Supporting Information for:

Syntheses and magnetic properties of a bis-tridentate

nitronyl nitroxide radical and its metal complexes

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Table of contents

Physical Measurements	3
Syntheses	3
EPR Spectrum for 1	5
Fig. S1 EPR spectrum of the radical ligand NIT-Pm2Py.	6
X-ray Crystallography	6
Table S1 Crystal data and structure refinements for Complexes 1-4	6
Table S2 Selected bond lengths (Å) for 1	7
Table S3 Selected bond lengths (Å) for 2	7
Table S4 Selected bond lengths (Å) for 3	7
Table S5 Selected bond lengths (Å) for 4	8
Magnetic measurements	8
Fig. S2 The field dependent magnetization curve of 1 at 2 K	8
Fig. S3 The field dependent magnetization curve of 2 at 2 K	9
Fig. S4 The field dependent magnetization curve of 3 at 2 K	9
Fig. S5The field dependent magnetization curve of 4 at 2 K	9
Table S6 Relaxation fitting parameters of the Cole-Cole plots of 4	10
Powder X-ray diffraction (PXRD) spectra	10
Fig. S6 The powder X-ray diffraction patterns for 1	10
Fig. S7 The powder X-ray diffraction patterns for 2	10
Fig. S8 The powder X-ray diffraction patterns for 3	11
Fig. S9 The powder X-ray diffraction patterns for 4	11
Computational details for CASSCF with MOLCAS 8.2	
Fig. S10 Calculated model structures of complexes 2–4	12
Table S7 Calculated spin-free energies for complexes 2–4	13
Table S8 Calculated weights of complexes 2–4	13
Table S9 Calculated zero-field splitting parameters of complexes 2–4	14
Table S10 Calculated values of complex $4_b(Co3)$	14
Fig. S11 Calculated orientations of the local magnetic axes of complexes 2-4	15
Fig. S12 Mn-radical couplings of <i>J</i> in complex 2	16
Reference	17

1. Physical Measurements

IR data were measured on KBr pellets using a Bruker Vector 22 FT-IR spectrometer in the 4000-400 cm⁻¹ range. Elemental analyses for C, H, and N were performed at Elementar Vario MICRO analyzer. Powder XRD patterns were obtained on Bruker D8X diffractometer equipped with monochromatized Cu-K α ($\lambda = 0.15418$ nm) radiation at room temperature, and the data were collected in the range of 5 ° ≤ 2 θ ≤ 50 ° on grinded crystalline samples for all compounds. Magnetic susceptibility measurements were performed using Quantum Design SQUID VSM magnetometer on micro crystalline samples for all compounds. All magnetic data were corrected for the diamagnetism of the sample holder. The diamagnetism of the sample was estimated according to Pascal's constants.

2. Syntheses

All the chemicals purchased were of reagent grade and were used without further purification. The synthesized precursor aldehyde of the radicals were prepared according to the literature procedure.^{S1} This new radical was synthesized by the reported method using 4,6-di(pyridin-2-yl)pyrimidine-2-carbaldehyde as the starting aldehyde.^{S2}





Firstly, a-1 (3.63 g, 33.9 mmol), a-2 (3.90 g, 32.1 mmol) and 75 mL methanol were added in a 500

mL flask placed in an ice bath. KOH solution (1.2 g in 225 mL H_2O) was then added, and the solution was stirred for three hours. Pale yellow precipitation was observed and filtrated. Chromatography (5:1 PE/EA) affords **a-3** as a fluffy white solid, yield: 3.70 g (55%).

Secondly, NaOH (0.8 g), acetamidine hydrochloride (1.7 g, 18 mmol) and EtOH (200 mL) were added in a 500 mL flask. **a-3** (3.6 g, 17 mmol) was then added in portions over a period of 20 min. Following the addition, the mixture was heated to reflux and a gradual color change from pale orange to peach and finally to dark yellow was observed with concomitant precipitation of a white solid (NaCl). Refluxing was continued for 2 h and then the mixture was cooled to room temperature. Air was bubbled through the solution for about 10 min, and the pH was lowered to neutral by addition of saturated ammonium chloride solution. All of the EtOH was removed under reduced pressure, affording a forest green aqueous solution containing a white precipitate. The flask was cooled in ice for 0.5 h, and then the off-white solid was collected by vacuum filtration, washed with cold distilled water and dried. Chromatography (4:1 hexanes/EtOAc) affords **a-4** as a fluffy white solid, yield: 1.63 g (38%).

Thirdly, **a-4** (1.32 g, 5.3 mmol) and SeO₂ (0.88 g, 8 mmol) were added to a 3-neck flask containing dioxane (50 mL), and the mixture was heated to 90 °C with stirring under a nitrogen atmosphere. At this temperature, distilled water (0.2 mL) was added to the reaction mixture and the solution was subsequently heated to 130 °C for 4 d. Over the course of the reaction a fine black solid precipitates out (Se) and the solution darkens to a salmon color. The reaction was stopped when all, or most, of **a-4** was reacted and the reaction flask was subsequently cooled to room temperature. Distilled water (50 mL) was added and the flask was cooled in an ice bath, affording an off-white solid which was collected by filtration. Trituration of the solid with CH₂Cl₂ (3 × 30 mL) and evaporation of the CH₂Cl₂ extracts under reduced pressure affords **a-5** as a crude tan solid, which was recrystallized from CH₂Cl₂/Et₂O (1:3) at -10 °C. More **a-5** can be recovered by evaporation of the dioxane/water filtrate. Combined yield: 0.28 g (20 %).

At last, **a-5** (0.28 g), **a-6** (0.30 g) and 50 mL EtOH were added into a 100 mL flask. The solution was then stirred for 1 d. Solid precipitates of **a-7** (about 0.5 g) were collected by filtration, which were used for the further reaction without purification. All **a-7** was added to 50 mL CH_2Cl_2 to give a suspension in CH_2Cl_2 . Excessive NaIO₄ aqueous solution (1g in 50 mL H₂O) was slowly added

dropwise in 15 minutes. Following the addition of NaIO₄ solution, the solid of **a-7** dissolved and the organic layer turned to deep purple. The product was then extracted by CH_2Cl_2 (50 mL × 3). After the extraction, all of the CH_2Cl_2 was removed under reduced pressure, affording a red precipitate. Silica gel chromatography (pure EtOAc) affords **1** as a red solid, yield: 0.17 g (40 %).

Purple needle-like crystals of **1** were obtained by the slow evaporation of its CH_2Cl_2 solution after 3 days. Anal. Calcd (%) for $C_{21}H_{21}N_6O_2$: C, 64.77; H, 5.87; N, 21.48. Found: C, 64.56; H, 5.44; N, 21.58. IR (KBr pellet, cm⁻¹): 3098(m), 1579(s), 1417(s), 1266(m), 1175(s), 992(m), 765(s), 646(s), 539(m).

(NIT-2-Pm)Mn₂(hfac)₄(2)

A solution of Mn(hfac)₂·2H₂O (46.90 mg, 0.10mmol, 2.0 eq) in 30 mL of dry boiling n-heptane was heated to reflux for 3 h and then cooled to 70 °C. Then, 10 mL of CH₂Cl₂ solution of NIT-2-Pm (11.76 mg, 0.05 mmol, 1.0 eq) was added. The solution was stirred for 30 min and was cooled to room temperature and filtered. After one week, yellow crystals of **2** were obtained. Yield: 21.4 mg (36%). Anal. Calcd (%) for $C_{31}H_{19}F_{24}Mn_2N_4O_{10}$: C, 31.73; H, 1.63; N, 4.78. Found: C, 31.31; H, 1.57; N, 4.54. IR (KBr pellet, cm⁻¹): 3105(m), 2221(m), 1645(s), 1410(s), 1250(s), 1190(s), 1140(s), 813(m), 647(m), 576(m).

$[(NIT-Pm2Py)Mn_2(hfac)_4] \cdot 0.5 C_7H_{16}(3).$

Complex **3** was prepared in the essentially identical way as that for **2** but using NIT-Pm2Py as the radical ligand. Yield: 24.4 mg (35%). Anal. Calcd (%) for $C_{44.5}H_{33}F_{24}Mn_2N_6O_{10}$: C, 38.40; H, 2.41; N, 6.10. Found: C, 38.25; H, 2.51; N, 6.29. IR (KBr pellet, cm⁻¹): 3124(m), 1658(s), 1555(s), 1498(s), 1325(s), 1266(s), 1214(s), 1143 (s), 801(m), 660 (m), 584(m).

[(NIT-Pm2Py)Co₂(H₂O)(hfac)₃][Co(hfac)₃] · 0.5 H₂O · 0.25 C₇H₁₆ (4).

Complex 4 was made in the similar way as that for 3 but using $Co(hfac)_2 \cdot 2H_2O$ as the metal salt. Also, the equivalence ratio of $Co(hfac)_2 \cdot 2H_2O$ and the NIT-ligand was changed from 2:1 to 3:1. Yield: 25.4 mg (27%). Anal. Calcd (%) for $C_{52.75}H_{34}Co_3F_{36}N_6O_{15.5}$: C, 34.05; H, 1.84; N, 4.51. Found: C, 34.31; H, 1.97; N, 4.54. IR (KBr pellet, cm⁻¹): 3288(m), 3098(m), 1647(s), 1528(s), 1375(s), 1258(s), 1206(s), 1148(s), 795(m), 673(m), 587(m).

3. EPR Spectrum of 1

The EPR spectrum of **1** at 300 K in CH₂Cl₂ solution shows five similar major lines in the ratio of 1:2:3:2:1, as expected for coupling with two identical nitrogen atoms of N-O groups in the radicals. The *g* value is estimated as 2.007 according to $g = hv/\beta H$ (v = 9.8544 GHz), and the nitrogen hyperfine coupling constants α^{N} is 7.33 G.



Fig. S1 EPR spectrum of the radical ligand NIT-Pm2Py.

4. X-ray Crystallography

Single-crystal X-ray crystallographic data were collected on a Bruker APEX II diffractometer with a CCD area detector (Mo-K α radiation, λ = 0.71073 Å). The APEX II program was used to determine the unit cell parameters and for data collection. The data were integrated and corrected for Lorentz and polarization effects using SAINT.^{S3} Absorption corrections were applied with SADABS.^{S4} The structures were solved by direct methods and refined by a full-matrix least-squares method on F² using the SHELXTL crystallographic software package.^{S5} All nonhydrogen atoms were refined anisotropically, and all hydrogen atoms were refined by the riding mode. Details of the data collections and structural refinement parameters are provided in Table S1. Selected bond lengths for compounds 1-4 are listed in Table S2-S5. They can be obtained free of charge from the

Cambridge Crystallographic Data Center via www. ccdc.cam.ac.uk/data_request/cif.

Complex	1	2	3	4
Formula	$C_{21}H_{21}N_6O_2$	C31H19F24Mn2N4O10	$C_{44.5}H_{33}F_{24}Mn_2N_6O_{10}$	C52.75H32C03F36N6O15.5
Mr / gmol ⁻¹	389.44	1173.38	1377.65	1858.60
Temperature / K	150	150	150	150
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\overline{1}$	$P\overline{1}$	<i>P</i> 2 ₁ /n	C2/c
a /Å	10.2375(8)	12.207(5)	17.143(2)	24.6425(19)
b/Å	10.7695(8)	12.761(5)	16.374(2)	20.7127(14)
c /Å	11.1404(8)	14.489(5)	21.215(3)	29.4191(19)
α/deg	66.602(2)	87.736(6)	90	90
β /deg	65.760(2)	77.249(6)	113.30(3)	100.068(2)
γ/deg	66.314(2)	80.846(5)	90	90
$V/\text{\AA}^3$	985.18(13)	2173.3(14)	5469.6(12)	14784.7(18)
Ζ	2	2	2	2
$ ho_{ m calc}/ m g~cm^{-1}$	1.313	1.793	1.673	1.694
μ (Mo–K α)(mm ⁻¹)	0.089	0.741	0.603	0.820
F (000)	410	1158	2752	7356
Refl.collected/unique	8807/8807	14313/7658	34189/9571	51159 / 13023
GOF on F ²	1.059	1.089	1.060	1.079
$R_1^{\rm a}/wR_2^{\rm b} (I \geq 2\sigma(I))$	0.0507/0.1420	0.0739/0.1948	0.0658/0.1785	0.0580/0.1340
R_1/wR_2 (all data)	0.0626/0.1516	0.1077/0.2275	0.0752/0.1859	0.0948/0.1500

 Table S1 Crystal data and structure refinements for Complexes 1-4

 $\overline{{}^{a} \mathbf{R}_{1} = \sum ||F_{o}| - |F_{c}|| \sum |F_{o}|} \cdot \mathbf{w} \mathbf{R}_{2} = \{\sum [\mathbf{w}(F_{o}^{2} - F_{c}^{2})^{2}] / \sum [\mathbf{w}(F_{o}^{2})^{2}] \}^{1/2}$

Table S2 Selected bond lengths (Å) for 1				
O(1)-N(6)	1.2767(17)	O(2)-N(5)	1.2779(16)	

	Table S3 Selected bond lengths (Å) for 2				
Mn(1)-O(4)	2.109(4)	Mn(1)-O(5)	2.114(3)		
Mn(1)-O(3)	2.118(4)	Mn(1)-O(2)	2.128(3)		
Mn(1)-O(1)	2.168(3)	Mn(1)-N(1)	2.359(4)		
Mn(2)-O(8)	2.119(4)	Mn(2)-O(9)	2.120(4)		
Mn(2)-O(6)	2.128(3)	Mn(2)-O(7)	2.140(3)		
Mn(2)-O(10)	2.154(3)	Mn(2)-N(2)	2.346(4)		

O(1)-N(3)	1.286(5)	O(6)-N(4)	1.293(5)
	Table S4 Selected I	bond lengths (Å) for 3	
Mn(1)-O(7)	2.158(3)	Mn(1)-O(2)	2.164(3)
Mn(1)-O(9)	2.194(3)	Mn(1)-O(10)	2.226(3)
Mn(1)-O(8)	2.241(3)	Mn(1)-N(6)	2.310(3)
Mn(1)-N(4)	2.440(3)	Mn(2)-O(4)	2.159(3)
Mn(2)-O(5)	2.182(3)	Mn(2)-O(6)	2.190(3)
Mn(2)-O(1)	2.203(3)	Mn(2)-O(3)	2.247(3)
Mn(2)-N(5)	2.306(4)	Mn(2)-N(3)	2.459(3)
O(1)-N(1)	1.287(4)	O(2)-N(2)	1.270(5)
	Table S5 Selected	bond lengths (Å) for 4	
N(2)-O(2)	1.278(5)	N(1)-O(3)	1.288(4)
Co(1)-O(7)	1.996(3)	Co(1)-O(8)	2.042(3)
Co(1)-O(3)	2.051(3)	Co(1)-N(3)	2.072(4)
Co(1)-O(6)	2.115(3)	Co(1)-N(4)	2.117(3)
Co(2)-O(2)	2.014(4)	Co(2)-O(5)	2.029(3)
Co(2)-O(4)	2.050(3)	Co(2)-N(6)	2.059(4)
Co(2)-N(5)	2.108(3)	Co(2)-O(1)	2.119(3)
Co(3)-O(14)	2.051(3)	Co(3)-O(13)	2.048(3)
Co(3)-O(10)	2.062(3)	Co(3)-O(15)	2.077(3)
Co(3)-O(12)	2.077(3)	Co(3)-O(11)	2.079(3)

5. Magnetic measurements



Fig. S2 The field dependent magnetization curve of 1 at 2 K.



Fig. S3 The field dependent magnetization curve of 2 at 2 K.



Fig. S4 The field dependent magnetization curve of 3 at 2 K.



Fig. S5 The field dependent magnetization curve of 4 at 2 K.

Temperature / K	$\chi_S \ / \ cm^3mol^{-1}K$	$\chi_T / \ cm^3 mol^{-1} K$	τ/s	α	
1.8	0.00020	11.44336	0.00045	0.29876	
2.0	0.24881	10.57657	0.00038	0.23623	
2.4	1.06102	9.50133	0.00028	0.13153	
2.6	1.18375	9.02897	0.00022	0.11230	
2.8	0.97498	8.50161	0.00016	0.10858	
3.0	1.04177	8.02128	0.00012	0.08176	
3.2	0.97347	7.59582	0.00009	0.07718	
3.4	1.06336	7.21499	0.00007	0.06789	
3.6	1.8544	6.86635	0.00005	0.05757	

 Table S6 Relaxation fitting parameters from the least-square fitting of the Cole-Cole plots of 4 according to the generalized Debye model.

6. Powder X-ray diffraction (PXRD) spectra of 1, 2, 3 and 4



Fig. S6 The powder X-ray diffraction patterns for 1 at room temperature.



Fig. S7 The powder X-ray diffraction patterns for complex 2 at room temperature.



Fig. S8 The powder X-ray diffraction patterns for complex 3 at room temperature.



Fig. S9 The powder X-ray diffraction patterns for complex 4 at room temperature.

7. Computational details for CASSCF with MOLCAS 8.2

Complex **4** has two types of structures: binuclear compound **4**_*a* and mononuclear **4**_*b* (Co3). Binuclear **2**, **3** and **4**_*a* have two types of individual Mn^{II} or Co^{II} fragments, and thus two individual Mn^{II} or Co^{II} fragments (see Figure S12 for the calculated model structures of **2**, **3**, **4**_*a* and **4**_*b* on the basis of X-ray determined geometry of complexes **2**–**4**) were calculated by complete-active-space self-consistent field (CASSCF) calculations with MOLCAS 8.2 program package.^{S6} During the calculations, individual Mn^{II} or Co^{II} fragments of **2**, **3** and **4**_*a* were calculated keeping the experimentally determined structure of the corresponding compound while replacing the neighboring Mn^{II} or Co^{II} ion by diamagnetic Zn^{II} , and the spin of the central radical was considered as 0.

The basis sets for all atoms are atomic natural orbitals from the MOLCAS ANO-RCC library: ANO-RCC-VTZP for Mn^{II} or Co^{II} ion; VTZ for close N; VDZ for distant atoms. The calculations employed the second order Douglas-Kroll-Hess Hamiltonian, where scalar relativistic contractions were taken into account in the basis set. And then, the spin-orbit couplings were handled separately in the restricted active space state interaction (RASSI-SO) procedure. For Mn^{II} or Co^{II} fragment, active electrons in 5 active spaces include all *d* electrons (CAS(5 in 5 for Mn^{II} , 7 in 5+5 ′ for Co^{II})) in the CASSCF calculation. To exclude all the doubts, we calculated all the roots in the active space. We have mixed the maximum number of spin-free states which was possible with our hardware (all from 1 sextet, all from 24 quadruplets, all from 75 doublets for Mn^{II} ; all from 10 quadruplets and 20 from 40 doublets for Co^{II}). SINGLE_ANISO^{S7} program was used to obtain zero-field splitting parameters D (E) (cm⁻¹), g tensors, energy levels, magnetic axes, *et al.*, based on the above CASSCF/RASSI calculations.





4_*a*



4_*b*

Fig. S10 Calculated model structures of complexes 2–4. H atoms are omitted for clarity.

spin-free	2(Mn1)	2(Mn2)	3(Mn1)	3(Mn2)	4_a(Co1)	4_a(Co2)	4_b(Co3)
states	E/cm^{-1}	E/cm^{-1}	E/cm^{-1}	E/cm^{-1}	E/cm ⁻¹	E/cm^{-1}	E/cm^{-1}
1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	25450.9	25952.5	27573.2	27171.1	1264.8	1177.2	390.2
3	26043.8	26118.3	28125.4	27965.8	1602.2	1363.1	452.0
4	26512.5	26867.6	29944.1	29774.0	8185.9	8554.7	7381.4
5	29262.2	29300.5	30728.1	30658.4	8806.3	9580.8	7490.1
6	29833.7	29957.7	31233.2	30935.4	9076.7	9661.8	7742.3
7	30358.1	30515.6	31318.4	31028.7	17474.1	18994.8	15943.7
8	31068.5	31098.8	31422.1	31132.8	23489.9	23348.5	22823.4
9	31240.4	31239.0	31524.7	31287.3	23872.9	24861.8	22880.5
10	31313.1	31326.1	31612.8	31308.3	25127.2	25698.1	23815.8

Table S7. Calculated spin-free energies (cm⁻¹) of the lowest ten terms (S=5/2 for Mn^{II} and of S=3/2 for Co^{II}) of individual Mn^{II} or Co^{II} fragments for complexes **2–4** using CASSCF/RASSI with MOLCAS 8.2.

	Spin- orbit states	Energy (cm ⁻¹)	Spin-free states, Spin, Weights				
	1	0.0	1,2.5,0.9995	2,1.5,0.0002	18,1.5,0.0001	3,1.5,0.0001	17,1.5,0.0001
2(Mn1)	2	0.1	1,2.5,0.9995	2,1.5,0.0001	4,1.5,0.0001	16,1.5,0.0001	5, 1.5, 0.0011
	1	0.0	1,2.5,0.9995	2,1.5,0.0001	3,1.5,0.0001	18,1.5,0.0001	17,1.5,0.0001
2(Mn2)	2	0.1	1,2.5,0.9996	4,1.5,0.0001	2,1.5,0.0001	18,1.5,0.0001	16,1.5,0.0001
2(M-1)	1	0.0	1,2.5,0.9996	18,1.5,0.0001	2,1.5,0.0001	17,1.5,0.0001	3,1.5,0.0001
3(MINI)	2	0.1	1,2.5,0.9996	11,1.5,0.0001	18,1.5,0.0001	2,1.5,0.0001	4,1.5,0.0000
2(14-2)	1	0.0	1,2.5,0.9996	18,1.5,0.0001	2,1.5,0.0001	17,1.5,0.0001	3,1.5,0.0001
3(MINZ)	2	0.1	1,2.5,0.9996	11,1.5,0.0001	18,1.5,0.0001	2,1.5,0.0001	4,1.5,0.0000
$4 \sigma(C_{2})$	1	0.0	1,1.5,0.8918	2,1.5,0.0656	3,1.5,0.0398	4,1.5,0.0008	6,1.5,0.0006
4_ <i>a</i> (C01)	2	80.4	1,1.5,0.9592	2,1.5,0.0201	3,1.5,0.0152	5,1.5,0.0021	4,1.5,0.0015
$\int g(\mathbf{C} \mathbf{a}^2)$	1	0.0	1,1.5,0.8802	2,1.5,0.0706	3,1.5,0.0456	4,1.5,0.0015	5,1.5,0.0005
4_ <i>a</i> (C02)	2	107.2	1,1.5,0.9532	3,1.5,0.0230	2,1.5,0.0197	5,1.5,0.0013	4,1.5,0.0011
$4 h(C_{2})$	1	0.0	1,1.5,0.5862	2,1.5,0.2279	3,1.5,0.1832	4,1.5,0.0007	19,0.5,0.0007
4_ <i>v</i> (C03)	2	222.2	1,1.5,0.8355	2,1.5,0.0839	3,1.5,0.0742	4,1.5,0.0021	5,1.5,0.0019

Table S8. Calculated weights of the five most important spin-free states for the lowest two spin-orbit states of individual Mn^{II} or Co^{II} fragments of complexes 2–4 using CASSCF/RASSI with MOLCAS 8.2.

Table S9. Calculated zero-field splitting parameters D(E) (cm⁻¹) and $g(g_x, g_y, g_z)$ tensors of the lowest spin-orbit states of complexes 2–4 using CASSCF/RASSI with MOLCAS 8.2.

	2(Mn1)	2(Mn2)	3(Mn1)	3Mn2)	4_a(Co1)	4_a(Co2)
CAS	(5, 10)	(5, 10)	(5, 10)	(5, 10)	(3, 5+5)	(3, 5+5)
Spin	$S_{\rm Mn} = 5/2$	$S_{\rm Co}=3/2$	$S_{\rm Co}=3/2$			
D(E)	0.04 (0.01)	0.03 (0.01)	0.03 (0.01)	0.04 (0.01)	39.2 (-5.1)	51.5 (-8.5)
	2.002	2.002	2.002	2.002	2.543	2.588
g	2.002	2.002	2.002	2.002	2.432	2.421
	2.002	2.002	2.002	2.002	2.083	2.018

Table S10. Calculated lowest two spin-orbit energies (cm⁻¹) and g(x, y, z) values of complex **4**_*b*(Co3) using CASSCF/RASSI with MOLCAS 8.2.

	E/cm^{-1}	g
1	0.0	5.559

F			4.564
			2.858
			0.320
	2	222.2	0.520
			5.343







3_a



Fig. S11 Calculated orientations of the local magnetic axes of the lowest spin-orbit state on Mn^{II} or Co^{II} ions of complexes 2–4 with CASSCF/RASSI calculation.

To fit the exchange interaction in complexes 2 and 3, we took two steps. Firstly, we calculated individual Mn^{II} fragments using CASSCF/RASSI to obtain the corresponding magnetic properties.



Fig. S12 Mn-radical couplings of J in complex 2.

For complexes 2 and 3, we only consider the Mn-radical couplings (see Fig. S12).

The Ising exchange Hamiltonian is:

$$\hat{H}_{exch} = -2J(\hat{S}_{Mn1}\hat{S}_{radical} + \hat{S}_{Mn2}\hat{S}_{radical})$$
(1)

The J is the parameter of the total magnetic interaction between magnetic center ions. The spin $S_{Mn} = 5/2$ is on Mn1 and Mn2 sites, and the spin $S_{radical} = 1/2$ is on the radical site. The exchange

coupling constants were fitted through comparison of the computed and measured magnetic susceptibilities using the POLY_ANISO program.^{S7}

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