Supporting Information

Tuning magnetic relaxation in a Tb-nitronyl nitroxide complex by using co-crystalline paramagnetic complex

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

Bond distances			
Tb(1)-O(1)	2.356(6)	Tb(1)-O(3)	2.346(7)
Tb(1)-O(9)	2.346(7)	Tb(1)-O(10)	2.392(7)
Tb(1)-O(11)	2.335(7)	Tb(1)-O(12)	2.380(7)
Tb(1)-O(13)	2.363(7)	Tb(1)-O(14)	2.365(7)
O(1)-N(4)	1.303(11)	O(2)-N(5)	1.264(11)
O(3)-N(1)	1.305(10)	O(4)-N(2)	1.267(11)
Angles			
O(1)-Tb(1)-O(3)	137.8(2)	O(1)-Tb(1)-O(9)	94.0(2)
O(1)-Tb(1)-O(10)	147.9(2)	O(1)-Tb(1)-O(11)	101.1(2)
O(1)-Tb(1)-O(12)	73.7(2)	O(1)-Tb(1)-O(13)	69.8(2)
O(1)-Tb(1)-O(14)	76.4(2)	O(3)-Tb(1)-O(9)	104.2(2)
O(3)-Tb(1)-O(10)	74.2(2)	O(3)-Tb(1)-O(11)	90.8(2)
O(3)-Tb(1)-O(12)	147.9(2)	O(3)-Tb(1)-O(13)	74.6(2)
Tb(1)-O(3)-N(1)	138.2(6)	Tb(1)-O(1)-N(4)	136.8(6)

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

Bond distances			
Gd(1)-O(8)	2.359(4)	Gd(1)-O(17)	2.365(4)
Gd(1)-O(9)	2.383(4)	Gd(1)-O(10)	2.377(4)
Gd(1)-O(11)	2.356(4)	Gd(1)-O(12)	2.405(4)
Gd(1)-O(13)	2.351(4)	Gd(1)-O(14)	2.393(4)
Cu(1)-O(2)	2.406(4)	Cu(1)-O(3)	1.928(4)
Cu(1)-O(4)	1.942(4)	O(2)-N(2)	1.298(6)
O(1)-N(1)	1.275(7)	O(8)-N(5)	1.309(6)
O(7)-N(4)	1.305(8)	O(18)-N(7)	1.276(6)
O(17)-N(8)	1.300(5)		
Angles			
O(8)-Gd(1)-O(17)	137.08(14)	O(8)- Gd (1)-O(9)	71.20(15)
O(8)- Gd (1)-O(10)	74.38(14)	O(8)- Gd (1)-O(11)	92.96(15)
O(8)- Gd (1)-O(12)	133.27(14)	O(8)- Gd (1)-O(13)	103.41(14)
O(8)- Gd (1)-O(14)	74.47(14)	O(17)- Gd (1)-O(9)	75.40(13)
O(17)- Gd (1)-O(10)	70.76(13)	O(17)- Gd (1)-O(11)	102.50(14)
O(17)- Gd (1)-O(12)	73.95(14)	O(17)- Gd (1)-O(13)	92.23(13)
O(17)- Gd (1)-O(14)	148.20(13)	O(2)-Cu(1)-O(3)	96.99(17)
O(2)-Cu(1)-O(4)	91.66(17)	O(2)-Cu(1)-O(3A)	83.01(17)
O(2)-Cu(1)-O(4A)	88.34(17)	Gd(1)-O(8)-N(5)	136.7(4)
Gd(1)-O(17)-N(8)	135.0(3)	Cu(1)-O(2)-N(2)	136.7(4)

A: -x+1,-y+1,-z

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

Bond distances			
Tb(1)-O(8)	2.347(5)	Tb(1)-O(17)	2.373(5)
Tb(1)-O(9)	2.368(5)	Tb(1)-O(10)	2.353(5)
Tb(1)-O(11)	2.361(6)	Tb(1)-O(12)	2.392(5)
Tb(1)-O(13)	2.334(6)	Tb(1)-O(14)	2.381(5)
Cu(1)-O(2)	2.413(6)	Cu(1)-O(3)	1.943(6)
Cu(1)-O(4)	1.927(6)	O(2)-N(2)	1.299(9)
O(1)-N(1)	1.265(9)	O(8)-N(5)	1.326(8)
O(7)-N(4)	1.287(10)	O(18)-N(7)	1.272(8)
O(17)-N(8)	1.285(8)		
Angles			
O(8)-Tb(1)-O(17)	137.53(18)	O(8)- Tb(1)-O(9)	71.4(2)
O(8)- Tb(1)-O(10)	74.83(18)	O(8)- Tb(1)-O(11)	92.7(2)
O(8)- Tb(1)-O(12)	148.4(2)	O(8)- Tb(1)-O(13)	103.6(2)
O(8)- Tb(1)-O(14)	74.11(19)	O(17)- Tb(1)-O(9)	75.46(18)
O(17)- Tb(1)-O(10)	70.86(19)	O(17)- Tb(1)-O(11)	102.72(19)
O(17)- Tb(1)-O(12)	73.93(18)	O(17)- Tb(1)-O(13)	91.45(19)
O(17)- Tb(1)-O(14)	148.09(18)	O(2)-Cu(1)-O(3)	88.0(2)
O(2)-Cu(1)-O(4)	83.0(2)	O(2)-Cu(1)-O(3A)	92.0(2)
O(2)-Cu(1)-O(4A)	97.0(2)	Tb(1)-O(8)-N(5)	138.0(5)
Tb(1)-O(17)-N(8)	134.9(5)	Cu(1)-O(2)-N(2)	138.0(5)

A: -x+1,-y+1,-z+1

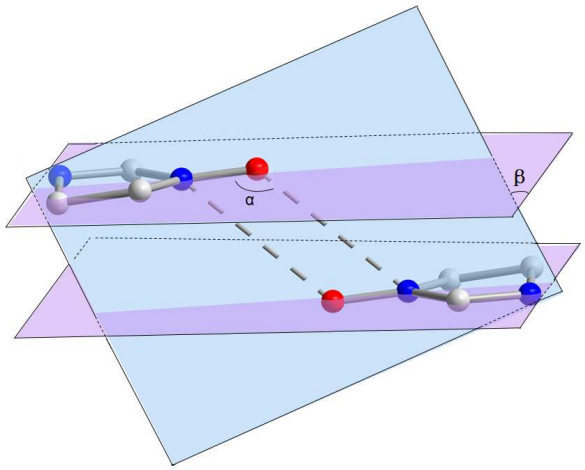

Chart S1. The relative disposition of neighboring nitronyl nitroxide moieties in **2** and **3**.

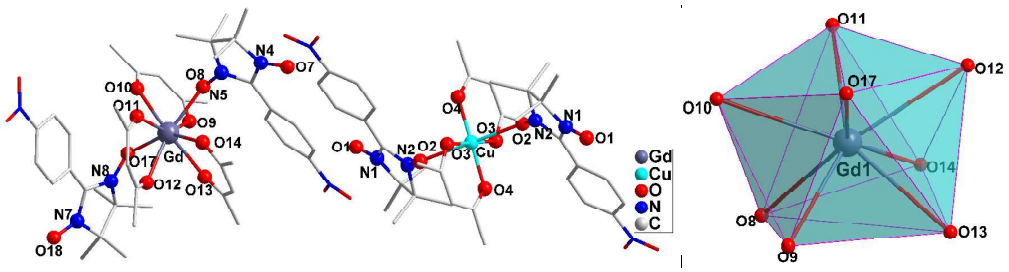

Figure S1. (left) Crystal structure of complex **2**(Hydrogen and fluorine atoms are omitted for clarity) and (right) the coordination polyhedron of Gd(III) in **2**.

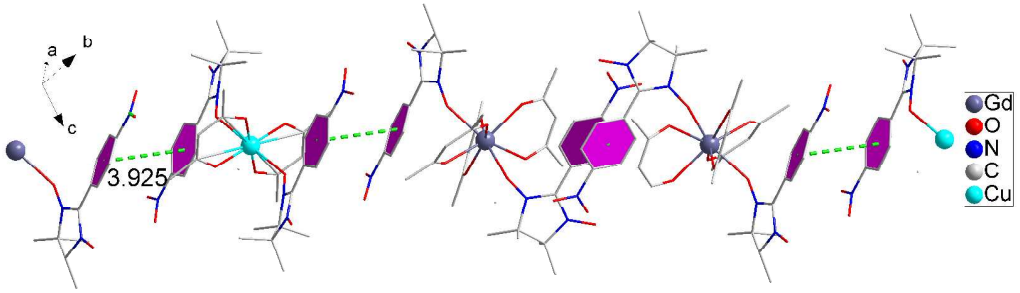

Figure S2. One-dimensional chain of **2** through π–π interactions. Hydrogen atoms and fluorine atoms are omitted for clarity.

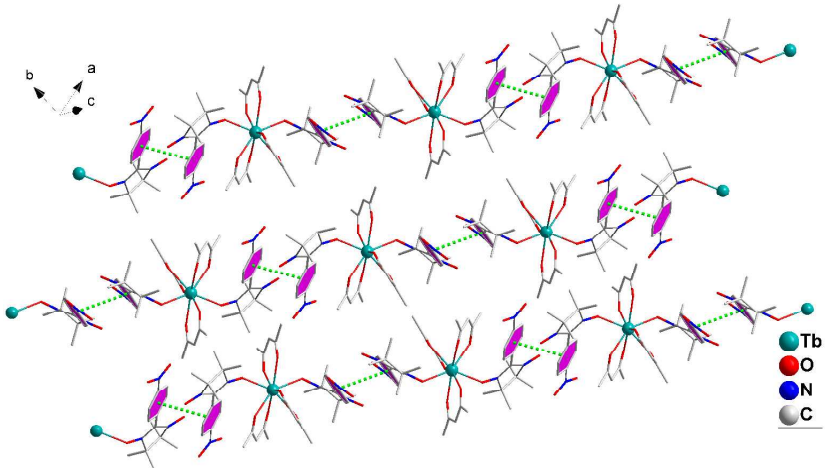

Figure S3. Packing arrangement of the chains in **1**. Heptane molecules, hydrogen atoms, and fluorine atoms are omitted for clarity.

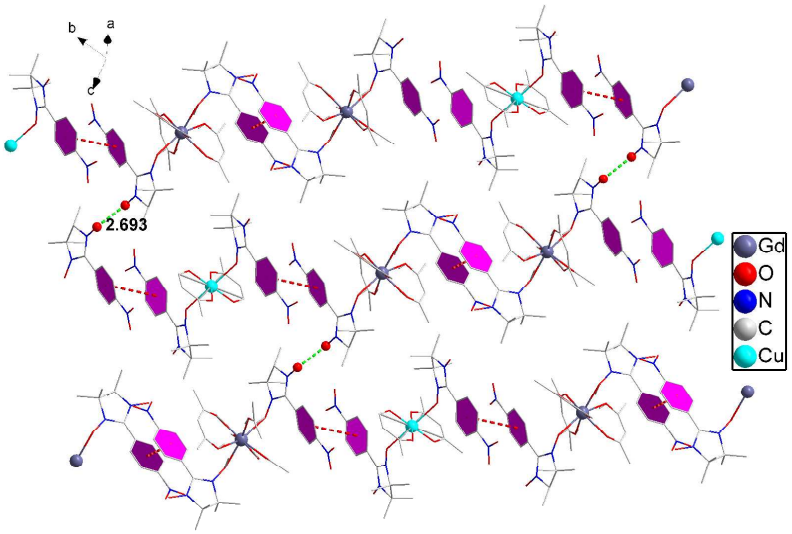

Figure S4. Packing arrangement of the chains in **2**. Hydrogen atoms, and fluorine atoms are omitted for clarity.

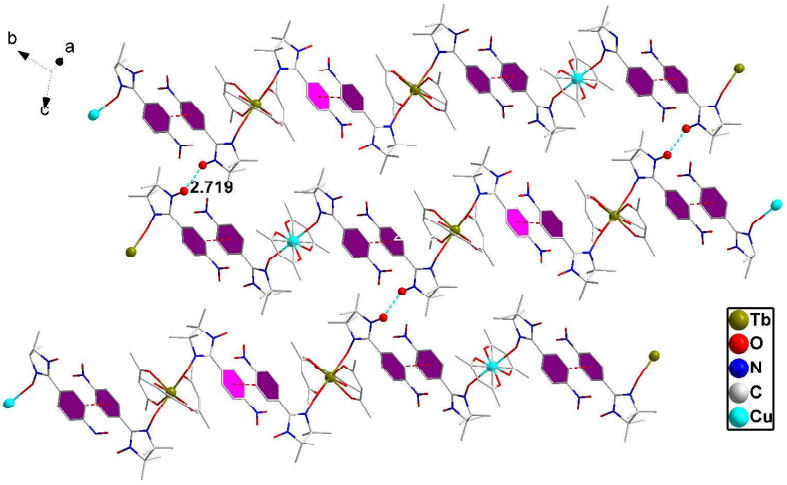

Figure S5. Packing arrangement of the chains in **3**. Hydrogen atoms and fluorine atoms are omitted for clarity.

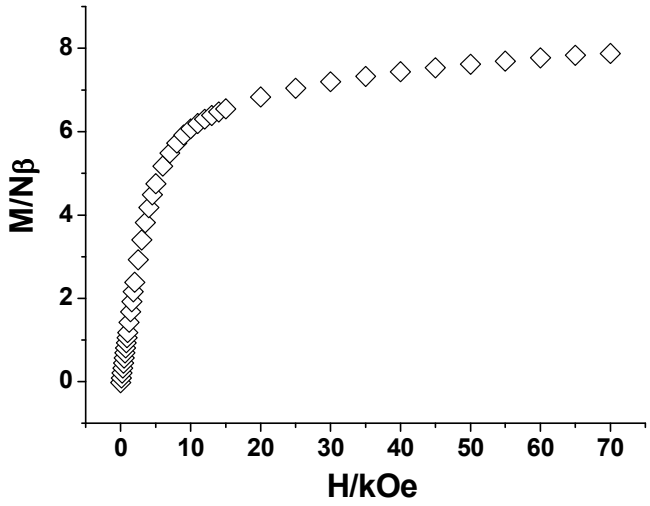

Figure S6. Field dependence of magnetization for **1** at 2.0 K.

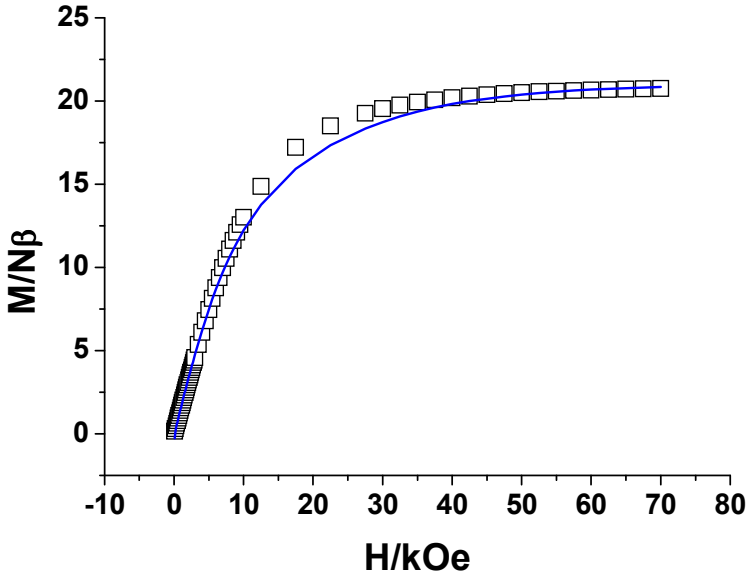

Figure S7. Field dependence of magnetization for **2** at 2.0 K. The solid blue line is the theoretical cure for the sum of the Brillouin function for two S = 7/2 spins (Gd(III)) and seven *S* = 1/2 spins (six radicals and one Cu(II)) with *g* = 2.

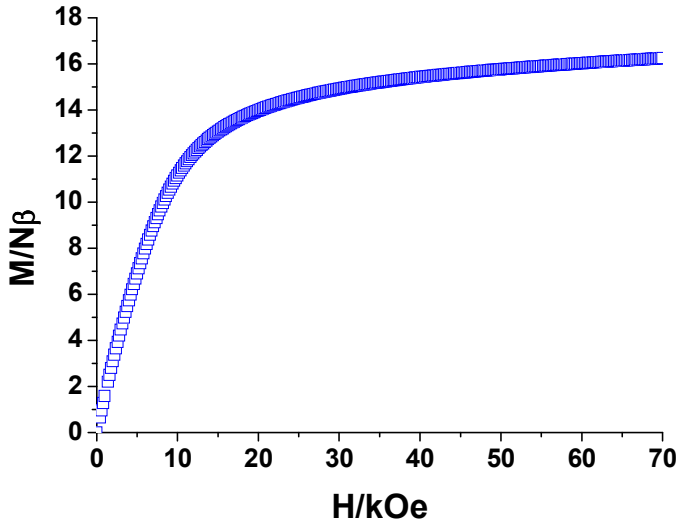

Figure S8. Field dependence of magnetization for **3** at 2.0 K.

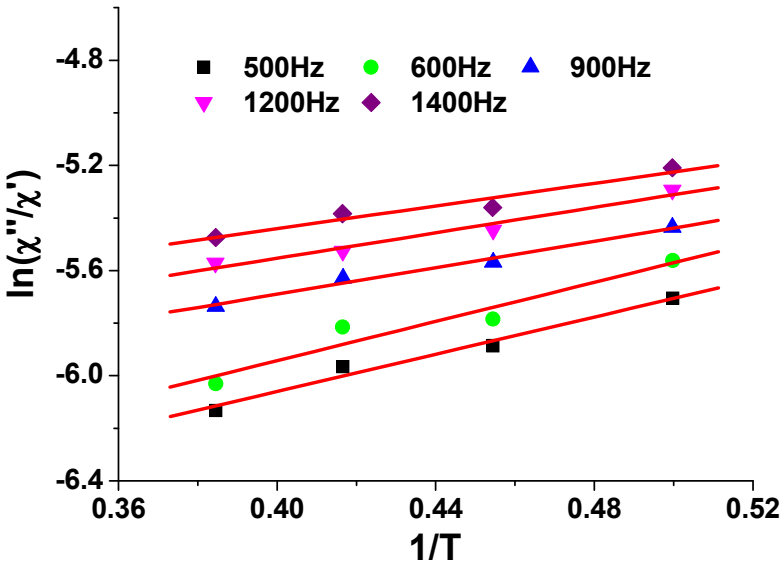

Figure S9. Plots of natural logarithm of χ''/χ' vs. 1/T for **1**. The solid line represents the best fitting results.

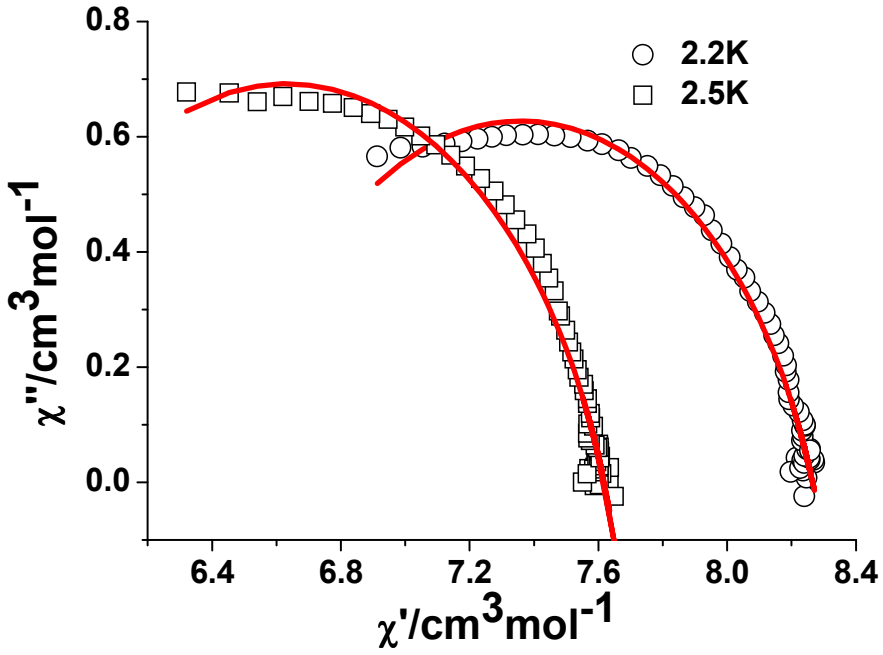

Figure S10. The Cole–Cole plots at 2.2 and 2.5 K of **3** in zero-dc field. The red solid line represents the best fitting results obtained with a Debye model.