# Electronic Supporting Information

# Efficient synthesis of manganese(II) carboxylates: From trinuclear cluster $[Mn_3(PhCO_2)_6(THF)_4]$ to a unique $[Mn(PhCO_2)_2]_n$ chiral 3D network

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Supporting Information

## Experimental Section

All manipulations were conducted under an argon atmosphere by using standard Schlenk techniques. All reagents were purchased from commercial vendors. Solvents were dried and distilled prior to use. The reactions were conducted in a 250ml Parr pressure vessel equipped with a pressure gauge, thermocouple and temperature controller. The infrared spectra were recorded on a FT-IR Perkin-Elmer System 2000 spectrometer. Elemental analyses were performed on a Vario EL apparatus (Elementar Analysensysteme GmbH).

**Synthesis of 1:** $[Mn(PhCO_2)_2]_n$: A mixture of manganese powder (1 g, 18.2 mmol), benzoic acid (4.274 g, 35 mmol) and MeCN (100 mL) was heated in a pressure reactor for 72 hours at 120°C. After cooling, reaction mixture was filtered, and about 70 mL of MeCN was distilled. After several hours light pink crystals of **1** formed, and were washed with MeCN and dried under vacuum, resulting in 4,47 g (86% yield after first crystallization based on benzoic acid). Elemental analysis (%) calcd for $Mn(PhCO_2)_2$ (297.165 g $mol^{-1}$): C 56.58, H 3.39; found: C 56.62, H 3.41; IR (Nujol): ν = 560w, 676m, 715s, 820w, 838w, 856w, 938w, 1002w, 1025w, 1070w, 1102w, 1157w, 1180m, 1307m, 1378s, 1403s, 1446s, 1504s, 1551s, 1594s, 1698w, 1790vw, 1825vw, 1917vw, 1965vw, 2853s, 2923vs, 2954s, 3056w $cm^{-1}$.

**Synthesis of 2**: $[Mn_3(PhCO_2)_6(THF)_4]$•THF: A mixture of manganese powder (1 g, 18.2 mmol), benzoic acid (4.274 g, 35 mmol) and THF (70 mL) was heated in a pressure reactor for 72 hours at 120°C. After cooling, reaction mixture was filtered, and about 40 mL of THF was distilled. After several hours light pink crystals of compound **2** formed, and were washed with cold THF and dried under vacuum, resulting in 5,40 g (74% yield after first crystallization based on benzoic acid). Elemental analysis (%) calcd for $C_{62}H_{70}Mn_3O_{17}$ (1252.02 g $mol^{-1}$): C 59.48, H 5.63; found: C 59.52, H 5.66; IR (Nujol): ν = 537w, 571w, 675m, 684m, 717s, 773vw, 819w 838w, 862w, 881w, 911w, 1025m, 1067m, 1099vw, 1143w, 1182w, 1309m, 1377s, 1404s, 1456s, 1516s, 1558s, 1627s, 1781vw, 1818vw, 1911vw, 1961vw, 2729vw, 2853vs, 2868s, 2923vs, 2954s, 3027w, 3056w $cm^{-1}$.

**Synthesis of 3**: $[Mn_6(^tBuCO_2)_{12}(THF)_4]_n$: A mixture of manganese powder (1 g, 18.2 mmol), pivalic acid (3.574 g, 35 mmol) and THF (70 mL) was heated in a pressure reactor for 72 hours at 120°C. After cooling, reaction mixture was filtered, and about 55 mL of THF was distilled, producing a highly viscous liquid. After two days in room temperature, light pink crystals of compound **3** formed, and were washed with cold THF and dried under vacuum, resulting in 3,52 g (65% yield after first crystallization based on benzoic acid). Elemental analysis (%) calcd for $C_{76}H_{140}Mn_6O_{28}$ (1831.54 g $mol^{-1}$): C 49.83, H 7.70; found: C 49.86, H 7.72; IR (Nujol): ν = 538w, 602w, 722w, 791w, 894w, 937w, 1033w, 1228m, 1309w, 1362m, 1377s, 1423s, 1456s, 1463s, 1483s, 1557s, 1568m, 1575m, 1695w, 2726w, 2854vs, 2923vs, 2955vs.

**Formation of 4:**

Compound **4** forms as an impurity during reflux synthesis of **1**.

$[Mn_6O_2(PhCO_2)_{10}(MeCN)_4]$: Elemental analysis (%) calcd for $C_{78}H_{62}Mn_6O_{22}N_4$ (1736.96 g $mol^{-1}$): C 53.93, H 3.60, N 3.22; found: C 53.97, H 3.61, N 3.17; IR (Nujol): ν = 561m, 609s, 673m, 689.43m 714s, 842m, 932w, 1024m, 1068m, 1175.40m, 1306m, 1398vs, 1447s, 1490m, 1568vs, 1605vs, 1621s, 1827vw, 1914vw, 1966vw, 2276m, 2304w, 2854s, 2923vs, 2954s, 3027w, 3064m

## X-Ray Crystallography

Data were collected using the 'oil drop technique' to mount crystals on a Nonius Kappa-CCD equipped with an Oxford Cryostream low-temperature device. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Crystal data for **1**, $C_{280}H_{200}Mn_{19}O_{80}$: $M$ = 5888.26, crystal dimensions 0.48 × 0.32 × 0.28 $mm^3$, orthorhombic, space group $P$ 21 21 2 (no. 18), $a$ = 38.8251(2) Å, $b$ = 17.6702(2) Å, $c$ = 19.4001(5) Å, $U$ = 13309.1(4) $Å^3$, $Z$ = 2, $F(000)$ = 5990, $D_c$ = 1.469 g $m^3$, $T$ = 100(2)K, $\mu$(Mo-K$\alpha$) = 0.952 $mm^{-1}$, Nonius Kappa-CCD diffractometer, $\theta_{max}$ = 27.49 °, 29808 unique reflections. The structure was solved by direct methods using the SHELXS97 [1] program and was refined by full matrix least–squares on $F^2$ using the program SHELXL97.[2] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at geometrically idealized coordinates with a fixed isotropic displacement parameter equal to 1.2. Refinement converged at $R1$ = 0.0844, $wR2$ = 0.1590 for all data, 133 parameters, and 144 restraints ($R1$ = 0.0768, $wR2$ = 0.1549 for 27733 reflections with $I_o > 2\sigma(I_o)$). The goodness-of-fit on $F^2$ was equal 1.165. A weighting scheme $w = [\sigma^2(F_o^2 + (0.0418P)^2 + 3.1964P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the final stage of refinement. The residual electron density = + 0.96 /- 0.74 $eÅ^{-3}$. CCDC-949071.

Crystal data for **2**, $C_{124}H_{143}Mn_6O_{34}$: $M$ = 2507.02, crystal dimensions 0.38 × 0.30 × 0.26 $mm^3$, triclinic, space group $P$ -1 (no. 2), $a$ = 11.4356(3) Å, $b$ = 12.0816(2) Å, $c$ = 21.5601(5) Å, $\alpha$ = 85.3518(12) °, $\beta$ = 89.0215(12) °, $\gamma$ = 82.4410(14) °, $U$ = 2943.28(11) $Å^3$, $Z$ = 1, $F(000)$ = 1309, $D_c$ = 1.444 g $m^3$, $T$ = 100(2)K, $\mu$(Mo-K$\alpha$) = 0.705 $mm^{-1}$, Nonius Kappa-CCD diffractometer, $\theta_{max}$ = 24.71 °, 9663 unique reflections. The structure was solved by direct methods using the SHELXS97 [1] program and was refined by full matrix least–squares on $F^2$ using the program SHELXL97.[2] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at geometrically idealized coordinates with a fixed isotropic displacement parameter equal to 1.2. Refinement converged

at $R1$ = 0.0530, $wR2$ = 0.1006 for all data and 749 parameters and restraints 6 ($R1$ = 0.0450, $wR2$ = 0.0971 for 8556 reflections with $I_o > 2\sigma(I_o)$). The goodness-of-fit on $F^2$ was equal 1.072. A weighting scheme $w = [\sigma^2(F_o^2 + (0.0418P)^2 + 3.1964P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the final stage of refinement. The residual electron density = + 0.69 /- 0.84 eÅ$^{-3}$. CCDC-949072.

Crystal data for **3**, $[C_{76}H_{140}Mn_6O_{28}]_n$: $M$ = 1831.52, crystal dimensions 0.34 × 0.32 × 0.22 mm$^3$, triclinic, space group $P$ -1 (no. 2), $a$ = 12.4470(13) Å, $b$ = 18.7120(16) Å, $c$ = 21.509(2) Å, $\alpha$ = 91.782(6) °, $\beta$ = 90.506(6) °, $\gamma$ = 108.686(4) °$U$ = 4742.3(8) Å$^3$, $Z$ = 2, $F$(000) = 1940, $D_c$ = 1.283 g m$^3$, $T$ = 100(2)K, $\mu$(Mo-K$\alpha$) = 0.843 mm$^{-1}$, Nonius Kappa-CCD diffractometer, $\theta_{max}$ = 23.26 °, 12491 unique reflections.

Twinned crystal with partially superimposed reciprocal lattices. The transformation matrix of indices of the twin components for crystals was determined roughly as:

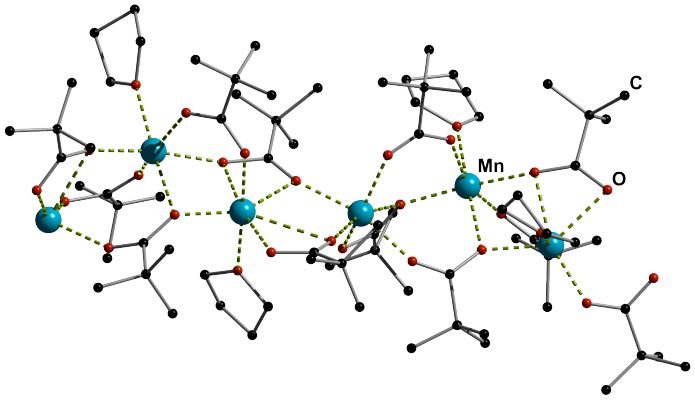
| -1.000 0.000 0.000|
| 0.000 -1.000 0.000|
| 0.072 0.087 1.000|

which comply with conditions: rotation twin axis [0 0 1] rotation angle 23% or reflection twin plane (1 1 24).

The structure was solved by direct methods using the SHELXS97 [1] program and was refined by full matrix least–squares on $F^2$ using the program SHELXL97.[2] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at geometrically idealized coordinates with a fixed isotropic displacement parameter equal to 1.2. Refinement converged at $R1$ = 0.2292, $wR2$ = 0.4142 for all data, 1027 parameters, and 42 restraints ($R1$ = 0.1761, $wR2$ = 0.3905 for 8611 reflections with $I_o > 2\sigma(I_o)$). The goodness-of-fit on $F^2$ was equal 1.156. A weighting scheme $w = [\sigma^2(F_o^2 + (0.0418P)^2 + 3.1964P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the final stage of refinement. The residual electron density = + 1.10 /- 1.06 eÅ$^{-3}$. CCDC-959486.

We were not able to obtain satisfactory refinement of the discussed structure due to the poor quality of crystals, therefore the geometric parameter could not be discussed.

a)




b)

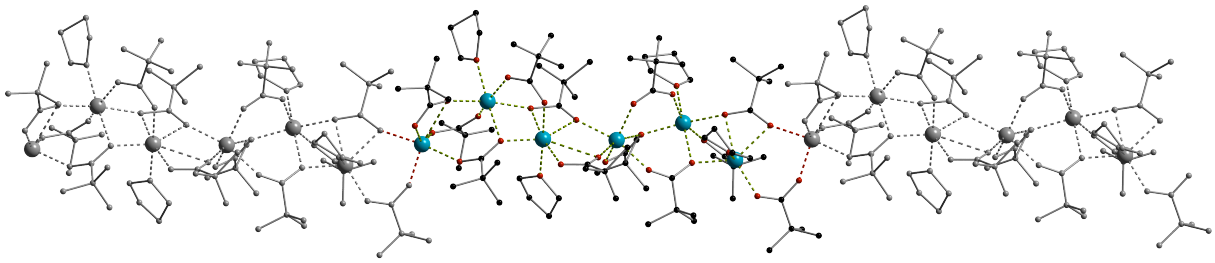


**Fig. S1.** a) Molecular structure of **3,** hydrogen atoms have been omitted for clarity; b) side view of a single 1D coordination polymer of **3.**

Compound **3** crystallizes in triclinic system, *P* -1 space group as a 1D coordination polymer. The constitutional repeating unit consists of six Mn(II) ions with distorted octahedral coordination spheres. Manganese centers are bridged by a total of twelve $^{t}BuCO_2^-$ ligands in four different coordination modes: $\eta^1{:}\eta^1{:}\mu_2$, $\eta^2{:}\eta^1{:}\mu_2$, $\eta^2{:}\eta^1{:}\mu_3$, and $\eta^2{:}\eta^2{:}\mu_3$. The remaining coordination sites are occupied by four terminally coordinated molecules of THF.

Crystal data for **4**, $C_{78}H_{62}Mn_6N_4O_{22}$: $M$ = 1736.86, crystal dimensions 0.34 × 0.30 × 0.24 $mm^3$, orthorhombic, space group *P* 21 21 2 (no. 18), $a$ = 17.5001(2) Å, $b$ = 18.4522(2) Å, $c$ = 24.6381(2) Å, $U$ = 7956.02(14) $Å^3$, $Z$ = 4, $F$(000) = 3536, $D_c$ = 1.450 g $m^3$, $T$ = 100(2)K, $\mu$(Mo-K$\alpha$) = 0.998 $mm^{-1}$, Nonius Kappa-CCD diffractometer, $\theta_{max}$ = 27.48 °, 9086 unique reflections. The structure was solved by direct methods using the SHELXS97 [1] program and was refined by full matrix least–squares on $F^2$ using the program SHELXL97.[2] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at geometrically idealized coordinates with a fixed isotropic displacement parameter equal to 1.2. Refinement converged at $R1$ = 0.0441, $wR2$ = 0.0802 for all data, 498 parameters, ($R1$ = 0.0345, $wR2$ = 0.0763 for 7767 reflections with $I_o > 2\sigma(I_o)$). The goodness-

of-fit on $F^2$ was equal 1.046. A weighting scheme $w = [\sigma^2(F_o^2 + (0.0418P)^2 + 3.1964P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the final stage of refinement. The residual electron density = + 0.37 /- 0.36 eÅ$^{-3}$. CCDC-959487.

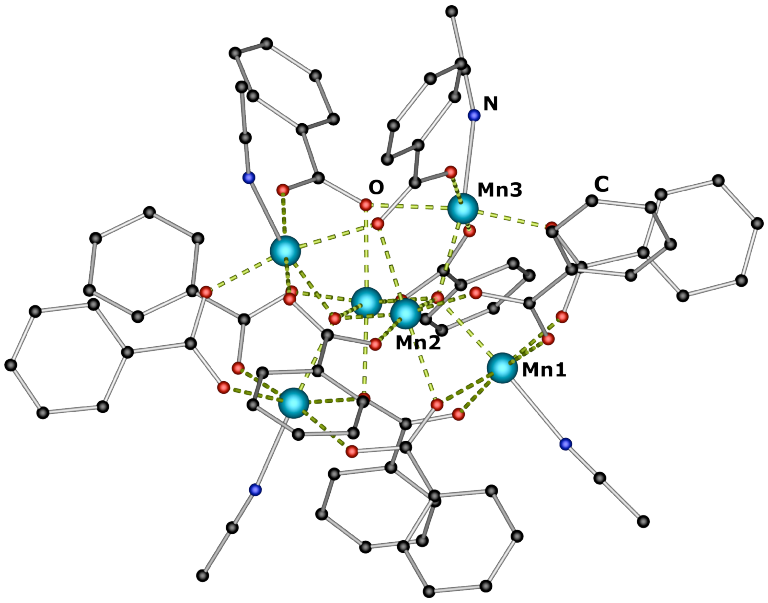



**Fig. S2.** Molecular structure of **4**. Hydrogen atoms have been omitted for clarity.

Compound **4** crystallizes in orthorhombic system, *P b c n* space group and is similar to those of $[Mn_6O_2(PhCO_2)_{10}(py)_2(MeCN)_2]$•2MeCN and $[Mn_6O_2(PhCO_2)_{10}(py)_4]$•$Et_2O$ which have been previously reported.[3] The structure of the molecule is shown in Figure S2. It has a hexanuclear mixed valence Mn(II), Mn(III) cluster structure and is best viewed as two $Mn_4(\mu_4$-O) tetrahedrons sharing an edge. The two manganese ions forming the shared edge are the inner atoms, while the four remaining atoms are considered outer. Six of benzoate ions are located along the edges of the tetrahedrons bridging inner and outer Mn cations in a $\eta^1{:}\eta^1{:}\mu_2$ fashion, while the four remaining benzoate ions are bridging three manganese ions in a $\eta^2{:}\eta^1{:}\mu_3$ fashion. Finally four MeCN molecules are terminally coordinated to the four outer Mn ions. The metal-oxygen distances between inner metal atoms are considerably shorter [Mn-O = 1,890(5)-1,892(2) Å] than between the outer [Mn-O = 2,198(5)-2,200(8) Å].

## Magnetic Section

Magnetic measurements were carried out on polycrystalline powder samples using a PPMS-9T system (Quantum Design) in the temperature range 2 – 300 K. Data were corrected for the sample-holder contribution and diamagnetism of the sample using standard procedures [4].

The temperature dependences of magnetization of **1**, **2** and **3** were measured in 0.1 T applied magnetic field and are presented in the form of χT vs T and 1/χ vs T in Figure S3 and Figure S4 by symbols.

Experimental $\chi$ *vs* T data of **1** were fitted with an analytical expression for the magnetic susceptibility ($\chi_M$) for linear trimers ($S_1$-$S_2$-$S_3$) presented in [5] that have been additionally modified by the term of intermolecular interactions in the frame of molecular field approximation [6]: $\chi_{calcd} = \chi_M \left[1 - zJ'\chi_M / N_A g^2 \mu_B{}^2\right]^{-1}$ (where $zJ'$ is an inter-centres interaction parameter). The theoretical curve matches the experimental data over the whole temperature range (solid line in Figure S3) with the agreement factor $R = \frac{\sum(\chi - \chi_{calcd})^2}{\sum \chi^2} =$ $3.4 \cdot 10^{-4}$.

Below the magnetic behaviour of **3** are discussed (the result for **1** and **2** are presented in the main article). The room temperature value of χT is 4.04 $cm^3K(mol(Mn))^{-1}$ (close to the one expected for isolated S = 5/2 spins, 4.37 $cm^3K(mol)^{-1}$). As the temperature decreases the χT product also decreases up to 0.99 $cm^3K(mol(Mn))^{-1}$ at 2 K. Magnetisation curves measured at low temperatures in the field range ± 9 T reveal no hysteresis. The M(H) dependence at 2 K (Figure S5), does not follow a Brillouin function for S = 5/2 spin system, does not saturate and at H > 5.5 T is linear. Magnetic moment measured at T = 2 K in H = 9 T is 2.14 $\mu_B$/Mn that is far below expected 5 $\mu_B$ per isolated Mn(II) ions. The 1/χ vs T reveals linear behaviour over 30 - 300 K temperature range (Figure S4) and a fit to the Curie-Weiss model gives: C = 4.4 $cm^3K(mol(Mn))^{-1}$, θ = -27.1 K. Additionally, temperature dependences of magnetization were measured in Zero Field Cooling and Field Cooling modes and the full superimposition of both curves was observed.

The basic magnetic characteristics described above indicate the paramagnetism of manganese ions at high temperatures and an intra-chains magnetic ordering of Mn(II) with dominant antiferromagnetic exchange interactions at low temperatures. Initial fitting of χ vs T with the Fisher's model [7] valid for uniform chains of classical spins with nearest-neighbours Heisenberg couplings gave unsatisfying results. That is reasonable as the chains in **3** are irregular. There are no identical bridging modes between two magnetic centres within Mn6

structural unit: Mn – Mn distances and the interaction angles varies and Mn ions are bridged by two or three carboxylates groups (see Figure S1). These structural differences affect the value of the exchange constant $J$ [8] that induces some distribution of $J$ value along the structural chains. Thus, to describe the experimental results, the model of chains with random exchange coupling between nearest neighbours was used [9]:

$$\chi_{calc} = \frac{N_A \mu_B{}^2 g^2 S(S+1)}{3k_B T}\left[\frac{1+F_0}{1-F_0}\right] \text{ where } F_0 = \frac{k_B T}{2\lambda S(S+1)} \ln \frac{(J-\lambda)\sinh\left(\frac{S(S+1)(J+\lambda)}{k_B T}\right)}{(J+\lambda)\sinh\left(\frac{S(S+1)(J-\lambda)}{k_B T}\right)} \text{ and}$$

$J$ and $\lambda$ – define the distribution of exchange coupling values (a uniform distribution of the exchange constant was assumed over a domain ranging from $J - \lambda$ to $J + \lambda$ ( $\lambda \geq 0$)), S = 5/2 and g = 2. The best fit for **3** is shown in Figure S3 as a solid line and the values obtained are: $J$ = -2.72 cm$^{-1}$, $\lambda$ = 4.05 (the agreement factor R = 6.15·10$^{-4}$).

*Comparison of the observed magnetic characteristics of **1**, **2** and **3**.*

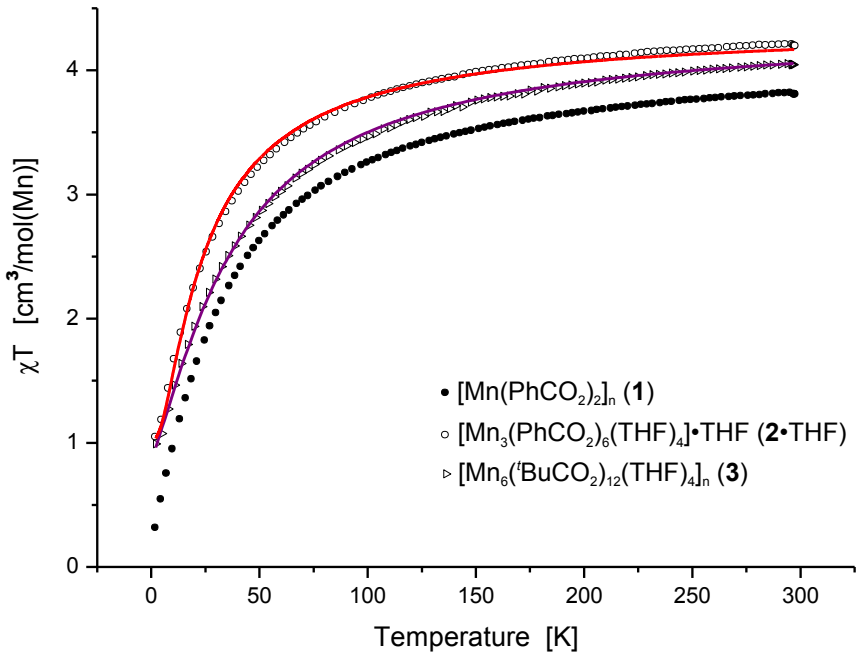



**Fig. S3.** Temperature dependences of the magnetic susceptibility, in the form of χT vs T for **1**, **2**, **3** measured at 0.1 T. The solid lines represent the best fit of the experimental data (see text for details). All curves are presented in cm$^3$K/mol(Mn).

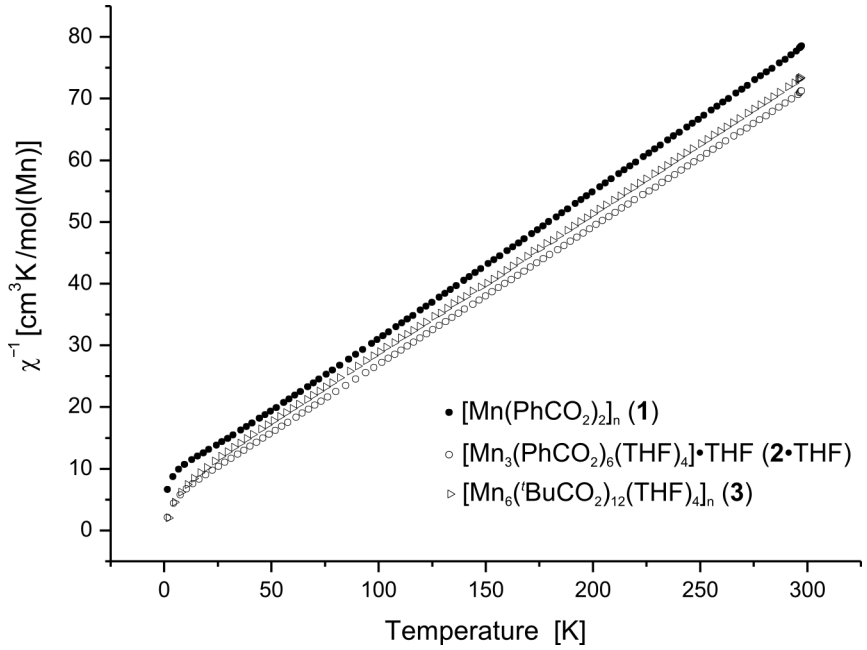



**Fig. S4.** The inverse of magnetic susceptibility versus temperature data for **1**, **2**, **3**.

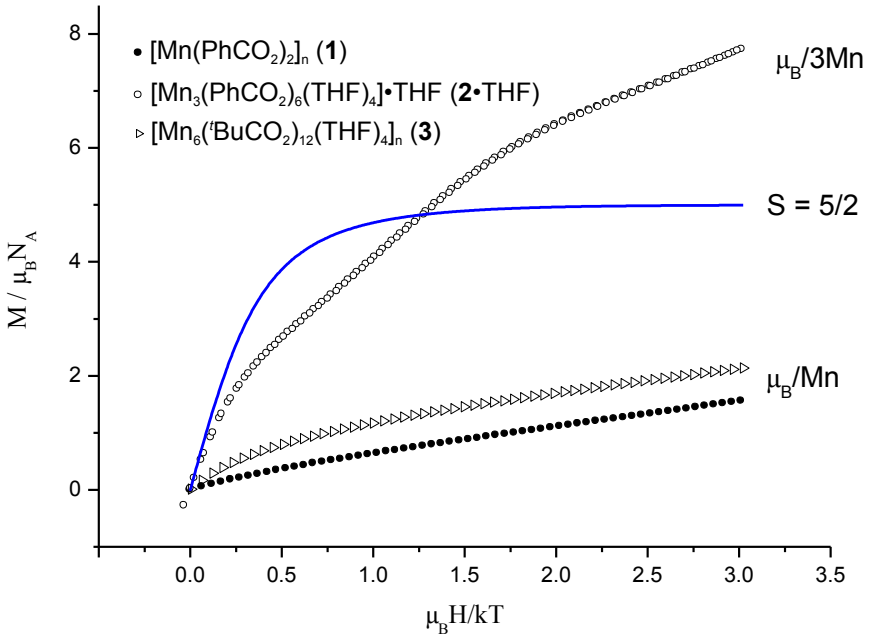



**Fig. S5.** Magnetization curves measured at 2 K for complexes **1**, **2**, **3**. Solid curve is the theoretical Brillouin function for S = 5/2 and g =2. The experimental data for **1** and **3** are presented in the form of $\mu_B$/Mn vs $\mu_B$H/kT and for **2** in $\mu_B$/3Mn vs $\mu_B$H/kT.

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