*Supporting Information*

# Wheel-shaped nanoscale 3*d*-4*f* $\{Co^{II}_{16}Ln^{III}_{24}\}$ clusters (Ln = Dy and Gd)

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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. Crystallographic measurements for **1** were carried out with the Oxford CCD diffractometer using mirror-monochromated Cu-K$\alpha$ radiation ($\lambda$ = 1.54178 Å) at 150(2) K. Powder X-ray diffraction measurement were performed on a Bruker D8 Advance X-ray diffractometer using Cu-K$\alpha$ radiation. 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**: $Co(NO_3)_2{\cdot}6H_2O$ (0.058 g, 0.2 mmol) and $Dy(NO_3)_3{\cdot}6H_2O$ (0.137 g, 0.3 mmol) dissolved in MeOH (10 mL) was added to the solution of pyacacH (0.045 g, 0.2 mmol) in MeOH (10 mL). Then $Et_3N$ (0.050 g, 0.5 mmol) was added dropwise. The resulting mixture was left under magnetic stirring for half an hour. Evaporation of the filtrate under ambient conditions afforded pink block-shaped crystals in about a week (yield 15 % based on Dy). IR (KBr, $cm^{-1}$): 3417 (br), 1552 (vs), 1446 (vs), 1386 (vs), 1326 (s), 1267 (s), 1169 (m), 1126 (m), 1051 (m), 1014(w), 951 (w), 773 (s), 704 (s), 650 (m). Elemental analyses (%, calc : found) for **1**: C 19.26 : 19.11, H 3.33 : 3.18, N 6.50 : 6.41.

**Synthesis of 2**: The procedure was the same as that employed for **1**, except that $Gd(NO_3)_3{\cdot}6H_2O$ (0.137 g, 0.3 mmol) was employed as lanthanide salts. The pink block-shaped crystals were obtained (yield 18 % based on Gd). IR (KBr, $cm^{-1}$): 3412 (br), 1552 (vs), 1446 (vs), 1390 (vs), 1321 (s), 1267 (s), 1169 (m), 1126 (m), 1053 (m), 1014(w), 951 (w), 768 (s), 704 (s), 650 (m). Elemental analyses (%, calc : found) for **2**: C 19.57 : 19.38, H 3.31 : 3.19, N 6.61 : 6.67.

Crystal data for **1**: $C_{228}H_{470}Co_{16}Dy_{26}N_{66}O_{307}$, $M$ = 14216.6, Monoclinic, space group $C2/m$, $a$ = 29.4047(13), $b$ = 35.5722(8), $c$ = 24.9143(11) Å, $\alpha$ = 90°, $\beta$ = 123.124(6)°, $\gamma$ = 90°, $V$ = 21825.1(21) $Å^3$, $T$ = 150(2) K, $Z$ = 2, $\rho_c$ = 2.163 g $cm^{-3}$, $F(000)$ = 13808, 52212 reflections collected, 11651 reflections used ($R_{int}$ = 0.0759), $R_1$ = 0.0767 ($I > 2\sigma(I)$), $wR_2$ = 0.2333 (all data). CCDC 926821. For **2**: $C_{228}H_{460}Co_{16}Gd_{26}N_{66}O_{302}$, $M$ = 13989.8, Monoclinic, space group $C2/m$, $a$ = 29.3969(9), $b$ = 35.5750(6), $c$ = 24.9218(6) Å, $\alpha$ = 90°, $\beta$ = 123.109(3)°, $\gamma$ = 90°, $V$ = 21831.3(12) $Å^3$, $T$ = 150(2) K, $Z$ = 2, $\rho_c$ = 2.128 g $cm^{-3}$, $F(000)$ = 13604, 46551 reflections collected, 13258 reflections used ($R_{int}$ = 0.0705), $R_1$ = 0.0775 ($I > 2\sigma(I)$), $wR_2$ = 0.2384 (all data). CCDC 926822. Some of the severely disordered guest molecules for both **1** and **2** were removed by the SQUEEZE program in structural refinement.

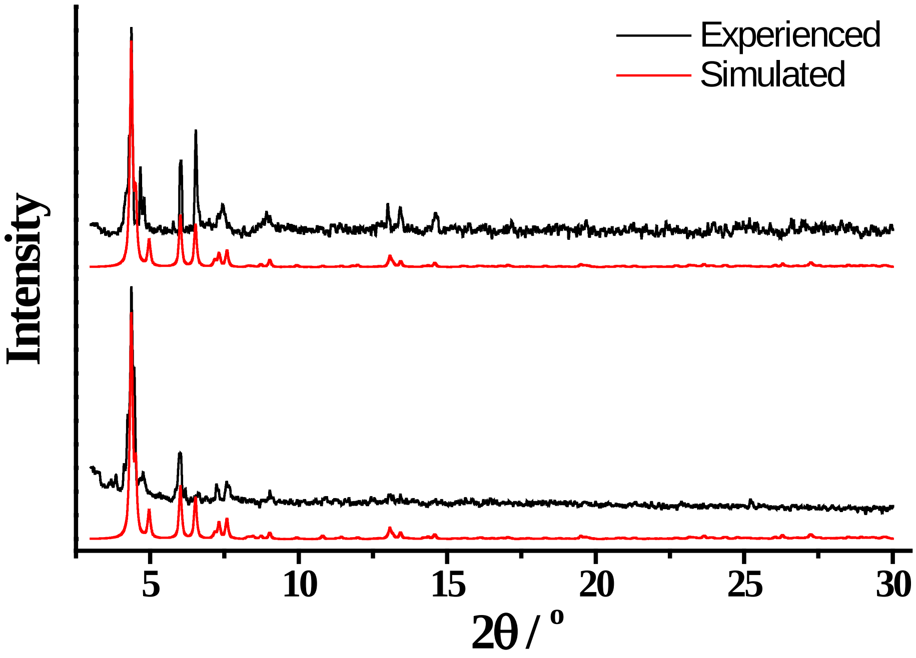

**Fig. S1** Powder X-ray diffraction pattern of compound **1** (top) and **2** (bottom). Red line is simulated based on single-crystal diffraction data.

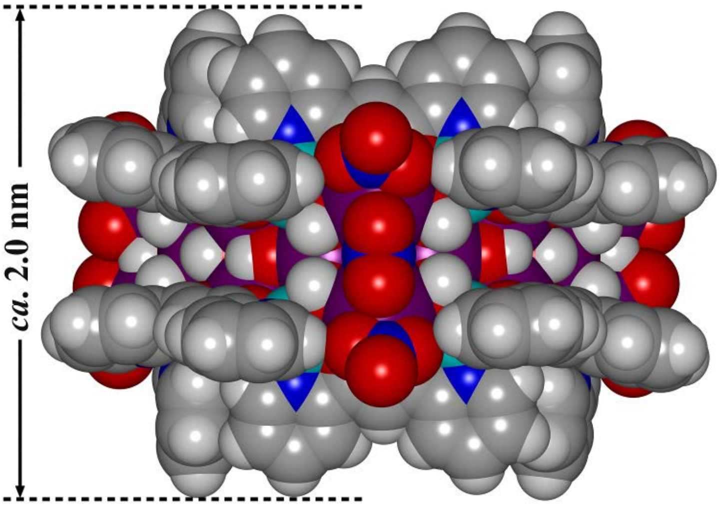

**Fig. S2** Space-filling representation (including hydrogen atoms) from the viewpoint parallel to the plane of the wheel for compound **1**, showing the thickness of the molecular wheel.

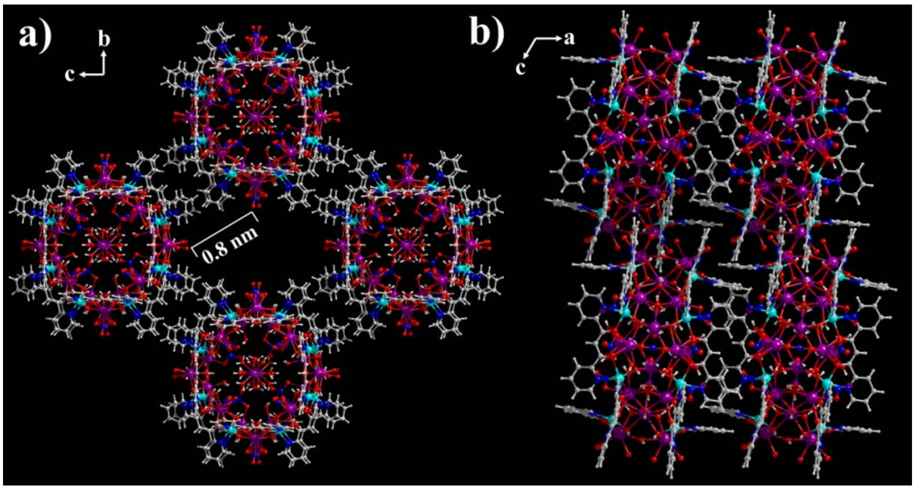

**Fig. S3** Ball and stick plots from viewpoints along the *a* axis (**a**) and the *b* axis (**b**), showing the packing mode of neighboring molecules for compound **1** (including hydrogen atoms) and the size of void on *bc* plane.

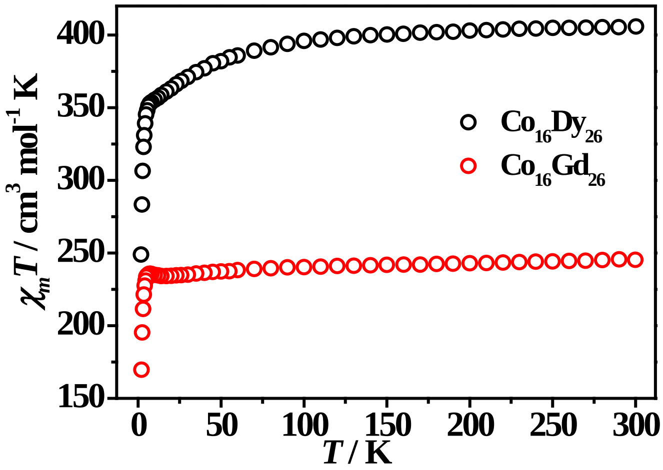

**Fig. S4** Plots of temperature dependence of $\chi_m T$ for **1** (black) and **2** (red) in a 500 G dc field between 1.8 and 300 K.

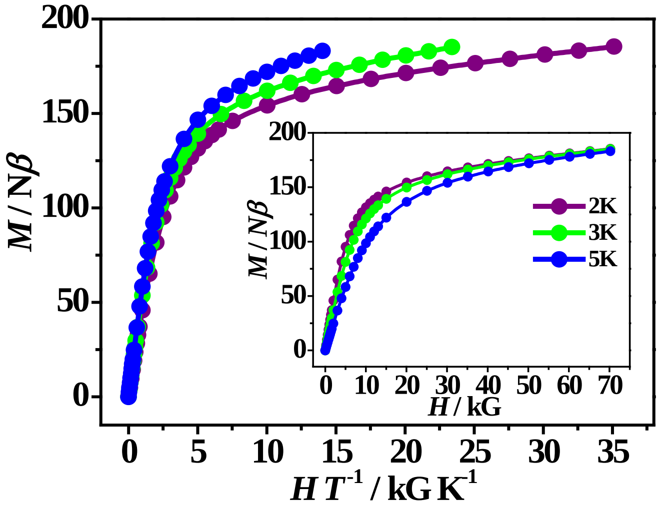

**Fig. S5** Plots of *M vs. H*/*T* (inset: *M vs. H*) for **1** at 2, 3 and 5 K.

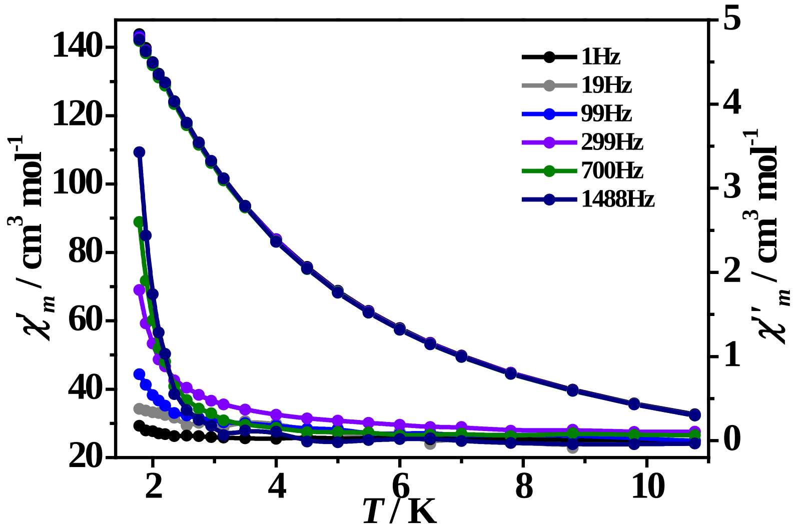

**Fig. S6** Plots of temperature dependence of the in-phase (upper) and out-of-phase (under) ac susceptibility in a 5 G ac field with a zero dc field for **1** at the indicated frequencies. Lines are only guides to the eye.

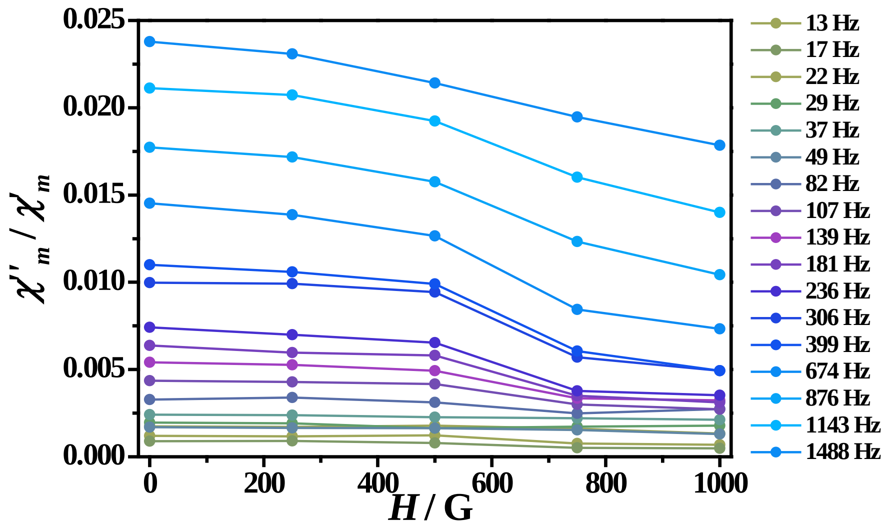

**Fig. S7** Plots of $\chi''_\mathrm{m}/\chi'_\mathrm{m}$ vs. $H_\mathrm{dc}$ at 1.8 K in a 5 G ac field for **1** at the indicated frequencies. Lines are only guides to the eye.

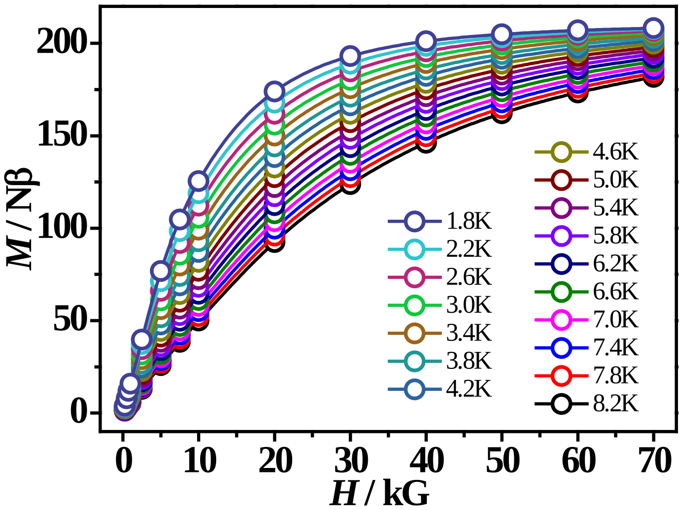

**Fig. S8** Field-dependence of the magnetization at indicated temperatures (1.8−8.2 K) for **2**.

**Table S1.** Bond valence sum (BVS) for Co atoms in **1** and **2**[a]

| atom | Co$^{II}$ | Co$^{III}$ | Co$^{IV}$ |
|---|---|---|---|
| | Compound **1** | | |
| Co1 | <u>1.874</u> | 1.846 | 1.473 |
| Co2 | <u>1.886</u> | 1.855 | 1.489 |
| Co3 | <u>1.912</u> | 1.883 | 1.504 |
| Co4 | <u>1.828</u> | 1.796 | 1.447 |
| | Compound **2** | | |
| Co1 | <u>1.897</u> | 1.875 | 1.474 |
| Co2 | <u>1.853</u> | 1.820 | 1.469 |
| Co3 | <u>1.893</u> | 1.864 | 1.487 |
| Co4 | <u>1.822</u> | 1.791 | 1.440 |

[a] The underlined value is the one closest to the charge calculated for each of Co atoms. The nearest integer can be taken as the oxidation state of the corresponding atom. Thus we can conclude that the Co ions are all divalent.[1]

**Table S2.** BVS for O(OH$^-$) atoms in **1** and **2**[b]

| Compound **1** | | Compound **2** | |
|---|---|---|---|
| atom | BVS | atom | BVS |
| O9 | 1.003 | O9 | 1.125 |
| O10 | 1.014 | O10 | 1.206 |
| O11 | 0.972 | O11 | 1.093 |
| O12 | 0.961 | O12 | 1.079 |
| O13 | 0.996 | O13 | 1.106 |
| O14 | 0.844 | O14 | 1.008 |
| O15 | 1.032 | O15 | 1.200 |
| O16 | 0.993 | O16 | 1.098 |
| O17 | 0.966 | O17 | 1.092 |
| O18 | 0.979 | O18 | 1.150 |
| O19 | 0.989 | O19 | 1.164 |
| O20 | 0.959 | O20 | 1.070 |
| O21 | 0.977 | O21 | 1.082 |
| O22 | 1.050 | O22 | 1.245 |

[b] The BVS values of ~0.8-1.2 for O atoms confirm fourteen OH$^-$ ions for both **1** and **2**.[1]

1 (*a*) I. D. Brown and D. Altermatt, *Acta Crystallogr.*, 1985, **B41**, 244; (*b*) W. Liu and H. H. Thorp, *Inorg. Chem.*, 1993, **32**, 4102.