Electronic Supplementary Information

A single-stranded {Gd_{18}} nanowheel with symmetric polydentate diacylhydrazone ligand

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General Materials and Methods

All reagents were used as received without further purification. IR spectra were recorded in the range of 4000-400 cm^{-1} on a Perkin-Elmer Spectrum One FT/IR spectrometer using a KBr pellet. Elemental microanalyses for C, H, and N were carried out on a Model 2400 II, Perkin-Elmer elemental analyzer. Magnetic susceptibility measurements were performed in the temperature range of 300-2 K using a Quantum Design MPMS SQUIDXL-5 magnetometer equipped with a 5 T magnetic field. The diamagnetic correction for the complex was estimated using Pascal's constants, and magnetic data were corrected for diamagnetic contributions of the sample holder.

X-ray Structure Determination

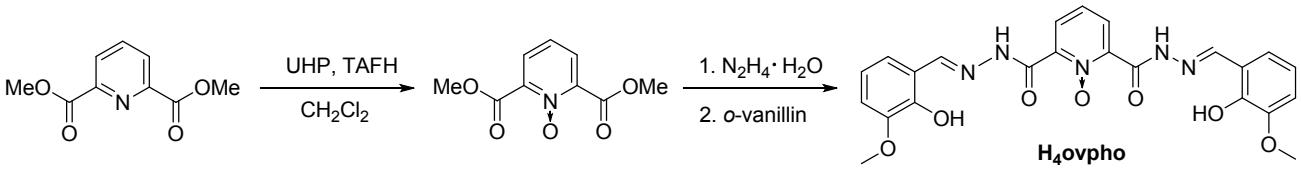
All the data for **1** were collected with a Bruker SMART CCD instrument by using graphite monochromatic Mo-$K\alpha$ radiation (λ = 0.71073 Å) at 120(2) K. Absorption effect was corrected by semi-empirical methods. The structure was solved by direct methods and was refined by full-matrix least-squares methods with SHELXL-97 crystallographic software package.[S1] The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and refined by using a riding model. The final cycle of full-matrix least-squares refinement was based on observed reflections and variable parameters. A summary of crystal data and relevant refinement parameters is given in Table S1. Selected bond lengths and bond angles are given in Table S3.

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

Identification	**1**	Identification	**1**
Formula	$C_{219}H_{324}N_{30}O_{147}Gd_{18}$	Z	6
Fw	8559.58	D_c/g cm^{-3}	1.504
Temp/K	120(2)	$m\mu$/mm^{-1}	3.190
Crystal system	Trigonal	F(000)	25056
Space group	$R\bar{3}c$	Reflns collected	95695
a/Å	33.1977(3)	Unique reflns	12353
b/Å	33.1977(3)	R_{int}	0.0963
c/Å	59.4184(8)	GOF	1.160
α/°	90.00	R_1, wR_2 ($I > 2\sigma(I)$)	R_1 = 0.0568
β/°	90.00		wR_2 = 0.1326
γ/°	120.00	R_1, wR_2 (all data)	R_1 = 0.0786
V/Å^3	56711.0(11)		wR_2 = 0.1545

Synthesis of H_4ovpho

The synthetic route for H_4ovpho is presented in Scheme S1. Starting from dimethyl 2,6-pyridinedicarboxylate, the dimethyl 2,6-pyridinedicarboxylate *N*-oxide was synthesized accord to the literature.[S2] Subsequently, the pyridine-2,6-dicarbohydrazide *N*-oxide (2.1 g, 1 mmol) and $N_2H_4 \cdot H_2O$ (10 ml) was refluxed in MeOH (100 ml) at 80 ˚C for 12 h. The *o*-vanillin (3.0 g, 2 mmol) was then added slowly and the reaction was keep at 80 ˚C for another 12 h. Upon cooling and filtering, yellow solid of *N*,*N*'-bis(*o*-vanillidene)pyridine-2,6-dicarbohydrazide *N*-oxide (H_4ovpho) was obtained with a yield of 84%. ESI-MS *m/z*: 478.14 $[M\text{-}H^+]^-$. Elemental analysis Calcd. (%): C, 57.62; H, 4.41; N, 14.61%. Found: C, 57.75; H, 4.33; N, 14.54%.



Scheme S1. Synthetic route of H_4ovpho.

Synthesis of 1

A mixture of $Gd(OAc)_3 \cdot 6H_2O$ (191 mg, 0.5 mmol), H_4ovpho (24 mg, 0.05 mmol) and Et_3N (0.1 mmol) in 1.5 mL CH_3OH-CH_3CN (*V*/*V* = 1/2) mixed solvent was sealed in a *Pyrex* tube and heated to 80 ˚C for 72 h. After cooled to room temperature at a rate of 0.5 ˚C/min, orange block-shaped crystals of **1** were obtained with a yield of 54% (based on ligand). Elemental analysis (%): calcd: C, 30.73; H, 3.82; N, 4.91; Found: C, 30.88; H, 3.93; N, 4.78. IR (KBr disk, cm^{-1}): 3432 (vs), 2975 (w), 1615 (s), 1563 (m), 1456 (m), 1385 (m), 1216 (m), 1085 (m), 1050 (m), 946 (m), 741 (m), 669 (w), 437 (w).

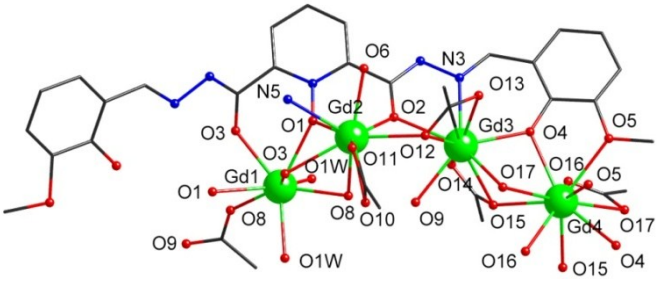
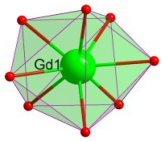
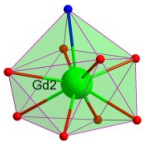
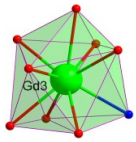
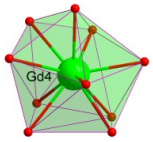


Fig. S1. The asymmetry unit of **1**.

Table S2. The coordination environments, geometries and donors of the Gd^{3+} ions in **1**.

No.	Coordination Environments	Coordination Gometries	Coordination Donors
Gd1		Eight-coordinated Bicapped trigonal prism	$O_{oxynitride}$, O_{enol}, $O_{acetate}$, O_{aqua}
Gd2		Nine-coordinated Mono-capped square antiprism	$O_{oxynitride}$, O_{phenol}, O_{enol}, $O_{acetate}$, $N_{acylhydrazone}$
Gd3		Nine-coordinated Mono-capped square antiprism	$O_{acetate}$, O_{phenol}, O_{enol}, $N_{acylhydrazone}$
Gd4		Ten-coordinated Bicapped dodecahedron	$O_{acetate}$, O_{phenol}, $O_{methoxyl}$

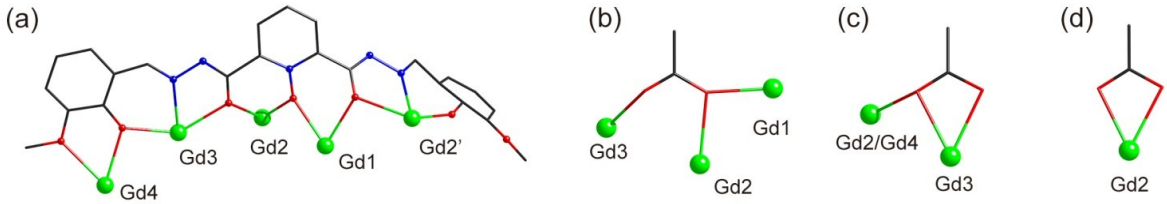


Fig. S2. The coordination modes of $ovpho^{4-}$ (a) and OAc^{-} ions (b-d) in **1**.

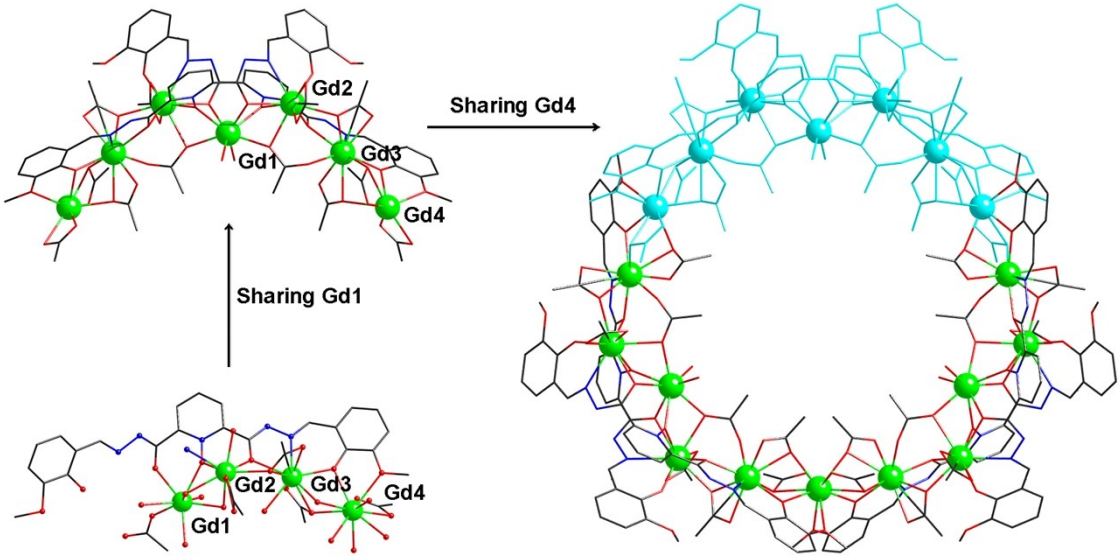


Fig. S3. The building units of **1**.

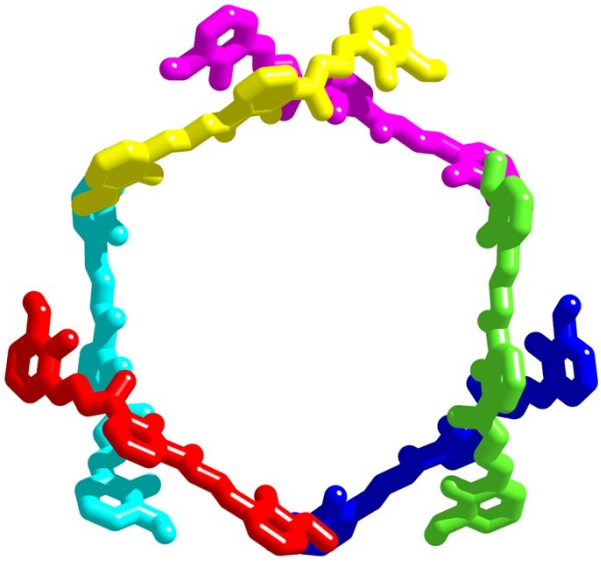


Fig. S4. The arrangement of six ligands in **1**.

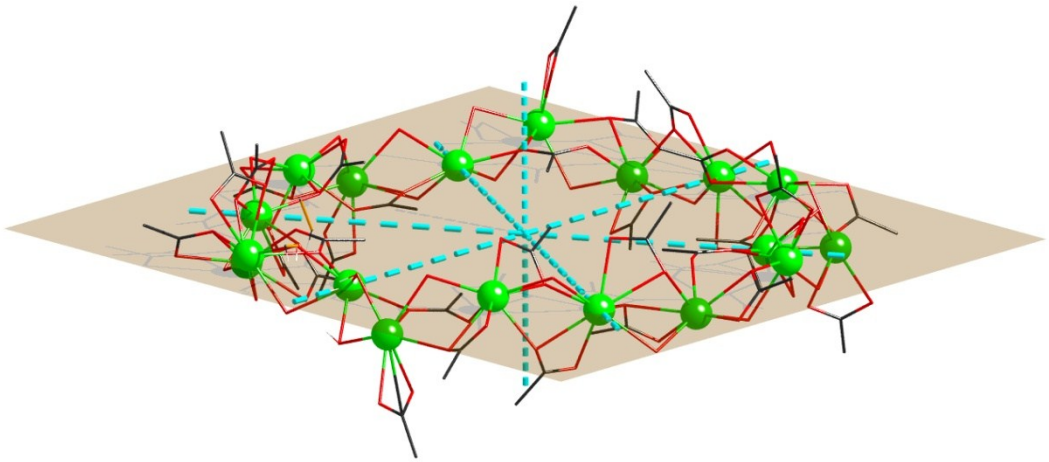


Fig. S5. The D_{3d} symmetry structure of **1** in a side-view.

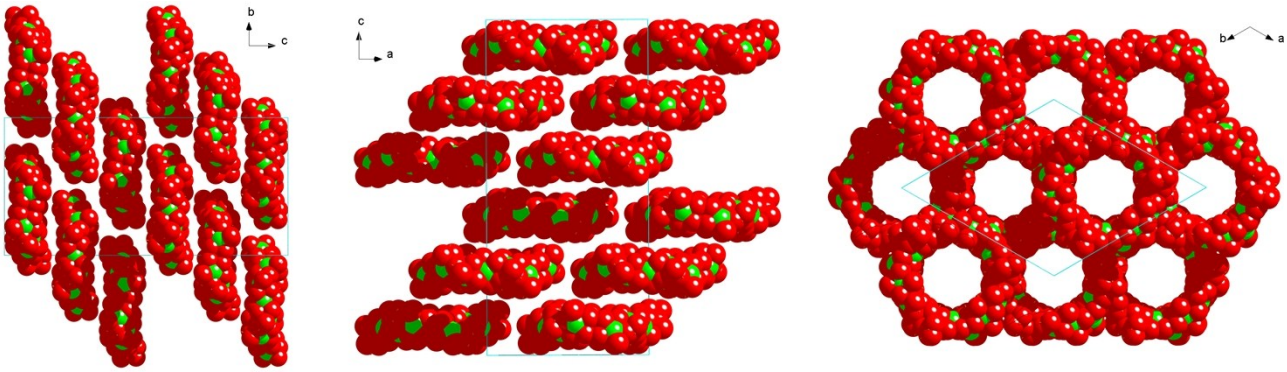


Fig. S6. Crystal packing diagram of the Gd−O cores of **1**.

Color code: Gd, green; O, red; cell edge, blue.

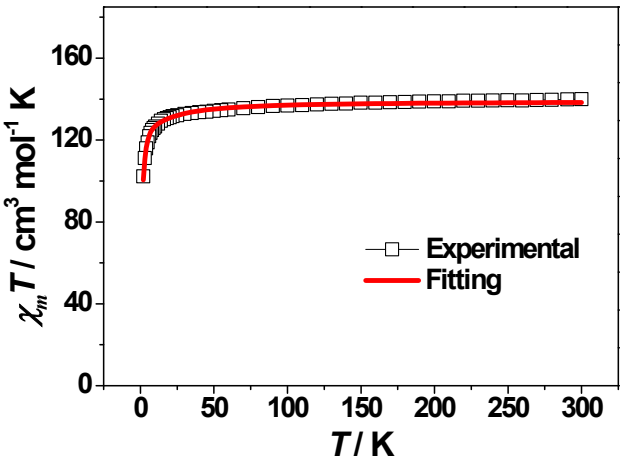


Fig. S7. The $\chi_m T$-T plot for **1**. The red line represents the best fitting.

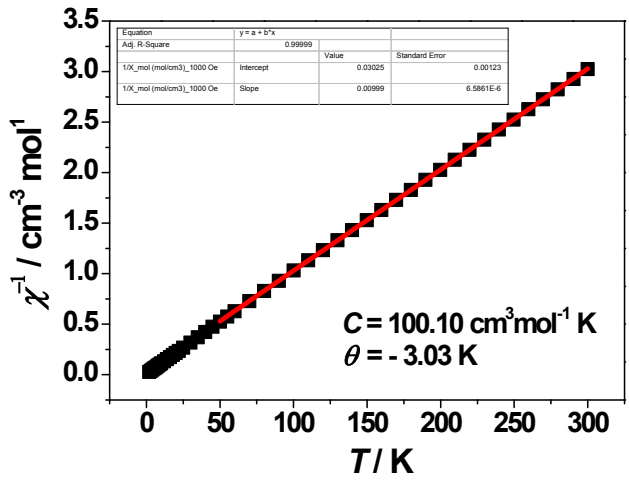


Fig. S8. The χ_m^{-1}-T plot for **1**.

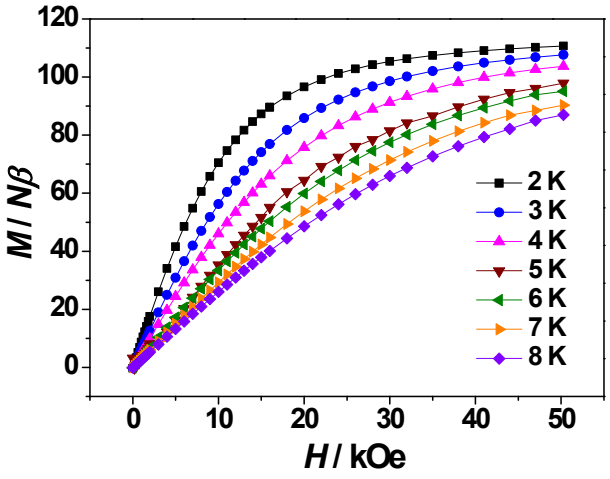


Fig. S9. The plot of M-H for **1** in the field rang of 0-50 kOe at 2-8 K.

Table S3. Selected bond lengths (Å) and angles (°) for **1**.

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Gd1-O8	2.334 (6)	Gd2-O10	2.467 (7)	Gd4-O15	2.379 (6)
Gd1-O8^{i}	2.335 (6)	Gd2-O8^{i}	2.550 (6)	Gd4-O4	2.439 (6)
Gd1-O1W^{i}	2.355 (7)	Gd2-N5'^{i}	2.552 (9)	Gd4-O4^{ii}	2.439 (6)
Gd1-O1W	2.355 (7)	Gd2-N5^{i}	2.552 (9)	Gd4-O16^{ii}	2.482 (7)
Gd1-O3^{i}	2.387 (6)	Gd3-O4	2.325 (6)	Gd4-O16	2.482 (7)
Gd1-O3	2.387 (6)	Gd3-O9^{i}	2.342 (6)	Gd4-O5	2.523 (6)
Gd1-O1^{i}	2.402 (6)	Gd3-O17^{ii}	2.343 (6)	Gd4-O5^{ii}	2.523 (6)
Gd1-O1	2.402 (6)	Gd3-O2	2.357 (6)	Gd4-O17^{ii}	2.589 (7)
Gd2-O6^{i}	2.236 (7)	Gd3-O13	2.462 (6)	Gd4-O17	2.589 (7)
Gd2-O1	2.416 (6)	Gd3-N3	2.471 (7)	O3-Gd2^{i}	2.454 (6)
Gd2-O12	2.424 (6)	Gd3-O12	2.485 (6)	O8-Gd2^{i}	2.550 (6)
Gd2-O2	2.449 (6)	Gd3-O14	2.506 (6)	O9-Gd3^{i}	2.342 (6)
Gd2-O3^{i}	2.454 (6)	Gd3-O15	2.534 (6)	O17-Gd3^{ii}	2.343 (6)
Gd2-O11	2.464 (8)	Gd4-O15^{ii}	2.379 (6)	O6-Gd2^{i}	2.236 (7)
N5-Gd2^{i}	2.552 (9)				
Bond Angle	Angle(°)	Bond Angle	Angle(°)	Bond Angle	Angle(°)
Gd1-O1-Gd2	101.6 (2)	Gd3-O4-Gd4	101.9 (2)	Gd4-O15-Gd3	97.7 (2)
Gd3-O2-Gd2	107.2 (2)	Gd1-O8-Gd2^{i}	99.6 (2)	Gd3^{ii}-O17-Gd4	97.1 (2)
Gd1-O3-Gd2^{i}	100.9 (2)	Gd2-O12-Gd3	104.0 (2)		

Symmetry codes: (i) $y-1/3, x+1/3, -z+5/6$; (ii) $-x-4/3, -x+y-2/3, -z+5/6$.

References

S1. (a) G. M. Sheldrick, *SHELXS−97, Program for Crystal Structure Solution and Refinement*. University of Göttingen, **1997**; (b) G. M. Sheldrick, *SHELXL 97, Program for the Refinement of Crystal Structure.* University of Göttingen, **1997**.

S2. S. Caron, N. M. Do and J. E. Sieser, *Tetrahedron Lett.,* 2000, **41**, 2299.