Selective Encapsulation of a Chloride Anion in a 1*H*-Pyrazole Cu²⁺.

Javier Pitarch-Jarque,[a] Hermas R. Jiménez,[a] Elina Kalenius,[b] Salvador Blasco,*[a] Alberto Lopera,[a] M. Paz Clares,[a] Kari Rissanen[b] and Enrique García-España*[a]

[a] Instituto de Ciencia Molecular, Universidad de Valencia, C/Catedrático José Beltrán Martínez 2, 46980 Paterna, Spain. E-mail: salvador.blasco@uv.es, enrique.garcia-es@uv.es

[b] University of Jyväskylä, Department of Chemistry, P.O. Box. 35, FI-40014; University of Jyväskylä, Finland

Contents

List of Figures

List of Tables
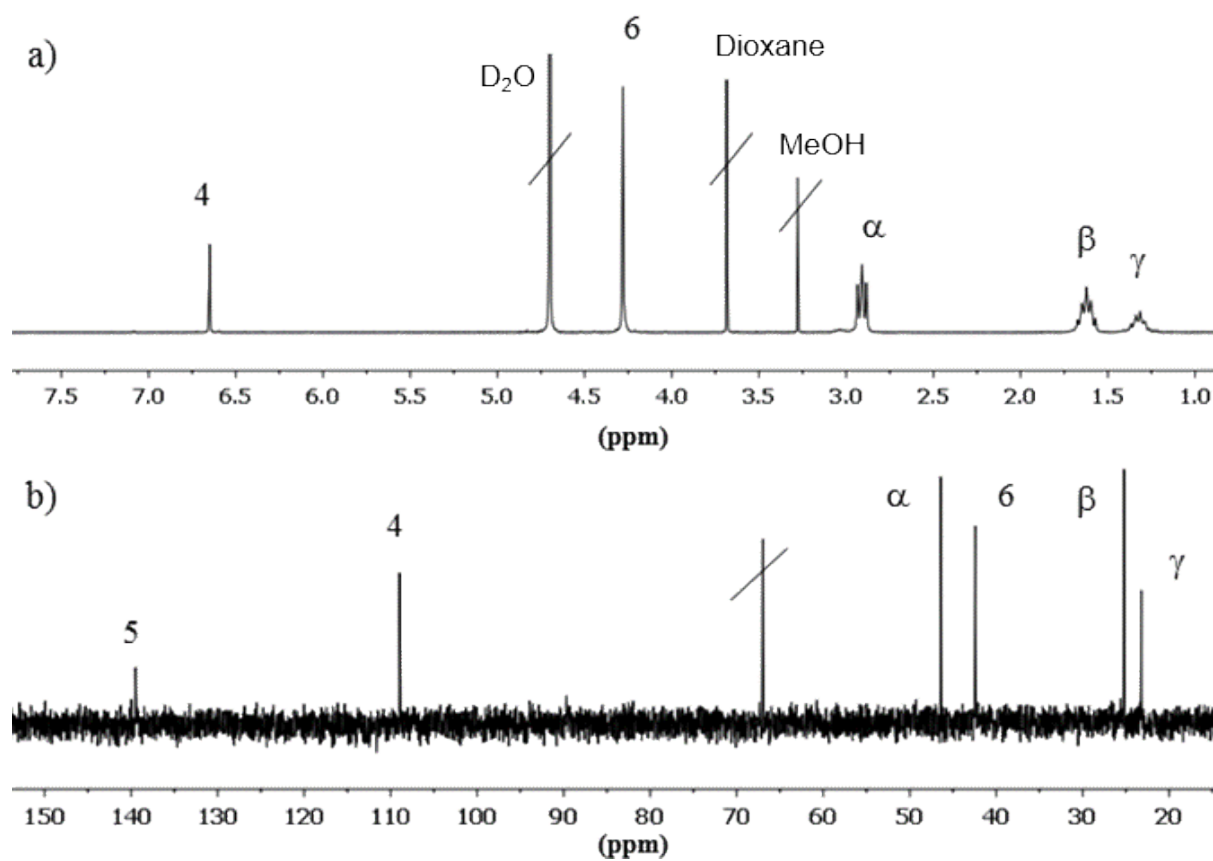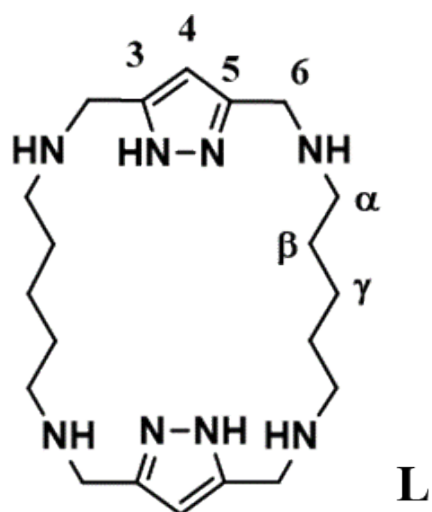
1 Ligand characterisation.

L

Figure S1: (a) ^{1}H NMR (300 MHz, D$_2$O) spectrum of **L**. (b) ^{13}C NMR (75 MHz, D$_2$O) spectrum of **L**.
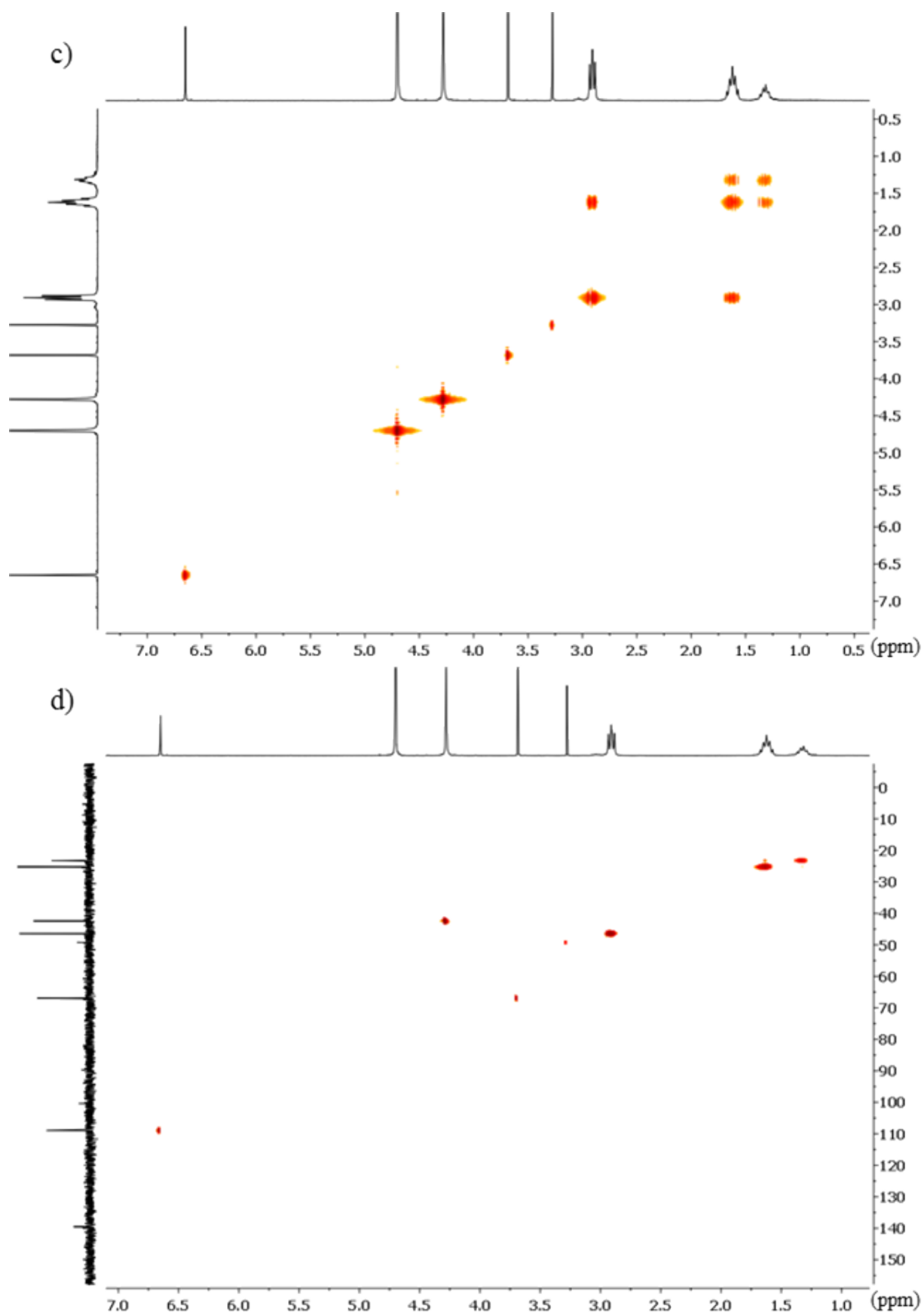
Figure S2: (c) COSY and (d) HSQC in D$_2$O of **L**.

2 Crystallographic information

Table S1: Crystallographic data

	1	2	3	4
Formula	$C_{40}H_{78.67}Cu_4F_{14}N_{16}$ $O_{5.33}P_2$	$C_{40}H_{74}Cl_4Cu_4N_{16}O_3$	$C_{80}H_{136}Br_4Cu_8N_{32}$	$C_{40}H_{60}ClCu_5$ $I_7N_{16}O_4$
Weight / g mol^{-1}	1451.27	1223.11	2374.16	2077.10
Density / g cm^{-3}	1.423	1.601	1.488	1.962
Size	$0.30 \times 0.10 \times 0.05$	$0.20 \times 0.20 \times 0.20$	$0.24 \times 0.09 \times 0.08$	$0.20 \times 0.10 \times 0.10$
System	orthorhombic	triclinic	monoclinic	orthorhombic
Space Group	I bam	$P-1$	$I\,2/m$	I mmm
Cell				
$a/\text{Å}$	13.861(3)	12.0598(7)	14.34035(14)	20.5739(9)
$b/\text{Å}$	20.5434(17)	14.3764(8)	18.7171(2)	14.4716(5)
$c/\text{Å}$	23.7890(18)	15.6936(6)	19.8559(2)	11.8083(4)
$\alpha/°$		108.589(4)		
$\beta/°$		90.753(4)	96.1863(10)	
$\gamma/°$		99.531(5)		
$V/\text{Å}^3$	6774.0(17)	2537.0(2)	5298.49(10)	3515.8(2)
Z	4	2	2	2
T/K	291.0(2)	120.0(1)	123(1)	291.0(2)
Θ range / $°$	3.21–32.40	3.03–32.33	1.80–26.62	3.84–23.65
$F(000)$	2981	1268	2424	1959
μ/cm^{-1}	1.373	1.920	3.136	4.677
Reflections				
- total	12959	27668	20584	9900
- unique	5683	14775	5669	2586
- $I > 2\sigma_I$	2350	7843	5318	1536
Parameters	209	663	320	117
Constraints	0	0	0	0
Restraints	0	9	61	0
Indices	$-20 < h < 8$	$-15 < h < 16$	$-18 < h < 14$	$-26 < h < 27$
	$-17 < k < 31$	$-20 < k < 20$	$-23 < k < 20$	$-20 < k < 17$
	$-34 < l < 15$	$-22 < l < 22$	$-24 < l < 24$	$-16 < l < 16$
R(int)	0.0945	0.0472	0.0186	0.0332
R(sigma)	0.1500	0.0901	0.0139	0.0347
$R1$	0.2068	0.1311	0.0519	0.0904
$R1(I > 2\sigma_I)$	0.0835	0.0607	0.0493	0.0553
$wR2$	0.2520	0.1755	0.1403	0.1925
$wR2(I > 2\sigma_I)$	0.2034	0.1326	0.1429	0.1623
GooF	0.921	1.018	1.039	1.033
CCDC number	1994846	1994845	1994844	1994847

Table S2: Hydrogen bonds of structure **1**

	distances / Å			angles / °
D–H···A	D–H	H···A	D···A	D–H···A
O(1)–H(1A)···(F6)	0.92	2.21	2.748(6)	117
O(1)–H(1A)···(F4)^i	0.92	2.21	3.067(6)	156
O(1)–H(1B)···(F2)	0.91	2.23	2.99(3)	141
O(1)–H(1B)···(F3)	0.91	2.29	2.84(2)	119
N(2)–H(2) ···(F5)	0.98	2.10	2.905(5)	138
N(2)–H(2) ···(F6)	0.98	2.19	3.087(6)	152
N(3)–H(3) ···(F5)	0.98	2.32	3.062(5)	132
N(3)–H(3) ···(F4)^i	0.98	2.09	3.034(6)	162

D: donor, A: acceptor, H: hydrogen. Symmetry operations: (i) $\frac{1}{2} - x$, $\frac{1}{2} - y$, $\frac{1}{2} - z$
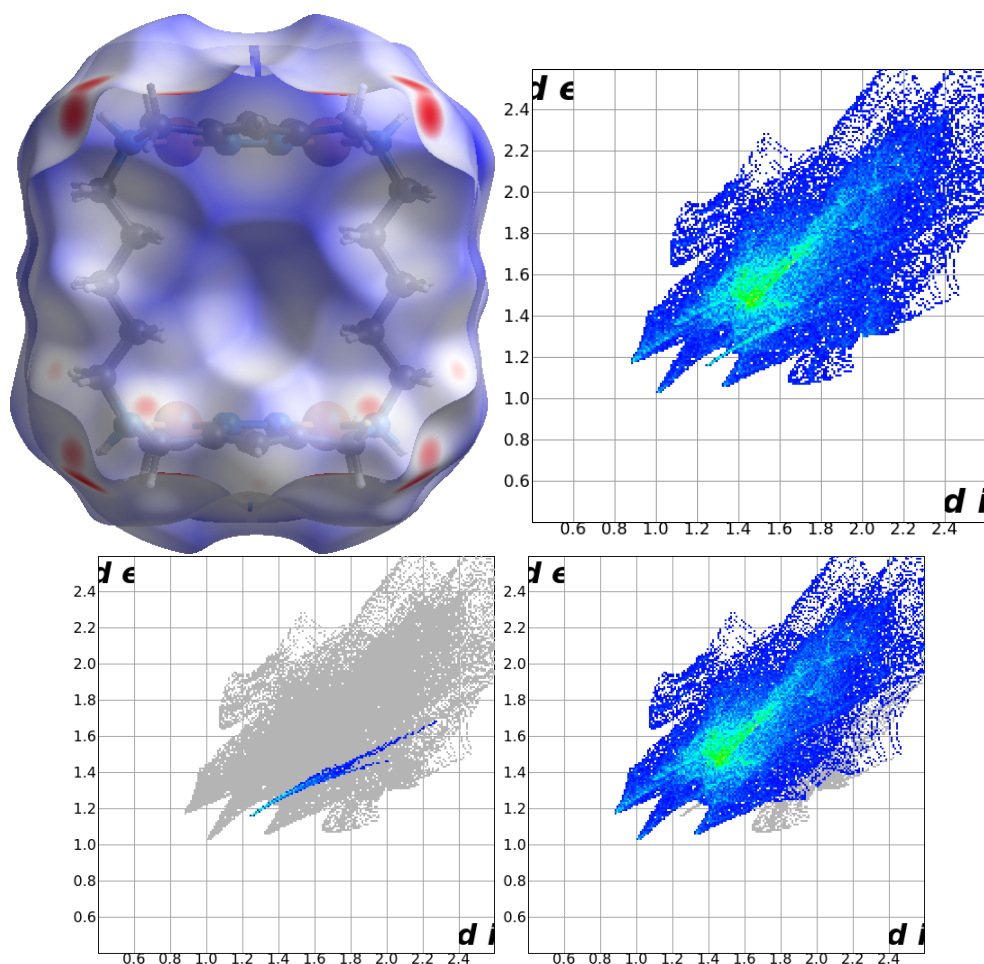

Figure S3: (top) Hirshfeld surface representation for structure **1**. (middle) Hirshfeld surface fingerprint for all interactions. (bottom left) Interactions involving copper from the inside and oxygen on the outside which represent 2.1 % of the Hirshfeld surface. (bottom right) Interactions involving hydrogen from the inside with any atom in the outside which account for 92.1 % of the Hirshfeld surface.

Table S3: Hydrogen bonds of structure **2**

D–H⋯A	distances / Å			angles / °
	D–H	H⋯A	D⋯A	D–H⋯A
N(16)–H(16)⋯O(3)	1.00	2.13	3.127(4)	175.5
N(4)–H(4)⋯Cl(2)^{i}	1.00	2.46	3.293(4)	140.2
N(5)–H(5)⋯O(1)^{ii}	1.00	2.17	3.021(5)	141.4
N(1)–H(1)⋯Cl(4)^{iii}	1.00	2.31	3.230(4)	152.4
O(3)–H(3A)⋯Cl(3)^{iii}	0.78	2.38	3.076(3)	149.2
O(3)–H(3B)⋯Cl(4)^{iv}	0.82	2.49	3.173(3)	141.2
C(6)–H(6B)⋯Cl(1)	0.99	2.66	3.28(1)	121.5
N(13)–H(13A)⋯Cl(3)^{ii}	1.00	2.40	3.303(4)	150.2
N(13)–H(13A)⋯O(1)^{ii}	1.00	2.50	3.238(5)	130.8
O(2)–H(2A)⋯Cl(2)^{iv}	0.80	2.43	3.154(5)	150.6
O(2)–H(2B)⋯Cl(4)^{v}	0.81	2.43	3.161(5)	150.0

D: donor, A: acceptor, H: hydrogen. Symmetry operations: (i) $-x$, $1-y$, $1-z$; (ii) $1-x$, $1-y$, $1-z$; (iii) x, $1+y$, z; (iv) $1-x$, $1-y$, $1-z$; (v) $1-x$, $-y$, $1-z$.
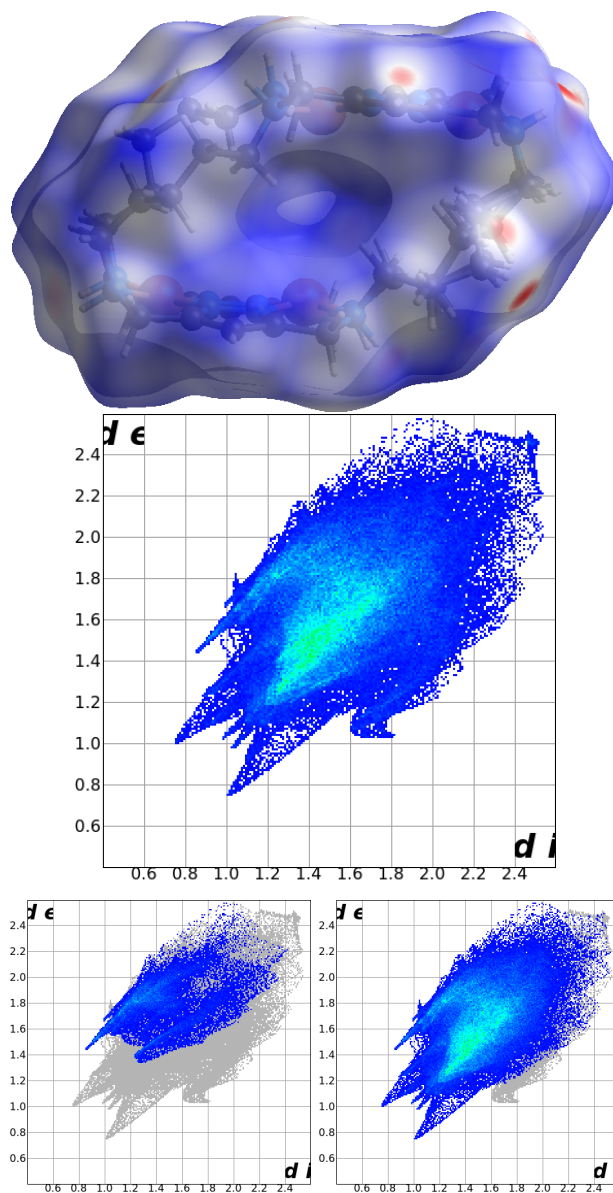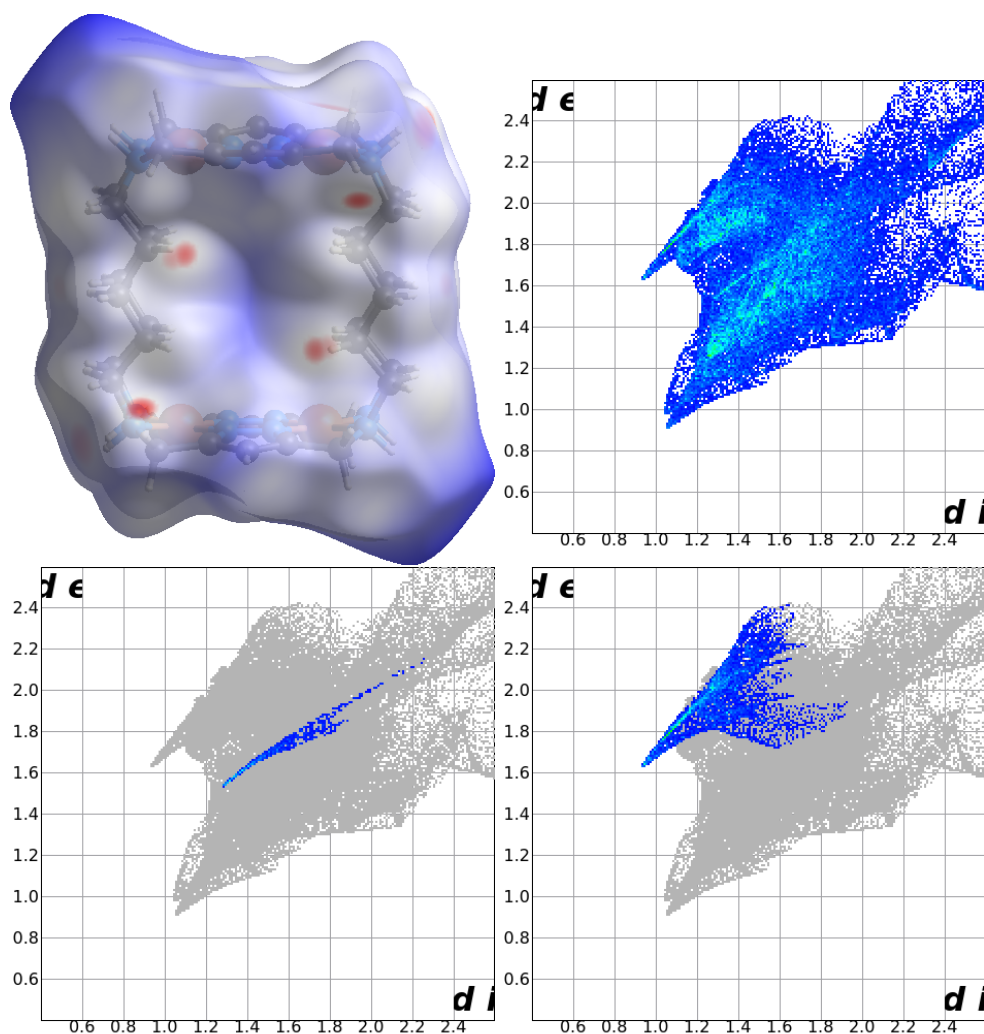

Figure S4: (top) Hirshfeld surface representation for structure **2**. (middle) Hirshfeld surface fingerprint for all interactions. (bottom left) Interactions involving chlorine outside with any atom in the inside which represent 15.7 % of the Hirshfeld surface. (bottom right) Interactions involving hydrogen from the inside with any atom in the outside which account for 89.7 % of the Hirshfeld surface.

Table S4: Hydrogen bonds of structure **3**

D–H⋯A	distances / Å			angles / °
	D–H	H⋯A	D⋯A	D–H⋯A
N(5)–H(5A)⋯ Br(1)^i	1.00	2.60	3.336(5)	130.6
N(1)–H(1)⋯ Br(2)^{ii}	1.00	2.58	3.433(3)	143.6

D: donor, A: acceptor, H: hydrogen. Symmetry operations: (i) $\frac{3}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$; (ii) $-x$, $-y$, $1 - z$.
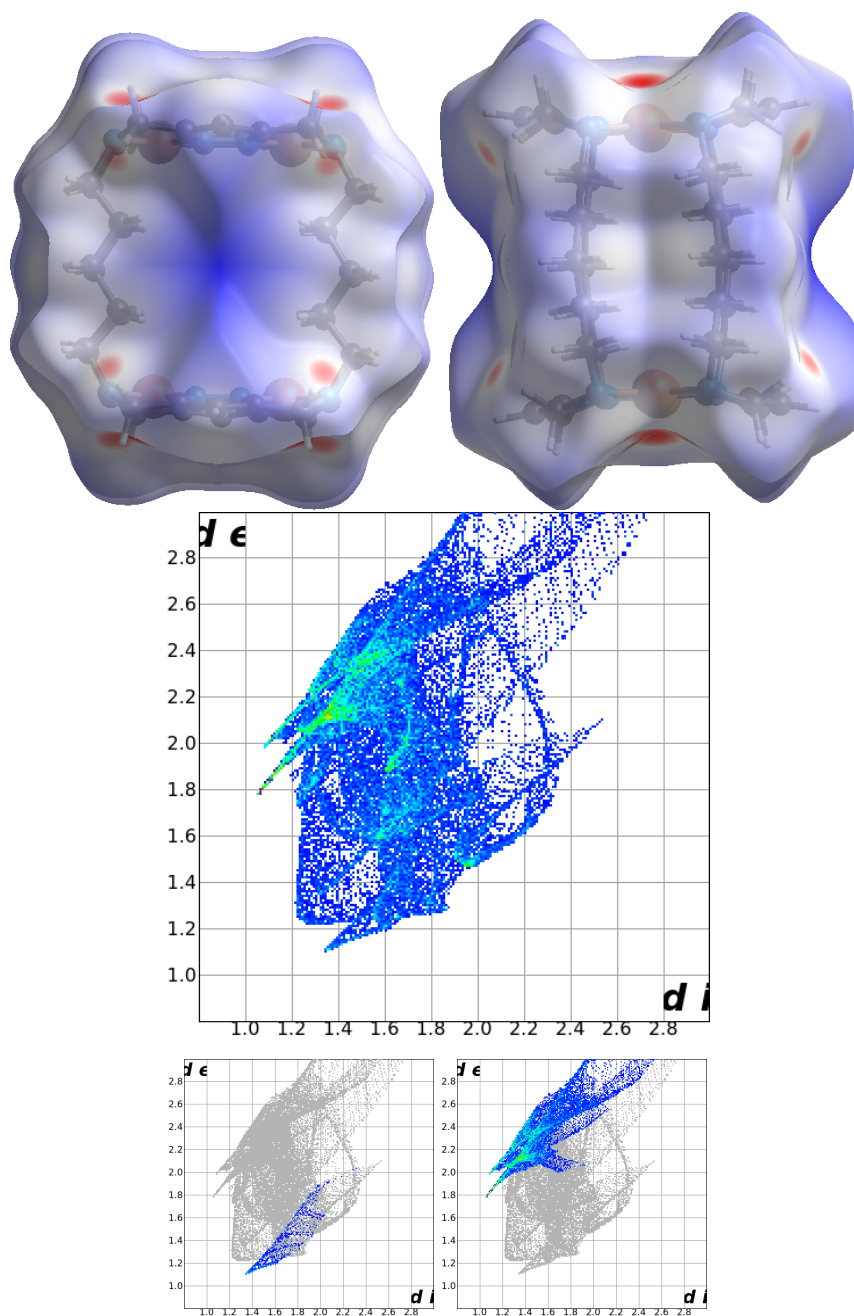

Figure S5: (top) Hirshfeld surface representation for structure 3. (middle) Hirshfeld surface fingerprint for all interactions. (bottom left) Interactions involving oxygen outside with copper inside which represent 0.12% of the Hirshfeld surface. (bottom right) Interactions involving hydrogen from the inside with any atom in the outside which account for 8.3% of the Hirshfeld surface.

Table S5: Hydrogen bonds of structure **4**

D–H⋯A	distances / Å			angles / °
	D–H	H⋯A	D⋯A	D–H⋯A
C(3)–H(3B)⋯(I2)	0.97	2.95	3.920(7)	178

D: donor, A: acceptor, H: hydrogen.

Figure S6: (top) Hirshfeld surface representation for structure **4**. (middle) Hirshfeld surface fingerprint for all interactions. (bottom left) Interactions involving oxygen outside with copper inside which represent 2.4 % of the Hirshfeld surface. (bottom right) Interactions involving hydrogen from the inside with iodine atoms in the outside which account for 38.0 % of the Hirshfeld surface.
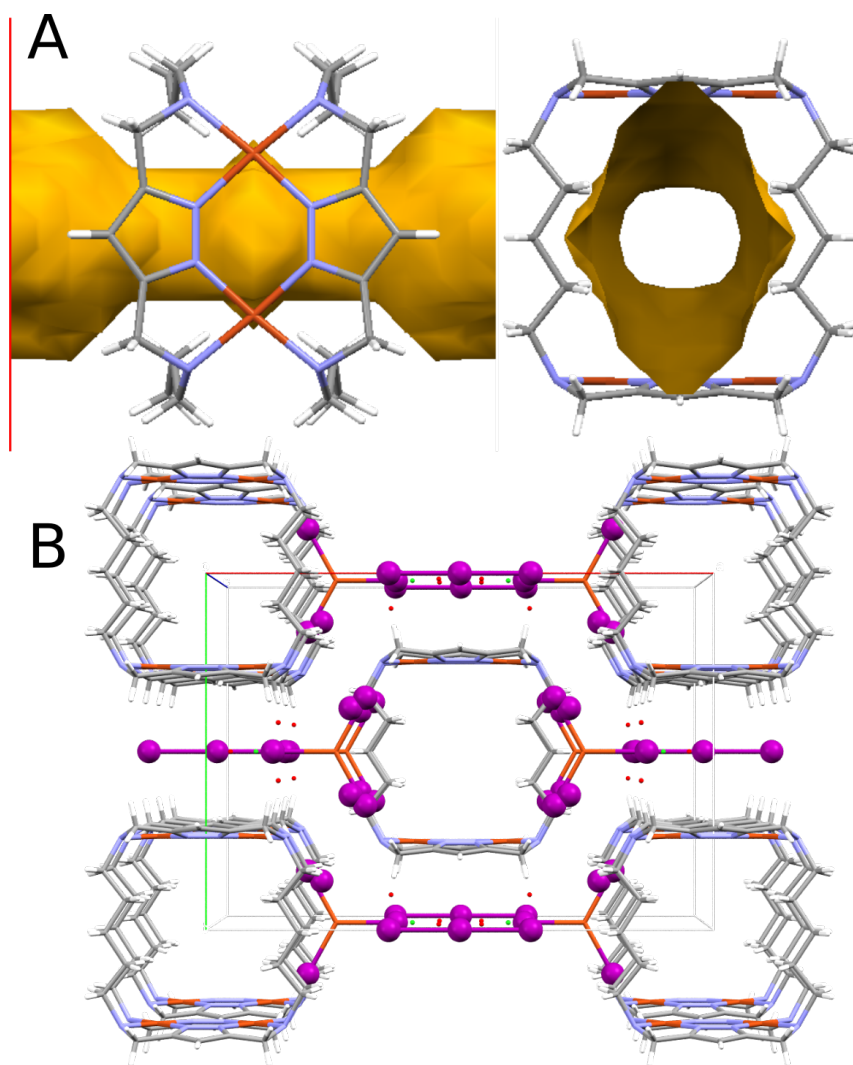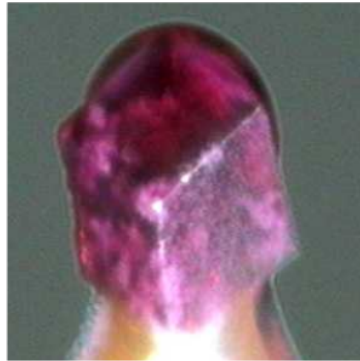
Figure S7: (A) Void channels as calculated by Mercury viewed down *b* and *c* axis. (B) Unit cell of **4** showing the arrangements of the anions in the lattice with respect to the $[Cu_4(H_{-2}L)_2]^{4+}$ cations.
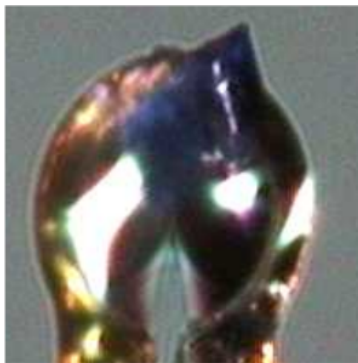
no halogen
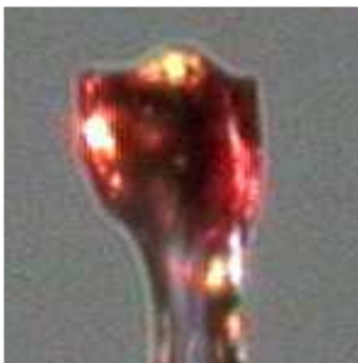(perchlorate counterion)

fluoride

chloride

bromide

iodide

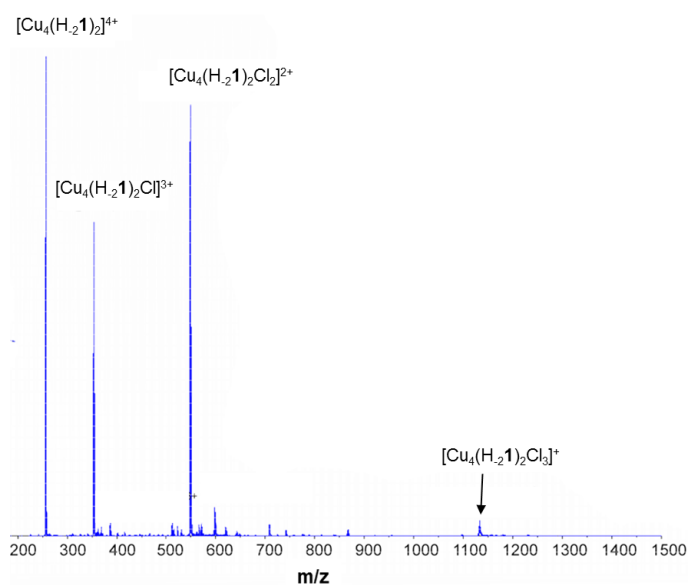**Figure S8:** Pictures of the crystals sampled.

3 Mass Spectroscopy

Figure S9: Mass Spectrum ESI($+$) of crystals of **3** dissolved in H_2O/CH_3CN.
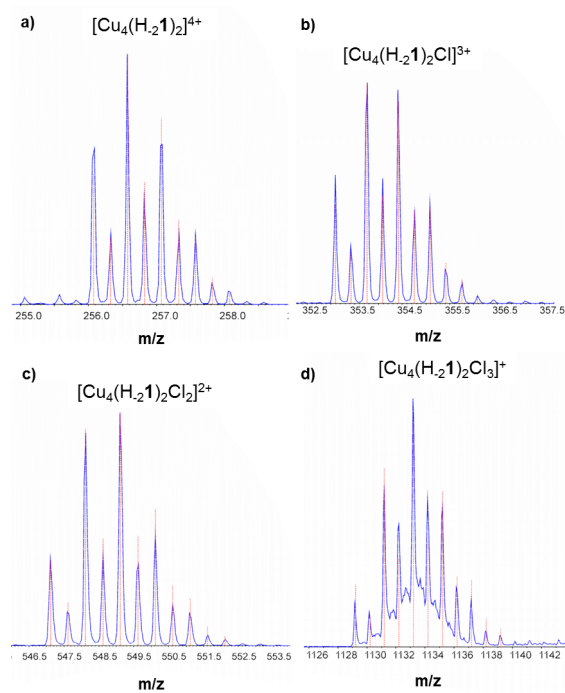

Figure S10: Detail of experimental (blue lines) and calculated (red lines) peaks for $m/z = 256.0744$ (a), 353.0892 (b), 547.1182 (c) and 1129.2057.

Table S6: The ions observed in the ESI(+)–MS spectrum measured from [Cu$_4$(H$_{-2}$**L**)] with chloride ions, their formulas, theoretical and experimental m/z values (monoisotopic) and absolute mass accuracies.

ion	charge	formula	m/z (calc)	m/z (exp)	$\Delta(m/z)$
[Cu$_4$(H$_{-2}$**L**)$_2$]$^{4+}$	+4	C$_{40}$H$_{68}$N$_{16}$Cu$_4$	256.0744	256.0783	0.0039
[Cu$_4$(H$_{-2}$**L**)$_2$Cl]$^{3+}$	+3	C$_{40}$H$_{68}$N$_{16}$Cu$_4$Cl	353.0892	353.0921	0.0029
[Cu$_5$(H$_{-2}$**L**)$_2$Cl$_2$]$^{3+}$	+3	C$_{40}$H$_{68}$N$_{16}$Cu$_5$Cl$_2$	385.7218	385.7254	0.0036
[Cu$_4$(H$_{-2}$**L**)$_2$Cl$_2$]$^{2+}$	+2	C$_{40}$H$_{68}$N$_{16}$Cu$_4$Cl$_2$	547.1182	547.122	0.0038
[Cu$_5$(H$_{-2}$**L**)$_2$Cl$_3$]$^{2+}$	+2	C$_{40}$H$_{68}$N$_{16}$Cu$_5$Cl$_3$	596.0674	596.0797	0.0123
[Cu$_4$(H$_{-2}$**L**)$_2$Cl$_3$]$^{+}$	+1	C$_{40}$H$_{68}$N$_{16}$Cu$_4$Cl$_3$	1129.2057	1129.183	0.0227

4   UV-vis titrations
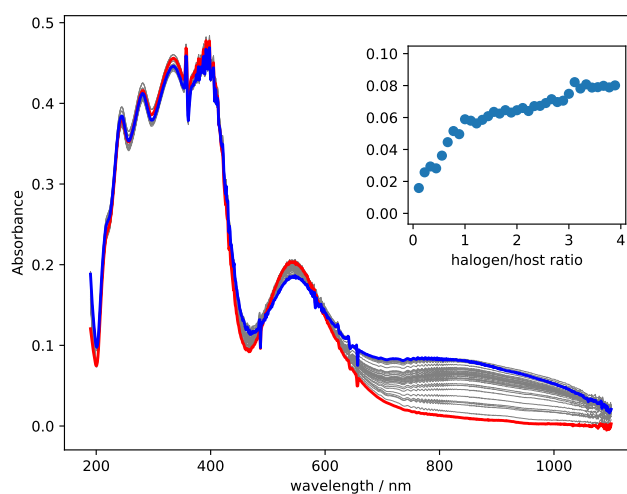
Figure S11: UV-vis spectra for the titration of a 0.002 M water solution of [Cu$_4$(H$_{-1}$**L**)$_2$](ClO$_4$)$_4$ with chloride and absorbance vs. chloride concentration at 812 nm (inset).