Electronic Supplementary Information:

Elucidating the Paramagnetic Interactions of an Inorganic-Organic Hybrid Radical-Functionalized Mn-Anderson Cluster

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1. General remarks

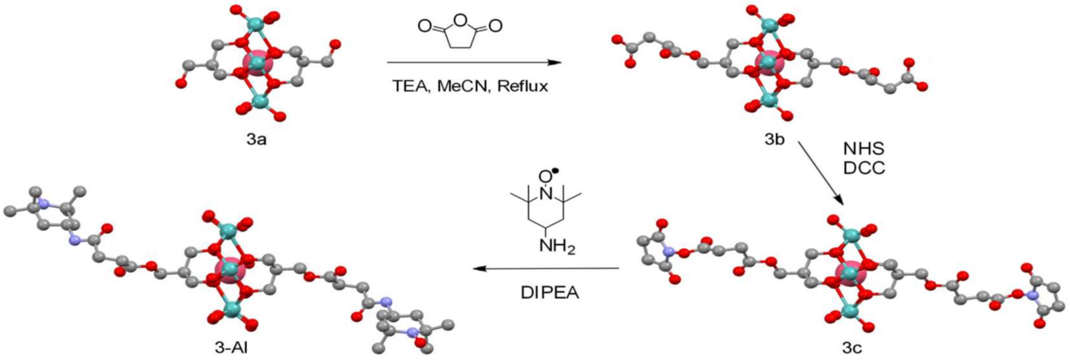
All starting materials were purchased from commercial sources and used without further purification. $[(n\text{-}C_4H_9)_4N]_3[MnMo_6O_{24}\{(CH_2)_3CNHCO(CH_2)_3COOH\}_2]$[1] and $[(n\text{-}C_4H_9)_4N]_3[MnMo_6O_{24}\text{-}\{(CH_2)_3CNHCO(CH_2)_2COOH\}_2]$[2] were synthesized according to our previous works and fully characterized. $Na_3(H_2O)_6[AlMo_6O_{24}H_6]\cdot 2H_2O$[3] was prepared according to published method. The FT-IR spectra were collected on a JASCO FT-IR 4100 spectrometer in transmission mode with intensities denoted as w = weak, m = medium, and s = strong. ^{1}H NMR was recorded on a Bruker 400 MHz NMR instrument. Element analyses of C, N and H content were determined by the microanalysis services within the School of Chemistry, University of Glasgow using an EA 1110 CHN, CE-440 Elemental Analyser. ESI-MS spectra were acquired from acetonitrile solutions on a Waters Synapt G2 HDMS instrument in negative mode. X-Band EPR spectra were recorded in acetonitrile solutions at room temperature on a Bruker Elexsys 500E spectrometer with an Elexsys super-high-Q cavity using a quartz flat-cell. Single-crystal X-ray diffractions were carried out on a Rigaku XtaLAB Synergy R HyPix-Arc diffractometer or a Bruker APEX II Quasar CCD diffractometer at 150 K (λ ($Mo_{k\alpha}$) = 0.71073 Å). Data collection and reduction were performed using CrysAlisPro or Apex3 software package. Structure solution and refinement were carried out by SHELXT-2018/3[4] and SHELXL-2018/3[5] using Olex2[6]. This type of compounds containing large TEMPO ligands and tetrabutylammonium (TBA) cations most often yield crystals with heavy disorders around these entities and the solvent areas. Low crystallinity and weak diffraction in high angle ranges result in poor crystal data; thus a few structures show extremely high wR2 and R1 values. Nevertheless, the clusters and associated ligands are clearly defined, satisfying the objective of structure analysis. In all structures, the Anderson clusters and their associated ligands were modeled and refined. Most TBA cations were found and were also included in the refinements with restraints. A few TBA cations and most solvent areas were disordered so badly that they could not be modeled even with restraints. Consequently, SQUEEZE (from PLATON) was used to calculate the void space and the electron count, and to produce new HKL files for further refinements. According to the SQUEEZE results, the number of TBA cations and solvent molecules N,N-dimethylformamide (DMF) or acetonitrile (ACN) masked were assessed for each compound. Details of the masked entities per unit cell are summarised as below. Compound **1-Mn**: 2DMF (279 Å^3 void and 72 electrons count from SQUEEZE); **2-Mn**: 10DMF (3641 Å^3 and 428 electrons); **3-Al**: 4TBA + 4DMF (3501 Å^3 and 754 electrons); **3a**: 4TBA + 20 ACN (7192 Å^3 and 1024 electrons); **3c**: 4TBA + 24DMF (5434 Å^3 and 1521 electrons). SQUEEZE procedure improved the quality of all structures applied. CCDC 2001278-2001283 contain the supplementary crystallographic data and can be obtained free of charge via www.ccdc.cam.ac.uk./data_request/cif.

2. Syntheses

$[(n\text{-}C_4H_9)_4N]_3[MnMo_6O_{24}\{(CH_2)_3CNHCO(CH_2)_3CONHC_9H_{17}NO\}_2]$ (**1-Mn**): $[(n\text{-}C_4H_9)_4N]_3[MnMo_6O_{24}\text{-}\{(CH_2)_3CNHCO(CH_2)_3COOH\}_2]$ (2.11 g, 1.0 mmol) was dissolved in 20 mL dry DMF. To this solution NHS (460 mg, 4 equiv) and DCC (1.24 g, 6 equiv) were added and stirred at room temperature for 24 hours. After the reaction, the white solid was filtered off and the resulting orange solution was set for diethyl ether diffusion to get the NHS-activated precursor, which was used directly for the next step without further purification. The obtained precursor, 4-amino-TEMPO (685 mg, 4 equiv), and DIPEA (700 µL, 4 equiv) were then dissolved in 50 mL dry DMF and stirred at room temperature overnight. The crude product was obtained by vapour diffusion of diethyl ether for two weeks. For purification, the crude product was dissolved in minimum amount of acetonitrile and added into an aqueous solution of *n*-tetrabutylammonium bromide (1.29 g, 3 equiv). The resulting precipitates were filtered, washed with water, and dried in air. Single crystals of **1-Mn** were obtained by diethyl ether diffusion into its DMF solution for 3 days. Total yield: 1.30 g (54.0 %). FT-IR (cm^{-1}): 2961 (m), 2933 (m), 2861 (m), 1645 (m), 1550 (m), 1460 (m), 1237 (w), 1067 (w), 1025 (w), 940 (s), 910 (s), 890 (s), 650 (s), 560 (m). ESI-MS: 2174.40 ({[**1-Mn**]-TBA}$^{1-}$). Element Analysis for $C_{84}H_{170}MnMo_6N_9O_{30}$ calc (%): C, 41.71; H, 7.03; N, 5.21; found (%): C, 40.44; H, 7.03; N, 5.54.

$[(n\text{-}C_4H_9)_4N]_3[MnMo_6O_{24}\{(CH_2)_3CNHCO(CH_2)_2CONHC_9H_{17}NO\}_2]$ (**2-Mn**): The synthetic procedure is similar to **1-Mn** by only replacing the starting material as $[(n\text{-}C_4H_9)_4N]_3[MnMo_6O_{24}\{(CH_2)_3CNH\text{-}CO(CH_2)_2COOH\}_2]$ (2.08 g, 1.0 mmol). Total yield: 1.06 g (44.3 %). FT-IR (cm^{-1}): 2961 (m), 2932 (m), 2871 (m), 1645 (m), 1550 (m), 1460 (m), 1232 (w), 1052 (w), 1024 (w), 942 (s), 910 (s), 887 (s), 650 (s), 564 (m). ESI-MS: 2146.37 ({[**2-Mn**]-TBA}$^{1-}$), 1350.15 ({2[**2-Mn**]-3TBA}$^{3-}$). Element Analysis for $C_{82}H_{166}MnMo_6N_9O_{30}$ calc (%):C, 41.23; H, 7.00; N, 5.28; found (%): C, 39.40; H, 7.05; N, 5.54.

$[(n\text{-}C_4H_9)_4N]_3[AlMo_6O_{24}\{(CH_2)_3CCH_2OCO(CH_2)_2CONHC_9H_{17}NO\}_2]$ (**3-Al**):



Scheme S1. The synthetic procedure of **3-Al**. Colour code: Mo, Teal; Al, Pink; C, Grey; O, Red; and N, Blue.

$[(n\text{-}C_4H_9)_4N]_3[AlMo_6O_{24}\{(CH_2)_3CCH_2OH\}_2]$ (**3a**) was prepared by using hydrothermal method[7] to graft pentareythriol on both sides of $Na_3(H_2O)_6[AlMo_6O_{24}H_6]\cdot 2H_2O$ (2.4 g, 2 mmol) cluster. Yield: 3.0 g (79.6 %). $[(n\text{-}C_4H_9)_4N]_3[AlMo_6O_{24}\{(CH_2)_3CCH_2OCO(CH_2)_2COOH\}_2]$ (**3b**) was obtained similarly to $[(n\text{-}C_4H_9)_4N]_3[MnMo_6O_{24}\{(CH_2)_3CNHCO(CH_2)_2COOH\}_2]$. However, a modification of the original procedure was needed. Typically, $[(n\text{-}C_4H_9)_4N]_3[AlMo_6O_{24}\{(CH_2)_3CCH_2OH\}_2]$ (1.88 g, 1 mmol), succinic anhydride (500 mg, 5 mmol), TEA (700 µL, 5 mmol), and a catalytic amount of DMAP were dissolved in dry acetonitrile 20 mL, and refluxed for 24 hours. The resulting brown solution gave prism single crystals after slow diethyl ether diffusion for 3 days. Yield: 1.12 g (53.8 %). The preparations of NHS-activated precursor, $[(n\text{-}C_4H_9)_4N]_3[AlMo_6O_{24}\{(CH_2)_3CCH_2OCO(CH_2)_2COON\text{-}(CO)_2C_2H_4\}_2]$ (**3c**), and final compound, $[(n\text{-}C_4H_9)_4N]_3[AlMo_6O_{24}\{(CH_2)_3CCH_2OCO(CH_2)_2CONH\text{-}C_9H_{17}NO\}_2]$ (**3-Al**), were similar to that of **1-Mn**. Total yield: 845 mg (35.4 %). FT-IR (cm^{-1}): 2962 (m), 2933 (m), 2871 (m), 1735 (m), 1654 (m), 1540 (w), 1460 (m), 1128 (w), 1024 (w), 941 (s), 922 (s), 900 (s), 655 (s), 575 (m). ESI-MS: 2148.57 ({[**3-Al**]-TBA}$^{1-}$), 952.88 ({[**3-Al**]-2TBA}$^{2-}$). Element

Analysis for $C_{84}H_{168}AlMo_6N_7O_{32}$ calc (%): C, 42.16; H, 7.03; N, 4.10; found (%): C, 41.89; H, 7.04; N, 4.84.

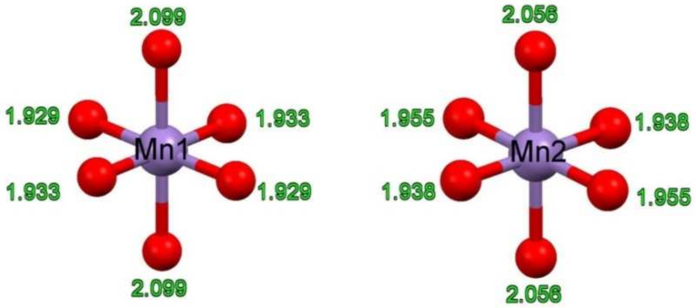


Fig. S1 The Mn-O distances in the crystal structure of **1-Mn**.

Table S1. The crystallographic data of **1-Mn**, **2-Mn**, **3-Al**, **3a**, **3b**, and **3c**.

	1-Mn·4DMF	**2-Mn**	**3-Al·DMF**	**3a·DMF**	**3b·4CH$_3$CN**	**3c**
Formula	$C_{96}H_{198}MnMo_6N_{13}O_{34}$	$C_{82}H_{166}MnMo_6N_9O_{30}$	$C_{87}H_{175}AlMo_6N_8O_{33}$	$C_{61}H_{133}AlMo_6N_4O_{27}$	$C_{74}H_{146}AlMo_6N_7O_{32}$	$C_{74}H_{140}AlMo_6N_5O_{36}$
F.W.	2709.24	2388.81	2463.96	1957.33	2248.59	2278.52
Cryst. Syst.	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P-1	P21/n	P21/c	P21/n	I2/a	C2/c
a/ Å	18.48700(10)	18.3321(2)	33.7469(11)	15.4262(2)	24.0446(2)	31.449(6)
b/ Å	19.4071(2)	20.0174(4)	12.8751(4)	54.1958(7)	14.31510(10)	15.681(3)
c/ Å	19.6357(2)	34.4565(6)	28.9950(7)	23.3363(3)	28.3267(2)	24.450(5)
α (^{o})	71.6880(10)	90	90	90	90	90
β (^{o})	79.9100(10)	93.5000(10)	105.212(3)	90.0190(10)	98.3250(10)	97.16(3)
γ (^{o})	74.2640(10)	90	90	90	90	90
V/ Å^3	6406.18(11)	12620.6(4)	12156.8(6)	19510.0(4)	9647.34(13)	11964(4)
Z	2	4	4	8	4	4
ρ	1.405	1.257	1.346	1.333	1.548	1.265
R_1	0.0346	0.1016	0.0899	0.0786	0.0304	0.0687
$wR2$	0.0950	0.3173	0.2555	0.2200	0.0852	0.1803

3. ESI-MS

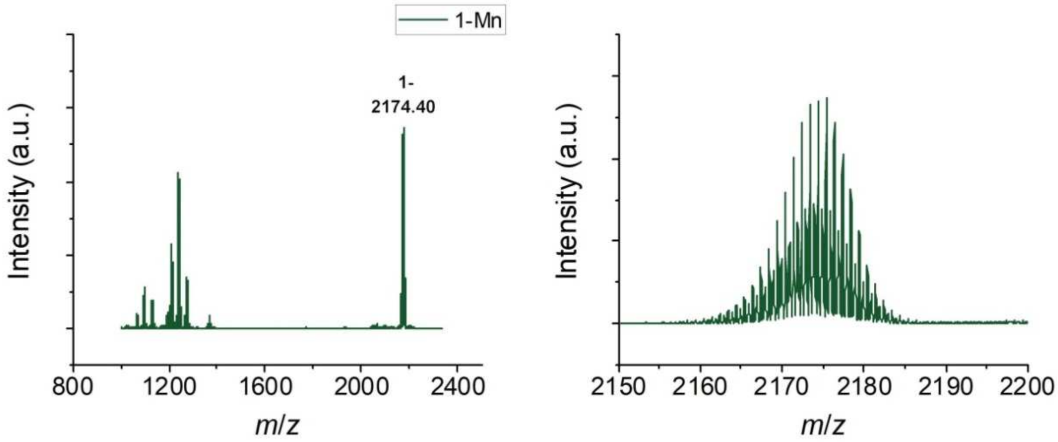


Fig. S2 The ESI-MS spectra of **1-Mn**.

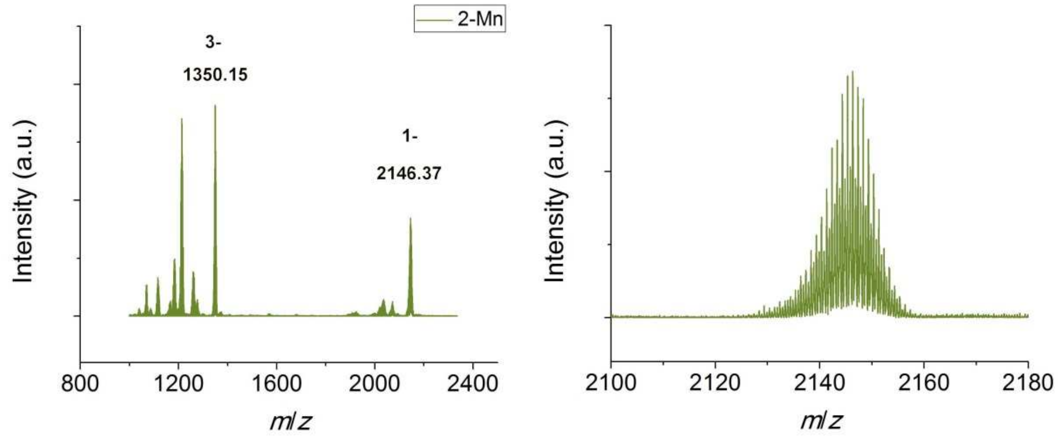


Fig. S3 The ESI-MS spectra of **2-Mn**.

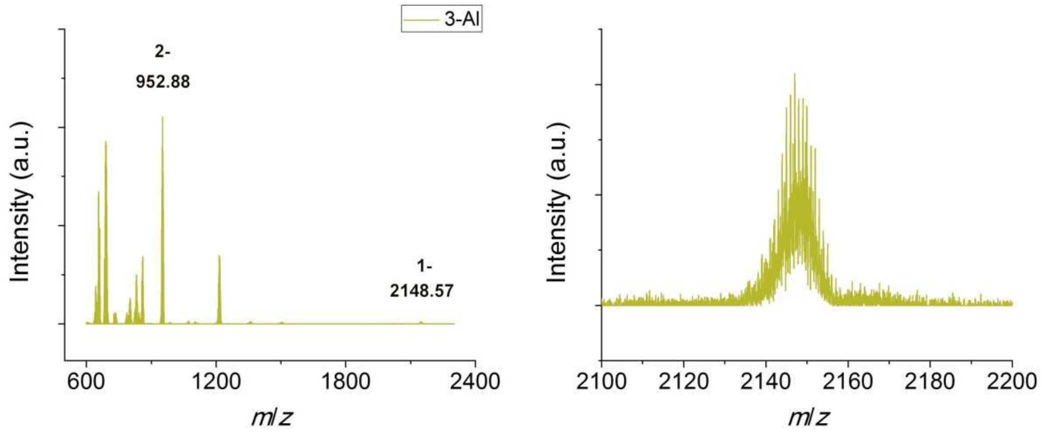


Fig. S4 The ESI-MS spectra of **3-Al**.

4. Evans NMR

The Evans NMR spectra were recorded on a 400.13 MHz Bruker NMR instrument with probe temperature of 300.1 K. For the sample preparation, *ca*. 5 mg of paramagnetic compound was dissolved in DMSO-d_6 500 µL and placed into a standard NMR tube. Then, to a one-end sealed capillary tube *ca*. 100 µL of DMSO-d_6/DMSO = 50:1 (v/v) mixture was added, and the capillary was carefully inserted into the NMR tube. Finally, the Evans NMR spectrum was acquired the same as a standard ^{1}H NMR. The 'solvent correction' of the Evans NMR is neglected due to the diluted system (10^{-6} mol/mL). Each sample went for three runs to avoid experimental errors.

The theoretic magnetic moment for paramagnetic complexes is given by the following equation.[8]

Equation S1:

$$\mu_{theo} = \mathrm{g}\sqrt{\mathrm{S}(\mathrm{S}+1) + \frac{L(L+1)}{4}}$$

where g is the gyromagnetic ratio (2.0 μ_B), S is the spin quantum number, which equals to half of the number of unpaired electrons (n), and L is the orbital quantum number, which usually can be omitted for early transition metal complexes due to small orbital contribution. Therefore, the magnetic moment can be simplified as follow. Leading to the spin-only case:

Equation S2: $\mu_{theo} = 2\sqrt{S(S+1)} = \sqrt{n(n+2)}$

Meanwhile, the magnetic moment can be calculated by measuring the magnetic susceptibility according to the following equation.[9]

Equation S3: $\mu_{\mathrm{exp}} = 2.83\sqrt{(\chi_{\mathrm{M}} \cdot \mathrm{T})}$

$$\mu_{exp} = \sqrt{\frac{3k}{N\beta^2}(\chi_{\mathrm{M}} \cdot \mathrm{T})}$$

with $\frac{3k}{N\beta^2} \approx 8$ -> $2.83 = \sqrt{8}$

where χ_{M} is the molar magnetic susceptibility (mL/mol), *T* is temperature (K), *k* is Boltzmann constant, *N* is Avogadro's number, and β is Bohr magneton of the electron.

According to the Evans method,[10] the magnetic susceptibility of a dissolved paramagnetic substance can be measured in a diamagnetic solvent using NMR technique and simplified in dilute solutions to eliminate the susceptibility contribution of pure solvent as follow.[11]

Equation S4:

$$\chi_M = \frac{\Delta_f \cdot M}{S \cdot F \cdot \frac{m}{V}} = \frac{\Delta_{ppm} \cdot F}{S \cdot F \cdot 10^6 \cdot c} = \frac{\Delta_{ppm}}{S \cdot 10^6 \cdot c} = \frac{3 \cdot \Delta_{ppm}}{4\pi \cdot 10^6 \cdot c}$$

where Δ_f is the shift in frequency (Hz) from the value found for the pure solvent and can be calculated by Δ_{ppm} (the shift in ppm), S is the shape factor of the magnet ($4\pi/3$ for a cylindrical sample in a superconducting magnet), F is the spectrometer radiofrequency in Hz, M is the molecular weight of the paramagnetic solute, m is the mass of the solute, V is the volume of deuterated pure solvent, and c is the molar centration of the solute (mol/mL).

Therefore, the calculation of magnetic moment can be obtained by the following equation.

Equation S5:

$$\mu_{exp} = 2.828\sqrt{\frac{3 \cdot T}{4\pi \cdot 10^6} \cdot \frac{\Delta_{ppm}}{c}}$$

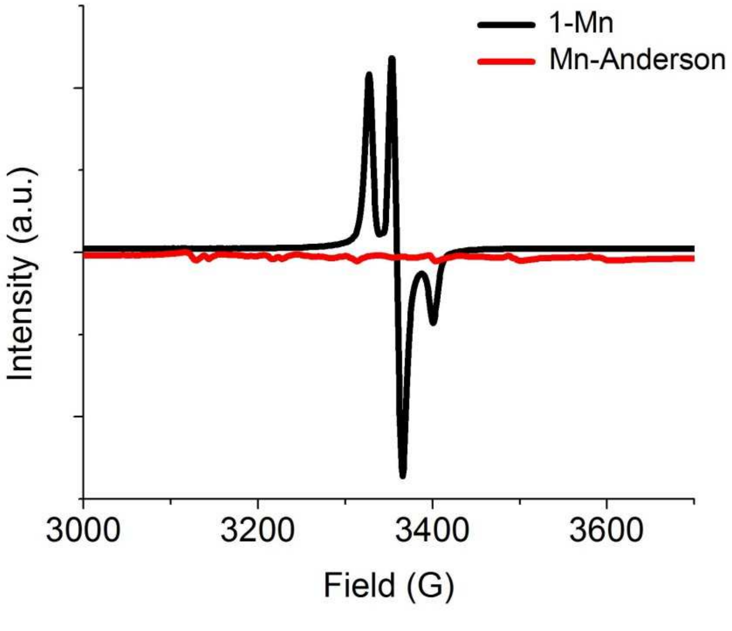


Fig. S5 The EPR spectra of **1-Mn** and Mn-Anderson performed in DMSO (1 x 10^{-4} M) at 100 K.

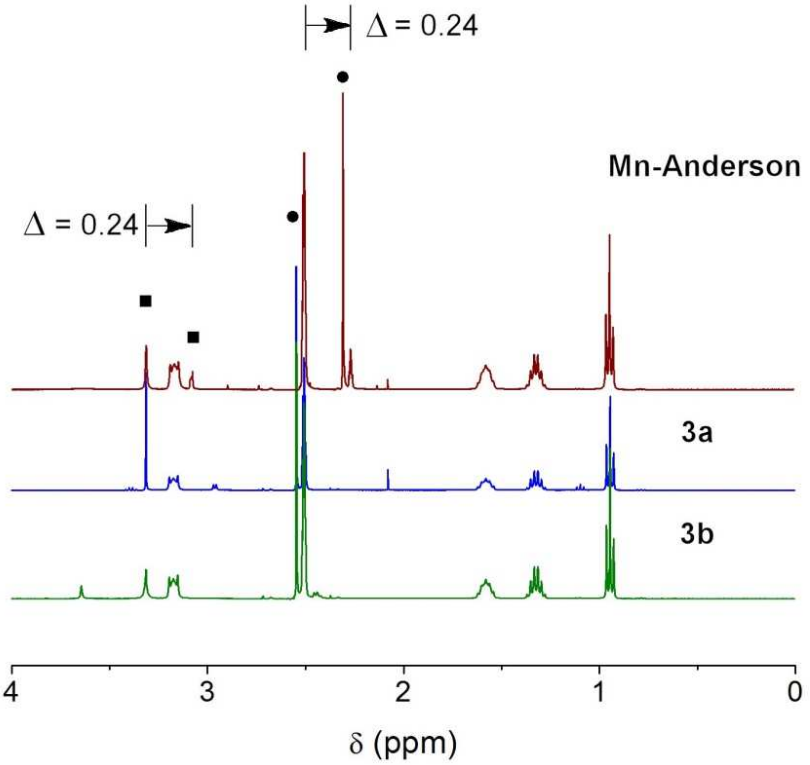


Fig. S6 The Evans NMR spectra of Mn-Anderson (red), **3a** (blue) and **3b** (green). Square and round dots indicate the solvent peaks of H_2O and DMSO, respectively.

Table S2 The data and calculation details of Evans NMR.

	M. W. (g mol^{-1})	mass (mg)	c (mol mL^{-1})	Δ_{ppm}	μ_{clcd} (μ_B)
Mn-Anderson	1882.18	5.9	6.27 x 10^{-6}	0.24	4.68
		4.8	5.10 x 10^{-6}	0.20	4.74
		5.0	5.31 x 10^{-6}	0.20	4.65
1-Mn	2416.87	6.0	4.96 x 10^{-6}	0.25	5.38
		4.6	3.81 x 10^{-6}	0.17	5.06
		5.6	4.63 x 10^{-6}	0.22	5.22
2-Mn	2388.82	5.3	4.44 x 10^{-6}	0.19	4.95
		4.9	4.10 x 10^{-6}	0.20	5.29
		4.5	3.77 x 10^{-6}	0.18	5.23
3-Al	2390.88	5.3	4.43 x 10^{-6}	0.04	2.28
		6.2	5.19 x 10^{-6}	0.04	2.10
		5.2	4.35 x 10^{-6}	0.04	2.30

5. References

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