Electronic Supplementary Information

Positioning a single Metal Organic Framework particle using the magnetic field.

Paolo Falcaro, Florance Lapierre, Benedetta Marmiroli, Mark J. Styles, Yonggang Zhu, Masahide Takahashi, Anita J. Hill, Cara M. Doherty

S.1 Experimental Detail

Precursors

Pluronic F127, 1,4-benzenedicarboxylic acid (BDC), 2-amino-1,4-benzenedicarboxylate (NH2-BDC), N,N-Diethylformamide (DEF), $Zn(NO_3)_2 \cdot 6H_2O$, carbon coated cobalt nanoparticles (<50 nm, Sigma-Aldrich), $AgNO_3$, tetraethyl orthosilicate (TEOS), (3-Glycidyloxypropyl)trimethoxysilane (GLYMO) where purchased from Aldrich and used without further purification.

Preparation of the magnetic framework composite (NH_2-MC-FCs)

The amino functionalized MOFs embedding cobalt nanoparticles (NH_2-MC-FCs) have been prepared by dissolving 0.075 g of BDC and 0.026 g of NH_2-BDC in 16.5 ml DEF under sonication for 10 minutes. 0.877 g of $Zn(NO_3)_2 \cdot 6H_2O$ have been added to the solution and further sonication for 10 minutes was performed.

Pluronic F127 (0.2 g) has been added to the MOF mother batch solution and after 20 minutes of sonication the surfactant was completely dissolved. Finally, 1.6 mg of carbon coated cobalt nanoparticles has been added. Sonication occurred until the particles have been homogeneously dispersed (the solution becomes dark and only partially transparent).

The vial containing the final solution has been heated at 95°C. Depending on the length of the solvothermal growth, different crystal sizes have been obtained. Typically, 36 hours are enough to induce the formation of cubic crystals used for the reaction within the capillary (80-100 micron).

The final MOF lattice will include 25% of the amino-functionalized ligands. An example of a unit cell with amino-functionalized ligands is presented in Figure S1.1

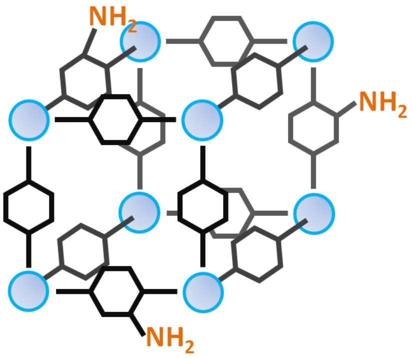


Figure S1.1: schematic of a random distribution of a 25% of NH_2-BDC and 75% of BDC in a Fm-3m unit cell.

Preparation of the Ag-solution.

A solution containing silver ions has been prepared adding 0.03g of $AgNO_3$ in 18 ml of methanol. After 1 h of sonication a transparent and colorless solution has been obtained.

Preparation of the Silica nanoparticles

Silica nanoparticles have been prepared using the classical Stöber approach. In particular tetraethoxyorthosilicate has been added to a mixture of ammonia and ethanol. The recipe and the calibration curve presented by Costacurta et al.[1] has been chosen to prepare particles of about 150 nm in diameter.

After 24 hours reaction, the particles have been washed 8 times with ethanol and then dried in the oven for 48 hours. An amount of 0.01 g of the silica nanoparticles has been added to 3 ml of toluene; then 30 µlof (3-Glycidyloxypropyl)trimethoxysilane (GLYMO) has been added in order to functionalize the silica nanoparticle surface. The solution has been kept at 50°C for 48 hours. According with the procedure proposed by Gopinath et al.[2] these conditions would ensure the partial functionalization with the epoxysilane. The particles have been centrifuged at 4000 rpm for 30 seconds and the solution has been replaced with fresh toluene. After 15 minutes of sonication, a new centrifugation and replacement of the solvent has been done. Following this procedure, 3 washing cycles with toluene and 2 with methanol have been performed. Finally, the powder has been dried under vacuum.

Preparation of the epoxy-SiO_2 functionalized colloidal solution

The epoxy-SiO_2 functionalized colloidal solution has been prepared by adding 0.01 g of the epoxyfunctionalized dried powder in 2 ml of methanol. The solution has been sonicated until the particles were homogenously dispersed.

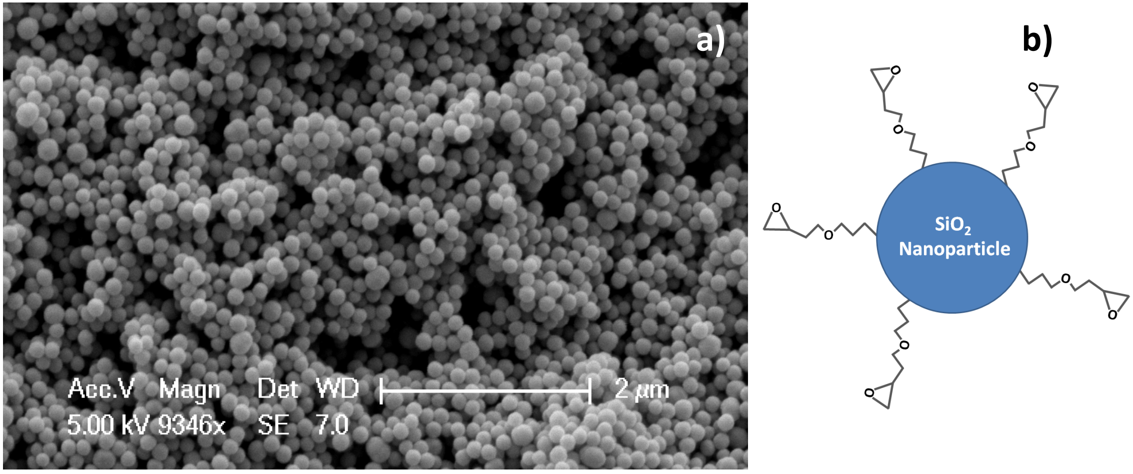


Fig. S1.1 SEM image of the functionalized silica nanoparticles from the colloidal solution (a); the particles have a functionalized surface as presented in the schematic (b)

Fabrication of the Microfluidic circuit presented in the TOC

The microfluidic circuit has been fabricated in two steps. First, a master in silicon and SU8 resin has been prepared with the microchannels in relief; finally a casting of PDMS (Polydimethysiloxane) has been performed in order to obtain the final circuit.

The master has been prepared as in the following. SU8-2025 has been purchased by MicroChem Corp. and has been spun on a silicon wafer at 2000 rpm for 1 minute. The post bake has been conducted on a hot plate at 65°C for 1 min and at 95°C for 5 minutes. The lithography has been performed with a conventional UV source with i-line (365 nm) radiation (Karl Suss MJB3 mask aligner) for 40 s. The post bake has been conducted on a hot plate at 65°C for 3 min and at 95°C for 5 min. The sample has then been developed in MicroChem´s SU8 developer for few minutes and rinsed in isopropanol.

The casting has been prepared using the following; Sylgard 184 PDMS kit has been purchased by Dow Corning Corp. The PDMS has been prepared with a ratio between resin and crosslinker of 10:1 in weight. The liquid PDMS has been poured on the master. The sample has been degassed for 5 minutes in a glass vacuum bell, and then put in an oven at 95°C for 3 hours. After cooling down, the cured PDMS with the microchannels has been peeled off the master.

The channels have been sealed with a glass slide by plasma oxygen bonding using a plasma reactive ion etching apparatus (Sistec s.r.l.) for 20 seconds at 50W.

Fabrication of the Microfluidic circuit presented in the Figure 3 (Main text)

The microfluidic chip was fabricated using the standard photolithography technique. First, a SU-8 mold was fabricated on a Si wafer using the following protocol:

The Si wafer was cleaned with acetone/isopropyl alcohol and dried under nitrogen flow. It was then treated by piranha etching (H2SO4/H2O2 3:1 v/v) for 10 minutes, following by a HF (5%) etching for 1 minute to remove the native oxide on the Si wafer to increase hydrophobicity and adhesion of the photoresist. The SU-8 2050 (MicroChem) solution was spin-coated (3000 rpm, 300 rpm.s-1, 30 s) and soft baked at 65°C then 95°C for 3 minutes and 9 minutes, respectively. After baking, the substrate was exposed to UV light at 200mJ/cm2 through a mask and post-baked at 65°C then 95°C for 2 minutes and 7 minutes, respectively. The photoresist was developed by immersion in a solution of SU-8 developer for 6 minutes, rinsed with isopropyl alcohol and deionised water, the dried under nitrogen flow.

The thickness of the photoresist was 55µm. The mold was coated with a hydrophobic monolayer of octadecyltrichlorosilane (OTS). This last step gives the total wafer hydrophobic property, necessary for the PDMS pealing. The static contact angle of the coated mold surface with water droplet was about 110°.

The microfluidic device was fabricated with poly(dimethylsiloxane) (PDMS). First, the PDMS was mixed with its curing agent (1:10 w/w) and de-gassed under vacuum for 20 minutes. PDMS was then poured on the SU-8 mold and heated on a hot plate for 10 minutes at 100°C. Tubing access points were made by creating holes in the PDMS with a 1.5 mm diameter puncher. The resulting PDMS chip was introduced in a plasma chamber with a glass slide (100 µm thick) and the sealing was produced after 30 seconds of air plasma and 10 minutes on a hot plate at 90°C. Silicon tubes with 1.5 mm diameter were inserted in each access, sealed with PDMS and the chip was finally cured to seal the connection.

S.2 Immiscibility between Dodecane and Methanol

The immiscibility between Methanol and Dodecane is evident if a dye is dissolved in the alcohol. In the present case, 60 mg of Sodium 4-[(1-hydroxynaphthalen-2-yl-hydrazinylidene]-7-nitro-3-oxo-Y-naphthalene-1-sulfonate, also called Eriochrome Black T, has been dissolved in 6 ml of methanol (dark solution in Figure S3.1). Injecting the coloured alcoholic solution in the alkane (colourless solution) macroscopic dark droplets are formed almost instantaneously.

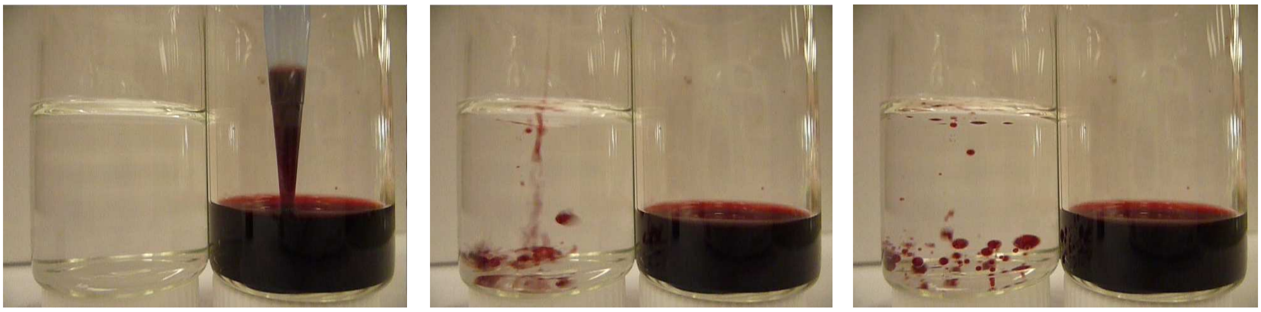


Figure S3.1: test of immiscibility between the dodecane (transparent solution) and methanol with a dye. After the injection of the methanol in dodecane, droplets of methanol can be clearly observed.

Ag-solution and dodecane

The Ag solution prepared as described in S1, is transparent, therefore the immiscibility with dodecane can be detected by the meniscus can be seen in **figure S3.1a**. The same vial uncovered has been exposed to UV light from the top for 2 hours. The formation of metallic silver is detected as a gray powder at the bottom part of the meniscus.

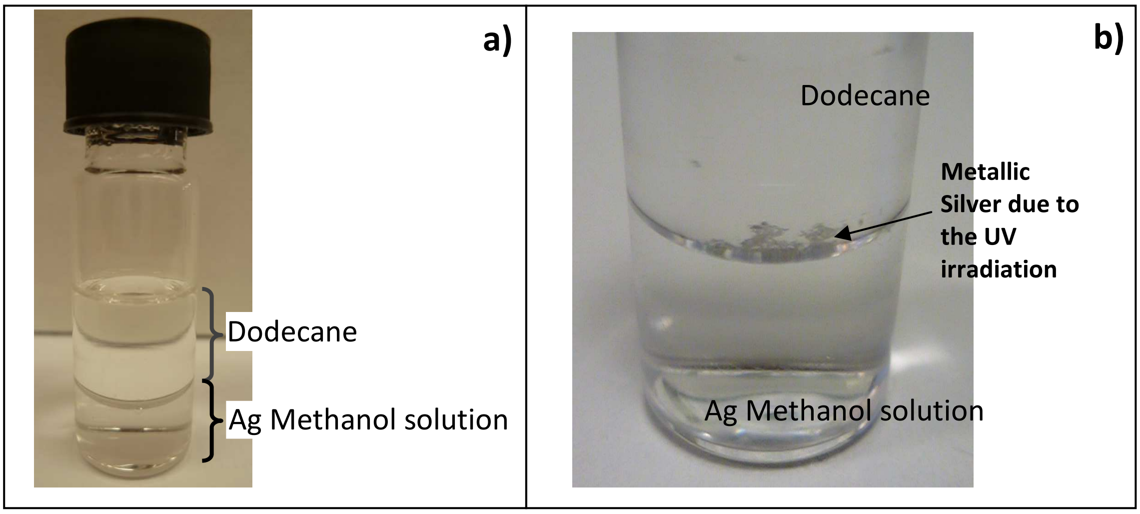


Figure S3.2: a) test of immiscibility between the dodecane (transparent solution) and Ag-solution. To prove the presence of silver ions, the solution has been exposed to UV light (254 and 364 nm) for 2 hours; the formation of metallic silver can be detected by eye.

Epoxy-SiO_2 functionalized colloidal solution and dodecane

The methanol Epoxy-SiO_2 functionalized colloidal solution is a white and opaque solution. Once it is mixed with dodecanel the separation can be clearly seen (Figure S3.3)

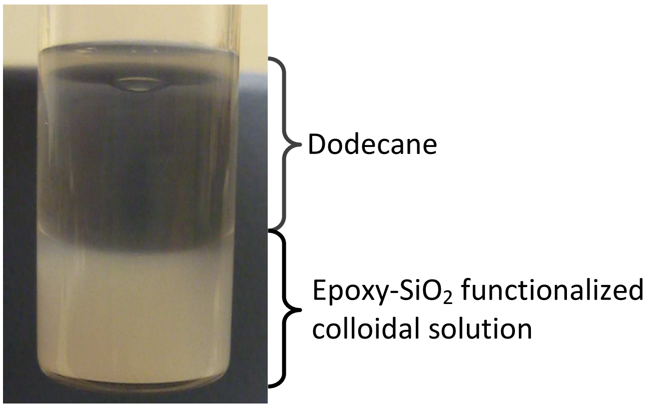
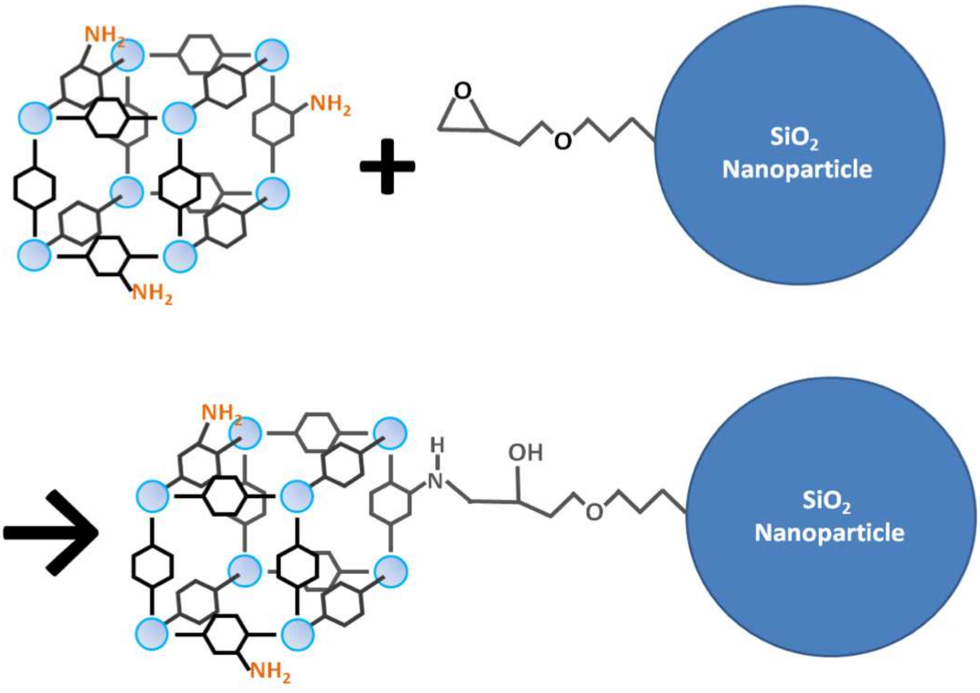


Figure S3.3

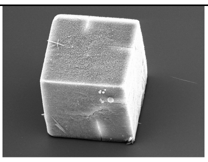
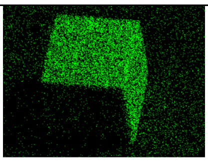
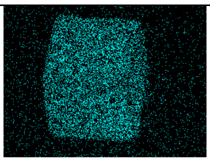
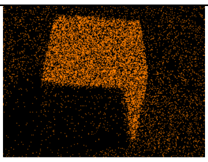
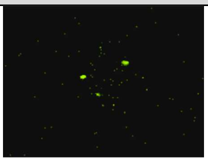
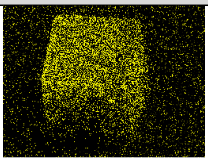
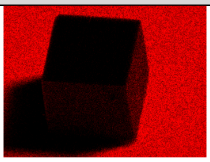
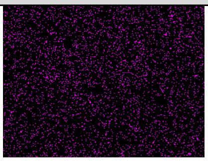
Reaction between the amino functionalized ligand and the epoxy silane

As Le Craz et al.[3] described, the amine undertakes nucleophilic attack on the α – carbon of the epoxy ring originating a pendant hydroxyl group. The same mechanism was used by Brusatin et al.[4] to react amino-silanes with epoxy-silanes and creating silane-based functional materials. In the present case, the reaction between NH_2-BDC and the epoxy-silane decorating the SiO_2 particles is represented in the following schematic.



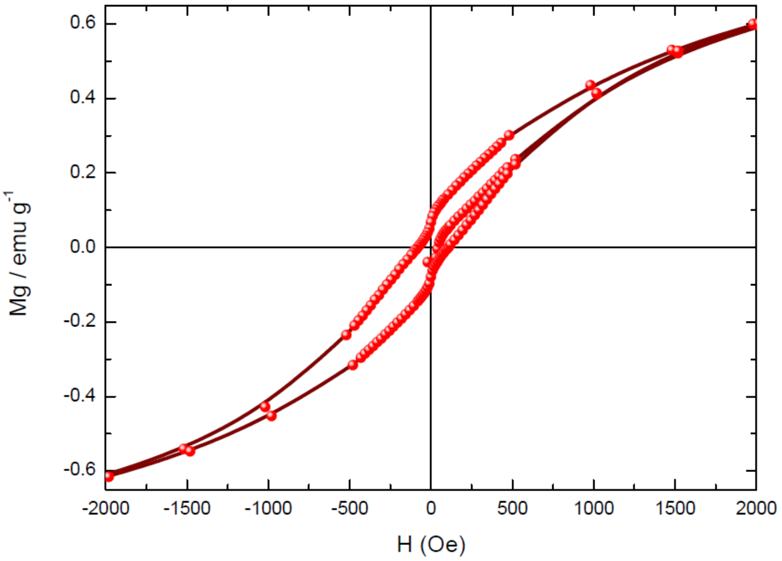
S.4 Energy dispersion X-Ray analysis (EDS).

The energy dispersive X-ray analysis has been performed using 20 KeV. Different contrasts have been applied in order to better highlight the different elements.

 **SEM of the crystal**	 **C Kα1_2 (framework)**	 **Zn Kα1 (framework)**	 **O Kα1 (framework)**
 **Co Kα1 (magnetic nanoparticles)**	 **Ag Kα1 (Uptaked metal ion)**	 **Si Kα1 (Substrate)**	 **Ir Kα1 (Sputtered conductive coating)**

The C, Zn and O signals are related to the metal organic framework elemental composition; the Co signal is due to the magnetic nanoparticles (clusters can be detected); the Ag signal is due to the uptaken ion once the porous crystal has been immersed in the Ag-solution; the Si signal is induced by the silicon wafer used as a substrate. The noise in the pictures is due to the fact that the mapping has been collected with a smaller spot channel in order to increase the resolution of the SEM images.

S.5 Magnetic Properties of the NH_2-MC-FCs



Magnetization curve of NH_2-MC-FCs. The measurement was performed at 300K. A magnetic response is a combination of the diamagnetic response of the MOF lattice and the ferromagnetic response of the cobalt particles. In fact, 1 emu at saturation has been measured.

References

[1] S. Costacurta, P. Falcaro, S. Vezzu', M. Colasuonno, P. Scopece, E. Zanchetta, M. Guglielmi, P. Alessandro P. *J. Sol-Gel Sci. Tech.* 60-3, 340-346.

[2] S. C. B. Gopinath, K. Awazu, M. Fujimaki, K. Shimizu, W. Mizutanic, K. Tsukagoshic *Analyst*, 2012, 137, 3520.

[3] S. Le Craza, R. A. Pethricka, *International Journal of Polymeric Materials*, 2011, 60(7), 441.

[4] G. Brusatin, A. Abbotto, L. Beverina, G. A. Pagani, M. Casalboni, F. Sarcinelli, P. Innocenzi, *Adv. Funct. Mater.* 2004, **14**, 1160.