A dinuclear dysprosocenium dication has been synthesised that is bound together by weak interactions between \([\text{Dy(Cp*)}_2]^+\) fragments and neutral \(\text{NEt}_3\AlMe_3\) molecules. The axiality of the \(\text{Dy}^{3+}\) crystal fields are perturbed by these equatorial interactions but a relatively large effective barrier to magnetisation reversal of 860(60) cm\(^{-1}\) and magnetic hysteresis up to 15 K are observed.
A double-dysprosocenium single-molecule magnet bound together with neutral ligands

Peter Evans, Daniel Reta, Conrad A. P. Goodwin, Fabrizio Ortu, Nicholas F. Chilton and David P. Mills*

Department of Chemistry, School of Natural Sciences, The University of Manchester, Oxford Road, Manchester, M13 9PL, U.K.

Abstract

A dinuclear dysprosocenium dication has been synthesised that is bound together by weak interactions between \([\text{Dy(Cp*})_2]^+\) fragments and neutral \(\text{NEt}_3\text{AlMe}_3\) molecules. The axiality of the Dy\(^{3+}\) crystal fields are perturbed by these equatorial interactions but a relatively large effective barrier to magnetisation reversal of 860(60) cm\(^{-1}\) and magnetic hysteresis up to 15 K are observed.

Introduction

The potential use of single-molecule magnets (SMMs) in high-density data storage devices requires them to retain magnetization on long timescales (i.e. months to years) at liquid nitrogen temperatures, but the best SMMs currently only have relaxation times of a few hours at liquid helium temperatures.\(^{1,2}\) The first lanthanide (Ln) SMM was reported in 2003\(^3\) and this field has grown rapidly\(^4\) since design criteria to build Ln SMMs with large effective barriers to magnetization reversal \((U_{\text{eff}})\) were popularised in 2011.\(^5\) For Dy\(^{3+}\) SMMs an axial ligand field is required to maximise \(U_{\text{eff}}\), but a report of magnetic hysteresis at \(T_H = 60\) K in the isolated dysprosocenium cation \([\text{Dy(C}_5\text{H}_2\text{Bu}_3-1,2,4)_2]^+\) in 2017 showed that a combination of charge-dense \(\pi\)-aromatic rings and an absence of equatorial anion interactions can provide high temperature magnetic remanence.\(^2a\) This report also predicted that the removal of substituted cyclopentadienyl ring C-H bonds would provide even higher hysteresis temperatures, and this hypothesis has now been proved correct, with \(T_H\) up to 80 K being reported in the last two years in peralkylated \{Ln(Cp\(^8\))\}_2-based SMMs.\(^2b-d\)

Prior to the synthesis of \([\text{Dy(C}_3\text{H}_7\text{Bu}_3-1,2,4)_2]^+\), much dysprosocene-based SMM research focused on the less bulky \{DyCp\(^*\)_2\} \((\text{Cp}^* = \text{C}_5\text{Me}_5)\) framework\(^7\) and the magnetic properties of a
hypothetical \([\text{DyCp}^*]^2\) cation were calculated.\(^8\) Two strategies were investigated in parallel to increase \(U_{\text{eff}}\) values for \{\text{DyCp}^*\} systems; in one approach the equatorial ligand field strength was progressively decreased,\(^9\) and a second tactic employed anionic radical ligands to promote magnetic exchange coupling between \{\text{DyCp}^*\} units.\(^10\) By utilising weakly coordinating equatorial anions \(U_{\text{eff}} = 662\ \text{cm}^{-1}\) and \(T_{\text{H}} < 1.8\ \text{K}\) was found for \([\text{Dy(Cp}^*)_2{\mu-\text{Fe(Cp)(CO)}}_2]\),\(^9b\) and by blocking the equatorial sites with neutral Lewis base ligands a \(U_{\text{eff}}\) of 546 cm\(^{-1}\) and a \(T_{\text{H}}\) of 5.2 K was found for \([\text{Dy(Cp}^*)_2(\text{NH}_3)_2][\text{BPh}_4]\).\(^9c\) Given the improvement of the magnetic properties with weakening equatorial ligand fields, we set out to probe the magnetic behaviour of \{\text{DyCp}^*\} fragments with even weaker equatorial interactions; we report our results herein.

**Results and Discussion**

**Synthesis**

The dinuclear Ln\(^{3+}\) complexes \([\{\text{Ln(Cp}^*)_2{\mu-\text{Me}_3\text{AlNEt}_3}\}_2][\text{Al(OC(CF}_3)_3]\}_4\] (1-Ln, Ln = Dy, Y) were prepared by the protonolysis reactions of parent \([\{\text{Ln(Cp}^*)_2{\mu-\text{Me}_4\text{Al}}\}_2]\) with two equivalents of \([\text{NEt}_3\text{H}][\text{Al(OC(CF}_3)_3]\}_4]\) in benzene at room temperature; the elimination of two equivalents of methane provides an entropic driving force (Scheme 1). After stirring reaction mixtures overnight the solvent was removed *in vacuo* and crystals of 1-Ln were grown from chlorobenzene in good yields (1-Dy: 76%; 1-Y: 75%). A doped sample 1-Dy@Y containing a 5 : 95 ratio of Dy : Y (composition confirmed by ICP-OES) was synthesized by recrystallizing a mixture of 1-Dy and 1-Y. \([\{\text{Ln(Cp}^*)_2{\mu-\text{Me}_3\text{Al}}\}_2]\)\(^11\) and \([\text{NEt}_3\text{H}][\text{Al(OC(CF}_3)_3]\}_4]\)\(^12\) were prepared by adapting literature procedures; see the ESI for full details. Elemental analysis results for the carbon and hydrogen content of 1-Ln were in close agreement with expected values.

![Scheme 1. Synthesis of 1-Ln.](image)
**NMR spectroscopy**

The paramagnetism of \textit{1-Dy} thwarted its assignment by NMR spectroscopy apart from the presence of two signals in the \textsuperscript{19}F\{\textsuperscript{1}H\} NMR spectrum at \(-81.40\) and \(-80.28\) ppm. The initial \textsuperscript{1}H NMR spectrum of a solution of \textit{1-Y} in \textit{C}_6\textit{D}_5\textit{Cl} contained the four resonances expected for the \{\textit{Y(Cp*)}_2(\mu-\textit{Me}_3\textit{AlNEt}_3)\} moieties, together with additional resonances for \textit{NEt}_3 and \textit{Cp*} protons. We interpret these data to propose that \textit{1-Y} establishes a monomer-dimer equilibrium in \textit{C}_6\textit{D}_5\textit{Cl} solution; this mixture is then subject to various ligand scrambling and decomposition processes promoted by \textit{C}_6\textit{D}_5\textit{Cl} to give a complex mixture of products. By analysis of \textit{NEt}_3 integrals in the initial \textsuperscript{1}H NMR spectrum we establish an initial dimer:monomer ratio of approximately 2:1, with the broadest signals attributed to the dimeric species.

Decomposition of \textit{1-Y} in \textit{C}_6\textit{D}_5\textit{Cl} solution was monitored by \textsuperscript{1}H NMR spectroscopy, with the number of species increasing rapidly over several hours at room temperature (see Supporting Information). These facile decomposition processes, together with the low solubility \textit{1-Y} in \textit{C}_6\textit{D}_5\textit{Cl} solution, precluded more detailed analysis of these equilibria by Diffusion Ordered \textsuperscript{1}H NMR spectroscopy and variable temperature (VT) experiments. However, a monomer-dimer equilibrium was previously established for \textit{C}_7\textit{D}_8 solutions of \{\textit{Y(Cp*)}_2(\mu-\textit{Me}_4\textit{Al})\}_2 \textsuperscript{2+} by VT \textsuperscript{1}H NMR spectroscopy,\textsuperscript{11a} thus it is reasonable to assume that similar processes are in operation here for \textit{1-Ln}. Four of the five expected resonances were observed in the \textsuperscript{13}C\{\textsuperscript{1}H\} NMR spectrum of \textit{1-Y}, with the \textit{AlMe}_3 groups not observed due to a combination of the poor solubility of the complex in \textit{C}_6\textit{D}_5\textit{Cl}, quadrupolar broadening by \textit{I} = 5/2 \textit{^{27}Al} nuclei and additional splitting by \textit{I} = 1/2 \textit{^{88}Y} nuclei. The \textsuperscript{19}F\{\textsuperscript{1}H\} NMR spectrum of \textit{1-Y} exhibits a single resonance at \(-74.66\) ppm.

**Structural characterisation**

The solid state structures of \textit{1-Ln} were determined by single crystal XRD; \textit{1-Dy\textcdot3C}_6\textit{H}_5\textit{Cl} is depicted in Fig. 1 and isostructural \textit{1-Y\textcdot3C}_6\textit{H}_5\textit{Cl} and \{\textit{[Ln(Cp*)}_2(\mu-\textit{Me}_4\textit{Al})}\}_2 \textsuperscript{2+} \textsuperscript{2+} \textsuperscript{(Ln = Y, Dy)} are shown in the ESI. Each \{\textit{[Dy(Cp*)}_2(\mu-\textit{Me}_3\textit{AlNEt}_3)\}_2\}^2\textsuperscript{2+} dication in \textit{1-Dy} is associated with two \textit{[Al\{OC(CF}_3)_3]_4} counterions and three co-crystallized chlorobenzene molecules in the lattice; the structural parameters of these latter components are unremarkable and there are no significant
interactions with the dication. The Dy$^{3+}$ centres in 1-Dy are related by inversion symmetry and exhibit bent metallocene motifs with Cp\textsubscript{centroid}−−Dy−−Cp\textsubscript{centroid} angles of 138.03(13)$^\circ$ and mean Dy−−Cp\textsubscript{centroid} distances of 2.343(4) Å. The range of Dy−−C\textsubscript{ring} distances is 2.580(8)−2.665(7) Å (mean 2.634 Å). The Dy$^{3+}$ coordination spheres are each completed by two Me groups of two separate {µ-Me\textsubscript{3}AlNEt\textsubscript{3}} moieties (mean Dy−−C\textsubscript{Me}: 2.794(8) Å) to give distorted pseudo-tetrahedral Dy$^{3+}$ geometries (C\textsubscript{Me}−−Dy−−C\textsubscript{Me}: 82.8(2)$^\circ$; range Cp\textsubscript{centroid}−−Dy−−C\textsubscript{Me}: 103.6(2)−107.8(2)$^\circ$) and a diamond-shaped Dy\textsubscript{2}Al\textsubscript{2}Me\textsubscript{4} core, with two Dy and two Al vertices and Me groups on each face; the two {Dy(Cp\textsubscript{*})\textsubscript{2}}$^+$ units are orthogonal to the Dy\textsubscript{2}Al\textsubscript{2} mean plane and the intramolecular Dy−−Dy distance is 7.365(2) Å.

As expected, the core Al−C bond lengths (mean 2.011(8) Å) are longer than the external Al−C distances (1.952(6) Å) as the latter do not interact with the Dy$^{3+}$ centres.

The equatorial interactions in 1-Dy likely arise from the electrostatic attraction of the Dy$^{3+}$ centres with C\textsubscript{δ}−−Al\textsubscript{δ+} partial dipoles. The two shortest equatorial Dy−−H distances that result from these interactions are 2.407 and 2.482 Å, which are shorter than the two shortest equatorial Dy−−H distances in [Dy(C\textsubscript{5}H\textsubscript{2}Bu\textsubscript{3},1,2,4)\textsubscript{2}][B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}] (mean 2.499 Å).\textsuperscript{2a} Each {µ-Me\textsubscript{3}AlNEt\textsubscript{3}} unit in 1-Dy also exhibits ca. 10 C−−C distances < 5 Å between its Me and Et groups and the Me groups of the Cp\textsubscript{*} ligands; it is postulated that the combined strength of these inter-ligand London dipole interactions is also crucial for binding the dication together as such forces are of particular importance in low-coordinate metal complexes.\textsuperscript{13} The bulk features of 1-Dy are most reminiscent of the dinuclear Dy$^{3+}$ complex [Dy(Cp\textsubscript{*})\textsubscript{2}{µ-Fe(Cp)(CO)}\textsubscript{2}]\textsubscript{2} (mean Dy−−Cp\textsubscript{centroid}: 2.342(10) Å; Cp\textsubscript{centroid}−−Dy−−Cp\textsubscript{centroid}: 141.5(3)$^\circ$; Dy−−Dy: 7.14(2) Å),\textsuperscript{9b} but this contains bridging {µ-Fe(Cp)(CO)}\textsubscript{2}−−C\textsuperscript{−−O, O}' anions rather than the neutral {µ-Me\textsubscript{3}AlNEt\textsubscript{3}} units in 1-Dy. The metrical parameters about the Dy$^{3+}$ centres of 1-Dy are similar to those seen for [Dy(Cp\textsubscript{*})\textsubscript{2}(NH\textsubscript{3})\textsubscript{2}][BP\textsubscript{h\textsubscript{4}}] (mean Dy−−Cp\textsubscript{centroid}: 2.350(3) Å; Cp\textsubscript{centroid}−−Dy−−Cp\textsubscript{centroid}: 140.25(6)$^\circ$),\textsuperscript{9c} which also contains neutral donors in the equatorial plane, though the dative Dy−−N distances in the literature complex (mean 2.47(1) Å)\textsuperscript{9c} are shorter than the two equatorial Dy−−C\textsubscript{Me} distances in 1-Dy.
Figure 1. Molecular structure of the dication of 1-Dy-3C₆H₅Cl, shown at the 50 % probability level; [Al{OC(CF₃)₃}]₄⁻ counterions and lattice solvent are omitted for clarity. Symmetry operation used to generate equivalent atoms: $i = 2 - x, 1 - y, z$. Selected bond lengths (Å) and angles (°): Dy(1)·∙∙∙Cp centroid 1: 2.388(3); Dy(1)·∙∙∙Cp centroid 2: 2.348(3); Dy(1)·∙∙∙C(21): 2.800(6); Dy(1)·∙∙∙C(23)$_i$: 2.788(6); range Dy(1)·∙∙∙C ring: 2.580(8)–2.665(7); Cp centroid 1·∙∙∙Dy(1)·∙∙∙Cp centroid 2: 138.03(13); Cp centroid 1·∙∙∙Dy(1)·∙∙∙C(21): 103.74(14); Cp centroid 1·∙∙∙Dy(1)·∙∙∙C(23)$_i$: 107.77(15); Cp centroid 2·∙∙∙Dy(1)·∙∙∙C(21): 107.29(14); Cp centroid 2·∙∙∙Dy(1)·∙∙∙C(23)$_i$: 103.56(15); C(21)·∙∙∙Dy(1)·∙∙∙C(23)$_i$: 82.80(17).

Magnetism

Although the Dy$^{3+}$ centres of 1-Dy have less axial geometries than several decamethyldysprosocene complexes in the literature, we envisioned that the combination of peralkylated Cp ligands and neutral equatorial ligands bound only through electrostatic interactions could endow favourable SMM properties for 1-Dy. The magnetic susceptibility temperature product ($\chi_M T$) of a microcrystalline sample of 1-Dy suspended in eicosane is 13.86 cm$^3$ K mol$^{-1}$ at 300 K (Fig. S21) was determined by SQUID magnetometry. This high-temperature value is in excellent agreement
with the Dy$^{3+}$ free-ion Curie value (14.17 cm$^3$ K mol$^{-1}$)$^{14}$ and the predicted value from \textit{ab initio} calculations (13.76 cm$^3$ K mol$^{-1}$ at 300 K, see below). As expected, the experimental $\chi_{d}T$ value decreases monotonically down to 12.08 cm$^3$ K mol$^{-1}$ at 10 K, as excited CF states are thermally depopulated (\textit{ab initio} predicted 12.34 cm$^3$ K mol$^{-1}$), followed by a sharp decrease below 12 K due to magnetic blocking. This correlates well with the temperature at which we observe divergence of the zero-field cooled, field-cooled (ZFC/FC) susceptibility curves (Fig. S24).

The dynamic magnetic behaviour of 1-Dy was probed by low temperature ac susceptibility measurements in zero-field. These data show slow relaxation of magnetization, with clear in-phase and out-of-phase maxima between 25 and 68 K (Fig. S28). We have used CCFIT$^2$\textsuperscript{15} to fit the data to a generalised Debye model, where we can obtain estimated standard deviations for the relaxation times (Fig. 2). Below 25 K, the maxima in the ac data fall out of the range of accessible frequencies and we turn to magnetisation decay measurements to access the lowest temperature regime. The dc magnetization decay data were fitted with stretched exponentials (Table S4), where we have used a similar model as that employed by CCFIT$^2$ to obtain estimated standard deviations for the relaxation times.\textsuperscript{12} Complex 1-Dy@Y presents a similar, yet faster relaxation profile (Table S5, Figs. S30 and S31).\textsuperscript{16}

In the high-temperature region (T > 46 K), an Orbach process dominates ($\tau^{-1} = \tau_0^{-1} \exp[-U_{\text{eff}}/kT]$) with an associated effective barrier of $U_{\text{eff}} = 860(60)$ cm$^{-1}$ (1,230(90) K) and $\tau_0 = 10^{-11.6(6)}$ s (ca. $2.5\times10^{-12}$ s); \textit{c.f.} structurally similar [Dy(Cp*)$_2$][µ-Fe(Cp)(CO)$_2$]$_2$, $U_{\text{eff}} = 662$ cm$^{-1}$ (952 K),\textsuperscript{9b} though the current record $U_{\text{eff}}$ value is 1,541 cm$^{-1}$ (2,217 K) for [Dy(C$_5$Pr$_5$)(Cp*)][B(C$_6$F$_5$)$_4$].\textsuperscript{2c} Below 46 K the relaxation rate is governed by a Raman process ($\tau^{-1} = CT^n$) with $C = 10^{6.6(2)}$ s$^{-1}$ K$^{-n}$ (ca. $2.5\times10^{-7}$ s$^{-1}$ K$^{-n}$) and $n = 4.5(2)$. The value of $n$ is higher than typical values extracted for isolated Ln metalloccenium cations (\textit{e.g.} [Dy(Cp*)$_2$]$^+$, $n = 2.15$;\textsuperscript{2a} [Dy(C$_5$Pr$_5$)(Cp*)], $n = 3.0$\textsuperscript{2c}), likely due to the influence of the equatorial ligand interactions in 1-Dy.\textsuperscript{17} From these data we can directly measure a 100 s blocking temperature of 10.5 K. The extrapolated Orbach and Raman relaxation plots intersect at 50.7 K; this value is far greater than the highest temperatures at which the FC/ZFC traces (Fig. S24) start to bifurcate (22 K), or the maxima in the ZFC data (8 K). Importantly, we do not observe a temperature-independent quantum tunnelling regime at the lowest temperatures, which may be due to a dipolar
exchange-bias between the two Dy$^{3+}$ centres; this is supported by relaxation in 1-Dy@Y being slightly faster at the lowest temperatures (Fig. S30). An immobilised powdered sample of 1-Dy was found to be EPR silent at X-band at 5 K, thus we cannot measure the Dy···Dy interaction here.

\[ U_{\text{eff}} = 1230(90) \text{ K}, \tau_0 = 10^{-11.6(6)} \text{ s}, C = 10^{-6.8(2)} \text{ s}^{-1} \text{ K}^{-n}, n = 4.5(2) \]

**Figure 2.** Temperature dependence of the magnetic relaxation rate of 1-Dy. Red circles are the relaxation rates extracted from AC susceptibility data (high temperature) and dc magnetisation decay data (low temperature); solid red lines are error bars. The solid green line is given by $\tau^{-1} = \tau_0^{-1} \exp[-U_{\text{eff}}/kT] + C T^n$, the dashed green line is given by $\tau^{-1} = \tau_0^{-1} \exp[-U_{\text{eff}}/kT]$ and the dotted orange line is given by $\tau^{-1} = C T^n$ with $U_{\text{eff}} = 855 \text{ cm}^{-1}$ (1,230 K), $\tau_0 = 2.51 \times 10^{-12}$ s, $C = 2.51 \times 10^{-7} \text{ s}^{-1} \text{ K}^{-n}$ and $n = 4.5$. 
Open magnetic hysteresis loops were observed for 1-Dy between 2 and 15 K at a sweep rate of ca. 20 Oe s\(^{-1}\) around the zero-field region (Fig. 3); the waist-restricted “butterfly” shapes of these loops is typical for Ln\(^{3+}\) SMMs and arises due to strongly-field dependent relaxation near zero field.\(^4\) The highest temperature at which we observe an open loop is \(T_{\text{H}} = 15\) K; c.f. 6.5 K at ca. 20 Oe s\(^{-1}\) for \([\{\text{Dy}(\text{Cp}^*)_2\}(\text{µ-2,2'-bipyrimidine}')]\{\text{BPh}_4\}\)\(^{10a}\) and 5.2 K at ca. 20 Oe s\(^{-1}\) for \([\text{Dy}(\text{Cp}^*)_2(\text{NH}_3)_2]\{\text{BPh}_4\}\).\(^9c\)

The current record value of \(T_{\text{H}} = 80\) K at ca. 25 Oe s\(^{-1}\) is seen for \([\text{Dy}(\text{C}_5\text{Pr}_5)(\text{Cp}^*)]\{\text{B}(\text{C}_6\text{F}_5)_4\}\),\(^2c\) thus it is evident that even the very weak neutral equatorial contacts in 1-Dy promote far more efficient magnetic relaxation than is observed for isolated \([\text{Dy}(\text{Cp}^*)_2]^+\) cations.\(^2\)

Figure 3. Magnetic hysteresis of solid 1-Dy, measured with a mean field sweep rate of 21(9) Oe s\(^{-1}\) for \(|H| < 10\) kOe, 49(12) Oe s\(^{-1}\) for 10 < \(|H| < 20\) kOe, and 88(17) Oe s\(^{-1}\) for 20 < \(|H| < 70\) kOe. Hysteresis loops recorded from 2–10 K in 2 K steps; inset shows zoomed zero-field region.
**Ab initio calculations**

Using a purely electrostatic model, equatorial ligands in Ln metallocene frameworks tend to increase Dy···Cp\textsubscript{centroid} distances and decrease Cp\textsubscript{centroid}···Ln···Cp\textsubscript{centroid} angles, which disrupts the axiality of the ligand field, lowering the $U_{\text{eff}}$ value and the purity of the $m_J = \pm 15/2$ ground state. The effect of molecular geometry and ligand vibrational modes on $T_H$ is a more complex relationship to fully disentangle. To probe the electronic structure of **1-Dy** we performed first-principles complete active space self-consistent field spin-orbit (CASSCF-SO) calculations on a model of **1-Dy**, where one of the Dy\textsuperscript{3+} centres was replaced by Lu\textsuperscript{3+} for computational efficiency (Fig. 4; see ESI for details). The predicted $U_{\text{eff}}$ for this model was 842 cm\textsuperscript{-1} (1,211 K), in excellent agreement with experimentally obtained values, thus we confidently assign the Orbach relaxation pathway as proceeding via the fifth excited doublet.

![Figure 4](image)

**Figure 4.** Energy barrier to magnetic relaxation for a model of **1-Dy** containing one Dy\textsuperscript{3+} and one Lu\textsuperscript{3+} centre. Electronic states from CASSCF-SO calculations, labelled with their dominant $m_J$ composition in the $J = 15/2$ basis. Arrows represent the Orbach relaxation pathway, where the opacity of the arrows is proportional to the transition probability approximated with the average matrix elements of magnetic moment connecting the states, $\gamma_0 = (1/3)[|<i | \mu_x | j>|^2 + |<i | \mu_y | j>|^2 + |<i | \mu_z | j>|^2]$, normalised from each departing state and commencing from $|\text{–15/2}>$. 

9
Conclusion

To conclude, the double-decamethyldysprosocenium dication $\{\text{Dy(Cp*$_2$)(µ-Me$_3$AlNEt$_3$)}\}_2$$^{2+}$ is held together by multiple weak dipolar interactions between the cationic $\{\text{Dy(Cp*$_2$)}\}^+$ fragments and neutral $\{\text{µ-Me$_3$AlNEt$_3$}\}$ moieties. This dication fulfils the design criteria for high-performance dysprosocenium SMMs of an axial ligand field, rigid charge-dense π-aromatic rings, an absence of ring C–H bonds and a lack of equatorial anion interactions. However, magnetic relaxation promoted by the equatorial electrostatic contacts of the $\{\text{µ-NEt$_3$AlMe$_3$}\}$ adducts have limited both the effective barrier to magnetisation reversal and maximum hysteresis temperature compared to dysprosocenium cations that lack such interactions. An alternative synthetic route is required to prepare an isolated decamethyldysprosocenium cation, which could represent the pinnacle of isolated $\{\text{Dy(CpR$_2$)}\}^+$ SMMs as it contains the smallest peralkylated Cp$^R$ rings. Although the $\{\text{Dy(Cp*$_2$)}\}^+$ cation would exhibit short Dy···Cp$_\text{centroid}$ distances, the Cp$_\text{centroid}$···Dy···Cp$_\text{centroid}$ angle is more difficult to predict and is also crucial for determining its magnetic parameters.

Acknowledgements

This work was supported by the EPSRC (EP/R002605X/1 for P.E., EP/P002560/1 for D.R. and F.O., Doctoral Prize Fellowship to C.A.P.G.), and the University of Manchester. N.F.C. thanks The University of Manchester for a Presidential Fellowship and The Royal Society for a University Research Fellowship. We thank B. L. L. Réant for providing Cp*H, Prof. R. E. P. Winpenny for stimulating discussions, the EPSRC UK National Electron Paramagnetic Resonance Service for access to the EPR facility and the SQUID magnetometer, and the University of Manchester for access to the Computational Shared Facility. Research data files supporting this publication are available from Mendeley Data at doi: 10.17632/vzwmzthy3z.2.
References

1. D. Gatteschi, R. Sessoli, J. Villain, *Molecular Nanomagnets*, Oxford University Press, 2006.
2. (a) C. A. P. Goodwin, F. Ortu, D. Reta, N. F. Chilton, D. P. Mills, *Nature* **2017**, *548*, 439; (b) K. R. McClain, C. A. Gould, K. Chakarawet, S. J. Teat, T. J. Groshens, J. R. Long, B. G. Harvey, *Chem. Sci.* **2018**, *9*, 8492; (c) F.-S. Guo, B. M. Day, Y.-C. Chen, M.-L. Tong, A. Mansikkamäki, R. A. Layfield, *Science* **2018**, *362*, 1400; (d) C. A. Gould, K. R. McClain, J. Yu, T. J. Groshens, F. Furche, J. R. Long, B. G. Harvey, *J. Am. Chem. Soc.* **2019**, *141*, 12967.
3. N. Ishikawa, M. Sugita, T. Ishikawa, S. Koshihara, Y. Kaizu, *J. Am. Chem. Soc.* **2003**, *125*, 8694.
4. R. A. Layfield, M. Murugesu, *Lanthanides and Actinides in Molecular Magnetism*, Wiley-VCH, 2015.
5. J. D. Rinehart, J. R. Long, *Chem. Sci.* **2011**, *2*, 2078.
6. See, for example: Y.-S. Ding, N. F. Chilton, R. E. P. Winpenny, Y.-Z. Zheng, *Angew. Chem. Int. Ed.* **2016**, *55*, 16071.
7. B. M. Day, F.-S. Guo, R. A. Layfield, *Acc. Chem. Res.* **2018**, *51*, 1880.
8. Y.-S. Meng, Y-Q. Zhang, Z-M. Wang, B-W. Wang, S. Gao, *Chem. Eur. J.* **2016**, *22*, 12724.
9. (a) S. Demir, J. M. Zadrozny, J. R. Long, *Chem. Eur. J.* **2014**, *20*, 9524; (b) T. Pugh, N. F. Chilton, R. A. Layfield, *Angew. Chem. Int. Ed.* **2016**, *55*, 11082; (c) S. Demir, M. D. Boshart, J. F. Corbey, D. H. Woen, M. I. Gonzalez, J. W. Ziller, K. R. Meihaus, J. R. Long, W. J. Evans, *Inorg. Chem.* **2017**, *56*, 15049.
10. (a) S. Demir, J. M. Zadrozny, M. Nippe, J. R. Long, *J. Am. Chem. Soc.* **2012**, *134*, 18546; (b) S. Demir, M. Nippe, M. I. Gonzalez, J. R. Long, *Chem. Sci.* **2014**, *5*, 4701; (c) F-S. Guo, R. A. Layfield, *Chem. Commun.* **2017**, *53*, 3130; (d) C. A. Gould, L. E. Darago, M. I. Gonzalez, S. Demir, J. R. Long, *Angew. Chem. Int. Ed.* **2017**, *56*, 10103.
11. (a) M. A. Busch, R. Harlow, P. L. Watson, *Inorg. Chim. Acta* **1987**, *140*, 15; (b) P. L. Watson, T. Herskovitz, *Am. Chem. Soc. Symp. Ser.* **1983**, *212*, 459; (c) P. L. Watson, *J. Am. Chem. Soc.* **1983**, *105*, 6491.
12. P. Evans, D. Reta, G. F. S. Whitehead, N. F. Chilton, D. P. Mills, *ChemRxiv* **2019**, DOI:10.26434/chemrxiv.10050128.v1.
13. D. J. Liptrot, P. P. Power, Nature Rev. Chem. 2017, 1, 0004.

14. D. A. Atwood, The Rare Earth Elements: Fundamentals and Applications, John Wiley and Sons Ltd., 2012.

15. D. Reta, N. F. Chilton, Phys. Chem. Chem. Phys. 2019, 21, 23567.

16. (a) F. Habib, P.-H. Lin, J. Long, I. Korobkov, W. Wernsdorfer, M. Murugesu, J. Am. Chem. Soc. 2011, 133, 8830; (b) Y.-N. Guo, G.-F. Xu, W. Wernsdorfer, L. Ungur, Y. Guo, J. Tang, H.-J. Zhang, L. F. Chibotaru, A. K. Powell, J. Am. Chem. Soc. 2011, 133, 11948; (c) J. Xiong, H.-Y. Ding, Y.-S. Meng, C. Gao, X.-J. Zhang, Z.-S. Meng, Y.-Q. Zhang, W. Shi, B.-W. Wang, S. Gao, Chem. Sci. 2017, 8, 1288; (d) E. Moreno Pineda, G. Taran, W. Wernsdorfer, Mario Ruben, Chem. Sci. 2019, 10, 5138.

17. (a) C. A. P. Goodwin, D. Reta, F. Ortu, N. F. Chilton, D. P. Mills, J. Am. Chem. Soc. 2017, 139, 18714; (b) C. A. P. Goodwin, D. Reta, F. Ortu, J. Liu, N. F. Chilton, D. P. Mills, Chem. Commun. 2018, 54, 9182.

18. (a) E. Moreno Pineda, N. F. Chilton, R. Marx, M. Dörfel, D. O. Sells, P. Neugebauer, S.-D. Jiang, D. Collison, J. van Slageren, E. J. L. McInnes, R. E. P. Winpenny, Nature Commun. 2014, 5, 5243; (b) M. J. Giansiracusa, E. Moreno-Pineda, R. Hussain, R. Marx, M. Martínez Prada, P. Neugebauer, S. Al-Badran, D. Collison, F. Tuna, J. van Slageren, S. Carretta, T. Guidi, E. J. L. McInnes, R. E. P. Winpenny, N. F. Chilton, J. Am. Chem. Soc. 2018, 140, 2504.
Supplementary information for:

A double-dysprosocenium single-molecule magnet bound together with neutral ligands

Peter Evans, Daniel Reta, Conrad A. P. Goodwin, Fabrizio Ortu, Nicholas F. Chilton, David P. Mills*  
Department of Chemistry, School of Natural Sciences, The University of Manchester, Oxford Road, Manchester, M13 9PL, U.K.

Contents

1. Synthesis  
2. Crystallography  
3. Molecular structures  
4. NMR spectroscopy  
5. ATR-IR spectroscopy  
6. Magnetic measurements  
7. CASSCF-SO electronic structure  
8. References
1. Synthesis

**General methods.** All manipulations were conducted under argon with rigorous exclusion of oxygen and water using Schlenk line and glove box techniques. Pentane, diethyl ether, toluene, and THF were dried by passing through columns containing alumina; n-hexane and benzene were dried by refluxing over potassium and distillation; chlorobenzene was dried by refluxing over CaH₂ and distillation. Solvents were stored over potassium mirrors, except for THF and chlorobenzene, which were stored over 4 Å molecular sieves. All solvents were degassed before use. For NMR spectroscopy C₅D₅Cl was dried by refluxing over CaH₂ and vacuum transferred and degassed by three freeze-pump-thaw cycles before use. MeLi (1.6 M in diethyl ether), and AlMe₃ (2.0 M in hexanes) were purchased from Sigma-Aldrich and were used as received. [Y(Cp*)₂(µ-Cl)₂K(THF)₂], [Dy(Cp*)₂(µ-Cl)₂K(THF)₂], [Y(Cp*)₂(µ-Me)₂Li] and [{Y(Cp*)₂(µ-Me₄Al)}₂] were prepared according to literature methods¹ and were adapted here for Dy analogues; we include additional experimental details of these procedures for convenience. During the preparation of [{Y(Cp*)₂(µ-Me₄Al)}₂] we obtained an improved single crystal XRD dataset over that previously reported,¹a as well as a dataset for the precursor [Y(Cp*)₂(µ-Me)₂Li(THF)]; we have included these data herein. [NEt₃H][Al{OC(CF₃)₃}₄]² was also prepared by published procedures.

¹H (400 MHz), ¹³C{¹H} (100 MHz and 125 MHz) and ¹⁹F{¹H} (376 MHz) NMR spectra were obtained on an Avance III 400 MHz or 500 MHz spectrometer at 298 K. These were referenced to the solvent used, or to external TMS (¹H, ¹³C) or C₂H₅F/CDCI₃ (¹⁹F). ATR-Fourier Transform infrared (ATR-FTIR) spectra were recorded as microcrystalline powders using a Bruker Tensor 27 spectrometer. Elemental and ICP-OES analyses were performed by Mrs Anne Davies and Mr Martin Jennings at The University of Manchester School of Chemistry Microanalysis Service, Manchester, UK. Low carbon values obtained for [Dy(Cp*)₂(µ-Me)₂Li] and 1-Dy@Y were attributed to incomplete combustion resulting from carbide formation, whilst low nitrogen values for 1-Dy and 1-Dy@Y are a consequence of the experimental limitations of the apparatus for the accurate measurement of nitrogen values < 1%.
[Y(Cp*)₂(µ-Me)₂Li]. A solution of MeLi in Et₂O (1.6 M, 4.1 ml, 6.6 mmol) was added dropwise to a cold (–78 °C) solution of [Y(Cp*)₂(µ-Cl)₂K(THF)₂] (1.9874 g, 3.24 mmol) in THF (50 mmol). The resultant pale yellow reaction mixture was allowed to warm slowly to room temperature overnight and volatiles were removed in vacuo to give a sticky yellow solid. The product was extracted into Et₂O (50 ml) and the pale yellow filtrate was reduced in volume to ca. 10 ml and was stored at –25 °C overnight to give pale yellow microcrystalline material. This was isolated by decantation of the supernatant solution and was dried under vacuum to give putative “[Y(Cp*)₂(µ-Me)₂Li(THF)ₓ].” This material was desolvated by heating under vacuum (75 °C, 0.01 Torr) for 24 h to give [Y(Cp*)₂(µ-Me)₂Li] as a yellow powder. Yield: 1.0847 g, 84%. This material was used without further purification for the next step. On one occasion several crystals of [Y(Cp*)₂(µ-Me)₂Li(Et₂O)] were grown from a saturated diethyl ether solution at –25 °C overnight to confirm the identity of the intermediate by single crystal XRD.

[{Y(Cp*)₂(µ-Me₄Al)}₂]. A solution of AlMe₃ in hexanes (2.0 M, 3.2 ml, 6.4 mmol) was added to a suspension of [Y(Cp*)₂(Me)₂Li] (0.9973 g, 2.52 mmol) in toluene (30 ml) at room temperature. The resultant yellow reaction mixture with pale solids was stirred for 16 hours and allowed to settle. The reaction mixture was filtered and volatiles were removed in vacuo from the yellow filtrate to give a pale yellow solid. This was washed with pentane (10 ml) and dried under vacuum to give [{Y(Cp*)₂(µ-Me₄Al)}₂], Yield: 0.1754 g, 16%. This material was used without further purification for the next step. On one occasion several crystals of [{Y(Cp*)₂(µ-Me₄Al)}₂]⋅(C₇H₈)₂ were grown from a saturated toluene solution at –25 °C overnight to confirm the identity of the product by single crystal XRD.

[Dy(Cp*)₂(µ-Me)₂Li]. A solution of MeLi in Et₂O (1.6 M, 3.3 ml, 5.3 mmol) was added dropwise to a pre-cooled (–78 °C) solution of [Dy(Cp*)₂(µ-Cl)₂K(THF)₂] (1.7912 g, 2.61 mmol) in THF (40 ml). The resultant yellow reaction mixture was allowed to warm to room temperature slowly overnight and the volatiles were removed in vacuo to give a tacky yellow solid. The product was extracted into diethyl ether (40 ml) and filtered. The yellow filtrate was reduced in volume to ca. 10 ml and was stored at –25 °C overnight to give “[Dy(Cp*)₂(µ-Me)₂Li(THF)ₓ]” as a yellow microcrystalline material. This was isolated by decantation of the supernatant solution and was desolvated by heating under vacuum (75
°C, 0.01 Torr) for 24 h to yield [Dy(Cp*)₂(µ-Me)₂Li] as a yellow powder. Yield: 0.9404 g, 77%. Anal. Calcd (%) for C₂₂H₃₆DyLi: C, 56.23; H, 7.72. Found: C, 53.77; H, 7.58. ¹H NMR (C₆D₅Cl, 400 MHz, 298 K): δ = -4.55 (br, v½ = 200 Hz, 6H, Li(CH₃)₂), -16.06 (br, v½ = 200 Hz, 30H, Cp-CH₃). The ¹³C[¹H] NMR spectrum could not be interpreted due to the paramagnetism of the sample. FTIR (ATR, microcrystalline): ū = 2960 (w, br), 2906 (w, br), 2859 (w, br), 1437 (w, br), 1385 (w), 1260 (w), 1137 (w), 1085 (w), 1021 (w, br), 945 (w, br), 798 (w), 589 (w), 512 (m), 485 (m) cm⁻¹.

[[Dy(Cp*)₂(µ-Me₄Al)]₂]. A solution of AlMe₃ in hexanes (2.0 M, 2.3 ml, 4.5 mmol) was added to a suspension of [Dy(Cp*)₂(µ-Me)₂Li] (0.8624 g, 1.84 mmol) in toluene (25 ml). The resulting yellow reaction mixture was filtered and the volatiles were removed in vacuo. The resultant solid was washed with pentane (10 ml) and dried in vacuo to give [[Dy(Cp*)₂(µ-Me₄Al)]₂] as a pale yellow powder. Yield: 0.1389 g, 15%. A small crop of crystals of [[Dy(Cp*)₂(µ-Me₄Al)]₂]·(C₇H₈)₂ were grown from a saturated toluene solution at -25 °C overnight to confirm the identity of the product by single crystal XRD. Anal. Calcd (%) for C₂₄H₄₂AlDy: C, 55.63; H, 8.14. Found: C, 55.42; H, 8.32. The ¹H and ¹³C[¹H] NMR spectra could not be interpreted due to the paramagnetism of the sample. FTIR (ATR, microcrystalline): ū = 2911 (w, br), 2858 (w, br), 1437 (w), 1380 (w), 1175 (w), 1098 (w), 1020 (w), 901 (m), 777 (w), 739 (m), 672 (m), 620 (m), 566 (m), 542 (m) cm⁻¹.

[[Y(Cp*)₂(µ-Me₃AlNEt₃)]₂][Al{OC(CF₃)₃}₄]₂ (1-Y). A slurry of [[Y(Cp*)₂(µ-Me₄Al)]₂] (0.1754 g, 0.20 mmol) and [NEt₃H][Al{OC(CF₃)₃}₄] (0.4200 g, 0.39 mmol) in benzene (15 ml) were stirred overnight to give a reaction mixture of a colourless solution and a pale yellow solid. The solvent was removed in vacuo and the product was extracted into chlorobenzene (15 ml) and filtered. The resultant pale yellow solution was reduced in volume to ca. 8 ml, layered with n-hexane (25 ml) and allowed to stand at room temperature overnight to afforded off-white crystals of [[Y(Cp*)₂(µ-Me₃AlNEt₃)]₂][Al{OC(CF₃)₃}₄]₂·(C₆H₅Cl)₃ (1-Y·3C₆H₅Cl). The crystals were dried in vacuo to afford an off-white crystalline solid, which elemental analysis results indicate is desolvated 1-Y. Yield: 0.4933 g, 75%. Anal. Calcd (%) for C₉₀H₁₀₈AlF₇₂N₂O₈Y₂: C, 36.04; H, 3.63; N, 0.93. Found: C, 36.43; H, 3.47; N, 0.78. ¹H NMR (C₆D₅Cl, 400 MHz, 298 K): δ = -0.74 (br m, 18H, Al(CH₃)₃), 0.95 (br m, 18H,
N(CH₂CH₃)₃), 1.73 (s, 60H, C₅(CH₃)₅), 2.52 (br m, 12H, N(CH₂CH₃)₃). A second species was identified in solution that arises from dynamic equilibria but this is not included in the assignment of the spectrum here. ¹³C{¹H} NMR (C₅D₅Cl, 100 MHz, 298 K): δ = 8.75, 9.00 (N(CH₂CH₃)₃), 10.98, 11.26 (C₅(CH₃)₅), 47.99 (N(CH₂CH₃)₃), 120.82, 122.86, 123.18 (C₅(CH₃)₅). Multiple signals arise from dynamic equilibria; Al(C₅H₅)₃ not observed due to quadrupolar broadening by I = 5/2 ²⁷Al nuclei and additional splitting by I = 1/2 ⁸⁸Y nuclei.

¹⁹F{¹H} NMR (C₆D₅Cl, 376 MHz, 298 K): δ = –74.66.

FTIR (ATR, microcrystalline): υ = 2915 (w, br), 1455 (w), 1398 (w), 1352 (w), 1297 (m), 1273 (m), 1239 (m), 1209 (s), 1163 (m), 1086 (w), 1043 (w), 969 (s), 895 (m), 830 (w), 805 (w), 789 (w), 744 (w), 726 (s), 688 (w), 688 (w), 560 (m), 536 (m), 442 (m) cm⁻¹.

[^{Dy(Cp*)₂(µ-Me₃AlNEt₃)}₂][Al{OC(CF₃)₃}₄]₂ (1-Dy). A slurry of [{Dy(Cp*)₂(µ-Me₄Al)}₂] (0.1389 g, 0.13 mmol) and [NEt₃H][Al{OC(CF₃)₃}₄] (0.2855 g, 0.27 mmol) in benzene (10 ml) were stirred overnight to give a reaction mixture of a colourless solution and a pale yellow solid. The solvent was removed in vacuo and the product was extracted into chlorobenzene (15 ml) and filtered. The resultant pale yellow solution was reduced in volume to ca. 5 ml, layered with n-hexane (20 ml) and allowed to stand at room temperature overnight to afford yellow crystals of [{Dy(Cp*)₂(µ-Me₃AlNEt₃)}₂][Al{OC(CF₃)₃}₄]·(C₆H₅Cl)₃ (1-Dy·3C₆H₅Cl). The crystals were dried in vacuo to afford a yellow crystalline solid, which elemental analysis results indicate is desolvated 1-Dy. Yield: 0.3606 g, 76%. Anal. Calcd (%) for C₉₀H₁₀₈Al₄F₇₂N₂O₈Dy₂: C, 34.35; H, 3.46; N, 0.89. Found: C, 34.53; H, 3.38; N, 0.14. ¹⁹F{¹H} NMR (C₆D₅Cl, 376 MHz, 298 K): δ = –81.40 (br, ν½ = 140 Hz), –80.28 (br, ν½ = 400 Hz); the presence of two signals is attributed to dynamic equilibrium processes in solution. The ¹H and ¹³C{¹H} NMR spectra could not be interpreted due to the paramagnetism of the sample.

FTIR (ATR, microcrystalline): υ = 2921 (w, br), 1453 (w), 1398 (w), 1352 (w), 1297 (m), 1274 (m), 1239 (m), 1209 (st), 1162 (m), 1087 (w), 1045 (w), 1022 (w), 969 (st), 830 (w), 805 (w), 789 (w), 755 (w), 742 (w), 726 (st), 689 (w), 653 (w), 560 (w), 536 (m), 442 (m) cm⁻¹.

[^{0.05Y(0.95Dy)(Cp*)₂(µ-Me₃AlNEt₃)}₂][Al{OC(CF₃)₃}₄]₂ (1-Dy@Y). A mixture of 1-Y (0.2643 g, 0.088 mmol) and 1-Dy (0.0146 g, 0.0046 mmol) was dissolved in chlorobenzene (5 ml), layered with
n-hexane (15 ml) and allowed to stand at room temperature overnight to afford off-white crystals of 
\[\left[[0.05\text{Dy}@0.95\text{Y}(\text{Cp}^*)_2(\mu-\text{Me}_3\text{AlNEt}_3)]_2\left[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4\right]_2(\text{C}_6\text{H}_5\text{Cl})_3\right] \quad (1-\text{Dy}@\text{Y} \cdot 3\text{C}_6\text{H}_5\text{Cl}) \]. The crystals were dried in vacuo to afford an off-white crystalline solid, which elemental analysis results indicate is desolvated 1-Dy@Y. Yield (0.2340 g, 88%).

\[\text{C}_{108}\text{H}_{123}\text{Al}_4\text{Cl}_3\text{F}_{72}\text{N}_2\text{O}_8\text{Dy}_{0.1}\text{Y}_{1.9}: \text{C, 38.79%; H, 3.71%; N, 0.84. Found: C, 34.51; H, 3.19; N, 0.0. Y/Dy composition (ICP-OES): Y, 94.6; Dy, 5.4.}\]

FTIR (ATR, microcrystalline): \(\tilde{\nu} = 2916\) (w, br), 1478 (w), 1454 (w), 1398 (w), 1352 (w), 1297 (w), 1273 (m), 1239 (m), 1208 (st), 1161 (m), 1085 (w), 1043 (w), 1023 (w), 969 (st), 831 (w), 793 (w, br), 754 (w), 725 (st), 688 (w), 653 (w), 560 (m), 536 (w), 441 (m) cm\(^{-1}\).
2. Crystallography

The crystal data for \([Y(Cp^*)(\mu-\text{Me})_2\text{Li(THF)}], \{[\text{Ln}(Cp^*)_2(\mu-\text{Me}_4\text{Al})]_2\}·(\text{C}_7\text{H}_8)_2 (\text{Ln} = \text{Dy}, \text{Y})\) and 1-\text{Ln}:3\text{C}_6\text{H}_5\text{Cl} (\text{Ln} = \text{Dy}, \text{Y}, 0.05\text{Dy@0.95Y}) are compiled in Tables S1–S2. Crystals were examined using a Rigaku XtaLAB AFC11 diffractometer equipped with a CCD area detector and graphite-monochromated Cu Kα (\(\lambda = 1.54178 \text{ Å}\)) or Mo Kα radiation (\(\lambda = 0.71073 \text{ Å}\)), apart from \([Y(Cp^*)(\mu-\text{Me})_2\text{Li(THF)}], \) which was examined using an Oxford Diffraction Supernova diffractometer equipped with a CCD area detector and mirror-monochromated Mo Kα radiation (\(\lambda = 0.71073 \text{ Å}\)).

Intensities were integrated from data recorded on 1° (\([Y(Cp^*)(\mu-\text{Me})_2\text{Li(THF)}]) 1-\text{Ln}:3\text{C}_6\text{H}_5\text{Cl} (\text{Ln} = \text{Y}, 0.05\text{Dy@0.95Y})\) or 0.5° (1-\text{Dy}:3\text{C}_6\text{H}_5\text{Cl}, \{[\text{Ln}(Cp^*)_2(\mu-\text{Me}_4\text{Al})]_2\}·(\text{C}_7\text{H}_8)_2) frames by \(\omega\) rotation. Cell parameters were refined from the observed positions of all strong reflections in each data set. A Gaussian grid face-indexed (\([Y(Cp^*)(\mu-\text{Me})_2\text{Li(THF)}]), 1-\text{Ln}:3\text{C}_6\text{H}_5\text{Cl}) or multi-scan (\{[\text{Ln}(Cp^*)_2(\mu-\text{Me}_4\text{Al})]_2\}·(\text{C}_7\text{H}_8)_2) absorption correction with a beam profile was applied.\(^3\) The structures were solved using SHELXS;\(^4\) the datasets were refined by full-matrix least-squares on all unique \(F^2\) values,\(^5\) with anisotropic displacement parameters for all non-hydrogen atoms, and with constrained riding hydrogen geometries; \(U_{iso}(H)\) was set at 1.2 (1.5 for methyl groups) times \(U_{eq}\) of the parent atom. The largest features in final difference syntheses were close to heavy atoms and were of no chemical significance. CrysAlisPro\(^3\) was used for control and integration, and SHELX\(^4,5\) was employed through OLEX2\(^6\) for structure solution and refinement. ORTEP-3\(^7\) and POV-Ray\(^8\) were employed for molecular graphics. CCDC 1964114–1964119 contain the supplementary crystal data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
Table S1. Crystallographic data for \([\text{Y(Cp}^*\text{)}_2(\mu-\text{Me})\text{Li(THF)}]\) and \([\{\text{Ln(Cp}^*\text{)}_2(\mu-\text{Me}_4\text{Al})\}_2]\)\(\text{C}_7\text{H}_8\)_2 (Ln = Dy, Y).

\(^a\)Conventional \(R = \sum |F_o| - |F_c|/\sum |F_o|; R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}; S = [\sum w(F_o^2 - F_c^2)^2/\text{no. data} - \text{no. params})]^{1/2}\) for all data.

|                  | \([\text{Y(Cp}^*\text{)}_2(\mu-\text{Me})\text{Li(THF)}]\) | \([\{\text{Dy(Cp}^*\text{)}_2(\mu-\text{Me}_4\text{Al})\}_2]\)\(\text{C}_7\text{H}_8\)_2 | \([\{\text{Y(Cp}^*\text{)}_2(\mu-\text{Me}_4\text{Al})\}_2]\)\(\text{C}_7\text{H}_8\)_2 |
|------------------|------------------------------------------------------------|------------------------------------------------------------|------------------------------------------------------------|
| **Formula**      | \(\text{C}_{26}\text{H}_{44}\text{LiYO}\)                | \(\text{C}_{76}\text{H}_{116}\text{Al}_2\text{Dy}_2\)     | \(\text{C}_{76}\text{H}_{116}\text{Al}_2\text{Y}_2\)     |
| **Formula weight** | 468.46                                                     | 1408.64                                                   | 1261.46                                                   |
| **Crystal size, mm** | \(0.17 \times 0.11 \times 0.08\)                         | \(0.242 \times 0.119 \times 0.059\)                     | \(0.471 \times 0.373 \times 0.339\)                     |
| **Crystal system** | monoclinic                                                 | Triclinic                                                 | triclinic                                                 |
| **Space group**  | \(P2_1/n\)                                                 | \(P-1\)                                                   | \(P-1\)                                                   |
| **a, Å**         | 9.2530(13)                                                 | 11.1938(3)                                                | 11.2354(3)                                                |
| **b, Å**         | 15.4572(12)                                                | 12.4457(7)                                                | 12.4540(3)                                                |
| **c, Å**         | 18.3771(16)                                                | 14.8073(5)                                                | 14.8193(2)                                                |
| **α, °**         | 90                                                         | 104.044(4)                                                | 103.8942(17)                                              |
| **β, °**         | 94.016(10)                                                 | 100.205(3)                                                | 100.2987(17)                                              |
| **γ, °**         | 90                                                         | 111.785(4)                                                | 111.860(2)                                                |
| **V, Å\(^3\)**  | 2621.9(5)                                                  | 1774.64(14)                                               | 1783.51(7)                                                |
| **Z**            | 4                                                          | 1                                                         | 1                                                         |
| **ρ\(_{\text{calc}}\), g cm\(^{-3}\)** | 1.187                                                      | 1.318                                                     | 1.174                                                     |
| **μ, mm\(^{-1}\)** | 2.237                                                      | 2.153                                                     | 2.688                                                     |
| **F(000)**       | 1000                                                       | 730                                                       | 676                                                       |
| **No. of reflections (unique)** | 4797 (2680)                                                   | 11216 (8687)                                              | 24477 (6466)                                              |
| **S**            | 0.993                                                      | 1.010                                                     | 1.141                                                     |
| **R(I\(wR_2\)) (F^2 > 2σ(F^2))** | 0.0954 (0.1760)                                             | 0.1023 (0.2489)                                           | 0.0444 (0.1278)                                           |
| **R_{int}**      | 0.1413                                                     | 0.1507                                                    | 0.0339                                                    |
| **Min./max. diff map, Å\(^3\)** | −0.630, 0.557                                                 | −3.336, 3.848                                             | −0.580, 1.855                                             |
Table S2. Crystallographic data for 1-Ln·3C₆H₅Cl (Ln = Dy, Y, 0.05Dy@0.95Y).

*Conventional \( R = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|}; \) \( R_w = \left[ \Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2 \right]^{1/2} ; S = \left[ \Sigma w(F_o^2 - F_c^2)^2 / \text{no. data} - \text{no. params} \right]^{1/2} \) for all data.

|                  | 1-Dy·3C₆H₅Cl | 1-Y·3C₆H₅Cl | 1-Dy@Y·3C₆H₅Cl |
|------------------|---------------|--------------|-----------------|
| Formula          | C₁₀₈H₁₂₃Al₄Cl₃Dy₂F₇₂ | C₁₀₈H₁₂₄Al₄Cl₃F₇₂ | C₁₀₈H₁₂₃Al₄Cl₃Dy₀.22F₇₂N₂O₈Y₁.78 |
| Formula weight   | 3484.35       | 3350.18      | 3353.36         |
| Crystal size, mm | 0.175 × 0.096 × | 0.160 × 0.116 × | 0.218 × 0.169 × |
| Crystal system   | monoclinic    | Monoclinic   | monoclinic      |
| Space group      | \( P2_1/c \)   | \( P2_1/c \)   | \( P2_1/c \)   |
| a, Å             | 13.8684(3)    | 100.02(10)   | 14.14639(9)     |
| b, Å             | 30.4814(7)    | 14.1215(2)   | 30.4739(2)      |
| c, Å             | 16.1283(5)    | 30.3026(3)   | 16.04187(10)    |
| α, °             | 90            | 16.0232(2)   | 90              |
| β, °             | 97.720(3)     | 90           | 98.2178(6)      |
| γ, °             | 90            | 98.4210(10)  | 90              |
| V, Å³            | 6756.1(3)     | 90           | 6844.58(8)      |
| Z                | 2             | 6782.70(15)  | 2               |
| \( \rho_{\text{calc}}, \text{g cm}^{-3} \) | 1.713         | 2            | 1.627           |
| \( \mu, \text{mm}^{-1} \) | 8.035         | 1.640        | 3.801           |
| F(000)           | 3464          | 3370         | 3368            |
| No. of reflections (unique) | 43524 (13559) | 39902 (13772) | 41213 (13952) |
| \( S^a \)        | 1.155         | 1.015        | 1.049           |
| \( R_1(wR_2)(F^2 > 2\sigma(F^2)) \) | 0.0720 (0.2050) | 0.0783 (0.2319) | 0.0452 (0.1251) |
| \( R_{\text{int}} \) | 0.0760        | 0.0272       | 0.0225          |
| Min./max. diff map, Å³ | −1.999, 1.122 | −0.840, 1.135 | −0.573, 1.126  |
Figure S1. Molecular structure of [Y(Cp*)(µ-Me)₂Li(THF)]. Displacement ellipsoids set at 50% probability level and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°):

Y(1)···Cₚcentroid₁: 2.37(2); Y(1)···Cₚcentroid₂: 2.45(2); Y(1)–C(21): 2.505(10); Y(1)–C(22): 2.500(10); Li(1)–C(21): 2.13(2); Li(1)–C(22): 2.13(2); Y(1)–O(1): 1.84(2); range Y(1)–Cring: 2.62(3)–2.69(2); Cₚcentroid₁···Y(1)···Cₚcentroid₂: 141.1(3); C(21)–Y(1)–C(22): 90.8(3); Y(1)–C(21)–Li(1): 77.2(7); Y(1)–C(22)–Li(1): 77.3(7); C(21)–Li(1)–C(22): 113.5(12).
Figure S2. Molecular structure of \([\{\text{Dy(Cp}^\ast)\_2\_\mu,\text{-Me}_4\text{Al}\}\_2\_\text{(C}_7\text{H}_8\}_2\). Displacement ellipsoids set at 50\% probability level and hydrogen atoms and lattice solvent are omitted for clarity. Selected bond lengths (Å) and angles (°): Dy(1)···C_{centroid1}: 2.355(7); Dy(1)···C_{centroid2}: 2.372(7); Dy(1)···C(21): 2.68(2); Dy(1)···C(22): 2.70(2); Al(1)···C(21): 2.04(2); Al(1)···C(22): 2.05(2); range Dy(1)···C_{ring}: 2.63(2)–2.67(2); C_{centroid1}···Dy(1)···C_{centroid2}: 138.7(2); C(21)···Dy(1)···C(22): 87.2(2); Dy(1)···C(21)···Al(1): 175.6(8); C(21)···Al(1)···C(22): 100.7(7).
**Figure S3.** Molecular structure of [{Y(Cp*)₂(µ-Me₂Al)}₂{(C₇H₈)₂}. Displacement ellipsoids set at 50% probability level and hydrogen atoms and lattice solvent are omitted for clarity. Selected bond lengths (Å) and angles (°): Y(1)∙∙∙C_{centroid}1: 2.351(2); Y(1)∙∙∙C_{centroid}2: 2.365(2); Y(1)∙∙∙C(21): 2.669(4); Y(1)∙∙∙C(22): 2.686(3); Al(1)–C(21): 2.039(3); Al(1)–C(22): 2.049(3); range Y(1)–C_{ring}: 2.627(3)–2.675(4); C_{centroid}1∙∙∙Y(1)∙∙∙C_{centroid}2: 138.65(5); C(21)∙∙∙Y(1)∙∙∙C(22): 87.39(10); Y(1)∙∙∙C(21)∙∙∙Al(1): 175.5(2); C(21)∙∙∙Al(1)∙∙∙C(22): 100.4(2).
Figure S4. Molecular structure of the dication of 1-Y\(\cdot3\)C\(_6\)H\(_5\)Cl, shown at the 50 % probability level; [Al\{OC(CF\(_3\))\(_3\}\}\(_4\)]\(^-\) counterions and lattice solvent are omitted for clarity. Selected bond lengths (Å) and angles (°): Y(1)···C\(_{\text{centroid}}\)\(_1\): 2.339(2); Y(1)···C\(_{\text{centroid}}\)\(_2\): 2.360(3); Y(1)···C(25): 2.776(5); Y(1)···C(27): 2.782(5); range Y(1)···C\(_{\text{ring}}\): 2.55(2)–2.65(3); C\(_{\text{centroid}}\)\(_1\)···Y(1)···C\(_{\text{centroid}}\)\(_2\): 137.99(10); C\(_{\text{centroid}}\)\(_1\)···Y(1)···C(25): 108.43(11); C\(_{\text{centroid}}\)\(_1\)···Y(1)···C(27): 107.19(11); C\(_{\text{centroid}}\)\(_2\)···Y(1)···C(25): 102.55(11); C\(_{\text{centroid}}\)\(_2\)···Y(1)···C(27): 104.08(11); C(21)···Y(1)···C(27): 83.01(13).
4. NMR spectroscopy

**Figure S5.** Initial $^1$H NMR spectrum of 1-Y in C$_6$D$_5$Cl.

**Figure S6.** Initial $^{13}$C{$^1$H} NMR spectrum of 1-Y in C$_6$D$_5$Cl.
Figure S7. Initial $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of 1-Y in C$_6$D$_5$Cl.

Figure S8. $^1\text{H}$ NMR spectra of 1-Y in C$_6$D$_5$Cl to show decomposition of the sample over time at room temperature (bottom 10 mins, middle 5 hrs, top 22 hrs).
Figure S9. Initial $^1$H NMR spectrum of 1-Dy in C$_6$D$_5$Cl, zoomed in the region +200 to –200 ppm; no other signals were observed between +400 to –400 ppm. The signals between 0 to +10 ppm are assigned to C$_6$D$_5$Cl.

Figure S10. Initial $^{19}$F{$^1$H} NMR spectrum of 1-Dy in C$_6$D$_5$Cl.
Figure S11. $^1$H NMR spectrum of [{Dy(Cp*)$_2$(µ-Me$_4$Al)}$_2$] in C$_6$D$_5$Cl, zoomed in the region +200 to –200 ppm.

Figure S12. $^1$H NMR spectrum of [{Dy(Cp*)$_2$(µ-Me$_4$Al)}$_2$] in C$_6$D$_5$Cl, zoomed in the region 0 to –400 ppm.
Figure S13. $^1$H NMR spectrum of $[\text{Dy}(\text{Cp}^*)_2(\mu-\text{Me})_2\text{Li}]$ in C$_6$D$_5$Cl, zoomed in the region +200 to –200 ppm; no other signals were observed between +400 to –400 ppm.
5. ATR-IR spectroscopy

Figure S14. ATR-IR spectrum of 1-Y recorded as a microcrystalline powder.

Figure S15. ATR-IR spectrum of 1-Dy recorded as a microcrystalline powder.
Figure S16. ATR-IR spectrum of 1-Dy@Y recorded as a microcrystalline powder.

Figure S17. ATR-IR spectra of 1-Y, 1-Dy and 1-Dy@Y in the region 1600–400 cm$^{-1}$ intended to show the similarities between all spectra.
Figure S18. ATR-IR spectrum of [Dy(Cp*)₂(µ-Me)₂Li] recorded as a microcrystalline powder.

Figure S19. ATR-IR spectrum of [{Dy(Cp*)₂(µ-Me₄Al)}₂] recorded as a microcrystalline powder.
6. Magnetic measurements

Magnetic measurements were made using a Quantum Design MPMS-XL7 superconducting quantum interference device (SQUID) magnetometer. A crystalline sample (1-Dy) with mass 32.3 mg was crushed with a mortar and pestle under an inert atmosphere, and then loaded into a borosilicate glass NMR tube along with ca. 15.8 mg powdered eicosane, which was then evacuated and flame-sealed to a length of ca. 5 cm. Similarly, 34.8 mg of doped sample containing a 5:95 ratio of Dy:Y (1-Dy@Y) was prepared with 16.8 mg of powdered eicosane to address the effect of intramolecular magnetic interactions. The eicosane was melted by heating the tube gently with a low-power heat gun in order to immobilize the crystallites. The NMR tube was then mounted in the centre of a drinking straw using friction by wrapping it with Kapton tape, and the straw was then fixed to the end of the sample rod. The measurements were corrected for the diamagnetism of the straw, borosilicate tube and eicosane using calibrated blanks, and the intrinsic diamagnetism of the sample using Pascals constants.9

![Figure S20](image.png)

*Figure S20.* Temperature dependence of the molar magnetic susceptibility $\chi_M T$ products of 1-Dy measured under a 0.1 T DC field.
Figure S21. Magnetisation curves of 1-Dy.

Figure S22. Temperature dependence of hysteresis loops of 1-Dy, showing an opening up to 15 K.
Figure S23. Temperature dependence of hysteresis loops of 1-Dy@Y, showing closing of the loops at 12 K; this lower temperature is attributed to noisy data as we observe open loops at 14 and 16 K.

Figure S24. Zero-field cooled (ZFC), field cooled (FC) measurements of 1-Dy under a 0.1 T (top) and 0.05 T (bottom) external field, showing a maximum at 8 K.
Figure S25. Zero-field cooled (ZFC), field cooled (FC) measurements of 1-Dy@Y under a 0.1 T (top) and 0.05 T (bottom) external field, showing a maximum at 8 K.

Figure S26. Zero-field cooled (ZFC), field cooled (FC) measurements of 1-Dy under a 0.1 T (top) and 0.05 T (bottom) external field. The curves overlap at 22 K.
Figure S27. Zero-field cooled (ZFC), field cooled (FC) measurements of 1-Dy@Y under a 0.1 T (top) and 0.05 T (bottom) external field. The curves overlap at 13 K. We used the same diamagnetic correction as for 1-Dy, and an effective molecular weight of 3600 g/mol, corresponding to a dilution of 8.4%, in line with the experimentally determined value of 5%.
Figure S28. In-phase (top) and out-of-phase (bottom) ac susceptibilities of 1-Dy in a zero field. Solid lines are fits to the generalized Debye model, giving $0.002 \leq \alpha \leq 0.1$.

Figure S29. Cole-Cole plot for 1-Dy. Solid lines are fits to the generalized Debye model, giving $0.002 \leq \alpha \leq 0.1$. 

S27
Table S3. Best fit parameters to the generalized Debye model for 1-Dy.

| T     | τ       | $\tau_{err, upper}^{Deby}$ | $\tau_{err, lower}^{Deby}$ | $\chi_S^{err}$ | $\chi_S^{err}$ | $\chi_T^{err}$ | $\chi_T^{err}$ | α       | $\alpha^{err}$ |
|-------|---------|----------------------------|----------------------------|----------------|----------------|----------------|----------------|---------|----------------|
| 25.00 | 1.57E+00| 3.27E+00                   | 7.55E-01                   | 4.00E-06       | 2.19E-08       | 1.88E-05       | 1.89E-07       | 1.24E-01| 5.87E-03       |
| 26.00 | 1.20E+00| 2.21E+00                   | 6.54E-01                   | 3.75E-06       | 2.09E-07       | 1.72E-05       | 1.28E-06       | 9.22E-02| 5.23E-02       |
| 27.00 | 1.15E+00| 2.25E+00                   | 5.88E-01                   | 3.73E-06       | 1.74E-08       | 1.71E-05       | 1.01E-07       | 1.08E-01| 4.25E-03       |
| 28.00 | 1.01E+00| 1.69E+00                   | 6.07E-01                   | 3.84E-06       | 2.09E-07       | 1.57E-05       | 1.03E-06       | 6.86E-02| 5.38E-02       |
| 30.00 | 7.85E-01| 1.52E+00                   | 4.05E-01                   | 3.32E-06       | 1.99E-08       | 1.53E-05       | 1.00E-07       | 1.05E-01| 5.48E-03       |
| 32.00 | 6.23E-01| 1.19E+00                   | 3.26E-01                   | 3.13E-06       | 1.85E-08       | 1.44E-05       | 7.47E-08       | 1.02E-01| 4.87E-03       |
| 34.00 | 4.92E-01| 9.26E-01                   | 2.62E-01                   | 2.97E-06       | 1.66E-08       | 1.36E-05       | 5.46E-08       | 9.82E-02| 4.20E-03       |
| 36.00 | 3.85E-01| 6.99E-01                   | 2.12E-01                   | 2.84E-06       | 1.55E-08       | 1.28E-05       | 4.18E-08       | 8.93E-02| 3.81E-03       |
| 38.00 | 3.00E-01| 5.50E-01                   | 1.63E-01                   | 2.69E-06       | 1.67E-08       | 1.23E-05       | 3.80E-08       | 9.21E-02| 3.96E-03       |
| 40.00 | 2.30E-01| 4.13E-01                   | 1.28E-01                   | 2.56E-06       | 1.75E-08       | 1.16E-05       | 3.36E-08       | 8.62E-02| 4.04E-03       |
| 42.00 | 1.70E-01| 2.88E-01                   | 1.01E-01                   | 2.47E-06       | 3.11E-08       | 1.11E-05       | 4.94E-08       | 7.21E-02| 6.93E-03       |
| 44.00 | 1.33E-01| 2.54E-01                   | 6.93E-02                   | 2.22E-06       | 3.56E-08       | 1.08E-05       | 8.04E-08       | 1.03E-01| 1.10E-02       |
| 46.00 | 9.19E-02| 1.62E-01                   | 5.22E-02                   | 2.26E-06       | 2.02E-08       | 1.02E-05       | 3.29E-08       | 8.17E-02| 5.51E-03       |
| 48.00 | 6.57E-02| 1.25E-01                   | 3.46E-02                   | 2.07E-06       | 3.58E-08       | 9.94E-06       | 6.09E-08       | 1.00E-01| 1.06E-02       |
| 50.00 | 4.00E-02| 6.79E-02                   | 2.36E-02                   | 2.10E-06       | 1.46E-08       | 9.45E-06       | 1.72E-08       | 7.25E-02| 3.73E-03       |
| 52.00 | 2.43E-02 | 4.26E-02 | 1.38E-02 | 3.57E-04 | 1.96E-06 | 2.91E-08 | 9.16E-06 | 3.52E-08 | 8.09E-02 | 8.10E-03 |
|-------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| 54.00 | 1.30E-02 | 2.10E-02 | 8.08E-03 | 7.40E-05 | 1.96E-06 | 1.46E-08 | 8.76E-06 | 1.16E-08 | 6.10E-02 | 3.30E-03 |
| 56.00 | 7.03E-03 | 1.19E-02 | 4.15E-03 | 8.83E-05 | 1.82E-06 | 2.83E-08 | 8.52E-06 | 2.35E-08 | 7.20E-02 | 7.02E-03 |
| 58.00 | 3.57E-03 | 5.99E-03 | 2.12E-03 | 6.59E-05 | 1.77E-06 | 4.10E-08 | 8.24E-06 | 6.03E-08 | 7.02E-02 | 1.14E-02 |
| 60.00 | 1.87E-03 | 3.15E-03 | 1.11E-03 | 2.78E-05 | 1.63E-06 | 4.07E-08 | 7.98E-06 | 2.16E-08 | 7.08E-02 | 8.35E-03 |
| 62.00 | 9.60E-04 | 1.61E-03 | 5.73E-04 | 1.49E-05 | 1.54E-06 | 4.83E-08 | 7.70E-06 | 3.30E-08 | 6.96E-02 | 9.59E-03 |
| 64.00 | 5.17E-04 | 8.84E-04 | 3.03E-04 | 8.19E-06 | 1.31E-06 | 5.65E-08 | 7.49E-06 | 1.62E-08 | 7.43E-02 | 8.39E-03 |
| 66.00 | 2.44E-04 | 2.53E-04 | 2.36E-04 | 7.68E-05 | 1.11E-06 | 1.33E-06 | 6.63E-06 | 3.50E-07 | 3.81E-04 | 1.80E-01 |
| 68.00 | 1.76E-04 | 1.90E-04 | 1.63E-04 | 3.91E-06 | 1.34E-06 | 9.87E-08 | 7.04E-06 | 1.30E-08 | 1.74E-03 | 1.05E-02 |
Table S4. Best fit parameters to the magnetisation decay curves for 1-Dy using a stretched exponential model function $M(t) = M_2 + (M_1 - M_2) \exp(t/\tau)^\beta$. $M_2$, $\tau$, and $\beta$ are the fitting parameters.

| T  | $\tau$   | $\beta$ | $M_2$   | M(t) vs t plots |
|----|----------|---------|---------|-----------------|
| 10.00 | 169.383 | 0.833   | 2.01E-04 | ![Graph](10.00.png) |
| 9.00  | 225.148 | 0.866   | 9.55E-04 | ![Graph](9.00.png) |
| 8.00  | 340.018 | 0.813   | 1.03E-03 | ![Graph](8.00.png) |
| Value  | Data Points | Fit Value | Error |
|--------|-------------|-----------|-------|
| 3.25   | 14269.790   | 0.587     | 2.59E-03 |
| 2.90   | 23288.330   | 0.555     | 2.51E-03 |
| 2.60   | 27906.488   | 0.563     | 1.09E-02 |
**Table S5.** Best fit parameters to the magnetisation decay curves for 1-Dy@Y using a stretched exponential model function \( M(t) = M_2 + (M_1 - M_2) \exp\left(\frac{t}{\tau}\right)\beta \). \( M_2 \), \( \tau \) and \( \alpha \) are the fitting parameters.

| T   | \( \tau \) | \( \beta \) | \( M_2 \) | M(t) vs t plots |
|-----|-------------|-------------|------------|----------------|
| 7.00| 200.000     | 0.666       | 0.00E+00   | ![Graph](image1) |
| 6.20| 318.346     | 0.657       | 0.00E+00   | ![Graph](image2) |
| 5.40| 486.245     | 0.585       | 6.69E-07   | ![Graph](image3) |
| 2.60 | 1758.841 | 0.343 | 2.53E-04 |
Figure S30. Temperature dependence of the magnetic relaxation rate of 1-Dy (red) and 1-Dy@Y (blue) over the whole temperature range (top) and below 10 K (bottom).
7. CASSCF-SO electronic structure

We used MOLCAS 8.0\textsuperscript{10} to perform CASSCF-SO calculations of the 1-Ln and 2-Ln complexes in order to determine their electronic structures. We employed the molecular geometry of the metal-containing molecules from single crystal XRD structure with no optimization, taking the largest disorder component only and substituting one Dysprosium center by Lutetium. Basis sets from the ANO-RCC library\textsuperscript{11,12} were employed with VTZP quality for Dy atoms, VDZP quality for the cyclopentadienyl C atoms and VDZ quality for all remaining atoms, employing the second-order DKH transformation. Cholesky decomposition of the two-electron integrals with a threshold of 10\textsuperscript{-8} was performed to save disk space and reduce computational demand. The molecular orbitals (MOs) were optimized in state-averaged CAS(9,7)SCF calculations considering 21, 224 and 490 roots for the sextet, quartet and doublet spin states, respectively. These sets of spin-free states were then used to construct and diagonalise the spin-orbit coupling Hamiltonian in the basis of all sextet, 128 quartet and 130 doublets with the RASSI module. The crystal field decomposition of the ground \( J = 15/2 \) multiplet of the \( ^6H \) term was performed with the SINGLE_ANISO\textsuperscript{13} module.
Table S6. Electronic structure of the monomer of 1-Dy (one of the Dysprosium centres has been substituted by Lutetium) calculated with CASSCF-SO at the solid-state geometry, quantised along the \( g_z \) direction of the ground doublet.

| Energy (cm\(^{-1}\)) | Energy (K) | \( g_1 \) | \( g_2 \) | \( g_3 \) | angle (deg) | Wavefunction | \(<J_z>\) |
|----------------------|------------|---------|---------|---------|------------|-------------|--------|
| 0.00                 | 0          | 0.00    | 0.00    | 19.80   | --         | 98%|\(±\) 15/2\) + 2%|\(±\) 11/2\) | ± 7.47 |
| 298.38               | 429.284    | 0.00    | 0.00    | 17.05   | 0.87       | 99%|\(±\) 13/2\) + 1%|\(±\) 9/2\) | ± 6.47 |
| 526.66               | 757.704    | 0.00    | 0.01    | 14.50   | 0.88       | 98%|\(±\) 11/2\) + 2%|\(±\) 15/2\) | ± 5.53 |
| 681.19               | 980.024    | 0.14    | 0.14    | 11.83   | 2.01       | 98%|\(±\) 9/2\) + 1%|\(±\) 13/2\) | ± 4.51 |
| 790.28               | 1136.97    | 1.68    | 2.48    | 8.54    | 4.26       | 89%|\(±\) 7/2\) + 8%|\(±\) 3/2\) | ± 3.22 |
| 841.62               | 1210.84    | 2.95    | 7.16    | 9.81    | 89.34      | 47%|\(±\) 5/2\) + 32%|\(±\) 1/2\) + 10%|\(±\) 3/2\) + 5%|\(±\) 7/2\) | ± 0.95 |
| 908.48               | 1307.03    | 0.38    | 1.19    | 14.99   | 89.40      | 47%|\(±\) 3/2\) + 36%|\(±\) 5/2\) + 10%|\(±\) 1/2\) + 4%|\(±\) 7/2\) | ± 0.13 |
| 1104.14              | 1588.52    | 0.03    | 0.04    | 19.43   | 89.45      | 53%|\(±\) 1/2\) + 33%|\(±\) 3/2\) + 10%|\(±\) 5/2\) | ± 0.05 |
8. References

1. (a) M. A. Busch, R. Harlow, P. L. Watson, *Inorg. Chim. Acta* **1987**, *140*, 15; (b) P. L. Watson, T. Herskovitz, *Am. Chem. Soc. Symp. Ser.* **1983**, *212*, 459; (c) P. L. Watson, *J. Am. Chem. Soc.* **1983**, *105*, 6491.

2. P. Evans, D. Reta, G. F. S. Whitehead, N. F. Chilton, D. P. Mills, *ChemRxiv* DOI:10.26434/chemrxiv.10050128.v1.

3. *CrysAlisPRO*, version 39.27b; Oxford Diffraction /Agilent Technologies UK Ltd: Yarnton, U.K., 2017.

4. G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112.

5. G. M. Sheldrick, *Acta Crystallogr., Sect. C* **2015**, *71*, 3.

6. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339.

7. L. J. Farrugia, *J. Appl. Crystallogr.* **2012**, *45*, 849.

8. *POV-Ray. Persistence of Vision Raytracer*; Persistence of Vision Pty. Ltd.: Williamstown, Victoria, Australia, 2013.

9. G. A. Bain, J. F. Berry, *J. Chem. Ed.* **2008**, *85*, 532.

10. F. Aquilante, J. Autschbach, R. K. Carlson, L. F. Chibotaru, M. G. Delcey, L. De Vico, I. Fernandez Galván, N. Ferré, L. M. Frutos, L. Gagliardi, M. Garavelli, A. Giussani, C. E. Hoyer, G. Manni, H. Lischka, D. Ma, P. Å. Malmqvist, T. Müller, A. Nenov, M. Olivucci, T. B. Pedersen, D. Peng, F. Plasser, B. Pritchard, M. Reiher, I. Rivalta, I. Schapiro, J. Segarra-Martí, M. Stenrup, D. G. Trehlar, L. Ungur, A. Valentini, S. Vancoillie, V. Veryazov, V. P. Vysotskiy, O. Weingart, F. Zapata, R. Lindh, *J. Comput. Chem.* **2016**, *37*, 506.

11. B. O. Roos, R. Lindh, P.-Å. Malmqvist, V. Veryazov, P.-O. Widmark, *J. Phys. Chem. A* **2004**, *108*, 2851.

12. B. O. Roos, R. Lindh, P.-Å. Malmqvist, V. Veryazov, P.-O. Widmark, *J. Phys. Chem. A* **2005**, *109*, 6575.

13. L. Ungur, L. F. Chibotaru, *Chem. Eur. J.* **2017**, *23*, 3708.
