Supporting Information for: **$Cu_3(BTC)_2$ for the Removal of Ammonia from Contaminated Air Streams and Its Characterization by MAS NMR**

Table S1. Raw nitrogen isotherm data collected for fresh $Cu_3(BTC)_2$.

P/Po	Volume (cc/g @ STP)		P/Po	Volume (cc/g @ STP)		P/Po	Volume (cc/g @ STP)
7.40E-06	131.5973333		8.23E-03	331.2526667		7.49E-01	409.658
1.57E-05	156.8873333		9.08E-03	332.1113333		8.02E-01	416.4306667
2.52E-05	170.5893333		1.27E-02	334.8726667		8.51E-01	428.3453333
3.49E-05	185.67		2.11E-02	340.0786667		9.02E-01	435.0033333
4.48E-05	203.4286667		3.14E-02	344.6293333		9.50E-01	436.262
5.48E-05	221.4473333		4.15E-02	347.8806667		9.93E-01	438.438
6.50E-05	238.1533333		5.18E-02	351.1833333		9.46E-01	438.6906667
7.52E-05	250.8346667		6.20E-02	353.2093333		8.98E-01	437.1193333
8.53E-05	259.518		7.15E-02	355.522		8.49E-01	434.9973333
9.46E-05	265.1073333		8.21E-02	357.5853333		7.98E-01	432.2026667
1.97E-04	287.442		9.22E-02	359.4126667		7.49E-01	427.9493333
2.97E-04	295.6933333		1.02E-01	361.2446667		6.99E-01	424.612
3.99E-04	300.5186667		1.50E-01	367.6473333		6.46E-01	423.442
5.03E-04	304.02		2.00E-01	372.6713333		5.98E-01	422.422
6.05E-04	306.5846667		2.50E-01	377.1646667		5.48E-01	419.8686667
7.07E-04	308.556		3.01E-01	380.7493333		4.98E-01	416.6246667
8.13E-04	310.228		3.51E-01	383.8613333		4.49E-01	390.7173333
9.07E-04	311.7653333		4.01E-01	386.6053333		3.98E-01	386.8566667
1.01E-03	312.8886667		4.51E-01	389.0866667		3.48E-01	383.2366667
2.05E-03	319.5493333		4.99E-01	392.3793333		2.98E-01	379.29
3.07E-03	322.9653333		5.50E-01	396.8306667		2.48E-01	375.13
4.08E-03	325.3213333		6.00E-01	399.7253333		1.98E-01	370.3893333
5.04E-03	327.0473333		6.50E-01	402.71		1.48E-01	365.5686667
6.08E-03	328.6513333		7.00E-01	405.8366667		9.83E-02	358.4426667
7.13E-03	330.0133333		7.49E-01	409.658		4.94E-02	347.6233333

Table S2. Raw nitrogen isotherm data collected for ammonia-exhausted $Cu_3(BTC)_2$ under dry conditions.

P/Po	Volume (cc/g @ STP)		P/Po	Volume (cc/g @ STP)		P/Po	Volume (cc/g @ STP)
2.22E-05	0.111683168		8.35E-03	0.87480198		8.01E-01	17.95490099
3.45E-05	0.130643564		9.41E-03	0.915346535		8.50E-01	19.32163366
4.57E-05	0.144950495		1.04E-02	0.99029703		9.00E-01	20.58920792
5.58E-05	0.15539604		2.29E-02	1.396237624		9.49E-01	22.85178218
6.47E-05	0.163217822		3.29E-02	1.811881188		9.96E-01	31.54118812
7.21E-05	0.168910891		4.27E-02	2.067970297		9.49E-01	25.1839604
7.84E-05	0.172920792		5.27E-02	2.312623762		8.98E-01	22.33806931
8.36E-05	0.175544554		6.27E-02	2.478168317		8.48E-01	20.3539604
1.08E-04	0.190792079		7.25E-02	2.946633663		7.96E-01	21.24836634
1.08E-04	0.19019802		8.19E-02	4.363267327		7.48E-01	19.87831683
2.07E-04	0.237376238		9.25E-02	3.252277228		6.98E-01	18.41193069
3.16E-04	0.271287129		1.02E-01	3.953564356		6.47E-01	17.11475248
4.20E-04	0.29509901		1.52E-01	5.523762376		5.97E-01	15.61465347
5.23E-04	0.313514851		2.02E-01	6.982524752		5.48E-01	14.06212871
6.25E-04	0.328613861		2.52E-01	7.947772277		4.97E-01	14.07811881
7.29E-04	0.341435644		3.02E-01	8.209752475		4.47E-01	12.88207921
8.30E-04	0.352128713		3.51E-01	9.567673267		3.97E-01	9.84009901
9.34E-04	0.364554455		4.01E-01	9.684455446		3.47E-01	9.316782178
1.01E-03	0.406039604		4.51E-01	11.57851485		2.97E-01	8.659059406
2.08E-03	0.515445545		5.01E-01	12.10529703		2.47E-01	7.361138614
3.17E-03	0.59509901		5.51E-01	13.06212871		1.97E-01	6.510148515
4.21E-03	0.656386139		6.01E-01	13.93490099		1.47E-01	4.928762376
5.25E-03	0.71		6.51E-01	14.5879703		9.72E-02	3.080940594
6.28E-03	0.78039604		7.01E-01	15.19019802		4.73E-02	1.151386139
7.32E-03	0.832277228		7.50E-01	17.15465347		8.01E-01	17.95490099

Table S3. Raw nitrogen isotherm data collected for ammonia-exhausted $Cu_3(BTC)_2$ under wet conditions.

P/Po	Volume (cc/g @ STP)		P/Po	Volume (cc/g @ STP)		P/Po	Volume (cc/g @ STP)
1.39E-05	2.986909091		8.17E-03	24.42672727		8.00E-01	137.5743636
2.08E-05	3.620727273		9.59E-03	21.55381818		8.52E-01	159.7570909
3.51E-05	4.562363636		1.02E-02	21.89018182		9.01E-01	266.4618182
4.26E-05	4.981454545		2.21E-02	24.32127273		9.52E-01	369.3545455
5.44E-05	5.496		3.27E-02	27.53490909		9.95E-01	440.0254545
6.00E-05	5.728909091		4.23E-02	32.42254545		9.47E-01	410.0854545
7.44E-05	6.226545455		5.27E-02	33.64054545		9.01E-01	361.3054545
8.07E-05	6.429090909		6.27E-02	31.52054545		8.50E-01	307.8127273
9.76E-05	6.889818182		7.27E-02	33.28527273		8.00E-01	197.9527273
1.04E-04	7.057090909		8.27E-02	35.40872727		7.49E-01	131.3129091
2.28E-04	9.108909091		9.26E-02	34.99618182		7.00E-01	104.7838182
3.00E-04	9.923636364		1.02E-01	32.36163636		6.49E-01	88.32090909
4.02E-04	10.83963636		1.52E-01	39.65454545		5.98E-01	79.06127273
5.11E-04	11.65690909		2.02E-01	48.22818182		5.48E-01	69.51545455
6.20E-04	12.33272727		2.51E-01	57.16581818		4.98E-01	60.31090909
7.28E-04	12.91654545		3.02E-01	59.64636364		4.47E-01	55.48327273
8.02E-04	13.28527273		3.51E-01	67.33872727		3.98E-01	48.38327273
9.29E-04	13.84963636		4.01E-01	72.82727273		3.48E-01	40.35472727
1.00E-03	14.37890909		4.51E-01	76.46181818		2.98E-01	31.83036364
2.03E-03	17.40981818		5.00E-01	86.48127273		2.48E-01	22.66090909
3.09E-03	19.394		5.50E-01	93.54818182		1.98E-01	14.836
4.05E-03	20.70854545		6.00E-01	99.996		1.48E-01	2.489818182
5.08E-03	21.84545455		6.50E-01	102.3325455		9.73E-02	-8.130909091
6.13E-03	22.80545455		7.00E-01	110.3447273		4.77E-02	-15.92727273
7.16E-03	23.67109091		7.49E-01	126.1750909			

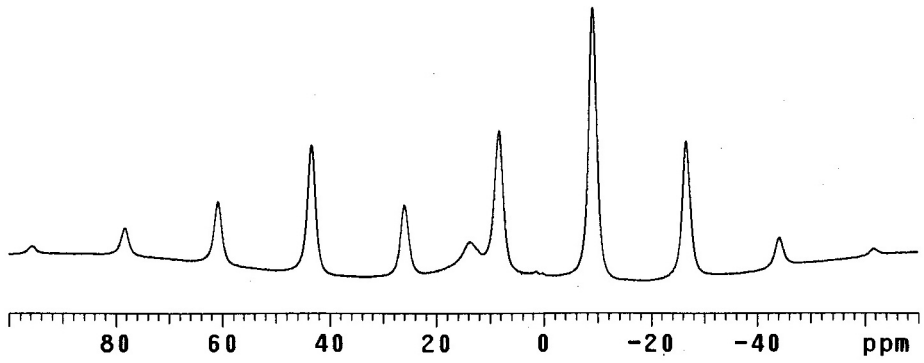

Figure S1. ^{1}H MAS NMR spectrum obtained for Soxhlet-Extracted (MeOH) $Cu_3(BTC)_2$.

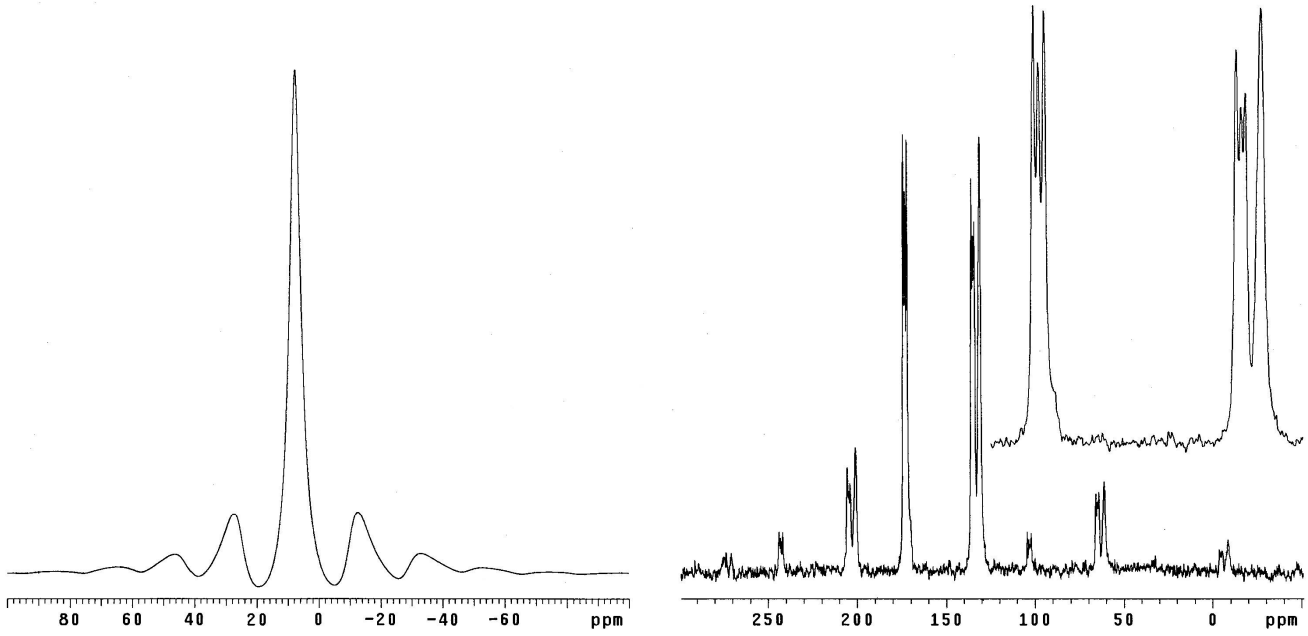

Figure S2. ^{1}H MAS (left) and ^{13}C CP-MAS (right) NMR spectra (9.4 T, υ_R = 7000 Hz) obtained for $(NH_4)_3$BTC. Inset shows splittings of CO_2^- (173.0, J_{CON} = 103 Hz) and =C< (134.8, J_{CCON} = 85 Hz) resonances attributed to ^{14}N (I = 1) J–couplings, which are smaller for the more distant =C< carbon. The methine (CH) carbon (131.0 ppm; furthest removed from the NH_4-groups) does not exhibit detectable splittings.

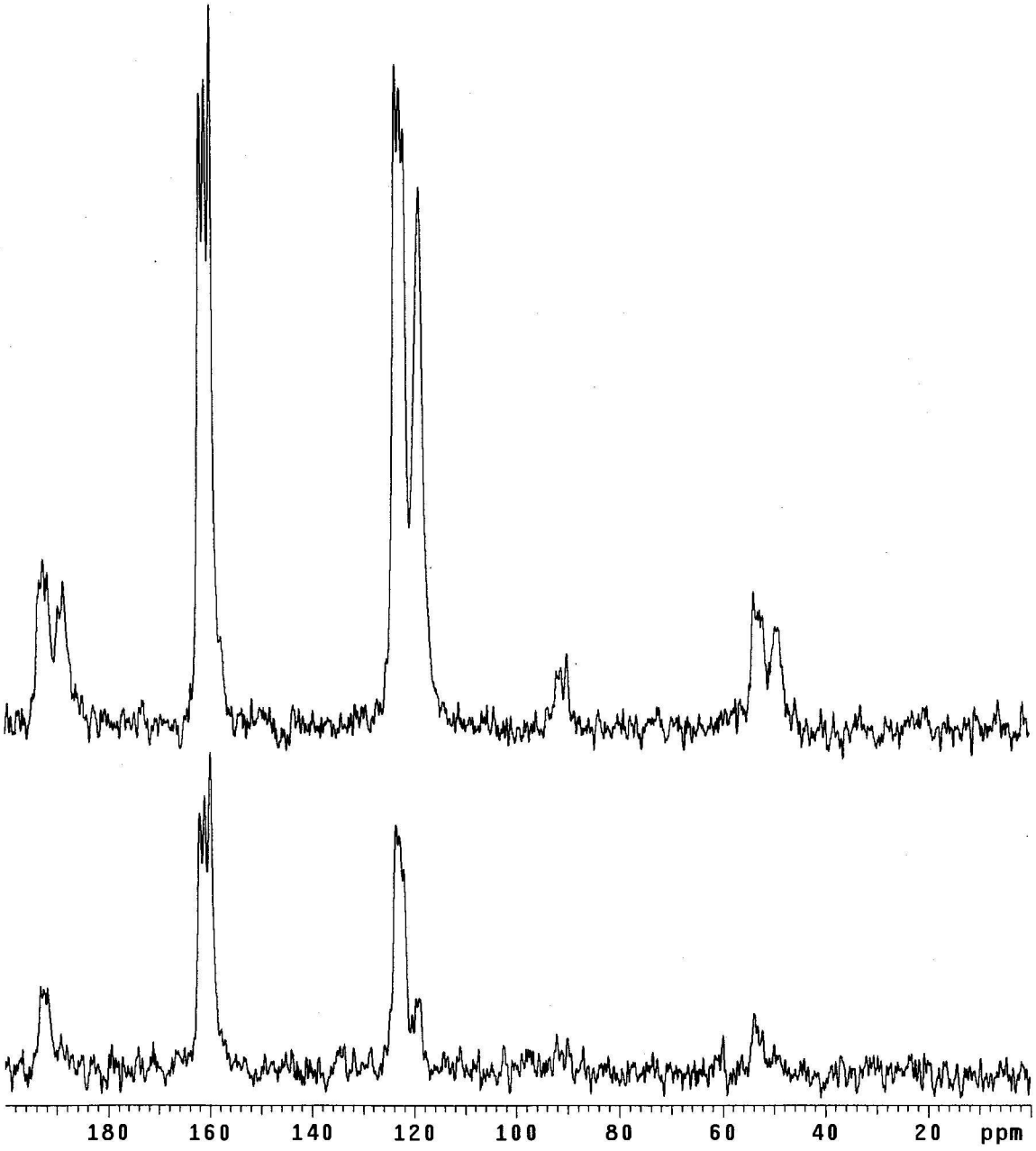

Figure S3. ^{13}C–^{1}H CP-MAS NMR dipolar recoupling spectra (9.4 T, υ_R = 7000 Hz) obtained for $(NH_4)_3BTC$. The top spectrum is the "S_o" spectrum obtained in the absence of ^{1}H recoupling pulses. The bottom spectrum, "S", shows the reduced signal intensity resulting from the applied ^{1}H recoupling pulses.

Figure S4. MAS NMR ^{13}C-^{1}H dipolar recoupling pulse sequence for Varian NMR spectrometers.

```
/* Modification of Varian XPOLAR1 sequence to
 * 13C-1H Dipolar Recoupling Pulse Sequence
 * Ishii et al. JACS 125 (2003) 3438-3439
 * George W. Wagner, U.S. Army ECBC
 */

/* xpol = 'y' gives cross polarization
          'n' gives direct polarization

   pw -    the observe 90 degree pulse

   pw2 -   proton 90 degree recoupling pulse

   cntct - hartmann-hahn contact time

   dipolr  - controls fine decoupler power during acquisition time.


 */

#include <standard.h>

static int table1[4] = {0, 1, 2, 3};
static int table2[4] = {1, 1, 3, 3};
static int table3[4] = {3, 0, 3, 0};
static int table4[4] = {1, 2, 1, 2};

pulsesequence()

{

/* declare new variables */

   double          dutycycle,
                   pw2,
                   cntct,
                   srate,
                   crossp,
                   dipolr;

   char            xpol[MAXSTR];

/* set variables */

   cntct = getval("cntct");
   at = getval("at");
   pw2 = getval("pw2");
   crossp  = getval("crossp");
   dipolr  = getval("dipolr");
   srate = getval("srate");
   getstr("xpol", xpol);


 /*check dutycycle -
      do not accept dm=y or decoupler duty cycles in excess of 20% */

   dutycycle = (d1 + d2) / (cntct + pw + d1 + d2 + at);
   fprintf(stdout, "Duty cycle is %5.2f%%. Doing ", (1.0 - dutycycle) * 100);

   if ((dutycycle < 0.8) || (dm[0] == 'y'))
```

```
   {
      fprintf(stdout, "ABORT! The duty cycle must be less than 20%%.\nPlease adj
      abort(1);
   }

/*begin pulse sequence*/


   if (xpol[0] == 'n')          /*direct polarization (dp)*/
   {
      fprintf(stdout, "Bloch decay");

      settable(t1,4,table1);
      settable(t3,4,table3);
      settable(t4,4,table4);
      setreceiver(t1);

      status(A);
      decpwrf(dipolr);
      delay(d1);
      rcvroff();
      delay(rof1);
      rgpulse(pw, t1, 0.0 , 0.0);
      status(B);
   }

   else
   {                            /* cross-polarization (cp)*/

      fprintf(stdout, "Cross polarization");

      settable(t1,4,table1);
      settable(t2,4,table2);
      settable(t3,4,table3);
      settable(t4,4,table4);
      setreceiver(t1);

      status(A);
      decpwrf(crossp);
      delay(d1);
      rcvroff();
      delay(rof1);

      decpulse(pw, t2);
      status(C);
      decphase(zero);
      rgpulse(cntct, t3, 0.0, 0.0);
      status(B);
      decpwrf(dipolr);
   }

 /* Begin Dipolar Rephasing Pulses */

      delay(0.5 / srate - pw2);
      decpulse(2.0 * pw2, t1);
      delay(0.5 / srate - pw - pw2);
      rgpulse(2.0 * pw, t1, 0.0, 0.0);
      delay(0.5 / srate - pw - pw2);
      decpulse(2.0 * pw2, t1);
      delay(0.5 / srate - pw2);

       status(C);

   fprintf(stdout, ".\n");

/*begin acquisition*/

   rcvron();
}
```

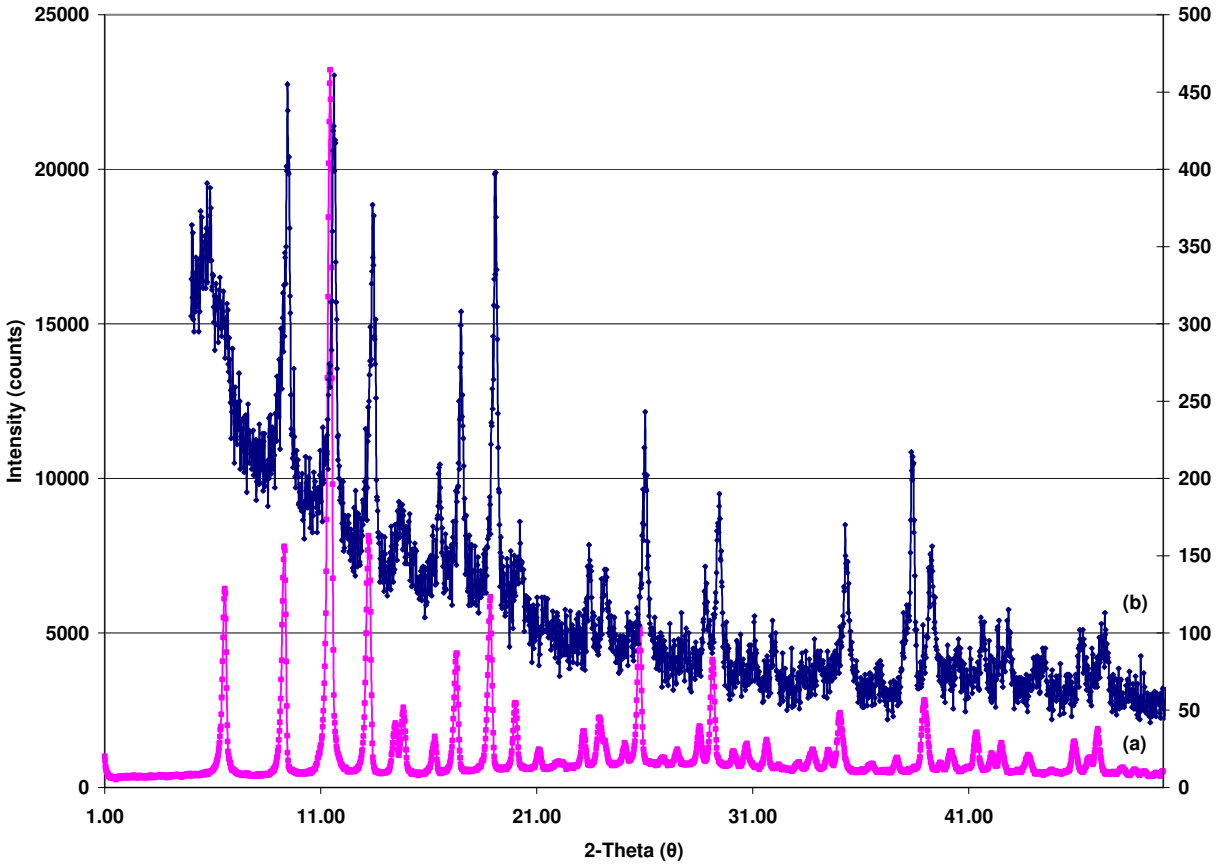

Figure S5. Comparison of X-ray patterns of different $Cu_3(BTC)_2$ starting materials. Sample (a) is a powder from well-formed framework $Cu_3(BTC)_2$ material whereas sample (b) indicates some differences from the well-formed framework $Cu_3(BTC)_2$ material.

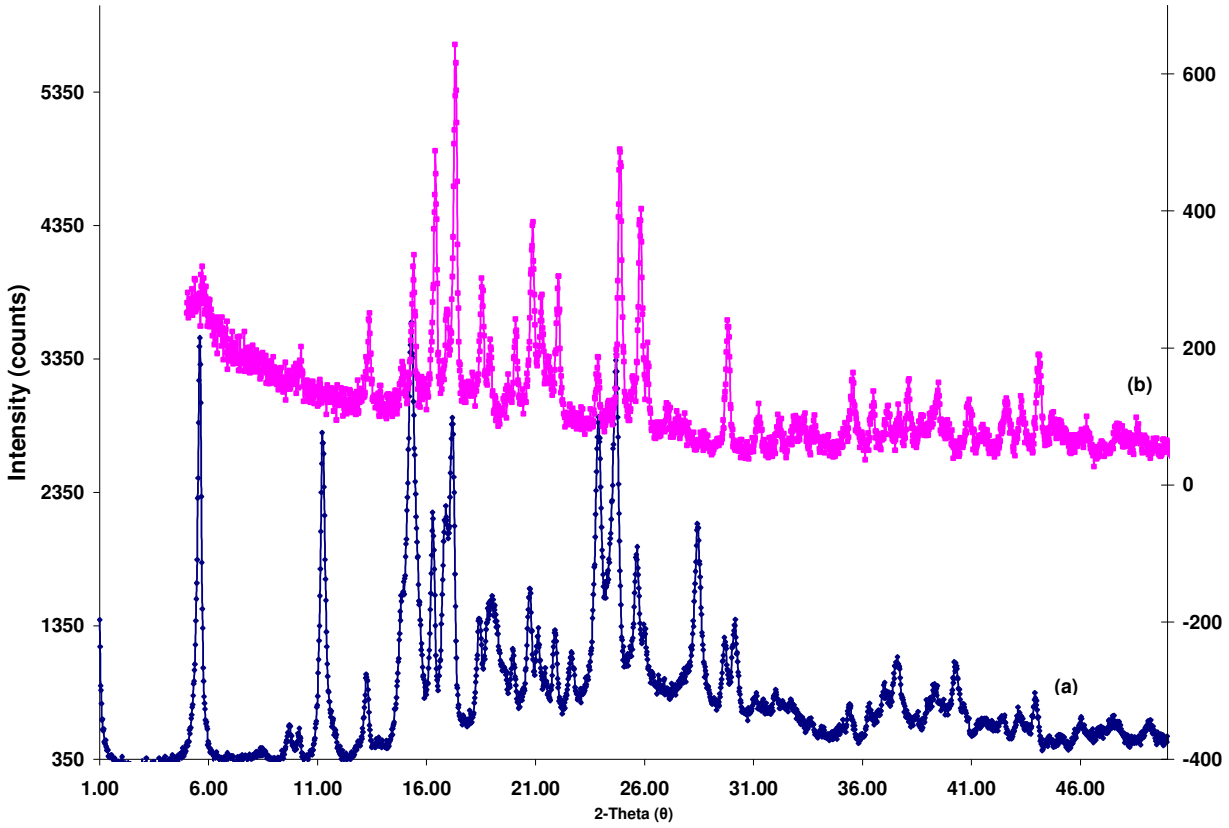

Figure S6. Comparison of X-ray patterns of different $Cu_3(BTC)_2$ materials exposed to humid ammonia vapors. Sample (a) is a powder from well-formed framework $Cu_3(BTC)_2$ material whereas sample (b) indicates some differences from the well-formed framework $Cu_3(BTC)_2$ material.

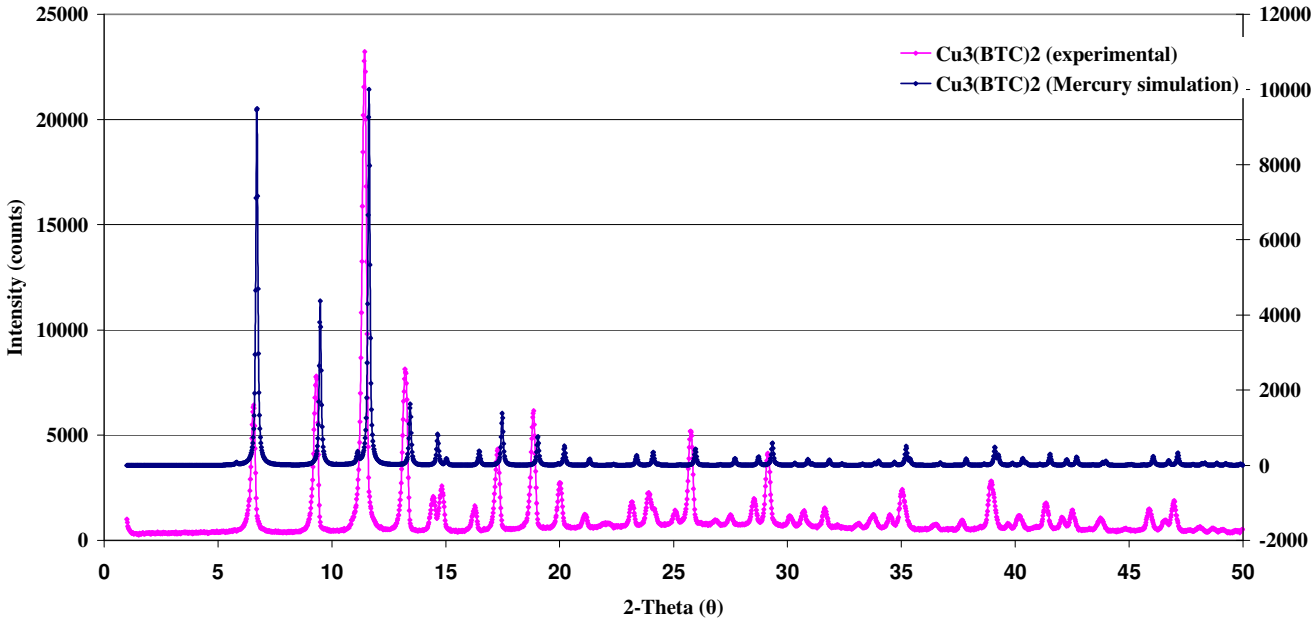

Figure S7. Comparison of PXRD pattern of experimental and Mercury simulation[1] of $Cu_3(BTC)_2$ material.

Table S4. Comparison of PXRD peak values of experimental and Mercury simulation of $Cu_3(BTC)_2$ material.

This paper		Mercury* simulation (Chiu data)	
2-Theta	Relative intensity[a]	2-Theta	Relative intensity[a]
6.5685245	0.2772	6.71554	0.9740
9.3212668	0.3360	9.48925	0.6613
11.44361	1.0000	11.6326	1.0000
13.208727	0.3507	13.4397	0.4039
14.826751	0.1117	14.6374	0.2884
17.285308	0.1872	17.4742	0.3719
18.861305	0.2653	19.0502	0.2761
19.996023	0.1181	20.2059	0.2274
25.753667	0.2240	25.9634	0.2088
29.136809	0.1783	29.3465	0.2433
38.95002	0.1219	39.0966	0.2189

*Mercury simulation conditions:

- 1-50° 2 theta

- 0.02101° (2 theta) Step size (exact experimental step size was 0.021013° (2 theta))

- FWHM 0.5 (2 theta)

[a] Relative intensity above.1 are only listed for peak PXRD values

References

[1] http://www.ccdc.cam.ac.uk/free_services/mercury/.