Electronic Supplementary Information

A novel trigonal propeller-shaped hybrid tri-Neodymium-polyoxometalate exhibiting single-molecule magnet behavior

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1. Materials and Physical Measurements

$[(n-C_4H_9)_4N]_2Mo_6O_{19}$ was synthesized according to the literature.[1] All other chemicals were obtained from commercial sources and used as received without further purification. Elemental analyses (C, H, N) was carried out on Vario MICRO elemental analyzer. Powder X-ray diffraction (PXRD) patterns were collected on Rigaku desktop MiniFlex 600 diffractometer with Cu Kα radiation (λ=1.5406 Å). IR spectra were recorded in the range 4000–400 cm^{-1} on a Perkin-Elmer FT-IR spectrum 2000 spectrometer with pressed KBr pellets. Thermal analyses were performed on a TGA/DSC 1 STAR^e system from room temperature to 1000°C at a heating rate of 10K/min under nitrogen. The dc magnetic susceptibilities were measured with a Quantum Design MPMS-XL SQUID susceptometer under an applied magnetic field of 1 kOe in the 2-300 K range. Diamagnetic corrections were made using Pascal'sconstants.[2] Ac magnetic susceptibility measurements were performed on a Physical Property Measurement System(PPMS) PPMS-9 T with a 3 Oe ac oscillating field under 500Oedcfield.

2. Experimental Section

Synthesis of (NH₂Me₂)₃{[Nd(Mo₄O₁₃)(DMF)₄]₃(BTC)₂}·8DMF (compound 1). A mixture of $[(n-C_4H_9)_4N]_2Mo_6O_{19}$ (0.08 mmol, 0.109 g) and H₃BTC (0.5 mmol, 0.105 g) were dissolved in N,N-dimethylformamide (DMF) (4 mL), and 2.5 mL of an ethanol (EtOH) solution of Nd(NO₃)₃·6H₂O (0.5 mmol, 0.219 g) was added dropwise to the solution. The mixed solution was stirred at room temperature for 30 minutes to give a clear solution. The solution was sealed in a glass bottle and heated at 80 °C for 24hours, and then slowly cooled down to the room temperature. Violet block-shaped single crystals suitable for X-ray data collection were obtained. Yield: 52% based on Mo. Elemental analysis found (calcd) for C₈₄H₁₇₀N₂₃O₇₁Mo₁₂Nd₃, C 24.26 (23.89); H 4.21 (4.06); N 7.80 (7.63).IR(cm^{-1}) :3418(m), 2931(w), 1658(s),1620(m), 1562(s), 1444(s), 1382(s), 1247(s), 1114(s), 1107(s), 931(s), 869(s), 725(m),686(m), 572(m), 453(m).

3. Crystallographic data collection and refinement

Suitable single crystal of **compound 1** was mounted on a loop for the X-ray measurement. Diffraction data was collected on SuperNova (Dual source) diffractometer equipped with the CrysAlispro X-ray crystallography data systems. The measurement was made by using graphic monochromatic Mo Kα radiation (λ = 0.71073 Å) at 100 K under a cold nitrogen stream. Using Olex2,[3] the structure was solved by the ShelXT[4] structure solution program using Intrinsic Phasing and refined with the ShelXL[5] refinement package using Least Squares minimization. The crystallographic data has been deposited at the Cambridge Crystallographic Data Center with reference number CCDC 1572984. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via*http://www.ccdc.cam.ac.uk/data_request/cif.

4. Crystal data for compound 1

Table S1. Crystal Data and Structure Refinement Parameters for **Compound 1**

Compound reference	**Compound1**
Chemical formula	$C_{54}H_{90}Mo_{12}N_{12}Nd_3O_{63}\cdot8(C_3H_7NO)\cdot3(C_2H_8N)$
Formula Mass	4222.42
Crystal system	Monoclinic
a/Å	35.7841(1)
b/Å	18.6471(6)
c/Å	23.5985(7)
α/°	90
β/°	120.260(3)
γ/°	90
Unit cell volume/Å^3	13601.1(9)
Temperature/K	100
Space group	C2/c
No. of formula units per unit cell, Z	4
No. of reflections measured	34634
No. of independent reflections	13229
R_{int}	0.0270
Final R_1^a values (I > 2σ(I))	0.0322
Final $wR(F^2)^b$ values (I > 2σ(I))	0.0756
Final R_1^a values (all data)	0.0374
Final $wR(F^2)^b$ values (all data)	0.0780
Goodness-of-fit on F^2	1.017

$^aR_1=\sum||F_o|-|F_c||/\sum|F_o|$. $^bwR_2=[\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)]^{1/2}$

Table S2. Selected bond lengths for **Compound 1**

	Bond lengths (Å)		Bond lengths (Å)		Bond lengths (Å)
Mo1—O4	1.7492	Mo3—O14	2.2024	Mo4—O25	1.7432
Mo1—O5	2.2512	Mo3—O17	1.9165	Mo5—O21	1.9083
Mo1—O8	1.9091	Mo3—O18	1.6968	Mo5—O22	1.6995
Mo1—O9	1.7080	Mo3—O19	1.9097	Mo5—O23	1.9136
Mo1—O10	2.2245	Mo3—O24	2.3142	Mo5—O24	2.2601
Mo2—O3	1.7530	Mo3—O26	1.7490	Mo5—O28	1.7467
Mo2—O5	2.3126	Mo4—O15	2.2250	Mo6—O19	1.8903

Mo2—O6	1.9102	Mo4—O16	1.7008	Mo6—O20	1.7039
Mo2—O7	1.6999	Mo4—O17	1.9182	Mo6—O21	1.9228
Mo2—O8	1.9142	Mo4—O23	1.9249	Mo6—O24	2.2729
Mo2—O11	2.2484	Mo4—O24	2.2762	Mo6—O27	1.7529

	Bond lengths (Å)		Bond lengths (Å)
Nd1—O1	2.4609	Nd2—O26	2.4669
Nd1—O2	2.4890	Nd2—O27	2.4688
Nd1—O3	2.4766	Nd2—O28	2.4598
Nd1—O4	2.5059	Nd2—O29	2.5404
Nd1—O5	2.6003	Nd2—O30	2.4952
Nd2—O24	2.5955	Nd2—O31	2.4882
Nd2—O25	2.4623	Nd2—O32	2.4780

5. Figures of compound 1
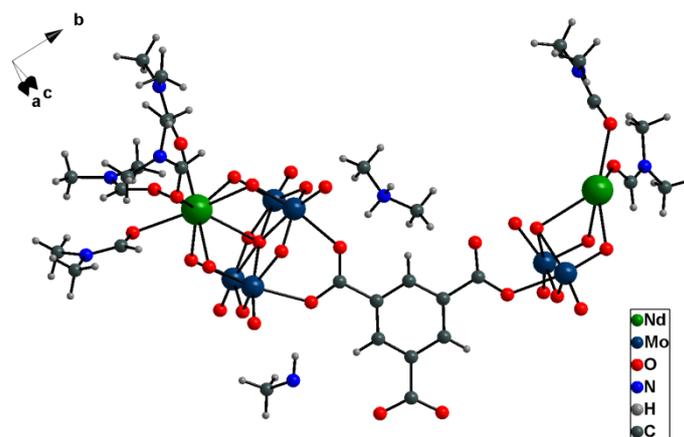
Fig. S1 The asymmetric unit of **complex 1**, containing one and a half Nd centers, one and a half {Mo_4O_{13}} POMs, a deprotonated BTC ligand, six coordinated DMF molecules, one and a half (NH_2Me_2)$^+$ cations and four uncoordinated DMF molecules (omitted for clarity). Nd (green), O (red), C (gray), N (blue),Mo (dark teal), H (light gray).
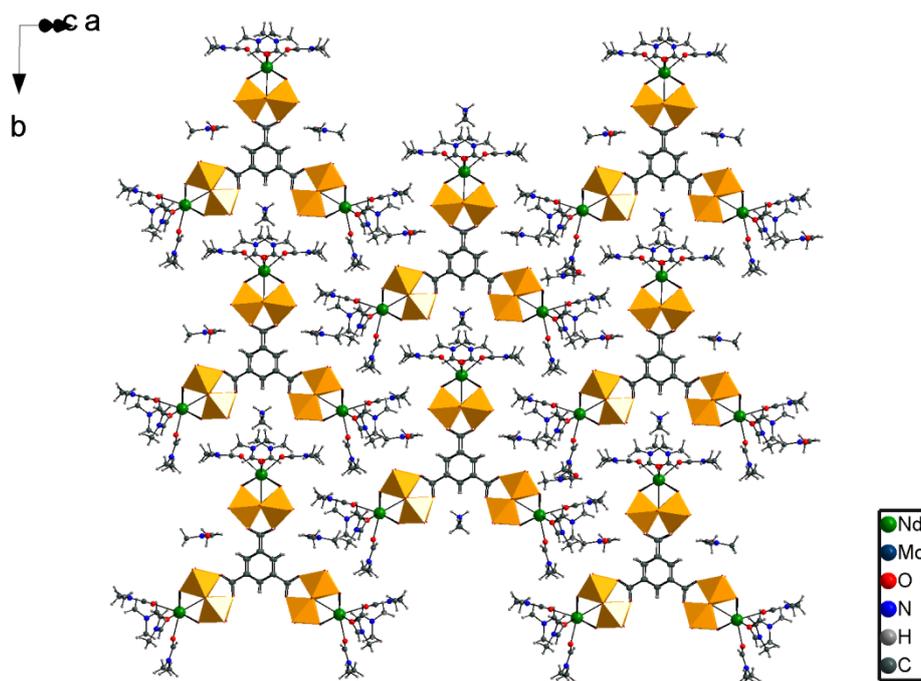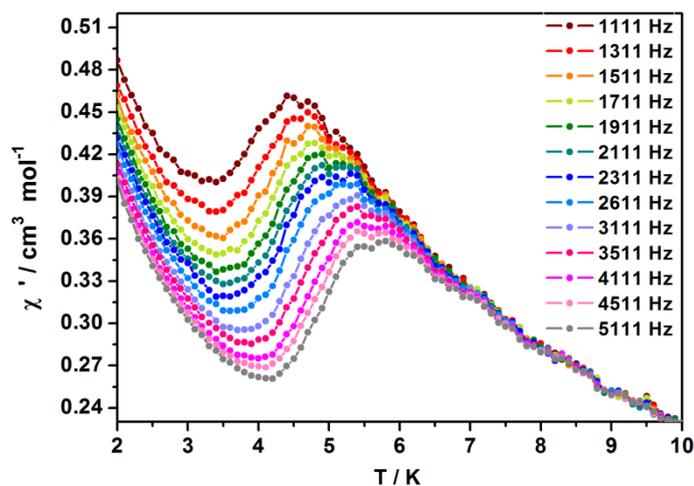
Fig.S2 The 2D hydrogen-bonded layer in **1**. Nd (green), MoO$_6$ octahedral (orange), O (red), C (gray), N (blue), H (light gray).
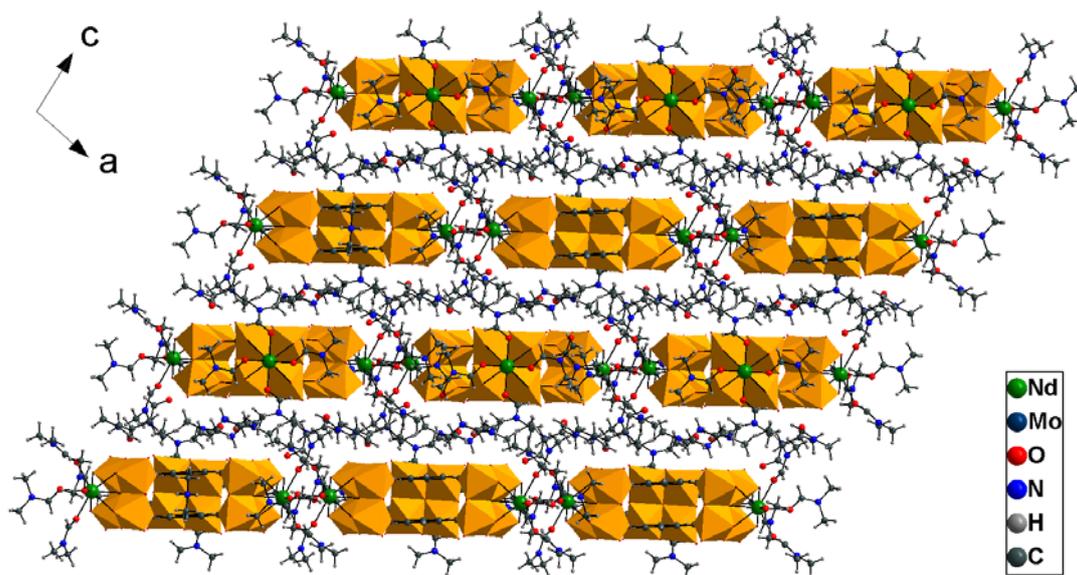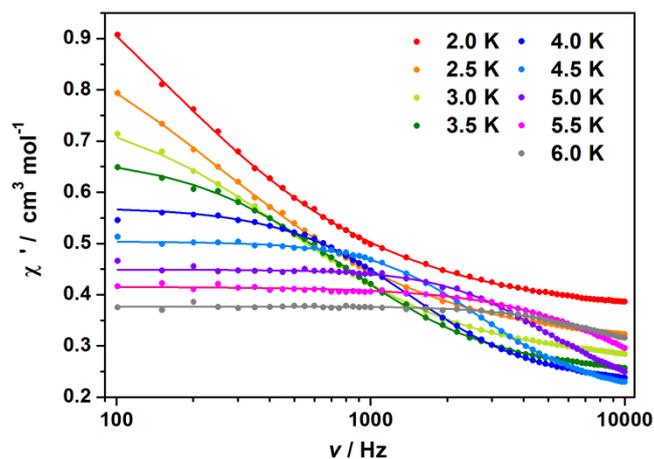

Fig. S3 The 3D packing view of **1** along the *b* axis. Nd (green), MoO$_6$ octahedral (orange), O (red), C (gray), N (blue), H (light gray).
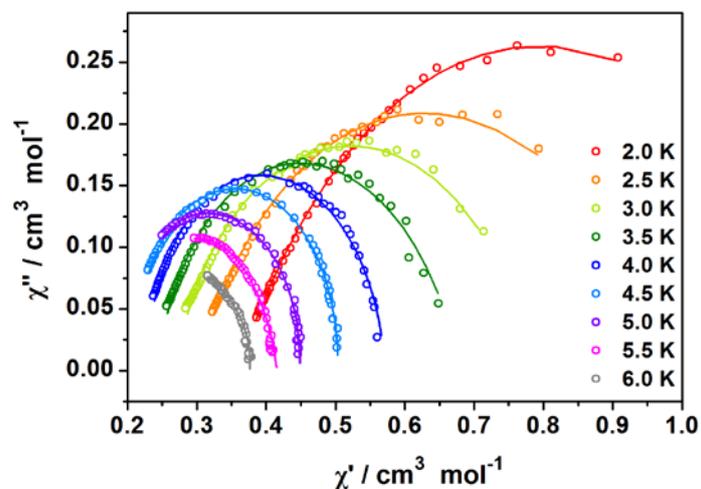
6. Magnetic data

Fig. S4 Temperature dependence of in-phase ac susceptibility at different ac frequency under a 500 Oe dc field for **1**(the solid lines are for eye guide).


Fig. S5 Frequency dependence of the in-phase ac susceptibility from 2.0 to 6.0 K under a 500 Oe dc field for **1** (the solid lines are the best fitting of experimental data the generalized Debye model).

Fig. S6 Cole−Cole plots at different temperatures (3.0 − 5.0 K) for **1** (the solid lines are the best fitting of experimental data to a generalized Debye model).
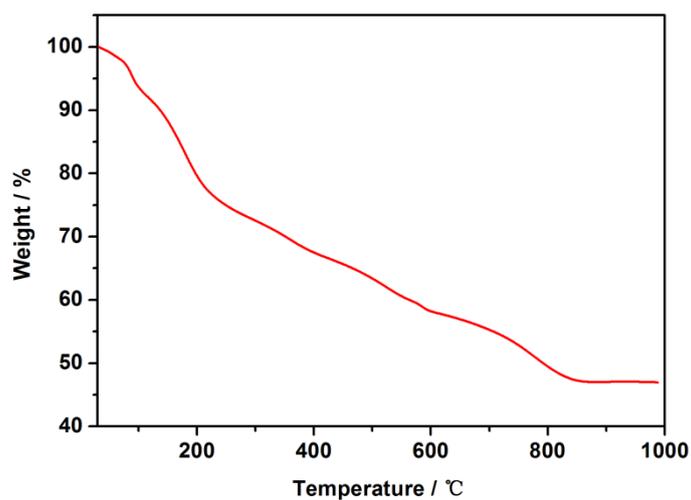
Table S3 Selected parameters obtained by fitting out-of-phase ac magnetic susceptibility (χ'') *vs* frequency (ν) plots of **1** using Debye model.

T/K	τ/ms	α
4.0	0.1075	0.07
4.5	0.0583	0.03
5.0	0.0297	0.04
5.5	0.0168	0.05
6.0	0.0125	0.04
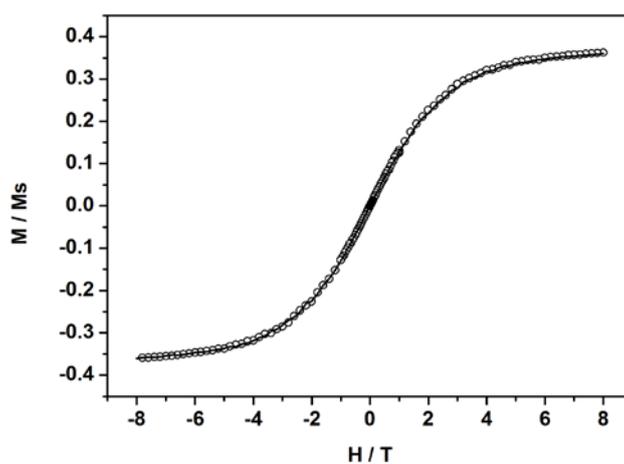
Fig. S7 Magnetization measurements *vs* applied field plot for **1** at 2.0 K.

7. Thermogravimetric analyses

Fig. S8 The TGA curve of complex **1**.
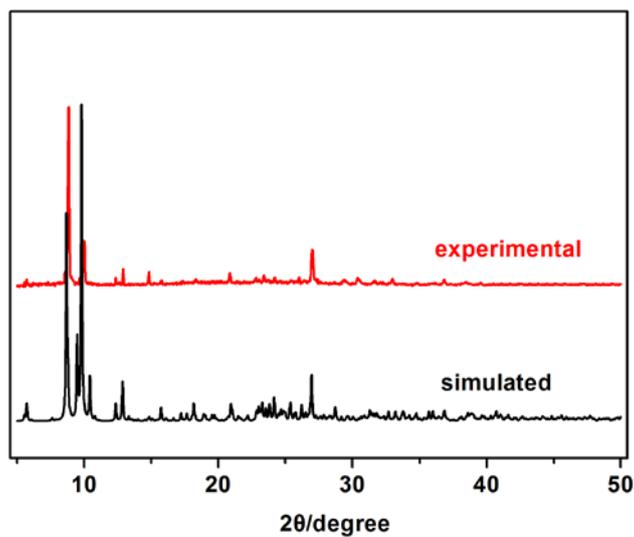
8. X-ray Powder Diffraction

Fig. S9 A comparison of PXRD patterns between the as-synthesized bulk material of **1** and the simulated one from the single crystal diffraction data of **1**.
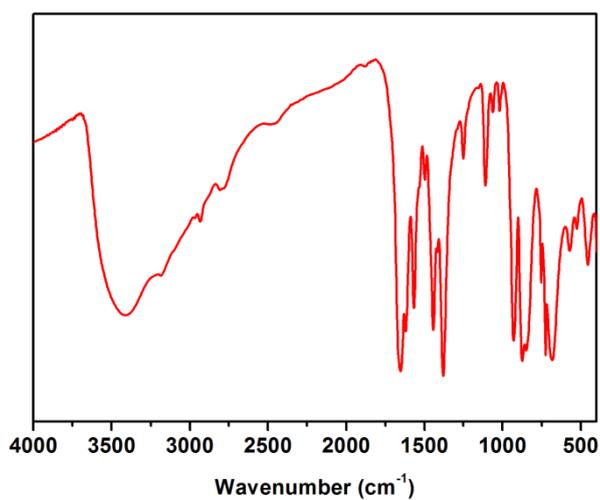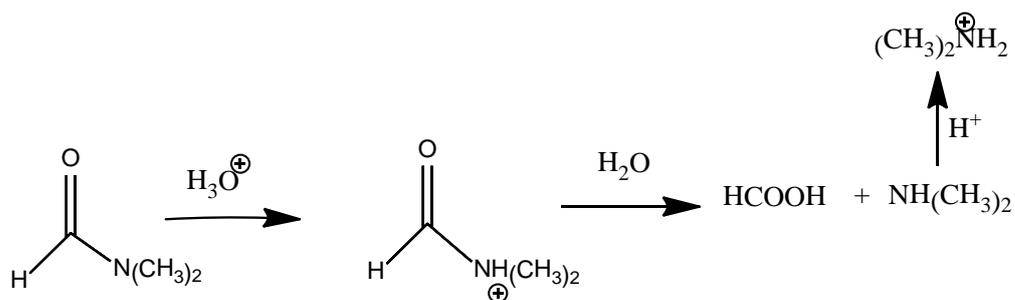
9. IR spectrum

Fig. S10 The IR spectrum of **compound 1**.

10. Hydrolysis mechanism of DMF and the formation of dimethylamine cations

H$_2$O sources: Nd(NO$_3$)$_3$·6H$_2$O and impurity of DMF and EtOH (there are always a very little amount of water in DMF and EtOH)

H$^+$ sources: H$_3$BTC

11. References

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S3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. J. Puschmann, *Appl. Cryst.*, 2009,**42**, 339.

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