Air-stable redox-active nanomagnets with lanthanide spins radical-bridged by a metal-metal bond

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Supplementary Figure 1. The synthesis procedure of the Ln$_2$@C$_{80}$(CH$_2$Ph).
**Supplementary Figure 2.** The first separation step of $\{\text{Gd}_2\} - 2$ analytical Buckyprep columns. The fraction between the orange lines contains $\{\text{Gd}_2\}$ and is separated further at the second step.

**Supplementary Figure 3.** The second separation step of $\{\text{Gd}_2\} - 2$ analytical BuckyPrep-D columns. The fraction between the orange lines contains $\{\text{Gd}_2\}$ and is separated further at the third step

**Supplementary Figure 4.** The third separation step of $\{\text{Gd}_2\} -$ recycling HPLC with semipreparative BuckyPrep column. The fraction between orange lines is pure $\{\text{Gd}_2\}$. 
Supplementary Figure 5. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass-spectra of Gd$_2$@C$_{80}$(CH$_2$Ph), linear positive (top) and reflector negative (bottom) ionization modes. Resolution in linear mode is not high enough for analysis of isotopic distribution. In the reflector mode, strong fragmentation does not allow for detection of molecular peak, but spectral resolution is sufficient to prove correct isotopic distribution of the Gd$_2$@C$_{80}^-$ fragment.
Supplementary Figure 6. Separation of Tb$_2$@C$_{80}$(CH$_2$Ph). Three steps HPLC separation were required to obtain the pure compound. (I) HPLC profile of the mixture of benzyl-derivatized Tb-EMFs. The highlighted fraction contained Tb$_2$@C$_{80}$(CH$_2$Ph) was collected for further separation. HPLC conditions: linear combination of two 4.6 × 250 mm Buckyprep columns; flow rate 1.6 mL/min; injection volume 800 µL; toluene as eluent; 40 °C. (II) Recycling HPLC separation of the fraction collected in the first step. The highlighted fraction was collected for further separation (10 × 250 mm Buckyprep column; flow rate 1.5 mL/min; injection volume 4.5 mL; toluene as eluent). (III) HPLC separation of the fraction collected in the second step. Pure Tb$_2$@C$_{80}$(CH$_2$Ph) was obtained as the highlighted fraction. (10 × 250 mm Buckyprep-D column; flow rate 1.0 mL/min; injection volume 4.5 mL; toluene as eluent).
**Supplementary Figure 7.** Matrix-assisted laser desorption/ionization time-of-flight (MALDI TOF) mass-spectra of Tb$_2$@C$_{80}$(CH$_2$Ph). Linear negative (top) and positive (bottom) ionization modes. Resolution in positive mode is not high enough for analysis of isotopic distribution. In the negative ion mode, strong fragmentation does not allow for detection of molecular peak, but spectral resolution is sufficient to prove correct isotopic distribution of the Tb$_2$@C$_{80}^-$ fragment.
Supplementary Figure 8. Separation of Tb$_2$Y$_2$-x@C$_{80}$(CH$_2$Ph). Four HPLC separation steps with toluene as eluent are required to obtain pure compounds. (I) HPLC profile of the mixture of benzyl-derivatized Tb-Y-EMFs (two 4.6 × 250 mm BuckyPrep columns; 1.6 mL min$^{-1}$). The highlighted fraction contains Tb$_2$Y$_2$-x@C$_{80}$(CH$_2$Ph). (II) Recycling HPLC of the fraction collected in the first step (10 × 250 mm Buckyprep column; 1.5 mL min$^{-1}$). The two highlighted fractions were collected for further separation. (III) HPLC of the first highlighted fraction collected in the second step (10 × 250 mm Buckyprep-D column; 1.0 mL min$^{-1}$). Highlighted fraction contains Y$_2$@C$_{80}$(CH$_2$Ph) and TbY@C$_{80}$(CH$_2$Ph). (IV) Recycling HPLC of the fraction collected in the third step (10 × 250 mm Buckyprep column; 1.0 mL min$^{-1}$). Pure Y$_2$@C$_{80}$(CH$_2$Ph) and TbY@C$_{80}$(CH$_2$Ph) are obtained. (V) HPLC of the second highlighted fraction collected in the second step (10 × 250 mm Buckyprep-D column; 1.0 mL min$^{-1}$). Highlighted fraction contains Tb$_2$@C$_{80}$(CH$_2$Ph) and TbY@C$_{80}$(CH$_2$Ph). (VI) Recycling HPLC of the fraction collected in the last step (10 × 250 mm Buckyprep column; 1.0 mL min$^{-1}$). Pure Tb$_2$@C$_{80}$(CH$_2$Ph) and TbY@C$_{80}$(CH$_2$Ph) are obtained.
Supplementary Figure 9. Matrix-assisted laser desorption/ionization time-of-flight (MALDI TOF) mass-spectra of \( Y_2@C_{80}(CH_2Ph) \). Linear negative (top) and positive (bottom) ionization modes. Resolution in positive mode is not high enough for analysis of isotopic distribution. In the negative ion mode, strong fragmentation does not allow for detection of molecular peak, but spectral resolution is sufficient to prove correct isotopic distribution of the \( Y_2@C_{80}^- \) fragment.
**Supplementary Figure 10.** Matrix-assisted laser desorption/ionization time-of-flight (MALDI TOF) mass-spectra of TbY@C$_{80}$(CH$_2$Ph). Linear negative (top) and positive (bottom) ionization modes. Resolution in positive mode is not high enough for analysis of isotopic distribution. In the negative ion mode, strong fragmentation does not allow for detection of molecular peak, but spectral resolution is sufficient to prove correct isotopic distribution of the TbY@C$_{80}^-$ fragment.
Supplementary Figure 11. First step separation of {TbGd} – 2 analytical Buckyprep columns. The fraction marked with orange contains {TbGd} and is further separated at the second step.

Supplementary Figure 12. Second step separation of {TbGd} – 2 analytical Buclyprep-D columns. Fraction F9 contains {TbGd} and is further separated at the third step.

Supplementary Figure 13. Third step separation of {TbGd} – recycling HPLC with semipreparative BuckyPrep column. The fraction marked with orange is a mixture of {Gd}, {TbGd}, and {Tb}$_2$. Longer runs of this fraction with recycling HPLC did not afford further separation into individual compounds.
Supplementary Figure 14. MALDI-TOF mass-spectra of the purified "{TbGd}" sample

Supplementary Figure 15. MALDI-TOF mass-spectrum of the \{TbGd\} sample showing experimental isotopic distribution compared to the simulated one for a mixture of 20\% \{Gd\}_2, 30\% \{Tb\}_2 and 50\% \{TbGd\}. 
Supplementary Figure 16. Separation of Ho$_2$@C$_{80}$(CH$_2$Ph). Three steps HPLC separation were required to obtain the pure compound (I) HPLC profile of the mixture of benzyl-derivatized Ho-EMFs. The highlighted fraction contained Ho$_2$@C$_{80}$(CH$_2$Ph) was collected for further separation. HPLC conditions: linear combination of two 4.6 × 250 mm Buckyprep columns; flow rate 1.6 mL/min; injection volume 800 µL; toluene as eluent; 40 °C. (II) Recycling HPLC separation of the fraction collected in the first step. The highlighted fraction was collected for further separation (10 × 250 mm Buckyprep column; flow rate 1.5 mL/min; injection volume 4.5 mL; toluene as eluent). (III) HPLC separation of the fraction collected in the second step. Pure Ho$_2$@C$_{80}$(CH$_2$Ph) was obtained as the highlighted fraction. (10 × 250 mm Buckyprep-D column; flow rate 1.0 mL/min; injection volume 4.5 mL; toluene as eluent).
Supplementary Figure 17. Matrix-assisted laser desorption/ionization time-of-flight (MALDI TOF) mass-spectra of Ho$_2$@C$_{80}$(CH$_2$Ph). Linear negative (top) and positive (bottom) ionization modes. Resolution in positive mode is not high enough for analysis of isotopic distribution. In the negative ion mode, strong fragmentation does not allow for detection of molecular peak, but spectral resolution is sufficient to prove correct isotopic distribution of the Ho$_2$@C$_{80}^-$ fragment.
Supplementary Figure 18. Separation of Er₂@C₈₀(CH₂Ph). Three steps HPLC separation were required to obtain the pure compound (I) HPLC profile of the mixture of benzyl-derivatized Er-EMFs. The highlighted fraction contained Er₂@C₈₀(CH₂Ph) was collected for further separation. HPLC conditions: linear combination of two 4.6 × 250 mm Buckyprep columns; flow rate 1.6 mL/min; injection volume 800 µL; toluene as eluent; 40 °C. (II) Recycling HPLC separation of the fraction collected in the first step. The highlighted fraction was collected for further separation (10 × 250 mm Buckyprep column; flow rate 1.5 mL/min; injection volume 4.5 mL; toluene as eluent). (III) HPLC separation of the fraction collected in the second step. Pure Er₂@C₈₀(CH₂Ph) was obtained as the highlighted fraction. (10 × 250 mm Buckyprep-D column; flow rate 1.0 mL/min; injection volume 4.5 mL; toluene as eluent).
Supplementary Figure 19. Matrix-assisted laser desorption/ionization time-of-flight (MALDI TOF) mass-spectra of Er$_2$@C$_{80}$(CH$_2$Ph). Linear negative (top) and positive (bottom) ionization modes. Resolution in positive mode is not high enough for analysis of isotopic distribution. In the negative ion mode, strong fragmentation does not allow for detection of molecular peak, but spectral resolution is sufficient to prove correct isotopic distribution of the Er$_2$@C$_{80}^-$ fragment.
**Supplementary Figure 20.** HPLC profiles of the purified M$_2$@C$_{80}$(CH$_2$Ph). HPLC conditions: linear combination of two 4.6 × 250 mm Buckyprep columns; flow rate 1.6 mL/min; injection volume 800 µL; toluene as eluent; 40 °C. The identical retention times for Tb$_x$Gd$_{2-x}$@C$_{80}$(CH$_2$Ph) indicates that the separation of these compounds by HPLC is an impossible mission.

**Supplementary Figure 21.** Air stability: HPLC trace of the freshly synthesized {Tb$_2$} and 8 months after the synthesis (during this time period the sample was studied in air by SQUID magnetometry and NMR spectroscopy and stored in solution).
Supplementary Figure 22. Molecular structure of Dy$_2$@C$_{80}$(CH$_2$Ph) determined with single-crystal X-ray diffraction at temperatures from 100K to 290K. The thermal ellipsoids were shown with 50%. The hexagon belt of the C$_{80}$ fullerene cage where the Dy$_2$ locates is highlighted with yellow bonds. Color code: grey for carbon, green for Dy, the deeper the green color, the higher occupancy of the Dy site.
Supplementary Figure 23. Molecular structure of Dy$_2$@C$_{80}$(CH$_2$Ph) determined with single-crystal X-ray diffraction at temperatures from 100K to 290K. The Dy sites are shown as spheres whose radii are scaling proportional to the site occupancy (the bigger the sphere, the higher the occupancy).
Supplementary Figure 24. UV-vis-NIR absorption spectra of \( \text{(Ln}_2 \) compounds (room temperature, toluene solution).
Supplementary Figure 25. FT-IR spectra of \(\{\text{Ln}_2\}\) compounds drop-casted on KBr substrates, room temperature.
Supplementary Figure 26. Raman spectra of \(\{\text{Ln}_2\}\) compounds drop-casted on KBr substrates (the same samples as used for IR measurement). Spectra were recorded at 77 K using excitation line \(\lambda = 656\) nm of a dye laser.
Supplementary Figure 27. $^1$H VT-NMR spectra of $\{\text{Tb}_2\}$

Supplementary Figure 28. $^1$H VT-NMR spectra of $\{\text{TbY}\}$
Supplementary Figure 29. $^1$H VT-NMR spectra of $\{\text{Dy}_2\}$

Supplementary Figure 30. $^1$H VT-NMR spectra of $\{\text{Ho}_2\}$
Supplementary Figure 31. $^1$H VT-NMR spectra of $\{\text{Er}_2\}$. 
Supplementary Figure 32. $^{13}$C NMR spectrum of $\{\text{Ho}_2\}$ measured at 308 K.

Supplementary Figure 33. $^{13}$C NMR spectrum of $\{\text{Ho}_2\}$ at 308 K, enhancement of the $-15 - 180$ ppm range.
Supplementary Figure 34. Experimental $\chi T$ curve of $\{\text{Gd}_2\}$ measured in the field of 1 T (dots) and compared to the calculated curves with different values of the exchange parameter $K_{\text{eff}}$. Calculated curves are close to the experimental data for $K_{\text{eff}}$ near 160 cm$^{-1}$.

Supplementary Figure 35. Experimental $\chi T$ of $\{\text{Gd}_2\}$ measured in the fields of 1, 3, 5, and 7 T (dots) compared to the calculated curves with the exchange parameter $K_{\text{eff}} = 160$ cm$^{-1}$ (black lines).
**Supplementary Figure 36.** Magnetization curves of \( \{\text{Gd}_2\} \) (dots) compared to the results of calculations for \( K_{\text{eff}} = 160 \text{ cm}^{-1} \) (lines).
Supplementary Figure 37. Q-band EPR spectra of \( \text{Gd}_2 \) in toluene (298 K is liquid solution, 160 – 105 K frozen solution)

Supplementary Figure 38. X-band EPR spectra of \( \text{Gd}_2 \) in toluene
Supplementary Figure 39. Zeeman energy diagrams for $\{\text{Gd}_2\}$ described as a weakly anisotropic giant spin $S = 15/2$ (Spin Hamiltonian Eq. 5) for the magnetic field applied in three principal directions of the ZFI tensor. Also shown are allowed transitions in X-band and Q-band EPR spectra.
**Supplementary Figure 40.** Relaxation of magnetization in \{\text{Tb}_2\} measured by first magnetizing the sample in the field of 5 Tesla, then sweeping the field fast to 0 Tesla and measuring the decay (colored dots). The curves are fitted with stretched exponential (black solid lines); see Ref. 2 for a discussion of fitting procedure. Note that the curves were measured for several different samples with slightly different sample amounts. Only selected temperatures are shown.

**Supplementary Figure 41.** Relaxation of magnetization in \{\text{Tb}_2\} measured by first magnetizing the sample at 5 Tesla, then sweeping the field fast to 0.3 Tesla and measuring the decay (colored dots). The curves are fitted with stretched exponential (red solid lines).
Supplementary Figure 42. Temperature dependence of $\chi''$ of $\{\text{Tb}_2\}$ measured in zero field (left) and corresponding Cole-Cole plots (right). Dots are experimental data, lines are results of the fit with generalized Debye model.

Supplementary Figure 43. Contribution of the second, fourth and sixth order axial terms for Tb$^{3+}$ (left) and Dy$^{3+}$ ions (right) at sites 1 and 2. The symbols represent the *ab initio* energy levels while the curves are expectation values of the LF Hamiltonian, Eq. (4), obtained by considering only the axial terms given in the legends. The data for the Dy ion is taken from Ref. 1.
Supplementary Figure 44. Experimental $\chi T$ curve of $\{\text{Tb}_2\}$ measured in the field of 1 T (dots) and compared to the calculated curves with different values of the exchange parameter $K_{\text{eff}}$. Calculated curves are close to the experimental data for $K_{\text{eff}}$ in the range from 48 to 53 cm$^{-1}$. Absolute experimental $\chi T$ values cannot be determined sufficiently accurate, and hence the experimental curves are scaled to reproduce the calculated data. Note that the experimental $\chi T$ values measured below the blocking temperature of magnetization (29 K) do not correspond to the equilibrium values.

Supplementary Figure 45. Experimental $\chi T$ of $\{\text{Tb}_2\}$ measured in the fields of 1, 3, 5, and 7 T (dots) compared to the calculated curves with the exchange parameter $K_{\text{eff}} = 50$ cm$^{-1}$ (black lines). Experimental $\chi T$ values are scaled to reproduce the calculated data. Note that the experimental $\chi T$ values measured below the blocking temperature of magnetization (29 K) do not correspond to the equilibrium values, especially in low fields.
Supplementary Figure 46. Magnetization curves of \( \{ \text{Tb}_2 \} \) measured above blocking temperature and compared to the results of calculations for \( K^{\text{eff}} = 50 \text{ cm}^{-1} \) (black lines).
Supplementary Figure 47. The spectrum (low-energy part only) of the effective spin Hamiltonian (Supplementary Equation 1) for \(\text{Tb}_2\) with \(K^{\text{eff}}\) of 55 cm\(^{-1}\). Transition probabilities for the low-energy range are visualized as lines of different thickness (thicker lines correspond to higher probabilities). The x-axis is the projection of magnetic moment upon the main anisotropy axis.
Supplementary Figure 48. Temperature dependence of $\chi''$ of $\{\text{Ho}_2\}$ measured in zero field (left) and corresponding Cole-Cole plots (right). Measurements are performed with MPMS-XL system between 1.9 and 16 K. Dots are experimental data, lines are results of the fit with generalized Debye model.

Supplementary Figure 49. Temperature dependence of $\chi''$ of $\{\text{Ho}_2\}$ measured in the field of 0.2 T (left) and corresponding Cole-Cole plots (right). Measurements are performed with MPMS-XL system between 1.9 and 16 K. Dots are experimental data, lines are results of the fit with generalized Debye model.
Supplementary Figure 50. Temperature dependence of $\chi''$ of \{Ho\} measured in zero field (left) and corresponding Cole-Cole plots (right). Measurements are performed with PPMS system between 13.1 and 19.9 K. Dots are experimental data, lines are results of the fit with generalized Debye model.

Supplementary Figure 51. Temperature dependence of $\chi''$ of \{Ho\} measured in the field of 0.2 T (left) and corresponding Cole-Cole plots (right). Measurements are performed with PPMS system between 13 and 19 K. Dots are experimental data, lines are results of the fit with generalized Debye model.
**Supplementary Figure 52.** Field dependence of $\chi''$ of {Ho2} measured at 1.8 K (left) and corresponding Cole-Cole plots (right). Measurements are performed with MPMS system. Dots are experimental data, lines are results of the fit with generalized Debye model.

**Supplementary Figure 53.** Field dependence of $\chi''$ of {Ho2} measured at 5 K (left) and corresponding Cole-Cole plots (right). Measurements are performed with MPMS system. Dots are experimental data, lines are results of the fit with generalized Debye model.
Supplementary Figure 54. Experimental $\chi T$ curve of $\{\text{Ho}_2\}$ measured in the field of 1 T (dots) and compared to the calculated curves with different values of the exchange parameter $K_{\text{eff}}$. Calculated curves are close to the experimental data for $K_{\text{eff}}$ of 40 cm$^{-1}$. Absolute experimental $\chi T$ values are not accurate enough and are scaled to reproduce the calculated data.

Supplementary Figure 55. Experimental $\chi T$ of $\{\text{Ho}_2\}$ measured in the fields of 1, 3, 5, and 7 T (dots) compared to the calculated curves with the exchange parameter $K_{\text{eff}} = 40$ cm$^{-1}$ (black lines).
Supplementary Figure 56. Magnetization curves of {Ho$_2$} (dots) compared to the results of calculations for $K^{\text{eff}} = 40 \text{ cm}^{-1}$ (lines). Whereas the curve calculated for 2 K shows saturation already after 2 T, the experimental curve show continuous growth of magnetization in the whole accessible field range. The deviation of the shape of experimental and calculated curves is seen at all temperatures. We suggest that this is caused by the limited applicability of the spin Hamiltonian (Supplementary Equation 1) for {Ho$_2$} with two non-collinear Ho spins.
Supplementary Figure 57. The spectrum (low-energy part only) of the effective spin Hamiltonian (Supplementary Equation 1) for $\text{Ho}_2$ with $K_{\text{eff}}$ of 40 cm$^{-1}$. Transition probabilities for the low-energy range are visualized as lines of different thickness (thicker lines correspond to higher probabilities). The x axis is the projection of magnetic moment upon the main anisotropy axis.
Supplementary Figure 58. AC measurements of $\{\text{Er}_2\}$. Temperature dependence of $\chi''$ in the field of 0.2 T (left) and Cole-Cole plots (right). Dots are experimental data, lines are results of the fit with generalized Debye model.

Supplementary Figure 59. AC measurements of $\{\text{Er}_2\}$. Field dependence of $\chi''$ at 1.8 K (left) and Cole-Cole plots (right).

Supplementary Figure 60. Relaxation times of $\{\text{Er}_2\}$: temperature dependence in the field of 0.2 T (left) and field dependence at 1.8 K (right).
Supplementary Figure 61. Experimental $\chi T$ curve of $\{\text{Er}_2\}$ measured in the field of 1 T (dots) and compared to the calculated curves with different values of the exchange parameter $K_{\text{eff}}$. Calculated curves are close to the experimental data for $K_{\text{eff}}$ of 20 cm$^{-1}$.

Supplementary Figure 62. Experimental $\chi T$ of $\{\text{Er}_2\}$ measured in the fields of 1, 3, 5, and 7 T (dots) compared to the calculated curves with the exchange parameter $K_{\text{eff}} = 20$ cm$^{-1}$ (black lines).
Supplementary Figure 63. Magnetization curves of \{Er_2\} (dots) compared to the results of calculations for $K^{\text{eff}} = 20 \text{ cm}^{-1}$ (lines). The deviation of the shape of experimental and calculated curves is seen at all temperatures. We suggest that this is caused by the limited applicability of the spin Hamiltonian (Supplementary Equation 1) for \{Er_2\} with isotropic exchange for two easy-plane Er spins.
Supplementary Figure 64. Left: low-temperature magnetization curves of TbY showing magnetic hysteresis below 5 K. The curves are normalized by the magnetization value of the sample measured at 7 T at 2 K. Right: Comparison between $\chi_{\text{FC}}$ and $\chi_{\text{ZFC}}$ showing divergence of the two curves below 5 K.

Supplementary Figure 65. Magnetization curves of TbY measured in the range of 2 – 300 K. The curves are normalized by the magnetization value of the sample measured at 7 T at 2 K.
Supplementary Figure 66. Temperature dependence of $\chi''$ in zero field (left) and corresponding Cole-Cole plots (right). Dots are experimental data, lines are results of the fit with generalized Debye model.

Supplementary Figure 67. Temperature dependence of $\chi''$ in the field of 0.3 T (left) and corresponding Cole-Cole plots (right). Dots are experimental data, lines are results of the fit with generalized Debye model.

Supplementary Figure 68. Field dependence of $\chi''$ at 1.8 K (left) and Cole-Cole plots (right).
Supplementary Figure 69. Experimental $\chi T$ curve of $\{\text{TbY}\}$ measured in the field of 1 T (dots) and compared to the calculated curves with different values of the exchange parameter $K_{\text{eff}}$. Calculated curves are close to the experimental data for $K_{\text{eff}}$ in the range from 30 to 40 cm$^{-1}$, however the low-temperature part is not reproduced well. Absolute experimental $\chi T$ values are not known and are scaled here to reproduce the calculated data. The optimal $K_{\text{eff}}$ value is smaller than for $\{\text{Tb}_2\}$, presumably because of the asymmetry of the unpaired electron distribution between Tb and Y.

Supplementary Figure 70. Experimental $\chi T$ of $\{\text{TbY}\}$ measured in the fields of 1, 3, 5, and 7 T (dots) compared to the calculated curves with the exchange parameter $K_{\text{eff}} = 35$ cm$^{-1}$ (black lines). Note that high-field curves are in better agreement with calculations than the curve measured at 1 T.
**Supplementary Figure 71.** Magnetization curves of \{TbY\} (dots) compared to the results of calculations for $K_{\text{eff}} = 35 \text{ cm}^{-1}$ (lines). Experimental points are normalized by the magnetization measured at 2 K and 7 T. Low-temperature curves show a noticeable deviation from the calculated ones. In particular, the calculated curve saturate at high fields, whereas experimental ones show continuous growth of magnetization in the whole accessible field range. We suggest that this is caused by the limited applicability of the spin Hamiltonian in Supplementary Equation 3 for \{TbY\} with one Tb spin and asymmetrically distributed unpaired electron. The kinetic term in the Hamiltonian (which is neglected in current simulations) may play a more important role here.
Supplementary Figure 72. Square-wave voltammetry (dark blue) and cyclic voltammetry of \{Gd_2\}

Supplementary Figure 73. Square-wave voltammetry (dark blue) of \{Tb_2\}

Supplementary Figure 74. Square-wave voltammetry (dark blue) and cyclic voltammetry of \{TbY\}
Supplementary Figure 75. Square-wave voltammetry (dark blue) and cyclic voltammetry of \{\text{Dy}_2\}\n
Supplementary Figure 76. Square-wave voltammetry (dark blue) and cyclic voltammetry of \{\text{Ho}_2\}\n
Supplementary Figure 77. Square-wave voltammetry (dark blue) and cyclic voltammetry of \{\text{Y}_2\}\n
Supplementary Figure 78. Reduction potential of $\{\text{Ln}_2\}$ versus the $4f^n5d^16s^2 \rightarrow 4f^{n-1}5d^26s^1$ excitation energies of corresponding lanthanide atoms.
## Supplementary Table 1. Crystal data and data collection parameters.

| Crystal | Dy$_2$I$_8$(7)-C$_{80}$(CH$_2$Ph)$\cdot$0.67(C$_7$H$_8$) | Dy$_2$I$_8$(7)-C$_{80}$(CH$_2$Ph)$\cdot$0.67(C$_7$H$_8$) | Dy$_2$I$_8$(7)-C$_{80}$(CH$_2$Ph)$\cdot$0.67(C$_7$H$_8$) | Dy$_2$I$_8$(7)-C$_{80}$(CH$_2$Ph)$\cdot$0.67(C$_7$H$_8$) |
|---------|-----------------------------------------------------------|-----------------------------------------------------------|-----------------------------------------------------------|-----------------------------------------------------------|
| Formula | C$_{91.66}$H$_{12.33}$Dy$_2$ C$_{91.66}$H$_{12.33}$Dy$_2$ C$_{91.66}$H$_{12.33}$Dy$_2$ C$_{91.66}$H$_{12.33}$Dy$_2$ | C$_{91.66}$H$_{12.33}$Dy$_2$ C$_{91.66}$H$_{12.33}$Dy$_2$ C$_{91.66}$H$_{12.33}$Dy$_2$ C$_{91.66}$H$_{12.33}$Dy$_2$ | C$_{91.66}$H$_{12.33}$Dy$_2$ C$_{91.66}$H$_{12.33}$Dy$_2$ C$_{91.66}$H$_{12.33}$Dy$_2$ C$_{91.66}$H$_{12.33}$Dy$_2$ | C$_{91.66}$H$_{12.33}$Dy$_2$ C$_{91.66}$H$_{12.33}$Dy$_2$ C$_{91.66}$H$_{12.33}$Dy$_2$ C$_{91.66}$H$_{12.33}$Dy$_2$ |
| Formula weight | 1438.27 | 1438.27 | 1438.27 | 1438.27 |
| Color, habit | Black, block | Black, block | Black, block | Black, block |
| Crystal system | triclinic | triclinic | triclinic | triclinic |
| Space group | P̅1 | P̅1 | P̅1 | P̅1 |
| a, Å | 10.890(2) | 10.910(2) | 10.920(2) | 10.930(2) |
| b, Å | 11.040(2) | 11.040(2) | 11.050(2) | 11.060(2) |
| c, Å | 19.300(4) | 19.320(4) | 19.320(4) | 19.320(4) |
| α, deg | 85.91(3) | 85.97(3) | 86.05(3) | 86.08(3) |
| β, deg | 88.89(3) | 88.94(3) | 89.03(3) | 89.08(3) |
| γ, deg | 78.06(3) | 78.05(3) | 78.05(3) | 78.05(3) |
| Volume, Å$^3$ | 2264.3(8) | 2270.9(8) | 2275.3(8) | 2279.6(8) |
| Z | 2 | 2 | 2 | 2 |
| T, K | 100 | 130 | 160 | 190 |
| Radiation (λ, Å) | Synchrotron Radiation (0.89429) | Synchrotron Radiation (0.89429) | Synchrotron Radiation (0.89429) | Synchrotron Radiation (0.89429) |
| Unique data ($R_{int}$) | 9024 (0.055) | 8999 (0.0574) | 9002 (0.0584) | 8849 (0.0626) |
| Parameters | 857 | 912 | 917 | 917 |
| Restraints | 770 | 788 | 776 | 782 |
| Observed data ($I > 2\sigma(I)$) | 7591 | 7165 | 6877 | 6440 |
| $R_1^o$ (observed data) | 0.0792 | 0.0771 | 0.0804 | 0.0834 |
| $wR_2^o$ (all data) | 0.2570 | 0.2253 | 0.2413 | 0.2517 |
| CCDC NO. | 1519744 | 1851777 | 1851780 | 1851783 |

$^a$For data with $I > 2\sigma(I)$, $R_1 = \frac{\sum |F_{o}|-|F_{c}|}{\sum |F_{o}|}$. $^b$For all data, $wR_2 = \sqrt{\frac{\sum w(F_o^2-F_c^2)^2}{\sum w(F_o^2)^2}}$. 
### Supplementary Table 1 (continued). Crystal data and data collection parameters

| Crystal | Dy$_2$I$_n$(7)-C$_{80}$(CH$_2$Ph)-0.67(C$_7$H$_8$) | Dy$_2$I$_n$(7)-C$_{80}$(CH$_2$Ph)-0.67(C$_7$H$_8$) | Dy$_2$I$_n$(7)-C$_{80}$(CH$_2$Ph)-0.67(C$_7$H$_8$) | Dy$_2$I$_n$(7)-C$_{80}$(CH$_2$Ph)-0.67(C$_7$H$_8$) |
|---------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| **Formula** | C$_{91.66}$H$_{12.33}$Dy$_2$ | C$_{91.66}$H$_{12.33}$Dy$_2$ | C$_{91.66}$H$_{12.33}$Dy$_2$ | C$_{91.66}$H$_{12.33}$Dy$_2$ |
| **Formula weight** | 1438.27 | 1438.27 | 1438.27 | 1438.27 |
| **Color, habit** | Black, block | Black, block | Black, block | Black, block |
| **Crystal system** | Triclinic | Triclinic | Triclinic | Triclinic |
| **Space group** | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| **a, Å** | 10.950(2) | 10.960(2) | 10.960(2) | 10.970(2) |
| **b, Å** | 11.060(2) | 11.070(2) | 11.080(2) | 11.080(2) |
| **c, Å** | 19.330(4) | 19.340(4) | 19.350(4) | 19.350(4) |
| **$α$, deg** | 86.14(3) | 86.17(3) | 86.18(3) | 86.20(3) |
| **$β$, deg** | 86.12(3) | 89.16(3) | 89.17(3) | 89.19(3) |
| **γ, deg** | 78.06(3) | 78.06(3) | 78.06(3) | 78.06(3) |
| **Volume, Å$^3$** | 2285.2(8) | 2290.6(8) | 2293.9(8) | 2296.0(8) |
| **T, K** | 220 | 250 | 270 | 290 |
| **Radiation (λ, Å)** | Synchrotron Radiation (0.89429) | Synchrotron Radiation (0.89429) | Synchrotron Radiation (0.89429) | Synchrotron Radiation (0.89429) |
| **Unique data ($R_{int}$)** | 8541 (0.0633) | 8864 (0.0702) | 8714 (0.0706) | 8217 (0.0688) |
| **Parameters** | 917 | 917 | 917 | 917 |
| **Restraints** | 788 | 782 | 782 | 782 |
| **Observed data ($I > 2σ(I)$)** | 6311 | 5888 | 5666 | 5296 |
| **R$_p$ ($R_{int}$)** | 0.0992 | 0.1057 | 0.1186 | 0.1300 |
| **wR$_2$ (all data)** | 0.2924 | 0.3398 | 0.3709 | 0.3990 |
| **CCDC NO.** | 1851781 | 1851779 | 1851778 | 1851782 |

$^a$For data with $I > 2σ(I)$, $R_1 = \frac{\sum|F_{o}| - |F_{c}|}{\sum|F_{o}|}$. $^b$For all data, $wR_2 = \sqrt{\frac{\sum[w(F_o^2 - F_c^2)^2]}{\sum[w(F_o^2)^2]}}$. 

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**Supplementary Table 2. Metal site occupancy in {Dy$_2$} as a function of temperatures**

| Dy sites | 100K       | 130K       | 160K       | 190K       | 220K       | 250K       | 270K       | 290K       |
|----------|------------|------------|------------|------------|------------|------------|------------|------------|
| Dy1A     | 0.6983(17) | 0.6028(17) | 0.5253(17) | 0.4781(18) | 0.441(2)   | 0.422(2)   | 0.409(2)   | 0.384(3)   |
| Dy2A     | 0.657(2)   | 0.497(2)   | 0.453(2)   | 0.439(2)   | 0.388(2)   | 0.376(2)   | 0.360(2)   | 0.339(3)   |
| Dy1B     | 0.3016(17) | 0.3491(18) | 0.346(2)   | 0.361(2)   | 0.372(3)   | 0.367(3)   | 0.361(3)   | 0.355(3)   |
| Dy2B     | 0.2910(18) | 0.3424(17) | 0.3798(17) | 0.4048(19) | 0.417(2)   | 0.422(2)   | 0.425(3)   | 0.421(3)   |
| Dy1C     | -          | 0.0481(19) | 0.0732(19) | 0.0909(19) | 0.109(2)   | 0.131(2)   | 0.149(2)   | 0.178(2)   |
| Dy2C     | 0.052(2)   | 0.0416(18) | 0.0645(17) | 0.0806(18) | 0.097(2)   | 0.121(2)   | 0.140(2)   | 0.167(2)   |
| Dy1D     | -          | -          | 0.056(2)   | 0.076(2)   | 0.097(2)   | 0.080(2)   | 0.081(3)   | 0.083(3)   |
| Dy2D     | -          | 0.119(2)   | 0.103(2)   | 0.070(2)   | 0.078(3)   | 0.080(2)   | 0.076(2)   | 0.074(2)   |
| Supplementary Table 3. Cartesian DFT-optimized molecule structure of \((\text{Tb}_2)\), Å |
|---|---|---|---|
| 96 | C | 12.32929061 | 9.58470405 | 13.65031467 |
| | C | 12.34624539 | 10.47782857 | 14.79336496 |
| | C | 11.13305511 | 10.26253475 | 15.55519808 |
| | C | 11.11122927 | 8.44864945 | 13.69294116 |
| | C | 10.37444906 | 9.25374887 | 14.86357693 |
| | C | 10.41384674 | 8.46895968 | 12.49169015 |
| | C | 11.03891736 | 8.78614382 | 12.25116539 |
| | C | 12.91588764 | 9.98374194 | 12.40485473 |
| | C | 12.26823530 | 9.53828686 | 11.20781234 |
| | C | 13.59945646 | 11.22906513 | 12.36520635 |
| | C | 12.93603598 | 11.74496805 | 14.74024253 |
| | C | 13.88560062 | 12.08672579 | 13.60314608 |
| | C | 13.35880649 | 12.78422633 | 15.50151848 |
| | C | 10.53020977 | 11.29045275 | 16.34725326 |
| | C | 11.17422055 | 12.57506590 | 16.30875367 |
| | C | 9.07708816 | 11.28040018 | 14.67966090 |
| | C | 8.95573774 | 9.29220697 | 14.87182290 |
| | C | 8.34176734 | 10.33470308 | 15.66612995 |
| | C | 8.99065742 | 8.43165094 | 12.53578377 |
| | C | 8.26553023 | 8.83826168 | 13.71356412 |
| | C | 8.20070800 | 8.79304836 | 11.38759087 |
| | C | 10.24974893 | 9.15387206 | 10.10959146 |
| | C | 8.83011636 | 9.20503775 | 10.18093708 |
| | C | 12.23341441 | 10.36737805 | 10.04384357 |
| | C | 10.97945359 | 10.14022719 | 9.34829422 |
| | C | 13.52518516 | 12.05468061 | 11.23491546 |
| | C | 12.82503577 | 11.65374612 | 10.05047099 |
| | C | 13.63249725 | 13.49772053 | 13.06117858 |
| | C | 13.54367675 | 13.45207250 | 11.66525967 |
| | C | 12.35983870 | 14.15176092 | 15.04031669 |
| | C | 12.96465988 | 14.51696247 | 13.78820242 |
| | C | 10.42241986 | 13.82021055 | 16.32186865 |
| | C | 11.16369926 | 14.77079822 | 15.50530467 |
| | C | 8.30189354 | 12.54314159 | 16.50483430 |
| | C | 8.97813332 | 13.83960984 | 16.38203554 |
| | C | 7.13093955 | 10.95516151 | 15.21268952 |
| | C | 7.11678723 | 12.31247890 | 15.86356206 |
| | C | 7.03209137 | 9.44752014 | 13.29155192 |
| | C | 6.99033755 | 9.42046183 | 13.68599953 |
| | C | 6.46169086 | 10.53969465 | 14.00977306 |
| | C | 6.38542916 | 10.48809364 | 11.13620355 |
| | C | 8.18223711 | 10.22940179 | 9.39905195 |
| | C | 6.99762239 | 10.86512123 | 9.89178937 |
| | C | 10.33826911 | 11.15182295 | 8.56401922 |
| | C | 8.88214283 | 11.15351801 | 8.52610151 |
| | C | 12.19167993 | 12.67532180 | 9.27686736 |
| | C | 10.98751858 | 12.44282491 | 8.51165395 |

**Tb**: 9.39879063 | 12.46499701 | 14.42576983
### Supplementary Table 4. Cartesian DFT-optimized molecule structure of (Dy₂), Å

|     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|
| 96  | C   | 12.3293402 | 9.58464014 | 13.65014868 |     |
|     | C   | 12.34659639 | 10.47771939 | 14.79316744 |     |
|     | C   | 11.33166717 | 10.26237178 | 15.55465269 |     |
|     | C   | 11.11138775 | 8.84462724 | 12.69276924 |     |
|     | C   | 10.37467301 | 9.25333984 | 14.86332672 |     |
|     | C   | 10.41383971 | 8.46892556 | 12.49167168 |     |
|     | C   | 11.03902522 | 8.78608272 | 11.25131181 |     |
|     | C   | 12.91608456 | 9.98362540 | 12.40479977 |     |
|     | C   | 12.68322339 | 9.53813848 | 11.20789327 |     |
|     | C   | 13.60069777 | 11.22895464 | 12.36527939 |     |
|     | C   | 12.93606490 | 11.74452227 | 14.73987488 |     |
|     | C   | 13.88588950 | 12.08667275 | 13.60308998 |     |
|     | C   | 12.35907578 | 12.78437971 | 15.50080586 |     |
|     | C   | 10.53005885 | 11.29074433 | 16.34516005 |     |
|     | C   | 11.17372747 | 12.5751760 | 16.30685359 |     |
|     | C   | 9.07726541 | 11.28431345 | 16.47831041 |     |
|     | C   | 8.95609490 | 9.29201521 | 14.87131687 |     |
|     | C   | 8.34231747 | 10.35304727 | 15.66482718 |     |
|     | C   | 8.90951420 | 8.43136935 | 12.53578427 |     |
|     | C   | 8.26543333 | 8.83806977 | 13.71342684 |     |
|     | C   | 8.20058873 | 8.79280911 | 13.8767087 |     |
|     | C   | 10.24987777 | 9.15357347 | 10.10978794 |     |
|     | C   | 8.83027981 | 9.20475559 | 10.18217488 |     |
|     | C   | 12.2372109 | 10.36716886 | 10.04393650 |     |
|     | C   | 10.97936797 | 10.14009287 | 9.34880941 |     |
|     | C   | 13.52535487 | 12.05472615 | 11.23499784 |     |
|     | C   | 12.82550332 | 11.65351113 | 10.05063072 |     |
|     | C   | 13.63254373 | 13.49770752 | 13.06109284 |     |
|     | C   | 13.54374548 | 13.45200315 | 11.66287860 |     |
|     | C   | 12.36036291 | 14.15211805 | 15.04025463 |     |
|     | C   | 12.96505363 | 14.51720410 | 13.78824094 |     |
|     | C   | 10.42237330 | 13.81982752 | 16.31941752 |     |
|     | C   | 11.16398026 | 14.77083861 | 15.50296236 |     |
|     | C   | 8.30219750 | 12.54317341 | 16.50371519 |     |
|     | C   | 8.97825872 | 13.83933198 | 16.38051238 |     |
|     | C   | 7.13149779 | 10.95551961 | 15.21155009 |     |
|     | C   | 7.11773516 | 12.31268586 | 15.68229309 |     |
|     | C   | 7.03206807 | 9.44733354 | 13.29144078 |     |
|     | C   | 6.99027578 | 9.40279057 | 11.85609955 |     |
|     | C   | 6.46136139 | 10.53945615 | 10.04579574 |     |
|     | C   | 6.38502454 | 10.48779547 | 11.13635300 |     |
|     | C   | 8.18277071 | 10.22987825 | 9.40010594 |     |
|     | C   | 6.99784322 | 10.86523829 | 9.89257276 |     |
|     | C   | 10.33814325 | 11.15214861 | 8.56615971 |     |
|     | C   | 8.88230461 | 11.15385402 | 8.52763673 |     |
|     | C   | 12.19184435 | 12.67544033 | 9.27755853 |     |
|     | C   | 10.98715879 | 12.44293397 | 8.51388015 |     |

Dy 9.39646248 | 12.46376818 | 14.43690575 |     |

H 15.46236101 | 12.54922390 | 15.03094601 |     |

H 15.44608571 | 10.85804563 | 14.49539888 |     |

H 16.61061217 | 14.29008832 | 13.70323257 |     |

H 18.41162411 | 17.94405644 | 12.07369516 |     |

H 19.29272823 | 12.99703536 | 10.58643268 |     |

H 16.55933466 | 10.18922168 | 12.38252755 |     |

H 18.36028728 | 10.69024765 | 10.75170511 |     |
### Supplementary Table 5. Cartesian DFT-optimized molecule structure of (H₂O), Å

| C     | 12.32935897 | 9.58481932 | 13.65001529 |
|-------|-------------|-------------|--------------|
| C     | 12.34640970 | 10.47780227 | 14.79288752 |
| C     | 11.13318774 | 10.26246182 | 15.55377409 |
| C     | 11.11139951 | 8.84443953  | 13.69217806 |
| C     | 10.37466887 | 9.25318529  | 14.86296443 |
| C     | 10.41388579 | 8.46866972  | 12.49174172 |
| C     | 10.03911460 | 8.78583761  | 11.25144837 |
| C     | 12.91606289 | 9.98361635  | 12.40487094 |
| C     | 12.26839670 | 9.53815272  | 11.20807306 |
| C     | 13.60017581 | 11.22903896 | 12.36529327 |
| C     | 12.93636963 | 11.74476050 | 14.73917157 |
| C     | 13.88573056 | 12.08667111 | 13.60305979 |
| C     | 12.35940949 | 12.78446566 | 15.50037676 |
| C     | 10.52963571 | 11.29118647 | 13.64323368 |
| C     | 11.17346354 | 12.57511876 | 16.30454575 |
| C     | 9.07731182  | 11.28444175 | 16.47779386 |
| C     | 8.95620874  | 9.29201971  | 14.87092370 |
| C     | 8.34289740  | 10.33577642 | 15.66364711 |
| C     | 8.90961627  | 8.43119487  | 12.53579336 |
| C     | 8.26557806  | 8.83793883  | 13.71333297 |
| C     | 8.20078608  | 8.79281276  | 11.38781585 |
| C     | 10.25002903 | 9.15335995  | 10.11014430 |
| C     | 8.83054327  | 9.20491859  | 11.18703038 |
| C     | 12.23361590 | 10.36719982 | 10.04435763 |
| C     | 10.9791202  | 10.14011547 | 9.34973032  |
| C     | 13.52523853 | 12.05459795 | 11.23521276 |
| C     | 12.82544919 | 11.65366717 | 10.05090573 |
| C     | 13.63241544 | 13.49762272 | 13.06121459 |
| C     | 13.54342211 | 13.45202505 | 11.66247283 |
| C     | 12.36942028 | 14.15236124 | 12.04026112 |
| C     | 12.96514569 | 14.51732988 | 13.78823709 |
| C     | 10.42213946 | 13.81946676 | 16.31797949 |
| C     | 11.16417438 | 14.77099892 | 15.50229715 |
| C     | 8.30221126  | 12.54313250 | 16.50363206 |
| C     | 8.97852116  | 13.83881438 | 16.37859970 |
| C     | 7.13227191  | 10.95597587 | 15.21042304 |
| C     | 7.11842887  | 12.31295282 | 12.68116505 |
| C     | 7.03220676  | 9.44745563  | 13.29416208 |
| C     | 6.99047498  | 9.42054044  | 11.85602061 |
| C     | 6.46137849  | 10.53943208 | 14.00097075 |
| C     | 6.38498986  | 10.48780765 | 11.13671931 |
| C     | 8.18337307  | 10.23033465 | 9.40128514  |
| C     | 6.99856887  | 10.86571143 | 8.93958188  |
| C     | 10.33790670 | 11.15260325 | 8.56792825  |
| C     | 8.88239586  | 11.15408824 | 8.52831224  |
| C     | 12.19196321 | 12.67546342 | 9.27827123  |
| C     | 10.98682191 | 12.44294787 | 8.51565006  |
| Ho    | 9.85628910  | 10.74179143 | 10.04800264 |
| Ho    | 9.66372675  | 16.45249032 | 12.85446873 |
| Ho    | 8.22971123  | 16.45802093 | 11.21072747 |
| Ho    | 15.36577831 | 11.89945367 | 14.14745361 |
| Ho    | 16.4551044  | 12.20584315 | 13.15297547 |
| Ho    | 16.99027311 | 13.49850141 | 13.05185715 |
| Ho    | 18.00419968 | 13.78322263 | 12.13522545 |
| Ho    | 18.49815097 | 12.77638737 | 11.30247334 |
| Ho    | 17.97525377 | 11.48431429 | 11.39458292 |
| Ho    | 16.96137233 | 11.20346213 | 12.31256511 |
| Ho    | 6.93854538  | 12.46205487 | 14.44688888 |
| Ho    | 9.39287952  | 12.46295020 | 10.46299080 |
| H     | 15.46246465 | 12.50332120 | 15.03072772 |
| H     | 15.44621556 | 10.85807002 | 14.49515275 |
| H     | 16.61063586 | 14.29007081 | 13.70319316 |
| H     | 18.41161600 | 14.79436435 | 12.07381814 |
| H     | 19.29233919 | 12.99699366 | 10.58651823 |
| H     | 16.55953486 | 10.18912896 | 12.38262739 |
| H     | 18.36025765 | 10.69021489 | 10.75171219 |
Supplementary Table 6. Cartesian DFT-optimized molecule structure of (Er$_2$), Å

| 96 | C | 12.32945447 | 9.58482630 | 13.64986302 |
|    | C | 12.34634674 | 10.47798358 | 14.79248747 |
|    | C | 11.33122128 | 10.26253581 | 15.55281939 |
|    | C | 11.11161044 | 8.84406062  | 13.69256705 |
|    | C | 10.37498922 | 9.25284479  | 14.86256878 |
|    | C | 10.41401204 | 8.46825011  | 12.49181011 |
|    | C | 11.03935640 | 8.78542538  | 11.25168623 |
|    | C | 12.91631914 | 9.98355463  | 14.04093318 |
|    | C | 12.26857593 | 9.53082412  | 11.20837292 |
|    | C | 13.60029533 | 11.22899757 | 12.36532563 |
|    | C | 12.93657255 | 11.74486668 | 14.73946202 |
|    | C | 13.85856888 | 12.08668440 | 12.60978784 |
|    | C | 12.35984595 | 12.78466868 | 15.49958707 |
|    | C | 10.52914611 | 12.29168670 | 16.34096712 |
|    | C | 11.17293597 | 12.57057241 | 16.30179284 |
|    | C | 9.07735117  | 12.8545159  | 16.47741044 |
|    | C | 8.95653361  | 9.29197538  | 14.87048868 |
|    | C | 8.34355183  | 10.33627374 | 15.66246166 |
|    | C | 8.99072408  | 8.43088039  | 12.53583344 |
|    | C | 8.26568576  | 8.83779691  | 13.71327228 |
|    | C | 8.20903881  | 8.79276784  | 11.38793335 |
|    | C | 10.25028688 | 9.15303602  | 11.05600881 |
|    | C | 8.83091848  | 9.20497754  | 10.18218440 |
|    | C | 12.23359003 | 10.36724893 | 10.04484914 |
|    | C | 10.97954536 | 10.14019662 | 9.35067701 |
|    | C | 13.52526861 | 12.05458297 | 11.23574950 |
|    | C | 12.82544782 | 11.65371704 | 10.05131475 |
|    | C | 13.63242551 | 13.49773055 | 13.06122286 |
|    | C | 13.54330522 | 13.45209691 | 11.66297348 |
|    | C | 12.36169376 | 14.15282942 | 15.04026516 |
|    | C | 12.96510802 | 14.51762481 | 13.78835848 |
|    | C | 10.42190006 | 13.81895088 | 16.31460044 |
|    | C | 11.16451212 | 14.77119445 | 15.50156829 |
|    | C | 8.30211364  | 12.54307915 | 16.50382848 |
|    | C | 8.97878599  | 13.83822094 | 16.37684478 |
|    | C | 7.13319432  | 10.95625713 | 15.20910354 |
|    | C | 7.11908755  | 12.31326234 | 15.68028572 |
|    | C | 7.03230166  | 9.44741316  | 13.29139206 |
|    | C | 6.99059538  | 9.42045602  | 11.8505057 |
|    | C | 6.46147739  | 10.53946294 | 14.00856689 |
|    | C | 6.38503738  | 10.48785115 | 11.13079421 |
|    | C | 8.18411728  | 10.23096087 | 9.40247439 |
|    | C | 6.99495533  | 10.86631811 | 9.89484572 |
|    | C | 10.33768802 | 11.15305457 | 8.56998136 |
|    | C | 8.88241364  | 11.15425684 | 8.52867026 |
|    | C | 12.19213095 | 12.67556067 | 9.27920082 |
|    | C | 10.98639307 | 12.44296821 | 8.51796124 |
|    | C | 12.85904918 | 14.45931211 | 10.91334715 |
### Supplementary Table 7, CAS compositions

| System \{LnY\}− | CAS problems composition X(Y)* | Number of states in RASSI-SO | ANISO° KD-mapping |
|-----------------|---------------------------------|------------------------------|-------------------|
| Tb              | CAS(8,7) 7(7), 140(5), 500(3), 490(1) | 250                          | 6 KD              |
| Ho              | CAS(10,7) 35(5)                     | 35                           | 8 KD              |
| Er              | CAS(11,7) 35(4), 112(2)             | 147                          | 8 KD              |

*X(Y), X-number roots for the system with the spin Y*
### Supplementary Table 8. CASSCF/SO-RASSI calculations summary for the $\{\text{TbY}\}$ molecule. Energies and state compositions of pseudo Kramers doublets and singlet states of the Tb1 and Tb2 ions in single-ion frame.

| pKD | $E$, cm$^{-1}$ | Tb1 Composition, % | $E$, cm$^{-1}$ | Tb2 Composition, % |
|-----|----------------|-------------------|----------------|-------------------|
| 1   | 0.0            | 100(±6)           | 0.0            | 100(±6)           |
| 2   | 266.7          | 100(±6)           | 256.1          | 100(±6)           |
| 3   | 511.0          | 99(±4)            | 507.8          | 99(±4)            |
| 4   | 708.8          | 99(±3)            | 705.2          | 99(±3)            |
| 5   | 847.6          | 91(±2) + 8(0)     | 839.3          | 87(±2) + 13(0)    |
| 6   | 928.6          | 97(±1)            | 911.1          | 96(±1)            |
| 5   | 1001.3         | 87(0) + 8(±2) + 5(±1) | 996.0         | 80(0) + 12(±2) + 8(±1) |

The contribution for the “$\pm X$” state means a sum of contributions for $|+X\rangle$ and $|-X\rangle$ states.

### Supplementary Table 9. CASSCF/SO-RASSI calculations summary for the $\{\text{HoY}\}$ molecule. Energies and state compositions of pseudo Kramers doublets and singlet states of the Ho1 and Ho2 ions in single-ion frame.

| pKD | $E$, cm$^{-1}$ | Ho1 Composition, % | $E$, cm$^{-1}$ | Ho2 Composition, % |
|-----|----------------|-------------------|----------------|-------------------|
| 1   | 0.0            | 64(±8) + 14(±7) + 10(±6) | 0.0            | 63(±8) + 19(±6) + 9(±4) |
| 2   | 165.6          | 31(±3) + 20(±2) + 18(±5) | 130.1          | 29(±5) + 29(±3) + 18(±4) |
| 3   | 262.7          | 40(±7) + 28(±6) + 20(±4) | 245.2          | 63(±7) + 19(±6) + 6(±3) |
| 4   | 305.6          | 40(±5) + 22(±2) + 20(±1) | 292.9          | 33(±2) + 29(±5) + 19(±4) |
| 5   | 378.8          | 27(±7) + 18(±6) + 14(±5) | 363.0          | 38(±4) + 19(±7) + 17(±3) |
| 6   | 399.8          | 28(±7) + 20(±8) + 17(±6)| 377.1          | 55(±1) + 15(±3) + 12(±4) |
| 7   | 407.4          | 40(±1) + 20(±0) + 11(±6) | 405.3          | 25(±6) + 24(±7) + 20(±1) |
| 4   | 448.6          | 32(±6) + 31(±4) + 16(±1) | 428.2          | 25(0) + 19(±6) + 14(±1) |
| 5   | 450.8          | 29(±4) + 24(±0) + 20(±3) | 436.0          | 30(±6) + 20(±5) + 14(±3) |
| 6   | 486.6          | 42(±3) + 17(±4) + 15(±0) | 451.0          | 45(±3) + 22(±5) + 14(±1) |
| 7   | 555.3          | 39(±3) + 23(±1) + 16(±2) | 526.5          | 42(±2) + 17(0) + 13(±4) |
| 8   | 581.2          | 29(±2) + 29(±0) + 17(±1) | 534.2          | 36(0) + 22(±2) + 13(±1) |
| 9   | 603.4          | 47(±2) + 42(±1) + 4(±6)  | 561.9          | 61(±1) + 10(±3) + 9(±2)  |

The contribution for the “$\pm X$” state means a sum of contributions for $|+X\rangle$ and $|-X\rangle$ states.
**Supplementary Table 10. CASSCF/SO-RASSI calculations summary for the \( \{\text{ErY}\} \) molecule. Energies and state compositions of Kramers doublets of the Er1 and Er2 ions in single-ion frame.**

| KD | \( E, \text{ cm}^{-1} \) | Composition, % | \( E, \text{ cm}^{-1} \) | Composition, % |
|----|-----------------|-----------------|-----------------|-----------------|
| 1  | 0.0             | 61|±0.5\rangle + 19|±1.5\rangle | 0.0             | 38|±0.5\rangle + 27|±1.5\rangle + 16|±2.5\rangle + 10|±4.5\rangle |
| 2  | 96.4            | 52|±1.5\rangle + 15|±2.5\rangle + 10|±4.5\rangle | 85.4            | 30|±1.5\rangle + 26|±0.5\rangle + 17|±2.5\rangle + 16|±3.5\rangle |
| 3  | 159.3           | 26|±5.5\rangle + 21|±4.5\rangle + 21|±2.5\rangle + 10|±6.5\rangle | 123.9           | 31|±4.5\rangle + 24|±5.5\rangle + 16|±3.5\rangle + 11|±1.5\rangle |
| 4  | 226.6           | 19|±2.5\rangle + 16|±3.5\rangle + 16|±6.5\rangle + 14|±5.5\rangle + 13|±4.5\rangle + 12|±0.5\rangle | 193.2           | 36|±2.5\rangle + 25|±3.5\rangle + 11|±0.5\rangle |
| 5  | 255.7           | 32|±3.5\rangle + 26|±2.5\rangle + 11|±5.5\rangle | 229.9           | 22|±2.5\rangle + 19|±3.5\rangle + 18|±0.5\rangle + 15|±1.5\rangle + 12|±4.5\rangle |
| 6  | 342.0           | 50|±6.5\rangle + 19|±7.5\rangle + 13|±5.5\rangle | 315.6           | 39|±6.5\rangle + 30|±7.5\rangle + 10|±5.5\rangle |
| 7  | 429.1           | 33|±4.5\rangle + 28|±3.5\rangle + 14|±5.5\rangle | 420.8           | 25|±4.5\rangle + 21|±5.5\rangle + 18|±6.5\rangle + 18|±7.5\rangle + 15|±3.5\rangle |
| 8  | 607.4           | 67|±7.5\rangle + 15|±5.5\rangle + 10|±4.5\rangle | 565.1           | 49|±7.5\rangle + 21|±6.5\rangle + 19|±5.5\rangle |
**Supplementary Table 11.** Ab-intio derived (SINGLE_ANISO) crystal field parameters in Stevens Notation \(B(q,k)\)(cm\(^{-1}\)) for Ln-ions in the [LnY\(^+\)] molecules. *

| index | \(\{\text{TbY}^+\}\), Tb1 | \(\{\text{Y Tb}^-\}\), Tb2 | \(\{\text{HoY}^+\}, \text{Ho1}\) | \(\{\text{Y Ho}^+\}, \text{Ho2}\) | \(\{\text{ErY}^+\}, \text{Er1}\) | \(\{\text{Y Er}^+\}, \text{Er2}\) |
|-------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| k     | \(B(q,k)\)      | \(B(q,k)\)      | \(B(q,k)\)      | \(B(q,k)\)      | \(B(q,k)\)      | \(B(q,k)\)      |
| 2     | -2   | -1.09E+00      | 2.15E-01        | -2.33E-01       | -1.16E-01       | -4.84E-02       | -3.03E-02       |
| 2     | -1   | 4.00E-01       | 9.18E-02        | -5.64E-01       | 2.16E-01        | -6.37E-01       | -1.03E+00       |
| 2     | 0    | -9.19E+00      | -9.15E+00       | -1.80E+00       | -1.76E+00       | 2.03E+00        | 1.98E+00        |
| 2     | 1    | -3.69E-02      | -4.18E-01       | -1.32E+00       | 1.54E+00        | -1.95E+00       | -2.12E+00       |
| 2     | 2    | 3.95E-01       | 1.42E+00        | -2.89E-01       | -4.40E-01       | 3.00E-01        | 3.40E-01        |
| 4     | -4   | -1.66E-03      | 1.22E-03        | -3.62E-04       | -9.31E-05       | 1.77E-04        | 2.97E-04        |
| 4     | -3   | -1.70E-03      | -4.37E-03       | -5.50E-04       | 9.20E-04        | -9.20E-04       | -2.38E-03       |
| 4     | -2   | 8.09E-03       | -2.09E-03       | -7.93E-04       | -6.91E-05       | -3.21E-04       | -8.29E-04       |
| 4     | -1   | 1.62E-03       | 1.53E-03        | 2.12E-03        | -1.27E-03       | 1.76E-04        | -8.43E-04       |
| 4     | 0    | 3.34E-03       | 3.20E-03        | 1.83E-04        | 2.75E-04        | -4.71E-04       | -5.13E-04       |
| 4     | 1    | 2.23E-04       | 7.48E-04        | 3.44E-03        | -4.40E-03       | 4.14E-03        | 3.81E-03        |
| 4     | 2    | -6.21E-03      | -9.07E-03       | -5.94E-04       | -1.10E-03       | 2.68E-03        | 1.86E-03        |
| 4     | 3    | -9.05E-03      | -1.82E-03       | -1.54E-03       | 2.70E-03        | -7.19E-04       | -3.00E-03       |
| 4     | 4    | 2.02E-04       | 1.67E-03        | -2.16E-04       | -8.68E-04       | 6.18E-05        | 3.38E-04        |
| 6     | -6   | 5.93E-05       | -2.27E-04       | -6.50E-06       | 1.68E-04        | -2.55E-05       | -1.19E-07       |
| 6     | -5   | -1.09E-03      | 1.05E-03        | -8.30E-04       | -2.43E-05       | 1.11E-03        | 1.27E-03        |
| 6     | -4   | -1.26E-04      | 1.40E-05        | 2.07E-04        | -9.97E-06       | 2.09E-04        | 2.51E-04        |
| 6     | -3   | 1.37E-04       | -1.65E-04       | 2.26E-05        | -1.33E-04       | 9.58E-04        | 6.99E-04        |
| 6     | -2   | -4.55E-06      | -1.05E-05       | 3.29E-04        | 1.55E-04        | -5.34E-05       | -2.43E-04       |
| 6     | -1   | -3.11E-04      | -1.86E-04       | 2.27E-04        | -2.21E-04       | 1.57E-04        | 2.54E-04        |
| 6     | 0    | 4.44E-06       | 2.34E-05        | -3.04E-05       | 8.33E-07        | 5.25E-05        | 9.62E-06        |
| 6     | 1    | -4.37E-05      | 1.47E-04        | 2.79E-04        | -5.41E-04       | 5.29E-04        | 8.33E-04        |
| 6     | 2    | -5.65E-05      | 1.06E-04        | 2.77E-04        | 1.81E-04        | -5.71E-04       | -2.19E-04       |
| 6     | 3    | -2.01E-04      | 1.65E-05        | -4.79E-04       | 4.21E-04        | -1.15E-04       | -4.16E-04       |
| 6     | 4    | -1.13E-04      | 1.24E-04        | 9.10E-05        | 1.67E-04        | -1.80E-04       | -4.18E-05       |
| 6     | 5    | 4.26E-04       | -3.22E-07       | -2.24E-04       | 8.63E-04        | -6.78E-04       | -5.25E-04       |
| 6     | 6    | 1.09E-04       | -1.37E-04       | -5.48E-05       | 5.59E-05        | -3.96E-05       | -1.90E-04       |

*Parameters are given in the local frame for each ion (i.e. z-axis coincides with the single-ion quantization axis). When constricting the global Hamiltonian Eq. 6, the local frames should be rotated appropriately.
**Supplementary Table 12.** Stevens factors for Ln$^{3+}$ ions from Ref. 11. $\alpha_j$, $\beta_j$ and $\gamma_j$, respectively, are the second, fourth and the sixth order Stevens factors.

| Stevens factor | Tb$^{3+}$ | Dy$^{3+}$ | Ho$^{3+}$ | Er$^{3+}$ |
|----------------|-----------|-----------|-----------|-----------|
| $\alpha_j$     | $-1.01 \times 10^{-2}$ | $-0.63 \times 10^{-2}$ | $-0.22 \times 10^{-2}$ | $+0.25 \times 10^{-2}$ |
| $\beta_j$      | $+1.22 \times 10^{-4}$ | $-0.59 \times 10^{-4}$ | $-0.33 \times 10^{-4}$ | $+0.44 \times 10^{-4}$ |
| $\gamma_j$     | $-1.12 \times 10^{-6}$ | $+1.04 \times 10^{-6}$ | $-1.29 \times 10^{-6}$ | $+2.07 \times 10^{-6}$ |

$10^2 \times \beta_j/\alpha_j$ | $-1.21$ | $+0.94$ | $-1.50$ | $+1.76$

$10^4 \times \gamma_j/\alpha_j$ | $+1.11$ | $-1.65$ | $+5.86$ | $+8.28$

**Supplementary Table 13.** The lowest energy spin states of {Tb$_2$} computed for $K^{\text{eff}}$ of 55 cm$^{-1}$

| $E$, cm$^{-1}$ | State composition, % $|J_z,\text{Tb}_1, J_z,\text{Tb}_2, S_z\rangle$ | $g$ | $\alpha$ |
|----------------|----------------------------------------------------------|---|---|
| 0.0            | 100|6,6,0.5⟩                                                  | 0.0000, 0.0000, 37.9956 |
| 248.5          | 54|6,5,0.5⟩ + 40|5,6,0.5⟩                                                | 0.0000, 0.0000, 34.9357 |
| 316.9          | 57|6,5,0.5⟩ + 43|6,5,0.5⟩                                                | 0.0000, 0.0000, 34.9917 |
| 492.0          | 42|5,5,0.5⟩ + 25|6,4,0.5⟩ + 22|4,6,0.5⟩                                               | 0.0000, 0.0000, 31.8760 |
| 551.8          | 47|4,6,0.5⟩ + 46|6,4,0.5⟩                                                | 0.0016, 0.0016, 31.9144 |
| 555.8          | 57|6,−6, 0.5⟩ + 17|6,−5, 0.5⟩ + 13|−6, 6,−0.5⟩                                            | 0.0016, 0.0016, 31.9144 |
| 558.5          | 19|6,−6, 0.5⟩ + 14|−5, 6,−0.5⟩ + 51|−6, 6,−0.5⟩                                            | 0.0020, 0.0025, 3.7545 |
| 626.2          | 51|5,5,0.5⟩ + 25|4,6,0.5⟩ + 23|6,4,0.5⟩                                               | 0.0000, 0.0000, 31.9758 |

**Supplementary Table 14.** The lowest energy spin states of {Ho$_2$} computed for $K^{\text{eff}}$ of 40 cm$^{-1}$

| $E$, cm$^{-1}$ | g-tensor | $\cos(\alpha)$ |
|----------------|----------|-----------------|
| 0.0            | 0.0000, 0.0001, 37.7316 | 1.00 |
| 175.0          | 0.0106, 0.0207, 31.4631 | 0.98 |
| 227.9          | 0.0125, 0.0401, 32.6911 | 1.00 |
| 259.6          | 0.2877, 1.2843, 27.3253 | 0.07 |
| 267.4          | 0.1288, 0.6484, 31.9671 | 0.99 |
| 295.0          | 0.1298, 0.2532, 32.3879 | 0.98 |
| 324.7          | 0.5773, 1.0813, 27.8297 | 1.00 |
| 353.9          | 2.2027, 5.7440, 18.7264 | 0.96 |

* $\alpha$ is the angle between the main direction of ground state and a given higher energy states. Note the strong rotation for the 4th state, which therefore has small $\mu_z$ component.

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**Supplementary Table 15.** Electrochemical potentials of \{Ln_2\}  

| \{Ln_2\} | $E(+/0)$ | $E(0/-)$ | $E(-/-2)$ | $E(-2/-3)$ | gap$_{EC}^b$ |
|-----------|----------|----------|-----------|-----------|------------|
| \{Gd_2\} | +0.52    | -0.86    | -1.45     | -1.78     | 1.38       |
| \{Tb_2\} | +0.51    | -0.79    | -1.36     | -1.71     | 1.30       |
| \{TbY\}  | +0.51    | -0.66    | -1.33     | -1.62     | 1.11       |
| \{Dy_2\} | +0.52    | -0.60    | -1.28     | -1.58     | 1.12       |
| \{Ho_2\} | +0.51    | -0.54    | -1.33     | -1.63     | 1.05       |
| \{Y_2\}  | +0.52    | -0.52    | -1.29     | -1.60     | 1.04       |
| \{Er_2\} | +0.50    | -0.42    | -1.34     | -1.61     | 0.92       |

$^a$ The values are referred versus Fe(Cp)$_2$^{+/0}$ redox couple. The first reduction and the first oxidation steps are reversible for all \{Ln_2\} compounds. For many of them reversibility is also found for the second reduction step, but at the third reduction step additional features appear on the reverse scan, which points to the low chemical stability of the \{Ln_2\}$^{3-}$ trianions in o-DCB.

$^b$ Electrochemical gap is defined as the difference between the first oxidation and the first reduction potentials, gap$_{EC} = E(+/0) - E(0/-)$
**Supplementary Note 1. Variable temperature X-ray crystallographic analysis of Dy$_2$@C$_{80}$(CH$_2$Ph)**

The structure measured at 100K showed a fully ordered fullerene cage as well as the attached benzyl group. However, the encapsulated Dy$_2$ presented as disordered, two positions with fractional occupancies of ca. 0.7 and 0.3 were obtained. To unravel the dynamics of the Dy$_2$ in the fullerene cage, variable temperature X-ray diffraction from 100 K to 290 K were conducted. As shown in Supplementary Figs. 22 and 23, the fullerene cage and the benzyl group are fully ordered even when the temperature risen to 290 K. On the other hand, temperature-dependent movement of Dy$_2$ was observed clearly. The Dy$_2$ site with the highest occupancy showed lower occupancy when the temperature rises, from ca. 0.7 at 100 K to ca. 0.35 at 290 K, simultaneously, new Dy$_2$ sites appeared and the site occupancies increased with the rising of the temperature. See Supplementary Table 2 and Supplementary Figs. 22 and 23 for details.
Supplementary Note 2. Axiality of the ligand field in {Ln₂} molecules

As follows from ab initio calculations (Supplementary Tables 8-11), single-ion magnetic anisotropy in {Ln₂} is rather high. For instance, the total LF splitting for Tb ions is ca 1000 cm⁻¹, and the energy of the first excited KD state is ca 260 cm⁻¹. Ligand field is indeed highly axial, resulting in high-spin ground states of Ising type.

The axiality of the ligand field in {Ln₂} may have several reasons. First, metal atoms transfer their valence electrons to the fullerene cage, resulting in accumulation of the negative charge on carbon atoms coordinated to the endohedral lanthanide ion. Note that this interaction also has considerable covalent contribution via overlap of π-electron density of the fullerene with vacant d-orbital of the lanthanide. Next, covalent Ln-Ln bonding results in a concentration of the electron density between two Ln ions. In Ref. ¹ we used a simple point-charge model to show that even relatively small negative charge located between two lanthanide ions may induce rather high axial magnetic anisotropy. Thus, metal-metal bond is important not only for exchange interactions, but also to support the axial ligand field. Finally, lanthanide ions in EMFs have no “equatorial” ligands – the situation which also facilitates imposing of the axial ligand field.
Supplementary Note 3. Magnetic anisotropy and ligand-field states of different lanthanide ions in similar ligand-field environments

The similarity of \{\text{Tb}_2\} and \{\text{Dy}_2\} and the different behavior of \{\text{Ho}_2\} and \{\text{Er}_2\} can be understood by analysis of the LF acting on the individual Ln ions,

\[
\hat{H}_{\text{LF}} = \alpha_J \sum_{m=-2}^{2} A_{2m}^{(i)} < r_i^2 > \hat{d}_{2m} + \beta_J \sum_{m=-4}^{4} A_{4m}^{(i)} < r_i^4 > \hat{d}_{4m} + \gamma_J \sum_{m=-6}^{6} A_{6m}^{(i)} < r_i^6 > \hat{d}_{6m}
\]

Here, the Stevens factors \(\alpha_J, \beta_J, \gamma_J\) are rational numbers depending on \(S, L, J\) and describe the angular shape of the \(4f\) charge distribution, \(< r_i^l >\) are the expectation values of \(r_i^l\) taken with the radial \(4f\) wave function, \(A_{lm}^{(i)}\) are the CF coefficients describing the charge distribution around the \(Ln^{3+}\) ion at site \(i\), and \(\hat{d}_{lm}\) are the standard Stevens operators expressed in polynomials of \((J_i, J_x, J_y, J_z)\).

For the axial parameters, \(m = 0\), the parameters \(B(l,0)\) given in Table S8 are equal to the product of the related Stevens factor, the coefficient \(A_{im}^{(i)}\) and \(< r_i^l >\). For other values of \(m\), another prefactor must be included as detailed in Ref. 9.

By chemical similarity of the Ln ions, similar charge distributions are expected for all \{\text{Ln}_2\}. Thus, the values of \(A_{im}^{(i)} < r_i^l >\), which are expectation values of the radial \(4f\) wave function with the \(lm\)-component of the molecular potential, do not essentially depend on the chosen Ln, except for a minor, smooth reduction with growing atomic number due to decreasing extension of the \(4f\) radial wave functions (lanthanide contraction). Indeed, the lowest–order axial LF term \(A_{20} < r^2 >\) is found from the \(B(2,0)\) of Supplementary Table 11 and Ref. 1 to obey the expectation. This term decays like 9 (Tb) : 8 (Dy) : 7 (Ho) : 6 (Er). In particular, it has the same, positive sign in all cases.

Supplementary Table 8 shows that states with different \(J_z\) hardly mix for Tb ions (and similar was observed for Dy in Ref. 1). Thus, the LF Hamiltonian is almost diagonal for the Tb and the Dy ions, i.e., only the axial LF parameters are relevant. We evaluated the LF levels of the Tb and Dy ions using only the axial LF parameters and assuming the non-axial parameters to be zero. The resulting levels (curves denoted as axial 2, 4, 6) are compared with the levels obtained by our \textit{ab-initio} calculations (crosses) in Supplementary Fig. 43. As expected for the case of small mixing, the diagonal LF terms describe the \textit{ab-initio} levels very well.

In order to estimate the relative importance of the individual axial terms \((l = 2, 4, 6)\), we repeated the calculation with fourth-order term set to zero (curves denoted as axial 2, 6) and finally with both fourth- and sixth-order terms set to zero (curves denoted as axial 2). For the Tb ions we find that the quantum chemical data are very well described by considering only the second-order axial LF term; the fourth order provides a minor correction and the sixth order has no influence that would be visible at the scale of the plot. For the Dy ions as well, the second order alone describes the levels reasonably well. However, a minor correction is provided by the fourth-order term and a somewhat larger correction by the sixth order.

The relatively larger influence of the sixth-order term in Dy as compared to Tb can be understood from a combination of two factors. First, the sixth-order term gains a larger importance in Dy due to the larger \(J\)-value of its ground state multiplet, \(= 15/2\), compared to \(J = 6\) for Tb. This value enters the expectation values of the Stevens operators in the power of \(l\), providing an enhancement by a factor of 2.4 for the
importance of order six vs. order two. Second, a factor of modulus 1.5 in favor of the Dy sixth-order contributions is gained by the ratio of the Stevens factors $\gamma_j/\alpha_j$, see Supplementary Table 12. In a very similar manner one can understand that the fourth-order term has more or less the same influence on the Tb and the Dy ions. Here, a factor of 1.6 due to the different $J$-values is partly compensated by a factor of 0.8 due to the ratio of the Stevens factors $\beta_j/\alpha_j$, see Supplementary Table 12.

Summarizing the discussion for the Tb and the Dy ions, the whole LF spectrum and the LF states of Tb$^{3+}$ in \{Tb$_2$\} can be described by a single parameter $B(2,0)$ and the same holds, with a grain of salt, for Dy$^{3+}$ in \{Dy$_2$\}. The sign of this parameter determines, whether the magnetic anisotropy is of uniaxial type, i.e., the ground state is $|J_z| = J$, or if it is of easy-plane type with a ground state $|J_z| = 0$ or $\frac{1}{2}$. For the two discussed ions, $B(2,0)$ is negative, implying a uniaxial ground state. The negative sign of $B(2,0)$ for both cases comes about by the same, positive sign of $A_{20}$ for both systems combined with the same, negative sign of the related Stevens factors.

Turning to the case of the Ho$^{3+}$ ions, it can be noted that the second-order Stevens factor $\alpha_j$ is negative as in Tb$^{3+}$ and Dy$^{3+}$. Thus, given the same sign of $A_{20}$ as in the other cases, also $B(2,0)$ is negative and Ho has a high-spin ground state like the previous cases. However, the effect of the sixth-order axial crystal field term is much stronger than in Tb or Dy, since the ratio $\gamma_j/\alpha_j$ provides a factor of 5.3 (as compared with Tb) and the larger $J = 8$ provides a factor of 3.2. Calculation of the LF levels from the axial terms alone (not shown) shows that the high-spin ground state is (just) not spoilt by the higher-order terms. However, by virtue of the larger pre-factors, the non-axial sixth-order LF parameters now produce a strong mixing of different $J_z$ states, see Supplementary Table 9. This mixing is present even in the ground state. It is responsible for an important contribution to transitions between (quasi) degenerate states. The importance of fourth-order terms is slightly enhanced, if compared to Tb and Dy, but their impact is much smaller than that of other terms.

Finally, the second-order Stevens factor of Er$^{3+}$ is positive, opposite to all the other cases. Thus, an easy-plane ground state is realized in Er which is not compatible with SMM behavior. The influence of sixth-order contributions to the LF Hamiltonian of Er$^{3+}$ in \{Er$_2$\} is similar to the case of Ho, since the ratio of the Stevens factors $\gamma_j/\alpha_j$ is somewhat larger in Er$^{3+}$ than in Ho$^{3+}$, while the value of $J = 15/2$ is smaller than in Ho. Fourth-order terms have the same, minor importance as in the other systems.

Summarizing all the considered cases, the LF ground states for \{Ln$_2$\} are solely determined by the sign of the related second-order Stevens factors, encoding the different shapes of the Ln-4f shells. Moreover, it is possible, in a decent approximation, to describe all LF spectra by one single parameter $A_{20}$, which is determined by the quadrupolar potential at the Ln sites, and appropriately scaled by the radial expectation value of the specific Ln-4f wave function. A refined description, which is needed to account for mixing of the pure $J_z$ states in the cases of Ho and Er, however, has to include all sixth-order terms.

The dominance of the axial second-order LF term can be attributed to the large, almost axially distributed charge on the Ln dimers, including the single-electron o-bond. The less important, though still significant for the Ho and Er systems, sixth-order contributions (axial and non-axial) can be attributed to the charge distribution on the carbon cage. This means that a transfer of the Ln dimers to other kinds of carbon cages will influence mainly the less important sixth-order terms and keep the present results qualitatively unaffected.
**Supplementary Note 4. Spectra of Model Hamiltonians**

Although the simple *Ising*-type Hamiltonian (Supplementary Equation 1) gives insights mostly in the ground state, the formal analysis of the complete Hamiltonian (Supplementary Equation 1) spectra can be made, and transition probability between different states *i* and *f* can be estimated as (see code PHI\textsuperscript{10} for details):

\[
T_{if} = \frac{1}{3} \sum_{\alpha=x,y,z} |\langle i | \hat{H}_Z(B_\alpha) | f \rangle|^2
\]

{\text{Tb}_2} and {\text{Ho}_2} molecules, with [\text{Ln}^{3+}\text{--e--Ln}^{3+}] spin distribution, are Kramers systems. Thus, the ground state tunneling is protected in both cases (Supplementary Figs. 47, 57) and shows infinitesimal tunneling probability either in case of {\text{Tb}_2} or {\text{Ho}_2}. On a whole the {\text{Tb}_2} molecule represents a similar Hamiltonian spectrum once reported for {\text{Dy}_2}\textsuperscript{11}. Transitions probabilities are very low up to 6-7 KD-states and even after this point they are not very high. Assuming the *K*\textsuperscript{eff} coupling in (Supplementary Equation 1) of 55 cm\textsuperscript{-1} one can estimate the barrier for the effective Orbach process, through the semi-degenerate exchange-excited doublets to be of 555.8 and 558.5 cm\textsuperscript{-1} (\textasciitilde800 K). For the non-collinear system, the Hamiltonian S1 is not expected to be fully adequate, but still, the formal spectrum and transition probabilities can be computed and the effective Orbach process barrier can be estimated. For the *K*\textsuperscript{eff} value of 40 cm\textsuperscript{-1}, there is a state with the energy of 259.6 cm\textsuperscript{-1} (374 K), which has an almost perpendicular orientation of the main anisotropy axis with respect to the ground state. Experimentally, an Orbach barrier of \textasciitilde330 K is found for {\text{Ho}_2}. 


Supplementary Methods

Magnetic properties

Magnetic susceptibility in the further discussion is defined as $\chi = M/H$ both in experiment and in theory. Note that in high field the $M/H$ ratio is significantly different from differential susceptibility defined as a derivative of magnetization with respect to the external field.

Simulations of magnetic properties are based on the spin Hamiltonian (all calculated curves are powder-averaged):

$$\hat{H}_{\text{spin}}([\text{Ln}_2]) = \hat{H}_{\text{LF}_1} + \hat{H}_{\text{LF}_2} - 2K^{\text{eff}}\hat{s}(\hat{J}_{\text{Ln}_1} + \hat{J}_{\text{Ln}_2})$$

(1)

where ligand field parameters in $\hat{H}_{\text{LF}_i}$ are obtained from ab initio calculations, and exchange constant $K^{\text{eff}}$ is the only unknown parameter. The value of $K^{\text{eff}}$ is varied to find the best fit to the experimental data.

For $\{\text{Gd}_2\}$, the spin Hamiltonian is reduced to the following form:

$$\hat{H}_{\text{spin}}([\text{Gd}_2]) = -2K^{\text{eff}}\hat{s}(S_{\text{Gd}_1} + S_{\text{Gd}_2})$$

(2)

Thus leaving only one unknown parameter, effective exchange constant $K^{\text{eff}}$.

For $\{\text{TbY}\}$, the spin Hamiltonian is reduced to the following form:

$$\hat{H}_{\text{spin}}([\text{TbY}]) = \hat{H}_{\text{LF}_{\text{Tb}}} - 2K^{\text{eff}}\hat{s} \cdot \hat{J}_{\text{Tb}}$$

(3)

where ligand-field parameters in $\hat{H}_{\text{LF}_{\text{Tb}}}$ are obtained from ab initio calculations.

In the fitting of the magnetic data we used the followed strategy: $\chi T$ curve measured for a given $\{\text{Ln}_2\}$ compound was fitted for only one value of the magnetic field, 1 T, to determine $K^{\text{eff}}$. This $K^{\text{eff}}$ value was then used to calculate $\chi T$ curves for other values of the magnetic field (3, 5, and 7 T) as well as to calculate magnetization curves at different temperatures. The agreement of the model and experiment is considered to be good, when a single $K^{\text{eff}}$ value can give a good agreement for the whole set of experimental data.

Due to the small mass of the sample, reliable estimations of the absolute magnetization values are possible only for $\{\text{Dy}_2\}$ (ref. 1), $\{\text{Er}_2\}$ and $\{\text{Ho}_2\}$, which show the highest yield in the synthesis. For other sample uncertainties in the mass determination introduced during the sample preparation are too large to allow accurate determination of the absolute magnetization values. We therefore use arbitrary units for these $\{\text{Ln}_2\}$ molecules.

DFT calculations

We used the VASP code, version 5.0, to optimize the molecular structures at the PBE-D level using PAW pseudopotentials with standard cutoffs as recommended. The 4f shells of the lanthanide elements do not contribute to chemical bonding. Thus, we included the 4f shell in the core potential, i.e., we used the so-called open-core approximation (here, implemented as unpolarized potential). The SCF calculations accounted for spin polarization of the valence states. This procedure is expected to provide realistic results for structures involving Ln ions. The pseudopotential configuration $5p^66s^25d^1$ was used for all Ln atoms. All molecular structures were optimized such that the residual forces for all atoms were below $10^{-4}$ eV/Å.
The broadening parameter was chosen to be 0.2 eV. The size of the cubic periodic calculation box was 25 Å³.

**Ab initio calculations**

Ab initio energies and wave functions of CF multiplets for the \{LnY\}⁻ molecule and model systems have been calculated using the quantum chemistry package MOLCAS 8.0. Single point complete active space self-consistent field with spin-orbit interactions calculations (CASSCF/SO-RASSI) were done to derive ab initio ligand field parameters (note that we use the term “ligand field” instead of “crystal field” to avoid possible confusion with the intermolecular interactions in crystals). Mixed atomic natural extended relativistic basis set (ANO-RCC) was employed with the minimal basis option for C and H atoms, and VDZ-quality of Y, Ln metals in the cluster. The use of \{LnY\}⁻ anions instead of neutral \{LnY\} molecule allows one to limit active space only to the 4f shell. Calculations for the neutral \{LnY\} molecule would require inclusion of the unpaired valence electron and corresponding valence orbital into the active space, which makes ab initio calculations less tractable. Besides, the crystal field parameters extracted from such calculations would then lose their clear physical meaning.

Depending on f-shell populations of the Ln-ions there are three ground state multiplets \(^7F_6\), \(^5I_8\) and \(^4I_{15/2}\) for Tb (with \(f^8\)), Ho (with \(f^{10}\)) and Er(\(f^{11}\)) respectively. Being non-Kramers, with an even number of electrons, ions Tb and Ho are represented by energetically close singlets, which can be grouped into several pseudo-KD. At the same time the Er-system, as a Kramers-system, has a full set of eight low-lying Kramers doublets.

Supplementary Tables 7 summarizes the CAS compositions, RASSI-SO setting and ANISO pseudo-spin mapping options for the different \{LnY\}⁻ molecule. For example, the active space of the CASSCF calculations includes eleven active electrons and the seven active orbitals (e.g. CAS (11,7)) was considered for \{ErY\}⁻ molecule. All 35 quartets and 112 doublets were used in the state-averaged CASSCF runs and when all 147 states were mixed in the state interaction problem with spin-orbit interaction included. The single ion magnetic properties and CF-parameters were calculated with use of SINGLE_ANISO module with mapping on eight low-lying Kramers doublets of Er\(^{13+}\). The results and properties for KD and pseudo-KD systems are shown in Supplementary Tables 8-10.
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