CHEMISTRY
A European Journal

Supporting Information

Tuning the Magnetic Interactions and Relaxation Dynamics of Dy_2 Single-Molecule Magnets

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Supporting Information

Contents of the Supporting Information:

1. Structure and Crystallographic Data

Table S1. Crystallographic data for compounds.

Compound	**1**	**1a**	**2**
Formula	$C_{36}H_{42}N_{12}O_{12}Dy_2$	$C_{36}H_{42}N_{12}O_{12}Y_2$	$C_{38}H_{44}N_{10}O_{22}Zn_2Dy_2$
Weight	1159.82	1012.64	1448.57
Crystal System	triclinic	triclinic	monoclinic
Space group	*P*-1	*P*-1	*C*2/*c*
a (Å)	9.4470(5)	9.4440(10)	26.516(2)
b (Å)	10.3586(5)	10.3109(12)	15.7286(13)
c (Å)	11.4659(6)	11.4602(12)	17.3844(14)
α (°)	79.9550(10)	79.907(2)	90
β (°)	71.1700(10)	71.378(2)	126.8940(10)
γ (°)	85.1040(10)	84.908(2)	90
V (Å ^{3})	1045.19(9)	1040.5(2)	5798.4(8)
Z	1	1	4
D_{calc} (g cm^{-3})	1.843	1.616	1.659
T(K)	191(2)	191(2)	191(2)
Color	Yellow	Yellow	Yellow
μ (mm^{-1})	3.623	2.851	3.442
F(000)	570	516	2840
R_{int}	0.0189	0.0332	0.0384
Reflns collected	5420	5260	16586
Unique reflns	3700	3650	5114
R1[$I > 2\sigma(I)$]	0.0347	0.0633	0.0389
*wR*2 (all data)	0.0911	0.1780	0.1274
GOF	1.053	1.021	1.099
$(\Delta p)_{max,min}$ (e/Å ^{3})	1.488, -1.106	1.100, -0.992	1.890, -0.550

Table S2. Selected bond distance (Å) and bond angle (°) for **1** and **2**.

		Compound **1**			
Dy(1)-O(2)	2.192(4)	Dy(1)-O(5)	2.363(4)	Dy(1)-O(4)	2.438(4)
Dy(1)-O(1)	2.314(4)	Dy(1)-O(1)#1	2.398(4)	Dy(1)-N(1)#1	2.574(5)
Dy(1)-O(6)#1	2.362(4)	Dy(1)-N(4)#1	2.430(5)	Dy(1)-Dy(1)#1	3.6769(5)
Dy(1)-O(1)-Dy(1)#1	102.55(14)				
		Compound **2**			
Zn(1)-O(9)	1.969(5)	Dy(1)-O(2)	2.284(4)	Dy(1)-O(2)#2	2.346(4)
Zn(1)-O(7)	1.978(6)	Dy(1)-O(1)	2.300(5)	Dy(1)-O(5)	2.376(5)
Zn(1)-N(4)	2.002(6)	Dy(1)-O(6)	2.306(5)	Dy(1)-O(4)	2.441(5)
Zn(1)-O(1)	2.158(4)	Dy(1)-O(8)	2.311(5)	Dy(1)-O(3)#2	2.504(5)
Zn(1)-N(1)	2.259(6)	Dy(1)-Dy(1)#2	3.7651(7)		
Zn(1)-O(1)-Dy(1)	110.19(18)	Dy(1)-O(2)-Dy(1)#2	108.83(17)		

Symmetry codes: #1, -*x*+1, -*y*, -z; #2, -*x*+2, *y*, -z+1/2.

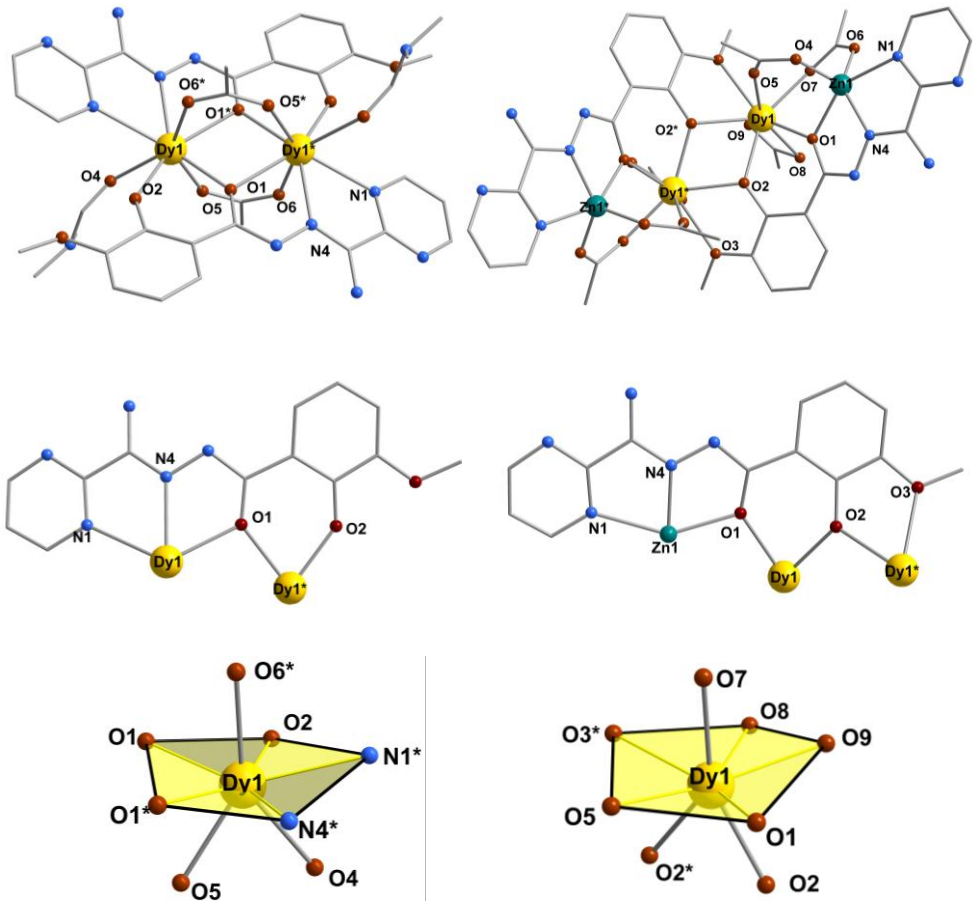

Figure S1. Molecular structures, coordination modes and coordination environments of **1** (left) and **2** (right). Solvent molecules and hydrogen atoms are omitted for clarity.

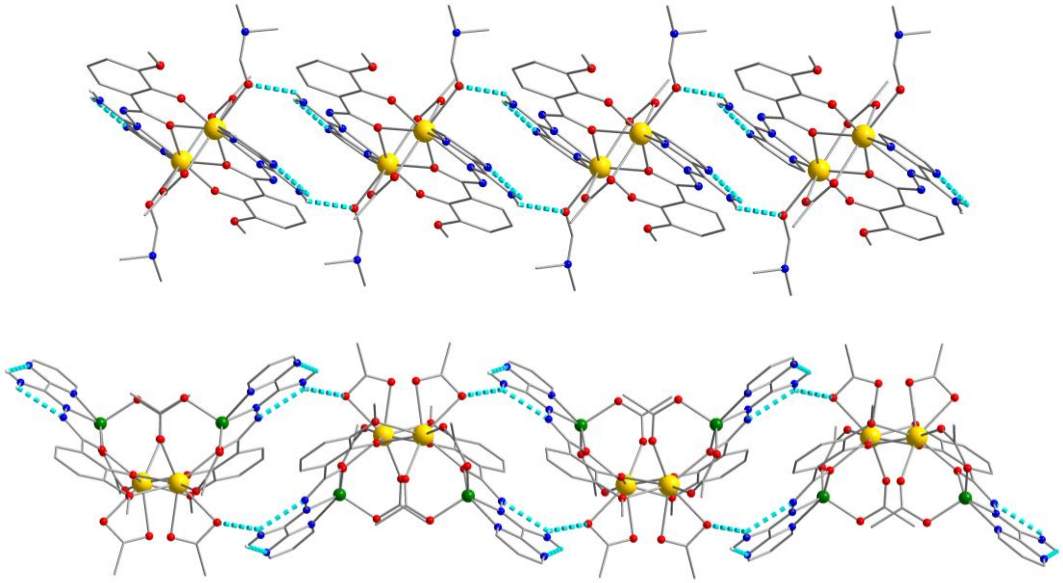

Figure S2. View along [001] direction for **1** (top) and **2** (bottom). The dash lines correspond to the intra- and intermolecular hydrogen bonding interactions.

2. Magnetic Data

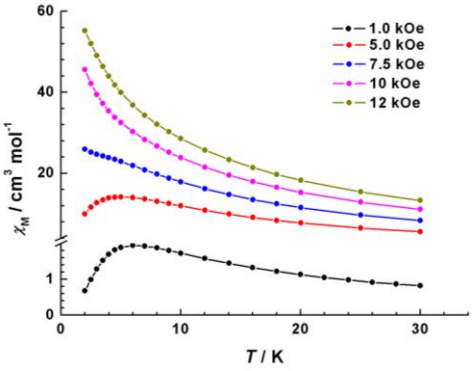

Figure S3. Temperature dependence of the magnetic susceptibility at different fields for **1**.

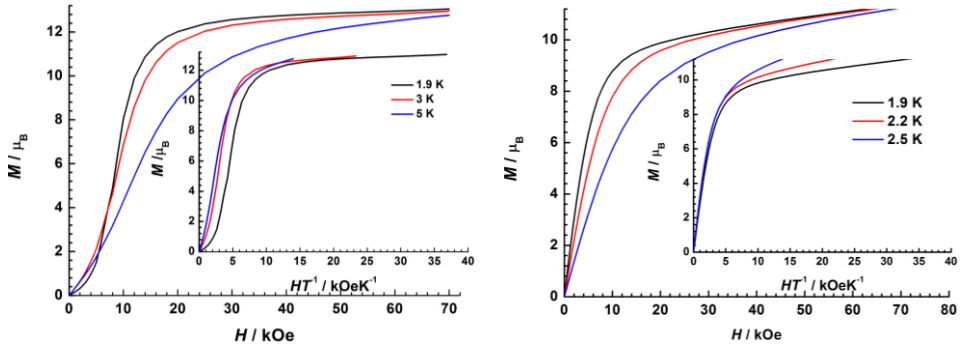

Figure S4. Field dependences of magnetization. Inset: plots of the reduced magnetization *M* vs. *H*/*T*. Left for **1** and right for **2**.

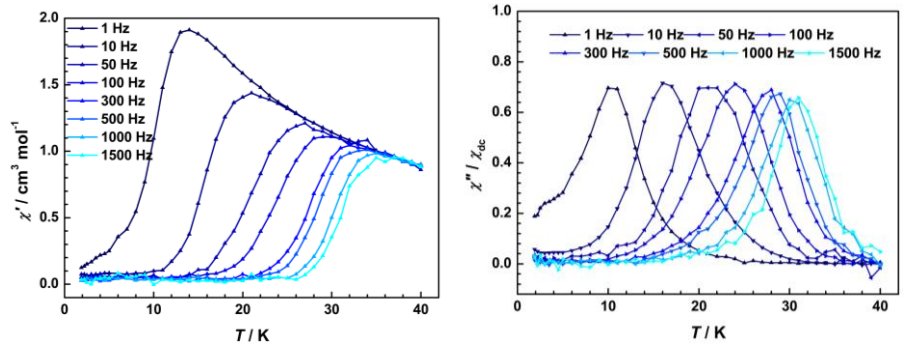

Figure S5. Temperature dependence of the ac susceptibility for **1** under zero-dc field.

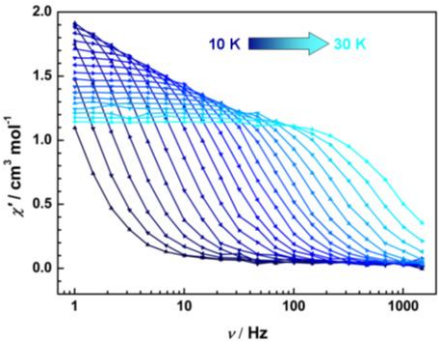

Figure S6. Frequency dependence of the in-phase (χ') parts of the ac susceptibility for **1** under zero-dc field.

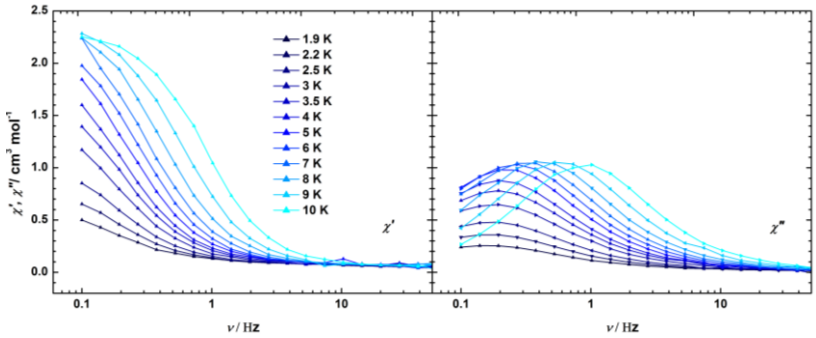

Figure S7. Frequency dependence of the in-phase (χ') and out-of-phase (χ'') parts of the ac susceptibility for **1**, measured between 1.9 and 10 K.

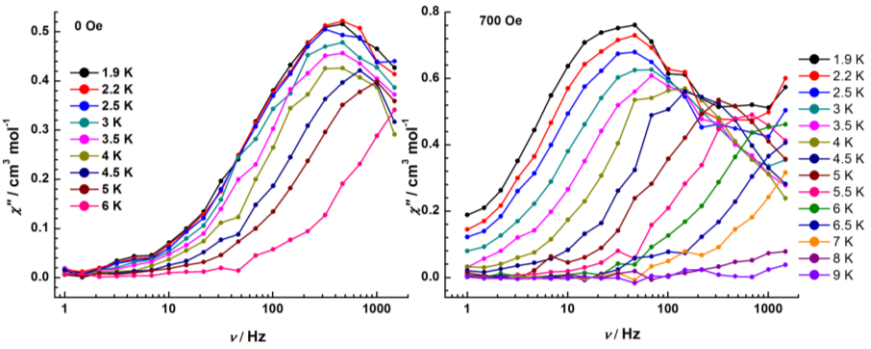

Figure S8. Frequency dependence of the out-of-phase (χ'') parts of the ac susceptibility for **2** under 0 Oe and 700 Oe field.

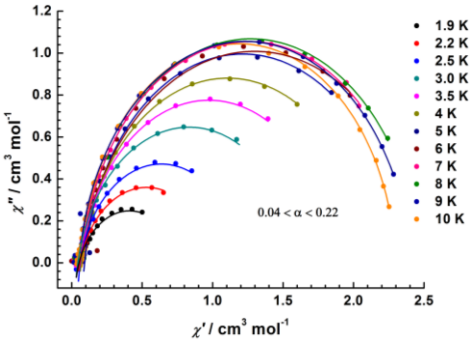

Figure S9. Cole-Cole plots for **1** at zero field. The solid lines are the best fits to the experiments with the generalized Debye model.

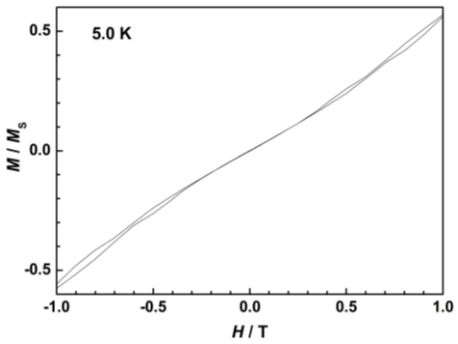

Figure S10. Magnetic hysteresis at 5 K at a sweep rate accessible with a conventional magnetometer for **1**.

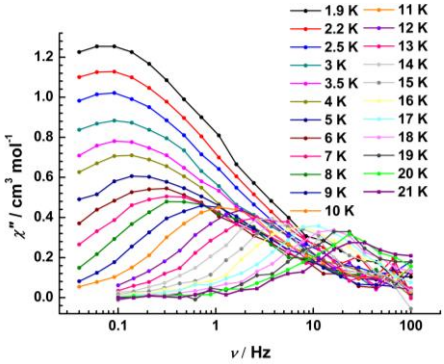

Figure S11. Frequency dependence of χ'' component of ac magnetic susceptibility for the diluted $Dy_{0.05}Y_{0.95}$ sample in zero static field.

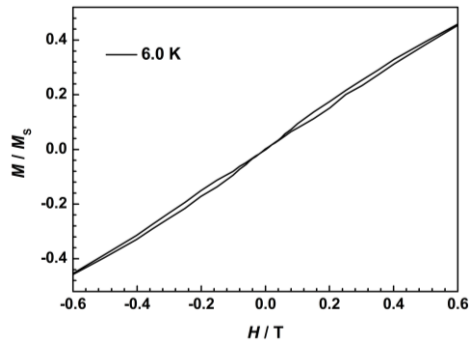

Figure S12. Magnetic hysteresis at 6 K at a sweep rate accessible with a conventional magnetometer for the diluted $Dy_{0.05}Y_{0.95}$ sample.

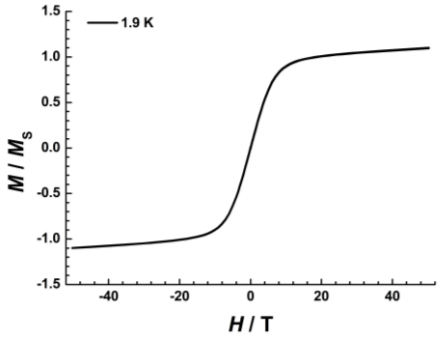

Figure S13. *M vs. H* data of **2** at 1.9 K.

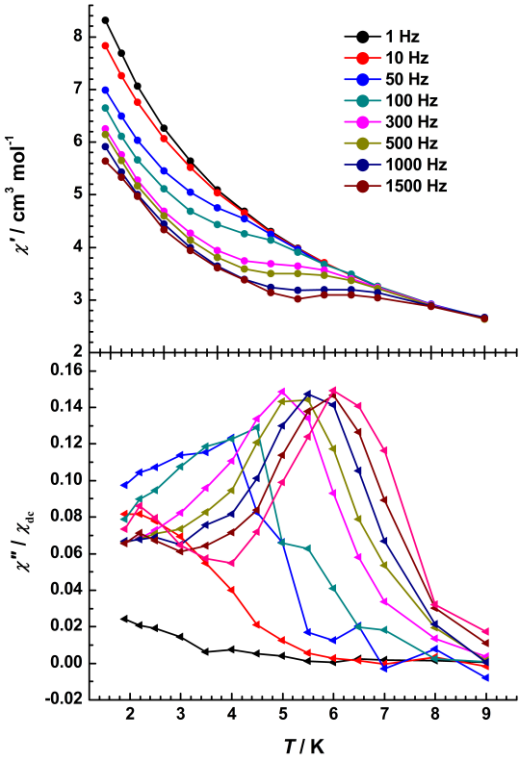

Figure S14. Temperature dependence of the out-of-phase (χ'') parts of the ac susceptibility for **2** under 700 Oe field.

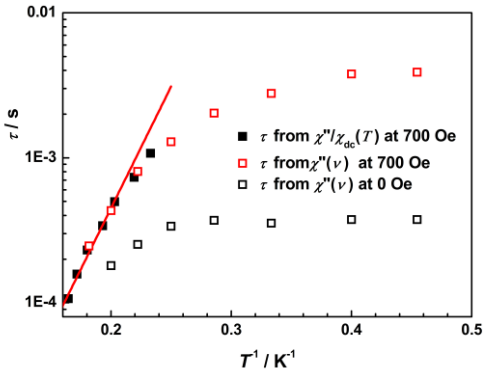

Figure S15. Magnetization relaxation time (τ) *vs.* T^{-1} plot for **2** at zero and 700 Oe.

3. *Ab initio* Calculations

Table S3. Atomic coordinates for **1** used in ab initio calculations.

Atom	Cartesian Coordinates		
	x	y	z
Dy1	5.98119800	0.86401700	1.02545800
Lu2	3.46580200	-0.86401700	-1.02545800
O3	3.71534800	0.92061100	0.55635900
O4	5.12865700	2.33472100	2.40981500
O5	5.15248800	3.98737200	4.40155700
O6	7.53638700	2.73512500	0.88438500
O7	5.92791400	1.80914900	-1.13951700
O8	4.34922700	0.83393400	-2.40874300
O9	5.73165200	-0.92061100	-0.55635900
O10	4.31834300	-2.33472100	-2.40981500
O11	4.29451200	-3.98737200	-4.40155700
O12	1.91061300	-2.73512500	-0.88438500
O13	3.51908600	-1.80914900	1.13951700
O14	5.09777300	-0.83393400	2.40874300
N15	1.78184600	-0.75201300	-2.96938900
N16	-0.27128100	0.16400400	-3.72513600
N17	-0.41442500	1.64690600	-1.43538400
N18	1.59159900	0.65764000	-0.75145900
N19	1.50809700	1.49464800	0.36125800
N20	7.61114400	4.95913000	1.05375800
N21	7.66515400	0.75201300	2.96938900
N22	9.71828100	-0.16400400	3.72513600
N23	9.86142500	-1.64690600	1.43538400
N24	7.85540100	-0.65764000	0.75145900
N25	7.93890300	-1.49464800	-0.36125800
N26	1.83585600	-4.95913000	-1.05375800
C27	0.69499000	0.01272000	-2.83217600
C28	-0.10007200	-0.48404400	-4.87001300
C29	0.95031200	-1.29251300	-5.11442500
C30	1.90225200	-1.42083500	-4.12820200
C31	0.61008000	0.80080800	-1.57152500
C32	2.66393700	1.55723400	0.98729500
C33	2.73663800	2.44234800	2.18255500
C34	3.96804300	2.79192400	2.78286500
C35	3.92468600	3.70365200	3.87199800
C36	2.73750700	4.23014500	4.31794200
C37	1.55297000	3.84970300	3.74443200
C38	1.54680300	2.97004900	2.68853000

C39	5.22189300	4.69596400	5.60968000
C40	7.47889300	3.82467800	1.43216800
C41	8.67016600	4.97368500	-0.03215900
C42	7.60264100	6.16816700	1.80950500
C43	5.30299200	1.62090900	-2.22865000
C44	5.78899700	2.43989300	-3.40997400
C45	8.75201000	-0.01272000	2.83217600
C46	9.54707200	0.48404400	4.87001300
C47	8.49668800	1.29251300	5.11442500
C48	7.54474800	1.42083500	4.12820200
C49	8.83692000	-0.80080800	1.57152500
C50	6.78306300	-1.55723400	-0.98729500
C51	6.71036200	-2.44234800	-2.18255500
C52	5.47895700	-2.79192400	-2.78286500
C53	5.52231400	-3.70365200	-3.87199800
C54	6.70949300	-4.23014500	-4.31794200
C55	7.89403000	-3.84970300	-3.74443200
C56	7.90019700	-2.97004900	-2.68853000
C57	4.22510700	-4.69596400	-5.60968000
C58	1.96810700	-3.82467800	-1.43216800
C59	0.77683400	-4.97368500	0.03215900
C60	1.84435900	-6.16816700	-1.80950500
C61	4.14400800	-1.62090900	2.22865000
C62	3.65800300	-2.43989300	3.40997400
H63	-0.46005900	2.17371200	-0.73216400
H64	-1.04449700	1.67700200	-2.04962900
H65	-0.75163000	-0.37291000	-5.55286500
H66	1.03215800	-1.75878000	-5.93770700
H67	2.65305700	-1.98671400	-4.26755900
H68	2.73722500	4.86031000	5.02866600
H69	0.73344400	4.19641200	4.07781800
H70	0.71991000	2.71742100	2.29725700
H71	4.92567800	5.61836300	5.46389100
H72	6.14525100	4.69574300	5.93556300
H73	4.64063000	4.26683400	6.27216500
H74	7.28658500	3.76360200	2.36050400
H75	7.05041500	6.04982400	2.61027500
H76	7.23304600	6.89318100	1.26279400
H77	8.51890700	6.39482700	2.07535700
H78	6.54803400	1.98523700	-3.83233500
H79	6.07062000	3.32575800	-3.10017100
H80	5.06335900	2.53632000	-4.06173900
H81	9.36095000	4.30999000	0.17687700
H82	9.07618800	5.86398900	-0.08039900

H83	8.25785800	4.75522500	-0.89403300
H84	9.90705900	-2.17371200	0.73216400
H85	10.49149700	-1.67700200	2.04962900
H86	10.19863000	0.37291000	5.55286500
H87	8.41484200	1.75878000	5.93770700
H88	6.79394300	1.98671400	4.26755900
H89	6.70977500	-4.86031000	-5.02866600
H90	8.71355600	-4.19641200	-4.07781800
H91	8.72709000	-2.71742100	-2.29725700
H92	4.52132200	-5.61836300	-5.46389100
H93	3.30174900	-4.69574300	-5.93556300
H94	4.80637000	-4.26683400	-6.27216500
H95	2.16041500	-3.76360200	-2.36050400
H96	2.39658500	-6.04982400	-2.61027500
H97	2.21395400	-6.89318100	-1.26279400
H98	0.92809300	-6.39482700	-2.07535700
H99	2.89896600	-1.98523700	3.83233500
H100	3.37638000	-3.32575800	3.10017100
H101	4.38364100	-2.53632000	4.06173900
H102	0.08605000	-4.30999000	-0.17687700
H103	0.37081200	-5.86398900	0.08039900
H104	1.18914200	-4.75522500	0.89403300

Table S4. Atomic coordinates for **2** used in ab initio calculations.

Atom	Cartesian Coordinates		
	x	y	z
Dy1	24.23767400	5.05254800	1.61652400
Lu2	23.64058300	5.05254800	5.32969300
Zn3	23.64841700	2.42749800	-0.85660700
Zn4	24.22984100	2.42749800	7.80282400
O5	22.70450200	3.60372800	0.68489700
O6	22.67206100	4.71256700	3.22582300
O7	21.22254700	5.61748200	5.13464300
O8	24.96465700	1.34940700	0.11669600
O9	25.44545800	3.12896600	1.27254700
O10	24.57164100	3.72321500	-2.00328900
O11	24.81028100	5.38966000	-0.59181800
O12	24.45308100	7.39863500	1.86853200
O13	22.58281900	6.75021900	1.01414800
O14	25.17375600	3.60372800	6.26132000
O15	25.20619600	4.71256700	3.72039400
O16	26.65571000	5.61748200	1.81157300
O17	22.91360000	1.34940700	6.82952000
O18	22.43280000	3.12896600	5.67367000
O19	23.30661700	3.72321500	8.94950600
O20	23.06797700	5.38966000	7.53803500
O21	23.42517700	7.39863500	5.07768500
O22	25.29543800	6.75021900	5.93206900
N23	23.40516000	1.08175600	-2.66595800
N24	21.68784500	-0.18958600	-3.69122000
N25	19.98914400	0.61814600	-1.71432600
N26	21.75704400	1.75088300	-0.72518500
N27	20.92137900	2.19059500	0.29313000
N28	24.47309800	1.08175600	9.61217500
N29	26.19041200	-0.18958600	10.63743600
N30	27.88911300	0.61814600	8.66054300
N31	26.12121400	1.75088300	7.67140200
N32	26.95687800	2.19059500	6.65308600
C33	22.19207800	0.59424900	-2.73542000
C34	24.26679100	0.75356500	-3.66204600
C35	23.83061800	-0.06691300	-4.67758200
C36	22.55748200	-0.48432100	-4.66230100
C37	21.24956500	0.98298000	-1.68376300
C38	21.50147000	3.14808400	0.97802700
C39	20.75187500	3.72480800	2.09497900

C40	21.35126700	4.45925500	3.12996500
C41	20.53507900	4.92923700	4.16495200
C42	19.19453300	4.66795900	4.19968300
C43	18.62651900	3.93032600	3.16886400
C44	19.37259500	3.47946100	2.12832100
C45	20.49243600	6.39175800	6.06404700
C46	25.59559400	1.96118000	1.02665100
C47	26.53273800	1.15026200	1.88103600
C48	25.03916200	4.85754500	-1.68932000
C49	25.91805100	5.53145200	-2.67290400
C50	23.32435100	7.65513400	1.50594000
C51	22.80856000	9.04436900	1.55456300
C52	25.68618000	0.59424900	9.68163700
C53	23.61146700	0.75356500	10.60826200
C54	24.04763900	-0.06691300	11.62379900
C55	25.32077500	-0.48432100	11.60851800
C56	26.62869300	0.98298000	8.62998000
C57	26.37678800	3.14808400	5.96819000
C58	27.12638200	3.72480800	4.85123800
C59	26.52699000	4.45925500	3.81625200
C60	27.34317900	4.92923700	2.78126500
C61	28.68372400	4.66795900	2.74653400
C62	29.25173800	3.93032600	3.77735300
C63	28.50566300	3.47946100	4.81789600
C64	27.38582200	6.39175800	0.88217000
C65	22.28266400	1.96118000	5.91956600
C66	21.34551900	1.15026200	5.06518100
C67	22.83909600	4.85754500	8.63553700
C68	21.96020700	5.53145200	9.61912100
C69	24.55390700	7.65513400	5.44027700
C70	25.06969800	9.04436900	5.39165400
H71	19.45218000	0.87623800	-1.09611300
H72	19.70119200	0.11948700	-2.35337800
H73	25.13850400	1.08016200	-3.65787800
H74	24.40691500	-0.32659800	-5.35970100
H75	22.26158000	-1.01006300	-5.36942600
H76	18.67276900	4.98181100	4.90125100
H77	17.71569100	3.74074000	3.19248100
H78	18.96627400	3.00629300	1.43786700
H79	19.85802100	6.93980500	5.59587200
H80	21.09509200	6.95255000	6.55722900
H81	20.02834500	5.81025500	6.66975700
H82	26.48444900	1.45774100	2.78821100
H83	27.42907900	1.25063100	1.55456300

H84	26.28052500	0.22463600	1.84213700
H85	25.39557200	6.13525900	-3.20637400
H86	26.32522700	4.87347600	-3.24110500
H87	26.60061400	6.02214500	-2.20889700
H88	22.25514400	9.15429700	2.33115000
H89	22.29333900	9.22280300	0.76408400
H90	23.54707700	9.65773600	1.59901900
H91	28.42607700	0.87623800	8.04233000
H92	28.17706500	0.11948700	9.29959500
H93	22.73975300	1.08016200	10.60409500
H94	23.47134200	-0.32659800	12.30591800
H95	25.61667800	-1.01006300	12.31564200
H96	29.20548900	4.98181100	2.04496600
H97	30.16256700	3.74074000	3.75373600
H98	28.91198400	3.00629300	5.50835000
H99	28.02023600	6.93980500	1.35034500
H100	26.78316500	6.95255000	0.38898800
H101	27.84991300	5.81025500	0.27645900
H102	21.39380800	1.45774100	4.15800500
H103	20.44917900	1.25063100	5.39165400
H104	21.59773200	0.22463600	5.10408000
H105	22.48268600	6.13525900	10.15259100
H106	21.55303000	4.87347600	10.18732200
H107	21.27764300	6.02214500	9.15511400
H108	25.62311400	9.15429700	4.61506600
H109	25.58491900	9.22280300	6.18213300
H110	24.33118000	9.65773600	5.34719800

Table S5. Contractions of the ANO-RCC basis sets used in ab initio calculations.

Basis set DZP	Basis set TZP
Dy.ANO-RCC...7s6p4d2f1g.	Dy.ANO-RCC...8s7p5d3f2g1h.
Lu.ANO-RCC...7s6p4d2f1g.	Lu.ANO-RCC...7s6p4d2f1g.
O.ANO-RCC...3s2p1d.	O.ANO-RCC...4s3p2d1f.
O.ANO-RCC...3s2p.	O.ANO-RCC...3s2p.
N.ANO-RCC...3s2p1d.	N.ANO-RCC...4s3p1d.
N.ANO-RCC...3s2p.	N.ANO-RCC...3s2p.
N.ANO-RCC...3s2p.	N.ANO-RCC...3s2p.
C.ANO-RCC...3s2p.	C.ANO-RCC...4s3p1d.
C.ANO-RCC...3s2p.	C.ANO-RCC...3s2p.
H.ANO-RCC...2s.	H.ANO-RCC...2s.

Analysis of the multiplet-specific crystal-field for Dy sites in 1 and 2

Recently, the extraction of the parameters of the multiplet-specific crystal-field for lanthanides methodology has been implemented in the SINGLE_ANISO program in MOLCAS. The results presented below use the ab initio CASSCF/RASSI wave function and energies to compute the parameters of the crystal-field splitting of the ground *J* multiplet.

The Crystal-Field Hamiltonian:

$$H_{CF} = \sum_{k,q} B_k^q O_k^q$$

where:

O_k^q -- Extended Stevens Operators (ESO)as defined in:

1. Rudowicz, C.; J. Phys. C: Solid State Phys.,18 (1985) 1415-1430.
2. Implemented in the "EasySpin" function in MATLAB, www.easyspin.org.

k - the rank of the ITO, = 2, 4, 6.

q - the component (projection) of the ITO, = $-k,\ -k+1,$ ... $0,\ 1,$ ... k;

Quantization axis was chosen the main magnetic axis of the ground Kramers doublet.

Table S6. Crystal field parameters acting on the ground-state multiplet J = 15/2 of Dy^{3+} in **1** and **2**.

k	*q*	**1**		**2**	
		DZP	TZP	DZP	TZP
	-2	-0.32329698E+00	-0.33118060E+00	-0.57549711E+00	0.63412551E+00
	-1	0.23026522E+00	0.33850134E+00	-0.21577904E+00	**0.15093508E+01**
2	0	**-0.23821018E+01**	**-0.23854524E+01**	**-0.63558197E+00**	-0.26039815E+00
	1	-0.51974857E+00	-0.53438314E+00	**-0.17041421E+01**	**-0.74956245E+00**

	2	0.80162185E+00	0.81989842E+00	0.16375381E+00	-0.29112892E+00
	-4	-0.45786295E-02	-0.47439615E-02	-0.14345807E-01	**-0.20450193E-01**
	-3	**-0.33125013E-01**	**-0.31104362E-01**	0.68248026E-02	**0.67078119E-01**
	-2	-0.76608673E-02	-0.70454649E-02	-0.54727926E-02	0.13263429E-02
	-1	0.25019842E-02	0.17786475E-02	0.16093820E-02	-0.83762120E-02
4	0	-0.56061109E-02	-0.59258889E-02	-0.20187580E-02	-0.33609549E-02
	1	0.82349406E-02	0.85967644E-02	**0.16219237E-01**	-0.39460537E-02
	2	**-0.19883018E-01**	**-0.21053832E-01**	-0.10209873E-03	0.64060252E-02
	3	**-0.47374247E-01**	**-0.50645308E-01**	**0.75408076E-01**	**-0.75567933E-01**
	4	-0.10157409E-02	-0.20166817E-02	**-0.26394764E-01**	0.57945827E-03
	-6	0.22442375E-04	0.26633670E-04	-0.66083905E-04	-0.13541371E-03
	-5	0.49906748E-04	0.22301303E-04	0.26921277E-03	0.20746918E-03
	-4	0.16649294E-05	-0.12926714E-04	0.32864503E-05	-0.47078425E-04
	-3	-0.10107183E-04	0.12062904E-04	-0.32704654E-03	0.26479228E-03
	-2	0.15111903E-03	0.14883464E-03	-0.10271557E-03	-0.16683671E-03
	-1	-0.47297345E-04	-0.47349928E-04	-0.21984360E-04	-0.30150366E-04
6	0	-0.32880951E-05	-0.33508682E-05	0.21829249E-04	0.53638119E-05
	1	-0.50273968E-04	-0.52413733E-04	0.65249106E-04	0.17571050E-03
	2	0.37662540E-04	0.46027730E-04	0.10306498E-03	-0.10669587E-03
	3	-0.26331572E-03	-0.27181267E-03	-0.10207392E-03	-0.36753077E-05
	4	0.12400368E-03	0.12537274E-03	-0.20004658E-04	0.74709978E-04
	5	0.23093813E-03	0.24463871E-03	0.47608070E-03	0.40552694E-03
	6	-0.10942614E-04	-0.84587819E-05	0.10710103E-03	0.14377611E-04

Table S7. Ab initio calculated atomic charges (LoProp) on all atoms in **1**. First coordinated atoms are highlighted. Atoms labels correspond to those in Table S3.

Atom	Atomic charges in **1**	
	DZP	TZP
Dy1	2.5244	2.5423
Lu2	1.4483	1.4566
O3	-0.7470	-0.7669
O4	-0.8719	-0.8958
O5	-0.4070	-0.4141
O6	-0.6769	-0.7023
O7	-0.7681	-0.7928
O8	-0.6209	-0.6438
O9	-0.7299	-0.7456
O10	-0.6781	-0.6777
O11	-0.4059	-0.4057
O12	-0.5677	-0.5668
O13	-0.6364	-0.6608
O14	-0.7494	-0.7733
N15	-0.2141	-0.2133

Atom	Atomic charges in **2**	
	DZP	TZP
Dy1	2.5499	2.5685
Lu2	1.4995	1.5027
Zn3	1.5118	1.5236
Zn4	1.5179	1.5181
O5	-0.8582	-0.8725
O6	-0.7992	-0.8109
O7	-0.3591	-0.3587
O8	-0.7747	-0.7931
O9	-0.7318	-0.7504
O10	-0.7772	-0.7954
O11	-0.7417	-0.7586
O12	-0.7371	-0.7550
O13	-0.7699	-0.7862
O14	-0.7126	-0.7123
O15	-0.7773	-0.7893

N16	-0.2993	-0.2999
N17	-0.4613	-0.4639
N18	-0.2306	-0.2283
N19	-0.4033	-0.4123
N20	-0.1444	-0.1622
N21	-0.3071	-0.3471
N22	-0.3048	-0.3362
N23	-0.4689	-0.4690
N24	-0.3478	-0.3675
N25	-0.3953	-0.4232
N26	-0.1385	-0.1391
C27	0.2233	0.2238
C28	0.0359	0.0356
C29	-0.2184	-0.2191
C30	0.0750	0.0748
C31	0.2810	0.2777
C32	0.4297	0.4638
C33	-0.1194	-0.1249
C34	0.2878	0.3077
C35	0.1295	0.1480
C36	-0.1909	-0.1864
C37	-0.2034	-0.1996
C38	-0.1070	-0.1016
C39	-0.1655	-0.1652
C40	0.3924	0.4399
C41	-0.2759	-0.2426
C42	-0.2641	-0.2323
C43	0.6421	0.6909
C44	-0.4346	-0.4123
C45	0.2253	0.2664
C46	0.0375	0.0766
C47	-0.2206	-0.2285
C48	0.0741	0.1094
C49	0.2714	0.2951
C50	0.4316	0.4720
C51	-0.1236	-0.1273
C52	0.2739	0.2721
C53	0.1357	0.1357
C54	-0.1922	-0.1928
C55	-0.2006	-0.2010
C56	-0.1096	-0.1103
C57	-0.1656	-0.1656
C58	0.3766	0.3778
C59	-0.2762	-0.2762

O16	-0.4510	-0.4487
O17	-0.7537	-0.7539
O18	-0.5736	-0.5731
O19	-0.7589	-0.7589
O20	-0.5809	-0.5804
O21	-0.6096	-0.6091
O22	-0.6537	-0.6533
N23	-0.2973	-0.2953
N24	-0.2960	-0.2962
N25	-0.4523	-0.4529
N26	-0.3537	-0.3512
N27	-0.3903	-0.3915
N28	-0.2964	-0.2964
N29	-0.2903	-0.2904
N30	-0.4427	-0.4429
N31	-0.3797	-0.3794
N32	-0.3759	-0.3762
C33	0.2187	0.2192
C34	0.0751	0.0751
C35	-0.2098	-0.2100
C36	0.0436	0.0432
C37	0.2690	0.2687
C38	0.4530	0.4633
C39	-0.0814	-0.0818
C40	0.2767	0.2831
C41	0.2009	0.2012
C42	-0.1984	-0.1985
C43	-0.1795	-0.1798
C44	-0.1295	-0.1290
C45	-0.1633	-0.1629
C46	0.6576	0.6852
C47	-0.4183	-0.4193
C48	0.6662	0.6923
C49	-0.4144	-0.4150
C50	0.6295	0.6564
C51	-0.4214	-0.4219
C52	0.2114	0.2115
C53	0.0767	0.0767
C54	-0.2078	-0.2078
C55	0.0416	0.0416
C56	0.2816	0.2814
C57	0.4130	0.4135
C58	-0.0690	-0.0693
C59	0.2745	0.2807

C60	-0.2638	-0.2638
C61	0.6407	0.6898
C62	-0.4347	-0.4125
H63	0.2701	0.2701
H64	0.2581	0.2579
H65	0.1596	0.1594
H66	0.1573	0.1570
H67	0.1905	0.1907
H68	0.1340	0.1237
H69	0.1351	0.1260
H70	0.1536	0.1449
H71	0.1251	0.1264
H72	0.1439	0.1429
H73	0.1266	0.1285
H74	0.1236	0.1078
H75	0.1549	0.1458
H76	0.1531	0.1413
H77	0.1298	0.1218
H78	0.1512	0.1426
H79	0.1458	0.1349
H80	0.1425	0.1322
H81	0.1465	0.1390
H82	0.1362	0.1281
H83	0.1677	0.1561
H84	0.2674	0.2678
H85	0.2572	0.2560
H86	0.1583	0.1459
H87	0.1556	0.1442
H88	0.1872	0.1771
H89	0.1344	0.1343
H90	0.1355	0.1353
H91	0.1518	0.1529
H92	0.1252	0.1251
H93	0.1440	0.1440
H94	0.1267	0.1267
H95	0.1254	0.1256
H96	0.1551	0.1551
H97	0.1536	0.1535
H98	0.1302	0.1302
H99	0.1515	0.1431
H100	0.1460	0.1355
H101	0.1421	0.1315
H102	0.1472	0.1474
H103	0.1364	0.1365

C60	0.1972	0.1979
C61	-0.1952	-0.1954
C62	-0.1787	-0.1788
C63	-0.1254	-0.1254
C64	-0.1197	-0.1188
C65	0.6049	0.6053
C66	-0.4425	-0.4426
C67	0.6173	0.6177
C68	-0.4396	-0.4396
C69	0.5875	0.5884
C70	-0.4441	-0.4440
H71	0.2746	0.2746
H72	0.2652	0.2650
H73	0.1755	0.1755
H74	0.1640	0.1638
H75	0.1670	0.1669
H76	0.1424	0.1422
H77	0.1408	0.1407
H78	0.1532	0.1531
H79	0.1399	0.1398
H80	0.1736	0.1736
H81	0.1307	0.1307
H82	0.1514	0.1516
H83	0.1465	0.1467
H84	0.1404	0.1403
H85	0.1523	0.1525
H86	0.1415	0.1413
H87	0.1426	0.1428
H88	0.1523	0.1525
H89	0.1402	0.1403
H90	0.1334	0.1332
H91	0.2774	0.2774
H92	0.2667	0.2666
H93	0.1783	0.1783
H94	0.1658	0.1658
H95	0.1682	0.1682
H96	0.1435	0.1433
H97	0.1414	0.1412
H98	0.1555	0.1554
H99	0.1262	0.1262
H100	0.1597	0.1599
H101	0.1202	0.1202
H102	0.1647	0.1649
H103	0.1599	0.1600

H104	0.1687	0.1686

H104	0.1561	0.1560
H105	0.1662	0.1662
H106	0.1562	0.1562
H107	0.1556	0.1557
H108	0.1639	0.1637
H109	0.1554	0.1556
H110	0.1492	0.1493

Modelling of the exchange interactions

- ### Estimation of the exchange interactions by BS-DFT calculation

The calculations were carried out on the experimental geometry, by substituting computationally the Dy with Gd. This substitution is necessary in order to avoid the near-degenerate ground state of the Dy^{III} ion (it is known that DFT methods are not appropriate for description of near-degenerate ground states). We have employed ORCA program package for these calculations [1].

Computational details: B3LYP functional, SVP basis sets on all atoms, TightSCF convergence thresholds, Grid6.

Further, the obtained energies of the high-spin state, and of the three low-spin states, corresponding to spin flip of one metal site, were used for the estimation of the exchange coupling constants. General equations derived from the [2] were employed for this case.

The obtained exchange parameters corresponding to Gd-Gd, were re-scaled for the interacting pair of Dy-Dy, by using the rescaling factor 49/25 (the spin of Gd) / (the spin of Dy). This approach was successfully used in [3] and [4].

The obtained values of exchange parameters are given in Table S8 below.

Table S8. Exchange coupling constants obtained within BS-DFT approach for the investigated complexes in two basis set models employed.

Exchange interaction	SVP	Def2-TZVP
Compound **1**	-0.47	-0.53
Compound **2**	-0.11	-0.13

These parameters are to be compared with the fitted Lines parameters (within Poly_Aniso), Table S9.

Table S9. Exchange coupling parameters obtained within Lines model. Note that these parameters were re-written in the Ising model and reported in Table 2 in the main text.

Exchange interaction	TZP
Compound **1**	-0.335 cm^{-1}
Compound **2**	0.093 cm^{-1}

- ### Estimation of the exchange interactions within Poly_Aniso

Localization of the magnetic orbitals observed in transition metal complexes and networks [5] is even more pronounced in lanthanide-containing mono- and polynuclear compounds. This fact allows treating electronic and magnetic structure of polynuclear compounds in a two-step procedure. In the first step, reasonable fragmentation of the cluster into mononuclear fragments is performed and reliable ab initio calculations for each fragment are done. In the second step, the magnetic interaction between the fragments is introduced in an effective way. The

exchange interaction between magnetic centers is considered within the Lines model [5], while the account of the dipole-dipole magnetic coupling is treated exactly. The Lines model [6] is an approximation allowing describing the anisotropic exchange interaction between magnetic sites via a single parameter. To this end, an isotropic Heisenberg model involving the true spins of the two centers is introduced with an effective parameter (the Lines exchange parameter). In a second step the matrix of this model is constructed in the basis of products of localized lowest states of the two centers obtained in fragment ab initio calculations of corresponding centers with spin-orbit coupling included. The obtained exchange matrix describes exactly the anisotropic exchange interaction in two limiting cases:

1) of two strongly axial doublets on the two sites (the case of extreme magnetic anisotropy)

2) of isotropic spins on the two sites (lack of magnetic anisotropy)

The Lines approximation is expected to be quite accurate for the description of the exchange interaction between a strongly axial doublet and an arbitrary isotropic spin. For all other cases, the Lines model [6] is a reasonable approximation. Efficient implementation of the Lines model was done in the program POLY_ANISO.

The dipolar magnetic coupling is computed exactly, while the exchange parameters are fitted (from comparison of computed and measured magnetic susceptibility and molar magnetization). Best-fitted values are given in Table S9 and Table 2 (main text).

References:

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