Electronic Supporting Information

# Growth and density control of nanometric nickel-iron cyanide-bridged objects on functionalized Si(100) surface

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## Experimental procedure for the surface functionalization

*Synthesis*.

The diluted Ni-complex (step *Ni0*) is prepared as followed: a Si-H(100) substrate (1cm × 1cm) is immersed in a mixture of neat distilled methyl 10-undecenoate and dec-1-ene in the ratio around 1/2000 beforehand degassed. The system is heated at 110°C overnight under Ar bubbling. After cooling the sample is sonicated in dichloromethane (3 times 10 minutes) and in isopropanol (once 10 minutes). To hydrolyse the ester, the surface is dipped into a solution of potassium tert-butoxide in DMSO (0.25 mol.L$^{-1}$) for 30 s at room temperature, then rinsed in acidified water (0.1 mol.L$^{-1}$ HCl). The grafting of the ligand *N*,*N*-bis[(pyridin-2-yl)methyl]propane-1,3-diamine is carried out by immersing the substrate for 10 minutes in a distilled dichloromethane solution containing the coupling agent EDC, then 10 mg of the ligand are added to the solution. The wafer is kept in the solution overnight at room temperature under Ar. Then the surface is rinsed with dichloromethane and isopropanol and dried under vacuum. Then the wafer is immersed in a methanolic solution containing $[Ni(H_2O)_6]Cl_2$ ($10^{-3}$ mol.L$^{-1}$) for 20 minutes. The wafer is rinsed thoroughly with methanol, and dried under vacuum.

The sequential growth (steps *Fe1*, *Ni1*, *Fe2*, etc) is carried out as followed: the substrate with dangling Ni complex anchoring groups is dipped 15 minutes in a water solution of $K_4[Fe(CN)_6]$ ($10^{-3}$ mol.L$^{-1}$). The wafer is rinsed thoroughly with water, and quickly with methanol to facilitate the drying under vacuum (step *Fe1*). Then, the surface is dipped 15 minutes in a methanolic solution of $NiCl_2(H_2O)_6$ ($10^{-3}$ mol.L$^{-1}$). The wafer is rinsed thoroughly with methanol, and dried under vacuum (step *Ni1*). These two procedures are repeated to complete the sequential growth.

*Physical measurements*.

•Atomic Force Microscopy (AFM) images are taken in tapping-mode with a Nanoscope III using Si tips and with the Nanosensor at a resonance frequency of 236 KHz.

•Attenuated Total Reflection Infra-red (ATR-FTIR) spectra are obtained on a IFS-66 spectrometer with 2 $cm^{-1}$ resolution. The silicon wafers have a trapezoidal form (0,5 mm x 17.5 mm x 35 mm), their two edges are cut to make an angle of 45° with the base and thus allow 75 internal reflections.

•Field Emission Gun Scanning Electron Microscope (FEG-SEM) images are obtained on a Zeiss SUPRA 55 VP. Experiments are performed under high vacuum pressure ($<1.10^{-3}$ Pa) and reduced high voltage (between 2 and 5 kV) conditions, in order to keep a good enough surface image quality and limit any charging effect.

Particles heights and widths are measured using imaging software capabilities over several fields of view to get a sufficient statistical and check reproducibility.

•X-ray Photoelectron Spectroscopy (XPS) studies were performed on a KRATOS Axis Ultra spectrometer using an Al Kα source monochromatized at 1486.6eV. The vacuum in the sample chamber is about $5x10^{-9}$ Torr during the measurements. The detector is calibrated to get the Au(4f)7/2 line at 84 eV. The Fe(2p) core levels are recorded with 150 Watt power source and 20 eV pass energy.

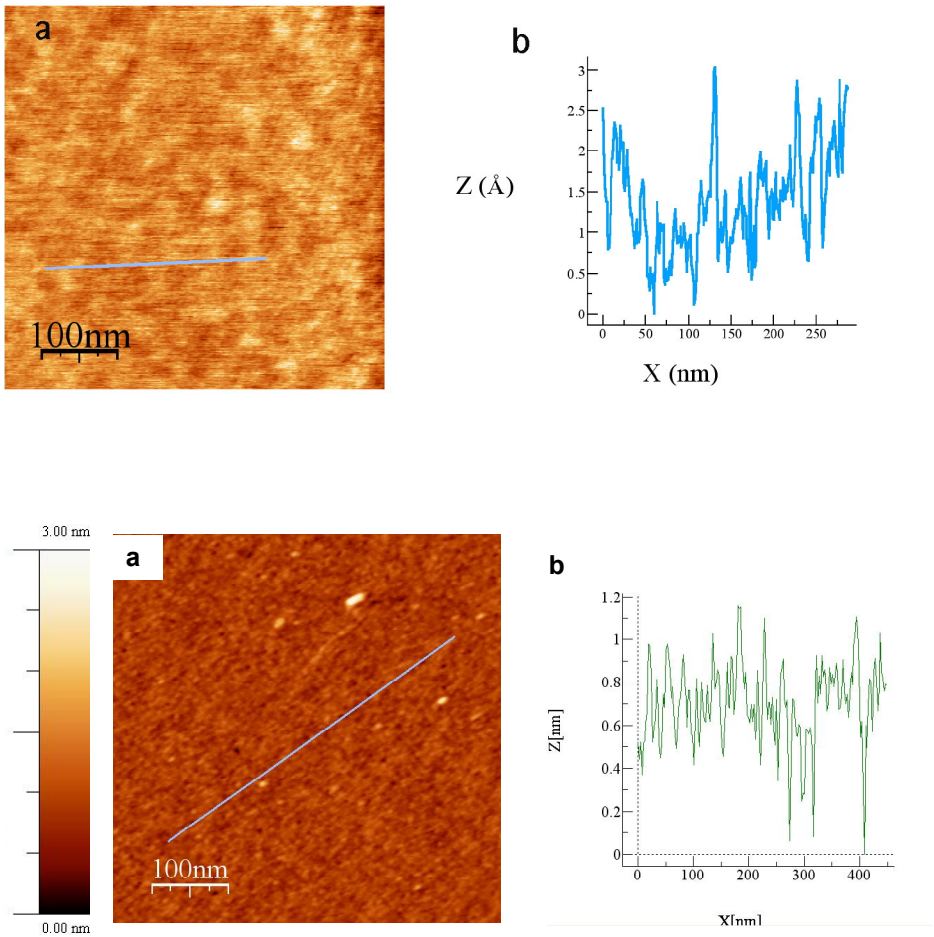



Figure S1. AFM image after hydrosylilation and before the reaction with the organic ligand (top); and AFM image at the step *Ni0* before the growth (bottom) - a) AFM image, b) profile of the AFM image, symbolized by the blue line on the image a.

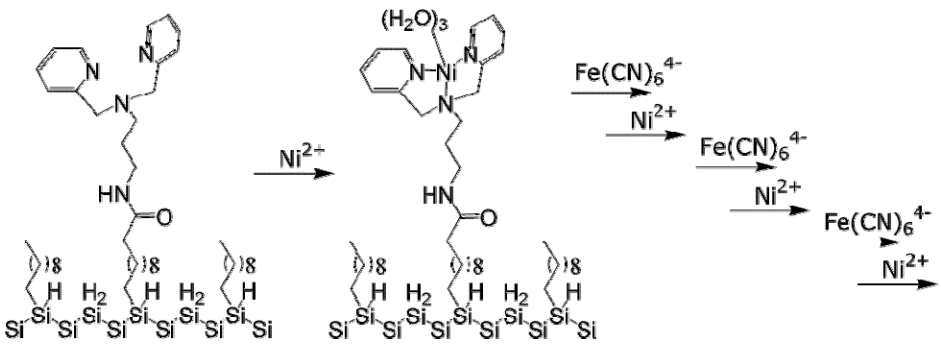



Figure S2. Sequential reaction from the monolayer of organic ligands diluted in alkyl chains to the step *Ni3* – the starting point is the metallation of the ligand cavity (*Ni0*), then the potassium ferrocyanide is added (*Fe1*), then the nickel chloride (*Ni1*), then the ferrocyanide (*Fe2*), then the nickel (*Ni2*), then the ferrocyanide (*Fe3*) and the nickel (*Ni3*).

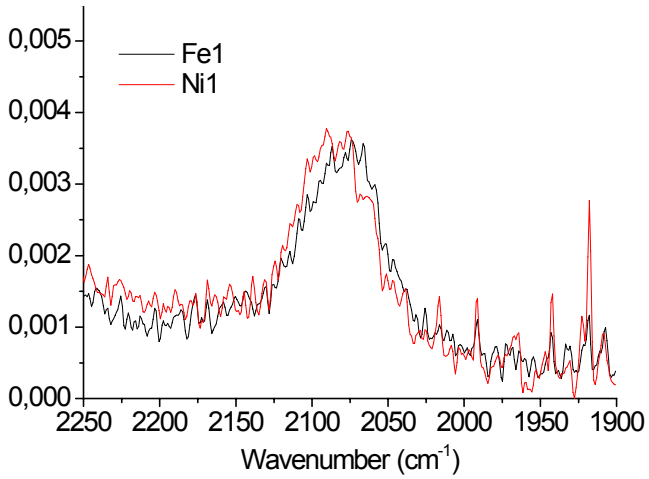
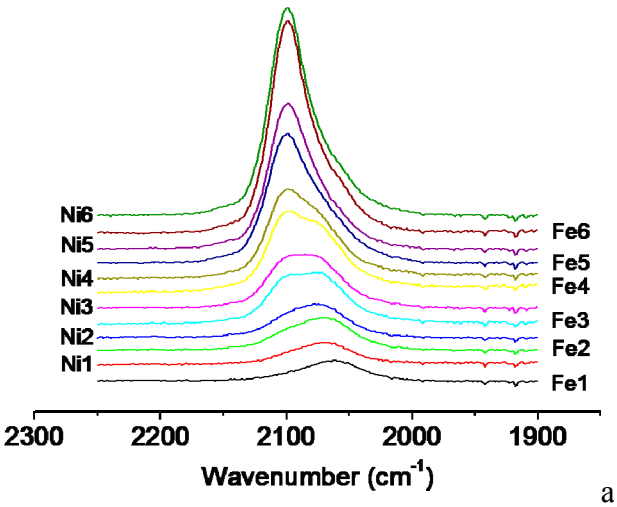



Figure S3. Attenuated Total Reflection Infra-red (ATR-FTIR) at steps Fe1 and Ni1 showing the blue shift of the cyanide vibration (from 2078 to 2084 $cm^{-1}$) upon addition of the Ni.




a b

Figure S4. Evolution of the ATR-FTIR spectra (absorbance) centered on the cyanide band from the step *Fe1* to the step *Ni6* for a surface made from pure undecenoic acid – a) spectra showing the absorbance for the different steps; the absorbance value of the baseline of all the spectra is the same but it was artificially shifted in the present figure in order to have a better view of the spectra evolution, b) peak area at each step.

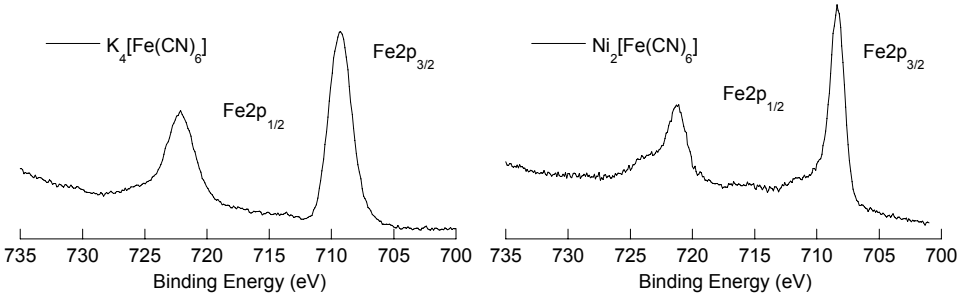



Figure S5. XPS spectra at the Fe2p edge for $K_4Fe(CN)_6$ (722.1 and 709.2 eV) and for the bulk $Ni_2[Fe(CN)_6]$ compound (721.3 and 708.3 eV).

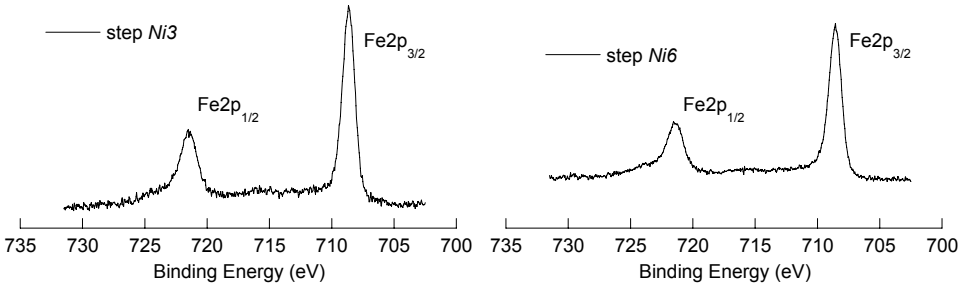



Figure S6. XPS spectra at the Fe2p edge for step *Ni3* (721.4 and 708.6 eV) and *Ni6* (721.4 and 708.6 eV).

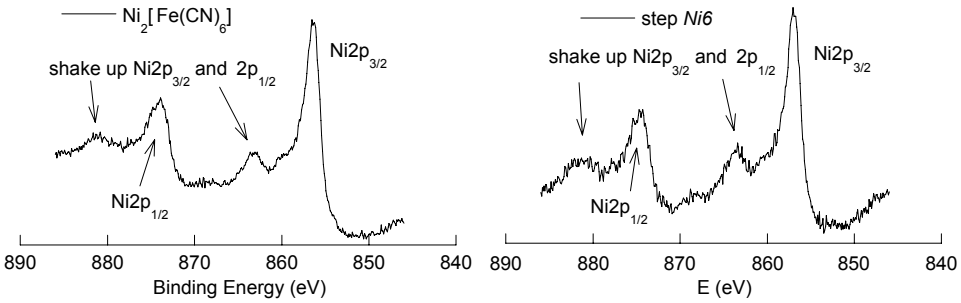



Figure S7. XPS spectra of the surface at the Ni2p edge for the bulk compound (874.1 and 856.5 eV) and for the step *Ni6* (874.6 and 856.9 eV).

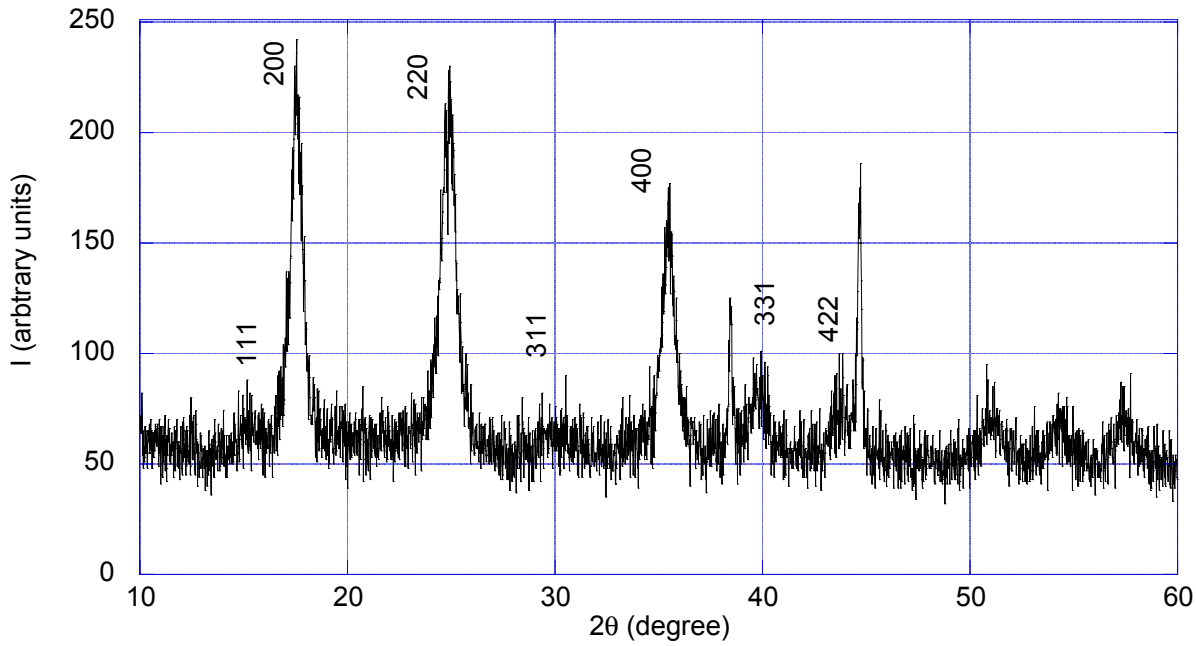



Figure S8. X-ray powder diffraction diagram of the $Ni_2Fe(CN)_6$ bulk compound showing the face centered cubic structure with a cell parameter of 1.01 nm corresponding to the distance between two metal ions of the same nature i.e. Fe-CN-Ni-NC-Fe.

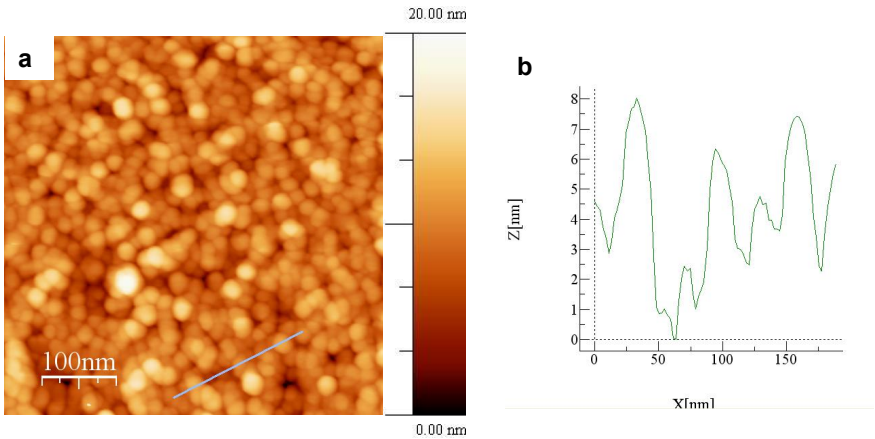



Figure S9. AFM image at the step *Ni6* of a surface where the organic layer was prepared from a solution containing a the ratio undecenoic acid/dec-1-ene = 1/100 - a) AFM image, b) profile of the AFM image, symbolized by the blue line on the image a.

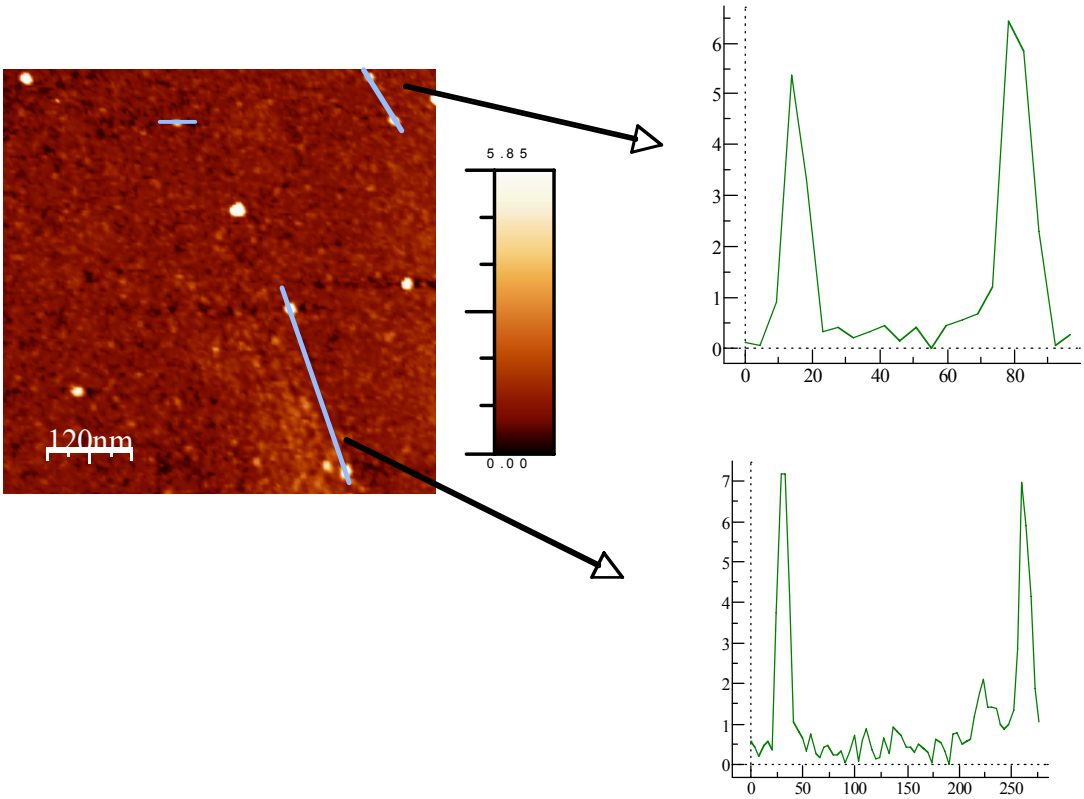



Figure S10. AFM image at the step *Ni6* of a surface where the organic layer was prepared from a solution containing a the ratio undecenoic acid/dec-1-ene = 1/ 40000) (left) and profile of the AFM image, symbolized by the blue line.