Supplementary Material (ESI) for Chemical Communications

Cyanide-bridged tetradecanuclear $Ru^{II}_3M^{II}_{11}$ clusters (M^{II} = Zn^{II} and Cu^{II}) based on the high connectivity building block $[Ru_3(HAT)(CN)_{12}]^{6+}$: structural and photophysical properties

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Supporting information

X-ray Structure Determinations. (**1**) A crystal of $[\{Zn^{II}(tren)\text{-}(\mu\text{–}CN)\}_{11}\{Ru_3(HAT)(CN)\}](ClO_4)_{16}\bullet 26.5H_2O\bullet 0.5CH_3CN$ (0.43 x 0.27 x 0.20 mm^3) was mounted on a Bruker-Nonius X8 Proteum diffractometer at 100 K. Formula: $C_{91}H_{250.5}O_{89.5}Cl_{16}N_{62.5}O_{89.5}Ru_3Zn_{11}$, F_w = 5242.52, monoclinic, $P2_1/c$, a = 18.9495(8), b = 37.4949(15), c = 29.2410(12) Å, β = 100.022(1)º, V = 20459.0(15) $Å^3$, Z = 4, σ_{calc} = 1.702 Mg/m^3, μ(Cu-K_α) = 5.942 mm^{-1}, λ = 1.54178 Å. 252142 reflections were measured which afforded 34754 reflections (R_{int} = 0.0679) after merging. Refinement of 2526 parameters converged at $R1$ = 0.0518 (selected data with $I > 2\sigma(I)$), w$R2$ = 0.1473 (all data). All non-hydrogen atoms were refined anisotropically. Lattice solvent molecules were refined with either 50 or 100% site occupancy, as required to generate reasonable thermal displacement parameters. Hydrogen atoms, except those belonging to the lattice water molecules which were not included in the refinement, were placed geometrically and refined with a riding model and with U_{iso} constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom. Atoms C31C and C34C are disordered over two closely spaced sites with site occupancies of 0.69/0.31 for C31C and 0.70/0.30 for C34C. Oxygen atoms O13, O14 and O61 of perchlorate groups are also disordered over two sites which refined with site occupancies of 0.58/0.42, 0.58/0.42 and 0.72/0.28 respectively. CCDC 686538. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/.

(**2**) Because of the poor quality of the data and the large amount of crystallographic disorder affecting perchlorate anions, *tren* ligands and solvent molecules, a complete resolution of the crystal structure was not possible, but the unit cell parameters and partial refinement confirm that it is isostructrual to **1**. Monoclinic, $P2_1/c$, a = 19.1721(8) Å, b = 35.6372(71) Å, c = 28.2563(57) Å, β = 96.930(30)º.

The programs used in the determination and refinement of the structures were SAINT [1] for control and integration, SADABS [2] for absorption correction and the SHELXTL suite of programs for structure solution and refinement [3].

[1] SAINT in APEX2. Bruker (2008). APEX2. Bruker AXS Inc., Madison, Wisconsin, USA.
[2] SADABS, Sheldrick, G. M. (2008). SADABS. University of Göttingen, Germany.
[3] SHELXTL *program system version 5.1; Bruker Analytical X-ray Instruments Inc.: Madison, WI, 1998.*

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

Empirical formula	C91 H250.50 Cl16 N62.50 O89.50 Ru3 Zn11	
Formula weight	5242.52	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 18.9495(8) Å	α= 90°
	b = 37.4949(15) Å	β= 100.022(1)°
	c = 29.2410(12) Å	γ = 90°
Volume	20459.0(15) $Å^3$	
Z	4	
Density (calculated)	1.702 Mg/m^3	
Absorption coefficient	5.942 mm^{-1}	
F(000)	10736	
Crystal size	0.43 x 0.27 x 0.20 mm^3	
Theta range for data collection	1.93 to 65.08°	
Index ranges	-22<=h<=22, -41<=k<=44, -34<=l<=34	
Reflections collected	252142	
Independent reflections	34754 [R(int) = 0.0679]	
Completeness to theta = 65.08°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7530 and 0.2385	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	34754 / 30 / 2526	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2sigma(I)]	R1 = 0.0518, wR2 = 0.1441	
R indices (all data)	R1 = 0.0541, wR2 = 0.1473	
Largest diff. peak and hole	1.540 and -1.727 $e.Å^{-3}$	

Table S2 Selected bond lengths (Å) and angles (º) in the crystal structure of **1**.

Ru(1A)-C(5A)	1.968(4)	Ru(1A)-C(3A)	1.971(5)
Ru(1A)-C(7A)	2.013(4)	Ru(1A)-C(01A)	2.028(5)
Ru(1A)-N(6)	2.106(3)	Ru(1A)-N(5)	2.134(3)
Ru(1B)-C(5B)	1.965(4)	Ru(1B)-C(3B)	1.985(4)
Ru(1B)-C(1B)	2.033(4)	Ru(1B)-C(7B)	2.058(4)
Ru(1B)-N(3)	2.119(3)	Ru(1B)-N(4)	2.142(3)
Ru(1C)-C(5C)	1.967(4)	Ru(1C)-C(3C)	1.977(4)
Ru(1C)-C(1C)	2.018(5)	Ru(1C)-C(7C)	2.039(5)
Ru(1C)-N(1)	2.115(3)	Ru(1C)-N(2)	2.124(3)
Zn(1A)-N(2A)	2.034(4)	Zn(1A)-N(13A)	2.060(4)
Zn(1A)-N(16A)	2.068(4)	Zn(1A)-N(19A)	2.072(5)
Zn(1A)-N(10A)	2.242(4)	Zn(2A)-N(4A)	2.035(4)
Zn(2A)-N(26A)	2.053(4)	Zn(2A)-N(29A)	2.062(4)
Zn(2A)-N(23A)	2.065(4)	Zn(2A)-N(20A)	2.283(4)
Zn(3A)-N(6A)	2.026(4)	Zn(3A)-N(33A)	2.067(4)
Zn(3A)-N(39A)	2.079(4)	Zn(3A)-N(36A)	2.079(4)
Zn(3A)-N(30A)	2.249(4)	Zn(4A)-N(8A)	2.012(4)
Zn(4A)-N(46A)	2.050(4)	Zn(4A)-N(43A)	2.074(4)
Zn(4A)-N(49A)	2.083(4)	Zn(4A)-N(40A)	2.265(4)
Zn(1B)-N(2B)	2.048(4)	Zn(1B)-N(13B)	2.064(4)
Zn(1B)-N(16B)	2.073(4)	Zn(1B)-N(19B)	2.082(4)
Zn(1B)-N(10B)	2.317(4)	Zn(2B)-N(4B)	2.034(3)
Zn(2B)-N(29B)	2.071(4)	Zn(2B)-N(23B)	2.073(4)
Zn(2B)-N(26B)	2.074(4)	Zn(2B)-N(20B)	2.277(4)
Zn(3B)-N(6B)	2.041(4)	Zn(3B)-N(36B)	2.070(4)
Zn(3B)-N(33B)	2.074(4)	Zn(3B)-N(39B)	2.074(4)
Zn(3B)-N(30B)	2.241(4)	Zn(4B)-N(46B)	2.045(4)
Zn(4B)-N(49B)	2.054(4)	Zn(4B)-N(8B)	2.072(4)
Zn(4B)-N(43B)	2.094(4)	Zn(4B)-N(40B)	2.340(4)
Zn(1C)-N(16C)	2.039(4)	Zn(1C)-N(2C)	2.051(4)
Zn(1C)-N(13C)	2.062(4)	Zn(1C)-N(19C)	2.092(4)
Zn(1C)-N(10C)	2.259(4)	Zn(2C)-N(4C)	2.022(4)
Zn(2C)-N(26C)	2.048(4)	Zn(2C)-N(23C)	2.078(4)
Zn(2C)-N(29C)	2.092(4)	Zn(2C)-N(20C)	2.288(4)
Zn(3C)-N(6C)	2.066(4)	Zn(3C)-N(39C)	2.066(4)
Zn(3C)-N(36C)	2.070(4)	Zn(3C)-N(33C)	2.077(4)
Zn(3C)-N(30C)	2.241(4)		

N(6)-Ru(1A)-N(5)	79.40(12)	N(3)-Ru(1B)-N(4)	79.47(12)
N(1)-Ru(1C)-N(2)	79.46(12)	N(2A)-C(1A)-Ru(1A)	176.9(4)
N(4A)-C(3A)-Ru(1A)	177.4(4)	N(6A)-C(5A)-Ru(1A)	174.8(4)
N(8A)-C(7A)-Ru(1A)	176.2(4)	N(2B)-C(1B)-Ru(1B)	173.7(4)
N(4B)-C(3B)-Ru(1B)	178.0(4)	N(6B)-C(5B)-Ru(1B)	178.7(4)
N(8B)-C(7B)-Ru(1B)	174.2(4)	N(2C)-C(1C)-Ru(1C)	178.1(4)
N(4C)-C(3C)-Ru(1C)	178.5(4)	N(6C)-C(5C)-Ru(1C)	175.7(4)
N(8C)-C(7C)-Ru(1C)	175.4(4)	C(1A)-N(2A)-Zn(1A)	172.3(5)
C(3A)-N(4A)-Zn(2A)	161.6(4)	C(5A)-N(6A)-Zn(3A)	160.0(4)
C(7A)-N(8A)-Zn(4A)	170.0(4)	C(1B)-N(2B)-Zn(1B)	163.4(3)
C(3B)-N(4B)-Zn(2B)	166.4(3)	C(5B)-N(6B)-Zn(3B)	160.4(3)
C(7B)-N(8B)-Zn(4B)	175.1(4)	C(1C)-N(2C)-Zn(1C)	138.0(3)
C(3C)-N(4C)-Zn(2C)	175.0(4)	C(5C)-N(6C)-Zn(3C)	141.3(3)
N(2A)-Zn(1A)-N(13A)	100.61(19)	N(2A)-Zn(1A)-N(16A)	98.5(2)
N(13A)-Zn(1A)-N(16A)	116.98(19)	N(2A)-Zn(1A)-N(19A)	96.3(2)
N(13A)-Zn(1A)-N(19A)	117.7(2)	N(16A)-Zn(1A)-N(19A)	118.9(2)
N(2A)-Zn(1A)-N(10A)	177.14(18)	N(13A)-Zn(1A)-N(10A)	81.78(18)
N(16A)-Zn(1A)-N(10A)	81.66(18)	N(19A)-Zn(1A)-N(10A)	81.17(19)
N(4A)-Zn(2A)-N(26A)	102.18(17)	N(4A)-Zn(2A)-N(29A)	95.17(19)
N(26A)-Zn(2A)-N(29A)	117.61(18)	N(4A)-Zn(2A)-N(23A)	100.00(17)
N(26A)-Zn(2A)-N(23A)	115.63(17)	N(29A)-Zn(2A)-N(23A)	119.43(18)
N(4A)-Zn(2A)-N(20A)	176.00(17)	N(26A)-Zn(2A)-N(20A)	80.79(15)
N(29A)-Zn(2A)-N(20A)	81.02(17)	(23A)-Zn(2A)-N(20A)	80.94(16)
N(6A)-Zn(3A)-N(33A)	103.22(16)	N(6A)-Zn(3A)-N(39A)	98.68(18)
N(33A)-Zn(3A)-N(39A)	114.14(19)	N(6A)-Zn(3A)-N(36A)	93.89(16)
N(33A)-Zn(3A)-N(36A)	119.94(17)	N(39A)-Zn(3A)-N(36A)	119.43(17)
N(6A)-Zn(3A)-N(30A)	174.51(16)	N(33A)-Zn(3A)-N(30A)	81.56(16)
N(39A)-Zn(3A)-N(30A)	81.57(18)	N(36A)-Zn(3A)-N(30A)	81.29(16)
N(8A)-Zn(4A)-N(46A)	102.13(18)	N(8A)-Zn(4A)-N(43A)	100.28(17)
N(46A)-Zn(4A)-N(43A)	114.71(17)	N(8A)-Zn(4A)-N(49A)	94.46(17)
N(46A)-Zn(4A)-N(49A)	118.94(17)	N(43A)-Zn(4A)-N(49A)	119.30(17)
N(8A)-Zn(4A)-N(40A)	175.28(17)	N(46A)-Zn(4A)-N(40A)	81.26(17)
N(43A)-Zn(4A)-N(40A)	81.08(15)	N(49A)-Zn(4A)-N(40A)	80.97(16)
N(2B)-Zn(1B)-N(13B)	101.85(15)	N(2B)-Zn(1B)-N(16B)	100.75(15)
N(13B)-Zn(1B)-N(16B)	116.77(15)	N(2B)-Zn(1B)-N(19B)	96.93(15)
N(13B)-Zn(1B)-N(19B)	113.71(15)	N(16B)-Zn(1B)-N(19B)	120.95(16)
N(2B)-Zn(1B)-N(10B)	176.67(13)	N(13B)-Zn(1B)-N(10B)	80.61(14)
N(16B)-Zn(1B)-N(10B)	79.96(14)	N(19B)-Zn(1B)-N(10B)	79.96(14)

N(4B)-Zn(2B)-N(29B)	95.95(15)	N(4B)-Zn(2B)-N(23B)	99.71(15)
N(29B)-Zn(2B)-N(23B)	119.14(16)	N(4B)-Zn(2B)-N(26B)	101.60(15)
N(29B)-Zn(2B)-N(26B)	120.36(15)	N(23B)-Zn(2B)-N(26B)	113.23(15)
N(4B)-Zn(2B)-N(20B)	176.60(14)	N(29B)-Zn(2B)-N(20B)	80.78(14)
N(23B)-Zn(2B)-N(20B)	81.19(14)	N(26B)-Zn(2B)-N(20B)	80.96(14)
N(6B)-Zn(3B)-N(36B)	98.75(15)	N(6B)-Zn(3B)-N(33B)	99.67(15)
N(36B)-Zn(3B)-N(33B)	115.43(16)	N(6B)-Zn(3B)-N(39B)	96.17(15)
N(36B)-Zn(3B)-N(39B)	121.49(16)	N(33B)-Zn(3B)-N(39B)	117.13(16)
N(6B)-Zn(3B)-N(30B)	177.30(15)	N(36B)-Zn(3B)-N(30B)	82.01(14)
N(33B)-Zn(3B)-N(30B)	82.29(14)	N(39B)-Zn(3B)-N(30B)	81.25(14)
N(46B)-Zn(4B)-N(49B)	117.31(17)	N(46B)-Zn(4B)-N(8B)	97.14(15)
N(49B)-Zn(4B)-N(8B)	103.06(16)	N(46B)-Zn(4B)-N(43B)	119.58(18)
N(49B)-Zn(4B)-N(43B)	112.90(17)	N(8B)-Zn(4B)-N(43B)	102.24(16)
N(46B)-Zn(4B)-N(40B)	79.25(15)	N(49B)-Zn(4B)-N(40B)	79.03(16)
N(8B)-Zn(4B)-N(40B)	176.37(14)	N(43B)-Zn(4B)-N(40B)	79.49(16)
N(16C)-Zn(1C)-N(2C)	105.51(15)	N(16C)-Zn(1C)-N(13C)	114.70(15)
N(2C)-Zn(1C)-N(13C)	98.49(15)	N(16C)-Zn(1C)-N(19C)	121.98(15)
N(2C)-Zn(1C)-N(19C)	91.10(15)	N(13C)-Zn(1C)-N(19C)	117.09(15)
N(16C)-Zn(1C)-N(10C)	82.82(14)	N(2C)-Zn(1C)-N(10C)	170.58(15)
N(13C)-Zn(1C)-N(10C)	81.54(14)	N(19C)-Zn(1C)-N(10C)	80.60(14)
N(4C)-Zn(2C)-N(26C)	106.81(18)	N(4C)-Zn(2C)-N(23C)	97.98(17)
N(26C)-Zn(2C)-N(23C)	115.56(19)	N(4C)-Zn(2C)-N(29C)	94.35(16)
N(26C)-Zn(2C)-N(29C)	113.52(18)	N(23C)-Zn(2C)-N(29C)	122.80(19)
N(4C)-Zn(2C)-N(20C)	171.43(18)	N(26C)-Zn(2C)-N(20C)	81.46(18)
N(23C)-Zn(2C)-N(20C)	79.96(17)	N(29C)-Zn(2C)-N(20C)	80.02(16)
N(6C)-Zn(3C)-N(39C)	100.51(16)	N(6C)-Zn(3C)-N(36C)	99.53(16)
N(39C)-Zn(3C)-N(36C)	117.3(2)	N(6C)-Zn(3C)-N(33C)	95.40(15)
N(39C)-Zn(3C)-N(33C)	118.19(19)	N(36C)-Zn(3C)-N(33C)	118.1(2)
N(6C)-Zn(3C)-N(30C)	176.68(14)	N(39C)-Zn(3C)-N(30C)	81.87(15)
N(36C)-Zn(3C)-N(30C)	81.30(16)	N(33C)-Zn(3C)-N(30C)	81.39(15)

Fig. S1 Main picture: Plot of $\chi_M T$ vs T for a polycrystalline sample of **2**. The magnetic susceptibility χ_M was measured under a 10000 Oe magnetic field between 2 – 300 K. Inset: plot of $1/\chi_M$ vs T (blue squares). Red line: linear fit according to the Curie Law.

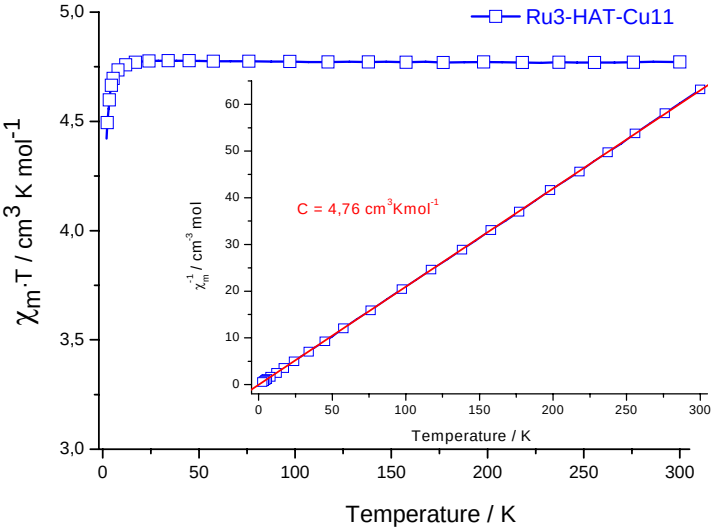

Fig. S2 Magnetic Field dependence of the magnetization, $M/N_A\beta$, at 2 K for a polycrystalline sample of **2** (N_A is the Avogadro's constant and β the electron Bohr magneton). Red line: Theoretical Brillouin function for eleven independent spin S=1/2 (g = 2.1).