

Electronic Supporting Information

Supergluing MOF Liquid Marbles

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Materials and Methods:

Ethyl-2-cyanoacrylate, 2-aminoterephthalic acid, triethylamine, glycerol, tetrabutylammonium hexafluorophosphate, dioxane, acetonitrile and caproic anhydride were purchased from Sigma Aldrich and neutral gamma phase alumina (200 m²/g surface, 40 µm APS microparticles) was purchased from Alfa Aesar. Sodium acetate, sodium hydroxide and dimethylformamide were obtained from Merck. Perfluorooctanoyl chloride was purchased from Lancaster. The superglue was purchased from 3M. Fluorinations were performed in a glovebox under inert atmosphere. All chemicals were used as received.

General:

XRD data was obtained using a Bruker D8 General Area Detector Diffraction System with a graphite monochromator and Cu K α wavelength of 1.5418 Å (40 kV, 40 mA) and a HI STAR Area Detector with a two dimensional multi wire proportional counter. A double pin-hole collimator used to control the beam size and divergence. Scanning Electron Microscopy (SEM) analysis was performed with a JEOL JSM 6360LA scanning electron microscope (tungsten source) with an accelerating voltage of 5 to 10 kV or with a JEOL FESEM JSM6700F field emission scanning electron microscope with an accelerating voltage of 5 to 10 kV. Prior to SEM analysis, samples were sputtered with gold using a JEOL JFC-1200 Fine Coater. Environmental SEM analysis was performed on an FEI Quanta 200 ESEM at an accelerating voltage of 10 kV and a pressure of 1.6 Torr. Fourier Transform Infrared Spectroscopy (FTIR) analysis was performed on a Perkin Elmer Spectrometer. Powder samples were ground with KBr and pelletized for FTIR analysis.

Synthesis of NH₂-MIL-53(Al)/ γ -Al₂O₃ microparticles

γ -Al₂O₃ microparticles (267.9 mg) and 2-aminoterephthalic acid (283.2 mg) and D.I. H₂O (to a total volume of 15mL) were placed in a a Telfon-insert of a 25 mL autoclave. The autoclave was sealed and placed in an oven at 120°C for 6 hours. The autoclave was then cooled by running water and the powder collected by filtration. Purification was performed by refluxing the yellow powder in EtOH overnight and filtration. The powder was placed in an oven and dried for several hours at 80 °C. As the porosity of the

MOF was not deemed necessary for our purposes, we did not reflux the material overnight in DMF to remove unreacted ligand residing in the MOF pores. Yield: 317.2 mg.

Synthesis of NH₂-MIL-53_{CA}(Al)/ γ -Al₂O₃ microparticles

NH₂-MIL-53(Al)/ γ -Al₂O₃ microparticles (100.2 mg), caproic anhydride (0.794 mL) and acetonitrile (2.146 mL) were refluxed for ~ 16 hours, then cooled and collected by via filtration, and washed with CHCl₃ and acetone and dried in an oven at 80 °C for several hours. Yield: 97.0 mg.

Synthesis of NH₂-MIL-53_F(Al)/ γ -Al₂O₃ microparticles

In an Ar-filled glovebox, NH₂-MIL-53 (Al)/ γ -Al₂O₃ microparticles (101.0 mg, pre-dried in oven at 80 °C) were placed in a 20 mL vial with 1,4-dioxane (1 mL) and Et₃N (0.1 mL). The vial was capped and chilled to 10 °C to freeze the dioxane, after which perfluorooctanoyl chloride (0.1 mL) was added and the mixture slowly allowed to thaw and then sit at room temperature for approximate 1 hour. The vial was brought out of the glovebox and 5 mL of EtOH was added to the mixture. The contents were filtered to collect the powder and washed with copious amounts of ethanol, then water, then ethanol again. The powder was placed in an oven to dry for several hours at 80 °C. Yield: 63.2 mg.

Preparation of liquid marble:

NH₂-MIL-53_{CA}(Al)/ γ -Al₂O₃ microparticles or NH₂-MIL-53_F(Al)/ γ -Al₂O₃ microparticles were placed in a petri-dish and 10 μ L of D.I. water was pipetted onto the powder and rolled gently until the surface is covered with the hydrophobic particles, giving a liquid marble. The liquid marble was carefully transferred by rolling into a separate petri-dish for further functionalization.

Preparation of liquid marble for ESEM studies.

Microparticles were placed in a petri-dish and 10 μ L of glycerol saturated with [Et₄N]PF₆ was pipetted onto the powder and rolled gently until the surface is covered with the hydrophobic particles, giving a liquid marble. The liquid marble was carefully transferred by rolling onto the ESEM sample holder for analysis.

Preparation of poly(ethyl-2-cyanoacrylate) encapsulated liquid marble (refer to Figure 3):

With ethyl-2-cyanoacrylate:

A liquid marble was placed in a petri-dish on a hot plate. The dish was insulated from the hotplate by a piece of cork to minimize heat transfer to the dish. Ethyl-2-cyanoacrylate (500 μ L) was placed on either an aluminium foil boat or or a glass petri-dish directly on the hotplate. The set-up is covered by a large crystallizing dish. The hotplate was turned on and set at 80 °C for 1.5 – 5 minutes, after which the crystallizing dish was removed and the liquid marble was found to be completely encapsulated with poly(ethyl-2-cyanoacrylate). The marble was able to roll on a glass surface even after encapsulation and retained its liquid core.

With superglue:

A liquid marble was placed in a petri-dish on a hot plate. The dish was insulated from the hotplate by a piece of cork to minimize heat transfer to the dish. Superglue (~1 mL) was placed on either an aluminium foil boat or or a glass petri-dish directly on the hotplate. The set-up is covered by a large crystallizing

dish. The hotplate was turned on and set at 80 °C for 7 minutes, after which the crystallizing dish was removed and the liquid marble was found to be completely encapsulated with poly(ethyl-2-cyanoacrylate). The marble was able to roll on a glass surface even after encapsulation and retained its liquid core.

Retention of water in liquid marble after encapsulation:

Right after polymerization of ethyl-2-cyanoacrylate on the liquid marble, the liquid marbles retain their aqueous core. However, depending on the degree of polymerization, the water slowly vaporizes. While we were able to determine approximately how long it takes for a normal liquid marble (without polymer) to dry by weighing the marble over a period of time and plotting the percentage loss of water over time (Figure S1), we were not able to do so with the polymerized marble. The reason for this is that a significant error is induced from the loss of some ethyl-2-cyanoacrylate monomer from the liquid marble wall. However, visual inspection and forced bursting of liquid marble approximately 4 hours after polymerization shows that there is still some liquid retained. While we do not notice a significant difference in how long it takes for the water to vaporize with versus without the polymeric shell, we do notice that the shell is significantly strengthened such that even after several hours, when a normal liquid marble has collapsed into its constituent powder and lost the water within, the shell of a polymerized marble is still intact, albeit buckled.

The time it takes for a non-encapsulated (without polymer) liquid marble to lose its water (10 μ L) is approximately 12700 seconds, based on the extrapolation of the trendline.

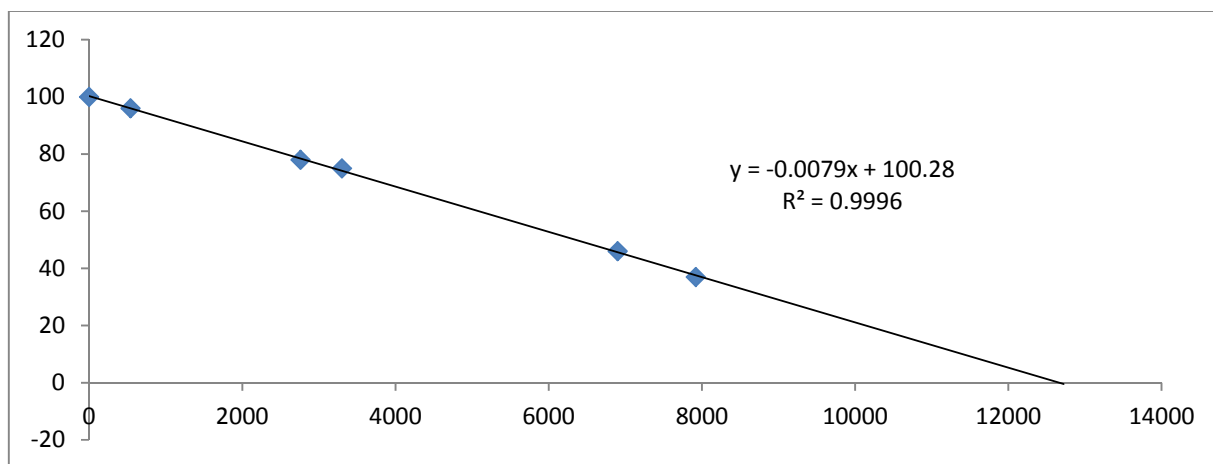


Figure S1. Plot of percentage weight loss of water against time (seconds) for a liquid marble formed from $\text{NH}_2\text{-MIL-53F(Al)/Al}_2\text{O}_3$ composite powder.

IR Spectroscopy

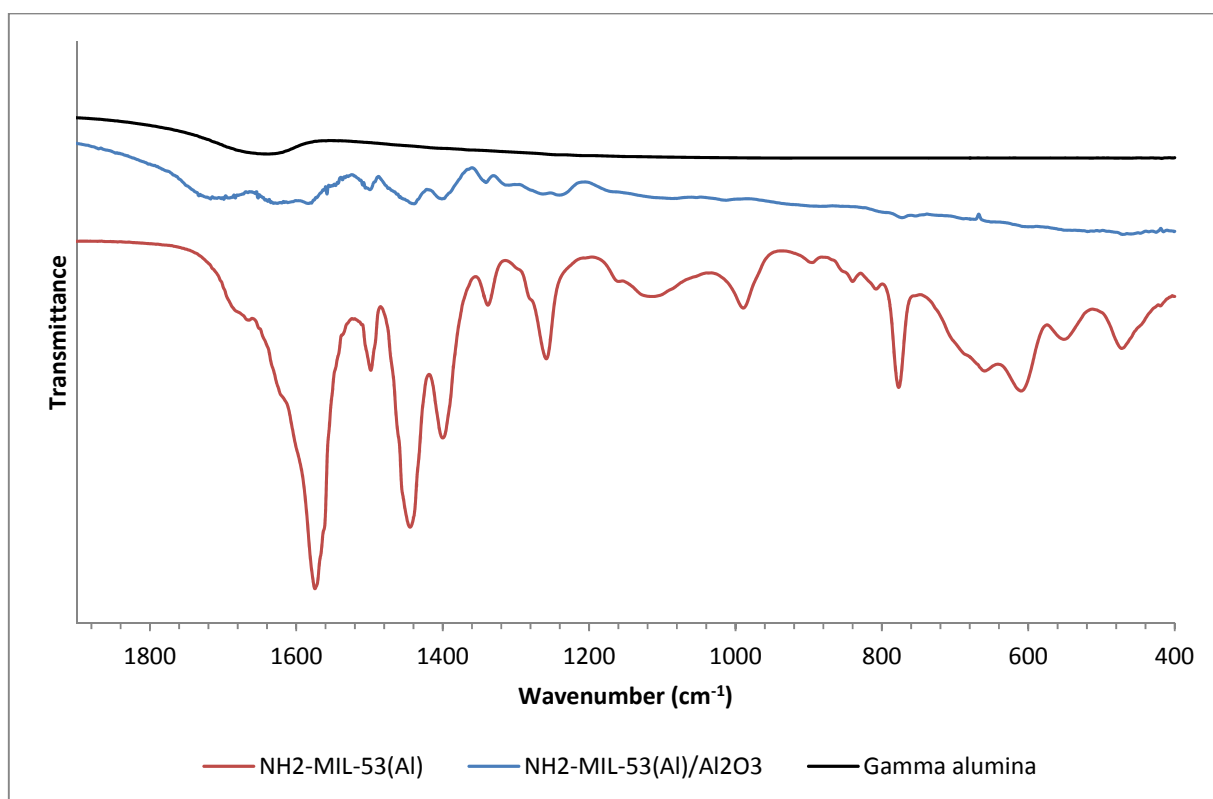


Figure S2. IR spectrum of NH₂-MIL-53(Al) (red), NH₂-MIL-53(Al) on γ -Al₂O₃ in a KBr pellet (blue) and spectrum of γ -Al₂O₃ microparticles (black). Due to the thin layer of NH₂-MIL-53(Al) crystallites on the relatively large γ -Al₂O₃ particles, the absorption bands of the MOF crystallites are weak compared to when a pure NH₂-MIL-53(Al) sample is used.

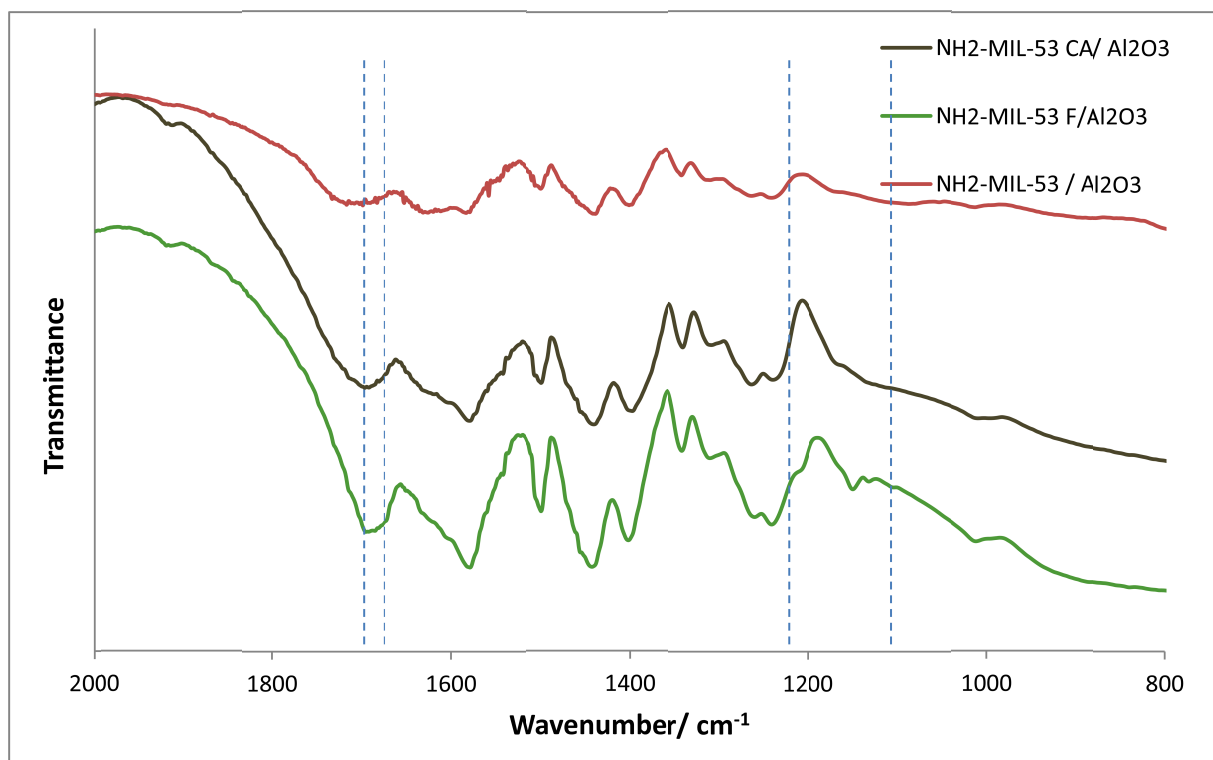


Figure S3. IR spectrum of NH₂-MIL-53(Al) MOF on γ -Al₂O₃ in a KBr pellet after fluorination (green) and spectrum of NH₂-MIL-53(Al) MOF on γ -Al₂O₃ in a KBr pellet after reaction with caproic anhydride (black). Absorption bands in the region 1100 – 1210 cm⁻¹ are attributed to C-F bond stretching vibrations. An absorption band at ~ 1690 cm⁻¹ is attributed to the amide C=O stretch. A band at ~ 1670 cm⁻¹ is attributed to the C=O stretch of free 2-aminoterephthalic acid.¹

Scanning Electron Microscopy

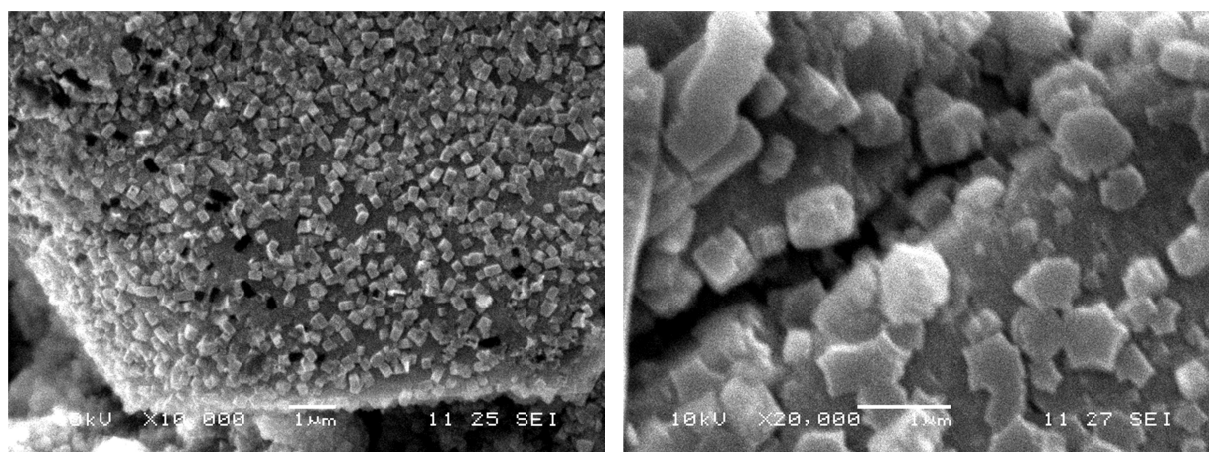


Figure S3. SEM images of NH₂-MIL-53(Al) crystallites on γ -Al₂O₃ microparticles after 4 hours reaction time.

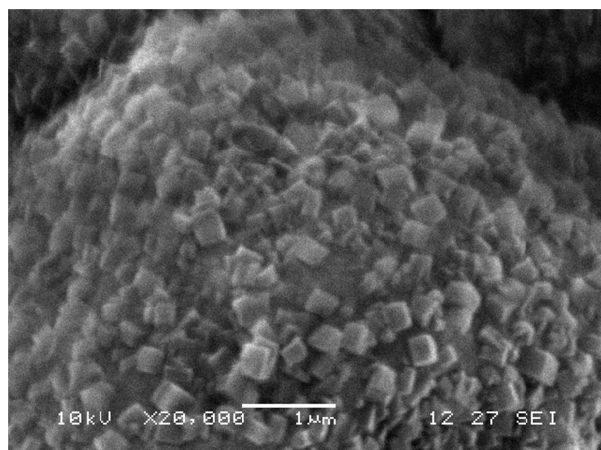


Figure S4. SEM images of NH₂-MIL-53(Al) crystallites on γ -Al₂O₃ microparticles after 6 hours reaction time. More coverage is observed, but the crystallites appear to be smaller.

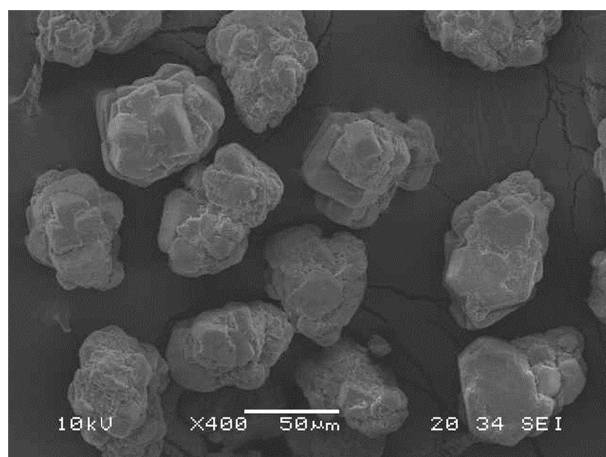


Figure S5. SEM images of γ -Al₂O₃ microparticles

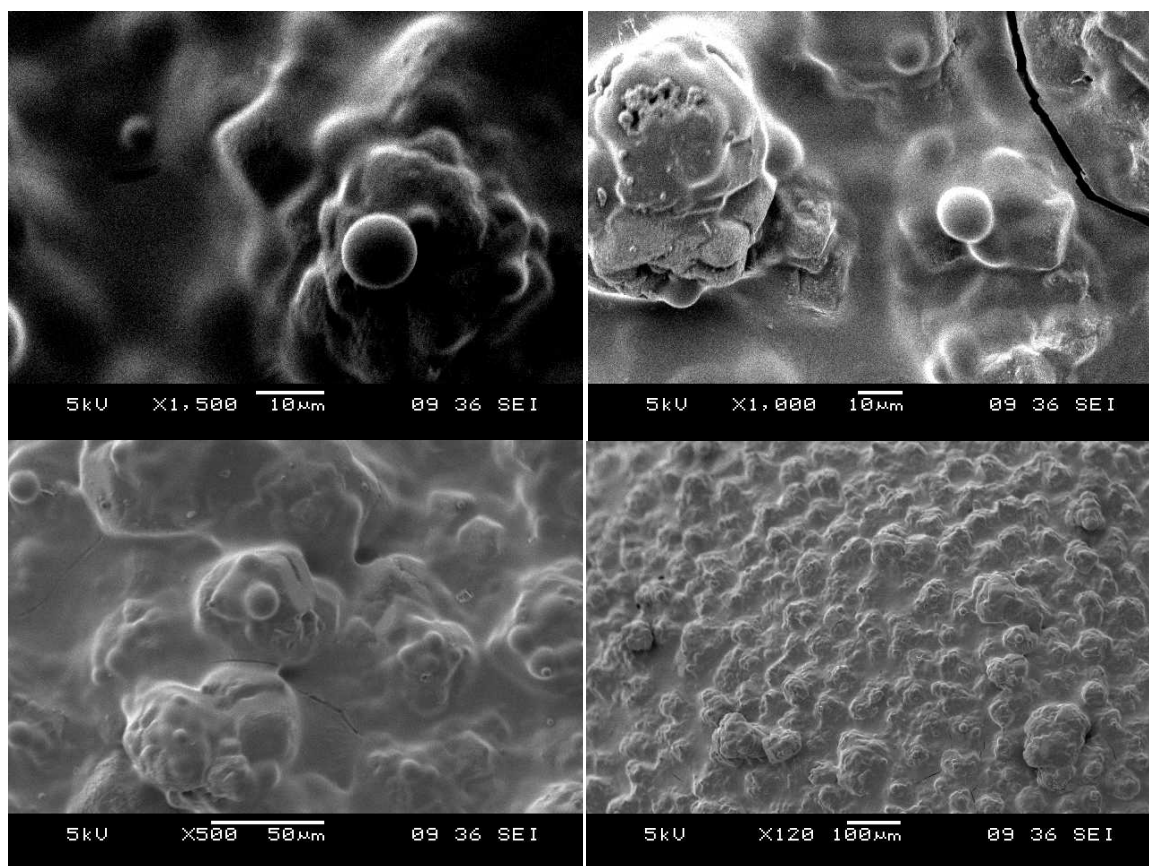


Figure S6. SEM images of poly(ethyl-2-cyanoacrylate) coating on microparticles, formed on a liquid marble using ethyl-2-cyanoacrylate.

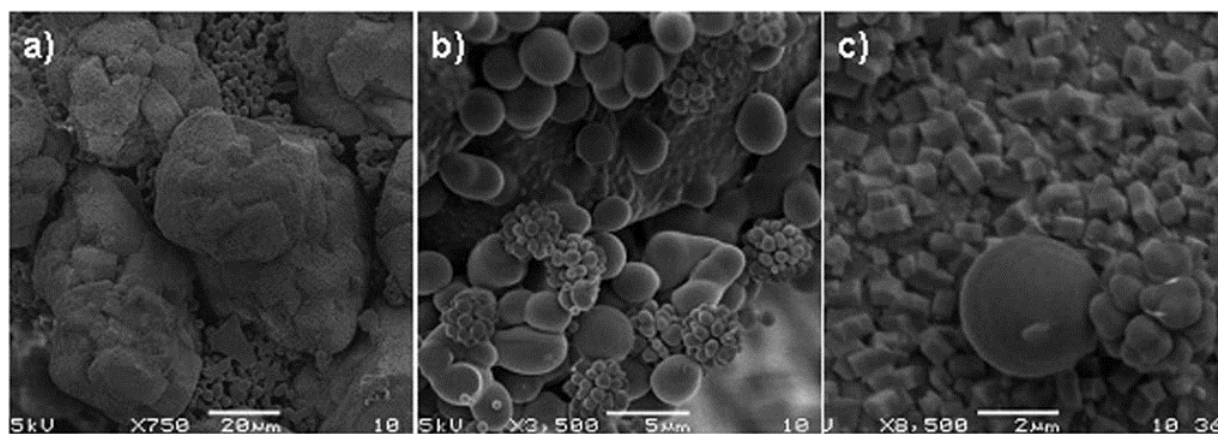


Fig. S7 SEM image of the polymer-microparticle composite shell of a liquid capsule formed using superglue. (a) The gaps between the microparticles are filled with micro-globules of poly(ethyl-2-cyanoacrylate). (b) Microglobules of poly(ethyl-2-cyanoacrylate) in raspberry-like shapes and spheres. (c) Close-up of the microparticle surface showing crystallites of modified NH₂-MIL-53(Al).

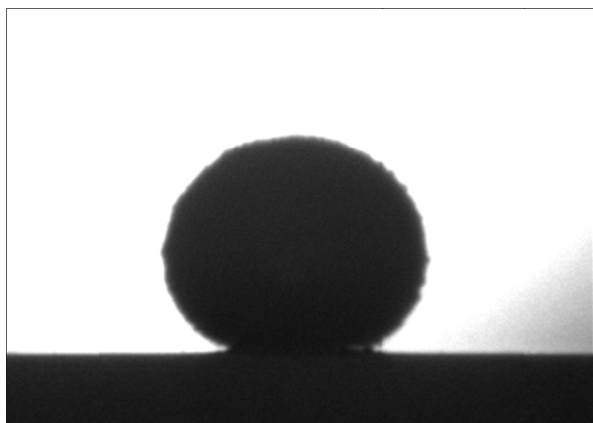


Figure S8. Side view of a liquid marble. The grainy texture arises from the microparticles, which are approximately 40 μm in diameter.

¹ S. Marx, W. Kleist, J. Huang, M. Maciejewski and A. Baiker, *Dalton Transactions*, 2010, **39**, 3795