Electronic Supporting Information

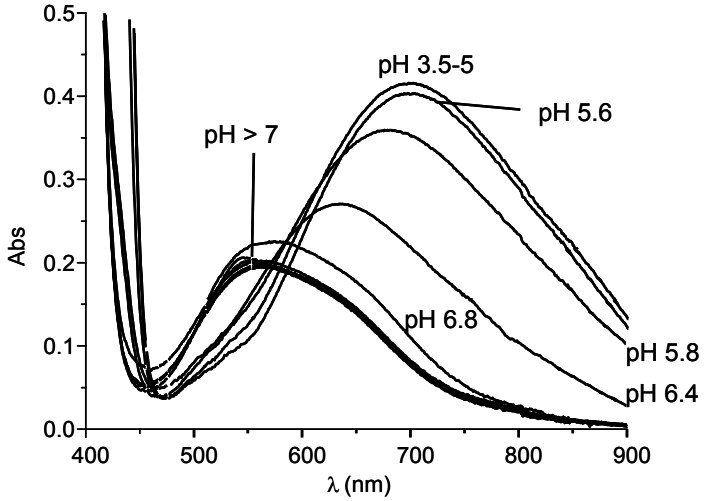

Figure S1. UV-vis spectra of L in the presence of 2 eq of Cu(II) at different pH values (Cu(II) = $1 \cdot 10^{-2}$ M, [L] = $5 \cdot 10^{-3}$ M, 298 K, 0.1 M NMe_4Cl)

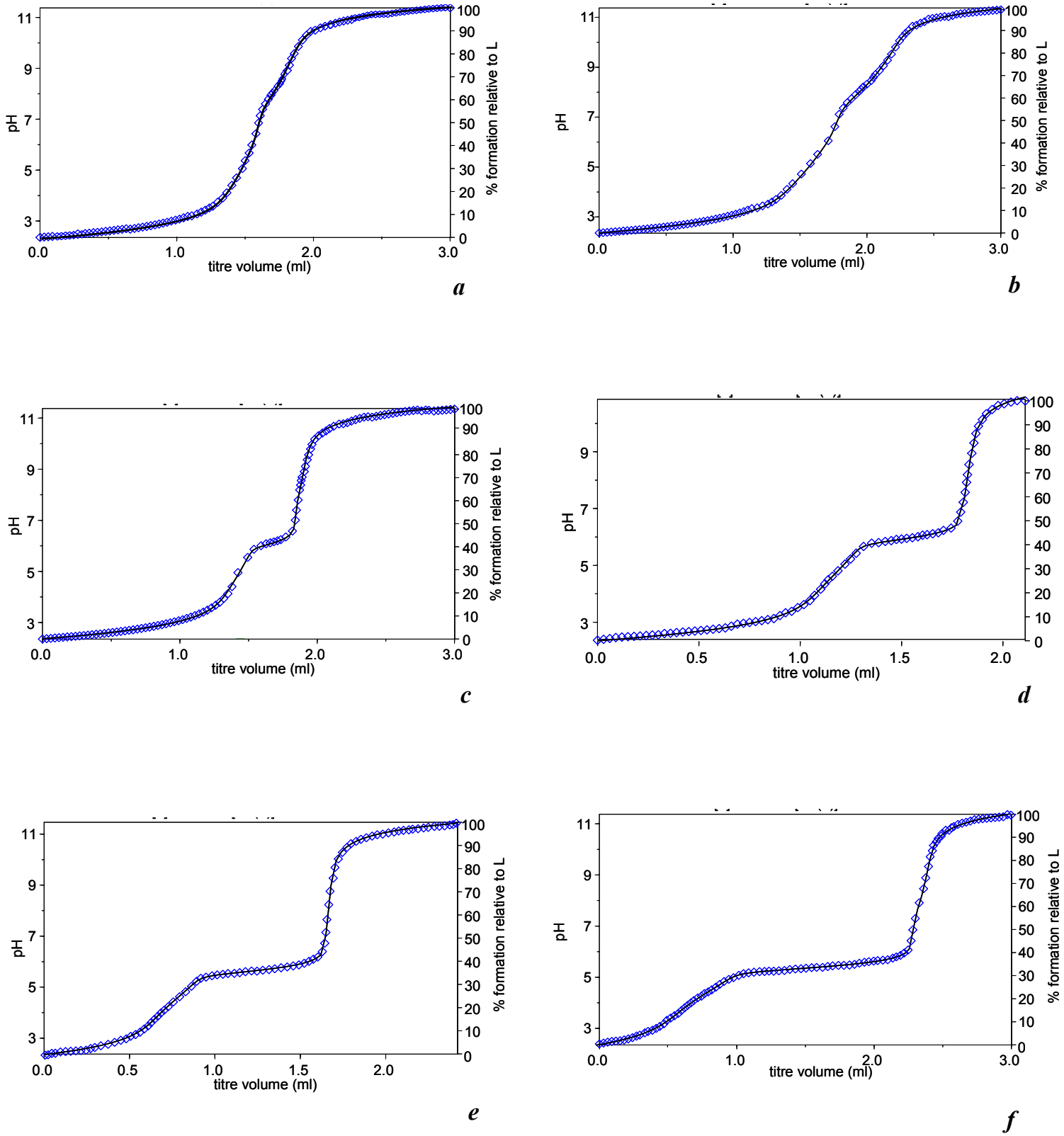

Figure S2. Theoretical (—) and experimental (◊) titration curves for the system Cu(II)/L with different ligand and metal concentrations (*a*: [L] = $5x10^{-4}$ M [Cu(II)] = $4x10^{-4}$ M, [NMe_4OH] = 0.1 M; *b*: [L] = $5x10^{-3}$ M, [Cu(II)] = $4x10^{-3}$ M, [NMe_4OH] = 0.3 M; *c*: [L] = $5x10^{-4}$ M, [Cu(II)] = $9x10^{-4}$ M, [NMe_4OH] = 0.1 M; *d*: [L] = $1x10^{-3}$ M, [Cu(II)] =$1.8x10^{-3}$ M, [NMe_4OH] = 0.2 M; *e*: [L] = $2x10^{-3}$ M, [Cu(II)] = $3.8x10^{-3}$ M, [NMe_4OH] = 0.3 M; *f*: [L] = 5 $x10^{-3}$ M, [Cu(II)] = $9x10^{-3}$ M, [NMe_4OH] = 0.3 M)

Table S1. Values of the variance of weighted square residuals (σ^2) for the titration curves relative to the system Cu(II)/L, reported in Figure S2

System Cu(II)/L

	σ^2	Cu(II) concentration	Ligand concentration
Curve *a*	3.3834	$4x10^{-4}$ M	$5x10^{-4}$ M
Curve *b*	2.5354	$4x10^{-3}$ M	$5x10^{-3}$ M
Curve *c*	3.7002	$9x10^{-4}$ M	$5x10^{-4}$ M
Curve *d*	4.5670	$1.8x10^{-3}$ M	$1x10^{-3}$ M
Curve *e*	4.8904	$3.8x10^{-3}$ M	$2x10^{-3}$ M
Curve *f*	3.0978	$9x10^{-3}$ M	$5\ x10^{-3}$ M
Entire set of curves *a-f*	3.6504		

Table S2. Protonation constants of ligand L determined in 0.1 mol dm^{-3} NMe_4Cl aqueous solutions, at 298.1 K

Equilibrium	Log K
$L + H^+ = [LH]^+$	9.31(5)
$[LH]^+ + H^+ = [LH_2]^{2+}$	8.2(2)
$[LH_2]^{2+} + H^+ = [LH_3]^{3+}$	7.2(1)
$[LH_3]^{3+} + H^+ = [LH_4]^{4+}$	4.2(2)
$[LH_4]^{4+} + H^+ = [LH_5]^{5+}$	3.0(2)
$[LH_5]^{5+} + H^+ = [LH_6]^{6+}$	2.9(1)

Table S3. Intermetallic distances in $[L_4Cu_8(\mu\text{-}OH)_8(\mu\text{-}NO_3)_3](NO_3)_5\cdot 32H_2O$

Cu1a···Cu3a	2.760(2)	Cu1b···Cu3b	2.760(2)
Cu2a···Cu4a	2.701(2)	Cu2b···Cu4b	2.701(2)
Cu1a···Cu2a	8.263(2)	Cu1b···Cu2b	7.753(2)
Cu3a···Cu4a	8.278(3)	Cu3b···Cu4b	7.800(2)

Table S4. O···O hydrogen bonding distances (Å) between water molecules in the hexameric cluster localized in the **a**-based channels.

Ow17····Ow3	2.65(2)	
Ow15····Ow17	2.80(2)	
Ow3····Ow15	2.74(2)	1-x,1-y,-z

Table S5. Hydrogen bonding distances (Å) involving the $NO_3\cdots(H_2O)_2\cdots NO_3$ group linking the hexameric clusters in the **a**-based channels (Ow6* is omitted from Figure 4a and 5 for clarity)

O81····Ow15	3.14(3)	
O83····Ow6	2.76(4)	
O83····Ow6*	3.16(5)	
O82····Ow6	3.21(4)	-x,-y+1,-z
O82····Ow6*	2.76(5)	-x,-y+1,-z
O82····N4a1	2.85(2)	
O83····N4a2	2.82(2)	

Table S6. O···O hydrogen bonding distances (Å) between water molecules in the hexameric cluster localized in the **b**-based channels.

Ow8···Ow5	2.65(2)	
Ow14···Ow5	2.82(2)	
Ow14···Ow5'	2.83(2)	-x+2,-y+1,-z+1

Table S7. Hydrogen bonding distances (Å) involving the $(NO_3)_2(H_2O)_2$ group linking the pentameric clusters in the **b**-based channels

O41···Ow8	3.21(2)	
O41···N4b2	2.81(1)	
O42···Ow19	2.93(2)	
N4b2···Ow19'	2.72(2)	1-x, 1-y, 1-z

Table S8. O···O hydrogen bonding distances (Å) for the water or water-nitrate chains localized in the **c** and **d** channels.

Ow1···Ow1'	1.84(3)	
Ow1···Ow2	3.21(3)	
Ow22···Ow2	2.75(3)	
Ow22···Ow32	2.79(3)	
Ow32···Ow1'	2.95(3)	x-1/2,-y+1/2,+z
Ow26···Ow29	2.88(3)	
O71'···Ow26	2.37(7)	-x+1/2+1,+y-1/2,-z+1
O72'···Ow29	3.53(5)	-x+2,-y+1,-z+1

Table S9. Crystallographic data for the single crystal structure determination of $[L_4Cu_8(\mu\text{-}OH)_8(\mu\text{-}NO_3)_3]\cdot(NO_3)_5\cdot 32H_2O$

formula	$C_{92}H_{200}Cu_8N_{32}O_{64}$
M/ g mol^{-1}	3287.16
Cryst syst	monoclinic
Space group	P $2_1/a$
a / Å	19.647(1)
b / Å	28.417(2)
c / Å	26.741(1)
β /deg	96.067(5)
V / Å^3	14846(1)
T / K	298
Z	4
Dc / g cm^{-3}	1.471
μ / mm^{-1}	2.079
Unique reflns	15340
Obsd reflns (I> 2sigma(I))	6102
R1,[a] wR2[b] (all data)	0.0795, 0.2542

[a] $R1 = \Sigma \, || Fo| - |Fc|| \, / \, \Sigma \, |Fo|$; [b] $wR2 = [\Sigma \, w(Fo^2 - Fc^2)^2 \, / \, \Sigma \, wFo^4]^{1/2}$