Electronic Supplemental Material for

Crystallization at Droplet Interfaces for the Fabrication of Geometrically Programmed Synthetic Magnetosomes

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Materials and Methods

A. Materials

The wells used to hold and observe droplets and the microfluidic devices used to generate droplets were fabricated using polydimethylsiloxand (PDMS, Sylgard® 184) purchased from Dow Corning Co. Silicone (Masterflex Tygon® Lab E-3603 tubing) and polyethylene (PE) tubing(IntramedicTM PE60 and PE160 by BD & Co.) were purchased from Fisher Scientific®. Sigmacote®, Asolectin (from soybean, lot # BCBR8705V), cobalt(II) chloride hexahydrate (CAS 7791-13-1), chloroform (CAS 67-66-3), and iron(III) chloride hexahydrate 97 % A.C.S reagent (CAS 10025-77-1) were purchased from Sigma-Aldrich. Iron(II) chloride tetrahydrate 98 % (CAS 13478-10-9) and n-hexadecane 95 % (CAS 544-76-3) were purchased from Alfa Aesar. Ammonium hydroxide (28.0 % - 30.0 %) (CAS 1336-21-6) in water (70.0 % – 72.0 %) (CAS 7732-18-5) was purchased from Fisher Scientific®.

B. Methods

B1. Preparation of droplet interface bilayers:

B1.1 Iron salt droplets: We prepared aqueous solutions of iron salts by first dissolving enough asolectin in chloroform to yield a final concentration of 2mg asolectin/1mL of desired aqueous solution. The chloroform was evaporated under a stream of nitrogen to yield a film of lipids; to this lipid film we added aqueous iron salt solution with a ratio of 2 parts iron(III) chloride hexahydrate to 1 part iron(II) chloride tetrahydrate at the desired concentration. The solution was mixed using ultrasonication for 1 hour.

B1.2 Ammonia droplets: We prepared aqueous solutions of ammonia by first dissolving enough asolectin in chloroform to yield a final concentration of 2mg asolectin/1mL of desired aqueous solution. The chloroform was evaporated under a stream of nitrogen to yield a film of lipids; to this lipid film we added aqueous ammonia solution at the desired concentration (typically a solution of 3 % ammonium hydroxide to 97 % water was used). The solution was mixed using ultrasonication for 1 hour.

B1.3 Hexadecane continuous phase: We prepared the continuous hexadecane phase by first dissolving enough asolectin in chloroform to yield a final concentration of 5 mg/1 mL of desired hexadecane. The chloroform was evaporated under a stream of nitrogen to yield a film of lipids; to this lipid film we added hexadecane and used ultrasonication for 1 hour to fully dissolve the asolectin.

B1.4 Droplet interface bilayer setup: To initiate growth of magnetic iron oxide (magnetite Fe_3O_4), a well/container is filled with 5 mg/mL asolectin/hexadecane and a droplet of 2 mg/mL asolectin/iron salt solution is placed in the hexadecane (submerged fully). Wait at least 2 minutes to allow spontaneous formation of a monolayer of asolectin around the droplet and then introduce a droplet of 2 mg/ml asolectin/ammonia solution. Gently bring the droplets into contact and diffusion of ammonia across the droplet-droplet interface will begin immediately and initiate the nucleation and growth of magnetite.

Supporting Videos:

Video S1: Directed growth of magnetite with a magnet on the left side of the droplets.

Video S2: Directed growth of magnetite with a magnet on the right side of the droplets.

Video S3: Reorientation and movement of a 3-domain magnetite droplet towards a magnet on the right.

Video S4: Rotation of a 3-domain magnetite droplet using a magnetic stir plate.

Video S5: Rotation of a single domain magnetite droplet using a rotating magnetic field generated by a rotating rare earth magnet. The magnet is moved twice to show that the droplet is not moving due to being slightly off from the center of the magnet but is moving due to the rotating field lines.

Video S6: Rotation of a single domain magnetite droplet using a rotating magnetic field generated by a rotating rare earth magnet. The magnet is flipped on its side to show that when the north-south field is facing up and down, the rotation of the magnet will not affect the droplet.

Video S7: Rotation of three single domain magnetite droplets using a rotating magnetic field generated by a rotating rare earth magnet.

Video S8: Rotation of three single domain magnetite droplets using a rotating magnetic field generated by a rotating rare earth magnet. The magnet is flipped on its side to show that when the north-south field is facing up and down, the rotation of the magnet will not affect the droplets.

Video S9: Rotation of a single domain magnetite droplet using a rotating magnetic field. We stop the rotation of the magnetic field and observe that after stopping the droplet continues to rotate until the edge of the droplet is aligned with the magnetic field.

Video S10: Rotation of a programmed magnetic domain droplet. This droplet will point its magnetic domain towards the north-south field lines.

Video S11: Multiplexed generation of magnetic droplets. Droplets are loaded into a well with ammonia solution on the bottom and hexadecane floating on top. The droplets will float on top of the ammonia solution while staying submerged in the hexadecane. After some time, the droplets each grow a magnetic domain and a magnet is used to move them around their environment.

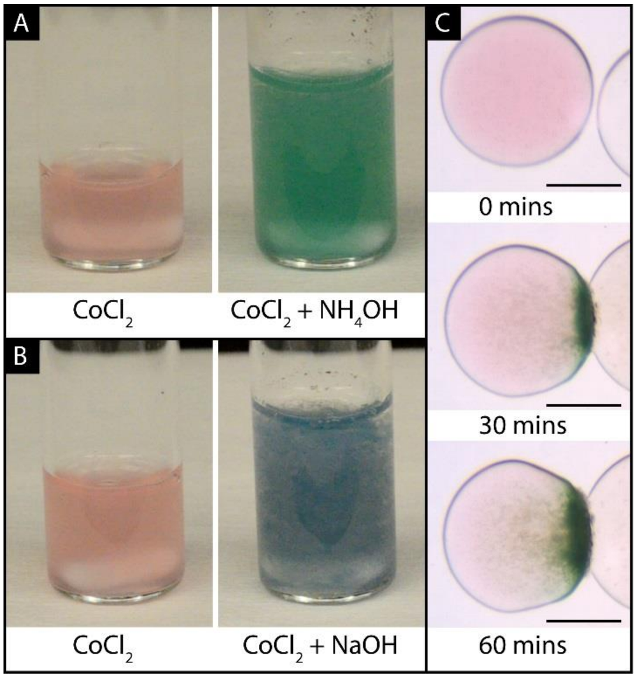

Fig. S1 – Cobalt control. (A) Images showing a solution of cobalt chloride before and after the addition of ammonium hydroxide. (B) Images showing a solution of cobalt chloride before and after the addition of sodium hydroxide. (C) Image sequence showing the precipitation reaction that occurs when a droplet of cobalt chloride is introduced to a droplet of ammonium hydroxide to form a DIB. Note the color change matches with (A).

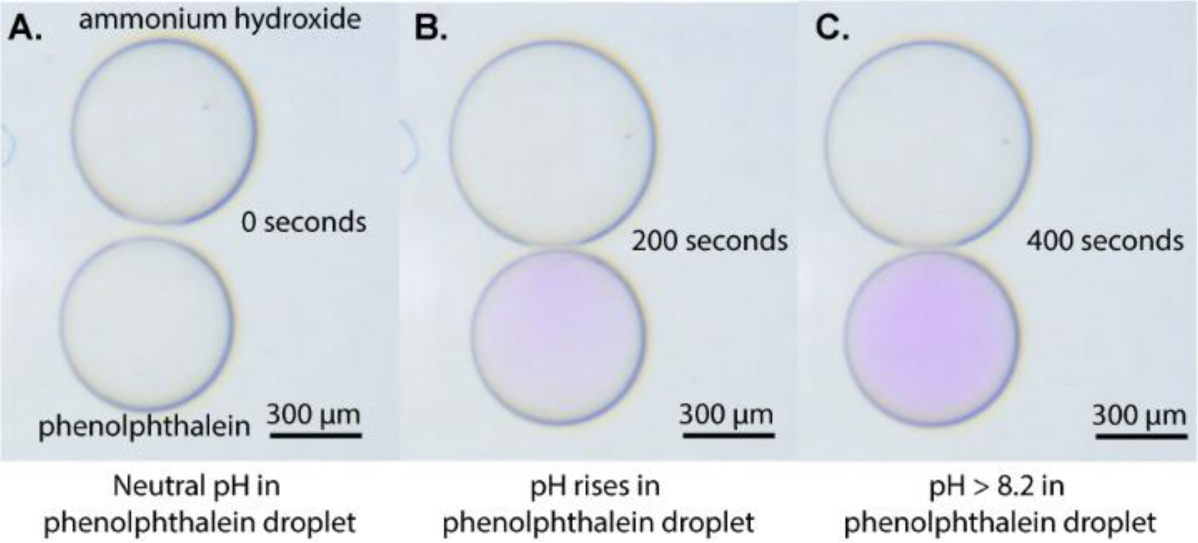

Fig. S2 – (A.) Two droplets, with base on top and pH indicator on bottom, just before coming into contact. (B.) A bilayer formed between droplets and base diffused for 200 seconds. (C.) After 400 seconds the pH indicator has stopped changing color.

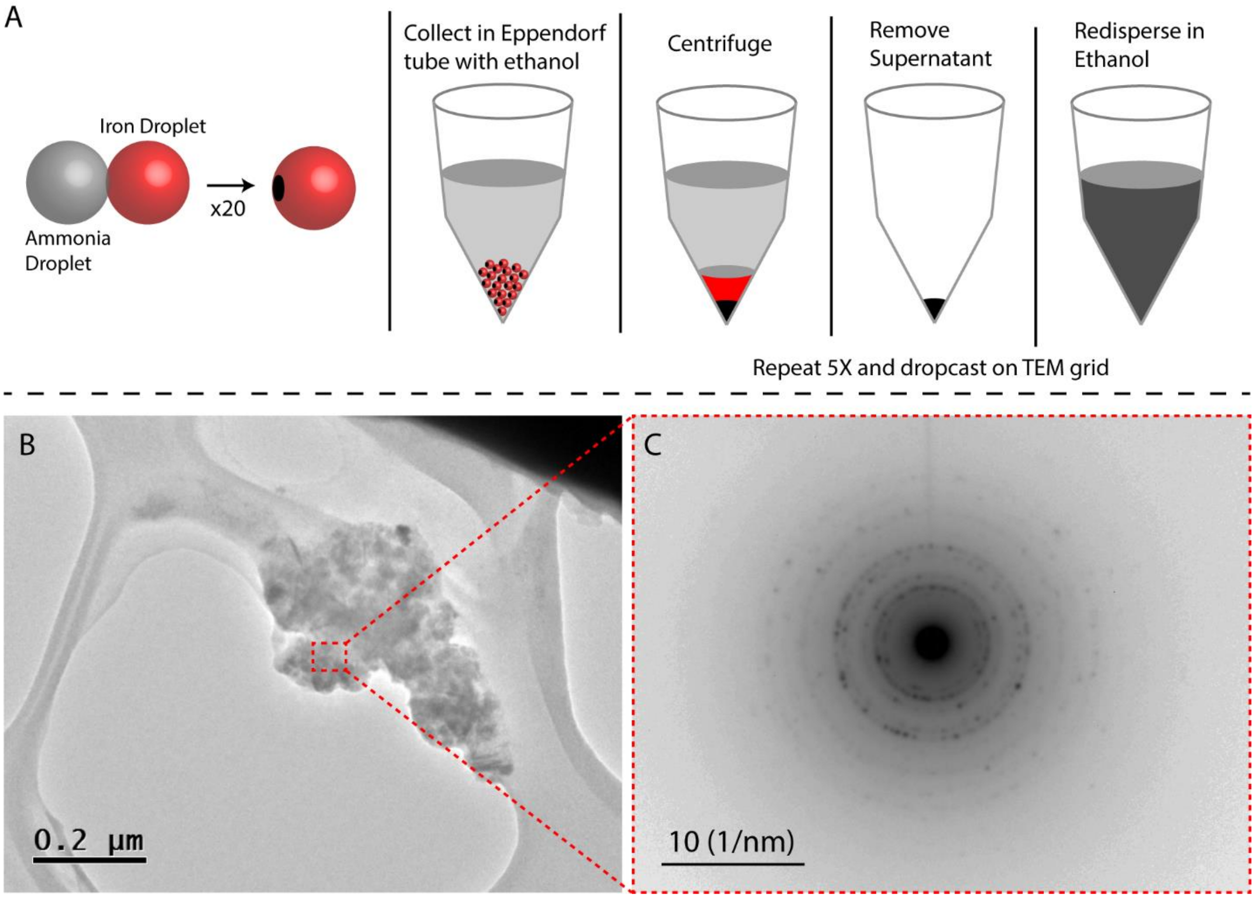

Fig. S3 – (A) Schematic illustrating the preparation of magnetite filled droplets for TEM analysis. (B) TEM image of magnetite particles on a lacey carbon TEM grid. (C) Electron diffraction ring pattern imaged from the denoted area of the magnetite particles.

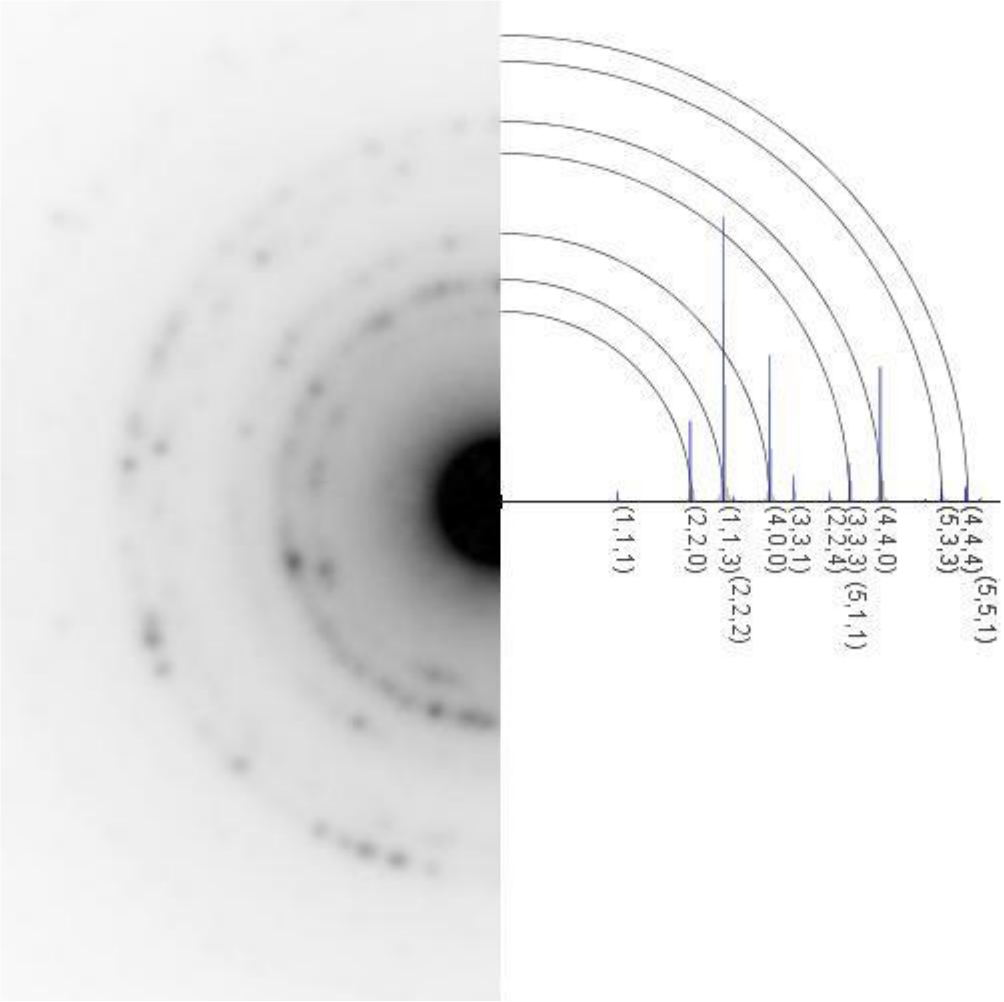

Fig. S4 – Electron diffractogram of a sample of DIB grown magnetite particles (left) and simulated ring pattern of magnetite (right)

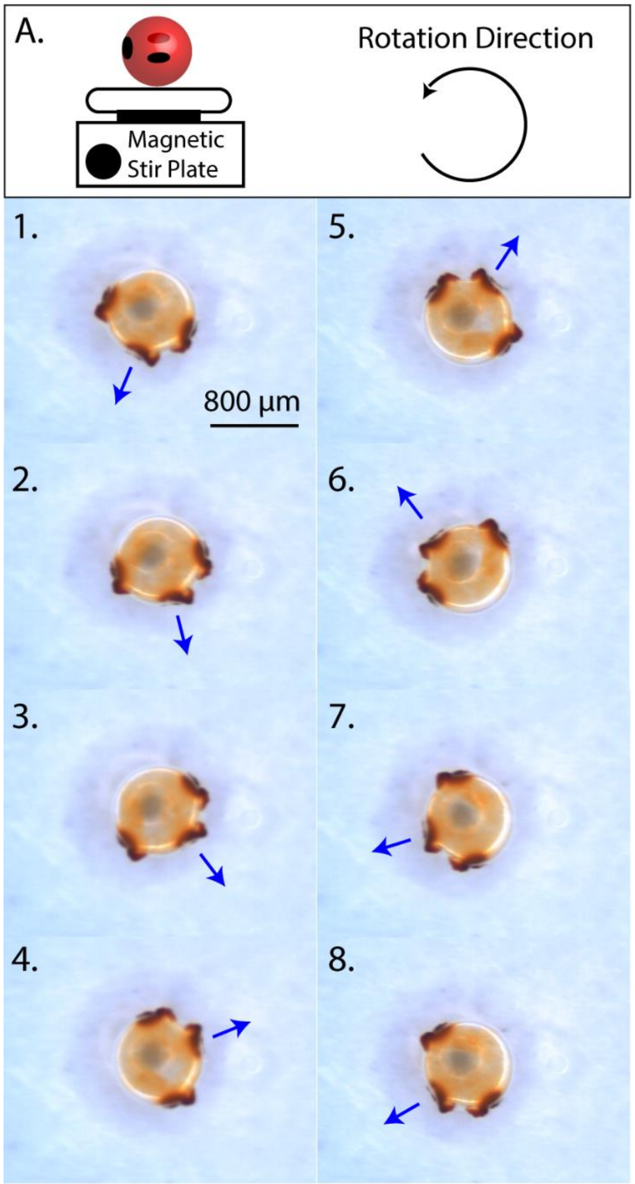

Fig. S5 – Image sequence showing the rotation of an asymmetric magnetite droplet using a magnetic stir plate. The stir plate rotates a magnet counterclockwise and the droplet rotates counterclockwise.

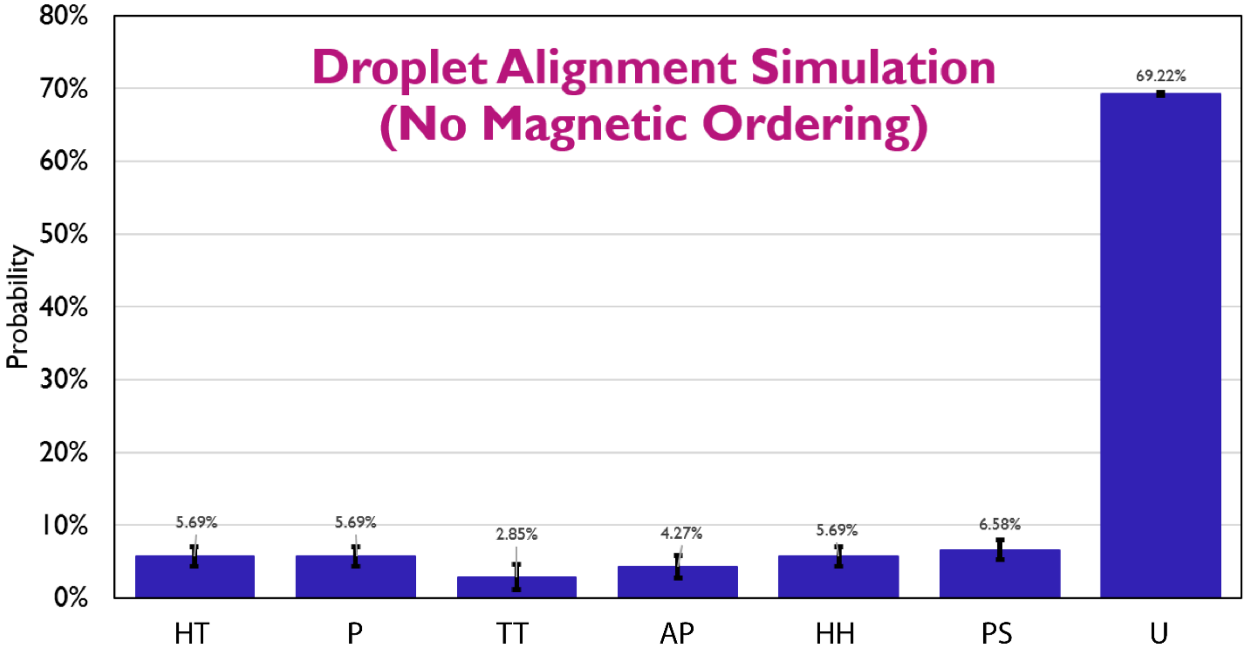

Fig. S6 – Random alignment simulation. Results of a simulation for alignment events in system where two droplets with randomly assigned angles are compared and measured. The labels are for the following alignment cases: head-to-tail (HT), parallel (P), tail-to-tail (TT), antiparallel (AP), head-to-head (HH), parallel skewed (PS), and unaligned (U).