Supporting information

Table S1. Selected bond lengths [Å] and angles [º] for $\{[Cu_4(bpy)_4(OH)_4(H_2O)_2]\}(NO_3)_2(C_7H_5O_2)_2 \cdot 6H_2O$ **1**[a]

Cu1–O1	1.921(3)	Cu1–O3	2.257(3)	Cu2–N4	2.015(3)
Cu1–O2	1.973(2)	Cu2–O1	1.920(3)	Cu2–O2$^{\#1}$	2.301(2)
Cu1–N1	2.008(3)	Cu2–O2	1.962(3)		
Cu1–N2	2.014(3)	Cu2–N3	1.990(3)		
O1–Cu1–O2	82.5(1)	N1–Cu1–O3	100.4(1)	O2–Cu2–O2$^{\#1}$	82.6(1)
O1–Cu1–O3	90.3(1)	N1–Cu1–N2	80.8(1)	O2–Cu2–N3	176.6(1)
O1–Cu1–N1	169.2(1)	N2–Cu1–O3	107.7(1)	O2–Cu2–N4	99.3(1)
O1–Cu1–N2	94.9(1)	O1–Cu2–O2	82.8(1)	N3–Cu2–O2$^{\#1}$	100.8(1)
O2–Cu1–O3	94.7(1)	O1–Cu2–O2$^{\#1}$	101.5(1)	N3–Cu2–N4	80.8(1)
O2–Cu1–N1	97.7(1)	O1–Cu2–N3	96.2(1)	N4–Cu2–O2$^{\#1}$	94.9(1)
O2–Cu1–N2	157.5(1)	O1–Cu2–N4	163.6(1)		

[a] Symmetry transformations used to generate equivalent atoms: #1 = –x+2, –y+1, –z+1

Table S2. Selected bond lengths [Å] and angles [º] for $\{[Cu_4(bpy)_4(OH)_4(H_2O)_2]\}(NO_3)_2(C_5H_6O_4)\cdot 8H_2O$ **2**

Cu1–O1	1.920(2)	Cu2–O3	2.296(2)	Cu3–N6	1.984(3)
Cu1–O2	1.962(2)	Cu2–N3	2.011(3)	Cu4–O4	1.913(2)
Cu1–O5	2.251(2)	Cu2–N4	2.002(3)	Cu4–O3	1.973(2)
Cu1–N1	2.016(3)	Cu3–O2	2.327(2)	Cu4–N7	1.998(3)
Cu1–N2	2.003(3)	Cu3–O3	1.949(2)	Cu4–N8	2.012(3)
Cu2–O1	1.911(2)	Cu3–O4	1.919(2)	Cu4–O6	2.260(2)
Cu2–O2	1.967(2)	Cu3–N5	2.016(3)		
O1–Cu1–O2	81.38(9)	O2–Cu2–O3	84.85(8)	N6–Cu3–O2	97.69(9)
O1–Cu1–O5	94.23(9)	O2–Cu2–N3	100.5(1)	N6–Cu3–N5	81.1(1)
O1–Cu1–N1	167.81(9)	O2–Cu2–N4	174.7(1)	O3–Cu4–O6	94.23(9)
O1–Cu1–N2	94.8(1)	N3–Cu2–O3	97.76(9)	O3–Cu4–N7	98.5(1)
O2–Cu1–O5	104.3(1)	N4–Cu2–O3	100.03(9)	O3–Cu4–N8	155.61(9)
O2–Cu1–N1	99.0(1)	N4–Cu2–N3	81.0(1)	O4–Cu4–O3	80.59(9)
O2–Cu1–N2	159.3(1)	O3–Cu3–O2	84.42(8)	O4–Cu4–O6	97.7(1)
N1–Cu1–O5	97.5(1)	O3–Cu3–N5	101.6(1)	O4–Cu4–N7	168.3(1)
N2–Cu1–O5	96.2(1)	O3–Cu3–N6	176.4(1)	O4–Cu4–N8	95.2(1)
N2–Cu1–N1	80.6(1)	O4–Cu3–O2	101.49(9)	N7–Cu4–O6	94.0(1)
O1–Cu2–O2	81.47(9)	O4–Cu3–O3	81.03(9)	N7–Cu4–N8	80.8(1)
O1–Cu2–O3	96.67(8)	O4–Cu3–N5	161.1(1)	N8–Cu4–O6	110.2(1)
O1–Cu2–N3	165.56(9)	O4–Cu3–N6	95.6(1)		
O1–Cu2–N4	95.9(1)	N5–Cu3–O2	97.36(9)		

Table S3. Selected bond lengths [Å] and angles [º] for $\{[Cu_4(bpy)_4(OH)_4(H_2O)_2]\}(C_5H_6O_4)_2 \cdot 16H_2O$ **3**[a]

Cu1–O1	1.91(3)	Cu2–O2$^{\#1}$	2.31(3)	Cu3–N6	2.01(4)
Cu1–O2	1.99(3)	Cu2–N3	1.98(4)	Cu4–O4	1.92(3)
Cu1–O3	2.25(4)	Cu2–N4	2.02(4)	Cu4–O5	1.96(3)
Cu1–N1	1.99(4)	Cu3–O4	1.91(3)	Cu4–O5$^{\#2}$	2.30(3)
Cu1–N2	2.01(4)	Cu3–O5	1.97(3)	Cu4–N7	2.03(4)
Cu2–O1	1.92(3)	Cu3–O6	2.24(4)	Cu4–N8	1.99(4)
Cu2–O2	1.95(3)	Cu3–N5	2.02(4)		
O1–Cu1–O2	81.2(1)	O2–Cu2–O2$^{\#1}$	84.6(1)	N6–Cu3–O6	98.5(2)
O1 Cu1 O3	91.3(2)	O2–Cu2–N3	175.7(2)	N6–Cu3–N5	80.7(2)
O1–Cu1–N1	168.6(2)	O2–Cu2–N4	100.9(1)	O4–Cu4–O5	81.8(1)
O1 Cu1 N2	94.7(2)	N3–Cu2–O2$^{\#1}$	98.9(1)	O4–Cu4–O5$^{\#2}$	99.8(1)
O2–Cu1–O3	98.8(1)	N3–Cu2–N4	80.9(2)	O4–Cu4–N7	163.2(1)
O2–Cu1–N1	98.2(2)	N4–Cu2–O2$^{\#1}$	100.7(1)	O4–Cu4–N8	95.8(1)
O2 Cu1 N2	156.5(2)	O4–Cu3–O5	81.7(1)	O5–Cu4–O5$^{\#2}$	85.3(1)
N1–Cu1–O3	100.0(2)	O4–Cu3–O6	92.0(1)	O5–Cu4–N7	100.4(1)
N1 Cu1 N2	81.2(2)	O4–Cu3–N5	95.3(1)	O5–Cu4–N8	176.3(1)
N2–Cu1–O3	104.5(2)	O4–Cu3–N6	169.5(2)	N7–Cu4–O5$^{\#2}$	97.0(1)
O1–Cu2–O2	82.1(3)	O5–Cu3–O6	96.6(1)	N8–Cu4–O5$^{\#2}$	97.9(1)
O1–Cu2–O2$^{\#1}$	96.4(1)	O5–Cu3–N5	157.2(1)	N8–Cu4–N7	81.1(2)
O1–Cu2–N3	95.1(2)	O5–Cu3–N6	98.1(1)		
O1–Cu2–N4	162.8(2)	N5–Cu3–O6	106.1(2)		

[a] Symmetry transformations used to generate equivalent atoms: #1 = –x, –y, –z+1, #2 = –x + 1, y+1, –z+1

Table S4a. Selected bond lengths [Å] and angles [º] for $[Cu_6(bpy)_6(OH)_6(H_2O)_2](C_8H_7O_2)_6 \cdot 12H_2O$ **4**[a]

Cu1–O1	1.911(4)	Cu3–O2	2.254(4)	Cu5–O5	1.923(5)
Cu1–O2	1.992(4)	Cu3–O3	1.947(4)	Cu5–O6	1.978(5)
Cu1–O4	2.207(5)	Cu3–O3$^{\#1}$	1.966(4)	Cu5–O7$^{\#2}$	2.380(5)
Cu1–N1	2.015(5)	Cu3–N5	1.997(5)	Cu5–N9	2.007(6)
Cu1–N2	1.997(5)	Cu3–N6	2.018(5)	Cu5–N10	2.016(6)
Cu2–O1	1.910(4)	Cu4–O5	1.934(5)	Cu6–O6	2.269(5)
Cu2–O2	1.974(4)	Cu4–O6	2.004(5)	Cu6–O7	1.962(4)
Cu2–O3$^{\#1}$	2.327(4)	Cu4–O8	2.203(5)	Cu6–O7$^{\#2}$	1.962(4)
Cu2–N3	2.007(5)	Cu4–N7	2.019(6)	Cu6–N11	2.026(5)
Cu2–N4	1.995(5)	Cu4–N8	2.013(6)	Cu6–N12	1.999(5)
O1–Cu1–O2	79.6(2)	O2–Cu3–O3	100.2(2)	O5–Cu5–O6	83.1(2)
O1–Cu1–O4	92.8(2)	O2–Cu3–O3$^{\#1}$	86.8(2)	O5–Cu5–O7$^{\#2}$	95.4(2)
O1–Cu1–N1	97.4(2)	O2–Cu3–N5	98.8(2)	O5–Cu5–N9	166.1(2)
O1–Cu1–N2	171.6(2)	O2–Cu3–N6	95.9(2)	O5–Cu5–N10	95.3(2)
O2–Cu1–O4	95.5(2)	O3–Cu3–O3$^{\#1}$	81.5(2)	O6–Cu5–O7$^{\#2}$	82.7(2)
O2–Cu1–N1	157.4(2)	O3–Cu3–N5	161.0(2)	O6–Cu5–N9	99.2(2)
O2–Cu1–N2	98.8(2)	O3–Cu3–N6	98.5(2)	O6–Cu5–N10	173.5(2)
O4–Cu1–N1	107.1(2)	O3$^{\#1}$–Cu3–N5	98.5(2)	O7$^{\#2}$–Cu5–N9	98.5(2)
O4–Cu1–N2	95.6(2)	O3$^{\#1}$–Cu3–N6	177.3(2)	O7$^{\#2}$–Cu5–N10	103.7(2)
N1–Cu1–N2	80.9(2)	N5–Cu3–N6	80.6(2)	N9–Cu5–N10	80.9(2)
O1–Cu2–O2	80.1(2)	O5–Cu4–O6	82.2(2)	O6–Cu6–O7	109.7(2)
O1–Cu2–O3$^{\#1}$	98.4(2)	O5–Cu4–O8	91.9(2)	O6–Cu6–O7$^{\#2}$	86.1(2)
O1–Cu2–N3	162.3(2)	O5–Cu4–N7	96.2(2)	O6–Cu6–N11	95.1(2)
O1–Cu2–N4	98.9(2)	O5–Cu4–N8	173.0(2)	O6–Cu6–N12	96.9(2)
O2–Cu2–O3$^{\#1}$	84.7(2)	O6–Cu4–O8	88.5(2)	O7–Cu6–O7$^{\#2}$	79.7(2)
O2–Cu2–N3	99.3(2)	O6–Cu4–N7	162.5(2)	O7–Cu6–N11	155.1(2)
O2–Cu2–N4	177.8(2)	O6–Cu4–N8	99.1(2)	O7–Cu6–N12	97.7(2)
O3$^{\#1}$–Cu2–N3	99.1(2)	O8–Cu4–N7	109.0(2)	O7$^{\#2}$–Cu6–N11	100.7(2)
O3$^{\#1}$–Cu2–N4	97.5(2)	O8–Cu4–N8	95.0(2)	O7$^{\#2}$–Cu6–N12	176.6(2)
N3–Cu2–N4	81.1(2)	N7–Cu4–N8	80.6(3)	N11–Cu6–N12	80.7(2)

[a]Symmetry transformations used to generate equivalent atoms: #1 = –x+1, –y+1, –z; #2 = –x, –y+1, –z+1

Table S4b. Hydrogen bonding contacts for $[Cu_6(bpy)_6(OH)_6(H_2O)_2](C_8H_7O_2)_6 \cdot 12H_2O$ **4**[a]

D–H···A	d(D–H)	d(H···A)	∠DHA	d(D···A)
O1–H1A···O20	0.87	1.90	176	2.768
O2–H2A···O13	0.90	2.04	175	2.934
O3–H3A···O14	0.87	1.87	175	2.731
O4–H4A···O22	0.85	1.83	177	2.679
O4–H4B···O12	0.79	1.96	169	2.733
O5–H5···O17$^{\#3}$	0.86	1.94	150	2.717
O6–H6···O9	0.86	2.00	172	2.852
O7–H7···O18$^{\#4}$	0.91	1.95	171	2.854
O8–H8B···O10	0.84	1.91	153	2.676
O8–HA···O16$^{\#3}$	0.85	1.85	160	2.669
O21–H21B···O9$^{\#4}$	0.88	1.91	172	2.784
O21–H21A···O18	0.88	1.96	154	2.784
O22–H22A···O19	0.85	1.82	163	2.642
O22–H22B···O23$^{\#4}$	0.84	1.89	161	2.707
O23–H23A···O11	0.88	1.86	172	2.734
O23–H23B···O11$^{\#4}$	0.84	1.98	178	2.828
O24–H24A···O28	0.86	2.06	156	2.871
O24–H24B···O26$^{\#5}$	0.86	2.03	167	2.864
O25–H25A···O14$^{\#1}$	0.88	2.10	174	2.979
O25–H25B···O20	0.73	2.19	175	2.922
O26–H26A···O27	0.76	1.98	158	2.697
O26–H26B···O17	0.86	1.89	170	2.744
O27–H27A···O16	0.87	1.87	161	2.709
O27–H27B···O5$^{\#6}$	0.86	1.89	164	2.730
O28–H28A···O13	0.89	1.94	166	2.812
O28–H28B···O12	0.82	1.95	175	2.764
O29–H29A···O15$^{\#3}$	0.86	1.88	178	2.745
O29–H29B···O10	0.82	2.04	156	2.807
O30–H30B···O21	0.88	2.05	149	2.837
O30–H30A···O32B_b$^{\#4}$	0.88	1.55	144	2.312
O30–H30A···O32A_a$^{\#4}$	0.88	2.03	155	2.844
O31–H31B···O15$^{\#7}$	0.77	1.95	177	2.715
O31–H31A···O29$^{\#4}$	0.82	2.06	162	2.848
O32–H32B_a···O26$^{\#5}$	0.85	1.99	163	2.818
O32–H32A_a···O28	0.89	2.25	162	3.100

[a] Symmetry transformations used to generate equivalent atoms: #1 = –x+1, –y+1, –z; #2 = –x, –y+1, –z+1; #3 = x–1, y, z; #4 = –x+1, –y+1, –z+1; #5 = x, y+1, z; #6 = x+1, y+1, z; #7 = x, y, z+1

Table S6 The IR spectrum data, elemental analyses data and fitted magnetic data of complexes **1–4**

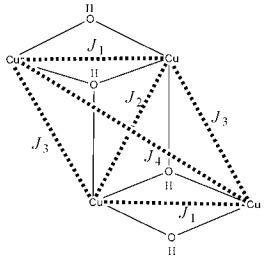
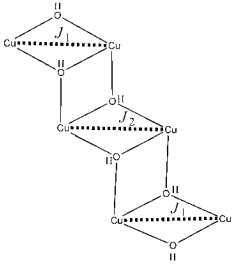
	1	**2**	**3**	**4**
IR data (ν cm^{-1}):	3381 vs, 3109 vw, 3022 vw, 1647 w, 1601 m, 1553 s, 1447 m, 1385 vs, 1319 w, 1161 w, 1030 w, 770 m, 729 m, 486 w.	3383 vs, 3109 vw, 3022 vw, 1651 m, 1601 m, 1556 s, 1447 s, 1385 vs, 1161 w, 1028 w, 770 m, 731 m, 489 w	3381 vs, 3107 vw, 3030 vw, 1647 w, 1601 m, 1558 s, 1448 m, 1396 vs, 1319 w, 1161 w, 1030 w, 770 m, 729 m, 490 w	3363 m, 3058 w, 1574 s, 1494 m, 1446 m, 1367 s, 1030 m, 769 s, 731 s
elemental analyses	Anal. Calcd. for $C_{54}H_{62}Cu_4N_{10}O_{22}$ (%): C, 44.44; H, 4.28; N, 9.60. Found (%): C, 44.26; H, 4.36; N, 9.51.	Anal. Calcd. for $C_{45}H_{57}Cu_4N_{10}O_{24}$ (%): C, 39.08; H, 4.15; N, 10.12. Found (%): C, 38.96; H, 4.05; N, 10.30.	Anal. Calcd. for $C_{50}H_{84}Cu_4N_8O_{30}$ (%): C, 39.17; H, 5.52; N, 7.31. Found (%): C, 39.25; H, 5.43; N, 7.37.	Anal. Calcd. for $C_{108}H_{124}Cu_6N_{12}O_{32}$ (%): C, 52.23; H, 5.03; N, 6.75. Found (%): C, 52.63; H, 5.33; N, 6.90.
Magnetic scheme				
Fitted parameters	J_1 = 64.1 cm^{-1}, J_2 = 5.7 cm^{-1}, g = 2.06	J_1 = 20.3 cm^{-1}, J_2 = 8.9 cm^{-1}, g = 2.32	J_1 = 35.4 cm^{-1}, J_2 = 3.4 cm^{-1}, g = 2.02	J_1 = 5.0 cm^{-1}, J_2 = –25.1cm^{-1}, g = 2.18

Figure S1. PXRD, I.R spectrum and TG curves for **1**.

Figure S2. PXRD, I.R spectrum and TG curves for **2**.

Figure S3. PXRD, I.R spectrum and TG curves for **3**.

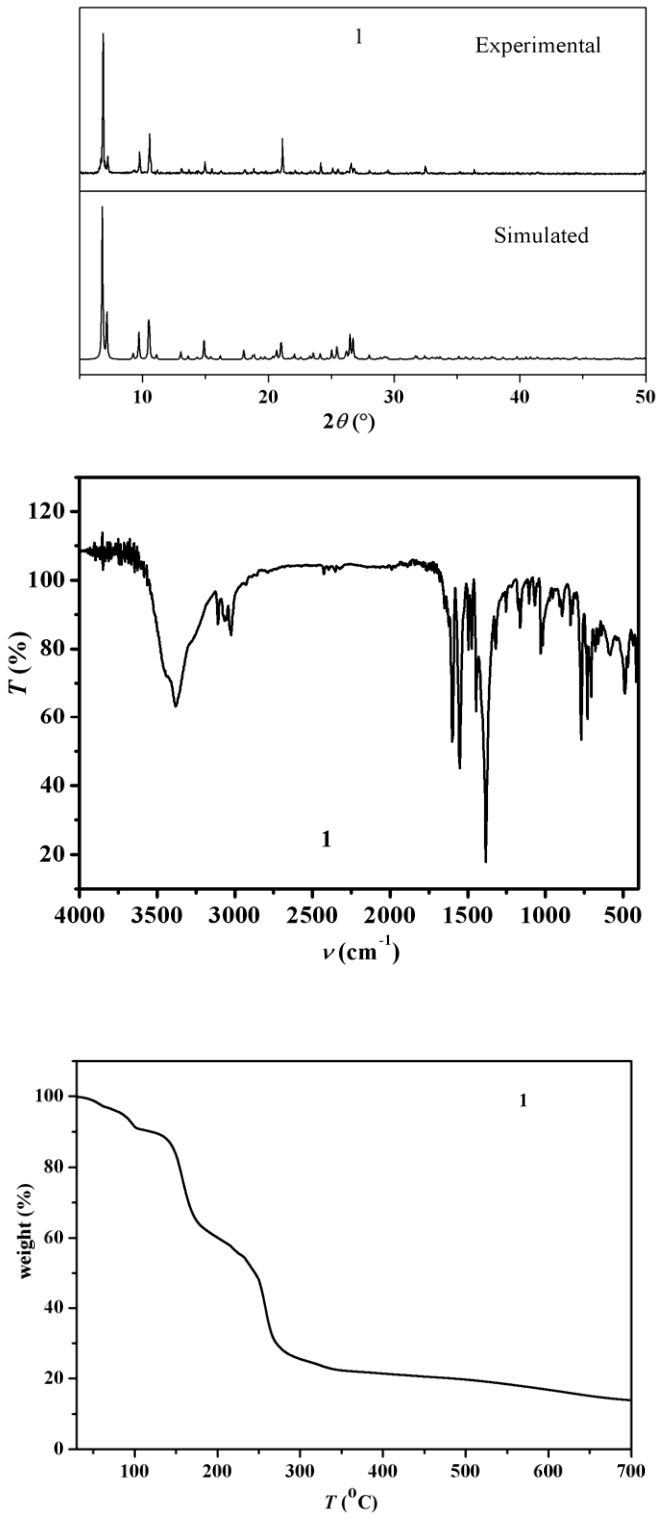
Figure S4. PXRD, I.R spectrum and TG curves for **4**.

Figure S5. 2D (4,4) topological supramolecular layers generated from the $[Cu_4(bpy)_4(\mu_2\text{-}OH)_2(\mu_3\text{-}OH)_2]^{4+}$ complex cations based on intercationic face-to-face $\pi\cdots\pi$ stacking interactions in **2**.

Figure S6. Hydrogen bonded network of disordered nitrate NO_3^-, benzoate $(C_7H_5O_2)^-$ anions and lattice water molecules in **1**.

Figure S7. Hydrogen bonded network of nitrate NO_3^-, glutarate $(C_5H_6O_4)^{2-}$ anions and lattice water molecules in **2**.

Figure S8. Hydrogen bonded network of glutarate $(C_5H_6O_4)^{2-}$ anions and lattice water molecules in **3**.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Simulated
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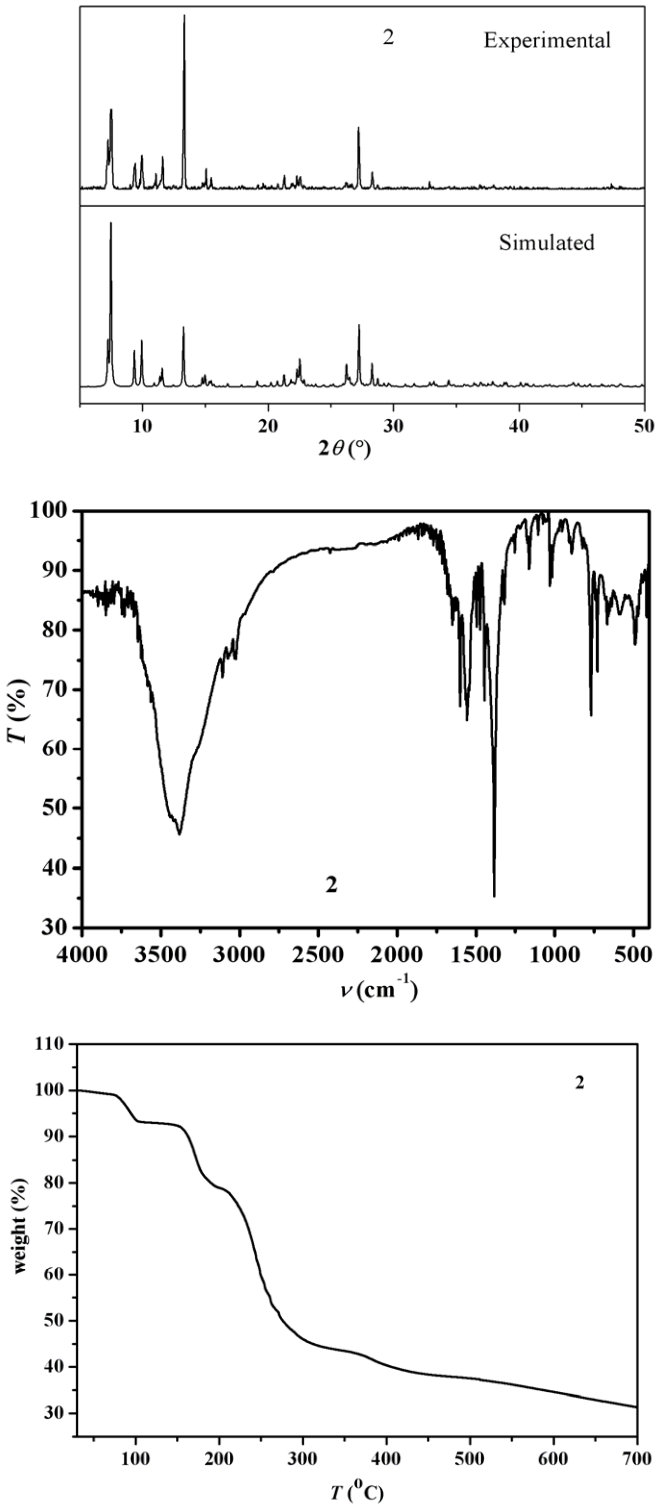
20
30
40
50
2θ (°)
120
100
80
60
40
20
T (%)
1
4000
3500
3000
2500
2000
1500
1000
500
ν (cm-1)
100
80
60
40
20
0
weight (%)
1
100
200
300
400
500
600
700
T (0C)

Figure S1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Experimental
Simulated
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20
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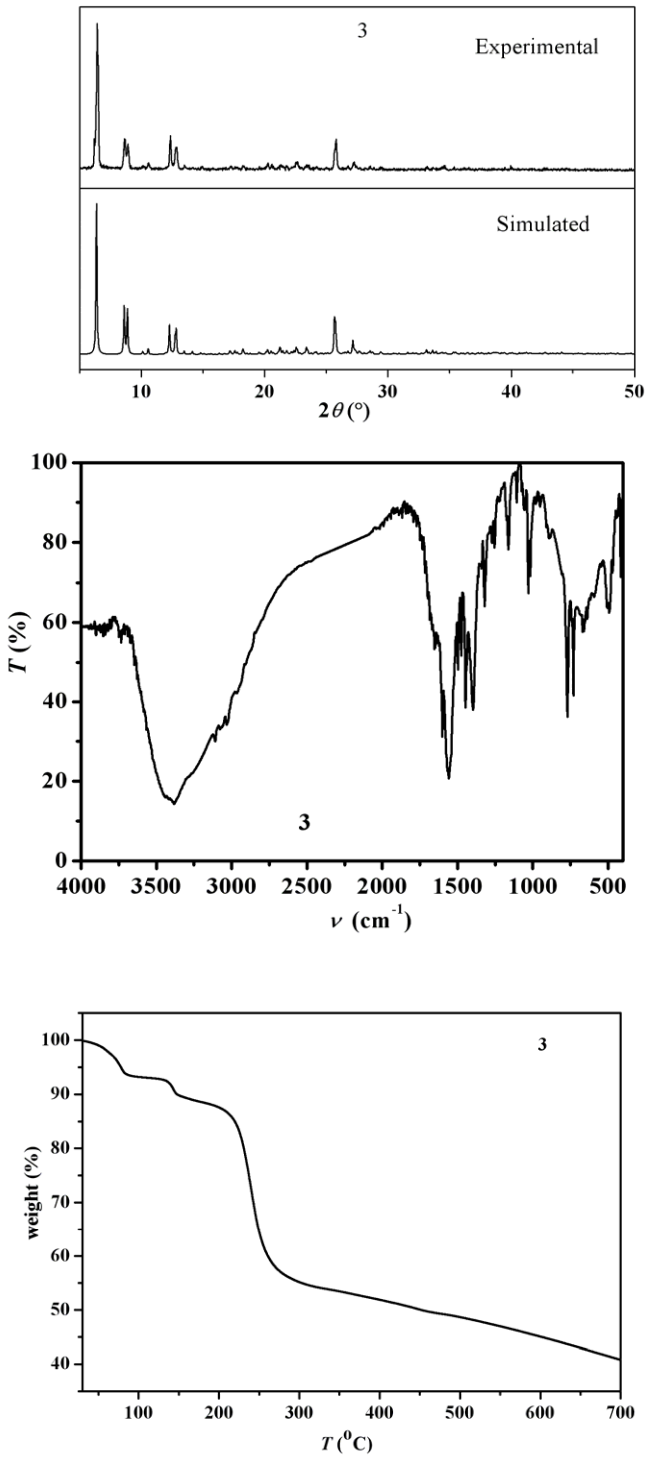
40
50
2θ (°)
100
90
80
70
60
50
40
30
T (%)
2
4000
3500
3000
2500
2000
1500
1000
500
ν (cm-1)
110
100
90
80
70
60
50
40
30
weight (%)
2
100
200
300
400
500
600
700
T (0C)

Figure S2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Experimental
Simulated
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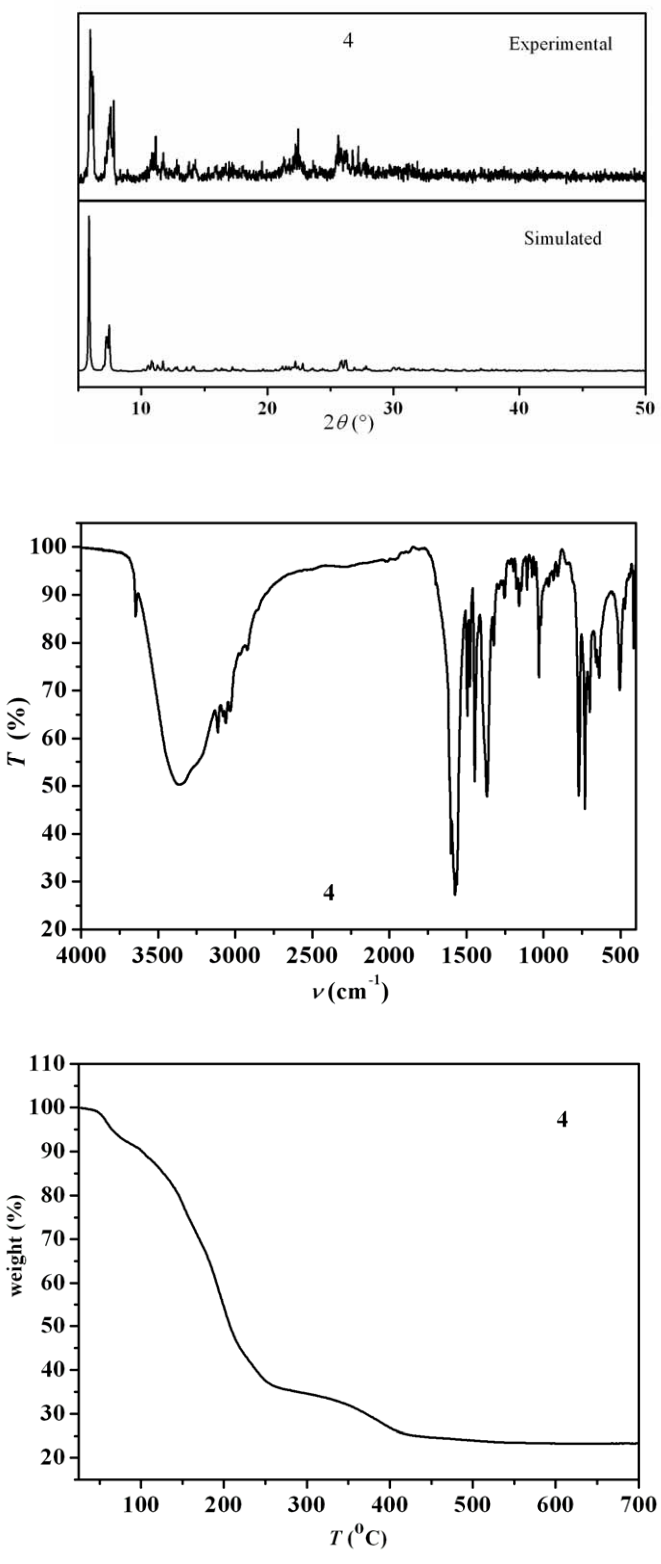
20
30
40
50
2θ (°)
100
80
60
40
20
0
T (%)
3
4000
3500
3000
2500
2000
1500
1000
500
ν (cm-1)
3
100
90
80
70
60
50
40
weight (%)
100
200
300
400
500
600
700
T (0C)

Figure S3


4
Experimental
Simulated
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20
30
40
50
2θ(°)
100
90
80
70
60
50
40
30
20
T (%)
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4000
3500
3000
2500
2000
1500
1000
500
ν(cm-1)
110
100
90
80
70
60
50
40
30
20
weight (%)
4
100
200
300
400
500
600
700
T (0C)

Figure S4

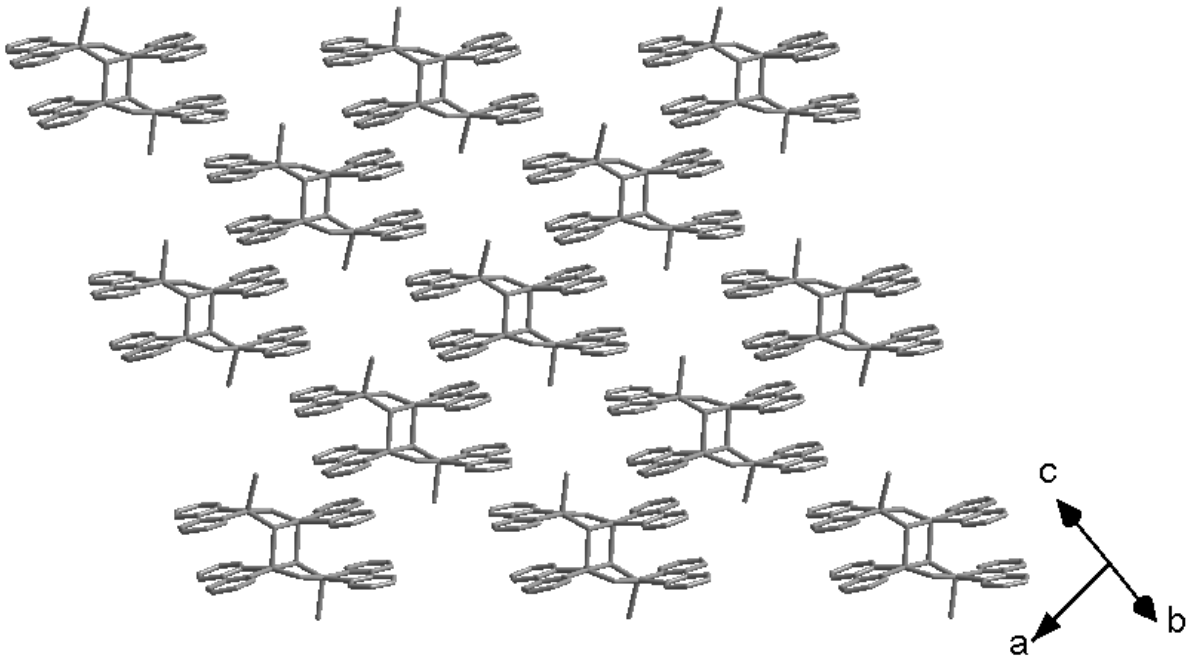

Figure S5

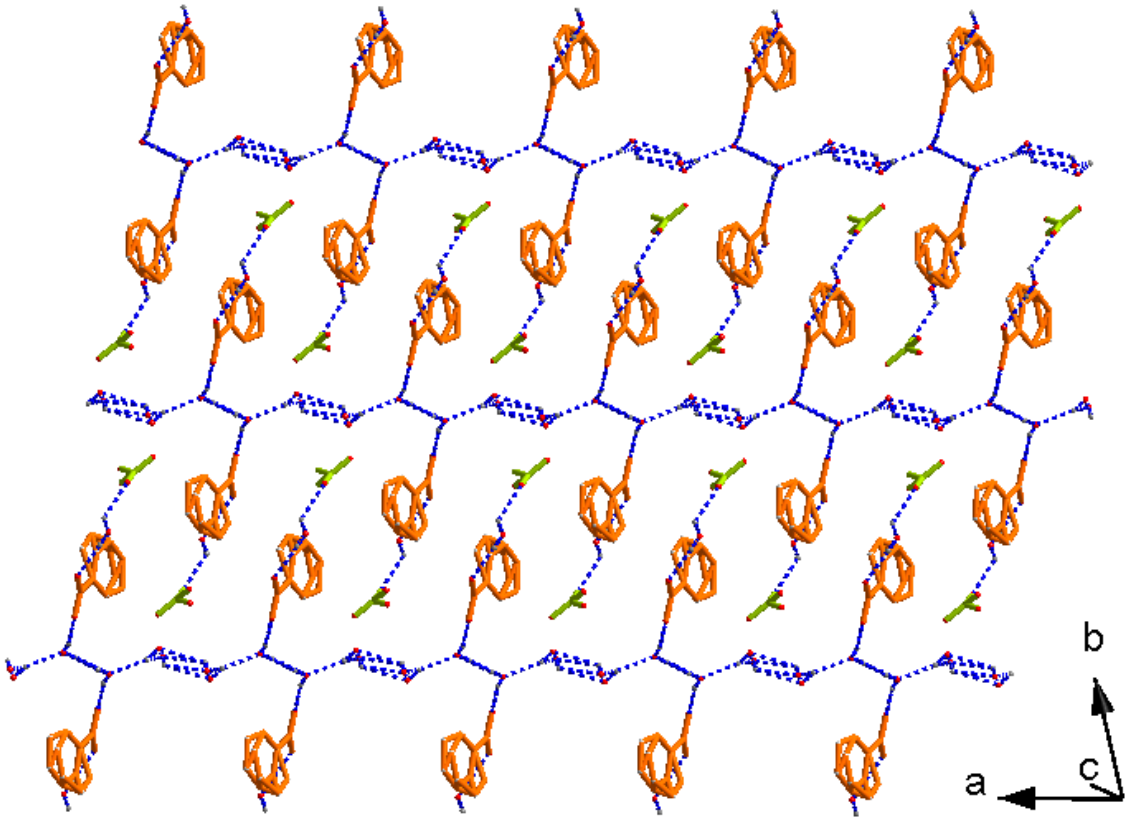

Figure S6

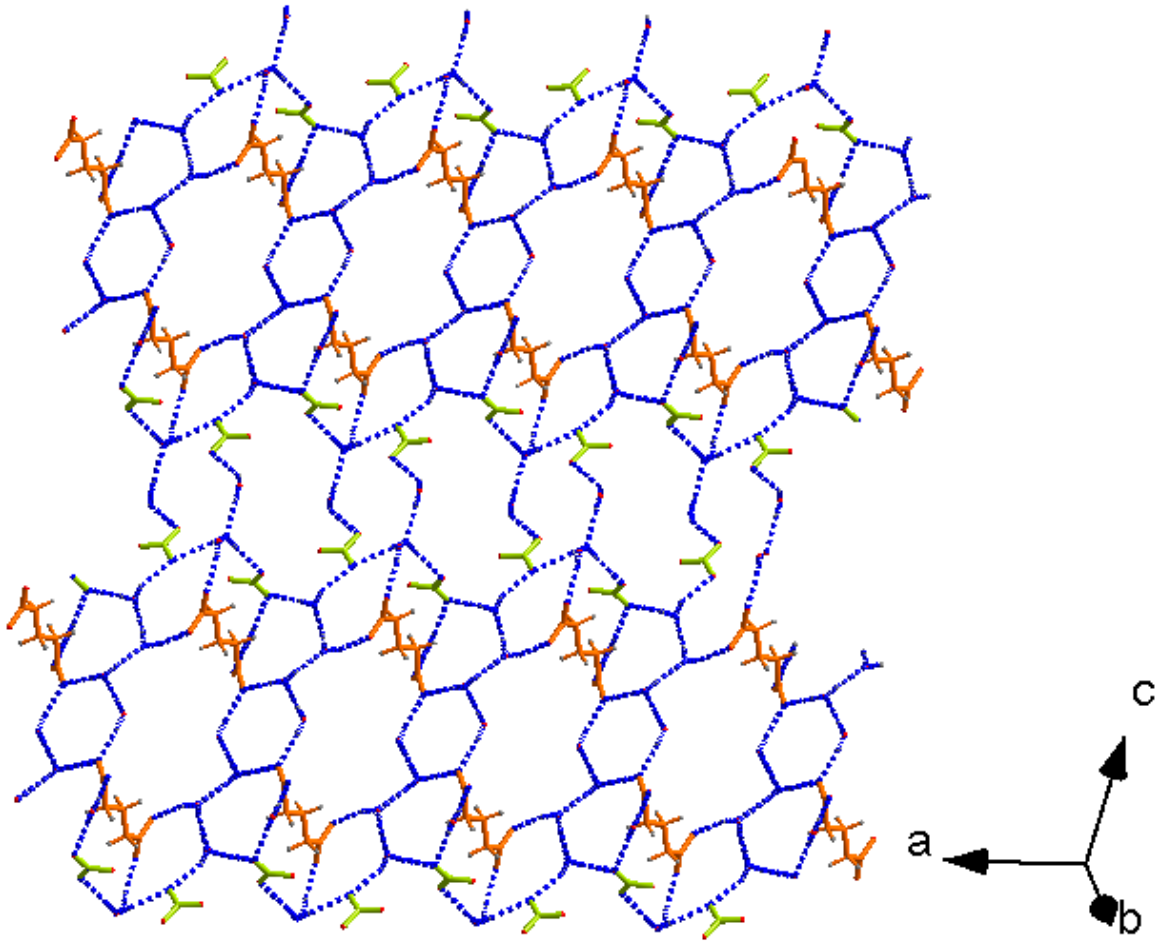

Figure S7

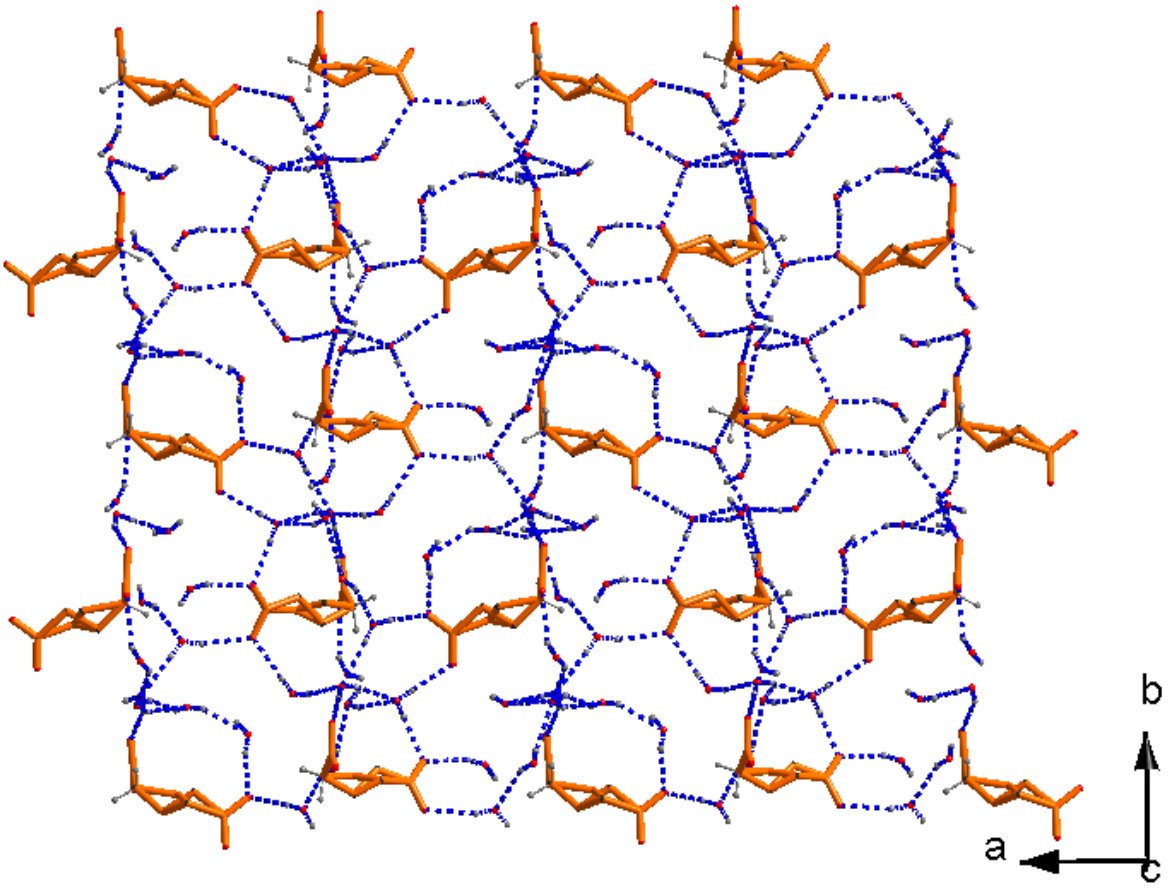

Figure S8