Macrocycle Based Dinuclear Dysprosium(III) Single Molecule Magnets with Local $D_{5h}$ Coordination Geometry

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1. Schematic drawing of the ligands

Scheme S1. Schematic drawing of the proligands H$_2$L$^1$ (top), H$_2$L$^2$ (middle), and H$_2$L$^3$ (bottom).
2. IR Spectroscopy

Fig. S1 IR(ATR) spectrum of a solid sample of complex Dy₄.

Fig. S2 IR(ATR) spectra of solid samples of complexes Dy₂·Cl, Dy₂⁺·Cl, and Dy₂·SCN.
3. Powder XRD and thermogravimetric analyses

**Fig. S3** Powder XRD analysis of Dy$_2$Cl. The black line is the simulated pattern based on the single crystal diffraction data.

**Fig. S4** Powder XRD analysis of Dy$_2^+$Cl. The black line is the simulated pattern based on the single crystal diffraction data.

**Fig. S5** Thermogravimetric analyses of Dy$_2$Cl (red line) and Dy$_2^+$Cl (black line).
4. Crystallographic Details

Table S1. Crystallographic data of complexes Dy₄, Dy₂·Cl, Dy₂⁺·Cl, and Dy₂·SCN.

|                | Dy₄            | Dy₂·Cl         | Dy₂⁺·Cl        | Dy₂·SCN        |
|----------------|----------------|----------------|----------------|----------------|
| empirical formula | C₇₂H₁₀₂Cl₄Dy₄O₳₃ | C₇₂H₁₀₂Cl₄Dy₂N₁₀ | C₆₂H₄Cl₄Dy₂N₁₀ | C₆₂H₄Dy₂N₁₄O₂S₄ |
| formula weight, g·mol⁻¹ | 2523.51       | 931.43         | 959.48         | 1086.03        |
| crystal size, mm³   | 0.500 x 0.300 x 0.150 | 0.210 x 0.180 x 0.160 | 0.160 x 0.150 x 0.100 | 0.210 x 0.080 x 0.050 |
| crystal system     | Monoclinic    | Monoclinic     | Monoclinic     | Triclinic      |
| space group        | P₂₁/n         | P₂₁/c          | P₂₁/c          | P-1            |
| T, K               | 133(2)        | 133(2)         | 133(2)         | 133(2)         |
| λ, Å                | 0.71073       | 0.71073        | 0.71073        | 0.71073        |
| a, Å               | 14.0320(2)    | 8.9982(3)      | 8.9524(3)      | 8.7415(4)      |
| b, Å               | 16.1940(3)    | 11.6001(3)     | 11.7805(5)     | 9.1291(4)      |
| c, Å               | 25.7815(4)    | 14.8941(5)     | 15.8173(6)     | 12.9791(5)     |
| α, °               | 90            | 90             | 90             | 79.287(3)      |
| β, °               | 96.4540(10)   | 103.545(3)     | 102.837(3)     | 73.578(3)      |
| γ, °               | 90            | 90             | 90             | 87.499(4)      |
| V, Å³              | 5821.31(16)   | 1511.41(8)     | 1626.46(11)    | 976.15(7)      |
| Z                  | 2             | 2              | 2              | 1              |
| ρ (cal), g·cm⁻³    | 1.440         | 2.047          | 1.959          | 1.847          |
| F(000)             | 2496          | 900            | 932            | 534            |
| θ range [°]        | 1.488 to 26.790 | 2.250 to 26.855 | 2.175 to 26.865 | 1.663 to 26.747 |
| Tmin / Tmax        | 0.8436 / 0.5310 | 0.4310 / 0.2492 | 0.8004 / 0.6557 | 0.8473 / 0.4952 |
| measured refl.    | 84214         | 19848          | 13782          | 13784          |
| unique refl. [Rint] | 12347, 0.0285 | 3205 / 0.0239  | 3450 / 0.0360  | 4139 / 0.0275  |
| goodness-of-fit (F²) | 1.048        | 1.115          | 1.071          | 1.118          |
| data / restr. / param. | 12347 / 119 / 636 | 3205 / 0 / 184  | 3450 / 31 / 241 | 4139 / 1 / 247 |
| R₁, wR₂ (I > 2σ(I)) | 0.0235, 0.0569 | 0.0248, 0.0589 | 0.0293, 0.0638 | 0.0229, 0.0537 |
| R₁, wR₂ (all data) | 0.0274, 0.0584 | 0.0275, 0.0600 | 0.0400, 0.0668 | 0.0282, 0.0558 |
| res. el. dens. [e·Å⁻³] | 0.736 / -0.686 | 1.257 / -0.717 | 1.882 / -0.700 | 1.492 / -0.336 |

Table S2. Selected bond distances (Å) in complex Dy₄.

| Dy(1)-O(6)     | 2.2608(18) | Dy(2)-O(6) | 2.2726(19) |
|----------------|------------|------------|------------|
| Dy(1)-O(5)     | 2.3152(18) | Dy(2)-O(8) | 2.320(2)   |
| Dy(1)-O(7)     | 2.351(2)   | Dy(2)-O(5) | 2.3890(18) |
| Dy(1)-O(5)#    | 2.4034(17) | Dy(2)-N(6)# | 2.411(2)  |
| Dy(1)-N(1)     | 2.424(2)   | Dy(2)-N(2)# | 2.431(2)  |
| Dy(1)-N(7)     | 2.429(2)   | Dy(2)-N(3)# | 2.517(2)  |
| Dy(1)-O(1)     | 2.5179(19) | Dy(2)-N(5)# | 2.531(2)  |
| Dy(1)-O(3)     | 2.5892(19) | Dy(2)-N(4)# | 2.570(2)  |
| Dy(1)-Dy(1)#   | 3.8066(2)  | Dy(1)-Dy(2) | 3.72071(18) |

Symmetry transformations used to generate equivalent atoms: # -x+1,-y+1,-z+1.
Table S3. Selected bond angles (°) in complex Dy₄⁺.

| Bond               | Angle 1  | Angle 2  | Angle 3  | Angle 4  |
|--------------------|----------|----------|----------|----------|
| O(6)-Dy(1)-O(7)    | 82.39(7) |          |          |          |
| O(5)-Dy(1)-O(7)    | 105.47(7)|          |          |          |
| O(7)-Dy(1)-N(1)    | 78.31(8) |          |          |          |
| O(5)#-Dy(1)-N(1)   | 74.10(7) |          |          |          |
| O(5)-Dy(1)-N(7)    | 80.54(7) |          |          |          |
| O(5)#-Dy(1)-N(7)   | 75.54(7) |          |          |          |
| N(1)-Dy(1)-N(7)    | 75.15(8) |          |          |          |
| O(6)-Dy(1)-O(1)    | 85.28(7) |          |          |          |
| O(7)-Dy(1)-O(1)    | 86.00(7) |          |          |          |
| N(7)-Dy(1)-O(1)    | 105.67(7)|          |          |          |
| O(6)-Dy(1)-O(3)    | 78.91(7) |          |          |          |
| O(5)#-Dy(1)-O(3)   | 82.41(6) |          |          |          |
| N(1)-Dy(1)-O(3)    | 109.12(7)|          |          |          |
| O(1)-Dy(1)-O(3)    | 78.54(7) |          |          |          |

Symmetry transformations used to generate equivalent atoms: # -x+1,-y+1,-z+1

Table S4. Selected bond distances (Å) and angles (°) in complexes Dy⁺⁺Cl, Dy⁺⁺⁺Cl, and Dy⁺⁺⁻SCN.

| Bond               | Distance 1  | Distance 2  | Distance 3  |
|--------------------|-------------|-------------|-------------|
| Dy(1)-N(1)         | 2.441(3)    | 2.447(4)    | 2.397(3)    |
| Dy(1)-N(2)         | 2.455(3)    | 2.452(3)    | 2.423(3)    |
| Dy(1)-N(5)         | 2.458(3)    | 2.453(4)    | 2.454(3)    |
| Dy(1)-N(3)         | 2.467(3)    | 2.469(4)    | 2.455(3)    |
| Dy(1)-N(4)         | 2.488(4)    | 2.547(4)    | 2.472(3)    |
| Dy(1)-Cl(2)        | 2.6030(11)  | 2.6050(12)  | 2.484(3)    |
| Dy(1)-Cl(1)        | 2.6143(12)  | 2.6123(12)  | 2.486(3)    |
| Cl(2)-Dy(1)-Cl(1)  | 169.18(4)   | 174.17(4)   | 2.550(3)    |

Table S5. Selected bond angles (°) in complexes Dy⁺⁺Cl, Dy⁺⁺⁺Cl, and Dy⁺⁺⁻SCN.

| Bond               | Angle 1  | Angle 2  | Angle 3  | Angle 4  | Angle 5  |
|--------------------|----------|----------|----------|----------|----------|
| N(1)-Dy(1)-N(2)    | 92.58(10)| 66.32(13)| 112.19(10)|          |          |
| N(2)-Dy(1)-N(5)    | 66.02(11)| 91.34(11)| 81.24(9) |          |          |
| N(1)-Dy(1)-N(3)    | 66.12(11)| 66.33(12)| 71.50(9) |          |          |
| N(5)-Dy(1)-N(4)    | 68.46(13)| 67.26(13)| 127.67(10)|          |          |
| N(3)-Dy(1)-N(4)    | 66.81(13)| 68.76(13)| 76.78(9) |          |          |
| N(1)-Dy(1)-Cl(2)   | 92.58(8) | 90.98(13)| 91.53(9) |          |          |
| N(2)-Dy(1)-Cl(2)   | 94.97(8) | 93.43(8) | 80.86(10)|          |          |
| N(5)-Dy(1)-Cl(2)   | 90.78(9) | 89.92(9) | 80.60(10)|          |          |
| N(3)-Dy(1)-Cl(2)   | 88.08(8) | 86.31(9) | 65.20(9) |          |          |
| N(4)-Dy(1)-Cl(2)   | 85.43(12)| 88.08(9) | 90.11(10)|          |          |
| N(1)-Dy(1)-Cl(1)   | 93.73(8) | 90.22(13)| 84.64(10)|          |          |
| N(2)-Dy(1)-Cl(1)   | 93.53(8) | 92.28(8) | 65.31(9) |          |          |
Fig. S6 Packing models along the $a$ and $b$ axes of complex $\text{Dy}_4$.

Fig. S7 Packing models along the $a$ and $b$ axes of complex $\text{Dy}_2\cdot \text{Cl}$. The green dash lines represent the hydrogen bondings.

Fig. S8 Packing models along the $a$ and $b$ axes of complex $\text{Dy}_2\cdot \text{Cl}$. The green dash lines represent the hydrogen bondings.
Fig. S9 Packing models along the $a$ and $b$ axes of complex $\text{Dy}_2\cdot\text{SCN}$.

Table S6. $\text{CShM}$ values calculated by $\text{SHAPE}$ 2.1\textsuperscript{1} for $\text{Dy}_4$.

| Central atom | Coordination Geometry                  | Dy1   | Dy2   |
|--------------|---------------------------------------|-------|-------|
| Dy           | Cube ($O_h$)                           | 10.878| 12.616|
|              | Square antiprism ($D_{4d}$)            | 1.358 | 2.900 |
|              | Triangular dodecahedron ($D_{2d}$)     | 2.124 | 2.075 |
|              | Johnson gyrobifastigium J26 ($D_{2d}$) | 15.159| 11.704|
|              | Johnson elongated triangular bipyramid ($D_{3h}$) | 28.301| 25.449|
|              | Biaugmented trigonal prism ($C_3v$)    | 2.147 | 1.898 |
|              | Snub diphenoid J84 ($D_{2d}$)          | 4.694 | 3.447 |

Fig. S10 Coordination polyhedron of Dy1 (left) and Dy2 (right) in complex $\text{Dy}_4$.

Table S7. $\text{CShM}$ values calculated by $\text{SHAPE}$ 2.1\textsuperscript{1} for $\text{Dy}_2\cdot\text{Cl}$ and $\text{Dy}_2^+\cdot\text{Cl}$.

| Central atom | Coordination Geometry                  | Dy$_2\cdot\text{Cl}$ | Dy$_2^+\cdot\text{Cl}$ |
|--------------|---------------------------------------|----------------------|------------------------|
| Dy           | Hexagonal pyramid ($C_{6v}$)           | 24.940               | 24.584                 |
|              | Pentagonal bipyramid ($D_{5h}$)        | 0.801                | 0.689                  |
|              | Capped octahedron ($C_{3v}$)           | 8.759                | 8.143                  |
|              | Capped trigonal prism ($C_{3v}$)       | 6.947                | 6.420                  |
|              | Johnson pentagonal bipyramid J13 ($D_{15}$) | 5.420               | 5.268                  |
|              | Johnson elongated triangular pyramid J7 ($C_{3v}$) | 24.391               | 23.565                 |
Fig. S11 Coordination polyhedra of the Dy$^{III}$ ions in complexes Dy$_2$·Cl (left) and Dy$_2^*$·Cl (right).

Table S8. CShM values calculated by SHAPE 2.1$^1$ for Dy$_2$·SCN.

| Central atom | Coordination Geometry | Dy$_2$·SCN |
|--------------|-----------------------|------------|
| Dy           | Cube ($O_h$)          | 8.776      |
|              | Square antiprism ($D_{4d}$) | 4.194      |
|              | Triangular dodecahedron ($D_{2d}$) | **2.600**  |
|              | Johnson gyrobiastigium J26 ($D_{2d}$) | 9.308      |
|              | Johnson elongated triangular bipyramid ($D_{3h}$) | 26.603     |
|              | Biaugmented trigonal prism ($C_3$) | 2.818      |
|              | Snub diphenoid J84 ($D_{3h}$) | 5.724      |

Fig. S12 Coordination polyhedra of the Dy$^{III}$ ions in complex Dy$_2$·SCN.
5. Direct current (dc) magnetic susceptibility measurements

Fig. S13 Molar magnetization ($M$) vs. field ($H$) for Dy$_4$ at 2.0 K.

Fig. S14 Molar magnetization ($M$) vs. field ($H$) for Dy$_2$Cl at 2.0 K.
Fig. S15 Molar magnetization \((M)\) vs. field \((H)\) for \(\text{Dy}_2^*\cdot\text{Cl}\) at 2.0 K.

Fig. S16 Molar magnetization \((M)\) vs. field \((H)\) for \(\text{Dy}_2^*\cdot\text{SCN}\) at 2.0 K.
6. Alternating current (ac) magnetic susceptibility measurements

Fig. S17 Temperature-dependent ac susceptibility of Dy\(_4\) at indicated dc fields with frequency of 1488 Hz.

Fig. S18 Field-dependent ac susceptibility of Dy\(_4\) at indicated temperatures with frequency of 1488 Hz.
Fig. S19 Temperature-dependent ac susceptibility of Dy$_4$ at indicated frequencies under zero (left) and 800 Oe (right) dc field.

Fig. S20 Temperature-dependent ac susceptibility of Dy$_2$-Cl (left) and Dy$_2^*$-Cl (right) at zero dc field with a frequency of 1488 Hz.

Fig. S21 Field-dependent ac susceptibility of Dy$_2$-Cl (left) and Dy$_2^*$-Cl (right) at 2 K with a frequency of 1488 Hz.
Fig. S22 Frequency-dependent ac susceptibility of $\text{Dy}_2 \cdot \text{Cl}$ (left) and $\text{Dy}_2^* \cdot \text{Cl}$ (right) at indicated temperatures under 300 Oe dc field.

Fig. S23 Cole-Cole plots (top) and plots of $\tau$ vs. $T^{-1}$ (bottom) for $\text{Dy}_2 \cdot \text{Cl}$ (left), $\text{Dy}_2^* \cdot \text{Cl}$ (middle), and $\text{Dy}_2 \cdot \text{SCN}$ (right) under indicated dc field. The red line represents the best fits using equation 1.
### 7. CC-Fit results

Table S9. CC-Fit$^2$ results for frequency-dependent ac susceptibility of Dy$_4$ under zero dc field.

| $T$ / K | $\chi_{S,tot}$ | $\Delta f_1$ | $\tau_1$/s | $\alpha_1$ | $\Delta f_2$ | $\tau_2$/s | $\alpha_2$ | Residual 2 |
|---------|----------------|--------------|------------|-------------|--------------|------------|-------------|-------------|
| 2       | 0.59044        | 8.13929      | 0.01481    | 0.32966     | 2.64099      | 0.09655    | 2.19926E-8  | 0.01591     |
| 2.5     | 0.5123         | 8.08732      | 0.01224    | 0.31826     | 2.93527      | 0.07771    | 3.18221E-8  | 0.00088     |
| 3       | 0.4305         | 8.05426      | 0.01076    | 0.32733     | 2.59776      | 0.05837    | 5.76599E-8  | 0.00764     |
| 3.5     | 0.37351        | 7.74295      | 0.00872    | 0.32463     | 2.23654      | 0.04503    | 1.18424E-7  | 0.00712     |
| 4       | 0.32768        | 7.29461      | 0.0066     | 0.32239     | 1.93835      | 0.03572    | 1.94098E-7  | 0.00725     |
| 4.5     | 0.274          | 6.84936      | 0.00482    | 0.32419     | 1.70276      | 0.02866    | 3.94594E-7  | 0.00647     |
| 5       | 0.22708        | 6.386        | 0.00344    | 0.32719     | 1.5474       | 0.02289    | 7.95211E-7  | 0.00522     |
| 6       | 0.13659        | 5.53512      | 0.00171    | 0.33536     | 1.37677      | 0.01423    | 1.36364E-6  | 0.00559     |
| 7       | 0.11242        | 4.80641      | 9.03371E-4 | 0.34297     | 1.2644       | 0.00879    | 1.63469E-6  | 0.00509     |
| 8       | 0.07596        | 4.23591      | 4.81184E-4 | 0.36112     | 1.1917       | 0.00533    | 2.83498E-6  | 0.00695     |
| 9       | 0.15701        | 3.64447      | 2.70302E-4 | 0.37318     | 1.14825      | 0.00328    | 2.66936E-6  | 0.00192     |
| 10      | 0.5111         | 2.92288      | 1.98751E-4 | 0.35343     | 1.05345      | 0.00212    | 1.89458E-5  | 0.00817     |
| 12      | 0.99713        | 1.94597      | 1.11583E-4 | 0.28187     | 0.84326      | 8.84435E-4 | 2.65224E-5  | 0.00364     |
| 14      | 0.90483        | 1.72157      | 3.72505E-5 | 0.24227     | 0.64899      | 3.7311E-4  | 9.21447E-7  | 0.00178     |
| 16      | 0.97553        | 1.52834      | 2.23824E-5 | 0.14896     | 0.39461      | 1.83002E-4 | 1.00345E-6  | 0.00139     |

Table S10. CC-Fit results for frequency-dependent ac susceptibility of Dy$_4$ under 800 Oe dc field.

| $T$ / K | $\chi_S$ | $\chi_T$ | $\tau$/s | $\alpha$ | Residual |
|---------|----------|----------|----------|----------|----------|
| 2       | 0.899    | 12.6174  | 0.02894  | 0.34231  | 0.07056  |
| 2.5     | 0.83     | 12.4717  | 0.02089  | 0.33558  | 0.09002  |
| 3       | 0.76931  | 11.6902  | 0.01471  | 0.32453  | 0.12673  |
| 3.5     | 0.72041  | 10.7396  | 0.01018  | 0.31072  | 0.15109  |
| 4       | 0.66365  | 9.8181   | 0.00696  | 0.29754  | 0.16413  |
| 4.5     | 0.61313  | 8.99414  | 0.00478  | 0.28615  | 0.15874  |
| 5       | 0.57009  | 8.2771   | 0.00332  | 0.27714  | 0.15522  |
| 6       | 0.50603  | 7.11298  | 0.0017   | 0.26438  | 0.1403   |
| 7       | 0.49822  | 6.21768  | 9.39959E-4| 0.25406  | 0.11875  |
| 8       | 0.59089  | 5.51423  | 5.58594E-4 | 0.24155  | 0.09559  |
| 9       | 0.77069  | 4.94512  | 3.47387E-4 | 0.22478  | 0.06007  |
| 10      | 1.00678  | 4.48003  | 2.18822E-4 | 0.20507  | 0.03133  |
| 12      | 1.55972  | 3.77789  | 9.01896E-5 | 0.15865  | 0.00468  |
Table S11. Parameters obtained from the fitting of the relaxation time (τ) vs. 1/T plots of Dy₄ under zero and 800 Oe dc field.

| dc Field | U_{eff} / K | n / s  | τ_{QTM} / s | A/τ₀ | C    | n    |
|----------|-------------|--------|-------------|-------|------|------|
| 0 Oe     | SR          | 59.21  | 9.2632E-6   | 0.1066 | 0    | 29684| 3    |
|          | FR          | 48.66  | 1.0839E-5   | 0.01414| 0    | 16781| 4.40712|
| 800 Oe   | 46.01       | 1.2087E-5| 0.10134   | 9.41073| 0.36298| 4.01693|

Table S12. CC-Fit results for frequency-dependent ac susceptibility of Dy₂Cl under 1200 Oe dc field.

| T / K | χ₅ | χ₉ | τ / s | α   | Residual |
|-------|----|----|------|-----|----------|
| 6     | 1.1397 | 3.44922 | 6.5531E-5 | 0.27193 | 0.00726 |
| 5.6   | 1.54109 | 3.64313 | 1.15704E-4 | 0.22785 | 0.00742 |
| 5.2   | 1.74555 | 3.86974 | 1.64343E-4 | 0.21238 | 0.00743 |
| 4.8   | 1.93081 | 4.12384 | 2.17445E-4 | 0.20528 | 0.00667 |
| 4.4   | 2.15013 | 4.42094 | 2.84882E-4 | 0.19433 | 0.0069 |
| 4     | 2.36507 | 4.7635 | 3.53657E-4 | 0.19766 | 0.00723 |
| 3.6   | 2.63061 | 5.16303 | 4.31948E-4 | 0.2013 | 0.01003 |
| 3.2   | 2.94591 | 5.62515 | 5.19721E-4 | 0.21235 | 0.01019 |
| 2.8   | 3.33487 | 6.18075 | 6.09794E-4 | 0.23033 | 0.01758 |
| 2.4   | 3.86546 | 6.81802 | 7.03546E-4 | 0.25244 | 0.01993 |
| 2     | 4.47729 | 7.61702 | 7.76157E-4 | 0.31706 | 0.03457 |

Table S13. CC-Fit results for frequency-dependent ac susceptibility of Dy₂*:Cl under 1200 Oe dc field.

| T / K | χ₅ | χ₉ | τ / s | α   | Residual |
|-------|----|----|------|-----|----------|
| 6     | 2.13221 | 3.5558 | 5.31887E-5 | 0.11228 | 0.00408 |
| 5.6   | 2.09976 | 3.77139 | 7.23319E-5 | 0.12661 | 0.00344 |
| 5.2   | 2.32506 | 4.01674 | 1.22483E-4 | 0.08761 | 0.01621 |
| 4.8   | 2.30376 | 4.29555 | 1.59001E-4 | 0.11594 | 0.00702 |
| 4.4   | 2.40194 | 4.61804 | 2.18446E-4 | 0.13551 | 0.01218 |
| 4     | 2.61389 | 4.97832 | 3.00672E-4 | 0.13002 | 0.02068 |
| 3.6   | 2.88533 | 5.41094 | 4.00273E-4 | 0.13047 | 0.02073 |
| 3.2   | 3.19282 | 5.91298 | 5.01834E-4 | 0.1421 | 0.04243 |
| 2.8   | 3.61486 | 6.51272 | 6.15237E-4 | 0.14721 | 0.05933 |
| 2.4   | 4.1006 | 7.25575 | 7.44169E-4 | 0.19283 | 0.06518 |
| 2     | 4.75651 | 8.12786 | 8.31683E-4 | 0.22474 | 0.10165 |
### Table S14. CC-Fit results for frequency-dependent ac susceptibility of Dy$_2$SCN under zero dc field.

| $T$ / K | $\chi_S$ | $\chi_T$ | $\tau$ / s | $\alpha$ | Residual |
|---------|----------|----------|-------------|---------|----------|
| 2       | 7.86539  | 8.5371   | 7.70218E-4  | 0.14204 | 0.00285  |
| 2.4     | 6.71108  | 7.30889  | 7.1906E-4   | 0.14849 | 0.00176  |
| 2.8     | 5.84562  | 6.37441  | 6.82227E-4  | 0.14875 | 0.00103  |
| 3.2     | 5.18467  | 5.67092  | 6.25023E-4  | 0.16672 | 8.58981E-4 |
| 3.6     | 4.67764  | 5.11506  | 6.11415E-4  | 0.17049 | 7.4554E-4 |
| 4       | 4.26489  | 4.66411  | 5.54544E-4  | 0.16664 | 7.58629E-4 |
| 4.4     | 3.92149  | 4.29602  | 4.98617E-4  | 0.15572 | 5.50063E-4 |
| 4.8     | 3.65469  | 3.98292  | 4.34641E-4  | 0.16145 | 4.80032E-4 |
| 5.2     | 3.40823  | 3.71984  | 3.99466E-4  | 0.16245 | 2.40736E-4 |
| 5.6     | 3.20394  | 3.49263  | 3.54213E-4  | 0.15223 | 2.10716E-4 |
| 6       | 3.02766  | 3.29277  | 3.08067E-4  | 0.1598  | 3.14756E-4 |
| 6.4     | 2.87414  | 3.11717  | 2.66174E-4  | 0.12979 | 2.72768E-4 |
| 6.8     | 2.74039  | 2.96045  | 2.0796E-4   | 0.14973 | 1.8885E-4 |
| 7.2     | 2.6145   | 2.82158  | 1.68795E-4  | 0.19989 | 1.79973E-4 |
| 7.6     | 2.48542  | 2.69619  | 1.35009E-4  | 0.162   | 1.8817E-4 |
| 8       | 2.41214  | 2.58167  | 1.02639E-4  | 0.19051 | 2.40235E-4 |
| 8.4     | 2.3207   | 2.47823  | 7.34E-4     | 0.162   | 1.8817E-4 |

### Table S15. Parameters obtained from the fitting of the relaxation time ($\tau$) vs. $1/T$ plots of Dy$_2$Cl, Dy$_2$Cl$^+$, and Dy$_2$SCN.

|          | $U_{\text{eff}}$ / K | $n$ / s | $\tau_{\text{QTM}}$ / s | $AH^4$ | $C$     | $n$     |
|----------|----------------------|---------|--------------------------|--------|---------|---------|
| Dy$_2$Cl | 19.08                | 1.37486E-5 | 1.57E-3                  | 321.65034 | 0.00849 | 7.57941 |
| Dy$_2$Cl$^+$ | 25.06              | 1.30265E-4 | 1.12E-3                  | 121.91791 | 2.49935 | 4.83978 |
| Dy$_2$SCN | 43.1                | 2.11156E-6 | 7.34E-4                  | 0      | 5.11551 | 3.07443 |

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8. Calculations with Magellan program

Fig. S24 Partial charges assigned to the ligands in complexes Dy$_2$·Cl (left), Dy$_2$·Cl* (middle), and Dy$_2$·SCN (right) with one negative charge in axial directions.

Fig. S25 Partial charges assigned to the ligands in complexes Dy$_2$·Cl (left), Dy$_2$·Cl* (middle), and Dy$_2$·SCN (right) with half negative charge in axial directions.

Fig. S26 Orientations of the main magnetic axes and local magnetizations of the ground states for the one (red) and half (blue) negative charge models of the Dy$_2$·Cl (left), Dy$_2$·Cl* (middle), and Dy$_2$·NCS (right).

Table S16. Minimal reorientation energies (cm$^{-1}$) and intersection angles (°) of anisotropy axes calculated from two different models by Magellan program$^3$ for complexes Dy$_2$·Cl, Dy$_2$·Cl*, and Dy$_2$·SCN.

|                  | Dy$_2$·Cl         | Dy$_2$·Cl*        | Dy$_2$·SCN        |
|------------------|-------------------|-------------------|-------------------|
| Center atom      | Center atom       | Center atom       | Center atom       |
| One charge       | Dy(1)             | 884.0             | Dy(1)             | 906.8             | Dy(1)             | 1217              |
| Half charge      | Dy(1)             | 205.4             | Dy(1)             | 223.3             | Dy(1)             | 509.4             |
| Deviation angle  | 1.082             | 0.885             | 4.497             |

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9. References

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