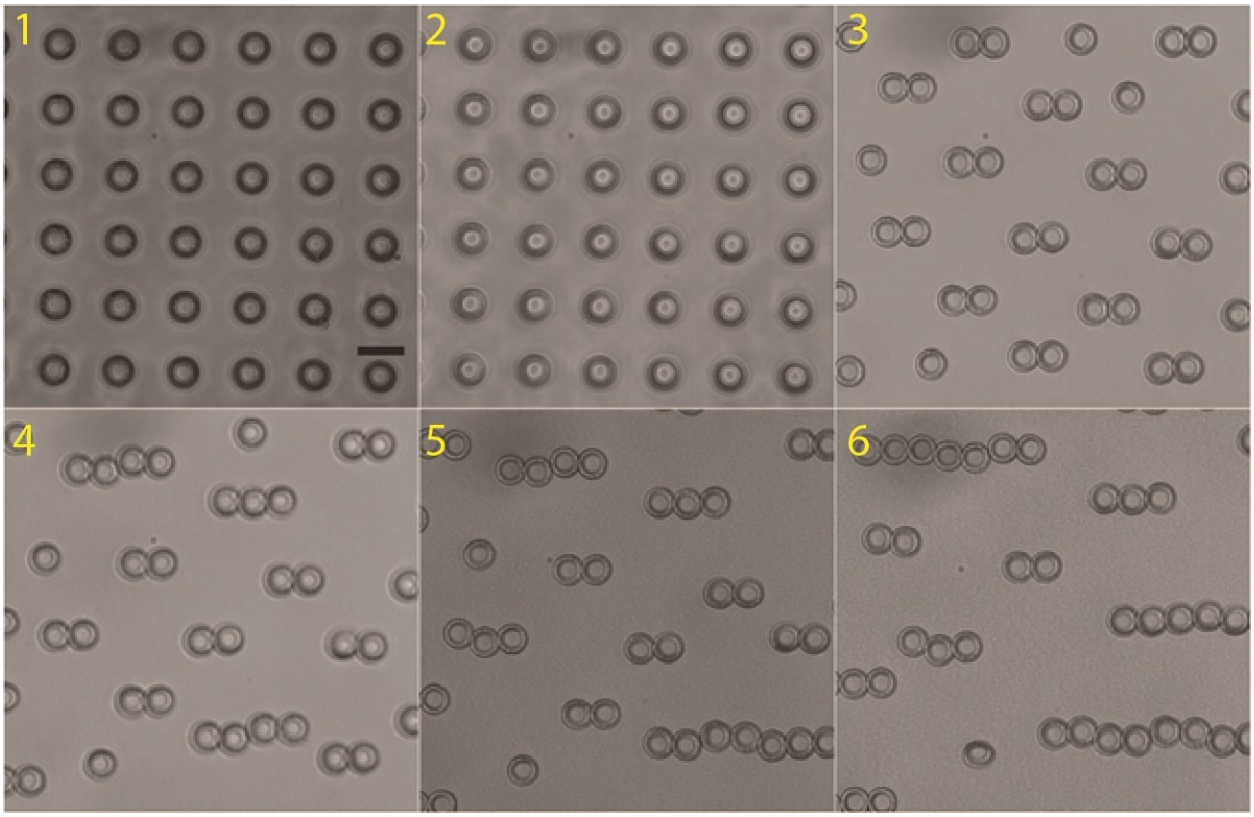
Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information



S1: The organisation of arrays of rings on application of a homogenous magnetic field. The montage proceeds from left to right and then down. Frame 1) a square array of the rings extracted from the PDMS mold with the polymer poly(1-vinyl-pyrrolidone-*co*-vinylacetate). Frame 2) dissolution of the polymer with ethanediol. Frame 3) application of a homogenous magnetic field and the formation of a square-centred lattice of dimers. Frames 4, 5 and 6) aggregation into chains with continued application of the field. The field strength was 25 mT and the timings for frames 3-6 after application of the magnetic field are 12, 180, 250 and 335 seconds. The scale bar is 10 microns.

S2: We give here a detailed description of the method for calculating annulus shapes. We normalize all lengths by the well radius, and suppose that the well is sufficiently deep that its height does not affect ring formation. Then for each annulus there are just two free parameters, the contact angle θ_c and the annulus width W. This determines the radius R(s=0)=1-W, and angle $\phi(s=0)=\theta_c$ at the inner edge of the annulus, and we set these as initial conditions. However, the contact angle with the outer wall should also be given by θ_c, i.e., $\phi(R=1)= \pi/2- \theta_c$. This condition cannot be satisfied trivially, as we also have to take into account the constant mean curvature condition which reads

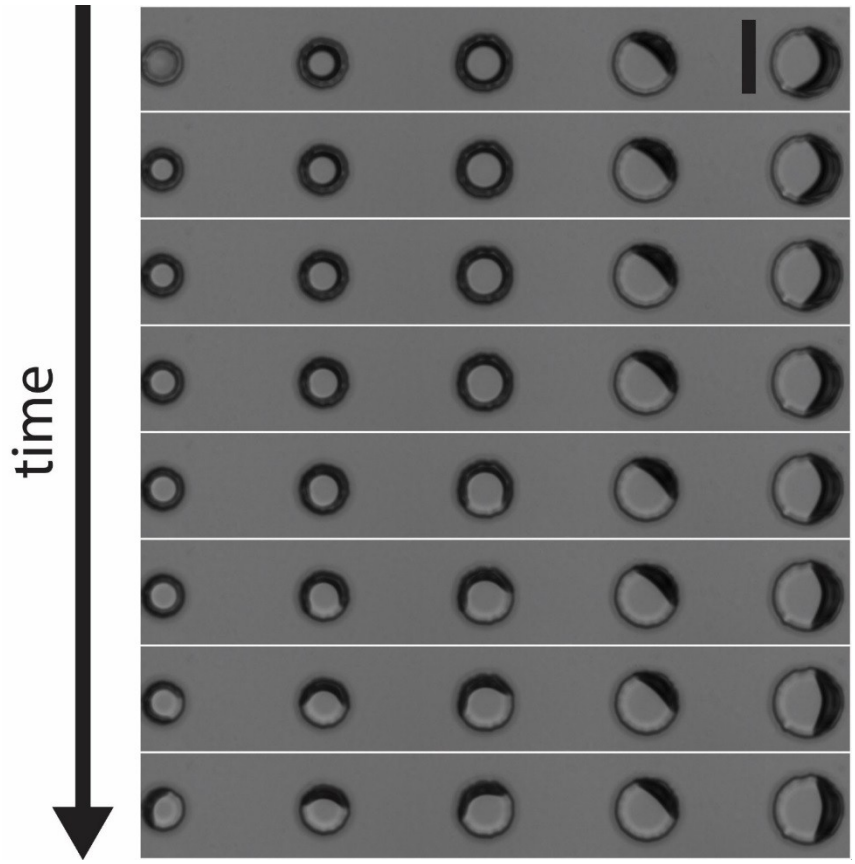
$2H=-d\phi/ds-\sin(\phi)/R$, (S1)

where the mean curvature H is an unknown constant which is different for each annulus. We therefore adopt the following strategy. We choose a value for H, and calculate the resulting annulus shape by the method of finite differences, that is, we move by small steps Δs outwards from the initial coordinates and solve the finite difference version of Eq. S1, i.e., $\phi(s+\Delta s)=\phi(s)+\Delta\phi$, where

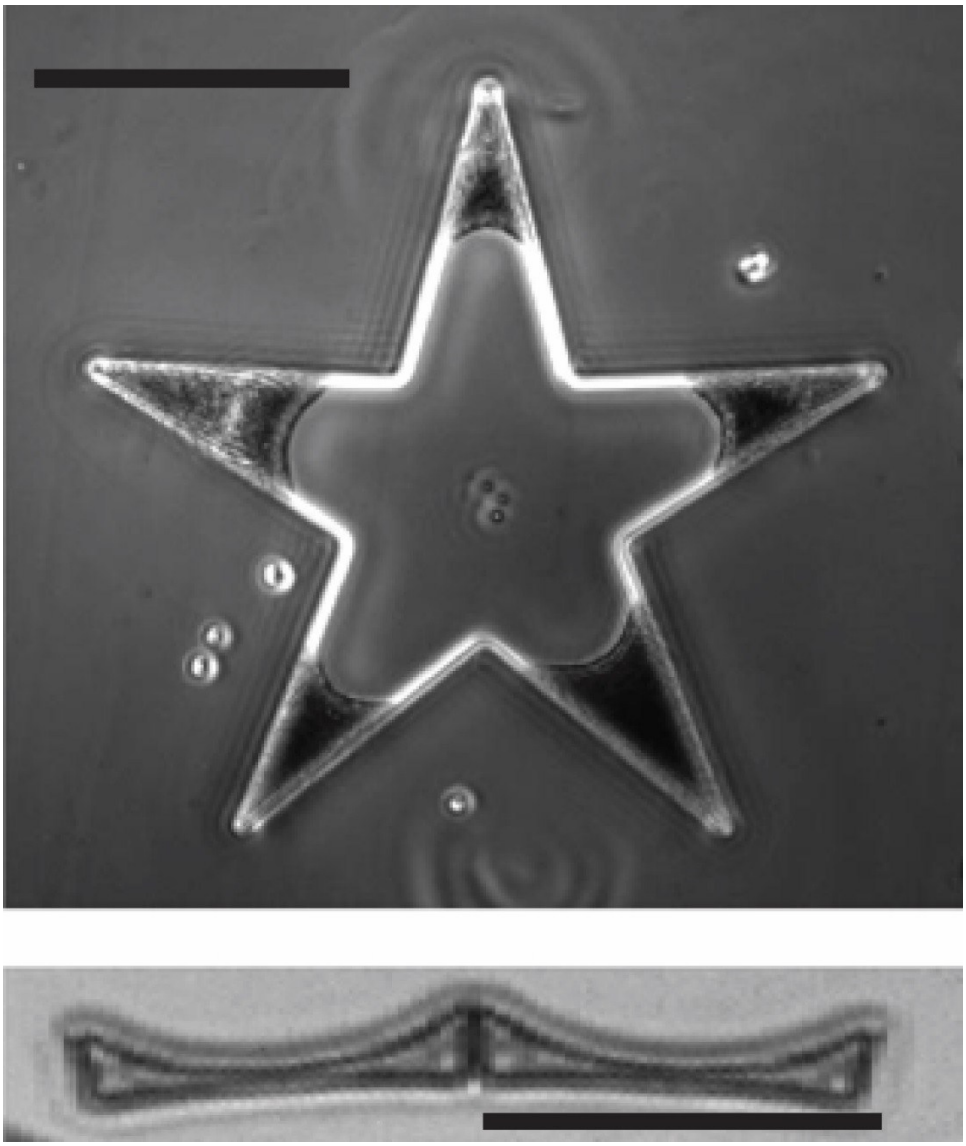
$\Delta\phi=[2H-\sin(\phi)/R]\Delta s$, (S1')

By comparing the contact angle at the outer edge of the well with its desired value θ_c, altering H and repeating the procedure, we iteratively approach the solution. When the contact angle matches θ_c to within some predefined tolerance the calculation halts and we accept the corresponding annulus shape as the solution. We perform these calculations in MATLAB with $\Delta s=10^{-4}$ and a tolerance of 0.06 degrees on the outer contact angle. From the annulus shape we can then calculate parameters such as the annulus volume and surface energy. By repeating this procedure with varying W, we build up an atlas of annulus shapes that allows us to calculate the expected shape for any given well radius and EPTPA volume fraction.

The surface energy U of the droplets is given by $U=\gamma_{LG} A_{LG}+ \gamma_{LS} A_{LS}+ \gamma_{GS} A_{GS}$ where γ and A are surface tension and interfacial area respectively and the three subscripts are for the liquid-gas, liquid-solid and gas-solid interfaces. Using the Young equation $\gamma_{GS}= \gamma_{LS} + \gamma_{LG}\cos(\theta)$, and the fact that $A_{LS}+A_{GS}=A_0$ is an arbitrary constant for a particular well geometry, we rewrite the surface energy as $U=\Delta U+U_0$, where the energy difference $\Delta U= \gamma_{LG} [A_{LG}-A_{LS}\cos(\theta)]$ and $U_0=\gamma_{GS}A_0$ is a constant energy offset. To calculate the area A_{LG} of the curved liquid-gas interface, we integrate the area numerically. In the arc-length angle parameterization, this is simply $A_{LG}=2\pi\int R\, ds$. To remove the dependence on the unknown γ_{LG}, we define a normalised energy difference $\Delta\tilde{U}=\Delta U/\Delta U_{M0}$ where ΔU_{M0} is the energy difference for the meniscus labelled M0, which is just touching the base of the well.



S3: A time series of bright-field micrographs showing that in the absence of particles the disc to ring shape transition is followed by a ring to 'moon' transition. The montage proceeds downwards and each image is 10 seconds apart. Rhodamine B dye was added to the solution to aid visualisation by making the droplet darker.



S4: Top: the wicking of the precursor material into the tips of a star-shaped PDMS well. The scale bar is 40 microns.

Bottom: A side view of two superparamagnetic ‘cuboids’ fabricated within wells of a rectangular cross section. Because of the wetting behaviour of the dispersion, more material settles at the corners of the well. Hence, on the application of a magnetic field the cuboids favourably connect at their ends. The scale bar is 20 microns