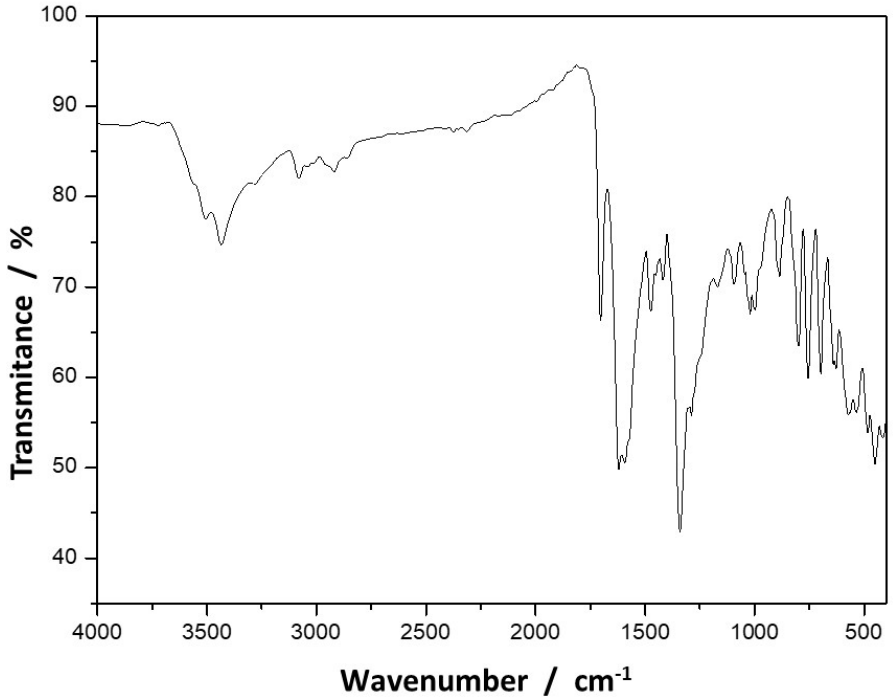

Figure S1. FTIR spectrum of **1**.

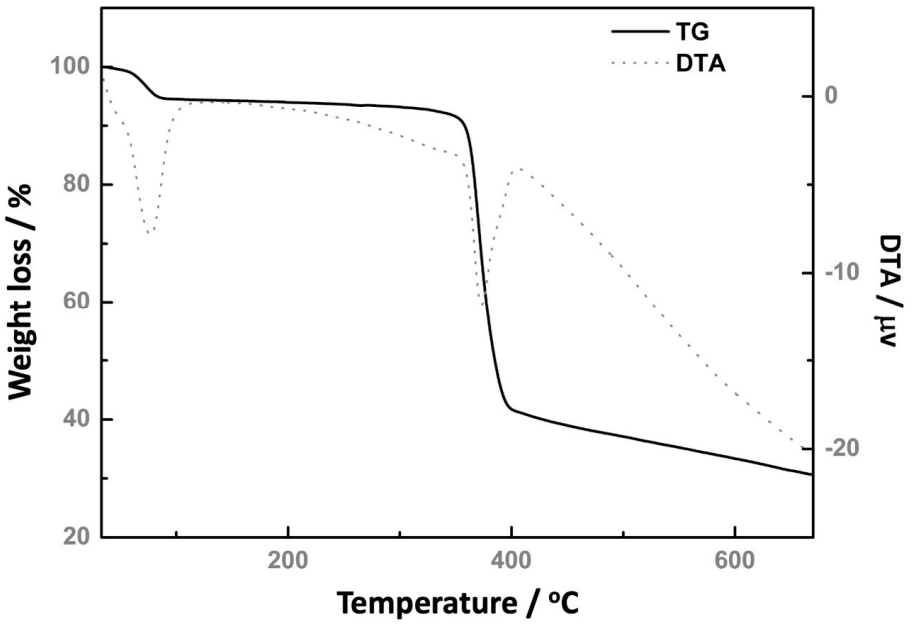

Figure S2. TG (solid line) and DTG (dashed line) curves for **1** in $N_{2(g)}$ atmosphere.

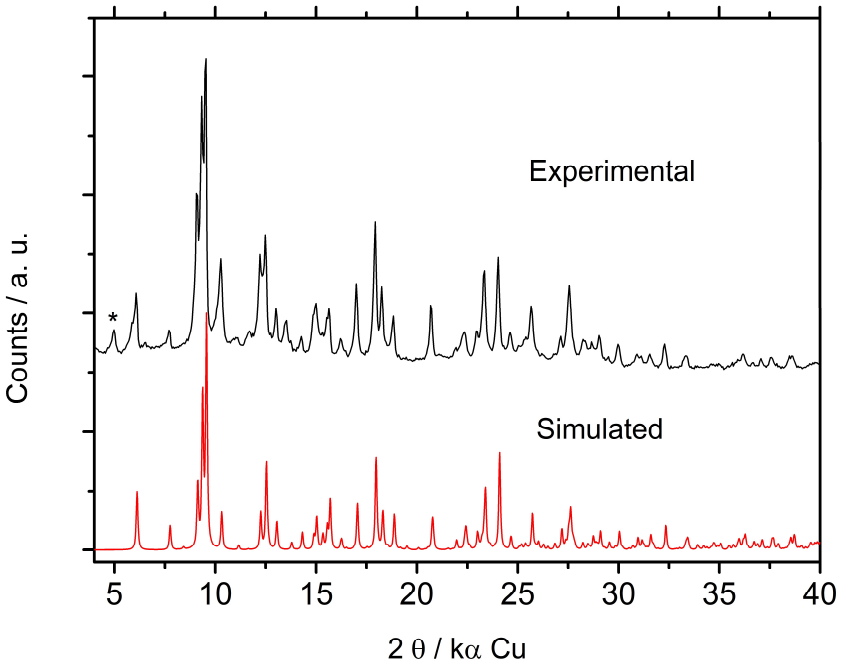

Figure S3. Experimental (solid black line) and simulated (solid red line) PXRD patterns for **1**.

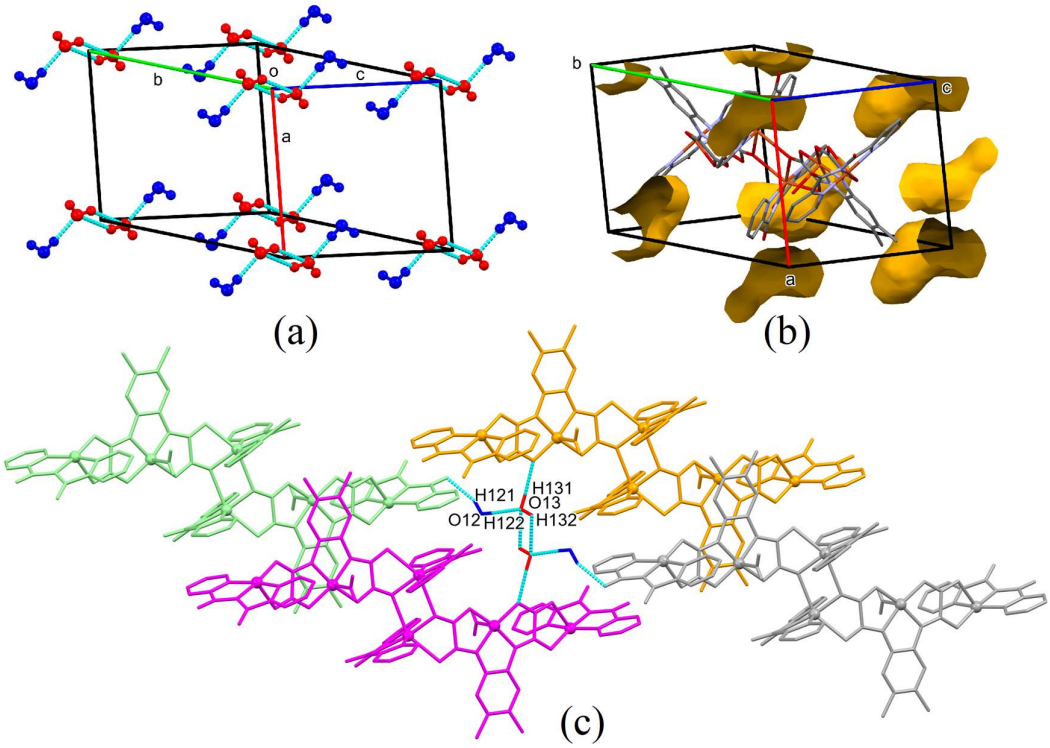

Figure S4. (a) View the crystallization water super-structure depicting the tetramer-cluster at the unit cell corner and (b) the calculated voids (surfaces in orange) surrounding a hexanuclear unit inside the unit cell in the same perspective view. View of each water-cluster surrounded by four hexanuclear units (c) being stabilized by the H bond network. The scheme color (red and blue) in (a) differentiates the independent symmetry of water molecules in the asymmetric unit. H bond is in dashed cyan lines. Non-water hydrogen atoms were omitted in some views for clarity.

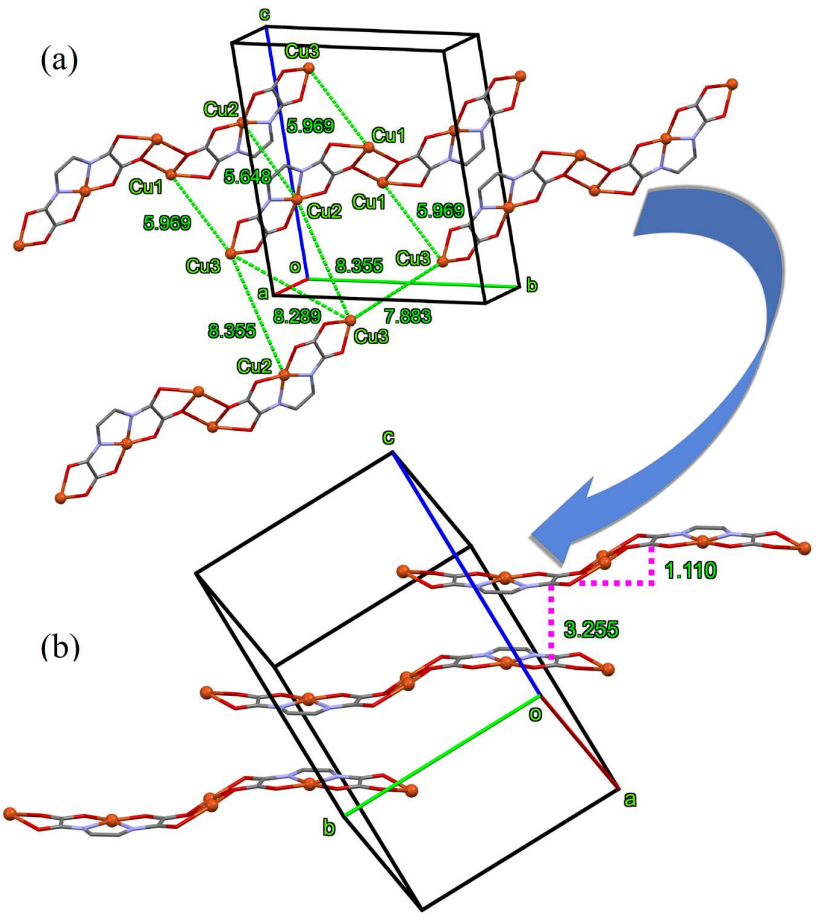

Figure S5 (a) Packing view of the hexanuclear units showing the chains along the crystallographic *b* axis showing the shortest interhexanuclear Cu···Cu distances (dashed green lines). (b) The perspective view of the star-like chain showing the parallel disposition of the hexanuclear units along the crystallographic *c* axis is shifted along the crystallographic *b* axis resulting in a stair-like chain formed along the crystallographic *b* axis with two-step rises (highlighted in magenta dashed lines). Just the copper atoms and part of the dmopba ligand were used to generate the illustration for clarity.

Table S1. Crystal data and structure refinement for **1**.

CCDC	2201495	
Empirical formula	$C_{36}H_{30}Cu_3N_8O_{13}$	
Molecular formula	$C_{72}H_{60}Cu_6N_{16}O_{26}$	
Empirical formula weight	973.30	
Measurement temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 10.781 Å	α = 98.24°
	b = 12.956 Å	β = 105.08°
	c = 15.572 Å	γ = 113.74°
Volume	1845.3 $Å^3$	
Z/Z′	1/0.5	
Density (calculated)	1.752 Mg/m^3	
Absorption coefficient	1.794 mm^{-1}	
F(000)	986	
Theta range for data collection	1.789 to 29.483°.	
Index ranges	–11<=h<=13, –17<=k<=17, –19<=l<=18	
Reflections collected	18486	
Independent reflections	8727 [R(int) = 0.0349]	
Completeness to theta = 25.242°	100.0 %	
Data / restraints / parameters	8727 / 9 / 552	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2σ(I)]	R1 = 0.0388, wR2 = 0.0855	
R indices (all data)	R1 = 0.0587, wR2 = 0.0954	
Largest diff. peak and hole	0.425 and –0.551 $e.Å^{-3}$	

Table S2. Bond lengths [Å] and angles [°] for **1**.

Cu1 Geometry		Cu2 Geometry		Cu3 Geometry	
N3–Cu1	2.022(2)	O3–Cu2	1.977(2)	N6–Cu3	2.000(2)
N4–Cu1	1.924(2)	O4–Cu2	1.969(2)	N7–Cu3	1.921(2)
N5–Cu1	1.997(2)	N1–Cu2	1.916(2)	N8–Cu3	2.004(2)
O1–Cu1	2.404(2)	N2–Cu2	1.918(2)	O5–Cu3	1.955(2)
O2–Cu1	1.969(2)	O11–Cu2	2.484(2)	O6–Cu3	2.274(2)
O2i–Cu1	2.629(2)	N1–Cu2–N2	83.61(9)	N7–Cu3–O5	170.62(9)
N4–Cu1–O2	170.27(9)	N1–Cu2–O4	167.74(8)	N7–Cu3–N6	82.07(9)
N4–Cu1–N5	82.37(9)	N2–Cu2–O4	84.68(8)	O5–Cu3–N6	100.12(8)
O2–Cu1–N5	98.91(8)	N1–Cu2–O3	84.72(8)	N7–Cu3–N8	82.13(9)
N4–Cu1–N3	81.97(9)	N2–Cu2–O3	167.93(8)	O5–Cu3–N8	95.14(9)
O2–Cu1–N3	96.77(8)	O4–Cu2–O3	106.75(7)	N6–Cu3–N8	164.06(9)
N5–Cu1–N3	164.28(9)	N1–Cu2–O11	90.46(9)	N7–Cu3–O6	109.38(8)
N4–Cu1–O1	113.19(8)	N2–Cu2–O11	88.75(9)	O5–Cu3–O6	79.69(7)
O2–Cu1–O1	76.41(7)	O3–Cu2–O11	94.41(8)	N6–Cu3–O6	93.40(8)
N5–Cu1–O1	94.47(8)	O4–Cu2–O11	92.87(8)	N8–Cu3–O6	93.83(9)
N3–Cu1–O1	90.37(8)				

Symmetry transformations used to generate equivalent atoms: (i) = –x+1, –y+1, –z+1

Table S3. Hydrogen bond lengths [Å] and angles [°] for **1**, where D and A are the donor and acceptor hydrogen atom, respectively.

	D—H	H•••A	D•••A	A—H•••A	Symmetry codes*
O12—H121•••O9	0.87	2.12	2.944(5)	158.2	
O13—H131•••O4	0.87	2.21	3.008(4)	152.9	
O11—H112•••O10^{ii}	0.87	1.93	2.799(3)	173.7	^{ii} -x+1, -y+2, -z+2
C14—H14•••O10^{ii}	0.93	2.47	3.349(4)	157.5	^{ii} -x+1, -y+2, -z+2
C34—H34•••O6^{ii}	0.93	2.62	3.328(4)	133.6	^{ii} -x+1, -y+2, -z+2
O11—H111•••O7^{iii}	0.87	2.08	2.929(3)	163.8	^{iii} -x, -y+1, -z+1
C35—H35•••O7^{iii}	0.93	2.51	3.316(4)	145.0	^{iii} -x, -y+1, -z+1
C35—H35•••O8^{iii}	0.93	2.52	3.285(4)	139.2	^{iii} -x, -y+1, -z+1
C15—H15•••O1^{iii}	0.93	2.55	3.314(3)	139.8	^{iii} -x, -y+1, -z+1
O12—H122•••O13^{iv}	0.87	2.13	2.996(6)	173.6	^{iv} -x+2, -y+3, -z+2
O13—H132•••O13^{v}	0.87	2.60	3.200(8)	127.5	^{v} -x+2, -y+2, -z+2

* Symmetry transformations used to generate equivalent atoms

Table S4. Shape measurements analysis for **1***.

			ML_6		
	HP-6	**PPY-6**	**OC-6**	**TPR-6**	**JPPY-6**
Cu1	33.980	21.179	4.338	11.172	24.305
			ML_5		
	PP-5	**vOC-5**	**TBPY-5**	**SPY-5**	**JTBPY-5**
Cu2	31.274	1.911	6.683	1.508	9.644
Cu3	25.562	2.323	6.920	2.334	9.061

*HP-6 = Hexagon; PPY-6 = Pentagonal pyramid; OC-6 = Octahedron; TPR-6 = Trigonal prism; JPPY-6 = Johnson pentagonal pyramid J2; PP-5 = Pentagon; vOC-5 = Vacant octahedron; TBPY-5 = Trigonal bipyramid; SPY-5 = Spherical square pyramid; JTBPY-5 = Johnson trigonal bipyramid J12.