

SUPPORTING INFORMATION

m-Carboranylphosphinate as Versatile Building Blocks to Design all Inorganic Coordination Polymers.

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Experimental section:

Materials, Instrumentation and Measurements.

Synthesis and characterization of polymer $[\text{Mn}(\text{MeOH})_2(1\text{-OPH}(\text{O})\text{-}1,7\text{-}closo\text{-C}_2\text{B}_{10}\text{H}_{11})_2]_n$, **1**.

Synthesis and characterization of $[\text{Mn}(\text{H}_2\text{O})_4][(1\text{-OPH}(\text{O})\text{-}1,7\text{-}closo\text{-C}_2\text{B}_{10}\text{H}_{11})_2]$, **2**.

Synthesis and characterization of polymer $[\text{Mn}(1\text{-OPH}(\text{O})\text{-}1,7\text{-}closo\text{-C}_2\text{B}_{10}\text{H}_{11})_2(\text{bpy})]_n$, **3**.

Synthesis and characterization of $[\text{Ni}(\text{H}_2\text{O})_6][(1\text{-OPH}(\text{O})\text{-}1,7\text{-}closo\text{-C}_2\text{B}_{10}\text{H}_{11})_2]$, **4**.

Scheme S1. Synthetic strategy for the preparation of Ni^{II} compound **4**.

Figure S1. IR spectra of compounds a) **1**, b) **2**, c) **3**, d) **4**

Figure S2. ^{11}B -NMR and $^{11}\text{B}\{^1\text{H}\}$ -NMR spectra of compounds a) polymer **1**, b) **2** and c) polymer **3**

Figure S3. ^{11}B -NMR, $^{11}\text{B}\{^1\text{H}\}$ -NMR, ^{31}P -NMR spectra of the compound **4**

Figure S4. Packing structure of a) Mn polymer **1** along the axis *a* and b) Mn polymer **3**

Figure S5. a) X-ray structures and labelling scheme for complex **4** (ORTEP plots with ellipsoids at 30% probability level). b) Packing of **4** along *a* axis.

Figure S6. Packing structure of Ni complex **4** along the *b* axis (a) and *c* axis (b).

Figure S7. Thermal gravimetric analysis (TGA/DCS) of a) polymer **1**; b) **2**; c) polymer **3**.

Figure S8. TEM images of polymers **1** (a) and **3** (b) from methanol at the same concentration (1gL^{-1}). Scale bars are 200 nm.

Figure S9. $^{11}\text{B}\{^1\text{H}\}$ -NMR spectra of compound **3** in MeOH, in MeOH/H₂O and of compound **2** in MeOH/H₂O

Table S1. Crystal Data for X-ray structures of Mn complexes, **1-3**.

Table S2. Selected bond lengths (Å) and angles (°) for Mn complexes **1-3**.

Table S3. Crystal Data for X-ray structures of Ni complex, **4**.

Table S4. Selected bond lengths (Å) and angles (°) for Ni complex **4**.

Table S5. Thermal gravimetric analysis (TGA) data for compounds **1-3**.

References.

Experimental Section

Materials:

All reagents used in the present work were obtained from Aldrich Chemical Co and were used without further purification. Reagent grade organic solvents were obtained from SDS and high purity de-ionized water was obtained by passing distilled water through a nano-pure Mili-Q water purification system. 1,7-*closo*-C₂B₁₀H₁₂ were purchased from Katchem and used as received. Bis(dimethylamino)chlorophosphine was purchased from Alfa Aesar. The Na[1-OPH(O)-1,7-*closo*-C₂B₁₀H₁₁] was synthesized as reported.¹

Instrumentation and Measurements:

Elemental analyses were performed using a Thermo Scientific™ FLASH 2000 CHNS Analyzer. IR spectra were obtained on PerkinElmer® Universal ATR Accessory. The ¹H-, ¹H{¹¹B}, ¹H{³¹P}-NMR (300.13 MHz), ¹³C{¹H}-NMR (75.47 MHz), ¹¹B-, ¹¹B{¹H}-NMR (96.29 MHz), ³¹P- and ³¹P{¹H}-NMR (121.48 MHz) spectra were recorded on a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories. All NMR spectra were performed in deuterium oxide and chloroform deuterated solvent at 22°C. The ¹¹B- and ¹¹B{¹H}-NMR shifts were referenced to external BF₃·OEt₂, the ¹H, ¹H{¹¹B}, ¹H{³¹P}, ¹³C{¹H}-NMR shifts were referenced to SiMe₄, ³¹P and ³¹P{¹H}-NMR shifts were referenced to external 85% H₃PO₄. Chemical shifts are reported in units of parts per million downfield from reference, and all coupling constants in Hz. ESI-MS spectra were recorded either in positive and negative-ion mode on a 6000 ESI Ion Trap LC/MS (Bruker Daltonics) using nitrogen as the nebuliser gas. Thermogravimetric Analyses (TGA) were performed on a Netzsch STA 449 thermal analyzer at a heating rate of 10°C/min in a Ar atmosphere.

Dynamic Light Scattering (DLS).

The light scattering setup (Zetasizer Nano ZS, Malvern Instruments Ltd, England) equipped with a He-Ne 633nm laser. Samples for DLS measurements were dissolved in filtered (200nm pore size

filter) methanol in concentration range 0.01 – 20 g/L, where solutions of lower concentrations were prepared by dilution of the stock solution by filtered (200nm pore size filter) methanol.

X-ray structure determination.

Measured crystals were prepared under inert conditions immersed in perfluoropolyether or paratone as protecting oil for manipulation. Suitable crystals were mounted on MiTeGen Micromounts and used for data collection. Diffraction data were collected using a Bruker D8 Venture (**1** and **2**) or Agilent Supernova (**3**) diffractometer. The data were processed with APEX2² (**1** and **2**) or CrysAlisPro³ (**3**) and corrected for absorption using TWINABS⁴ (**1**), SADABS⁵ (**2**) or using the SCALE3 ABSPACK algorithm implemented in CrysAlisPro (**3**). The structures were solved by direct methods⁶ (**1**, **2**) or charge flipping⁷ (**3**), which revealed the position of all non-hydrogen atoms. These atoms were refined on F^2 by a full-matrix least-square procedure using anisotropic displacement parameters⁶. All hydrogen atoms were located in different Fourier maps and included as fixed contributions riding on attached atoms with isotropic thermal displacement parameters 1.2 (C–H, B–H) or 1.5 (CH₃, O–H) times. Additional crystal data and more information about the X-ray structural analyses are shown in Tables S1–S4. In **1**, one coordinated methanol molecule and one phosphinate group are disordered over two alternative positions (0.70:0.30 and 0.76:0.24 ratio, respectively). **1** was treated as a two-component non-merohedral twin; the exact twin matrix identified by the integration program was found to be 1 0 1 0 -1 0 0 0 -1. The structure of **1** was solved using direct methods with only the no overlapping reflections of component 1. The structure was refined using the HKLF 5 routine with all reflections of component 1 (including the overlapping ones), resulting in a BASF value of 0.4063(16).

The crystal of **4** was measured at 170 K on a Bruker Kappa Apex II diffractometer using Mo K α (λ = 0.71073) radiation. The *Denzo-Scalepac*⁸ program package was used for cell refinement and data reduction. Multi-scan absorption corrections (*SADABS*⁵) were applied to the intensities before structure solution. The structure **4** was solved by charge flipping method using the *SUPERFLIP*⁹

software. Structural refinements were carried out using *SHELXL-2014*.¹⁰ In **4**, the P-H and H₂O hydrogen atoms were located from the difference Fourier map and refined isotropically. All other H-atoms were positioned geometrically and constrained to ride on their parent atoms, with C-H = 1.12 Å, B-H = 1.12 Å, and $U_{\text{iso}} = 1.2 \cdot U_{\text{eq}}$ (parent atom). The crystallographic details are summarized in Table **S4**. The crystallographic data as well as details of the structure solution and refinement procedures are reported in supporting information.

CCDC 1534777-1534780, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/products/csd/request/

Synthesis and characterization of coordination polymer [Mn(MeOH)₂(1-OPH(O)-1,7-*closo*-C₂B₁₀H₁₁)₂]_n, **1.**

100 mg (0.43 mmols) of Na[1-OPH(O)-1,7-*closo*-C₂B₁₀H₁₁] in 1 mL of MeOH was mixed with 43 mg (0.22 mmols) of MnCl₂·4H₂O in 1 mL of MeOH at room temperature. The solution was stirred for 2h. Afterward, the solution was filtered, to remove the NaCl formed, and the solvent was evaporated under vacuum to obtain a white solid. The latter was recrystallized from MeOH. After several days, air-stable, colourless crystals of **1** suitable for X-ray diffraction analysis were obtained. Yield: 0.112g (97%). ¹¹B{¹H}NMR (MeOH, 25°C): δ=14.0, 4.9, 1.8. ¹¹BNMR(CD₃OD, 25°C): δ=13.9, 4.9, 2.3 (20B). IR (KBr): ν [cm⁻¹] = 3064 (w, ν_{s} (C_c-H)), 2976 (w, ν_{s} (C-H)), 2595 (vs, ν_{s} (B-H)), 2383 (m, ν_{s} (P-H)), 1615 (m, O-H), 1191, 1097, 1078 (vs, ν (P=O)). Anal. Found (calcd.) (%) for C₄H₂₄B₂₀MnP₂O₄: C 10.25 (10.24); H 5.19 (5.15). ESI-MS (m/z) at the positive ion mode: 767.4 (100%), 281.1 (12%).

The solubility of polymer **1** in MeOH is >100 g/L.

Synthesis and characterization of $[\text{Mn}(\text{H}_2\text{O})_4][(\text{1-OPH}(\text{O})\text{-1,7-closo-C}_2\text{B}_{10}\text{H}_{11})_2]$, **2**.

By recrystallization of **1** in a $^i\text{PrOH}/\text{H}_2\text{O}$ solution and after slow diffusion, colorless needles suitable for X-ray diffraction were obtained, after a few days, corresponding to complex **2**, that was obtained quantitatively. ^{11}B NMR ($\text{MeOH}/\text{H}_2\text{O}$): $\delta = -2.1$ (s, $^1\text{J}(\text{B,H})= 36$, 1B), -4.0 (s, $^1\text{J}(\text{B,H})= 133$, 1B), -7.5 (s, $^1\text{J}(\text{B,H})= 135$, 4B), -9.8 (s, $^1\text{J}(\text{B,H})= 160$, 3B), -11.9 (s, 1B). IR (KBr): ν [cm^{-1}] = 3295, 3199 (vs broad, H_2O), 3064 (w, $\nu_s(\text{C}_c\text{-H})$), 2600 (vs, $\nu_s(\text{B-H})$), 2396 (s, $\nu_s(\text{P-H})$), 1657 (m, H_2O), 1170, 1016-1099 (vs, $\nu(\text{P=O})$). Anal. Found (calcd.) (%) for $\text{C}_4\text{H}_{26}\text{B}_{20}\text{MnP}_2\text{O}_5$: C 9.89(9.86); H 5.39(5.38). ESI-MS (m/z) at the positive ion mode: 321.2 (100%), 344.2 (97%), 417 (37%).

Synthesis and characterization of coordination polymer $[\text{Mn}(\text{1-OPH}(\text{O})\text{-1,7-closo-C}_2\text{B}_{10}\text{H}_{11})_2(\text{bpy})]_n$, **3**.

Two synthetic procedures have been followed. Procedure 1: 100 mg (0.43 mmols) of $[\text{Na}[\text{1-OPH}(\text{O})\text{-1,7-closo-C}_2\text{B}_{10}\text{H}_{11}]$ in 1 mL of EtOH was mixed with 43 mg (0.22 mmols) of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in 1 mL of EtOH at room temperature. The solution was stirred for 2h. Afterward, the solution was filtered, to remove the NaCl formed, and thus was added a solution of 2,2'-bpy (34 mg, 0.217 mmol) in EtOH (2 mL). The light-yellow solution was stirred for 1 h and filtered. Yellow crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of an ethanol solution of the complex. After several days, air-stable, colourless crystals of **3** suitable for X-ray diffraction analysis were obtained. Yield: 0.129g (95%). Procedure 2: A solution of 2,2'-bpy (5.86 mg, 0.037mmol) in EtOH (0.5 mL) was added to a solution of complex **1** (20 mg, 0.037 mmol) in EtOH (0.5 mL). A slightly yellow solution was formed and stirred for 30 min and filtered. The volume of the solution was reduced to give a precipitate corresponding to complex **3**, that was washed with diethyl ether. Yield: 0.0230g (98 %). ^{11}B $\{^1\text{H}\}$ NMR (MeOH , 25°C): $\delta = 3.3$, -0.6 . IR (KBr): ν [cm^{-1}] = 3064 (w, $\nu_s(\text{C}_c\text{-H})$), 2988, 2906 (w, $\nu_s(\text{C-H})$), 2581 (vs, $\nu_s(\text{B-H})$), 2335 (m, $\nu_s(\text{P-H})$), 1594, 1473, 1439, (m, $\nu(\text{C=C})$ and $\nu(\text{N=C})$), 1223, 1085 (vs, $\nu(\text{P=O})$). Anal. Found (calcd.)

(%) for C₁₄H₃₂B₂₀P₂O₄N₂Mn: C 25.15(26.88); H 4.85(5.16); N 3.81(4.48). ESI-MS (m/z) at the positive ion mode: 1044.6 (17 %), 575.2 (100 %), 418.2 (22 %).

The solubility of polymer **3** in MeOH is >192 g/L.

Synthesis and characterization of [Ni(H₂O)₆][1-OPH(O)-1,7-*closo*-C₂B₁₀H₁₁]₂, **4.**

100 mg (0.43 mmols) of Na[1-OPH(O)-1,7-*closo*-C₂B₁₀H₁₁] in 1 mL of EtOH was mixed with 28.2 mg (0.22 mmols) of NiCl₂ in 1 mL of EtOH at room temperature. The solution was stirred for 2h. Afterward, the solution was filtered, to remove the NaCl formed, and the solvent was evaporated giving a pale-green solid. Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of an ethanol solution of the complex. Yield: 0.120g (95 %). ¹¹B NMR (EtOH): δ = -3.3 (d, ¹J(B,H)=142, 2B), -8.2 (d, ¹J(B,H)=149, 2B), -10.5 (d, ¹J(B,H)=230, 4B), -13.2 (d, ¹J(B,H)=259, 2B). ³¹P{¹H} NMR (EtOH): δ = 13.00 (1P). IR (KBr): ν [cm⁻¹] = 3326 (vs broad, H₂O), 3058 (vs, ν_s(C_c-H)), 2601 (vs, ν_s(B-H)), 2380 (vs, ν_s(P-H)), 1654 (w, H₂O), 1153, 1100, 1097, 1063 (vs, ν(P=O)). Anal. Found (calcd.) (%) for C₄B₂₀H₃₆O₁₀P₂Ni: C 8.37(8.27), H 6.20(6.24). ESI-MS (m/z) at the positive ion mode: 348.2 (100%), 324.2 (91 %).

Scheme S1. Synthetic strategy for the preparation of Ni^{II} compound **4**.

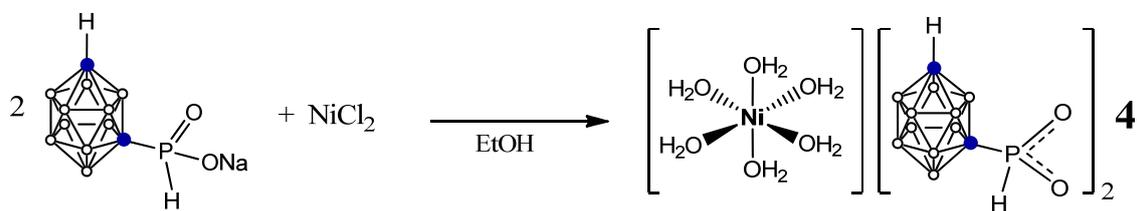
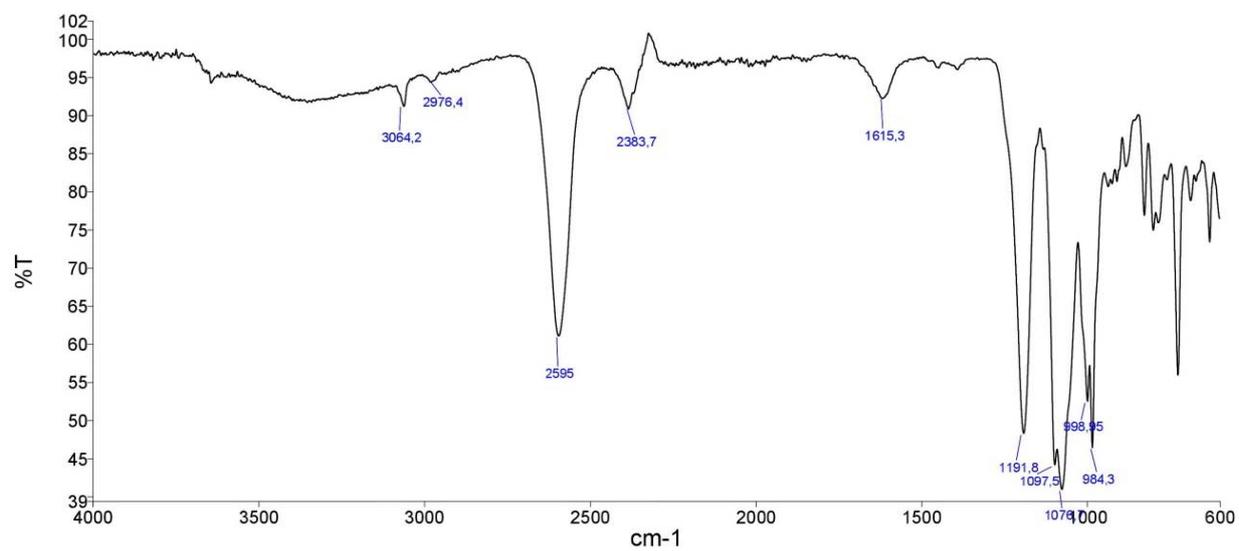
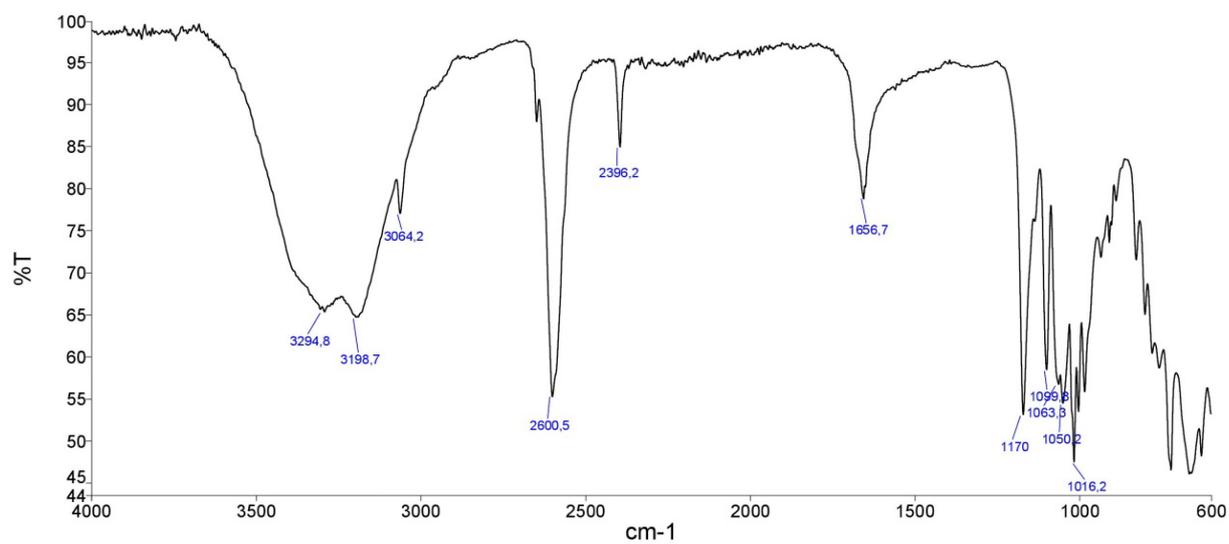


Figure S1. IR spectra of compounds a) polymer **1**, b) **2**, c) polymer **3**, d) **4**

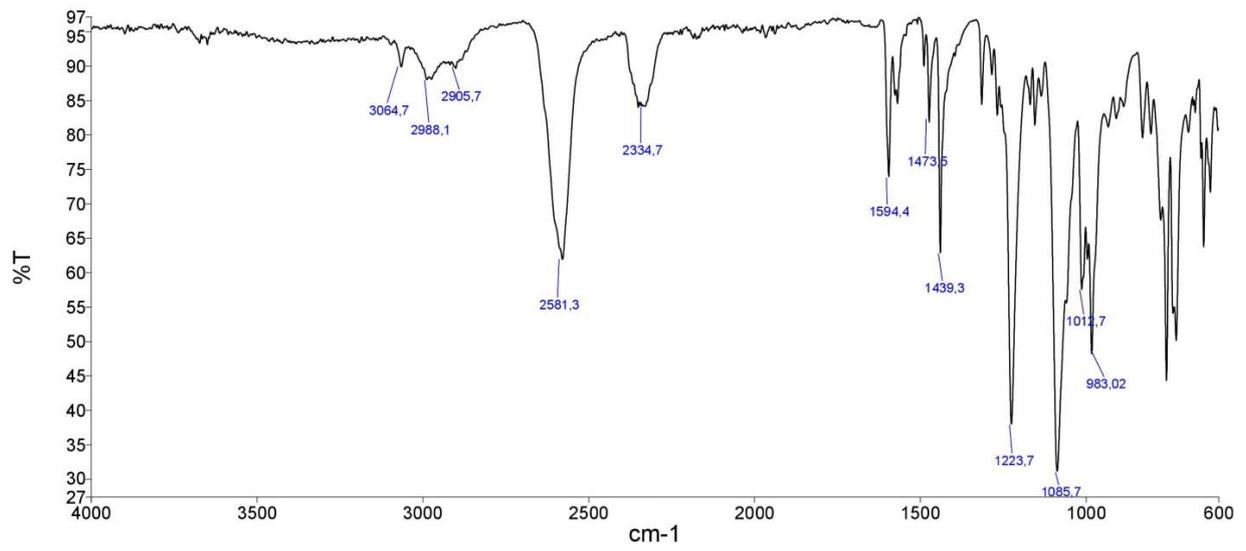
a)



b)



c)



d)

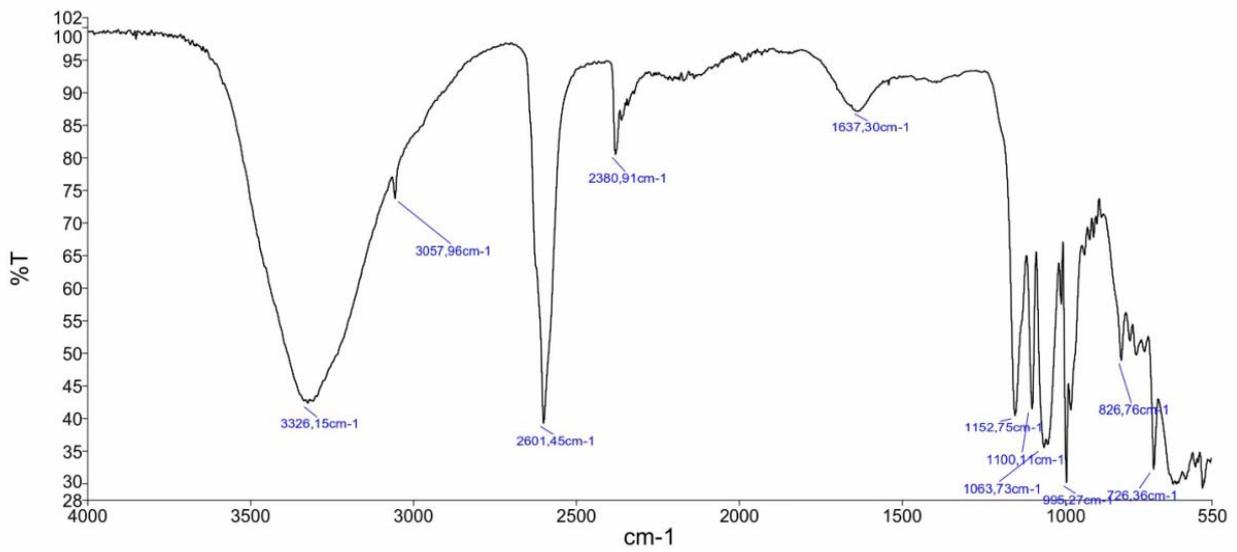
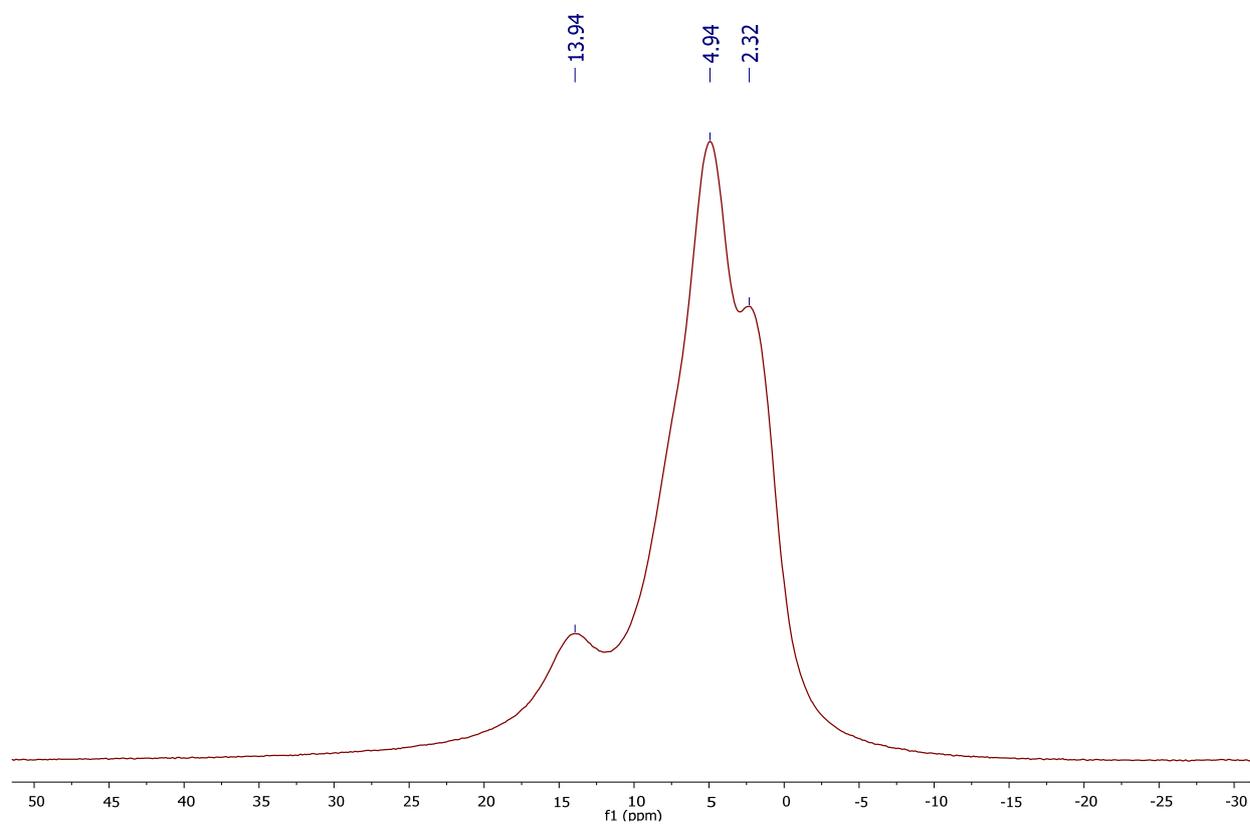


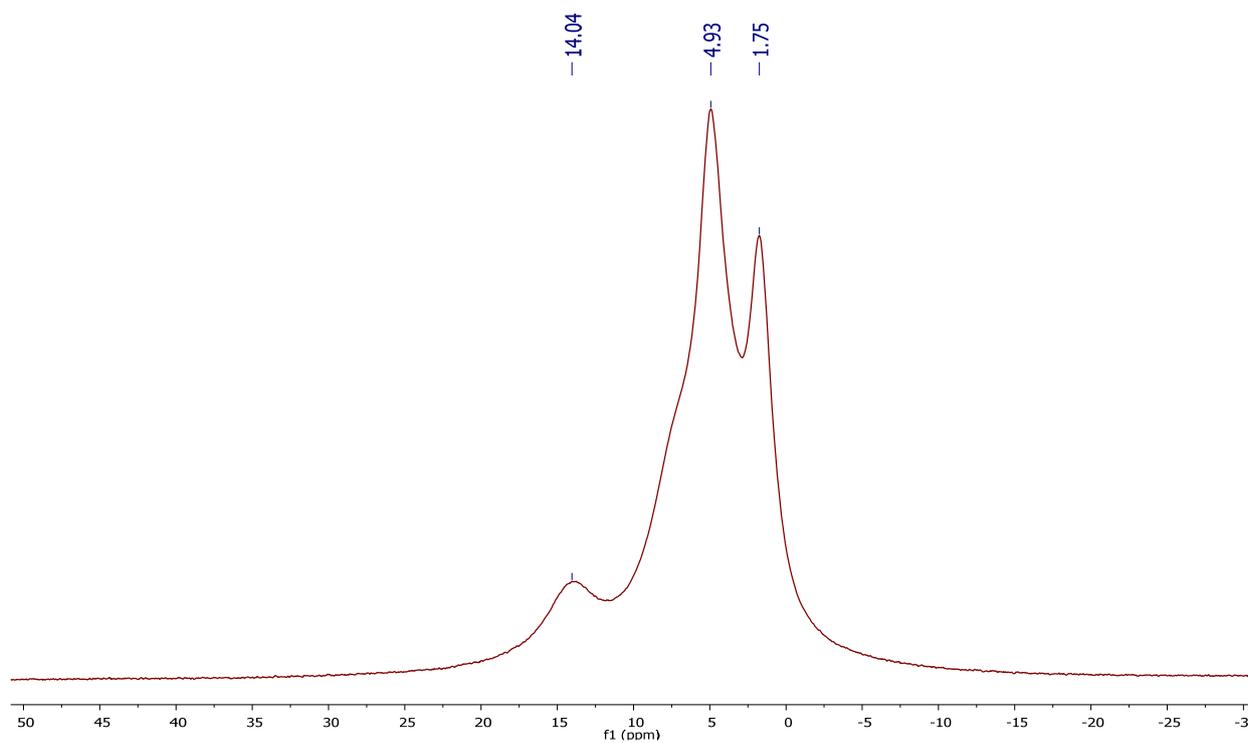
Figure S2. ^{11}B -NMR and $^{11}\text{B}\{^1\text{H}\}$ -NMR spectra of compounds a) polymer **1**, b) **2** and c) polymer **3**

a)

^{11}B -NMR spectrum of **1**.

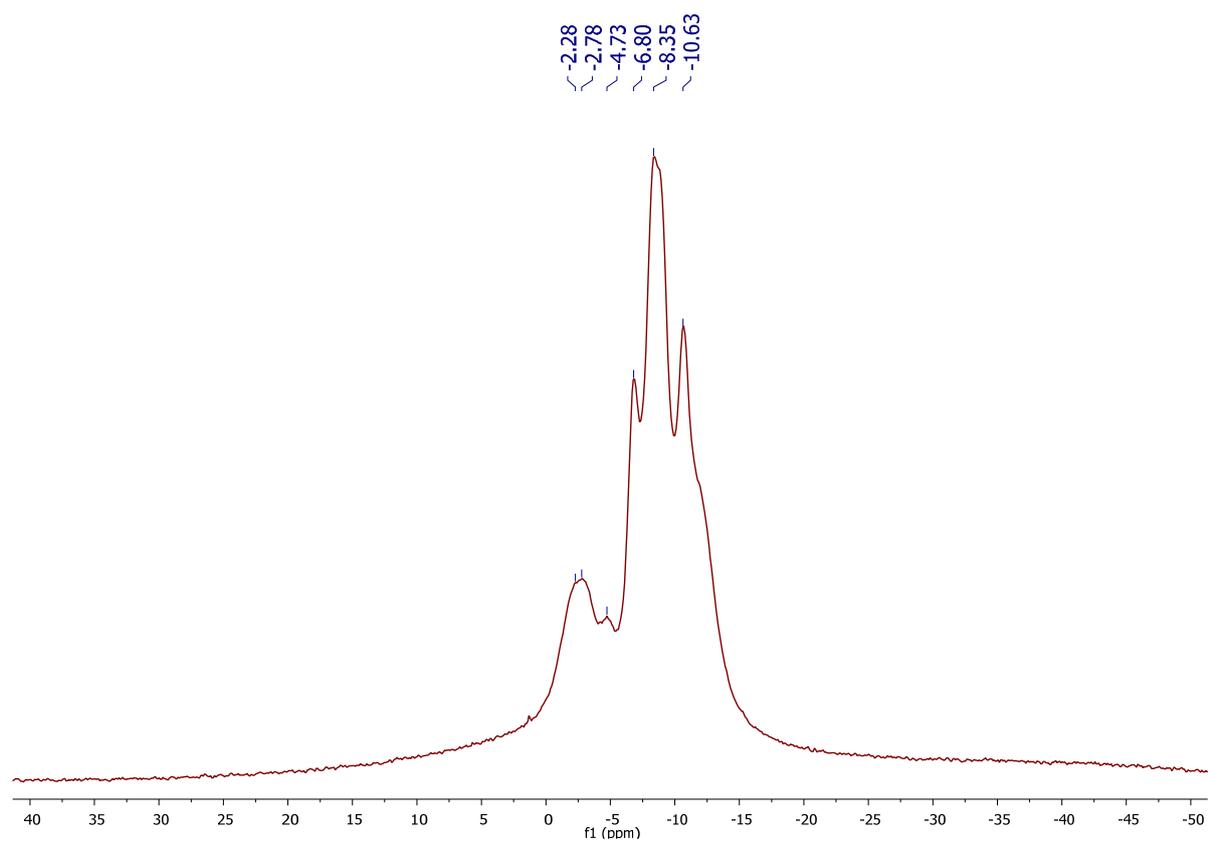


$^{11}\text{B}\{^1\text{H}\}$ -NMR spectrum of polymer **1**.

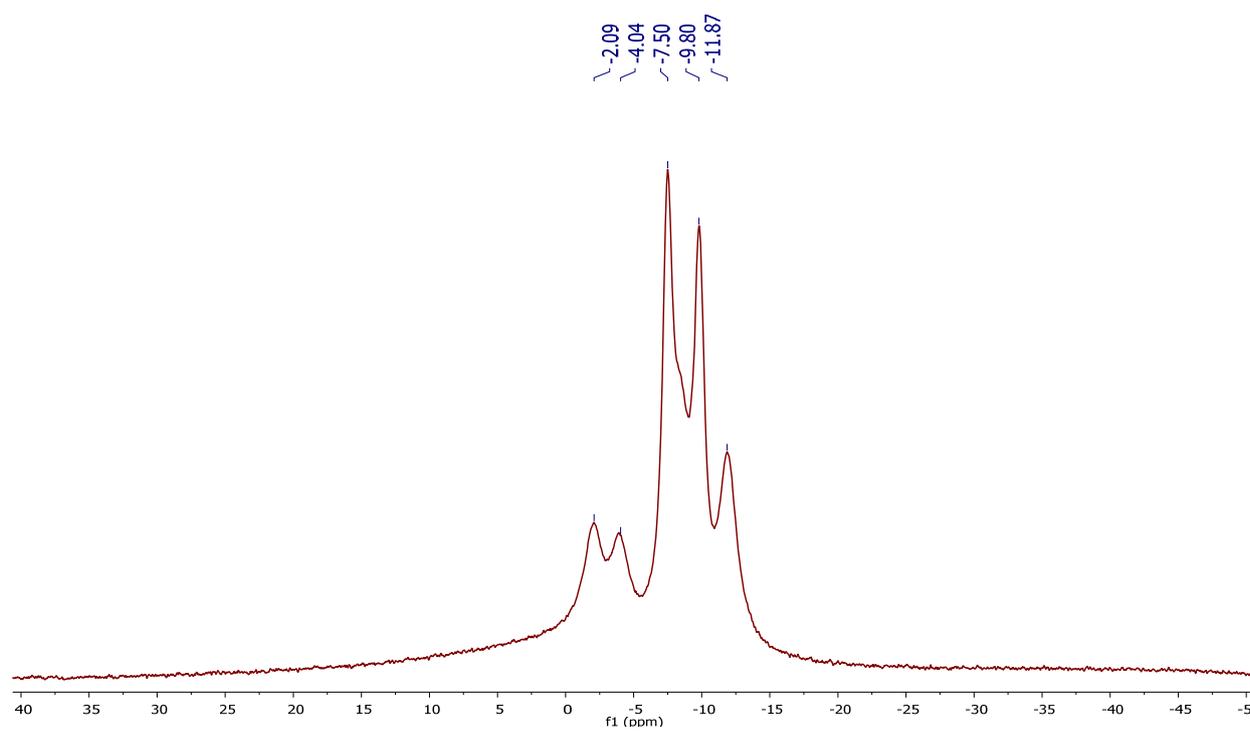


b)

^{11}B -NMR spectrum of **2**.

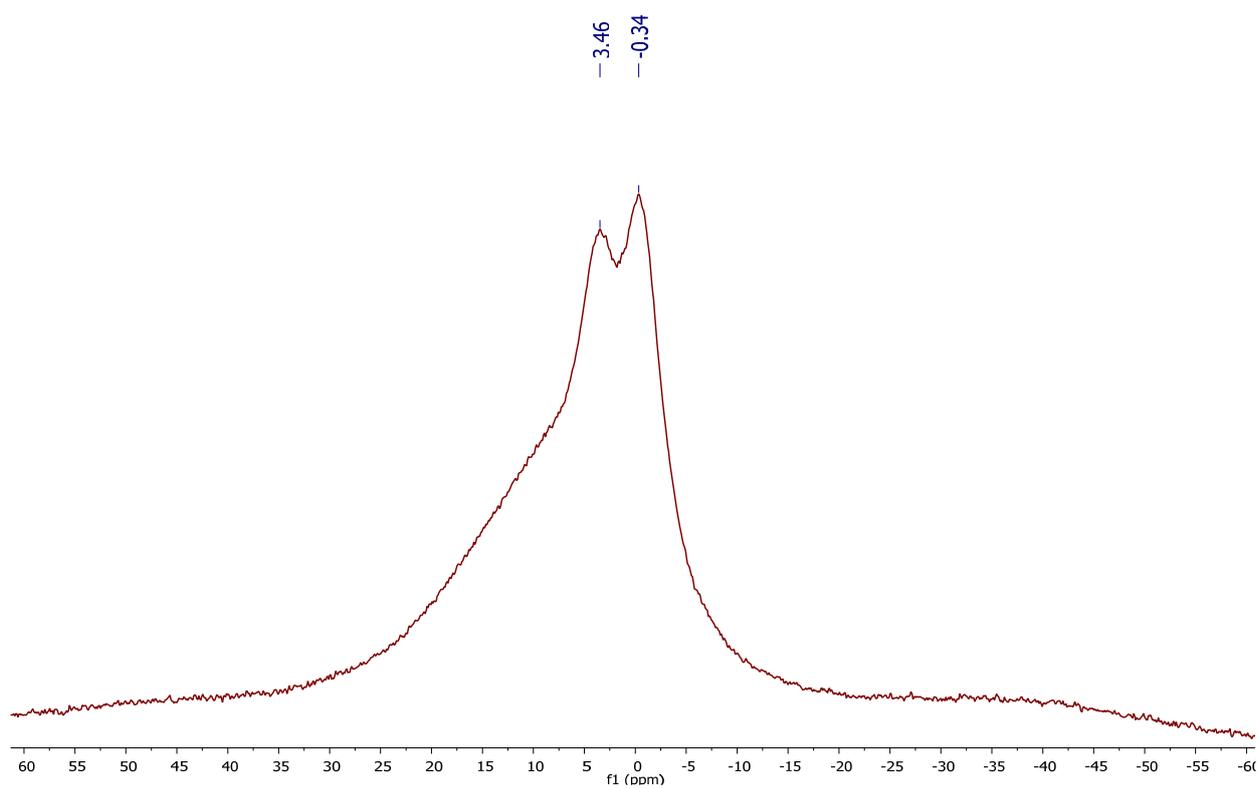


$^{11}\text{B}\{^1\text{H}\}$ -NMR spectrum of **2**.



c)

^{11}B -NMR spectrum of polymer **3**.



$^{11}\text{B}\{^1\text{H}\}$ -NMR spectrum of **3**.

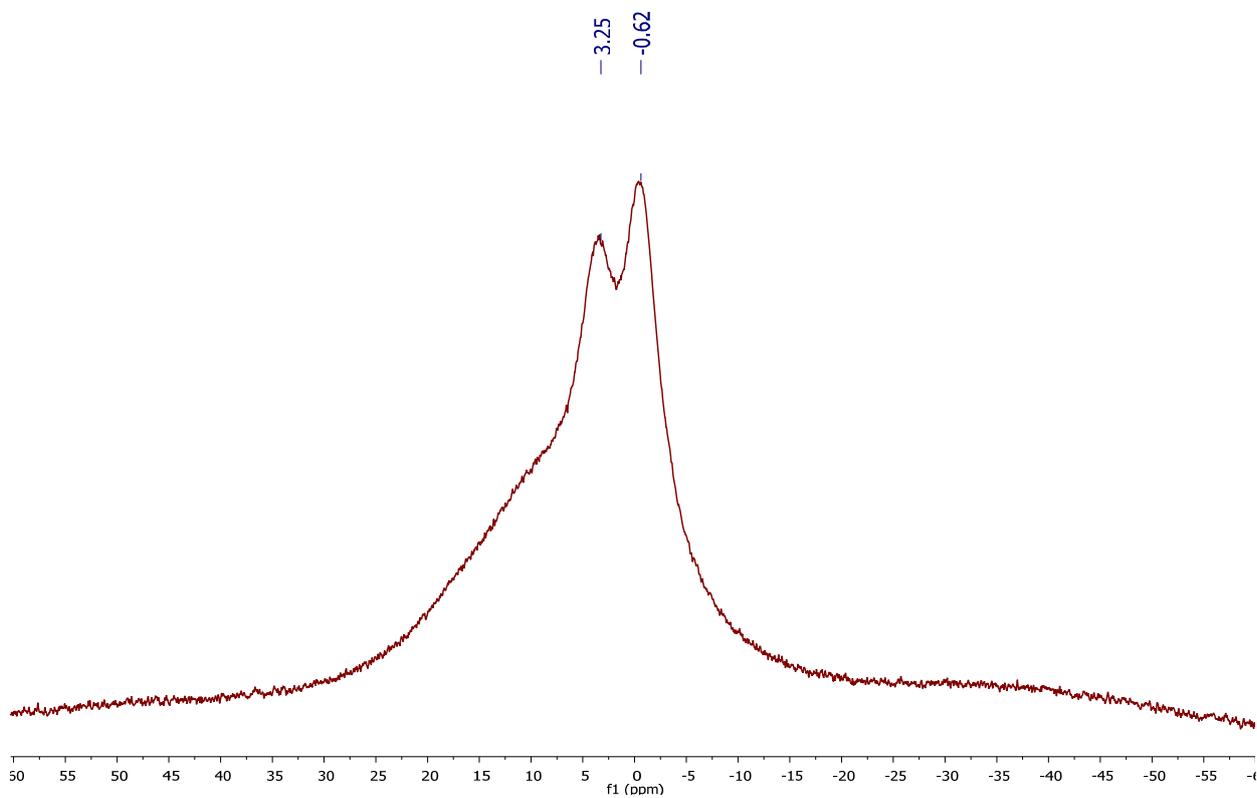
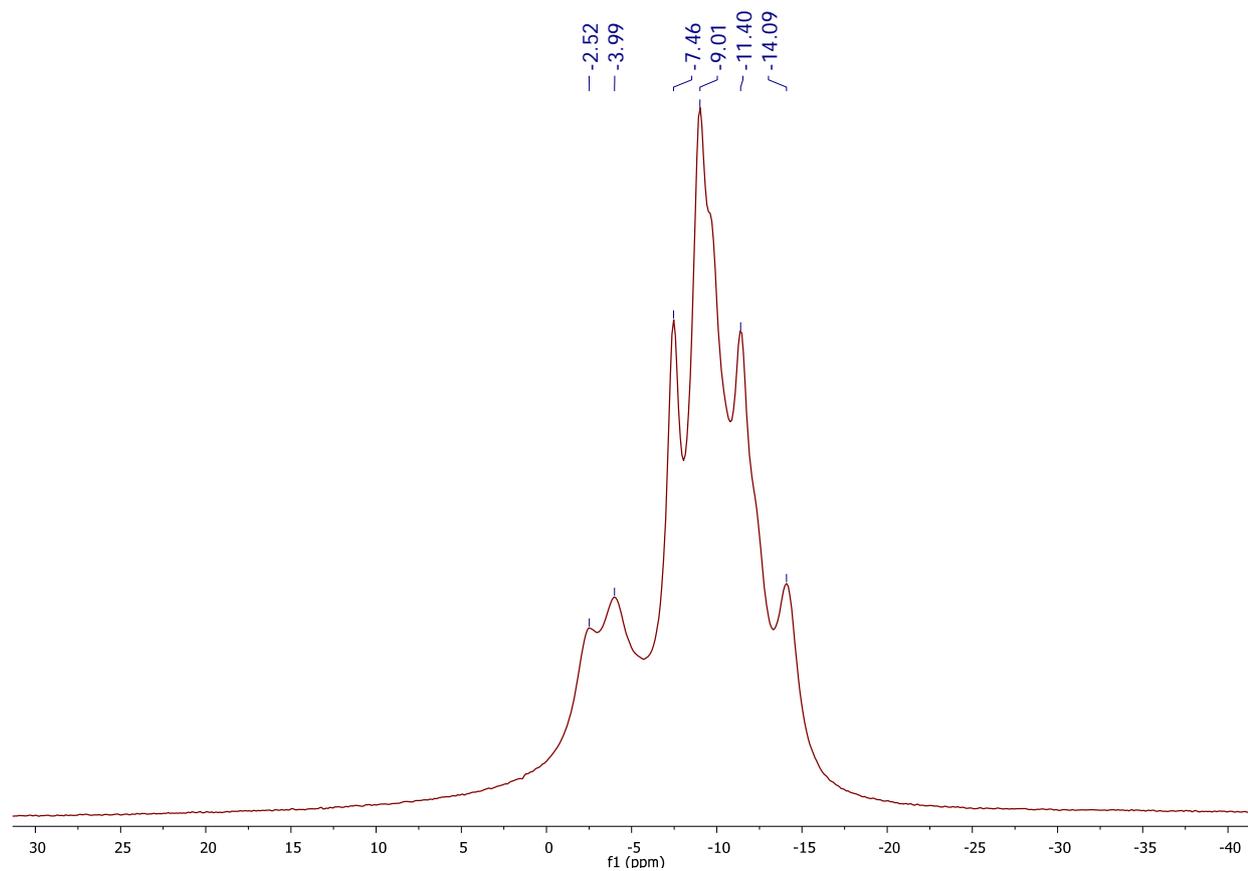
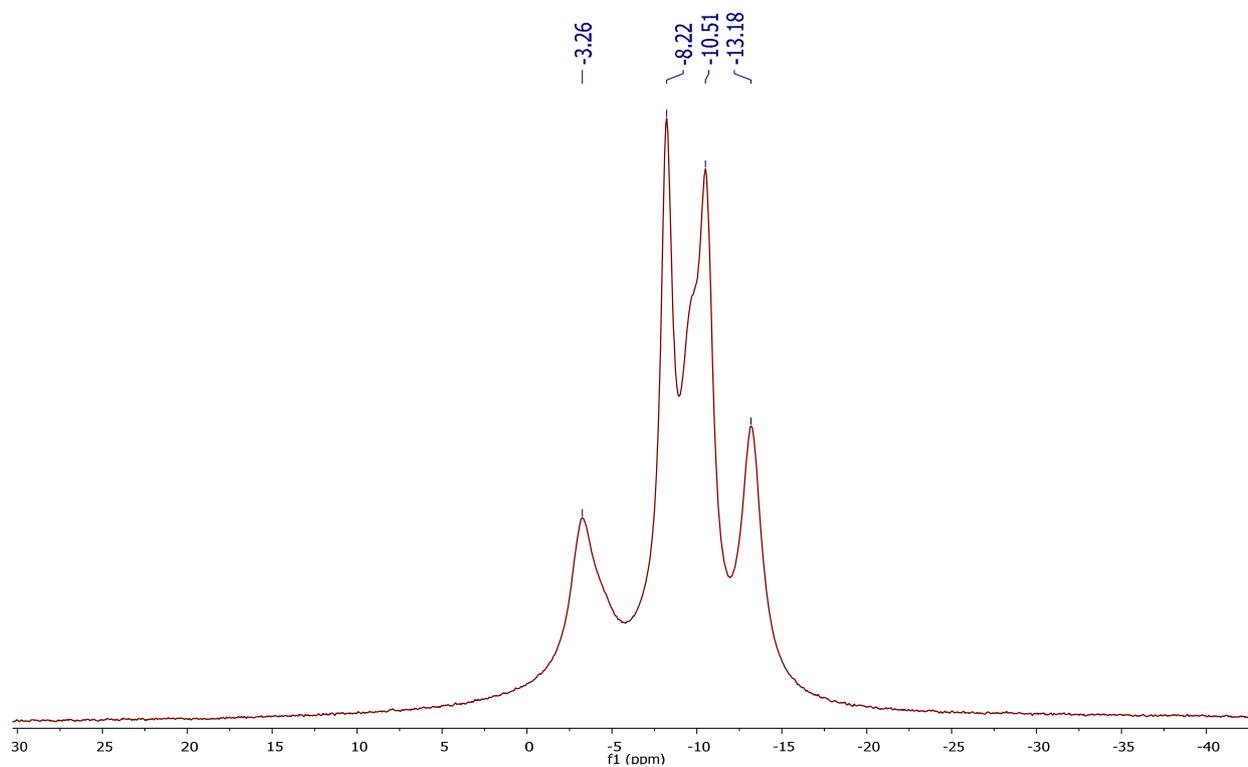


Figure S3. ^{11}B -NMR, $^{11}\text{B}\{^1\text{H}\}$ -NMR, ^{31}P -NMR spectra of the compound **4**

^{11}B -NMR spectrum of **4**.



$^{11}\text{B}\{^1\text{H}\}$ -NMR spectrum of **4**.



^{31}P -NMR spectrum of **4**.

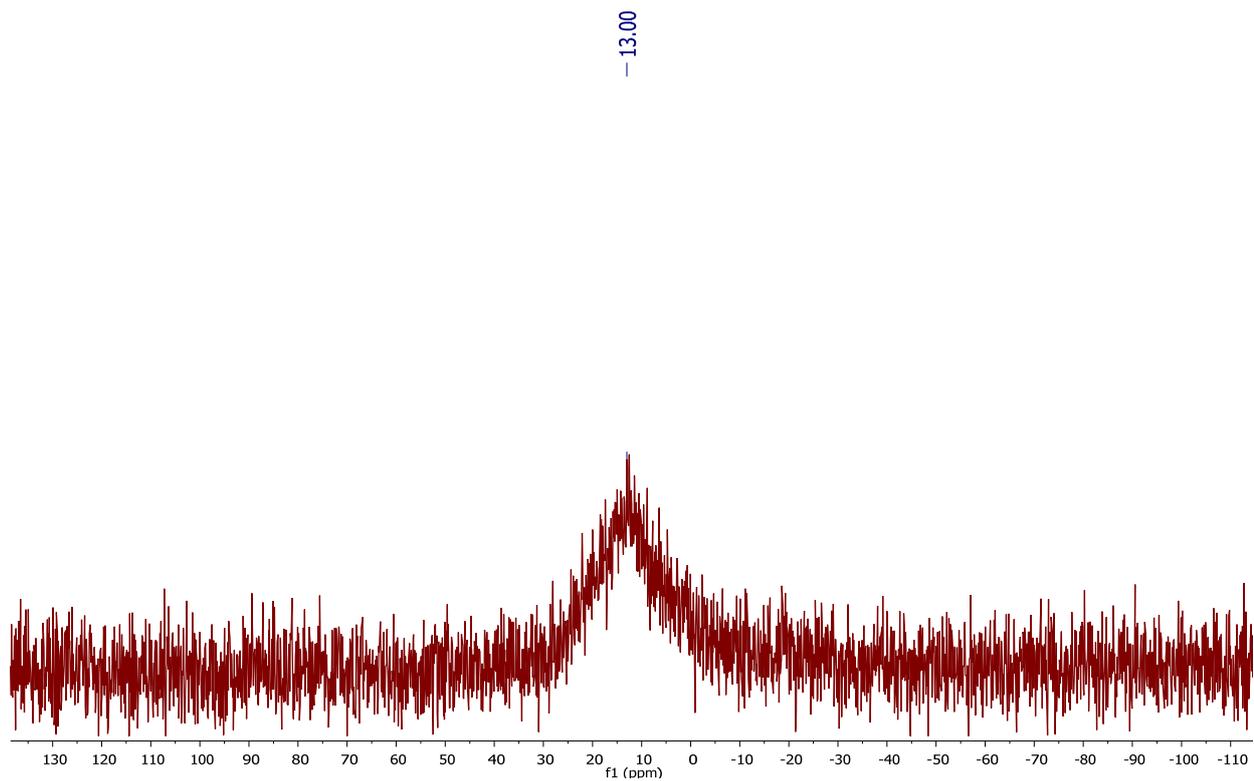
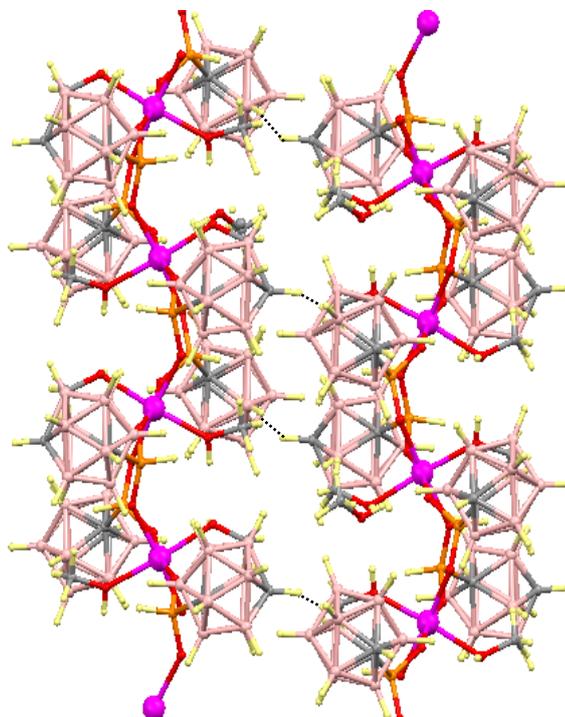


Figure S4. Packing structure of a) Mn coordination polymer **1** along the axis *a* and b) coordination polymer **3**

a)



b)

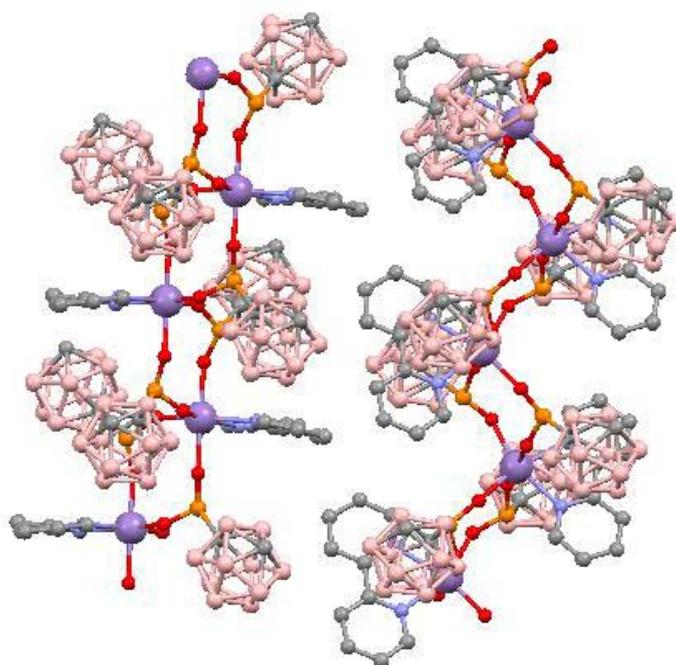


Figure S5. a) X-ray structures and labelling scheme for complex **4** (ORTEP plots with ellipsoids at 30% probability level). b) Packing of **4** along *a* axis.

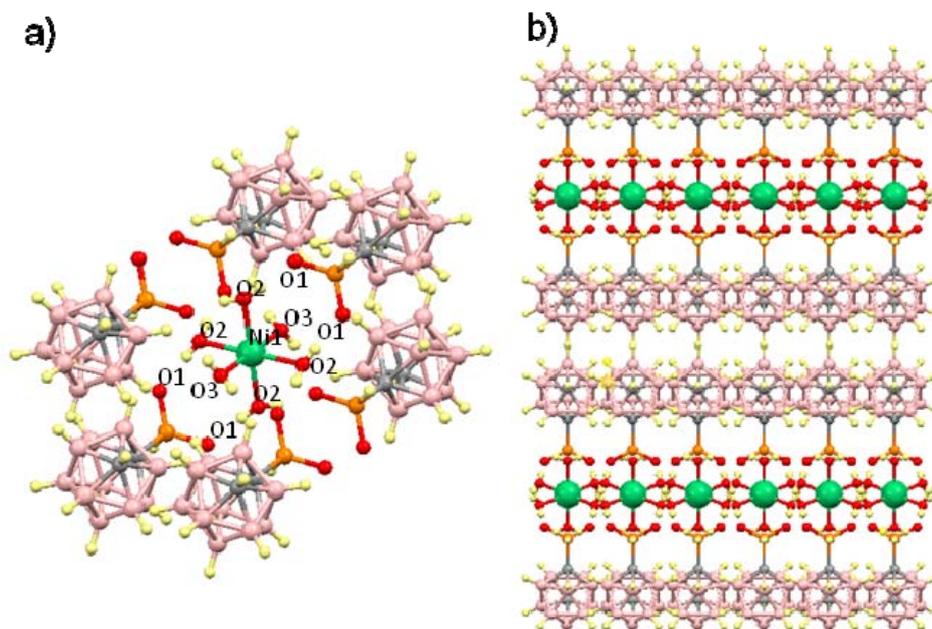
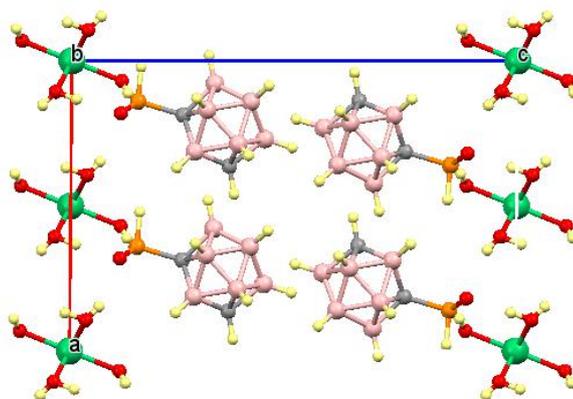


Figure S6. Packing structure of Ni complex **4** along the *b* axis (a) and *c* axis (b).

a)



b)

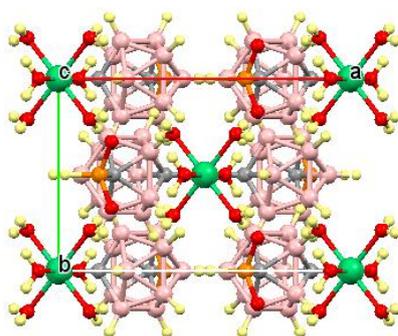
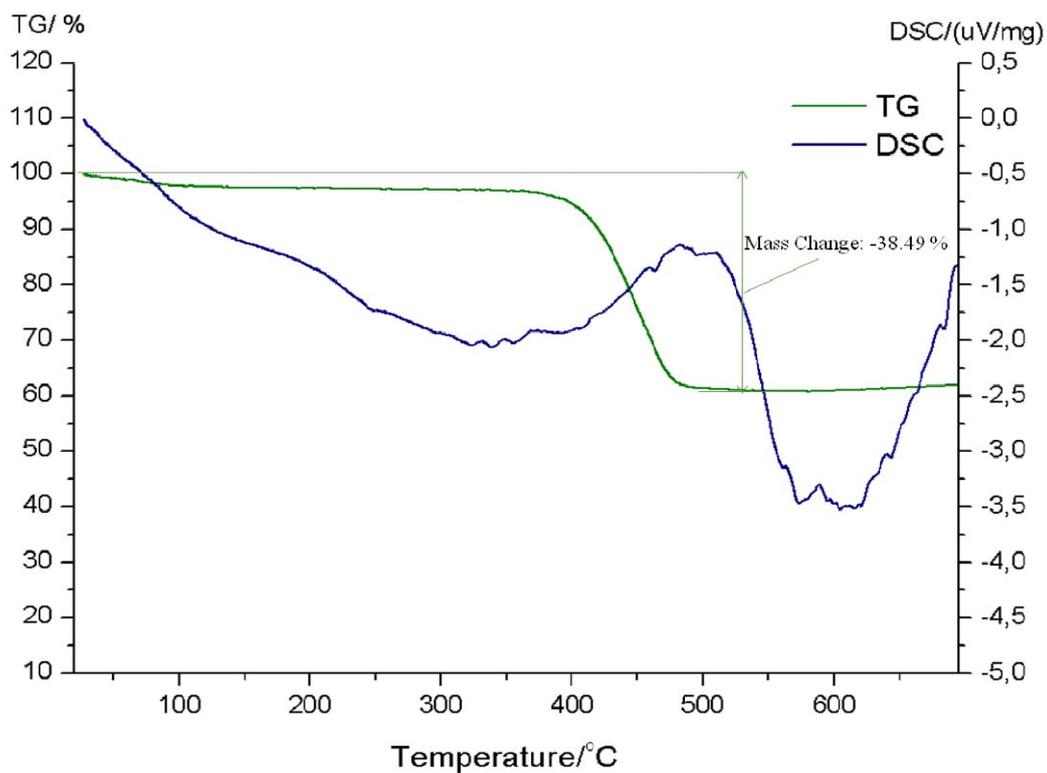
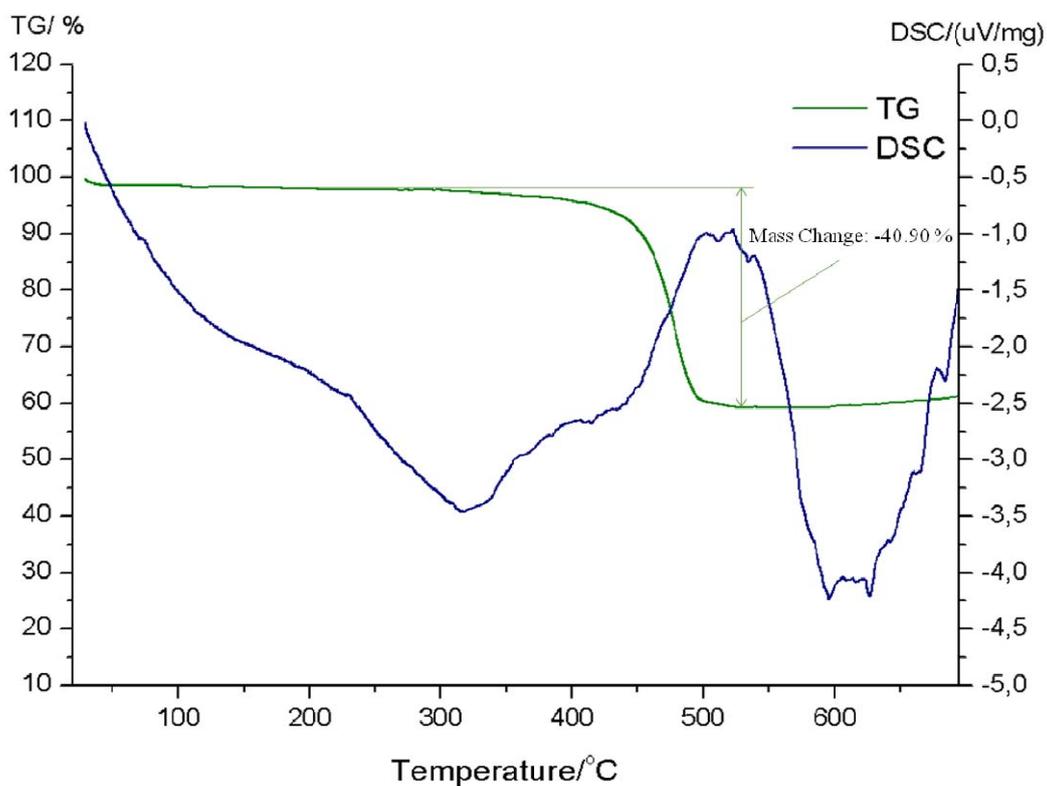


Figure S7. Thermal gravimetric analysis (TGA/DCS) of a) polymer **1**, b) **2**, c) polymer **3**.

a)



b)



c)

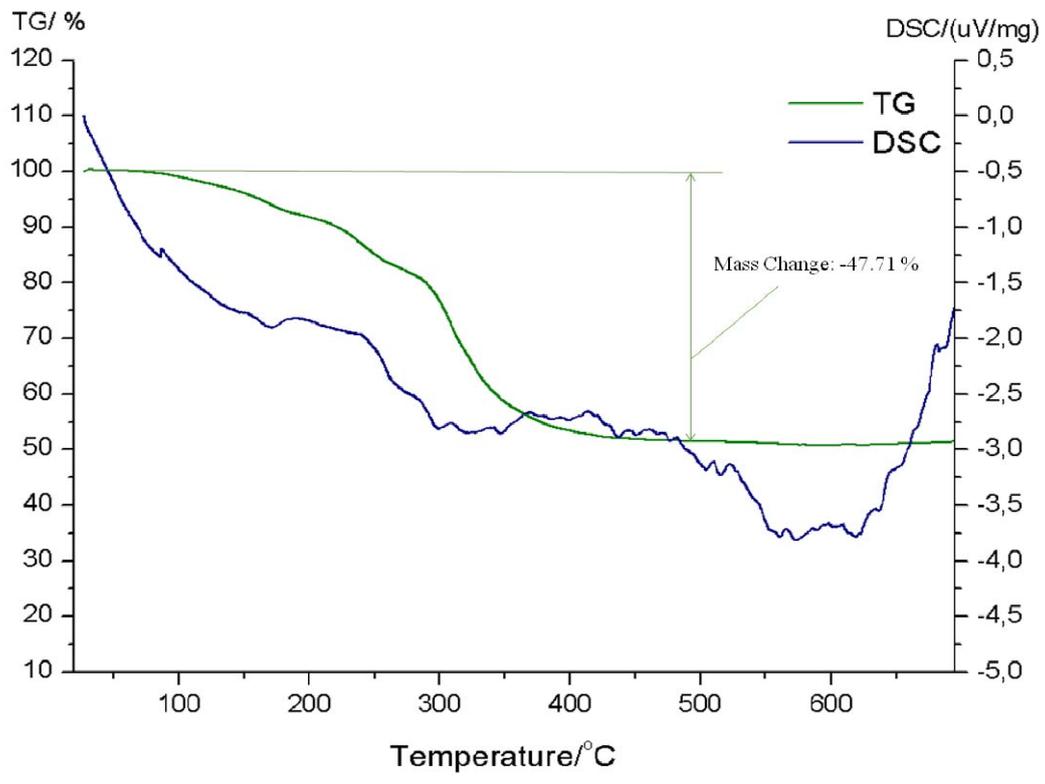
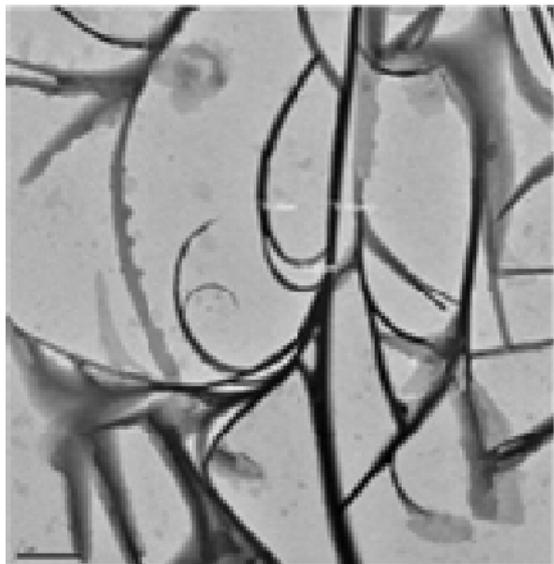


Figure S8. TEM images of polymers **1** (a) and **3** (b) from methanol at the same concentration (1gL⁻¹). Scale bars are 200 nm.

a)



b)

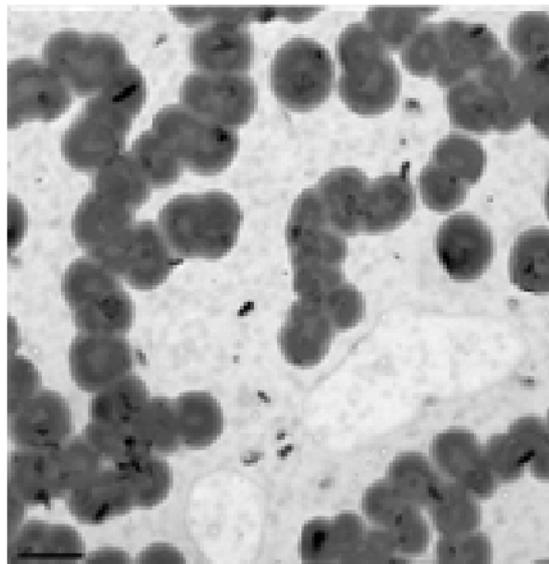


Figure S9. $^{11}\text{B}\{^1\text{H}\}$ -NMR spectra of compound **3** in MeOH, in MeOH/H₂O and of compound **2** in MeOH/H₂O

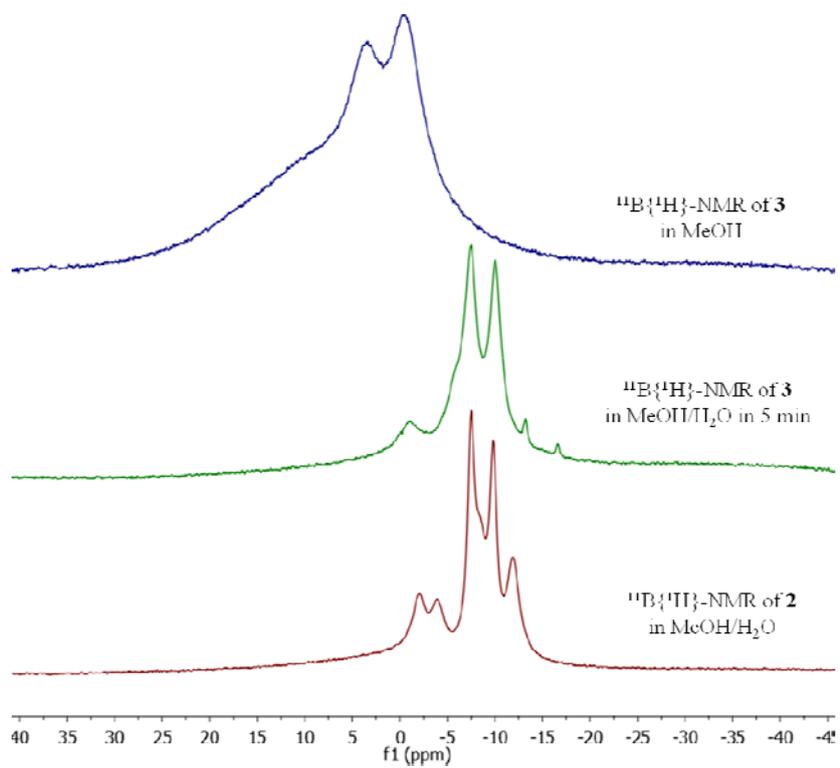


Table S1. Crystal Data for X-ray structures of Mn complexes **1-3**.

	1	2	3
Empirical formula	C ₇ H ₃₆ B ₂₀ MnO 7P ₂	C ₄ H ₃₆ B ₂₀ MnO ₁₀ P ₂	C ₁₄ H ₃₂ B ₂₀ MnN ₂ O ₄ P ₂
Formula weight	565.44	577.41	625.49
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	<i>P2(1)/c</i>	<i>C2/c</i>	<i>Pbca</i>
a [Å]	14.9010(5)	12.3311(6)	23.89183(18)
b [Å]	19.7357(7)	6.9027(4)	10.17927(7)
c [Å]	10.3827(4)	32.9093(15)	26.1625(2)
α [°]	90	90	90
β [°]	110.3470(10)°	100.5020(17)°	90
γ [°]	90	90	90
V [Å ³]	2862.84(18)	2754.2(2)	6362.75(8)
Formula Units/Cell	4	4	8
ρ _{calc.} [g cm ⁻³]	1.312	1.392	1.306
μ [mm ⁻¹]	5.026	0.634	4.530
R ₁ ^[a] , [I > 2σ(I)]	0.0456	0.0365	0.0434
wR ₂ ^[b] [all data]	0.1263	0.0880	0.1259

[a] $R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$

[b] $wR_2 = [\frac{\sum \{w(F_o^2 - F_c^2)^2\}}{\sum \{w(F_o^2)^2\}}]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0042P)^2]$ and $P = (F_o^2 + 2F_c^2)/3$

Table S2. Selected bond lengths (Å) and angles (°) for Mn complexes **1-3**.

	1		2		3
Mn(1)-O(2)	2.213(3)	Mn(1)-O(1)	2.1883(13)	Mn(8)-O(1)	2.1007(18)
Mn(1)-O(4)	2.244(3)	Mn(1)-O(1)#1	2.1883(13)	Mn(8)-O(4)#1	2.1117(16)
Mn(1)-O(14)	2.218(3)	Mn(1)-O(3)	2.1839(14)	Mn(8)-O(2)#1	2.1358(18)
Mn(1)-O(15)#1	2.110(3)	Mn(1)-O(3)#1	2.1839(14)	Mn(8)-O(3)	2.1437(16)
Mn(1)-O(34)	2.137(3)	Mn(1)-O(4)#1	2.1619(14)	Mn(8)-N(2)	2.2750(17)
Mn(1)-O(35)	2.125(3)	Mn(1)-O(4)	2.1620(14)	Mn(8)-N(1)	2.3184(18)
O(2)-Mn(1)-O(4)	171.89(13)	O(1)-Mn(1)-O(1)#1	180.0	O(1)-Mn(8)-O(4)#1	108.49(9)
O(2)-Mn(1)-O(14)	89.72(12)	O(3)-Mn(1)-O(1)#1	90.78(5)	O(1)-Mn(8)-O(2)#1	87.95(8)
O(14)-Mn(1)-O(4)	82.20(11)	O(3)#1-Mn(1)-O(1)#1	89.22(5)	O(4)#1-Mn(8)-O(2)#1	94.22(7)
O(15)#1-Mn(1)-O(2)	88.07(11)	O(3)#1-Mn(1)-O(1)	90.78(5)	O(1)-Mn(8)-O(3)	88.67(7)
O(15)#1-Mn(1)-O(4)	92.12(12)	O(3)-Mn(1)-O(1)	89.22(5)	O(4)#1-Mn(8)-O(3)	88.84(6)
O(15)#1-Mn(1)-O(14)	86.41(11)	O(3)#1-Mn(1)-O(3)	180.0	O(2)#1-Mn(8)-O(3)	176.03(7)
O(15)#1-Mn(1)-O(34)	92.85(12)	O(4)#1-Mn(1)-O(1)#1	89.97(5)	O(1)-Mn(8)-N(2)	158.62(8)
O(15)#1-Mn(1)-O(35)	172.89(11)	O(4)#1-Mn(1)-O(1)	90.03(5)	O(4)#1-Mn(8)-N(2)	92.88(8)
O(34)-Mn(1)-O(2)	99.41(14)	O(4)-Mn(1)-O(1)	89.97(5)	O(2)#1-Mn(8)-N(2)	90.75(7)
O(34)-Mn(1)-O(4)	88.68(13)	O(4)-Mn(1)-O(1)#1	90.03(5)	O(3)-Mn(8)-N(2)	91.63(7)
O(34)-Mn(1)-O(14)	170.82(13)	O(4)#1-Mn(1)-O(3)#1	89.89(6)	O(1)-Mn(8)-N(1)	87.71(8)
O(35)-Mn(1)-O(2)	87.02(11)	O(4)#1-Mn(1)-O(3)	90.11(6)	O(4)#1-Mn(8)-N(1)	163.80(8)
O(35)-Mn(1)-O(4)	92.02(11)	O(4)-Mn(1)-O(3)#1	90.11(6)	O(2)#1-Mn(8)-N(1)	86.14(7)
O(35)-Mn(1)-O(14)	88.44(10)	O(4)-Mn(1)-O(3)	89.89(6)	O(3)-Mn(8)-N(1)	91.63(7)
O(35)-Mn(1)-O(34)	93.01(12)	O(4)#1-Mn(1)-O(4)	180.0	N(2)-Mn(8)-N(1)	70.92(7)

Table S3. Crystal Data for X-ray structures of Ni complex, **4**.

4	
Empirical formula	C ₄ H ₃₆ B ₂₀ NiO ₁₀ P ₂
Formula weight	581.18
Crystal system	Monoclinic
Space group	<i>C2/m</i>
a [Å]	11.2676(5)
b [Å]	7.4372(5)
c [Å]	17.0406(9)
α [°]	90
β [°]	90.492(3)
γ [°]	90
V [Å ³]	1427.94(14)
Formula Units/Cell	2
ρ _{calc.} [g cm ⁻³]	1.352
μ [mm ⁻¹]	0.829
R1 ^[a] , [I > 2σ(I)]	0.0405
wR2 ^[b] [all data]	0.0917

^a $R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$. ^b $wR2 = \frac{[\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]}^{1/2}$.

Table S4. Selected bond lengths (Å) and angles (°) for Ni complex, **4**.

Ni(1)-O(2)	2.049(2)
Ni(1)-O(3)	2.062(2)
P(1)-O(1)	1.5052(15)
P(1)-H(1C)	1.29(3)
O(2)-Ni(1)-O(3)	86.61(6)
O(2)#1-Ni(1)-O(3)	93.39(6)
O(3)-Ni(1)-O(3)#2	98.50(9)
O(3)#2-Ni(1)-O(3)#1	81.50(9)
O(1)#3-P(1)-O(1)	116.09(12)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z #2 x,-y,z, #3 x,-y+1,z

Table S5. Thermal gravimetric analysis (TGA) data for compounds **1-3**.

Compound	% weight loss (T[°C])
1	38.49 (483)
2	40.90 (507)
3	47.71 (430)

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