Supplementary Information

Modulation of Slow Magnetic Relaxation by Tuning Magnetic Exchange in {Cr₂Dy₂} Single Molecule Magnets

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Structural diagrams – Figures S1 – S3.



Figure S1. The molecular structure of compound **4**. The H-atoms are omitted for clarity. Colour scheme; Cr^{III}, yellow; Dy^{III}, purple; O, red; N, blue; C, light grey.



Figure S2. The molecular structure of compound **5**. The H-atoms are omitted for clarity. Colour scheme; Cr^{III}, yellow; Dy^{III}, purple; O, red; N, blue; C, light grey.



Figure S3. The molecular structure of compound **1**. The H-atoms are omitted for clarity. Colour scheme; Cr^{III}, yellow; Dy^{III}, purple; O, red; N, blue; C, light grey.

Experimental magnetic data. Figures S4 – S15



Figure S4. Isothermal magnetization versus field plots for 3.



Figure S5. Isothermal magnetization versus field plots for 4.



Figure S6. Isothermal magnetization versus field plots for 5.



Figure S7. Reduced magnetization plots for 3.



Figure S8. Reduced magnetization plots for 4.



Figure S9. Reduced magnetization plots for 5.



Figure S10. Frequency dependence of χ_M ' (top) and χ_M " (bottom) for **3** in a zero applied dc field, with an ac field of 3.5 Oe.



Figure S11. Frequency dependence of χ_M ' (top) and χ_M " (bottom) for **4** in a zero applied dc field, with an ac field of 3.5 Oe.



Figure S12. Magnetization relaxation time (τ) plotted as $\ln(\tau)$ versus T^{-1} for compound **3**. The solid red line represents a fit to the Arrhenius law in the thermally activated regime. (inset) Cole-Cole plots of **3** at temperatures between 2.2 and 4.5 K. The solid lines are fits of the experimental data using a generalized Debye model.



Figure S13. Magnetization relaxation time (τ) plotted as $\ln(\tau)$ versus T^{-1} for compound 4. The solid red line represents a fit to the Arrhenius law in the thermally activated regime. (inset) Cole-Cole plots of 4 at temperatures between 2.5 and 5 K. The solid lines are fits of the experimental data using a generalized Debye model.



Figure S14. Plot of magnetization (M) versus field (H) for 3, sweeping the field with an average sweep rate of 0.004 T/s, at the temperatures indicated.



Figure S15. Plot of magnetization (M) versus field (H) for 4, sweeping the field with an average sweep rate of 0.004 T/s, at the temperatures indicated.

Computational details

The entire molecules were calculated; just the neighbouring Dy^{III} and Cr^{III} ions were replaced by diamagnetic Lu^{III} and Sc^{III} respectively.

Two basis set approximations have been employed: 1 - small, and 2 - large. Table S1 shows the contractions of the employed basis sets for all elements.

Table SI. Contractions of the employed basis sets	is of the employed basis sets.
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Basis 1	Basis 2
Dy.ANO-RCC7s6p4d2f1g.	Dy.ANO-RCC8s7p5d3f2g1h.
Lu.ANO-RCC7s6p4d2f.	Lu.ANO-RCC7s6p4d2f.
Sc.ANO-RCC5s4p2d.	Sc.ANO-RCC5s4p2d.
N.ANO-RCC3s2p.	O.ANO-RCC3s2p1d. (close)
O.ANO-RCC3s2p.	O.ANO-RCC3s2p. (distant)
C.ANO-RCC3s2p.	N.ANO-RCC3s2p.
H.ANO-RCC2s.	C.ANO-RCC3s2p.
	H.ANO-RCC2s.

Active space of the CASSCF method included 9 electrons in 7 orbitals (4*f* orbitals of Dy^{3+} ion).

We have mixed 21 sextets, 128 quartet and 130 doublet states by spin-orbit coupling. On the basis of the resulting spin-orbital multiplets the SINGLE_ANISO program computed the local magnetic properties (g-tensors, magnetic axes, local magnetic susceptibility, etc.)

Spin-orbit energies, cm ⁻¹						
3		4		5		
Dy_basis1	Dy_basis2	Dy_basis1	Dy_basis2	Dy_basis1	Dy_basis2	
0	0	0	0	0	0	
175	169	180	171	179	171	
309	283	328	297	336	317	
355	314	369	328	402	362	
411	367	433	387	459	414	
519	461	550	487	568	509	
617	523	655	559	646	548	
812	700	856	736	836	720	

Table S2. Energies of the lowest Kramers doublets (cm⁻¹) of Dy^{III} centers.

Table S3. The g tensors of the lowest Kramer	rs doublets (KD) of Dy ^{III} centers
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KD		3 (cm ⁻¹)		4 (cm ⁻¹)		5 (cm ⁻¹)	
		Dy_basis1	Dy_basis2	Dy_basis1	Dy_basis2	Dy_basis1	Dy_basis2
		g	g	g	g	g	g
1	gx gy gz	0.008837 0.012755 19.722495	0.012285 0.017181 19.704312	0.009597 0.013896 19.722680	0.014296 0.020128 19.707470	0.006482 0.011026 19.677604	0.009686 0.015627 19.669433
2	gx gy g7	0.067602 0.100180 16.743886	0.156964 0.253112 16.634500	0.069917 0.099146 16.711846	0.161136 0.253787 16.611940	0.027444 0.036429 16.705398	0.059436 0.088131 16.698683

3	gx	0.654221	1.714799	1.036987	2.055509	0.358573	0.985818
	gy	1.300003	3.475127	2.119652	4.033140	0.660653	1.875169
	gz	12.991998	12.817272	12.847352	13.231827	13.126713	12.605420
4	gx	2.841344	1.308860	2.073753	0.263524	3.072936	2.036262
	gy	4.163448	4.233186	3.585894	5.501648	4.989272	4.170956
	gz	13.833060	11.982456	14.381287	10.977896	13.509446	15.137712

BS-DFT calculations

In order to gain some information about the exchange coupling constants we performed BS-DFT calculations at the B3LYP/TZVP(magnetic ions)/SVP level. TightSCF and Grid5 were used. To estimate the exchange constant between chromium ions we substituted Dy^{III} ions by Gd^{III}. Another calculation was carried out on {Gd₂Sc₂} (with the geometry of {Dy₂Cr₂}) to investigate the exchange interaction between Gd^{III} ions and then to rescale the exchange coupling constant to the spin of dysprosium ions. Finally, we calculated the Gd1Cr1ScLu and Gd1Cr2ScLu compounds (all with the experimental geometry of Dy_2Cr_2 complex) to calculate the interaction between Gd^{III} and Cr^{III} ions and then to rescale it to the spin of Dy^{III} . In all cases we applied the Yamaguchi's formula to estimate the exchange coupling

constants: $J_{ab} = \frac{E^{LS} - E^{HS}}{\langle S^2 \rangle^{HS} - \langle S^2 \rangle^{LS}}$

The chromium ions were considered isotropic with a g-factor of 2.00.



Figure S16. (a) The magnetic orbitals of 4; (b) Spin density plots of high and low spin respectively (b). Blue colour corresponds to spin α and red one to spin β .



Figure S17. (a) The magnetic orbitals of **5**; (b) Spin density plots of high and low spin respectively. Blue colour corresponds to spin α and red one to spin β .



Figure S18. Calculated (solid lines) and experimental (symbols) magnetization curves of 3. The intermolecular interaction zJ' was set to -0.03 cm⁻¹.



Figure S19. Calculated (solid lines) and experimental (symbols) magnetization curves of 4.



Figure S20. Calculated (solid lines) and experimental (symbols) magnetization curves of the 5. The intermolecular interaction zJ' was set to +0.05 cm⁻¹.



Figure S21. The orientation of local magnetic moments in the ground exchange doublet state in **4**. The dashed lines correspond to the main magnetic axes of Dy centers.



Figure S22. The orientation of local magnetic moments in the ground exchange doublet state in **5**. The dashed lines correspond to the main magnetic axes of Dy centers.



Figure S23. Low-lying exchange spectrum and the position of magnetization blocking barrier (dashed green line) in **1**. Each exchange state is placed in accordance with the value of its magnetic moment (bold black lines). The horizontal blue arrows show the tunnelling transitions within each doublet state (Δ_{tun} are corresponding tunnelling gaps), while vertical arrows (red and dark-green) show the spin-phonon transitions (the numbers are averaged transition moments in μ_B connecting the corresponding states). Red arrows correspond to the

maximal transition probability from a given state, thus outlining the relaxation barrier of reversal of magnetization within the ground exchange doublet.