# Supporting Information

# Lanthanide-radical complexes deriving from a nitronyl nitroxide ligand with chelating and bridging function: structure and magnetic properties

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

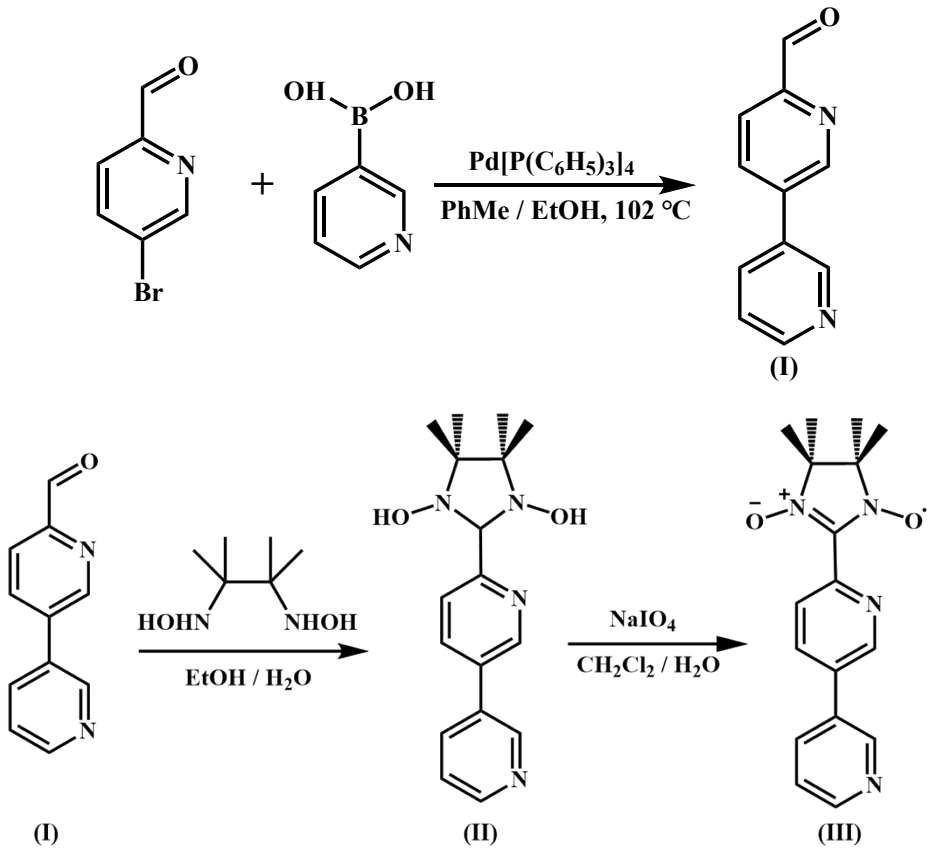
| **1 Gd** | | | |
|---|---|---|---|
| *Bond distances* | | | |
| Gd(1)-O(2) | 2.384(4) | Gd(2)-O(15) | 2.366(4) |
| Gd(1)-N(8) | 2.691(5) | Gd(2)-N(4) | 2.698(5) |
| Gd(1)-O(6) | 2.421(4) | Gd(2)-O(13) | 2.398(4) |
| Gd(1)-O(1) | 2.403(4) | Gd(2)-O(12) | 2.393(4) |
| Gd(1)-O(5) | 2.366(4) | Gd(2)-O(11) | 2.395(4) |
| Gd(1)-O(3) | 2.398(4) | Gd(2)-O(14) | 2.401(4) |
| Gd(1)-O(4) | 2.404(4) | Gd(2)-O(9) | 2.444(4) |
| Gd(1)-O(7) | 2.347(4) | Gd(2)-O(10) | 2.355(4) |
| Gd(1)-N(3) | 2.777(5) | Gd(2)-N(7) | 2.771(5) |
| O(15)-N(5) | 1.292(6) | N(1)-O(7) | 1.289(6) |
| N(2)-O(8) | 1.258(7) | N(46)-O(16) | 1.266(7) |
| *Angles* | | | |
| O(2)-Gd(1)-N(8) | 69.08(14) | O(15)-Gd(2)-O(11) | 99.10(15) |
| O(2)-Gd(1)-N(3) | 72.45(14) | O(15)-Gd(2)-O(14) | 79.91(14) |
| N(8)-Gd(1)-N(3) | 126.79(15) | O(15)-Gd(2)-O(9) | 65.86(14) |
| O(6)-Gd(1)-N(8) | 125.40(15) | O(15)-Gd(2)-N(7) | 65.11(14) |
| O(6)-Gd(1)-N(3) | 107.57(15) | N(4)-Gd(2)-N(7) | 128.09(15) |
| O(1)-Gd(1)-N(8) | 68.77(14) | O(13)-Gd(2)-N(4) | 68.48(14) |
| O(1)-Gd(1)-N(3) | 66.07(14) | O(12)-Gd(2)-N(4) | 69.77(14) |
| O(5)-Gd(1)-N(8) | 66.34(14) | O(12)-Gd(2)-N(7) | 138.21(14) |
| O(5)-Gd(1)-N(3) | 136.00(14) | O(11)-Gd(2)-N(4) | 128.51(14) |
| O(3)-Gd(1)-N(8) | 70.10(14) | O(11)-Gd(2)-N(7) | 69.65(14) |
| O(3)-Gd(1)-N(3) | 139.51(14) | O(14)-Gd(2)-N(4) | 70.34(14) |
| O(4)-Gd(1)-N(8) | 129.06(14) | O(14)-Gd(2)-N(7) | 66.33(14) |
| O(4)-Gd(1)-N(3) | 71.54(14) | O(9)-Gd(2)-N(4) | 124.06(14) |
| O(7)-Gd(1)-N(8) | 126.66(15) | O(9)-Gd(2)-N(7) | 107.78(14) |
| O(7)-Gd(1)-N(3) | 65.92(14) | O(10)-Gd(2)-N(4) | 66.97(15) |
| O(15)-Gd(2)-N(4) | 132.35(15) | O(10)-Gd(2)-N(7) | 134.88(14) |
| O(15)-Gd(2)-O(13) | 136.94(14) | N(5)-O(15)-Gd(2) | 129.4(4) |
| O(15)-Gd(2)-O(12) | 135.90(14) | N(1)-O(7)-Gd(1) | 132.6(3) |

| 2 Nd | | | |
|---|---|---|---|
| *Bond distances* | | | |
| Nd(1)-O(2) | 2.454(6) | Nd(2)-O(8) | 2.403(6) |
| Nd(1)-O(3) | 2.426(6) | Nd(2)-O(12) | 2.433(6) |
| Nd(1)-O(7) | 2.419(7) | Nd(2)-O(9) | 2.447(5) |
| Nd(1)-O(4) | 2.451(6) | Nd(2)-O(11) | 2.451(6) |
| Nd(1)-O(1) | 2.381(6) | Nd(2)-O(10) | 2.446(6) |
| Nd(1)-O(6) | 2.429(8) | Nd(2)-O(14) | 2.402(6) |
| Nd(1)-O(5) | 2.450(6) | Nd(2)-O(13) | 2.470(6) |
| Nd(1)-N(2) | 2.686(7) | Nd(2)-N(6) | 2.728(8) |
| Nd(1)-N(1) | 2.792(8) | Nd(2)-N(3) | 2.796(8) |
| O(1)-N(4) | 1.291(10) | O(16)-N(5) | 1.261(11) |
| O(8)-N(8) | 1.279(10) | O(15)-N(7) | 1.248(12) |
| *Angles* | | | |
| O(2)-Nd(1)-N(1) | 65.5(2) | O(8)-Nd(2)-O(12) | 98.1(2) |
| O(3)-Nd(1)-N(2) | 69.7(2) | O(8)-Nd(2)-O(9) | 81.2(2) |
| O(3)-Nd(1)-N(1) | 72.3(2) | O(8)-Nd(2)-O(11) | 136.4(2) |
| O(7)-Nd(1)-N(2) | 66.3(2) | O(8)-Nd(2)-O(10) | 136.0(2) |
| O(7)-Nd(1)-N(1) | 135.3(2) | O(8)-Nd(2)-O(13) | 66.4(2) |
| O(4)-Nd(1)-N(2) | 128.9(2) | O(8)-Nd(2)-N(6)#1 | 133.1(2) |
| O(4)-Nd(1)-N(1) | 72.5(2) | O(8)-Nd(2)-N(3) | 64.0(2) |
| O(1)-Nd(1)-O(2) | 76.0(2) | O(12)-Nd(2)-N(6)#1 | 128.7(2) |
| O(1)-Nd(1)-O(3) | 134.2(2) | O(12)-Nd(2)-N(3) | 69.6(2) |
| O(1)-Nd(1)-O(7) | 73.7(2) | O(9)-Nd(2)-N(6)#1 | 70.1(2) |
| O(1)-Nd(1)-O(4) | 105.0(2) | O(9)-Nd(2)-N(3) | 66.4(2) |
| O(1)-Nd(1)-O(6) | 69.5(2) | O(11)-Nd(2)-N(6)#1 | 70.2(2) |
| O(1)-Nd(1)-O(5) | 140.2(2) | O(11)-Nd(2)-N(3) | 137.1(2) |
| O(1)-Nd(1)-N(2) | 126.1(2) | O(10)-Nd(2)-N(6)#1 | 68.4(2) |
| O(1)-Nd(1)-N(1) | 65.1(2) | O(10)-Nd(2)-N(3) | 73.5(2) |
| O(6)-Nd(1)-N(2) | 123.9(2) | O(14)-Nd(2)-O(8) | 76.0(2) |
| O(6)-Nd(1)-N(1) | 108.3(2) | O(14)-Nd(2)-N(6)#1 | 66.7(2) |
| O(5)-Nd(1)-N(2) | 70.0(2) | O(14)-Nd(2)-N(3) | 134.4(2) |
| O(5)-Nd(1)-N(1) | 139.3(2) | O(13)-Nd(2)-N(6)#1 | 122.0(2) |
| N(2)-Nd(1)-N(1) | 127.4(2) | O(13)-Nd(2)-N(3) | 109.0(2) |
| N(8)-O(8)-Nd(2) | 128.9(6) | N(6)#1-Nd(2)-N(3) | 128.8(2) |
| N(4)-O(1)-Nd(1) | 131.9(5) | O(2)-Nd(1)-N(2) | 68.9(2) |

**Table S2.** Selected bond distances (Å) and angles (deg) for complex **2**.

**Table S3.** Selected bond distances (Å) and angles (deg) for complex **3**.

| **3 Dy** | | | |
|---|---|---|---|
| *Bond distances* | | | |
| Dy(1)-O(5) | 2.337(8) | Dy(2)-O(20) | 2.313(7) |
| Dy(1)-O(4) | 2.368(8) | Dy(2)-O(17) | 2.318(7) |
| Dy(1)-O(2) | 2.315(8) | Dy(3)-O(9) | 2.352(9) |
| Dy(1)-O(3) | 2.343(7) | Dy(3)-O(11) | 2.320(9) |
| Dy(1)-O(6) | 2.293(9) | Dy(3)-O(8) | 2.297(8) |
| Dy(1)-O(1) | 2.305(9) | Dy(3)-O(10) | 2.328(8) |
| Dy(1)-O(7) | 2.332(9) | Dy(3)-O(13) | 2.330(10) |
| Dy(1)-N(1) | 2.604(9) | Dy(3)-N(2) | 2.619(9) |
| Dy(2)-O(19) | 2.350(7) | Dy(3)-O(14) | 2.312(9) |
| Dy(2)-O(18) | 2.353(7) | Dy(3)-O(12) | 2.359(10) |
| Dy(2)-O(15) | 2.322(7) | O(8)-N(7) | 1.303(11) |
| Dy(2)-O(16) | 2.331(8) | O(22)-N(8) | 1.254(13) |
| Dy(2)-N(4) | 2.543(9) | O(1)-N(5) | 1.287(12) |
| Dy(2)-N(3) | 2.570(8) | O(21)-N(6) | 1.254(13) |
| *Angles* | | | |
| O(1)-Dy(1)-O(5) | 141.3(3) | O(16)-Dy(2)-N(4) | 112.1(3) |
| O(1)-Dy(1)-O(4) | 78.9(3) | O(16)-Dy(2)-N(3) | 78.6(3) |
| O(1)-Dy(1)-O(2) | 82.1(3) | N(4)-Dy(2)-N(3) | 141.8(3) |
| O(1)-Dy(1)-O(3) | 141.3(3) | N(7)-O(8)-Dy(3) | 125.3(7) |
| O(1)-Dy(1)-O(7) | 70.1(3) | O(18)-Dy(2)-N(3) | 119.6(3) |
| O(1)-Dy(1)-N(1) | 70.3(3) | O(15)-Dy(2)-N(4) | 74.9(3) |
| O(6)-Dy(1)-O(1) | 109.8(4) | O(7)-Dy(1)-N(1) | 117.1(3) |
| O(6)-Dy(1)-N(1) | 76.3(3) | O(9)-Dy(3)-N(2) | 70.3(3) |
| O(4)-Dy(1)-N(1) | 71.8(3) | O(11)-Dy(3)-N(2) | 78.9(3) |
| O(2)-Dy(1)-N(1) | 141.2(3) | O(8)-Dy(3)-O(9) | 83.5(3) |
| O(3)-Dy(1)-N(1) | 144.2(3) | O(8)-Dy(3)-O(10) | 143.4(3) |
| O(5)-Dy(1)-N(1) | 76.3(3) | O(8)-Dy(3)-O(13) | 71.8(3) |
| N(5)-O(1)-Dy(1) | 127.6(7) | O(8)-Dy(3)-N(2) | 69.0(3) |
| O(20)-Dy(2)-N(4) | 143.5(2) | O(8)-Dy(3)-O(14) | 80.3(3) |
| O(20)-Dy(2)-N(3) | 72.5(3) | O(8)-Dy(3)-O(12) | 141.5(4) |
| O(17)-Dy(2)-N(4) | 76.2(3) | O(10)-Dy(3)-N(2) | 77.1(3) |
| O(17)-Dy(2)-N(3) | 76.3(3) | O(13)-Dy(3)-N(2) | 119.2(3) |
| O(19)-Dy(2)-N(4) | 77.1(3) | O(14)-Dy(3)-N(2) | 136.4(3) |
| O(19)-Dy(2)-N(3) | 139.1(3) | O(12)-Dy(3)-N(2) | 146.2(3) |
| O(18)-Dy(2)-N(4) | 75.5(3) | O(14)-Dy(3)-O(11) | 142.4(3) |




**Sceme S1.** The synthesis of NIT-2Py-3Py radical ligand.

**Table S4.** SHAPE analyses for complexes **1–2**.

| Complex | CSAPR-9 | MFF-9 | JCSAPR-9 | TCTPR-9 |
|---|---|---|---|---|
| **1 Gd1** | **0.505** | 0.912 | 0.915 | 1.413 |
| **1 Gd2** | **0.611** | 1.079 | 1.033 | 1.706 |
| **2 Nd1** | **0.528** | 0.804 | 1.071 | 1.368 |
| **2 Nd2** | **0.724** | 1.072 | 1.204 | 1.750 |

MFF-9: $C_s$, Muffin; CSAPR-9: $C_{4v}$, Spherical capped square antiprism; JCSAPR-9: $C_{4v}$, Capped square antiprism J10; TCTPR-9: $D_{3h}$, Spherical tricapped trigonal prism.

**Table S5.** SHAPE analysis for complex **3**.

| Complex | SAPR-8 | JBTPR-8 | BTPR-8 | TDD-8 |
|---|---|---|---|---|
| **3 Dy1** | **0.359** | 2.035 | 1.904 | 2.096 |
| **3 Dy2** | **0.394** | 2.257 | 2.047 | 2.143 |
| **3 Dy3** | **0.462** | 2.006 | 1.911 | 2.113 |

SAPR-8: $D_{4d}$, Square antiprism; JBTPR-8: $C_{2v}$, Biaugmented trigonal prism J50; BTPR-8: $C_{2v}$, Biaugmented trigonal prism; TDD-8: $D_{2d}$, Triangular dodecahedron.

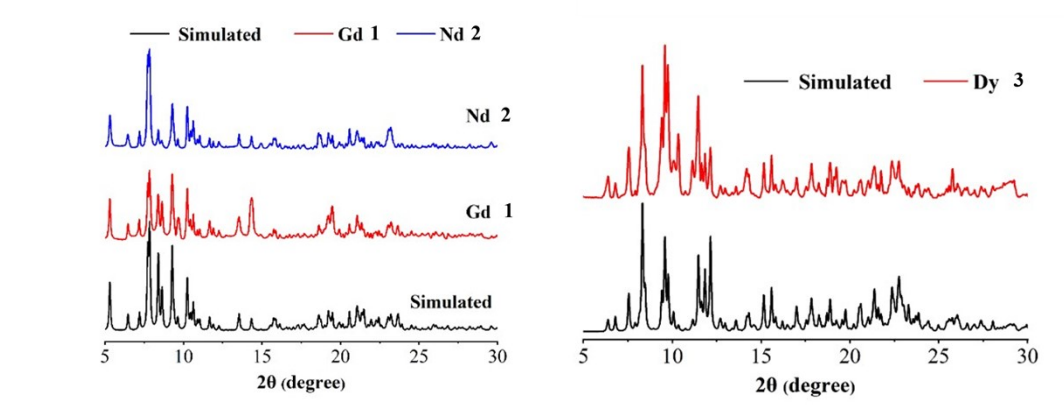



**Fig. S1.** The PXRD pattern of complexes **1-3**.

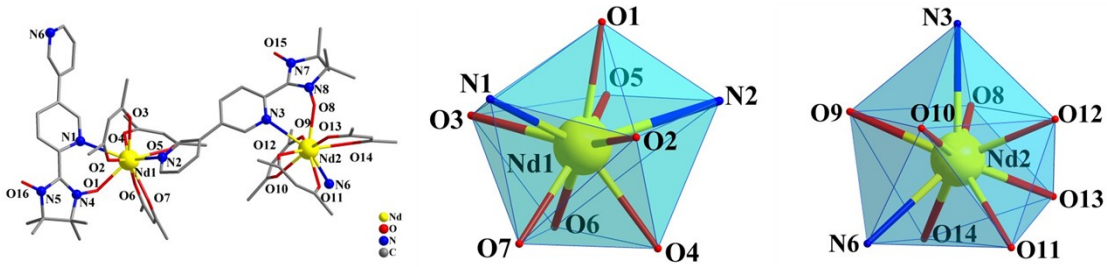



**Fig. S2.** Asymmetric structural unit of **2** (H and F atoms are omitted for clarity) (left); the coordination polyhedra of $Nd^{III}$ ions in **2** (right).

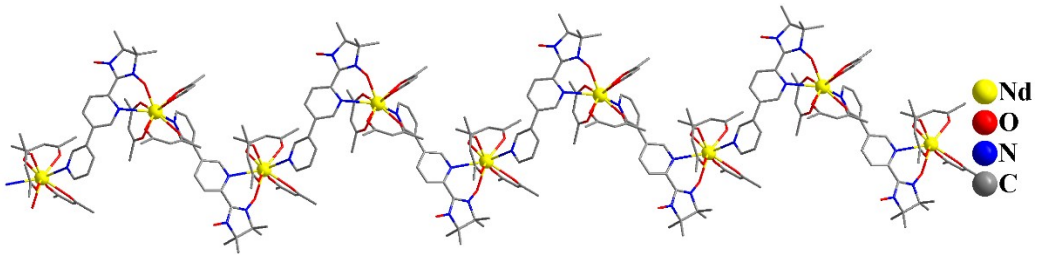



**Fig. S3.** One-dimensional structure of **2** (H and F atoms are omitted for clarity).

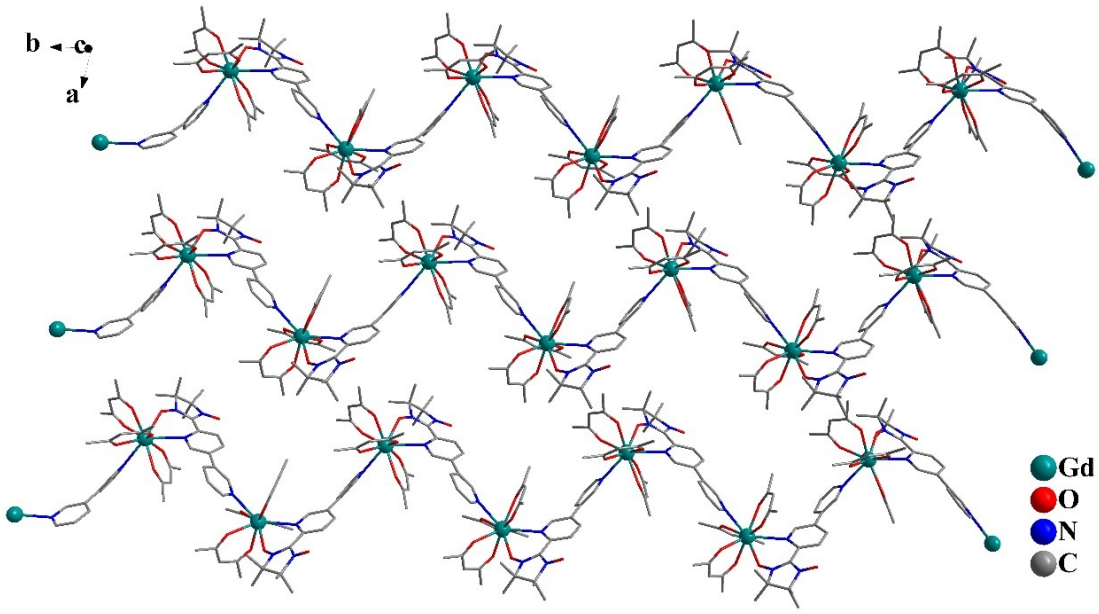



**Fig. S4.** Crystal packing diagram of **1** (H and F atoms are omitted).

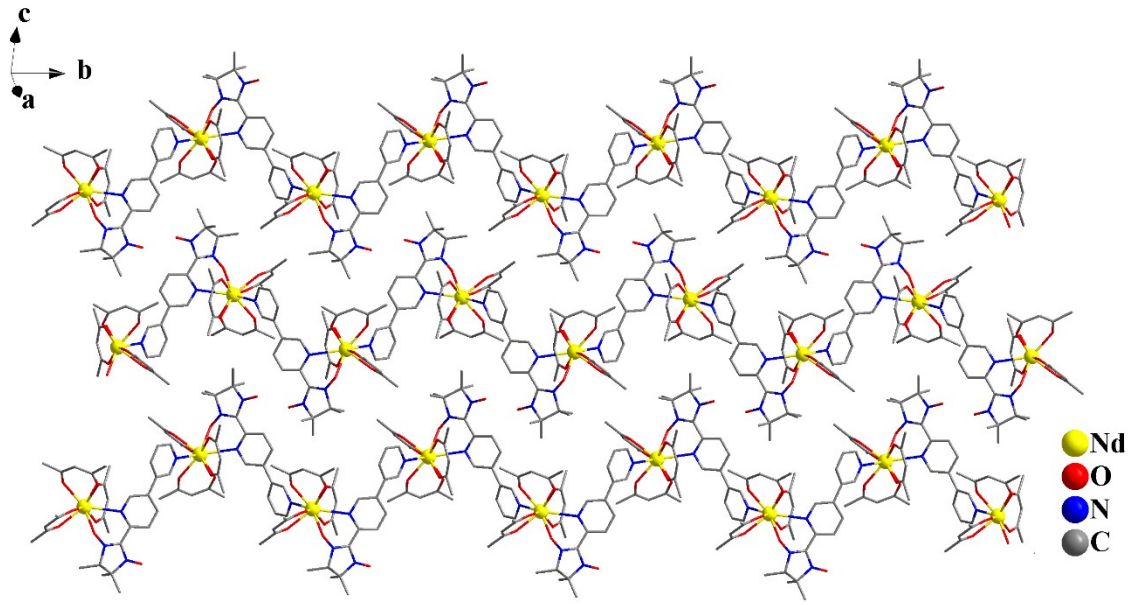



**Fig. S5**. Crystal packing diagram of **2** (H and F atoms are omitted).

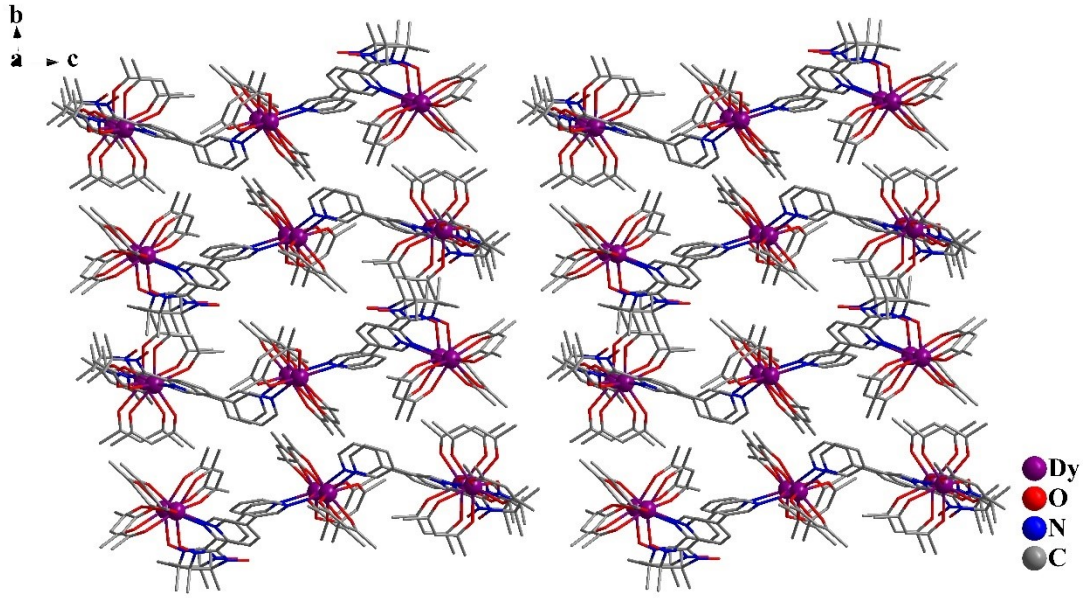



**Fig. S6**. Crystal packing diagram of **3** (H and F atoms are omitted).

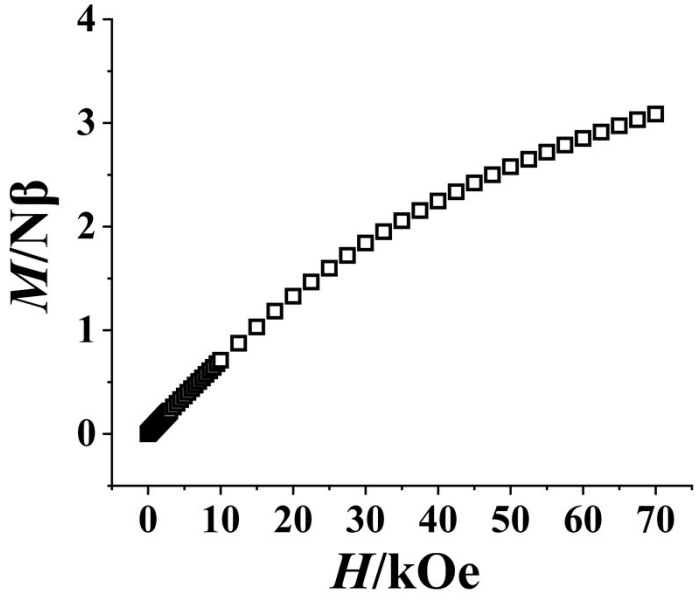



**Fig. S7.** Magnetization versus applied field curve measured at 2 K for complex **2**.

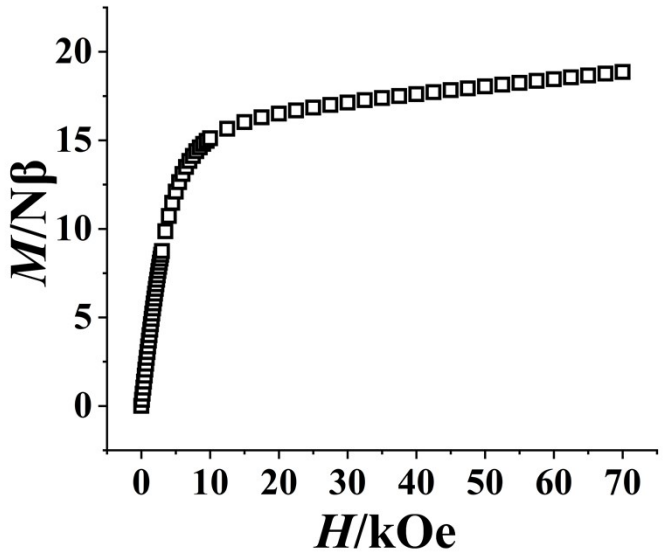



**Fig S8.** Magnetization versus applied field curve measured at 2 K for complex **3**.

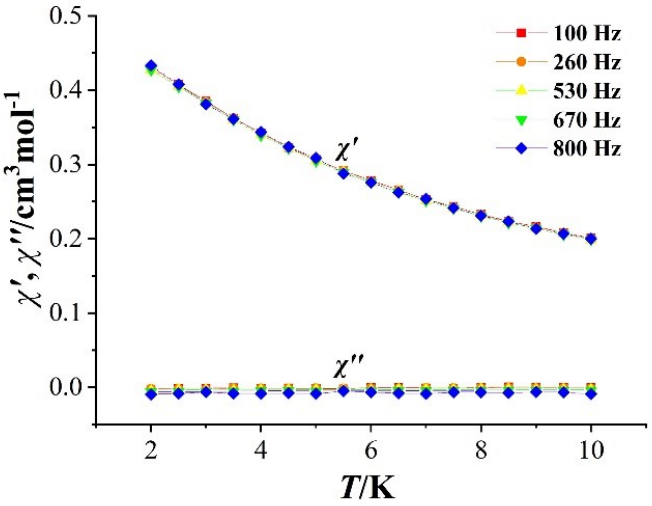



**Fig. S9.** Frequency-dependent ac signals of $\chi'$ and $\chi'$ under 0 Oe dc field for **2**.

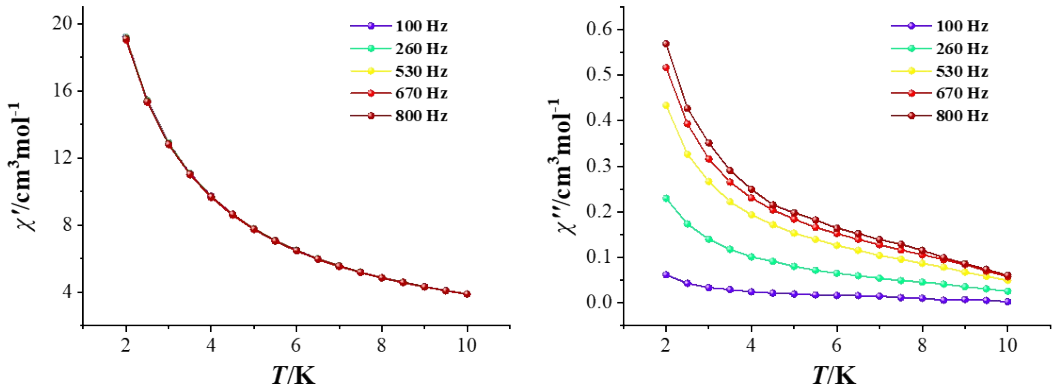



**Fig. S10.** Variable temperature $\chi'$ and $\chi''$ curves for complex **3** under a zero dc field.

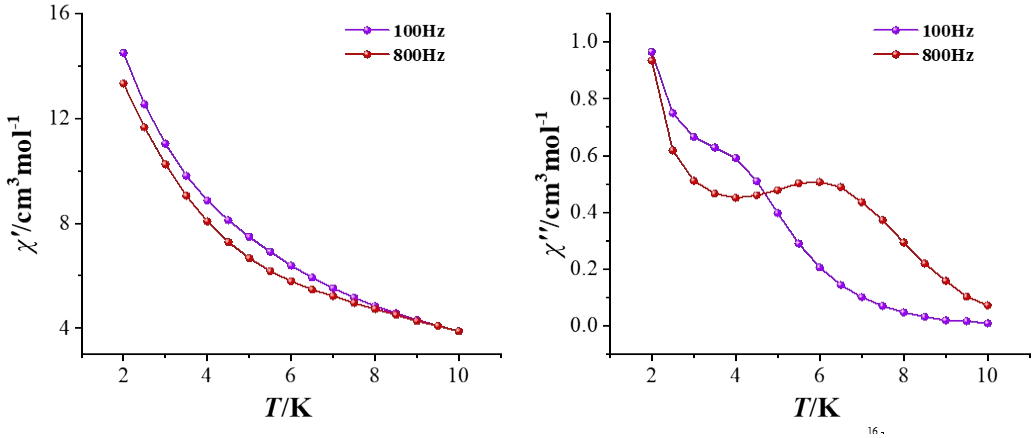



**Fig. S11.** Variable temperature $\chi'$ and $\chi''$curves for complex **3** under 1000 Oe dc field.