

Strong intramolecular Dy^{III}–Dy^{III} magnetic couplings up to 15.00 cm^{−1} in phenoxy-bridged dinuclear 4f complexes

Wei Zhang,^a Shao-Min Xu,^a Zhao-Xia Zhu,^a Jing Ru,^{*b} Yi-Quan Zhang^{*c} and Min-Xia Yao^{*a}

^a College of Chemistry & Molecular Engineering, Nanjing Tech University, Nanjing, 211816, P. R. China.

^b School of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng, 252059, P. R. China

^c Jiangsu Key Lab for NSLSCS, School of Physical Science and Technology, Nanjing Normal University, Nanjing 210023, China

Table S1 Selected bond lengths (Å) and angles (°) for **1–3**.

1		2		3	
Gd(1)–O(1)	2.317(3)	Tb(1)–O(1)	2.304(5)	Dy(1)–O(1)	2.298(6)
Gd(1)–O(2)	2.325(3)	Tb(1)–O(2)	2.306(5)	Dy(1)–O(2)	2.300(6)
Gd(1)–O(3)	2.332(2)	Tb(1)–O(3)	2.320(5)	Dy(1)–O(3)	2.320(6)
Gd(1)–O(4)	2.332(3)	Tb(1)–O(4)	2.322(4)	Dy(1)–O(4)	2.319(6)
Gd(1)–O(6)	2.370(2)	Tb(1)–O(6)	2.357(4)	Dy(1)–O(6)	2.302(6)
Gd(1)–O(6)'	2.332(2)	Tb(1)–O(6)'	2.324(4)	Dy(1)–O(6)'	2.357(5)
Gd(1)–N(1)	2.604(3)	Tb(1)–N(1)	2.593(6)	Dy(1)–N(1)	2.579(8)
Gd(1)–N(2)	2.601(4)	Tb(1)–N(2)	2.605(6)	Dy(1)–N(2)	2.590(9)
O(1)–Gd(1)–O(2)	75.35(10)	O(1)–Tb(1)–O(2)	76.02(17)	O(1)–Dy(1)–O(2)	76.3(2)
O(1)–Gd(1)–O(3)	78.26(9)	O(1)–Tb(1)–O(3)	77.86(17)	O(1)–Dy(1)–O(3)	77.7(2)
O(1)–Gd(1)–O(4)	110.68(9)	O(1)–Tb(1)–O(4)	110.21(16)	O(1)–Dy(1)–O(4)	110.0(2)
O(1)–Gd(1)–O(6)	79.53(9)	O(1)–Tb(1)–O(6)	79.91(16)	O(1)–Dy(1)–O(6)	146.0(2)
O(1)–Gd(1)–O(6)'	145.84(9)	O(1)–Tb(1)–O(6)'	145.86(16)	O(1)–Dy(1)–O(6)'	80.3(2)
O(1)–Gd(1)–N(1)	76.34(10)	O(1)–Tb(1)–N(1)	75.84(16)	O(1)–Dy(1)–N(1)	75.6(2)
O(1)–Gd(1)–N(2)	142.83(10)	O(1)–Tb(1)–N(2)	143.84(18)	O(1)–Dy(1)–N(2)	143.7(3)
O(2)–Gd(1)–O(3)	73.93(9)	O(2)–Tb(1)–O(3)	73.44(16)	O(2)–Dy(1)–O(3)	74.5(2)
O(2)–Gd(1)–O(4)	143.55(9)	O(2)–Tb(1)–O(4)	143.49(16)	O(2)–Dy(1)–O(4)	144.1(2)
O(2)–Gd(1)–O(6)	106.25(9)	O(2)–Tb(1)–O(6)	85.27(16)	O(2)–Dy(1)–O(6)	105.9(2)
O(2)–Gd(1)–O(6)'	85.06(9)	O(2)–Tb(1)–O(6)'	106.73(16)	O(2)–Dy(1)–O(6)'	83.9(2)
O(2)–Gd(1)–N(1)	142.50(10)	O(2)–Tb(1)–N(1)	142.80(17)	O(2)–Dy(1)–N(1)	142.1(2)
O(2)–Gd(1)–N(2)	74.56(11)	O(2)–Tb(1)–N(2)	75.29(18)	O(2)–Dy(1)–N(2)	75.4(3)
O(3)–Gd(1)–O(6)	152.58(9)	O(3)–Tb(1)–O(4)	73.03(15)	O(3)–Dy(1)–O(6)'	152.2(2)

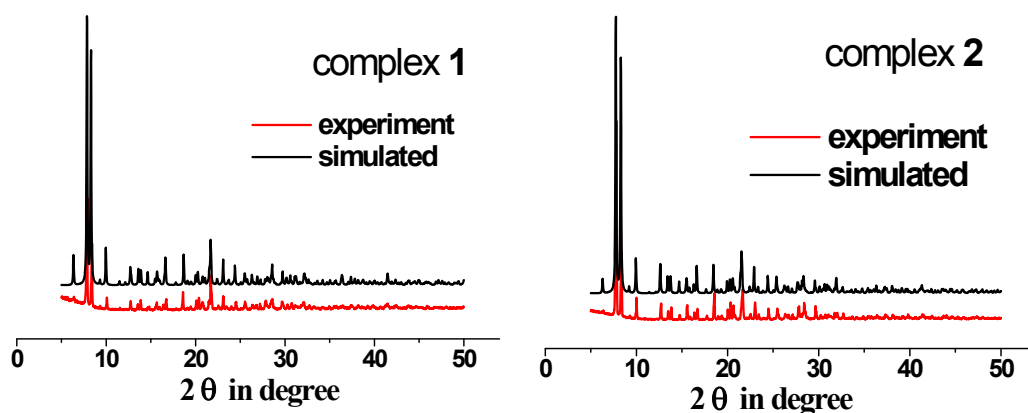
* To whom correspondence should be addressed. Email: yaomx@njtech.edu.cn; hptx214@163.com; zhangyiquan@nynu.edu.cn Fax: +86-25-58139528.

O(3)-Gd(1)-N(1)	123.07(9)	O(3)-Tb(1)-O(6)	152.26(16)	O(3)-Dy(1)-N(1)	122.7(2)
O(3)-Gd(1)-N(2)	72.85(10)	O(3)-Tb(1)-O(6)'	135.10(16)	O(3)-Dy(1)-N(2)	73.1(3)
O(3)-Gd(1)-O(4)	72.45(9)	O(3)-Tb(1)-N(1)	122.92(17)	O(4)-Dy(1)-O(3)	72.7(2)
O(4)-Gd(1)-O(6)	131.18(9)	O(3)-Tb(1)-N(2)	73.21(18)	O(4)-Dy(1)-O(6)'	131.7(2)
O(4)-Gd(1)-N(1)	70.48(9)	O(4)-Tb(1)-O(6)	131.00(15)	O(4)-Dy(1)-N(1)	70.5(2)
O(4)-Gd(1)-N(2)	82.42(10)	O(4)-Tb(1)-O(6)'	87.98(15)	O(4)-Dy(1)-N(2)	81.5(2)
O(6)-Gd(1)-N(1)	65.95(9)	O(4)-Tb(1)-N(1)	70.22(16)	O(6)-Dy(1)-O(3)	136.1(2)
O(6)-Gd(1)-N(2)	118.73(9)	O(4)-Tb(1)-N(2)	81.61(17)	O(6)-Dy(1)-O(4)	88.2(2)
O(6)'-Gd(1)-O(3)	135.63(9)	O(6)-Tb(1)-N(1)	66.24(16)	O(6)-Dy(1)-O(6)'	66.4(2)
O(6)'-Gd(1)-O(4)	88.47(9)	O(6)-Tb(1)-N(2)	118.85(17)	O(6)-Dy(1)-N(1)	84.5(2)
O(6)'-Gd(1)-O(6)	66.82(11)	O(6)'-Tb(1)-O(6)	66.67(18)	O(6)-Dy(1)-N(2)	65.1(2)
O(6)'-Gd(1)-N(1)	84.47(9)	O(6)'-Tb(1)-N(1)	84.22(16)	O(6)'-Dy(1)-N(1)	66.8(2)
O(6)'-Gd(1)-N(2)	65.02(9)	O(6)'-Tb(1)-N(2)	64.94(17)	O(6)'-Dy(1)-N(2)	118.4(2)
N(1)-Gd(1)-N(2)	139.67(11)	N(1)-Tb(1)-N(2)	138.86(18)	N(1)-Dy(1)-N(2)	139.2(3)

Table S2 Continuous Shape Measures (CShMs) of the coordination geometry for Ln^{III} ions in compounds **1-3**.

Complex	CU-8	SAPR-8	TDD-8
1	9.759	1.410	2.901
2	9.970	1.384	2.801
3	9.781	1.353	2.745

CU-8	O _h	Cube
SAPR-8	D _{4d}	Square antiprism
TDD-8	D _{2d}	Triangular dodecahedron



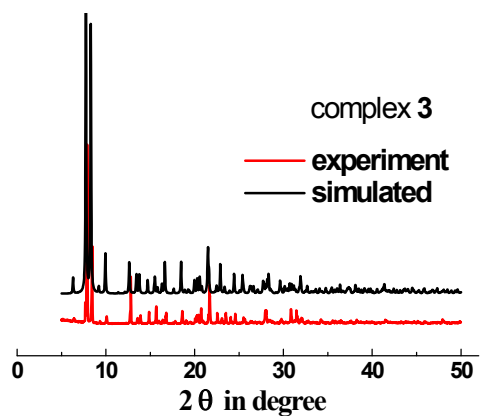


Fig. S1 PXRD patterns for complexes 1-3.

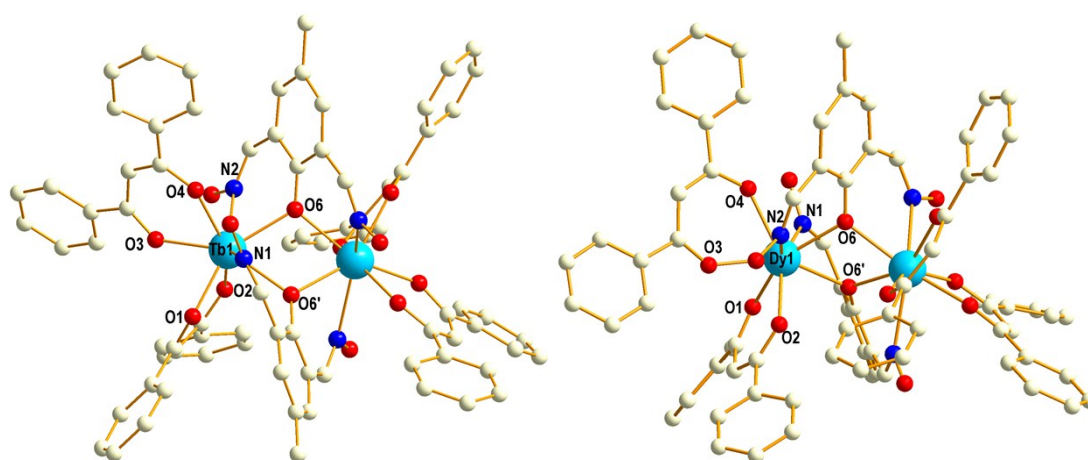


Fig. S2. Molecular structures of $[\text{Tb}_2(\text{dbm})_2(\text{LH}_2)_2] \cdot \text{H}_2\text{O}$ (**2**, left) and $[\text{Dy}_2(\text{dbm})_2(\text{LH}_2)_2] \cdot \text{H}_2\text{O}$ (**3**, right). Hydrogen atoms and the solvent water molecules have been omitted for clarity.

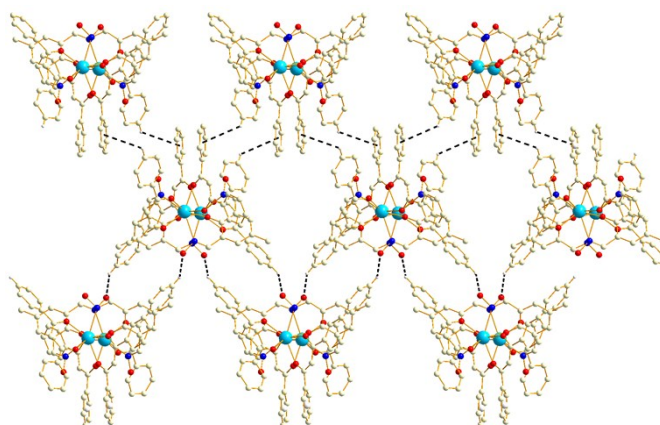


Fig. S3. 2D supramolecular framework of **1** generated by intermolecular $\text{C-H} \cdots \text{O}_{\text{oxime}}$ and $\text{C-H} \cdots \pi$ interactions.

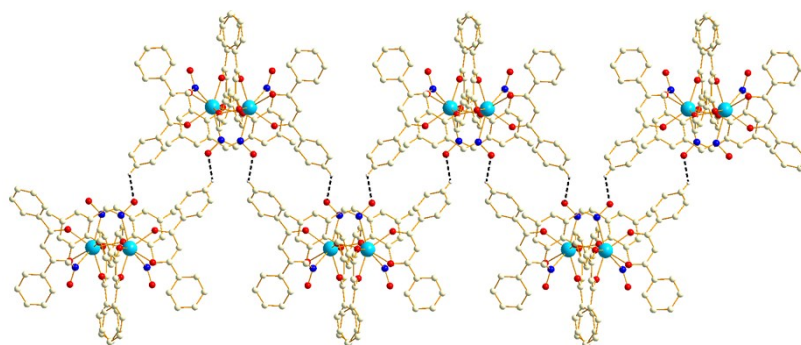


Fig. S4. One-dimensional supramolecular chain of **2** generated by intermolecular C–H $\cdots$ O_{oxime} H-bonding interactions.

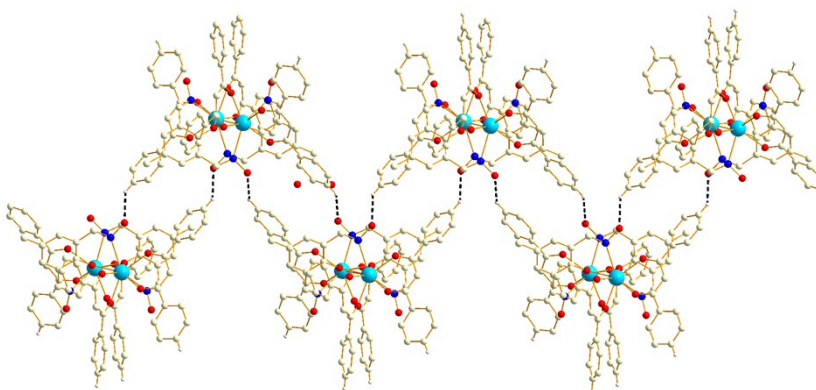


Fig. S5. One-dimensional supramolecular chain of **3** generated by intermolecular C–H $\cdots$ O_{oxime} H-bonding interactions.

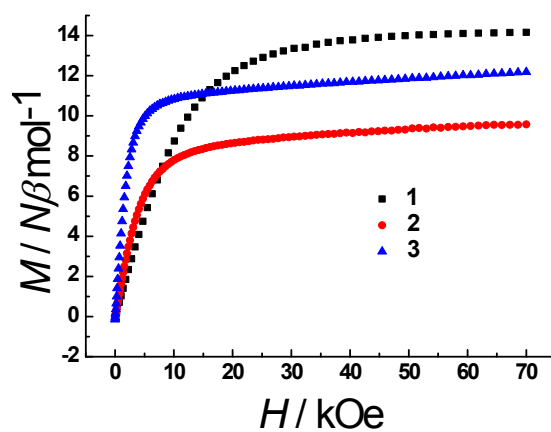


Fig. S6 Field dependence of magnetization for **1-3** at 2.0 K

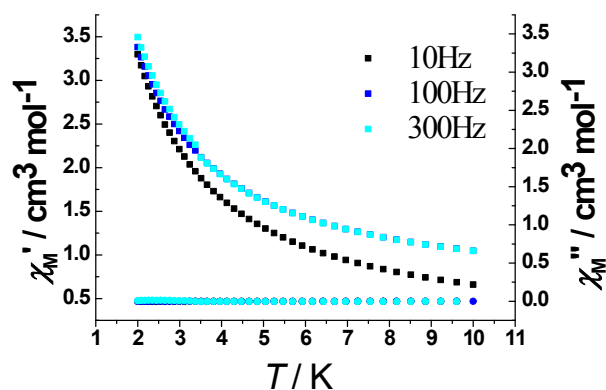


Fig. S7 Temperature dependence of the in-phase χ' and out-of-phase χ'' at different frequencies in a 3 Oe ac field oscillating at 10–300 Hz with a zero dc field for **2**

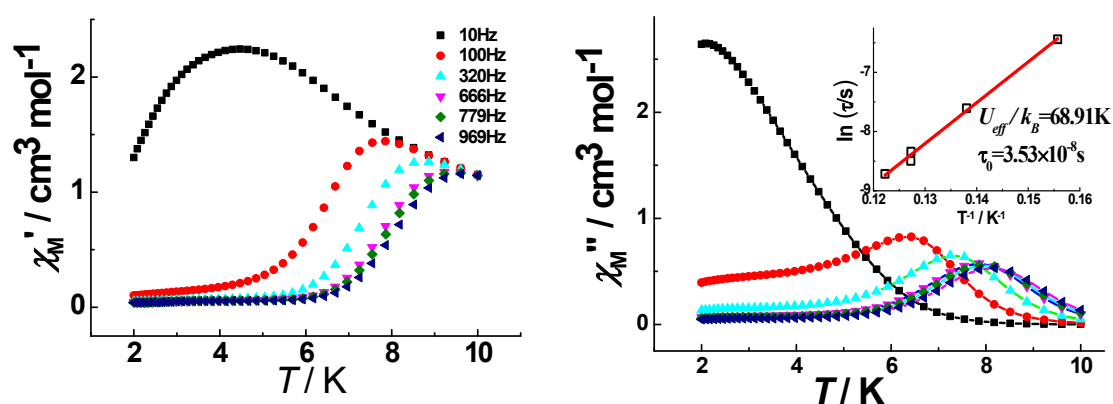


Fig. S8 Temperature dependence of the in-phase χ' and out-of-phase χ'' at different frequencies in a 3 Oe ac field oscillating at 10–969 Hz with a zero dc field for **3**; Inset: The Arrhenius fits for the $\ln \tau$ vs T^{-1} plots from ac- T data of **3**. The red solid line represents the best fits of these data.

Computational details

Although there is only a crystallographically independent Dy^{III} ion in complex **3**, both Dy^{III} fragments are calculated. Complete-active-space self-consistent field (CASSCF) calculations on individual Dy^{III} fragments indicated as Dy1 and Dy1' (see Fig. S9 for the calculated model structures of Dy1 and Dy1') 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 was calculated keeping the experimentally determined structure of the corresponding compound while the other Dy^{III} ion was replaced 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. For individual Dy^{III} fragment, 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). SINGLE_ANISO^{S2} program was used to obtain the energy levels, *g* tensors, *m_J* values, magnetic axes, *et al.*, based on the above CASSCF/RASSI-SO calculations.

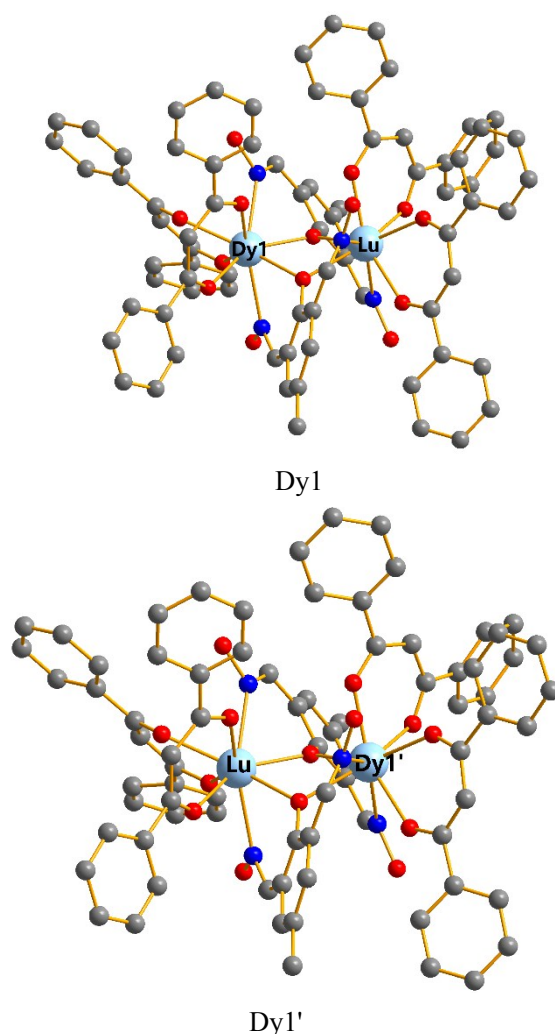


Fig. S9. Calculated model structures of Dy1 and Dy1'; H atoms are omitted.

Table S3. 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 Dy1 and Dy1' using CASSCF/RASSI-SO with MOLCAS 8.4.

KDs	Dy1			Dy1'		
	E/cm^{-1}	g	m_J	E/cm^{-1}	g	m_J
1	0.0	0.012			0.013	
		0.022	$\pm 15/2$	0.0	0.022	$\pm 15/2$
		19.100			19.104	
2	51.9	0.456			0.438	
		0.815	$\pm 13/2$	52.1	0.790	$\pm 13/2$
		15.578			15.569	
3	74.6	1.255			1.240	
		2.228	$\pm 9/2$	75.0	2.176	$\pm 9/2$
		12.620			12.622	
4	122.5	5.388			5.372	
		5.935	$\pm 7/2$	123.1	5.905	$\pm 7/2$
		7.504			7.505	
5	173.5	1.233			1.266	
		2.318	$\pm 3/2$	173.9	2.367	$\pm 3/2$
		11.513			11.493	
6	246.5	0.233			0.233	
		0.353	$\pm 5/2$	246.9	0.351	$\pm 5/2$
		14.445			14.454	
7	388.5	0.154			0.154	
		0.243	$\pm 1/2$	389.0	0.245	$\pm 1/2$
		17.248			17.249	
8	573.5	0.008			0.008	
		0.018	$\pm 11/2$	574.3	0.018	$\pm 11/2$
		19.331			19.331	

Table S4. Wave functions with definite projection of the total moment $|m_J\rangle$ for the lowest two KDs of individual Dy^{III} fragments for Dy1 and Dy1' using CASSCF/RASSI-SO with MOLCAS 8.4.

	E/cm^{-1}	wave functions
Dy1	0.0	$87.27\% \pm 15/2\rangle + 9.50\% \pm 11/2\rangle$
	51.9	$53.03\% \pm 13/2\rangle + 11.20\% \pm 11/2\rangle + 16.42\% \pm 9/2\rangle + 8.04\% \pm 5/2\rangle$
Dy1'	0.0	$87.49\% \pm 15/2\rangle + 9.51\% \pm 11/2\rangle$
	52.1	$53.42\% \pm 13/2\rangle + 11.27\% \pm 11/2\rangle + 16.42\% \pm 9/2\rangle + 7.87\% \pm 5/2\rangle$

To fit the exchange interaction in compound **3**, we took two steps to obtain them. Firstly, we calculated individual Dy^{III} fragment using CASSCF/RASSI-SO to obtain the corresponding magnetic properties. Then, the exchange interaction between the

magnetic centers is considered within the Lines model,^{S3} while the account of the dipole-dipole magnetic coupling is 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}

The Ising exchange Hamiltonians for **3** is:

$$\hat{H}_{exch} = -J \hat{S}_{Dy1}^z \hat{S}_{Dy1'}^z \quad (1)$$

The *J* is parameter of the exchange magnetic interaction between Dy^{III} ions. The $\hat{S}_{Dy}^z = 1/2$ is the ground pseudospin on the Dy^{III} sites. The dipolar magnetic coupling can be calculated exactly, while the exchange coupling constants were fitted through comparison of the computed and measured magnetic susceptibility using the POLY_ANISO program.^{S2}

Table S5. 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 **3**.

	<i>E</i>	Δ_t	<i>g_z</i>
1	0.0	2.3×10^{-6}	37.485
2	7.0	5.7×10^{-6}	7.377

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