Suplementary Information for

Synthesis and structural characterization of six Cu(II)-based coordination polymers using the thermally tunable 1,2,3,4-cyclobutanetetracarboxylic acid

P. Díaz-Gallifa,[a] O. Fabelo,*[b] J. Pasán,*[a] L. Cañadillas-Delgado,[c] M. A. Ramirez,[d,e] A. G. Gallardo[e] and C. Ruiz-Pérez[a]

Table S1. Selected bond lengths (Angstroms) and angles (Degrees) for **1-6** compounds.

Compound 1					
Cu(1)-O(1)	1.9084(2)	O(1)-Cu(1)-O(1w)	91.820(4)	O(1w)-Cu(1)-O(3)^{I}	91.081(4)
Cu(1)-O(1w)	1.9655(2)	O(1)-Cu(1)-O(2w)	90.479(4)	O(1w)-Cu(1)-O(4)^{II}	104.292(4)
Cu(1)-O(2w)	1.9851(2)	O(1)-Cu(1)-O(4)^{II}	91.623(3)	O(2w)-Cu(1)-O(3)^{I}	86.448(4)
Cu(1)-O(3)^{I}	1.9124(2)	O(1)-Cu(1)-O(3)^{I}	176.894(5)	O(2w)-Cu(1)-O(4)^{II}	88.247(3)
Cu(1)-O(4)^{II}	2.4193(3)	O(1w)-Cu(1)-O(2w)	167.175(5)	O(3)^{I}-Cu(1)-O(4)^{II}	88.737(4)
Compound 2					
Cu(1)-O(3)	1.962(2)	Cu(2)-O(2w)	1.961(3)	Cu(3)-O(1H)	1.923(2)
Cu(1)-O(4w)	1.965(3)	Cu(2)-O(3w)	2.367(3)	Cu(3)-O(1w)	1.9808(4)
Cu(1)-O(3w)	2.501(5)	Cu(2)-O(7)^{III}	1.984(2)	Cu(3)-O(6)^{IV}	1.969(2)
Cu(2)-O(2)	1.956(2)	Cu(3)-O(1)	1.939(2)	Cu(3)-O(8)^{V}	2.342(2)
Cu(2)-O(1H)	1.923(2)				
O(3)-Cu(1)-O(4w)	93.71(11)	O(1H)-Cu(2)-O(7)^{III}	90.93(10)	O(1H)-Cu(3)-O(1w)	174.44(8)
O(3)-Cu(1)-O(4w)^{VI}	86.29(11)	O(2w)-Cu(2)-O(3w)	95.12(14)	O(1H)-Cu(3)- O(6)^{IV}	94.44(10)
O(2)-Cu(2)-O(1H)	94.56(10)	O(2w)-Cu(2)-O(7)^{III}	90.11(11)	O(1H)-Cu(3)- O(8)^{V}	86.97(9)
O(2)-Cu(2)-O(2w)	86.07(11)	O(3w)-Cu(2)- O(7)^{III}	83.90(12)	O(1w)-Cu(3)- O(6)^{IV}	90.48(7)
O(2)-Cu(2)-O(3w)	88.30(12)	O(1)-Cu(3)- O(1H)	90.61(11)	O(1w)-Cu(3)- O(8)^{V}	90.41(6)
O(2)-Cu(2)-O(7)^{III}	170.98(10)	O(1)-Cu(3)- O(1w)	85.05(7)	O(6)^{IV}-Cu(3)- O(8)^{V}	90.36(9)
O(1H)-Cu(2)-O(3w)	97.28(13)	O(1)-Cu(3)- O(6)^{IV}	168.06(10)		
O(9)-Cu(2)-O(2w)	167.60(11)	O(1)-Cu(3)- O(8)^{V}	100.71(10)		
Compound 3					
Cu(1)-O(5)	1.96(2)	Cu(1)-O(6)^{IX}	1.99(3)	Cu(3)-O(2)	1.95(3)
Cu(1)-O(1w)	2.13(2)	Cu(2)-O(1)	1.96(3)	Cu(3)-O(1H)^{X}	1.93(3)
Cu(1)-O(3)^{VII}	1.99(3)	Cu(2)-O(1H)	1.93(3)	Cu(3)-O(2w)^{X}	2.47(4)
Cu(1)-O(4)^{VIII}	1.96(3)	Cu(2)-O(2w)	2.50(5)		
O(5)-Cu(1)-O(1w)	91.1(11)	O(3)^{VII}-Cu(1)-O(4)^{IX}	168.4(12)	O(2)-Cu(3)-O(1H)^{X}	91.8(12)
O(5)-Cu(1)-O(3)^{VII}	86.6(12)	O(4)^{VIII}-Cu(1)-O(6)^{IX}	88.3(14)	O(2)^{XI}-Cu(3)-O(1H)^{XI}	88.2(12)
O(5)-Cu(1)-O(4)^{VIII}	90.6(13)	O(1)-Cu(2)-O(1H)	88.5(11)	O(2)-Cu(3)-O(2w)^{XI}	86.2(13)
O(5)-Cu(1)-O(6)^{IX}	168.3(12)	O(1)-Cu(2)-O(2w)	86.0(12)	O(2)-Cu(3)-O(2w)^{X}	93.8(13)
O(1w)-Cu(1)-O(4)^{VIII}	94.4(12)	O(1)-Cu(2)-O(2w)^{X}	94.0(12)	O(1H)^{X}-Cu(3)-O(2w)^{X}	82.4(12)
O(1w)-Cu(1)-O(3)^{VII}	97.1(12)	O(1)-Cu(2)-O(1H)^{X}	91.5(11)	O(2)^{XII}-Cu(3)-O(1H)^{XI}	97.6(12)
O(1w)-Cu(1)-O(6)^{IX}	98.6(11)	O(1H)-Cu(2)-O(2w)	81.6(12)		
O(3)^{VII}-Cu(1)-O(6)^{IX}	92.2(13)	O(2w)-Cu(2)-O(1H)^{X}	98.4(12)		
Compound 4					
Cu(1)-O(2)	1.954(3)	Cu(1)-O(2w)	1.983(4)	Cu(1)-O(2)^{XIV}	2.267(3)
Cu(1)-O(1w)	1.960(4)	Cu(1)-O(4)^{XIII}	1.918(3)		
O(2)-Cu(1)-O(1w)	87.98(15)	O(1w)-Cu(1)-O(2w)	167.1(2)	O(2w)-Cu(1)-O(2)^{XIV}	99.1(2)
O(2)-Cu(1)-O(2w)	93.3(2)	O(1w)-Cu(1)-O(4)^{XIII}	87.09(15)	O(4)^{XV}-Cu(1)-O(2)^{XIV}	107.45(12)
O(2)-Cu(1)-O(4)^{XIII}	173.95(14)	O(1w)-Cu(1)-O(2)^{XIV}	93.7(2)		
O(2)-Cu(1)-O(2)^{XIV}	76.36(14)	O(2w)-Cu(1)-O(4)^{XIII}	90.8(2)		
Compound 5					
Cu(1)-O(2)	1.906(2)	Cu(1)-O(1w)	1.953(2)		
O(2)-Cu(1)-O(1w)	91.56(8)	O(2)-Cu(1)-O(1w)^{XV}	88.44(8)		
Compound 6					

Cu(1)-O(2)	1.975(4)	Cu(2)-O(10)	1.943(4)	Cu(3)-O(15)^{XVIII}	1.949(4)
Cu(1)-O(10)	2.238(4)	Cu(2)-O(5)^{XVII}	2.008(4)	Cu(4)-O(4)	2.426(4)
Cu(1)-O(11)	1.967(4)	Cu(2)-O(16)^{XVIII}	1.948(4)	Cu(4)-O(6)	1.996(4)
Cu(1)-O(2w)	1.951(5)	Cu(3)-O(3)	1.963(4)	Cu(4)-O(1w)	1.965(4)
Cu(1)-O(14)^{XVI}	1.948(4)	Cu(3)-O(6)^{XVII}	2.409(4)	Cu(4)-O(7)^{XXI}	1.954(4)
Cu(2)-O(2)	2.165(4)	Cu(3)-O(8)^{XIX}	1.955(4)	Cu(4)-O(12)^{XXII}	2.453(4)
Cu(2)-O(3)	1.971(4)	Cu(3)-O(12)^{XX}	1.938(4)	Cu(4)-O(13)^{XXII}	1.989(4)
O(2)-Cu(1)-O(10)	74.4(15)	O(3)-Cu(2)-O(5)^{XVII}	89.2(2)	O(4)-Cu(4)-O(6)	98.9(2)
O(2)-Cu(1)-O(11)	176.9(2)	O(3)-Cu(2)-O(16)^{XVIII}	91.2(2)	O(4)-Cu(4)-O(1w)	86.9(2)
O(2)-Cu(1)-O(2w)	88.6(2)	O(10)-Cu(2)-O(5)^{XVII}	92.4(2)	O(4)-Cu(4)-O(7)^{XXIII}	97.0(2)
O(2)-Cu(1)-O(14)^{XVI}	88.8(2)	O(10)-Cu(2)- O(16)^{XVIII}	89.2(2)	O(4)-Cu(4)-O(12)^{XXII}	174.12(14)
O(10)-Cu(1)-O(11)	102.8(2)	O(5)^{XVII}-Cu(2)-O(16)^{XVIII}	140.4(2)	O(4)-Cu(4)-O(13)^{XXII}	82.1(2)
O(10)-Cu(1)-O(2w)	97.0(2)	O(3)-Cu(3)-O(6)^{XVII}	92.62(14)	O(6)-Cu(4)-O(1w)	89.0(2)
O(10)-Cu(1)-O(14)^{XVI}	97.8(2)	O(3)-Cu(3)-O(8)^{XIX}	91.5(2)	O(6)-Cu(4)-O(7)^{XXIII}	88.4(2)
O(11)-Cu(1)-O(2w)	90.4(2)	O(3)-Cu(3)-O(12)^{XX}	178.5(2)	O(6)-Cu(4)-O(12)^{XXII}	85.4(2)
O(11)-Cu(1)-O(14)^{XVI}	93.0(2)	O(3)-Cu(3)-O(15)^{XX}	90.4(2)	O(6)-Cu(4)-O(13)^{XXII}	178.8(2)
O(14)$^{a-7}$-Cu(1)-O(2w)	163.6(2)	O(6)^{XVII}-Cu(3)-O(8)^{XIX}	83.2(2)	O(1w)-Cu(4)-O(7)^{XXIII}	175.6(2)
O(2)-Cu(2)-O(3)	100.27(14)	O(6)^{XVII}-Cu(3)-O(12)^{XX}	87.86(14)	O(1w)-Cu(4)-O(12)^{XXII}	89.2(2)
O(2)-Cu(2)-O(10)	76.8(2)	O(6)^{XVII}-Cu(3)-O(15)^{XVIII}	98.4(2)	O(1w)-Cu(4)-O(13)^{XXII}	91.7(2)
O(2)-Cu(2)-O(5)^{XVII}	101.7(2)	O(8)^{XIX}- Cu(3)-O(12)^{XX}	90.0(2)	O(7)^{XXIII}-Cu(4)-O(12)^{XXII}	87.1(2)
O(2)-Cu(2)-O(16)^{XVIII}	117.2(2)	O(8)^{XIX}- Cu(3)-O(15)^{XVIII}	177.5(2)	O(7)^{XXIII}-Cu(4)-O(13)^{XXII}	90.9(2)
O(3)-Cu(2)-O(10)	176.9(2)	O(12)^{XX}-Cu(3)-O(15)^{XVIII}	88.2(2)	O(12)^{XXII}-Cu(4)-O(13)^{XXII}	93.6(2)

Symmetry codes: (I) = -1/4+*y*, 5/4-*x*, -1/4-*z*; (II) = -1/4+*y*, 5/4-*x*, -3/4-*z*; (III)= *x*, -1+*y*, *z*; (IV) = -1+*x*, -1+*y*, *z*; (V) = -*x*, 1-*y*, 1-*z*; (VI) = -*x*, -*y*, -*z*; (VII) = 1+*x*, *y*, *z*; (VIII) = 2-*x*, 1-*y*, -*z*; (IX) = 3-*x*, 1-*y*, -*z*; (X) = 2-*x*, -*y*, 1-*z*; (XI) = -1+*x*, *y*, *z*; (XII) = 1-*x*, -*y*, 1-*z*; (XIII) = -1/2+*x*, 1/2+*y*, -*z*; (XIV) = -*x*, 1-*y*, -*z*; (XV)= -*x*, 1-*y*, -*z*; (XVI) = -1+*x*, *y*, *z*; (XVII) = 1+*x*, *y*, *z*; (XVIII) = 2-*x*, 2-*y*, 1-*z*; (XIX) = 1-*x*, 2-*y*, -*z*; (XX) = *x*, 1+*y*, *z*; (XXI) = -*x*, 2-*y*, *z*; (XXII) = -1+*x*, 1+*y*, *z*; (XXIII) = -*x*, 2-*y*, -*z*.

Table S2. Relevant torsion angles (°)

	Torsion angle	*(1)*	*(2)*	*(3)*	*(4)*
1	C(1)-C(3)-C(1)^{I}-C(3)^{I}	0.0	0.0	0.0	0.0
2	C(1)-C(3)-C(5)-C(7)	-11.906(3)	11.777(2)	-11.695(2)	12.016(3)
3	C(1)-C(3)-C(5)-C(7)	16.18(2)	-16.38(2)	16.14(2)	-15.99(2)
4	C(1)-C(3)-C(1)^{II}-C(3)^{II}	-7.885(2)	7.764(2)	7.764(2)	-7.885(2)
5	C(1)-C(1)^{III}-C(1)^{IV}-C(1)^{V}	-16.936(1)	-16.936(1)	-16.936(1)	-16.936(1)
6	C(1)-C(3)-C(5)-C(7)	13.381(7)	-13.496(7)	13.561(7)	-13.544(7)
6	C(9)-C(11)-C(13)-C(15)	-16.976(7)	16.873(7)	-16.966(7)	16.827(7)

Symmetry codes: (I) = 3/2-*x*, 3/2-*y*, -1/2-*z*; (II) = 1/2-*x*, 1/2-*y*, *z*; (III) = 3/4-*y*, 3/4+*x*, 3/4-*z*; (IV) = -*x*, 3/2+*y*, *z*; (V) = -3/4+*y*, 3/4-*x*, 3/4-*z*

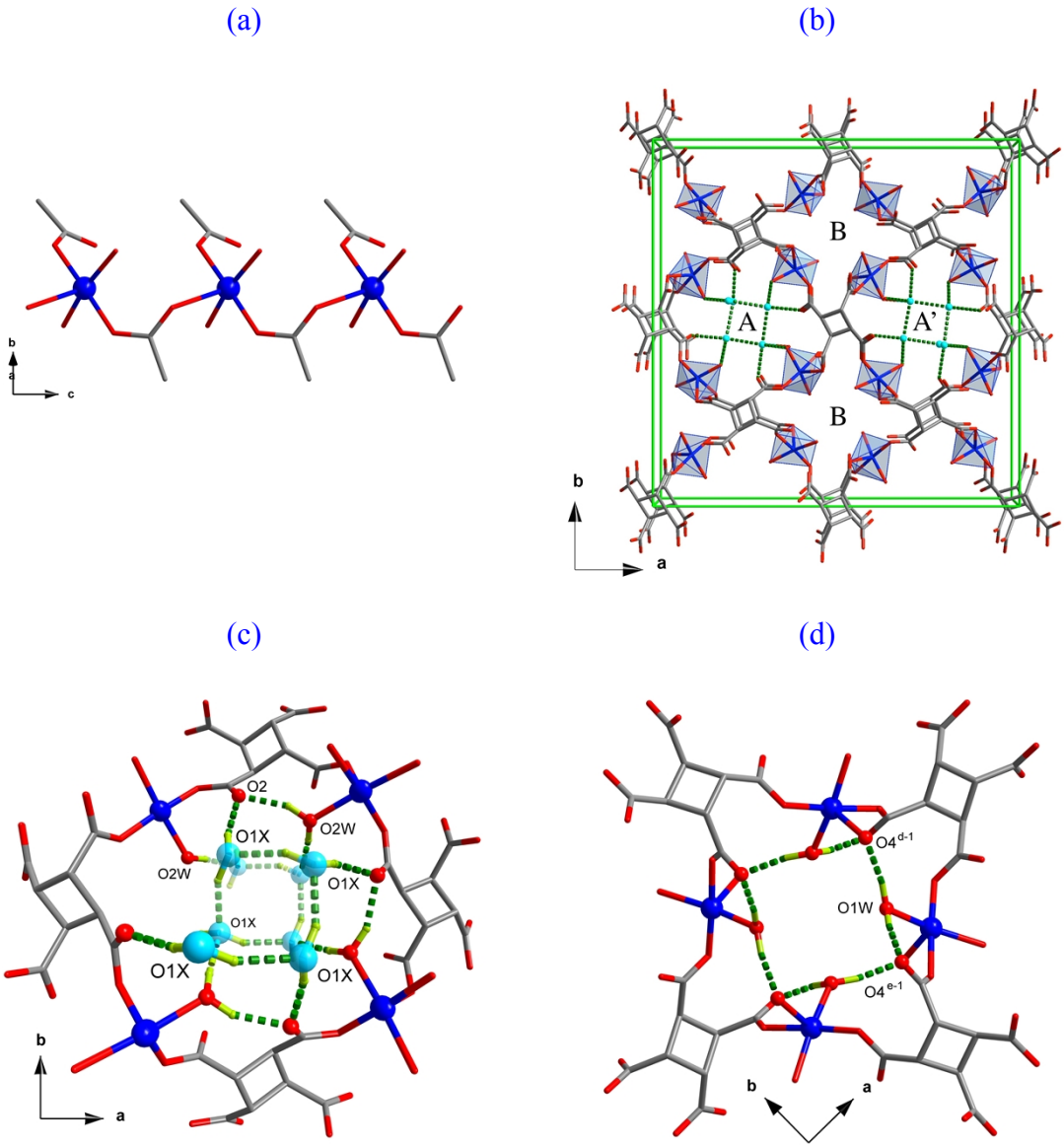
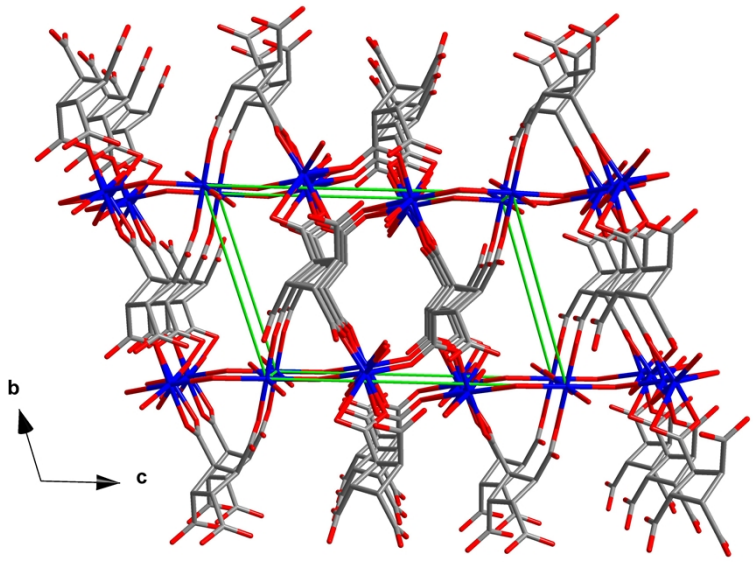


Figure S1. (a) A view of the carboxylate-bridged Cu(II) chains running along the *c*-axis. (b) View of a fragment of the network of **1** along the *c*-axis showing the two types of channels, A and B. (c and d) Central projection along the *c*-axis of the A (c) and B (d) cavities present on compound **1** with the atom labels of the atoms involved on the H-bonds. The crystallization water molecules and the H-bonds are represented as light blue balls and dashed green lines, respectively.

(a)



(b)

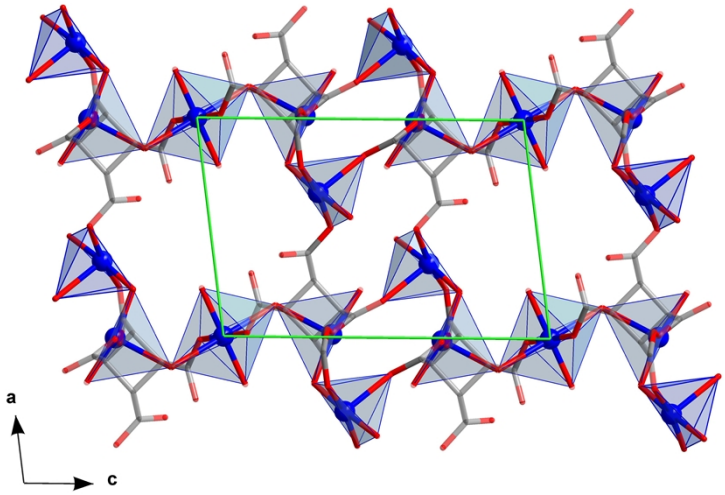


Figure S2. (a) Central projection of a fragment of crystal packing of **2** along the *a*-axis. (b) Fragment of *ac* layer along the *b* axis.

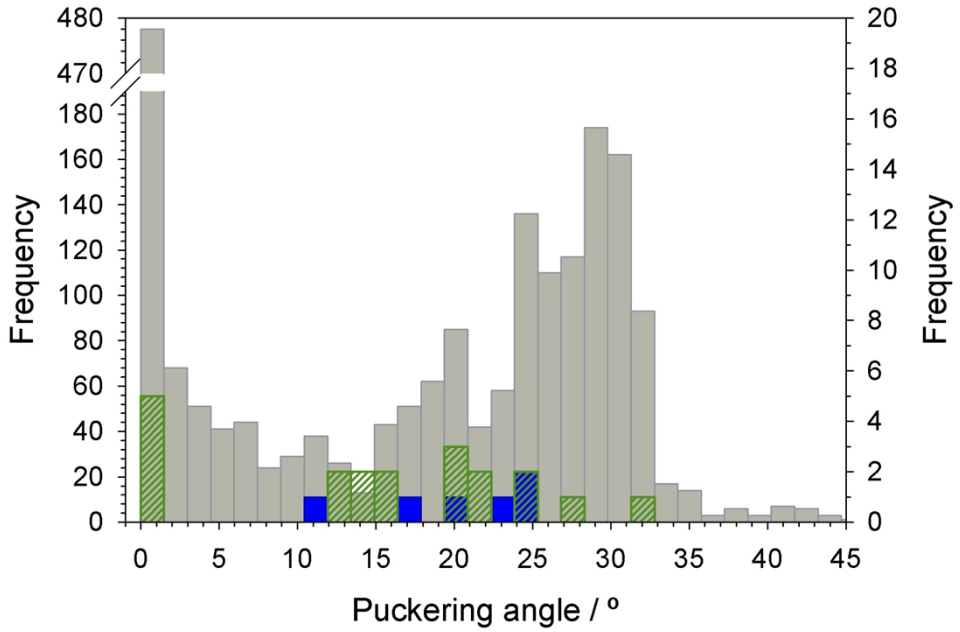


Figure S3: Distribution of the puckering angles reported in CSD for cyclobutane ring and the 1,2,3,4-cyclobutanetetracarboxyliate ligand-containing structures, represented as grey and green bars respectively, together with the angles presented in this work (blue bars). Frequency axis of grey bars are on the left side, while that of blue and green bars is on the right side.

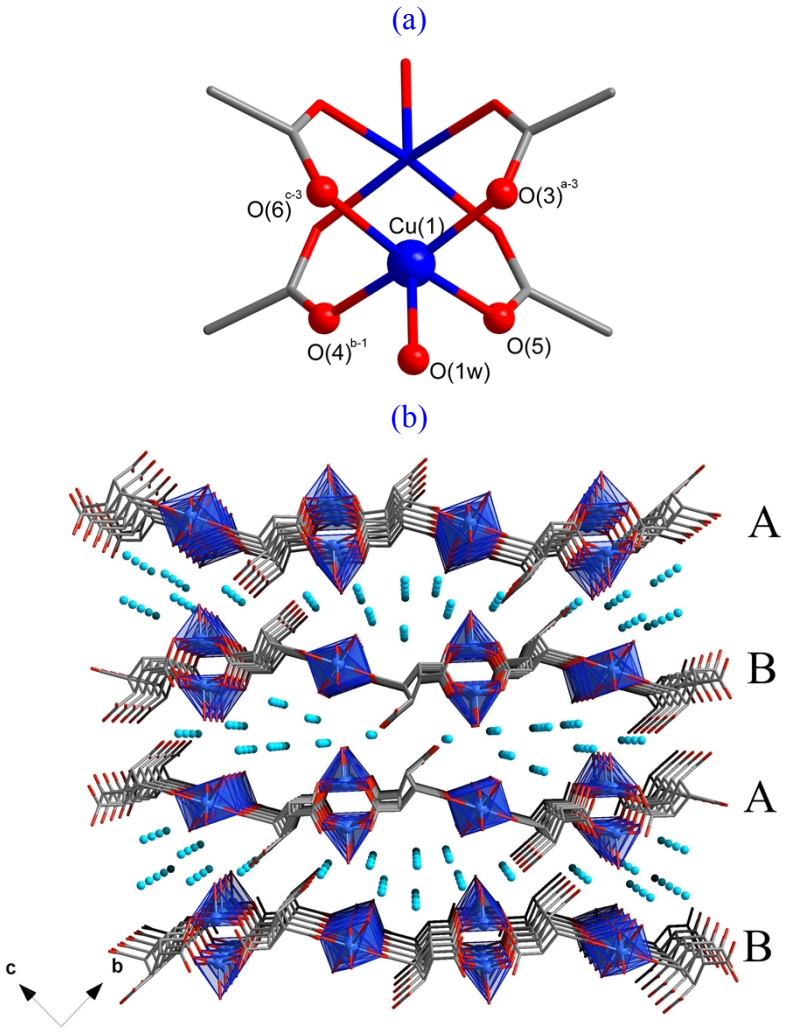


Figure S4: (a) View of the carboxylate di-copper paddle wheel units of compound **3.** (b) Projection along the *a* axis of the 3D supramolecular network with the crystallization water molecules represented as light blue balls. For sake of the clarity the hydrogen atoms are omitted.

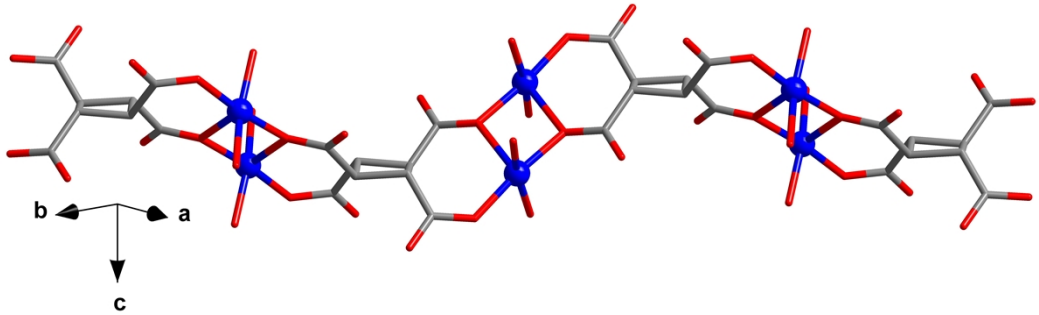


Figure S5: View of a fragment of the corrugated $[Cu_2(cbut)H_2O)_2]_n$ chain of **4** running

along the [1 -1 0] direction**.** The hydrogen atoms were omitted for clarity.

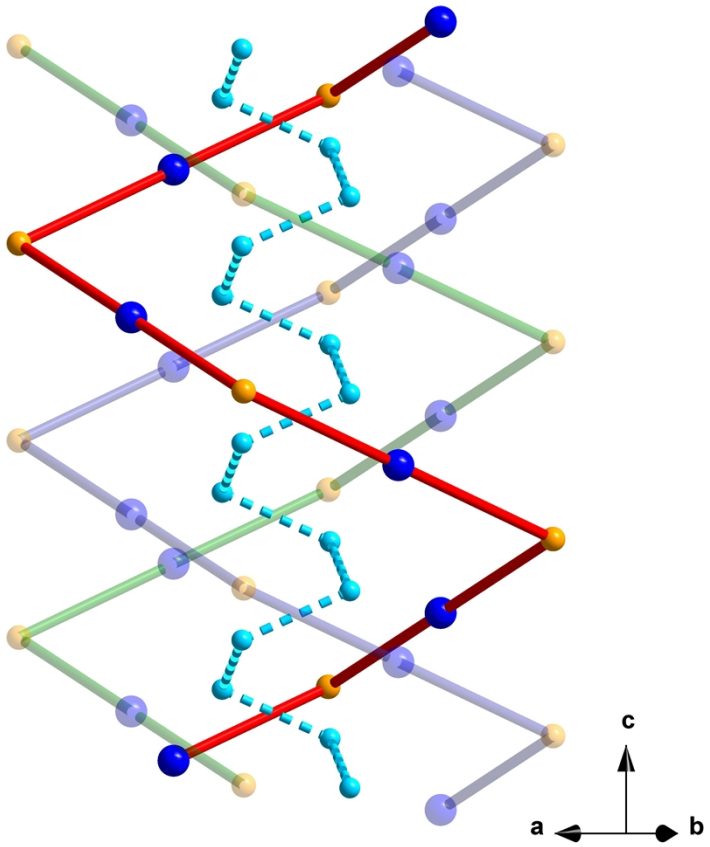


Figure S6: Schematic representation downs the *a* axis showing the opposite handedness between the molecular helix (counter-clockwise outer helix) and the helical water chains (clockwise inner helix) of the compound **5**. The molecular helix is represented as yellow (*ttt*-cbut) and blue balls (copper atoms) while the light blue balls and the dashed line represents the helical water chain. For sake of clarity transparent mode has been used to represent two of the three interpenetrated networks.

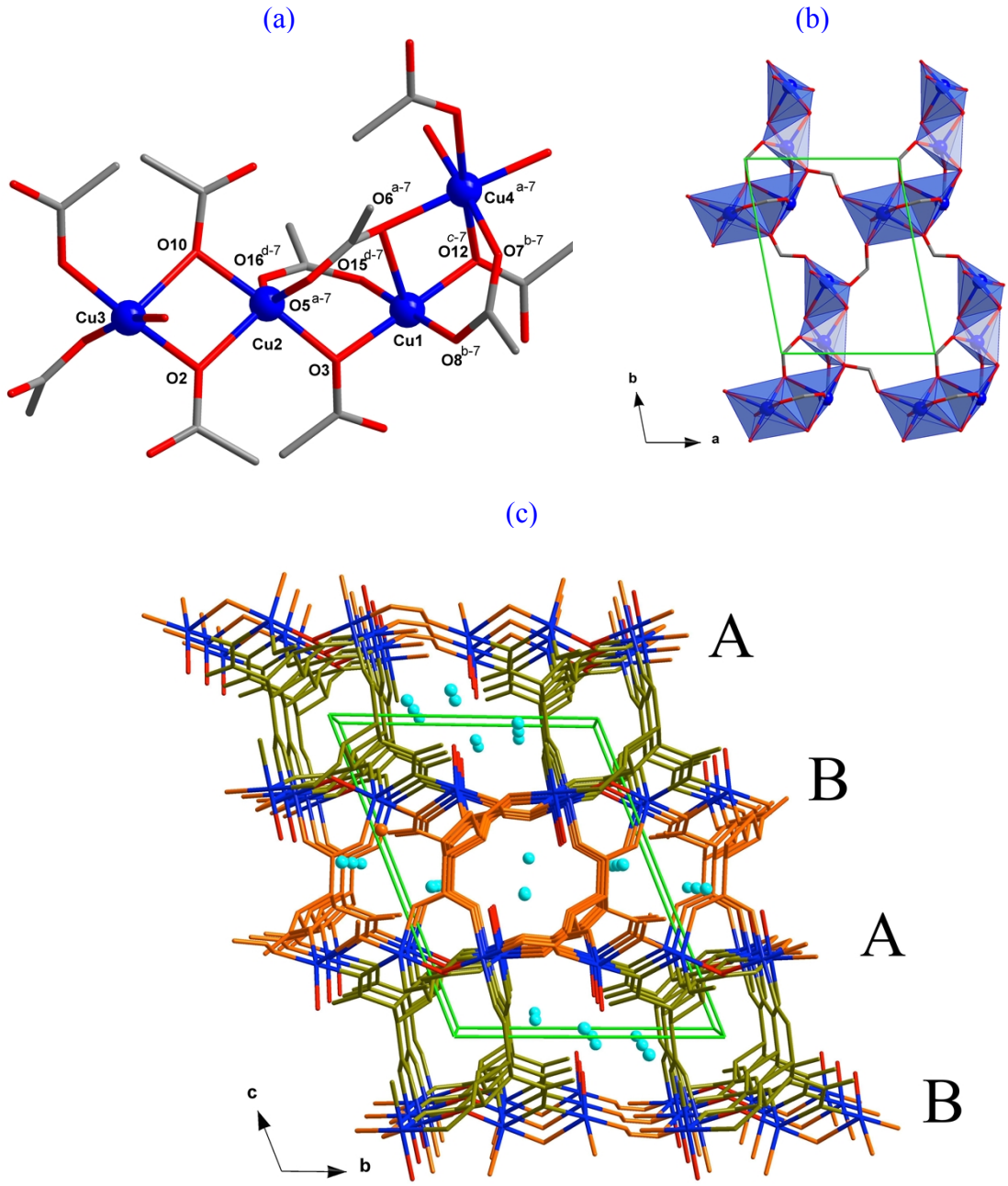


Figure S7: (a) View of the secondary building unit and the bridges involved in **6**. (b) Fragment of the organic-inorganic *ab* layers along the *c* axis. (c) Portion of the 3D structure showing the alternated *ttt*-cbut-a (orange sticks) and *ttt*-cbut-b (green sticks) pillared layers. For sake of clarity the hydrogen atoms have been omitted.

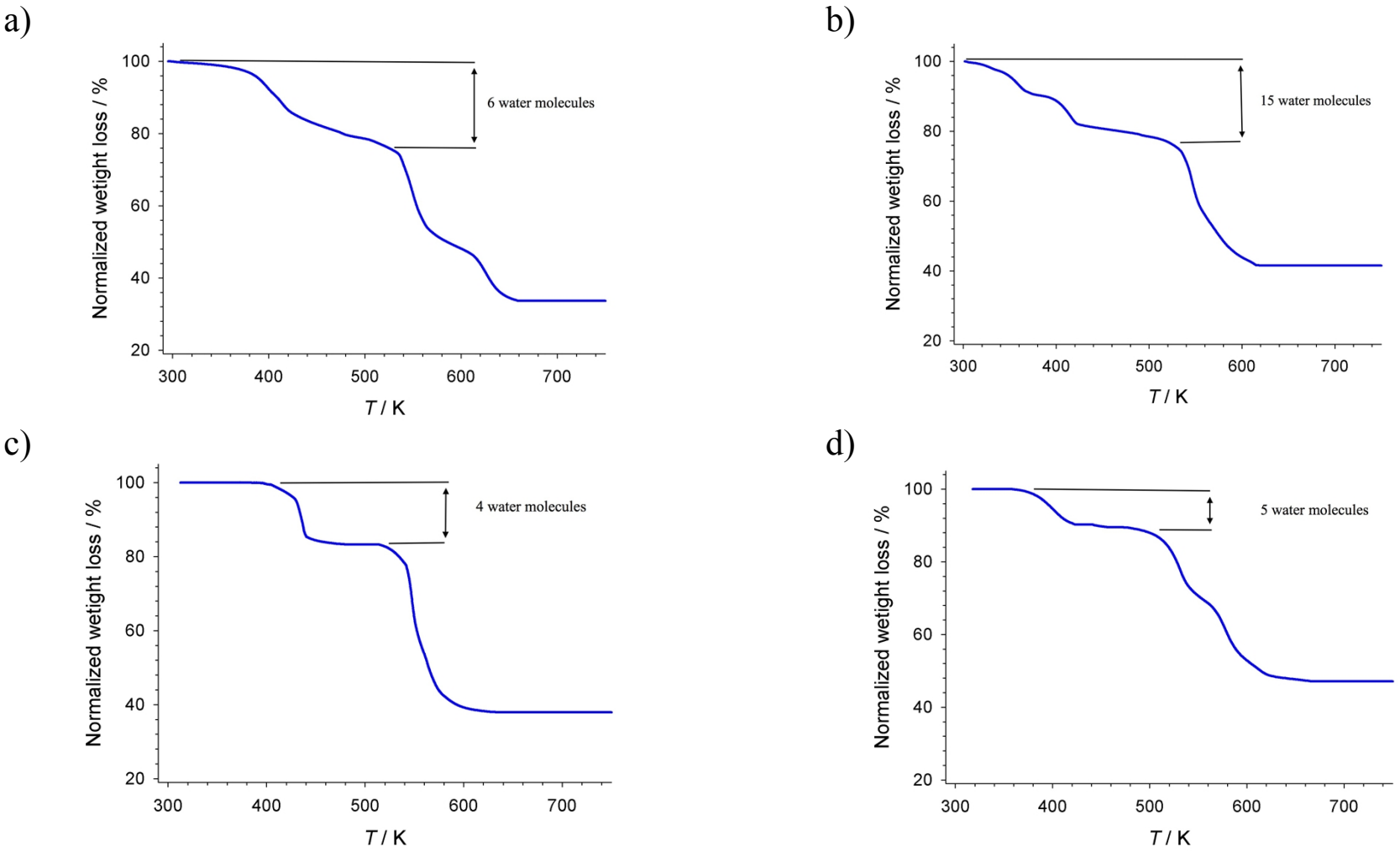
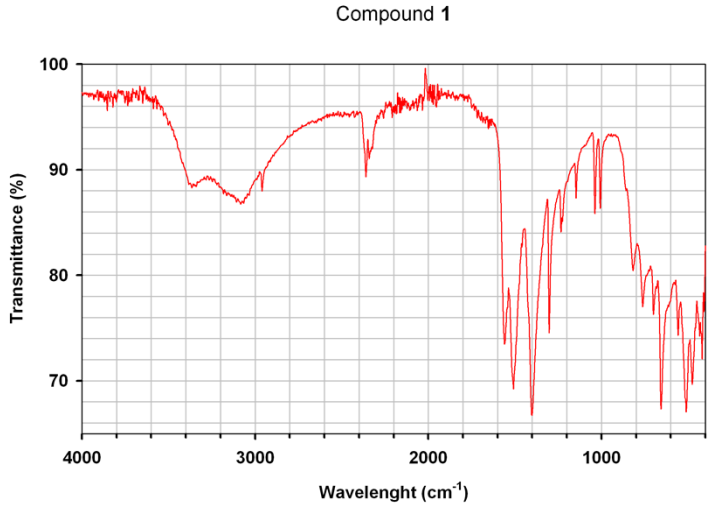
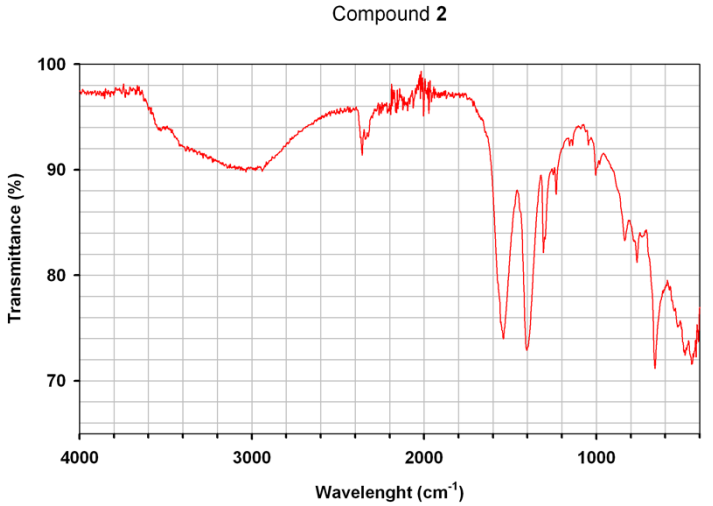


Figure S8: TGA measurements of compounds **1**, **2**, **4** and **6** [a), b), c) and d), respectively], with detail of the loss of coordinated and uncoordinated water molecules.

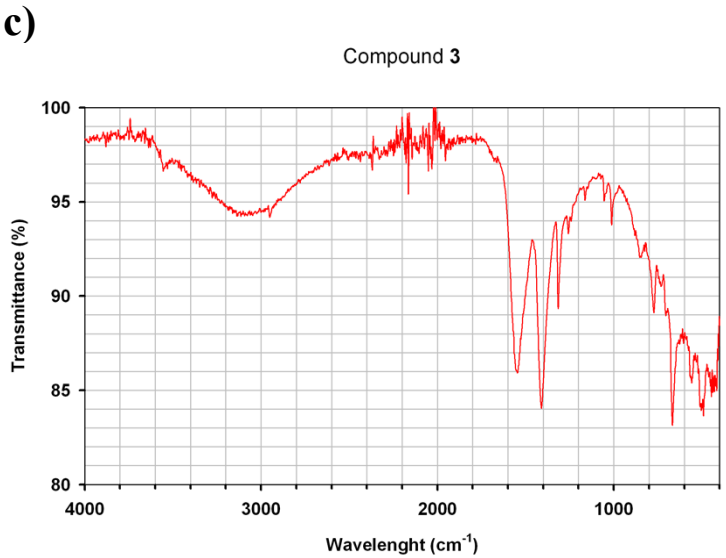
a)


Compound 1
Transmittance (%)
100
90
80
70
4000
3000
2000
1000
Wavelenght (cm-1)

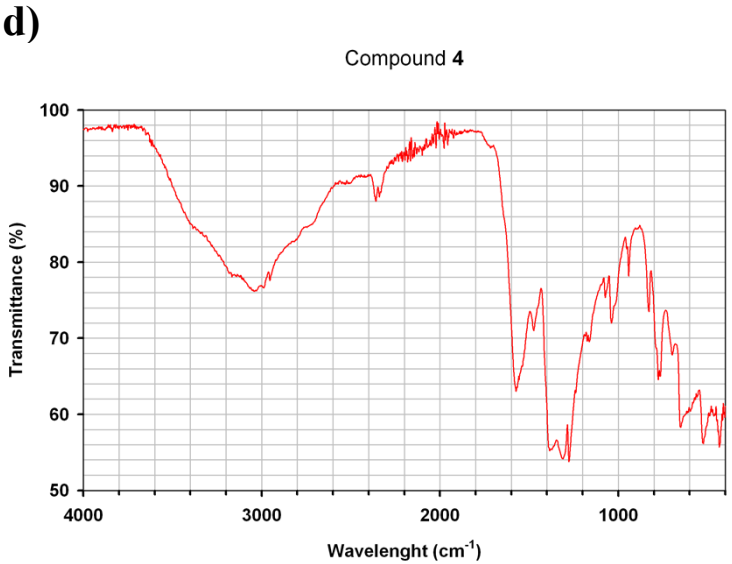
b)


Compound 2
Transmittance (%)
100
90
80
70
4000
3000
2000
1000
Wavelenght (cm-1)

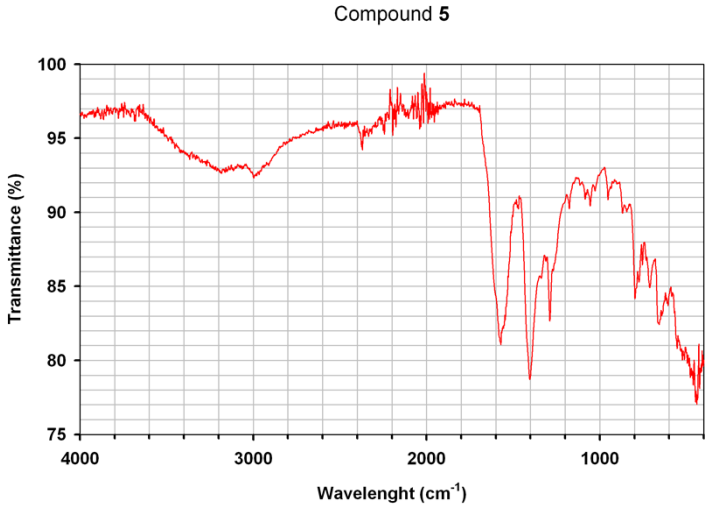
c)


Compound 3
Transmittance (%)
100
95
90
85
80
4000
3000
2000
1000
Wavelenght (cm-1)

d)


Compound 4
Transmittance (%)
100
90
80
70
60
50
4000
3000
2000
1000
Wavelenght (cm-1)

e)



f)

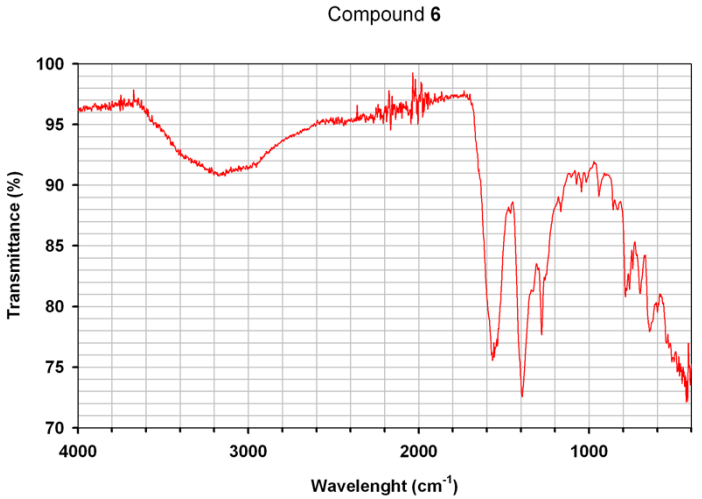
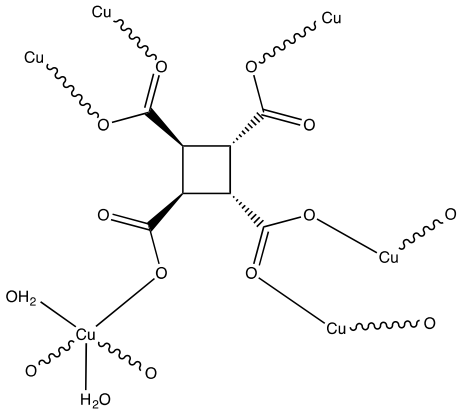


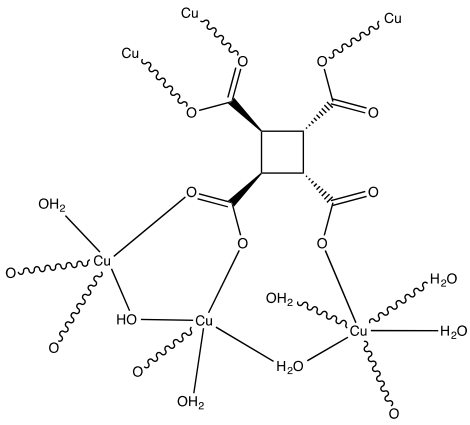
Figure S9: IR measurements of compounds **1- 6** [a) - f), respectively].

Scheme S1: Structural representation of formulae of **1-6** compounds [a)-f), respectively].

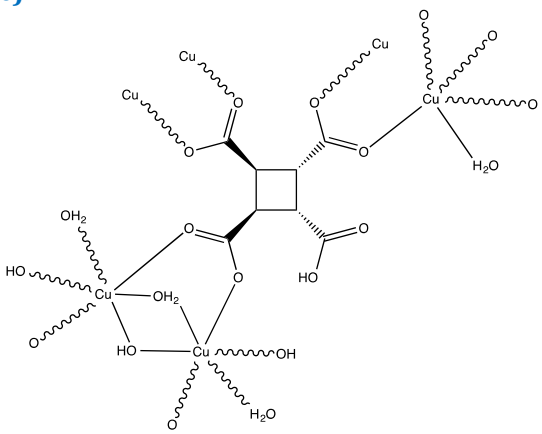
a)



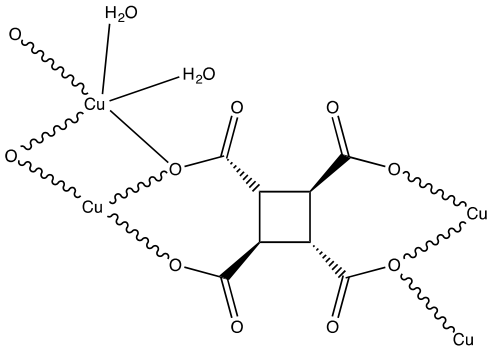
b)



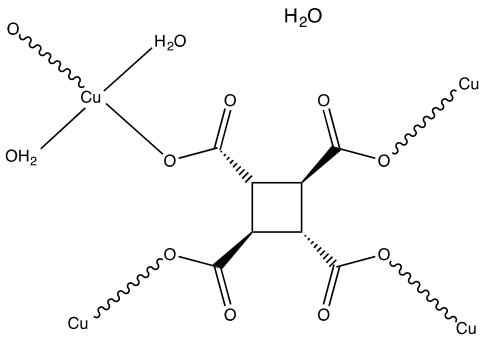
c)



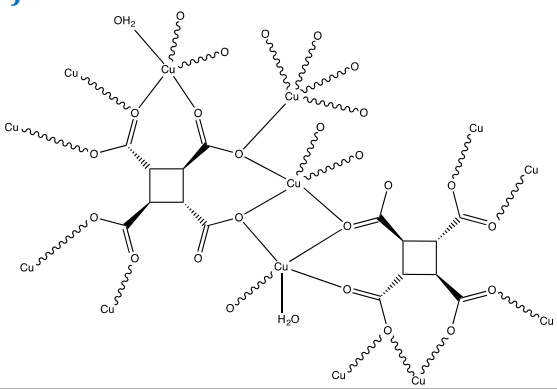
d)



e)



f)



Scheme S2: Coordination modes of the known examples of CPs involving the cbut ligand with at least a metal-ligand coordination bond.