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Two polymeric 36-metal pure lanthanide nanosize clusters†

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Two rarely seen 2D coordination polymers based on huge 36-metal pure lanthanide clusters, $\{[Gd_{36}(NA)_{36}(OH)_{49}(O)_6(NO_3)_6(N_3)_3(H_2O)_{20}]Cl_2 \cdot 28H_2O\}_n$ (**1**) and $\{[Dy_{36}(NA)_{36}(OH)_{49}(O)_6(NO_3)_6(N_3)_3-(H_2O)_{20}]Cl_2 \cdot 28H_2O\}_n$ (**2**) (HNA = nicotinic acid), were synthesized and structurally characterized. The spherical Ln_{36} skeleton can be viewed as the aggregation of one cyclohexane chair-like Ln_{24} wheel and two identical tripod-like Ln_6 units. The coordination of the carboxylic groups of the NA ligands with the Ln(III) cations results in a square layer. Additionally, compound **1** possesses a large MCE of 39.66 J kg^{-1} K^{-1} and compound **2** exhibits slow relaxation of the magnetization.

Introduction

The synthesis of high-nuclearity metal clusters remains one of the most fascinating research frontiers due to their structural diversity and rich physical properties such as magnetism, optics and catalysis. As we know, the cluster chemistry based on paramagnetic 3d and 3d/4f ions is well established, and many huge clusters of manganese,[1] cobalt,[2] nickel,[3] iron[4] and 3d/4f clusters[5] have been synthesized and investigated. However, the synthesis of high-nuclearity pure lanthanide clusters, especially over thirty nuclei, continues to be a challenge. The most important reason may be that lanthanide ions have variable and high coordination numbers as well as poor directionality. Until now, there has been only one report of lanthanide clusters with the number of lanthanide ions over thirty.[6] Furthermore, the assembly of the high-nuclearity clusters into metal–organic frameworks or coordination polymers is also an attractive topic, since the particular characteristics of the clusters can be incorporated into the obtained frameworks. Yaghi *et al.* proposed that the different types of metal clusters should possibly self-assemble into coordination polymers,[7] but it is rarely realized. On the other hand, the magnetocaloric effects of polynuclear clusters have recently attracted much attention for their potential applications in

energy-efficient and environmentally friendly magnetic refrigerants. For Gd(III) ions, the magnetic isotropy, high spin ground state and existence of low-lying excited spin states make them a perfect candidate for molecular refrigerants.[8] In general, high-nuclearity Gd(III) compounds will lead to high magnetic density, which will endow large magnetocaloric effects (MCEs). Herein, we wish to report two 2D coordination polymers based on huge 36-metal pure lanthanide clusters, $\{[Gd_{36}(NA)_{36}(OH)_{49}(O)_6-(NO_3)_6(N_3)_3(H_2O)_{20}]Cl_2 \cdot 28H_2O\}_n$ (**1**) and $\{[Dy_{36}(NA)_{36}(OH)_{49}(O)_6-(NO_3)_6(N_3)_3(H_2O)_{20}]Cl_2 \cdot 28H_2O\}_n$ (**2**) (HNA = nicotinic acid). Of them, a new magnetic coolant is found based on huge Gd_{36} clusters with a $-\Delta S_m$ value of 39.66 J kg^{-1} K^{-1} ($\Delta H = 7$ T at 2.5 K). Additionally, an isostructural ferromagnetic Dy_{36} complex showing slow relaxation of magnetization is also reported here.

Results and discussion

$\{[Gd_{36}(NA)_{36}(OH)_{49}(O)_6(NO_3)_6(N_3)_3(H_2O)_{20}]Cl_2 \cdot 28H_2O\}_n$ (**1**) and $\{[Dy_{36}(NA)_{36}(OH)_{49}(O)_6(NO_3)_6(N_3)_3(H_2O)_{20}]Cl_2 \cdot 28H_2O\}_n$ (**2**) (HNA = nicotinic acid) were synthesized by the slow hydrolysis of lanthanide ions under hydrothermal conditions. The N_3^- anions act as weak bases to cause the hydrolysis of lanthanide ions at high temperature as well as the ligands to bridge two lanthanide ions. This method is very different from that for the syntheses of the Dy_{26} clusters,[9] in which the source of the lanthanide cation is Dy_2O_3. Single-crystal X-ray diffraction analyses reveal that compounds **1** and **2** are isostructural and crystallize in triclinic space group $P\bar{1}$. Therefore, the cluster unit structure of **1** was taken as the example to be described in detail (Fig. 1). In the asymmetric unit of **1**, there are eighteen Gd(III) cations, eighteen NA$^-$ anions, twenty-four and a half OH$^-$ groups, three NO$_3^-$ anions, three O^{2-} anions, one and a half N$_3^-$ anions, one Cl$^-$ anion, ten coordination water molecules and fourteen lattice water molecules. Of the Gd(III) ions, Gd9 is in a

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mono-capped trigonal prism NO_6 coordination sphere; Gd5, Gd14 and Gd10 are in O_9 environments; the other Gd(III) cations lie in eight-coordination O_8 environments. The Gd–N distances are in the range of 2.433(6)–2.610(8) Å and the Gd–O distances are in the range of 2.295(6)–2.574(6) Å, which are all in good agreement with the reported lengths.[10] Through a centre symmetry operation, this Gd_{18} fragment can further form a sphere-like Gd_{36} cluster. To better understand the arrangement, we simplify the structure of **1** as a backbone of Gd(III) cations. As shown in Fig. 2, the cationic Gd_{36} cluster can be viewed as the aggregation of two types of cluster units, i.e. one wheel-like Gd_{24} unit and two identical tripod-like Gd_6 units. In the Gd_{24} unit, six Gd_4 cubanes, which are well-known subunits for constructing high-nuclearity lanthanide clusters,[11] are joined together with two similar neighbours. Different from the reported metallacrowns or wheels,[12] in the Gd_{24} unit six tetrahedral Gd_4 clusters here adopt an up and down arrangement and form a cyclohexane chair-like structure (see Fig. S1†). The centroid···centroid separations of the Gd_4 units are in the range of 7.83–7.90 Å and the centroid···centroid angles of the Gd_4 units are 79.60, 80.15 and 81.49°, respectively. The two triangles constructed from three centroids of the 'up' Gd_4 units and three centroids of the 'down' Gd_4 units respectively are almost equilateral, with lengths of the sides of 10.09, 10.13 and 10.24 Å as well as angles of 59.37, 59.77 and 60.86°, respectively. The planes of these two equilateral triangles are parallel and the separation between them is 5.24 Å. However, it should be noted that they are not eclipsed and have a staggered conformation, where the staggered angle between them is ca. 60°. In each tripod-like Gd_6 unit, the six Gd(III) cations are not coplanar, with the Gd···Gd separations in the range of 3.65–3.90 Å. The dihedral angle between the centric triangular Gd(III) unit and the plane constructed by the outer three Gd(III) cations is 2.90° and the average separation of the above planes is 1.48 Å. These two tripod-like units cover the wheel-like Gd_{24} unit to form a compressed sphere. Similar to the incorporation of one iodine ion into the Dy_{26} cluster centre, the Gd_{36} sphere captures two Cl⁻ anions as guests. In the skeleton of this Gd_{36} cluster, there are six pentagonal windows, which are occupied by six NO_3^- anions respectively. As in the Dy_{26} clusters and $La_{20}Ni_{30}$ cluster, the NO_3^- anions adopt a rare μ_5-$\eta^2(O,O')$:$\eta^1(O)$:$\eta^1(O')$:$\eta^1(O'')$:$\eta^1(O'')$ coordination mode to bridge five nonplanar Gd(III) cations.[13] The size of this huge Gd_{36} cluster is ca. 1.0 nm × 1.7 nm × 1.7 nm, which is estimated from the Gd···Gd separations. According to the method for the topological analysis of high nuclearity Mn and Co clusters suggested by Kostakis, Blatov, Proserpio et al.,[14] this D_{3d}-symmetric Gd_{36} unit has six topologically non-equivalent Gd(III) vertexes, i.e. four Gd(III) cations in one tetrahedral Gd_4 unit and two Gd(III) cations of a tripod-like Gd_6 unit (see Fig. S2†). Accordingly, it can be signed as **3,4,5,6,6,6M36-1**. Different from the formation of the tetramers in Dy_{26} clusters, compound **1** is not isolative. And upon packing, **1** extends its structure through the coordination of carboxylic groups of the NA ligands with the Gd(III) cations to form a square layer (see Fig. S3†). To date, this type of coordination polymer based on high-nuclearity lanthanide clusters has rarely been seen.[8h,15]

The temperature dependencies of the magnetic susceptibilities of compound **1–2** were measured up to 300 K with an applied direct-current (dc) magnetic field of 1000 Oe using the polycrystalline powder (Fig. 3). The $\chi_m T$ values of 279.60 cm³ K mol⁻¹ for **1** and 498.69 cm³ K mol⁻¹ for **2** at 300 K are in close agreement with the expected values of 283.68 cm³ K mol⁻¹ for 36 Gd(III) cations ($^8S_{7/2}$, $g = 2$) and 510.12 cm³ K mol⁻¹ for 36 Dy(III) cations ($^6H_{15/2}$, $g = 4/3$), respectively. For **1**, the $\chi_m T$ value slightly decreases on lowering the temperature down to 50 K and then decreases quickly to 122.55 cm³ K mol⁻¹ at 2 K, thus suggesting the presence of dominant antiferromagnetic interactions between the Gd(III) cations. To estimate the intramolecular exchange constant, fitting the curve of $1/\chi_m$ vs T in the range of 2–300 K gives $C = 280.90$ cm³ K mol⁻¹ and $\theta = -2.43$ K. For **2**, upon cooling the $\chi_m T$ value increases gradually to reach a maximum of 548.64 cm³ K mol⁻¹ at about 36 K, before quickly decreasing to 292.79 cm³ K mol⁻¹ at 2 K. The increase of the $\chi_m T$ product may be due to the magnetic anisotropy of the Dy(III) cations. The decrease at the low temperature may be owing to a combination of large magnetic anisotropy, intermolecular antiferromagnetic interactions and thermal population of the excited states of the Dy(III) ions (Stark sublevels of the $^6H_{15/2}$ state).[16] Below 8 K, the field-dependence of the magnetization rises rapidly at low magnetic fields. At high fields, the magnetization increases without any sign of saturation to reach 223.18 μ_B around 7 T at 2 K. The non-superposition of the M vs. H/T curves at different magnetic fields (Fig. S4†) and the lack of saturation at high field suggest the presence of significant magnetic anisotropy and/or low lying excited states.

Considering the low M_w/N_{Gd} ratio of 347, compound **1** is a good candidate for molecular refrigerants. To evaluate the MCEs, we calculate the magnetic entropy change ΔS_m from the experimental magnetization data according to the Maxwell equation $\Delta S_m(T)_{\Delta H} = \int[\partial M(T, H)/\partial T]_H dH$. As shown in Fig. 4, the maximum of the $-\Delta S_m$ for **1** is 39.66 J kg⁻¹ K⁻¹ at 2.5 K for $\Delta H = 7$ T. This value is smaller than that of 49.64 J kg⁻¹ K⁻¹ calculated for 36 isolated Gd(III) spins using the equation $-\Delta S_m = nR\ln(2S + 1) = 36R\ln(8) = 74.9R$. However, this value is still among the largest for Gd-based polynuclear complexes, which is comparable to 41.26 J kg⁻¹ K⁻¹ for $\{Gd_{42}^{III}Co_9^{II}Co^{III}\}^{8o}$ and 46.12 J kg⁻¹ for $\{Gd_{24}^{III}\}^{17}$ but much larger than 19.0 J kg⁻¹ K⁻¹ for $\{Mn_4^{III}Gd_4^{III}\}$,[8l] 28.6 J kg⁻¹ K⁻¹ for $\{Co_6^{II}Gd_8^{III}\}^{18}$ and 22.3 J kg⁻¹ K⁻¹ for $\{Co_4^{II}Gd_6^{III}\}$.[19]
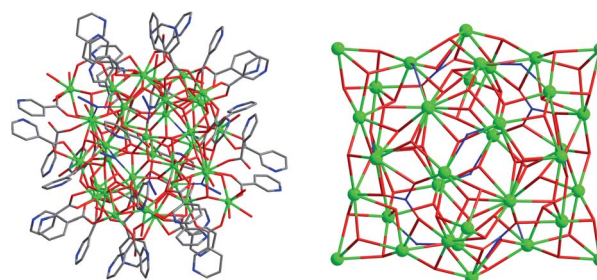

Fig. 1 The 36-metal Gd(III) cluster (left). For clarity, only the bridge atoms and Gd(III) cations are shown (right). Green, Gd; red, oxygen; blue, nitrogen.
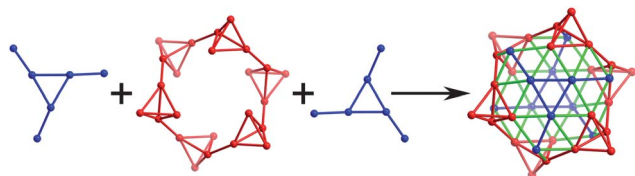
Fig. 2 Illustration of the structure of the Gd$_{36}$ cluster. The Gd(III) cations of the wheel-like Gd$_{24}$ units are in red and their joints are also in red. The Gd(III) cations of the two tripod-like Gd$_6$ units are in blue and their joints are also in blue. Additionally, the joints between the Gd(III) cations of the wheel-like Gd$_{24}$ units and the Gd(III) cations of the two tripod-like Gd$_6$ units are in green.
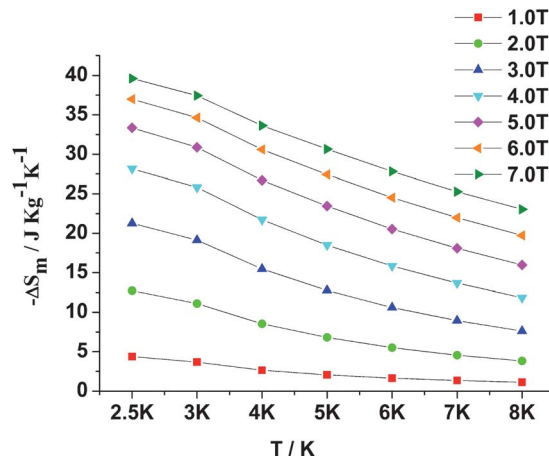

Fig. 4 Values of $-\Delta S_m$ calculated from the magnetization data using the Maxwell equation for **1** at various fields (1–7 T) and temperatures (2.5–8 K).

Accordingly, the volumetric magnetic entropy change for **1** is 91.34 mJ cm^{-3} K^{-1}. This large MCE may be attributed to the high spin density in **1**.

To verify the validity of the ΔS_m values calculated from the experimental magnetization data, we also carried out temperature-dependent heat capacity (C) measurements in applied magnetic fields up to 7 T with the temperature in the range of 2–25 K. As seen in Fig. 5, the heat capacity data normalized to the gas constant R vs. T at different magnetic fields are presented. Further, the corresponding magnetic entropy $S_m(T)$ at $T > 2.5$ K can be obtained using the equation $S_m(T) = \int_0^T C_m(T)/T dT$. The value of S_m at $T = 2.5$ K is obtained from the magnetization data.[8o] As shown in Fig. 5, the $-\Delta S_m$ values obtained from the C data are in agreement with those calculated from the magnetization data.

For **2**, the dynamics of the magnetization were investigated using alternating-current (ac) magnetic susceptibility measurements, at the zero static field with an oscillation of 3.0 Oe from 111 to 9111 Hz given in Fig. 6 as plot of χ'' vs T. Strikingly, frequency-dependent out-of-phase signals are observed, indicating slow relaxation of the magnetization.[20] However, the absence of the maxima of the out-of-phase susceptibility signals is likely owing to the fast quantum tunneling of the magnetization.

Conclusions

In conclusion, two 36-metal lanthanide compounds **1** and **2** were synthesized by the slow hydrolysis of lanthanide ions under hydrothermal conditions, which is demonstrated as a good method to synthesize high-nuclearity lanthanide clusters. Importantly, **1** and **2** stand as the examples of the highest nuclearity among the reported Gd(III) and Dy(III) clusters, respectively. At the same time, **1** possesses a large MCE of 39.66 J Kg^{-1} K^{-1} and **2** exhibits slow relaxation of the magnetization. Further investigations are now ongoing.

Experimental section

Materials and methods

All reactants were reagent grade and used as purchased without further purification. Elemental analyses for C, H, N were carried out on a German Elementary Vario EL III instrument. The FT-IR spectra were performed on a Nicolet Magna 750 FT-IR spectrometer using KBr pellets in the range of 4000–400 cm^{-1}. The
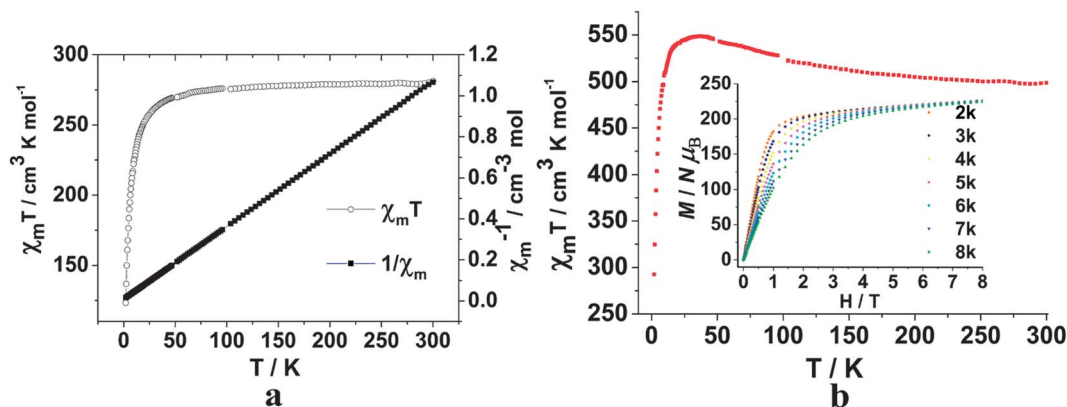

Fig. 3 Plots of the temperature dependence of $\chi_m T$ and $1/\chi_m$ under a 1000 Oe dc field between 2 and 300 K for **1** (a). Plots of the temperature dependence of $\chi_m T$ under a 1000 Oe dc field between 2 and 300 K for **2** (b). Inset: M vs. H data at various temperatures for **2**.
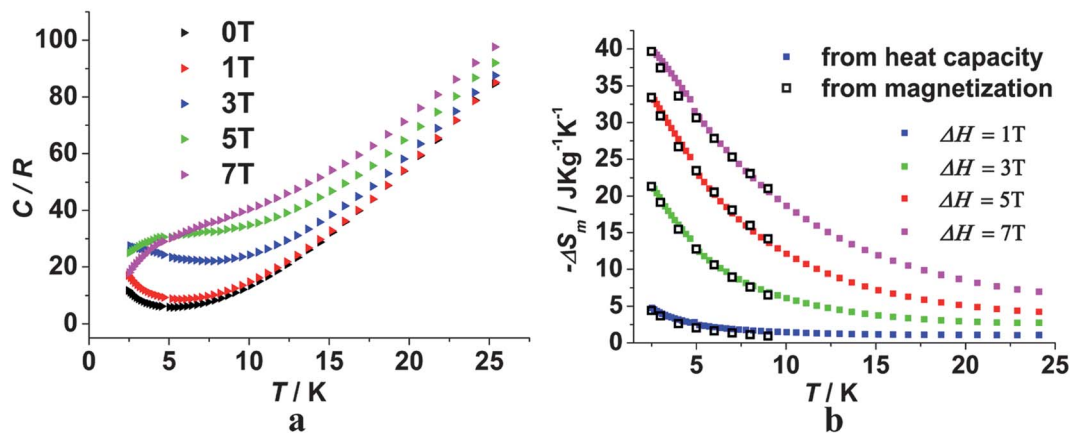
Fig. 5 Temperature dependence of the heat capacities normalized to the gas constant R for **1** at different applied fields (a). Temperature dependence of $-\Delta S_m$ obtained from the C (filled dots) data and magnetization data (hollow dots) at different applied fields (b).
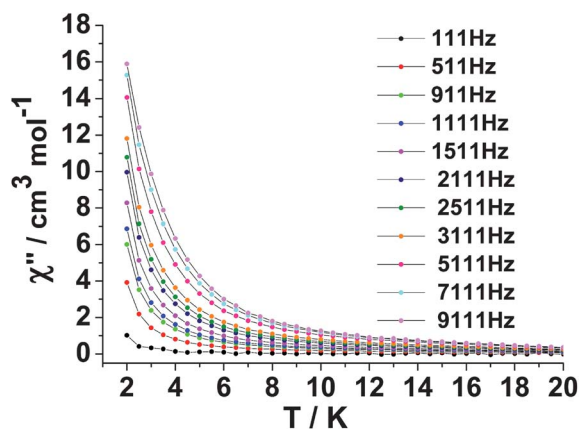

Fig. 6 Frequency dependence of the out-of-phase (χ'') ac susceptibility components for **2** at zero dc field.

power X-ray diffraction (XRD) patterns were collected using a Rigaku DMAX2500 X-ray diffractometer using Cu Kα radiation ($\lambda = 0.154$ nm). Magnetic data were recorded on polycrystalline samples with Quantum Design PPSM-9T and MPMS-XL systems.

Syntheses

(65 mg, 1.0 mmol) NaN_3 was added to a solution of 0.49 mg (0.4 mmol) nicotinic acid and 75 mg (0.2 mmol) $GdCl_3 \cdot 6H_2O$ in 5 mL H_2O. Then 100 μL 2 mol L^{-1} HNO_3 was quickly added into the above mixture in a fume hood (pH = 4.61). A Teflon-lined bomb was sealed and raised to the temperature of 180 °C for three days. Cooling the bomb slowly at 1 °C per 10 min afforded the expected colorless prism crystals **1** (pH = 4.91). Yield, *ca.* 7 mg (10.14%, based on Gd). Anal. calcd for complex **1**: calcd C, 20.89; H, 2.35; N, 5.75; found C, 21.38; H, 2.55; N, 5.95%.

For **2**, 65 mg (1.0 mmol) NaN_3 was added to a solution of 0.49 mg (0.4 mmol) nicotinic acid and 76 mg (0.2 mmol) $DyCl_3 \cdot 6H_2O$ in 5 mL H_2O. Then 100 μL 2 mol L^{-1} HNO_3 was quickly added into the above mixture in a fume hood (pH = 4.60). A Teflon-lined bomb was sealed and raised to the temperature of 180 °C for three days. Cooling the bomb slowly at 1 °C per 10 min afforded the expected colorless prism crystals **2** (pH = 4.89). Yield, *ca.* 8 mg (11.42%, based on Dy). Anal. calcd for complex **2**: calcd C, 20.58; H, 2.31; N, 5.67; found C, 21.39; H, 2.52; N, 5.55%.

X-Ray data collection and structural determination

The data of complexes **1** and **2** were collected on a Rigaku MM007 CCD diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 123 K. These two structures were resolved by direct methods and refined by full-matrix least-squares fitting on F^2 using the SHELX-97 software package.[21] All non-hydrogen atoms were refined with anisotropic thermal parameters except several solvent molecules. In both **1** and **2**, there are six sites co-occupied by OH^- anions and N_3^- anions. At each site, one OH^- anion and one N_3^- anion appear alternately, with occupancy factors of 0.5 and 0.5. The hydrogen atoms on the aromatic rings were located at geometrically calculated positions and refined by riding. More details on the crystallographic studies as well as atomic displacement parameters are given in the ESI† as CIF files. CCDC reference numbers 921120 and 921121 for complexes **1–2**.

Crystal and refinement details for complexes 1 and 2

1, $C_{216}H_{289}Cl_2Gd_{36}N_{51}O_{193}$, $M = 12\,419.88$, colorless crystals, 0.08 mm × 0.09 mm × 0.12 mm. Triclinic, space group $P\bar{1}$, $a = 21.545(3)$ Å, $b = 23.046(3)$ Å, $c = 23.372(3)$ Å, $\alpha = 94.5350(10)°$, $\beta = 115.1930(10)°$, $\gamma = 115.6790(10)°$, $V = 8956(2)$ Å^3, $Z = 1$. $F(000) = 5824$, $2\theta_{max} = 51°$, 70 025 reflections collected, 32 100 unique ($R_{int} = 0.0866$). Final $R_1 = 0.0400$, $wR_2 = 0.1371$, GooF = 1.067, R indices based on 32 100 reflections with $I > 2\sigma(I)$ (refinement on F^2).

2, $C_{216}H_{289}Cl_2Dy_{36}N_{51}O_{193}$, $M = 12\,608.88$, colorless crystals, 0.08 mm × 0.12 mm × 0.16 mm. Triclinic, space group $P\bar{1}$, $a = 21.545(4)$ Å, $b = 22.886(5)$ Å, $c = 23.170(4)$ Å, $\alpha = 94.32°$, $\beta = 115.373(2)°$, $\gamma = 115.6390(10)°$, $V = 8816(3)$ Å^3, $Z = 1$. $F(000) = 5896$, $2\theta_{max} = 52°$, 97 598 reflections collected, 34 416 unique ($R_{int} = 0.1222$). Final $R_1 = 0.0422$, $wR_2 = 0.1232$, GooF = 1.066, R indices based on 34 416 reflections with $I > 2\sigma(I)$ (refinement on F^2).

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