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Magnetic Nano-organocatalyst: impact of the surface functionalization on catalytic activity.

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Supporting information

1) **Experimental details**
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1) Experimental details

Materials

Boc-Pro-Osu (≥ 98 %), 1-mercapto-dodecanoic acid 99.6%), 1-dodecanthiol (≥ 98%), dimethylamine (40 wt% in H_2O), and tris(trimethyl-silyl) phosphite were purchased from Sigma-Aldrich, and were used without further purification. 4-p-nitobenzaldehyde (99%), cyclohexanone (99%), n-butyraldehyde (99%), trans- β-Nitrostyrene, TFA (99%), DMF (99%), were purchased from Alpha Aesar and were used without further purification. Peptide **6** (H-L-Pro-L-Pro-Glu-AHX-Cys-NH_2 (HPLC > 95%) was purchased from Eurogentec. Solvents: methanol (RS HPLC), isopropanol (HPLC), dichloromethane (RE amylene stabi-lized), ethyl acetate, hexane and diethylether (RE stabilized) were purchased from Carlo Erba SDS. All the other reagents were obtained from commercial suppliers and were used without purification.

Water was purified with a millipore system (resistivity 18.2 MΩ cm).

^{1}H NMR spectra (400 MHz), proton-decoupled ^{13}C NMR spectra (100.63 MHz) were recorded on a Bruker Avance III 400 spectrometer. Chemical shifts are reported in parts per million (ppm) on the δ scale. The residual solvent peaks were used as internal references (^{1}H NMR: $CHCl_3$ 7.26 ppm, H_2O 4.79 ppm; ^{13}C NMR: $CDCl_3$ 77.2 ppm). Data are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, qt = quintuplet, m = multiplet and coupling constant(s) are given in Hz. FTIR spectra were recorded as KBr pellets or between NaCl plates (for liquid product) on a Thermo Scientific Nicolet 380 FTIR spectrophotometer and are reported in wavenumbers (cm^{-1}). High resolution Mass Spectrometry experiments were realized on a LTQ Orbitrap Velos (Thermo Scientific) in positive and negative modes using an ESI source. MS spectra were recorded in the Orbitrap mass analyzer allowing a mass accuracy around 1-2 ppm. For MALDI-MS of nanoparticles, the nanoparticles were mixed with the matrix HCCA and the solution was then deposited onto the MALDI target to be analyzed by MALDITOF/ MS (Ultraflex TOF/TOF, Bruker Daltonique) in positive and negative mode.

Specific optical rotation were measured on a Perkin Elmer 341 polarimeter at 26°C using a Hg lamp (□ = 589 nm) in water.

UV-visible spectra were recorded on a Varian Cary 50 Scan UV-Visible spectrophotometer. The number of particles was determined by UV from the iron concentration (ε_{480} = 420 L.mol-1.cm-1), considering an average diameter of 10 nm, a density value of 4.85 $g.cm^{-3}$, and a molecular weight of 160 $g.mol^{-1}$ for γ-Fe_2O_3.

The hydrodynamic diameter and the zeta potential of the nano complex were determined by dynamic laser light scattering (DLS) on a Nano-ZS (Red Badge) ZEN 3600 device (Malvern Instruments, Malvern, UK).

TEM images were obtained using a FEI CM10 microscope (Philips), and samples were prepared by depositing a drop of nanoparticles suspension on carbon-coated copper grids placed on a filter paper. The average particle diameters were deduced from TEM data measurements, simulating the diameter distribution with a log-normal function (g(d)):

$$g(d) = \frac{1}{\sigma d\sqrt{2\pi}} \exp\left(-\frac{\left(\ln \frac{d}{d_{med}} \right)^2}{2\sigma^2} \right)$$

σ corresponding to the distribution's length and $\ln(d_{med})$ to the medium of (d).

Quantification of MNPs coating and grafting per particle was evaluated by Energy-dispersive X-ray (EDX), FTIR and Thermogravimetric analysis (TGA) respectively. EDX microanalyses were performed using a TM 3000 tabletop microscope equipped with a Swift EDX-ray 3000 microanalysis system (Oxford Instruments). Samples were deposited as powder on a copper surface, and data were collected using a 15 kV accelerating voltage, studying ratio of iron vs Pd and knowing the average number of iron atoms/particles. The TGA curves were recorded using a LabsSys evo TG-DTA-DSC 16000 device manufactured by Setaram Instrumentation.

The magnetic behavior of the as-synthesized nanoparticles was characterized at room temperature using a vibrating magnetometer was characterized at room temperature using a vibrating magnetometer, VSM (Dautum Design, Versalab).

Chemicals reactions under microwave irradiation were performed using Mono Wave 300 (Anton, Paar) in sealed vessel.

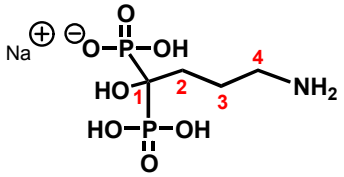
Chemical synthesis and characterization

Nanoparticles synthesis

The bare maghemite nanoparticles, γ-Fe_2O_3 nanocrystals (average diameter 10.5 nm and size distribution σ = 0.2), were synthesized according to the following procedure (Lalatonne 2008). Dimethylamine ($(CH_3)_2NH$) was added to an aqueous solution of ferrous dodecyl sulfate ($Fe(DS)_2$). The final concentrations after the reactants were mixed were $1.4.10^{-2}$ mol.L^{-1} and 1.4 mol.L^{-1} respectively for $Fe(DS)_2$ and dimethylamine. The solution was stirred vigorously for 2 h at 28 °C. 12 mL of HCl (1 M) were then added in order to reach the isoelectric point (around pH = 7), inducing nanoparticles precipitation. The precipitate was isolated from the supernatant using magnetic separation. After 10 washings at neutral pH, the nanoparticles were then dispersed at pH=2 in distilled water. At this stage bare γ-Fe_2O_3 nanocrystals were produced

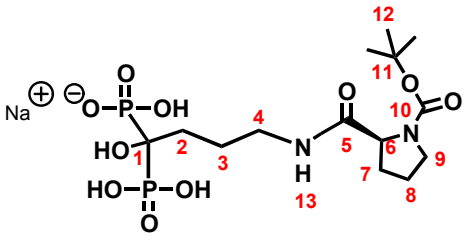
*Synthesis of **1***

Sodium 4-amino-1-hydroxybutylidene bisphosphonic acid (Alendronate) was synthesized and purified according to original process described by Kieczykowski *et al.*[1]

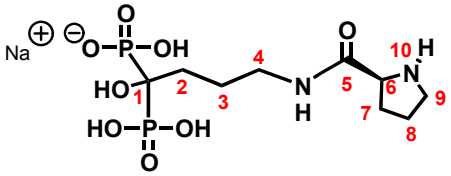


NMR ^1H (D_2O, 25°C): δ = 3.04 (t, $^3J_{H-H}$ = 6.5 Hz, 2 H, *4*) ; 2,0-1,8 (m, 4 H, *2*, *3*) ppm.
NMR $^{13}C\{^1H\}$ (D_2O, 25°C): δ = 72.9 (t, J_{C-P} = 139.7 Hz, *1*); 39.7 (s, *4*); 30.4 (s, *2*); 21,2 (t, J_{C-P} = 6.7 Hz, *3*) ppm.
NMR $^{31}P\{^1H\}$ (D_2O, 25°C): δ = 18.4 (s) ppm.
IR (KBr): 3486 ; 3346 ; 3244 ; 2960 ; 2800 ; 2710 ; 2566 ; 1644 ; 1545 ; 1231 ; 1178 ; 1063 ; 1018 ; 953 ; 926 ; 866 ; 660 ; 576 ; 547 ; 472 cm^{-1}.

Alendronate (500 mg, 1.85 mmol) were solubilized in 50 mL pure water and pH was adjusted to 7 with NaOH (1M) (10 mL). (Boc)-L-Pro-OSu (1.20 mg, 3.7 mmol) previously solubilized in 10 mL of DMF and DIPEA (700 µL, 4.1 mmol) were added to the water solution. The resulting mixture was stirred for 4 days and then washed twice with 15 mL Et_2O. The white product was obtained after acidic precipitation with 75% yield. Classical deprotection was performed using 6 mL of CH_2Cl_2/TFA (1/1) mixture for 30 min at room temperature. Then solvents were removed by reduced pressure. The product was washed twice with 10 mL Et_2O. After crystallization, a white powder was obtained with 75% yield. The product (**1**) is obtained as a TFA salt.



NMR ^1H (D_2O, 25°C): δ = 8.20 (d, 5.28 Hz, 1H, *13*) ; 4.04 (m, 1H, *6*) ; 3.4-3.25 (t, 2H, *4*) ; 3.2-3.0 (m, 2H, *9*) ; 2.2-2.04 (m, 2H, *7*) ; 1.89-1.82 (m, 6H, *2*, *3*, *8*) ; 1 ,26 (s, 9H, *12*) ppm.
NMR $^{13}C\{^1H\}$ (D_2O, 25°C): δ = 175.9 (*10*) ; 156.0 (*5*) ; 81.9(*12*) ; 72.9 (t, J_{C-P} = 134.4 Hz, *1*) ; 61.0 (*6*) ; 47.2 (*9*) ; 46.8(*4*) ; 40.0 (*8*) ; 31.0(*7*) ; 27.5 (*12*) ; 23.5 (*2* et *3*) ppm.
NMR $^{31}P\{^1H\}$ (D_2O, 25°C): δ = 18.09 (s) ppm.



NMR ^1H (D_2O, 25°C): δ = 4.20 (dd, 1H, *6*) ; 3.35-3.10 (m, 4H, *9*, *4*) ; 2.34-2.2 (m, 2H, *7*) ; 2-1.62 (m, 6H, *2*, *3*, *8*) ppm.

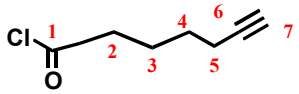
NMR $^{13}C\{^{1}H\}$ (D_2O, 25°C): δ = 169.33 (*5*) ; 73.35 (t, $J_{C,P}$ = 138.3 Hz,*1*) ; 59.78 (*6*); 46.34 (*4*) ;40.02 (*9*) ; 30.79 (*8*); 29.64(*7*) ; 23.50 (*3*); 23.16 (*2*) ppm.
NMR $^{31}P\{^{1}H\}$ (D_2O, 25°C): δ = 18.26 ppm.
IR (KBr): 3400 ; 3294 ; 3103 ; 2983 ; 2786 ; 2394 ; 1685 ; 1681 ; 1573 ; 1441 ; 1435 ; 1385 ; 1206 ; 1138 ; 1068 ; 930 ; 840 ; 801 ; 722 ; 667 ; 580 ; 538 ; 461 cm^{-1}.
HR-MS: (ESI-Q Tof) $C_9H_{21}N_2O_8P_2$ m/z $(M + H)^+$: 347.08; calc: 347.08.
$[\alpha_D]^{25}$ (589 nm acidic pH, H_2O) = -91.3°.

*Synthesis of MNPs **2***

To 4 mL of an aqueous solution of **1** (43 mg, 83 µmol, pH = 4), an aqueous solution of bare γ-Fe_2O_3 nanoparticles (4 mL, [Fe] = 0.16 M, pH = 4) was added. The resulting mixture was vigorously stirred for 2 h at 90°C. The nanoparticles **2** were then washed 5 times by filtration using 30 KDa Amicon filters, in order to remove the excess of unbound **1**. MNPs **2** are dispersed in pure water and pH of the solution was adjusted to 7 using NaOH solution (0.1M).

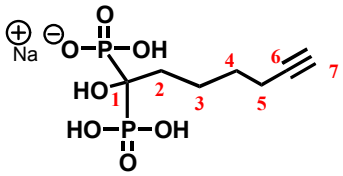
IR (KBr): 3124, 1624, 1514, 1471, 1396, 1119, 1024, 682, 579, 476, 417.

Synthesis of 6-heptynoic acyl chloride
6-heptynoic acid (1 g, 9 mmol) was dissolved in dichloromethane under inert atmosphere. Oxalyl chloride (3.7 mL, 5 eq.) was added dropwise to the reaction mixture. The solution was then stirred for 16 h at room temperature. The solvent and the oxalyl chloride in excess were evaporated and the remaining oil was used without further purification.



NMR ^{1}H ($CDCl_3$, 25°C): δ= 2.93 (t, J^3_{H-H}= 7.2 Hz, 2H, ***2***) ; 2.22 (td, J^3_{H-H}= 7.2 Hz, J^4_{H-H}= 2.7 Hz, 2H, ***5***) ; 1.97 (t, J^4_{H-H}= 2.7 Hz, 1H, ***7***) ; 1.83 (qt, J^3_{H-H}= 7.2 Hz, 2H, ***3***) ; 1.58 (qt, J^3_{H-H}= 7.2 Hz, 2H, ***4***).
NMR ^{13}C ($CDCl_3$, 25°C): δ= 179.8 ; 83.8 ; 68.7 ; 32.5 ; 27.7 ; 23.7 ; 18.1.

(1-hydroxy-1-phosphonohept-6-ynyl)phosphonic Acid (BPheptyne) synthesis:
Tris(trimethylsilyl)phosphite (6.7 mL, 20 mmol) was added dropwise at -20°C to the previously obtained 6-heptynoic acyl chloride without solvent and under inert atmosphere. When the addition was completed, the reaction mixture was allowed to stand at room temperature for 4 h. The evolution of the reaction was monitored by 31P NMR {1H}. Then, volatile fractions were evaporated under reduced pressure (0.1 Torr) before being hydrolyzed with methanol. After methanol evaporation the product was dissolved in water at pH = 2.3 and lyophilized. The product was then precipitate twice in a water/methanol mixture (1:9).
The sodium salt of HMBPheptyne was obtained as a white powder (1.95g, 84%).



NMR ^{1}H (D_2O, 25°C): δ=2.29 (t, J^4_{H-H} = 2.6 Hz, 1H, ***7***) ; 2.20 (td, J^3_{H-H}= 7.2 Hz, J^4_{H-H}= 2.6 Hz, 2H, ***5***); 1.91 (m, 2H, ***2***) ; 16.63 (m, 2H, ***3***) ; 1.51(qt, 2H, ***4***).
NMR ^{13}C (D_2O, 25°C): δ= 86.5 ; 74,0 (t, J^1_{P-C} = 134.5 Hz, ***1***) ; 68.9 ; 33.1 ; 28.7 ; 23.0 ; 17.5.
NMR ^{31}P (D_2O, 25°C): δ= 18.4 (td, J^3_{P-H}= 13.9 Hz).
IR (KBr, pH=7): 3541, 3261, 2953, 2866, 2113, 1725, 1467, 1448, 1383, 1329, 1265, 1227, 1167, 1058,986, 947, 911, 755, 738, 673, 656, 597, 547, 487, 455 cm^{-1}.
SM-HR (ESI,-Q Tof) $C_5H_9O_7P_2$: m/z (M-H)-: 271.01359 ; calc: 271.0137.

Coating of MNPs with 3
Coating with BPheptyne **3** was achieved by adding a 5 mL solution of the **3** (60 mg, 0.2 mmol) at pH = 2 to 20 mL of an aqueous solution of γFe2O3 nanocrystals ([Fe] =0.1-0.15 M). The solution was stirred at room temperature for 2 h. The MNP@3 were collected under a magnetic field and washed ten times with acidic water (pH = 2). The as-synthesized nanoparticles were then dispersed in distilled water and adjusted to pH = 7. The average number of molecules of **3** per nanocrystal was measured by ATG and EDX measurement.

IR (KBr): ν= 2957.3, 2923.3, 2853.2, 1122.8, 1075.8, 633.0, 586.0, 451.6 cm^{-1}

*Synthesis of **4***

Synthesis of $H_2N(CH_2)_3N_3$: Sodium azide (7.8g, 120 mmol) reacted with 3-bromopropylamine hydrogen bromide (8.6 g, 40 mmol) in 40 mL of water, at 80°C for 24h. Then, 100 mL of NaOH (2M) was added to this mixture, and organic phase was extracted 3 times with 150 mL of Et_2O. The organic phase was dried under $MgSO_4$ and solvent was removed by reduced pressure. Yellow oil was obtained with 90% yield.

NMR ^1H (D_2O, 25°C): δ = 3.40 (t, J^3_{H-H}= 6.7 Hz, 2H) ; 2,84 (t, J^3_{H-H}= 6.8 Hz, 2H) ; 1.78 (m, 2H) ppm.

NMR $^{13}C\{^1H\}$ (D_2O, 25°C): δ = 49.19 ; 39.32 ; 32.57 ppm.

A solution of $H_2N(CH_2)_3N_3$ (3 mmol, 276 mg, 6 mL) in CH_2Cl_2 was added drop wise to 6 mL of a solution (Boc)-L-Pro-OSu (3 mmol, 1 g) in CH_2Cl_2 at 0°C with DIPEA (3 mmol, 500 µL). The resulting mixture was stirred for 18 h at room temperature. Then, solvent was removed under reduced pressure. The product was extracted tree times with Et_2O. The organic layer was then washed two times with $KHSO_4$ (1M) and two times with $NaHCO_3$. After that, the organic phase was dried over $MgSO_4$, filtered and solvent was removed by reduced pressure.

The crude product was solubilized with 3 mL of CH_2Cl_2 and 3 mL of TFA were added. The mixture was stirred for 30 min. at room temperature. Then both TFA and CH_2Cl_2 were removed by reduced pressure. After 2 washing steps with Et_2O, the product precipitated and was filtered. The yellow product was obtained as an oil (**4**)

IR (NaCl): 3320, 2101, 1684, 1431, 1384 cm^{-1}.

NMR ^1H (D_2O, 500 MHz, 298 K): δ = 8. 36 (s, 1H); 4.32-4.23 (m, 1H); 3.45-3.15 (m, 6H); 2.45-2.25 (m, 1H); 2.15-1.90 (m, 5H).

NMR $^{13}C\{^1H\}$ (D_2O, 120.7 MHz, 298 K): δ = 169.7; 59.7, 48.5; 46.3; 46.1; 29.7; 28.7; 23.7 ppm.

*Deprotection of **5***

N-Boc-*cis*-4-azido-L-proline (1 g, 9.39 mmol) was dissolved in 3mL of CH_2Cl_2 and 3 mL of TFA were added. The mixture was stirred 30 min at room temperature and both CH_2Cl_2 and TFA were removed by reduced pressure. The product was washed two times with Et_2O and lyophilized after being dissolved in HCl (1M). An orange powder was obtained with quantitative yield.

NMR ^1H (D_2O, 500 MHz, 25°C): δ = 4.63-4.65 (m, 1H) ; 4.50-4.42 (m, 1H) ; 3.58-3.44 (m, 2H) ; 2.68-2.53 (m, 1H) ; 2.52-2.41 (m, 1H).

NMR $^{13}C\{^1H\}$ (D_2O, 120.7 MHz, 25°C): δ = 172.22 ; 59.10 ; 58.81 ; 50.90 ; 34.18 ppm.

CuAAC procedure is performed according to Guénin et al. [2].

First, 5 equivalents of Azido-Proline (**4** or **5**), Copper Sulfate hexahydrate (5%) and sodium ascorbate (20%) were added to 2.5 mL of MNP@**3** ([Fe] = 0.1 – 0.2M, [BPheptyne] = 2 – 5 mM) and reacted in a sealed vial under microwave irradiations for 8 min ($T°C_{max}$ = 100°C). The as synthesized nanoparticles are washed 5 times by magnetic separation with acidic pure water (pH = 2) and then solubilized in water at pH 7.

Thiolyne reaction procedure is performed according to Demay-Drouard et al.[3] .

An aqueous solution of MNP@**3** ([Fe] = 0.1-0.15 M, [BPheptyne] = 2.5-3.8 mM, pH = 7, V = 3 mL) and 3 mL of DMF were mixed with radical initiator, 1-hydroxycyclohexylphenylketone (10 %). Thiol molecules were added (2 equivalents per BPheptyne, 10 for double functionalization) and the mixture was mixed for one and an half hour under UV irradiation (360 nm). The as functionalized MNPs are then washed 5 times with ethanol and 5 times with HCl 0.01M using magnetic separation (for **6**, only two ethanol washing were performed). MNPs are dispersed in water and pH is adjusted to 7.

General procedure for aldolisation

Catalyst (10 mol %, 0.04 mmol) was dissolved in 420 µL iPrOH. To this mixture, 60.4 mg of 4-p-nitrobenzakdehyde (0.4 mmol) and 210 µL of cyclohexanone (2 mmol) were added. The resulting mixture was mechanically mixed (600 rpm) at room temperature. The reaction was monitored by ^1H NMR. After reaction, crude mixture was extract tree times with Et_2O. Organic phase was then wash and dried with $MgSO_4$ and solvent was removed under reduced pressure. The product, orange powder, was purified on silica column using hexane/AcOEt gradient. With MNPs: catalyst (2µmol), 4-p-nitrobenzaldehyde (0.02 mmol) and cylohexanone (0.1 mmol), iPrOH (21 µL).Water was remove from MNPs by magnetic separation.

NMR ^1H ($CDCl_3$, 25°C): δ = 8.2 (d, J = 8.5 Hz, 2H) ;7.51 (d, J = 7,6 Hz, 2H) ; 4.9 (d, J = 8.1 Hz, 1H) ; 4.09 (d, J = 4,1 Hz, 2H) ; 2.67-2.57 (m 1H) ; 2.54-2.50 (m, 1H) ; 2.42-2.32 (m, 1H) ; 2.16-2.10 (m, 1H); 1.91-1.80 (m, 1H) ; 1.77-1.70 (m 1H) ; 1.66-1.52 (m, 2H) ; 1.44-1.37 m 1H) ppm.

NMR $^{13}C\{^1H\}$ ($CDCl_3$, 25°C): δ =214.0 ; 148.5 (2) ; 127.9 (2) ; 123. 5 (2) 70.1 ; 57.1 ; 42.6 ; 30.7 ; 27.6 ; 24.6 ppm.

General procedure for Michael addition

Catalyst (18.8 µmol) was first dissolved in 1 mL $CHCl_3$/iPrOH (9/1) and NMM (0.188 mmol, 23 µL) and mechanically stirred (600 rpm) for 5 min. at room temperature. Then trans-β-Nitrostyrene (0.7 mmol, 105 mg) and n-butyraldehyde (2.1 mmol, 191 µL) were added. The reaction was monitored by ^{1}H NMR. After reaction, crude mixture was extract tree times with CH_2Cl_2, and three times with water. Organic phase was then dried on $MgSO_4$ and solvent and excess of aldehyde were removed under reduced pressure. The yellow-orange product was purified on silica column (Hexane/AcOEt). With MNPs: catalyst (1 µmol), trans-β-Nitrostyrene (32.3 µmol, 4.8 mg), n-butyraldehyde (97 µmol, 8.8 µL), $CHCl_3$/iPrOH (9/1) (50 µL), NMM (30 mol %). Water was removed from MNPs by centrifugation.

NMR ^{1}H ($CDCl_3$, 25°C): δ = 9.77 (d = J = 2.6 Hz, 1H) ; 7.31 (m, 3H) ; 7.20 (m, 2H) ; 4,75 (dd, J = 5 et 11.3 Hz, 1H) ; 4.65(dd, J = 9.64 et 12.6 Hz, 1H) ; 3.80 (dt, J = 3.8 ; 9.7Hz, 1H) ; 2.68 (m, 1H) ; 1.52 (m, 2H) ; 0.85 (t, J = 7.5 Hz, H) ppm.
NMR ^{13}C{^{1}H} ($CDCl_3$, 25°C): δ =202.1; 136.54; 129.3 (2), 128.1; 128.0 (2); 64; 49.5; 25.33; 14.14; 10.79 ppm.
HPLC, hexane/iPrOH (97/3) t(SR) = 10.1 min ; t(RS) = 12.6 min ; t(RR) = 18.4 min et t (SS) = 21.3 min.

2) Figures

MNPs	ζ Potential (± 5 mV)	D_h (± 5 nm)	Nbr Cat/NP	Stability on pH range
2	-36	25	400	5.5-10
MNP@3	-40	20	-	3.5-10
MNP@**3-4**	-37	28	150	4-10
MNP@**3-5**	-45	26	250	5-10
MNP@**3-6**	-44	25	150	3.5-11
MNP@**3-5-7**	-14	30	150	-
MNP@**3-5-8**	-39	30	150	-

Table1. ζ Potential, D_h, Mean number of catalysts/NP and pH stability of **2**, MNP@**3**, MNP@**4**, MNP@**3-5**, MNP@**3-6**, MNP@**3-5-7**, MNP@**3-5-8**.

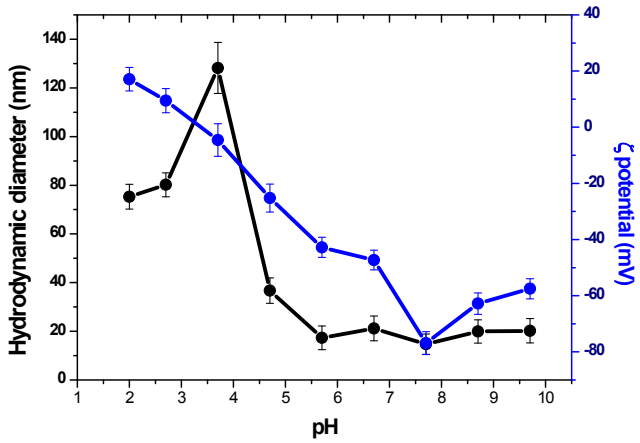


Figure1. Hydrodynamic diameter (D_h) et Zeta (ζ) potential vs pH of **2**.

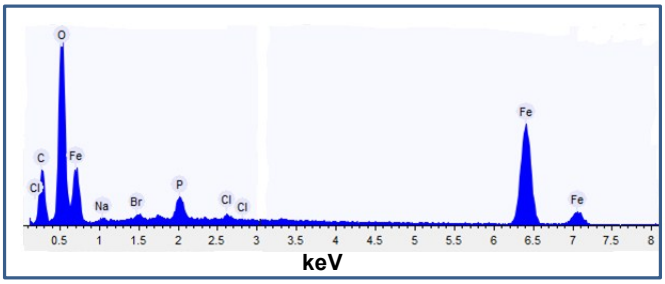


Figure2. EDX spectra for **2**.

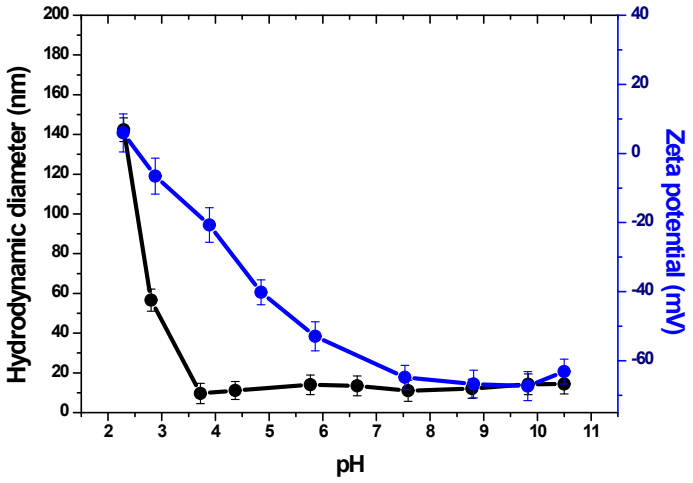


Figure3. D_h and ζ potential vs pH of MNP@**3**.

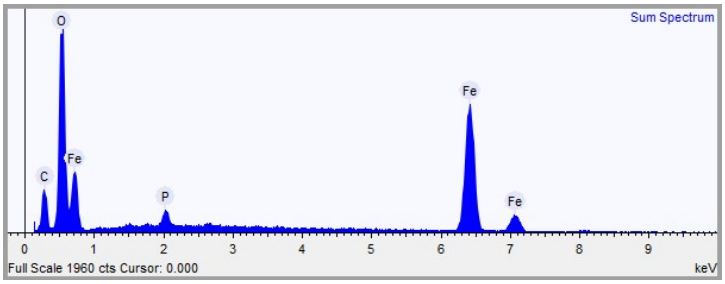


Figure4. EDX spectra for MNP@**3**.

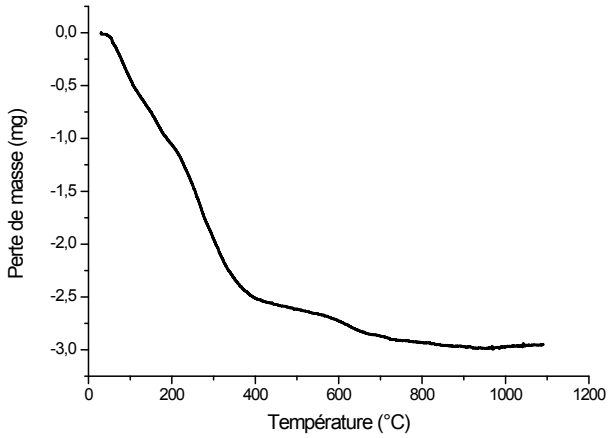


Figure5. TGA curve of MNP@**3**.

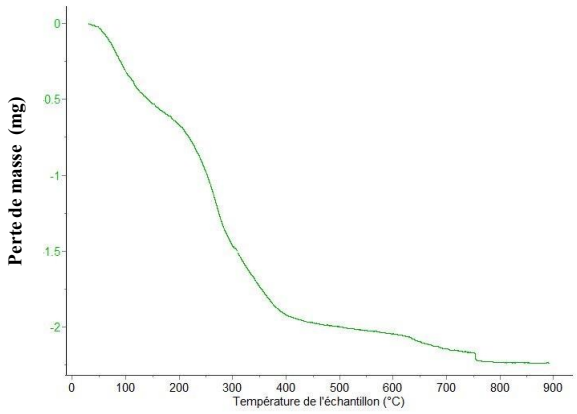


Figure6. TGA curve of MNP@**3-4**.

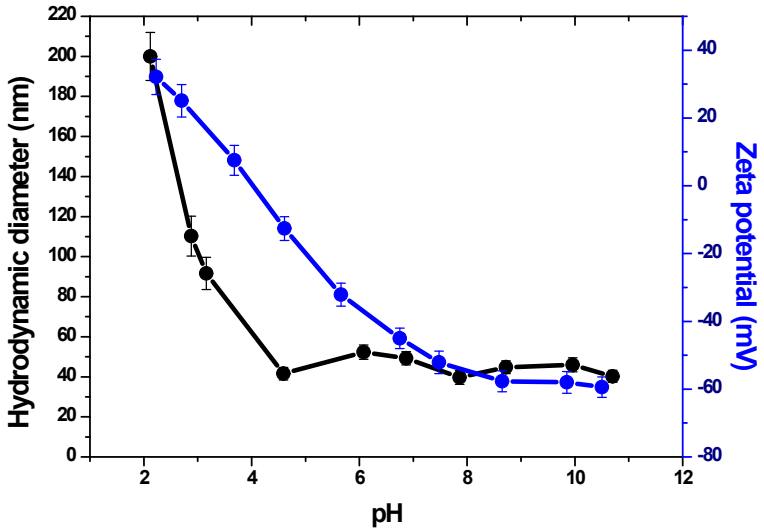


Figure7. D_h and ζ potential vs pH of MNP@**3-4**.

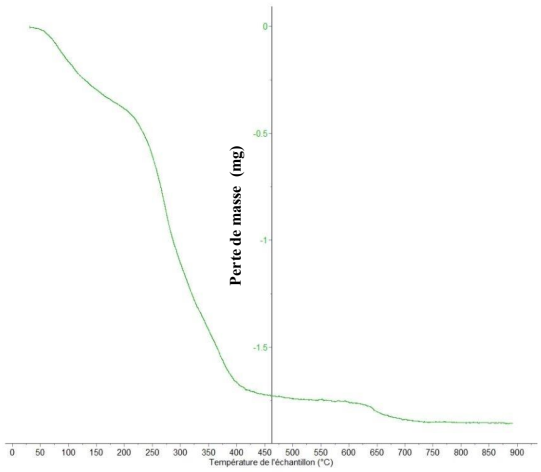


Figure8. TGA curve of MNP@**3-5**.

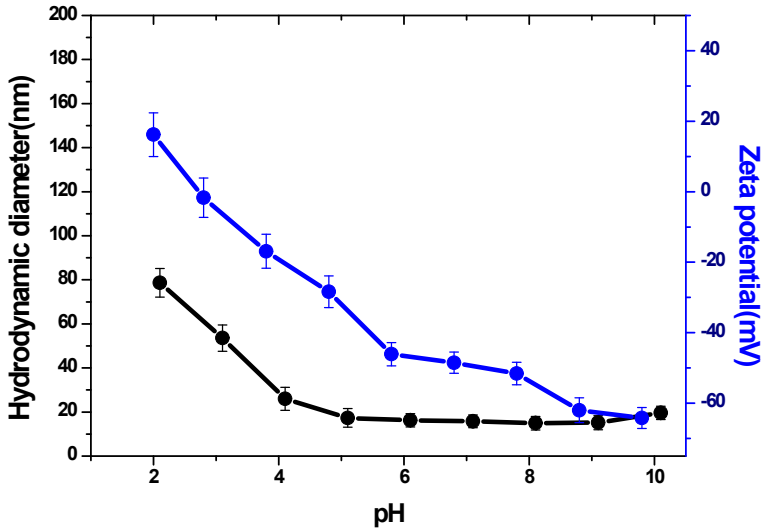


Figure9. D_h and ζ potential vs pH of MNP@**3-5**.

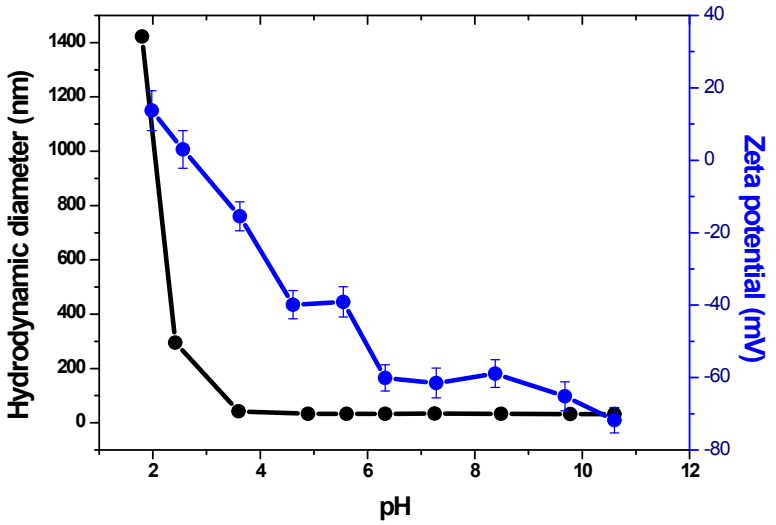


Figure10. D_h and ζ potential vs pH of MNP@**3-6**.

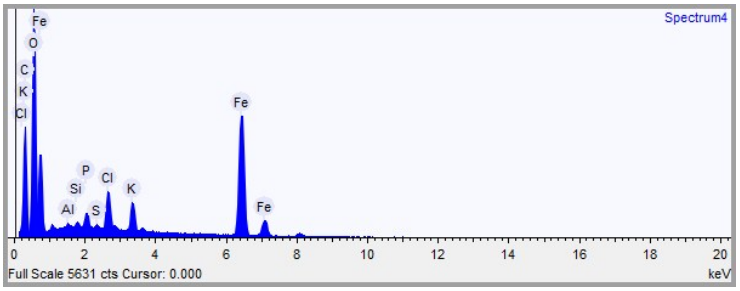


Figure11. EDX spectrum of MNP@3-**6**.

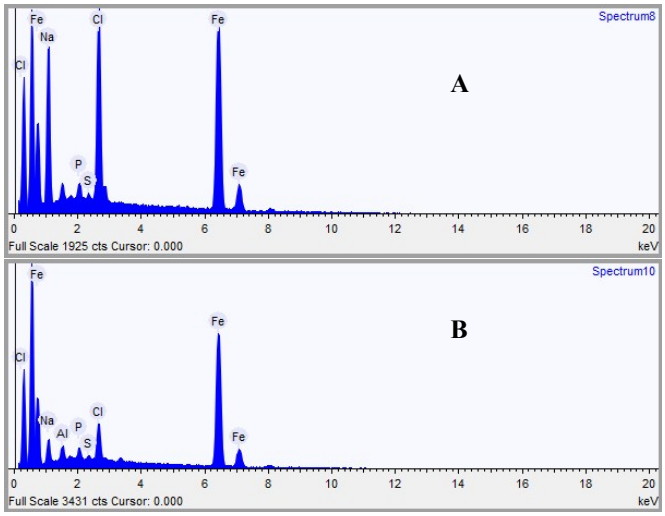


Figure12. EDX spectrum of MNP@**3-5-7**(**A**) and MNP@**3-5-8** (**B**).

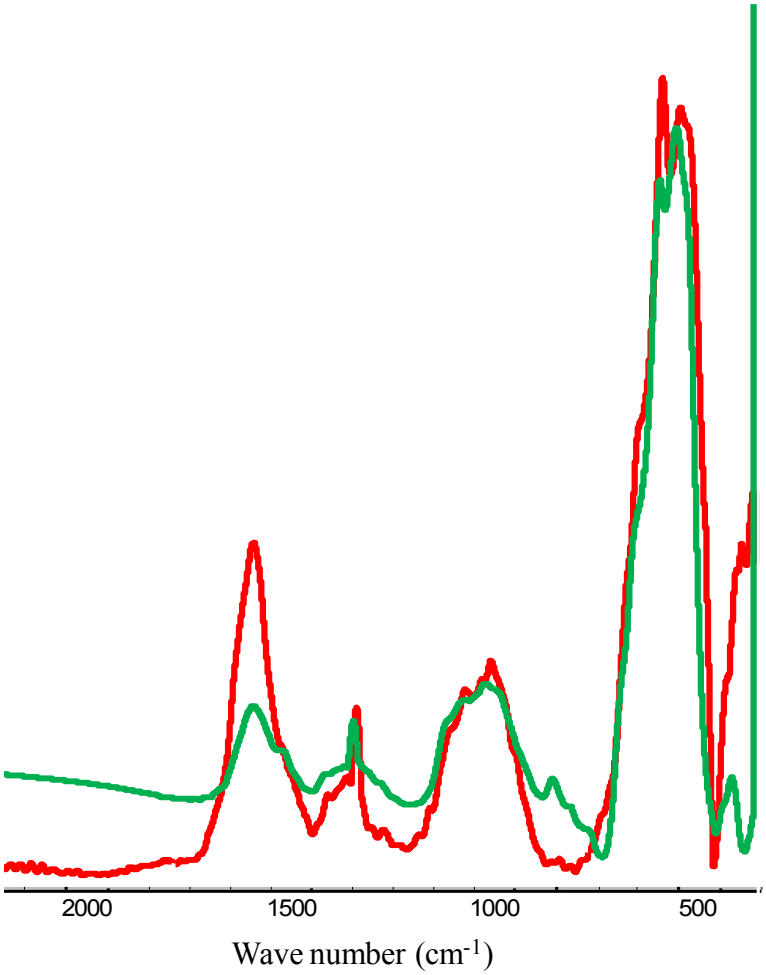


Figure13. FTIR spectrum of MNP@**3-5-7**(green) and MNP@**3-5-8** (red).

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