

Supporting Information for:

A new breakthrough in low-coordinate Dy(III) single-molecule magnet

Zhenhua Zhu,^{a, b} Xu Ying,^{a, c} Chen Zhao,^{a, c} Yi-Quan Zhang,^{*, d} and Jinkui Tang^{*, a}

^a State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China

^b University of Chinese Academy of Sciences, Beijing 100049, P. R. China

^c University of Science and Technology of China, Hefei 230026, P. R. China

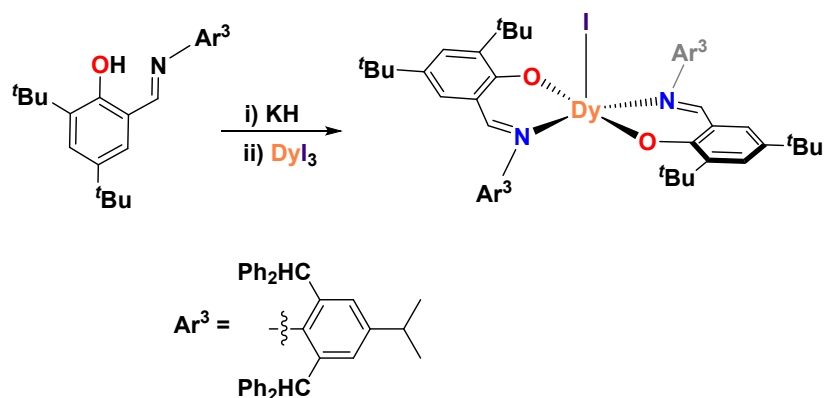
^d Jiangsu Key Laboratory for NSLSCS, School of Physical Science and Technology, Nanjing Normal University, Nanjing 210023, P. R. China

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Experimental details:

General procedures: All synthetic experiments were performed in the standard Schlenk line and a Mikrouna glovebox under an atmosphere of purified Ar (99.999%) with rigorous exclusion of air and moisture (< 0.1 ppm O₂/H₂O). All solvents were dried and degassed before use in the standard Schlenk line and stored over activated 4 Å molecular sieves in the glovebox. The ligand HL and anhydrous DyI₃ were synthesized according to the literature procedures.^{1,2} Chemicals were purchased from Aldrich, Alfa Aesar and used without further purification.



Scheme S1 Synthetic protocol toward **5-Dy-I**.

Synthesis of 5-Dy-I

A solution of 1 equiv KH/KO^tBu in THF (5 ml) was added dropwise to a solution of HL (0.4 g) in THF (10 ml) at -60 °C. The mixture was warmed to room temperature then transferred into the glovebox and stirred for 1 h. Then, a suspension of DyI₃ (0.16 g) in THF (10 ml) was added dropwise to the solution at room temperature. A white precipitate was gradually produced after stirring 12 h. The mixture was filtered giving a yellow solution. All volatile components were removed *in vacuo* and the residue was extracted with toluene (8ml), which was allowed to stand undisturbed at room temperature for several days to yield light yellow rod crystals. Washing the crystals with cold hexane afford crystalline **5-Dy-I** in a reproducible yield (67%).

X-ray crystallography

Single crystals of **5-Dy-I** were grown from a concentrated toluene solution at room temperature for slow evaporation. X-ray diffraction data were collected on a Bruker Apex II CCD diffractometer equipped with an Oxford low temperature apparatus using MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). Structures were solved in Olex2 with SHELXT using intrinsic phasing and were refined with SHELXL using least squares minimization.³⁻⁵ All hydrogen atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms. The crystal data have been deposited at the Cambridge Structural Database (CCDC-2071880), which can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal data and structure refinement for **5-Dy-I**.

	5-Dy-I
CCDC ref. code	2071880
empirical formula	C ₁₀₀ H ₁₀₄ DyIN ₂ O ₂ ·2(C ₇ H ₈)
formula weight	1839.51
crystal system	Monoclinic
space group	<i>P2(1)/n</i>
<i>a</i> (Å)	17.7162(4)
<i>b</i> (Å)	25.8219(5)
<i>c</i> (Å)	20.9529(5)
β (°)	90.00
α (°)	92.1670(10)
γ (°)	90.00
<i>V</i> (Å ³)	9578.4(4)
<i>Z</i>	4
<i>T</i> (K)	180(2)
ρ_{calc} (g/cm ³)	1.276
<i>F</i> (000)	3812
Reflections collected	101844
Independent reflections	16900
R_{int}^{\dagger}	0.0891
GOF on F^2	1.033
R_1^a	0.0441
R_w^b	0.0852

Table S2. The continuous shape measure values of the first coordination sphere of **5-Dy-I**.

SHAPE	Pentagon	Vacant octahedron	Trigonal bipyramid	Spherical square pyramid	Johnson trigonal bipyramid
Symmetry	D_{5h}	C_{4v}	D_{3h}	C_{4v}	D_{3h}
5-Dy-I	34.042	9.360	3.112	4.840	9.235

Table S3. Important bonding distances for **5-Dy-I**.

Compound	Dy-N1/Å	Dy-N2/Å	Dy-O1/Å	Dy-O2/Å	Dy-I1/Å
5-Dy-I	2.420(3)	2.410(4)	2.126(3)	2.129(3)	2.9376(4)

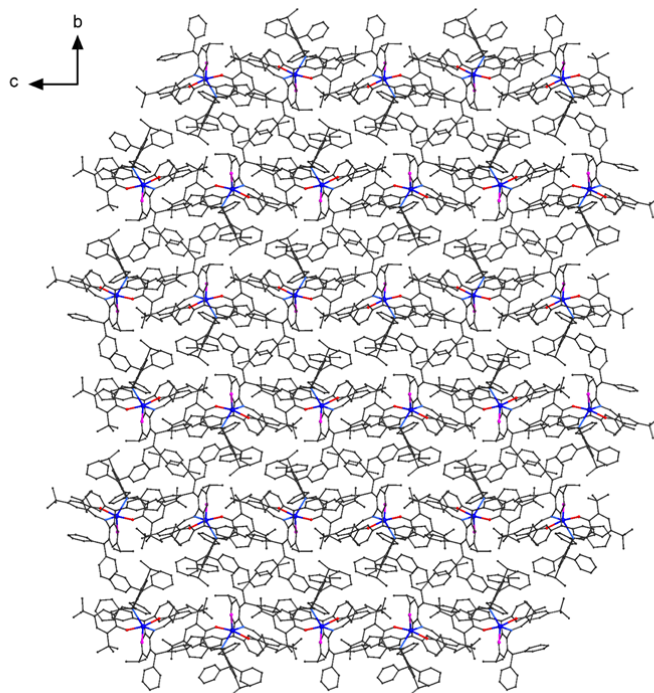


Fig. S1 The packing diagram for **5-Dy-I** shown along the crystallographic *a* axis gives the shortest intermolecular Dy...Dy distance of 13.4697(6) Å.

Magnetic measurements

The magnetic characteristics were explored using a Quantum Design MPMS XL-7 SQUID magnetometer equipped with a 7 T magnet. Dc magnetic susceptibility measurements were performed in the temperature range 1.9-300 K under a 1000 Oe dc field. Ac magnetic susceptibility measurements were measured under a zero dc field using an oscillating field of 3 Oe. The magnetic hysteresis measurements were performed using field sweep rate of 200 Oe/s. The samples were restrained in eicosane and sealed in borosilicate NMR tubes. The experimental magnetic data are corrected for the diamagnetism estimated from Pascal's constants and sample holder calibration.⁶

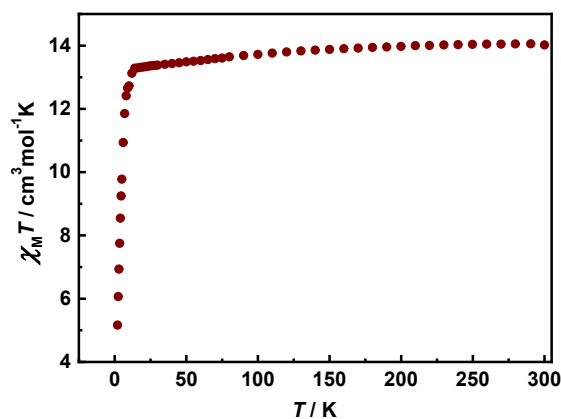


Fig. S2 Temperature dependence of $\chi_m T$ values for **5-Dy-I**.

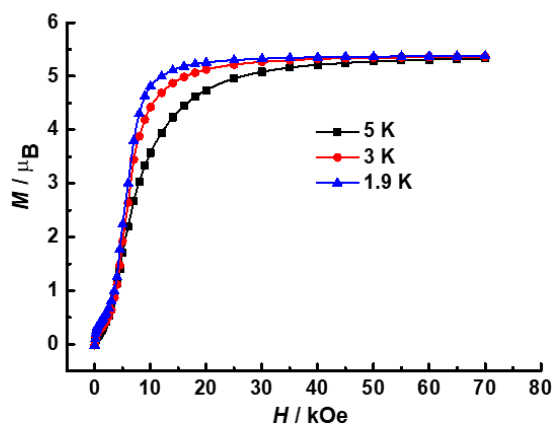


Fig. S3 Molar magnetization (M) vs. field (H) for **5-Dy-I** at the temperature of 5 K, 3 K and 1.9 K.

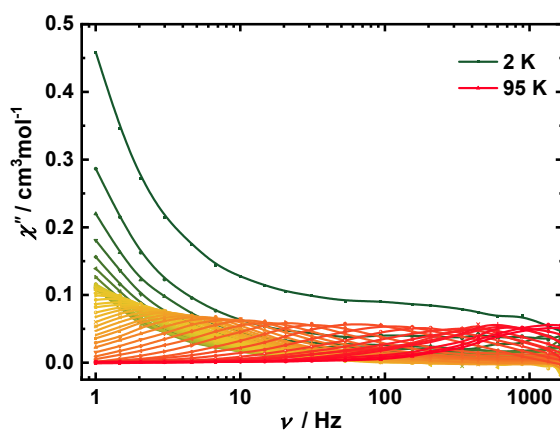


Fig. S4 Plots of $\chi''(\nu)$ for **5-Dy-I** in zero dc field in the temperature of 2-95 K.

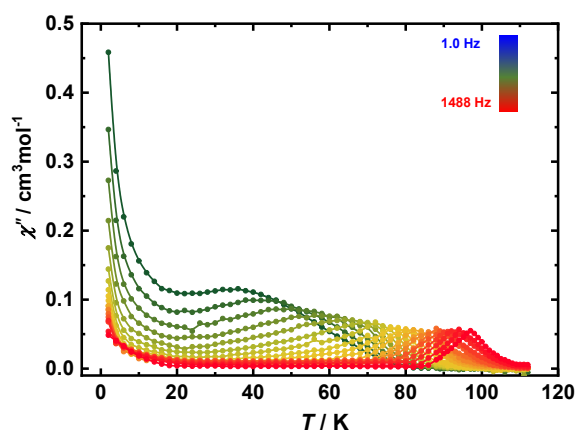


Fig. S5 Plots of $\chi''(T)$ for **5-Dy-I** in zero dc field in the frequency of 1.0-1488 Hz.

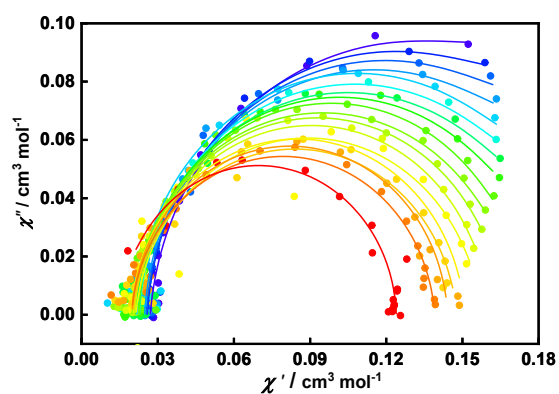


Fig. S6 Core-core plots of χ'' vs. χ' in the temperature of 48-90 K.

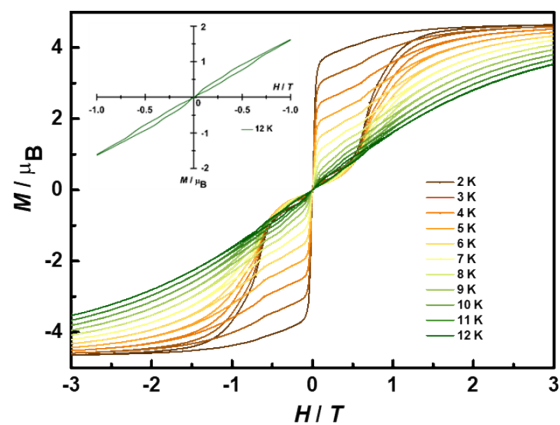


Fig. S7 Magnetic hysteresis of **5-Dy-I**, measured with a mean field sweep rate of 11.5 Oe/s for $|H| < 0.5$ T, 27.6 Oe/s for 0.5 T $< |H| < 1.0$ T, 43.9 Oe/s for 1.0 T $< |H| < 2.0$ T, 62.8 Oe/s for 2.0 T $< |H| < 3.0$ T. Inset: Amplified hysteresis loop at 12 K.

Quantum chemical calculations

Complete-active-space self-consistent field (CASSCF) calculations on individual Dy^{III} fragment on the basis of X-ray structures of **5-Dy-I** have been carried out with MOLCAS 8.2 program package.⁷⁻⁹ Basis sets employed here are from the MOLCAS ANO-RCC library with ANO-RCC-VTZP for Dy^{III} ion, VTZ for close O and N and VDZ for distant atoms. The calculations employed the second order Douglas-Kroll-Hess Hamiltonian, where scalar relativistic contractions were taken into account in the basis set and the spin-orbit couplings were handled separately in the restricted active space state interaction (RASSI-SO) procedure. For the fragment of individual Dy^{III} ion, active electrons in 7 active orbitals include all *f* electrons (CAS(9 in 7)) in the CASSCF calculation. To exclude all the doubts, we calculated all the roots in the active space. We have mixed the maximum number of spin-free state which was possible with our hardware (all from 21 sextets, 128 from 224 quadruplets, 130 from 490 doublets). SINGLE_ANISO program was used to obtain energy levels, *g* tensors, *m_J* values, magnetic axes, *et al.*, based on the above CASSCF/RASSI-SO calculations.¹⁰⁻¹²

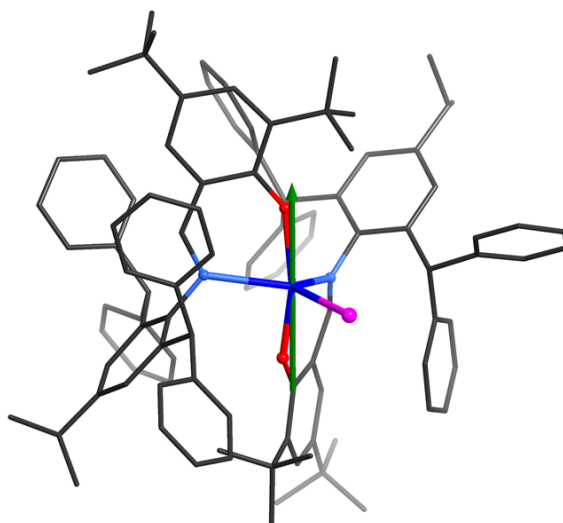


Fig. S8 Orientation of the principal magnetic axis of the ground KD for **5-Dy-I**.

Table S4. Ab initio results for the $J = 15/2$ multiplet of Dy(III) in **5-Dy-I**.

KDs	E/cm^{-1}	g	m_j	g_{zz} Angle/ $^\circ$	Wavefunctions
1	0.0	0.000 0.000 19.843	$\pm 15/2$	–	99.90% $ \pm 15/2\rangle$
2	402.6	0.005 0.006 17.069	$\pm 13/2$	7.3	97.90% $ \pm 13/2\rangle$
3	771.3	0.076 0.084 14.317	$\pm 11/2$	12.4	88.10% $ \pm 11/2\rangle + 9.60\% \pm 9/2\rangle$
4	1035.1	0.214 0.263 12.496	$\pm 9/2$	32.2	56.20% $ \pm 9/2\rangle + 31.30\% \pm 7/2\rangle + 6.20\% \pm 11/2\rangle$
5	1117.0	0.634 1.853 15.643	$\pm 5/2$	75.7	37.10% $ \pm 1/2\rangle + 29.70\% \pm 3/2\rangle + 23.70\% \pm 5/2\rangle + 7.10\% \pm 9/2\rangle$
6	1184.3	1.258 3.920 9.940	$\pm 3/2$	72.8	35.40% $ \pm 1/2\rangle + 29.10\% \pm 5/2\rangle + 13.00\% \pm 7/2\rangle + 12.00\% \pm 3/2\rangle + 9.20\% \pm 9/2\rangle$
7	1240.3	2.478 4.304 14.067	$\pm 1/2$	91.2	50.20% $ \pm 3/2\rangle + 26.50\% \pm 1/2\rangle + 10.90\% \pm 7/2\rangle + 6.30\% \pm 9/2\rangle$
8	1356.7	0.173 0.795 17.893	$\pm 7/2$	63.2	42.30% $ \pm 7/2\rangle + 38.00\% \pm 5/2\rangle + 11.70\% \pm 9/2\rangle$

Table S5. Calculated crystal-field parameters $B(k,q)$ for 5-Dy-I.

k	q	5-Dy-I
	-2	0.4141
	-1	0.1694×10^1
2	0	-0.7250×10^1
	1	-0.4647×10^1
	2	0.4120
	-4	-0.5951×10^{-2}
	-3	0.2943×10^{-2}
	-2	-0.4604×10^{-2}
	-1	-0.9978×10^{-2}
4	0	-0.1049×10^{-1}
	1	0.2260×10^{-1}
	2	0.5525×10^{-2}
	3	0.2720×10^{-2}
	4	0.3201×10^{-3}
	-6	0.1500×10^{-3}
	-5	0.3825×10^{-3}
	-4	-0.7253×10^{-4}
	-3	-0.5072×10^{-4}
	-2	0.9808×10^{-4}
	-1	-0.3727×10^{-4}
6	0	0.5129×10^{-4}
	1	0.1407×10^{-3}
	2	-0.9651×10^{-4}
	3	0.2792×10^{-4}
	4	-0.2954×10^{-5}
	5	0.2896×10^{-4}
	6	0.6690×10^{-4}

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