# ELECTRONIC SUPPORTING INFORMATION (ESI)

## A family of mono-, di-, and tetranuclear $Dy^{III}$ complexes bearing the ligand 2,6-diacetylpyridine bis(picolinoylhydrazone) and exhibiting slow relaxation of magnetization

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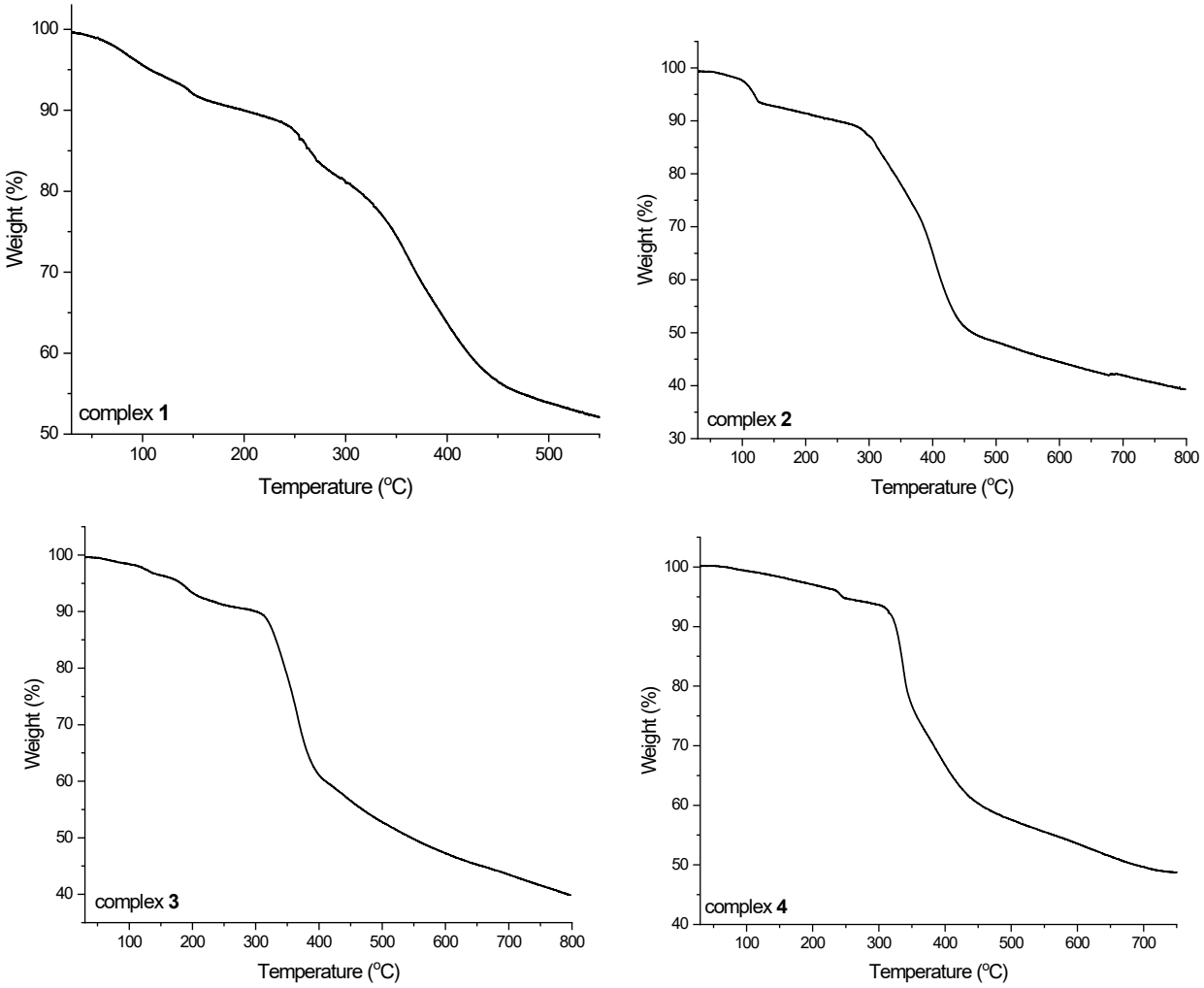


**Fig. S1** Thermogravimetric (TG) plots for complexes **1**-**4** at heating rate 10 °C $min^{-1}$.

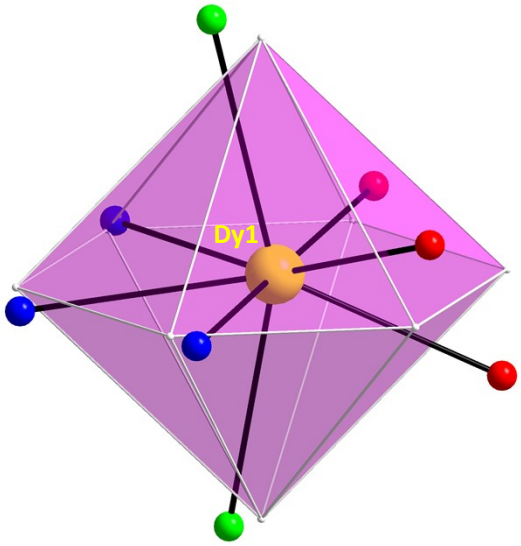


**Fig. S2** The hexagonal bipyramidal coordination polyhedron of the $Dy^{III}$ center in complex **1**. The smaller white spheres define the vertices of the ideal polyhedron.

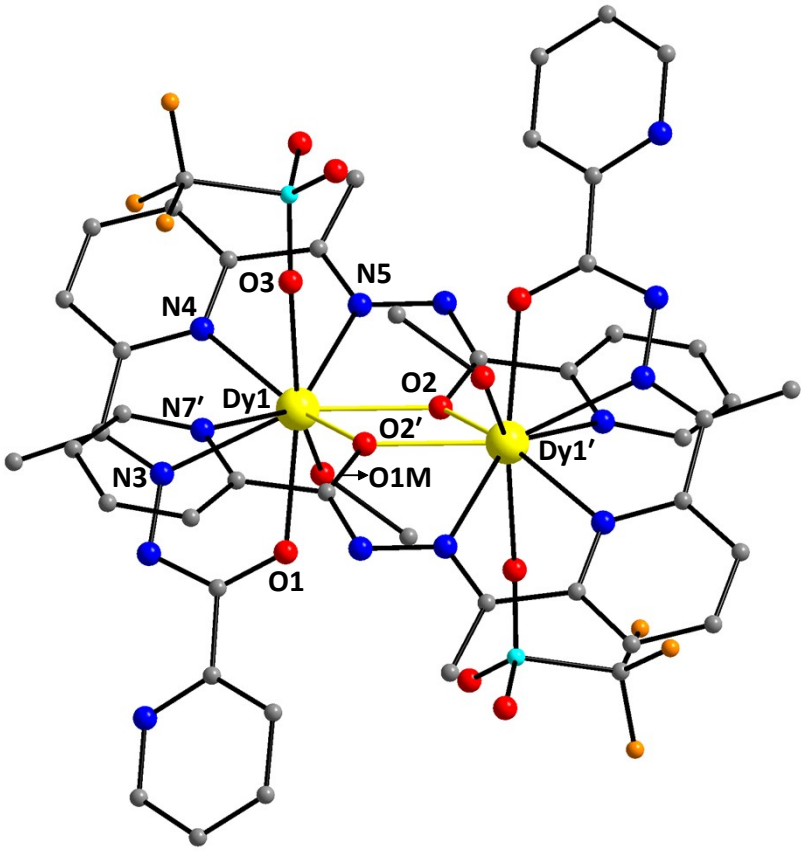


**Fig. S3** Partially labelled representation of the $[Dy_2(O_3SCF_3)_2(LH)_2(MeOH)_{1.42}(H_2O)_{0.58}]^{2+}$ cation that is present in the crystal of **2**, highlighting with yellow thick bonds the $\{Dy_2(\mu\text{-}OR)_2\}^{4+}$ core. H atoms are omitted for clarity. Color scheme: $Dy^{III}$, yellow; O, red; N, blue; S, cyan; F, orange;

C, grey. The coordinated MeOH molecules are shown in the figure since they are the sites with the highest occupancy (over the $H_2O$ molecules). Symmetry code: (′) 1-*x*, 1-*y*, 1-*z*.

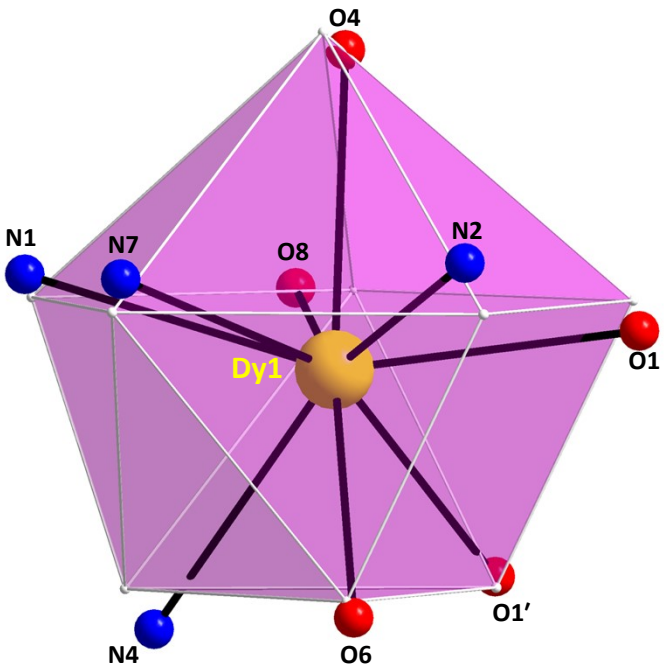


**Fig. S4** The muffin coordination polyhedron of the $Dy^{III}$ centers in complex **3**·2MeOH with the corresponding atom labelling scheme as discussed in the main text. The smaller white spheres define the vertices of the ideal polyhedron.

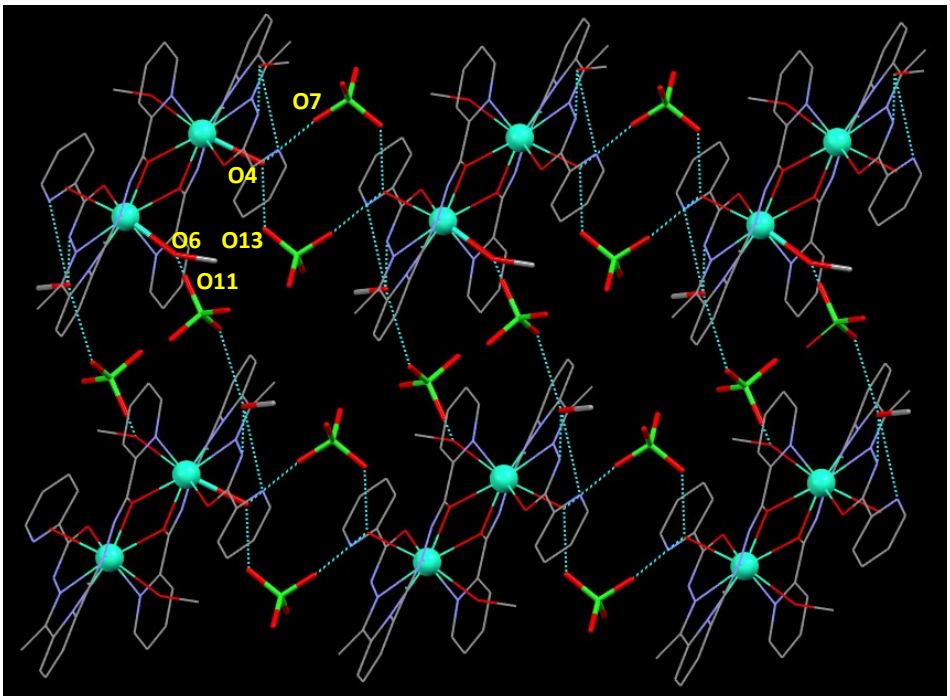


**Fig. S5** A portion of the H-bonded network developed in the crystal of **3**·2MeOH. The groups involved into the interactions are showed in capped sticks. The H-bonds are represented by the blue dashed lines.

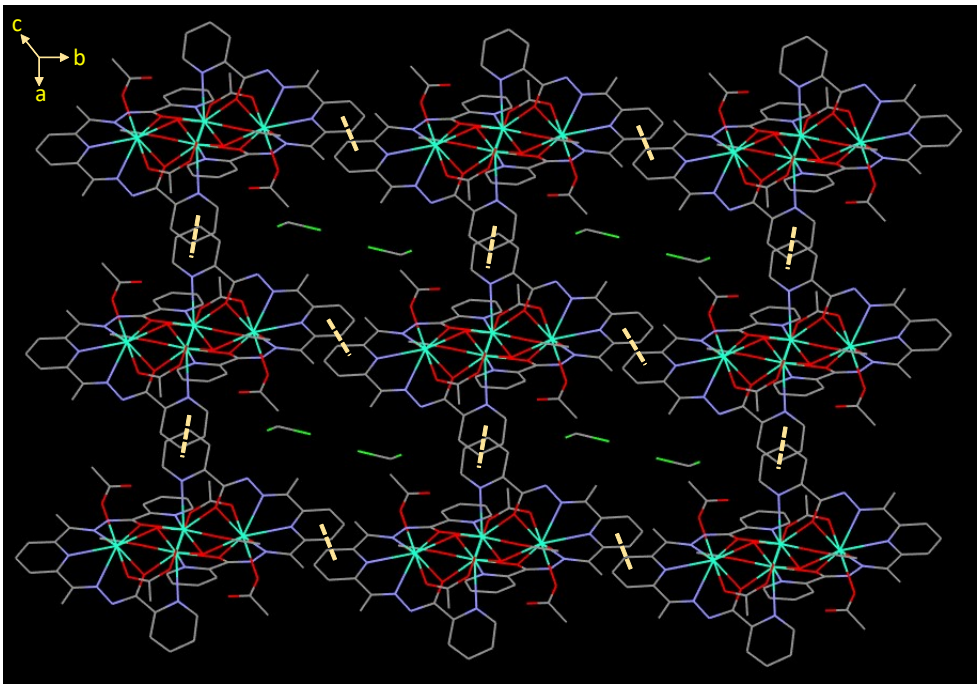

**Fig. S6** A portion of the supramolecular 2-D network developed in the crystal of **4**·2$CH_2Cl_2$ through an array of intermolecular $\pi$-$\pi$ stacking interactions (dashed yellow lines) between the pyridyl groups of the $L^{2-}$ ligands. The lattice $CH_2Cl_2$ solvate molecules are 'trapped' in the resulting cavities.

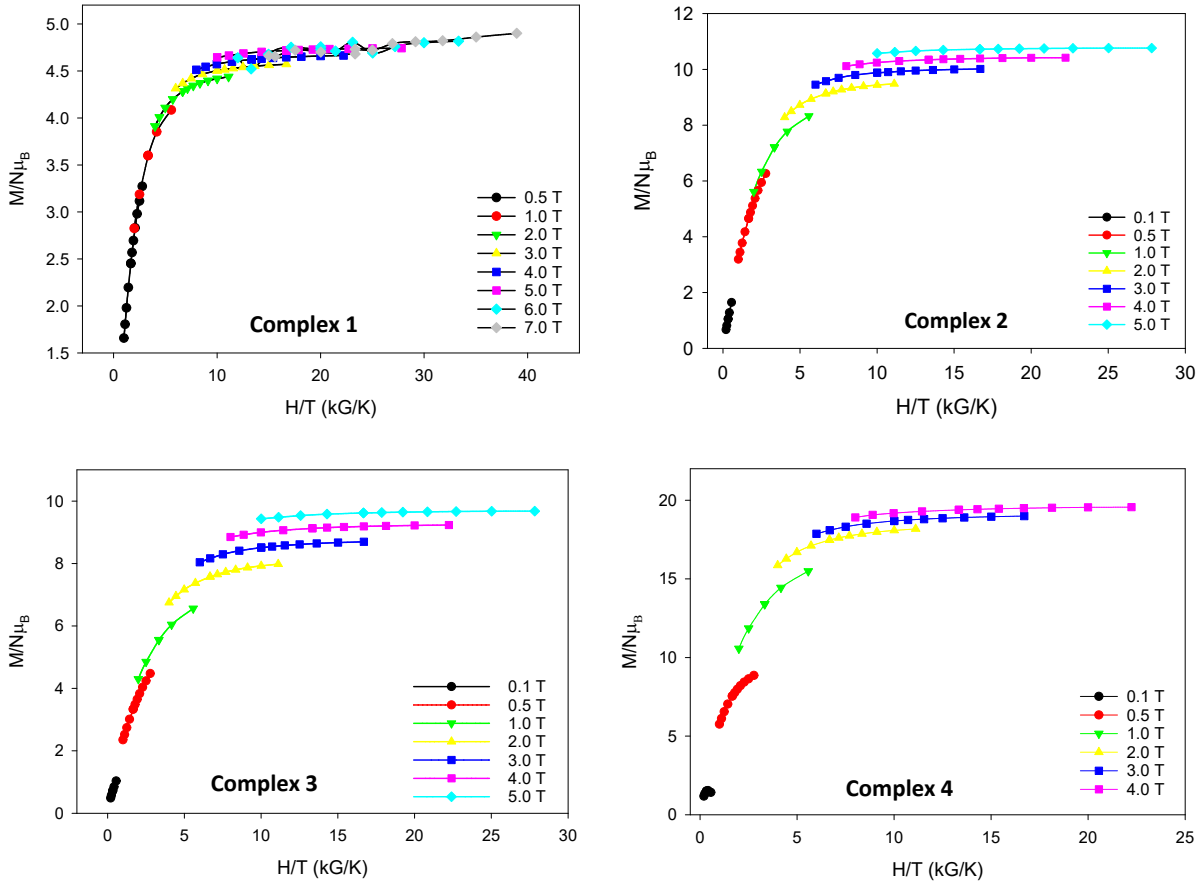


**Fig. S7** Plots of reduced magnetization ($M/N\mu_B$) *vs* $H/T$ for complexes **1**-**4** at different fields and temperatures. The solid lines are guides for the eye only.

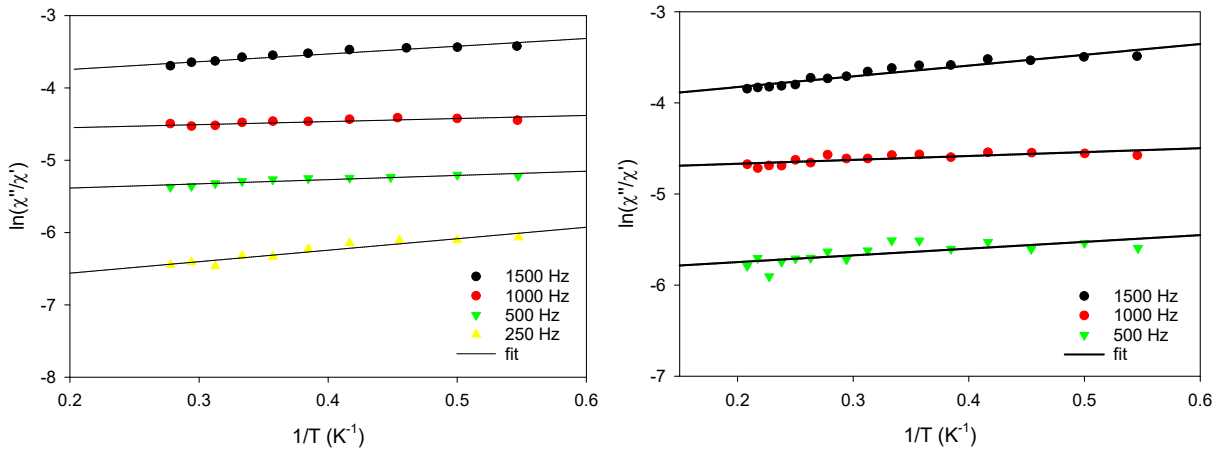


**Fig. S8** Debye plots of the dinuclear complexes **2** (left) and **3** (right) for the indicated ac frequencies. The solid lines correspond to the fit of the data by applying Equation 1 [$\ln(\chi''/\chi') = \ln(\omega\tau_0) + U_{\text{eff}}/k_BT$]; see the text for the fit parameters.

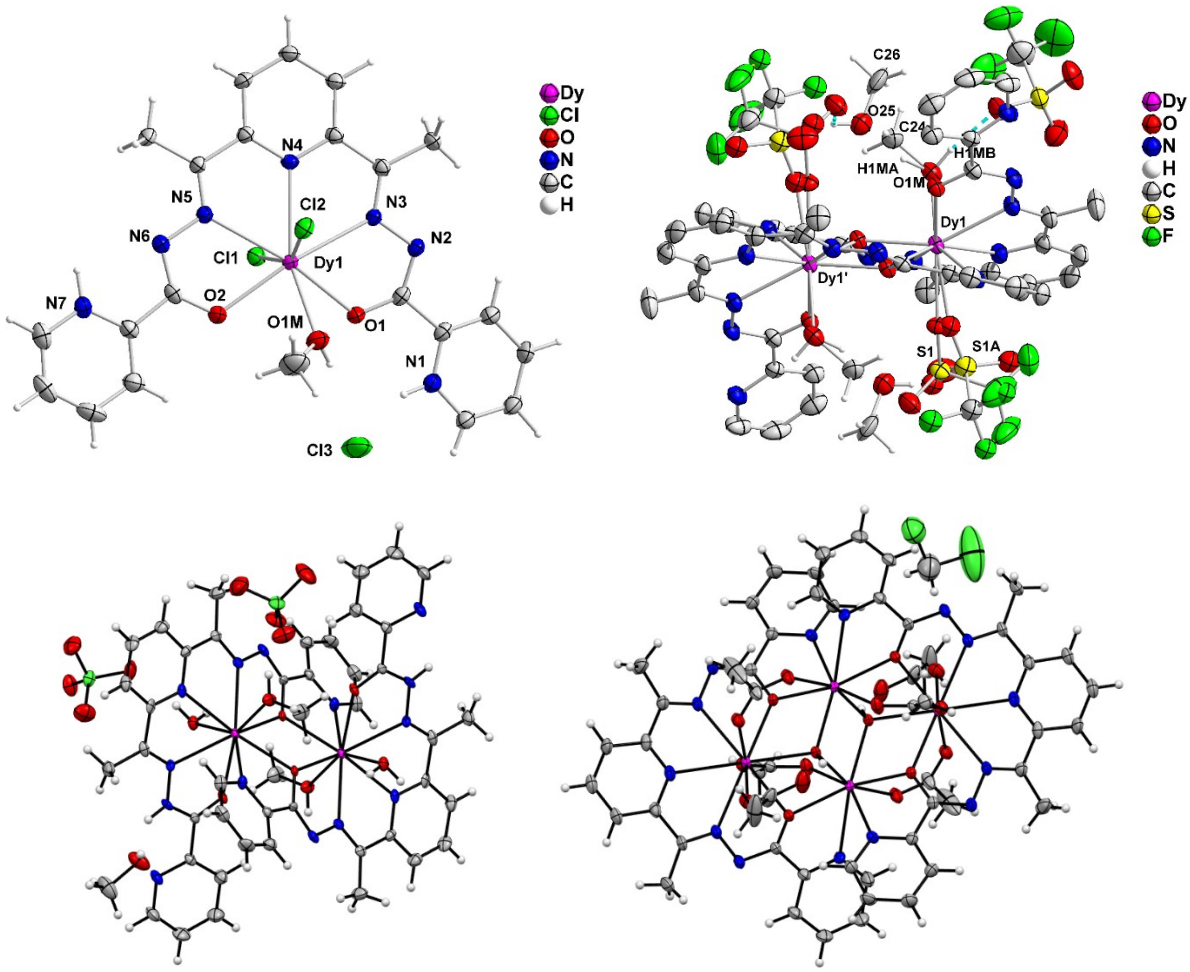

**Fig. S9** ORTEP representations of complexes **1** (top, left), **2** (top, right), **3** (bottom, left), and **4** (bottom, right); thermal ellipsoids are at the 50% probability level. For complex **2**: The disordered sites of methanol and triflate anion are indicated and those labeled as (O1M, C24) and S1 are the sites with the highest occupancy. The dashed cyan lines indicate hydrogen bonds of H1M with O6' atom (O1M···O6': 2.704(3)Å) of lattice triflate anion and H2M with O5A' (O25···O5': 2.98(1)Å) of the coordinated one. Symmetry code ('): 1-*x*, 1-*y*, 1-*z*.

**Table S1** Selected bond distances (Å) and angles (°) for complex **1**

| **Bond distances (Å)** | |
|---|---|
| Dy1-O1 | 2.382(2) |
| Dy1-O2 | 2.342(2) |
| Dy1-O1M | 2.486(3) |
| Dy1-N3 | 2.531(3) |
| Dy1-N4 | 2.581(3) |
| Dy1-N5 | 2.542(3) |
| Dy1-Cl1 | 2.6674(8) |
| Dy1-Cl2 | 2.7037(9) |
| N2-C6 | 1.307(4) |
| N3-C7 | 1.293(4) |
| N5-C14 | 1.290(4) |
| N6-C16 | 1.313(4) |
| N2-N3 | 1.392(4) |
| N5-N6 | 1.390(4) |
| **Bond angles (°)** | |
| O2-Dy1-N3 | 170.4(9) |
| O1-Dy1-N5 | 160.9(9) |
| O1M-Dy1-N4 | 148.0(9) |
| O1M-Dy1-Cl1 | 128.5(7) |
| Cl1-Dy1-Cl2 | 155.6(3) |
| O1M-Dy1-N5 | 124.0(9) |
| N3-Dy1-N5 | 123.5(9) |

| | |
|---|---|
| O2-Dy1-N4 | 125.7(8) |
| O1-Dy1-N4 | 122.6(8) |

**Table S2** Selected bond distances (Å) and angles (°) for complex **2**[a]

| **Bond distances (Å)** | | | |
|---|---|---|---|
| Dy1-O1 | 2.373(2) | Dy1-N5 | 2.500(2) |
| Dy1-O2 | 2.331(2) | Dy1-N4 | 2.525(2) |
| Dy1-O3 | 2.383(2) | Dy1-N3 | 2.530(2) |
| Dy1-O2′ | 2.397(2) | Dy1-N7′ | 2.638(2) |
| Dy1-O1M | 2.423(2) | Dy1···Dy1′ | 3.971(3) |
| Dy1-O3A | 2.422(2) | | |
| **Bond angles (°)** | | | |
| Dy1-O2-Dy1′ | 114.3(1) | O2-Dy1-N3 | 150.0(1) |
| O1-Dy1-O3 | 140.7(1) | O2-Dy1-N3′ | 120.8(1) |
| O2-Dy1-O1M′ | 125.5(1) | O3-Dy1-N3 | 116.8(1) |
| O1-Dy1-N5 | 143.1(1) | N5-Dy1-N3 | 119.1(1) |
| O2-Dy1-N5′ | 120.2(1) | O2-Dy1-N7′ | 128.9(1) |
| O2-Dy1-N4 | 125.7(1) | O1M-Dy1-N7′ | 138.2(1) |
| O1-Dy1-N4 | 123.5(1) | N5-Dy1-N7′ | 144.6(1) |
| O2-Dy1-N4′ | 155.8(1) | | |

[a] Symmetry code: (′) 1-*x*, 1-*y*, 1-*z*.

**Table S3** Selected bond distances (Å) and angles (°) for complex **3**·2MeOH[a]

| **Bond distances (Å)** | | | |
|---|---|---|---|
| Dy1-O1 | 2.315(3) | Dy1-N1 | 2.537(4) |
| Dy1-O1′ | 2.389(3) | Dy1-N2 | 2.491(4) |
| Dy1-O4 | 2.409(3) | Dy1-N4′ | 2.600(4) |
| Dy1-O6 | 2.406(3) | Dy1-N7 | 2.512(4) |
| Dy1-O8 | 2.399(3) | Dy1···Dy1′ | 3.958(4) |
| **Bond angles (°)** | | | |

| | | | |
|---|---|---|---|
| O1-Dy1-O4′ | 128.1(1) | O1-Dy1-N4′ | 128.1(1) |
| O1-Dy1-N1′ | 119.8(1) | O1-Dy1-N7′ | 155.1(1) |
| O1-Dy1-N1 | 151.5(1) | O6-Dy1-N1 | 116.5(1) |
| O1-Dy1-N2 | 119.7(1) | O8-Dy1-O6 | 143.9(1) |
| O1-Dy1-N7 | 126.6(1) | O8-Dy1-N2 | 142.2(1) |
| O4-Dy1-N4′ | 139.1(1) | O8-Dy1-N7 | 122.7(1) |
| O6-Dy1-O4 | 142.5(1) | N2-Dy1-N1 | 120.4(1) |
| N2-Dy1-N4 | 142.7(1) | | |

[a] Symmetry code: (′) 1-*x*, 1-*y*, 1-*z*.

**Table S4** Selected bond distances (Å) and angles (°) for complex **4**·2$CH_2Cl_2$[a]

| **Bond distances (Å)** | | | |
|---|---|---|---|
| Dy1-O8 | 2.299(4) | Dy2-O9′ | 2.370(4) |
| Dy1-O1′ | 2.316(4) | Dy2-O6 | 2.376(5) |
| Dy1-O5 | 2.332(4) | Dy2-O2 | 2.415(4) |
| Dy1-O1 | 2.332(4) | Dy2-O3 | 2.419(4) |
| Dy1-O2 | 2.344(4) | Dy2-O1 | 2.434(4) |
| Dy1-O3′ | 2.380(4) | Dy2-N2 | 2.604(5) |
| Dy1-N6′ | 2.567(5) | Dy2-N3 | 2.611(5) |
| Dy1-N7 | 2.615(4) | Dy2-N4 | 2.615(5) |
| Dy1···Dy2 | 3.793(4) | Dy2-O4 | 2.350(4) |
| Dy1′···Dy2 | 3.946(5) | Dy1···Dy1′ | 3.720(5) |
| **Bond angles (°)** | | | |
| Dy1-O2-Dy2 | 105.7(2) | Dy1-O3-Dy2′ | 110.7(2) |
| Dy1-O1-Dy1′ | 106.4(1) | Dy1···Dy1′···Dy2 | 59.2(1) |
| Dy1-O1-Dy2′ | 112.4(2) | Dy1′···Dy2···Dy1 | 57.4(1) |
| Dy1-O1-Dy2 | 105.5(1) | Dy2···Dy1···Dy1′ | 63.4(1) |

[a] Symmetry code: (′) 1-*x*, 1-*y*, 1-*z*.

**Table S5** Continuous Shape Measures (CShM) values for the potential coordination polyhedra of the 8-coordinate $Dy^{III}$ center in the structure of complex **1**

| Polyhedron[a,b] | Dy1 |
|---|---|
| OP | 33.07 |
| HPY | 21.67 |
| **HBPY** | **5.29** |
| CU | 6.95 |
| SAPR | 6.36 |
| TDD | 5.64 |
| JGBF | 7.85 |
| JETBPY | 25.29 |
| JBTPR | 6.77 |
| BTPR | 5.71 |
| JSD | 7.71 |
| TT | 7.66 |
| ETBPY | 20.82 |

[a] Abbreviations: OP, Octagon; HPY, Heptagonal pyramid; HBPY, Hexagonal bipyramid; CU, Cube; SAPR, Square antiprism; TDD, Triangular dodecahedron; JGBF, Johnson gyrobifastigium; JETBPY, Johnson elongated triangular bipyramid; JBTPR, Biaugmented trigonal prism; BTPR, Biaugmented trigonal prism; JSD, Snub diphenoid; TT, Triakis tetrahedron; ETBPY, Elongated trigonal bipyramid. [b] The value in boldface indicates the closest polyhedron according to the Continuous Shape Measures.

**Table S6** Continuous Shape Measures (CShM) values for the potential coordination polyhedra of the 9-coordinate $Dy^{III}$ centers in the structures of complexes **2** and **3**·2MeOH

| Polyhedron[a,b] | Dy1 / Dy1′ (**2**) | Dy1 / Dy1′ (**3**) |
|---|---|---|
| EP | 30.60 | 30.54 |
| OPY | 22.59 | 22.83 |
| HBPY | 16.24 | 17.16 |
| JTC | 15.12 | 14.80 |
| JCCU | 6.95 | 6.54 |
| CCU | 5.73 | 5.34 |
| JCSAPR | 3.77 | 3.62 |

| | | |
|---|---|---|
| CSAPR | 2.77 | 2.65 |
| JTCTPR | 3.72 | 3.52 |
| TCTPR | 3.54 | 3.37 |
| JTDIC | 11.16 | 11.44 |
| HH | 5.80 | 5.94 |
| **MFF** | **2.50** | **2.44** |

[a] Abbreviations: EP, Enneagon; OPY, Octagonal pyramid; HBPY, Heptagonal bipyramid; JTC, Johnson triangular cupola; JCCU, Capped cube; CCU, Spherical-relaxed capped cube; JCSAPR, Capped square antiprism, CSAPR-9, Spherical capped square antiprism; JTCTPR, Tricapped trigonal prism; TCTPR, Spherical tricapped trigonal prism; JTDIC, Tridiminished icosahedron, HH, Hula-hoop; MFF, Muffin. [b] The value in boldface indicates the closest polyhedron according to the Continuous Shape Measures.

**Table S7** Continuous Shape Measures (CShM) values for the potential coordination polyhedra of the 8- and 9-coordinate $Dy^{III}$ centers in the structure of complex **4**·$2CH_2Cl_2$

| Polyhedron[a,c] | Dy1 / Dy1′ | Polyhedron[b,c] | Dy2 / Dy2′ |
|---|---|---|---|
| OP | 32.37 | EP | 32.75 |
| HPY | 22.83 | OPY | 21.61 |
| HBPY | 12.20 | HBPY | 14.84 |
| CU | 8.15 | JTC | 14.89 |
| SAPR | 2.71 | JCCU | 7.46 |
| TDD | 2.68 | CCU | 6.40 |
| JGBF | 12.58 | JCSAPR | 5.20 |
| JETBPY | 25.85 | CSAPR | 4.12 |
| JBTPR | 3.10 | JTCTPR | 4.85 |
| **BTPR** | **2.22** | TCTPR | 4.88 |
| JSD | 4.13 | JTDIC | 12.05 |
| TT | 8.90 | HH | 4.34 |
| ETBPY | 23.82 | **MFF** | **3.16** |

[a] Abbreviations: OP, Octagon; HPY, Heptagonal pyramid; HBPY, Hexagonal bipyramid; CU, Cube; SAPR, Square antiprism; TDD, Triangular dodecahedron; JGBF, Johnson gyrobifastigium;

JETBPY, Johnson elongated triangular bipyramid; JBTPR, Biaugmented trigonal prism; BTPR, Biaugmented trigonal prism; JSD, Snub diphenoid; TT, Triakis tetrahedron; ETBPY, Elongated trigonal bipyramid. [b] Abbreviations: EP, Enneagon; OPY, Octagonal pyramid; HBPY, Heptagonal bipyramid; JTC, Johnson triangular cupola; JCCU, Capped cube; CCU, Spherical-relaxed capped cube; JCSAPR, Capped square antiprism, CSAPR-9, Spherical capped square antiprism; JTCTPR, Tricapped trigonal prism; TCTPR, Spherical tricapped trigonal prism; JTDIC, Tridiminished icosahedron, HH, Hula-hoop; MFF, Muffin. [c] The values in boldface indicate the closest polyhedron according to the Continuous Shape Measures.

**Table S8** Crystallographic data for compounds **1**-**4**.

| Parameter | **1** | **2** | **3**·2MeOH | **4**·2$CH_2Cl_2$ |
|---|---|---|---|---|
| Formula | $C_{22}H_{23}Cl_3DyN_7O_3$ | $C_{50}H_{51.15}Dy_2F_{12}N_{14}O_{20.57}S_4$ | $C_{46}H_{56}Cl_4Dy_2N_{14}O_{26}$ | $C_{56}H_{58}Cl_4Dy_4N_{14}O_{18}$ |
| $F_w$ | 702.32 | 1858.56 | 1687.84 | 2006.96 |
| Crystal system | Triclinic | Triclinic | Triclinic | Triclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| $a$ / Å | 8.1076(3) | 9.8622(2) | 11.7041(3) | 10.8636(9) |
| $b$ / Å | 12.3845(4) | 13.8457(3) | 11.8358(2) | 12.8360(10) |
| $c$ / Å | 13.8914(4) | 13.8813(3) | 12.0835(2) | 14.6728(11) |
| $\alpha$ / ° | 96.823(1) | 102.154(1) | 83.959(2) | 69.412(2) |
| $\beta$ / ° | 94.345(1) | 107.256(1) | 88.819(2) | 83.157(3) |
| $\gamma$ / ° | 97.571(1) | 97.596(1) | 65.389(2) | 84.392(3) |
| $V$ / Å$^3$ | 1366.93(8) | 1730.70(6) | 1512.88(6) | 1898.3(3) |
| $Z$ | 2 | 1 | 1 | 1 |
| $T$ / °C | -93 | -83 | -100 | -123 |
| Radiation / $\mu$ (mm$^{-1}$) | Mo Kα / 3.063 | Mo Kα / 2.375 | Cu Kα / 15.524 | Mo Kα / 4.101 |
| $\rho_{calcd}$ / g cm$^{-3}$ | 1.706 | 1.783 | 1.853 | 1.756 |
| Reflections collected/unique ($R_{int}$) | 23881/5946 (0.0253) | 32057/7562 (0.0320) | 45553/5388 (0.1439) | 150248/9340 (0.0346) |
| Reflections with $I>2\sigma(I)$ | 5538 | 7052 | 5162 | 8382 |
| No. of parameters | 375 | 545 | 424 | 438 |
| $R_1$ [$I>2\sigma(I)$], $wR_2$ [$I>2\sigma(I)$][a,b] | 0.0268, 0.0740 | 0.0268, 0.0628 | 0.0485, 0.1270 | 0.0391, 0.1014 |
| $R_1$ (all data), $wR_2$ (all data)[a,b] | 0.0291, 0.0751 | 0.0294, 0.0640 | 0.0497, 0.1281 | 0.0460, 0.1151 |
| $(\Delta/\sigma)_{max}$ | 0.052 | 0.056 | 0.001 | 0.001 |
| $\Delta\rho_{max}/\Delta\rho_{min}$ (e Å$^{-3}$) | 1.949 / -0.992 | 1.217 / -0.860 | 2.196 / -1.855 | 3.200 / -2.477 |
| CCDC number | 2205399 | 2205400 | 2205298 | 2205303 |

[a] $R_1 = \Sigma(|F_o| - |F_o|) / \Sigma(|F_o|)$.

[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$, $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2, 0) + 2F_c^2] / 3$.