Supplementary Information

for

Tailor-made copper(II) coordination polymers based on the C3 symmetric methanetriacetate as a ligand

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Table S1. Selected bond distances (Å) and angles (°) for complexes **1**-**3**

		1			
Cu(1)–N(1)	2.211(2)	O(2)–Cu(1)–N(2)	94.05(9)	N(6)–Cu(2)–N(8)	95.07(11)
Cu(1)–N(2)	1.995(2)	O(2)–Cu(1)–N(4)	93.17(10)	O(3)–Cu(2)–N(7)	95.25(11)
Cu(1)–N(3)	2.049(2)	N(2)–Cu(1)–N(4)	172.78(10)	N(5)–Cu(2)–N(7)	108.31(12)
Cu(1)–N(4)	2.006(2)	O(2)–Cu(1)–N(3)	159.91(9)	N(6)–Cu(2)–N(7)	99.75(12)
Cu(1)–O(2)	1.976(2)	N(2)–Cu(1)–N(3)	92.59(9)	N(8)–Cu(2)–N(7)	77.55(13
Cu(2)–N(5)	1.998(3)	N(4)–Cu(1)–N(3)	80.58(10)	N(12)–Cu(3)–N(9)	176.08(13)
Cu(2)–N(6)	2.016(3)	O(2)–Cu(1)–N(1)	101.95(9)	N(12)–Cu(3)–O(6)	94.95(11)
Cu(2)–N(7)	2.203(3)	N(2)–Cu(1)–N(1)	78.49(9)	N(9)–Cu(3)–O(6)	88.04(11)
Cu(2)–N(8)	2.034(3)	N(4)–Cu(1)–N(1)	100.03(10)	N(12)–Cu(3)–N(11)	80.74(13)
Cu(2)–O(3)	1.952(2)	N(3)–Cu(1)–N(1)	97.94(9)	N(9)–Cu(3)–N(11)	97.34(13)
Cu(3)–N(9)	2.013(3)	O(3)–Cu(2)–N(5)	93.59(11)	O(6)–Cu(3)–N(11)	159.24(11)
Cu(3)–N(10)	2.179(3)	O(3)–Cu(2)–N(6)	164.97(10)	N(12)–Cu(3)–N(10)	98.91(11)
Cu(3)–N(11)	2.025(3)	N(5)–Cu(2)–N(6)	80.81(12)	N(9)–Cu(3)–N(10)	78.10(12)
Cu(3)–N(12)	1.983(3)	O(3)–Cu(2)–N(8)	89.08(11)	O(6)–Cu(3)–N(10)	98.53(10)
Cu(3)–O(6)	2.024(2)	N(5)–Cu(2)–N(8)	173.26(12)	N(11)–Cu(3)–N(10)	102.20(11)
		2[a]			
Cu(1)–O(2)	1.9557(17)	O(2)–Cu(1)–N(1)	94.44(8)	O(4)–Cu(2)–O(6a)	89.47(8)
Cu(1)–N(1)	1.982(2)	O(2)–Cu(1)–N(4)	90.69(8)	O(4) –Cu(2)–N(5)	94.14(8)
Cu(1)–N(4)	1.995(2)	N(1)–Cu(1)–N(4)	174.67(8)	O(6a) –Cu(2)–N(5)	166.92(8)
Cu(1)–N(2)	2.035(2)	O(2)–Cu(1)–N(2)	162.84(8)	O(4)–Cu(2)–N(6)	171.33(8)
Cu(1)–N(3)	2.158(2)	N(1)–Cu(1)–N(2)	80.69(8)	O(6a) –Cu(2)–N(6)	93.89(8)
Cu(2)–O(4)	1.9530	N(4)–Cu(1)–N(2)	93.98(8)	N(5)–Cu(2)–N(6)	80.87(8)
Cu(2)–O(6a)	1.9772(18)	O(2)–Cu(1)–N(3)	100.63(8)	O(4)–Cu(2)–O(1W)	93.85(8)
Cu(2)–N(5)	2.009(2)	N(1)–Cu(1)–N(3)	100.73(8)	O(6a)–Cu(2)–O(1W)	100.72(7)
Cu(2)–N(6)	2.010(2)	N(4)–Cu(1)–N(3)	79.69(8)	N(5)–Cu(2)–O(1W)	91.58(8)
Cu(2)–O(1W)	2.287(2)	N(2)–Cu(1)–N(3)	96.45(8)	N(6)–Cu(2)–O(1W)	93.36(8)
		3[b]			
Cu(1)–O(2)	1.9201(11)	O(2)–Cu(1)–O(4a)	89.81(5)	N(2)–Cu(1)–N(1)	80.28(5)
Cu(1)–O(4a)	1.9739(11)	O(2)–Cu(1)–N(2)	93.87(5)	O(2)–Cu(1)–O(4b)	86.46(4)
Cu(1)–N(2)	2.0046(13)	O(4a)–Cu(1)–N(2)	175.23(5)	O(4a)–Cu(1)–O(4b)	76.34(4)
Cu(1)–N(1)	2.0065(13)	O(2)–Cu(1)–N(1)	173.33(5)	N(2)–Cu(1)–O(4b)	106.88(5)
Cu(1)–O(4b)	2.3769(11)	O(4a)–Cu(1)–N(1)	95.87(5)	N(1)–Cu(1)–O(4b)	98.25(4)

[a] Symmetry codes for **2**: (a) = -*x*+2, -*y*+1, -*z*+1.

[b] Symmetry codes for **3**: (a) = -*x*, -*y*+2, -*z*+1; (b) = *x*+1, *y*, *z*.

Table S2. Selected bond distances (Å) and angles (°) for complexes **4**-**6**

		4[a]			
Cu(1)–O(2)	1.9714(15)	O(2)–Cu(1)–O(7)	92.50(6)	O(9)–Cu(3)–N(6)	169.63(7)
Cu(1)–O(7)	1.9752(15)	O(2)–Cu(1)–N(2)	91.98(7)	O(9)–Cu(3)–N(5)	93.04(7)
Cu(1)–N(2)	1.9829(18)	O(7)–Cu(1)–N(2)	170.38(7)	N(6)–Cu(3)–N(5)	81.69(7)
Cu(1)–N(1)	1.9900(19)	O(2)–Cu(1)–N(1)	173.18(7)	O(9)–Cu(3)–O(3)	92.36(6)
Cu(1)–O(6a)	2.3076(14)	O(7)–Cu(1)–N(1)	93.27(7)	N(6)–Cu(3)–O(3)	95.01(7)
Cu(2)–O(6a)	1.9459(14)	N(2)–Cu(1)–N(1)	81.78(8)	N(5)–Cu(3)–O(3)	164.62(7)
Cu(2)–O(1)	1.9689(14)	O(2)–Cu(1)–O(6a)	85.78(6)	O(9)–Cu(3)–O(11b)	84.93(6)
Cu(2)–N(4)	1.9888(17)	O(7)–Cu(1)–O(6a)	83.09(5)	N(6)–Cu(3)–O(11b)	88.55(6)
Cu(2)–N(3)	1.9939(18)	N(2)–Cu(1)–O(6a)	105.73(6)	N(5)–Cu(3)–O(11b)	110.55(6)
Cu(2)–O(7)	2.3186(14)	N(1)–Cu(1)–O(6a)	98.52(6)	O(3)–Cu(3)–O(11b)	84.27(6)
Cu(3)–O(9)	1.9621(14)	O(6a)–Cu(2)–O(1)	93.18(6)	O(11)–Cu(4)–O(10b)	91.20(6)
Cu(3)–N(6)	1.9835(18)	O(6a)–Cu(2)–N(4)	94.40(7)	O(11)–Cu(4)–N(8)	175.63(6)
Cu(3)–N(5)	1.9929(18)	O(1)–Cu(2)–N(4)	171.48(7)	O(10b)–Cu(4)–N(8)	93.15(7)
Cu(3)–O(3)	2.0035(14)	O(6a)–Cu(2)–N(3)	172.26(7)	O(11)–Cu(4)–N(7)	94.05(7)
Cu(3)–O(11b)	2.3238(15)	O(1)–Cu(2)–N(3)	91.45(7)	O(10b)–Cu(4)–N(7)	172.07(7)
Cu(4)–O(11)	1.9394(14)	N(4)–Cu(2)–N(3)	81.45(7)	N(8)–Cu(4)–N(7)	81.58(7)
Cu(4)–O(10b)	1.9679(14)	O(6a)–Cu(2)–O(7)	83.43(6)	O(11)–Cu(4)–O(3b)	86.03(6)
Cu(4)–N(8)	1.9852(17)	O(1)–Cu(2)–O(7)	88.99(6)	O(10b)–Cu(4)–O(3b)	88.99(6)
Cu(4)–N(7)	1.9865(17)	N(4)–Cu(2)–O(7)	88.03(6)	N(8)–Cu(4)–O(3b)	94.43(6)
Cu(4)–O(3b)	2.3116(15)	N(3)–Cu(2)–O(7)	102.86(6)	N(7)–Cu(4)–O(3b)	97.28(6)
		5[b]			
Cu(1)–O(7)	1.937(4)	O(7)–Cu(1)–O(1)	91.29(18)	O(10)–Cu(2)–N(3)	166.3(3)
Cu(1)–O(1)	1.970(5)	O(7)–Cu(1)–N(1)	167.9(2)	N(4)–Cu(2)–N(3)	80.8(4)
Cu(1)–N(1)	2.011(5)	O(1)–Cu(1)–N(1)	93.4(2)	O(3)–Cu(3)–O(11)	92.8(2)
Cu(1)–N(2)	2.027(5)	O(7)–Cu(1)–N(2)	94.76(19)	O(3)–Cu(3)–N(6)	171.6(3)
Cu(1)–O(9)	2.320(5)	O(1)–Cu(1)–N(2)	173.9(2)	O(11)–Cu(3)–N(6)	92.5(2)
Cu(2)–O(6a)	1.949(6)	N(1)–Cu(1)–N(2)	80.5(2)	O(3)–Cu(3)–N(5)	93.4(3)
Cu(2)–O(10)	1.951(5)	O(7)–Cu(1)–O(9)	103.53(16)	O(11)–Cu(3)–N(5)	164.3(3)
Cu(2)–N(4)	1.982(7)	O(1)–Cu(1)–O(9)	94.5(2)	N(6)–Cu(3)–N(5)	79.9(3)
Cu(2)–N(3)	2.005(8)	N(1)–Cu(1)–O(9)	87.18(18)	O(3)–Cu(3)–O(1W)	99.0(3)
Cu(3)–O(3)	1.933(6)	N(2)–Cu(1)–O(9)	84.95(19)	O(11)–Cu(3)–O(1W)	89.3(3)
Cu(3)–O(11)	1.945(5)	O(6a)–Cu(2)–O(10)	92.8(2)	N(6)–Cu(3)–O(1W)	87.6(3)
Cu(3)–N(6)	1.986(7)	O(6a)–Cu(2)–N(4)	163.5(3)	N(5)–Cu(3)–O(1W)	104.0(3)
Cu(3)–N(5)	2.014(7)	O(10)–Cu(2)–N(4)	94.8(3)		
Cu(3)–O(1W)	2.347(9)	O(6a)–Cu(2)–N(3)	94.9(3)		
		6			
Cu(1)–O(2)	1.9082(12)	O(2)–Cu(1)–N(2)	175.47(6)	N(1)–Cu(1)–N(3)	160.24(6)
Cu(1)–N(2)	1.9571(14)	O(2)–Cu(1)–N(1)	101.75(6)	O(2)–Cu(1)–O(1W)	96.07(5)
Cu(1)–N(1)	2.0163(15)	N(2)–Cu(1)–N(1)	80.31(6)	N(2)–Cu(1)–O(1W)	88.03(5)
Cu(1)–N(3)	2.0246(14)	O(2)–Cu(1)–N(3)	97.39(6)	N(1)–Cu(1)–O(1W)	87.50(5)
Cu(1)–O(1W)	2.2435(12)	N(2)–Cu(1)–N(3)	80.26(6)	N(3)–Cu(1)–O(1W)	95.36(5)

[a] Symmetry codes for **4**: (a) = -*x*+1, -*y*, -*z*+2; (b) = -*x*+1, -*y*+1, -*z*+2.

[b] Symmetry codes for **5**: (a) = -*y*+2/3, *x*-*y*+1/3, *z*+1/3.

Table S3. Geometrical parameters of the π-π interactions of compounds **1-5**[a]

	d (Å)[b]	*ϑ* (°)[c]	*γ* (°)[d]
	1		
$bpy_{N(1)N(2)}$ – $bpy_{N(1a)N(2a)}$	3.590(1)	16.7(1)	0.0
$bpy_{N(3)N(4)}$ – $bpy_{N(9b)N(10b)}$	3.661(1)	22.3(1)	4.8(1)
$bpy_{N(3)N(4)}$ – $bpy_{N(3b)N(4b)}$	3.634(1)	15.4(6)	0.0
$bpy_{N(5)N(6)}$ – $bpy_{N(5a)N(6a)}$	3.652(1)	17.7(9)	0.0
$bpy_{N(11)N(12)}$ – $bpy_{N(11c)N(12c)}$	3.573(1)	14.0(7)	0.0
	2		
$bpy_{N(1)N(2)}$ – $bpy_{N(1b)N(2b)}$	3.607(1)	19.6(5)	0.0
$bpy_{N(3)N(4)}$ – $bpy_{N(3b)N(4b)}$	3.490(2)	18.4(2)	0.0
$bpy_{N(5)N(6)}$ – $bpy_{N(5c)N(6c)}$	3.703(2)	20.4(5)	0.0
	3		
$bpy_{N(1)N(2)}$ – $bpy_{N(1c)N(2c)}$	3.864(1)	26.5(3)	0.0
	4		
$bpy_{N(1)N(2)}$-$bpy_{N(7c)N(8c)}$	3.651(1)	20.3(7)	17.9(6)
$bpy_{N(5)N(6)}$-$bpy_{N(3e)N(4e)}$	3.717(1)	23.0(6)	5.6(9)
	5		
$bpy_{N(1)N(2)}$ – $bpy_{N(3)N(4)}$	3.706(7)	23.5(2)	16.4(2)
$bpy_{N(3)N(4)}$ – $bpy_{N(5b)N(6b)}$	3.767(6)	26.1(4)	11.2(2)
$bpy_{N(1)N(2)}$ – $bpy_{N(5c)N(6c)}$	3.905(7)	3.1(2)	12.5(2)

[a]Symmetry codes for **1**: (a) = -*x*+1, -*y*, -*z*, (b) = -*x*+1,-*y*+1,-*z*, (c) = -*x*+1,-*y*,-*z*+1. For **2**: (b) = -*x*+2,-*y*,-*z*+1, (c) = -*x*+3,-*y*-1,-*z*. For **3**: (c) = -*x*+1,-*y*+2,-*z*. For **4**: (c) = -*x*,*y*-1/2,-*z*+3/2, (d) = *x*,-*y*+1/2,*z*-1/2, (e) = *x*,-*y*+1/2,*z*+1/2. For **5**: (b) = *x*-1/3, *y*+1/3, *z*+1/3, (c) –*y*, *x*-*y*, *z*.

[b] Shortest centroid-centroid separation.

[c] Off-set angle. Dihedral angle between the normal of the pyridyl ring and the vector defined by the centroid-centroid line.

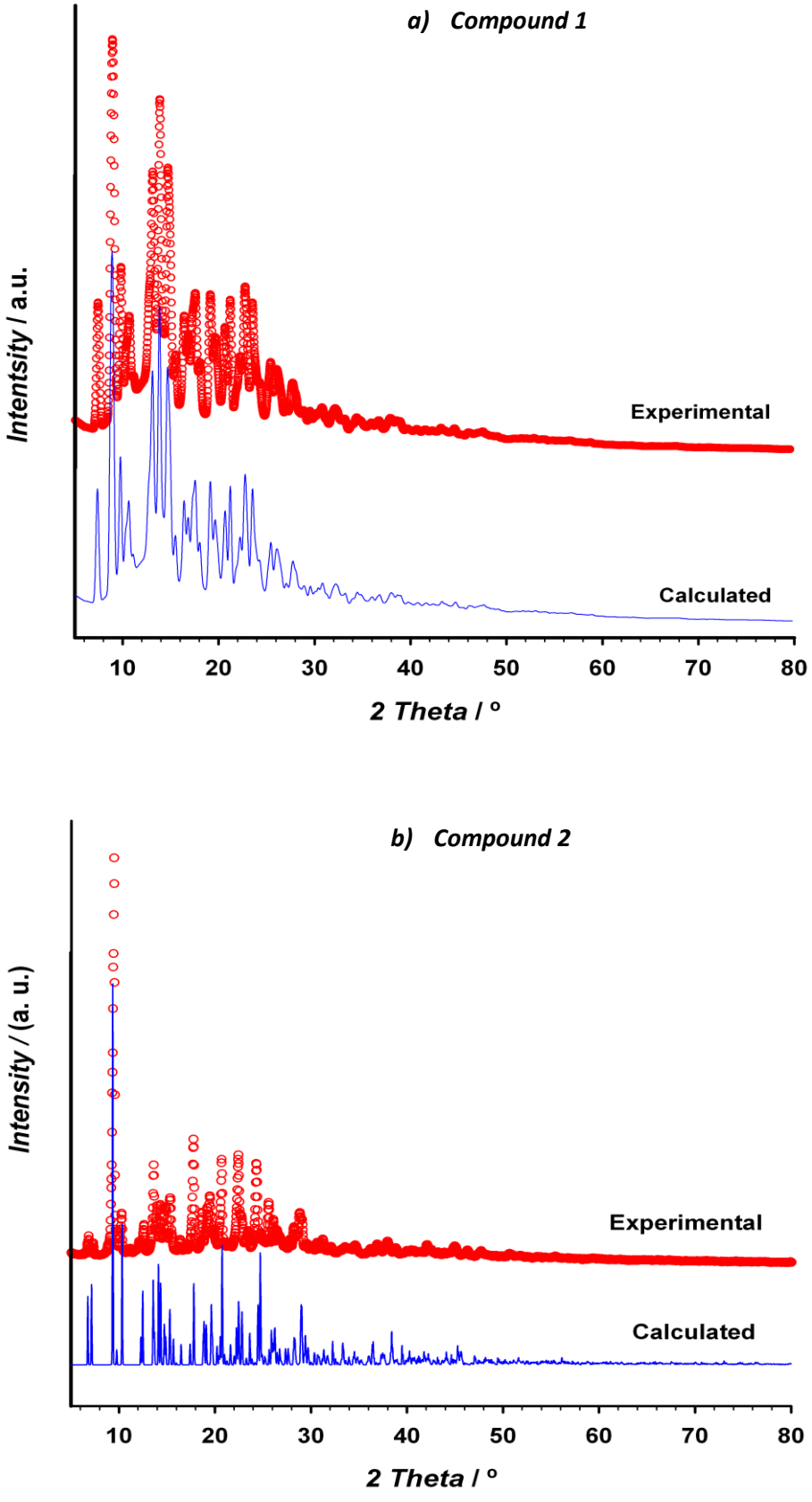
[d] Dihedral angle between the two bipyridine mean planes.

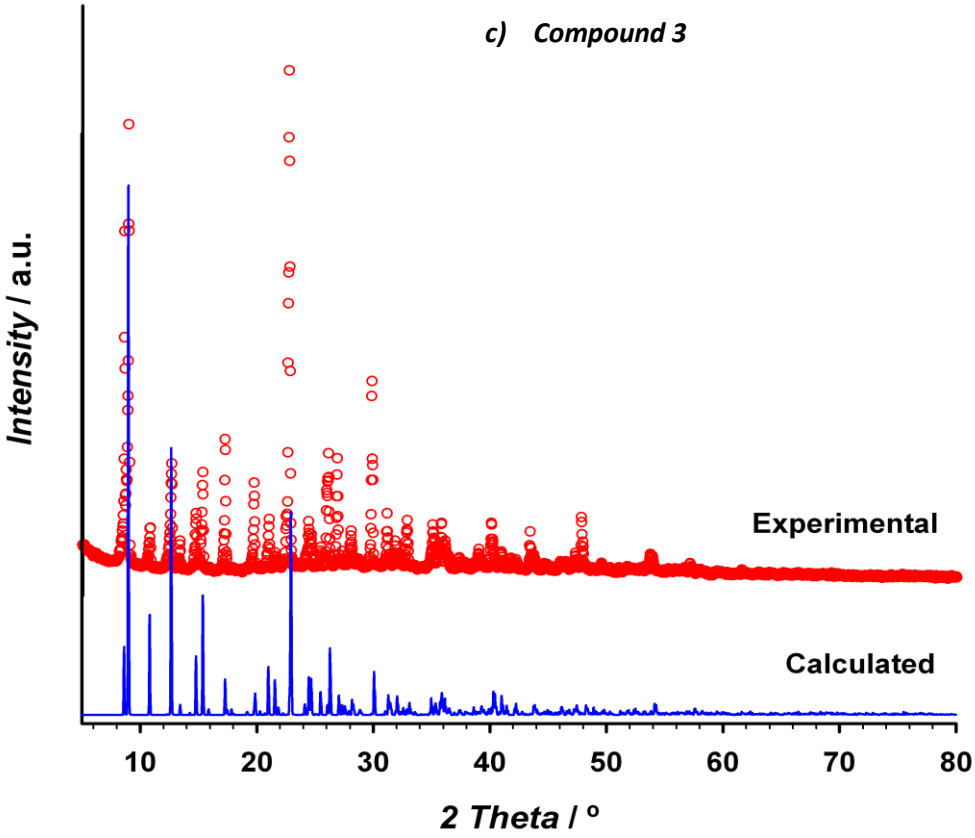
Table S4. Geometrical parameters of the hydrogen bonds in complexes **2** and **4**[a]

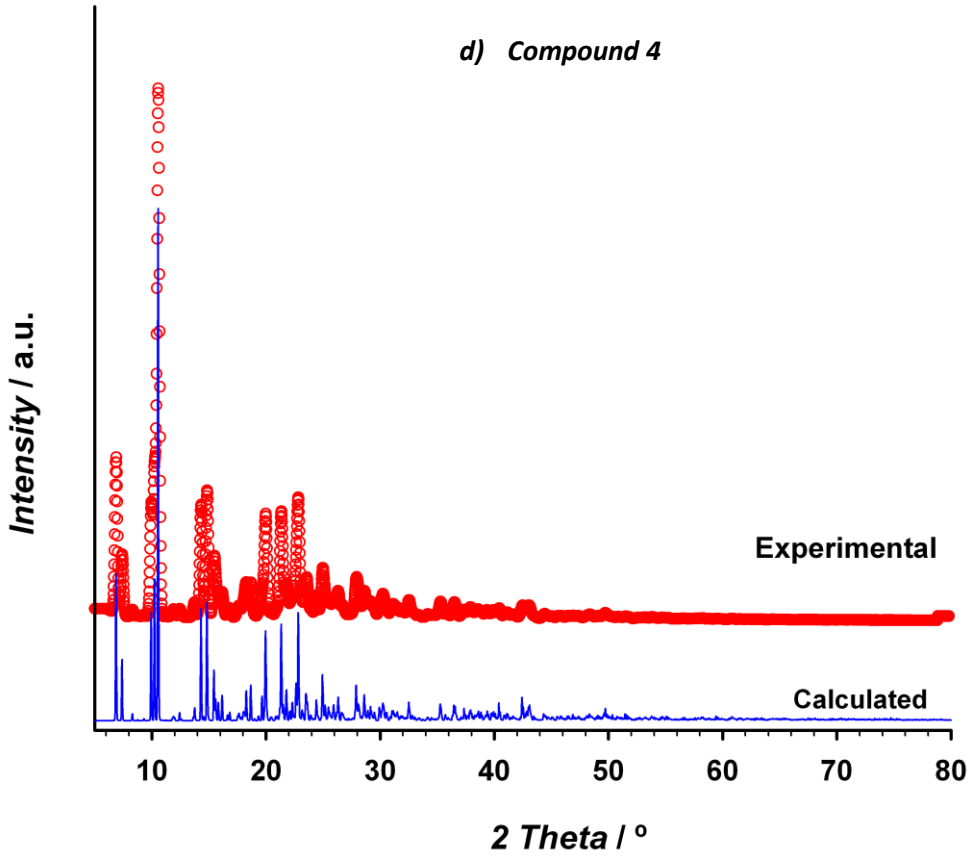
2				
D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (º)
O(1W)–H···O(5Wg)	0.83(5)	1.97(5)	2.795(5)	170(4)
O(1W)–H···O(5a)	0.85(2)	1.95(6)	2.754(4)	156(4)
O(2W)–H···O(3W)	0.85(3)	1.99(3)	2.831(5)	172(2)
O(2W)–H···O(9Wd)	0.86(7)	2.19(6)	2.831(4)	132(7)
O(3W)–H···O(3)	0.84(3)	1.94(2)	2.744(3)	160(3)
O(3W)–H···O(4W)	0.83(6)	2.21(5)	2.946(8)	148(5)
O(4W)–H···O(10Wd)	0.86(7)	2.25(6)	2.897(6)	131(5)
O(5W)–H···O(6W)	0.85(4)	1.95(5)	2.765(5)	157(5)
O(5W)–H···O(2We)	0.84(5)	2.08(5)	2.892(7)	161(4)
O(6W)–H···O(4W)	0.85(2)	2.26(6)	2.774(6)	119(4)
O(6W)–H···O(5)	0.86(3)	1.85(3)	2.667(3)	158(4)
O(7W)–H···O(7Wf)	0.86(4)	2.25(5)	2.833(6)	125(4)
O(8W)–H···O(4)	0.85(3)	2.03(3)	2.876(3)	174(3)
O(9W)–H···O(8W)	0.91(4)	2.01(4)	2.870(3)	157(4)
O(9W)–H···O(10)	0.91(5)	2.25(6)	2.776(6)	116(4)
O(10W)–H···O(3Wa)	0.88(2)	1.90(2)	2.779(4)	179(2)
O(10W)–H···O(11W)	0.88(2)	1.84(3)	2.707(3)	169(4)
O(11W)–H···O(6)	0.87(3)	1.96(3)	2.766(3)	154(3)
O(11W)–H···O(10)	0.87(2)	2.03(2)	2.870(3)	161(2)
4				
D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (º)
O(1W)–H···O(4)	0.85(2)	1.89(2)	2.714(2)	163(3)
O(1W)–H···O(8)	0.84(4)	2.38(6)	2.819(4)	113(3)
O(2W)–H···O(16)	0.89(7)	2.05(6)	2.921(5)	165(4)
O(2W)–H···O(18f)	0.92(5)	2.03(3)	2.846(11)	146(3)
O(3W)–H···O(5)	0.83(3)	2.00(3)	2.815(3)	169(3)
O(3W)–H···O(1W)	0.83(4)	2.24(4)	3.064(4)	168(3)

[a]Symmetry codes for **2**: (a) = -*x*+2, -*y*+1, -*z*+1; (b) = *x*, *y*+1, *z*; (c) = -*x*+2, -*y*+2, -*z*+1; (d) = *x*, *y*+1, *z*-1; (e) = -*x*+2, -*y*+2, -*z*; (f) = -*x*+1, -*y*+1, -*z*+1; (g) = *x*, *y*-1, *z*. Symmetry codes for **4**: (f) –*x*+1, *y*+1/2, -*z*+5/2.

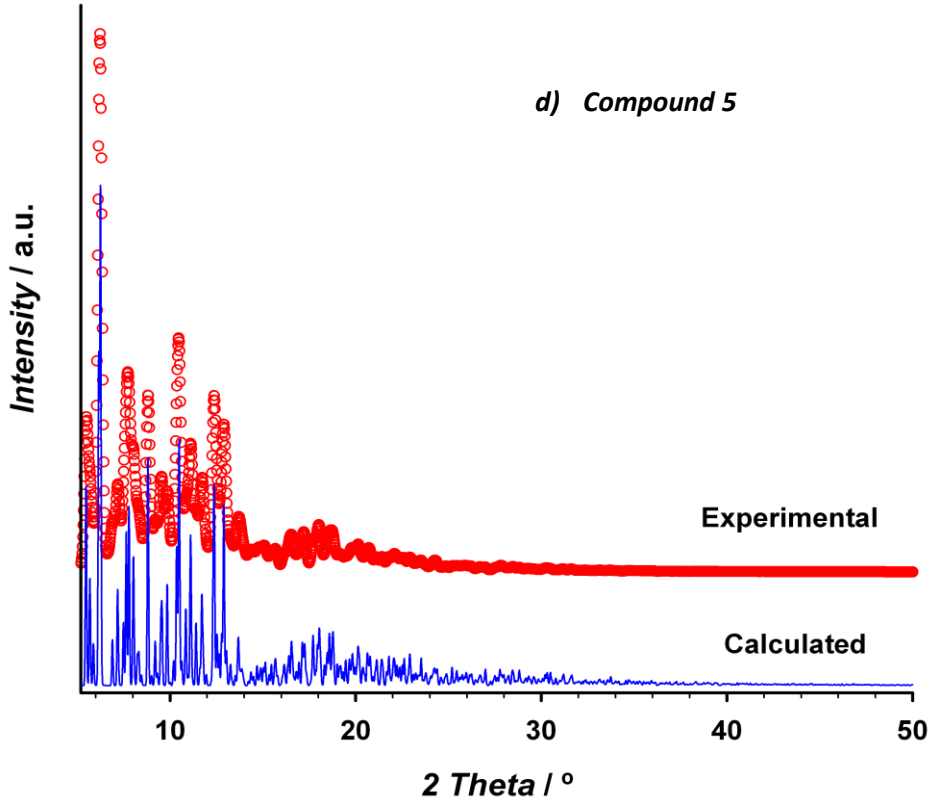
Figure S1. X-Ray powder diffraction patterns of the compounds **1-6** (red) together with the theoretical ones (blue).




c) Compound 3
Intensity / a.u.
Experimental
Calculated
10
20
30
40
50
60
70
80
2 Theta / °


d) Compound 4
Intensity / a.u.
Experimental
Calculated
10
20
30
40
50
60
70
80
2 Theta / °

d) Compound 5



e) Compound 6

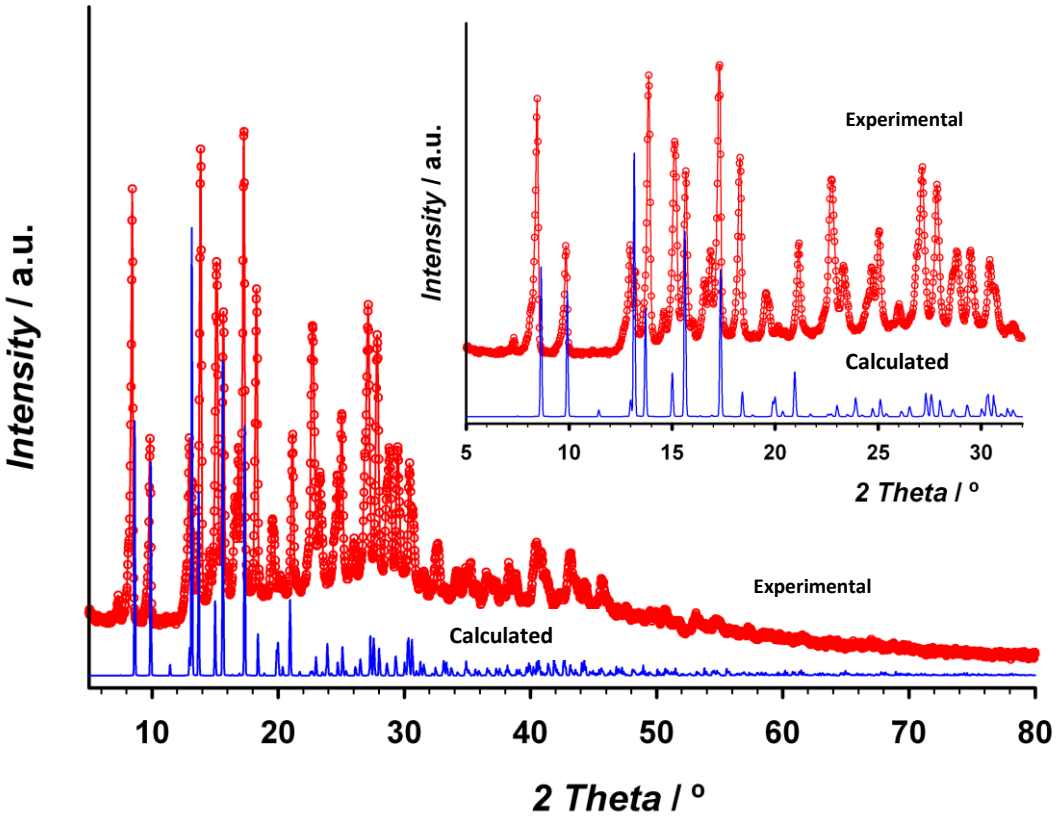
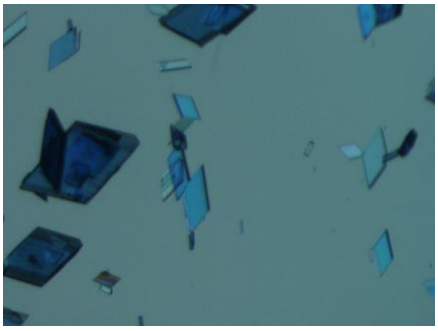
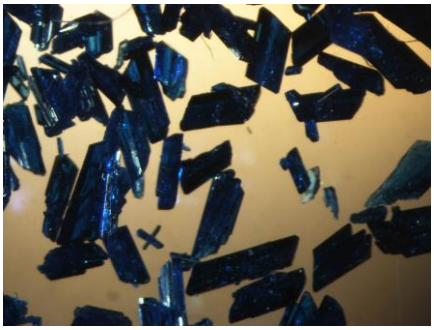


Figure S2. Optical microscope images with polarized light of crystals of **1**-**6**.



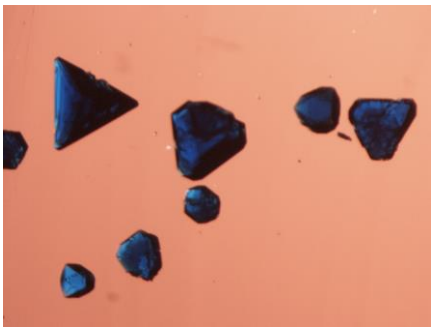
a) Compound **1**

b) Compound **2**

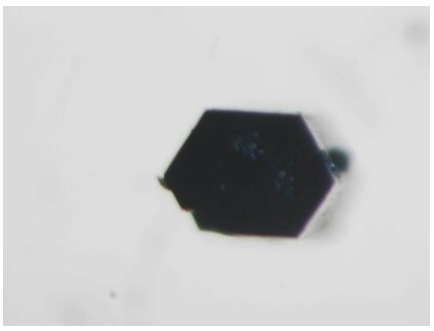


c) Compound **3**

d) Compound **4**



e) Compound **5**



f) Compound **6**

Figure S3. Thermogravimetric curves of **1-6**.

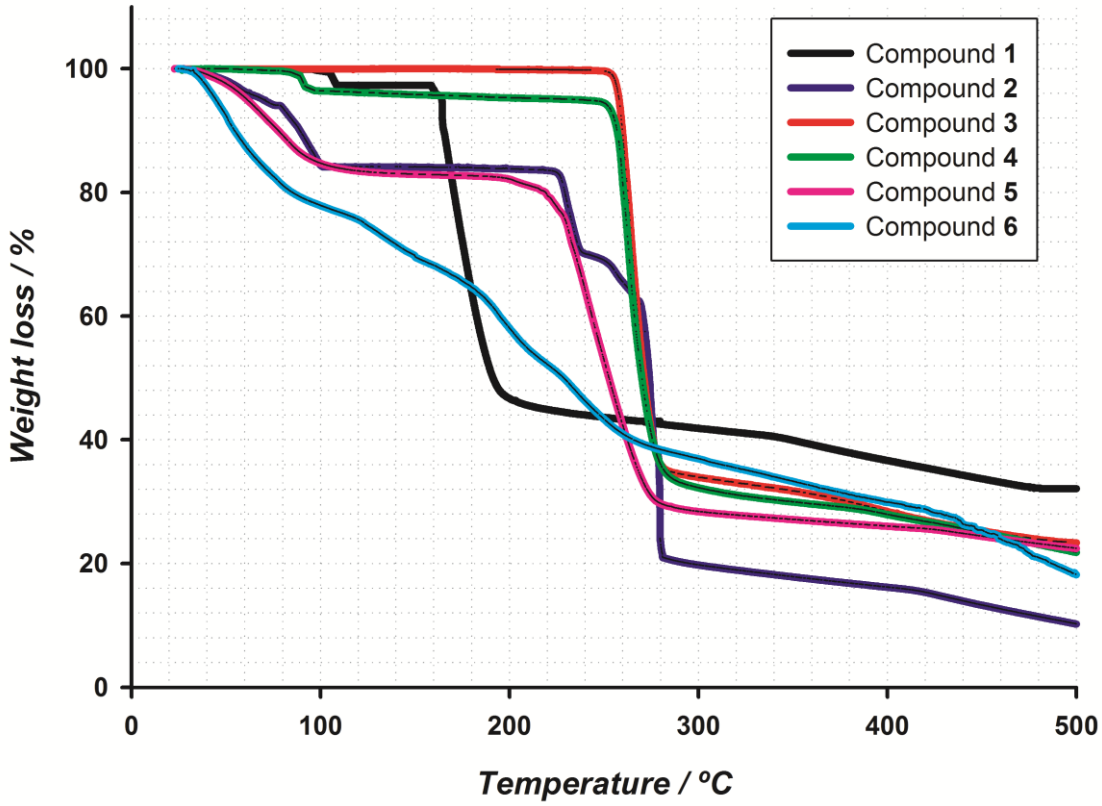


Figure S4. A view of the crystal packing of **1**. Each trinuclear molecule is depicted in one colour, except those related by a translation along the *c* axis. π-π interactions are depicted as orange dashed lines.

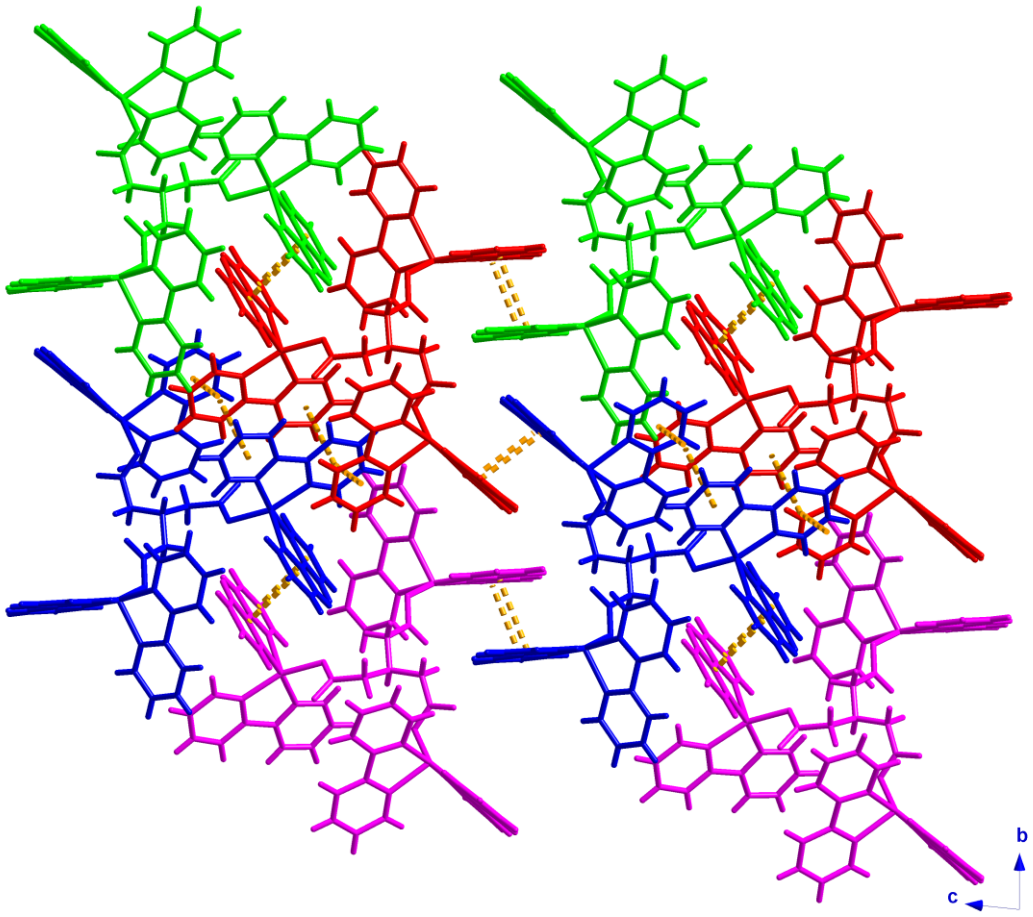


Figure S5. A view of the crystal packing of **2** showing the π-π type interactions between the bpy coligands. Each tetranuclear unit is depicted in a different colour. The π-π type interactions are shown as dashed orange lines linking the centroids of the pyridyl rings.

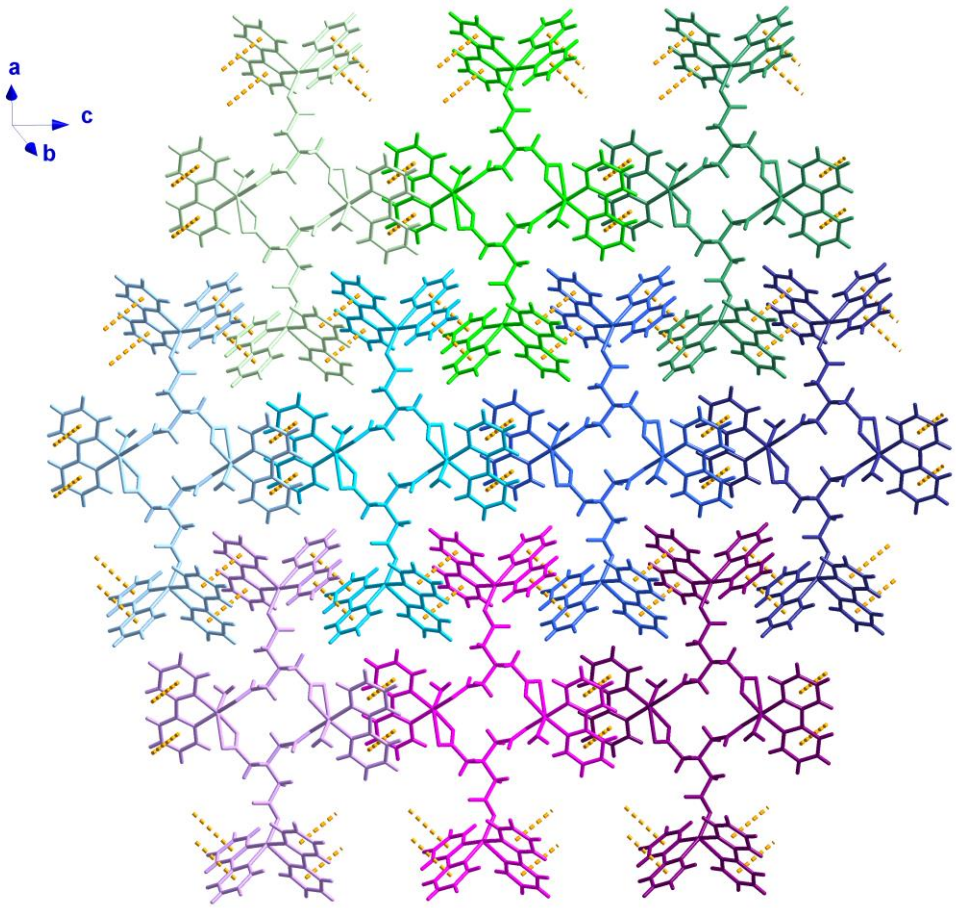


Figure S6. A view of the crystal packing of **2**. Each layer of π-π interacting tetranuclear molecules is separated from the adjacent layers by the water molecules of crystallization and the perchlorate anions. Colour code: pale green (H), red (O), and bright green (Cl), red bold lines (unit cell).

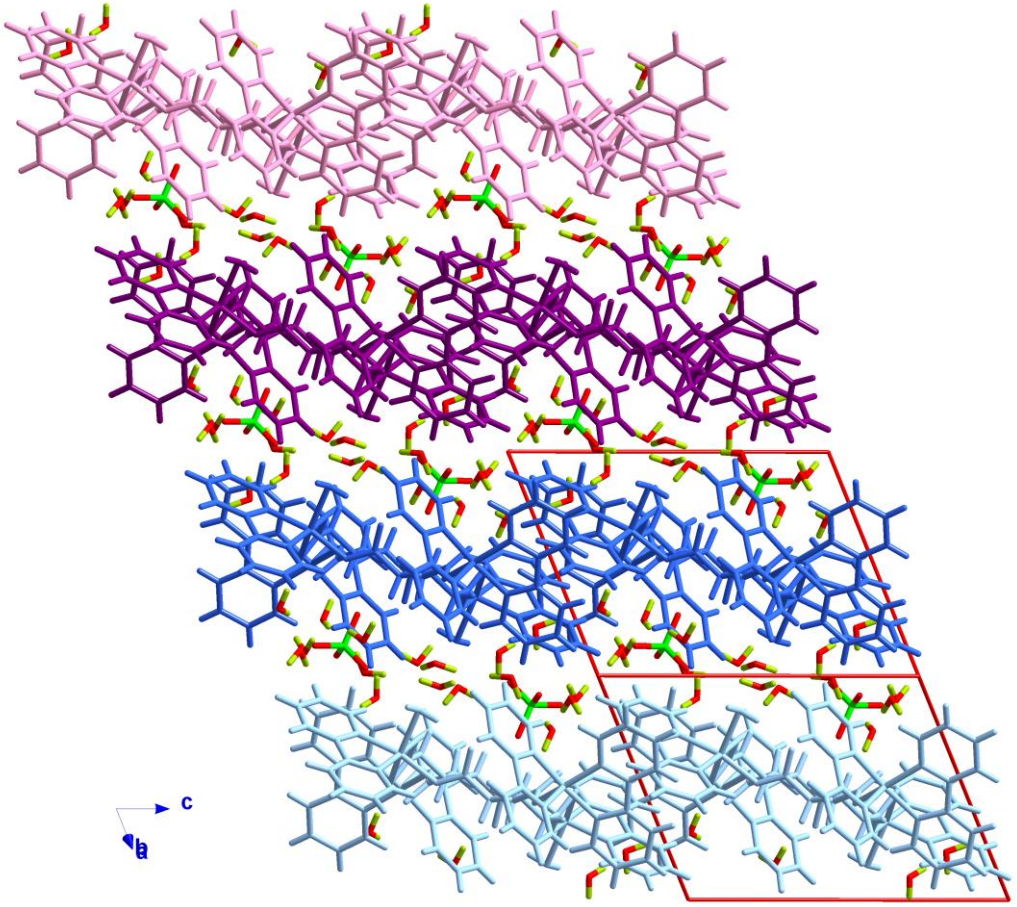


Figure S7. A central projection of the hydrogen bonded water cluster which occupies the interlayer space in **2.** Hydrogen bonds are depicted in dashed lines [see Table S4 for details; symmetry codes are listed in the Table S4 except for (h) = -*x*+2, -*y*+1, -*z*].

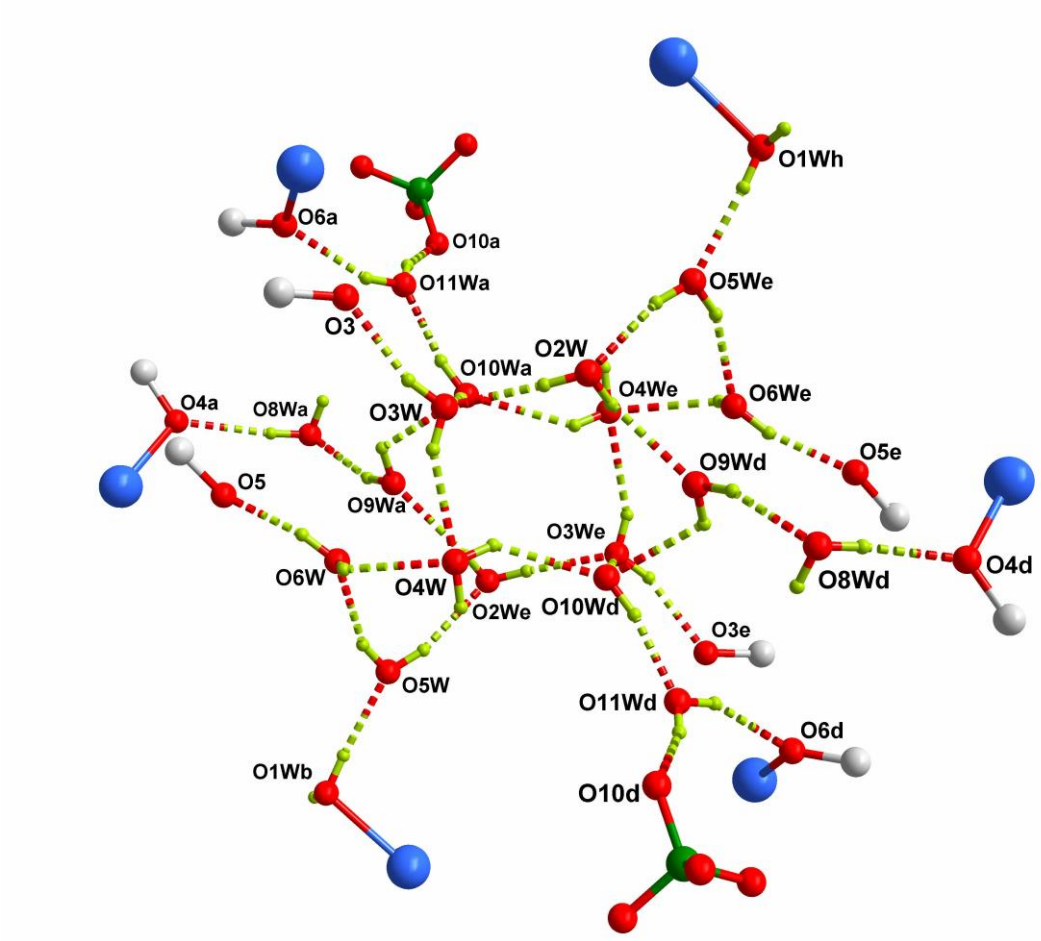


Figure S8. A view along the crystallographic *a* axis of the supramolecular arrangement of the $[Cu(bpy)(Hmta)]_n$ chains in **3**. Each of these chains are depicted in one color with the carboxylic hydrogen bond in pink dashed lines and the π-π interactions between bpy ligands in dashed orange lines.

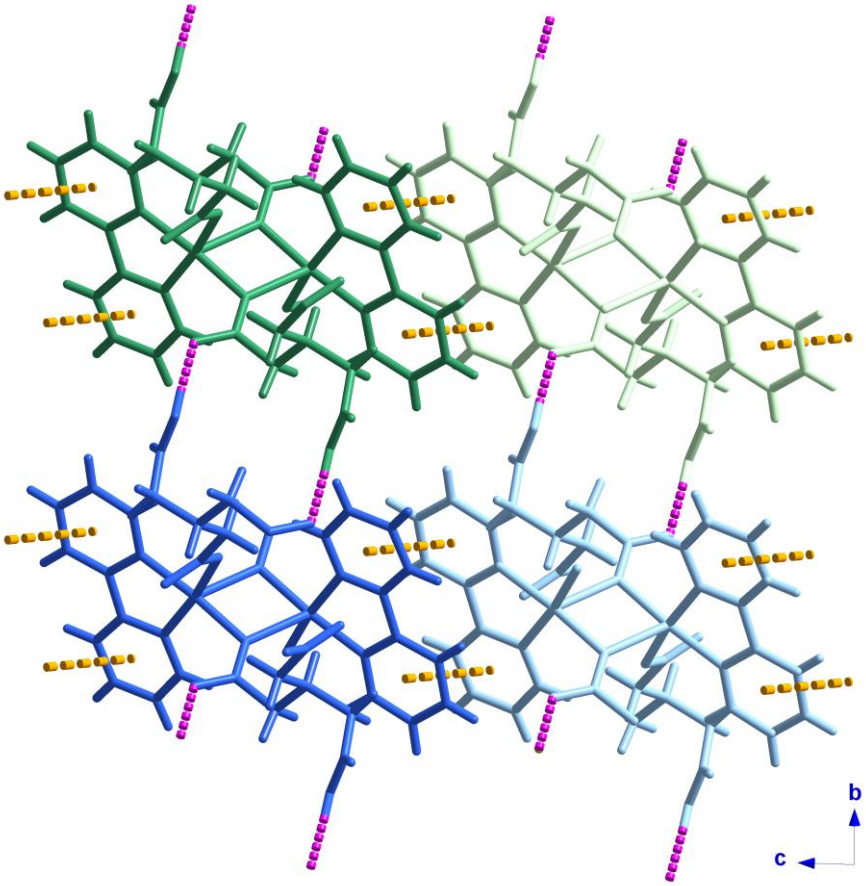


Figure S9. A view along the crystallographic *b* axis of the supramolecular arrangement of the copper(II) ladder-like chains in **4**. A central chain (blue) is linked to its four adjacent ones (green) through π-π type interactions involving the bpy coligands.

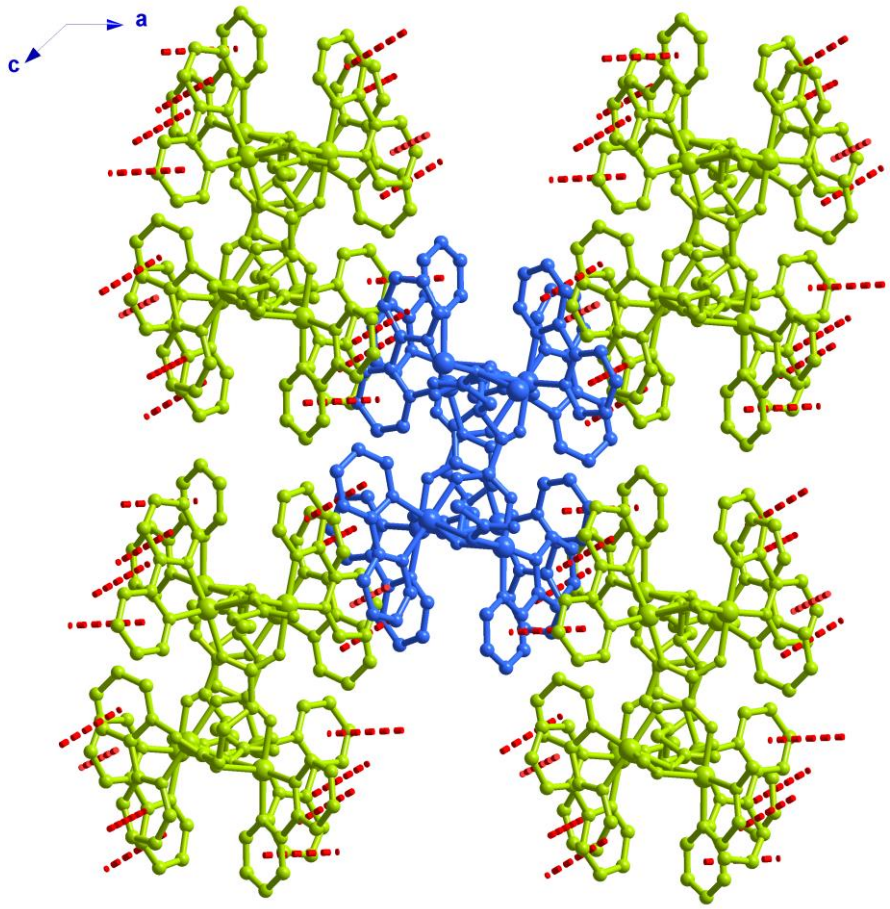


Figure S10. A view along the crystallographic *b* axis of the $[4^26][4^26^58^3]$ topology of the supramolecular 3D network of **4**. The dinuclear $Cu_2(bpy)_2$ nodes are the yellow spheres whereas the mta connectors are the grey ones.

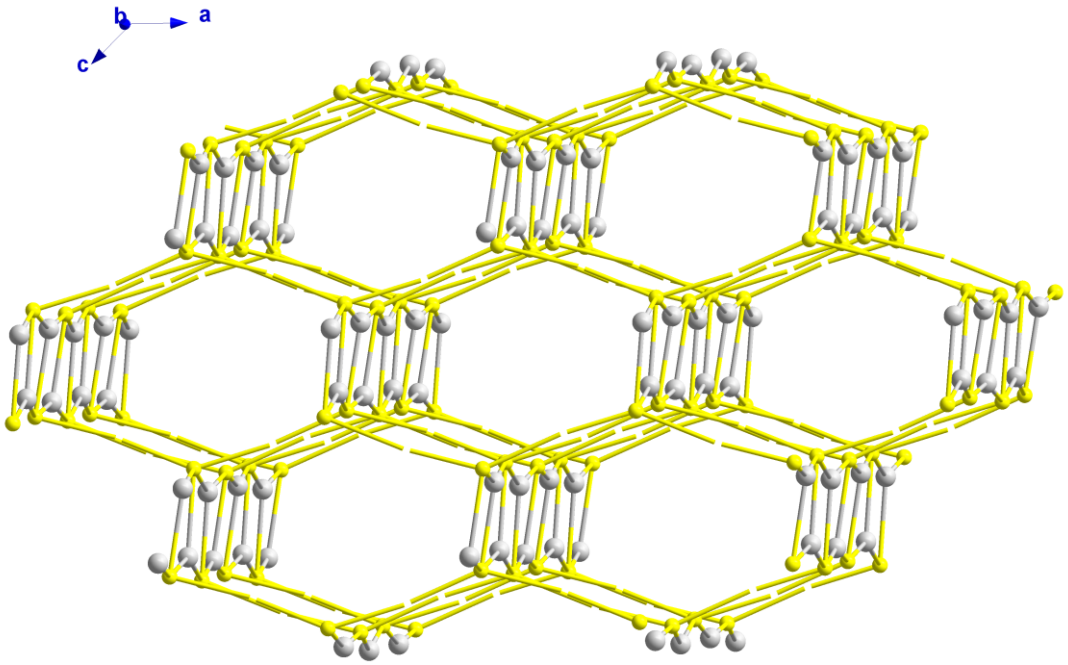


Figure S11. A view of the coordination modes of the two crystallographically independent mta^{3-} ligands in **4**, along with the numbering scheme.

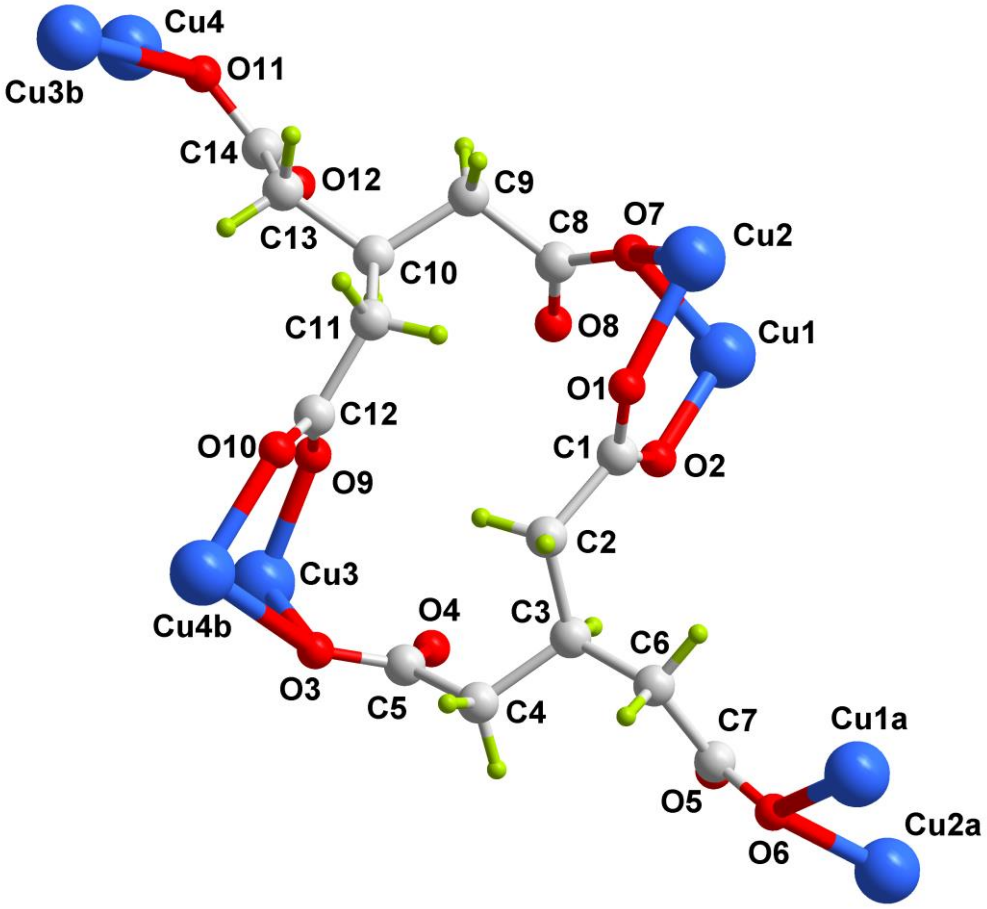


Figure S12. A view along the crystallgraphic *c* axis of the simplified topology of **5**, corresponding to the $[(6^3)_2(6^68^9)]$ Schäfli notation. It is a trinodal 3,3,6-connected net, where the mta ligands (green spheres) act as nodes and the copper(II) ions (blue spheres) act as linear linkers. The unit cell is depicted as red lines.

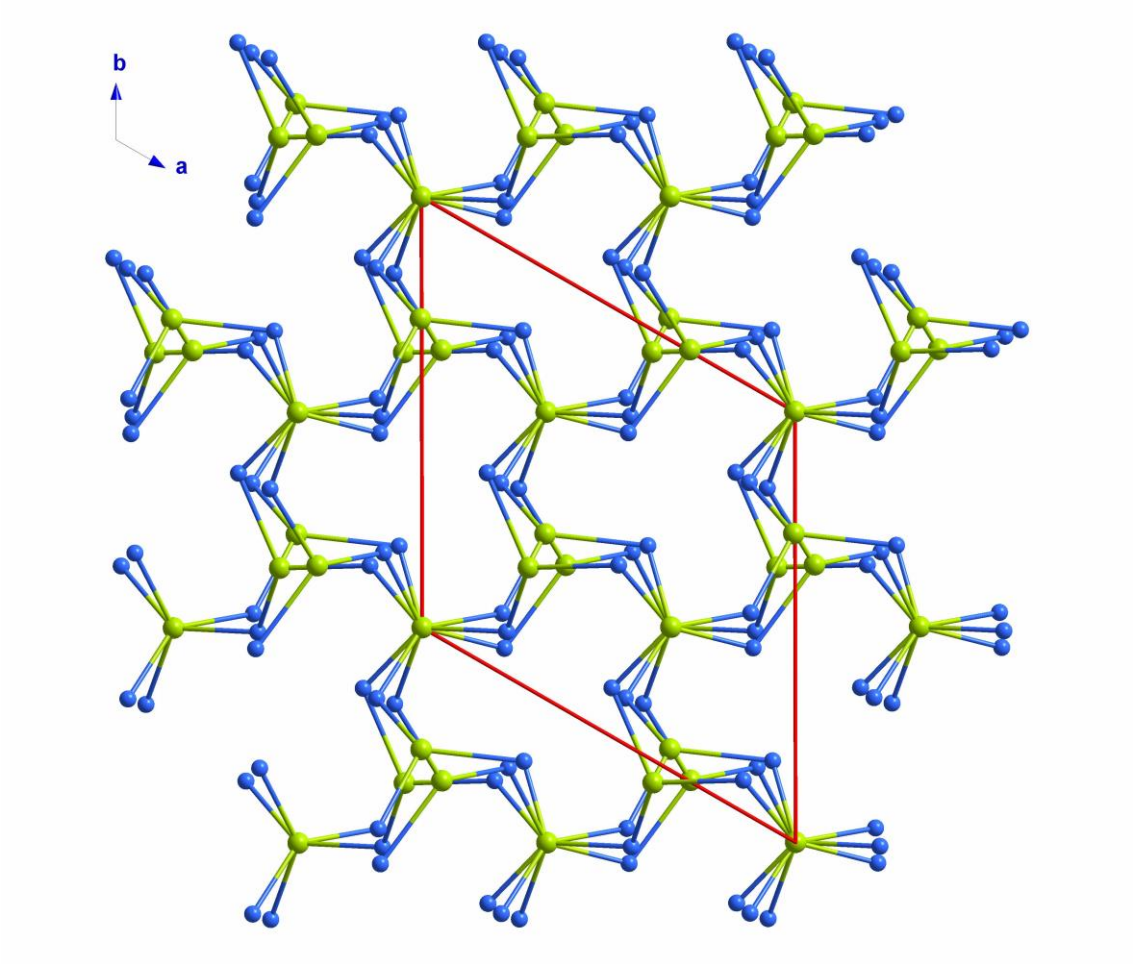


Figure S13. Temperature dependence of the $X_M T$ for product for **1**(o) and **2** (□).

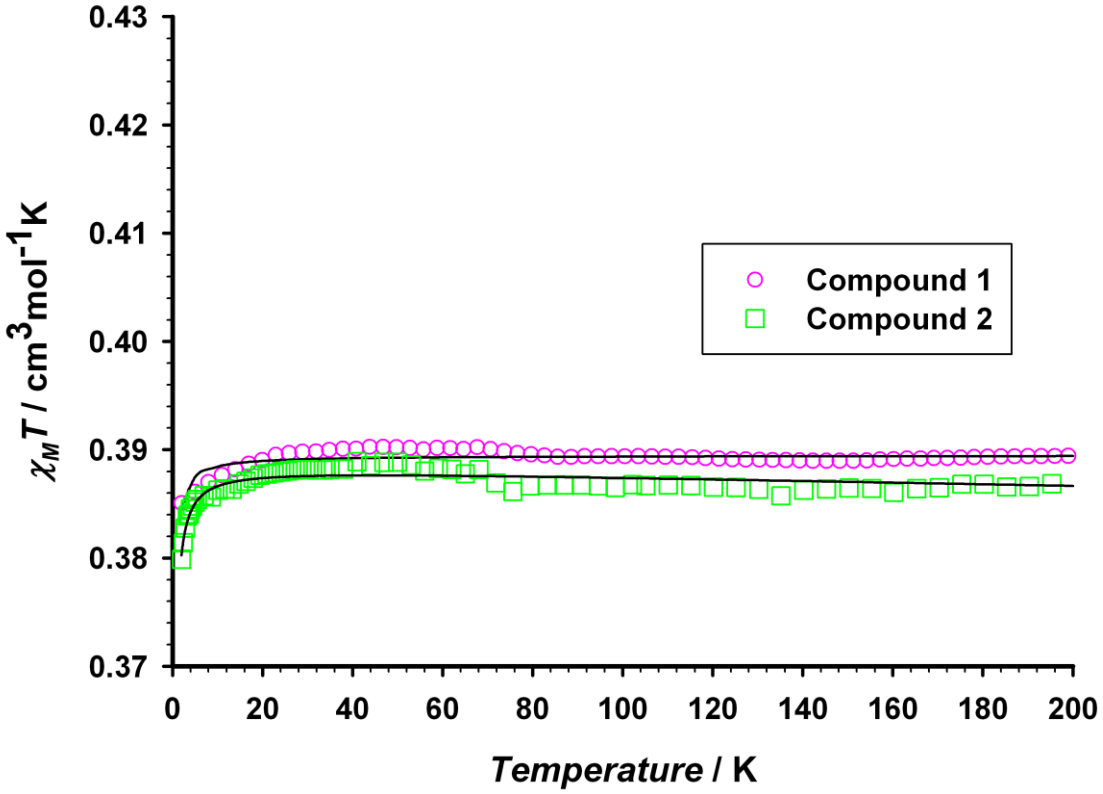


Figure S14. Temperature dependence of the $X_M T$ product for **3** (o) and **4** (◊).

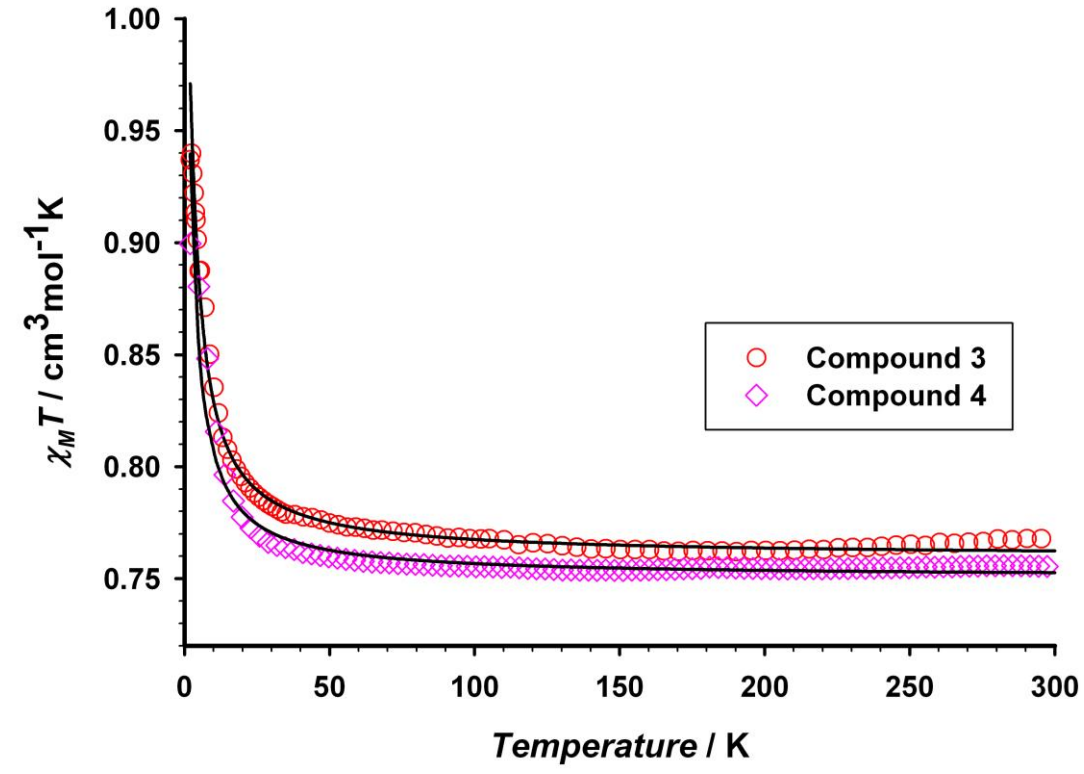


FIgure S15. Temperature dependence of $X_M T$ product for **5**(o).