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# Supporting Information

# Slow relaxation of magnetization in unprecedented Cu-Ln-Rad hetero-tri-spin chains constructed from multidentate nitronyl nitroxide

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**Table S1**. Selected bond lengths [Å] and angles [°] for **1**.

| | | | |
|---|---|---|---|
| *Bond distances* | | | |
| Gd(1)-O(2) | 2.354(8) | Gd(1)-O(9) | 2.326(9) |
| Gd(1)-O(6) | 2.378(8) | Gd(1)-O(5) | 2.334(9) |
| Gd(1)-O(11) | 2.429(9) | Gd(1)-O(10) | 2.361(10) |
| Gd(1)-O(7) | 2.391(9) | Gd(1)-O(8) | 2.359(9) |
| Cu(2)-O(15) | 1.935(8) | Cu(2)-O(13) | 1.943(8) |
| Cu(2)-O(14) | 1.920(8) | Cu(2)-O(12) | 2.180(9) |
| Cu(2)-N(3) | 2.007(9) | Cu(3)-O(16)#1 | 1.998(8) |
| Cu(3)-O(16) | 1.998(8) | Cu(3)-O(17)#1 | 2.276(9) |
| Cu(3)-O(17) | 2.276(9) | Cu(3)-N(4)#1 | 2.029(9) |
| Cu(3)-N(4) | 2.029(9) | Cu(1)-O(4)#2 | 1.944(9) |
| Cu(1)-O(4) | 1.943(9) | Cu(1)-O(3)#2 | 1.939(8) |
| Cu(1)-O(3) | 1.939(8) | Cu(1)-O(1) | 2.423(9) |
| Cu(1)-O(1)#2 | 2.423(9) | O(2)-N(2) | 1.294(12) |
| O(1)-N(1) | 1.258(12) | | |
| *Angles* | | | |
| O(2)-Gd(1)-O(6) | 73.0(3) | O(2)-Gd(1)-O(11) | 74.4(3) |
| O(2)-Gd(1)-O(10) | 144.9(3) | O(2)-Gd(1)-O(7) | 73.1(3) |
| O(2)-Gd(1)-O(8) | 142.0(3) | O(9)-Gd(1)-O(2) | 99.6(3) |
| O(9)-Gd(1)-O(6) | 82.1(3) | O(9)-Gd(1)-O(5) | 145.5(3) |
| O(9)-Gd(1)-O(11) | 141.6(3) | O(9)-Gd(1)-O(10) | 73.2(3) |
| O(9)-Gd(1)-O(7) | 70.5(3) | O(9)-Gd(1)-O(8) | 83.9(3) |
| O(6)-Gd(1)-O(11) | 129.1(3) | O(6)-Gd(1)-O(7) | 131.4(3) |
| O(5)-Gd(1)-O(2) | 96.1(3) | O(5)-Gd(1)-O(6) | 73.4(3) |
| O(5)-Gd(1)-O(11) | 72.4(3) | O(5)-Gd(1)-O(10) | 76.2(3) |
| O(5)-Gd(1)-O(7) | 143.9(3) | O(5)-Gd(1)-O(8) | 102.0(3) |
| O(10)-Gd(1)-O(6) | 72.0(3) | O(10)-Gd(1)-O(11) | 132.1(3) |
| O(10)-Gd(1)-O(7) | 131.5(3) | O(7)-Gd(1)-O(11) | 71.5(3) |
| O(8)-Gd(1)-O(6) | 144.3(3) | O(8)-Gd(1)-O(11) | 79.6(3) |
| O(8)-Gd(1)-O(10) | 72.5(3) | O(8)-Gd(1)-O(7) | 72.6(3) |
| O(15)-Cu(2)-O(13) | 174.1(4) | O(15)-Cu(2)-O(12) | 97.0(4) |
| O(15)-Cu(2)-N(3) | 89.5(4) | O(13)-Cu(2)-O(12) | 88.7(4) |
| O(13)-Cu(2)-N(3) | 90.9(4) | O(14)-Cu(2)-O(15) | 90.1(4) |
| O(14)-Cu(2)-O(13) | 87.7(4) | O(14)-Cu(2)-O(12) | 95.0(4) |
| O(14)-Cu(2)-N(3) | 161.6(4) | N(3)-Cu(2)-O(12) | 103.2(4) |
| O(16)#1-Cu(3)-O(16) | 180.0 | O(16)#1-Cu(3)-O(17) | 92.9(3) |
| O(16)-Cu(3)-O(17) | 87.1(3) | O(16)-Cu(3)-O(17)#1 | 92.9(3) |
| O(16)#1-Cu(3)-O(17)#1 | 87.1(3) | O(16)#1-Cu(3)-N(4)#1 | 90.4(3) |
| O(16)-Cu(3)-N(4) | 90.4(3) | O(16)#1-Cu(3)-N(4) | 89.6(3) |
| O(16)-Cu(3)-N(4)#1 | 89.6(3) | O(17)#1-Cu(3)-O(17) | 180.0 |
| N(4)-Cu(3)-O(17)#1 | 90.2(4) | N(4)#1-Cu(3)-O(17)#1 | 89.8(4) |
| N(4)#1-Cu(3)-O(17) | 90.2(4) | N(4)-Cu(3)-O(17) | 89.8(4) |
| N(4)#1-Cu(3)-N(4) | 180.0(5) | O(4)-Cu(1)-O(4)#2 | 180.0 |
| O(4)#2-Cu(1)-O(1)#2 | 80.8(3) | O(4)-Cu(1)-O(1)#2 | 99.2(3) |
| O(4)#2-Cu(1)-O(1) | 99.2(3) | O(4)-Cu(1)-O(1) | 80.8(3) |
| O(3)-Cu(1)-O(4)#2 | 87.4(4) | O(3)-Cu(1)-O(4) | 92.6(4) |
| O(3)#2-Cu(1)-O(4)#2 | 92.6(4) | O(3)#2-Cu(1)-O(4) | 87.4(4) |
| O(3)#2-Cu(1)-O(3) | 180.0 | O(3)#2-Cu(1)-O(1)#2 | 87.3(4) |
| O(3)-Cu(1)-O(1) | 87.3(4) | O(3)-Cu(1)-O(1)#2 | 92.7(4) |
| O(3)#2-Cu(1)-O(1) | 92.7(4) | O(1)-Cu(1)-O(1)#2 | 180.0 |
| N(2)-O(2)-Gd(1) | 138.8(7) | N(1)-O(1)-Cu(1) | 158.2(8) |

#1 -x+1,-y+1,-z  #2 -x+1,-y,-z+1

**Table S2**. Selected bond lengths [Å] and angles [°] for **2**.

| Bond distances | | | |
|---|---|---|---|
| Tb(1)-O(9) | 2.324(5) | Cu(3)-O(16) | 1.989(5) |
| Tb(1)-O(8) | 2.326(6) | Cu(3)-N(4) | 2.028(6) |
| Tb(1)-O(5) | 2.333(5) | Cu(3)-N(4)#1 | 2.028(6) |
| Tb(1)-O(2) | 2.338(4) | Cu(3)-O(17) | 2.285(5) |
| Tb(1)-O(10) | 2.353(5) | Cu(3)-O(17)#1 | 2.285(5) |
| Tb(1)-O(6) | 2.365(5) | Cu(1)-O(4)#2 | 1.937(5) |
| Tb(1)-O(7) | 2.377(5) | Cu(1)-O(4) | 1.937(5) |
| Tb(1)-O(11) | 2.402(5) | Cu(1)-O(3) | 1.939(5) |
| Cu(2)-O(15) | 1.930(5) | Cu(1)-O(3)#2 | 1.939(5) |
| Cu(2)-O(13) | 1.936(5) | Cu(1)-O(1) | 2.397(5) |
| Cu(2)-O(14) | 1.945(5) | Cu(1)-O(1)#2 | 2.397(5) |
| Cu(2)-N(3) | 2.011(5) | O(2)-N(2) | 1.303(7) |
| Cu(2)-O(12) | 2.180(6) | O(1)-N(1) | 1.274(8) |
| Cu(3)-O(16)#1 | 1.989(5) | | |
| Angles | | | |
| O(9)-Tb(1)-O(8) | 82.8(2) | O(13)-Cu(2)-O(12) | 88.7(2) |
| O(9)-Tb(1)-O(5) | 145.88(19) | O(14)-Cu(2)-O(12) | 95.2(3) |
| O(8)-Tb(1)-O(5) | 102.0(2) | N(3)-Cu(2)-O(12) | 102.9(2) |
| O(9)-Tb(1)-O(2) | 100.80(17) | O(16)#1-Cu(3)-O(16) | 180.0(2) |
| O(8)-Tb(1)-O(2) | 141.9(2) | O(16)#1-Cu(3)-N(4) | 89.4(2) |
| O(5)-Tb(1)-O(2) | 95.76(17) | O(16)-Cu(3)-N(4) | 90.6(2) |
| O(9)-Tb(1)-O(10) | 73.49(18) | O(16)#1-Cu(3)-N(4)#1 | 90.6(2) |
| O(8)-Tb(1)-O(10) | 72.6(2) | O(16)-Cu(3)-N(4)#1 | 89.4(2) |
| O(5)-Tb(1)-O(10) | 75.87(19) | N(4)-Cu(3)-N(4)#1 | 180 |
| O(2)-Tb(1)-O(10) | 145.17(17) | O(16)#1-Cu(3)-O(17) | 92.38(18) |
| O(9)-Tb(1)-O(6) | 82.88(18) | O(16)-Cu(3)-O(17) | 87.62(18) |
| O(8)-Tb(1)-O(6) | 144.36(19) | N(4)-Cu(3)-O(17) | 89.6(2) |
| O(5)-Tb(1)-O(6) | 73.68(19) | N(4)#1-Cu(3)-O(17) | 90.4(2) |
| O(2)-Tb(1)-O(6) | 73.10(16) | O(16)#1-Cu(3)-O(17)#1 | 87.62(18) |
| O(10)-Tb(1)-O(6) | 72.10(18) | O(16)-Cu(3)-O(17)#1 | 92.38(18) |
| O(9)-Tb(1)-O(7) | 70.46(18) | N(4)-Cu(3)-O(17)#1 | 90.4(2) |
| O(8)-Tb(1)-O(7) | 72.0(2) | N(4)#1-Cu(3)-O(17)#1 | 89.6(2) |
| O(5)-Tb(1)-O(7) | 143.4(2) | O(17)-Cu(3)-O(17)#1 | 180 |
| O(2)-Tb(1)-O(7) | 73.59(18) | O(4)#2-Cu(1)-O(4) | 180 |
| O(10)-Tb(1)-O(7) | 131.71(19) | O(4)#2-Cu(1)-O(3) | 87.1(2) |
| O(6)-Tb(1)-O(7) | 131.88(19) | O(4)-Cu(1)-O(3) | 92.9(2) |
| O(9)-Tb(1)-O(11) | 141.5(2) | O(4)#2-Cu(1)-O(3)#2 | 92.9(2) |
| O(8)-Tb(1)-O(11) | 79.3(2) | O(4)-Cu(1)-O(3)#2 | 87.1(2) |
| O(5)-Tb(1)-O(11) | 71.8(2) | O(3)-Cu(1)-O(3)#2 | 180 |
| O(2)-Tb(1)-O(11) | 74.60(17) | O(4)#2-Cu(1)-O(1) | 99.8(2) |
| O(10)-Tb(1)-O(11) | 131.01(18) | O(4)-Cu(1)-O(1) | 80.2(2) |
| O(6)-Tb(1)-O(11) | 129.18(19) | O(3)-Cu(1)-O(1) | 87.3(2) |
| O(7)-Tb(1)-O(11) | 71.7(2) | O(3)#2-Cu(1)-O(1) | 92.7(2) |
| O(15)-Cu(2)-O(13) | 173.5(2) | O(4)#2-Cu(1)-O(1)#2 | 80.2(2) |
| O(15)-Cu(2)-O(14) | 90.3(2) | O(4)-Cu(1)-O(1)#2 | 99.8(2) |
| O(13)-Cu(2)-O(14) | 87.6(2) | O(3)-Cu(1)-O(1)#2 | 92.7(2) |
| O(15)-Cu(2)-N(3) | 89.1(2) | O(3)#2-Cu(1)-O(1)#2 | 87.3(2) |
| O(13)-Cu(2)-N(3) | 90.9(2) | O(1)-Cu(1)-O(1)#2 | 180 |
| O(14)-Cu(2)-N(3) | 161.8(3) | N(2)-O(2)-Tb(1) | 138.9(4) |
| O(15)-Cu(2)-O(12) | 97.5(2) | N(1)-O(1)-Cu(1) | 157.7(5) |

#1 -x+1,-y+1,-z  #2 -x+1,-y,-z+1

**Table S3**. Selected bond lengths [Å] and angles [°] for **3**.

| *Bond distances* | | | |
|---|---|---|---|
| Dy(1)-O(5) | 2.319(6) | Dy(1)-O(9) | 2.323(6) |
| Dy(1)-O(2) | 2.331(5) | Dy(1)-O(8) | 2.334(7) |
| Dy(1)-O(10) | 2.357(6) | Dy(1)-O(6) | 2.360(6) |
| Dy(1)-O(7) | 2.371(6) | Dy(1)-O(11) | 2.400(6) |
| Cu(2)-O(15) | 1.926(6) | Cu(2)-O(14) | 1.941(6) |
| Cu(2)-O(13) | 1.947(6) | Cu(2)-N(3) | 2.009(6) |
| Cu(2)-O(12) | 2.185(7) | Cu(3)-O(16)#1 | 1.997(6) |
| Cu(3)-O(16) | 1.997(6) | Cu(3)-N(4)#1 | 2.038(7) |
| Cu(3)-N(4) | 2.038(7) | Cu(3)-O(17)#1 | 2.287(6) |
| Cu(3)-O(17) | 2.287(6) | Cu(1)-O(4) | 1.931(6) |
| Cu(1)-O(4)#2 | 1.931(6) | Cu(1)-O(3)#2 | 1.950(5) |
| Cu(1)-O(3) | 1.950(5) | Cu(1)-O(1)#2 | 2.414(6) |
| Cu(1)-O(1) | 2.414(6) | O(2)-N(2) | 1.299(8) |
| O(1)-N(1) | 1.262(9) | | |
| *Angles* | | | |
| O(5)-Dy(1)-O(9) | 145.7(2) | O(5)-Dy(1)-O(2) | 96.8(2) |
| O(9)-Dy(1)-O(2) | 99.5(2) | O(5)-Dy(1)-O(8) | 101.0(2) |
| O(9)-Dy(1)-O(8) | 83.9(2) | O(2)-Dy(1)-O(8) | 142.4(2) |
| O(5)-Dy(1)-O(10) | 75.5(2) | O(9)-Dy(1)-O(10) | 73.9(2) |
| O(2)-Dy(1)-O(10) | 145.1(2) | O(8)-Dy(1)-O(10) | 72.0(2) |
| O(5)-Dy(1)-O(6) | 74.1(2) | O(9)-Dy(1)-O(6) | 82.1(2) |
| O(2)-Dy(1)-O(6) | 73.1(2) | O(8)-Dy(1)-O(6) | 143.8(2) |
| O(10)-Dy(1)-O(6) | 72.1(2) | O(5)-Dy(1)-O(7) | 143.5(2) |
| O(9)-Dy(1)-O(7) | 70.6(2) | O(2)-Dy(1)-O(7) | 73.5(2) |
| O(8)-Dy(1)-O(7) | 72.4(3) | O(10)-Dy(1)-O(7) | 131.6(2) |
| O(6)-Dy(1)-O(7) | 132.0(2) | O(5)-Dy(1)-O(11) | 71.5(2) |
| O(9)-Dy(1)-O(11) | 142.1(2) | O(2)-Dy(1)-O(11) | 74.8(2) |
| O(8)-Dy(1)-O(11) | 79.8(2) | O(10)-Dy(1)-O(11) | 131.0(2) |
| O(6)-Dy(1)-O(11) | 128.9(2) | O(7)-Dy(1)-O(11) | 71.9(2) |
| O(15)-Cu(2)-O(14) | 90.1(3) | O(15)-Cu(2)-O(13) | 173.7(3) |
| O(14)-Cu(2)-O(13) | 88.0(3) | O(15)-Cu(2)-N(3) | 89.3(2) |
| O(14)-Cu(2)-N(3) | 162.6(3) | O(13)-Cu(2)-N(3) | 90.8(3) |
| O(15)-Cu(2)-O(12) | 97.5(3) | O(14)-Cu(2)-O(12) | 95.0(3) |
| O(13)-Cu(2)-O(12) | 88.6(3) | N(3)-Cu(2)-O(12) | 102.4(3) |
| O(16)#1-Cu(3)-O(16) | 180.0 | O(16)#1-Cu(3)-N(4)#1 | 90.4(3) |
| O(16)-Cu(3)-N(4)#1 | 89.6(3) | O(16)#1-Cu(3)-N(4) | 89.6(3) |
| O(16)-Cu(3)-N(4) | 90.4(3) | N(4)#1-Cu(3)-N(4) | 180.0 |
| O(16)#1-Cu(3)-O(17)#1 | 87.5(2) | O(16)-Cu(3)-O(17)#1 | 92.5(2) |
| N(4)#1-Cu(3)-O(17)#1 | 89.8(3) | N(4)-Cu(3)-O(17)#1 | 90.2(3) |
| O(16)#1-Cu(3)-O(17) | 92.5(2) | O(16)-Cu(3)-O(17) | 87.5(2) |
| N(4)#1-Cu(3)-O(17) | 90.2(3) | N(4)-Cu(3)-O(17) | 89.8(3) |
| O(17)#1-Cu(3)-O(17) | 180.0 | O(4)-Cu(1)-O(4)#2 | 180.0 |
| O(4)-Cu(1)-O(3)#2 | 87.2(2) | O(4)#2-Cu(1)-O(3)#2 | 92.8(2) |
| O(4)-Cu(1)-O(3) | 92.8(2) | O(4)#2-Cu(1)-O(3) | 87.2(2) |
| O(3)#2-Cu(1)-O(3) | 180.0 | O(4)-Cu(1)-O(1)#2 | 99.0(2) |
| O(4)#2-Cu(1)-O(1)#2 | 81.0(2) | O(3)#2-Cu(1)-O(1)#2 | 87.6(3) |
| O(3)-Cu(1)-O(1)#2 | 92.4(3) | O(4)-Cu(1)-O(1) | 81.0(2) |
| O(4)#2-Cu(1)-O(1) | 99.0(2) | O(3)#2-Cu(1)-O(1) | 92.4(3) |
| O(3)-Cu(1)-O(1) | 87.6(3) | O(1)#2-Cu(1)-O(1) | 180.0 |
| N(2)-O(2)-Dy(1) | 139.8(5) | N(1)-O(1)-Cu(1) | 158.8(6) |

#1 -x+1,-y+1,-z #2 -x+1,-y,-z+1

**Table S4**. Selected bond lengths [Å] and angles [°] for **4**.

| *Bond distances* | | | |
|---|---|---|---|
| Ho(1)-O(2) | 2.319(7) | Ho(1)-O(9) | 2.318(8) |
| Ho(1)-O(6) | 2.349(8) | Ho(1)-O(5) | 2.314(8) |
| Ho(1)-O(11) | 2.397(8) | Ho(1)-O(10) | 2.342(9) |
| Ho(1)-O(7) | 2.358(8) | Ho(1)-O(8) | 2.316(9) |
| Cu(2)-O(15) | 1.919(8) | Cu(2)-O(13) | 1.944(8) |
| Cu(2)-O(14) | 1.935(8) | Cu(2)-O(12) | 2.183(9) |
| Cu(2)-N(3) | 2.005(9) | Cu(3)-O(16)#1 | 1.994(8) |
| Cu(3)-O(16) | 1.994(8) | Cu(3)-O(17)#1 | 2.282(8) |
| Cu(3)-O(17) | 2.282(8) | Cu(3)-N(4)#1 | 2.027(9) |
| Cu(3)-N(4) | 2.027(9) | Cu(1)-O(4) | 1.932(8) |
| Cu(1)-O(4)#2 | 1.932(8) | Cu(1)-O(3)#2 | 1.941(7) |
| Cu(1)-O(3) | 1.941(7) | Cu(1)-O(1)#2 | 2.420(8) |
| Cu(1)-O(1) | 2.420(8) | O(2)-N(2) | 1.304(11) |
| O(1)-N(1) | 1.254(12) | | |
| *Angles* | | | |
| O(2)-Ho(1)-O(6) | 73.2(3) | O(2)-Ho(1)-O(11) | 74.6(3) |
| O(2)-Ho(1)-O(10) | 145.2(3) | O(2)-Ho(1)-O(7) | 73.4(3) |
| O(2)-Ho(1)-O(8) | 142.4(3) | O(9)-Ho(1)-O(2) | 99.5(3) |
| O(9)-Ho(1)-O(6) | 82.2(3) | O(9)-Ho(1)-O(11) | 141.8(3) |
| O(9)-Ho(1)-O(10) | 74.2(3) | O(9)-Ho(1)-O(7) | 70.6(3) |
| O(9)-Ho(1)-O(8) | 84.1(3) | O(6)-Ho(1)-O(11) | 129.0(3) |
| O(6)-Ho(1)-O(7) | 132.1(3) | O(5)-Ho(1)-O(2) | 97.0(3) |
| O(5)-Ho(1)-O(9) | 146.3(3) | O(5)-Ho(1)-O(6) | 74.8(3) |
| O(5)-Ho(1)-O(11) | 71.2(3) | O(5)-Ho(1)-O(10) | 75.5(3) |
| O(5)-Ho(1)-O(7) | 142.8(3) | O(5)-Ho(1)-O(8) | 100.2(3) |
| O(10)-Ho(1)-O(6) | 72.1(3) | O(10)-Ho(1)-O(11) | 131.0(3) |
| O(10)-Ho(1)-O(7) | 131.8(3) | O(7)-Ho(1)-O(11) | 71.6(3) |
| O(8)-Ho(1)-O(6) | 143.8(3) | O(8)-Ho(1)-O(11) | 79.7(3) |
| O(8)-Ho(1)-O(10) | 71.9(3) | O(8)-Ho(1)-O(7) | 72.7(3) |
| O(15)-Cu(2)-O(13) | 173.9(4) | O(15)-Cu(2)-O(14) | 90.2(3) |
| O(15)-Cu(2)-O(12) | 97.5(3) | O(15)-Cu(2)-N(3) | 89.5(3) |
| O(13)-Cu(2)-O(12) | 88.5(4) | O(13)-Cu(2)-N(3) | 90.4(3) |
| O(14)-Cu(2)-O(13) | 88.0(3) | O(14)-Cu(2)-O(12) | 94.9(4) |
| O(14)-Cu(2)-N(3) | 162.4(4) | N(3)-Cu(2)-O(12) | 102.6(4) |
| O(16)#1-Cu(3)-O(16) | 180.0 | O(16)#1-Cu(3)-O(17)#1 | 87.5(3) |
| O(16)-Cu(3)-O(17) | 87.5(3) | O(16)-Cu(3)-O(17)#1 | 92.5(3) |
| O(16)#1-Cu(3)-O(17) | 92.5(3) | O(16)-Cu(3)-N(4) | 90.5(4) |
| O(16)#1-Cu(3)-N(4)#1 | 90.5(4) | O(16)-Cu(3)-N(4)#1 | 89.5(4) |
| O(16)#1-Cu(3)-N(4) | 89.5(4) | O(17)#1-Cu(3)-O(17) | 180.0 |
| N(4)-Cu(3)-O(17) | 90.1(3) | N(4)-Cu(3)-O(17)#1 | 89.9(3) |
| N(4)#1-Cu(3)-O(17)#1 | 90.1(3) | N(4)#1-Cu(3)-O(17) | 89.9(3) |
| N(4)#1-Cu(3)-N(4) | 180.0 | O(4)-Cu(1)-O(4)#2 | 180.0 |
| O(4)-Cu(1)-O(3) | 92.9(3) | O(4)-Cu(1)-O(3)#2 | 87.1(3) |
| O(4)#2-Cu(1)-O(3)#2 | 92.9(3) | O(4)#2-Cu(1)-O(3) | 87.1(3) |
| O(4)#2-Cu(1)-O(1)#2 | 80.7(3) | O(4)-Cu(1)-O(1)#2 | 99.3(3) |
| O(4)-Cu(1)-O(1) | 80.7(3) | O(4)#2-Cu(1)-O(1) | 99.3(3) |
| O(3)#2-Cu(1)-O(3) | 180.0 | O(3)#2-Cu(1)-O(1) | 92.5(4) |
| O(3)-Cu(1)-O(1)#2 | 92.5(4) | O(3)#2-Cu(1)-O(1)#2 | 87.5(4) |
| O(3)-Cu(1)-O(1) | 87.5(4) | O(1)#2-Cu(1)-O(1) | 180.0 |
| N(2)-O(2)-Ho(1) | 139.0(6) | N(1)-O(1)-Cu(1) | 158.1(8) |

#1 -x+1,-y+1,-z  #2 -x+1,-y,-z+1

**Table S5.** SHAPE analysis for the Ln coordination spheres for **1-4**.

| Compound | SAPR-8 | TDD-8 | JBTPR-8 | BTPR-8 | JSD-8 |
|---|---|---|---|---|---|
| **1 Gd** | 2.293 | **0.400** | 2.770 | 2.154 | 2.556 |
| **2 Tb** | 2.187 | **0.446** | 2.768 | 2.181 | 2.606 |
| **3 Dy** | 2.347 | **0.398** | 2.822 | 2.223 | 2.560 |
| **4 Ho** | 2.394 | **0.402** | 2.883 | 2.292 | 2.545 |

**Table S6.** Distances (Å) and angles (°) for the hydrogen bonds in compounds **1-4**.

| D–H···A | Compound | d(D–H) | d(H···A) | d(D···A) | <(DHA) |
|---|---|---|---|---|---|
| O11-H11B···O17 | **1 Gd** | 0.852 | 2.258 | 2.751 | 117.03 |
| O11-H11B···O17 | **2 Tb** | 0.850 | 2.143 | 2.730 | 125.94 |
| O11-H11B···O17 | **3 Dy** | 0.852 | 2.184 | 2.761 | 124.90 |
| O11-H11B···O17 | **4 Ho** | 0.851 | 2.166 | 2.759 | 126.64 |

**Table S7.** Magnetic relaxation parameters for β-diketone Dy(III) complexes possessing triangular dodecahedron ($D_{2d}$) coordination spheres.

| Compound | $U_{eff}/k_B$ (K) | $\tau_0$ (s) | α | $H_{dc}$ (Oe) | Ref. |
|---|---|---|---|---|---|
| $Dy(BTFA)_3(H_2O)_2$ | 93.09<br>296.50 | $1.10 \times 10^{-6}$<br>$6.27 \times 10^{-12}$ | 0.03-0.41<br>below 0.18 | 0<br>1200 | 21a |
| $[Dy(Phen)(tfmb)_3]$ | 63.56<br>118.50 | $4.48 \times 10^{-6}$<br>$1.5 \times 10^{-7}$ | below 0.21<br>- | 0<br>1200 | 21b |
| $[Dy_4(hfac)_8(IMPhThio)_2(OH)_4][Dy(hfac)_3(NITPhThio)_2]$ | 32 | $2.96 \times 10^{-9}$ | 0.50-0.15 | 5000 | 21c |
| $[Dy^{III}(hfac)_3(tmphen)]$ | 35.09 | $9.16 \times 10^{-9}$ | 0.20–0.41 | 3500 | 21d |
| $[Dy(dbpy)(tcpb)_3]\cdot 0.5(1,4\text{-dioxane})$ | 149.87(FR);<br>79.69(SR)<br>178.56 | $1.42 \times 10^{-15}$ (FR);<br>$1.08 \times 10^{-9}$ (SR)<br>$1.84 \times 10^{-12}$ | -<br>0.26–0.36 | 0<br>1000 | 21e |
| $[Dy(thd)_2(NO_3)(TPPO)_2]$ | 20.7 | $1.59 \times 10^{-6}$ | 0.12–0.23 | 1000 | 21f |
| $[Dy(9Accm)_2(NO_3)(dmf)_2]$ | 23 | $1.3 \times 10^{-6}$ | 0.3-0.4 | 1000 | 21g |
| [Dy(L)(tmpd)] | 96.63 | $3.38 \times 10^{-6}$ | 0.262 - 0.356 | 0 | 21h |
| $[Dy_2Cu_2(hfac)_{10}(NIT\text{-}3py)_2(H_2O)_2]$ | 13.14 | $1.77 \times 10^{-6}$ | - | 2000 | 21i |
| $[Ln(hfac)_3(pz)_2]$ | 28.32 | $4.70 \times 10^{-6}$ | 0.203–0.009 | 0 | 21j |
| $\{[Ln(hfac)_3][Cu(hfac)_2]_2(3,5\text{-}bPy\text{-}Ph\text{-}Nit)(H_2O)\}_n$ | 17.8 (FR,LT)<br>47.6 (SR)<br>12.7(FR,HT)<br>19.8(FR,LT)<br>41.9(SR) | $6.2 \times 10^{-8}$(FR,LT)<br>$4.4 \times 10^{-8}$ (SR)<br>$2.4 \times 10^{-6}$(FR,HT)<br>$2.0 \times 10^{-8}$(FR,LT)<br>$9.9 \times 10^{-8}$(SR) | 0.13-0.41 (FR)<br>0.02-0.10 (SR)<br>0.13-0.47(FR)<br>0.03−0.21(SR) | 0<br>1000 | this work |

BTFA = 3-benzoyl-1,1,1-trifluoroacetone; tfmb = 4,4,4-trifluoro-1-(4-methylphenyl)-1,3-butanedione; Phen = 1,10-phenanthroline; NITPhThio = (2-(benzo[d]thiophen-2-yl)-4,4,5,5-tetramethylimidazolin-1-oxyl-3-oxide; IMPhThio = 2-(benzo[d]thiophen-2-yl)-4,4,5,5-tetramethylimidazolin-1-oxyl; tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline;dbpy = 4,4′-dimethyl-2,2′-bipyridyl; tcpb = 1-(4-chlorophenyl)-4,4,4-trifluoro-1,3-butanedione; thd = 2,2,6,6-tetramethyl-3,5-heptanedione; Tppo = Triphenylphosphane oxide; 9Accm = 1,7-di-9-anthracene-1,6-heptadiene-3,5-dione; $H_2L$ = N,N0-bis(2-hydroxy-5-methyl-3-formylbenzyl)-N,N0-bis-(pyridin-2-ylmethyl)ethylenediamine; tmpd = 4,4,4-trifluoro-1-(4-methoxyphenyl)-1,3-butanedione; NIT-3py = 2-(3-pyridyl)-4,4,5,5 -tetramethylimidazoline-1-oxyl-3-oxide; pz = pyrazole.

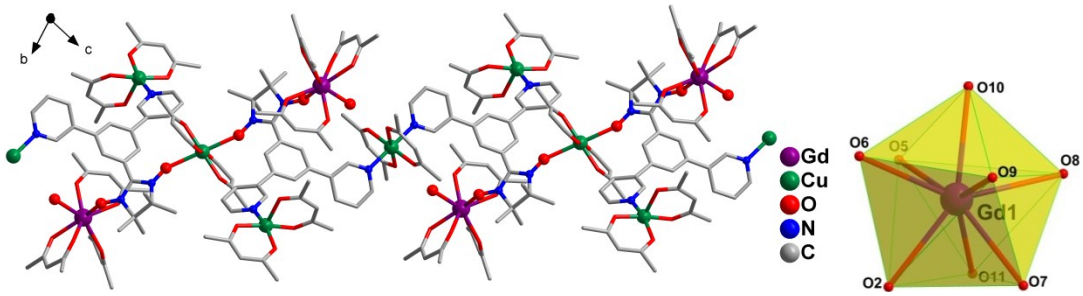


**Fig. S1** One-dimensional structure of **1** and local coordination geometry of Gd(III) ion (Fluorine and Hydrogen atoms are omitted for the sake of clarity).

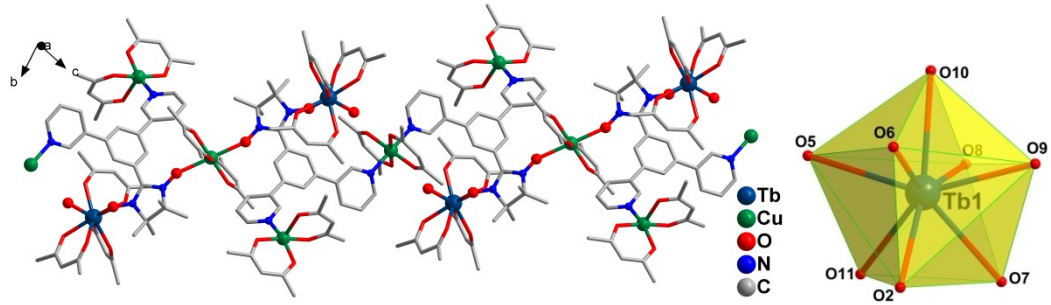


**Fig. S2** One-dimensional structure of **2** and local coordination geometry of Tb(III) ion (Fluorine and Hydrogen atoms are omitted for the sake of clarity).

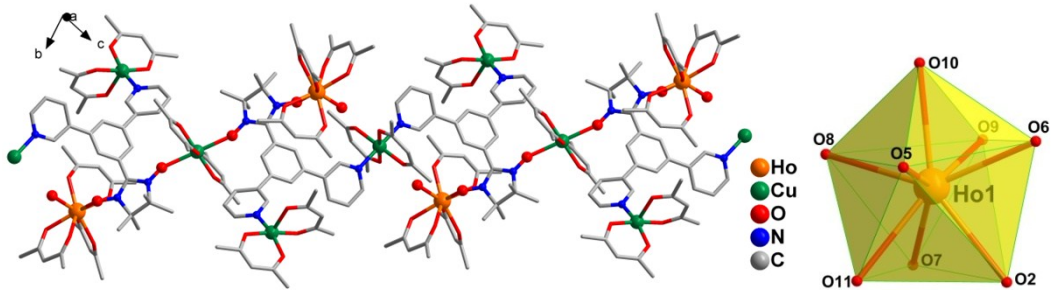


**Fig. S3** One-dimensional structure of **4** and local coordination geometry of Ho(III) ion (Fluorine and Hydrogen atoms are omitted for the sake of clarity).

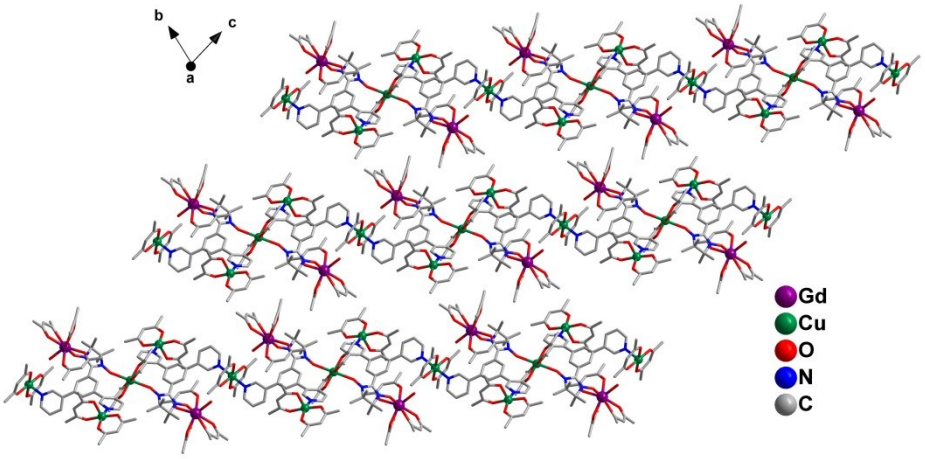


**Fig. S4** Packing arrangement of the chains in **1** (H and F atoms are omitted for clarity).

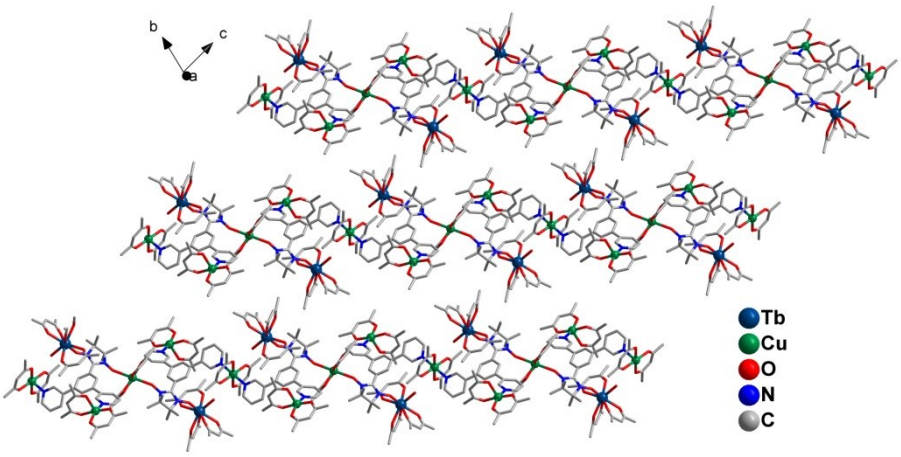


**Fig. S5** Packing arrangement of the chains in **2** (H and F atoms are omitted for clarity).

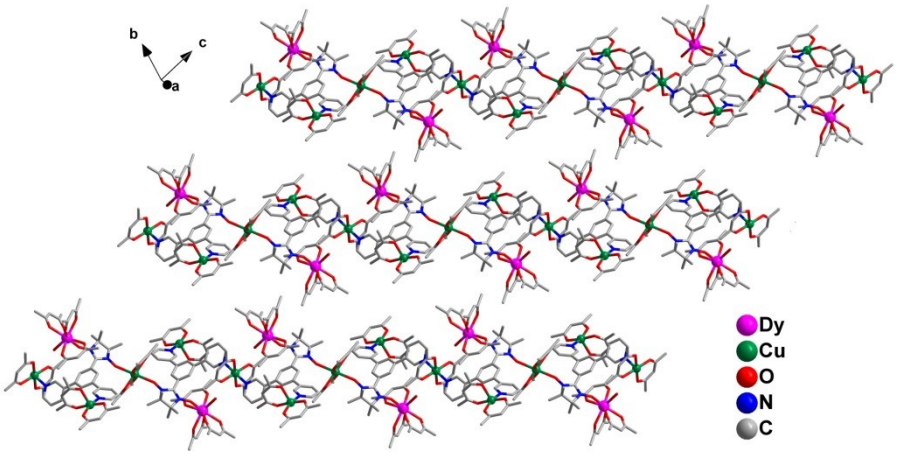


**Fig. S6** Packing arrangement of the chains in **3** (H and F atoms are omitted for clarity).

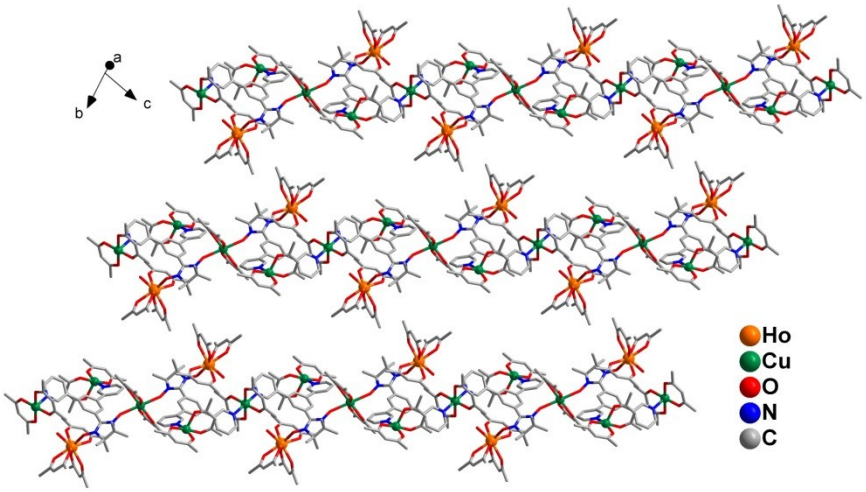


**Fig. S7** Packing arrangement of the chains in **4** (H and F atoms are omitted for clarity).

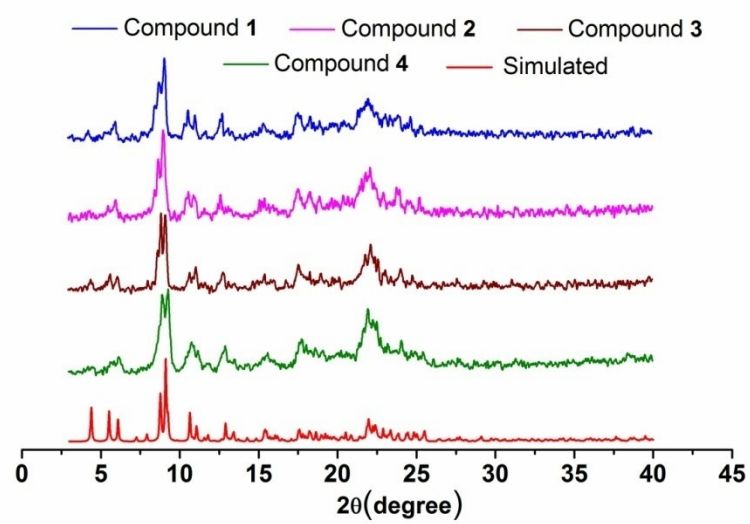


**Fig. S8** Powder X-ray diffraction patterns of complexes **1**-**4**.

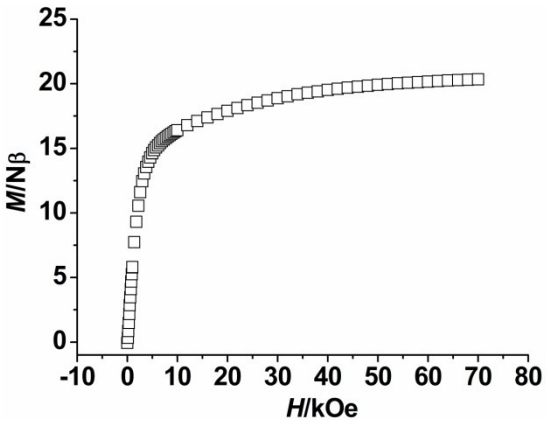


**Fig. S9** Plot of magnetization *vs* field for **2** at 2 K.

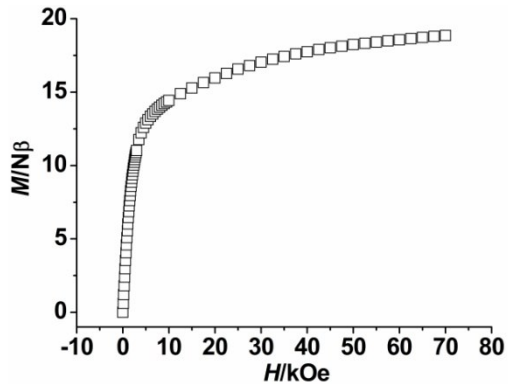


**Fig. S10** Plot of magnetization *vs* field for **3** at 2 K.

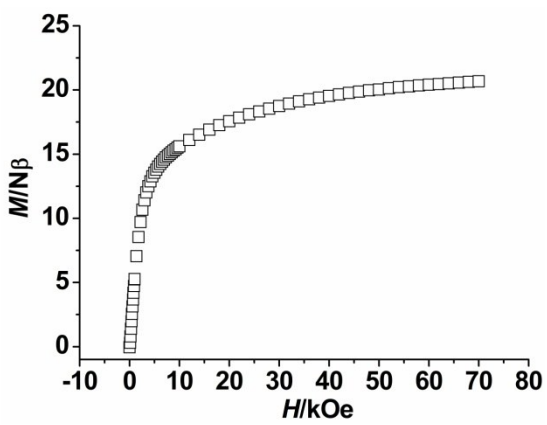


**Fig. S11** Plot of magnetization *vs* field for **4** at 2 K.

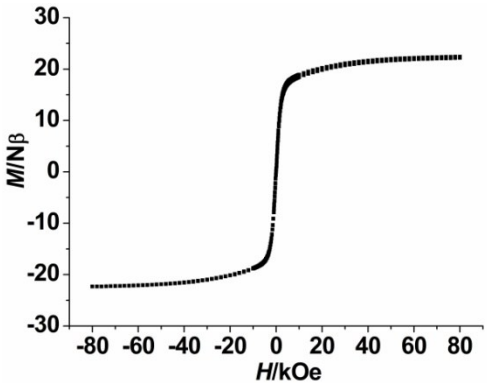


**Fig. S12** *M* vs *H* behavior for **3** at 2 K recorded from 80 kOe to -80 kOe.

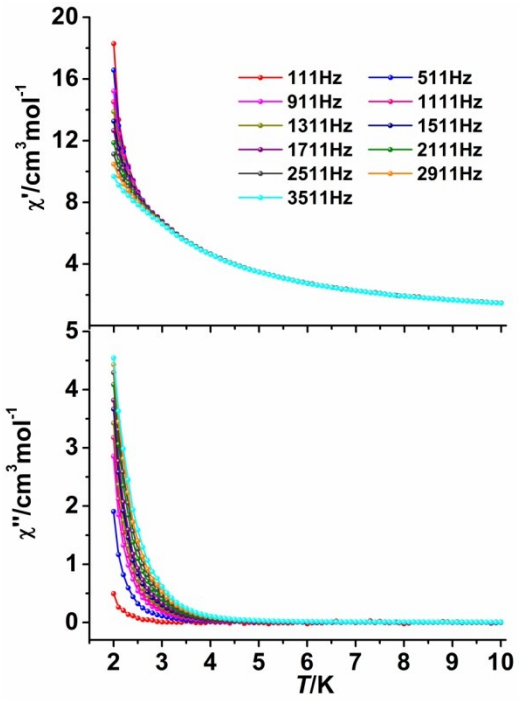


**Fig. S13** Temperature-dependent ac signals of the χ′ (top) and χ″ (bottom) under zero dc field for compound **2**.

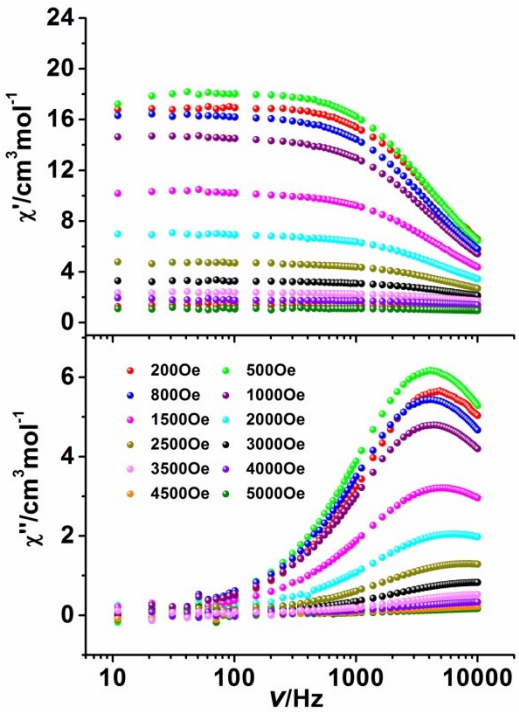


**Fig. S14** Frequency dependence of the χ′ (top) and χ″ (bottom) components of the ac susceptibility, between 0 and 5000 Oe and between 10 and 10000 Hz, for **2** at 2 K.

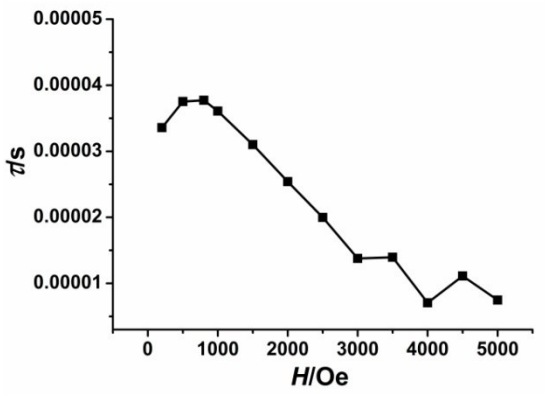


**Fig. S15** The $\tau$ versus $H$ plot for complex **2** at 2.0 K under the applied dc field.

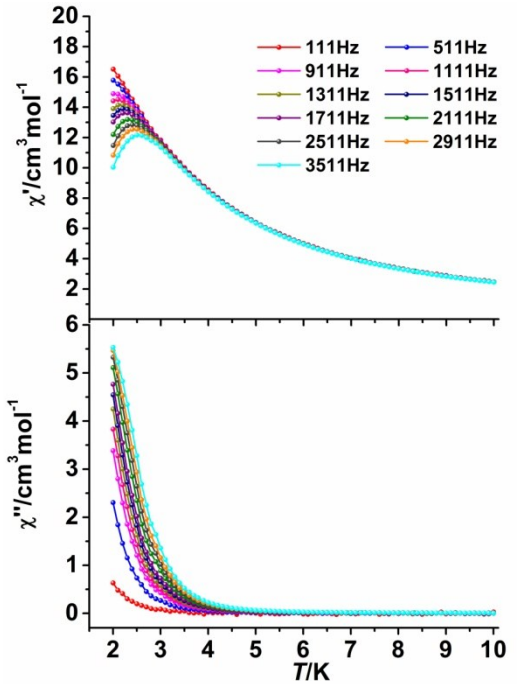


**Fig. S16** Temperature-dependent ac signals of the χ′ (top) and χ″ (bottom) under 800 Oe dc field for compound **2**.

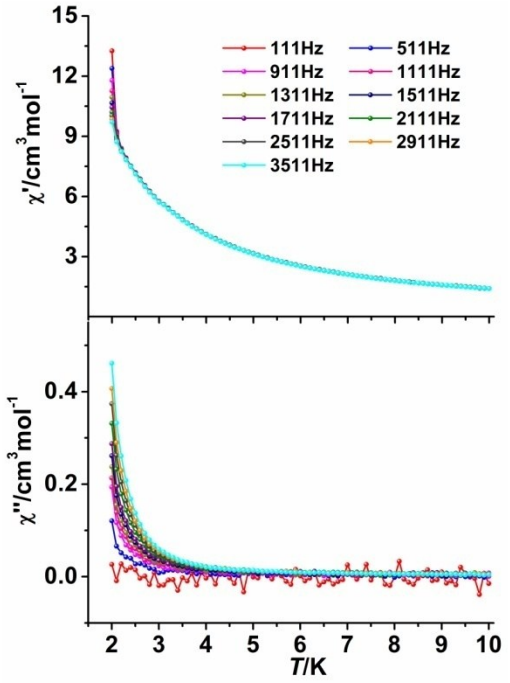


**Fig. S17** Temperature-dependent ac signals of the χ′ (top) and χ″ (bottom) under zero dc field for compound **4**.

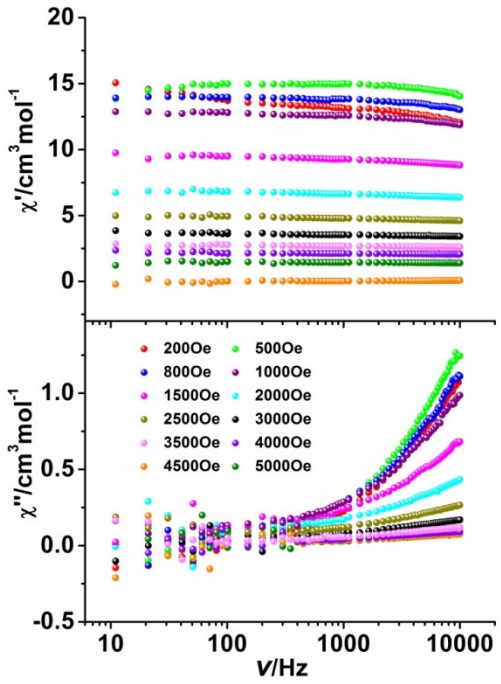


**Fig. S18** Frequency dependence of the χ′ (top) and χ″ (bottom) components of the ac susceptibility, between 0 and 5000 Oe and between 10 and 10000 Hz, for **4** at 2 K.

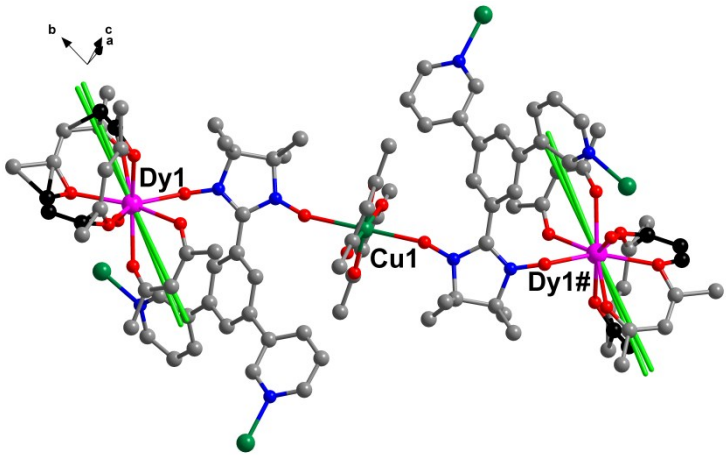


**Fig. S19** The Magellan predicted easy axes (bright green lines) of the Dy centers (black ball represent the disorder C atoms (occupancies: 50%)).

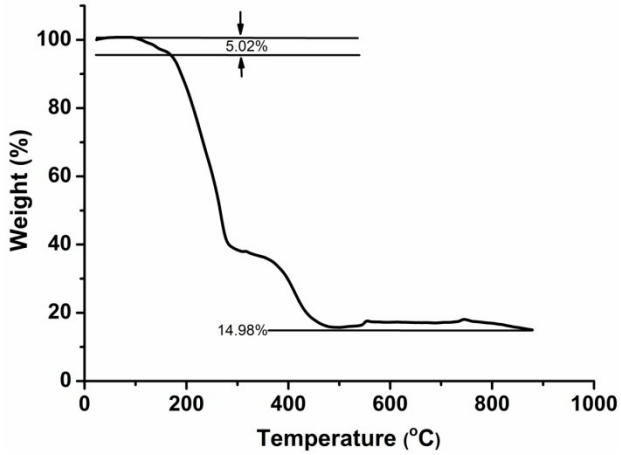


**Fig. S20** The TG curve of complex **1**.