

## Electronic Supplementary Information

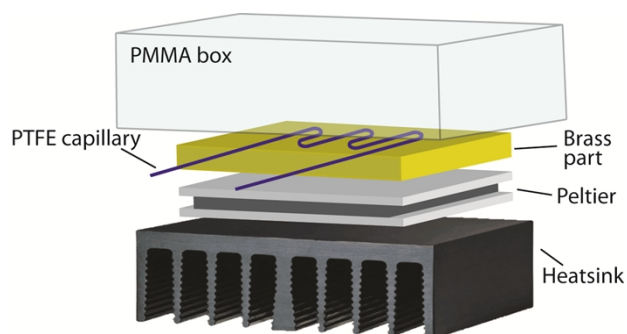
### Continuous chemical operations and modifications on magnetic $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles confined in nanoliter droplets for the assembly of fluorescent and magnetic $\text{SiO}_2@\gamma\text{-Fe}_2\text{O}_3$

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#### 1. Microfluidic droplets heater



**Figure S1:** Scheme of the microfluidic heater: a serpentine is milled on a brass surface in order to hold the PTFE capillary where droplets flow. The metal part is prepared by micro-milling machine (MiniTech machine). Temperature is controlled by a Peltier (by Radiospares), connected to an electronic PID control system (3508, by Eurotherm) which can be programmed in order to warm or cool down the temperature of the Brass part and so of the capillary. The feedback is guaranteed by a thermocouple fixed in the metal. All the parts are placed in contact by thermal grease (Metal Oxide Heatsink Compound by Radiospares) and PMMA transparent box is placed around in order to avoid thermal dispersions and isolate the system.

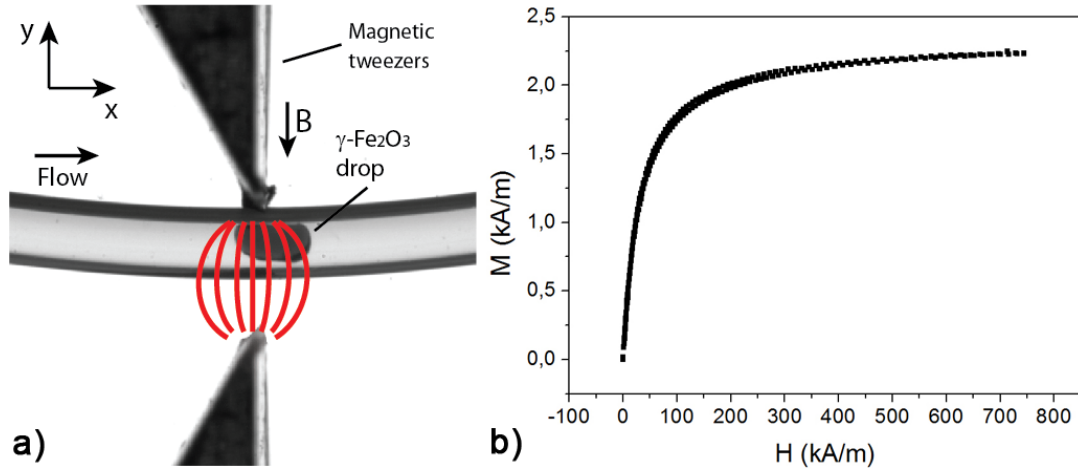
#### 2. Evaluation of magnetic and colloidal forces

The magnetic field applied by the magnetic tweezers on the  $\gamma\text{-Fe}_2\text{O}_3$  NPs confined in droplet results in the trapping of the droplet. This behaviour is different than what we observed for micrometric particles where, switching ON the magnetic field, a cluster of particles in correspondence of the tweezers is immediately formed.<sup>1</sup> This difference is due to the colloidal force which keeps the NPs stable in the water phase solution.

In order to estimate the magnetic force applied by the magnetic tweezers to the  $\gamma\text{-Fe}_2\text{O}_3$  NPs we used the same approach that we presented in ref <sup>1</sup>. The magnetic force  $F_m$  can be expressed as  $F_m \approx V \cdot M \cdot \vec{\nabla} B$ , where  $V$  is the total volume of the NPs,  $M$  is the magnetization and  $\vec{\nabla} B$  is the gradient of the magnetic field  $B$ . Therefore, at first we evaluated the magnetic field and its gradient simulating the system by Comsol Multiphysics. Since the droplet trapped is not symmetrically placed compare to the magnetic tweezers and the magnetic field lines schematized in red (see Figure S2a), we took into account the contribution of  $B$  and  $\vec{\nabla} B$  in both  $X$  and  $Y$  orientation. Then, considering the total volume of the NPs presented in a droplet and their magnetization curves showed in Figure S2b, we obtained values of  $F_m$  having an order of magnitude of hundreds of pN. In particular it is found between 50-150pN along  $X$  and 100-300pN along  $Y$ .

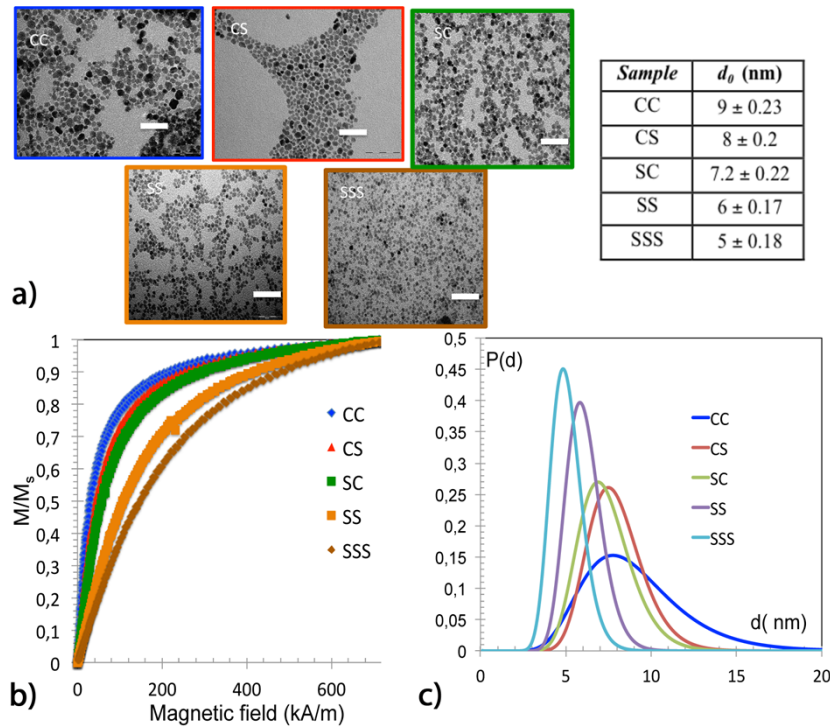
For the estimation of the colloidal force of the ferrofluid we followed the approach presented by Cousin et al.<sup>2</sup> where the same  $\gamma\text{-Fe}_2\text{O}_3$  NPs that we used were considered. In the DLVO model the colloidal stability is ensured due to two contributions: the Van der Waals and the electrostatic interactions between the NPs. Therefore considering that the  $\gamma\text{-Fe}_2\text{O}_3$  NPs are dispersed in nitric acid which presents an ionic strength  $I$  of  $10^{-3}$  M, the NPs average radius  $R$  of 5nm, the debye length<sup>3</sup>  $\kappa^{-1}$  of 6nm, the effective charge<sup>3</sup>  $Z$  of about 200 and a distance between the surfaces of 2 NPs of  $2R$  (=10nm), we calculated a colloidal force of 75pN.

The roughly estimated magnetic and the colloidal forces are both in the range of hundreds of pN, which explain why the super-paramagnetic NPs are effected by the magnetic tweezers (in fact the droplet is stopped), but the colloidal suspension remains stable.



**Figure S2:** (a) Scheme of the magnetic field applied by the magnetic tweezers on the droplet containing the  $\gamma\text{-Fe}_2\text{O}_3$  NPs. (b) Magnetization curve ( $M$ ) as function of the applied magnetic field strength ( $H$ ).

### 3. $\gamma\text{-Fe}_2\text{O}_3$ magnetic nanoparticles

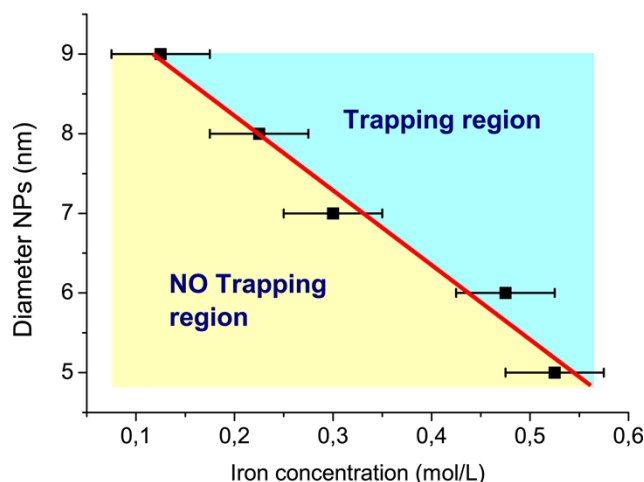


**Figure S3:** (a) Transmission electron micrographs of size-sorted maghemite samples. (b) Magnetization  $M$  of samples normalized to magnetization saturation  $M_s$  as a function of the applied magnetic field is well fitted by Langevin's law weighted by the log normal distribution of particle diameter (solid lines). (c) Size distributions deduced from the fit of magnetization curves for samples. The corresponding characteristic diameters and polydispersity index are indicated in the table. Scale bars in all figures are 50 nm.

### 4. Phase diagram for trapping $\gamma\text{-Fe}_2\text{O}_3$ droplet by magnetic tweezers

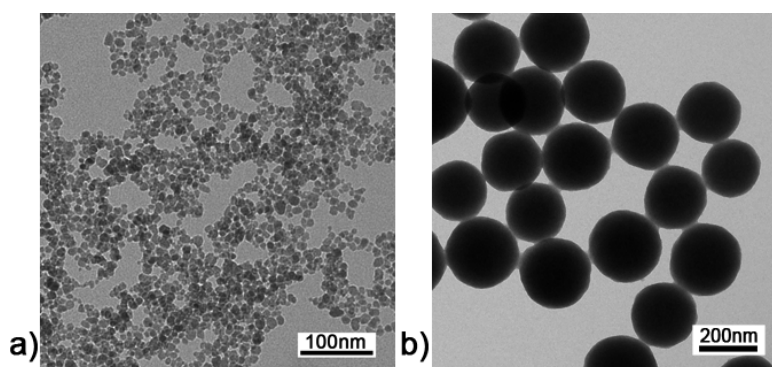
The capability of trapping the magnetic maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) droplet depends on magnetic field gradient from the tweezers, NPs stability, diameter and quantity. Figure S3 reports the phase diagram of the magnetic tweezers capability in trapping or not the  $\gamma\text{-Fe}_2\text{O}_3$  as function of NPs diameter (between 5-9nm) and iron concentration, at constant magnetic field (about 0.3T) and flow rate (0.02 $\mu\text{L/s}$ ). It shows that

the higher is the concentration and the higher is diameter of NPs, the easier is the droplet trapping. In other words, a minimal critical concentration of NPs is needed in order to facilitate the droplet manipulation. This concentration is smaller for larger particles. These observations follow the expected behaviour considering that higher concentration and diameter correspond to less stable colloidal solution and that the magnetic force is proportional to the quantity of magnetisable material presents in the droplet.



**Figure S4:** Phase diagram describing when the  $\gamma\text{-Fe}_2\text{O}_3$  droplet can be trapped (blue zone) or not (yellow zone) by the magnetic tweezers. We evaluate different concentrations in the two regions and the black points refer to the average values of the interval between the smaller and the higher concentration found for the trapping condition, which corresponds to the error bar extremities. Droplets of 50nL were used for the characterization.

## 5. TEM image of NPs



**Figure S5:** TEM images of a)  $\gamma\text{-Fe}_2\text{O}_3$  (average diameter  $9\pm0.23$  nm) and b) RITC-SiO<sub>2</sub> ( $200\pm4$  nm) NPs used for the nanoassembly reactions.

## 6. Preparation of the NPs' sample for the TEM characterization

The assembly generated by the droplet microfluidic approach was characterized by TEM image. In order to prepare the sample without diluting the NPs dispersed in droplet, we placed the droplet kept in the Teflon capillary directly on a TEM grid (CF300-Cu by Electron Microscopy Sciences) and then, 1 $\mu$ L of Ethanol was deposited on it. As a matter of fact, the volume of the droplet (about 250nL) is not enough to cover all the grid and the ethanol help to spread the solution. After the deposition, the grid was dried at room temperature overnight before making the observation. During the direct droplet deposition on the grid, some oil is inevitably deposited as well; in order to deposit as less oil as possible, the capillary was placed on the grid just at the last moment and removed immediately after the droplet touched the grid. This expedient allows depositing a quantity of oil which does not create any problem during the TEM characterization.

**Movie 1 - micrometric particles:** Droplets of 200nL flowing in correspondence of the magnetic tweezers. When the first droplet containing micrometric magnetic beads (diameter 1 $\mu$ m, MyOne by Life Technology) pass close to the magnetic tip, the magnetic field is switched ON and the beads are aggregated and extracted by the droplet. This happens because the magnetic force is higher than the capillary force and the beads cluster can be extracted breaking the original droplet in two droplets. Additionally, since the beads are not stably dispersed in the solution, when they experience the magnetic field gradient they immediately precipitate.

**Movie 2 - droplet trapping:** Droplet of 50nL of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> can be blocked by the magnetic field applied by the magnetic tweezers. The oil flow is never stopped (0,02 $\mu$ L/s) and the droplet stays blocked at the tweezers until the magnetic field is ON.

**Movie 3 - destabilization by acetone:** Droplet of 100nL of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> + sodium citrate after 5 minutes at 60°C is blocked at the tweezers. The incoming droplet of Acetone/water (50/50% w/w) destabilizes the colloidal suspension, resulting in the precipitation and extraction of the NPs, as happened for the unstable beads solutions (see Movie 1).

**Movie 4 - mixing with citrate:** Droplet of 50nL of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> is blocked by the magnetic tweezers and mixed with the following droplet containing the sodium citrate solution. Immediately after the merging, the solution in the droplet looks unstable.

**Movie 5 - washing:** In order to wash the NPs from the acetone, two water droplets are flowing through the cluster.

**Movie 6 - mixing with MOPS:** The washed cluster of NPs is mixed with the following droplet of MOPS.

**Movie 7 – homogeneous magnetic field:** RITC-SiO<sub>2</sub>@ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoassemblies confined in a water phase droplet in experience a magnetic field oriented as indicated by the arrow. In detail, at first the magnetic field is OFF and NPs are distributed homogenously in the droplet; when the magnetic field is switched ON, the NPs are immediately oriented following the magnetic field lines indicated by the white arrow.

**Movie 8 - magnetic field gradient:** RITC-SiO<sub>2</sub>@ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoassemblies confined in a water phase droplet in the presence of a magnet, which is moved on the right and on the left side of the droplet. The NPs experience a magnetic field gradient which attracts them to the magnet.

## ESI Reference

- 1 A. Ali-Cherif, S. Begolo, S. Descroix, J.-L. Viovy and L. Malaquin, *Angew. Chem. Int. Ed. Engl.*, 2012, **51**, 10765–9.
- 2 F. Cousin, E. Dubois and V. Cabuil, *Phys. Rev. E*, 2003, **68**, 021405.
- 3 I. T. Lucas, S. Durand-Vidal, O. Bernard, V. Dahirel, E. Dubois, J. F. Dufrêche, S. Gourdin-Bertin, M. Jardat, G. Meriguet and G. Roger, *Mol. Phys.*, 2014, **112**, 1463–1471.