The Slow Magnetic Relaxation Regulated by the Coordination Configuration and Intermolecular Dipolar Field in Two Mononuclear Dy^{III} Single-Molecule Magnets (SMMs)

Sheng Zhang,*[a,c] Wenjiao Mo,[a] Bing Yin,*[b] Gaini Zhang,[a] Desuo Yang,*[a] Xingqiang Lü,[c] Sanping Chen*[b]

[a.] *College of Chemistry and Chemical Engineering, Baoji University of Arts and Sciences, Baoji 721013, China.*

[b.] *Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, College of Chemistry and Materials Science, Northwest University, Xi'an, Shaanxi 710069, China.*

[c.] *School of Chemical Engineering, Shaanxi Key Laboratory of Degradable Medical Material, Northwest University, Xi'an 710069, Shaanxi, China*

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

Dy(1)-O(6)	2.305(5)
Dy(1)-O(1)	2.318(6)
Dy(1)-O(4)	2.329(6)
Dy(1)-O(2)	2.327(6)
Dy(1)-O(5)	2.337(5)
Dy(1)-O(3)	2.374(6)
Dy(1)-N(1)	2.520(7)
Dy(1)-N(2)	2.540(7)
O(6)-Dy(1)-O(1)	76.9(2)
O(6)-Dy(1)-O(4)	144.7(2)
O(1)-Dy(1)-O(4)	132.6(2)
O(6)-Dy(1)-O(2)	106.4(2)
O(1)-Dy(1)-O(2)	71.8(2)
O(4)-Dy(1)-O(2)	73.6(2)
O(6)-Dy(1)-O(5)	71.01(19)
O(1)-Dy(1)-O(5)	126.6(3)
O(4)-Dy(1)-O(5)	73.8(2)
O(2)-Dy(1)-O(5)	76.8(2)
O(6)-Dy(1)-O(3)	144.1(2)
O(1)-Dy(1)-O(3)	76.4(2)
O(4)-Dy(1)-O(3)	70.8(2)
O(2)-Dy(1)-O(3)	87.6(2)
O(5)-Dy(1)-O(3)	144.1(2)
O(6)-Dy(1)-N(1)	90.2(2)
O(1)-Dy(1)-N(1)	143.3(2)
O(4)-Dy(1)-N(1)	75.1(2)
O(2)-Dy(1)-N(1)	144.8(2)

O(5)-Dy(1)-N(1)	79.4(3)
O(3)-Dy(1)-N(1)	97.0(2)
O(6)-Dy(1)-N(2)	73.3(2)
O(1)-Dy(1)-N(2)	79.7(3)
O(4)-Dy(1)-N(2)	124.1(3)
O(2)-Dy(1)-N(2)	150.6(2)
O(5)-Dy(1)-N(2)	128.2(2)
O(3)-Dy(1)-N(2)	78.5(2)
N(1)-Dy(1)-N(2)	63.6(2)

Table S2 Selected bond lengths (Å) and angles (°) for **2**.

Dy(1)-O(3)	2.314(5)
Dy(1)-O(2)	2.321(6)
Dy(1)-O(6)	2.325(6)
Dy(1)-O(4)	2.328(6)
Dy(1)-O(1)	2.327(6)
Dy(1)-O(5)	2.327(6)
Dy(1)-N(1)	2.538(8)
Dy(1)-N(2)	2.558(8)
O(3)-Dy(1)-O(2)	75.6(2)
O(3)-Dy(1)-O(6)	77.4(2)
O(2)-Dy(1)-O(6)	74.0(2)
O(3)-Dy(1)-O(4)	72.2(2)
O(2)-Dy(1)-O(4)	121.8(2)
O(6)-Dy(1)-O(4)	139.5(2)
O(3)-Dy(1)-O(1)	115.1(2)
O(2)-Dy(1)-O(1)	71.4(2)
O(6)-Dy(1)-O(1)	138.0(2)
O(4)-Dy(1)-O(1)	80.3(2)
O(3)-Dy(1)-O(5)	80.4(2)
O(2)-Dy(1)-O(5)	141.0(2)
O(6)-Dy(1)-O(5)	71.1(2)
O(4)-Dy(1)-O(5)	77.8(2)
O(1)-Dy(1)-O(5)	147.6(2)
O(3)-Dy(1)-N(1)	146.0(2)
O(2)-Dy(1)-N(1)	82.4(3)
O(6)-Dy(1)-N(1)	71.7(3)
O(4)-Dy(1)-N(1)	141.7(2)
O(1)-Dy(1)-N(1)	80.8(2)
O(5)-Dy(1)-N(1)	102.3(3)
O(3)-Dy(1)-N(2)	148.4(2)
O(2)-Dy(1)-N(2)	132.1(2)

O(6)-Dy(1)-N(2)	120.5(2)
O(4)-Dy(1)-N(2)	78.7(2)
O(1)-Dy(1)-N(2)	70.7(2)
O(5)-Dy(1)-N(2)	81.8(2)
N(1)-Dy(1)-N(2)	63.7(2)

Table S3 Dy^{III} ion geometry analysis by SHAPE 2.1 software.

Configuration	ABOXIY, **1**	ABOXIY, **2**
Square antiprism (D_{4d})	1.885	0.944
Triangular dodecahedron (D_{2d})	0.561	1.712
Johnson gyrobifastigium J26 (D_{2d})	14.375	13.836
Johnson elongated triangular bipyramid J14 (D_{3h})	28.529	26.514
Biaugmented trigonal prism J50 (C_{2v})	2.697	2.280
Biaugmented trigonal prism (C_{2v})	2.126	1.734
Snub siphenoid J84 (D_{2d})	3.417	4.249

S H A P E v2.1 Continuous Shape Measures calculation
(c) 2013 Electronic Structure Group, Universitat de Barcelona
Contact: llunell@ub.edu

Dy structures of **1**

SAPR-8 5 D4d Square antiprism
TDD-8 6 D2d Triangular dodecahedron
JGBF-8 7 D2d Johnson gyrobifastigium J26
JETBPY-8 8 D3h Johnson elongated triangular bipyramid J14
JBTPR-8 9 C2v Biaugmented trigonal prism J50
BTPR-8 10 C2v Biaugmented trigonal prism
JSD-8 11 D2d Snub diphenoid J84

Structure [ML8]	SAPR-8	TDD-8	JGBF-8	JETBPY-8	JBTPR-8	BTPR-8	JSD-8
ABOXIY,	1.885,	0.561,	14.856,	28.529,	2.697,	2.126,	3.417

S H A P E v2.1 Continuous Shape Measures calculation
(c) 2013 Electronic Structure Group, Universitat de Barcelona
Contact: llunell@ub.edu

Dy structures of **2**

SAPR-8 5 D4d Square antiprism
TDD-8 6 D2d Triangular dodecahedron
JGBF-8 7 D2d Johnson gyrobifastigium J26
JETBPY-8 8 D3h Johnson elongated triangular bipyramid J14
JBTPR-8 9 C2v Biaugmented trigonal prism J50
BTPR-8 10 C2v Biaugmented trigonal prism
JSD-8 11 D2d Snub diphenoid J84

Structure [ML8]	SAPR-8	TDD-8	JGBF-8	JETBPY-8	JBTPR-8	BTPR-8	JSD-8
ABOXIY,	0.944,	1.712,	13.836,	26.514,	2.280,	1.734,	4.249

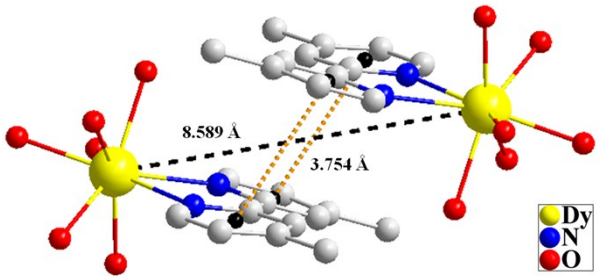
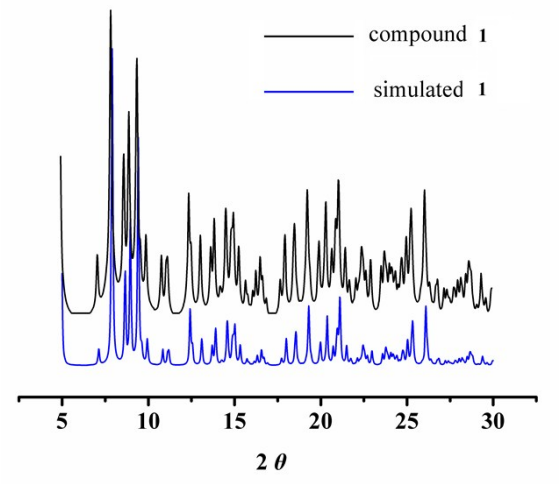
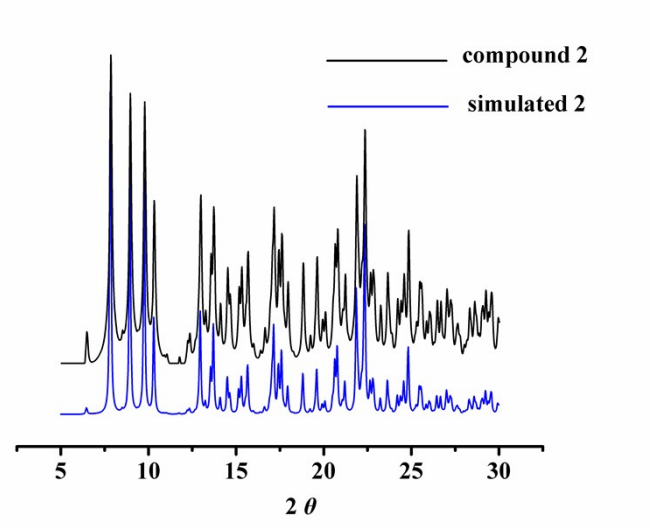


Fig. S1 the neutral molecules are assisted by weak π···π stacking between benzene rings from two adjacent dbpy molecules.



(a)



(b)

Fig. S2 XRPD curves of **1** (a) and **2** (b)**.**

The magnetic susceptibility data of **1** under a zero dc field were described by the sum of two modified Debye functions:[1]

$$\chi''(\omega) = \Delta\chi_1 \frac{(\omega\tau_1)^{1-\alpha_1}\cos(\pi\alpha_1/2)}{1+2(\omega\tau_1)^{1-\alpha_1}\sin(\pi\alpha_1/2)+(\omega\tau_1)^{(2-2\alpha_1)}} + \Delta\chi_2 \frac{(\omega\tau_2)^{1-\alpha_2}\cos(\pi\alpha_2/2)}{1+2(\omega\tau_2)^{1-\alpha_2}\sin(\pi\alpha_2/2)+(\omega\tau_2)^{(2-2\alpha_2)}}$$

$$\Delta\chi_1, \tau_1, \alpha_1, \Delta\chi_2, \tau_2, \alpha_2$$

$$\chi'(\omega) = \chi_{S,tot} + \Delta\chi_1 \frac{1+(\omega\tau_1)^{1-\alpha_1}\sin(\pi\alpha_1/2)}{1+2(\omega\tau_1)^{1-\alpha_1}\sin(\pi\alpha_1/2)+(\omega\tau_1)^{(2-2\alpha_1)}} + \Delta\chi_2 \frac{1+(\omega\tau_2)^{1-\alpha_2}\sin(\pi\alpha_2/2)}{1+2(\omega\tau_2)^{1-\alpha_2}\sin(\pi\alpha_2/2)+(\omega\tau_2)^{(2-2\alpha_2)}}$$

$$\chi_{S,tot}, \Delta\chi_1, \tau_1, \alpha_1, \Delta\chi_2, \tau_2, \alpha_2$$

1 (a) G. Cuccinota, M. Perfetti, J. Luzon, M. Etienne, P. E. Car, A. Caneschi, G. Calvez, K. Bernot and R. Sessoli, *Angew. Chem. Int. Ed.*, 2012, **51**, 1606-1610; (b) M. Grahl, J. Kotzler, and I. Sessler, J. Magn. Magn. Mater. 1990, **90–91**, 187–188; (c) Y. N. Guo, G. F. Xu, W. Wernsdorfer, L. Ungur, Yang Guo, J. K. Tang, H. J. Zhang, Liviu F. Chibotaru, and A. K. Powell, *J. Am. Chem. Soc.*, 2011, **133**, 11948–11951.

Table S4. Relaxation fitting parameters from Least-Squares Fitting of $\chi(\omega)$ data for **1** under a zero applied dc field.

T(K)	$\chi_{S,tot}$ (cm^3mol^{-1})	$\Delta\chi_1$ (cm^3mol^{-1})	$\Delta\chi_2$ (cm^3mol^{-1})	α_1	α_2	τ_1(s)	τ_2(s)
2.0	6.776	1.021	0.350	0.321	0.020	0.00120	0.04370
2.2	6.270	0.898	0.405	0.324	0.006	0.00111	0.04340
2.4	5.762	0.777	0.311	0.327	0.010	0.00109	0.04296
2.6	5.260	0.744	0.300	0.318	0.002	0.00107	0.04059
2.8	4.923	0.653	0.267	0.320	0.022	0.00107	0.03875
3.0	5.242	0.606	0.284	0.305	0.039	0.00106	0.03627
3.2	4.311	0.552	0.250	0.308	0.040	0.00102	0.03142
3.4	4.081	0.493	0.239	0.302	0.059	9.9650×10^{-4}	0.02714
3.6	3.881	0.433	0.297	0.347	0.079	9.6128×10^{-4}	0.02256
3.8	3.679	0.394	0.233	0.287	0.085	9.1259×10^{-4}	0.01817
4.0	3.512	0.349	0.232	0.277	0.098	8.5504×10^{-4}	0.01430
4.2	3.363	0.311	0.224	0.270	0.111	7.8340×10^{-4}	0.01088
4.4	3.220	0.276	0.228	0.258	0.130	7.1608×10^{-4}	0.00833
5.0	2.484	0.250	0.269	0.218	0.141	4.1192×10^{-4}	0.00284
5.5	1.622	0.245	0.307	0.185	0.150	1.8996×10^{-4}	0.00129
6.0	1.100	0.171	0.455	0.138	0.154	1.1802×10^{-4}	8.6186×10^{-4}
6.5	0.702	0.202	0.841	0.092	0.165	9.0160×10^{-5}	6.09071×10^{-4}

The magnetic susceptibility data of **2** under a zero dc field were described by the

modified Debye functions:[2]

$$\chi'(\omega) = \chi_S + (\chi_T - \chi_S)\frac{1+(\omega\tau)^{1-\alpha}\sin(\frac{\pi}{2}\alpha)}{1+2(\omega\tau)^{1-\alpha}\sin(\frac{\pi}{2}\alpha)+(\omega\tau)^{(2-2\alpha)}}$$

$$\chi''(\omega) = (\chi_T - \chi_S)\frac{(\omega\tau)^{1-\alpha}\cos(\frac{\pi}{2}\alpha)}{1+2(\omega\tau)^{1-\alpha}\sin(\frac{\pi}{2}\alpha)+(\omega\tau)^{(2-2\alpha)}}$$

$$\chi''_{\omega=\tau^{-1}} = (\chi_T - \chi_S)\frac{\cos(\frac{\pi}{2}\alpha)}{2+2\sin(\frac{\pi}{2}\alpha)} = \frac{1}{2}(\chi_T - \chi_S)\tan\frac{\pi}{4}(1-\alpha)$$

2 (a) H. X. Zhang, S. Y. Lin, S. F. Xue, C. Wang and J. K. Tang, *Dalton Trans.*, 2014, **43**, 6262−6268; (b) K. Suzuki, R. Sato and N. Mizuno, *Chem. Sci.*, 2013, **4**, 596−600; (c) K. S. Cole and R. H. Cole, *J. Chem. Phys.*, 1941, **9**, 341−351.

Table S5 Relaxation fitting parameters from Least-Squares Fitting of $\chi(\omega)$ data of **2** under a zero applied dc field.

T(K)	$\Delta\chi_1$ (cm^3mol^{-1})	$\Delta\chi_2$ (cm^3mol^{-1})	τ(s)	α
2.0	0.318	2.941	6.8321×10^{-4}	0.151
2.2	0.287	2.673	6.7971×10^{-4}	0.152
2.4	0.264	2.451	6.7689×10^{-4}	0.151
2.6	0.244	2.261	6.7409×10^{-4}	0.150
2.8	0.226	2.103	67010×10^{-4}	0.150
3.0	0.242	2.182	6.6255×10^{-4}	0.148
3.2	0.198	1.845	6.6306×10^{-4}	0.150
3.4	0.189	1.738	6.5858×10^{-4}	0.150
3.6	0.176	1.642	6.5379×10^{-4}	0.149
3.8	0.167	1.557	6.4867×10^{-4}	0.149
4.0	0.159	1.480	6.4192×10^{-4}	0.148
4.2	0.152	1.410	6.3570×10^{-4}	0.147
4.4	0.145	1.346	6.2696×10^{-4}	0.146
4.6	0.139	1.288	6.1728×10^{-4}	0.143
4.8	0.134	1.235	6.0597×10^{-4}	0.141
5.0	0.129	1.186	5.9299×10^{-4}	0.139
5.2	0.123	1.140	5.7810×10^{-4}	0.136
5.5	0.117	1.078	5.5297×10^{-4}	0.131
5.7	0.113	1.040	5.3372×10^{-4}	0.128
6.0	0.106	0.988	5.0223×10^{-4}	0.122
6.5	0.0939	0.911	4.4472×10^{-4}	0.115
7.0	0.0828	0.846	3.8553×10^{-4}	0.111
7.5	0.0711	0.790	3.2798×10^{-4}	0.108
8.0	0.0588	0.740	2.75243×10^{-4}	0.109
10.0	0.0223	0.594	1.2853×10^{-4}	0.123

12.0	0.0558	0.495	6.9160×10^{-5}	0.0834
14.0	0.0127	0.425	2.5046×10^{-5}	0.0790

Table S6 Relaxation fitting parameters from Least-Squares Fitting of $\chi(\omega)$ data of **1** under 1000 Oe dc field.

T(K)	$\Delta\chi_1$ (cm^3mol^{-1})	$\Delta\chi_2$ (cm^3mol^{-1})	τ(s)	α
2	0.291	3.113	8.1696×10^{-4}	0.356
2.2	0.269	2.826	8.0601×10^{-4}	0.354
2.4	0.254	2.589	8.0342×10^{-4}	0.351
2.6	0.231	2.386	7.8291×10^{-4}	0.351
2.8	0.218	2.218	7.6989×10^{-4}	0.347
3	0.208	2.073	7.5666×10^{-4}	0.343
3.2	0.200	1.944	7.3858×10^{-4}	0.337
3.4	0.194	1.832	7.1610×10^{-4}	0.329
3.6	0.190	1.730	6.8764×10^{-4}	0.319
3.8	0.185	1.639	6.4997×10^{-4}	0.307
4	0.180	1.556	6.0408×10^{-4}	0.295
4.2	0.173	1.482	5.5086×10^{-4}	0.283
4.4	0.164	1.414	4.9229×10^{-4}	0.272
4.6	0.153	1.352	4.3111×10^{-4}	0.265
4.8	0.140	1.295	3.7121×10^{-4}	0.262
5	0.127	1.243	3.1574×10^{-4}	0.263

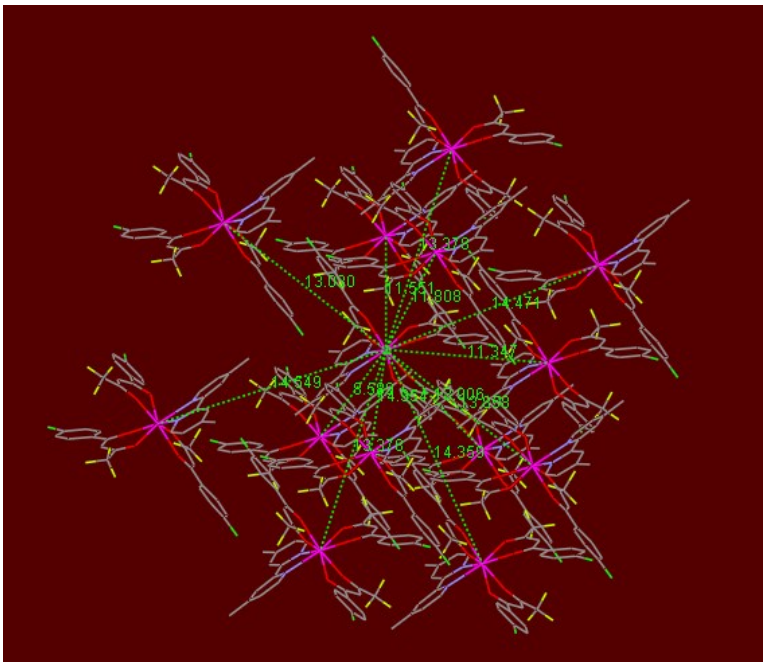


Fig. S3 The nearest-neighbour numbers and distances between adjacent dysprosium centers in **1**.

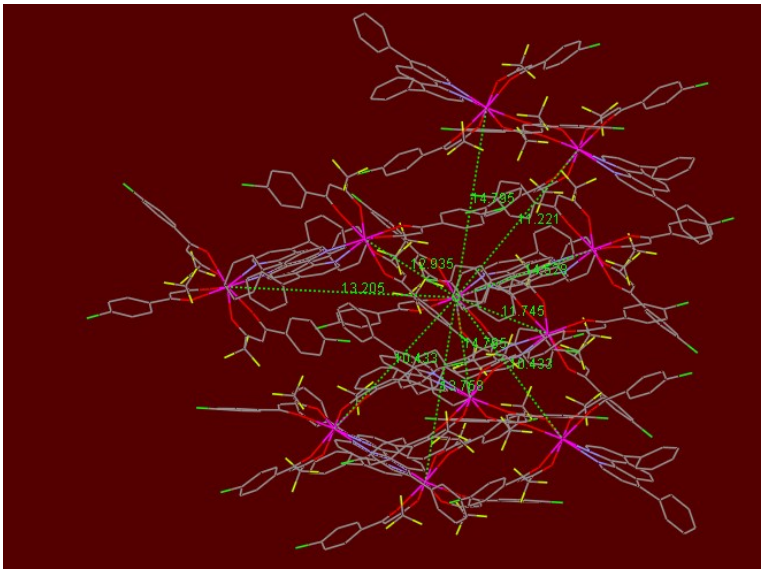


Fig. S4 The nearest-neighbour numbers and distances between adjacent dysprosium centers in compound **2**.

Table S7 The nearest-neighbour distances r_{nn} and use the value R, which is the sum of all the nearest-neighbour r_{nn}^{-3}, as a semi-quantitative parameter describing the internal dipolar field.

1	r_{nn} (Å)	model_dipolar (r_{nn}^{-3})		**2**	r_{nn} (Å)	model_dipolar (r_{nn}^{-3})	
d1	8.589	0.001578237		d1	10.433	0.000881	
d2	13.03	0.000452029		d2	14.795	0.000309	
d4	14.359	0.000337775		d4	14.528	0.000326	
d5	13.906	0.000371872		d5	11.745	0.000617	
d6	13.378	0.000417663		d6	13.768	0.000383	
d7	14.549	0.000324714		d7	13.205	0.000434	
d8	11.551	0.000648845		d8	12.935	0.000462	
d9	13.378	0.000417663		d9	10.433	0.000881	
d10	14.471	0.000329993		d10	14.795	0.000309	
d11	11.347	0.000684474				Average Value	0.004602
d12	13.858	0.000375749					
d13	14.954	0.000299039					
d14	11.808	0.000607395					
		Average Value	0.006845449				