Supplementary information

Unquenched orbital angular momentum in quasi-linear two-coordinate transition metal complexes featuring sterically bulky carbazole ligands

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Table of Contents

General considerations 3

Syntheses 3

1,8-bis(dipheylmethyl)-3,6-ditertbutylcarbazole, $^{(tbu)2}carbH^{(Ph2Me)2}$ (**1**) 3

$Mn(^{(tbu)2}carb^{(Ph2CH)2})_2$ (**2-Mn**) 3

$Fe(^{(tbu)2}carb^{(Ph2CH)2})_2$ (**2-Fe**) 4

$Co(^{(tbu)2}carb^{(Ph2CH)2})_2$ (**2-Co**) 4

NMR Spectra 5

X-ray Crystallography 7

Cyclic Voltammetry 10

Powder XRD 13

Magnetic Measurement 14

Theoretical Calculation 21

References 30

General considerations

All air- and moisture-sensitive manipulations were carried out using standard glove box or Schlenk line techniques unless otherwise mentioned. Solvents for air- and moisture-sensitive manipulations were dried and deoxygenated using a Glass Contour Solvent Purification System and stored over 4 Å activated molecular sieves or Na-sand in an inert atmosphere prior to use. Diphenylmethanol, 3,6-ditertbutyl carbazole, hydrochloric acid, zinc chloride (anhydrous), manganese chloride (anhydrous), cobalt chloride (anhydrous) and iron chloride (anhydrous) were purchased from commercial sources and used without further purification. Benzyl potassium[1] was prepared using literature procedure. Deuterated solvents for NMR spectroscopy were purchased from Cambridge Isotope Laboratories and distilled from sodium metal (for C_6D_6) or CaH_2 (for $CDCl_3$) and stored over 4 Å molecular sieves in the glove box. ^1H and ^{13}C $\{^1H\}$ NMR spectra were recorded on an Agilent 400 MHz or a Varian INOVA 600 MHz spectrometer. Chemical shifts were referenced to the ^1H and ^{13}C resonances of the deuterated solvents. Elemental analysis of the synthesized compounds was performed by Robertson Microlit Laboratories.

Syntheses

1,8-bis(dipheylmethyl)-3,6-ditertbutylcarbazole, $^{(tbu)2}$carbH$^{(Ph2CH)2}$ (1)

10.0 g 3,6-ditertbutylcarbazole (35.78 mmol, 1 equiv) and 13.30 g diphenylmethanol (71.56 mmol, 2 equiv) were melted together in a 100 mL Schlenk flask under N_2. A solution of anhydrous 2.44 g $ZnCl_2$ (17.89 mmol, 0.5 equiv) and 2.95 mL HCl (35.78 mmol, 1 equiv) was dropwise added to the melt while stirring. The reaction mixture solidifies almost immediately. The mixture was heated at 160 °C for 6 hours. After cooling to room temperature, the resulting solid was dissolved in 200 mL of dichloromethane (DCM) and extracted with deionized water (2 × 150 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure to yield an off-white solid. The crude product was washed with ethyl acetate, affording a white solid, which was filtered and dried under vacuum overnight. The dried product was stored in a glovebox for further use. Yield 13.5 g (60%). Recrystallization from a mixture of DCM and hexane generated single crystals suitable for X-ray diffraction. Anal. calcd. for $C_{46}H_{45}N \cdot 0.13\ CH_2Cl_2$: C 88.95%; H 7.32%; N 2.25%. Found C 88.44%; H 7.00%; N 2.23%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, m-*H*Ar), 6.98-7.24 (m, 22H, m-*H*Ar, H_{Ph}), 6.87 (s, 1H, N*H*), 5.45 (s, 2H, C*H*Ph_2), 1.31 (s, 18H, C(CH_3)$_3$). ^{13}C NMR (400MHz, $CDCl_3$) δ 142.22, 142.17, 136.52, 129.13, 128.47, 126.58, 125.62, 124.51, 123.36, 114.58, 54.19, 34.63, 31.92. IR (ATR, cm^{-1}) 3440 (s), 2959 (br), 2875 (w), 1599 (m), 1491 (s), 1432 (m), 1364 (m), 1304 (w), 1255 (s), 1156 (w), 1077 (m), 1029 (m), 958 (w), 919 (w), 874 (s), 755 (s), 734 (s), 696 (s), 673 (w). UV-vis (toluene, λ_{max}, nm [ε(M^{-1}, cm^{-1})]): 298.

Mn($^{(tbu)2}$carb$^{(Ph2CH)2}$)$_2$ (2-Mn)

To a stirring solution of 200 mg $^{(tbu)2}$carbH$^{(Ph2CH)2}$ (0.348 mmol, 2 equiv) in THF, a solution of 45 mg KBn (0.348 mmol, 2 equiv) in THF was added dropwise. The resulting solution of the

deprotonated ligand was yellow in color and glowed blue when shone with a white light. This deprotonated ligand solution was slowly added to a 20 mL vial charged with a suspension of 21.8 mg $MnCl_2$ (0.174 mmol, 1 equiv, anhydrous) in THF and stirred at room temperature overnight. The following day, the solvent was removed under vacuum leaving a yellow oily residue. The residue was then extracted with pentane and the bright yellow pentane extract was filtered through a pipette filter over a pad of celite. The pentane extract was then set up for slow diffusion in toluene forming X-ray quality yellow crystals of **2-Mn**. Yield 48 mg (23%). Anal. calcd. for $C_{92}H_{88}N_2Mn$: C 86.55%; H 6.94%; N 2.19%. Found C 84.32%; H 7.04%; N 2.04%. IR (ATR, cm^{-1}) 3448 (br), 2961 (s), 1600 (w), 1493 (s), 1363 (w), 1259 (w), 1031 (w), 871 (w), 701 (s). UV-vis (toluene, λ_{max}, nm [$\varepsilon(M^{-1}, cm^{-1})$]): 298.

Fe($^{(tbu)2}$carb$^{(Ph2CH)2}$)$_2$ (2-Fe)

To a stirring solution of 200 mg $^{(tbu)2}$carbH$^{(Ph2CH)2}$ (0.348 mmol, 2 equiv) in THF, a solution of 45 mg KBn (0.348 mmol, 2 equiv) in THF was added dropwise. The resulting solution of the deprotonated ligand was yellow in color and glowed blue when shone with a white light. This deprotonated ligand solution was slowly added to a 20 mL vial charged with a suspension of 22 mg $FeCl_2$ (0.174 mmol, 1 equiv, anhydrous) in THF and stirred at room temperature for 48 hours. Afterwards, the solvent was evaporated off under vacuum and the crude material was then extracted with pentane. The deep red pentane extract was filtered through a pipette filter over a pad of celite. Slow diffusion of the pentane extract into toluene yielded X-ray quality red crystals of **2-Fe**. Yield 43.5 mg (21%). Anal. calcd. for $C_{92}H_{88}N_2Fe$: C 86.49%; H 6.94%; N 2.19%. Found C 87.35%; H 7.08%; N 1.95%. IR (ATR, cm^{-1}) 3438 (w), 2961 (br), 1599 (w), 1493 (s), 1363 (w), 1260 (m), 1095 (br), 1030 (m), 870 (w), 800 (m), 701 (s), 627 (w). UV-vis (toluene, λ_{max}, nm [$\varepsilon(M^{-1}, cm^{-1})$]): 298.

Co($^{(tbu)2}$carb$^{(Ph2CH)2}$)$_2$ (2-Co)

To a stirring solution of 200 mg $^{(tbu)2}$carbH$^{(Ph2CH)2}$ (0.348 mmol, 2 equiv) in THF, a solution of 45 mg KBn (0.348 mmol, 2 equiv) in THF was added dropwise. The resulting solution of the deprotonated ligand was yellow in color and glowed blue when shone with a white light. This deprotonated ligand solution was slowly added to a 20 mL vial charged with a suspension of 23 mg $CoCl_2$ (0.174 mmol, 1 equiv, anhydrous) in THF and stirred at room temperature for 48 h. Afterwards, solvent was removed under vacuum leaving a brown residue. The residue was then extracted with pentane and the deep blue pentane extract was filtered through a pipette filter over a pad of celite. The pentane extract was then set up for slow diffusion into toluene forming X-ray quality blue crystals of **2-Co**. Yield 42 mg (20%). Anal. calcd. for $C_{92}H_{88}N_2Co$: C 86.28%; H 6.93%; N 2.18%. Found C 86.11% H 7.01%; N 1.85%. IR (ATR, cm^{-1}) 3444 (w), 2962 (br), 1599 (w), 1493 (s), 1363 (w), 1261 (m), 1092 (br), 1032 (m), 872 (w), 804 (m), 701 (s). UV-vis (toluene, λ_{max}, nm [$\varepsilon(M^{-1}, cm^{-1})$]): 298.

NMR Spectra

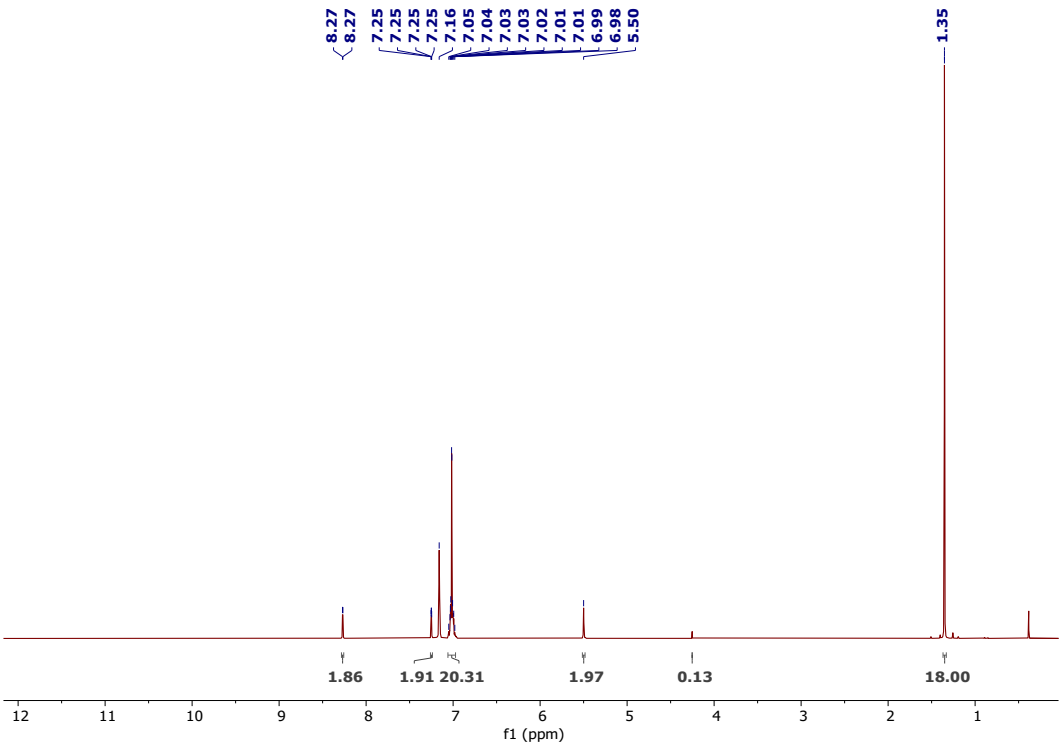

Figure S1:

Figure S1: ^{1}H NMR spectrum of $^{(tbu)2}$carbH$^{(Ph2CH)2}$ **(1)** in C_6D_6.

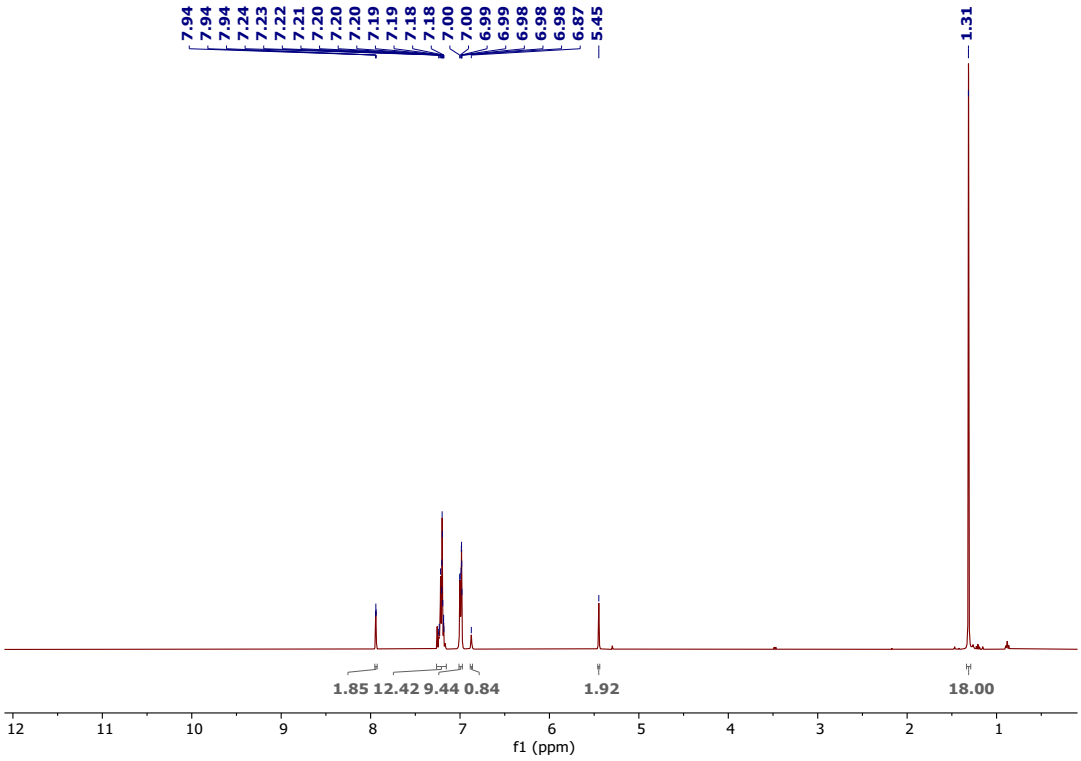

Figure S2: ^{1}H NMR spectrum of $^{(tbu)2}$carbH$^{(Ph2CH)2}$ **(1)** in $CDCl_3$.

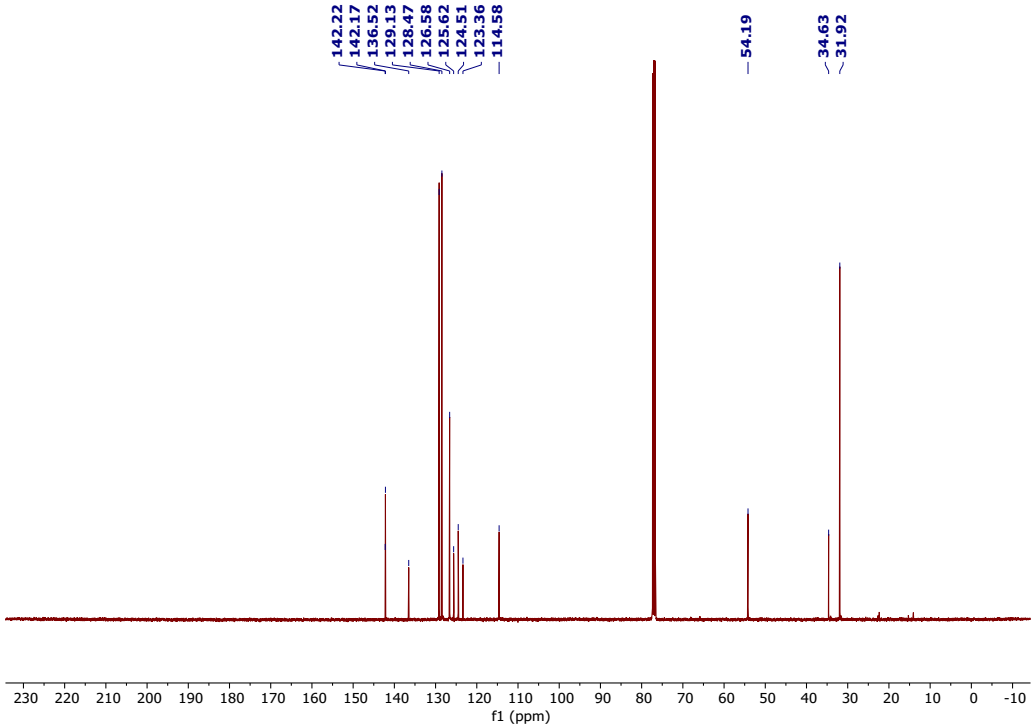

Figure S3: ^{13}C NMR spectrum of $^{(tbu)2}$carbH$^{(Ph2CH)2}$ **(1)** in $CDCl_3$.

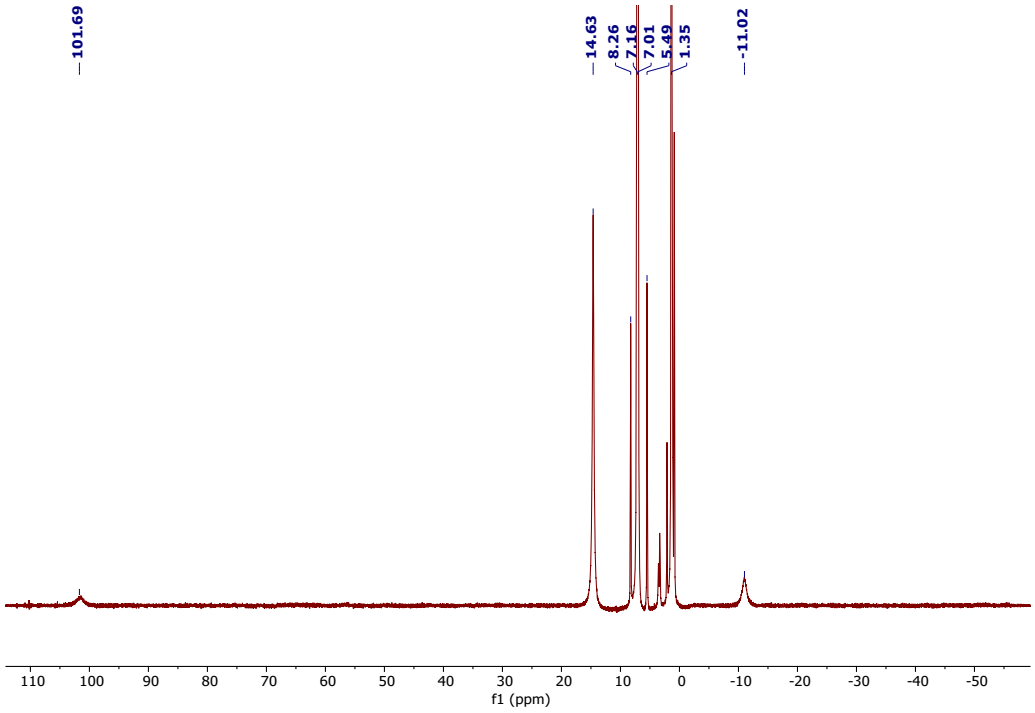

Figure S4: ^{1}H NMR spectrum of Co($^{(tbu)2}$carb$^{(Ph2CH)2}$)$_2$ **(2-Co)** in C_6D_6.

X-ray Crystallography

Suitable crystals of the compounds were selected under polybutene oil and mounted to a MiTeGen Micromount and mounted at 100 K to a D8-Venture diffractometer equipped with a Mo sealed tube X-ray source, a Triumph monochromator, and a Photon 2 CMOS area detector. Unit cells were determined from reflections harvested with a signal to noise ratio (I/σ) of at least 8 from a series of 3 ω scans of 6° with 0.5° frames using APEX3.[2] The data were integrated using SAINT and corrected for absorption using SADABS.[3,4] All structures were solved using the intrinsic phasing routine of SHELXT.[5] The non-hydrogen atoms were located from a Fourier difference map of the electron density and anisotropically refined using the least-squares algorithm of SHELXL.[6,7] Hydrogen atoms were then placed in calculated positions and refined with riding thermal parameters. A summary of refinement parameters can be found in Table **S1**.

Table S1: Crystallographic details of compounds **1, 2-Mn, 2-Fe and 2-Co.**

Compound	**1**	**2-Mn**	**2-Fe**	**2-Co**
Empirical formula	$C_{46}H_{45}N$	$C_{92}H_{88}N_2Mn$	$C_{92}H_{88}N_2Fe$	$C_{92}H_{88}N_2Co$
Formula weight	611.83	1276.58	1277.49	1280.57
Temperature / K	100 (1)	100 (1)	150 (1)	100 (1)
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	C2/c	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a / Å	13.5105 (9)	11.8910 (4)	11.9927 (9)	12.0213 (5)
b / Å	22.1840 (15)	12.5457 (4)	12.5791 (10)	12.5284 (4)
c / Å	11.7721 (4)	24.7931 (8)	24.7232 (15)	24.5267 (10)
α / °	90	98.369 (2)	98.610 (3)	98.474 (1)
β / °	107.1339 (17)	101.632 (2)	101.715 (2)	101.769 (1)
γ / °	90	95.547 (2)	95.375 (3)	95.374 (1)
Volume / $Å^3$	3371.7 (5)	3553.7 (2)	3581.0 (4)	3547.5 (2)
Z	4	2	2	2
$\rho_{calc}g/cm^3$	1.205	1.193	1.185	1.199
μ/mm^{-1}	0.068	0.235	0.259	0.291
F(000)	1312	1358.0	1360	1362
Crystal size/mm^3	0.033 x 0.121 x 0.174	0.266 x 0.118 x 0.089	0.093 x 0.193 x 0.287	0.091 x 0.103 x 0.171
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.156 to 25.686	2.374 to 26.435	2.246 to 25.738	2.109 to 26.393
Index ranges	-16 ≤ h ≤ 16, -26 ≤ k ≤ 26, -14 ≤ l ≤ 14	-14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -30 ≤ l ≤ 30	-14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -30 ≤ l ≤ 30	-14 ≤ h ≤ 15, -15 ≤ k ≤ 15, -30 ≤ l ≤ 30
Reflections collected	22233	92341	23463	43584
Independent reflections	3204	14557	13481	14510
R (int)	0.1232	0.1047	0.0728	0.1119
Data / restraints / parameters	3204/0/216	14557/216/948	13481/210/948	14510/210/948
Goodness-of-fit on F^2	1.126	1.054	1.039	0.981
Final R indexes	R_1 = 0.0741	R_1 = 0.0573	R_1 = 0.0922	R_1 = 0.0578
$[I>=2\sigma (I)]^{a,b}$	wR_2 = 0.1486	wR_2 = 0.1190	wR_2 = 0.2807	wR_2 = 0.1272
Final R indexes [all data]	R_1 = 0.1078	R_1 = 0.0888	R_1 = 0.1432	R_1 = 0.1184
	wR_2 = 0.1364	wR_2 = 0.1089	wR_2 = 0.2558	wR_2 = 0.1085
Largest diff. peak/hole / e $Å^{-3}$	0.212/-0.298	0.297/-0.532	0.923/-0.694	0.379/-0.460

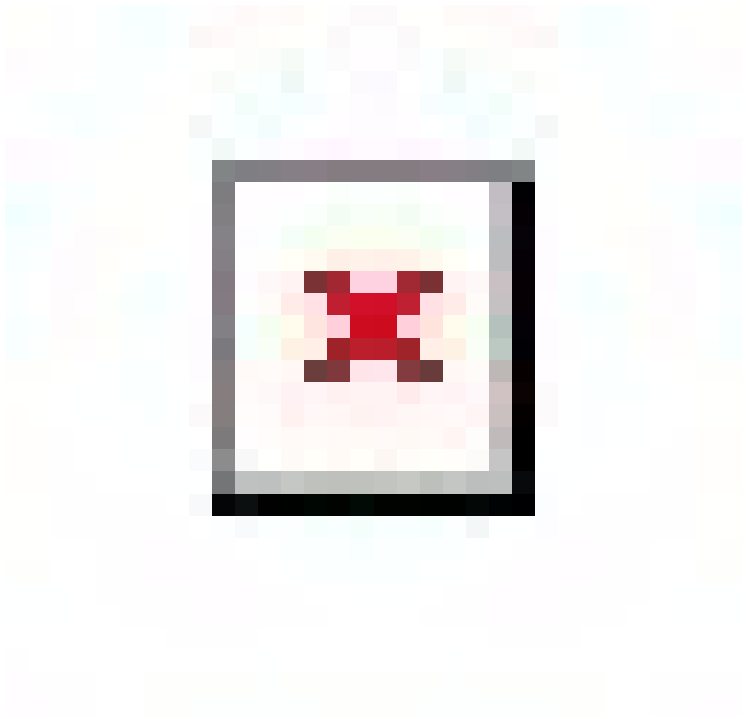

Fig S5: Crystal structure of **Mn($^{(tbu)2}$carb$^{(Ph2CH)2}$)$_2$ (2-Mn)**. All atoms are drawn as 50% probability thermal ellipsoids. All hydrogen atoms are omitted for clarity.

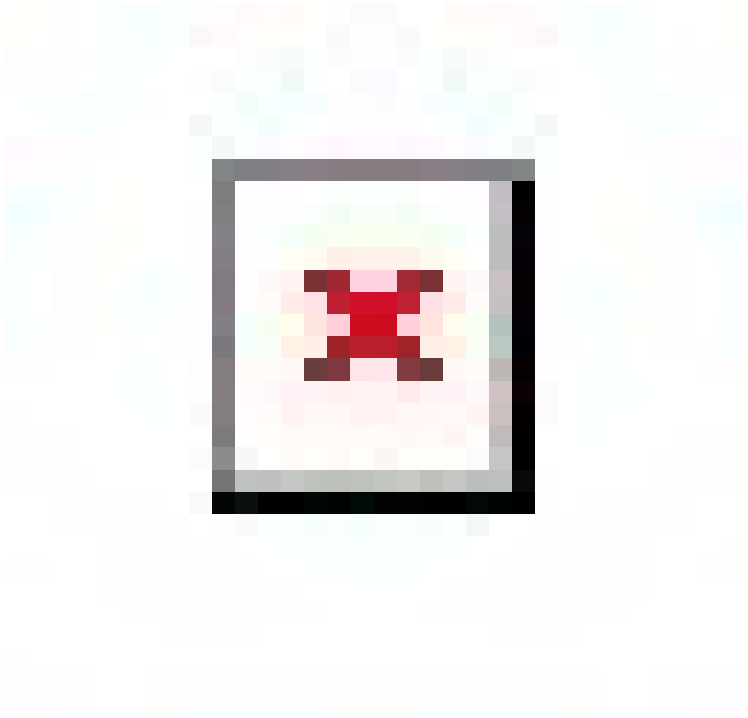

Fig S6: Crystal structure of **Fe($^{(tbu)2}$carb$^{(Ph2CH)2}$)$_2$ (2-Fe)**. All atoms are drawn as 50% probability thermal ellipsoids. All hydrogen atoms are omitted for clarity.

Cyclic Voltammetry

Cyclic voltammetry measurements were conducted in a nitrogen filled glovebox using a 1 mM solutions of the compounds in DCM with 100 mM $[nBu_4N][PF_6]$ as the supporting electrolyte, using a Bio-Logic SP200 potentiostat/galvanostat and the EC-Labsoftware suite. A glassy carbon electrode, a gold wire and a silver wire were used as the working electrode, the counter electrode and the quasi-reference electrode respectively. After the completion of the measurements, Ferrocene was added as the internal standard, and all potentials were references versus the Fc^+/Fc^0 couple.

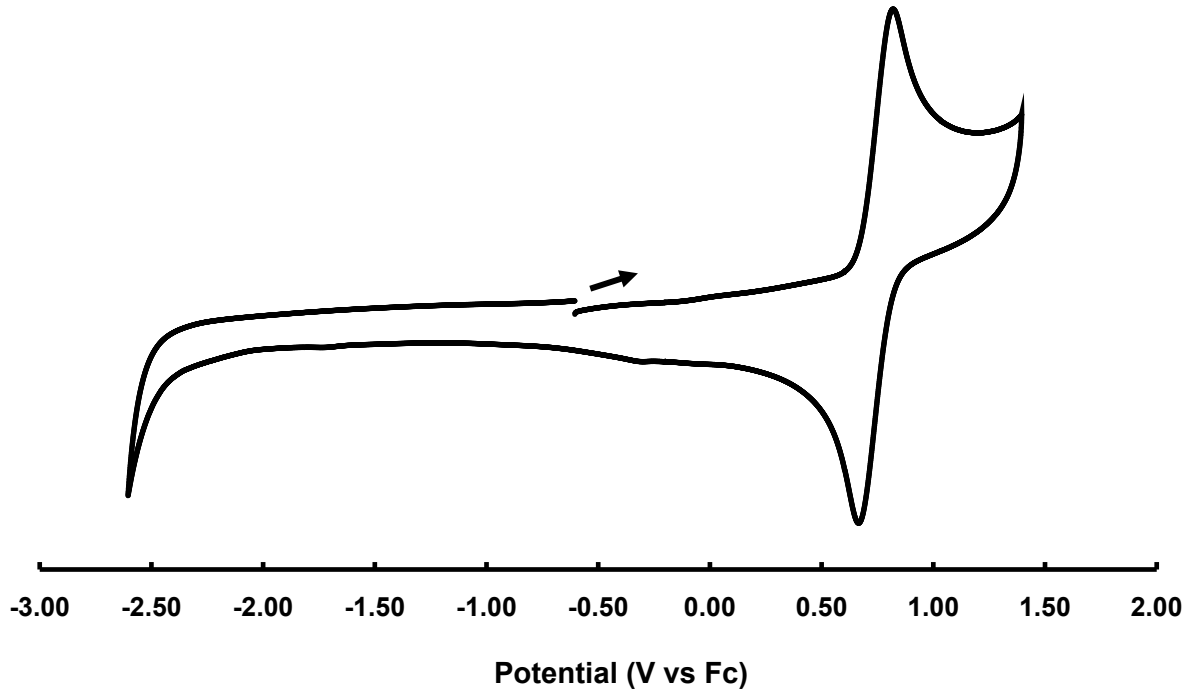

Fig S7: Cyclic voltammogram of **1** in DCM**.**

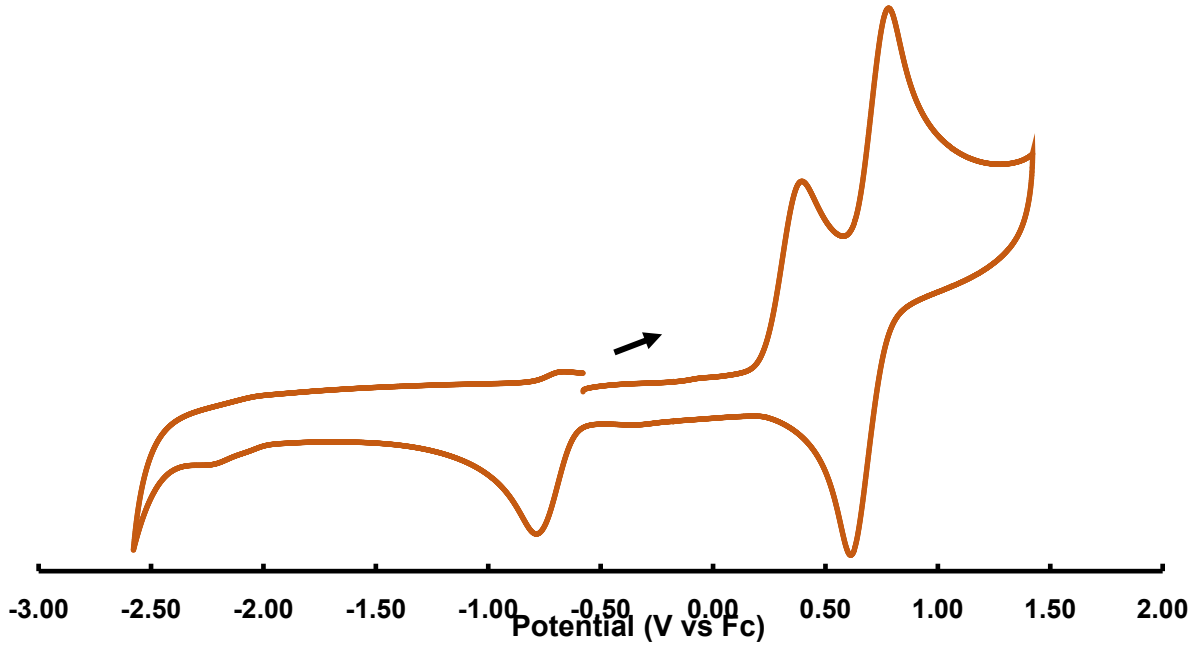

Fig S8: Cyclic voltammogram of **2-Mn** in DCM**.**

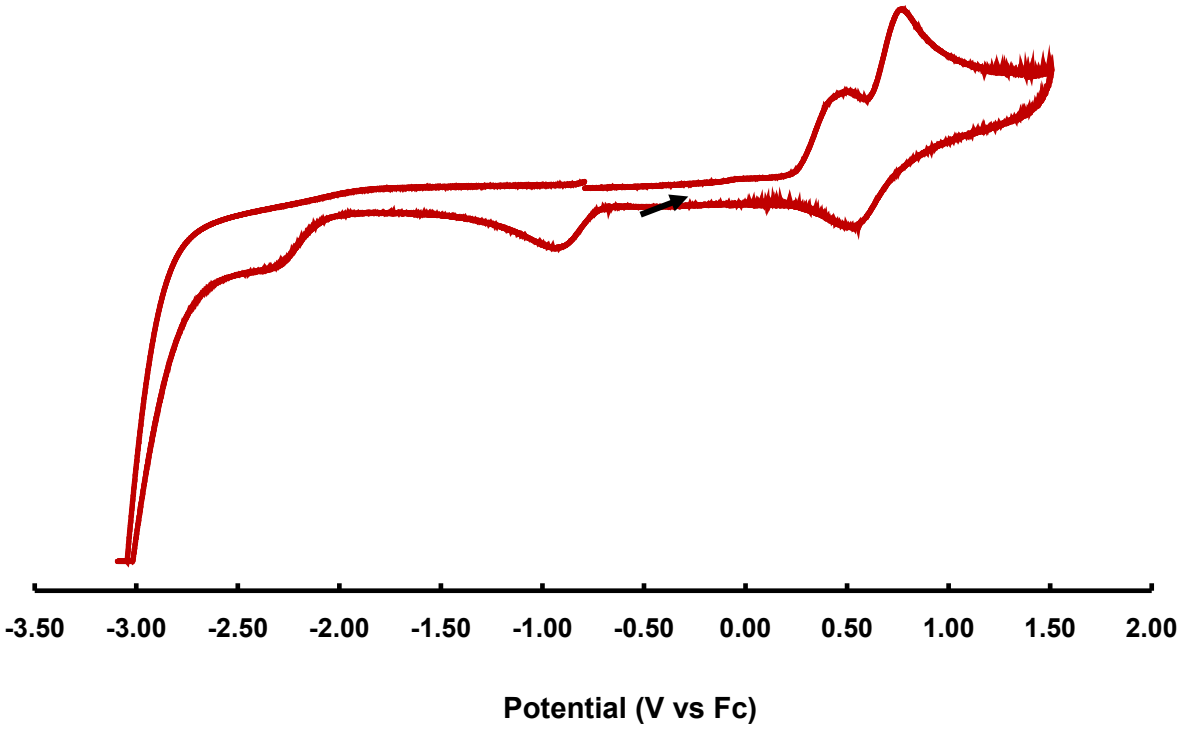

Fig S9: Cyclic voltammogram of **2-Fe** in DCM**.**

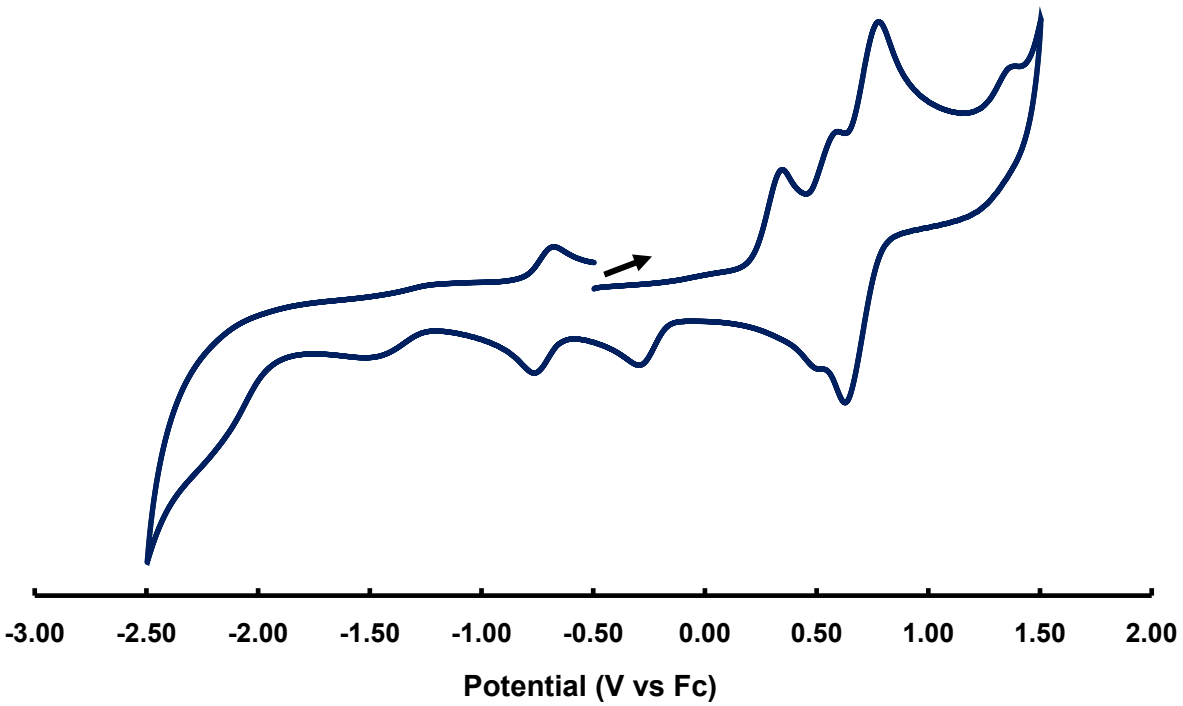

Fig S10: Cyclic voltammogram of **2-Co** in DCM.

Powder XRD

Due to the highly sensitive nature of the compounds, multiple attempts were required to obtain the powder diffractograms. Refer to Fig S11 and S12 for the powder diffractograms of 2-Mn and 2-Fe. Attempts to obtain a powder diffractogram of 2-Co was unsuccessful, which is perhaps due to its extreme air-sensitivity.

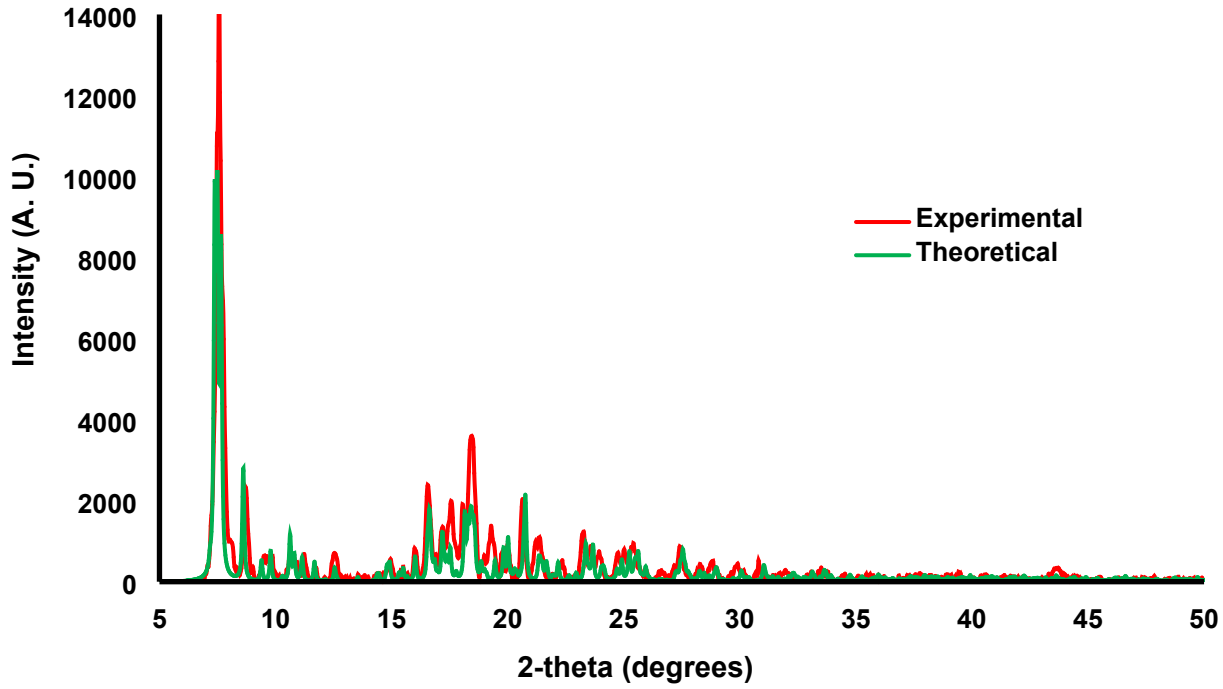

Fig S11: Powder XRD pattern of **2-Mn**.

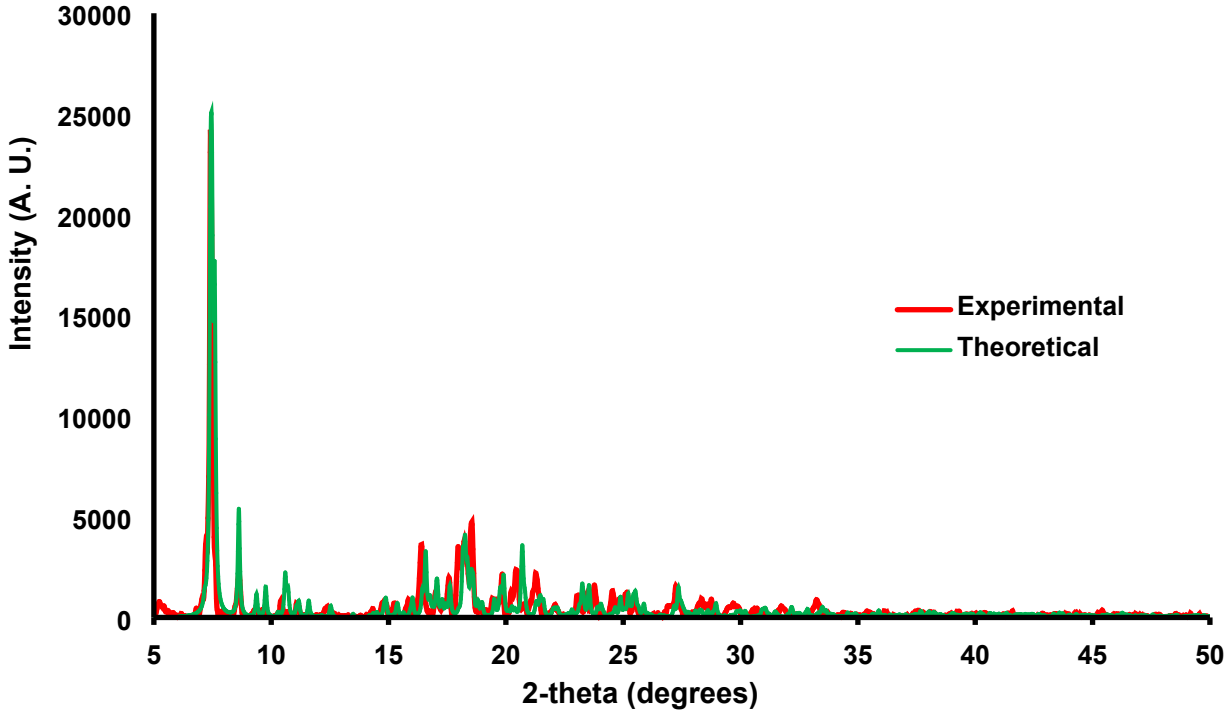

Fig S12: Powder XRD pattern of **2-Fe**.

Magnetic Measurement

Magnetic data were collected on microcrystalline samples of **2-Mn** and **2-Fe**, mixed with warmed eicosane and sealed in polycarbonate capsules. **2-Co** was added to a 4mm/5mm inner/outer diameter quartz tube, covered in eicosane, and flame sealed under vacuum. Variable-temperature DC susceptibility data, VHVT (variable field fixed temperature) magnetization data, and AC susceptibility data for complexes **2-Mn**, **2-Fe** and **2-Co** were measured with a MPMS 3 Quantum Design SQUID magnetometer at the University of Wisconsin–Madison. Susceptibility data were obtained by cooling to ~2 K in the absence of a magnetic field and subsequently measuring the magnetic moment from the starting temperatures to 300 K in an applied 1000 G DC magnetic field. VHVT data were collected for the complexes at temperatures of 2, 4, 6, and 8 K as the field strength was increased from 0 to 7 T. Experimental susceptibility data were corrected for underlying diamagnetism using Pascal's constants.[8] AC susceptibility data were collected at temperatures between 2-10 K for the complexes **2-Mn** and **2-Co** and between 2-6 K for **2-Fe**, at frequencies between 1-1000 Hz. More AC susceptibility data was collected for compound **2-Fe** between 1.8-2.7 K at more frequencies between 1-1000 Hz and further data was collected for compound **2-Fe** at 2 and 2.5 K in an applied DC magnetic field ranging from 0– 5000 Oe. For compound **2-Co**, AC susceptibility data was collected at 1.8 K in an applied DC magnetic

field ranging from 0-2000 Oe at frequencies between 1-1000 Hz. Under an applied field of 1500 Oe using a 2 Oe switching field, final AC susceptibility data was collected for **2-Co** between 2-7K at frequencies between 1-1000Hz. The DC susceptibility data for the complexes were modeled simultaneously with the following Hamiltonian (equation 1) and equation 2, using the fitting program PHI.[9]

$$\hat{\mathrm{H}} = D\hat{S}^2 + \mu_B g_{iso} S.H \tag{1}$$

$$\chi_{exp} = \frac{\chi_{calc}}{1 - \left(\frac{2zJ}{N_A \mu_B^2 g^2}\right)\chi_{calc}} \tag{2}$$

In equation (1), *D* is the axial zero field splitting parameter, S is the spin of the system, μ_B is the Bohr magneton, g_{iso} is the isotropic gyromagnetic factor or the *g*-factor, *H* is the applied field. In equation (2), χ_{exp} and χ_{calc} are experimental and calculated magnetic susceptibilities and *zJ* is intermolecular interactions.

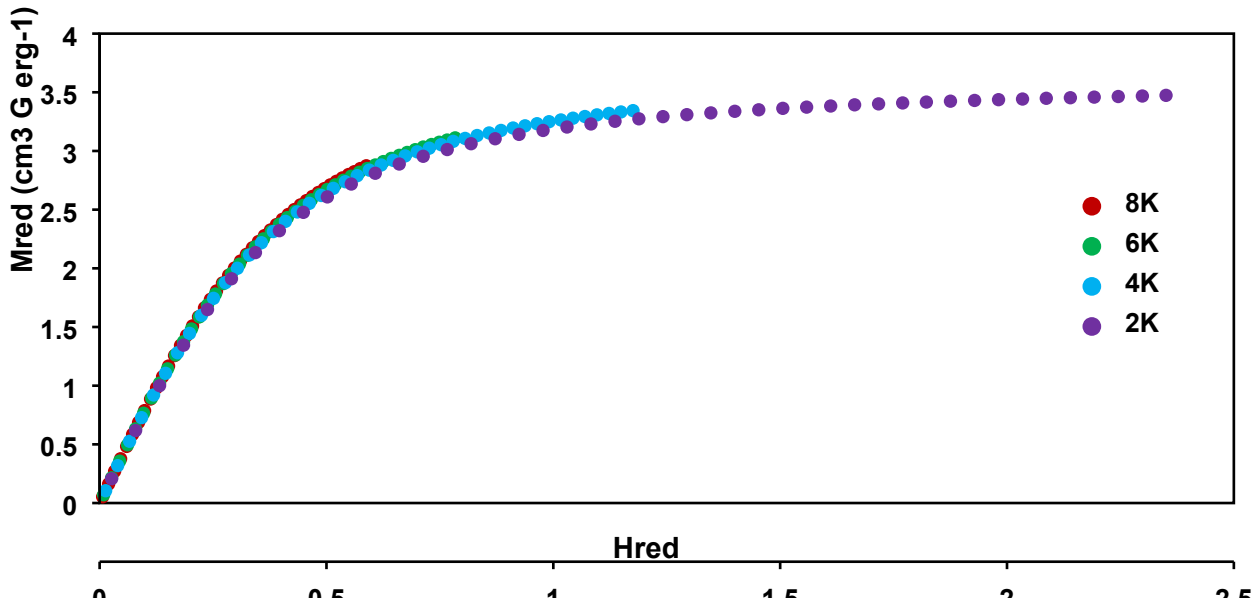

Fig S13: Reduced magnetization plot of **2-Mn**.

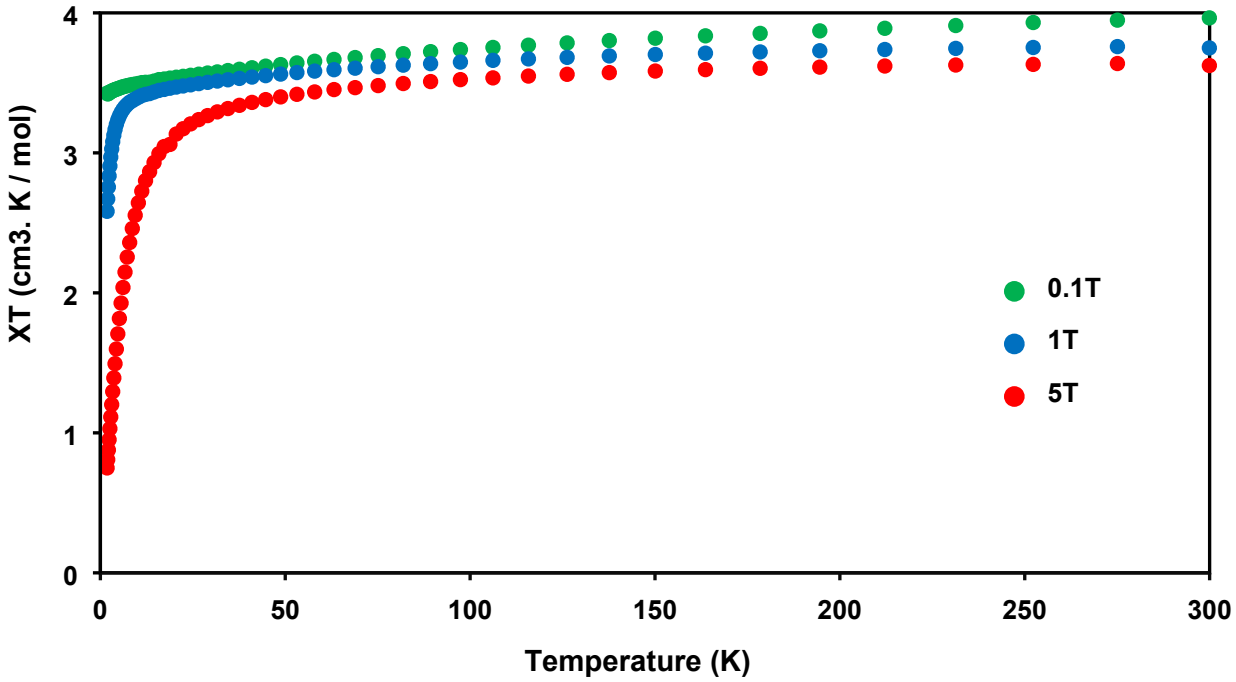

Fig S14: DC magnetic susceptibility plot of **2-Mn** at different field strengths of 0.1 T, 1T and 5T.

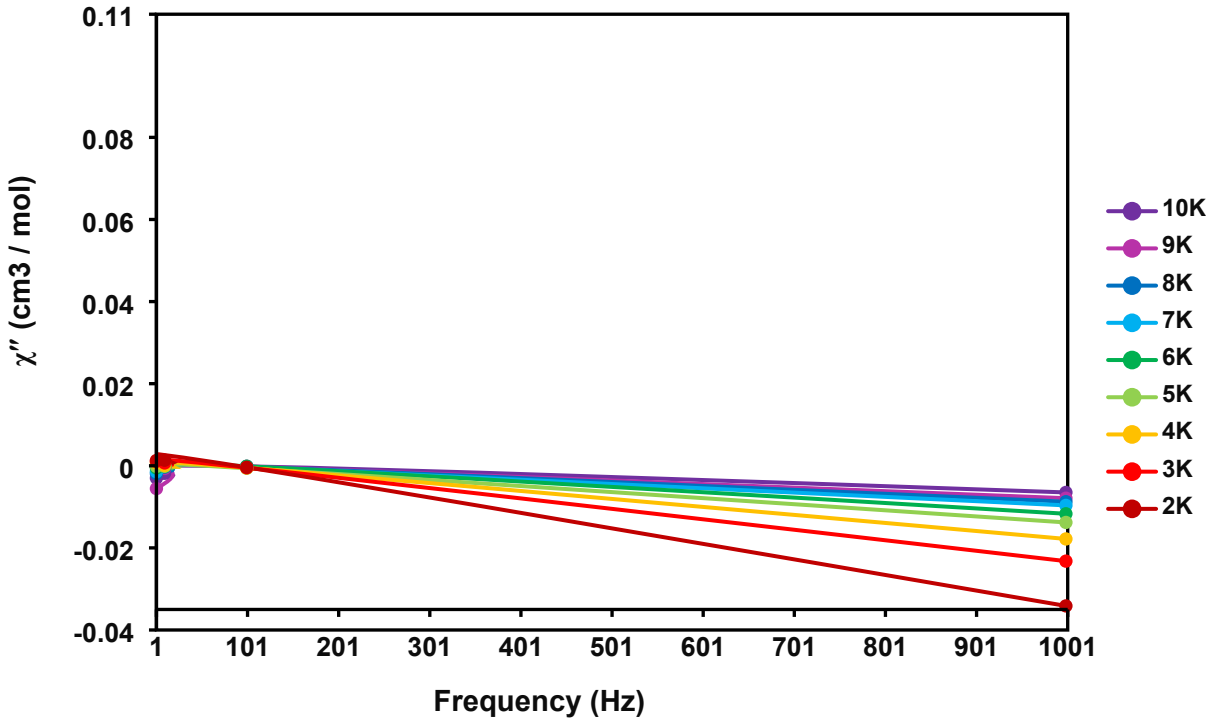

Fig S15: Out-of-phase magnetic susceptibility of **2-Mn**.

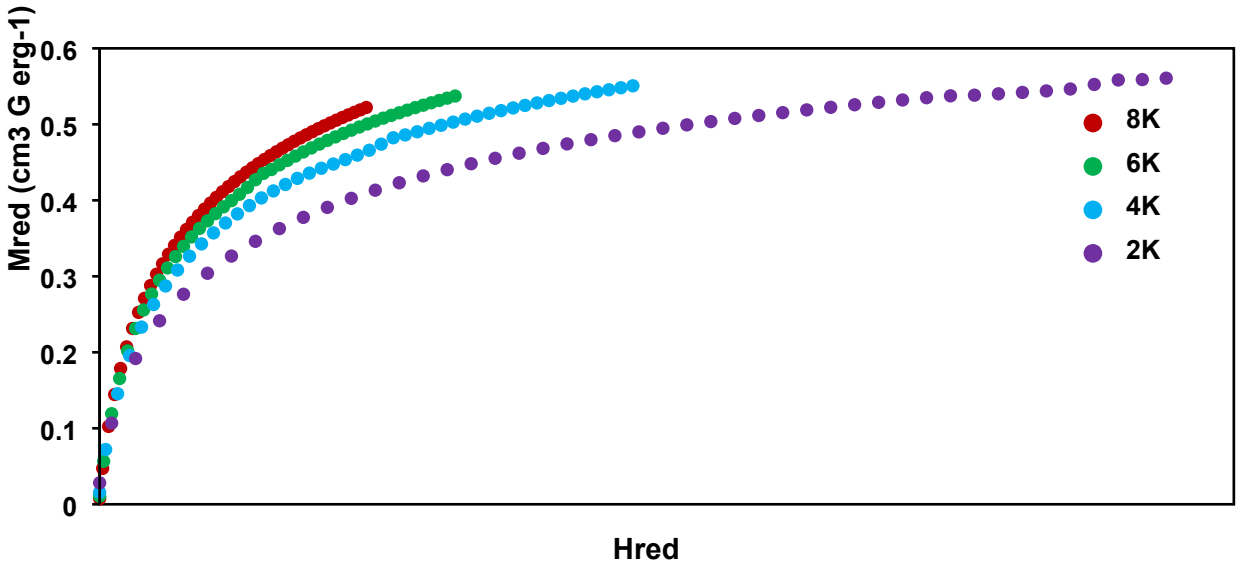

Fig S16: Reduced magnetization plot of **2-Fe**.

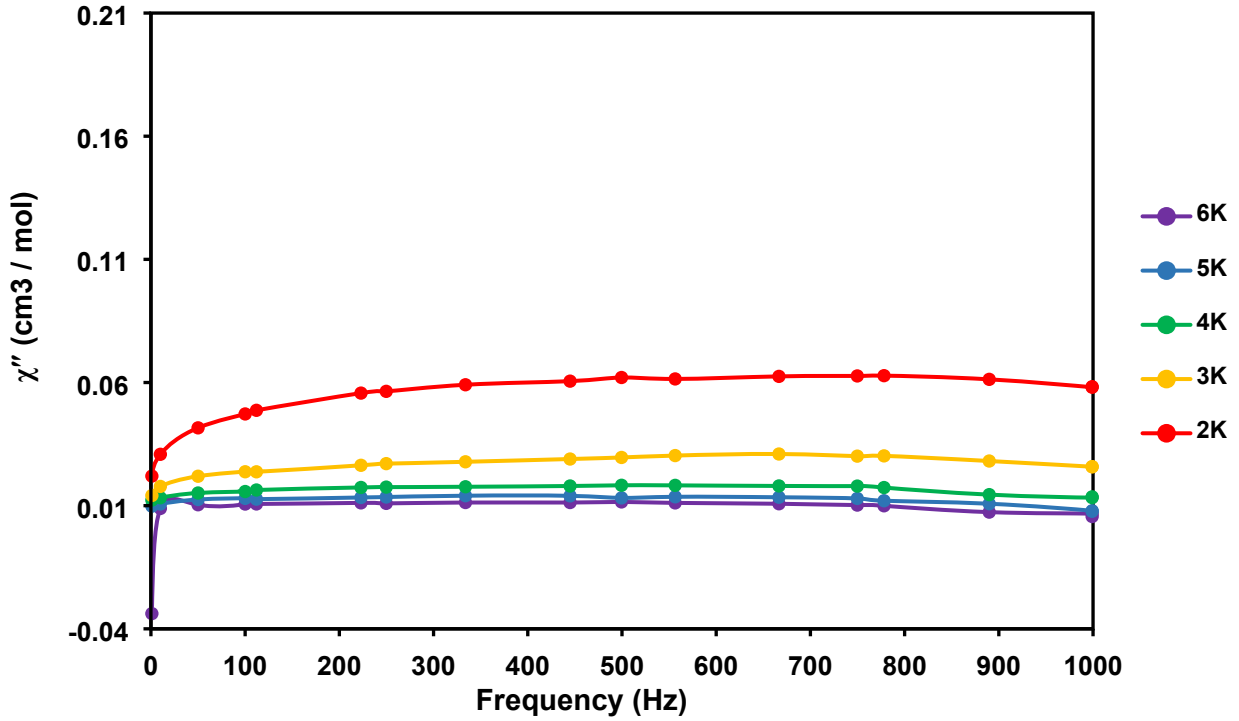

Fig S17: Out-of-phase AC magnetic susceptibility of **2-Fe** at temperatures ranging from 2-6 K.

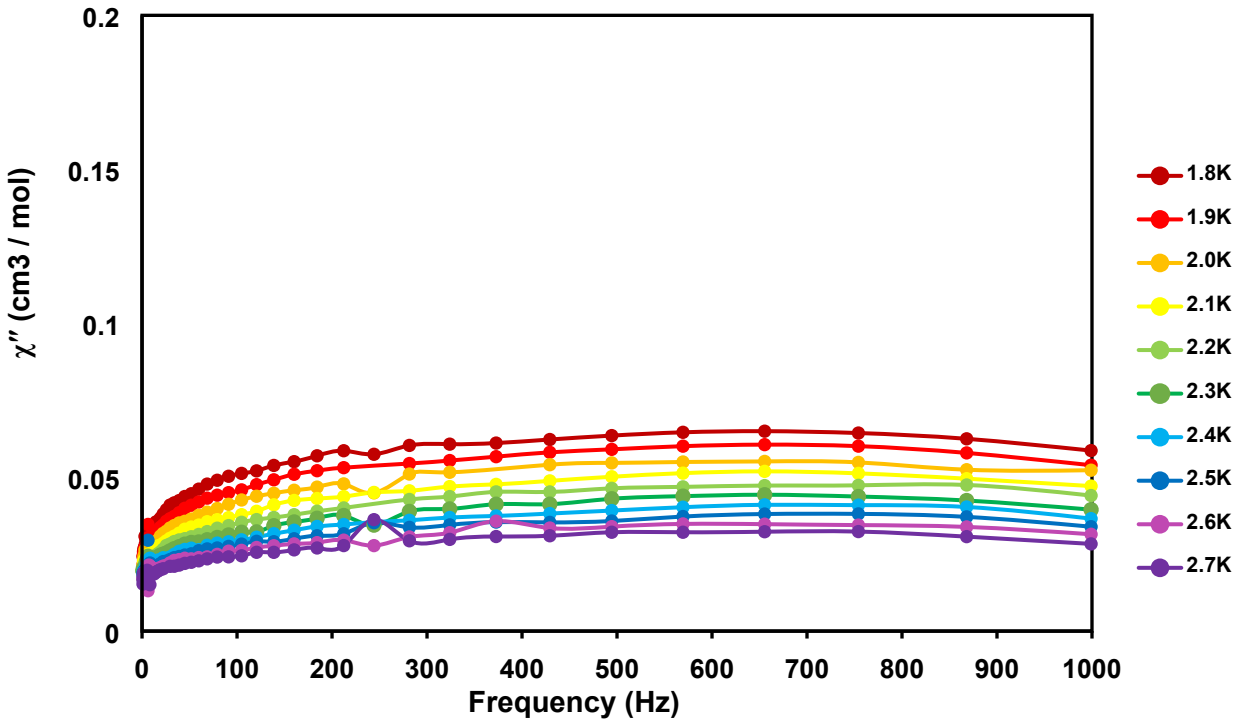

Fig S18: Out-of-phase AC magnetic susceptibility of **2-Fe** at temperatures ranging from 1.8-2.7 K.

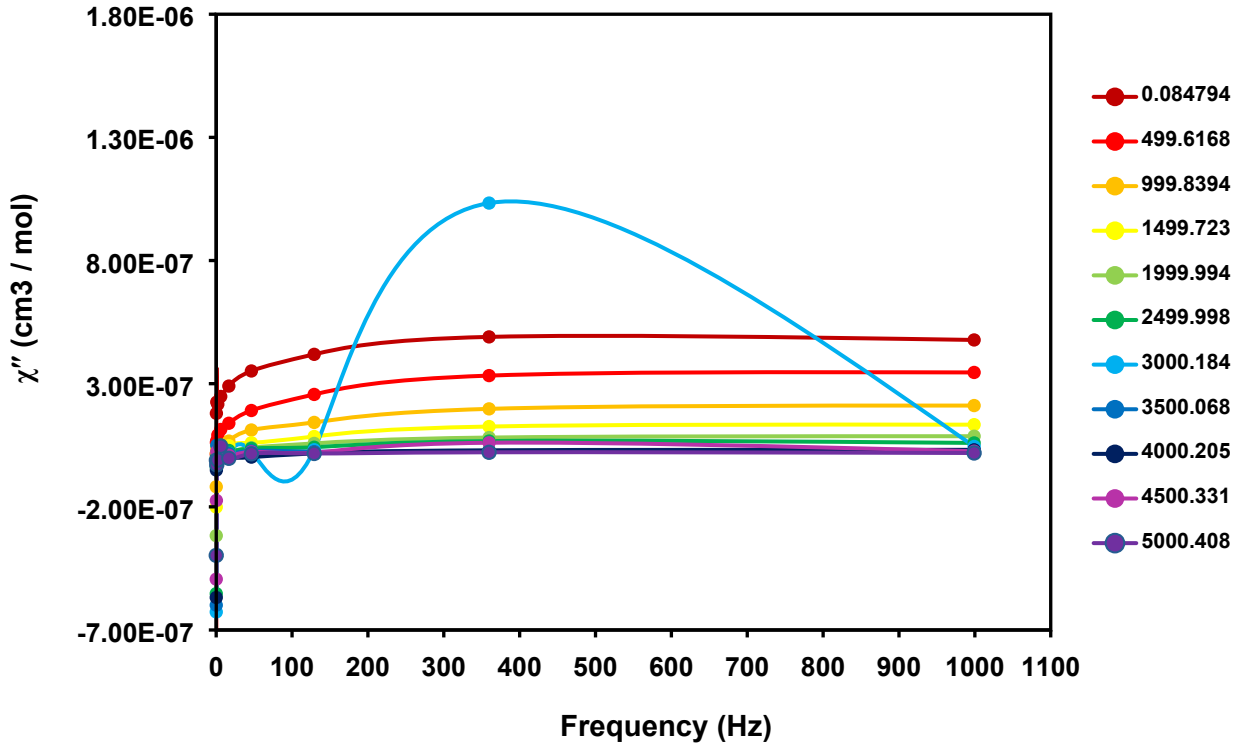

Fig S19: χ″ vs frequency plot of **2-Fe** at 2 K at different applied DC fields from 0-5000 Oe.

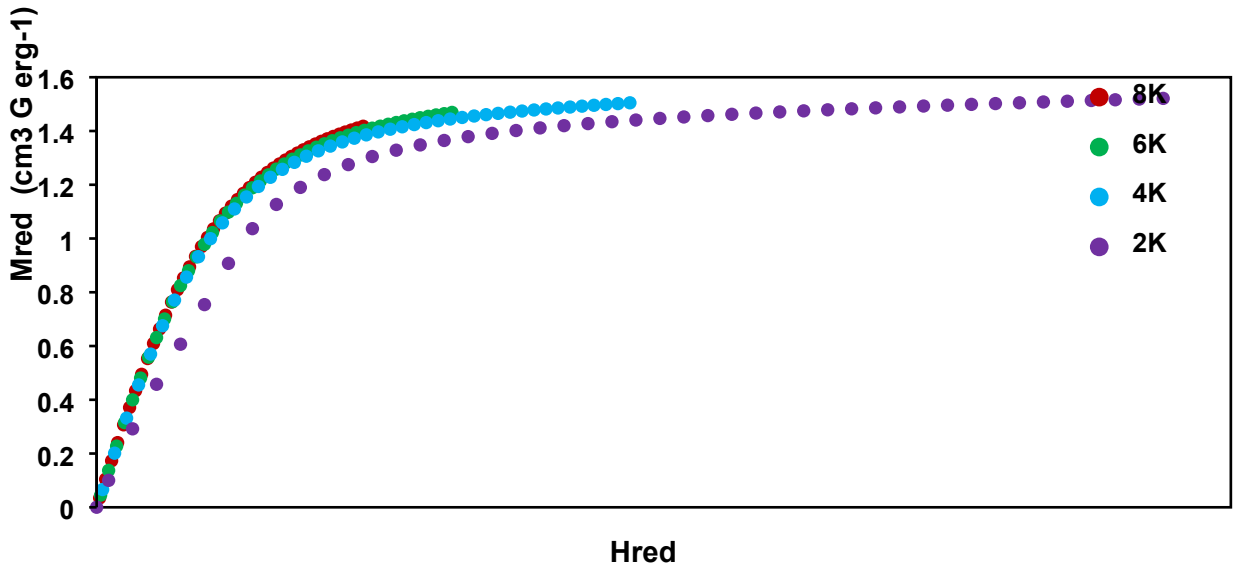

Fig S20: Reduced magnetization plot of **2-Co**.

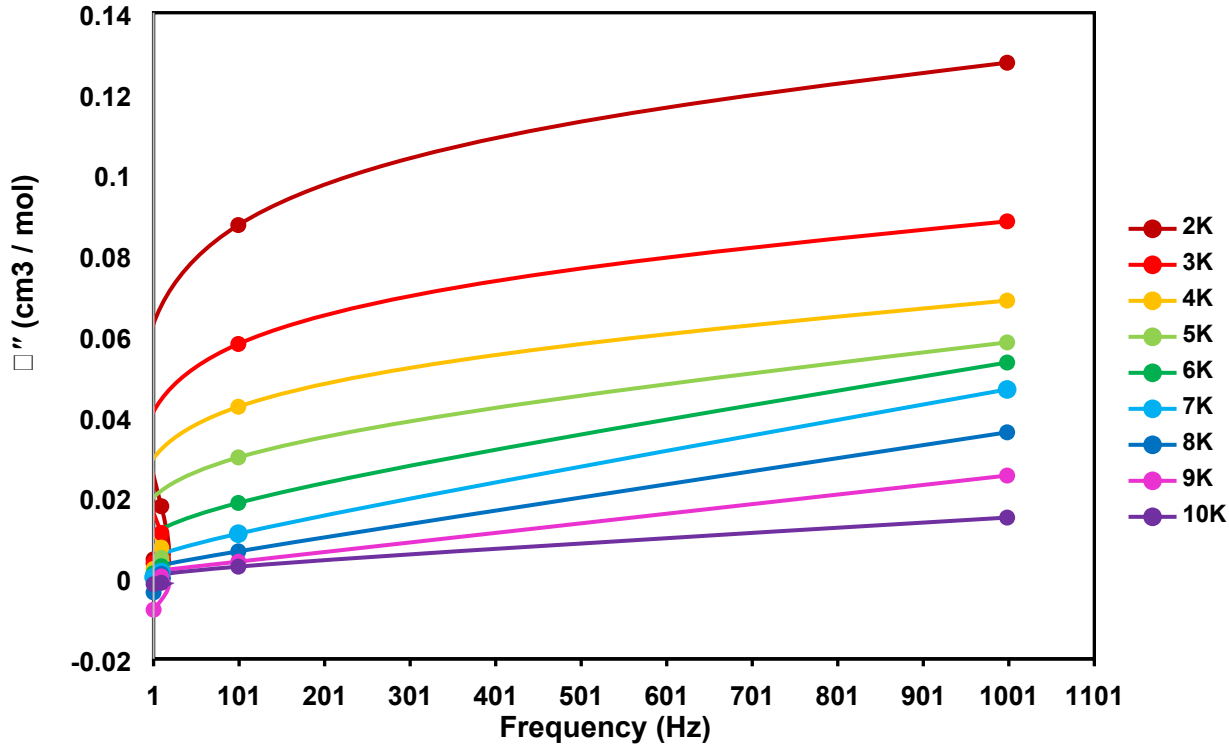

Fig S21: Out-of-phase AC magnetic susceptibility of **2-Co** at temperatures ranging from 2-10 K.

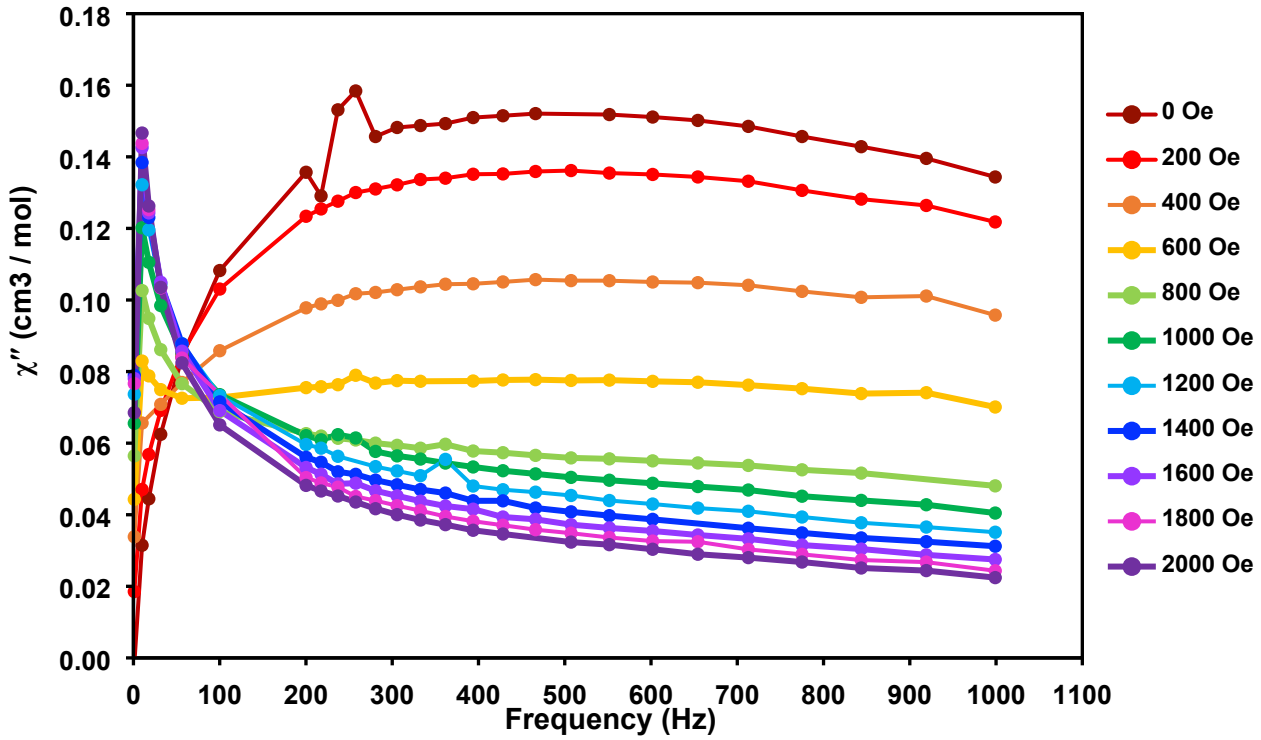

Fig S22: χ'' vs frequency plot of **2-Co** at 1.8 K at different applied DC fields from 0-2000 Oe.

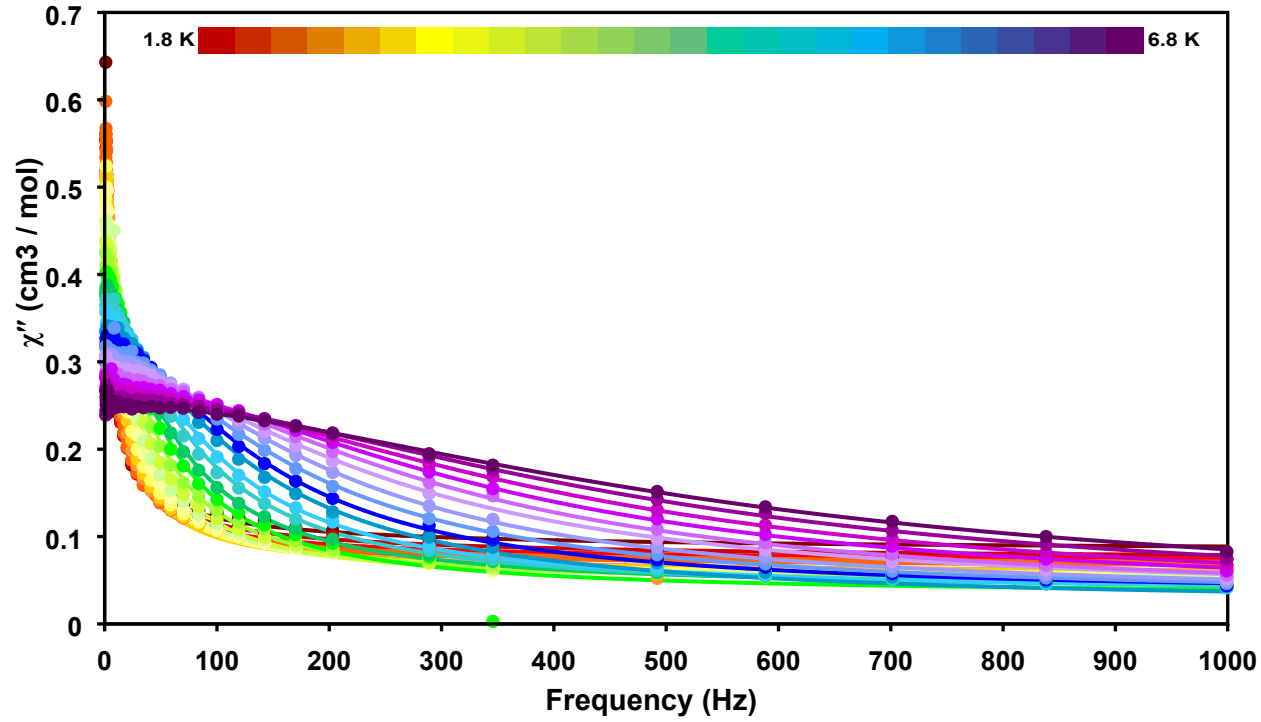

Fig S23: In-phase AC magnetic susceptibility plot of **2-Co** at 1500 Oe. The solid lines are fits to the data obtained from CC-fit2.

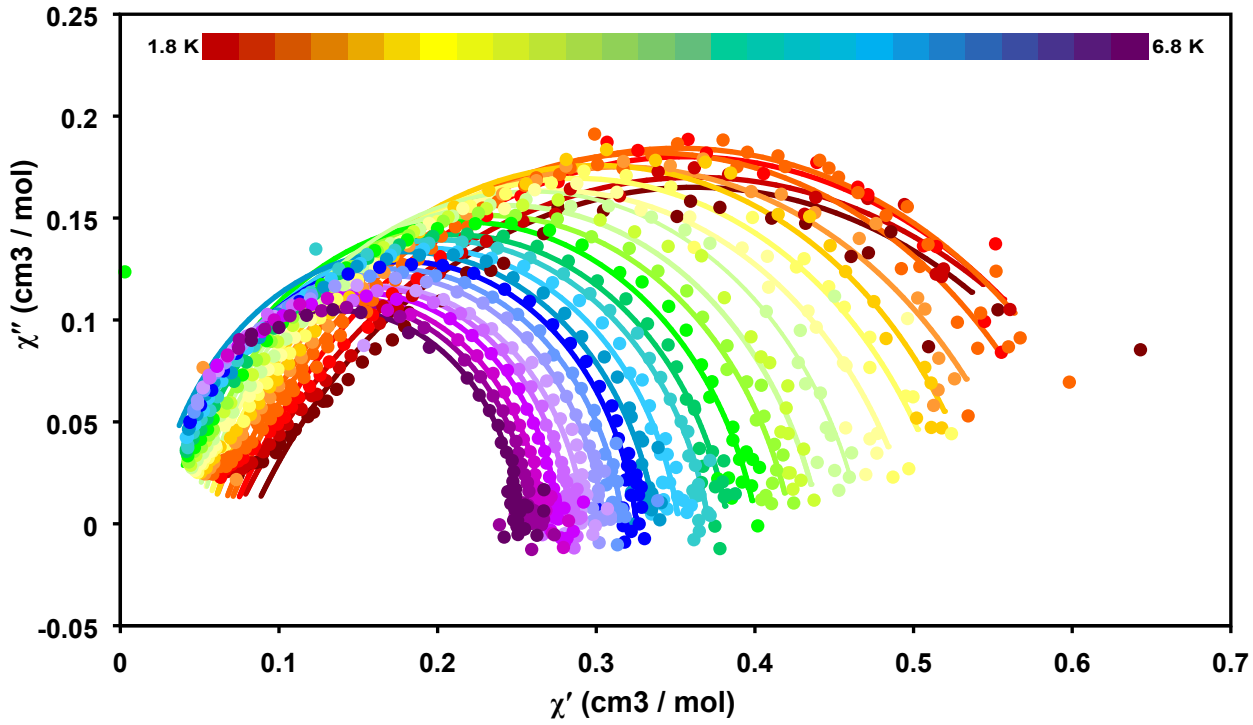

Fig S24: Cole-Cole plot of **2-Co**. The solid lines are fits to the data obtained from CC-fit2.

Theoretical Calculation

All calculations involving ground and excited state energies and wavefunctions were done on the experimentally obtained crystal structure. For single point energy calculation, a B3LYP functional with RIJCOSX approximation was used. Basis set def2-SVP was used for all atoms except cobalt and nitrogen, for which the def2-TZVP basis set was employed.

$Co(^{(tbu)2}carb^{(Ph2CH)2})_2$ **(2-Co)**

Table S2: Comparison of geometry optimized and experimental values of selected bond lengths and bond angles of **2-Co**

	Optimized	**Experimental**
Co-N_1 (Å)	1.9164	1.914 (2)
Co-N_2 (Å)	1.9340	1.945 (3)
N_1-Co-N_1 (°)	134.0	140.21 (10)
Co---C_{ipso}	2.4788	2.532 (3)

Table S3: Orbital composition from single-point DFT calculation on the experimental structure of **2-Co**

Orbital	**Loewdin composition***	**N_{occ}**

	Co (d contribution)	N_1 (s and p)	N_2 (s and p)	
313	8.7 d_{xz} + 39.5 d_{yz} + 4.3 d_{xy}			2.0
318	3.5 d_{z2} + 2.4 d_{yz} + 39.4 d_{x2-y2}			2.0
337	6.7 d_{z2} + 1.2 d_{x2-y2} + 2.4 d_{xy}	13.7 p_y		2.0
338	6.0 d_{xz} + 3.1 d_{yz}		4.2 p_z + 12.9 p_x + 3.8 p_y	2.0
339	4.3 d_{z2} + 2.9 d_{yz} + 86.9 d_{xy}			1.0
340	68.3 d_{xz} + 6.2 d_{yz} + 4.1 d_{x2-y2}	2.4 p_z	3.7 p_z + 1.7 p_x	1.0
341	61.0 d_{z2} + 6.1 d_{yz} + 4.1 d_{x2-y2}	1.4 p_z + 2.0 p_x + 3.0 p_y		1.0

*****Orbital compositions are from the QROs.

Table S4: Configuration state functions from the CASSCF/NEVPT2 calculation of **2-Co** with seven quartets

Root	Energy difference (eV)	Configuration	Weight
0	0	221221100000	0.47258
		222121100000	0.37453
		222112100000	0.06105
		221121200000	0.04286
		221212100000	0.01211
		221112200000	0.01043
1	0.061	222121100000	0.39263
		221221100000	0.30553
		221212100000	0.13649
		222211100000	0.04619
		221122100000	0.03557
		222112100000	0.03411
		221121200000	0.00871
		221112200000	0.00815
		222111200000	0.00575
		221211200000	0.00358
2	0.344	222211100000	0.44225
		221122100000	0.31643
		221211200000	0.05577
		222111200000	0.05276
		221221100000	0.04534
		222121100000	0.02564
		221121200000	0.01695
		221212100000	0.01065
		221112200000	0.01028
3	0.529	222112100000	0.74166
		221212100000	0.07189
		221121200000	0.05546
		221112200000	0.04992
		221221100000	0.03228
		222111200000	0.00903
		222121100000	0.00612
		221122100000	0.00611

		221211200000	0.00373
4	0.591	222111200000	0.52948
		221211200000	0.23392
		221122100000	0.12868
		221212100000	0.04289
		222211100000	0.01847
		221121200000	0.01786
		222112100000	0.00345
5	0.607	221212100000	0.34328
		222111200000	0.25335
		221211200000	0.14641
		221121200000	0.10067
		222112100000	0.05478
		221221100000	0.02652
		222121100000	0.02619
		221112200000	0.02327
		221122100000	0.00277
6	0.697	221211200000	0.51088
		221212100000	0.20777
		222111200000	0.11125
		221121200000	0.05
		221112200000	0.03315
		221221100000	0.0264
		222112100000	0.02292
		222121100000	0.01108
		221122100000	0.00371

Input file for single point DFT calculation:

```
!uks B3LYP RIJCOSX SlowConv def2-SVP def2/J  NormalPrint TightSCF UCO UNO D4
%scf
        MaxIter 125
        CNVDIIS 1
        CNVSOSCF 1
end
 %basis NewGTO 27 "def2-TZVP" end
        NewGTO 7 "def2-TZVP" end
end
%pal nprocs 16
end
%maxcore 4000
 * xyz 0 4
(cartesian coordinates)
```

Input file for geometry optimization:

```
!UKS B3LYP RIJCOSX SlowConv dkh dkh-def2-SVP def2/J  NormalPrint tightscf Tightopt UCO
UNO D4
%scf
   MaxIter 125
   CNVDIIS 1
   CNVSOSCF 1
end
%basis NewGTO 27 "def2-TZVP" end
        NewGTO 7 "def2-TZVP" end
end
%pal nprocs 16
end
%maxcore 10000
* xyz 0 4
(cartesian coordinates)
```

Input file for printing quasi restricted orbitals (QRO):

```
!B3LYP RIJCOSX SlowConv def2-SVP def2/J  NormalPrint TightSCF MORead D4 noiter
%moinp "SN08506.qro"
%basis NewGTO 27 "def2-TZVP" end
        NewGTO 7 "def2-TZVP" end
end
%pal nprocs 16
end
%maxcore 4000
* xyz 0 4
(cartesian coordinates)
```

Input file to generate initial CASSCF starting orbitals:

```
!RIJCOSX def2-SVP autoaux NormalPrint TightSCF MORead XYZFile PATOM
%moinp "SN08506printQRO.gbw"
%casscf nel 7
         norb 5
         mult 4
         nroots 7
         end
%basis NewGTO 27 "def2-TZVP" end
        NewGTO 7 "def2-TZVP" end
end
%pal nprocs 8
```

```
end
%maxcore 10000
* xyz 0 4
(cartesian coordinates)
```

Input file for CASSCF calculation of initial active space:

```
RIJCOSX def2-SVP autoaux NormalPrint MOread
%moinp "SN08506printQRO_CASinitial.gbw"
 %scf
   rotate { 277, 335 } end
end
 %casscf nel 11
            norb 7
            mult 4
            nroots 7
            end
 %basis NewGTO 27 "def2-TZVP" end
          NewGTO 7 "def2-TZVP" end
end
 %pal nprocs 8
end
 %maxcore 20000
 * xyz 0 4
(cartesian coordinates)
```

Input file for CASSCF calculation of final active space and second d-subshell preparation:

```
!RIJCOSX def2-SVP autoaux NormalPrint MOread
%moinp "SN08506printQRO_CAS11e7o_2.0_1.gbw"
%casscf nel 11
            norb 7
            mult 4
            nroots 7
            extorbs doubleshell
            end
%basis NewGTO 27 "def2-TZVP" end
          NewGTO 7 "def2-TZVP" end
end
%pal nprocs 8
end
%maxcore 20000
* xyz 0 4
```

(cartesian coordinates)

Input file for CASSCF/NEVPT2 calculation of electronic structure and magnetic properties:

```
!RIJCOSX def2-SVP autoaux NormalPrint TightSCF MOread DLPNO-NEVPT2
%moinp "SN08506printQRO_CAS11e7o_2.0_1_DoubleShell.gbw"
%casscf nel 11
          norb 12
          mult 4
          nroots 7
          trafostep ri
          rel
             dosoc true
             gtensor true
          end
end
%basis NewGTO 27 "def2-TZVP" end
        NewGTO 7 "def2-TZVP" end
end
%pal nprocs 8
end
%maxcore 20000
* xyz 0 4
(cartesian coordinates)
```

Cartesian Coordinates of 2-Co

```
* xyz 0 4

Co       0.60704      0.24972      1.79762
N        0.00000      0.00000      0.00000
N        0.00000     -0.00000      3.62803
C       -0.91059      0.90151     -0.59669
C       -2.07778      1.48947     -0.07006
C       -2.67919      2.47623     -0.84412
H       -3.42454      2.93423     -0.47262
C       -2.26442      2.84634     -2.13791
C       -1.21683      2.13671     -2.69350
H       -0.96295      2.29042     -3.59574
C       -0.53616      1.19578     -1.92625
C        0.61014      0.38371     -2.22129
C        1.36084      0.23506     -3.38598
H        1.13492      0.72914     -4.16551
C        2.43424     -0.63191     -3.40061
```

C	2.72278	-1.33464	-2.21206
H	3.46172	-1.93099	-2.21608
C	1.99509	-1.20854	-1.03597
C	0.91130	-0.32962	-1.03310
C	-2.73784	0.91958	1.18648
H	-2.01164	0.74316	1.85102
C	-3.76264	1.84088	1.86129
C	-3.50013	2.38739	3.10244
H	-2.65670	2.24376	3.51418
C	-4.47560	3.15669	3.75896
H	-4.29754	3.50938	4.62265
C	-5.67887	3.39834	3.16198
H	-6.33135	3.92971	3.60240
C	-5.94386	2.86709	1.91520
H	-6.77529	3.04774	1.49201
C	-5.01123	2.07796	1.28259
H	-5.21991	1.69013	0.44101
C	-3.41060	-0.41580	0.88083
C	-3.78468	-1.24541	1.93360
H	-3.56596	-0.99605	2.82406
C	-4.46877	-2.42190	1.70858
H	-4.70697	-2.97799	2.44092
C	-4.80683	-2.79668	0.42041
H	-5.29076	-3.59864	0.26370
C	-4.43327	-1.98846	-0.63246
H	-4.65253	-2.24380	-1.52079
C	-3.74250	-0.80797	-0.40974
H	-3.49329	-0.26247	-1.14655
C	3.31792	-0.80064	-4.63742
C	3.84309	-2.24212	-4.74999
H	4.41221	-2.44322	-3.97791
H	4.36519	-2.33600	-5.57394
H	3.08660	-2.86425	-4.76946
C	4.50506	0.16573	-4.51684
H	5.04054	-0.07078	-3.73121
H	4.17091	1.08252	-4.42021
H	5.06012	0.10404	-5.32186
C	2.54059	-0.49075	-5.91947
H	3.08158	-0.73797	-6.69802
H	2.33626	0.46717	-5.95425
H	1.70490	-1.00309	-5.92629
C	2.39443	-2.02923	0.18323
H	1.56311	-2.17543	0.71864
C	3.35973	-1.25843	1.07010
C	4.48305	-0.60700	0.54275
H	4.64561	-0.63158	-0.39293
C	5.35774	0.07335	1.37380
H	6.12018	0.50395	1.00381

C	5.13229	0.13252	2.74434
H	5.72488	0.61421	3.30890
C	4.03239	-0.51887	3.27794
H	3.87903	-0.49699	4.21514
C	3.15784	-1.20095	2.45453
H	2.40509	-1.63980	2.83458
C	2.91092	-3.42070	-0.22735
C	4.16939	-3.88004	0.09359
H	4.74985	-3.33471	0.61150
C	4.60065	-5.13765	-0.33397
H	5.47080	-5.44369	-0.10641
C	3.77168	-5.92895	-1.07946
H	4.06712	-6.78126	-1.37948
C	2.50631	-5.48482	-1.39308
H	1.92555	-6.03720	-1.90286
C	2.07407	-4.24313	-0.97301
H	1.19884	-3.94753	-1.19497
C	-0.95772	-0.90288	4.14394
C	-1.19166	-2.24613	3.82311
C	-2.17818	-2.91039	4.54713
H	-2.36208	-3.81418	4.31830
C	-2.92076	-2.33459	5.59456
C	-2.66450	-1.00565	5.90722
H	-3.14966	-0.57913	6.60376
C	-1.69553	-0.30079	5.19685
C	-1.12849	1.01174	5.40170
C	-1.38492	2.01372	6.33401
H	-2.09791	1.91875	6.95529
C	-0.58747	3.15455	6.34757
C	0.47943	3.22314	5.45251
H	1.04473	3.98598	5.48627
C	0.76329	2.24294	4.51871
C	-0.09407	1.13179	4.46964
C	-0.30405	-3.01185	2.85006
H	0.03444	-2.34238	2.18869
C	-1.02099	-4.08524	2.04643
C	-1.49249	-3.83124	0.78222
H	-1.38503	-2.96876	0.39920
C	-2.13329	-4.85061	0.05346
H	-2.47141	-4.67371	-0.81650
C	-2.26975	-6.11085	0.60782
H	-2.68713	-6.80569	0.11304
C	-1.80632	-6.35245	1.86341
H	-1.91863	-7.21343	2.24806
C	-1.18232	-5.36935	2.57190
H	-0.84977	-5.56203	3.44081
C	0.93004	-3.58775	3.55271
C	1.78827	-4.43760	2.84103

H	1.57852	-4.67626	1.94588
C	2.93314	-4.92773	3.42763
H	3.50846	-5.49591	2.92847
C	3.25606	-4.60882	4.72615
H	4.04657	-4.95520	5.12287
C	2.42224	-3.78438	5.44484
H	2.63794	-3.56043	6.34267
C	1.26265	-3.27274	4.86092
H	0.69517	-2.70297	5.36582
C	-3.93860	-3.19492	6.36664
C	-3.24997	-4.47242	6.85774
H	-2.92486	-4.98488	6.08844
H	-3.89103	-5.01457	7.36384
H	-2.49494	-4.23557	7.43555
C	-5.08908	-3.56683	5.42644
H	-5.50642	-2.74925	5.08198
H	-5.75526	-4.09136	5.91737
H	-4.74203	-4.09614	4.67866
C	-4.50471	-2.46540	7.57999
H	-3.77497	-2.23874	8.19384
H	-5.14826	-3.04544	8.03764
H	-4.95303	-1.64522	7.28776
C	1.95353	2.28069	3.58989
H	2.30867	1.34525	3.57182
C	3.11598	3.14816	4.05311
C	3.82432	2.75647	5.18629
H	3.54466	1.98833	5.66966
C	4.92868	3.46796	5.62042
H	5.40600	3.17818	6.38885
C	5.33675	4.59447	4.94397
H	6.09197	5.08574	5.24352
C	4.63995	5.00182	3.82845
H	4.91156	5.78378	3.36344
C	3.53911	4.27677	3.37547
H	3.07608	4.55977	2.59564
C	1.52496	2.58239	2.15592
C	2.33440	2.14272	1.10087
H	3.06467	1.55997	1.27383
C	2.06801	2.56038	-0.20928
H	2.61080	2.25204	-0.92584
C	1.02018	3.41902	-0.45912
H	0.85261	3.71520	-1.34591
C	0.20657	3.85272	0.58416
H	-0.52068	4.43884	0.40701
C	0.45554	3.43349	1.87686
H	-0.10828	3.72642	2.58327
C	-2.96755	3.98197	-2.94180
C	-3.76796	3.29924	-4.05680

H	-3.15779	2.79506	-4.63452
H	-4.23563	3.97699	-4.58602
H	-4.42177	2.68581	-3.65905
C	-1.90946	4.91766	-3.55310
H	-1.41534	5.36522	-2.83544
H	-2.35222	5.58997	-4.11326
H	-1.28824	4.39460	-4.10146
C	-3.92627	4.82730	-2.10028
H	-4.62285	4.25141	-1.72024
H	-4.34130	5.51262	-2.66422
H	-3.42934	5.25964	-1.37372
C	-0.70707	4.30921	7.34670
C	-1.55619	3.89603	8.53964
H	-2.48348	3.76287	8.24983
H	-1.52516	4.59793	9.22212
H	-1.20850	3.05979	8.91403
C	-1.36919	5.45781	6.59435
H	-0.77949	5.75923	5.87270
H	-1.53520	6.20087	7.21244
H	-2.22037	5.15313	6.21551
C	0.64061	4.81796	7.89200
H	1.14563	4.06687	8.26760
H	0.47864	5.48479	8.59268
H	1.15407	5.22673	7.16501

$Mn(^{(tbu)2}carb^{(Ph2CH)2})_2$ **(2-Mn)**

Table S5: SA-CASSCF transition energies between different states for **2-Mn** from NEVPT2 calculation

Lowest root (Root 0, Mult 6) -4790.241729141 Eh (-130349.104 eV)

State	Root	Multiplicity	DE (eV)
1	0	4	3.001
2	1	4	3.104
3	2	4	3.164
4	3	4	3.371
5	4	4	3.400
6	0	2	4.624
7	1	2	4.649
8	2	2	4.684
9	3	2	4.723
10	4	2	4.785
11	1	6	7.471
12	2	6	7.711

Table S6: Configuration state functions from the CASSCF/NEVPT2 calculation of **2-Mn** with three sextets

Root	Energy difference (eV)	Configuration	Weight
0	0	2211111	0.99907
1	7.471	2112111	0.41457
		2111112	0.35042
		2111211	0.19526
		2121111	0.03248
2	7.711	2121111	0.48578
		2111211	0.34114
		2112111	0.12537
		2111112	0.02517
		2111121	0.01412

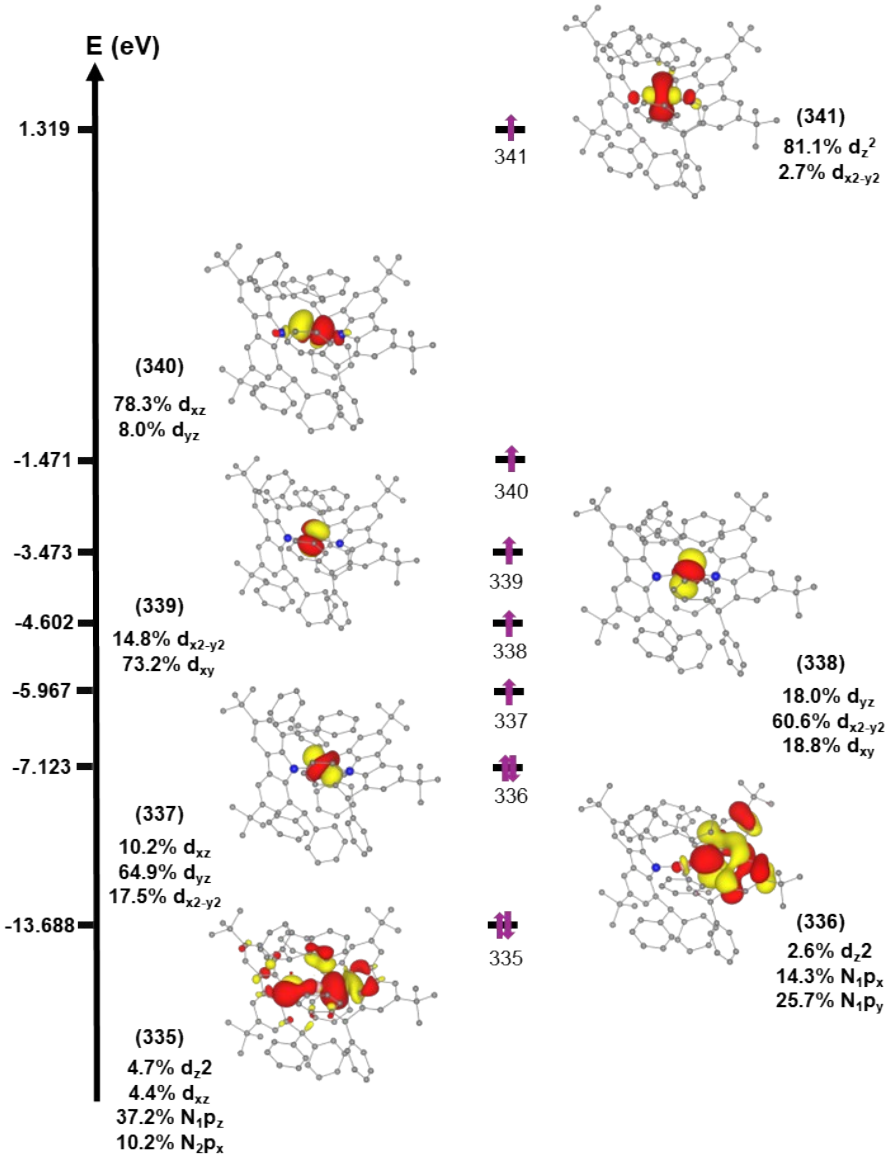

Fig S25: Orbital energy diagram depicting orbital contributions and electron occupations of seven active space orbitals (3d metal + two ligand orbitals) of 2-Mn in ground state from CASSCF/NEVPT2 calculation. H-atoms are omitted for clarity. (isosurface value 0.028)

Cartesian Coordinates of 2-Mn

* xyz 0 6

Mn	0.63263	0.22196	1.90874
N	0.00000	0.00000	0.00000
N	0.00000	0.00000	3.82416
C	-0.87641	0.93671	-0.57801

C	-2.03668	1.53409	-0.04133
C	-2.63172	2.53999	-0.79327
H	-3.37312	2.99676	-0.41390
C	-2.20735	2.92930	-2.08565
C	-1.15531	2.23322	-2.64393
H	-0.88190	2.41571	-3.53538
C	-0.49361	1.26093	-1.89698
C	0.65417	0.44737	-2.19723
C	1.41052	0.29968	-3.35752
H	1.20717	0.81466	-4.12959
C	2.46372	-0.60503	-3.37888
C	2.72905	-1.32458	-2.19968
H	3.46299	-1.92751	-2.20200
C	1.98357	-1.20959	-1.02911
C	0.92492	-0.29738	-1.02547
C	-2.69263	0.96005	1.21936
H	-1.95661	0.77284	1.87025
C	-3.68629	1.87254	1.92398
C	-3.41759	2.36217	3.19251
H	-2.57219	2.19021	3.59034
C	-4.36815	3.10069	3.89214
H	-4.17869	3.40095	4.77319
C	-5.58327	3.39642	3.31128
H	-6.22389	3.91992	3.77880
C	-5.85836	2.92635	2.04687
H	-6.68642	3.14172	1.63452
C	-4.93755	2.14093	1.36976
H	-5.16192	1.78251	0.51917
C	-3.37347	-0.37814	0.91988
C	-3.75072	-1.19908	1.98143
H	-3.52255	-0.94944	2.86896
C	-4.44740	-2.36608	1.76474
H	-4.69522	-2.91250	2.50169
C	-4.79141	-2.74791	0.47640
H	-5.28116	-3.54762	0.32309
C	-4.40582	-1.94298	-0.58309
H	-4.62391	-2.20003	-1.47113
C	-3.70430	-0.76541	-0.36385
H	-3.45136	-0.22249	-1.10088
C	3.33003	-0.79377	-4.62474
C	3.85786	-2.23045	-4.71874
H	4.46023	-2.40658	-3.96615
H	4.34566	-2.34425	-5.56118
H	3.10557	-2.85716	-4.68930
C	4.51818	0.18903	-4.52547
H	5.03877	-0.00831	-3.71863
H	4.18068	1.10742	-4.48015
H	5.09087	0.08983	-5.31511

C	2.52957	-0.50548	-5.89682
H	3.05196	-0.77618	-6.68023
H	2.33441	0.45383	-5.94998
H	1.68873	-1.00855	-5.87486
C	2.34253	-2.03747	0.19700
H	1.49057	-2.19439	0.69670
C	3.26469	-1.25338	1.13568
C	4.39177	-0.57593	0.64061
H	4.56781	-0.57289	-0.29273
C	5.24638	0.08816	1.50538
H	6.01354	0.53117	1.16252
C	4.98805	0.11068	2.87467
H	5.56922	0.57970	3.46210
C	3.88290	-0.55300	3.37435
H	3.70807	-0.54648	4.30788
C	3.02816	-1.22894	2.51108
H	2.27053	-1.68139	2.86291
C	2.88889	-3.41393	-0.18289
C	4.11948	-3.87982	0.22890
H	4.65953	-3.34157	0.79539
C	4.58333	-5.13188	-0.17504
H	5.43346	-5.43716	0.11905
C	3.82284	-5.92317	-0.99173
H	4.14513	-6.76941	-1.27960
C	2.57029	-5.47260	-1.39325
H	2.02935	-6.01983	-1.95015
C	2.10925	-4.23910	-0.99160
H	1.24839	-3.94784	-1.26878
C	-0.99265	-0.88290	4.31369
C	-1.25639	-2.22049	3.95332
C	-2.25604	-2.88187	4.65872
H	-2.45588	-3.77739	4.41222
C	-2.99155	-2.31094	5.71335
C	-2.71101	-1.00080	6.06018
H	-3.19326	-0.58166	6.76295
C	-1.71892	-0.29535	5.37666
C	-1.13558	1.00040	5.59898
C	-1.38320	2.00991	6.54375
H	-2.09358	1.91368	7.16709
C	-0.59130	3.14489	6.56551
C	0.48031	3.22075	5.65022
H	1.03576	3.99131	5.67168
C	0.76608	2.23655	4.72539
C	-0.08004	1.11571	4.66983
C	-0.37900	-2.97612	2.96157
H	-0.01435	-2.29032	2.33211
C	-1.11655	-3.99779	2.09953
C	-1.48254	-3.70311	0.79722

H	-1.29624	-2.84607	0.43275
C	-2.12378	-4.66935	0.01980
H	-2.36708	-4.46907	-0.87650
C	-2.40705	-5.90504	0.54486
H	-2.85293	-6.55335	0.01247
C	-2.05051	-6.20842	1.82488
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C	-1.39444	-5.26469	2.59295
H	-1.12861	-5.48821	3.47719
C	0.83431	-3.62072	3.64440
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H	1.44391	-4.69597	2.01678
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H	3.89394	-5.13684	5.19202
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H	2.53327	-3.71630	6.43137
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H	-2.59754	-4.21349	7.56846
C	-5.15111	-3.55888	5.49859
H	-5.58039	-2.74546	5.15917
H	-5.81302	-4.10332	5.97348
H	-4.78359	-4.07121	4.74862
C	-4.62978	-2.44431	7.65653
H	-3.92329	-2.22313	8.29863
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H	2.29880	1.37673	3.71093
C	3.11945	3.14862	4.28367
C	3.80698	2.71021	5.41531
H	3.51332	1.92881	5.86845
C	4.91057	3.39694	5.88641
H	5.37046	3.08026	6.65499
C	5.34830	4.53653	5.24999
H	6.10717	5.00704	5.57531
C	4.67457	4.98745	4.13598
H	4.96837	5.77451	3.69289
C	3.56583	4.29448	3.65457
H	3.11035	4.61386	2.88431
C	1.52397	2.68927	2.36243
C	2.29353	2.26269	1.27695

H	3.03250	1.68351	1.42311
C	1.98877	2.67777	-0.01535
H	2.51224	2.37090	-0.74703
C	0.93589	3.52796	-0.23691
H	0.74115	3.82631	-1.11765
C	0.15141	3.95475	0.83248
H	-0.58079	4.54056	0.67713
C	0.43025	3.53164	2.12017
H	-0.12013	3.81207	2.84132
C	-2.89385	4.07066	-2.87542
C	-3.69036	3.39656	-4.00560
H	-3.07579	2.90157	-4.58746
H	-4.15595	4.08097	-4.52951
H	-4.34483	2.77756	-3.62038
C	-1.85319	5.01904	-3.47286
H	-1.34612	5.44470	-2.75097
H	-2.30665	5.70716	-4.00378
H	-1.24225	4.51293	-4.04792
C	-3.85848	4.88596	-2.02420
H	-4.55792	4.29805	-1.66882
H	-4.26858	5.58499	-2.57497
H	-3.37068	5.29881	-1.28154
C	-0.81675	4.30874	7.53572
C	-1.68449	3.88481	8.72370
H	-2.58538	3.66500	8.40714
H	-1.73456	4.61951	9.36947
H	-1.28796	3.09807	9.15302
C	-1.50658	5.43401	6.75598
H	-0.92817	5.72429	6.01990
H	-1.67552	6.19084	7.35588
H	-2.35675	5.10792	6.39447
C	0.50270	4.85074	8.08829
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H	0.31710	5.54106	8.75806
H	1.02905	5.23675	7.35750

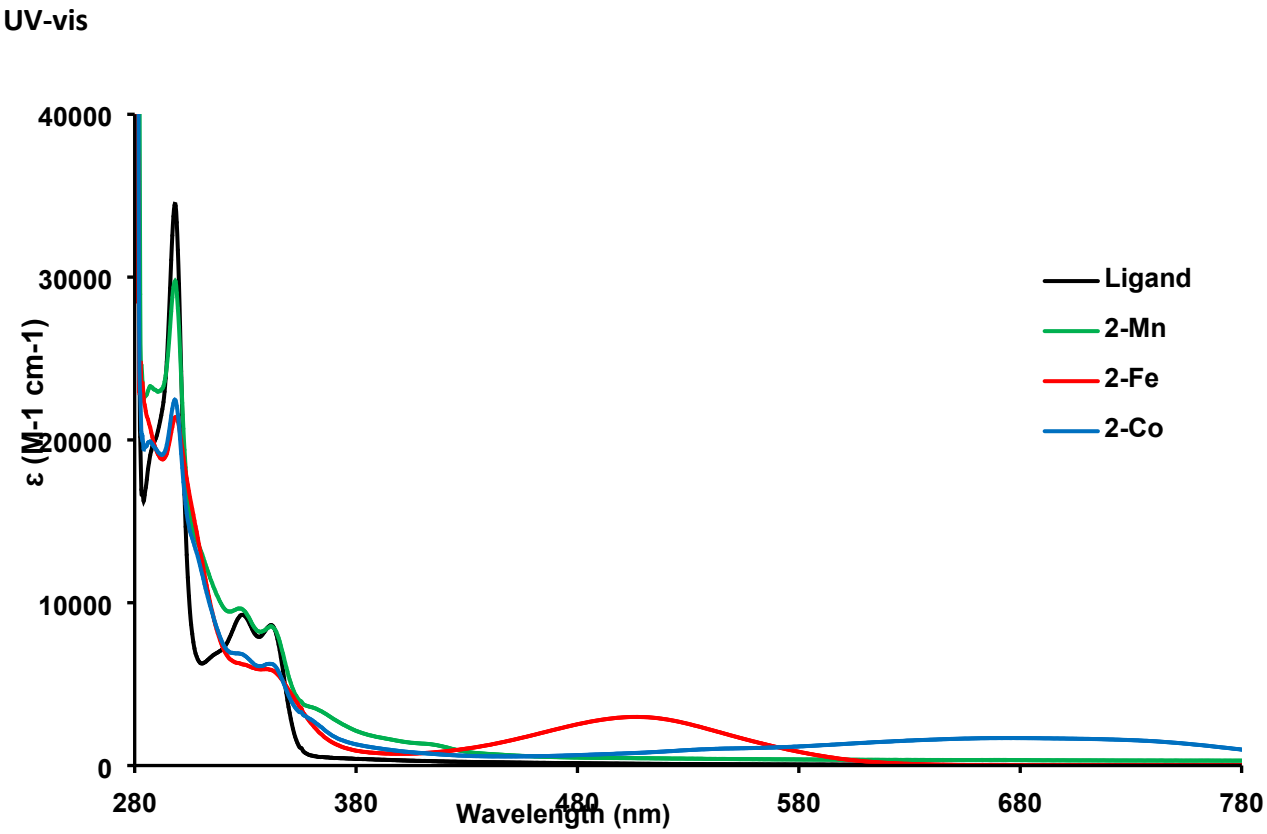

Fig S26: Extinction coefficient vs wavelength plot for protonated ligand, 2-Mn, 2-Fe and 2-Co in toluene.

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