Electronic Supplementary Information

Molecular Pac-Men and Tacos: Layered Cu(II) cages from ligands with premeditated high binding site concentrations

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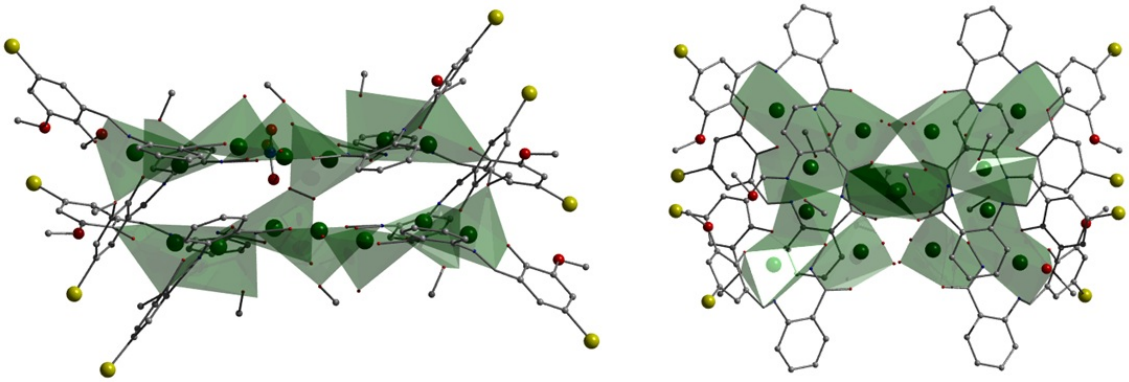

Figure S1 Polyhedral representations of the crystal structure in **3** as viewed parallel (left) and perpendicular (right) to the $\{Cu_7\}$ planes. Hydrogen atoms and NO_3^- counter anions have been omitted for clarity.

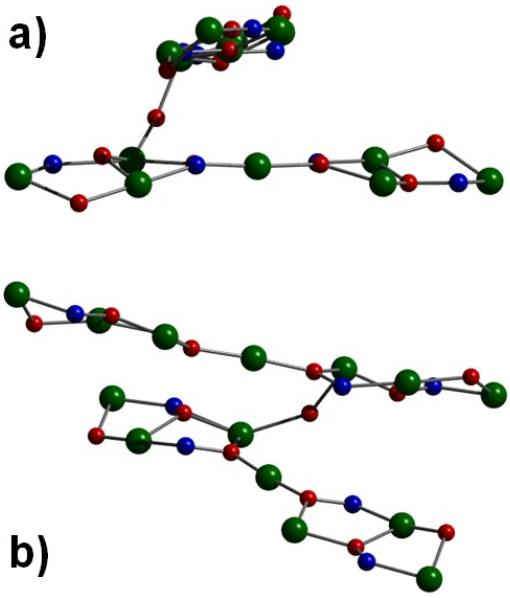

Figure S2 The criss-cross orientation of the $\{Cu_7\}$ planes in **3** as viewed parallel (a) and off-set (b).

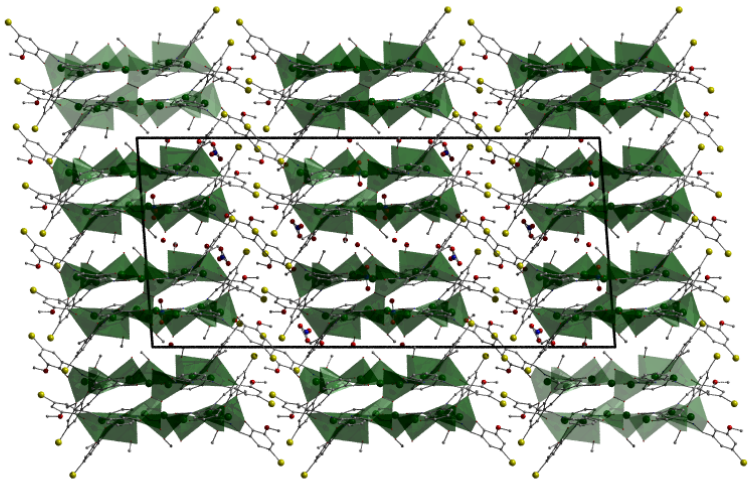

Figure S3 Crystal packing arrangement observed in **3** as viewed along the *b* unit cell direction.

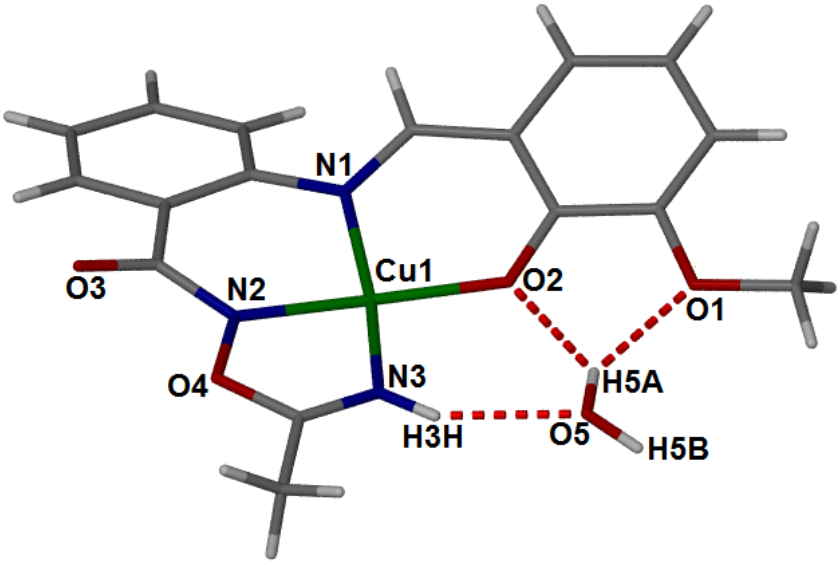

Figure S4 The monomeric unit in **1** and its extensive H-bonding (dashed red lines) with a juxtaposed water of crystallisation. H-bond distances (Å): N3(H3H)···O5 = 2.142, O5(H5A)···O1 = 2.206 and O5(H5A)···O2 = 2.303.

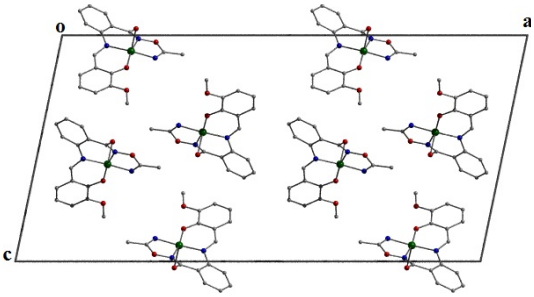

Figure S5 Packing arrangement of 1D units of **6** as viewed down the *b* axis of the unit cell. Hydrogen atoms and H_2O solvents of crystallisation have been removed for clarity.

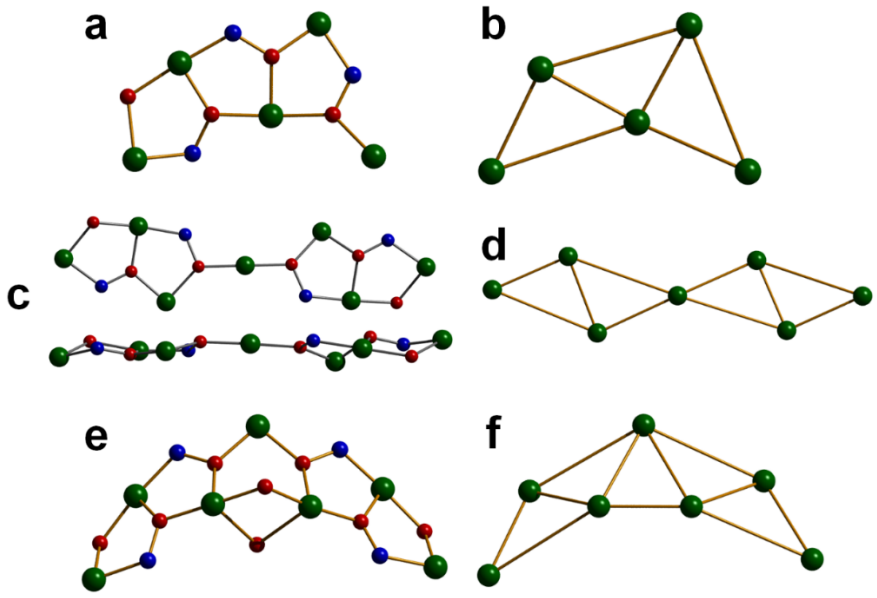

Figure S6 (a) A $\{Cu_5\}$ layer within the structure in **1**. (b) A skeletal representation of a $\{Cu_5\}$ layer in **1**. (c) A $\{Cu_7\}$ layer observed within the structures of **2-4** as viewed perpendicular and parallel to their heptanuclear planes. **(d)** A skeletal representation of a $\{Cu_7\}$ layer observed in complexes **2-4**. (e) A $\{Cu_7\}$ within the structure in **5**. (f) A skeletal representation of a $\{Cu_7\}$ layer in the structure of **5**.

Table S1 Crystallographic data obtained from complexes **1**-**4**

	1	**2**.3MeOH.7H_2O	**3**	**4**.4MeOH.4H_2O
Formula[a]	$C_{74}H_{60}N_{12}O_{38}Cl_4Cu_{10}$	$C_{125.5}H_{125}N_{16}O_{57}Cu_{14}$	$C_{123}H_{101.17}N_{20}O_{42.58}Br_8Cu_{14}$	$C_{122}H_{124}N_{20}O_{60}Cu_{14}$
M_W	2502.54	3827.01	4013.52	3643.88
Crystal System	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	*P*-1	C2/c	$P2_1/c$
a/Å	23.6341(10)	15.4185(6)	47.208(3)	18.989(4)
b/Å	25.5162(8)	22.8429(7)	16.6283(12)	13.838(3)
c/Å	16.5739(9)	25.1092(9)	21.3697(15)	26.748(5)
α/°	90.00	71.435(3)	90.00	90.00
β/°	104.244(5)	77.204(3)	94.2850(10)	91.05(3)
γ/°	90.00	80.405(3)	90.00	90.00
V/Å^3	9687.7(8)	8130.8(5)	16728(2)	7028(2)
Z	4	2	4	2
T/K	150(2)	173(2)	173(2)	150(2)
λ[b]/Å	0.71073	0.71073	0.71073	0.71073
D_c/g cm^{-3}	1.716	1.563	1.594	1.722
μ(Mo-Ka)/ mm^{-1}	2.348	1.882	3.723	2.169
Meas./indep.(R_{int}) refl.	8858/5297 (0.1077)	28668/13027 (0.1112)	19105 / 12747(0.0572)	12859/8415(0.1128)
wR2 (all data)[c]	0.1766	0.2446	0.1503	0.2302
*R*1[d,e]	0.0658	0.0861	0.0551	0.0948
Goodness of fit on F^2	1.010	0.937	1.058	1.050

[a] Includes guest molecules (does not include SQUEEZE results obtained on **2**-**4**).[b] Mo-Kα radiation, graphite monochromator. [c] $wR2= [\Sigma w(|F_o^2|- |F_c^2|)^2/ \Sigma w|F_o^2|^2]^{1/2}$. [d]For observed data. [e] $R1= \Sigma||F_o|- |F_c||/ \Sigma|F_o|$.

Table S2 Crystallographic data obtained from complex **5** and **6**.

Complex	**5**	**6**·H_2O
Formula[a]	$C_{246}H_{202}N_{32}O_{94}Cl_4Cu_{30}$	$C_{17}H_{17}N_3O_5Cu_1$
M_W	7158.38	406.88
Crystal System	Triclinic	Monoclinic
Space group	*P*-1	*C*2/*c*
a/Å	18.6255(5)	36.1459(12)
b/Å	20.6535(7)	5.2200(2)
c/Å	38.2976(12)	18.0068(7)
α/°	92.913(3)	90.00
β/°	99.064(3)	101.697(3)
γ/°	103.632(3)	90.00
V/Å^3	14079.1(8)	3327.0(2)
Z	2	8
T/K	150(2)	150(2)
λ[b]/Å	0.71073	0.71073
D_c/g cm^{-3}	1.689	1.625
μ(Mo-Ka)/ mm^{-1}	2.340	1.348
Meas./indep., (R_{int}) refl.	51469/25059 (0.1034)	3047/2627, (0.0249)
wR2 (all data)	0.3398	0.0842
*R*1[d,e]	0.1234	0.0315
Goodness of fit (GOOF) on F^2	1.054	1.066

[a] Includes guest molecules (does not include SQUEEZE results on complex **5**). [b] Mo-Kα radiation, graphite monochromator. [c] $wR2= [\sum w(|F_o^2|- |F_c^2|)^2/ \sum w|F_o^2|^2]^{1/2}$. [d] For observed data. [e] $R1= \sum||F_o|- |F_c||/ \sum|F_o|$.