Supporting Information

Chimeric design of heterospin 2*p*-3*d*, 2*p*-4*f*, and 2*p*-3*d*-4*f* complexes using a novel family of paramagnetic dissymmetric compartmental ligands

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1. Syntheses

The Mannich base was synthesized following the procedure published by Fenton et al.⁶

Synthesis of the nitronyl-nitroxide compartmental ligand HL (Scheme S1)

To a methanolic solution (30 mL) of [2,3-bis(hydroxyamino)-2,3-dimethylbutane]•H₂SO₄ (0.5000 g, 2 mmoles), which was deprotonated with 0.7 mL Et₃N, 0.6400 g (2 mmoles) of Mannich base were added under stirring at room temperature. The resulting mixture was stirred at room temperature for three days, then concentrated under reduced pressure giving the condensation product as a pale yellow oil which was solubilized in 5 ml dichloromethane. To the obtained solution were added 0.217 g NaIO₄ (considering yield = 50 % to avoid the overoxidation) in minimum amount of water. The mixture was vigorously stirred for 15 minutes at 0° C, then dried over anhydrous MgSO₄ and concentrated under reduced pressure to obtain a purple oil. The stable nitronyl nitroxide radical was purified on a column chromatograph (SiO₂) using methanol as eluent. After removing the solvent, the resulting compound is still contaminated with the Mannich base precursor. Second purification was carried out by extraction method. A solution of radical in ether was washed several times with water. Organic solution was dried over anhydrous magnesium sulphate and concentrated

under reduced pressure to obtain a deep blue sticky solid (0.270 g, yield = 30%). FTIR (cm⁻¹): 2944 (w), 2822(w), 1638 (m), 1453 (s), 1400 (s), 1360 (vs), 1263 (w), 1211 (m), 1163 (w), 1123 (m), 1068 (w), 1024 (w), 968 (w), 924 (w), 861 (m), 808 (w), 651 (m), 624 (w), 541 (w), 452 (w).





Synthesis of [Dy(hfac)₃(HL)] 1. To 20 mL hot *n*-heptane solution of $[Dy(hfac)_3(H_2O)_3]$ (0.0278 g, 0.0339 mmol), a chloroform solution (2 mL) of HL (0.0150 g, 0.0339 mmol) was added. The resulting mixture was stirred for one minute, then it was left to cool down at room temperature. Blue crystals were obtained after several days. FTIR (cm⁻¹): 1660 (m), 1529 (m), 1460 (m), 1253 (s), 1191 (s), 1132 (vs), 793 (m), 659 (s), 583 (m).

Synthesis of $[Co_2(hfac)_3(L)]$ 2. To 20 mL hot *n*-heptane solution of $[Co(hfac)_2(H_2O)_2]$ (0.0520 g, 0.1025 mmol), a chloroform solution (2 mL) of HL (0.0150g, 0.0339 mmol) was added. The resulted mixture was stirred for one minute, then it was cooled down to room temperature. Deep purple crystals were obtained after several days. FTIR (cm⁻¹): 1643 (m), 1525 (m), 1451 (m), 1252 (s), 1194 (s), 1135 (vs), 793 (m), 666 (m), 584 (m).

Synthesis of $[CoDy(hfac)_4(L)]$ 3. To 20 mL hot *n*-heptane mixed solution of $[Co(hfac)_2(H_2O)_2]$ (0.0258 g, 0.0508 mmol) and $[Dy(hfac)_3(H_2O)_3]$ (0.0312 g, 0.0381 mmol), a chloroform solution (2 mL) of HL (0.015g, 0.0339 mmol) was added and the mixture was stirred for one minute. The resulting solution was cooled down to room temperature and purple crystals were obtained after several days. FTIR (cm⁻¹): 1648 (m), 1512 (m), 1454 (m), 1254 (s), 1201 (s), 1135 (vs), 797 (m), 660 (m), 584 (m).

2. Crystallographic data

Compound	1	2	3
Formula	C _{37.5} H ₄₁ O ₉ N ₄ F ₁₈ BrDy	C ₃₄ H ₃₂ O ₉ N ₄ F ₁₈ BrCo ₂	C ₃₉ H ₃₃ O ₁₁ N ₄ F ₂₄ BrCoDy
Formula weight/ g	1276.15	1180.40	1491.03
mol ⁻¹			
T/K	273(2)	293(2)	293(2)
λ/Å	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P -1	P -1	P 21/c
Unit cell			
a/Å	11.5622(4)	12.8538(6)	22.9813(8)
b/Å	13.0505(5)	12.8545(5)	12.2926(4)
c/Å	18.3593(8)	14.0294(6)	20.8211(7)
α/deg	80.656(2)	92.824(2)	90
β/deg	83.118(2)	92.716(2)	112.084(2)
γ/deg	68.474(2)	92.592(2)	90
V/Å3	2537.38(18)	2310.02(17)	5450.4(3)
Ζ	2	2	4
Calculated density/g	1.670	1.697	1.817
cm ⁻³			
Absorption	2.377	1.708	2.536
coefficient/cm ⁻¹			
F(000)	1258	1174	2908
Crystal size/mm ×	0.15 x 0.02 x 0.01	0.3 x 0.2 x 0.1	0.279 x 0.177 x 0.078
mm × mm			
θ range/deg	2.142 to 19.692	2.192to 30.577	2.111 to 21.731
Limiting indices	-10 < h < 10	-18 < h < 18	-23 < h < 23
-	-12 < k < 12	-18 < k < 18	-12 < k < 12
	-17 < 1 < 17	-19 < 1 < 19	-21 < 1 < 21
Collected reflections	42575	75532	80299
Symmetry	4522	13956	6428
independent			
reflections			
R _{int}	0.056	0.1420	0.1327
Completeness/%	49.2	99.9	99.7
Max and min	0.7454 and 0.6457	0.7454 and 0.6076	0.7454 and 0.6181
transmission			
Data/restraints/	4522 / 6 / 714	13956 / 0 / 728	6428 / 0 / 757
parameters			
GOF on F ²	1.086	0.995	1.058
Final R indices	$R[F^2 > 2\sigma(F^2)] = 0.0290$	$R[F^2 > 2\sigma(F^2)] = 0.0618$	$R[F^2 > 2\sigma(F^2)] = 0.0448$
	$wR(F^2) = 0.0679$	$wR(F^2) = 0.1065$	$wR(F^2) = 0.0840$
Largest diff peak	0.538 and -0.442	0.662 and -0.637	0.975 and -0.724
and hole/e $Å^{-3}$			

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3. Bond distances and angles

Table S2.	Selected	bond	lengtł	ıs f	or 1	-3	,

1	2	3
N(1) - O(1) = 1.266(6)	N(1) - O(1) = 1.266(4)	N(1) - O(1) = 1.265(9)
N(2) - O(2) = 1.308(6)	N(2) - O(2) = 1.311(3)	N(2) - O(2) = 1.300(8)
Dy(1) - O(2) = 2.325(4)	Co(1) - O(2) = 2.041(3)	Dy(1) - O(2) = 2.327(5)
Dy(1) - O(3) = 2.249(4)	Co(1) - O(3) = 2.054(2)	Dy(1) - O(3) = 2.336(5)
Dy(1) - O(4) = 2.432(4)	Co(1) - O(4) = 2.055(3)	Dy(1) - O(4) = 2.385(6)
Dy(1) - O(5) = 2.332(4)	Co(1) - O(5) = 2.067(2)	Dy(1) - O(5) = 2.333(6)
Dy(1) - O(6) = 2.360(5)	Co(1) - O(6) = 2.102(3)	Dy(1) - O(6) = 2.322(6)
Dy(1) - O(7) = 2.409(4)	Co(1) - O(7) = 2.117(3)	Dy(1) - O(7) = 2.348(6)
Dy(1) - O(8) = 2.355(4)	Co(2) - N(3) = 2.172(3)	Dy(1) - O(8) = 2.412(5)
Dy(1) - O(9) = 2.372(4)	Co(2) - N(4) = 2.170(3)	Dy(1) - O(9) = 2.341(5)
	Co(2) - O(3) = 1.985(2)	Co(1) - N(3) = 2.155(7)
	Co(2) - O(7) = 2.6642(1)	Co(1) - N(4) = 2.155(7)
	Co(2) - O(8) = 2.044(2)	Co(1) - O(3) = 2.024(5)
	Co(2) - O(9) = 2.035(3)	Co(1) - O(8) = 2.490(5)
		Co(1) - O(10) = 2.036(6)
		Co(1) - O(11) = 2.027(6)

 Table S3. Selected angles for 1-3

1	2	3
O(2) - Dy(1) - O(3) = 73.38(13)	O(2) - Co(1) - O(3) = 89.41(9)	O(2) - Dy(1) - O(3) = 75.66(18)
O(2) - Dy(1) - O(4) = 148.51(14)	O(2) - Co(1) - O(4) = 92.49(11)	O(2) - Dy(1) - O(4) = 75.29(19)
O(2) - Dy(1) - O(5) = 94.17(14)	O(2) - Co(1) - O(5) = 94.42(11)	O(2) - Dy(1) - O(5) = 71.3(2)
O(2) - Dy(1) - O(6) = 140.19(15)	O(2) - Co(1) - O(6) = 94.95(11)	O(2) - Dy(1) - O(6) = 145.34(19)
O(2) - Dy(1) - O(7) = 75.53(14)	O(2) - Co(1) - O(7) = 170.86(11)	O(2) - Dy(1) - O(7) = 131.4(2)
O(2) - Dy(1) - O(8) = 115.03(14)	O(3) - Co(1) - O(4) = 177.48(10)	O(2) - Dy(1) - O(8) = 129.73(18)
O(2) - Dy(1) - O(9) = 73.40(14)	O(3) - Co(1) - O(5) = 92.10(9)	O(2) - Dy(1) - O(9) = 77.38(19)
O(3) - Dy(1) - O(4) = 77.56(14)	O(3) - Co(1) - O(6) = 100.45(10)	O(3) - Dy(1) - O(4) = 82.49(18)
O(3) - Dy(1) - O(5) = 83.86(14)	O(3) - Co(1) - O(7) = 82.28(10)	O(3) - Dy(1) - O(5) = 142.52(18)
O(3) - Dy(1) - O(6) = 146.24(15)	O(4) - Co(1) - O(5) = 86.11(11)	O(3) - Dy(1) - O(6) = 95.4(2)
O(3) - Dy(1) - O(7) = 137.54(14)	O(4) - Co(1) - O(6) = 81.04(11)	O(3) - Dy(1) - O(7) = 146.51(19)
O(3) - Dy(1) - O(8) = 82.74(14)	O(4) - Co(1) - O(7) = 95.93(12)	O(3) - Dy(1) - O(8) = 69.95(17)
O(3) - Dy(1) - O(9) = 123.36(16)	O(5) - Co(1) - O(6) = 164.38(10)	O(3) - Dy(1) - O(9) = 97.97(18)
O(4) - Dy(1) - O(5) = 70.67(14)	O(5) - Co(1) - O(7) = 89.70(11)	O(4) - Dy(1) - O(5) = 72.57(19)
O(4) - Dy(1) - O(6) = 70.19(15)	O(6) - Co(1) - O(7) = 82.89(10)	O(4) - Dy(1) - O(6) = 70.3(2)
O(4) - Dy(1) - O(7) = 121.31(15)	N(3) - Co(2) - N(4) = 82.86(12)	O(4) - Dy(1) - O(7) = 119.8(2)
O(4) - Dy(1) - O(8) = 72.28(14)	N(3) - Co(2) - O(3) = 90.87(11)	O(4) - Dy(1) - O(8) = 132.47(19)
O(4) - Dy(1) - O(9) = 134.74(14)	N(3) - Co(2) - O(7) = 93.03(9)	O(4) - Dy(1) - O(9) = 151.6(2)
O(5) - Dy(1) - O(6) = 94.44(15)	N(3) - Co(2) - O(8) = 173.75(12)	O(5) - Dy(1) - O(6) = 101.7(2)
O(5) - Dy(1) - O(7) = 70.28(15)	N(3) - Co(2) - O(9) = 90.39(11)	O(5) - Dy(1) - O(7) = 70.9(2)
O(5) - Dy(1) - O(8) = 142.49(15)	N(4) - Co(2) - O(3) = 106.29(11)	O(5) - Dy(1) - O(8) = 146.84(19)
O(5) - Dy(1) - O(9) = 142.78(16)	N(4) - Co(2) - O(7) = 174.91(10)	O(5) - Dy(1) - O(9) = 91.65(19)
O(6) - Dy(1) - O(7) = 71.09(15)	N(4) - Co(2) - O(8) = 91.77(12)	O(6) - Dy(1) - O(7) = 72.3(2)
O(6) - Dy(1) - O(8) = 78.31(16)	N(4) - Co(2) - O(9) = 98.42(13)	O(6) - Dy(1) - O(8) = 74.53(19)
O(6) - Dy(1) - O(9) = 76.40(16)	O(3) - Co(2) - O(7) = 70.66(9)	O(6) - Dy(1) - O(9) = 137.3(2)
O(7) - Dy(1) - O(8) = 137.32(15)	O(3) - Co(2) - O(8) = 93.71(10)	O(7) - Dy(1) - O(8) = 76.7(2)
O(7) - Dy(1) - O(9) = 72.64(16)	O(3) - Co(2) - O(9) = 155.22(10)	O(7) - Dy(1) - O(9) = 74.3(2)
O(8) - Dy(1) - O(9) = 71.74(16)	O(7) - Co(2) - O(8) = 92.49(9)	O(8) - Dy(1) - O(9) = 72.47(18)
	O(7) - Co(2) - O(9) = 84.56(9)	N(3) - Co(1) - O(3) = 89.7(2)
	O(8) - Co(2) - O(9) = 87.23(11)	N(3) - Co(1) - O(10) = 88.2(3)
		N(3) - Co(1) - O(11) = 174.4(3)
		N(3) - Co(1) - N(4) = 83.5(3)
		N(4) - Co(1) - O(3) = 105.5(2)
		N(4) - Co(1) - O(10) = 92.7(3)
		N(4) - Co(1) - O(11) = 93.1(3)
		O(3) - Co(1) - O(10) = 161.2(2)
		O(3) - Co(1) - O(11) = 95.5(2)
		O(10) - Co(1) - O(11) = 87.5(2)

4. Powder X-Ray diffraction



Figure S1. Powder X-ray diffraction pattern for compound 1 and the calculated pattern from the crystal structure determined by single crystal data



Figure S2: Powder X-ray diffraction pattern for compound **2** and the calculated diffractogram from the crystal structure determined by single crystal data



Figure S3: Powder X-ray diffraction pattern of compound **3** at room temperature and the calculated diffractogram from the crystal structure determined by single crystal data

5. Ab Initio Calculations and simulation of magnetic properties

All the calculations were performed with MOLCAS 8.1 Quantum Chemistry Software Package.^{S1} The *divide et impera* approach was adopted, as described in previous paper.^{S2}

For compound **1**, the geometries resolved obtained by the crystal structures x-ray diffraction were employed without further modifications. For compound **3**, x-ray structures were employed modeling $-CF_3$ and CH_3 groups by hydrogens atoms to reduce the number of primitive functions. No further optimization was carried out. To verify the adopted structural approximation on 3, we have also performed the CASSCF/CASSI-SO calculations on **1** substituting the $-CF_3$ and CH_3 for hydrogens atoms, **1***.

The energy ladders of the electronic states for Dy^{III} and Co^{II} ions have been computed within the CASSCF/CASSI-SO method and doping the radical with an extra electron in order to turn it into a diamagnetic ligand. The single ion anisotropies of the two metal ions in **3** have also been computed on the individual center by diamagnetic substitution. The chosen active space for Dy^{III} consists of nine electrons in the seven 4*f*-orbitals of the lanthanide ion: CAS (9,7). Due to hardware limitations, only the 21 sextuplets were computed and included in the following spin-orbit calculation. The chosen active space for Co^{II} consists of 7 electrons in the five 3*d*-orbitals of the metal ion: CAS (7,5). The 10 quadruplets and the 40 doublets were computed and included in the following spin-orbit calculation.

The g-tensors were computed with the SINGLE_ANISO module. Both are Kramers' ions due to their odd number of electrons. Their magnetic anisotropy was investigated within the pseudospin framework and their anisotropy axes were calculated with a pseudospin $S = \frac{1}{2}$.

The energy ladder and magnetic anisotropy computed for 1, 1*, and 3 have been reported in Table S5 and Table S6-S7, respectively. The small differences computed between 1 and 1* justify the reliability of the adopted structural simplification. Significant deviations have been computed only from the second excited state ahead with small effect on the magnetic properties, at least at low temperature and for the single ion anisotropy.

In order to compute the isotropic magnetic coupling between the radical and the metal ions, CASSCF calculations were performed without spin-orbit contribution for the two compounds. In compound **3**, the exchange couplings between the metal ions and the radical were computed substituting them in turn by a diamagnetic equivalent ion: replacing Dy^{III} by

La^{III} and Co^{II} by Zn^{II}. For the Dy^{III}-nitronyl-nitroxide radical (NNit) interactions in **1** and **3**, the chosen active space consisted of nine electrons in the seven 4*f*-orbitals of the lanthanide ion and the unpaired electron in the π^* orbital of the O₂-N₂-C_{π}-N₁-O₁ system on the radical, CAS (10,8). For the Co^{II}-NNit interaction in **3**, the active space consisted of the five 3*d* orbitals and the π^* molecular orbital of the radical, CAS (8,6). Calculations were performed converging on both the ferromagnetic and antiferromagnetic states resulting from the lanthanide ions: the lowest septuplet and quintuplet state for the interaction Dy^{III}-NNit; the lowest quintuplet and triplet for the exchange Co^{II}-NNit. The values of the exchange coupling constants were computed within the Heisenberg model without spin-orbit coupling.

The $\chi_{\rm M}T$ curves were simulated by means of the POLY_ANISO^{S3} software with the Lines' model (see Table S9 and S10). In the Lines model the Heisenberg isotropic exchange interaction is firstly computed between isotropic spin multiplets (S = 5/2 for Dy and S = 3/2for Co) and then projected on the basis of the previously computed spin-orbit states. In our models, for compound 1 only the exchange coupling interaction between the lanthanide and the coordinated isotropic $S = \frac{1}{2}$ of the radical was taken into account, while for compound **3** the three exchange coupling interactions between the lanthanide, the cobalt ion and the radical were considered, in agreement with the results of the ab initio calculation. To reproduce the $\chi_M T$ curve of compound 1, the energy of the first excited doublet was shifted 80 cm⁻¹ upward. Such a correction is used in literature in order to overcome limitations of the employed method:^{S4} extension of the basis set, unaccounted dynamical electronic correlation and the correct inclusion of the Madelung electrostatic potential.^{S5} The exchange interaction involved only the six lowest states in energy of the lanthanide ion, the four lowest of the Cobalt ion and the isotropic doublet of the radical. In order to reproduce the high temperature data also, the single ion crystal field splitting for the two inequivalent lanthanides was included in the model. In this Hamiltonian, the exchange coupling constant J_{Lines} is the only parameter of the methodology, because all the information about crystal field splitting and magnetic anisotropy are computed by *ab initio* calculation.

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Table S4. Contractions of the basis sets employed in the calculations.

etion
D-RCC8S7P5D3F2G1H
-RCC6S5P3D2F1G
-RCC7S6P4D2F
-RCC5S4P2D1F
-RCC5S4P1D
RCC4S3P2D1F
RCC4S3P2D1F
RCC3S2P
RCC2S

Compound	1	1*		3
Energy level (cm ⁻¹)	Dy	Dy	Dy	Со
1	0.000	.000	0.000	0.000
2	0.000	.000	0.000	0.000
3	112.531	98.170	140.797	132.124
4	112.531	98.170	140.797	132.124
5	215.490	161.035	178.363	1096.691
6	215.490	161.035	178.363	1096.691
7	285.629	178.859	229.729	1355.810
8	285.629	178.859	229.729	1355.810
9	321.419	224.317	275.502	1533.178
10	321.419	224.317	275.502	1533.178
11	354.075	256.749	343.242	1671.687
12	354.075	256.749	343.242	1671.687
13	378.896	277.452	429.786	5451.310
14	378.896	277.452	429.786	5451.310
15	556.928	467.884	562.921	5546.553
16	556.928	467.884	562.921	5546.553
17	3058.707	3048.877	3054.163	7509.578
18	3058.707	3048.877	3054.163	7509.578
19	3149.552	3111.371	3149.816	7564.646
20	3149.552	3111.371	3149.816	7564.646
21	3216.018	3161.303	3198.312	8332.111
22	3216.018	3161.303	3198.312	8332.111
23	3262.558	3181.645	3242.350	8450.095
24	3262.558	3181.645	3242.350	8450.095
25	3289.253	3193.464	3284.169	13720.841
26	3289.253	3193.464	3284.169	13720.841
27	3344.580	3235.784	3328.849	14418.602
28	3344.580	3235.784	3328.849	14418.602
29	3418.196	3315.098	3426.211	14425.885
30	3418.196	3315.098	3426.211	14425.885
31	5680.481	5652.440	5665.844	17894.996
32	5680.481	5652.440	5665.844	17894.996
33	5753.916	5698.718	5738.045	18782.646
34	5753.916	5698.718	5738.045	18782.646
35	5794.992	5735.808	5782.673	19535.552
36	5794.992	5735.808	5782.673	19535.552
37	5828.991	5751.397	5832.898	20031.114
38	5828.991	5751.397	5832.898	20031.114
39	5893.250	5808.139	5896.763	21280.048
40	5893.250	5808.139	5896.763	21280.048
41	5970.505	5854.047	5954.499	21754.577
42	5970.505	5854.047	5954.499	21754.577

 Table S5. Computed Energy levels at CASSCF/RASSI-SO level for 1, 1*, and 3.

Table S6. Compound 1: values of the main anisotropy axes for Dy and their orientations in the crystal frame.

	1	Value	a	b'	с*
	g _x	0.055	0.623422	0.0778704	0.070468
Dy	$\mathbf{g}_{\mathbf{y}}$	0.116	-0.678844	0.0583780	-0.445390
	gz	19.23	-0.387965	0.229829	0.892559

1	*	Value	a	b'	c *
	g _x	0.082	0.630194	0.772287	0.080178
Dy	gy	0.162	-0.685277	0.601779	-0.410192
	gz	19.11	-0.365036	0.203556	0.908468

Table S7. Compound **3**: values of the main anisotropy axes for Dy and Co and their orientations in the crystal frame.

		Value	a	b'	c*
	\mathbf{g}_1	0.025	-0.005575	0.616216	0.787557
Dy	\mathbf{g}_2	0.044	-0.120925	0.781374	-0.612235
	g ₃	19.8	-0.992646	-0.098648	0.070160
	\mathbf{g}_1	1.947	0.803778	0.487388	-0.341164
Со	\mathbf{g}_2	3.704	-0.238447	0.789300	0.565817
	g ₃	6.688	0.545053	-0.373442	0.750638



Figure S4. In-phase $\pi^*(NO) - f(Dy)$ magnetic orbitals in compounds 1 (left) and 3 (right).



Figure S5. Thermal dependence of the (left) in-phase χ' and (right) out-of-phase χ'' susceptibility components for compound 1 measured without external dc magnetic field.



Figure S6. Frequency dependence of the out-of-phase $(\chi \Box \Box)$ components of the ac magnetic susceptibility for compound 1 at H = 1 kOe. Solid lines represent the fits to the data as described in the text.

T (K)	$\chi_{S,tot}(cm^3.mol^{-1})$	$\Delta \chi (cm^3.mol^{-1})$	α	$\tau(s)$
2.0	0.44	6.64	0.55	6.1E-3
2.3	0.46	5.51	0.46	2.05E-3
2.6	0.37	4.98	0.418	7.82E-4
2.9	0.28	4.61	0.397	3.24E-4
3.2	0.26	4.25	0.376	1.51E-4
3.5	0.28	3.89	0.357	7.9E-5
3.8	0.3	3.6	0.346	4.47E-5
4.1	0.35	3.32	0.331	2.81E-5
4.5	0.24	3.2	0.34	1.5E-5

Table S8: Summary of the fit parameters using modified Debye function for compound 1.



Figure S7. Arrhenius plot for 1 at H = 1 kOe. The solid line represents the fit to Arrhenius law.



Figure S8. Low lying exchange states and transition moments for **1**. The thick black horizontal lines indicate the Kramers' doublets as a function of the projection of the magnetic moment on the chosen quantisation axis (the one of the ground multiplet). The dotted arrows show the possible pathways of different Orbach processes. The dashed green lines represent the presence of quantum tunnelling between the connecting states. The numbers reported for each arrow are the mean absolute value for the corresponding matrix element of the transition magnetic moment.



Figure S9. Thermal dependence of the in-phase χ' susceptibility components for compound 3 measured without external dc magnetic field (left) and under H_{ext} = 1.5 kOe (right).



Figure S10. Low lying exchange states and transition moments for 3. See Figure S8 for the legend.

Table S9. Compound 1: energy and values of the main anisotropy axes of ground and first

 excited exchange doublets computed within POLY_ANISO software.

Energy (cm ⁻¹)	Δ_{tun} (cm ⁻¹)	g _x	\mathbf{g}_{y}	gz
0.02750188	0.055	0	0	21.225508713
20.35845105	0.228	0	0	17.225626521

 Table S10. Compound 3: energy and values of the main anisotropy axes of low lying

 exchange doublets within POLY_ANISO software.

Energy (cm ⁻¹)	g _x	\mathbf{g}_{y}	gz
0	0.023512787	0.026142566	18.701640695
2.162	0.029051134	0.030623601	14.798816948
6.768	0.007785101	0.008092576	25.575389258
9.067	0.000881785	0.011931634	21.616072267