Supplementary Information

for

Magnetic relaxation versus 3D long-range ordering in $\{Dy_2Ba(\alpha\text{–}fur)_8\}_n$ furoate polymer

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S1. Literature survey of dinuclear Dy complexes

Table S1. Summary of Dy-dinuclear complexes in the literature (updated June 2013), classified according to the ferromagnetic or antiferromagnetic character of the dimer interaction. The intradimer distance ($d_{\mathrm{Dy\text{-}Dy}}$), minimum inter-dimer distance (d_{inter}), effective barrier energy (U_{eff}) and characteristic attempt rate (τ_0) for thermally activated slow relaxation process, the quantum tunneling relaxation time (τ_T), and the exchange (J), dipolar (J_{dip}) magnitude of the intradimer interactions are given. For comparison purposes, all coupling parameters are given with the exchange Hamiltonian defined as $H_{ex} = -2\sum_{ij} J_{ij} S_i S_j$ in the effective $S^*=1/2$ model, and J_{ij} expressed in thermodynamic units (K).

Ref.	Formula	Bond type	$d_{\mathrm{Dy\text{-}Dy}}$ [Å]	d_{inter} [Å]	*Dy-X-Dy Angle* [°]	U_{eff}/k_B [K]	τ_0 [s]	τ_{QT} [s]	J_{dip}/k_B [K]	J/k_B [K]
[11]	**ANTIFERRO**									
[a]	$[\{Cp'_2Dy(\mu\text{-}SSiPh_3)\}_2]$	S bridged	4.277	9.7223	101.43	192	2.38×10^{-7}	-	-1.58	-3.15
[b]	$[K(18\text{-}crown\text{-}6)]\{[(Me_3Si)_2N]_2(THF)Dy\}_2(\mu\text{-}\eta^2:\eta^2\text{-}N2)$	N_2^{3-} bridge	4.188	13.917	143.04	178	8×10^{-9}	-	-	-
[c]	$[Dy(hfac)_3(PyNO)]_2$	O bridge of pyridine- N-oxide ligand	4.076	12.476	116.25	167	5.6×10^{-11}	0.45	-	-1.75
[d]	$[(Cp^*_2Dy)_2(\mu\text{-}bpym.)](BPh_4)$	Radical anion $bpym^{\cdot-}$ bridge	6.426	10.341	117.64x2	126.3	1.03×10^{-7}	-	-	-
[e]	$[Dy_2(valdien)_2(NO_3)_2]$	Phenoxo groups of $valdien^{2n}$ ligands	3.768	10.481	108.22	76	6.04×10^{-7}	0.064	-	-0.15
[f]	$[Dy_2(hfac)_6(H_2O)_4pz].2pz$	Pirazine ring bridge	8.09	6.4119		110.78	8.4×10^{-10}	0.0035	-	-
[g]	$[\{Dy(tta)_3(L^1)\}_2]$	Nitroxide groups	4.104	12.399		87.1	5.48×10^{-7}	-	-	-1.64
[h]	$\{[Dy(hfac)_3(PyNONIT)]_2\}_2$	Double-μ2-O atoms of N-oxide groups	4.087	11.844	116.4, 115.5	5	10^{-5}	-	-	-1.79
[10]	**FERROMAGNETIC**									
[a]	$Dy_2ovph_2Cl_2(MeOH)_3].MeCN$	Alkoxido groups of two $ovph^{2-}$ ligands.	3.864	7.5071	112.3-111.5	(A)198 (B)150	7.3×10^{-9} 2.3×10^{-8}	35	3.8	4.2
[b]	$\{Dy(hfac)_3.2H_2O\}_2$	H_2O bridges	3.781	9.848	107.87	92	2.92×10^{-9}	0.0041	0.0018	1.62
[c]	$(2)\{Dy(notpH_4)(NO_3)\text{-}(H_2O)\}_2$	μ_3-O(P) and O-P-O bridges	4.055	9.269	109.5	81.8	1.19×10^{-7}	0.368	-	0.04
[d]	$[Dy_2(L1)_2(acac)_2(H_2O)]$	Phenoxide bridging O atoms	3.84	5.90	110.8	(A)80 (B)36	8.3×10^{-8} 4.2×10^{-7}	-	-	-
[e]	$[Dy_2(hmi)_2(NO_3)_2(MeOH)_2]_\infty.MeCN$ $[Dy_2(hmi)_2(NO_3)_2(MeOH)_2]$	Phenoxide groups of two hmi ligands	3.801 3.750	8.853 9.697	106.41, 107.68	71 56	7×10^{-8} 3×10^{-7}	1.2×10^{-2} 0.3×10^{-2}	-	-
[f]	$(1)[Dy_2(ovph)_2.(NO_3)_2(H_2O)_2]$ $(2)[Dy2(Hovph)(ovph)(NO_3)_2.(H_2O)_4].NO_3.2CH_3OH.3H_2O$	Carbonyl O atoms from the $ovph^{2-}$ ligands	3.8258 3.8926		110.12 111.1	69 1.3	5.3×10^{-7} 10^{-5}	4×10^{-3}	-	-
[g]	$[Dy_2(HBpz_3)_4(\mu\text{-}ox)].2CH_3CN.CH_2Cl_2$	Oxalate bridges	6.143	8.63		42		0.0082	-	-
[h]	$(1)\ [Dy_2(piv)_5(\mu_3\text{-}OH)(H_2O)]_n$	Carboxilate and hydroxyl bridges	3.790- 4.175	4.908	100.22-107.7	4.5	1.1×10^{-7}		- -	- -
This work	$\{\mathbf{Dy_2Ba(\alpha\text{-}fur)_8}\}_n$	Two furoic bridges	4.471	8.176	Dy-O-C 146.6° O-C-O 120.5°	67.6	9.0×10^{-9}	0.07	0.623	0.528

Table S1 summarizes a list of reported dinuclear Dy-complexes. The type of Dy-Dy bridge, the intradimer Dy distance, the angle between the Dy atom and the neighbor bridging atoms have been collected from the literature, together with the intradimer interaction and dipolar contribution, when specified. AF coupling between the Dy dimer atoms has been achieved using different types of bonds, including S, N_2^{3-} bridges, O bridges of pyridine- N-oxide ligands, radical anion $bpym^{\bullet-}$ bridges, phenoxo groups of valdien^{2n} ligands, pirazine ring bridges, nitroxide groups and double-μ2-oxygen groups. In these AF complexes, there seems to be a correlation between the intradimer distance and the total intradimer coupling, see Fig. S1, (no separate information about the dipolar contributions is available for all complexes). On the other hand, a number of complexes with ferromagnetic coupling have been reported, where the Dy-Dy coupling path is usually provided by a bridge containing one or more O atoms, forming part of different groups, (alkoxido groups of ovph^{2-} ligands, H_2O bridges, μ_3-O(P) and O-P-O bridges, phenoxide bridging O atoms, phenoxide groups of hmi ligands, carbonyl O atoms from ovph^{2-} ligands, oxalate bridges, carboxilate and hydroxyl bridges). In these complexes there is not a clear correlation between the ferromagnetic coupling and the Dy-Dy intradimer distance or angle. The function of the bridging O atom plays a major role. Comparing e.g. the complexes reported by Guo [10a] and Yi [10b], where the Dy dimer atoms are separated by similar distances and angles, the alkoxido groups of ovph^{2-} ligands in Guo's complex provides a weak ferromagnetic coupling and the large coupling is mainly from dipolar origin, whereas the H_2O bridges in Yi's complex provide a major exchange path. The absence of complete information about the orientation of the EAM axis of the Dy atoms and nature of the interactions for all the reported complexes precludes drawing firmer conclusions on the factors leading to strong interactions. In the case of $\{Dy_2Ba(\alpha\text{-fur})_8\}_n$ the intradimer distance is the largest among all the reported dinuclear complexes. The ferromagnetic exchange is mediated by two Dy-O-C-O-Dy bridges provided by α-fur ligands, and this indirect path via a carbon atoms leads to a very weak exchange coupling, compared to Dy-O-Dy paths of other complexes. The very weak intradimer coupling in $\{Dy_2Ba(\alpha\text{-fur})_8\}_n$, mainly of dipolar origin, implies that slow relaxation of the magnetization would be owed to spin relaxation of each of the individual ions, and not of the dimers.

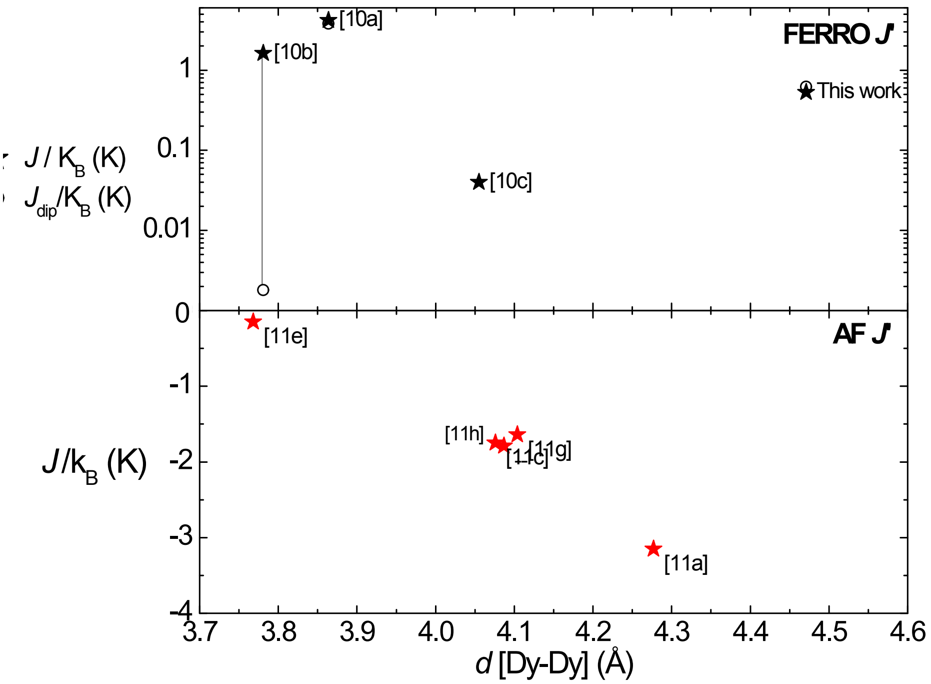

Fig. S1. Intradimer total coupling and dipolar contribution as a function of Dy-Dy intradimer distance, for the Ferromagnetic (Top) and AF (Bottom) Dy dinuclear complexes summarized in Table S1.

S2. Additional structural information

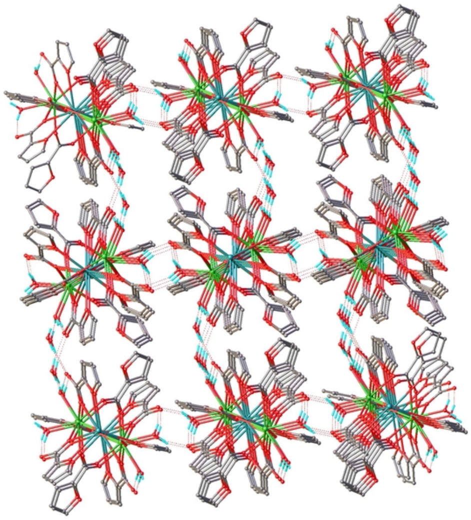

Fig. S2. View of 3D supramolecular network. Color code: Dy (green), Ba (blue), O (red), C (grey).

S3. *Ab initio* calculations

Table S2. *Ab initio* calculated eigenstates of Dy(III) in terms of the free ion wave functions. The numbers in the table indicate the weight of the combined $\pm M_J$ states.

Levels	Energy (K)	±15/2	±13/2	±11/2	±9/2	±7/2	±5/2	±3/2	±1/2
Ground	0.000	0.793	0.025	0.142	0.007	0.014	0.008	0.004	0.007
1st	73.408	0.015	0.179	0.009	0.260	0.091	0.176	0.131	0.140
2nd	104.440	0.037	0.273	0.126	0.110	0.207	0.019	0.156	0.072
3rd	148.507	0.027	0.192	0.216	0.064	0.094	0.176	0.026	0.206
4th	184.017	0.021	0.034	0.121	0.176	0.140	0.103	0.219	0.186
5th	219.372	0.024	0.067	0.087	0.119	0.233	0.267	0.162	0.040
6th	259.305	0.013	0.029	0.036	0.034	0.075	0.186	0.283	0.344
7th	614.048	0.070	0.201	0.263	0.230	0.145	0.065	0.020	0.005

S4. Relaxation experiments as a function of the magnetic field

The real and imaginary susceptibility as a function of the frequency, χ', $\chi''(f)$, were measured at T=5 K at different constant fields between 0-5 kOe (Fig. S3a). The determined field-dependence of the relaxation rate, $\tau(H$, 5K) showed a peak at ~500 Oe, and a minimum at the field H≈2 kOe where the intensity of χ'' was maximum (Fig. S3b). A similar behavior has been reported in other Dy dimers by Sulway *et al.* [4e]. Thereafter, χ', $\chi''(f)$ measurements were performed at this particular field, H=2 kOe, at different constant temperatures between 2-6.75 K (Figure 9a).

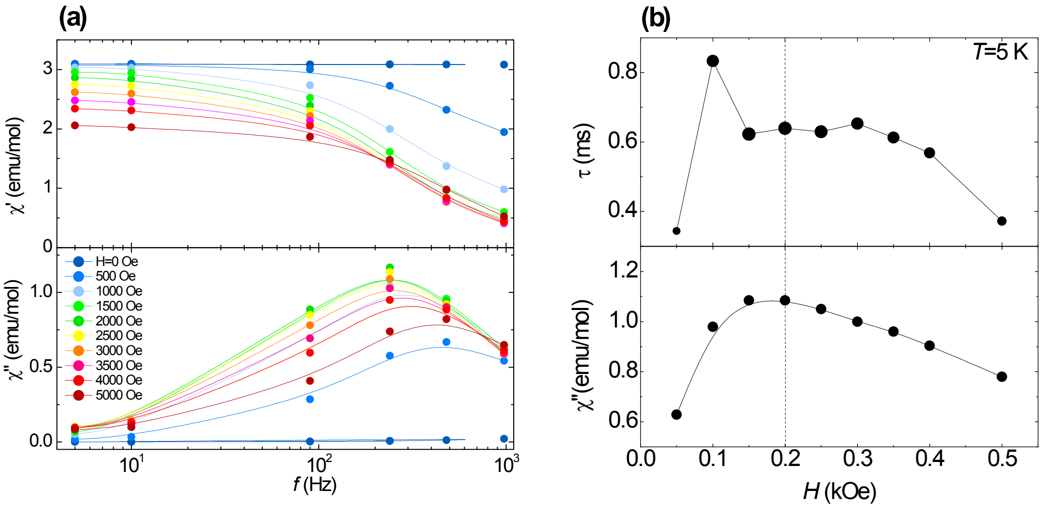

Fig. S3. (a) Susceptibility curves, χ', $\chi''(f)$, (per mols of Dy ions) , at different constant frequencies, at 5 K; (b) Field dependence of the relaxation rate, $\tau(H)$, and intensity of the peak χ'' (H) obtained from these curves.

Figure S4 shows susceptibility measurements as a function of the frequency, χ', $\chi''(f)$, performed at fixed temperatures of T=4 K and T=2.5 K as a function of the applied field, ranging between H=0 to 40 kOe. These data were used to determine the field-dependence of the relaxation rate $\tau(H)$ at 4 K and 2.5 K shown in Figures 10a and 10c.

S5. Comparison of physical parameters of two furoate polymeric Dy(III) complexes:

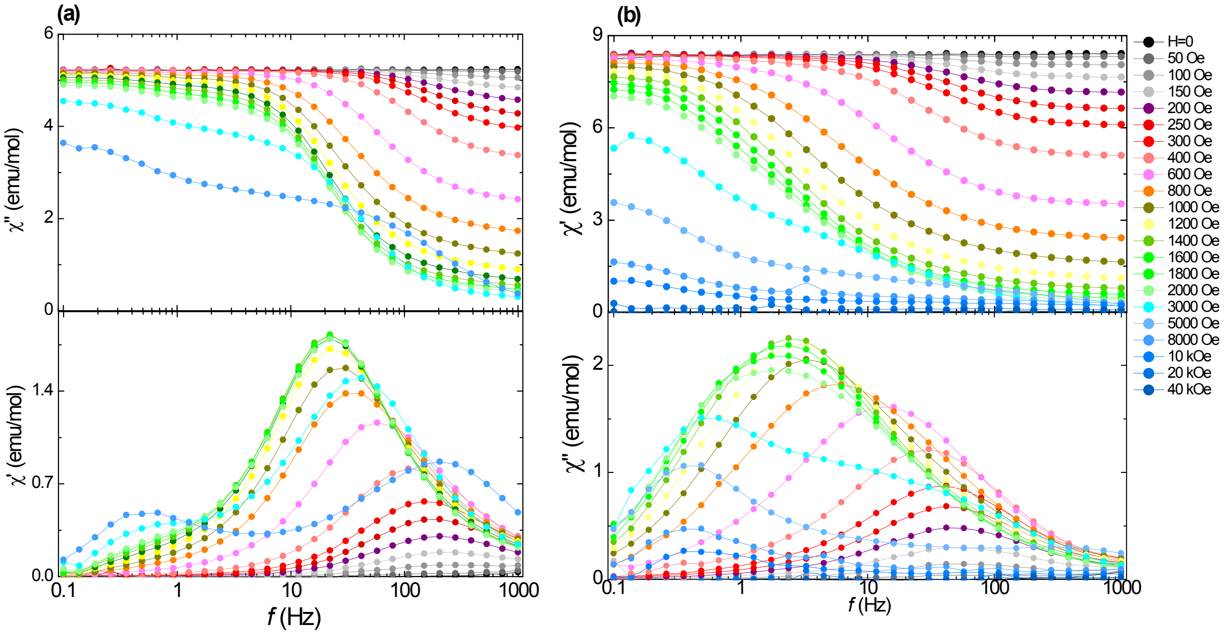

Fig. S4. Real and imaginary susceptibility curves as a function of the frequency at different applied constant fields, χ', χ''(f), measured at (a) T=4.0 K and (b) T=2.5 K.

Table S3. Transition temperature, exchange constants, calculated gyromagnetic factors of the ground state and energy gap between the ground and the first excited doublet states, activation energies and characteristic relaxation time prefactors of the different processes, and tunneling characteristic parameters, and slow direct process characteristic time.

	$\{Dy_2Ba(\alpha\text{-fur})_8.2H_2O\}_n$	$\{Dy(\alpha\text{-fur})_3\}_n$ Ref. [5]	
	This work	Site A	Site B
Coordination geometry	Distorted square antiprismatic	Distorted bicapped trigonal prism	
T_N (K)	0.250(5)	0.668(1)	
$J'/k_B=J''/k_B$ (K)	0.528(1)	0.755(1)	
J'''/k_B (K)	-0.021(1)	-0.135(1)	
g_x*(calculated)	0.1	0.1	0.1
g_y*(“)	0.3	0.7	0.1
g_z*(“)	18.7	18.8	19.5
Δ/k_B (K) (“l)	73.4	34.5	152.4
H	0	0	0
U/k_B(K) (TAQT)		29(3)	80(3)
τ_o(s)		$5(3)\times10^{-8}$	$6(4)\times10^{-11}$
H (kOe)	2	4	4
U/k_B (K) (Orbach)	68(3)	38(5)	79(3)
τ_o(s)	$1.(0)\times10^{-9}$	$2(1)\times10^{-8}$	$7(1)\times10^{-10}$
τ_T(s) (QT)	10^{-5}		3×10^{-4}
σ_{dip} (Oe)	200		500
$\sigma_{\xi,dip}=T_N$(K)	0.25		0.66
Δ_T/k_B (K)	7×10^{-4}		2×10^{-4}
τ_s(s) (direct)	$2(1)\times10^{-1}$		$4(1)\times10^{-1}$

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(Numbered according to main text)

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