Supporting Information

Unique Nanoscale {$Cu^{II}_{36}Ln^{III}_{24}$} (Ln = Dy and Gd) Metallo-rings †

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Experimental details

General Remarks: All chemicals were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with an Elementar Vario-EL CHNS elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000-400 cm^{-1} on a Bio-Rad FTS-7 spectrometer. Magnetic susceptibility was measured by a Quantum Design MPMS-XL7 SQUID. Data were corrected for the diamagnetic contribution calculated from Pascal constants.

Synthesis of 1: $Cu(NO_3)_2 \cdot 3H_2O$ (0.14 g, 0.6 mmol) and $Dy(NO_3)_3 \cdot 6H_2O$ (0.18 g, 0.4 mmol) dissolved in MeCN (20 mL) was added to the solution of $PhCO_2H$ (0.06 g, 0.5 mmol) in MeOH (10 mL). Then Et_3N (0.09 g, 0.9 mmol) was added dropwise. The resulting mixture was left under magnetic stirring for an hour. Evaporation of the filtrate under ambient conditions afforded blue block-shaped crystals in a few weeks (yield 40 % based on Dy). IR (KBr, cm^{-1}): 3449 (m), 3064 (w), 1596 (m), 1544 (s), 1493 (w), 1413 (s), 1306 (w), 1178 (m), 1071 (m), 1025 (m), 843 (w), 718 (s), 687 (m). Elemental analyses (calc: found) for **1**: C 32.21 : 32.18, H 3.44 : 3.36, N 1.92 : 1.94.

Synthesis of 2: The procedure was the same as that employed for **1**, except that $Gd(NO_3)_3 \cdot 6H_2O$ (0.18 g, 0.4 mmol) was employed as lanthanide salts. The blue block-shaped crystals were obtained (yield 45 % based on Gd). IR (KBr, cm^{-1}): 3445 (m), 3063 (w), 1596 (m), 1546 (s), 1493 (w), 1409 (s), 1305 (w), 1177 (m), 1070 (m), 1025 (m), 844 (w), 718 (s), 687 (m). Elemental analyses (calc: found) for **2**: C 32.91 : 32.52, H 3.42 : 3.29, N 2.41 : 2.37.

Crystal data for **1**: $C_{470}H_{598}Cu_{36}Dy_{24}N_{24}O_{297}$, $M = 17523.16$, triclinic, $a = 21.277(4)$, $b = 30.998(5)$, $c = 32.288(5)$ Å, $\alpha = 70.341(3)^{\circ}$, $\beta = 73.958(3)^{\circ}$, $\gamma = 89.499(3)^{\circ}$, $V = 19189(6)$ Å^3, $T = 173(2)$ K, space group $P\bar{1}$, $Z = 1$, $\rho_c = 1.516$ g cm^{-3}, $\mu = 3.356$ mm^{-1}, total data 135081, unique data 66196, $R_1 = 0.0676$ ($I > 2\sigma(I)$) $wR_2 = 0.1862$ (all data). For **2**: $C_{478}H_{592}Cu_{36}Gd_{24}N_{30}O_{289}$, $M = 17443.26$, triclinic, $a = 20.779(3)$, $b = 31.700(5)$, $c = 31.802(5)$ Å, $\alpha = 68.777(2)^{\circ}$, $\beta = 74.614(2)^{\circ}$, $\gamma = 87.823(3)^{\circ}$, $V = 18788(5)$ Å^3, $T = 173(2)$ K, space group $P\bar{1}$, $Z = 1$, $\rho_c = 1.542$ g cm^{-3}, $\mu = 3.159$ mm^{-1}, total data 133290, unique data 64828, $R_1 = 0.0610$ ($I > 2\sigma(I)$), $wR_2 = 0.1755$ (all data). The data of **1** and **2** were recorded on a Bruker SMART CCD diffractometer with Mo-Ka radiation ($\lambda = 0.71073$ Å). Some of the severely disordered guest molecules for both **1** and **2** were removed by SQUEEZE in structural refinement. One “Alert_level_A” for complex **1** is attributed to some benzene rings of the benzoates are disordered for the complexity and large dimension of the structure.

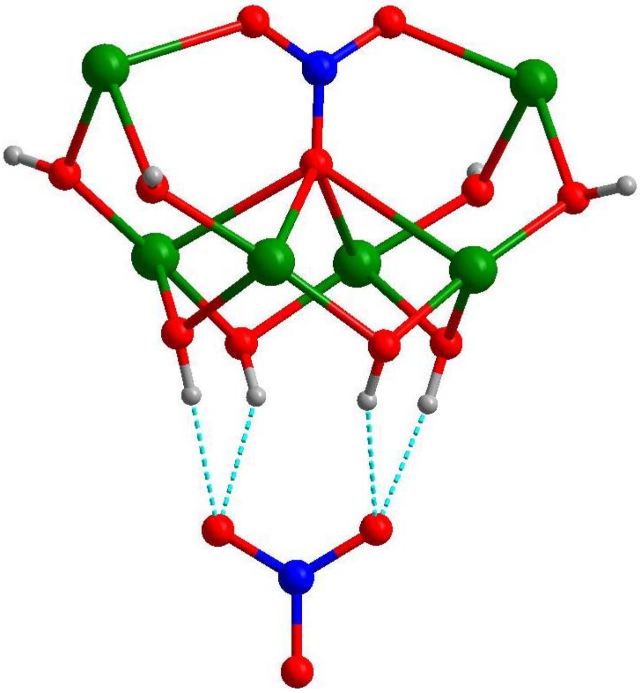

Fig. S1 H-bonds from between the nitrate counter anion and the OH^- groups of the cluster.

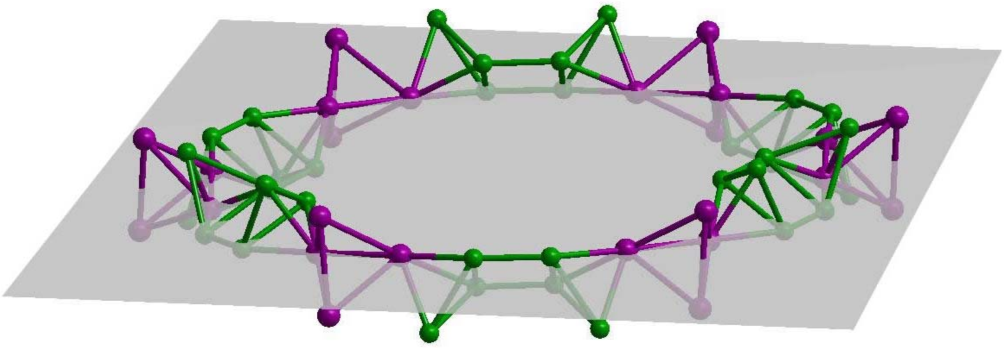

Fig. S2 Side view of the $\{Dy_{24}Cu_{36}\}$ ring of compound **1**.

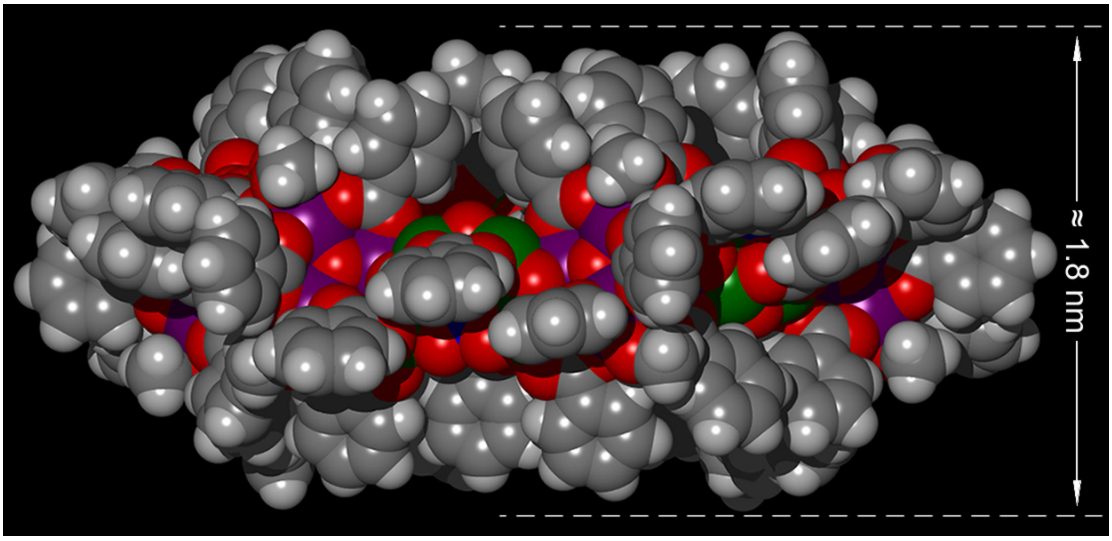

Fig. S3 Space-filling representation (including hydrogen atoms) from the viewpoint parallel to the plane of the ring of compound **1**, showing the thickness of the molecule.

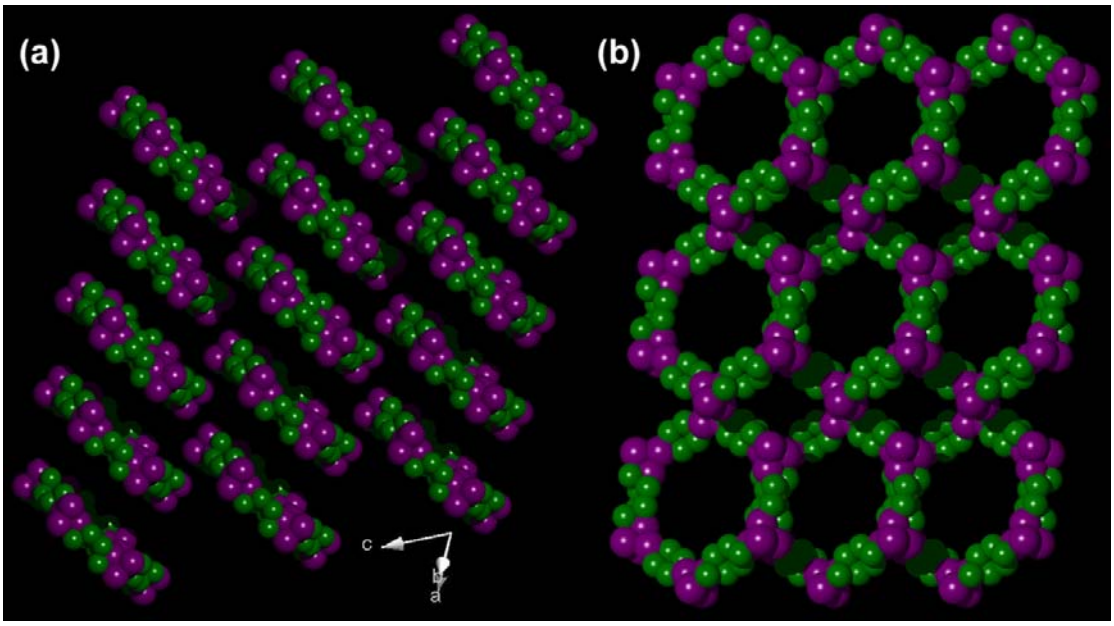

Fig. S4 Space-filling representations (including only metal ions) along the *ab* plane (**a**) and the *c* axis (**b**) showing the packing mode of the molecule in the lattice for compound **1**.

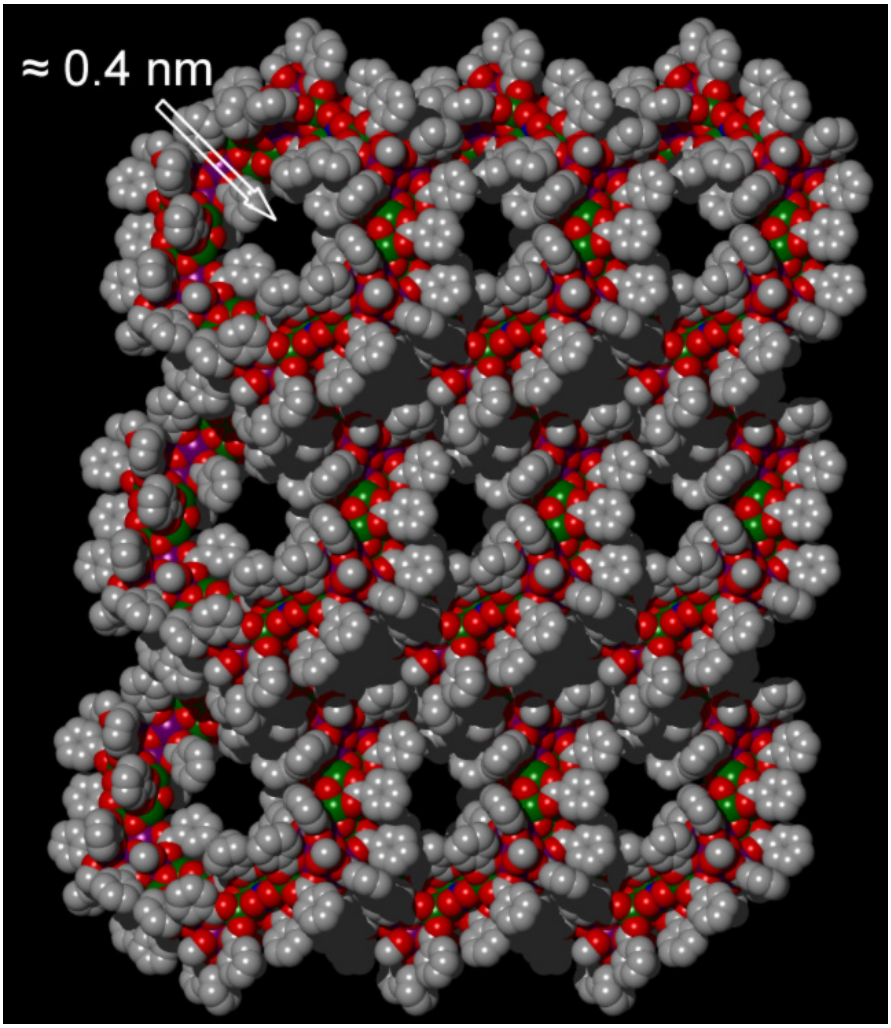

Fig. S5 A view along the *c* axis showing the oblate tubules of compound **1**.

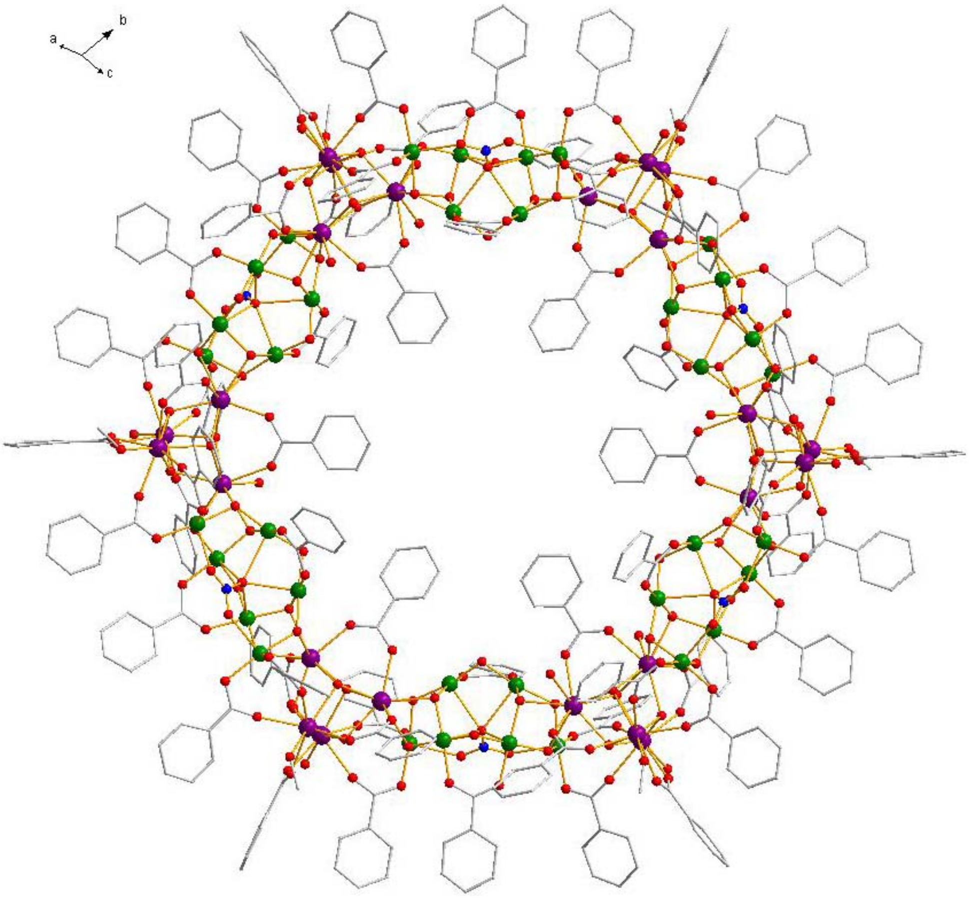

Fig. S6 The structure of the complete $\{Gd_{24}Cu_{36}\}$ ring of compound **2**, excluding hydrogen atoms.

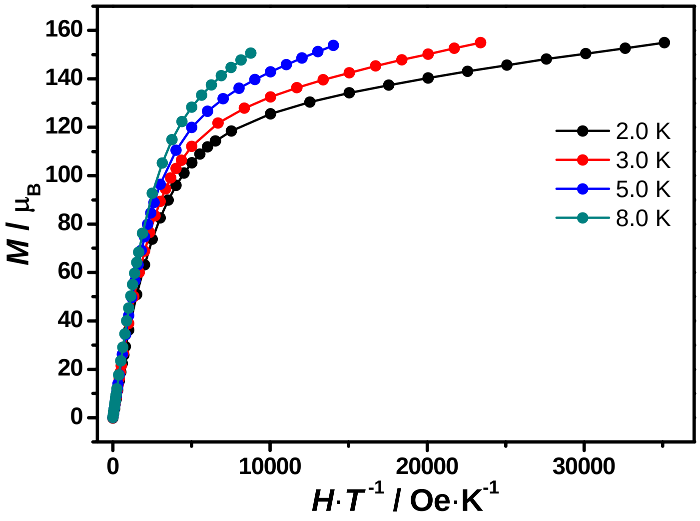

Fig. S7 Plots of *M*(*H*/*T*) for **1** at 2.0, 3.0, 5.0 and 8.0 K.

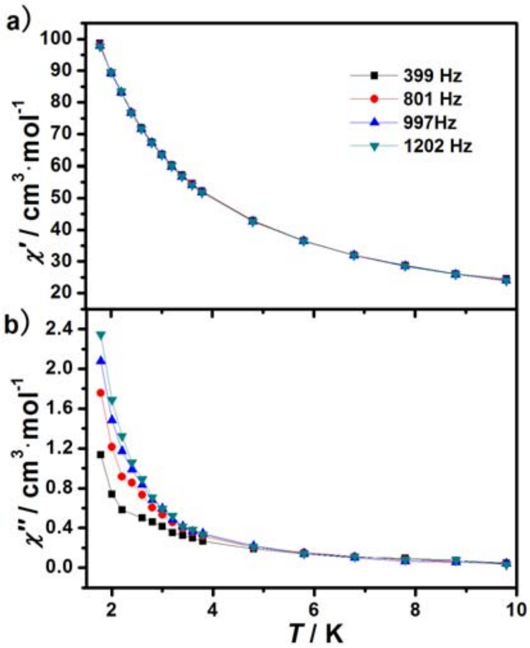

Fig. S8 Plots of temperature dependence of the in-phase (**a**) and out-of-phase (**b**) ac susceptibility for **1** at the indicated frequencies.

Table S1. BVS for O(OH$^-$) atoms in **1**

atom	BVS	atom	BVS
O1	1.18314	O19	1.20918
O2	1.15315	O20	1.31819
O3	1.15017	O21	1.09519
O4	1.11817	O22	1.11316
O5	0.99915	O23	1.28417
O6	1.26521	O24	1.2702
O7	1.28418	O25	1.26116
O8	1.30518	O26	1.11116
O9	1.0592	O27	1.14517
O10	1.09119	O28	1.13515
O11	1.28717	O29	1.15215
O12	1.25918	O30	1.20417
O13	1.2892	O31	1.2942
O14	1.13913	O32	1.34121
O15	1.13416	O33	1.09319
O16	1.17916	O34	1.03816
O17	1.12312	O35	0.98114
O18	1.27119	O36	0.96417

Table S2. BVS for O(OH$^-$) atoms in **2**

atom	BVS	atom	BVS
O1	1.30613	O19	1.22513
O2	1.28812	O20	1.34415
O3	1.26514	O21	1.07213

O4	1.24913	O22	1.12016
O5	0.99011	O23	1.31815
O6	1.25515	O24	1.27813
O7	1.29012	O25	1.28515
O8	1.34914	O26	1.23413
O9	1.09916	O27	1.25512
O10	1.09916	O28	1.29214
O11	1.34214	O29	1.25113
O12	1.26513	O30	1.26315
O13	1.30814	O31	1.31015
O14	1.26615	O32	1.30114
O15	1.31015	O33	1.11415
O16	1.26914	O34	1.05614
O17	1.24614	O35	0.96514
O18	1.28716	O36	0.93514

Bond valence sum (BVS)[19] were performed on the O(OH^-) atoms. The BVS values of ~0.9-1.3 confirm 72 OH^- ions for each **1** and **2**.

19 (*a*) I. D. Brown and D. Altermatt, *Acta Crystallogr.*, 1985, **B41**, 244; (*b*) W. Liu and H. H. Thorp, *Inorg. Chem.*, 1993, **32**, 4102; (*c*) G. P. Shields, P. R. Raithby, F. H. Allen and W. D. S. Motherwell, *Acta Crystallogr.*, 1999, **B56**, 455.