Supplementary Information

Self-assembly of neutral hexanuclear circular copper(II) *meso*-helicates: topological control by sulfate ions

Harold B. Tanh Jeazet, Kerstin Gloe, Thomas Doert, Olga N. Kataeva, Anne Jäger, Gerhard Geipel, Gert Bernhard, Bernd Büchner, and Karsten Gloe*

Experimental Section

L^{1} was synthesized with a slightly modification of the previously reported method.[1] 4,4'-Diaminodiphenylsulfide (1 g, 4.62 mmol) was dissolved in acetonitrile (30 mL) and stirred under a nitrogen atmosphere. A solution of 2-pyridinecarboxyaldehyde (0.99 g, 9.24 mmol) in acetonitrile was added dropwise and the mixture was refluxed for 5 h. The brown solution was then concentrated by rotary evaporation to produce a brown solid (1.619 g, 89%). IR (KBr): $\tilde{\nu}$ = 3430m, 3050w, 1626s, 1586s, 1483s, 1467m, 1345m, 1087m, 881m, 831s, 771m, 739m, 711w cm^{-1}; ESI-MS (MeOH): m/z 395 [M + H]; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): d = 8.71 (d, *J* = 4.3, 0.9 Hz, 2H, H_{Py}), 8.60 (s, 2H, H_{im}), 8.18 (d, *J* = 7.9 Hz, 2H, H_{Py}), 7.81 (t, *J* = 1.6 Hz, 2H, H_{Py}), 7.40 (dd, *J* = 1.9, 2.0 Hz, 2H, H_{Py}), 7.35 (m, 4H, H_{Ph}), 7.24 (d, *J* = 3.0 Hz, 4H, H_{Ph}). elemental analysis Calc. for $C_{24}H_{18}N_4S$ (%): C 73.07, H 4.60, N 14.20, S 8.13; Found: C 72.49, H 4.73, N 14.10, S 7.68.

L^{2} and **L**^{3} were prepared *via* the previously reported method.[2]

[Cu**L**^{1}$(SO_4)]_6 \cdot 24H_2O$ (**1**): Copper(II) sulfate pentahydrate (6.33 mg, 0.025 mmol) in methanol /water (2:1) (1.5 ml) was slowly layered on the top of a acetonitrile solution (1 ml) containing ligand **L**^{1} (15.0 mg, 0.038 mmol). Dark brown needles of the title compound were obtained by slow diffusion of diethylether into the resulting solution after 3 weeks. The crystals were collected, washed with ether, and dried under vacuum (0.021 g, 89%). IR (KBr): $\tilde{\nu}$ = 3430m, 3063w, 1630m, 1593m, 1483s, 1351w, 1088m, 890w, 837m, 769w, 745w, 690w cm^{-1}; ESI-MS (MeOH): m/z 457 [Cu(**L**^{1}**)$_2$** + 2MeOH]$^{2+}$, 554 {[Cu**L**^{1}$(SO_4)]$ + H}; elemental analysis indicated the stoichiometric formula of [Cu**L**^{1}$(SO_4)]_6 \cdot 22H_2O$, Cal. for $C_{144}H_{152}Cu_6N_{24}O_{46}S_{12}$ (%): C 46.48%, H 4.12%, N 9.03%, S 10.34%; Found: C 46.51%, H 4.36%, N 9.04%, S 9.94%; UV/Vis (MeCN): 418 (ε = 4734), 325 (ε = 5213), 309 (ε = 8530) nm.

[Cu**L**^{2}$(SO_4)]_6 \cdot 24H_2O$ (**2**): The same procedure was used as for the preparation of (**1**). The complex (green block-like crystals) was obtained after 3 days (0.022 g, 91%). IR (KBr): $\tilde{\nu}$ = 3428s, 3063m, 2854w, 1630s, 1598s, 1503s, 1481m, 1363w, 1129s, 863w, 817w, 785m, 745w, 709w cm^{-1}; ESI-MS (MeOH): m/z 439 [Cu(**L**^{2}**)$_2$** + 2MeOH]$^{2+}$, 536 {[Cu**L**^{2}$(SO_4)]$ + H}; elemental analysis indicated the stoichiometric formula of [Cu**L**^{2}$(SO_4)]_6 \cdot 18H_2O$, Cal. for $C_{150}H_{156}Cu_6N_{24}O_{42}S_6$ (%): C 50.88%, H 4.44%, N 9.49%, S 5.43%; Found: C 51.50%, H 4.41%, N 9.66%, S 5.30%; UV/Vis (MeCN): 401 (ε = 912), 327 (ε = 2160), 300 (ε = 5324) nm.

[Cu**L**^{3}$(SO_4)]_6 \cdot 24H_2O$ (**3**): The same procedure was used as for the preparation of (**1**). The complex (dark green needles) was obtained after 2 months (0.020 g, 85%). IR (KBr): $\tilde{\nu}$ = 3435m, 3063w, 1630m, 1598m, 1494s, 1349w, 1243m, 1130m, 872w, 838m, 775w, 747w, 695w cm^{-1}; ESI-MS (MeOH): m/z 441 [Cu(**L**^{3}**)$_2$** + 2MeOH]$^{2+}$, 538 {[Cu**L**^{3}$(SO_4)]$ + H}; elemental analysis indicated the stoichiometric formula of [Cu(**L**^{3}$)SO_4]_6 \cdot 18H_2O$, Cal. for $C_{144}H_{144}Cu_6N_{24}O_{48}S_6$ (%): C 48.69%, H 4.09%, N 9.46%, S 5.42%; Found: C 48.22%, H 4.28%, N 9.04%, S 5.57%; UV/Vis (MeCN): 425 (ε = 4397), 336 (ε = 4615), 309 (ε = 7003) nm.

Thermogravimetric Analysis

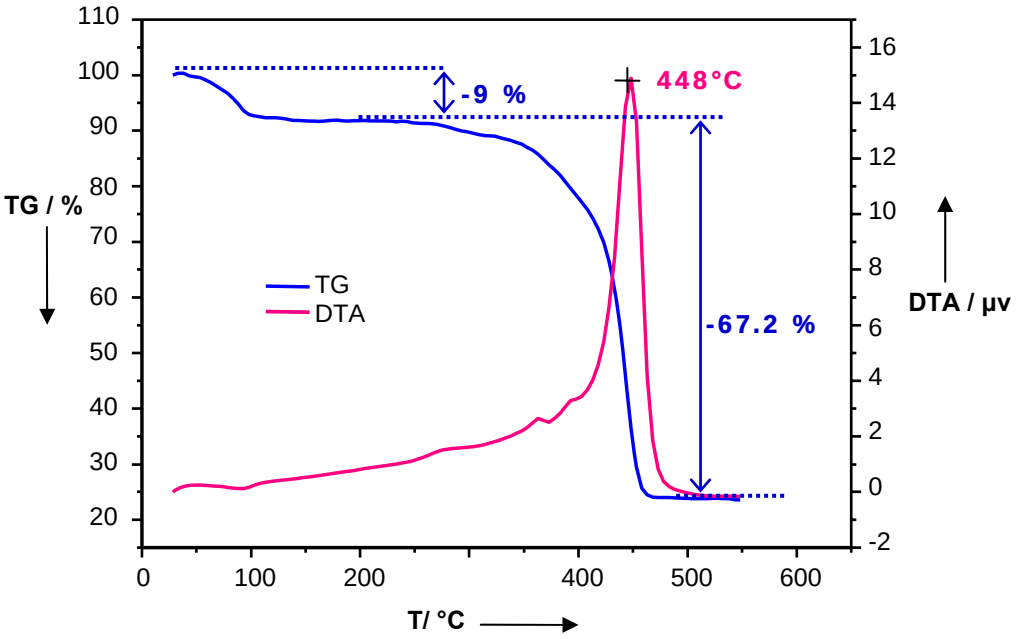


Figure S1: Thermogravimetric measurements (static air, heating rate: 5 K·min^{-1}) of $[CuL^{1}(SO_4)]_6 \cdot 24H_2O$ (**1**) show a weight loss of 9 % in the temperature range between 30 and 150 °C (calc.: 9.2 %) corresponding with the loss of 19 moles of H_2O.

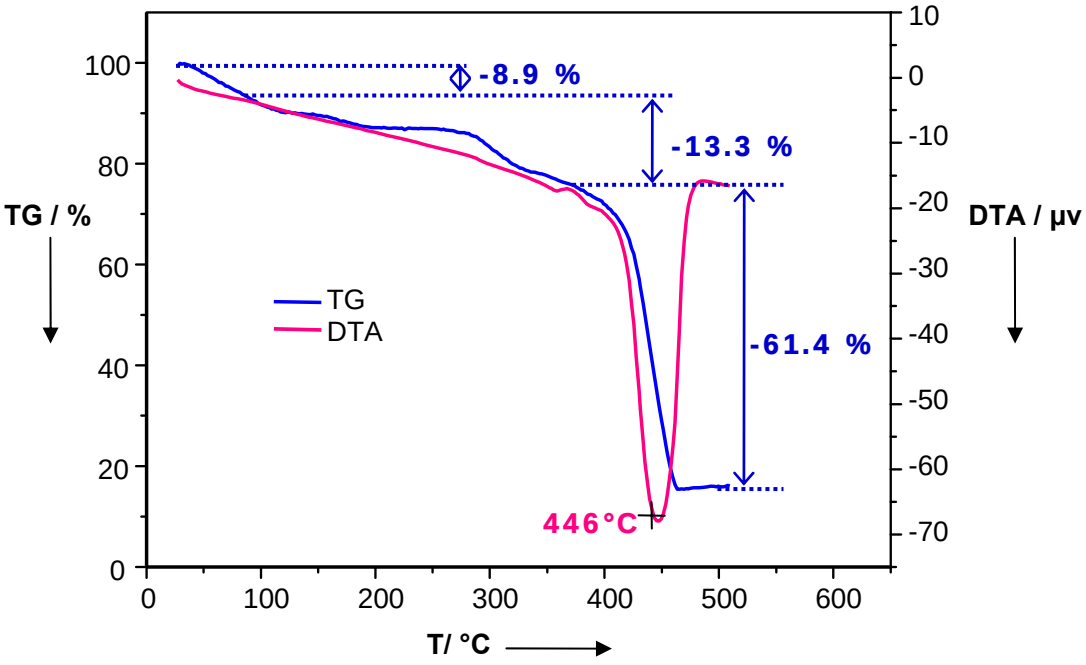


Figure S2: Thermogravimetric measurements (static air, heating rate: 5 K·min^{-1}) of $[CuL^{2}(SO_4)]_6 \cdot 24H_2O$ (**2**) show a weight loss of 8.9 % in the temperature range between 30 and 110 °C (calc.: 8.88 %) corresponding with the loss of 18 moles of H_2O.

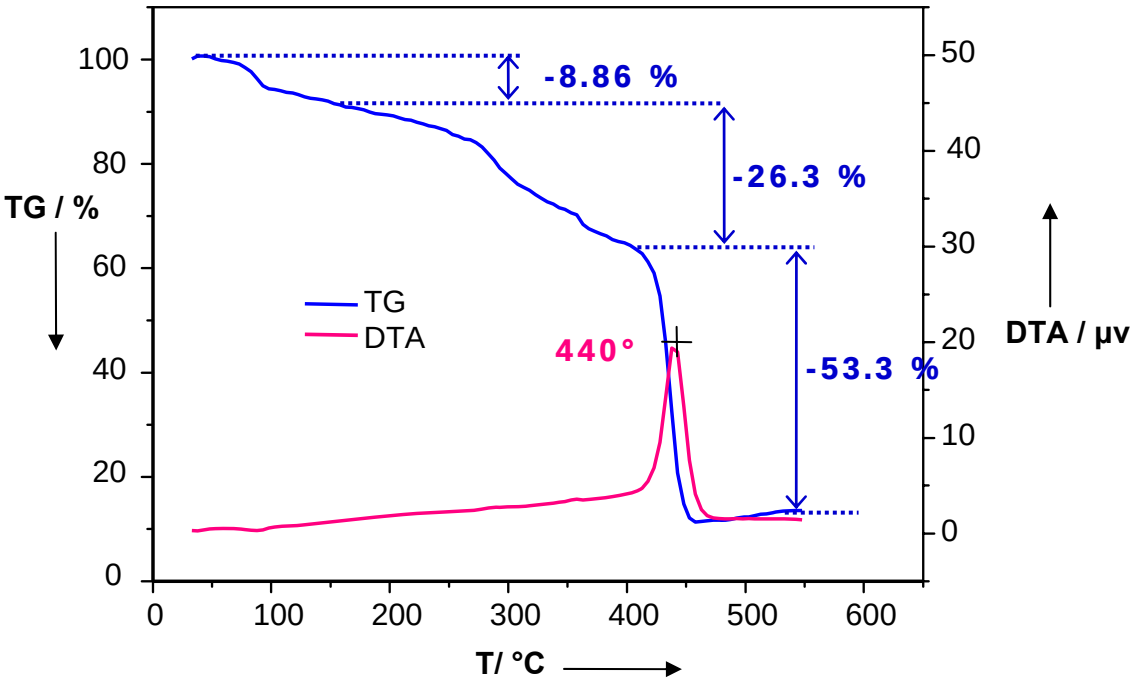


Figure S3: Thermogravimetric measurements (static air, heating rate: 5 $K \cdot min^{-1}$) of $[CuL^3(SO_4)]_6 \cdot 24H_2O$ (**3**) show a weight loss of 8.86 % in the temperature range between 30 and 150 °C (calc.: 8.85 %) corresponding with the loss of 18 moles of H_2O.

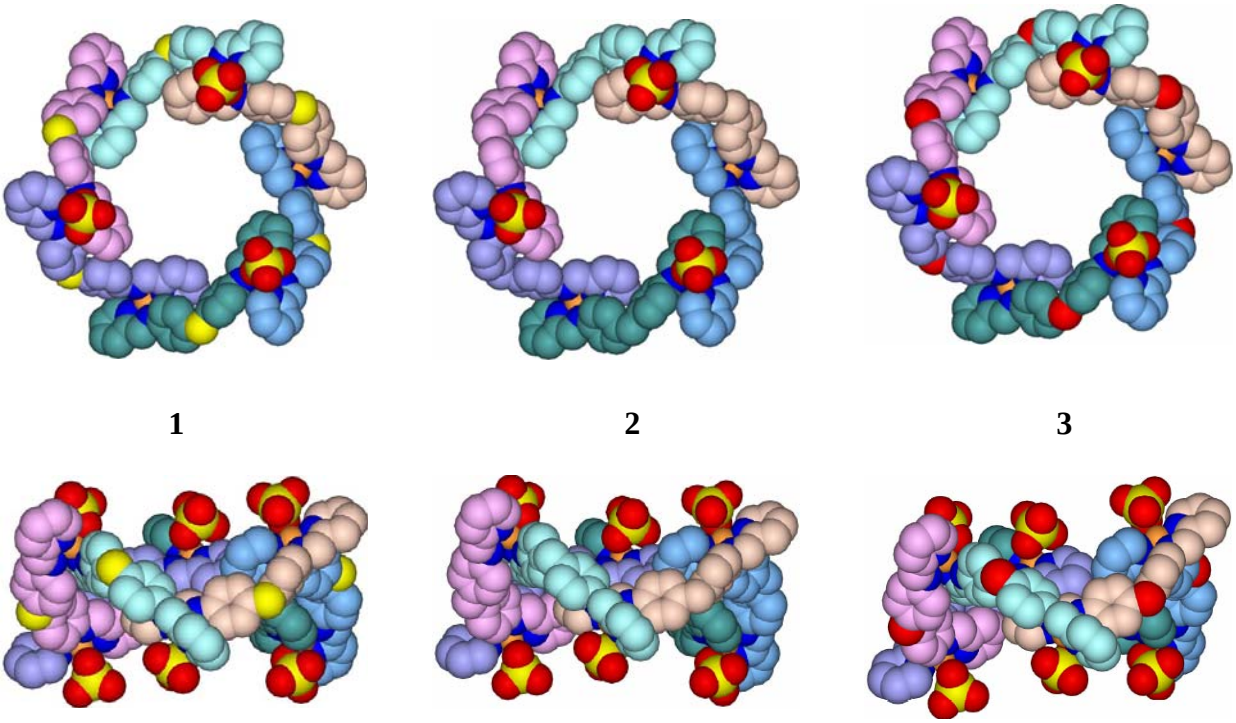
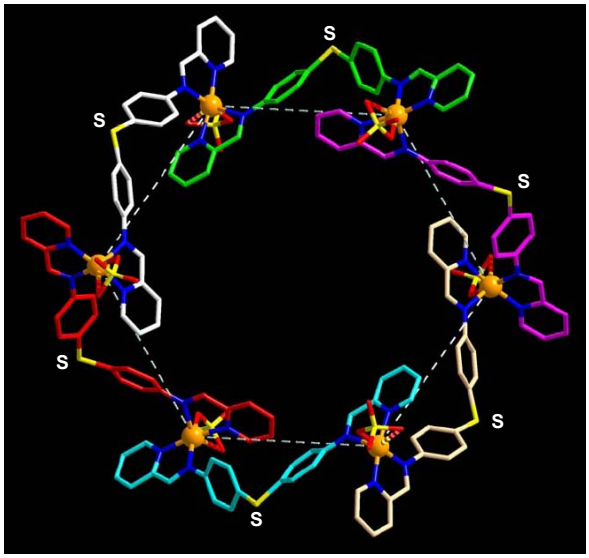
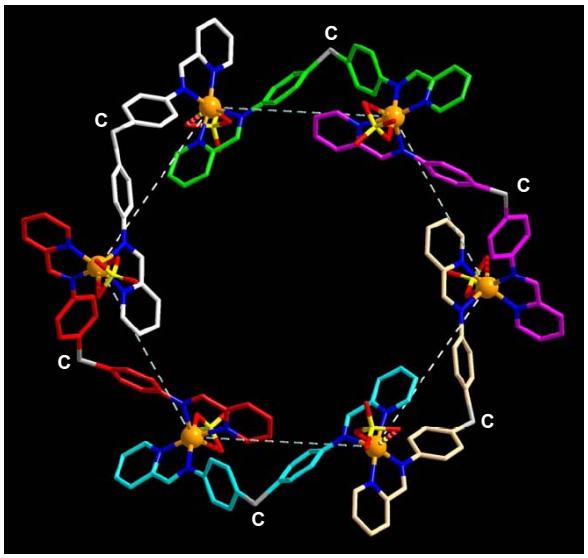


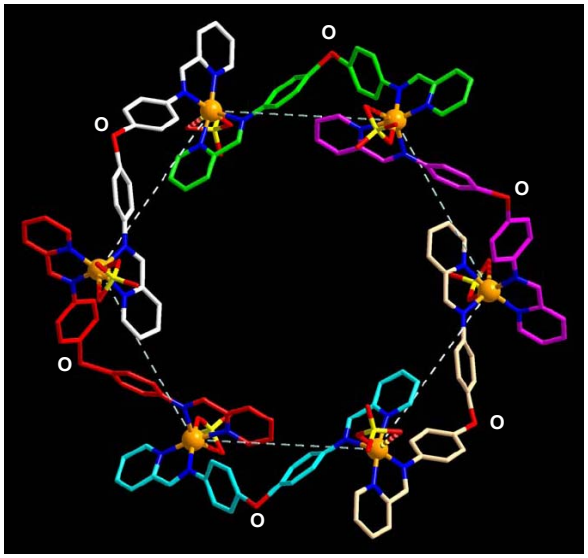
Figure S4. Space-filling representation of the crystal structures of $[CuL^1(SO_4)]_6$ (**1**), $[CuL^2(SO_4)]_6$ (**2**) and $[CuL^3(SO_4)]_6$ (**3**). Top: top view; Bottom: side view. The ligands are shown in different patterns. Cu in orange, N in blue, O in red, S in yellow. Hydrogen atoms are omitted for clarity.



(1)



(2)



(3)

Figure S5. Ball-and-stick representation of the crystal structures of the circular *meso*-helicates $[CuL^{1}(SO_4)]_6$ (**1**), $[CuL^{2}(SO_4)]_6$ (**2**) and $[CuL^{3}(SO_4)]_6$ (**3**). Cu in orange, N in blue, O in red, S in yellow. The ligands are shown in different colors. Hydrogen atoms are omitted for clarity.

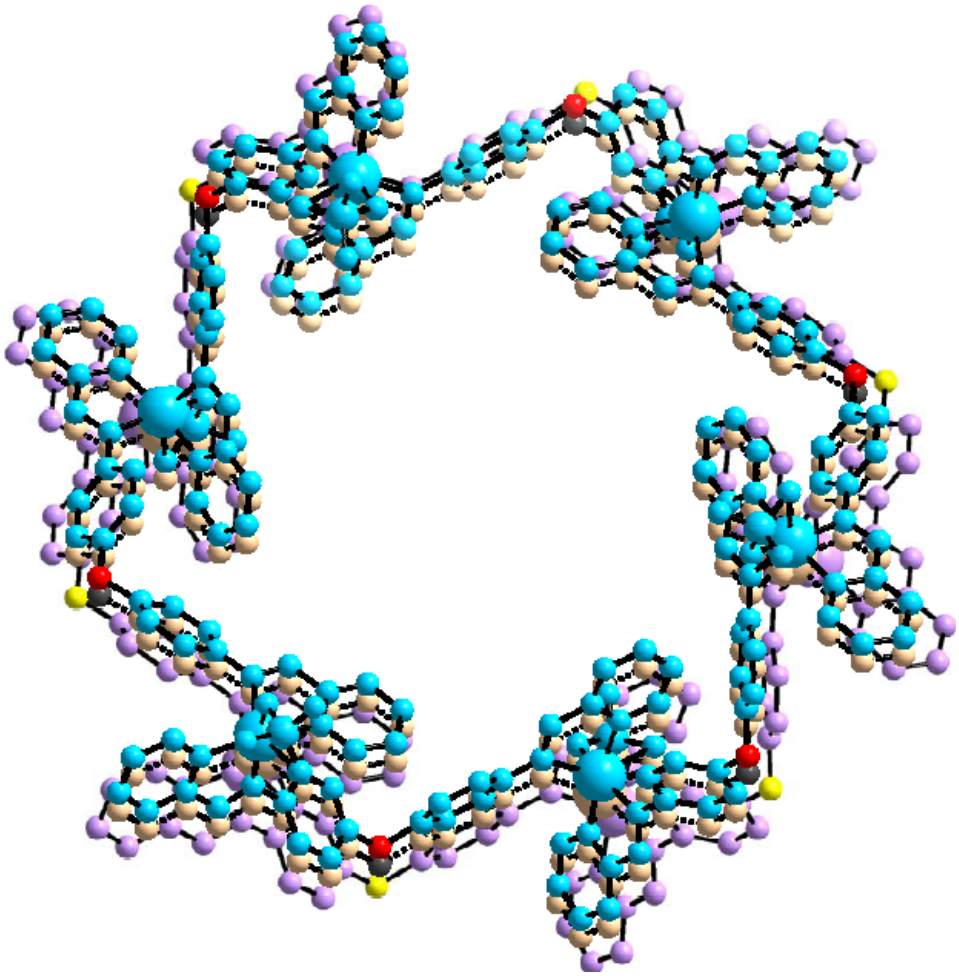


Figure S6. Overlay of the structures of the hexanuclear circular *meso*-helicates $[Cu\mathbf{L}^{1}(SO_4)]_6$ (**1**) in violet, $[Cu\mathbf{L}^{2}(SO_4)]_6$ (**2**) in light brown and $[Cu\mathbf{L}^{3}(SO_4)]_6$ (**3**) in blue. Color of the bridging atoms: S yellow, C black, O red. Hydrogen atoms are omitted for clarity.

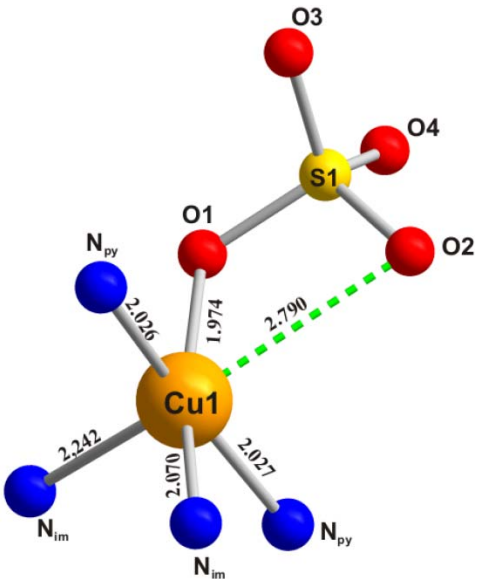


Figure S7. Coordination geometry around the Cu(II) ion in $[Cu\mathbf{L}^{1}(SO_4)]_6$ (**1**).

Table S1. Selected Bond lengths [Å] and angles [°] of the circular *meso*-helicates **1**, **2** and **3**

atoms	$[Cu\mathbf{L}^{1}(SO_4)]_6 \cdot 24H_2O$ (**1**)	$[Cu\mathbf{L}^{2}(SO_4)]_6 \cdot 24H_2O$ (**2**)	$[Cu\mathbf{L}^{3}(SO_4)]_6 \cdot 24H_2O$ (**3**)
Cu – N1	2.027(3)	2.020(3)	2.022(2)
Cu – N16	2.026(3)	2.018(3)	2.017(2)
Cu – N8	2.242(4)	2.246(2)	2.261(2)
Cu – N23	2.070(3)	2.045(2)	2.051(2)
Cu – O1	1.974(3)	1.959(2)	1.963 (2)
Cu – O2	2.790(3)	2.770(2)	2.792(2)
O1 – Cu – N1	93.81(12)	93.91(11)	93.01(7)
O1 – Cu – N16	93.19(12)	92.65(10)	92.83(8)
O1 – Cu – N8	90.55(12)	93.36 (9)	93.27 (8)
O1 – Cu – N23	165.41(13)	163.34(9)	164.14(8)
N1 – Cu – N16	169.63(15)	170.64(10)	171.05(10)
N1 – Cu – N23	91.51(12)	91.96(10)	92.65(8)
N16 – Cu – N23	79.92(12)	79.94(10)	79.99(8)
N1 – Cu – N8	77.71(12)	77.90(11)	77.94(8)
N8 – Cu – N23	103.85(12)	103.12(9)	102.39(8)
N8 – Cu – N16	109.86(13)	108.37(11)	108.49(8)
O2 – Cu – N1	82.56(8)	82.67(8)	81.46(8)
O2 – Cu – N16	94.80(8)	95.21(10)	95.99(10)
O2 – Cu – N8	141.17(8)	144.06(10)	143.20(10)
O2 – Cu – N23	109.82(8)	107.52(10)	108.75(10)

Table S2. π–π interactions in **(1)**, **(2)** and **(3).**

Cg	*Cg*	*Cg*···*Cg* [Å]	*β* [°]	*CgI*···perp [Å]
$[Cu\mathbf{L}^{1}(SO_4)]_6 \cdot 24H_2O$ (**1**)				
*Cg*4	*Cg*5^{i}	3.640	25	0.52
*Cg*4	*Cg*7	3.940	18	3.05
$[Cu\mathbf{L}^{2}(SO_4)]_6 \cdot 24H_2O$ (**2**)				
*Cg*4	*Cg*5^{ii}	3.613	24	6.64
*Cg*5	*Cg*6	3.899	18	3.16
$[Cu\mathbf{L}^{3}(SO_4)]_6 \cdot 24H_2O$ (**3**)				
*Cg*4	*Cg*5^{i}	3.630	25	0.32
*Cg*4	*Cg*7	3.926	19	3.09

Symmetry codes: (i) = 2/3+x-y,1/3+x,1/3-z ; (ii) = x-y,-1+x,-z

Table S3. CH···O and CH···*Cg* interactions in **(1)**, **(2)** and **(3).**

C – H	*A*	H···*A* [Å]	C···*A* [Å]	C–H···*A* [°]
$[Cu\mathbf{L}^{1}(SO_4)]_6 \cdot 24H_2O$ (**1**)				
C2 – H2	O2	2.542(3)	3.143(5)	121
C4 – H4	O3^{i}	2.577(3)	3.468(5)	156
C7 – H7	O3^{ii}	2.430(3)	3.276(5)	148
C25 – H25	O4^{ii}	2.581(3)	3.250(5)	128
C22 – H22	O4^{iii}	2.242(4)	3.164(6)	164
$[Cu\mathbf{L}^{2}(SO_4)]_6 \cdot 24H_2O$ (**2**)				
C17 – H17A	O2	2.487(3)	3.101(4)	122
C18 – H18A	O2^{iv}	2.527(3)	3.192(5)	127
C7 – H7A	O3^{v}	2.208(3)	3.118(4)	160
C19 – H19A	O4 ^{iv}	2.462(4)	3.353(5)	156
C22 – H22A	O4^{vi}	2.411(2)	3.272(4)	151
C15 – H15A	*Cg*4^{vii}	3.165	4.038	148
C15 – H15A	*Cg*7^{vii}	3.312	3.637	101
C15 – H15B	*Cg*7^{vii}	3.188	3.637	109
$[Cu\mathbf{L}^{3}(SO_4)]_6 \cdot 24H_2O$ (**3**)				
C17 – H17	O1	2.599(2)	3.088(3)	112
C2 – H2	O2	2.465(2)	3.072(3)	122
C3 – H3	O2^{i}	2.569(2)	3.213(3)	125
C4 – H4	O3^{i}	2.478(2)	3.390(3)	161
C7 – H7	O3^{viii}	2.452(2)	3.301(3)	149
C22 – H22	O4^{iii}	2.193(2)	3.097(3)	158
C28 – H28	Cg6^{ix}	3.112	3.600	114

Symmetry codes: (i) = 2/3+x-y,1/3+x,1/3-z ; (ii) = 4/3-y,2/3+x-y,-1/3+z ; (iii) = -1/3+y,1/3-x+y,1/3-z ; (iv) = 1+y,1-x+y,-z ; (v) = x-y,-1+x,-z ; (vi) = 5/3-x+y,4/3-x,1/3+z ; (vii) = 5/3-x,1/3-y,1/3-z ; (viii) = 4/3-y,2/3+x-y,-1/3+z ; (ix) = 1-x,1-y,-z

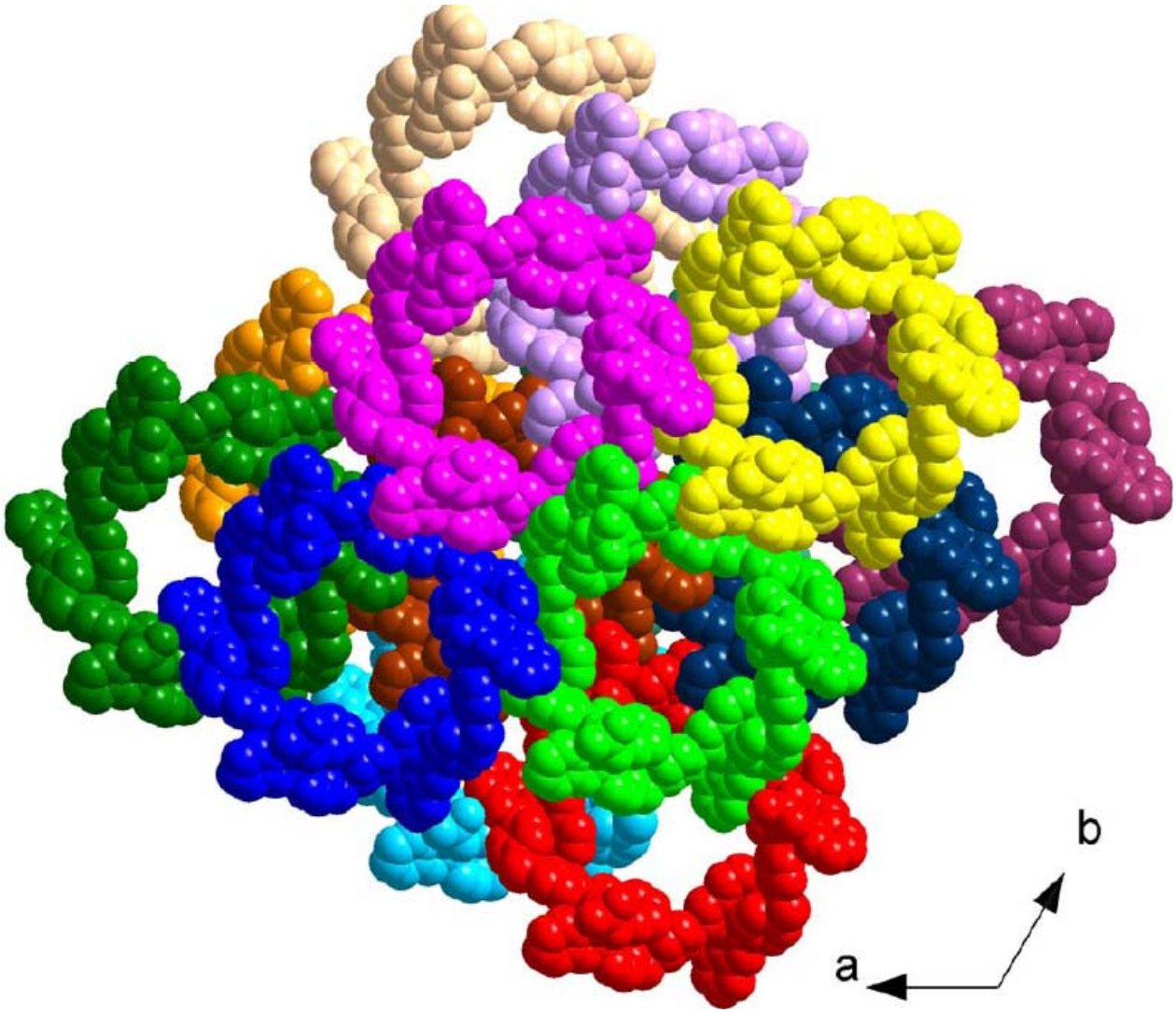
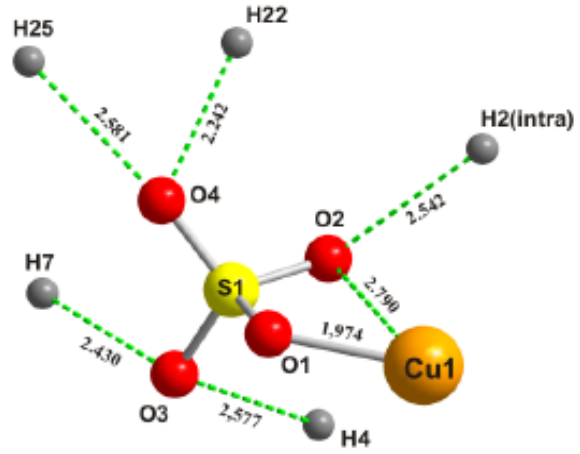
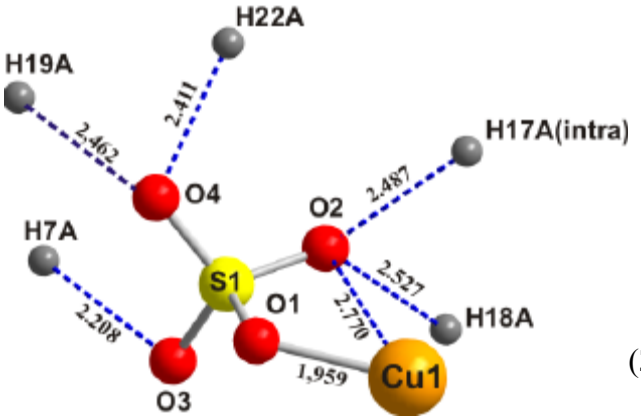


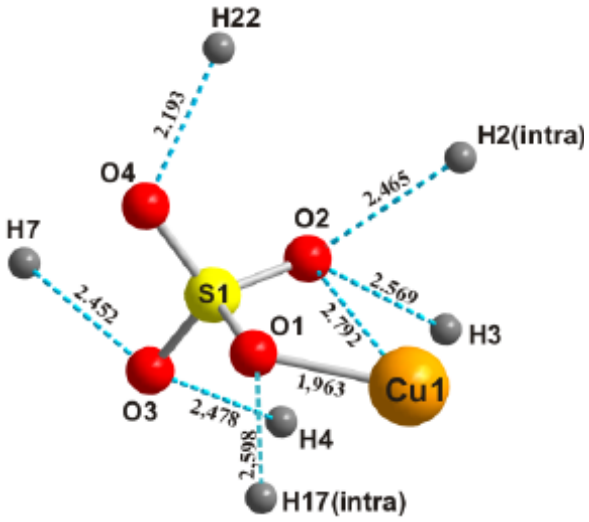
Figure S8. Top view of the packing of the hexanuclear circular *meso*-helicates $[Cu\mathbf{L}(SO_4)]_6$; each *meso*-helicates is shown in a different color. Hydrogen atoms are omitted for clarity.



(1)



(2)



(3)

Figure S9. Intra- and intermolecular hydrogen bonds (Å) of sulfate oxygen atoms in the circular *meso*-helicates **(1)**, **(2)** and **(3)**.

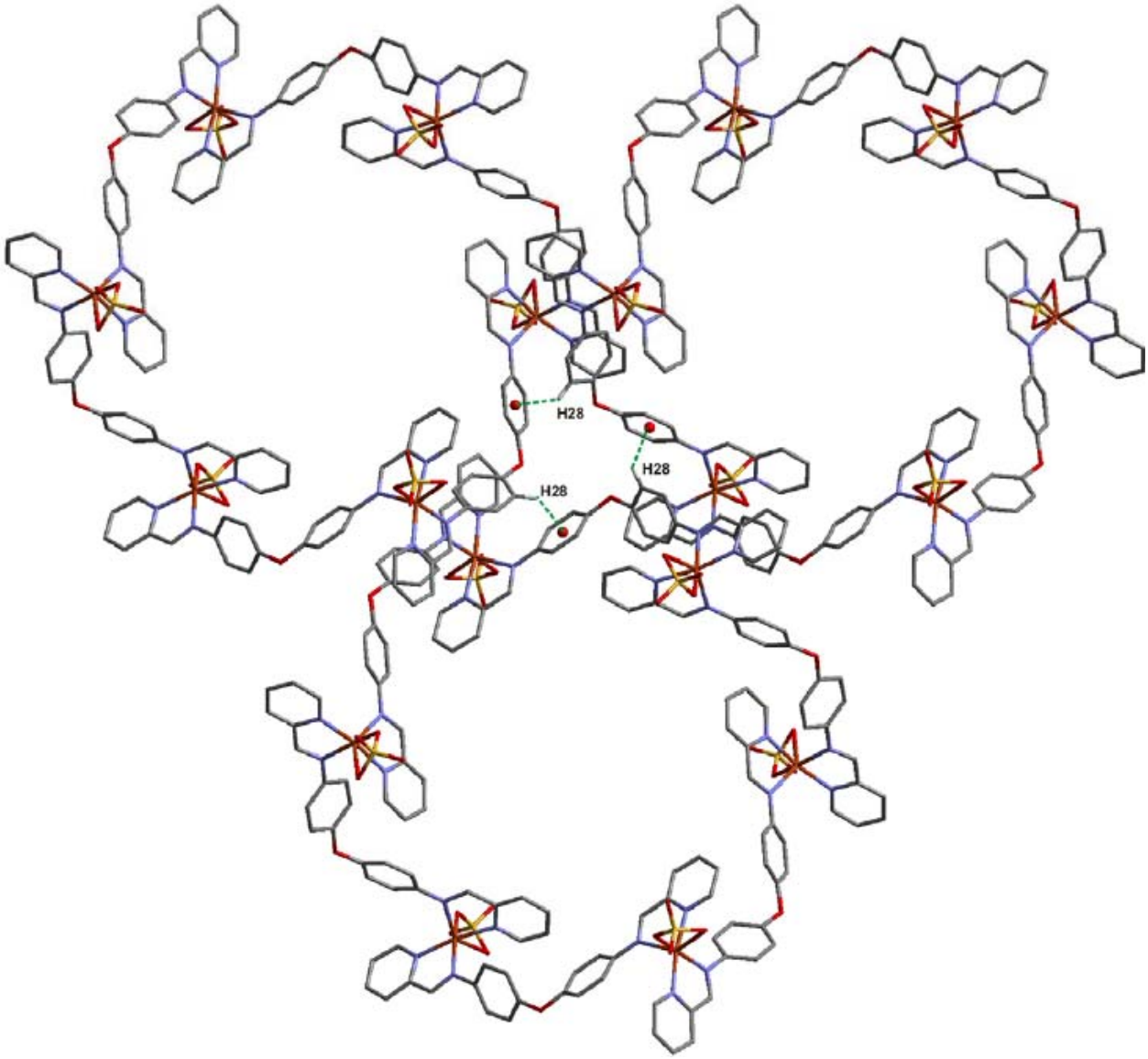


Figure S10. Wireframe representation of three single helicates of the assembly showing additional CH–π interactions in $[Cu\mathbf{L}^{3}(SO_4)]_6$ (**3**).

References

1 Y. Parajo, J. Malina, I. Meistermann, G. J. Clarkson, M. Pascu, A. Rodger, M. J. Hannon, P. Lincoln, *Dalton Trans*., 2009, 4868.

2 a) N. Yoshida, K. Ichikawa, *Chem. Commun.,* 1997, 1091; b) M. J. Hannon, C. L. Painting, N. W. Alcock, *Chem. Commun.*, 1999, 2023; c) N. Yoshida, K. Ichikawa, M. Shiro**,** *J. Chem. Soc., Perkin Trans*.2, 2000, 17; d) C. He, C. Y. Duan, C. J. Fang, Q. J. Meng, *J. Chem. Soc., Dalton Trans*., 2000, 2419; e) M. J. Hannon, V. Moreno, M. J. Prieto, E. Moldrheim, E. Sletten, I. Meistermann, C. J. Isaac, K. J. Sanders, A. Rodger, *Angew. Chem. Int. Ed.*, 2001**, 40,** 879; f) L. Xu, X.-T. Chen, Y. Xu, D.-R. Zhu, X.-Z. You, L.-H. Weng, *J. Mol. Struct.*, 2001**, 559***,*** 361; g) J. Keegan, P. E. Kruger, M. Nieuwenhuyzen, N. Martin, *Cryst. Growth Des*., 2002, **2**, 329.