SUPPORTING INFORMATION

Merging Icosahedral Boron Clusters and Magnetic Nanoparticles: Aiming towards Multifunctional Nanohybrids Materials.

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Redox titration analysis.

Geometry calculations.

Surface coverage values calculations.

Figure S1. Particle size distribution histograms from three batches of freshly prepared **1**-MNPs, prepared following the same synthesis, and mean particle size diameter.

Figure S2. X-ray diffraction patterns corresponding to **1**-MNPs (black) and the typical magnetite/maghemite spinel structure (red).

Figure S3. a) Images of **1**-MNP colloidal suspension in water at different pH. b) DLS studies in water at different pH.

Figure S4. ^{1}H-NMR, ^{1}H{^{11}B}-NMR, ^{11}B-NMR, ^{11}B{^{1}H}-NMR, ^{31}P-NMR spectra of the mother liquor after **1**-MNPs sterilization. Spectra were run in D_2O.

Figure S5. Thermogravimetric Analysis of the ligand Na[**1**] and the **1**-MNP.

Redox titration analysis.

The ratio of Fe^{2+} and Fe^{3+} ions forming **1**-MNPs nanoparticle core was determined by redox titration analysis.

Samples of freshly prepared **1**-MNPs: Powder samples of **1**-MNPs (about 0.5 mg) before sterilization were decomposed in 0.1 mL HCl (37 wt.%) and diluted to 1mL by Milli-Q water giving a yellowish solution (with Fe^{2+} and Fe^{3+} ions).

Preparation of the **1**-MNPs samples after sterilization: About 0.1 mL HCl (37 wt.%) was added to 1 mL of **1**-MNPs suspensions after sterilization to decompose the nanoparticles.

In both samples, each of the obtained clear yellow solutions was analyzed by titration with $K_2Cr_2O_7$ (oxidizing solution) (5 mM). To know the end point of titration (oxidation of all Fe^{2+} to Fe^{3+}) the indicator sodium diphenylamine sulphonate was added to the prepared solution. The Fe^{2+} content was determined by the first titration. Then by addition of $SnCl_2$ (reductive agent) Fe^{3+} was reduced to Fe^{2+}. The total iron content $Fe^{2+/3+}$ was determined by the second titration. The Fe^{3+} content was calculated as follows: $Fe^{2+/3+}{}_{content}$ - $Fe^{2+}{}_{content}$. Titration was done in triplicate (n=3).

Before sterilization:

n	$W_{1\text{-MNPs}}$, µg	Fe^{2+} content, wt.%$_{Fe2+/totFe}$	Fe^{3+} content, wt.%$_{Fe3+/totFe}$
1	540	23.57	76.43
2	528	26.67	73.33
3	546	25.00	75.00
MEAN	538	25.08	74.92

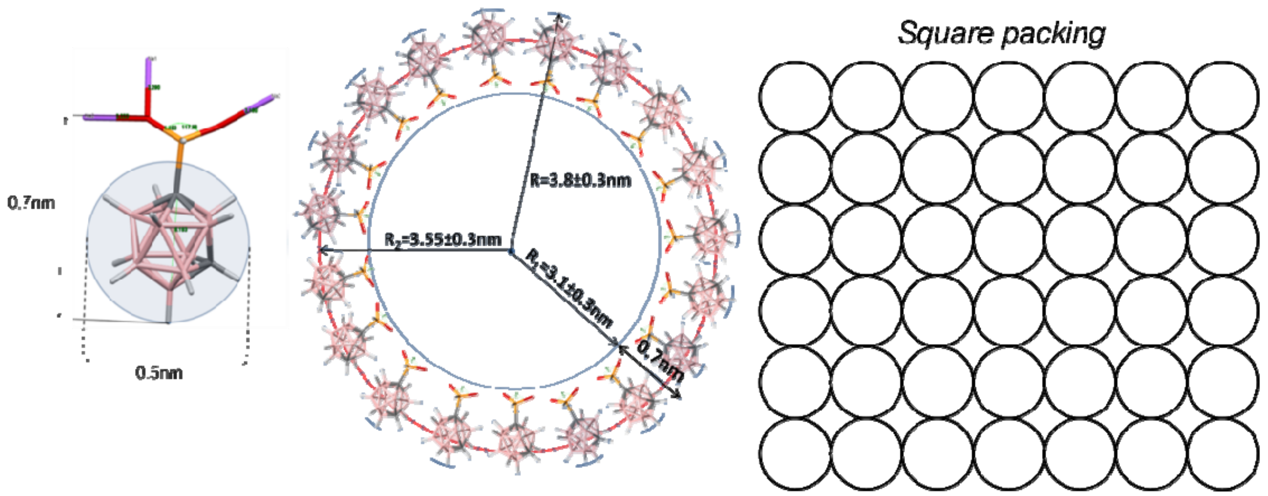
25.08 % of Fe^{2+} content corresponds to magnetite/maghemite ratio $2Fe_3O_4{\cdot}Fe_2O_3$ (Fe_8O_{11}).

*After sterilization in 1mL of suspension of **1**-MNPs:*

n	Fe^{2+} content, wt.%$_{Fe2+/totFe}$	Fe^{3+} content, wt.%$_{Fe3+/totFe}$
1	14.31	85.69
2	15.94	84.05
3	13.89	86.11
MEAN	14.71	85.28

14.71 % of Fe^{2+} content corresponds to magnetite/maghemite ratio $Fe_3O_4{\cdot}2Fe_2O_3$ (Fe_7O_{10})

Geometry calculations



$R_2 = 3.55 \pm 0.3$ nm

$A_2 = 4\pi R_2^2 = 132.732 \div 186.265$ nm^2 (158 ± 27 nm^2)

For square packing: $A_{[\mathbf{carboranylphosphate}]} = 0.5 \times 0.5 = 0.25$nm^2

$n_{max} = A_2/A_{[\mathbf{carboranylphosphate}]} = 530.928 \div 745.060$ (638 ± 107) – maximum number of *meta*-carboranylphosphates that can fit one nanoparticle with core diameter of 6.2 ± 0.6 nm.

Surface coverage values calculations.

Energy Dispersive X-ray (EDX) analysis of **1**-MNPs before sterilization was performed for 3 (n = 3) bathes, prepared following the same synthesis. Average:

Fe 92,89 (At%) – 13 Fe

P 7.11 (At%) – 1 P

Fe:P = 13:1

For freshly prepared **1**-MNPs the core composition is $2Fe_3O_4{\cdot}Fe_2O_3$ (Fe_8O_{11}).

Fe_8O_{11} : $C_2B_{10}H_{11}$-P(H)OO$^-$ = 1.625 : 1

(from geometry calculations) $d = 6.2 \pm 0.6$ nm - diameter of nanoparticle core.

$m_{MNPs} = (1/6)\pi d^3 \rho_{MNPs} = (66.4 \pm 19)$E-20 g (taking the density of magnetite to be $\rho_{Magnetite} = 5.175$g/cm^3 according to https://www.mindat.org/min-2538.html).

$Mole_{MNPs} = m_{MNPs}/M_{2Fe3O4{\cdot}Fe2O3} = N_{Fe8O11}/N_A$, where $M_{Fe8O11} = 622.75$ g/mol is molecular weight of magnetite/maghemite couple $2Fe_3O_4{\cdot}Fe_2O_3$, N_{Fe8O11} – number of Fe_8O_{11} units that contain one nanoparticle core with diameter 6.2 ± 0.6 nm.

$N_{Fe8O11} = m_{MNPs} N_A / M_{Fe8O11} = 642 \pm 182$ Fe_8O_{11}/NP

Taking into account EDX results before sterilization, Fe_8O_{11} : $C_2B_{10}H_{11}$-P(H)OO$^-$ = 1.625 : 1, each nanoparticle bears $n_{[\mathbf{carboranylphosphate}]} = N_{Fe8O11} / 1.625 = 395 \pm 112$ *meta*-carboranylphosphinates.

The saturation of surface of the nanoparticles core (%) $s_{CBP} = n_{[\mathbf{carboranylphosphate}]}/n_{max} \cdot 100\% = 61.29 \pm 7.43$ %.

$s_{[carboranylphosphate](ICP)} = 61.29 \pm 7.43$ %, $n_{CBP} = 395 \pm 112$ CBP/NP

Energy Dispersive X-ray (EDX) analysis of **1**-MNPs after sterilization was performed for 3 (n = 3) bathes, prepared following the same synthesis. Average:

Fe 55,34 (At%) – 70 Fe

P 0.79 (At%) – 1 P

Fe:P = 70:1

For **1**-MNPs after sterilization the core composition is $Fe_3O_4 \cdot 2Fe_2O_3$ (Fe_7O_{10}).

Fe_7O_{10} : $C_2B_{10}H_{11}$-P(H)OO$^-$ = 10 : 1. $Mole_{MNPs} = m_{MNPs}/M_{Fe7O10} = N_{Fe7O10}/N_A$, where M_{Fe7O10} = 550.91 g/mol is molecular weight of magnetite/maghemite couple Fe_7O_{10}, N_{Fe7O10} – number of Fe_7O_{10} units that contain one nanoparticle core with diameter 6.2 ± 0.6 nm.

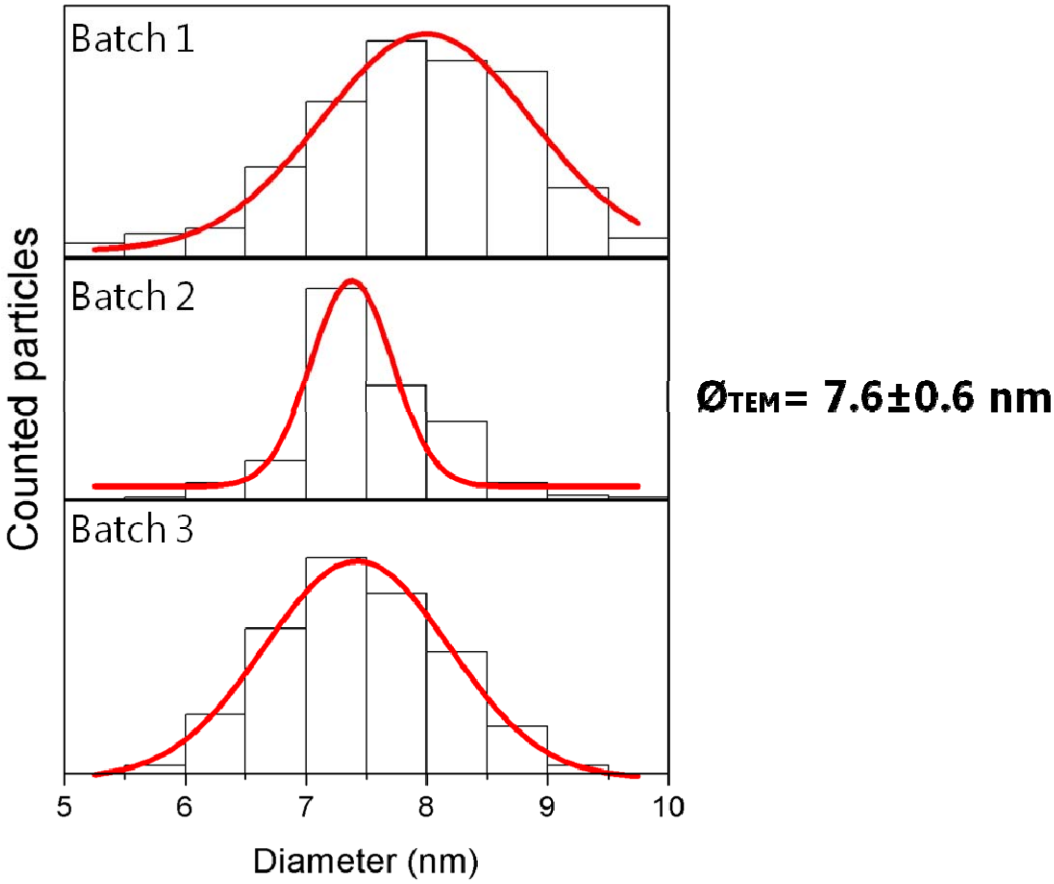
$N_{Fe7O10} = m_{MNPs} N_A/M_{Fe7O10} = 726 \pm 205$ Fe_7O_{10}/NP

Taking into account EDX results after sterilization, Fe_7O_{10} : $C_2B_{10}H_{11}$-P(H)OO$^-$ = 10 : 1, each nanoparticle bears $n_{[\mathbf{carboranylphosphate}]} = 73 \pm 21$ *meta*-carboranylphosphinates. The saturation of surface of the nanoparticles core (%)) $s_{[\mathbf{carboranylphosphate}]} = n_{[\mathbf{carboranylphosphate}]}/n_{max} \cdot 100\% = 11.21 \pm 1.41$ %.

$s_{[carboranylphosphate](ICP)} = 11.21 \pm 1.41$ %.

%, $n_{[carboranylphosphate]\,(ICP)} = 73 \pm 21$ $_{[carboranylphosphate]}$/NP

Figure S1. Particle size distribution histograms from three batches of freshly prepared **1**-MNPs, prepared following the same synthesis, and mean particle size diameter.



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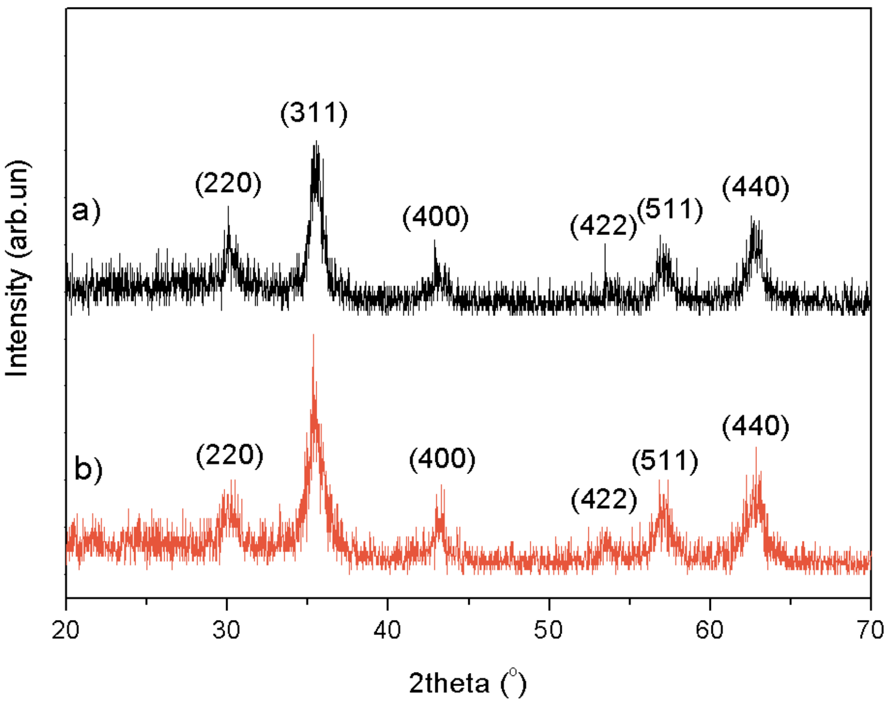


Figure S3. a) Images of **1**-MNP colloidal suspension in water at different pH. b) DLS studies in water at different pH.

a) b)

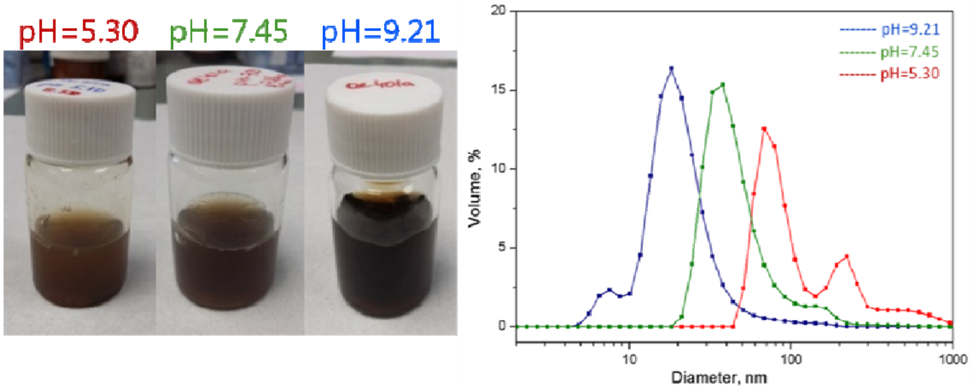
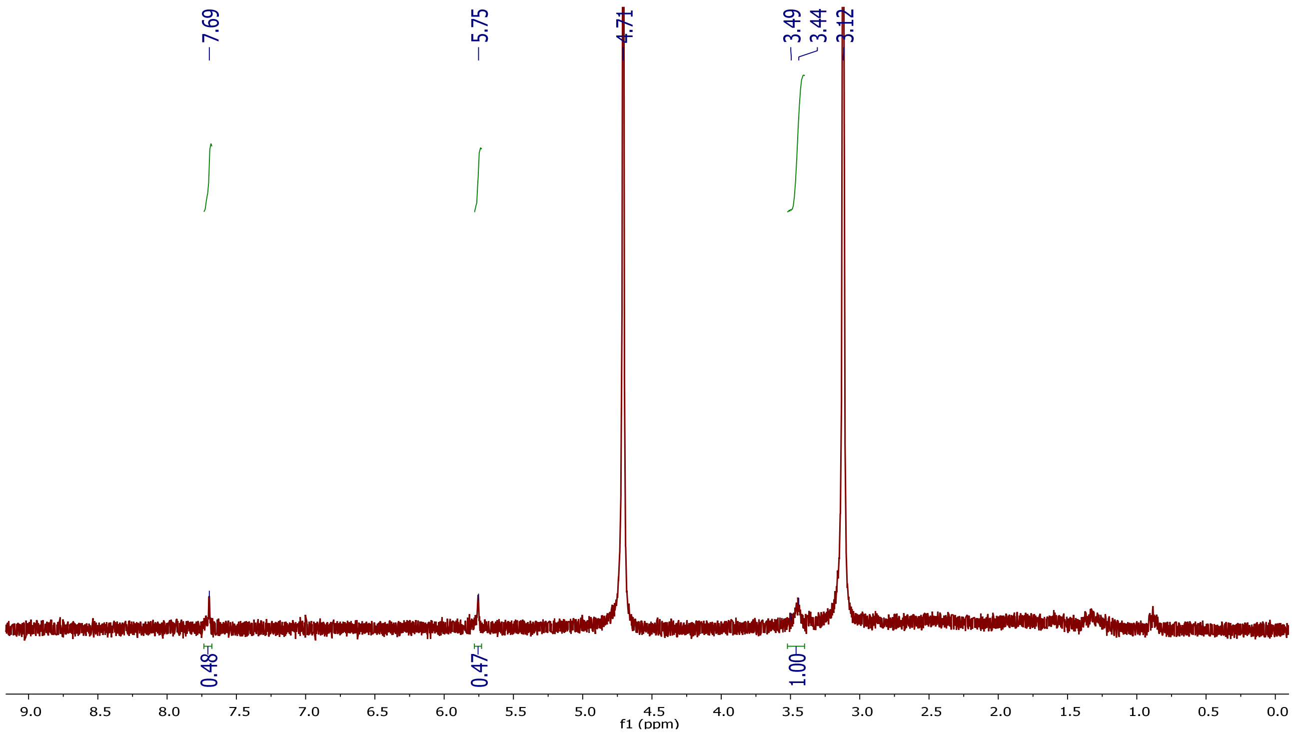
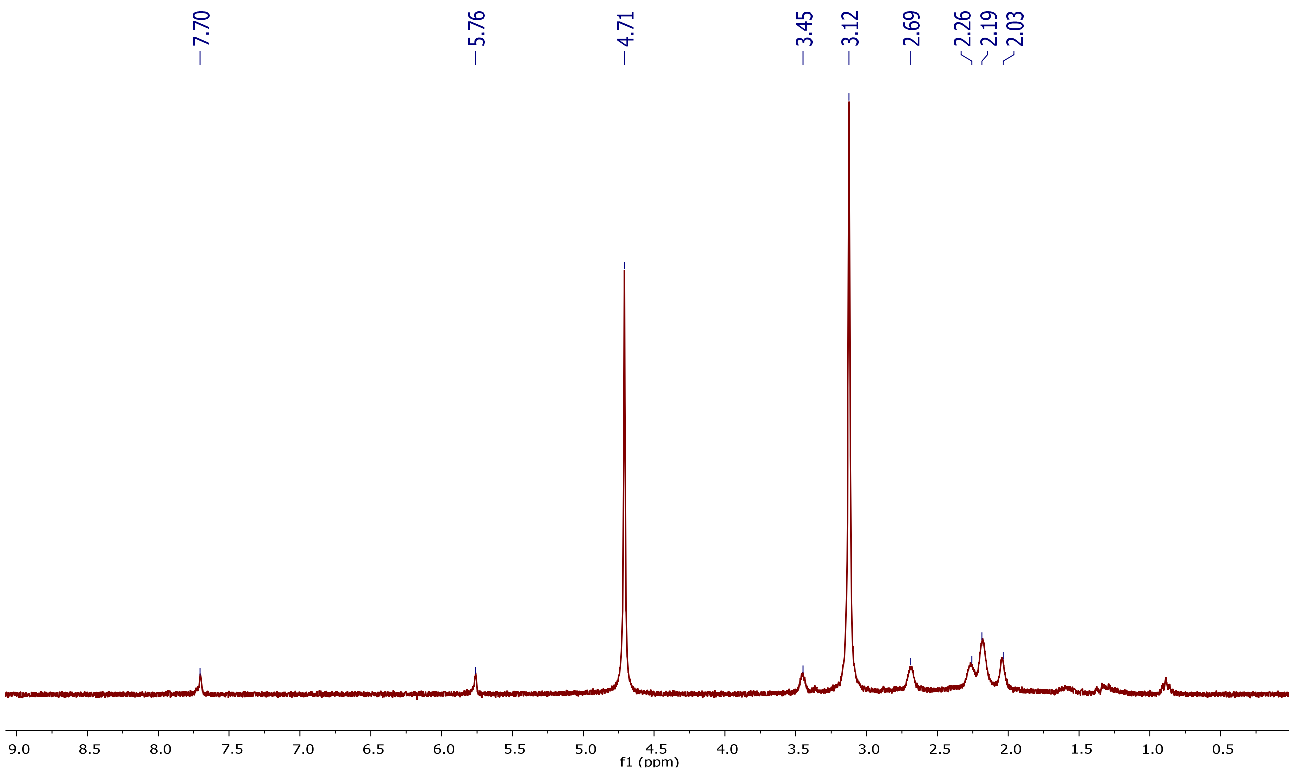


Figure S4. ^{1}H-NMR, $^{1}H\{^{11}B\}$-NMR, ^{11}B-NMR, $^{11}B\{^{1}H\}$-NMR, ^{31}P-NMR spectra of the mother liquor after **1**-MNPs sterilization. Spectra were run in D_2O.

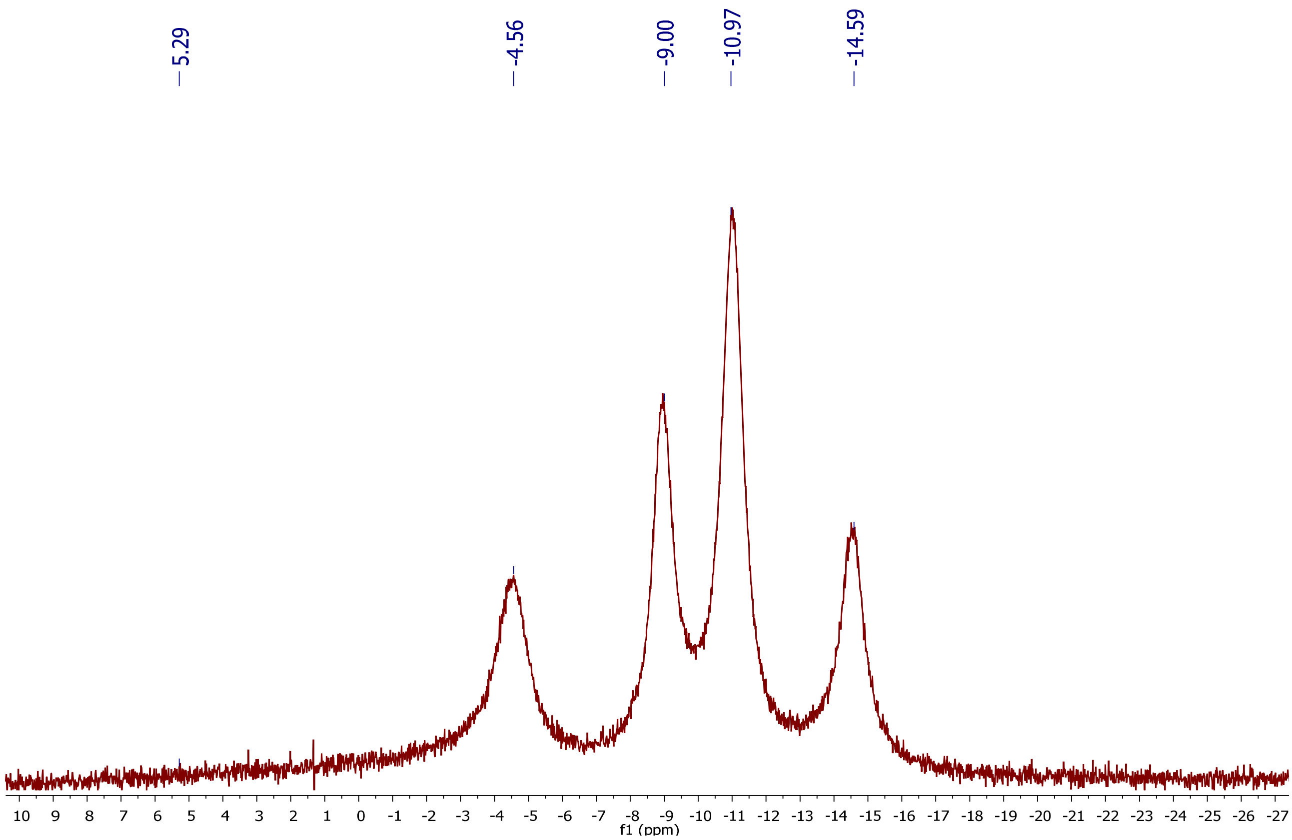
^{1}H-NMR



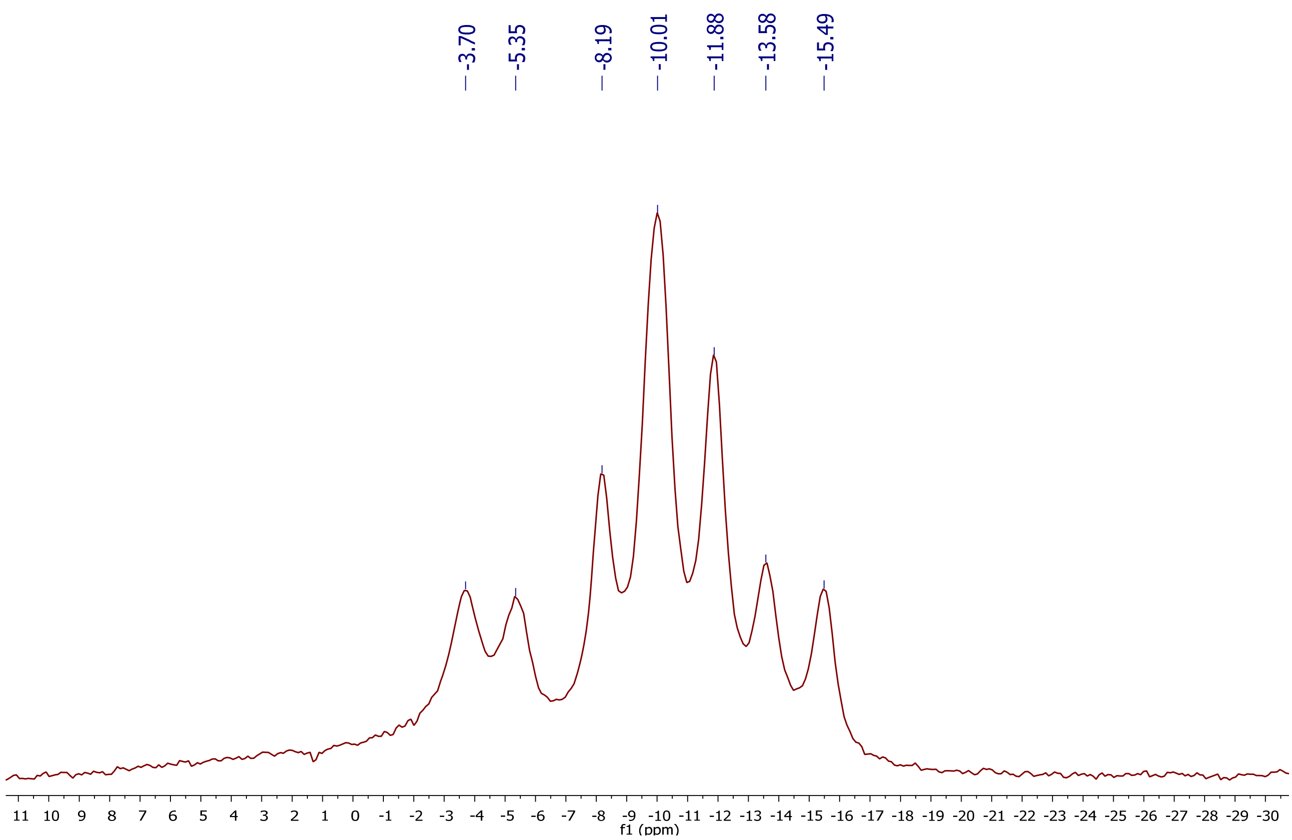
$^{1}H\{^{11}B\}$-NMR



$^{11}B\{^{1}H\}$-NMR



^{11}B-NMR



^{31}P-NMR

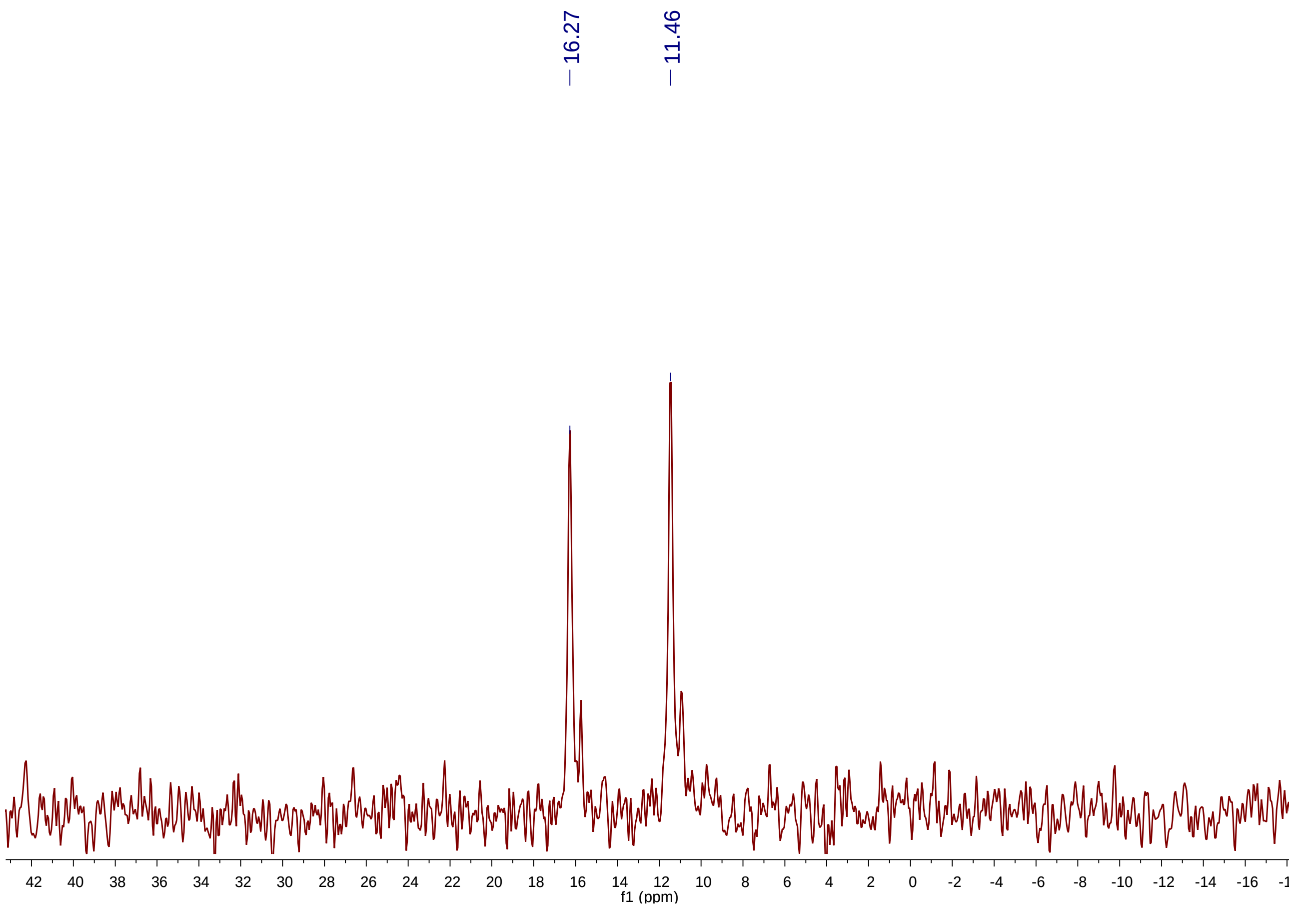

16.27
11.46
42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0 -2 -4 -6 -8 -10 -12 -14 -16
f1 (ppm)

Figure S5. Thermogravimetric Analysis of the ligand Na[**1**] and the **1**-MNP.