Journal Name

ARTICLE

Supporting Information

Hybrid materials based on transition Metal-BTC-Benzimidazole: Solvent assisted crystallographic and structural switching

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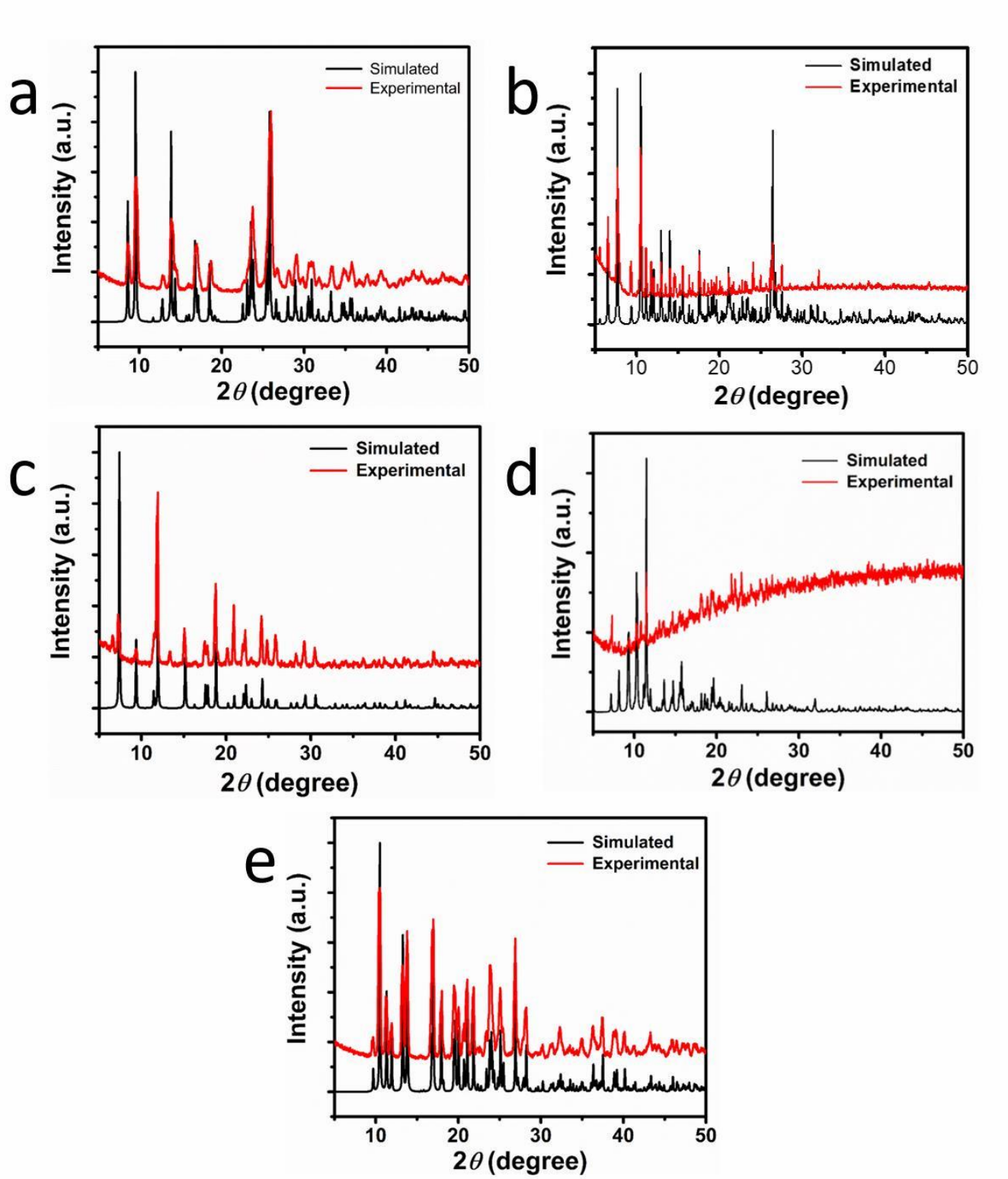


Figure S1. PXRD pattern for (a) $[Zn_2(H_2O)_2(HBTC)_2(BIm)_2](H_2O)_3$, **1,** (b) $[2\text{-}HABI]_2[Zn_2(BTC)_2(2\text{-}ABI)(H_2O)].(H_2O)_5$, **2**, (c) $[Cu_3(BTC)_2(BIm)_6]$[solvent], **3**, (d) $[Co_4(BTC)_3(BIm)_6]$[solvent], **4** and (e) $[(CH_3CH_2)_2NH_2][Zn(BTC)(BIm)].(H_2O)$, **5**.

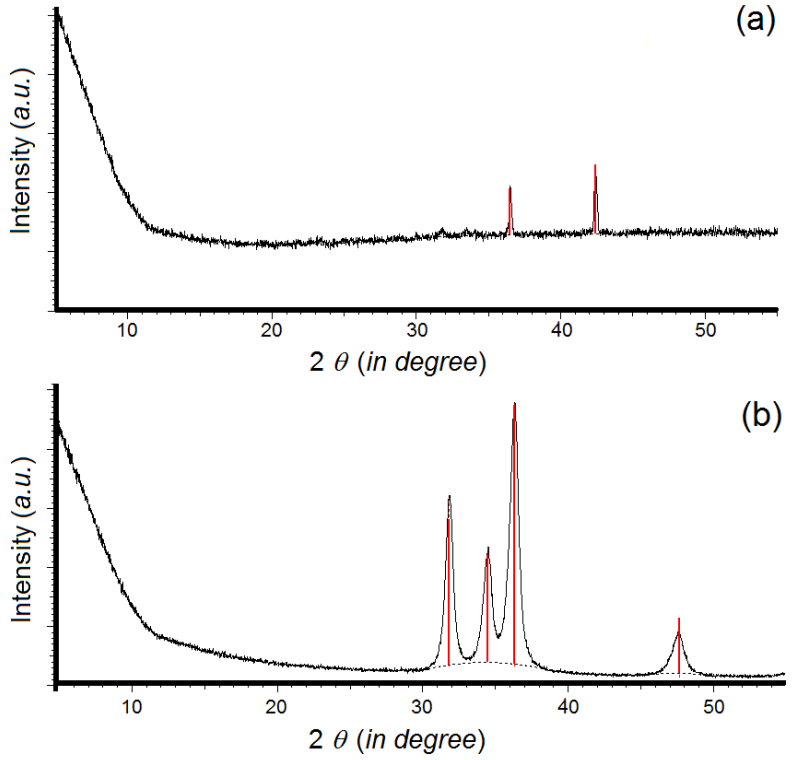


Figure S2. Post calcination PXRD analysis of (a) $[Co_4(BTC)_3(BIm)_6][solvent]$, **4** showing formation of CoO (PDF-00-043-1004) as final product and (b) Post calcination PXRD analysis of $[Zn_2(H_2O)_2(HBTC)_2(BIm)_2](H_2O)_3$, **1,** $[2\text{-}HABI]_2[Zn_2(BTC)_2(2\text{-}ABI)(H_2O)].(H_2O)_5$, **2**, $[(CH_3CH_2)_2NH_2][Zn(BTC)(BIm)].(H_2O)$, **5**, whereas the ZnO (PDF-01-075-0576) as calcined product.

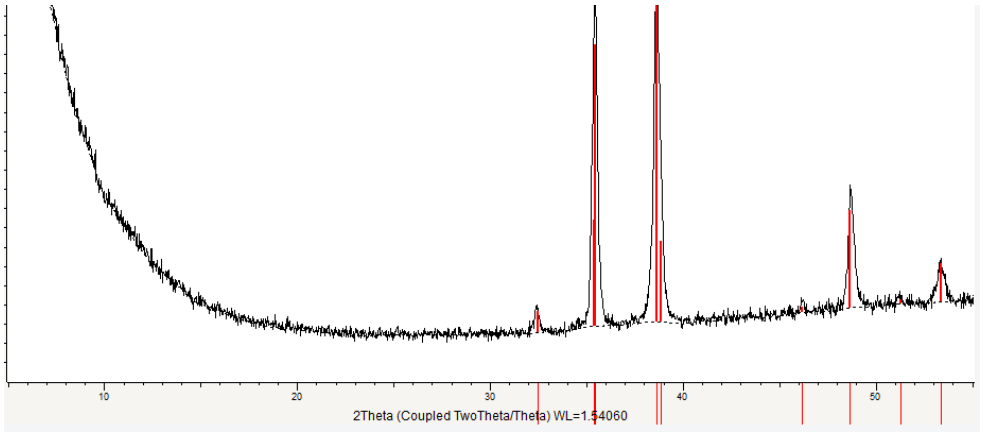
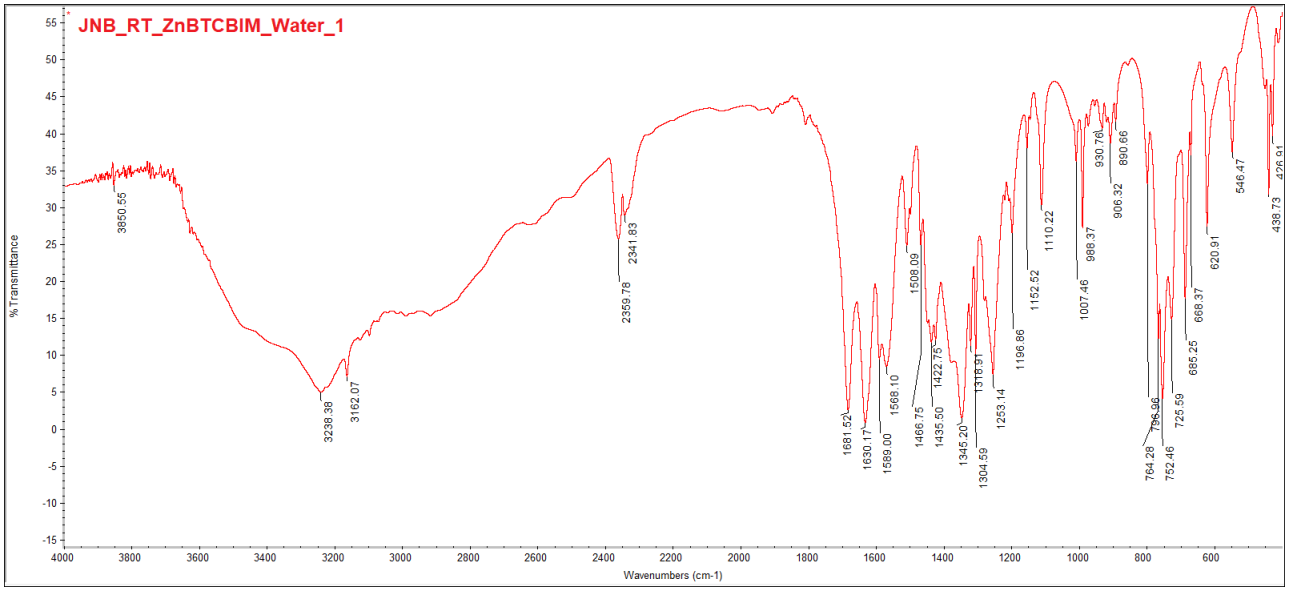
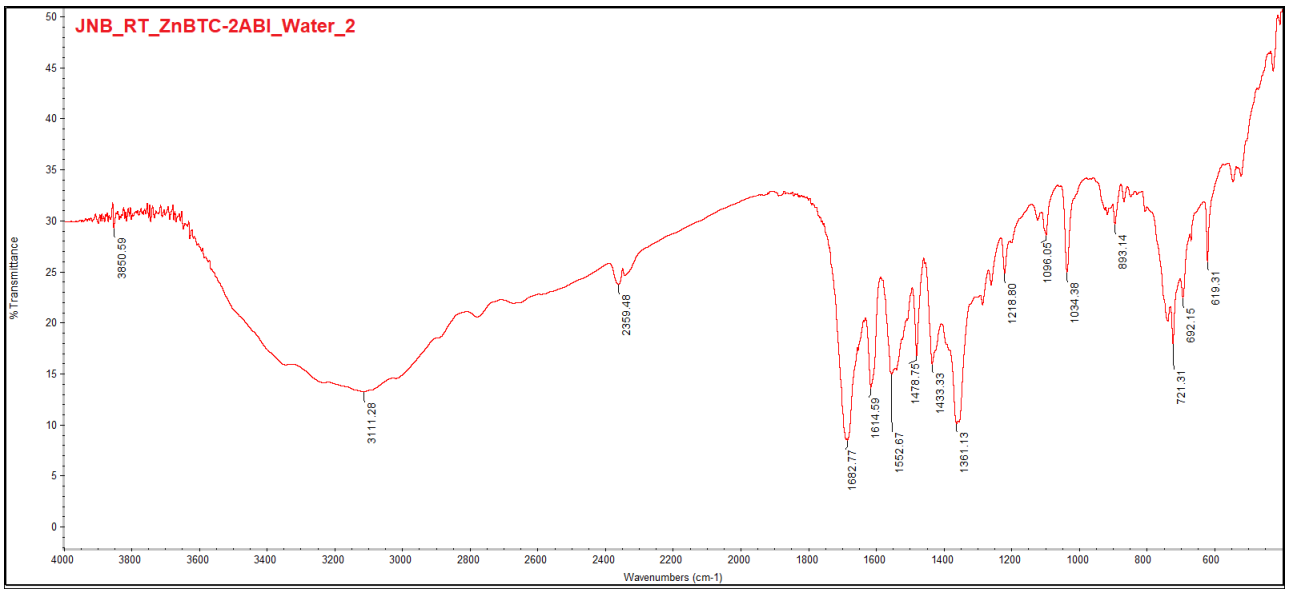
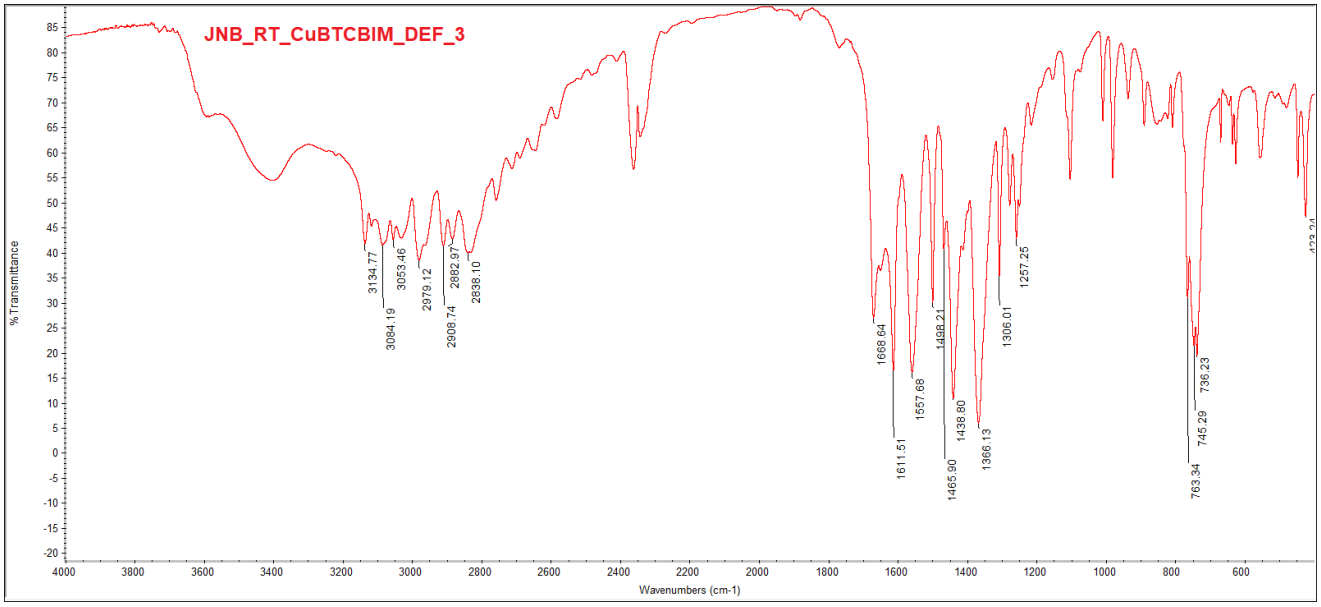


Figure S3. Post calcination PXRD analysis of $[Cu_3(BTC)_2(BIm)_6][solvent]$, **3**, showing formation of CuO (COD-9016326).



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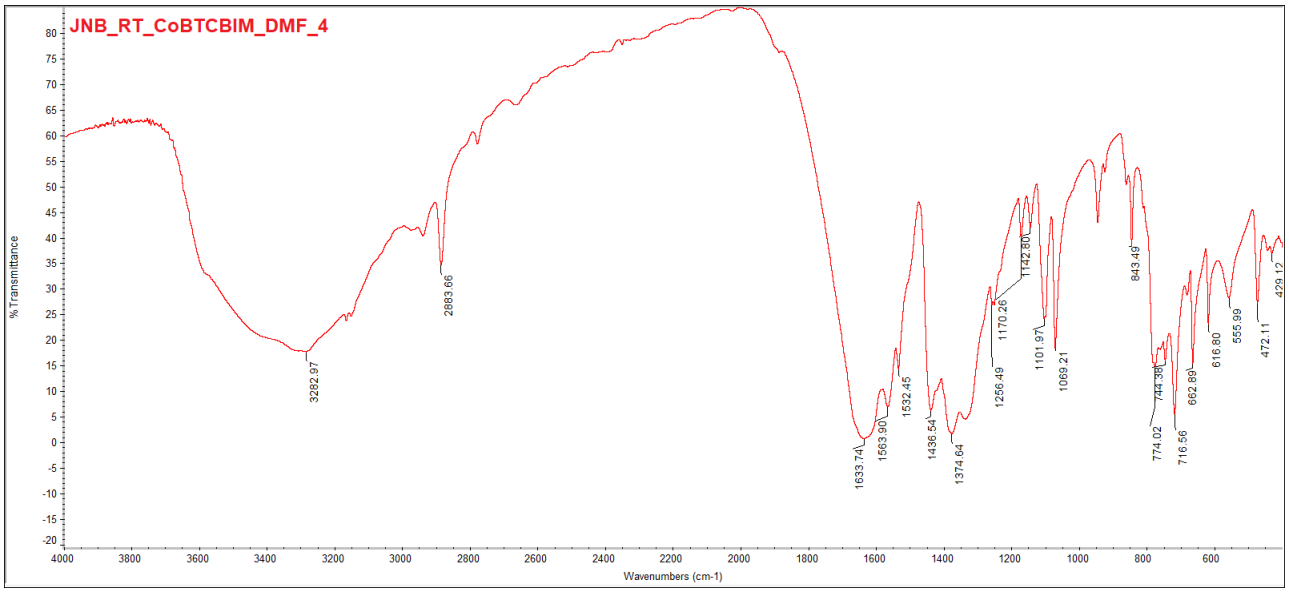
3053.46
2979.12
2908.74
2882.97
2838.10
1668.64
1611.51
1557.68
1498.21
1465.90
1438.80
1366.13
1306.01
1257.25
763.34
745.29
736.23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% Transmittance
Wavenumbers (cm-1)
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1633.74
1563.90
1532.45
1436.54
1374.64
1256.49
1170.26
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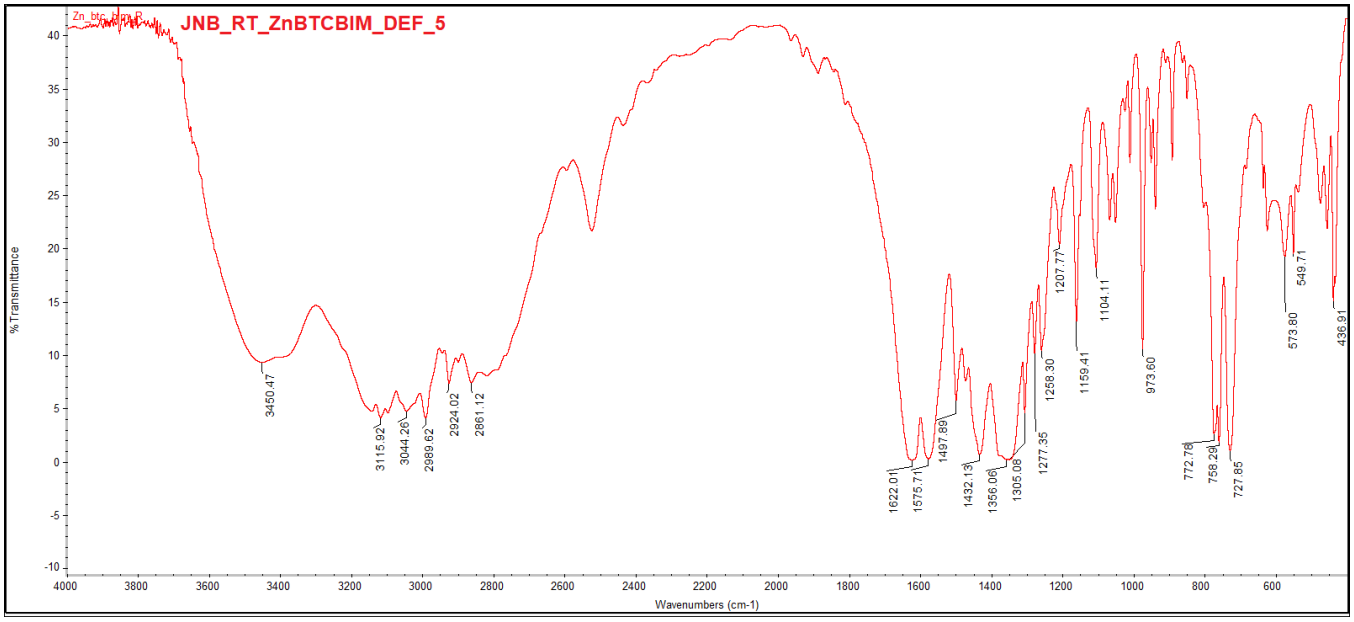

Figure S4. FTIR Spectra diagram of 1-5.

Table S1. Selected bond length tables of **1-5**

$[Zn_2(H_2O)_2(HBTC)_2(BIm)_2](H_2O)_3$, **1**					
Zn1-O1	1.9581(9)	Zn1-O4^a	1.9722(8)	Zn1-O1W	2.0313(10)
Zn1-N1	1.9693(10)				
$[2\text{-HABI}]_2[Zn_2(BTC)_2(2\text{-ABI})(H_2O)].(H_2O)_5$, **2**					
Zn1-O1	1.9506(18)	Zn1-O6^b	1.9675(19)	Zn1-O7	1.9770(17)
Zn1-N1	1.975(2)	Zn2 – O3	1.9766(18)	Zn2-O9^c	1.9845(18)
Zn2-O12^d	2.0195(18)	Zn2-O1W	2.023(2)		
$[Cu_3(BTC)_2(BIm)_6]$[solvent], **3**					
Cu1-O1^e	1.9702(9)	Cu1-O1	1.9702(9)	Cu1-N1	1.9851(14)
Cu1-N1^e	1.9851(14)				
$[Co_4(BTC)_3(BIm)_6]$[solvent], **4**					
Co1-Co1^f	2.8713(8)	Co1-O3	2.024(2)	Co1-O4^f	2.058(2)
Co1-O7	2.048(2)	Co1-O8^f	2.039(2)	Co1-N5	2.025(3)
Co2-O1	1.971(2)	Co2-O5^g	2.405(3)	Co2-O6^g	2.019(2)
Co2-N1	2.037(3)	Co2-N3	2.014(3)		
$[(CH_3CH_2)_2NH_2][Zn(BTC)(BIm)].(H_2O)$, **5**					
Zn1-O1	1.951(2)	Zn1-O3^h	1.980(2)	Zn1-O6^i	1.986(2)
Zn1-N1	2.027(3)				

Symmetry transformations used to generate equivalent atoms:

a) x+1/2,-y+3/2,z+1/2, b) -x+1,-y+1,-z+1 c) x,y,z-1 d) x-1,y,z-1 e) 1-x,1-y,1-z; f) -x+1,-y+1,-z+1 g) -x+1/2,y-1/2,-z+1/2 h) x-1/2,-y+1/2,z i) -x+1,-y+1,z-1/2.

Table S2. Classical Hydrogen bonding table for complexes **1-5**.[#]

D—H···A		D—H	H···A	D—A	∠D—H···A
$[Zn_2(H_2O)_2(HBTC)_2(BIm)_2](H_2O)_3$, **1**					
O6—H6A···O3W	1/2+x,-1/2+y,z	0.82	1.80(2)	2.6057(17)	170
N2—H2···O5	-1/2+x,1/2-y,-1/2+z	0.86	2.03	2.8233(14)	152
O1W—H1W1···O4	1-x,y,1/2-z	0.82(3)	1.93(2)	2.7254(13)	163
O1W—H2W1···O2	1/2-x,3/2-y,-z	0.81(3)	1.85(3)	2.6459(15)	169
O2W—H1W2···O3	-1/2+x,-1/2+y,z	0.84(2)	1.98(3)	2.8064(13)	170
O3W—H1W3···O2	1/2-x,3/2-y,-z	0.78(2)	2.16(2)	2.8517(18)	148
O3W—H2W3···O2W		0.77(3)	2.15(2)	2.8876(16)	163
$[2\text{-HABI}]_2[Zn_2(BTC)_2(2\text{-ABI})(H_2O)].(H_2O)_5$, **2**					
O1W—H1WA···O4W	x,y,-1+z	0.88	2.05	2.669(8)	127
N2—H2···O5W	-1+x,y,z	0.86	1.91	2.749(5)	163
O1W—H1WB···O12	-x,-y,1-z	0.88	1.87	2.734(3)	168
O6W—H6WA		0.85			
N3—H3A···O7		0.86	2.12	2.893(4)	149
N3—H3B···O4W	-1+x,y,z	0.86	2.10	2.934(7)	163
O6W—H6WB		0.85			
N4—H4A···O2	1+x,y,z	0.86	1.84	2.683(4)	167
N5—H5···O3	1-x,-y,1-z	0.86	2.14	2.915(3)	149
N5—H5···O10	1-x,-y,-z	0.86	2.14	2.915(3)	149
O5W—H5WA		0.85			

O5W—H5WB···O1	x,y,-1+z	0.85	2.02	2.858(4)	167
O5W—H5WB···O6	1-x,1-y,1-z	0.85	2.58	3.056(4)	116
N6—H6A···O10	1-x,-y,1-z	0.86	1.99	2.760(3)	148
N6—H6B···O6W	1+x,y,z	0.86	2.09	2.875(6)	153
N7—H7···O4	2-x,1-y,1-z	0.86	1.93	2.774(4)	167
O2W—H2WA···O3W	x,y,-1+z	0.85	1.95	2.757(10)	159
N8—H8···O5	x,y,-1+z	0.86	2.02	2.766(4)	144
O2W—H2WB···O9	x,y,-1+z	0.85	2.15	2.983(5)	167
O4W—H4WA···O8	x,y,-1+z	0.85	2.32	2.701(6)	107
N9—H9A···O5	x,y,-1+z	0.86	2.39	3.067(4)	136
N9—H9B···O2W	2-x,1-y,-z	0.86	1.99	2.850(6)	176
O4W—H4WB···O8	x,y,-1+z	0.85	2.31	2.701(6)	108
O3W—H3WA···O5	1-x,1-y,1-z	0.85	2.47	3.316(9)	177
O3W—H3WB		0.85			
$[Cu_3(BTC)_2(BIm)_6]$[solvent], **3**					
N2—H2···O2	y, -x+y,-z	0.86	1.88	2.729(5)	170
$[Co_4(BTC)_3(BIm)_6]$[solvent], **4**					
N2—H2A···O9	1/2+x,1/2-y,1/2+z	0.86	1.93	2.762(5)	161
N4—H4A···O2	1/2-x,-1/2-y,-z	0.86	1.83	2.687(5)	175
N6—H6A···O9	x,-1+y,z	0.86	2.04	2.851(5)	158
$[(CH_3CH_2)_2NH_2][Zn(BTC)(BIm)].(H_2O)$, **5**					
N1A—H1···O2	1/2+x,1/2-y,z	0.89	1.84	2.726(7)	170

N1A—H2···O1W	1/2-x,1/2+y,1/2+z	0.89	1.90	2.785(9)	171
N2—H2A···O4	1/2-x,1/2+y,-1/2+z	0.86	1.89	2.700(4)	157
O1W—H1W···O3		0.87	2.10	2.904(6)	155
O1W—H2W···O5	-x,-y,-1/2+z	0.87	1.90	2.754(6)	168

[#]Where 'D' is a donor and 'A' is acceptor, the bond lengths are in (Å) and angles are in (°).