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Slow magnetic relaxation in two-dimensional 3d-4f complex based on phenyl pyrimidyl substituted nitronyl nitroxide radical

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Table S1 Selected bond lengths(Å)and bond angles(°)for **1**.

Tb(1)-O(3)	2.351(5)	Cu(2)-O(19)	1.950(5)
Tb(1)-O(8)	2.353(5)	Cu(2)-O(22)	1.963(5)
Tb(1)-O(5)	2.354(5)	Cu(2)-O(20)	1.961(5)
Tb(1)-O(2)	2.363(5)	Cu(2)-N(6)	2.314(6)
Tb(1)-O(7)	2.361(5)	Cu(2)-O(1)#1	2.531(5)
Tb(1)-O(9)	2.370(5)	Cu(3)-O(16)	1.961(5)
Tb(1)-O(4)	2.379(5)	Cu(3)-O(15)	1.959(5)
Tb(1)-O(6)	2.383(5)	Cu(3)-O(17)	1.974(5)
Cu(1)-O(14)	1.954(5)	Cu(3)-O(18)	1.976(5)
Cu(1)-O(13)	1.959(5)	Cu(3)-N(5)	2.346(6)
Cu(1)-O(11)	1.966(5)	Cu(3)-N(2)#2	2.403(6)
Cu(1)-O(12)	1.970(5)	O(1)-N(4)	1.287(8)
Cu(1)-N(1)#1	2.293(6)	O(2)-N(3)	1.308(7)
Cu(1)-O(10)	2.481(5)	O(9)-N(8)	1.300(7)
Cu(2)-O(21)	1.940(5)	O(10)-N(7)	1.253(8)
O(3)-Tb(1)-O(2)	73.33(17)	O(21)-Cu(2)-N(6)	94.4(2)
O(8)-Tb(1)-O(2)	91.00(17)	O(19)-Cu(2)-N(6)	88.1(2)
O(5)-Tb(1)-O(2)	105.86(17)	O(22)-Cu(2)-N(6)	94.0(2)
O(2)-Tb(1)-O(9)	135.78(17)	O(20)-Cu(2)-N(6)	96.2(2)
O(7)-Tb(1)-O(9)	73.86(17)	O(21)-Cu(2)-O(1)#1	86.14(19)
O(9)-Tb(1)-O(6)	150.42(17)	O(19)-Cu(2)-O(1)#1	91.44(18)
O(9)-Tb(1)-O(4)	70.73(16)	O(22)-Cu(2)-O(1)#1	77.44(19)
N(8)-O(9)-Tb(1)	133.4(4)	O(20)-Cu(2)-O(1)#1	92.4(2)
N(3)-O(2)-Tb(1)	135.6(4)	N(6)-Cu(2)-O(1)#1	171.5(2)
O(14)-Cu(1)-N(1)#1	97.3(2)	N(4)-O(1)-Cu(2)#3	140.5(5)
O(13)-Cu(1)-N(1)#1	96.1(2)	N(5)-Cu(3)-N(2)#2	177.5(2)
O(11)-Cu(1)-O(10)	91.8(2)	O(16)-Cu(3)-N(5)	93.0(2)
O(12)-Cu(1)-O(10)	88.6(19)	O(15)-Cu(3)-N(5)	88.4(2)
N(1)#1-Cu(1)-O(10)	176.9(2)	O(17)-Cu(3)-N(5)	89.41319)
O(11)-Cu(1)-N(1)#1	89.7(2)	O(18)-Cu(3)-N(5)	93.5(2)
O(12)-Cu(1)-N(1)#1	88.6(2)	O(16)-Cu(3)-N(2)#2	88.2(2)
O(14)-Cu(1)-O(10)	85.5(2)	O(15)-Cu(3)-N(2)#2	93.7(2)
O(13)-Cu(1)-O(10)	82.3(2)	O(17)-Cu(3)-N(2)#2	88.48(19)
N(7)-O(10)-Cu(1)	152.6(5)	O(18)-Cu(3)-N(2)#2	85.3(2)

Symmetry transformations used to generate equivalent atoms: #1: x,-y-1/2,z-1/2; #2: x-1,-y+1/2,z-1/2; #3:x,-y+1/2,z+1/2

Table S2 Selected bond lengths(Å)and bond angles(°)for **2**.

Ho(1)-O(4)	2.308(5)	Cu(2)-O(15)	1.953(5)
Ho(1)-O(6)	2.317(6)	Cu(2)-O(18)	1.956(6)
Ho(1)-O(9)	2.322(5)	Cu(2)-O(16)	1.979(6)
Ho(1)-O(8)	2.325(5)	Cu(2)-N(8)	2.278(6)
Ho(1)-O(2)	2.331(5)	Cu(2)-O(7)#1	2.466(5)
Ho(1)-O(3)	2.353(5)	Cu(3)-O(21)	1.946(6)
Ho(1)-O(5)	2.360(6)	Cu(3)-O(19)	1.944(6)
Ho(1)-O(1)	2.373(6)	Cu(3)-O(20)	1.968(6)
Cu(1)-O(11)	1.902(8)	Cu(3)-O(22)	1.970(7)
Cu(1)-O(14)	1.917(6)	Cu(3)-N(4)#2	2.321(7)
Cu(1)-O(12)	1.964(6)	Cu(3)-N(7)	2.452(7)
Cu(1)-O(13)	2.007(6)	O(7)-N(1)	1.276(8)
Cu(1)-N(3)#1	2.354(6)	O(8)-N(2)	1.305(7)
Cu(1)-O(10)	2.541(5)	O(9)-N(5)	1.301(7)
Cu(2)-O(17)	1.927(5)	O(10)-N(6)	1.269(8)
O(4)-Ho(1)-O(9)	98.44(18)	O(17)-Cu(2)-N(8)	96.2(2)
O(6)-Ho(1)-O(9)	96.13(19)	O(15)-Cu(2)-N(8)	91.0(2)
O(9)-Ho(1)-O(8)	137.01(19)	O(18)-Cu(2)-N(8)	92.4(2)
O(8)-Ho(1)-O(2)	74.46(18)	O(16)-Cu(2)-N(8)	91.0(2)
O(9)-Ho(1)-O(3)	72.58(19)	O(17)-Cu(2)-O(7)#1	83.9(2)
O(8)-Ho(1)-O(1)	71.20(18)	O(15)-Cu(2)-O(7)#1	89.1(2)
O(8)-Ho(1)-O(5)	72.90(19)	O(18)-Cu(2)-O(7)#1	80.9(2)
N(2)-O(8)-Ho(1)	136.8(5)	O(16)-Cu(2)-O(7)#1	95.8(2)
N(5)-O(9)-Ho(1)	138.1(5)	N(8)-Cu(2)-O(7)#1	173.2(2)
O(11)-Cu(1)-N(3)#1	104.4(3)	N(1)-O(7)-Cu(2)#3	150.6(6)
O(14)-Cu(1)-N(3)#1	89.1(2)	O(21)-Cu(3)-N(4)#2	88.5(2)
O(12)-Cu(1)-N(3)#1	86.1(2)	O(19)-Cu(3)-N(4)#2	90.7(2)
O(13)-Cu(1)-N(3)#1	92.0(2)	O(20)-Cu(3)-N(4)#2	88.6(3)
O(11)-Cu(1)-O(10)	91.5(2)	O(22)-Cu(3)-N(4)#2	102.7(3)
O(14)-Cu(1)-O(10)	91.9(2)	O(21)-Cu(3)-N(7)	86.7(2)
O(12)-Cu(1)-O(10)	92.9(2)	O(19)-Cu(3)-N(7)	94.3(2)
O(13)-Cu(1)-O(10)	72.2(2)	O(20)-Cu(3)-N(7)	83.0(2)
N(3)#1-Cu(1)-O(10)	164.1(2)	O(22)-Cu(3)-N(7)	85.9(2)
N(6)-O(10)-Cu(1)	139.8(6)	N(4)#2-Cu(3)-N(7)	170.4(2)

Symmetry transformations used to generate equivalent atoms: #1: x,-y-1/2,z-1/2; #2: x-1,-y-1/2,z-1/2

Table S3 Selected bond lengths(Å)and bond angles(°)for **3**.

Yb(1)-O(5)	2.254(5)	Cu(2)-O(9)	1.935(5)
Yb(1)-O(3)	2.280(5)	Cu(2)-O(12)	1.947(5)
Yb(1)-O(2)	2.290(6)	Cu(2)-O(10)	1.957(6)
Yb(1)-O(8)	2.296(6)	Cu(2)-N(3)	2.268(6)
Yb(1)-O(21)#1	2.302(5)	Cu(2)-O(22)#3	2.462(5)
Yb(1)-O(6)	2.313(6)	Cu(3)-O(13)	1.933(6)
Yb(1)-O(4)	2.330(5)	Cu(3)-O(15)	1.954(6)
Yb(1)-O(7)	2.334(6)	Cu(3)-O(16)	1.951(5)
Cu(1)-O(19)	1.907(6)	Cu(3)-O(14)	1.962(6)
Cu(1)-O(17)	1.950(6)	Cu(3)-N(5)	2.308(8)
Cu(1)-O(18)	1.943(6)	Cu(3)-N(4)	2.439(6)
Cu(1)-O(20)	1.964(6)	O(1)-N(1)	1.284(8)
Cu(1)-O(1)#2	2.558(6)	O(2)-N(2)	1.305(8)
Cu(1)-N(6)	2.327(7)	O(21)-N(7)	1.299(8)
Cu(2)-O(11)	1.920(5)	O(22)-N(8)	1.266(8)
O(5)-Yb(1)-O(2)	98.28(18)	O(11)-Cu(2)-N(3)	96.6(2)
O(3)-Yb(1)-O(2)	74.99(18)	O(12)-Cu(2)-N(3)	92.0(2)
O(2)-Yb(1)-O(8)	96.3(2)	O(10)-Cu(2)-N(3)	90.8(2)
O(2)-Yb(1)-O(21)#1	136.8(2)	O(9)-Cu(2)-O(22)#3	89.2(3)
O(21)#1-Yb(1)-O(6)	150.1(2)	O(11)-Cu(2)-O(22)#3	83.0(2)
O(21)#1-Yb(1)-O(4)	71.45(18)	O(12)-Cu(2)-O(22)#3	81.3(2)
O(21)#1-Yb(1)-O(7)	73.07(19)	O(10)-Cu(2)-O(22)#3	95.9(2)
N(2)-O(2)-Yb(1)	137.9(5)	N(3)-Cu(2)-O(22)#3	173.2(2)
N(7)-O(21)-Yb(1)#4	136.2(5)	N(8)-O(22)-Cu(2)#2	149.6(6)
O(18)-Cu(1)-N(6)	86.4(2)	O(13)-Cu(3)-N(5)	87.4(2)
O(17)-Cu(1)-N(6)	104.7(2)	O(16)-Cu(3)-N(5)	91.3(2)
O(20)-Cu(1)-N(6)	93.5(2)	O(15)-Cu(3)-N(5)	89.3(3)
O(19)-Cu(1)-O(1)#2	91.4(2)	O(14)-Cu(3)-N(5)	103.1(3)
O(18)-Cu(1)-O(1)#2	93.2(2)	O(13)-Cu(3)-N(4)	87.3(2)
O(17)-Cu(1)-O(1)#2	89.9(2)	O(16)-Cu(3)-N(4)	94.2(2)
O(20)-Cu(1)-O(1)#2	71.9(2)	O(15)-Cu(3)-N(4)	82.2(3)
N(6)-Cu(1)-O(1)#2	165.3(2)	O(14)-Cu(3)-N(4)	85.6(2)
N(1)-O(1)-Cu(1)#3	139.0(6)	N(5)-Cu(3)-N(4)	170.0(2)
O(9)-Cu(2)-N(3)	91.4(2)	O(19)-Cu(3)-N(6)	89.5(3)

Symmetry transformations used to generate equivalent atoms: #1:x+1,-y+3/2,z+1/2;#2:x-1,y,z; #3:x+1,y,z;#4:x-1,-y+3/2,z-1/2.

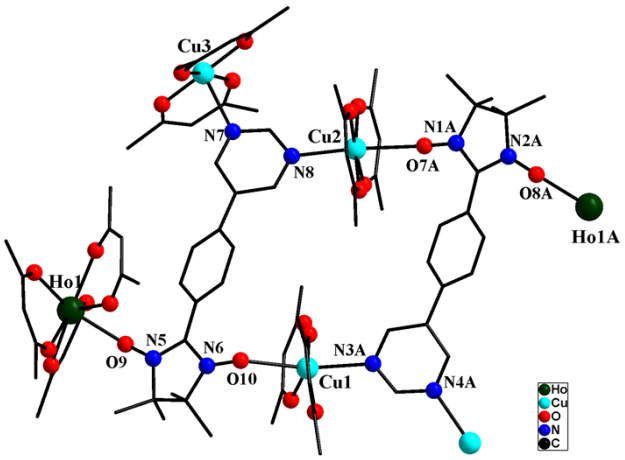

Figure S1. Crystal structure of complex **2**. Hydrogen atoms and fluorine atoms are not shown for the sake of clarity. (A:x,-1/2-y,-1/2+z;B:1+x,y,z)

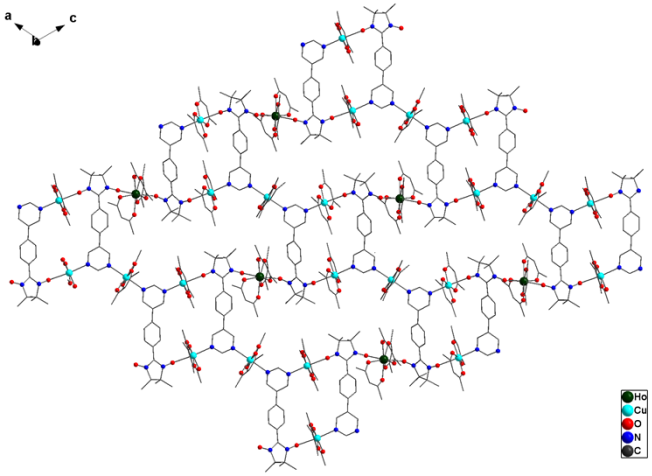

Figure S2. The two-dimensional layer structure of complex **2**, all hydrogen atoms and fluorine atoms are omitted for clarity.

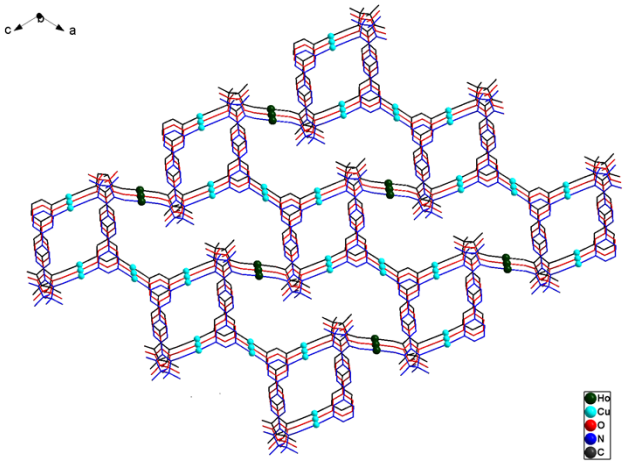

Figure S3. Crystal packing arrangement for complex **2**.

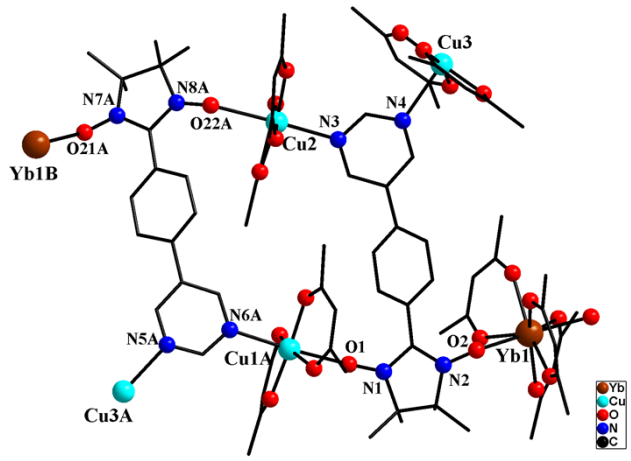

Figure S4. Crystal structure of complex **3**. Hydrogen atoms and fluorine atoms are not shown for the sake of clarity. (A:1+x, y, z;B:x,3/2-y,-1/2+z)

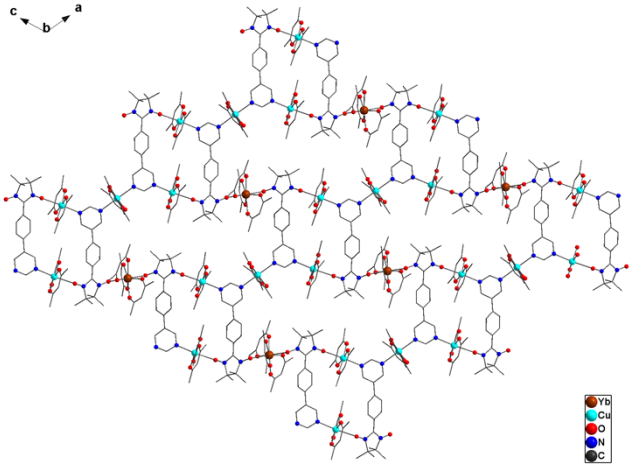

Figure S5. The two-dimensional layer structure of complex **3**, all hydrogen atoms and fluorine atoms are omitted for clarity.

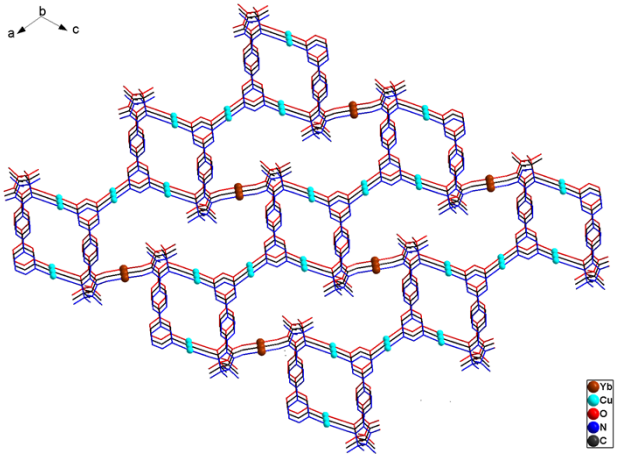

Figure S6. Crystal packing arrangement for complex **3**.

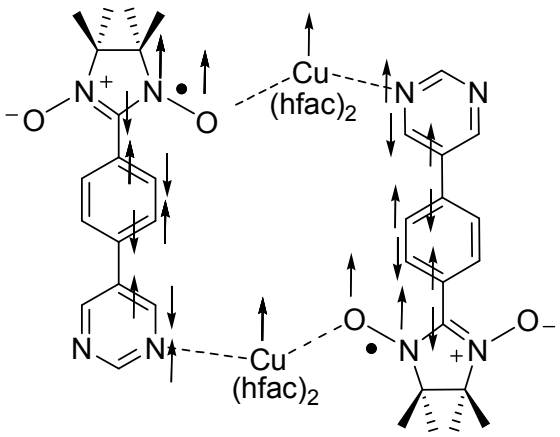

Chart S1. Spin polarization mechanism for the magnetic coupling mediated by NITPhPyrim ligand.

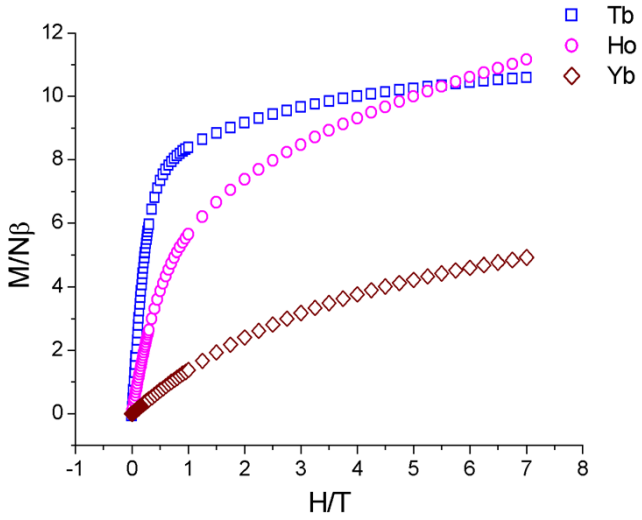

Figure S7. *M* versus *H/T* plots for complexes **1-3** at 2.0 K.

Table S4. Relaxation fitting parameters from Least-Squares Fitting of χ(ω) data.

T	$\chi_{S,tot}$	$\Delta\chi_1$	τ_1	α_1	$\Delta\chi_2$	τ_2	α_2
2.5	2.07	1.04	0.71	0.26	2.11	0.00035	0.25
3.0	2.36	0.44	0.39	0.036	1.96	0.00018	0.13

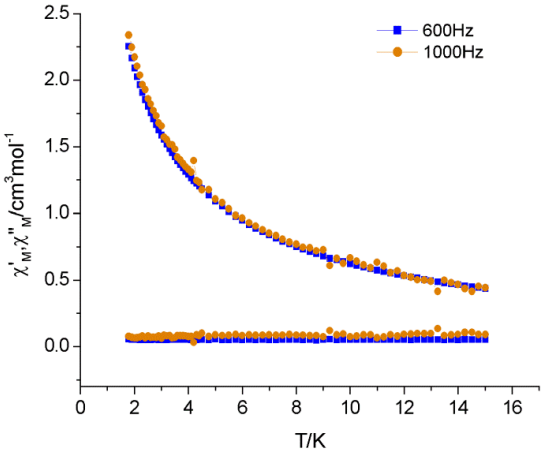

Figure S8.Temperature dependence of the in-phase and out-of-phase components of the ac magnetic susceptibility for **2** in zero dc fields with an oscillation of 3.0 Oe.

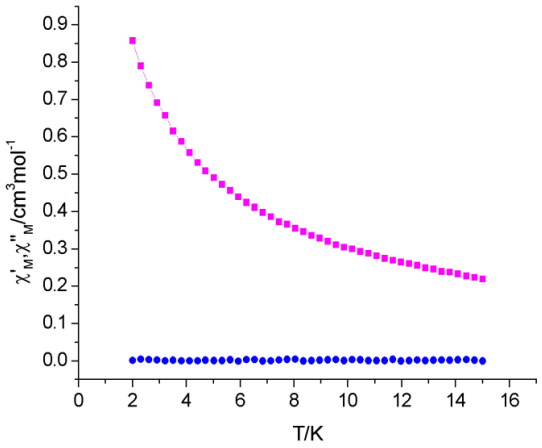

Figure S9.Temperature dependence of the in-phase and out-of-phase components of the ac magnetic susceptibility for **3** in zero dc fields with an oscillation of 3.0 Oe. (AC frequency:100Hz)