

Electronic supplementary information for:

**Patterned 2D assembling of magnetic iron oxide nanoparticles via “click chemistry”**

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**Chemicals.** Tetrahydrofuran (THF), dimethyl formamide (DMF), methanol and ethanol were purchased from Carlo Erba and used as received. Iron stearate was purchased from Strem Chemicals. Oleic acid, methanesulfonyl chloride and 11-undec-1-ynol were purchased from Alfa Aesar. Triethylamine was from Fluka and octyl ether from Aldrich.

**Synthesis of iron oxide nanoparticles coated with oleic acid (NP@OA).** NP@OA were synthesized by the thermal decomposition method,<sup>1</sup> based on our previous work.<sup>2, 3</sup> Iron stearate (Fe(stearate)<sub>2</sub>) (1.38 g, 2.2×10<sup>-3</sup> mol) was dissolved in octyl ether (20 mL) in the presence of oleic acid (1.24 g, 3.3×10<sup>-3</sup> mol). The mixture was kept at 110°C for 30 min to avoid water residues and to completely dissolve the reactants. The temperature was then carefully raised to reflux with a heating rate of 5 °C.min<sup>-1</sup> without stirring for 120 min under air. After cooling to room temperature the black suspension was washed three times with a mixture of chloroform and ethanol (v:v, 1:3) and

centrifuged (14000 rpm, 10 min). The 10 nm obtained nanoparticles were easily suspended in tetrahydrofuran (THF) at concentration of 5 mg.mL<sup>-1</sup>.

**Synthesis of azido-terminated iron oxide nanoparticles.** The functionalization of nanoparticles was achieved by direct exchange at the nanoparticles surface between oleic acid and azidoalkyl-phosphonic acid. NPs were functionalized by two molecules with different alkylene chains lengths: 2-(azidoethyl)phosphonic acid (H<sub>2</sub>PO<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>N<sub>3</sub>: AP2) and 12-(azidododecyl)phosphonic acid (H<sub>2</sub>PO<sub>3</sub>(CH<sub>2</sub>)<sub>12</sub>N<sub>3</sub>: AP12). Azidoalkyl phosphonic acid AP2 (10 mg) or AP12 (20 mg) was solubilized in 2 mL of THF. AP2 was added to a 18 mL suspension of oleic acid coated NPs (5 mg.mL<sup>-1</sup>) in a THF/DMF (v:v,9:1) mixture. DMF was used to enable the stability of NPs functionalized by the short alkylene chain AP2 which is hydrophilic. In contrast, long alkylene chain AP12 was added to a 18 mL suspension of oleic acid coated NPs (5 mg.mL<sup>-1</sup>) in a THF. The medium was stirred for 15 h at room temperature. The excess of azido phosphonic acid and desorbed oleic acid were removed by ultrafiltration (using a 30 kD membrane, Millipore) in 50 mL of the corresponding solvent.

**Synthesis of 11-(undec-1-ynyl)thioacetate (HCC(CH<sub>2</sub>)<sub>9</sub>SCOCH<sub>3</sub>).** The synthesis of 11-(undecynyl)thioacetate was carried out following a similar two-step reaction pathway published earlier by Collman *et al.*<sup>4</sup>

**Synthesis of 11-(undec-1-ynyl)methylsulfonate (HCC(CH<sub>2</sub>)<sub>9</sub>OSO<sub>2</sub>CH<sub>3</sub>).** 0.79 g of 11-undec-1-ynol (3.5 mmol) were solubilized in 35 mL of THF and followed by the addition of 1 mL of methanesulfonyl chloride. A mixture of 1.27 g of triethylamine (12.6 mmol) and 5 mL of THF was slowly added during 5 minutes to the stirring 11-undec-1-ynol solution. The reaction was carried out at room temperature for 2 hours. 35 mL of ice-cold water were added, and the organic phase was extracted twice with diethyl ether (2x35 mL). The combined organic phases were then washed several times using HCl (1

M), H<sub>2</sub>O, NaHCO<sub>3</sub> (1 M), and H<sub>2</sub>O. After drying over MgSO<sub>4</sub>, the solvent was removed via rotary evaporation yielding a pale yellow oil (0.83 g, 3.36 mmol, yield 71 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 4.18 (t, 2H) ; 2.96 (s, 3H) ; 2.15 (td, 2H) ; 1.90 (t, 1H) ; 1.71 (m, 2H) ; 1.49 (m, 2H) ; 1.2-1.4 (m, 10H).

**Synthesis of 11-(undec-1-ynyl)thioacetate (HCC(CH<sub>2</sub>)<sub>9</sub>SCOCH<sub>3</sub>).** 0.79 g of 11-(undec-1-ynyl) methylsulfonate (3.2 mmol) and 0.77 g of potassium thioacetate (7.1 mmol) were dissolved in 30 mL of methanol. The solution was degassed and refluxed under N<sub>2</sub> for three hours. After cooling to room temperature, excess methanol was removed *via* rotary evaporation and 30 mL of ice cold water were added. The mixture was extracted three times with diethyl ether (30 mL) and washed three times with water (3x30 mL). The solution was dried over MgSO<sub>4</sub> and the solvent removed by rotary evaporation yielding a yellow oil (0.60 g, yield 83 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 2.82 (t, 2H); 2.29 (s, 3H); 2.13 (td, 2H); 1.90 (t, 1H); 1.51 (m, 4H); 1.2-1.4 (m, 10H).

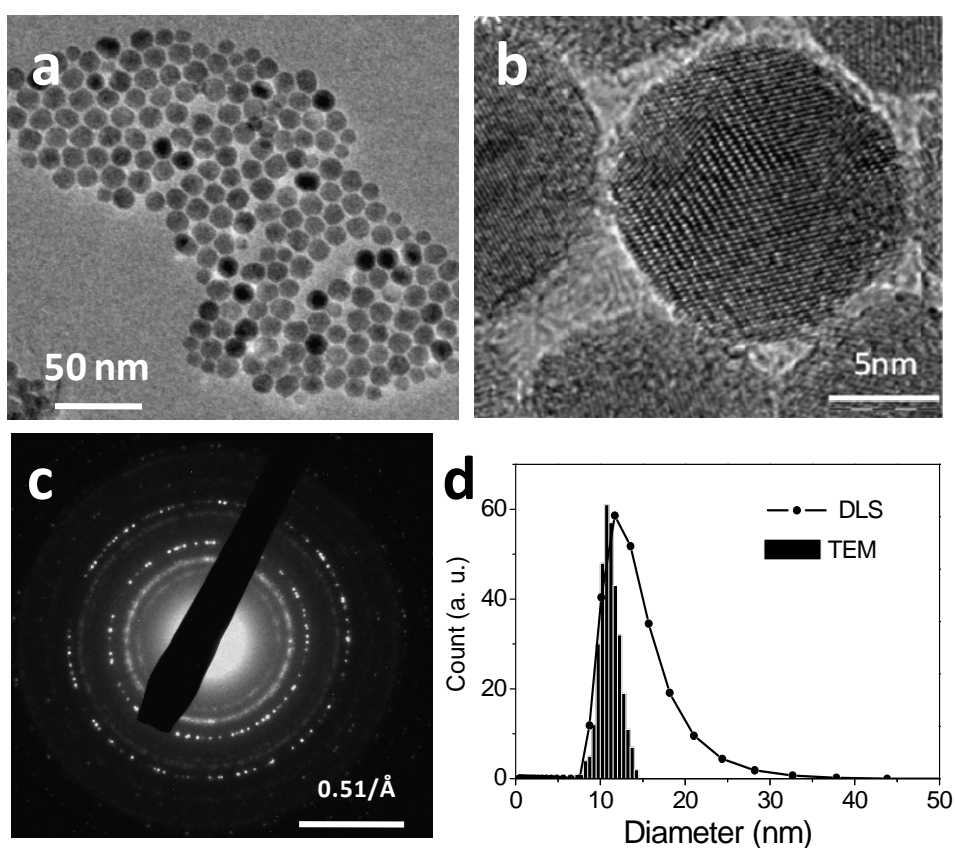
**Preparation of self-assembled monolayers.** Ion sputtered gold substrates were cleaned under O<sub>2</sub>/H<sub>2</sub> plasma and then soaked in a 10 mM ethanolic solution of 11-(undec-1-ynyl)thioacetate at room temperature for 15 h. The alkyne terminated SAM was then rinsed with copious amount of pure ethanol and use directly after drying under air. The obtained SAMs were named SAM-CC. The same process was applied to prepare SAM-CH<sub>3</sub> starting from commercial dodecanethiol (Aldrich).

**Nanoparticles assembly via the copper catalyzed alkyne-azide cycloaddition (CuAAC) “click” reaction.** The CuAAC “click” reaction was performed as reported by Moitra *et al.*<sup>5, 6</sup> Alkyne-terminated SAM were immersed in 20 mL of a solution of azidoalkyl-phosphonic acid coated iron oxide nanoparticles (NP@AP2 or NP@AP12) in the medium which was used for their preparation (5 mg/mL). 2 mL of triethylamine (14.8 mmol) and 1.3 mg of  $\text{CuBr}(\text{PPh}_3)_3$  ( $2.7 \cdot 10^{-3}$  mmol) were added. The mixture temperature was raised to reflux and kept constant during the whole time of the experiment. Two different samples were prepared according to the reaction time, SAM-1h and SAM48h.

**Characterization of NPs.** Transmission electronic microscopy (TEM), high resolution TEM (HRTEM) and electron diffraction (ED) were performed with a TOPCON model 002B TEM, operating at 200 kV, with a point-to-point resolution of 0.18 nm. The size distribution was calculated from the size measurements of more than 300 nanoparticles by using the Image J software. Granulometry measurements were performed by dynamic light scattering (DLS) on NPs suspensions using a nano-size MALVERN (nano ZS) apparatus. Fourier transform infrared FTIR spectroscopy was performed using Digilab Excalibur 3000 spectrophotometer (CsI beamsplitter) in the energy range  $4000\text{--}400\text{ cm}^{-1}$ . Samples were gently ground and diluted in nonabsorbent KBr matrices. All spectra were normalized with respect to the Fe-O stretching bond ( $590\text{ cm}^{-1}$ ).

**Characterization of SAMs.** Polarization Modulation Infrared Reflection-Absorption Spectroscopy (PM-IRRAS) was performed on gold substrates after being immersed in thioacetate solution, using a IF66S Bruker spectrometer with a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector. Typical data was derived from 2000 scans at a resolution of  $1\text{ cm}^{-1}$ ,  $85^\circ$  beam angle of incidence and 74 kHz modulation frequency. X-ray photoelectron spectroscopy (XPS) was performed with a ThermoVGScientific photoelectron spectrometer equipped with a twin anode, providing unchromatized Al KR radiation (1486.6 eV). The spectrometer, which was equipped with a

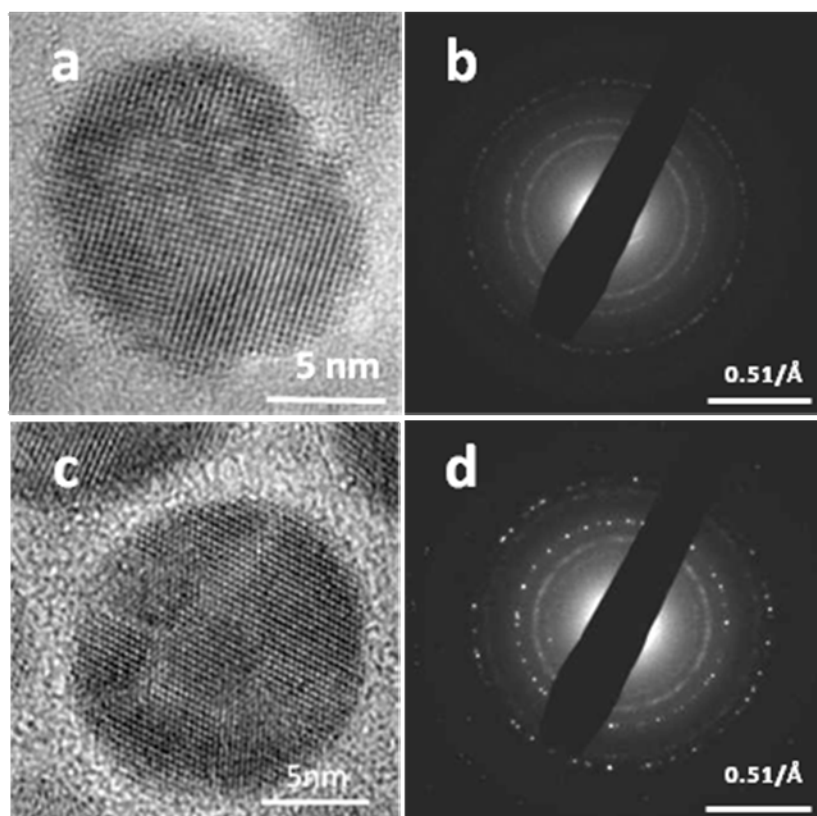
multichannel detector, operated in the constant resolution mode with pass energy of 20 eV. The total resolution of the system was estimated to be 0.55 eV. The energy scale is referred to the Au 4f7/2 line at a binding energy of 84 eV. The spectra were fitted by using a linear background and the Gaussian function. Scanning electronic microscopy (SEM) were studied after being immersed in the suspension of nanoparticles with a JEOL 6700 scanning electronic microscope equipped with a field emission gun (SEM-FEG) operating at an accelerating voltage of 3 kV.



**Figure S1.** Nanoparticles coated with oleic acid (NP@OA). a) TEM micrograph, b) HRTEM micrograph, c) electron diffraction pattern and d) size distribution calculated from TEM micrographs and hydrodynamic diameter of a NP@OA suspension in THF measured by dynamic light scattering.

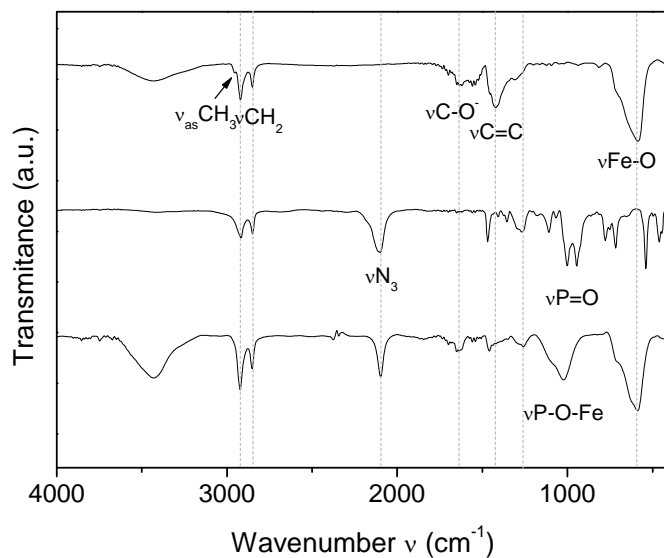
The thermal decomposition reaction yields spherical shaped NP@OA with narrow size distribution (centred at  $11.2 \pm 1.0$  nm) as observed by TEM (Figure S1a,d). NPs are single crystal as

shown by HRTEM (Figure S1b) and their structure can be indexed in the spinel structure (magnetite or maghemite) as shown by the electron diffraction pattern (Figure S1c). NPs coated by oleic acid lead to a highly stable suspension in THF which is featured by a hydrodynamic diameter centred at  $13.0 \pm 2.1$  nm as shown by granulometric measurements (Figure S1d).



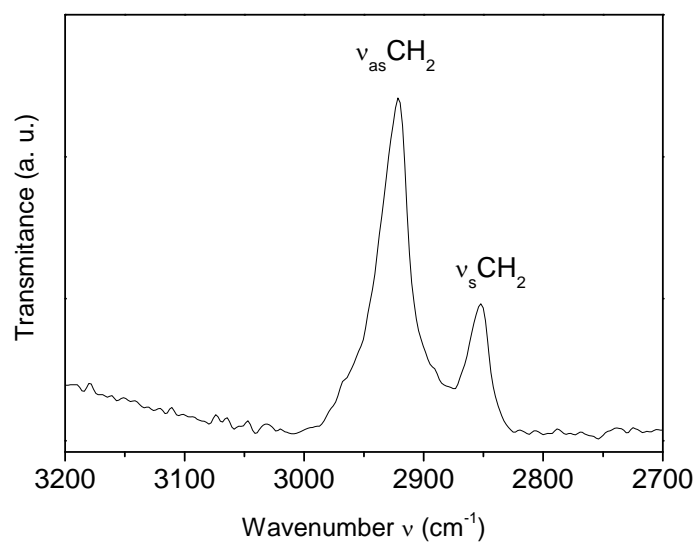
**Figure S2.** Azide-terminated nanoparticles (a,b) NP@AP2 and (c,d) NP@AP12. (a,c) HRTEM micrographs and (b,d) electron diffraction patterns.

After replacement of the oleic acid by azido-alkyl phosphonic acid (AP2 and AP12), the structure of NPs remain unchanged. High resolution TEM and electron diffraction show that all NPs are single crystal in the spinel structure (magnetite or maghemite) (Figure S2).

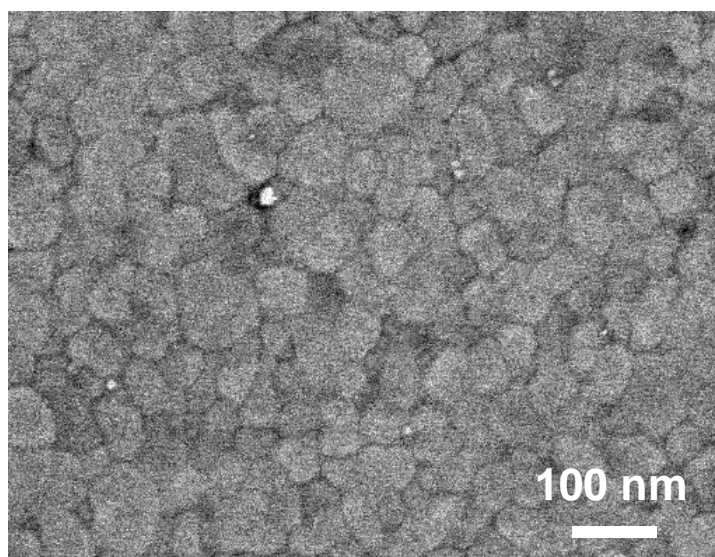


**Figure S3.** FTIR spectra of NPs coated with oleic acid (NP@OA), 2-azidoethyl-phosphonic acid (NP@AP2), 11-azidododecyl phosphonic acid (NP@AP12).

NP@OA and NP@AP12 spectra are normalized with respect to the  $\nu\text{Fe-O}$  stretching band at  $589\text{ cm}^{-1}$  which shows the presence of iron oxide NPs in all samples. AP12 and NP@AP12 spectra are normalized with respect to the  $\nu\text{N}_3$  stretching band at  $1196\text{ cm}^{-1}$  which refers to azide groups.

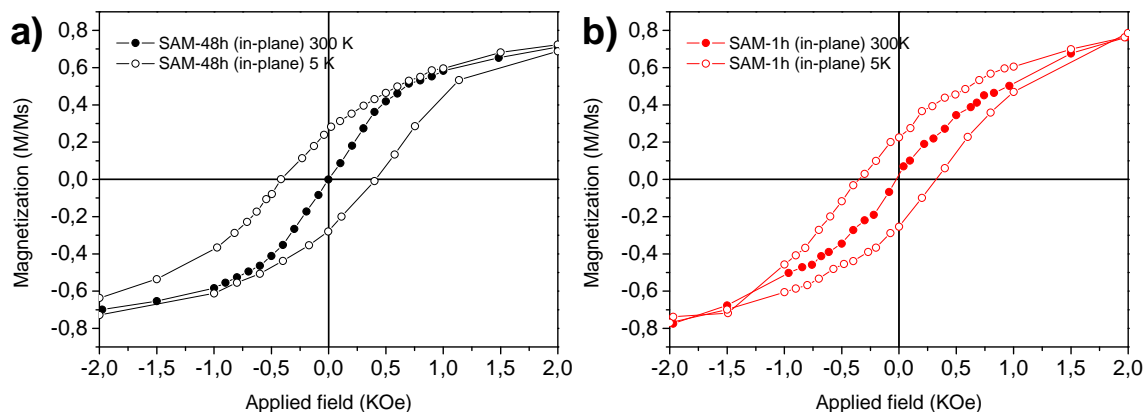


**Figure S4.** PM-IRRAS spectrum of alkyne-terminated SAM.



**Figure S5.** SEM micrograph of methylene-terminated SAM after performing the CuAAC "click" reaction for 48 h.





**Figure S6.** Magnetization versus an applied magnetic field recorded in the plane of the film at 300 K and 5 K for SAM-48h (a) and SAM-1h (b).

## References

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