

Substituted poly(vinylphosphonate) coatings of magnetite nanoparticles and clusters

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Synthesis of substituted vinylphosphonic acids

1-Phenylvinylphosphonic acid **2**:

Acetophenone (12 g, 0.1 mol) was put in a 250 mL 2 necked flask under Ar atmosphere, cooled in an ice bath, and PCl₃ (12 mL, 0.138 mmol) was added dropwise, and the mixture stirred for 1 h at room temperature. After cooling in an ice bath again, AcOH (17.17 mL, 0.3 mol) was also added dropwise, and the reaction stirred over night at room temperature. The mixture was poured on ice (350 g), and left standing for 24 h. The solution was then reduced by rotary evaporation to ca. 10-15 mL of a solid/liquid mixture and refluxed with 25 mL HCl (conc.) for 35 h. After leaving the product in the freezer 9.145 g of a white solid could be obtained by suction filtration and air drying.

¹H-NMR (D₂O, 500 MHz): [1,2] δ[ppm] = 7.51-7.42 (m, 2H, CH_{ortho}), 7.37-7.27 (m, 3H, CH_{meta+para}), 6.08 (dd, 1H, J₁ = 21.9 Hz, J₂ = 1.0 Hz, C=CH-H_Z), 5.99 (dd, 1H, J₁ = 45.0 Hz, J₂ = 1.0 Hz, C=CH-H_E). ¹³C-NMR (D₂O, 125 MHz): δ[ppm] = 141.7 (d, J = 171.7 Hz, C-PO₃H₂), 137.1 (d, J = 12.1 Hz, C_{ipso}), 129.5 (d, J = 8.1 Hz, C_{ortho}), 128.6 (C_{para}), 128.3 (C_{meta}), 127.3 (d, J = 5.5 Hz, C=CH₂). ³¹P-NMR (D₂O, 202 MHz): δ[ppm] = 14.67.

Disodium 1-(4-hydroxyphenyl)vinylphosphonate **3**:

Acetophenone (13.62 g, 0.1 mol) was put in a 250 mL 2 necked flask under Ar atmosphere, cooled in an ice bath, and PCl₃ (11 mL, 0.127 mmol) was added dropwise, and the mixture stirred for 1 h at room temperature. After cooling in an ice bath again, AcOH (17 mL, 0.3 mol) was also added dropwise, and the reaction stirred over night at room temperature. The mixture was poured on ice (180 g), and stirred until all ice dissolved. The solution was then reduced by rotary evaporation to ca. 20 mL and refluxed with 25 mL HCl (conc.) over night. The product did not precipitate upon cooling in the freezer. Sodium hydroxide (15 g) was then added portionwise, followed by ethanol (150 mL). The precipitate was filtered off, the filtrate reduced by rotary evaporation again and another 10 g of sodium hydroxide added. The basic solution was evaporated and the residue dried in a vacuum oven (50°C) for 3 days. A pink solid was obtained (20.8 g). NMR showed that the substance was not pure.

¹³C-NMR (D₂O, 125 MHz): δ[ppm] = 154.7 (d, J = 166.6 Hz), 147.9 (d, J = 10.2 Hz), 141.8 (d, J = 9.0 Hz), 129.3 (C_{para}), 114.3, 113.8 (d, J = 10.1 Hz).

Allenylphosphonic acid **4**:

Phosphorous trichloride (14 mL) was dissolved in dichloromethane (160 mL), a solution of allyl alcohol in dichloromethane (100 mL) was added under ice cooling over 1.5 h, the solvent was evaporated under vacuum at room temperature, 60 mL of chloroform added and the solution refluxed over night. After evaporating the solvent, the remaining oil was added dropwise to an ice cooled 50% aq. dioxane solution, the solvent evaporated and put in a freezer to obtain 7.6 g of the product as a white solid.

¹H-NMR (D₂O, 500 MHz): [3] δ[ppm] = 5.30 (t, 1H, J = 6.9 Hz), 4.70 (dd, 2H, J₁ = 13.6 Hz, J₂ = 6.9 Hz). ¹³C-NMR (D₂O, 125 MHz): δ[ppm] = 213.4, 80.8 (d, J = 188.6 Hz), 75.3 (d, J = 15.6 Hz). ³¹P-NMR (D₂O, 202 MHz): δ[ppm] = 13.04.

4-Methylpenta-2,4-diene-2-ylphosphonic acid **5**:

Phosphorous acid (10 g, 122 mmol) was stirred with acetic acid (9.7 g, 162 mmol) and acetic anhydride (24.7 g, 242 mmol) was added slowly. After addition of phenothiazine (20 mg) mesityl oxide (14.2 g, 145 mmol) was added dropwise. The reaction was stirred at 50 °C over night, water (10 mL) added and the mixture stirred for another 5 h at 50°C. After removing the remaining acetic acid by rotary evaporation, 28 g of a brown sap-like semi-solid remained. ³¹P-NMR showed that the product was not pure.

Synthesis of magnetite nanoparticles

Magnetite nanoparticles **8**:

A solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (3.028 g, 8 mmol) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (1.084 g, 4 mmol) in water (16 mL) was made and degassed by bubbling Ar gas through it. Ammonia solution (40 mL, 25%) was degassed in a 100 mL 3 necked flask fitted with a thermometer and condenser, then heated to 80°C. The iron chloride solution was quickly added and the reaction stirred for 3 h at the same temperature. After magnetic separation the sample was washed with water (3x) and dried in the oven (60°C) over night to obtain 1.3 g magnetic nanoparticles as brown powder.

Adsorption of RECl_3 RE = Gd: **9a**, Er: **9b**, Tb: **9c**, Eu: **9d**

RECl_3 ($\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, 1 mmol) was dissolved in water (13.2 mL) and stirred with PMVP coated magnetite nanoparticles (6.85 mL, 500 mg) for 24 h. After washing with water (3x), magnetic separation and drying, 481 mg (Gd), 485 mg (Er), 518 mg (Tb) and 505 mg (Eu) were obtained.

Synthesis of magnetite clusters

Magnetite clusters **10**:

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (2.16 g), NaOAc (11.6 g) and sodium acrylate (0.4 g) were stirred with a mixture of ethylene glycol (40 mL) and diethylene glycol (40 mL) for 2 hours. The mixture was poured into a 100 mL teflon lined autoclave and heated to 200°C for 10 h, washed with ethanol (2x) and water (3x) and magnetically separated. The magnetite clusters were then suspended in water (40 mL)

Ligand exchange for clusters **10** to obtain PMVP coated clusters **11**:

The suspension of magnetite clusters **10** was stirred with a solution of poly(methylvinylphosphonic acid) **6** (1 g) for 24 h, magnetically separated, washed with water (3x) and dried in an oven to obtain 553 mg of a black powder.

One pot solvothermal reaction to get PPVP coated magnetite clusters **13**:

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1.085 g), NaOAc (2.88 g) and ethylene glycol (30 mL) were stirred for 10 min and then heated to reflux. The mixture turned darker slowly, and when it was completely black at 2 h, phenylvinylphosphonic acid **2** (0.5 g, 2.71 mmol) and NaOH (436 mg) were added. The mixture was refluxed for another 6 h, cooled down, washed with EtOH, water (3x), acetone (2x) and magnetically separated, then dried in an oven to obtain 280 mg of a brown powder.

One pot solvothermal reaction to get PHVP coated magnetite clusters **14**:

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1.085 g), NaOAc (2.88 g) and ethylene glycol (30 mL) were stirred for 10 min and then heated to reflux for 3 h. Disodium 1-(4-hydroxyphenyl)vinylphosphonate **3** (1 g) was added, and the mixture was refluxed for another 3 h, cooled down, washed with EtOH and water (3x) and magnetically separated, then dried in an oven to obtain 207 mg of a black powder. The magnetic separation in water worked poorly.

One pot solvothermal reaction to get PAVP coated magnetite clusters **15**:

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1.085 g), NaOAc (2.88 g) and ethylene glycol (30 mL) were stirred for 10 min and then heated to reflux. The mixture turned darker slowly, and when it was completely black at 2 h, allenylphosphonic acid **4** (1.3 g, 10.8 mmol) and NaOH (433 mg) were added. The mixture was refluxed for another 6 h, cooled down, washed with EtOH (2x), water (3x) and magnetically separated, then dried in an oven to obtain 489 mg of a brown powder.

One pot solvothermal reaction to get PMPP coated magnetite clusters **16**:

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1.085 g), NaOAc (2.88 g) and ethylene glycol (30 mL) were stirred for 10 min and then heated to reflux for 3 h. 4-Methylpenta-2,4-diene-2-ylphosphonic acid **5** (540 mg) and NaOH (460 mg) were added, and the mixture was refluxed for another 3 h, cooled down, washed with EtOH and water (3x) and magnetically separated, then dried in an oven to obtain 460 mg of a brown powder. In the washings larger (mm-sized) transparent pieces of hydrogel could be found.

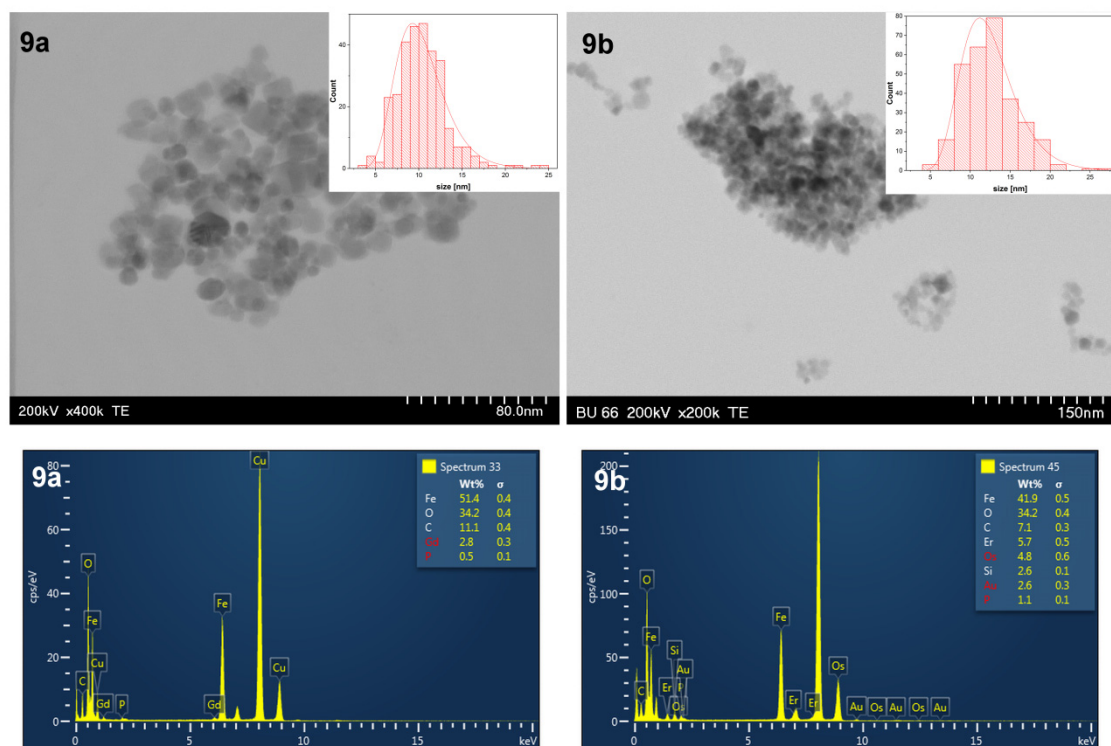


Figure S1: TEM (top) with size distribution and EDX (bottom) of MNP **9a** and **9b**; peaks of Au are from the sample holder, Si is an artifact of the device, and Os is a misinterpretation of the evaluation software

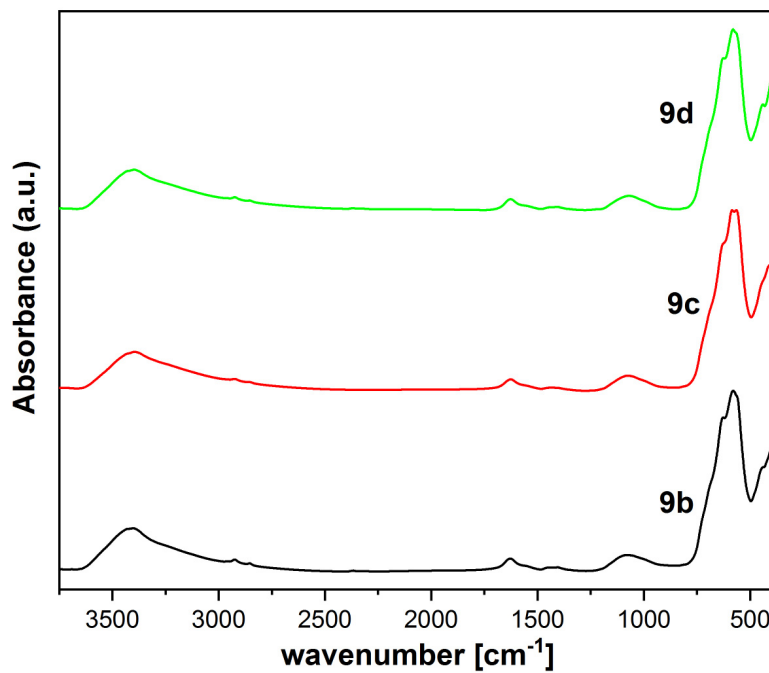


Figure S2: FTIR spectra of MNP **9a**, **9b** and **9c**

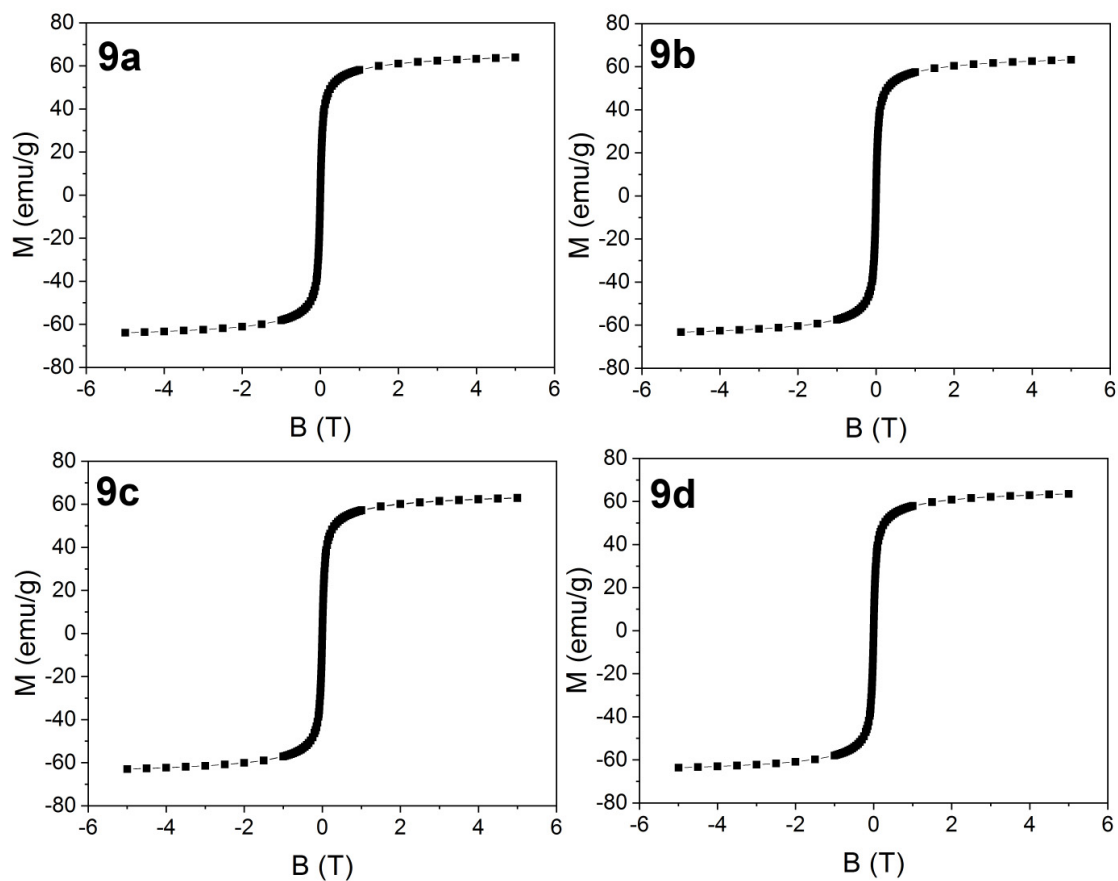


Figure S3: Magnetization of MNP **9a**, **9b**, **9c** and **9d**

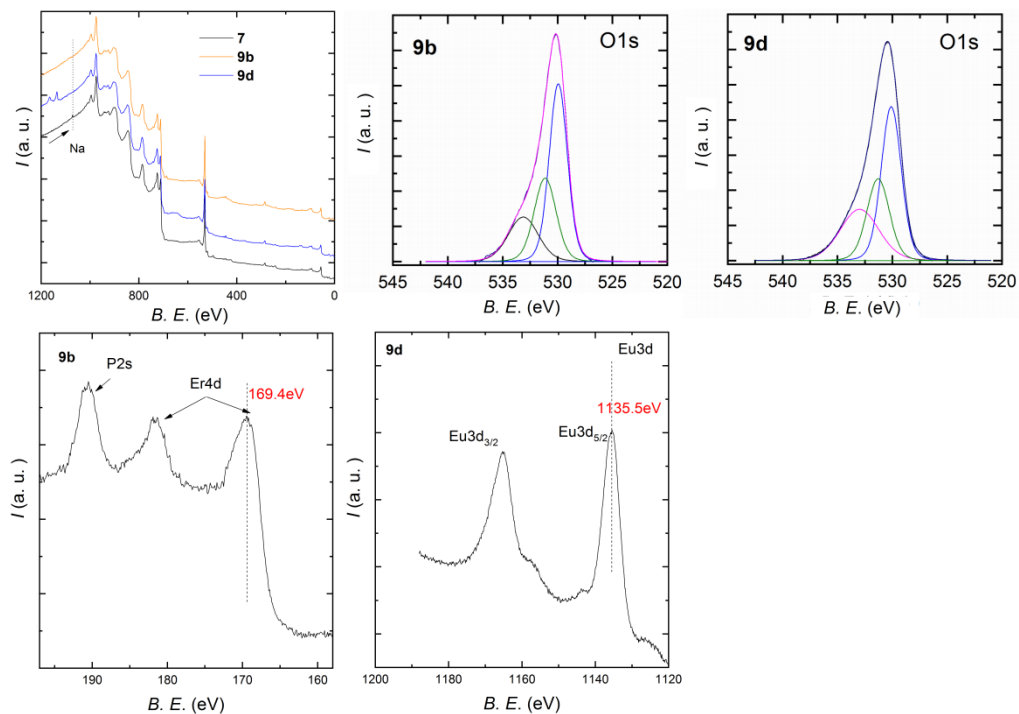


Figure S4: XPS survey spectra of **7**, **9a** and **9b** (top left); O1s spectra of **9b** and **9d** (top right); Er4d and P2s spectra of **9b** (bottom left); Eu3d spectrum of **9d** (bottom right)

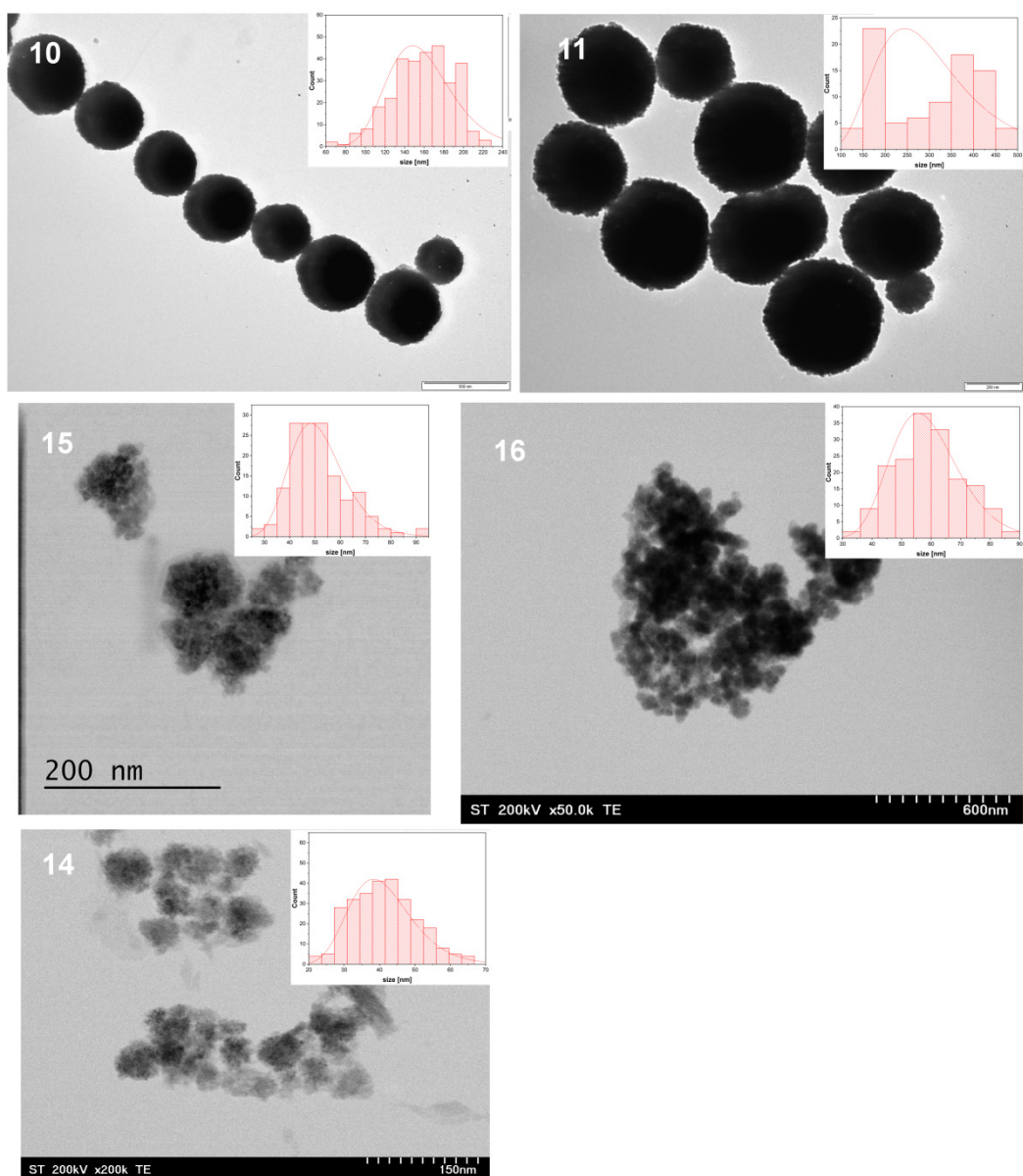


Figure S5: TEM results of magnetite clusters **10** (scalebar 200 nm), **11** (scalebar 500 nm), **15**, **16** and **14** and their size distributions

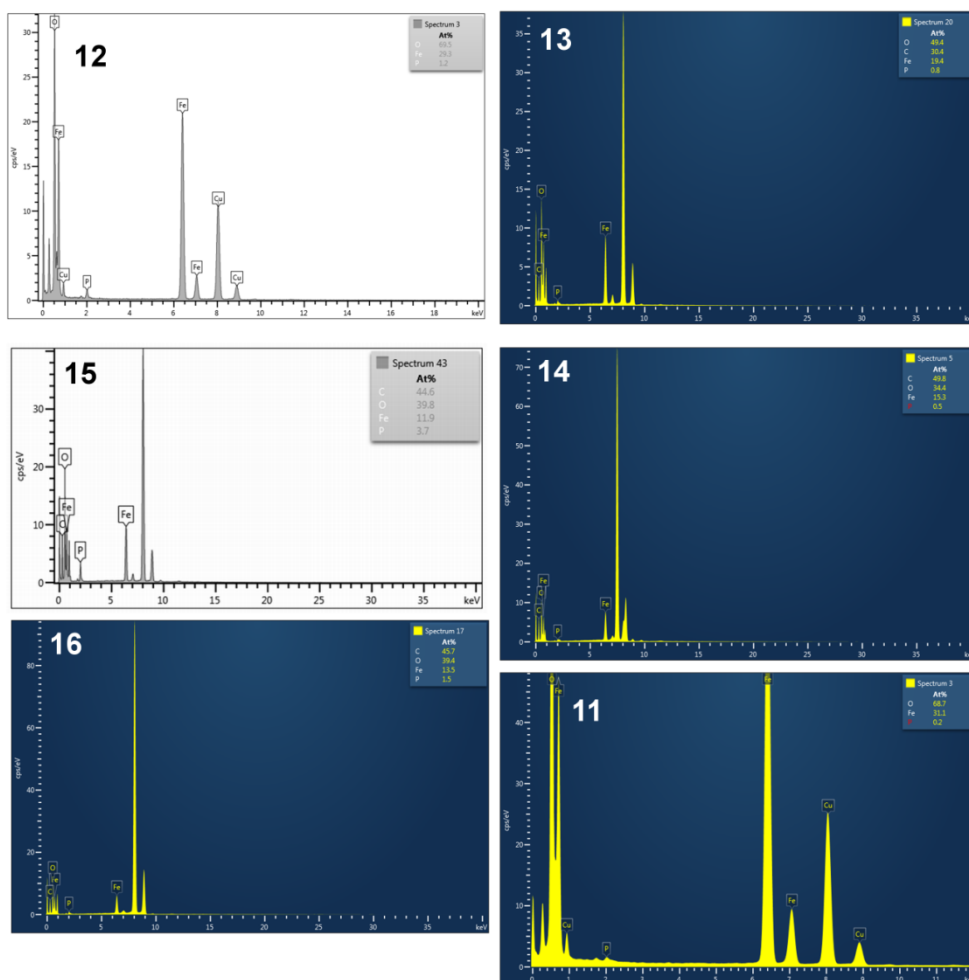


Figure S6: EDX of magnetite clusters 11, 12, 13, 14, 15 and 16

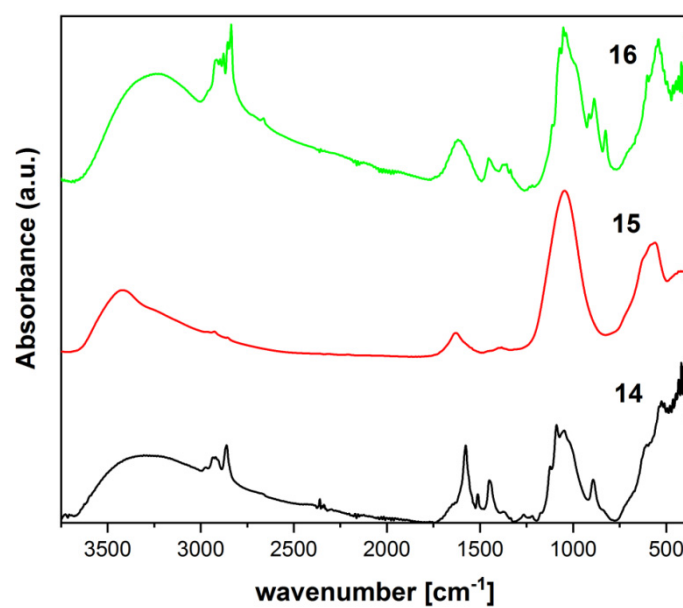


Figure S7: FTIR spectra of clusters 14, 15 and 16

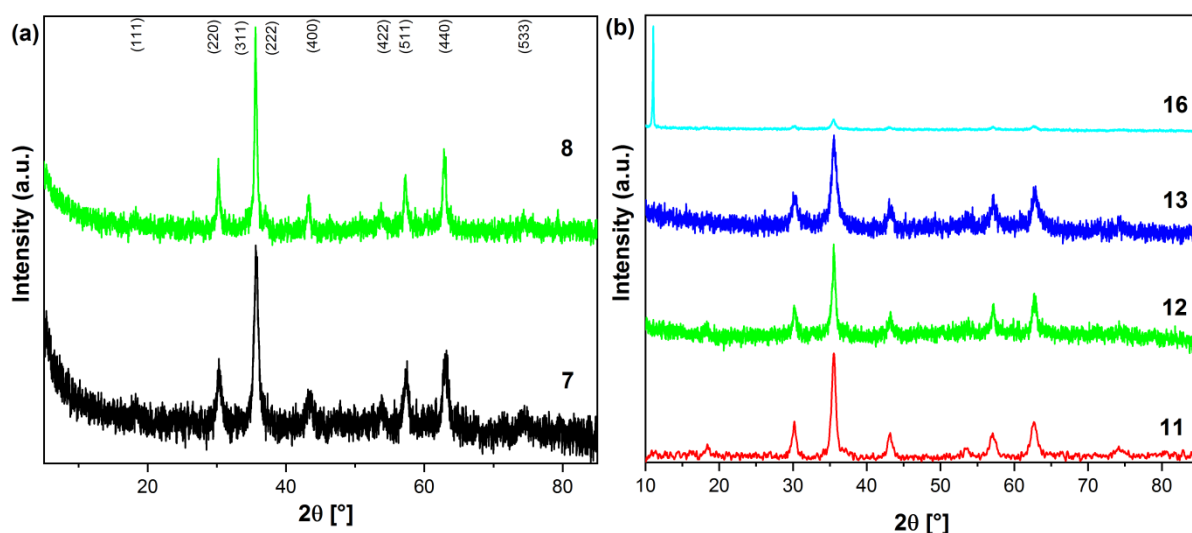


Figure S8: XRD patterns of samples (a): 7 and 8; (b): 11,12, 13 and 16. The values in brackets represent the planes representing the specific reflection, the reflections are the same as magnetite (JCPDS file No. 19-0629)

1. Kenyon, G.L.; Westheimer, F.H. The Stereochemistry of Unsaturated Phosphonic Acids1. *Journal of the American Chemical Society* **1966**, *88*, 3557-3561, doi:10.1021/ja00967a016.
2. Dong, K.W.; Wang, Z.; Ding, K.L. Rh(I)-Catalyzed Enantioselective Hydrogenation of α -Substituted Ethenylphosphonic Acids. *Journal of the American Chemical Society* **2012**, *134*, 12474-12477, doi:10.1021/ja305780z.
3. Macomber, R.S.; Kennedy, E.R. Phosphorus-containing products from the reaction of propargyl alcohols with phosphorus trihalides. 4. Alkyl substituent effects on oxaphospholene formation. *The Journal of Organic Chemistry* **1976**, *41*, 3191-3197, doi:10.1021/jo00881a028.