Supporting Information for

Macrocycle supported dimetallic lanthanide complexes with slow magnetic relaxation in Dy$_2$ analogues

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Fig. S1. ^1H NMR spectrum of the Schiff base ligand HL in CDCl$_3$.

Peak labels (left to right): 8.3237, 7.4903, 7.2083, 4.3894, 3.6622, 3.3175, 3.1556, 2.7960, 2.7353, 2.7107, 2.6646, 2.2302, 2.1846, 1.8317, 1.6286

Fig. S2. Experimental and simulated powder X-ray diffraction patterns for **1**$_{Dy}$-**6**$_{Gd}$. The data were collected at room temperature. The good fit of the experimental and simulated patterns indicates the phase purity of these compounds.
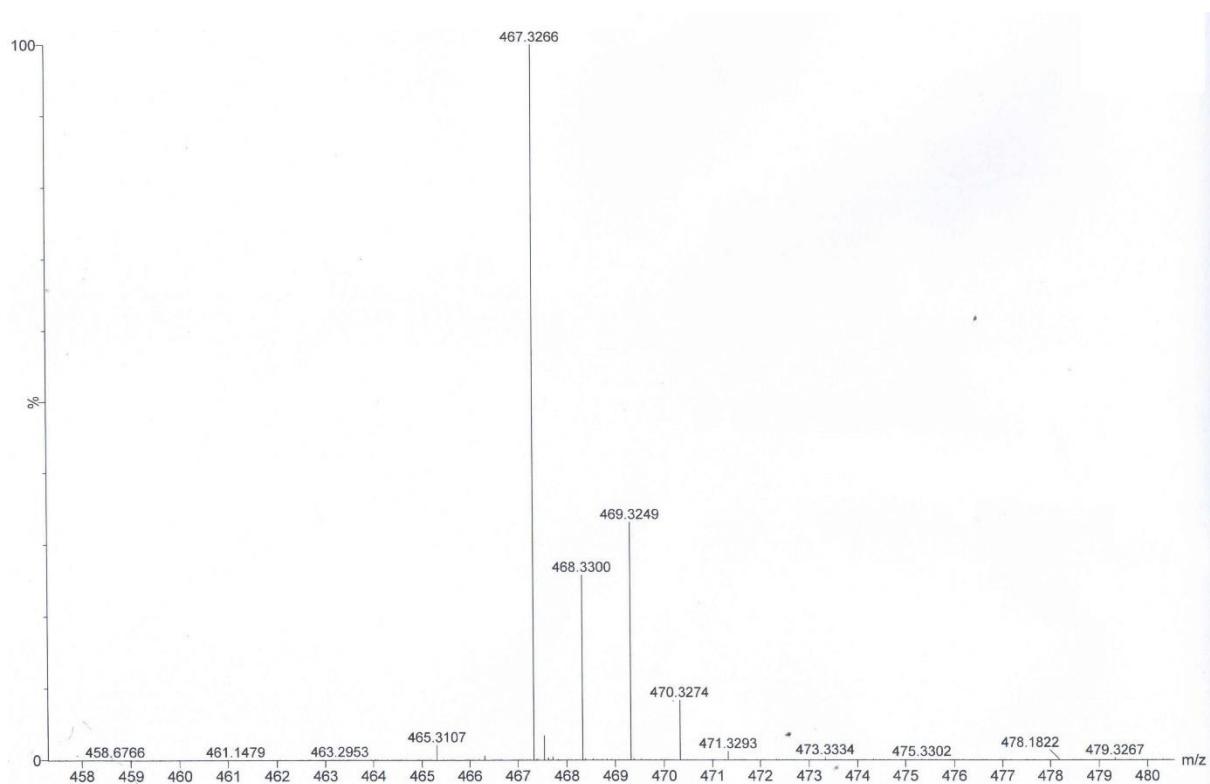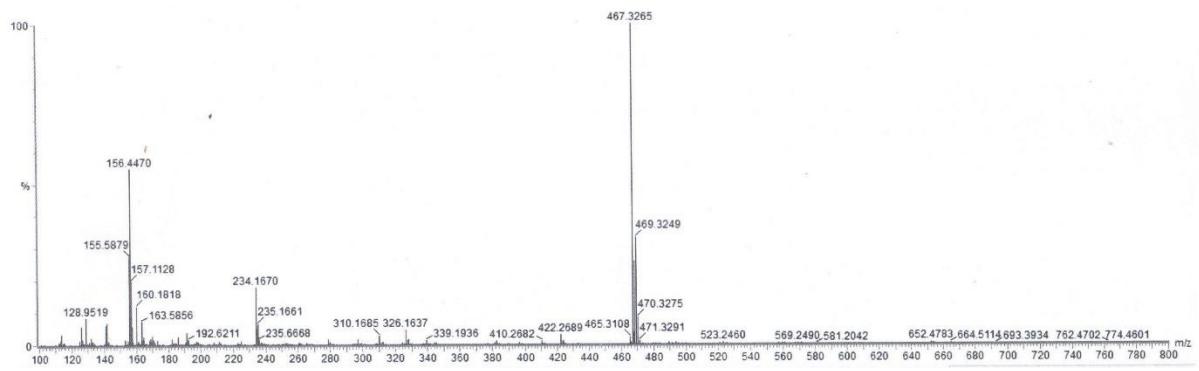
Fig. S3. Electrospray ionization mass spectrum (ESI-MS positive) of the Schiff base ligand in methanol (top) and its expanded view at bottom.
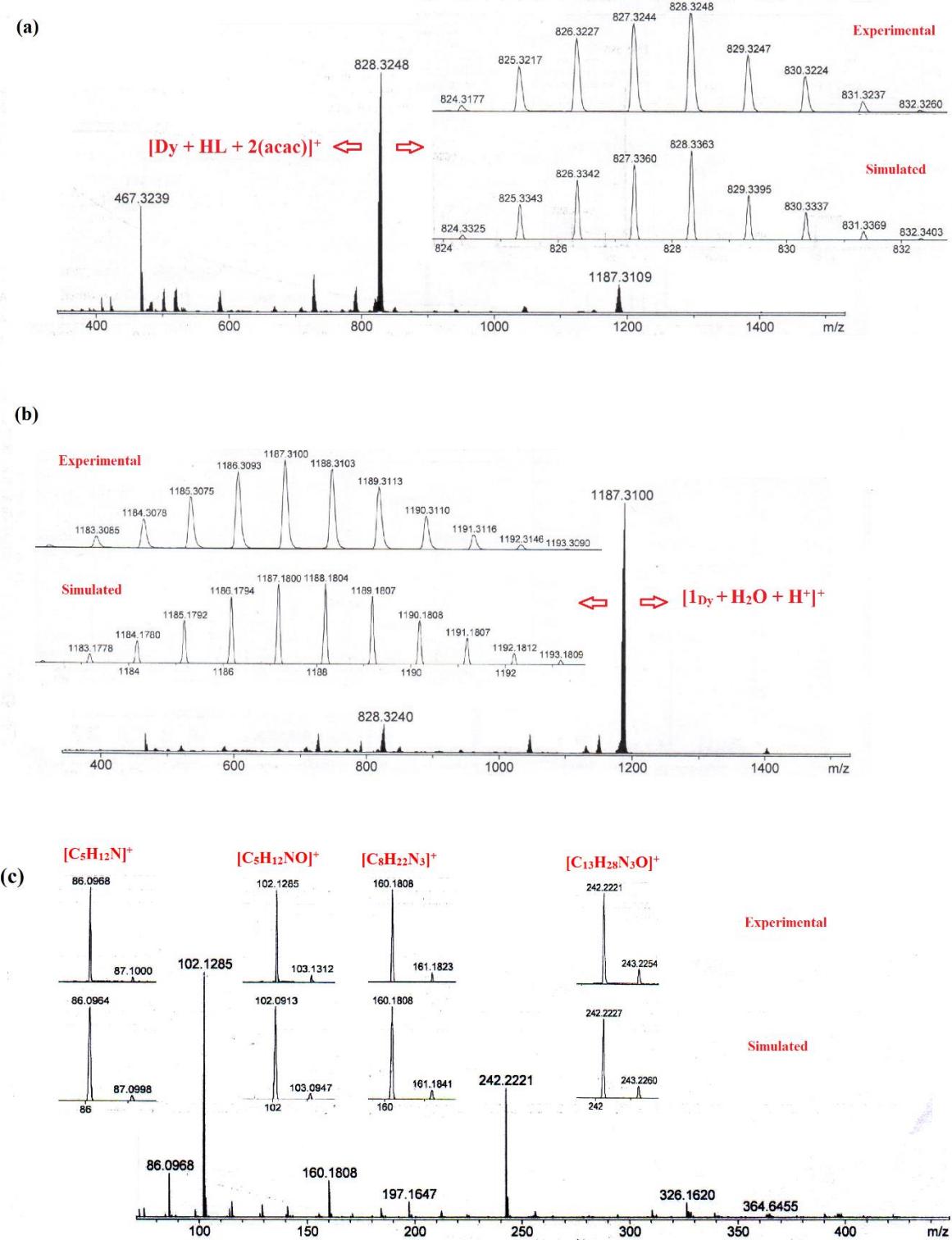
Fig. S4. Electrospray ionization mass spectra (ESI-MS positive) of a reaction mixture recorded after 5 min (top) and 1 h (bottom) of mixing.
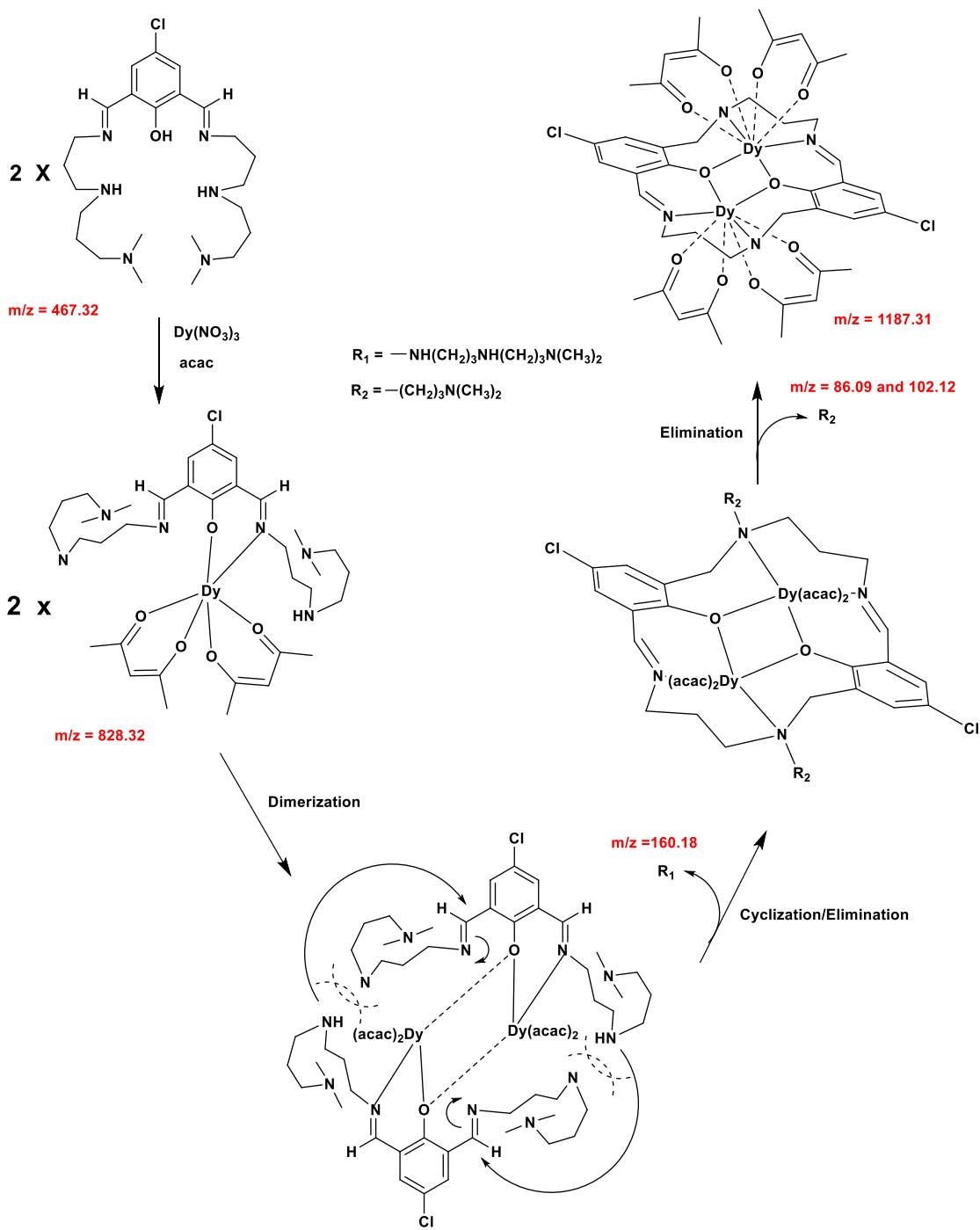
Scheme S1. Probable mechanism for the *in-situ* transformation of the Schiff base leading to the macrocyclic ligand.
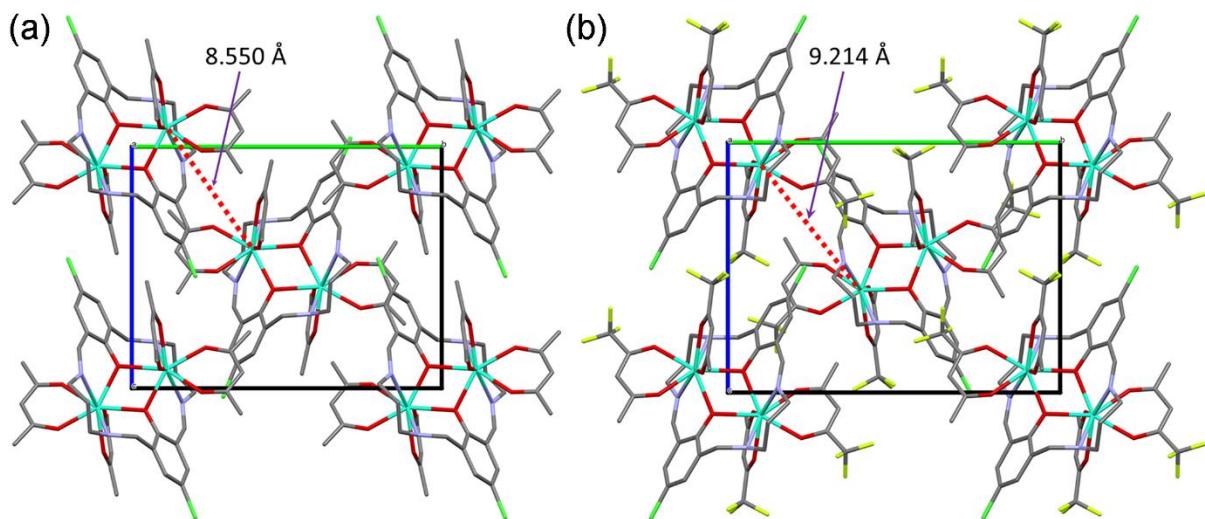
Fig. S5. Crystal packing of complexes 1_{Dy} and 4_{Dy} along the *a* axis. The numbers show the shortest Dy-Dy distances between the adjacent Dy$_2$ units.
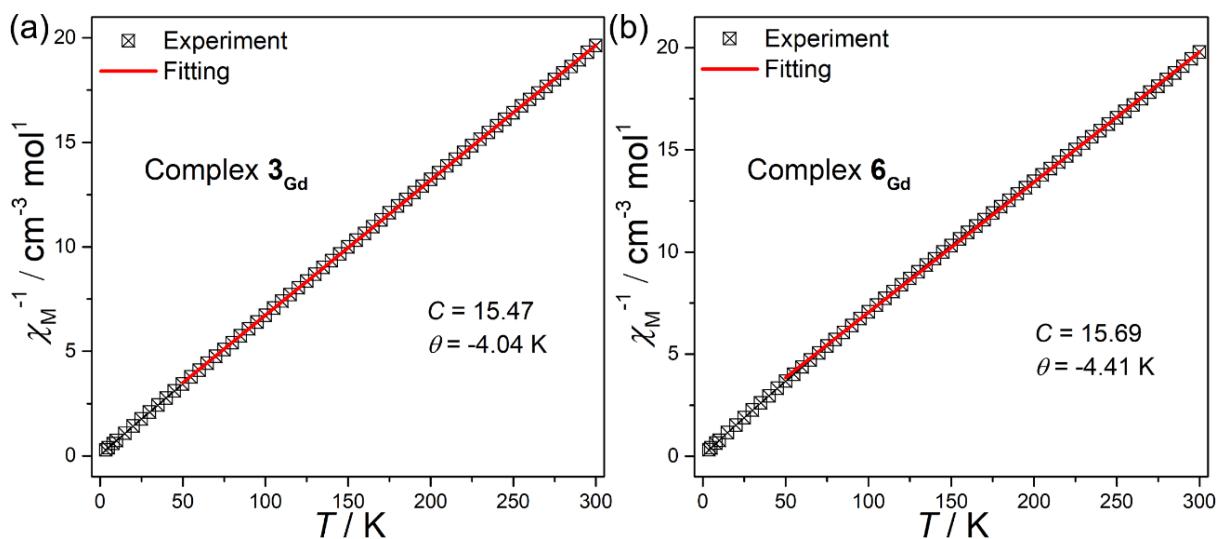
Fig. S6. The plot of $1/\chi_M$ versus T for 3_{Gd} (a)and 6_{Gd} (b), and the linear fit of Curie-Weiss law. The solid lines represent the best fits according to the Curie-Weiss law.
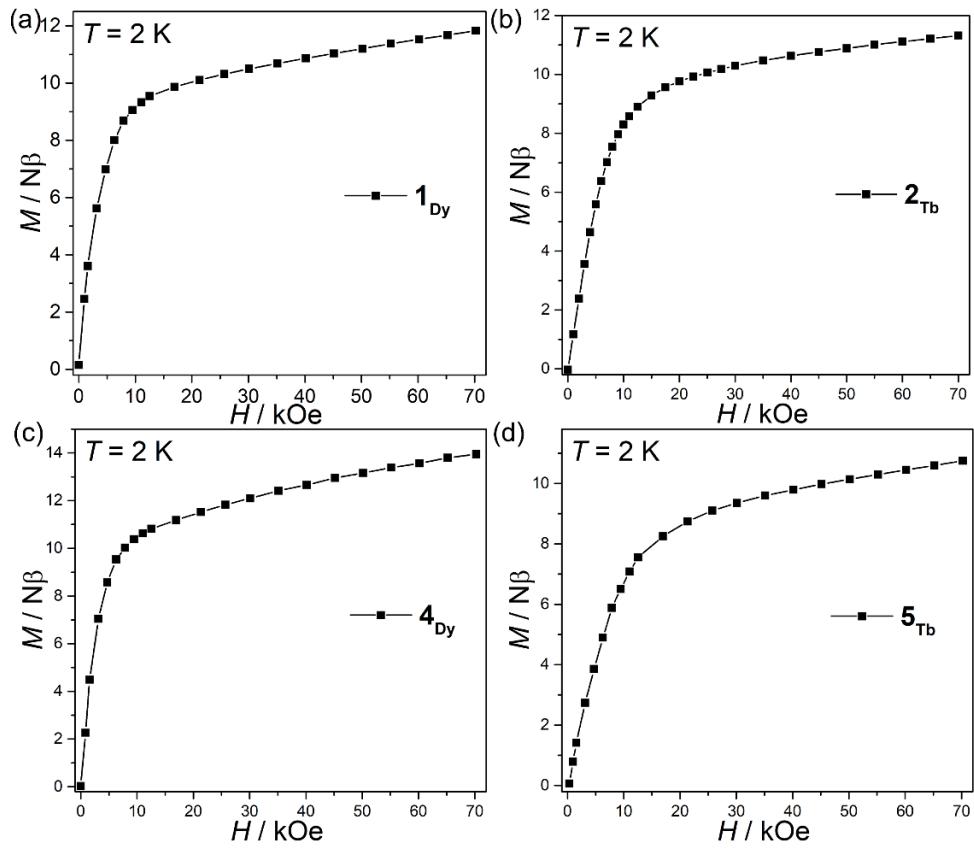
Fig. S7. Field dependent magnetization curves for compounds 1_{Dy}, 2_{Tb}, 4_{Dy} and 5_{Tb} at 2.0 K.
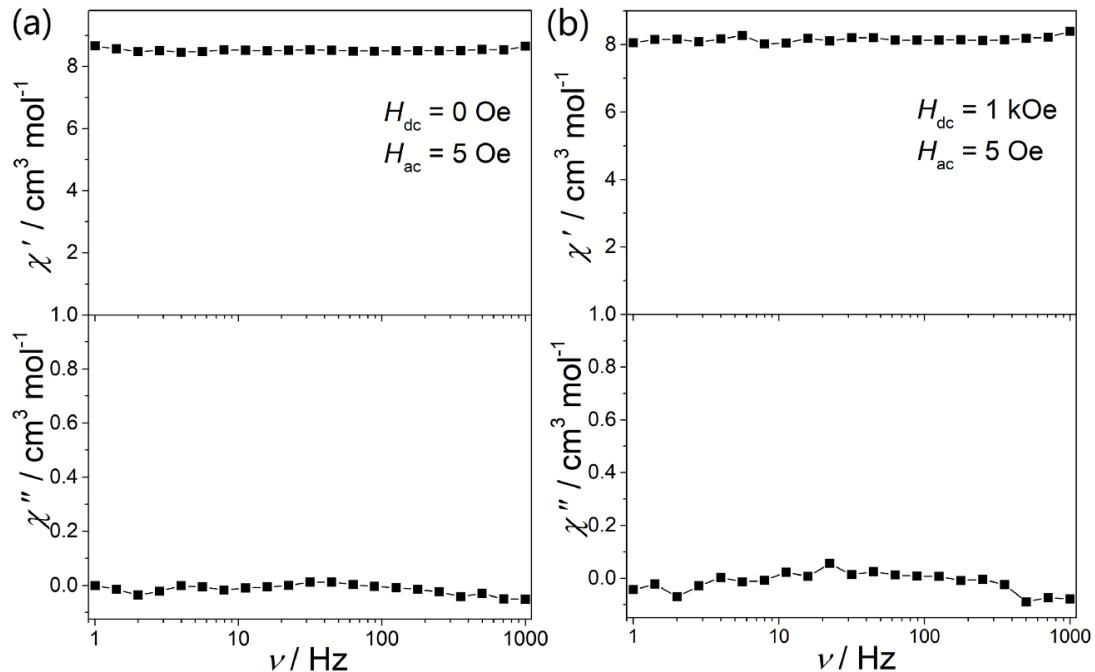
Fig. S8. Frequency dependent in-phase (χ') and out-of phase (χ'') signals of the ac susceptibility for 2_{Tb} under applied H_{dc} = 0 and 1 kOe.
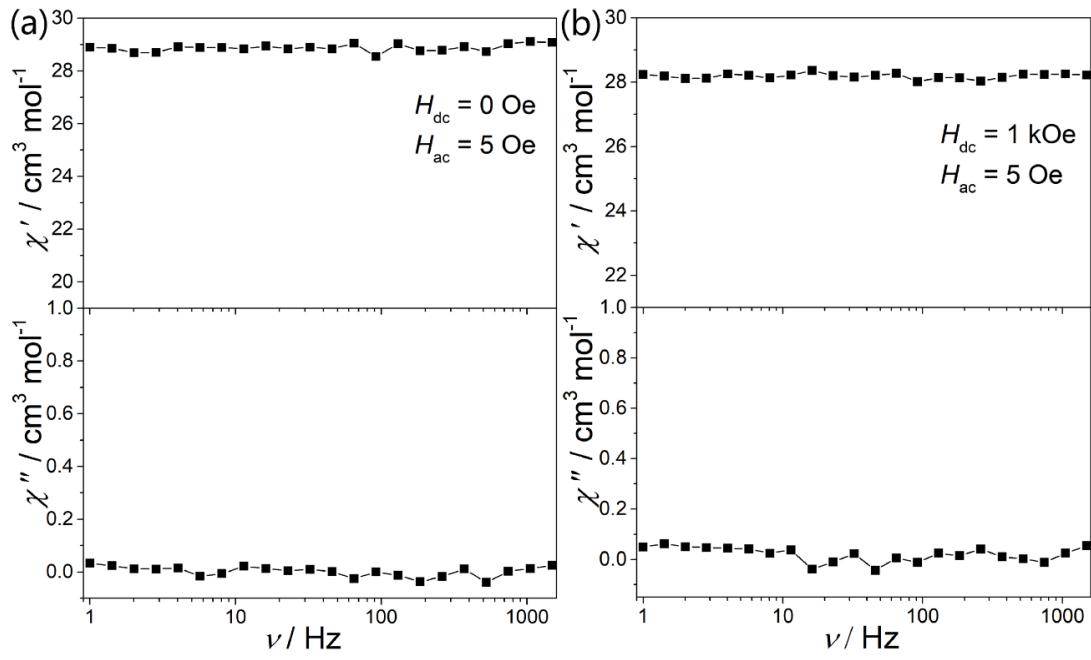
Fig. S9. Frequency dependent in-phase (χ') and out-of phase (χ'') signals of the ac susceptibility for **5$_{Tb}$** under applied H_{dc} = 0 and 1 kOe.
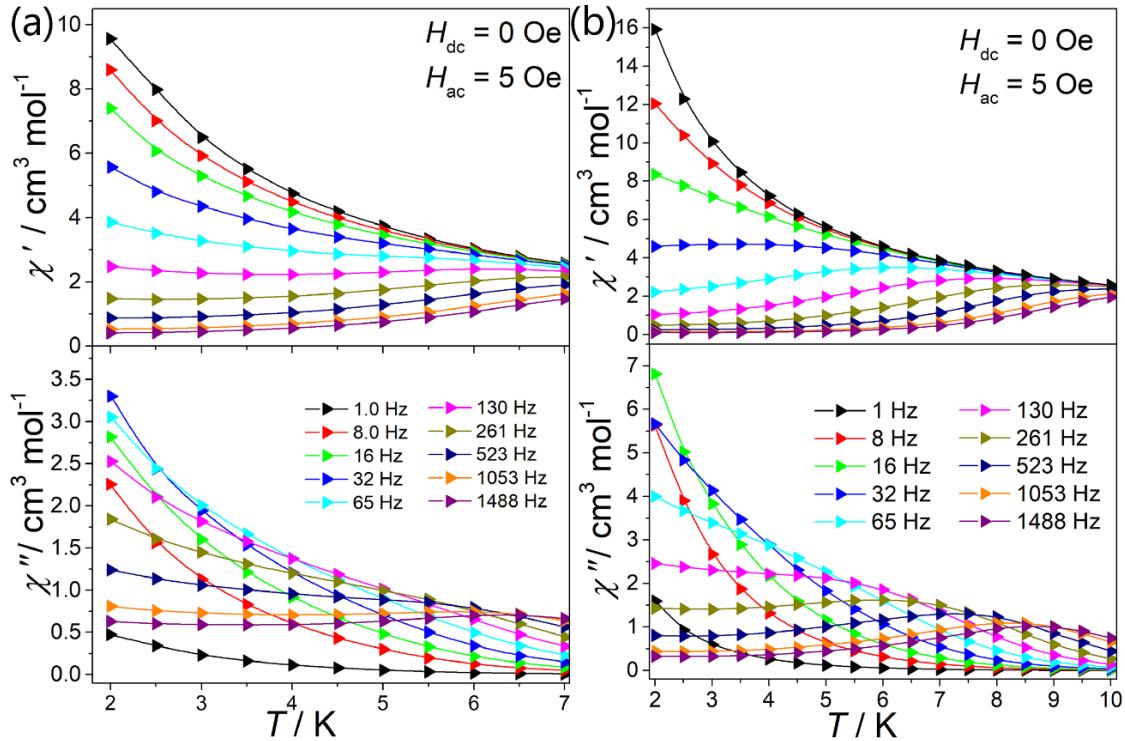
Fig. S10. Temperature dependent in-phase (χ') and out-of phase (χ'') signals of the ac susceptibility for **1$_{Dy}$** and **4$_{Dy}$** under zero dc field.

Electrostatic model for 1$_{Dy}$ and 4$_{Dy}$

Electrostatic calculations. The electrostatic calculations were performed on the complete monometallic structures using the X-Ray geometry with no optimization. The charge on the ligands is expected to have a dominant role in the determination of the electrostatic potential experienced by Dy^{III}, and thus, the electrostatic field produced by charge on the ligands could be calculated within a minimal valence bond model. Within this model, the charge is delocalized as a resonance hybrid that can be seen as a weighted sum of all "chemically stable" Lewis structures. The electrostatic calculations were implemented in a MAGELLAN program. This model does not take account different electron withdrawing or donating groups in the charged ligands. The partial charges assigned to the formally charged ligands in complexes 1$_{Dy}$ and 4$_{Dy}$ were shown in Fig. S11.
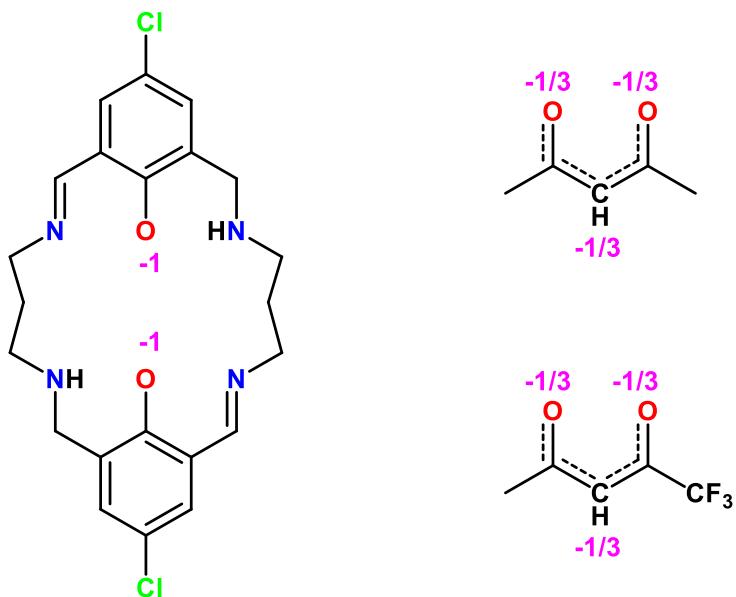
Fig. S11. Partial charges assigned to the formally charged ligands in complexes 1$_{Dy}$ and 4$_{Dy}$.
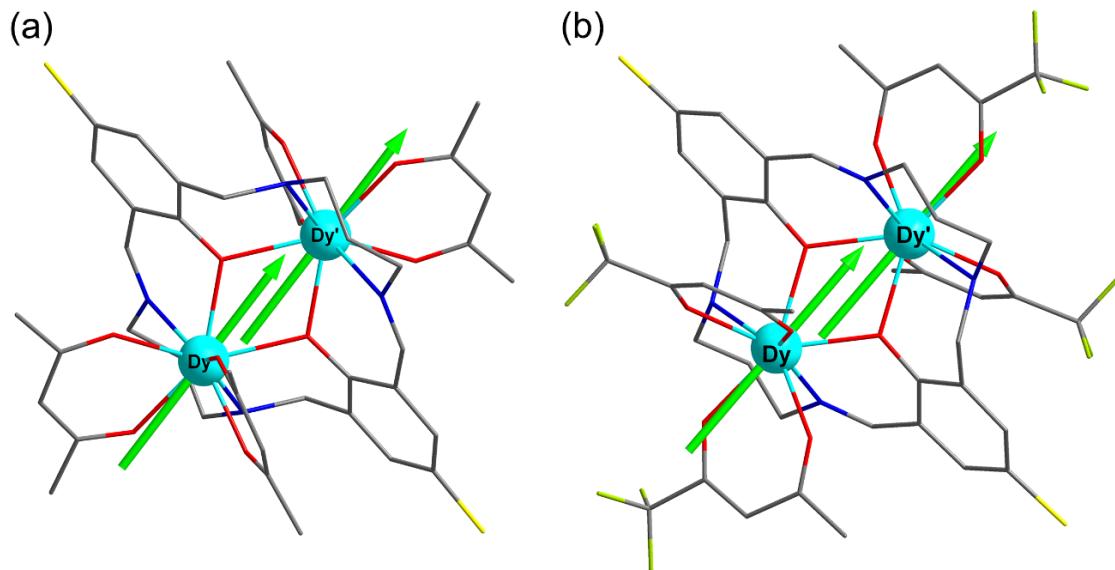
Fig. S12. Ground state magnetic anisotropy of complexes 1_{Dy} (a) and 4_{Dy} (b). The Green rods represent the orientations of the electrostatic anisotropy axes for each of the two Dy^{III} ions in complexes 1_{Dy} and 4_{Dy} as calculated by electrostatic model.

Table S1. Selected bond lengths (Å) for complex 1_{Dy}–6_{Gd}.

	1_{Dy}	2_{Tb}	3_{Gd}	4_{Dy}	5_{Tb}	6_{Gd}
Ln–O1	2.302(2)	2.306(2)	2.327(2)	2.2990(19	2.307(2)	2.328(2)
Ln–O1′	2.371(2)	2.378(3)	2.405(2)	2.3402(19)	2.353(2)	2.381(2)
Ln–O2	2.321(2)	2.309(2)	2.357(2)	2.335(2)	2.349(2)	2.377(2)
Ln–O3	2.302(2)	2.330(2)	2.330(3)	2.324(2)	2.334(2)	2.358(2)
Ln–O4	2.323(2)	2.320(3)	2.345(3)	2.341(2)	2.349(3)	2.374(2)
Ln–O5	2.337(2)	2.338(3)	2.354(3)	2.364(2)	2.372(3)	2.393(2)
Ln–N1	2.595(2)	2.601(3)	2.624(3)	2.573(2)	2.592(3)	2.608(2)
Ln–N2	2.588(2)	2.593(3)	2.611(3)	2.564(2)	2.572(3)	2.595(2)
Ln···Ln′	3.891(1)	3.901(2)	3.939(1)	3.874(1)	3.895(1)	3.935(1)

Table S2. SHAPE analysis of the Ln^{III} ion in complexes 1_{Dy}–6_{Gd}.

Label	Shape	Symmetry	1_{Dy}	2_{Tb}	3_{Gd}	4_{Dy}	5_{Tb}	6_{Gd}
OP-8	Octagon	D_{8h}	29.655	29.746	29.967	29.614	29.667	29.812
HPY-8	Heptagonal pyramid	C_{7v}	23.089	22.981	22.916	23.103	23.084	22.967
HBPY-8	Hexagonal bipyramid	D_{6h}	15.228	15.228	15.136	15.982	15.928	15.768
CU-8	Cube	O_h	9.516	9.474	9.373	9.645	9.562	9.415
SAPR-8	Square antiprism	D_{4d}	**0.711**	**0.715**	**0.738**	**0.719**	**0.732**	**0.759**
TDD-8	Triangular dodecahedron	D_{2d}	1.928	1.927	1.908	2.262	2.222	2.173
JGBF-8	Johnson gyrobifastigium J26	D_{2d}	14.799	14.738	14.685	15.450	15.464	15.376
JETBPY-8	Johnson elongated triangular bipyramid J14	C_{3h}	26.661	26.599	26.499	26.851	26.789	26.805
JBTPR-8	Biaugmented trigonal prism J50	C_{2v}	2.858	2.850	2.889	2.686	2.706	2.687
BTPR-8	Biaugmented trigonal prism	C_{2v}	2.403	2.394	2.411	2.209	2.194	2.158
JSD-8	Snub diphenoid J84	D_{2d}	4.960	4.986	5.014	5.026	5.091	5.073
TT-8	Triakis tetrahedron	T_d	10.226	10.185	10.080	10.484	10.400	10.266
ETBPY-8	Elongated trigonal bipyramid	D_{3h}	22.882	22.798	22.704	22.496	22.423	22.359

Table S3. Relaxation fitting parameters from the least-square fitting of the Cole-Cole plots of 1_{Dy} under 2.0 K-7.0 K according to the generalized Debye model.

T / K	χ_S / cm^{3}mol^{-1}K	χ_T / cm^{3}mol^{-1}K	τ / s	α	R
2.0	0.09772	10.3948	0.00421	0.27892	0.10645
2.5	0.11156	8.22078	0.00338	0.2899	0.09519
3.0	0.14739	6.72181	0.00265	0.29167	0.07716
3.5	0.17321	5.68125	0.0021	0.29922	0.06261
4.0	0.20167	4.88581	0.00162	0.30654	0.04711
4.5	0.23683	4.26460	0.0012	0.31286	0.0359
5.0	0.27400	3.78384	8.44849E-4	0.31827	0.0291
5.5	0.30472	3.3875	5.49351E-4	0.31964	0.01956
6.0	0.32661	3.07392	3.37829E-4	0.32397	0.01335
6.5	0.32983	2.80968	1.93784E-4	0.33039	0.00906
7.0	0.29719	2.59099	1.07626E-4	0.34125	0.00549

Table S4. Relaxation fitting parameters from the least-square fitting of the Cole-Cole plots of **4Dy** under 2.0 K-10.0 K according to the generalized Debye model.

T / K	χ_S / cm^{3}mol^{-1}K	χ_T / cm^{3}mol^{-1}K	τ / s	α	R
2.0	6.86965E-4	16.1494	0.00931	0.12744	0.32776
2.5	0.08033	12.5575	0.00705	0.11972	0.30968
3.0	0.06263	10.2857	0.00549	0.12471	0.10584
3.5	0.05662	8.59557	0.00426	0.12479	0.07755
4.0	0.05857	7.34936	0.0033	0.12304	0.06592
4.5	0.05897	6.38985	0.00253	0.12444	0.05484
5.0	0.06854	5.66259	0.00193	0.12219	0.04426
5.5	0.07805	5.10091	0.00149	0.12397	0.0393
6.0	0.09391	4.62589	0.00114	0.12211	0.03583
6.5	0.11715	4.21506	8.46843E-4	0.1233	0.02997
7.0	0.1517	3.86827	6.21474E-4	0.125	0.02964
7.5	0.18891	3.57869	4.43622E-4	0.13162	0.02116
8.0	0.2364	3.32169	3.06309E-4	0.13671	0.01664
8.5	0.31043	3.0887	2.0806E-4	0.1361	0.01211
9.0	0.37057	2.89992	1.38155E-4	0.14039	0.00727
9.5	0.50749	2.73676	9.7337E-5	0.1303	0.00577
10.0	0.66957	2.58259	6.95075E-5	0.11459	0.00329

Table S5. Parameters fitted from the Arrhenius plots considering multiple relaxation processes for **1Dy** and **4Dy**.

	Value	Standard error	R^2
Complex **1Dy**			
n	2.88	0.15	
C	8.19	1.91	
τ_{QTM}	0.0056	3×10^{-4}	0.9998
τ_0	1.1×10^{-8} s	3×10^{-9}	
U_{eff}	66.7 K	2.4	
Complex **4Dy**			
n	2.86	0.07	
C	4.40	0.53	
τ_{QTM}	0.013	6×10^{-4}	0.9998
τ_0	3.3×10^{-8} s	6×10^{-9}	
U_{eff}	79.0 K	1.8	

Computational details

Both of binuclear complexes 1_{Dy} and 4_{Dy} with central symmetrical structures have one type of magnetic center Dy^{III} ion. Complete-active-space self-consistent field (CASSCF) calculations on individual Dy^{III} fragments for 1_{Dy} and 4_{Dy} (see Figure S13 for the calculated complete structures of 1_{Dy} and 4_{Dy}) on the basis of single-crystal X-ray determined geometry have been carried out with MOLCAS 8.4[S1] program package. Each individual Dy^{III} fragment in 1_{Dy} and 4_{Dy} was calculated keeping the experimentally determined structure of the corresponding compound while replacing the neighboring Dy^{III} ion by diamagnetic Lu^{III}.

The basis sets for all atoms are atomic natural orbitals from the MOLCAS ANO-RCC library: ANO-RCC-VTZP for Dy^{III}; VTZ for close N and O; 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. Active electrons in 7 active spaces 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 for Dy^{II}. SINGLE_ANISO[S2] program was used to obtain the energy levels, g tensors, magnetic axes, *et al.,* based on the above CASSCF/RASSI-SO calculations.

1_{Dy} 4_{Dy}
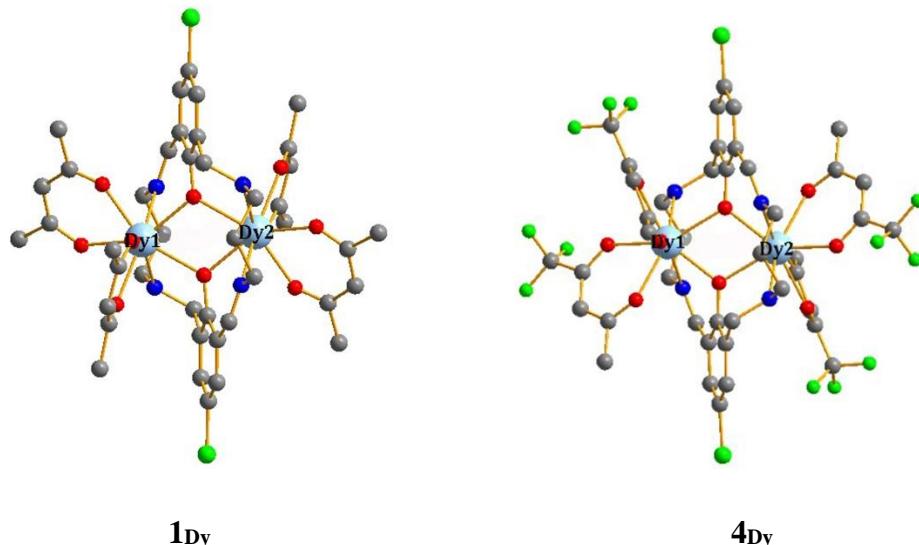
Fig. S13. Calculated complete structures of complexes 1_{Dy} and 4_{Dy}; H atoms are omitted.

Table S6. Calculated energy levels (cm^{-1}), g (g_x, g_y, g_z) tensors and predominant m_J values of the lowest eight Kramers doublets (KDs) of individual Dy^{III} fragments for complexes **1$_{Dy}$** and **4$_{Dy}$** using CASSCF/RASSI-SO with MOLCAS 8.4.

KDs	**1$_{Dy}$**			**4$_{Dy}$**		
	E/cm^{-1}	g	m_J	E/cm^{-1}	g	m_J
1	0.0	0.017 0.034 19.159	±15/2	0.0	0.005 0.009 19.498	±15/2
2	96.9	0.245 0.305 15.736	±13/2	143.1	0.146 0.240 15.964	±13/2
3	175.1	0.177 0.604 12.802	±11/2	224.4	0.561 0.785 13.214	±11/2
4	231.5	2.316 2.776 9.962	±7/2	304.5	0.946 2.062 10.678	±9/2
5	272.0	8.496 6.080 3.486	±3/2	378.2	0.122 3.616 7.278	±5/2

6	313.3	1.500 2.107 14.679	±1/2	430.3	9.628 7.452 3.313	±1/2
7	355.0	0.358 1.043 18.087	±5/2	490.1	0.520 1.273 18.407	±3/2
8	491.4	0.004 0.008 19.753	±9/2	591.0	0.015 0.020 19.775	±7/2

Table S7. Wave functions with definite projection of the total moment | m_J > for the lowest two KDs of individual Dy^{III} fragments for complexes 1_{Dy} and 4_{Dy}.

	E/cm^{-1}	wave functions
1_{Dy}	0.0	88.3%|±15/2>+8.0%|±11/2>
	96.9	72.5%|±13/2>+18.0%|±9/2>
4_{Dy}	0.0	93.7%|±15/2>
	143.1	68.5%|±13/2>+21.9%|±9/2>

To fit the exchange interactions in complexes 1_{Dy} and 4_{Dy}, we took two steps to obtain them. Firstly, we calculated individual Dy^{III} fragments using CASSCF/RASSI-SO to obtain the corresponding magnetic properties. Then, the exchange interactions between the magnetic centers were considered within the Lines model,[S3] while the account of the dipole-dipole magnetic couplings were treated exactly. The Lines model is effective and has been successfully used widely in the research field of d and f-elements single-molecule magnets.[S4]

For complexes 1_{Dy} and 4_{Dy}, there is only one type of $\tilde{J}_1$.

The Ising exchange Hamiltonian is:

$$\hat{H}_{exch} = -\tilde{J}\hat{\tilde{S}}_{Dy1}\hat{\tilde{S}}_{Dy2} \qquad (1)$$

The $\tilde{J}_{total}$ is the parameter of the total magnetic interaction ($\tilde{J}_{total} = \tilde{J}_{dip} + \tilde{J}_{exch}$) between magnetic center ions. The $\tilde{S}_{Dy} = 1/2$ is the ground pseudospin on the Dy^{III} site. The dipolar magnetic coupling can be calculated exactly, while the exchange coupling constant was fitted through comparison of the computed and measured magnetic susceptibilities using the POLY_ANISO program.[S2]

Table S8. Exchange energies E (cm^{-1}), the energy difference between each exchange doublets Δ_t (cm^{-1}) and the main values of the g_z for the lowest two exchange doublets of **1**$_{\text{Dy}}$ and **4**$_{\text{Dy}}$.

	1$_{\text{Dy}}$			**4**$_{\text{Dy}}$		
	E	Δ_t	g_z	E	Δ_t	g_z
1$_{\text{Dy}}$	0.00	0.72×10^{-5}	38.318	0.00	0.34×10^{-6}	38.997
4$_{\text{Dy}}$	1.29	0.12×10^{-4}	0.000	1.86	0.62×10^{-6}	0.000

Reference

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