

Supporting Information

Cycloheptatrienyl trianion: An elusive bridge in the search of exchange coupled dinuclear organolanthanide single-molecule magnets

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General Procedures and Starting Materials. All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions using a standard Schlenk-line or nitrogen-atmosphere glovebox. Tetrahydrofuran (THF), toluene, and n-hexanes were dried on columns of activated alumina using a J.C. Mayer solvent purification system. Pentanes was dried *via* distillation over calcium hydride and subsequent passage over activated alumina. All solvents were of least reagent grade and were stored over 3Å molecular sieves. Anhydrous toluene-d₈ and anhydrous chloroform-d was purchased from CDN Isotopes and Sigma Aldrich respectfully, and used without further purification. Anhydrous LnCl₃ was purchased from Strem Chemicals, sodium *bis*(trimethylsilyl)amide, potassium, and 1,3-cycloheptadiene was purchased from Sigma Aldrich; these chemicals were used as received. Triethylamine was purchased from Alfa Aesar and dried by refluxing over calcium hydride, distillation, and storage over 3Å sieves. Potassium cycloheptadienide¹ and lanthanide *tris*(bis(trimethylsilylamido))² were prepared from previously reported procedures with modifications as described below. Infrared spectra were recorded on a Nicolet Nexus 550 FT-IR spectrometer using transmission mode in the 4000-600 cm⁻¹ range; solid samples were prepared under an inert atmosphere and sandwiched between transparent NaCl plates. Elemental analyses were carried out with a Costech EOS 4010 CHNSO analyzer. NMR spectra were acquired on a Bruker Avance-II 300 MHz spectrometer at 298 K

Preparation of K(C₇H₉). Under an inert atmosphere, K⁰ (360 mg, 9.22 mmol) was added to a reaction vessel containing 6 mL of THF and 0.96 mL of Et₃N (6.91 mmol). With vigorous stirring 1,3-cycloheptadiene (2 mL, 18.4 mmol) was added slowly to the vessel at 0 °C. Following the addition of the diene, the vessel was allowed to gradually warm to room temperature for 16 h. Addition of n-hexanes and subsequent exposure to -35 °C yielded yellow needle-like crystals. Collection of the crystals over a fine frit and subsequent washings with n-hexanes provided the product in 70% yield. IR (neat, cm⁻¹): 2826 (w), 1557 (m), 1529 (m), 1444 (m), 1363 (m), 1318 (m), 1274 (w), 1235 (w), 1215 (w), 1155 (m), 1125 (m), 1041 (m), 1006 (w), 948 (w), 889 (s), 867 (s), 771 (w), 710 (s), 634 (w), 541 (s). ¹H NMR (CDCl₃, 298 K, δ/ppm): 5.79 (m, 5H, C_{sp3}-H), 2.13 (m, 4H, C_{sp2}-H).

Preparation of [Ln(N(SiMe₃)₂)₃], Ln = Gd, Dy, Er. Under an inert atmosphere, a slurry of LnCl₃ (1.86 mmol) in THF was combined with a THF solution of NaN(SiMe₃)₂ (5.57 mmol) at -35 °C. The reaction mixture was gradually warmed to room temperature over 16 h. Solvent was removed

under reduced pressure and the subsequent solid treated with n-pentanes. The solution was filtered over Celite, the collection of the filtrate and storage at -35 °C, resulted in the formation of needle-like crystals of $[\text{Ln}(\text{N}(\text{SiMe}_3)_2)_3]$. Unit cell determinations matched previously reported structures for Ln = Dy and Er, however; no previous report of Ln = Gd exists.

Select characterizations for $[\text{Gd}(\text{N}(\text{SiMe}_3)_2)_3]$. Yield = 52 % IR (neat, cm^{-1}): 2934 (br), 1436 (m), 1235 (s), 1186 (w), 1094 (w), 1045 (w), 978 (s), 807 (w), 765 (w), 655 (m), 601 (s). ^1H NMR (CDCl_3 , 298 K, δ/ppm): -11.67 (br, s, $\text{Si}(\text{CH}_3)_3$, FWHM: 5233.11 Hz).

Select characterizations for $[\text{Dy}(\text{N}(\text{SiMe}_3)_2)_3]$. Yield = 49 % IR (neat, cm^{-1}): 2944 (br), 1424 (m), 1236 (s), 1090 (w), 1048 (w), 974 (s), 827 (m), 768 (m), 656 (s), 604 (s). ^1H NMR (CDCl_3 , 298 K, δ/ppm): -102.37 (br, s, $\text{Si}(\text{CH}_3)_3$, FWHM: 846.39 Hz).

Select characterizations for $[\text{Er}(\text{N}(\text{SiMe}_3)_2)_3]$. Yield = 51 % IR (neat, cm^{-1}): 2945 (br), 1423 (m), 1235 (s), 1090 (w), 1050 (w), 972 (s), 827 (m), 769 (m), 654 (m), 603 (m). ^1H NMR (CDCl_3 , 298 K, δ/ppm): 62.86 (br, s, $\text{Si}(\text{CH}_3)_3$, FWHM: 2670.44 Hz).

Preparation of $[\text{KGd}_2(\text{C}_7\text{H}_7)(\text{N}(\text{SiMe}_3)_2)_4]$ (1**).** Under an inert atmosphere, $\text{Gd}(\text{N}(\text{SiMe}_3)_2)_3$ (58%, 0.350 mmol) was added to a cold solution of $\text{K}(\text{C}_7\text{H}_9)$ (80 mg, 0.605 mmol) at -35 °C in 10 mL of toluene. The reaction mixture was stirred for 12 h, gradually warming to room temperature. The filtrate was then collected and solvent was removed under reduced pressure to achieve an orange-brown oil. Subsequent treatment with toluene and n-hexanes yielded X-ray quality crystals of **1**, (yield = 22 - 26 %). Isolated X-ray diffraction quality crystals are air and moisture sensitive. Bulk purity of compound **1** was determined by X-ray powder diffraction, *vide infra*. IR (neat, cm^{-1}): 2940 (w), 2892 (w), 1587 (br), 1494 (w), 1433 (br), 1240 (s), 1180 (w), 1066 (w), 992 (m), 931 (w), 872 (m), 815 (s), 740 (m), 693 (w), 655 (m). ^1H NMR (toluene- d_8 , 298 K, δ/ppm): -196.04 (br, s, 17.8H, $\text{Si}(\text{CH}_3)_3$, FWHM: 24.52 Hz), -196.93 (br, s, 7H, C_7H_7 , FWHM: 34.76 Hz), -197.28 (br, s, 16.9H, $\text{Si}(\text{CH}_3)_3$, FWHM: 34.46 Hz), -198.09 (br, s, 35.8H, $\text{Si}(\text{CH}_3)_3$, FWHM: 26.38 Hz). ^1H NMR integrations have been calibrated to seven protons on C_7H_7 . Anal. Calcd. for $\text{C}_{31}\text{H}_{79}\text{Gd}_2\text{KN}_4\text{Si}_8$: C, 34.28; H, 7.33; N, 5.16. Found: C, 34.60; H, 7.12; N, 4.93.

Preparation of $[\text{KDy}_2(\text{C}_7\text{H}_7)(\text{N}(\text{SiMe}_3)_2)_4]$ (2**).** Compound **2** was prepared in an analogous manner to **1**. X-ray quality crystals of **2**, (yield = 22 - 26 %). Isolated X-ray diffraction quality crystals are air and moisture sensitive. Bulk purity of compound **2** was determined by X-ray

powder diffraction, *vide infra*. IR (neat, cm^{-1}): 2939 (w), 2891 (w), 1595 (br), 1494 (w), 1421 (br), 1241 (s), 1180 (w), 1083 (w), 999 (m), 932 (w), 879 (m), 820 (s), 729 (m), 694 (w), 662 (m). ^1H NMR (toluene- d_8 , 298 K, δ/ppm): 95.43 (br, s, 17.5H, $\text{Si}(\text{CH}_3)_3$, FWHM: 3604.57 Hz), -34.12 (br, s, 17.9H, $\text{Si}(\text{CH}_3)_3$, FWHM: 3739.31 Hz), -76.68 (br, s, 36.9H, $\text{Si}(\text{CH}_3)_3$, FWHM: 305.09 Hz), -100.81 (br, s, 7H, C_7H_7 , FWHM: 256.67 Hz). ^1H NMR integrations have been calibrated to seven protons on C_7H_7 . Anal. Calcd. for $\text{C}_{31}\text{H}_{79}\text{Dy}_2\text{KN}_4\text{Si}_8$: C, 33.95; H, 7.26; N, 5.11. Found: C, 33.71; H, 6.97; N, 5.43.

Preparation of $[\text{KEr}_2(\text{C}_7\text{H}_7)(\text{N}(\text{SiMe}_3)_2)_4]$ (3**).** Compound **3** was prepared in an analogous manner to **1**. X-ray quality crystals of **3**, (yield = 22 - 26 %). Isolated X-ray diffraction quality crystals are air and moisture sensitive. Bulk purity of compound **3** was determined by X-ray powder diffraction, *vide infra*. IR (neat, cm^{-1}): 2949 (w), 2892 (w), 1662 (w), 1603 (w), 1495 (w), 1435 (br), 1249 (s), 1180 (m), 1079 (w), 988 (m), 931 (m), 882 (w), 822 (s), 728 (m), 693 (w), 661 (m). ^1H NMR (toluene- d_8 , 298 K, δ/ppm): 45.98 (br, s, 17.6H, $\text{Si}(\text{CH}_3)_3$, FWHM: 723.42 Hz), 40.81 (br, s, 37.2H, $\text{Si}(\text{CH}_3)_3$, FWHM: 758.32 Hz), 15.85 (br, s, 7H, C_7H_7 , FWHM: 1807.98 Hz), -98.44 (br, s, 17.8H, $\text{Si}(\text{CH}_3)_3$, FWHM: 963.65 Hz). ^1H NMR integrations have been calibrated to seven protons on C_7H_7 . Anal. Calcd. for $\text{C}_{31}\text{H}_{79}\text{Er}_2\text{KN}_4\text{Si}_8$: C, 33.65; H, 7.20; N, 5.06. Found: C, 33.26; H, 7.09; N, 4.86.

Preparation of $[\text{K}(\text{THF})_2\text{Er}_2(\text{C}_7\text{H}_7)(\text{N}(\text{SiMe}_3)_2)_4]$ (4**).** Under an inert atmosphere, $\text{Er}(\text{N}(\text{SiMe}_3)_2)_3$ (223 mg, 0.350 mmol) was added to a cold solution of $\text{K}(\text{C}_7\text{H}_9)$ (80 mg, 0.605 mmol) at $-35\text{ }^\circ\text{C}$ in 10 mL of toluene. The reaction mixture was stirred for 12 h, gradually warming to room temperature. The filtrate was collected, extracted into THF, and the subsequent filtrate was evaporated to dryness with reduced pressure to achieve an orange-brown oil. Treatment with toluene and n-hexanes yielded x-ray quality crystals of **4**, (yield = 32 %). Isolated X-ray diffraction quality crystals are air and moisture sensitive. IR (neat, cm^{-1}): 2941 (s), 2884 (s), 1461 (w), 1425 (m), 1369 (w), 1243 (s), 1181 (w), 1085 (s), 1052 (m), 989 (m), 869 (m), 818 (m), 753 (m), 711 (w), 691 (w), 662 (m), 603 (m). ^1H NMR (toluene- d_8 , 298 K, δ/ppm): 45.15 (br, s, 17.9H, $\text{Si}(\text{CH}_3)_3$, FWHM: 914.35 Hz), 40.86 (br, s, 35.7H, $\text{Si}(\text{CH}_3)_3$, FWHM: 883.96 Hz), 35.62 (br, s, 7.9H, THF, FWHM: 570.66 Hz), 21.36 (br, s, 7.9H, THF, FWHM: 594.09 Hz), 15.60 (br, s, 7H, C_7H_7 , FWHM: 110.97 Hz), -99.35 (br, s, 17.7H, $\text{Si}(\text{CH}_3)_3$, FWHM: 184.19 Hz). ^1H NMR

integrations have been calibrated to seven protons on C_7H_7 . Anal. Calcd. for $C_{39}H_{95}Er_2KN_4O_2Si_8$: C, 37.46; H, 7.66; N, 4.48. Found: C, 37.91; H, 7.29; N, 4.51.

X-ray Powder Diffraction (XRPD). XRPD experiments were performed using a RIGAKU Ultima IV diffractometer, equipped with a Cu-K α radiation source ($\lambda = 1.541836 \text{ \AA}$), and a graphite monochromator. Scanning of the 2θ range was performed from 5-35°. XRPD pattern was consistent in 2θ values with the generated pattern from XRD, with slight discrepancies in some intensities of peaks attributed to preferred orientation and some broad amorphous character present.

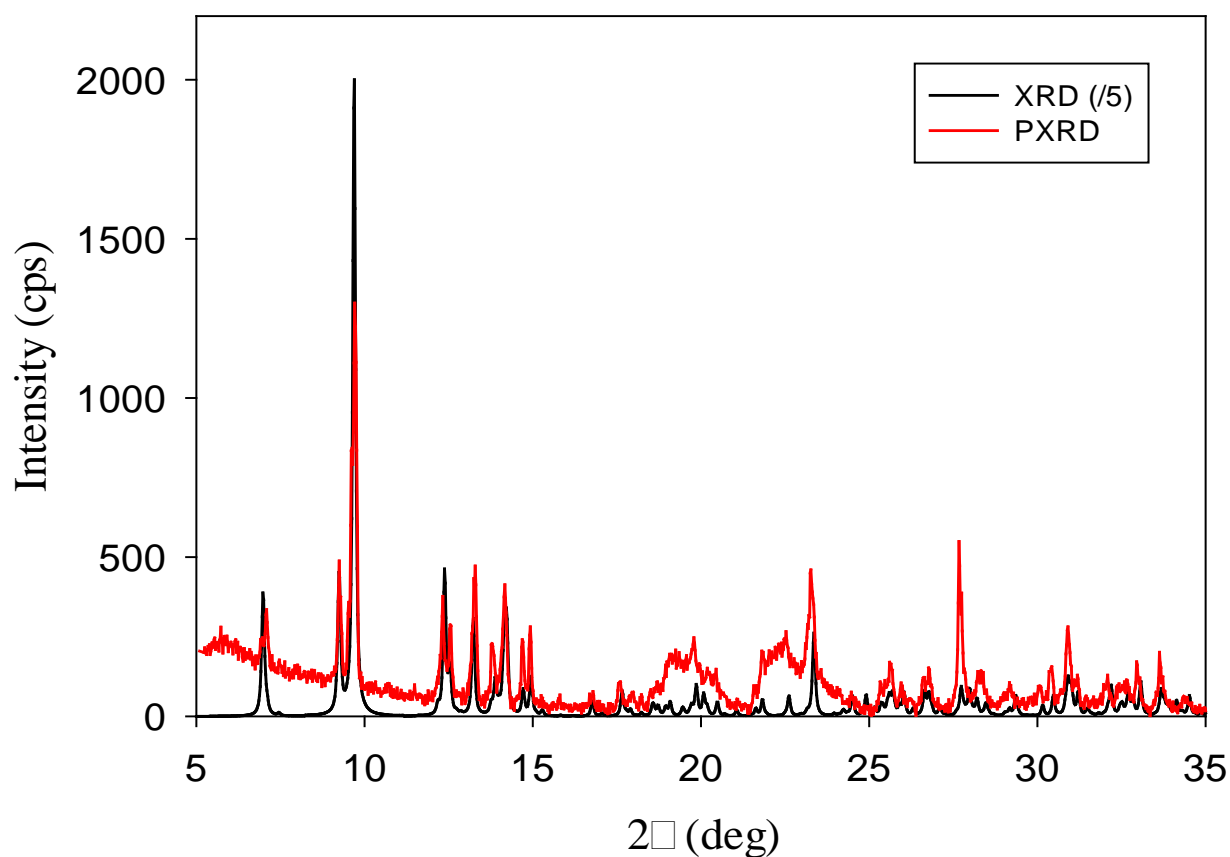


Figure S1. X-ray powder diffraction of $[KGd_2(C_7H_7)(N(SiMe_3)_2)_4]$, **1**, (red) in the 5-35° 2θ region, as compared with the theoretical pattern generated from single crystal X-ray data (black).

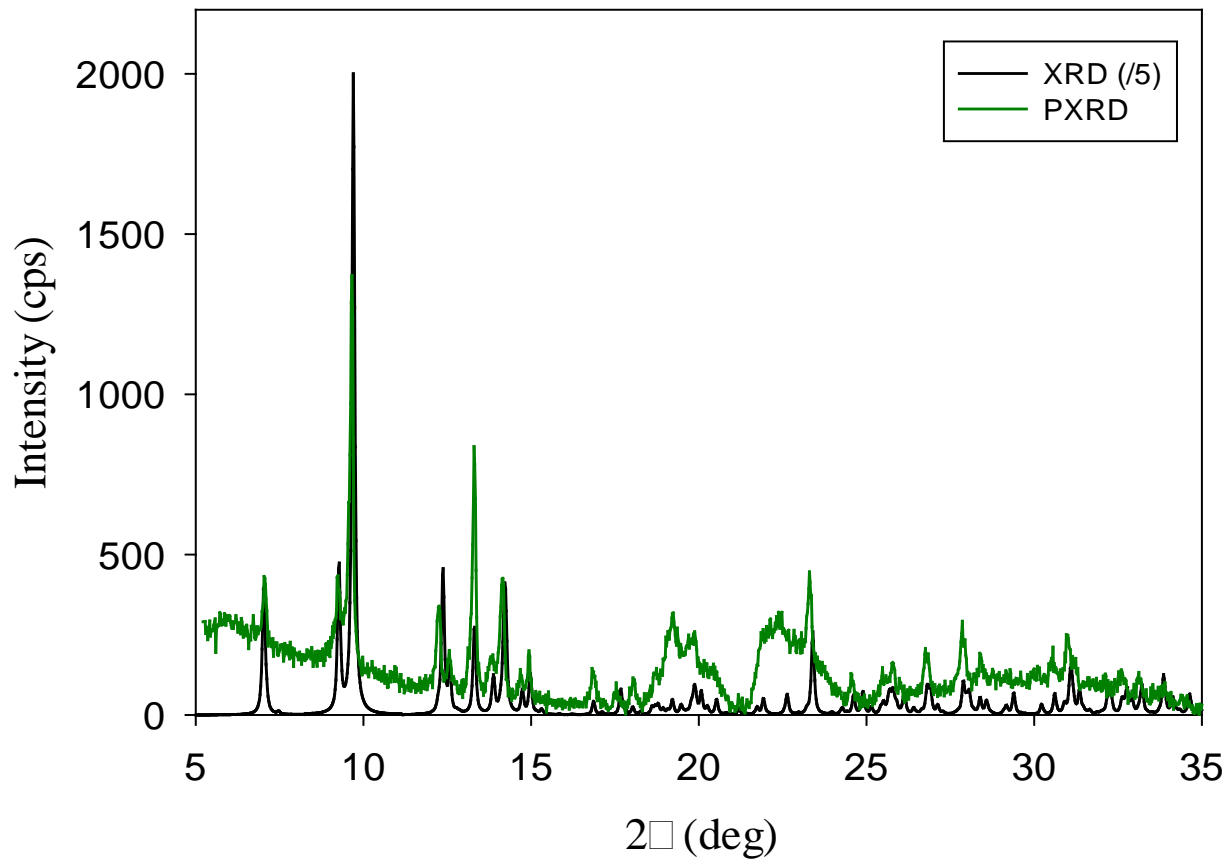


Figure S2. X-ray powder diffraction of $[\text{KDy}_2(\text{C}_7\text{H}_7)(\text{N}(\text{SiMe}_3)_2)_4]$, **2**, (green) in the $5\text{-}35^\circ 2\theta$ region, as compared with the theoretical pattern generated from single crystal X-ray data (black).

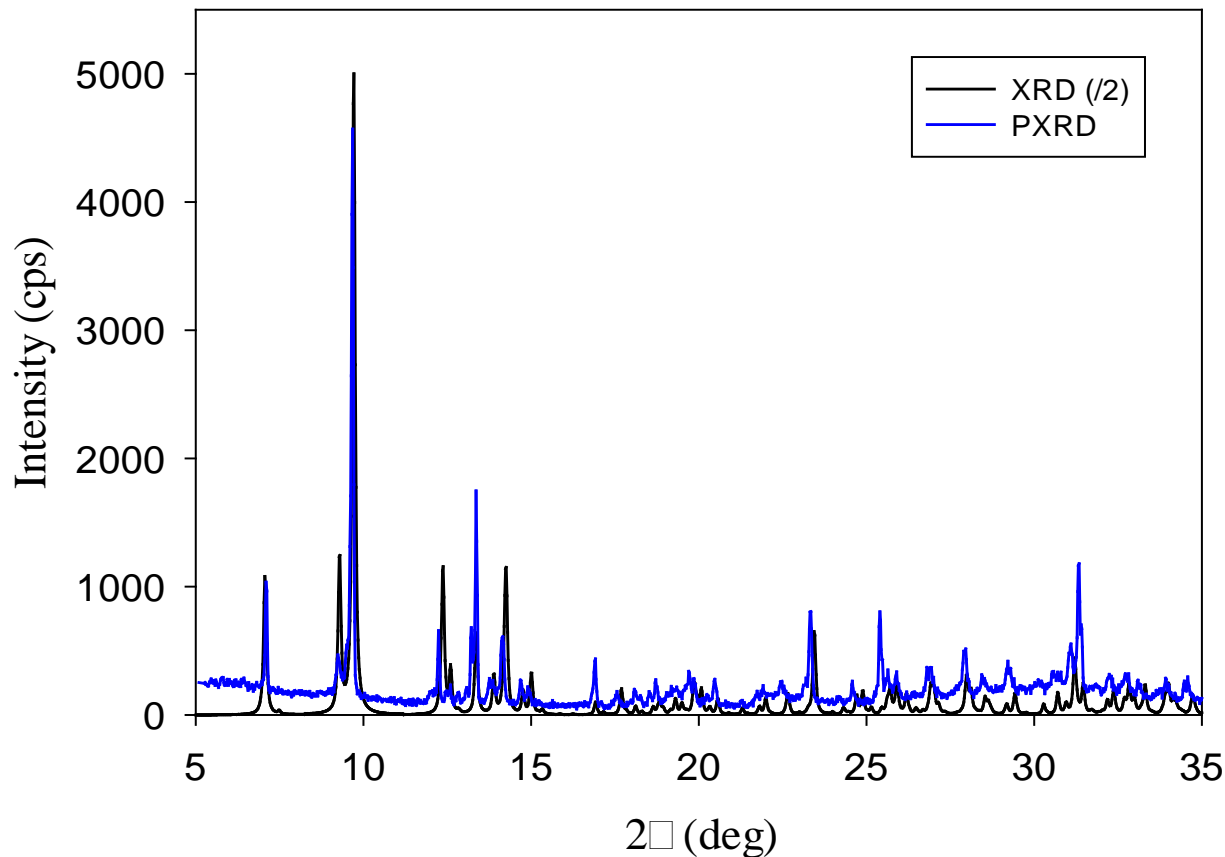


Figure S3. X-ray powder diffraction of $[\text{KEr}_2(\text{C}_7\text{H}_7)(\text{N}(\text{SiMe}_3)_2)_4]$, **3**, (blue) in the $5\text{-}35^\circ$ 2θ region, as compared with the theoretical pattern generated from single crystal X-ray data (black).

Single Crystal X-ray Diffraction Studies. Data collection results for compounds represent the best data sets obtained in several trials for each sample. The crystals were mounted on thin glass fibers using paraffin oil. Prior to data collection crystals were cooled to 200.15 K. Data were collected on a Bruker AXS KAPPA single crystal diffractometer equipped with a sealed Mo tube source (wavelength 0.71073 \AA) APEX II CCD detector. Raw data collection and processing were performed with APEX II software package from BRUKER AXS.³ Diffraction data was collected with a sequence of 0.30° ω scans at 0.00 , 120.0 , and 240.0° in φ . Initial unit cell parameters were determined from 60 data frames with 0.3° ω scan each, collected at the different sections of the

Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied.⁴ Systematic absences in the diffraction data-set and unit-cell parameters were consistent with monoclinic $P2_1/n$ (№11) for compounds **1-3**, and monoclinic $C2/c$ (№15) for compound **4**. Solutions in the centrosymmetric space groups for all samples yielded chemically reasonable and computationally stable results of refinement. Structures were solved by direct methods, completed with difference Fourier synthesis, and refined with full-matrix least-squares procedures based on F^2 .

For all the compounds all hydrogen atoms positions were calculated based on the geometry of related non-hydrogen atoms. All hydrogen atoms were treated as idealized contributions during the refinement. All scattering factors are contained in several versions of the SHELXTL program library, with the latest version used being v.6.12.⁵ Crystallographic data and selected data collection parameters are reported in Table S1.

Table S1. Crystallographic data and selected data collection parameters for dinuclear compounds **1-4**.

| Compound | 1 | 2 | 3 | 4 |
|---------------------------------------|----------------------------|----------------------------|----------------------------|-------------------------------|
| Empirical formula | $C_{31}H_{79}Gd_2KN_4Si_8$ | $C_{31}H_{79}Dy_2KN_4Si_8$ | $C_{31}H_{79}Er_2KN_4Si_8$ | $C_{39}H_{95}Er_2KN_4O_2Si_8$ |
| Formula weight | 1086.30 | 1096.80 | 1106.32 | 1250.52 |
| Crystal size, mm | 0.290x0.203x0.139 | 0.210x0.140x0.120 | 0.800x0.543x0.430 | 0.677x0.530x0.200 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2_1/n$ | $P2_1/n$ | $P2_1/n$ | $C2/c$ |
| Z | 4 | 4 | 4 | 4 |
| a, Å | 14.1700(7) | 14.1259(4) | 14.09464(7) | 20.1042(7) |
| b, Å | 14.2848(7) | 14.2954(4) | 14.2965(8) | 18.7574(6) |
| c, Å | 25.4039(12) | 25.2343(6) | 25.1055(13) | 16.5696(6) |
| α , ° | 90 | 90 | 90 | 90 |
| β , ° | 95.518(2) | 95.2741(13) | 95.170(3) | 107.8505(17) |
| γ , ° | 90 | 90 | 90 | 90 |
| Volume, Å ³ | 5118.3(4) | 5074.1(2) | 5038.3(5) | 5947.6(4) |
| Calculated density, Mg/m ³ | 1.410 | 1.436 | 1.459 | 1.397 |

| | | | | |
|--|---------------------------|---------------------------|---------------------------|---------------------------|
| Absorption coefficient, mm ⁻¹ | 2.861 | 3.217 | 3.606 | 3.066 |
| T (K) | 200(2) | 200(2) | 200(2) | 200(2) |
| F(000) | 2208 | 2224 | 2240 | 2560 |
| Θ range for data collection, ° | 1.584 to 30.595 | 1.723 to 28.424 | 1.598 to 30.659 | 1.520 to 28.381 |
| Limiting indices | h = ±19, k = ±20, l = ±36 | h = ±18, k = ±18, l = ±33 | h = ±20, k = ±20, l = ±35 | h = ±26, k = ±25, l = ±22 |
| Reflections collected / unique | 25502 | 58488 | 26202 | 23004 |
| R(int) | - | 0.0334 | - | 0.0258 |
| Completeness to Θ = 28.32, % | 99.6 | 99.3 | 99.5 | 98.1 |
| Max. and min. transmission | 0.746071 and 0.531793 | 0.7457 and 0.5770 | 0.746065 and 0.304526 | 0.7457 and 0.4771 |
| Data / restraints / parameters | 15195 / 0 / 416 | 12645 / 0 / 415 | 15164 / 0 / 416 | 7321 / 657 / 286 |
| Goodness-of-fit on F ² | 1.055 | 1.019 | 1.063 | 1.071 |
| Final R indices [I > 2σ(I)] | R1 = 0.0330, wR2 = 0.0626 | R1 = 0.0299, wR2 = 0.0642 | R1 = 0.0443, wR2 = 0.1120 | R1 = 0.0384, wR2 = 0.1251 |
| R indices (all data) | R1 = 0.0544, wR2 = 0.0725 | R1 = 0.0424, wR2 = 0.0693 | R1 = 0.0648, wR2 = 0.1336 | R1 = 0.0438, wR2 = 0.1325 |
| Largest diff. peak/hole, e·Å ⁻³ | 2.022 and -0.913 | 1.430 and -1.064 | 3.653 and -2.021 | 1.380 and -2.107 |

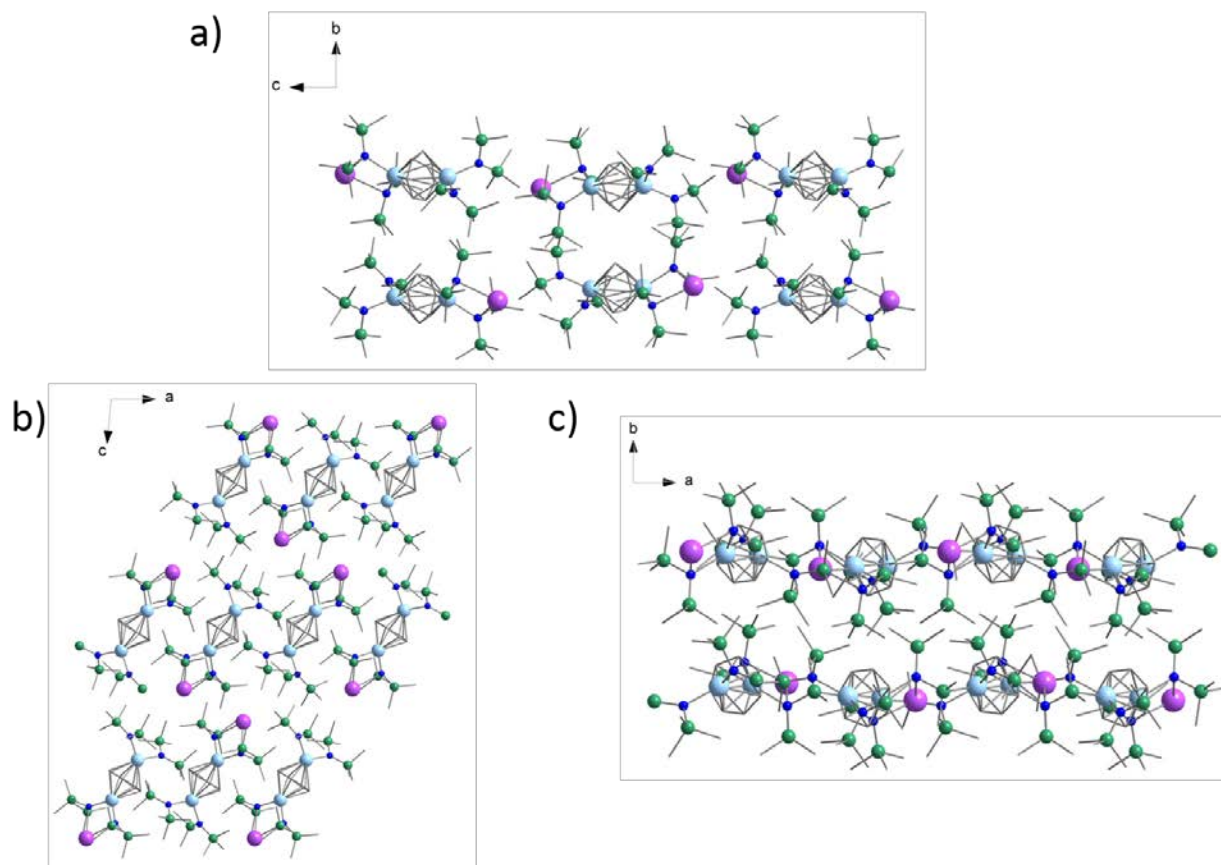


Figure S4. Crystallographic packing diagrams of $[\text{KEr}_2(\text{C}_7\text{H}_7)(\text{N}(\text{SiMe}_3)_2)_4]$ (**3**), (a) along the *a*-axis, (b) along the *b*-axis, and (c) along the *c*-axis. Isostructural compounds **1** and **2** exhibit analogous packing arrangements. Colour code: Er; light blue, Si; green, K; purple, N; royal blue, C; grey.

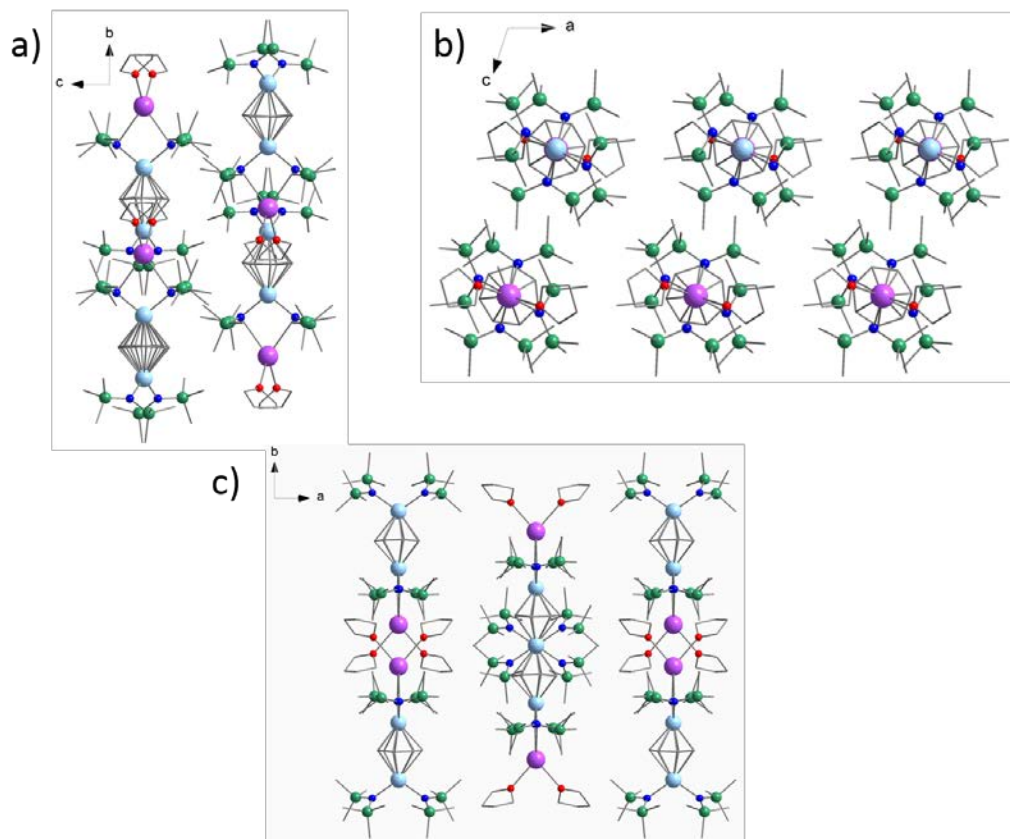


Figure S5. Crystallographic packing diagrams of $[\text{K}(\text{THF})_2\text{Er}_2(\text{C}_7\text{H}_7)(\text{N}(\text{SiMe}_3)_2)_4]$ (**4**) (a) along the a -axis, (b) along the b -axis, and (c) along the c -axis. Colour code: Er; light blue, Si; green, K; purple, N; royal blue, O; red, C; grey.

Magnetic Measurements. The magnetic susceptibility measurements were obtained using a Quantum Design SQUID magnetometer MPMS-XL7 operating between 1.8 and 300 K. DC measurements were performed on a polycrystalline samples of 12 mg, 15 mg, 11 mg, and 21 mg of **1-4** respectively. Samples were wrapped in a polyethylene bag, and subjected to a field of 0 to 7 T. The magnetization data were collected at 100 K to check for ferromagnetic impurities that were absent in all of the samples. Diamagnetic corrections were applied for the sample holder and the inherent diamagnetism of the sample was estimated with the use of Pascals constants.

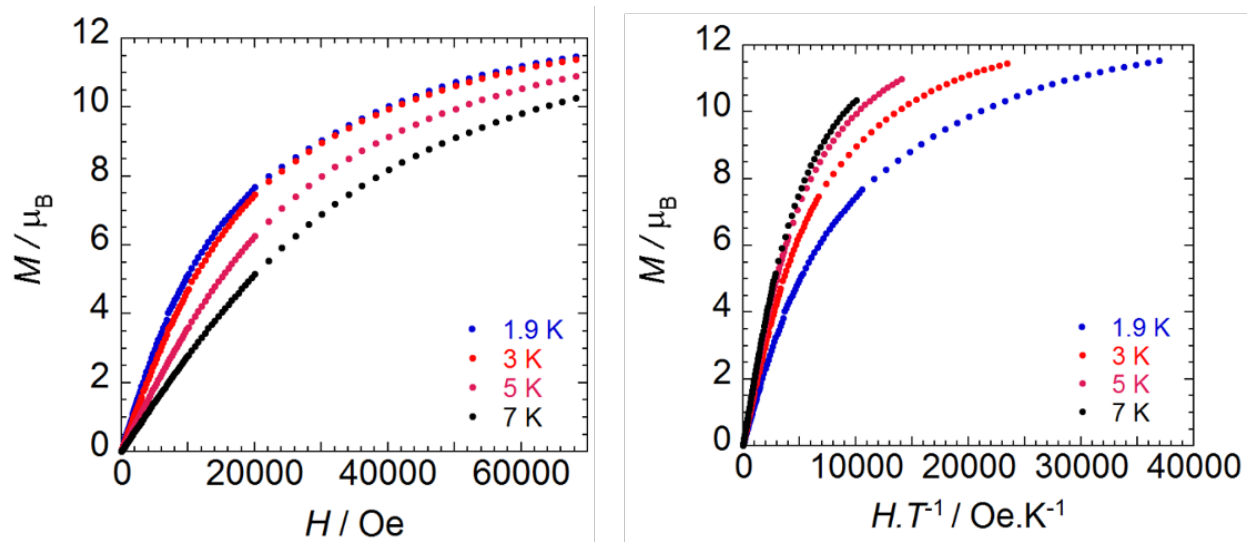


Figure S6. Solid state field dependence of the magnetization (left) and reduced magnetization (right) for **1** at the indicated temperatures.

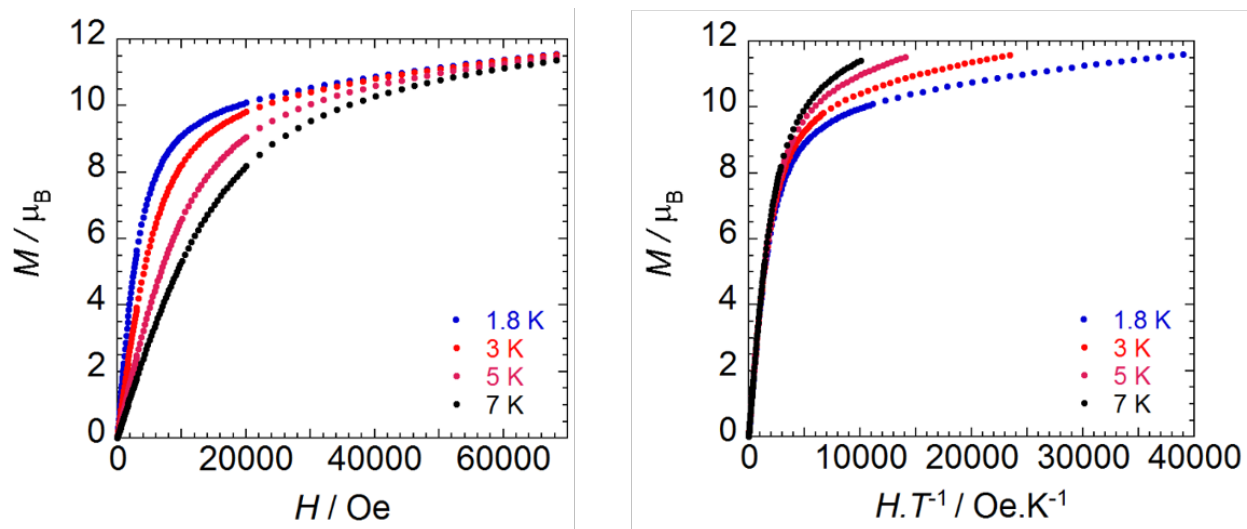


Figure S7. Solid state field dependence of the magnetization (left) and reduced magnetization (right) for **2** at the indicated temperatures.

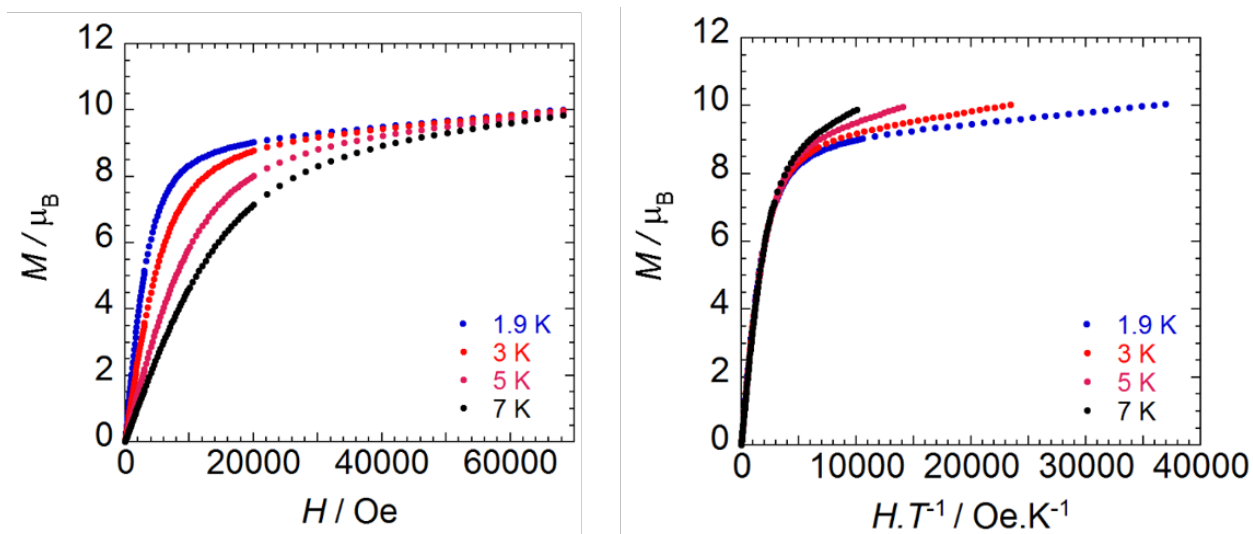


Figure S8. Solid state field dependence of the magnetization (left) and reduced magnetization (right) for **3** at the indicated temperatures.

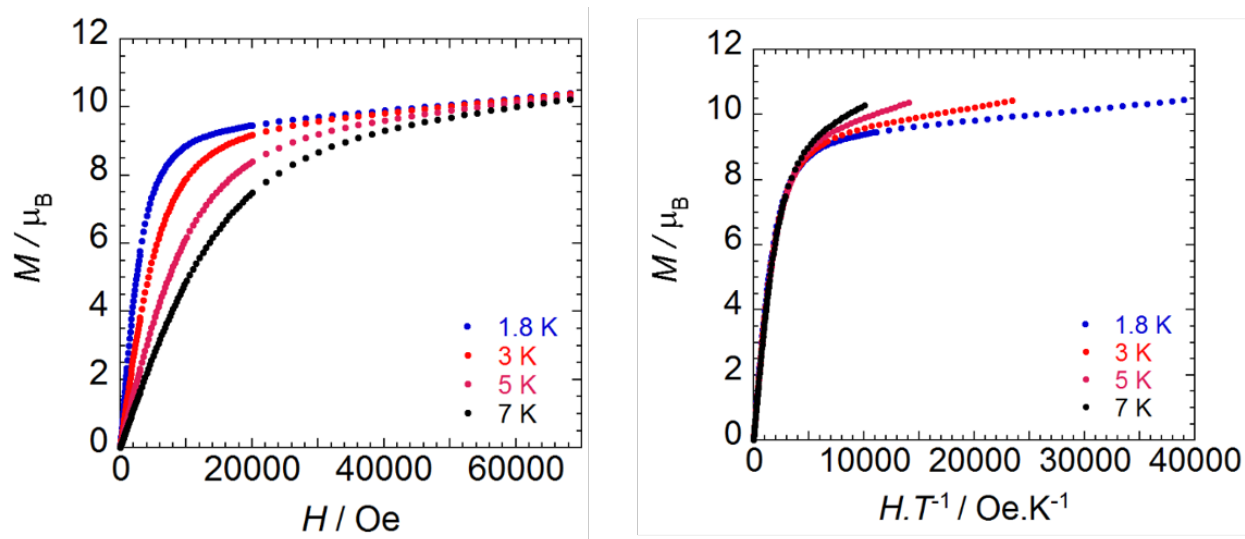


Figure S9. Solid state field dependence of the magnetization (left) and reduced magnetization (right) for **4** at the indicated temperatures.

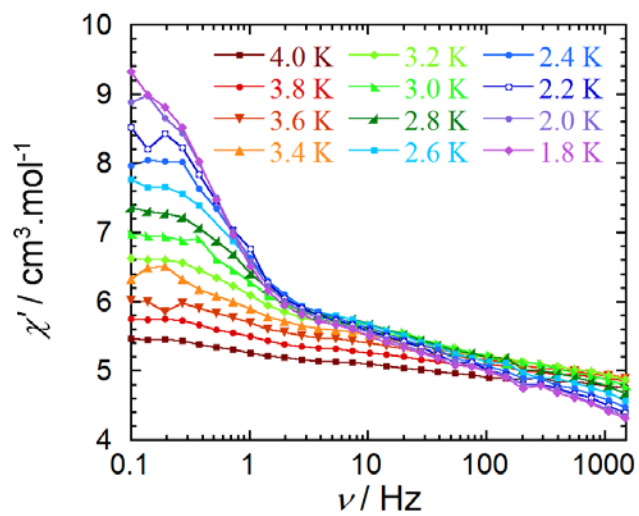


Figure S10. Variable temperature in-phase (χ') magnetic susceptibility of **2** under a static dc field of 2000 Oe at the indicated temperatures.

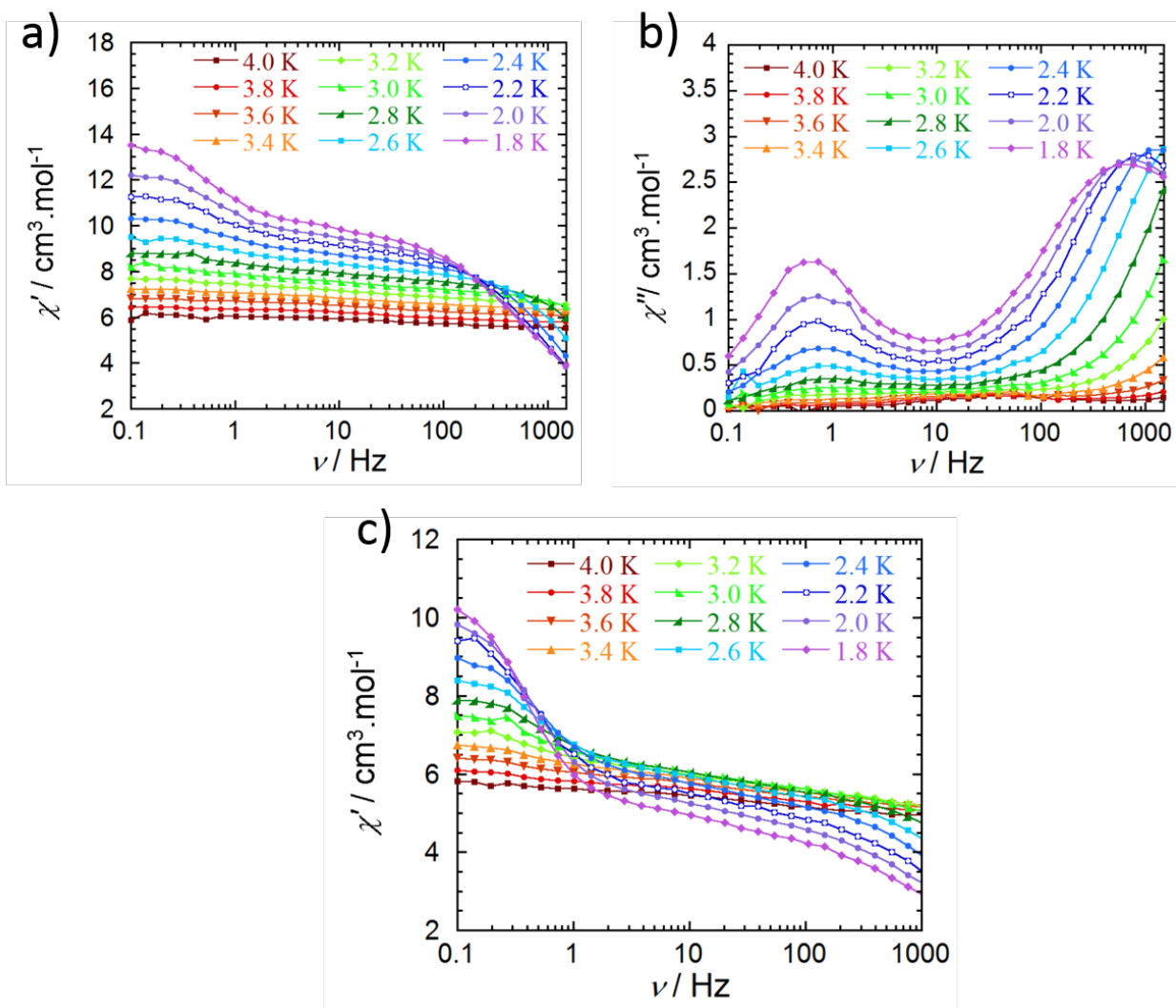


Figure S11. Variable temperature in-phase (χ') (left) and out-of-phase (χ'') (right) magnetic susceptibility of **4** under a static dc field of 1000 Oe for a) and b), and a static dc field of 2000 Oe for c).

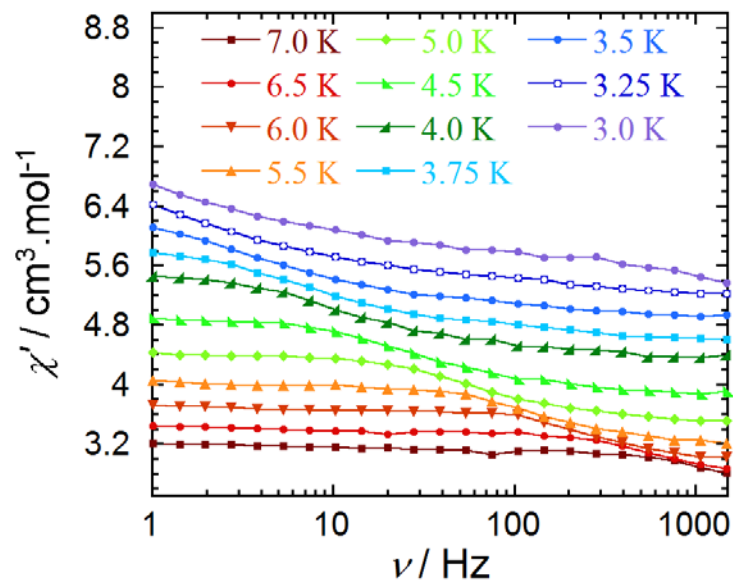


Figure S12. Variable temperature in-phase (χ') magnetic susceptibility of **3** under a static dc field of 800 Oe at the indicated temperatures.

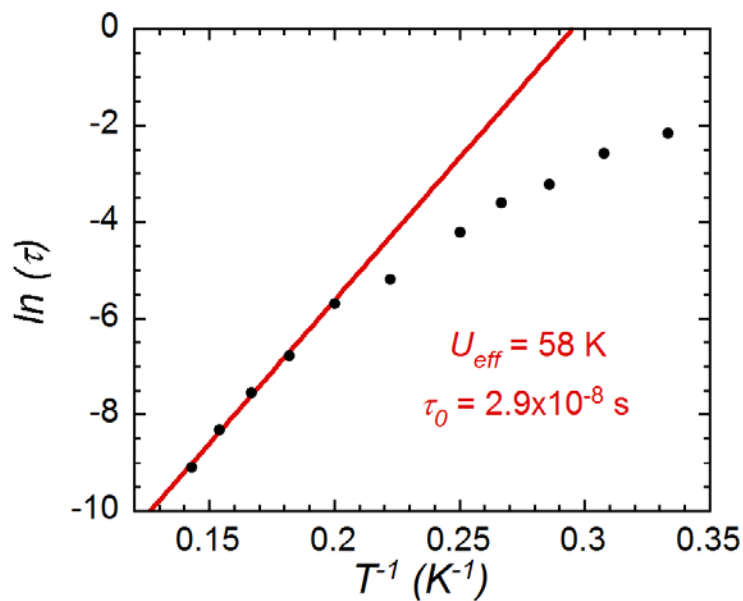


Figure S13. Plot of $\ln(\tau)$ versus T for **3** at $H_{dc} = 800$ Oe. The solid lines represent the Arrhenius fit of the frequency-dependent data.

Supplementary details and results of the *ab initio* investigation

All atoms were described with ANO-RCC basis sets.

MB- basis = minimal

VDZP-basis = medium

VTZP-basis = large

Active space of the CASSCF method included the $4f^n$ configuration only. Active orbitals have a weight of ~95% on the atomic $4f$ basis of the lanthanide.

For Dy sites in 2, 21 spin sextet, 128 spin quartet and 130 spin doublet states were mixed by the spin-orbit coupling within RASSI method.

Table S2: Energies of the spin-free states (CASSCF, cm^{-1}) obtained (cm^{-1}) for compound 2

| Spin | center Dy1 | | | center Dy2 (closer to K) | | |
|-----------|------------|-----------|-----------|--------------------------|-----------|-----------|
| | MB | VDZP | VTZP | MB | VDZP | VTZP |
| 5/2 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| | 2.474 | 4.246 | 3.178 | 3.137 | 4.691 | 1.722 |
| | 409.135 | 227.343 | 211.574 | 323.618 | 171.324 | 142.252 |
| | 415.058 | 230.054 | 217.847 | 326.966 | 173.509 | 153.125 |
| | 902.801 | 587.152 | 589.227 | 748.301 | 498.397 | 489.099 |
| | 914.863 | 636.990 | 638.454 | 793.749 | 571.281 | 566.165 |
| | 1297.404 | 905.348 | 896.145 | 1144.466 | 802.836 | 801.952 |
| | 1411.179 | 952.155 | 972.300 | 1193.025 | 847.156 | 825.479 |
| | 1543.080 | 1065.365 | 1072.233 | 1378.895 | 972.410 | 950.893 |
| | 1766.843 | 1233.284 | 1277.700 | 1421.885 | 1042.853 | 1084.803 |
| | 1784.372 | 1246.257 | 1287.899 | 1473.743 | 1068.972 | 1100.454 |
| | 7864.661 | 7826.886 | 7847.631 | 7730.022 | 7747.265 | 7756.298 |
| | 7948.126 | 7926.369 | 7945.621 | 7833.453 | 7862.842 | 7871.222 |
| | 8150.293 | 8027.948 | 8059.192 | 7941.128 | 7908.270 | 7926.140 |
| | 8192.636 | 8131.564 | 8178.854 | 7990.573 | 8023.747 | 8067.599 |
| | 8255.602 | 8162.603 | 8212.629 | 8037.712 | 8041.310 | 8084.381 |
| | 8448.307 | 8268.844 | 8310.793 | 8282.155 | 8177.179 | 8199.736 |
| | 8456.183 | 8286.725 | 8324.144 | 8300.024 | 8200.042 | 8215.927 |
| | ... | ... | ... | ... | ... | ... |
| | 3/2 | 24089.220 | 24878.442 | 25045.965 | 24025.489 | 24826.678 |
| 24089.769 | | 24878.859 | 25050.191 | 24026.355 | 24829.323 | 24928.182 |
| 24212.016 | | 24938.925 | 25250.447 | 24098.607 | 24859.535 | 24953.101 |
| 24216.611 | | 24943.391 | 25276.157 | 24107.254 | 24867.875 | 24961.299 |
| 24437.654 | | 25142.728 | 25284.207 | 24319.195 | 25043.514 | 25138.292 |
| 24457.534 | | 25169.667 | 25307.902 | 24340.013 | 25061.376 | 25160.230 |
| 24494.047 | | 25172.825 | 25332.565 | 24379.566 | 25083.920 | 25173.699 |
| 24523.677 | | 25199.999 | 25360.688 | 24389.836 | 25099.942 | 25189.484 |
| 24526.219 | | 25220.129 | 25434.223 | 24402.741 | 25142.018 | 25248.532 |
| 24540.219 | | 25248.783 | 25442.568 | 24430.176 | 25177.239 | 25279.846 |
| 24631.527 | | 25326.897 | 25483.973 | 24515.567 | 25236.432 | 25334.083 |
| 24673.884 | | 25339.456 | 25496.477 | 24524.512 | 25269.491 | 25359.367 |
| 24681.209 | | 25378.389 | 25515.506 | 24553.713 | 25291.210 | 25385.392 |
| 24721.840 | | 25386.406 | 25549.553 | 24590.790 | 25326.020 | 25418.702 |
| 24724.455 | | 25408.220 | 25555.914 | 24604.023 | 25328.256 | 25421.254 |
| 24750.429 | | 25437.287 | 25564.352 | 24618.946 | 25338.147 | 25441.142 |
| 24759.203 | | 25443.368 | 25574.061 | 24637.113 | 25340.991 | 25444.941 |
| 24773.311 | | 25454.697 | 25600.410 | 24659.376 | 25375.470 | 25470.667 |
| ... | | ... | ... | ... | ... | ... |
| 1/2 | | 36261.082 | 37383.117 | 37552.313 | 36120.008 | 37288.335 |
| | 36263.201 | 37386.673 | 37556.093 | 36122.074 | 37291.596 | 37440.843 |
| | 36270.563 | 37394.315 | 37563.033 | 36125.220 | 37293.950 | 37443.636 |
| | 36273.153 | 37398.981 | 37567.972 | 36127.495 | 37297.703 | 37447.211 |
| | 36474.471 | 37557.726 | 37726.943 | 36322.087 | 37452.840 | 37604.295 |
| | 36485.801 | 37566.070 | 37734.584 | 36327.348 | 37454.787 | 37605.889 |
| | 36501.045 | 37571.716 | 37740.569 | 36343.198 | 37469.735 | 37620.570 |
| | 36504.919 | 37575.333 | 37744.192 | 36347.072 | 37473.026 | 37623.793 |
| | 36526.645 | 37615.652 | 37788.478 | 36377.230 | 37521.774 | 37678.168 |
| | 36577.834 | 37658.792 | 37832.372 | 36408.520 | 37547.097 | 37704.275 |
| | 36596.897 | 37690.621 | 37867.466 | 36454.019 | 37600.812 | 37763.060 |
| | 36614.602 | 37710.534 | 37889.328 | 36463.701 | 37605.239 | 37767.691 |
| | 36643.208 | 37744.925 | 37926.952 | 36504.200 | 37652.193 | 37818.028 |
| | 36677.199 | 37756.758 | 37935.608 | 36525.104 | 37661.801 | 37828.946 |

| | | | | | | |
|--|-----------|-----------|-----------|-----------|-----------|-----------|
| | 36680.591 | 37766.668 | 37947.545 | 36533.498 | 37675.009 | 37842.896 |
| | 36713.633 | 37809.614 | 37984.848 | 36600.470 | 37728.882 | 37884.106 |
| | 36715.801 | 37811.426 | 37986.956 | 36601.855 | 37729.942 | 37885.495 |
| | 37784.444 | 38989.541 | 39160.535 | 37671.830 | 38905.462 | 39057.197 |
| | 37786.932 | 38995.480 | 39167.174 | 37677.426 | 38915.036 | 39068.446 |
| | 37861.250 | 39026.889 | 39196.933 | 37707.601 | 38922.724 | 39073.348 |
| | 37866.167 | 39036.762 | 39207.592 | 37716.807 | 38935.853 | 39088.201 |
| | ... | ... | ... | ... | ... | ... |

Table S3: Energies of the spin-orbit states (RASSI, cm⁻¹) obtained for compound 2

| center Dy1 | | | center Dy2 (closer to K) | | |
|------------|--------|--------|--------------------------|--------|--------|
| MB | VDZP | VTZP | MB | VDZP | VTZP |
| 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 246.5 | 126.3 | 115.9 | 188.2 | 86.3 | 69.1 |
| 246.5 | 126.3 | 115.9 | 188.2 | 86.3 | 69.1 |
| 532.8 | 332.2 | 327.7 | 440.8 | 279.3 | 269.6 |
| 532.8 | 332.2 | 327.7 | 440.8 | 279.3 | 269.6 |
| 823.3 | 534.4 | 530.4 | 697.1 | 456.7 | 440.6 |
| 823.3 | 534.4 | 530.4 | 697.1 | 456.7 | 440.6 |
| 1084.2 | 721.6 | 720.3 | 932.7 | 626.2 | 614.0 |
| 1084.2 | 721.6 | 720.3 | 932.7 | 626.2 | 614.0 |
| 1278.1 | 856.9 | 851.3 | 1129.9 | 777.8 | 754.3 |
| 1278.1 | 856.9 | 851.3 | 1129.9 | 777.8 | 754.3 |
| 1478.2 | 987.6 | 1010.3 | 1254.0 | 855.6 | 853.6 |
| 1478.2 | 987.6 | 1010.3 | 1254.0 | 855.6 | 853.6 |
| 1720.0 | 1171.7 | 1213.7 | 1376.3 | 982.4 | 1021.0 |
| 1720.0 | 1171.7 | 1213.7 | 1376.3 | 982.4 | 1021.0 |
| 3542.3 | 3660.3 | 3638.0 | 3505.3 | 3641.7 | 3622.5 |
| 3542.3 | 3660.3 | 3638.0 | 3505.3 | 3641.7 | 3622.5 |
| 3816.8 | 3832.3 | 3806.3 | 3740.4 | 3784.9 | 3753.6 |
| 3816.8 | 3832.3 | 3806.3 | 3740.4 | 3784.9 | 3753.6 |
| 4087.3 | 4015.1 | 3986.2 | 3982.2 | 3949.9 | 3912.7 |
| 4087.3 | 4015.1 | 3986.2 | 3982.2 | 3949.9 | 3912.7 |
| 4296.8 | 4158.2 | 4125.8 | 4177.1 | 4080.6 | 4038.1 |
| 4296.8 | 4158.2 | 4125.8 | 4177.1 | 4080.6 | 4038.1 |
| 4448.0 | 4258.6 | 4228.4 | 4334.4 | 4187.2 | 4132.1 |
| 4448.0 | 4258.6 | 4228.4 | 4334.4 | 4187.2 | 4132.1 |
| 4657.2 | 4397.3 | 4389.7 | 4443.8 | 4267.8 | 4245.7 |
| 4657.2 | 4397.3 | 4389.7 | 4443.8 | 4267.8 | 4245.7 |
| 4969.3 | 4624.0 | 4634.3 | 4646.2 | 4445.6 | 4451.3 |
| 4969.3 | 4624.0 | 4634.3 | 4646.2 | 4445.6 | 4451.3 |
| 6084.7 | 6266.4 | 6233.4 | 6008.4 | 6224.0 | 6193.4 |
| 6084.7 | 6266.4 | 6233.4 | 6008.4 | 6224.0 | 6193.4 |
| ... | ... | ... | ... | ... | ... |

Table S4: Energies of the spin-free states (CASSCF, cm⁻¹) obtained for compound 3

| Spin | center Er1 | | | center Er2 (closer to K) | | |
|------|------------|-----------|-----------|--------------------------|---------|-----------|
| | MB | VDZP | VTZP | MB | VDZP | VTZP |
| 3/2 | 0.000 | 0.000 | 0.000 | 0.000 | 0.0 | 0.000 |
| | 3.111 | 4.869 | 3.639 | 6.519 | 7.7 | 4.239 |
| | 115.020 | 83.264 | 103.620 | 13.112 | 30.0 | 61.022 |
| | 115.532 | 90.264 | 109.525 | 19.018 | 39.3 | 67.175 |
| | 208.705 | 174.102 | 180.176 | 174.309 | 163.5 | 168.959 |
| | 225.265 | 178.531 | 185.630 | 196.966 | 170.1 | 177.354 |
| | 250.142 | 211.531 | 224.979 | 208.022 | 186.1 | 203.275 |
| | 331.753 | 235.651 | 243.624 | 283.585 | 210.3 | 215.495 |
| | 335.571 | 248.422 | 261.508 | 291.255 | 212.7 | 222.247 |
| | 615.665 | 470.409 | 487.767 | 542.054 | 434.5 | 453.861 |
| | 619.424 | 476.582 | 494.186 | 542.885 | 435.3 | 454.801 |
| | 741.919 | 547.178 | 563.698 | 618.887 | 477.9 | 493.705 |
| | 743.180 | 549.694 | 566.305 | 620.105 | 479.1 | 495.265 |
| | 17253.938 | 17958.383 | 18068.673 | 17239.930 | 17941.3 | 18061.140 |
| | 17255.091 | 17966.345 | 18074.171 | 17243.016 | 17952.1 | 18067.521 |
| | 17639.830 | 18186.170 | 18278.450 | 17642.016 | 18185.6 | 18270.283 |
| | 17728.391 | 18249.966 | 18338.134 | 17695.745 | 18233.6 | 18309.931 |

| | | | | | | |
|-----|-----------|-----------|-----------|-----------|-----------|-----------|
| | 17769.056 | 18277.684 | 18382.060 | 17755.403 | 18242.3 | 18345.953 |
| | 17796.354 | 18339.970 | 18449.867 | 17772.773 | 18337.9 | 18448.962 |
| | 18135.229 | 18530.618 | 18643.304 | 17999.665 | 18443.8 | 18554.713 |
| | 18245.623 | 18648.720 | 18764.638 | 18126.210 | 18579.4 | 18693.855 |
| | 27530.849 | 28380.737 | 28531.265 | 27474.428 | 28330.4 | 28474.845 |
| | 27553.281 | 28389.772 | 28542.028 | 27482.672 | 28341.5 | 28484.964 |
| | 27595.406 | 28402.192 | 28553.636 | 27503.386 | 28358.3 | 28510.501 |
| | 27788.547 | 28584.501 | 28740.514 | 27686.884 | 28515.0 | 28667.136 |
| | 27904.512 | 28701.883 | 28861.079 | 27809.020 | 28644.7 | 28802.327 |
| | 27957.205 | 28786.810 | 28949.534 | 27919.759 | 28760.5 | 28925.305 |
| | 28013.568 | 28806.147 | 28975.199 | 27924.083 | 28766.2 | 28931.057 |
| | 28040.107 | 28831.305 | 28994.709 | 27957.147 | 28789.1 | 28949.676 |
| | 28058.863 | 28854.509 | 29024.224 | 27965.354 | 28806.2 | 28975.011 |
| | ... | ... | ... | ... | ... | ... |
| 1/2 | 17292.960 | 17917.565 | 18047.449 | 17272.905 | 17900.137 | 18028.308 |
| | 17293.828 | 17918.150 | 18047.840 | 17273.474 | 17900.339 | 18028.644 |
| | 17359.103 | 17954.359 | 18079.612 | 17316.738 | 17923.701 | 18047.227 |
| | 17360.155 | 17955.560 | 18081.586 | 17317.281 | 17925.000 | 18049.450 |
| | 17436.118 | 17999.013 | 18122.387 | 17389.535 | 17968.823 | 18091.160 |
| | 17444.193 | 18004.287 | 18128.581 | 17390.593 | 17970.177 | 18092.616 |
| | 17486.853 | 18027.891 | 18148.572 | 17437.897 | 17996.689 | 18114.068 |
| | 17512.791 | 18047.999 | 18171.694 | 17442.450 | 18005.342 | 18128.631 |
| | 17521.760 | 18053.603 | 18176.005 | 17461.098 | 18015.889 | 18136.485 |
| | 17590.885 | 18099.097 | 18222.979 | 17497.246 | 18043.753 | 18168.278 |
| | 17591.059 | 18099.310 | 18223.231 | 17497.878 | 18043.895 | 18168.440 |
| | 22684.858 | 23581.286 | 23735.519 | 22690.617 | 23581.266 | 23737.894 |
| | 22686.390 | 23583.902 | 23738.691 | 22690.776 | 23583.034 | 23741.053 |
| | 22984.278 | 23758.116 | 23905.564 | 22934.928 | 23724.486 | 23868.703 |
| | 22999.233 | 23774.992 | 23921.506 | 22952.129 | 23742.978 | 23888.024 |
| | 23207.804 | 23917.549 | 24057.737 | 23151.279 | 23882.481 | 24029.039 |
| | 23249.583 | 23942.855 | 24094.834 | 23188.001 | 23900.294 | 24034.078 |
| | 23320.529 | 23988.260 | 24132.885 | 23267.761 | 23951.322 | 24084.377 |
| | 23531.999 | 24145.694 | 24307.567 | 23374.910 | 24055.665 | 24217.778 |
| | 23533.754 | 24148.034 | 24310.608 | 23379.610 | 24056.240 | 24220.339 |
| | 25264.357 | 26378.113 | 26519.679 | 25424.708 | 26462.900 | 26593.309 |
| | 25265.522 | 26378.425 | 26519.895 | 25431.372 | 26463.937 | 26593.646 |
| | 25560.670 | 26619.260 | 26782.028 | 25551.428 | 26617.055 | 26803.143 |
| | 25586.694 | 26635.600 | 26793.250 | 25603.612 | 26649.577 | 26830.279 |
| | 25721.001 | 26722.130 | 26911.222 | 25663.649 | 26676.372 | 26865.063 |
| | 25850.257 | 26798.002 | 26984.473 | 25795.742 | 26753.362 | 26937.043 |
| | 25884.486 | 26841.710 | 27016.340 | 25857.828 | 26828.239 | 27004.424 |
| | 26146.747 | 27001.672 | 27177.492 | 26088.933 | 26968.171 | 27138.390 |
| | 26166.878 | 27030.175 | 27207.926 | 26101.906 | 26987.275 | 27167.555 |
| | 26519.826 | 27257.286 | 27429.725 | 26419.012 | 27193.587 | 27358.130 |
| | ... | ... | ... | ... | ... | ... |

Table S5: Energies of the spin-orbit states (RASSI, cm⁻¹) obtained for compound 3

| center Er1 | | | center Er2 (closer to K) | | |
|------------|--------|--------|--------------------------|--------|--------|
| MB | VDZP | VTZP | MB | VDZP | VTZP |
| 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 130.9 | 99.6 | 121.5 | 12.4 | 37.7 | 73.9 |
| 130.9 | 99.6 | 121.5 | 12.4 | 37.7 | 73.9 |
| 173.1 | 142.2 | 148.3 | 138.1 | 130.3 | 138.4 |
| 173.1 | 142.2 | 148.3 | 138.1 | 130.3 | 138.4 |
| 237.5 | 198.8 | 211.0 | 177.7 | 168.5 | 188.0 |
| 237.5 | 198.8 | 211.0 | 177.7 | 168.5 | 188.0 |
| 318.5 | 247.3 | 261.5 | 259.6 | 214.4 | 231.1 |
| 318.5 | 247.3 | 261.5 | 259.6 | 214.4 | 231.1 |
| 440.8 | 323.5 | 334.7 | 366.3 | 276.1 | 285.1 |
| 440.8 | 323.5 | 334.7 | 366.3 | 276.1 | 285.1 |
| 662.1 | 508.0 | 525.2 | 563.6 | 454.9 | 475.7 |
| 662.1 | 508.0 | 525.2 | 563.6 | 454.9 | 475.7 |
| 751.2 | 557.7 | 573.0 | 618.8 | 483.1 | 500.5 |
| 751.2 | 557.7 | 573.0 | 618.8 | 483.1 | 500.5 |
| 6342.5 | 6640.4 | 6594.9 | 6328.7 | 6634.0 | 6590.4 |
| 6342.5 | 6640.4 | 6594.9 | 6328.7 | 6634.0 | 6590.4 |
| 6445.3 | 6731.1 | 6699.2 | 6354.0 | 6678.6 | 6664.0 |
| 6445.3 | 6731.1 | 6699.2 | 6354.0 | 6678.6 | 6664.0 |

| | | | | | |
|---------|---------|---------|---------|---------|---------|
| 6488.9 | 6757.1 | 6722.5 | 6435.1 | 6732.1 | 6698.1 |
| 6488.9 | 6757.1 | 6722.5 | 6435.1 | 6732.1 | 6698.1 |
| 6573.1 | 6823.6 | 6789.9 | 6508.5 | 6787.8 | 6759.7 |
| 6573.1 | 6823.6 | 6789.9 | 6508.5 | 6787.8 | 6759.7 |
| 6691.0 | 6901.7 | 6866.9 | 6617.3 | 6856.6 | 6823.3 |
| 6691.0 | 6901.7 | 6866.9 | 6617.3 | 6856.6 | 6823.3 |
| 6868.4 | 7041.3 | 7010.3 | 6775.7 | 6989.0 | 6962.0 |
| 6868.4 | 7041.3 | 7010.3 | 6775.7 | 6989.0 | 6962.0 |
| 6973.3 | 7100.4 | 7066.3 | 6852.2 | 7028.9 | 6996.5 |
| 6973.3 | 7100.4 | 7066.3 | 6852.2 | 7028.9 | 6996.5 |
| 10259.3 | 10710.8 | 10665.3 | 10227.0 | 10694.2 | 10652.4 |
| 10259.3 | 10710.8 | 10665.3 | 10227.0 | 10694.2 | 10652.4 |
| ... | ... | ... | ... | ... | ... |

Table S6: Energies of the spin-free states (CASSCF, cm⁻¹) obtained for compound 4

| Spin | center Er1 (closer to K) | | center Er2 | |
|-----------|--------------------------|-----------|------------|-----------|
| | MB | VTZP | MB | VTZP |
| 3/2 | 0.000 | 0.000 | 0.000 | 0.000 |
| | 4.289 | 3.971 | 3.278 | 4.644 |
| | 11.047 | 55.444 | 78.646 | 76.283 |
| | 15.708 | 60.947 | 79.520 | 81.932 |
| | 164.763 | 164.963 | 191.388 | 181.490 |
| | 185.434 | 173.560 | 218.862 | 187.682 |
| | 209.498 | 196.178 | 231.046 | 208.715 |
| | 282.097 | 213.211 | 322.865 | 241.982 |
| | 290.020 | 220.784 | 326.843 | 248.471 |
| | 541.452 | 449.134 | 612.684 | 482.300 |
| | 543.130 | 452.390 | 613.781 | 484.145 |
| | 632.411 | 499.354 | 775.525 | 581.542 |
| | 633.834 | 501.969 | 775.934 | 582.357 |
| | 17223.296 | 18045.865 | 17191.770 | 18026.327 |
| | 17226.649 | 18052.120 | 17193.894 | 18032.905 |
| | 17638.290 | 18274.982 | 17630.826 | 18288.316 |
| | 17694.880 | 18324.399 | 17719.116 | 18376.710 |
| | 17754.726 | 18345.399 | 17768.964 | 18378.526 |
| | 17778.286 | 18438.286 | 17835.010 | 18443.366 |
| | 18012.271 | 18558.975 | 18149.643 | 18640.460 |
| | 18129.892 | 18697.099 | 18245.684 | 18766.845 |
| | 27486.646 | 28484.081 | 27542.082 | 28529.310 |
| | 27495.699 | 28493.087 | 27555.129 | 28551.803 |
| | 27513.128 | 28520.379 | 27593.624 | 28557.443 |
| | 27703.935 | 28679.509 | 27810.496 | 28754.126 |
| | 27818.730 | 28809.408 | 27929.105 | 28879.216 |
| | 27906.946 | 28918.089 | 27945.863 | 28943.805 |
| | 27914.418 | 28918.681 | 27978.126 | 28950.970 |
| | 27952.200 | 28944.944 | 28019.763 | 28978.911 |
| | 27962.976 | 28966.223 | 28059.603 | 29019.666 |
| | ... | ... | ... | ... |
| | 1/2 | 17265.233 | 18023.205 | 17273.547 |
| 17265.754 | | 18023.429 | 17274.152 | 18035.933 |
| 17315.335 | | 18045.826 | 17353.320 | 18076.984 |
| 17316.181 | | 18048.458 | 17353.590 | 18078.798 |
| 17388.200 | | 18089.072 | 17437.498 | 18123.360 |
| 17391.558 | | 18092.943 | 17439.879 | 18126.899 |
| 17438.405 | | 18116.237 | 17495.183 | 18153.414 |
| 17446.860 | | 18128.474 | 17505.539 | 18167.374 |
| 17464.103 | | 18136.694 | 17519.597 | 18173.113 |
| 17495.280 | | 18168.386 | 17575.671 | 18215.887 |
| 17496.265 | | 18168.449 | 17575.958 | 18216.071 |
| 22676.350 | | 23726.109 | 22646.659 | 23709.474 |
| 22677.330 | | 23728.745 | 22647.261 | 23711.162 |
| 22938.901 | | 23871.372 | 22989.981 | 23910.107 |
| 22955.784 | | 23891.298 | 23007.480 | 23929.275 |
| 23154.372 | | 24030.040 | 23239.419 | 24084.649 |
| 23202.963 | | 24046.468 | 23259.128 | 24096.172 |
| 23281.885 | | 24094.948 | 23350.788 | 24152.340 |

| | | | | |
|--|-----------|-----------|-----------|-----------|
| | 23375.581 | 24220.846 | 23506.782 | 24296.385 |
| | 23383.195 | 24222.312 | 23511.404 | 24297.051 |
| | 25416.021 | 26587.281 | 25288.450 | 26533.507 |
| | 25424.433 | 26587.837 | 25291.270 | 26534.043 |
| | 25522.609 | 26784.141 | 25511.306 | 26762.373 |
| | 25567.855 | 26812.561 | 25572.436 | 26793.569 |
| | 25659.612 | 26847.132 | 25609.953 | 26832.520 |
| | 25784.139 | 26920.471 | 25775.198 | 26921.135 |
| | 25845.175 | 26995.745 | 25829.973 | 26989.127 |
| | 26081.222 | 27133.520 | 26108.544 | 27156.314 |
| | 26092.526 | 27159.819 | 26123.561 | 27179.356 |
| | 26420.169 | 27363.981 | 26509.243 | 27428.644 |
| | ... | ... | ... | ... |

Table S7: Energies of the spin-orbit states (RASSI, cm⁻¹) obtained for compound 4:

| center Er1 (closer to K) | | center Er2 | |
|--------------------------|---------|------------|---------|
| MB | VTZP | MB | VTZP |
| 0.0 | 0.0 | 0.0 | 0.0 |
| 0.0 | 0.0 | 0.0 | 0.0 |
| 7.1 | 67.8 | 87.6 | 88.1 |
| 7.1 | 67.8 | 87.6 | 88.1 |
| 130.2 | 136.3 | 162.1 | 149.1 |
| 130.2 | 136.3 | 162.1 | 149.1 |
| 174.7 | 181.9 | 216.6 | 199.0 |
| 174.7 | 181.9 | 216.6 | 199.0 |
| 257.7 | 228.3 | 304.1 | 248.5 |
| 257.7 | 228.3 | 304.1 | 248.5 |
| 367.2 | 288.9 | 433.7 | 331.6 |
| 367.2 | 288.9 | 433.7 | 331.6 |
| 567.1 | 476.4 | 663.9 | 522.9 |
| 567.1 | 476.4 | 663.9 | 522.9 |
| 633.0 | 507.5 | 783.6 | 589.3 |
| 633.0 | 507.5 | 783.6 | 589.3 |
| 6325.9 | 6589.6 | 6340.8 | 6594.8 |
| 6325.9 | 6589.6 | 6340.8 | 6594.8 |
| 6348.3 | 6655.9 | 6410.0 | 6673.7 |
| 6348.3 | 6655.9 | 6410.0 | 6673.7 |
| 6431.5 | 6696.1 | 6470.3 | 6712.3 |
| 6431.5 | 6696.1 | 6470.3 | 6712.3 |
| 6506.1 | 6756.7 | 6555.8 | 6778.5 |
| 6506.1 | 6756.7 | 6555.8 | 6778.5 |
| 6617.3 | 6825.2 | 6681.6 | 6862.0 |
| 6617.3 | 6825.2 | 6681.6 | 6862.0 |
| 6778.6 | 6962.6 | 6868.7 | 7007.7 |
| 6778.6 | 6962.6 | 6868.7 | 7007.7 |
| 6865.7 | 7004.8 | 7001.1 | 7081.9 |
| 6865.7 | 7004.8 | 7001.1 | 7081.9 |
| 10223.5 | 10651.2 | 10253.2 | 10663.6 |
| 10223.5 | 10651.2 | 10253.2 | 10663.6 |
| ... | ... | ... | ... |

All states correspond to the 4f-4f transitions, i.e. are of ligand field type. No charge transfer states were considered. For the modeling of the exchange interaction between Ln sites the VTZP results were employed.

Analysis of the multiplet-specific crystal-field for Dy sites in 1 and 2

Recently, the extraction of the parameters of the multiplet-specific crystal-field for lanthanides methodology has been implemented in the SINGLE_ANISO program in MOLCAS. The results presented below use the ab initio CASSCF/RASSI wave function and energies to compute the parameters of the crystal-field splitting of the ground J multiplet.

The Crystal-Field Hamiltonian:

$$H_{CF} = \sum_{k,q} B_k^q O_k^q$$

where:

O_k^q -- Extended Stevens Operators (ESO) as defined in:

1. Rudowicz, C.; J. Phys. C: Solid State Phys., 18 (1985) 1415-1430.

2. Implemented in the "EasySpin" function in MATLAB, www.easyspin.org.

k - the rank of the ITO, = 2, 4, 6.

q - the component (projection) of the ITO, = $-k, -k + 1, \dots, 0, 1, \dots, k$;

Quantization axis was chosen the main magnetic axis of the ground Kramers doublet.

Table S8. Parameters of the *ab initio* crystal field for the individual Ln sites in compounds 2-4. (TZP basis)

| Rank | Proj. | Compound 2 | | Compound 3 | | Compound 4 | |
|------|--------------|---------------|---------------|---------------|---------------|---------------|---------------|
| | | Dy1 | Dy2 | Er1 | Er2 | Er1 | Er2 |
| 2 | -2 | -0.535140E-01 | -0.140417E+00 | -0.546539E+00 | 0.194653E-01 | -0.189670E+00 | -0.202116E-03 |
| | -1 | 0.201439E+01 | -0.837609E+00 | -0.371786E+00 | 0.126786E+00 | 0.401697E+00 | -0.248221E+00 |
| | 0 | -0.551468E+01 | -0.471389E+01 | -0.244231E+01 | -0.204053E+01 | -0.205323E+01 | -0.236264E+01 |
| | 1 | 0.231254E+00 | -0.468048E+00 | -0.269014E+00 | -0.417252E-01 | 0.228275E-01 | -0.964296E-01 |
| | 2 | 0.649035E+01 | 0.518941E+01 | 0.231406E+01 | 0.218899E+01 | 0.244990E+01 | 0.311724E+01 |
| 4 | -4 | -0.467820E-02 | -0.841583E-02 | 0.126499E-01 | 0.268865E-02 | 0.860376E-02 | -0.257562E-02 |
| | -3 | -0.709719E-01 | 0.278916E-01 | -0.580828E-02 | 0.190522E-02 | -0.101570E-02 | 0.307589E-02 |
| | -2 | -0.117192E-02 | -0.427150E-02 | 0.288370E-02 | 0.513570E-03 | 0.160784E-02 | -0.615698E-03 |
| | -1 | -0.287663E-01 | 0.141000E-01 | 0.269479E-02 | -0.596242E-03 | -0.167835E-02 | 0.944818E-03 |
| | 0 | 0.292096E-02 | 0.518216E-02 | 0.269434E-03 | -0.144163E-03 | -0.940719E-04 | 0.911350E-04 |
| | 1 | 0.407627E-02 | 0.109271E-02 | 0.355323E-03 | -0.126146E-03 | 0.122872E-02 | 0.430922E-03 |
| | 2 | 0.423533E-01 | 0.483016E-01 | -0.192298E-01 | -0.178598E-01 | -0.178150E-01 | -0.201671E-01 |
| | 3 | 0.757695E-02 | 0.744148E-02 | 0.101029E-01 | -0.784807E-03 | -0.240173E-02 | 0.157817E-01 |
| 4 | 0.302131E-01 | 0.338922E-01 | -0.415297E-01 | -0.471105E-01 | -0.442765E-01 | -0.407549E-01 | |
| 6 | -6 | 0.262912E-05 | -0.173971E-07 | 0.811522E-04 | 0.136673E-04 | 0.386364E-04 | -0.397995E-05 |
| | -5 | -0.352270E-03 | 0.114006E-03 | -0.124379E-03 | 0.171786E-05 | -0.160369E-03 | 0.983794E-04 |
| | -4 | -0.252467E-05 | -0.158880E-04 | -0.842563E-04 | -0.156848E-04 | -0.350193E-04 | 0.157681E-04 |
| | -3 | 0.598729E-04 | -0.857549E-05 | 0.971150E-04 | -0.426555E-04 | -0.484972E-04 | -0.510964E-05 |
| | -2 | 0.299320E-05 | 0.767148E-05 | 0.151308E-04 | 0.248996E-05 | -0.132274E-05 | 0.469280E-05 |
| | -1 | 0.662807E-04 | -0.420457E-04 | -0.158505E-04 | 0.191147E-04 | 0.384596E-05 | 0.967831E-05 |
| | 0 | -0.178829E-05 | -0.595496E-05 | -0.207138E-04 | -0.197021E-04 | -0.194103E-04 | -0.210516E-04 |
| | 1 | -0.688711E-04 | 0.240167E-04 | 0.292318E-04 | 0.166737E-04 | -0.304174E-04 | 0.371577E-06 |
| | 2 | -0.115581E-03 | -0.104506E-03 | 0.518185E-04 | 0.982957E-05 | 0.196359E-04 | 0.665648E-04 |
| | 3 | -0.700622E-05 | -0.463034E-04 | -0.750018E-04 | -0.797069E-04 | 0.456875E-04 | -0.163746E-03 |
| | 4 | 0.120817E-03 | 0.114721E-03 | 0.187624E-03 | 0.188058E-03 | 0.170024E-03 | 0.162188E-03 |
| | 5 | 0.672395E-04 | -0.540420E-04 | 0.122807E-03 | -0.122831E-03 | 0.106352E-03 | 0.310352E-03 |
| | 6 | 0.135509E-04 | 0.856097E-06 | -0.556321E-04 | -0.985607E-04 | -0.124296E-03 | -0.171449E-03 |

References

1. Yasuda, H.; Ohnuma, Y.; Yamauchi, M.; Tani, H.; Nakamura, A., *Bulletin of the Chemical Society of Japan* **1979**, *52* (7), 2036-2045.
2. Bradley, D. C.; Ghotra, J. S.; Hart, F. A., *Journal of the Chemical Society-Dalton Transactions* **1973**, (10), 1021-1027; Schuetz, S. A.; Day, V. W.; Sommer, R. D.; Rheingold, A. L.; Belot, J. A., *Inorganic Chemistry* **2001**, *40* (20), 5292-+.
3. v.2012, A. S. S.; Bruker AXS: Madison, W., 2005.
4. Blessing, R. H., *Acta Crystallographica Section A* **1995**, *51*, 33-38.
5. Sheldrick, G. M., *Acta Crystallographica Section A* **2008**, *64*, 112-122.