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SUPPORTING INFORMATION

Synthesis, structure, magnetic and luminescent properties of two dysprosium single-molecule magnets based on phenoxide dye ligands.

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Experimental Section

General Procedure. All operations were carried out in atmosphere of argon using Schlenk techniques or in a nitrogen filled glovebox. After drying over KOH, THF was purified by distillation from sodium/benzophenone ketyl. Hexane, C_6D_6 and toluene were dried over Na/K alloy, transferred under vacuum, and stored in the glovebox. Pyridine was dried over CaH_2 and was degassed by freeze-pump-thaw metods, then condensed in a vacuum prior to use. 1-(2,4-dimetylphenylazo)-2-naphthol (orange dye Sudan-II) and anthrone were purchased from Aldrich and were used after recrystallization from hot acetone. KH was purchased from Aldrich and was used without further purification. $DyCl_3$[1] and $Dy[N(SiMe_3)_2]_3$[2] were synthesized according to the previously published procedures. Lanthanide metal analysis was carried out by complexometric titration.[3] IR spectra were recorded as Nujol mulls on a Bruker-Vertex 70 spectrophotometer. Elemental analysis was performed in the microanalytical laboratory of IOMC.

Synthesis of 1. $Dy[N(SiMe_3)_2]_3$ (0.400 g, 0.60 mmol) was dissolved in toluene (10 mL) and sudan-II (0.500 g, 1.80 mmol) was added gradually. The saturated red solution was heated at 60 ^{o}C within 1 h, and gradually the red colour changed to orange. Cooling the solution to room temperature and its subsequent concentration afforded **1** in 90% yield (0.53 g). Elemental analysis calcd. (%) for $C_{122}H_{102}Dy_2N_{12}O_6$ (2157.24 g/mol^{-1}): C, 67.93; H, 4.77; N, 7.79; Dy, 15.07; found C, 67.65; H, 4.56; N, 7.81; Dy, 15.00. IR (Nujol, KBr) ν/cm^{-1}: 1616 (m), 1595 (m), 1553 (s), 1302 (m), 1264 (m), 1210 (m), 1172 (m), 1147 (s), 1097 (s), 1029 (s), 982 (s), 865 (m), 811 (s), 752 (s), 639 (m), 597 (w), 574 (w), 536 (m), 519 (m).

Synthesis of 2. KH (0.150 g, 3.80 mmol) was added to a solution of anthrone (0.500 g, 2.60 mmol) in THF (10 mL) under vigorous stirring. After the completion of hydrogen evolution, the orange luminescent solution was stirred for another 2 h at room temperature. The solution was filtered from the excess of KH and slowly added to the suspension of $DyCl_3$ (0.232 g, 0.86 mmol) in THF (10 mL). The colour of the solution instantly changed to yellow and an insoluble yellow precipitate formed. THF was removed in vacuum, the solid residue was dissolved in pyridine and centrifuged from the precipitate of KCl. Complex **2** was isolated as yellow crystals by slow diffusion of hexane into the pyridine solution of the complex in 65% yield (0.54 g). Elemental analysis calcd. (%) for $C_{57}H_{42}DyN_3O_3$ (979.43 g/mol^{-1}): C, 70.11; H, 4.03; N, 4.30, Dy, 16.64; found (%): C, 69.80; H, 3.82; N, 4.01; Dy, 16.59. IR (Nujol, KBr) ν/cm^{-1}: 1659 (s), 1600 (s), 1400 (w), 1346 (w), 1309 (s), 1217 (w), 1170 (w), 1151 (w), 1118 (w), 1090 (w), 1036 (w), 1006 (w), 959 (m), 933 (s), 862 (w), 811 (m), 663 (m), 628 (m), 574 (w).

X-Ray crystallography.
X-ray diffraction data for all studied complexes were collected on a SMART APEX II area-detector diffractometer (graphite monochromator, ω-scan technique), using MoKα-radiation (0.71073Å). The intensity data were integrated by the SAINT program[1] and were corrected for absorption and decay using SADABS[4] for the other complexes. All structures were solved by direct methods using SHELXS,[5] and were refined on F^2_{hkl} using SHELXL-2014/2017.[5-6]All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal calculated positions (C-H distance = 0.95 Å for aromatic hydrogen atoms) and refined as riding atoms with relative isotropic displacement parameters taken as Uiso(H)=1.2Ueq(C). The SHELXTL program suite[7] was used for molecular graphics. Crystal data, data collection and structure refinement details are summarized in Table S1.

CCDC 1972626-1972627 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Magnetic Measurements.

Magnetic susceptibility data were collected with a Quantum Design SQUID MPMS-XL magnetometer working in the range 1.8–350 K with the magnetic field up to 7 Tesla. The samples were prepared in a glove box. The data were corrected for the sample holder and the diamagnetic contributions calculated from the Pascal's constants. The ac magnetic susceptibility measurements were carried out in the presence of a 3 Oe oscillating field in zero or applied external dc field.

Photoluminescence measurements

The solid samples were sealed in a quartz tube in an argon atmosphere (glove box). The emission and excitation spectra were recorded at 77 K and 295 K using a spectrofluorimeter Edinburgh FLS-920. The excitation source was a 450 W Xe arc lamp. The emission spectra were corrected for detection and optical spectral response of the spectrofluorimeter.

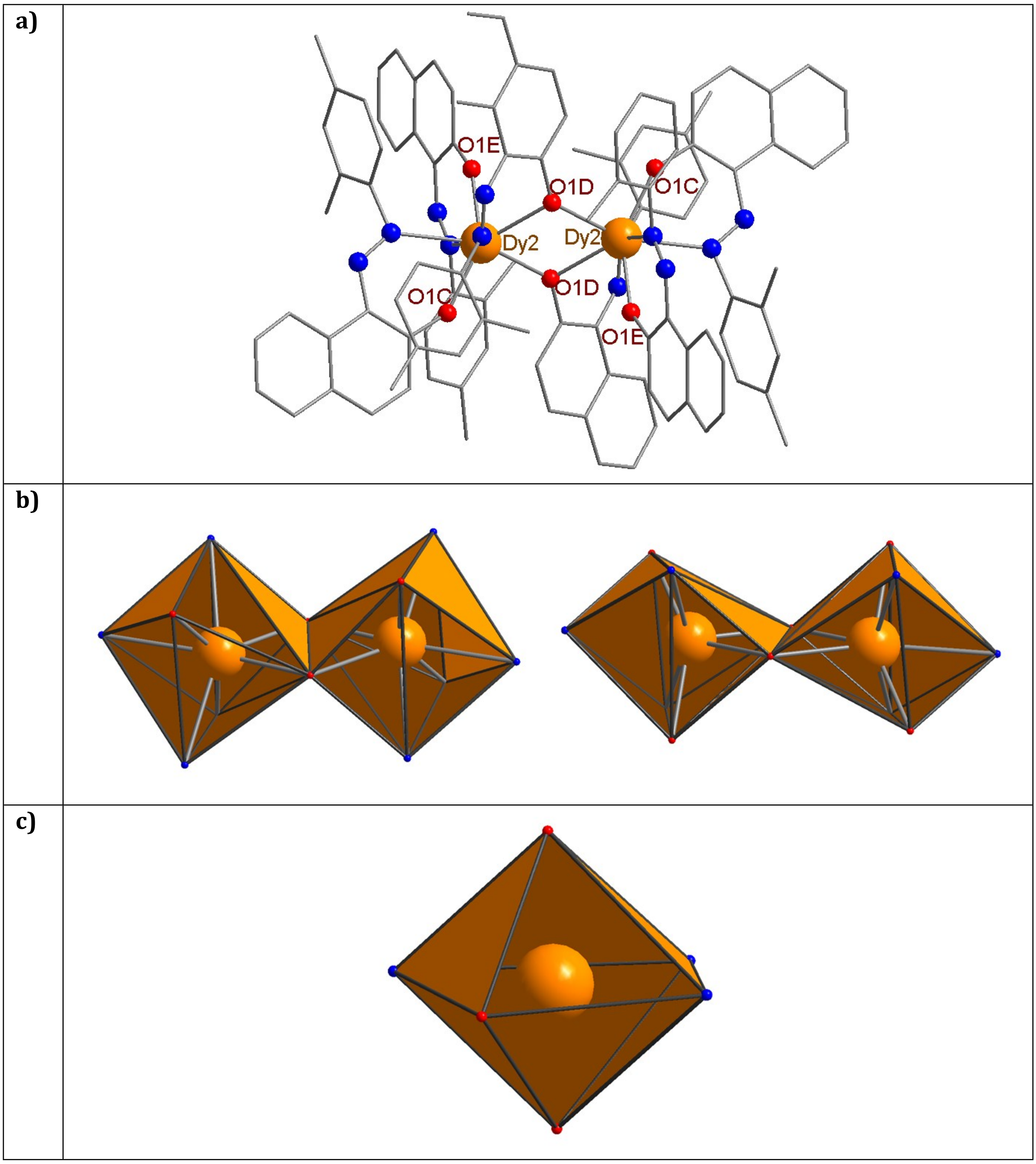

Figure S1: a) Molecular structure of one of the two crystallographically independent dinuclear complexes **1**. Colour code: orange, Dy; blue, N; grey, C; Hydrogen atoms have been omitted for clarity. b) Coordination polyhedrons of the Dy^{3+} ions in the two crystallographically independent complexes in **1**. c) Coordination polyhedral of the Dy^{3+} ion in **2**.

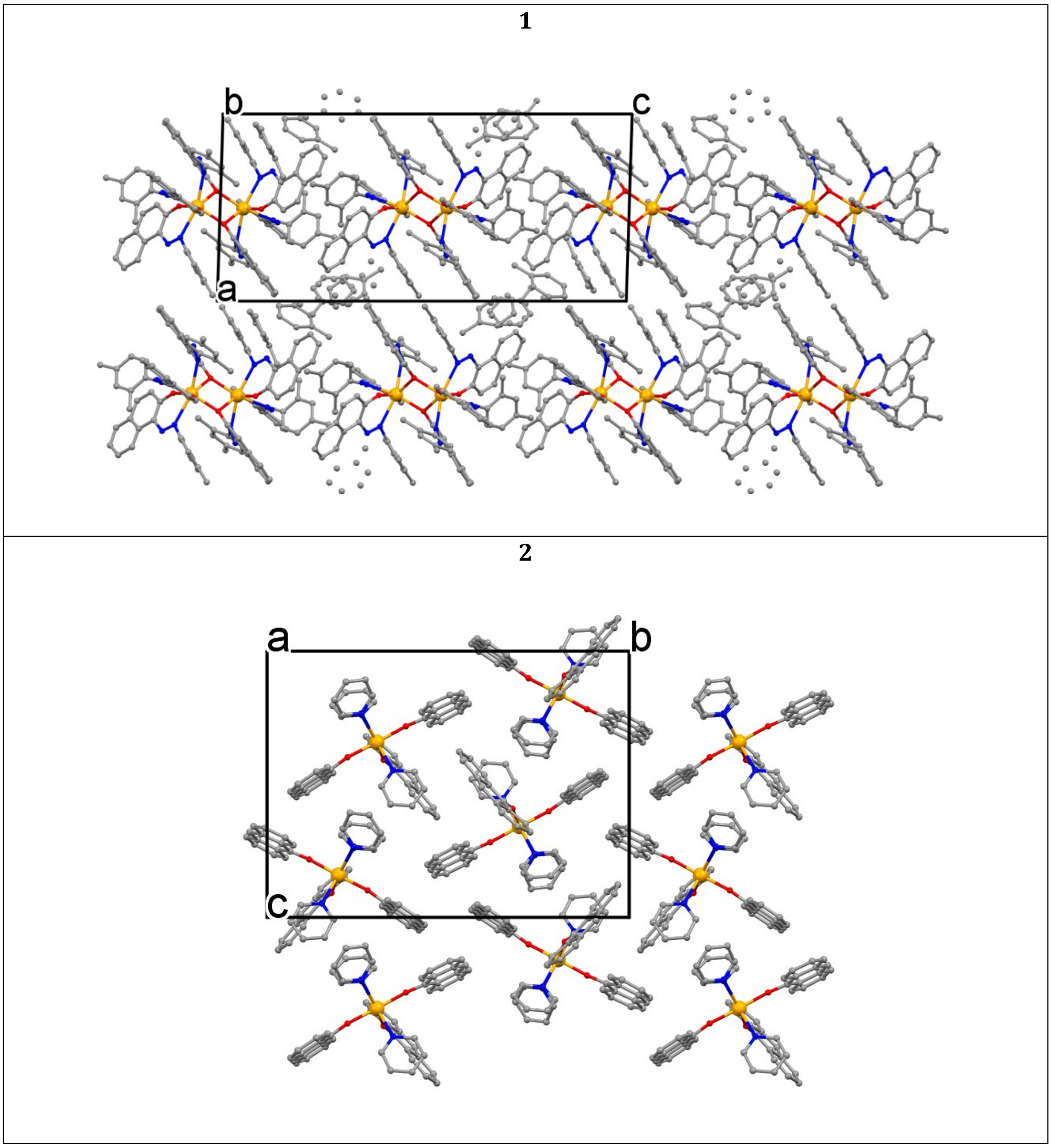

Figure S2: Perspective view of the crystal packing for **1** and **2** along the *b* and *c* crystallographic axes. Hydrogen atoms have been omitted for clarity.

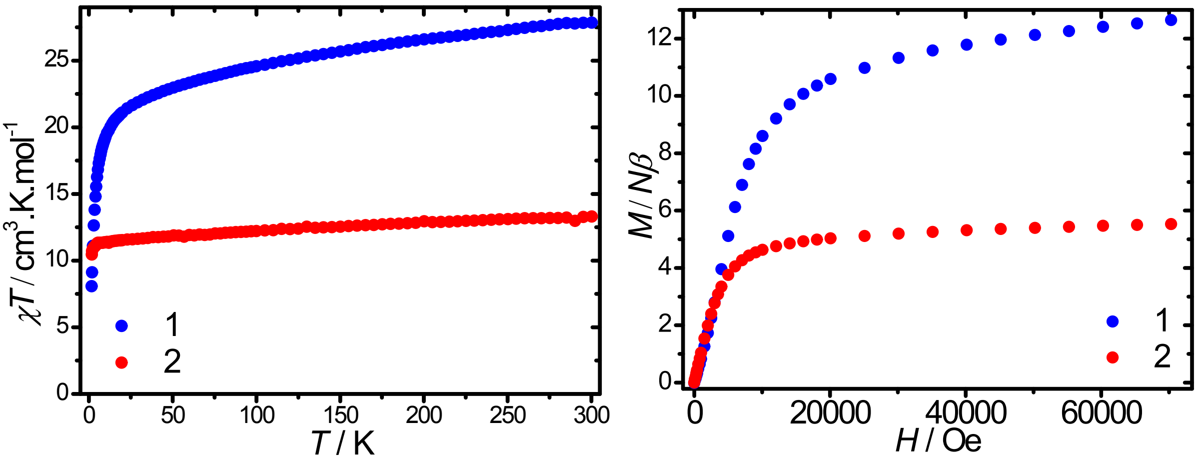

Figure S3: Left: temperature dependence of χT under an applied magnetic field of 1000 Oe for **1** and **2**. Right: field dependence of the magnetization at 1.8 K for **1** and **2**.

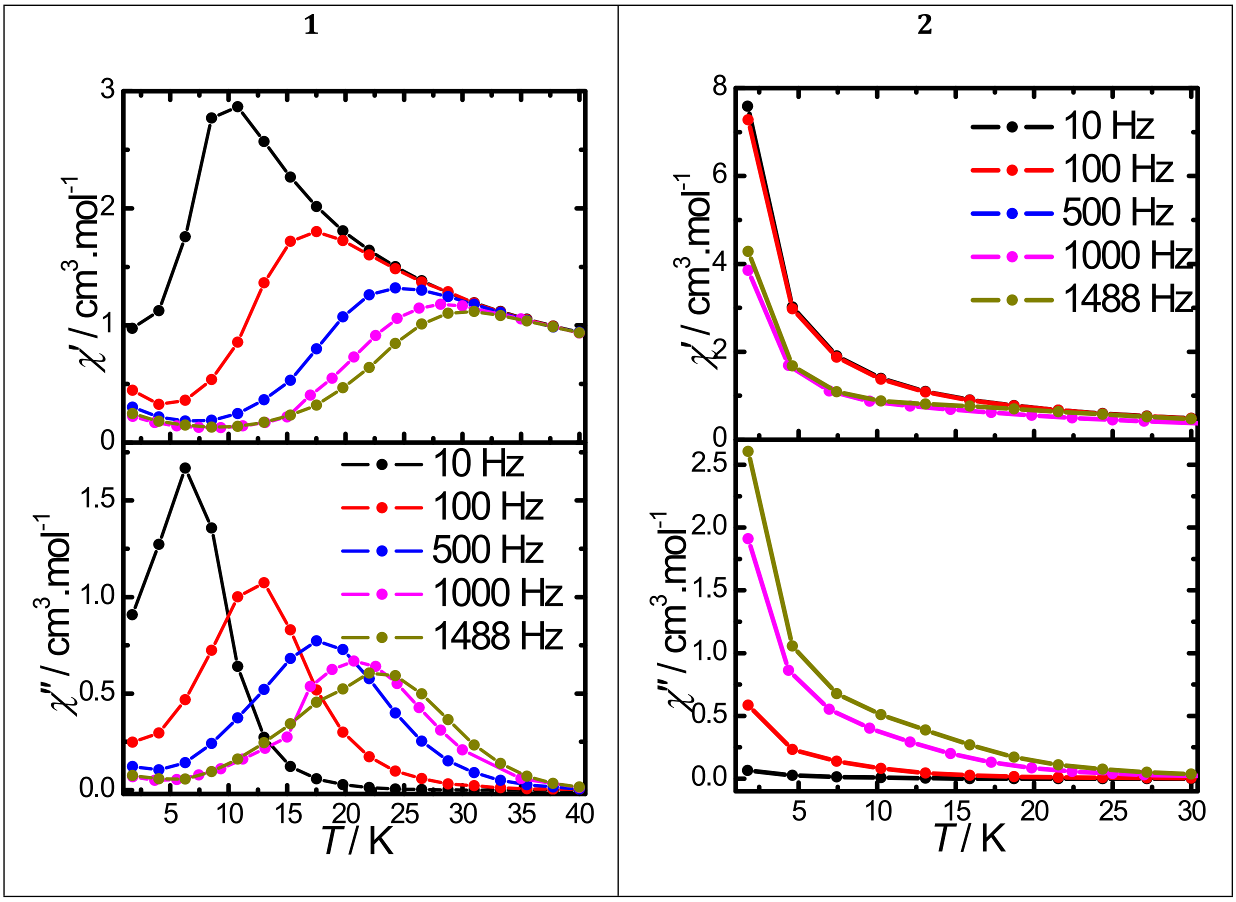

Figure S4. Temperature dependence of χ' and χ'' for **1** and **2** for different frequencies under a zero-dc field.

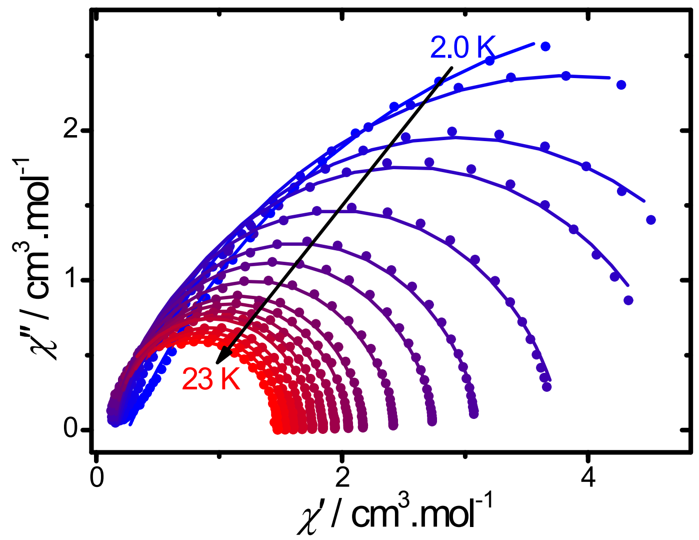

Figure S5: Cole-Cole (Argand) plots obtained using the ac susceptibility data for **1** (0 Oe). The solid lines correspond to the best fit obtained with a generalized Debye model.

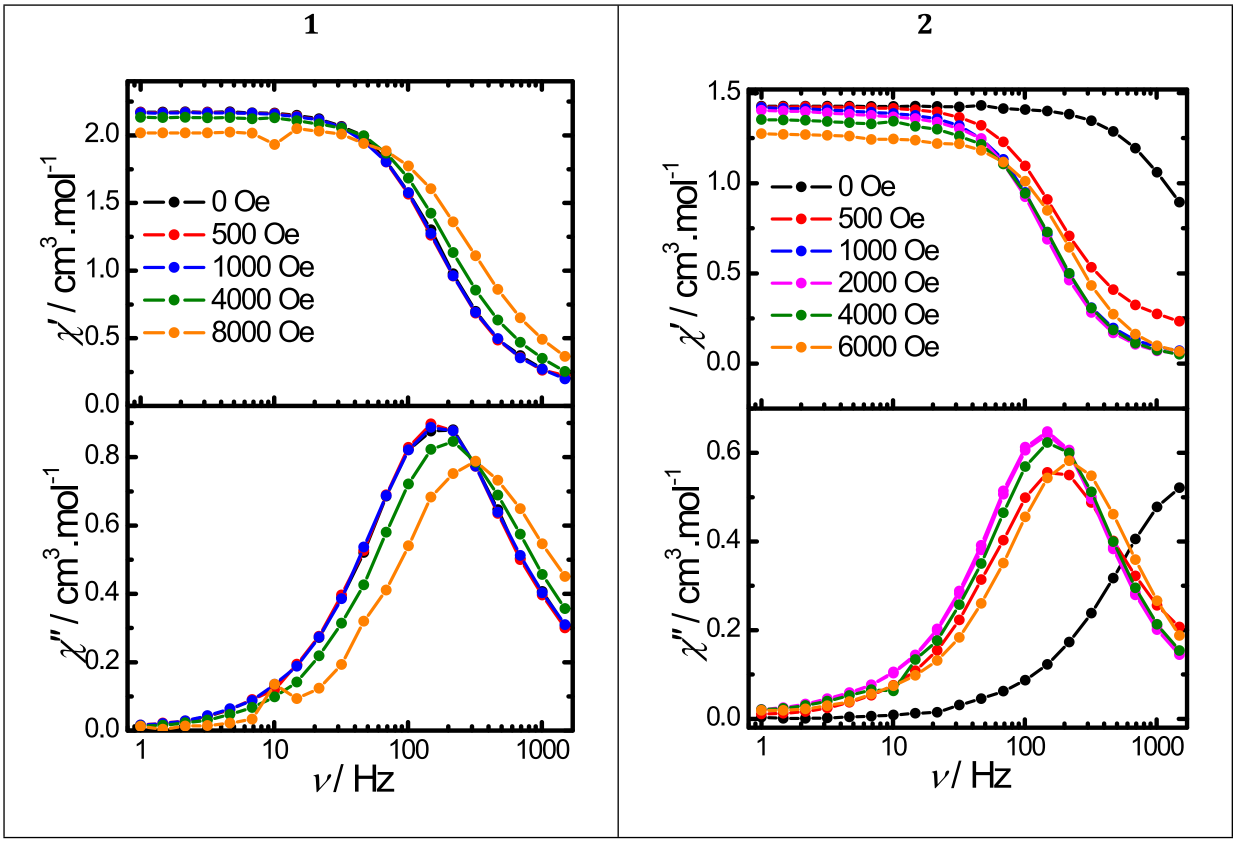

Figure S6. Frequency dependence of χ' and χ'' for **1** (15 K) and **2** (10 K) under various dc fields.

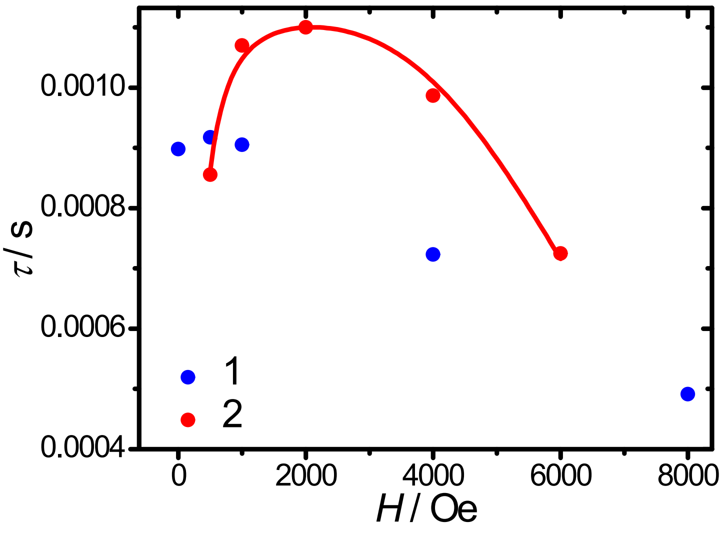

Figure S7. Field dependence of the relaxation time for **1** (15 K) and **2** (10 K). The solid line corresponds to the fit with Eq. 2.

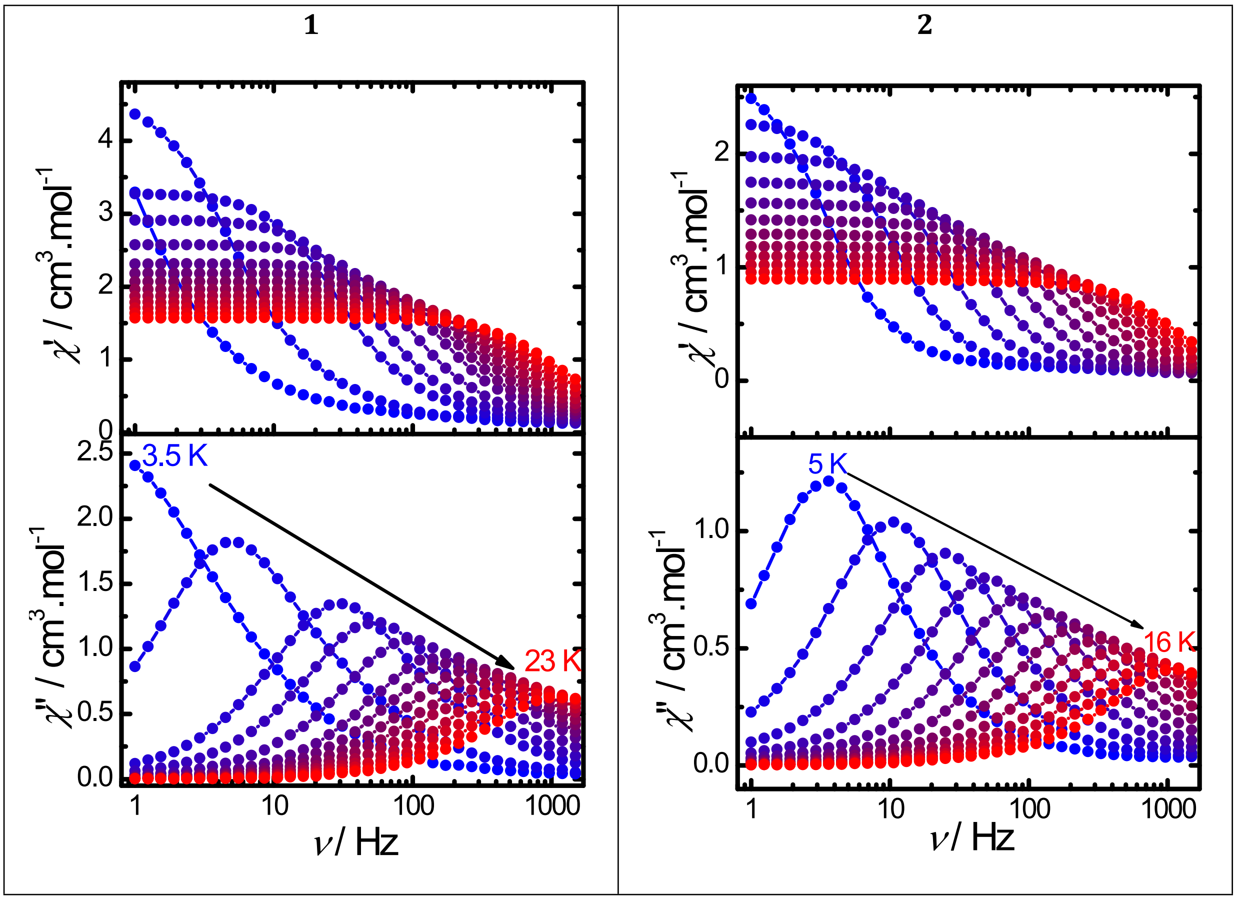

Figure S8. Frequency dependences of χ' and χ'' for **1** (under 500 Oe) and **2** (under 1000 Oe).

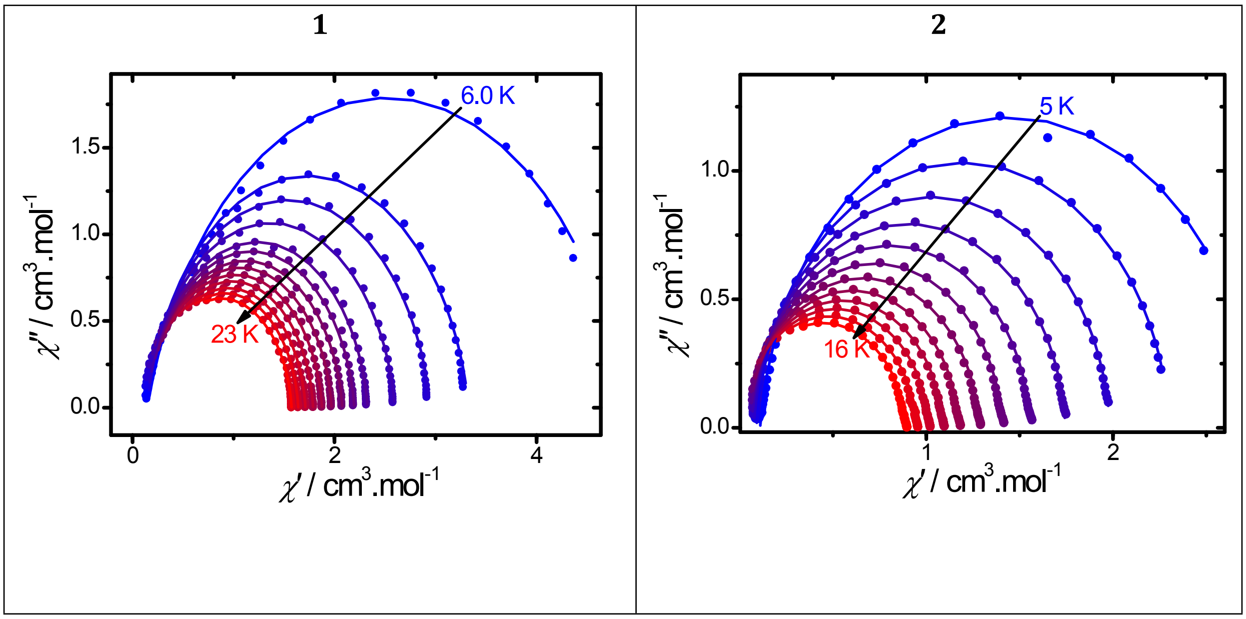

Figure S9: Cole-Cole (Argand) plot obtained using the ac susceptibility data for **1** (under 500 Oe) and **2** (under 1000 oOe). The solid lines correspond to the best fit obtained with a generalized Debye model.

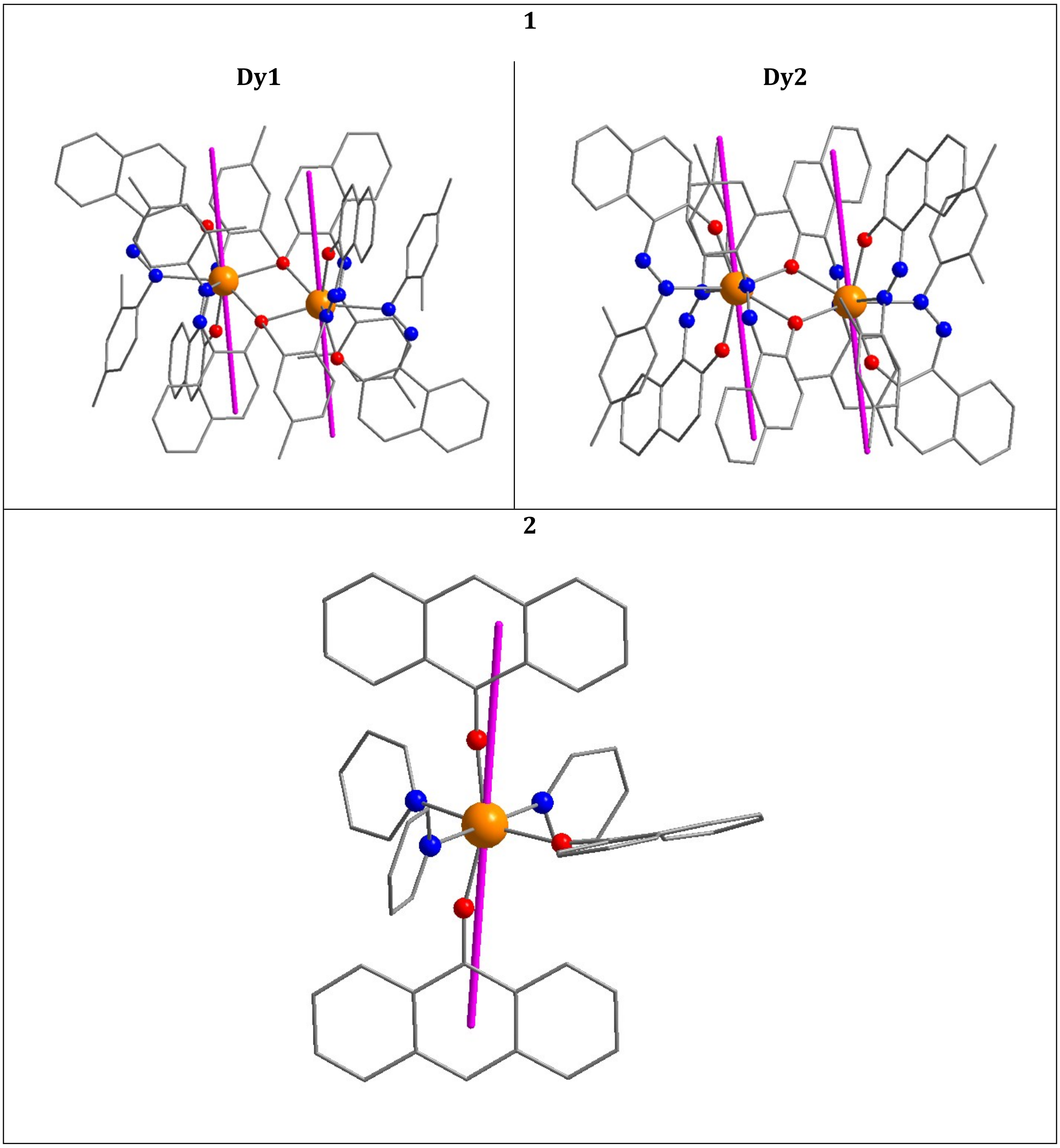

Figure S10: Anisotropic axes (purple) obtained from the MAGELLAN package.[8]

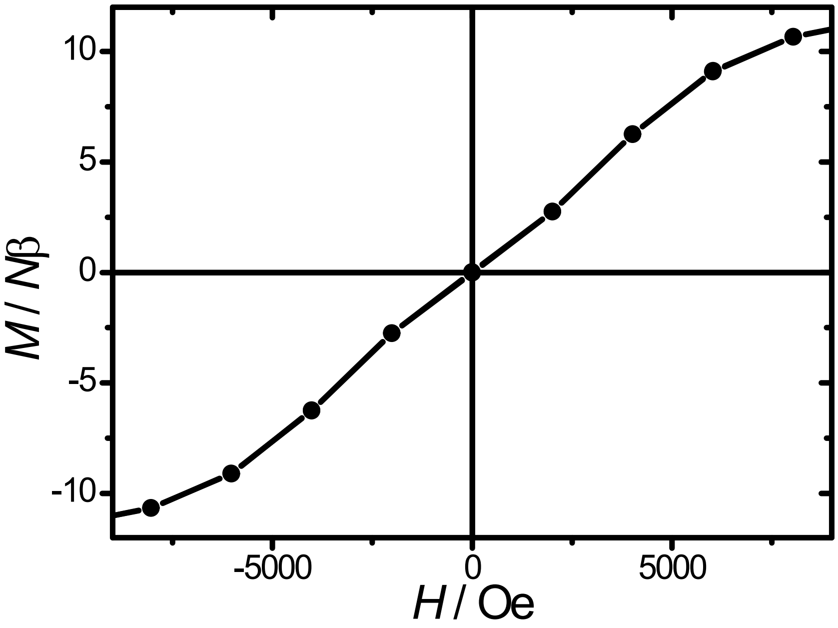

Figure S11: Hysteresis loop at 1.8 K for **1** obtained with a mean 35 Oe.s^{-1} sweep rate.

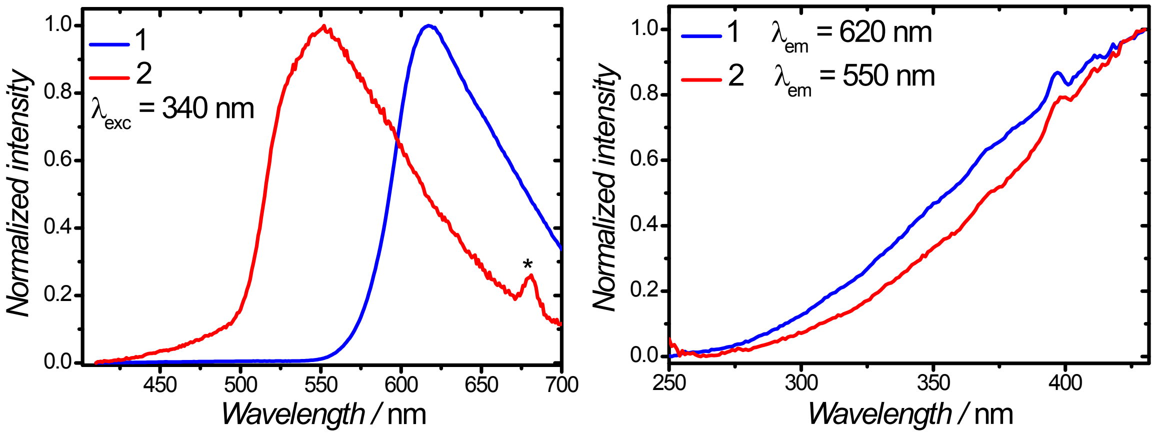

Figure S12: Left: Emission spectra for complexes **1** and **2** excited at 340 nm. The * symbol corresponds to the excitation of second order. Right: Excitation spectra for **1** and **2**.

Table S1. The crystal data and structures refinement details for complexes **1**–**2.**

	1	**2**
Formula	$C_{132.50}H_{118}Dy_2N_{12}O_6$	$C_{57}H_{42}DyN_3O_3$
MW	2299.38	979.43
T, K	120	120
Crystal system	Triclinic	Monoclinic
Space group	P-1	$P2_1/c$
Z (Z')	2(2*0.5)	4(1)
a, Å	13.328(3)	11.3117(6)
b, Å	14.307(3)	23.0212(12)
c, Å	29.016(6)	17.7515(10)
α, °	90.480(5)	90
β, °	91.743(5)	107.3737(14)
γ, °	94.143(5)	90
V, Å^3	5515.7(19)	4411.8(4)
$d_{выч}$, g·cm^{-3}	1.384	1.475
μ, cm^{-1}	14.08	17.44
F(000)	2354	1980
$2\theta_{max}$, °	55	58
Number of measured refl. (Rint)	59999 (0.1170)	41712 (0.1005)
Number of independent refl.	25321	11729
Observed refl. with $I>2\sigma(I)$	11562	7758
Parameters	1355	577
R1	0.0741	0.0464
wR2	0.2079	0.1032
GOF	0.943	0.978
Residual density, e·Å^{-3}(d_{min}/d_{max})	2.389/ -2.370	0.758 /-1.255

Table S2. SHAPE analysis for compounds **1-2**.

	HP	**HPY**	**PBPY**	**COC**	**CTPR**	**JPBPY**	**JETPY**
Dy1 (1)	31.408	18.413	8.514	1.610	3.008	9.781	17.430
Dy2 (1)	31.711	18.092	8.612	1.663	2.872	10.038	17.867

HP: Heptagon
HPY: Hexagonal Pyramid
PBPY: Pentagonal Bipyramid
COC: Capped Octahedron
CTPR: Capped Trigonal Prism
JPPY: Johnson Pentagonal Pyramid J13
JETPY: Johnson Elongated Triangular Pyramid J13

	HP	**PPY**	**OC**	**TPR**	**JPPY**
2	30.984	20.405	2.532	10.514	23.232

HP: Hexagon
PPY: Pentagonal Pyramid
OC: Octahedron
TPR: Trigonal Prism
JPPY: Johnson Pentagonal Pyramid

Table S3. Fitting of the Cole-Cole plots with a generalized Debye model under a zero-dc field for **1**.

T (K)	χ_S (cm^3. mol^{-1})	χ_T (cm^3. mol^{-1})	α
2	0.257	9.47	0.316
3.5	0.197	7.47	0.266
5	0.171	5.7	0.216
6	0.158	4.87	0.185
8	0.148	3.8	0.138
10	0.139	3.13	0.115
11.5	0.135	2.77	0.102
13.25	0.136	2.44	0.093
15	0.148	2.18	0.0826
16	0.144	2.06	0.0808
17	0.152	1.95	0.0767
18	0.163	1.85	0.0685
19	0.1	1.77	0.0716
20	0.166	1.68	0.0643
21	0.169	1.61	0.0623
22	0.19	1.54	0.0525
23	0.185	1.48	0.0578

Table S4: Fit parameters of the field dependence of the relaxation time for **2**.

Compound	***D* ($s^{-1}K^{-1}Oe^{-4}$)**	***B_1* (s^{-1})**	***B_2* (Oe^{-2})**	***K***
2 (10 K)	3.93×10^{-14}	167100	0.00245	885.82

Table S5. Fitting of the Cole-Cole plots with a generalized Debye model for **1** under a 500 Oe dc field.

T (K)	χ_S (cm^3. mol^{-1})	χ_T (cm^3. mol^{-1})	α
6.5	0.14543	4.89256	0.17815
10	0.14301	3.32987	0.11106
11.5	0.13902	2.94796	0.10058
13.25	0.13865	2.59806	0.09056
15	0.14629	2.32878	0.08386
16	0.1541	2.19577	0.07775
17	0.16215	2.07729	0.07674
18	0.16443	1.97029	0.06945
19	0.16172	1.87631	0.06976
20	0.18432	1.78774	0.05906
21	0.1857	1.71156	0.06217
22	0.19346	1.64011	0.05624
23	0.18229	1.57388	0.06144

Table S6. Fitting of the Cole-Cole plots with a generalized Debye model for **2** under a 1000 Oe dc field.

T (K)	χ_S (cm^3. mol^{-1})	χ_T (cm^3. mol^{-1})	α
5	0.10953	2.77306	0.06192
6	0.08986	2.30344	0.0443
7	0.07528	1.98284	0.03756
8	0.06386	1.74431	0.03591
9	0.05395	1.55746	0.03613
10	0.04505	1.40731	0.03953
11	0.03973	1.28356	0.04043
12	0.02918	1.17591	0.04421
13	0.01965	1.09	0.04793
14	0.01218	1.01533	0.05036
15	0.0032	0.94961	0.05387

16	2.16679E-12	0.89091	0.05435

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