Supplementary Information

Circular serendipity: *in-situ* ligand transformation for the self-assembly of an hexadecametallic [Cu^{II}_{16}] wheel

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Experimental details

Synthesis of $[Cu_{16}(L^1)_4(L^2)_8(L^3)_8]\cdot 8H_2O$ ($1\cdot 8H_2O$)

$CuCl_2\cdot 2H_2O$ (0.085 g, 0.500 mmol) and acacdoH_2 (0.130 g, 1 mmol) were dissolved in ethanol (25 mL) to produce a bright green solution. $Ln(AcO)_3.xH_2O$ (Nd: 0.197g, 0.500 mmol; Gd: 0.203g, 0.500 mmol; Er: 0.208g, 0.500 mmol) dissolved in 15 mL of H_2O were added and the resulted dark green solution was gently heated at (~40-50 ^oC) for ~20 min. The solution was left undisturbed to evaporate. X-ray quality dark green crystals of $\mathbf{1}\cdot 8H_2O$ were formed in approximately 2 weeks. The crystals were collected by vacuum filtration, washed with H_2O (2 x 3mL) and ethanol (3 mL) and dried in air. Yield: 37% (Gd), 28% (Nd, Er). Anal. Calcd. for $\mathbf{1}\cdot 8H_2O$ ($C_{100}H_{152}Cu_{16}N_{40}O_{64}$): C 30.37, H 3.87, N 14.17. Found C 30.42, H 3.82, N 14.23. IR (KBr pellets, cm^{-1}): 3420 (b, m), 3105 (w), 2969 (w), 2927 (w), 1622 (vs), 1564 (m), 1542 (m), 1433 (m), 1362 (m), 1346 (m), 1291 (m), 1224 (w), 1124 (vs), 1087 (s), 1037 (s), 1006 (s), 954 (m), 917 (m), 800 (m), 764 (s), 726 (w), 613 (m), 560 (w), 534 (m), 496 (w), 466 (w).

Synthesis of $[Cu_2Cl_4(acacdoH_2)_2]$ (2)

$acacdoH_2$ (0.065 g, 0.500 mmol) was dissolved in ethanol (5 mL) and added to an ethanol solution (5 mL) of $CuCl_2 \cdot 2H_2O$ (0.085 g, 0.500 mmol) to produce a clear bright green solution, which was left undisturbed at room temperature. X-ray quality green needle crystals of **1** were formed within 10 mins. The crystals were collected by filtration, washed with ethanol (3 mL) and dried in air. Yield 75%. Anal. Calcd. for **2** ($C_{10}H_{20}Cl_4Cu_2N_4O_4$): C 22.70, H 3.81, N 10.59. Found C 22.78, H 3.72, N 10.65. IR (KBr pellets, cm^{-1}): 3366 (s), 3193(s), 2870 (w), 1672 (w), 1440 (m), 1397 (s), 1357 (s), 1248 (w), 1223 (m), 1071 (s), 1018 (m), 995 (w), 862 (w), 637 (m), 534 (w), 456 (w).

Table S1. Crystal data and structure refinement for complexes **1** and **2**.

Complex	**1**·$8H_2O$[a]	**2**[b]
Empirical formula	C100 H152 Cu16 N40 O64	C10 H20 Cl4 Cu2 N4 O4
Formula weight	3955.26	529.18
Temperature	293(2) K	296(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Tetragonal	Monoclinic
Space group	P4/nnc	C2/c
Unit cell dimensions	a = 21.974(3) Å, α = 90.00° b = 21.974(3) Å, β = 90.00° c = 16.490(3) Å, γ = 90.00°	a = 13.184(3) Å, α = 90.00° b = 12.091(3) Å, β = 103.716(3)° c = 11.922(3) Å, γ = 90.00°
Volume	7962(2) $Å^3$	1846.2(8) $Å^3$
Z	2	4
Density (calculated)	1.650 g/cm^3	1.904 g/cm^3
Absorption coefficient	2.185 mm^{-1}	2.905 mm^{-1}
F(000)	4016	1064
Crystal size	0.23 x 0.20 x 0.14 mm^3	0.42 x 0.36 x 0.28 mm^3

θ range for data collection	2.80 to 25.92°	2.67 to 25.24°
Index ranges	-26<=h<=26, -26<=k<=26, -20<=l<=20	-15<=h<=15, -13<=k<=14, -14<=l<=14
Reflections collected	59330	6713
Independent reflections	3859 [R_{int} = 0.0514]	1670 [R_{int} = 0.0201]
Completeness to θ = 25.92°	99%	99.2%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3859 / 12 / 262	1670 / 0 / 111
Goodness-of-fit	1.167	1.099
Final R indices [>2σ(I)]	R_{obs} = 0.0632, wR_{obs} = 0.1549	R_{obs} = 0.0261, wR_{obs} = 0.0689
R indices [all data]	R_{all} = 0.0817, wR_{all} = 0.1639	R_{all} = 0.0316, wR_{all} = 0.0709
Largest diff. peak and hole	0.468 and -0.370 e·Å^{-3}	0.433 and -0.303 e·Å^{-3}
CCDC	1026037	1026038

[a] $R = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2] / \Sigma[w(|F_o|^4)]\}^{1/2}$ and calc $w=1/[\sigma^2(Fo^2)+(0.0357P)^2+38.4540P]$ where $P=(Fo^2+2Fc^2)/3$.

[b] $R = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2] / \Sigma[w(|F_o|^4)]\}^{1/2}$ and calc $w=1/[\sigma^2(Fo^2)+(0.0304P)^2+3.6596P]$ where $P=(Fo^2+2Fc^2)/3$