

Supplementary information

Conductivity experiments

De-supersaturation rates were determined using conductivity measurements normalized to the control as described in ref R1. These rates were then used to calculate the % inhibition, and results from these experiments are also shown in R1. After obtaining the conductivity results, samples were collected by filtration onto 0.22 μm membranes. The solids were washed with ultrapure water and dried in a dessicator. Subsequently, a portion of the sample was prepared for Scanning Electron Microscopy (SEM) and viewed using a Philips XL30 scanning electron microscope or Zeiss Evo microscope. Selected samples were also set in resin for ultramicrotomy. The thin sections were viewed with a Jeol 2011 TEM at 200 kV.

The barium ion degree of complexation with the phosphonated and sulfonated calixarene are unknown and would require a study in its own right. For this reason, the supersaturation has been defined as:

$$S = c/c_0$$

where c is the concentration of the barium ion added and c_0 is the equilibrium barium ion concentration. Similarly, the %inhibition was calculated according to:

$$\%inhibition = 100 * [(k_0 - k) / k_0]$$

where k is the rate of de-supersaturation in the linear region of the conductivity versus time curve in the presence of calixarene and k_0 is the de-supersaturation rate for the control run.

Low supersaturation morphology experiments for *p*-sulfonated calix[4]arene

Morphology experiments were undertaken with the *p*-sulfonated calix[4]arene additive to ascertain if its impact was the same or otherwise as previously observed for *p*-phosphonated calix[4]arene. Due to the high concentrations of sulfonated calixarene required to observe major morphological changes, lower barium sulfate supersaturations were used so that the impact of the sulfonated calixarene could be increased.²¹

The experiment consisted of equilibrating barium chloride and *p*-sulfonated calix[4]arene at the desired concentration in a 25 mL cleaned glass vial in a water bath. A cleaned glass cover slip was added to the bottom of the vial and a stoichiometric amount of sodium sulfate was added to initiate crystallization. The total volume of solution was kept constant at 20 mL. After three days the cover slips were harvested, and tissue paper used to soak up excess fluid followed by preparing the glass cover for SEM. This consisted of placing the glass cover slip on a carbon coated SEM stub, painting the circumference with carbon paint to reduce charging, and then drying in a dessicator before sputtering with gold.

55 Nephelometry

Turbidity experiments were undertaken using a UV-Vis instrument (UV-916, GBC scientific equipment Pty. Ltd, Melbourne, Australia) operated at 900 nm wavelength using a quartz flow cell. At this wavelength little absorption by the solids or solution occurs and the instrument acts like a turbidity meter,²² measuring the optical density of the slurry. The barium chloride concentration, sodium sulfate concentrations, pH and temperature were all equivalent to those used in the conductivity experiments. The flow rate through the cell was 67 mL/min and this was achieved using a Masterflex[®] peristaltic pump and Tygon[®] tubing.

Atomic force microscopy (AFM)

AFM experiments were performed on a PicoPlus[®] using a standard silicon nitride cantilever with a flow-through cell attachment. The same procedure was used for all samples. A freshly cleaved mineralogical barium sulfate sample was fixed to a metallic stub and the flow cell was flushed with filtered ultrapure water (resistivity >18 M Ω cm) using a precision, dual syringe pump (from Kd Scientific) run at 0.2 mL/min and Gelman 0.2 μm Supor[®] membrane filters attached to the syringes. One syringe had the water replaced with barium chloride solution (0.1 mM) and the other with sodium sulfate solution (0.1 mM). This was then flushed through the cell at a rate of 0.2 mL/min as per the water. Finally, the barium chloride solution was replaced with a solution containing barium chloride plus the calixarene at a known concentration and the sodium sulfate solution was topped up as necessary. This was then flushed through the cell at a rate of 0.2 mL/min, as per the water run. In this way, the rate of growth of barium sulfate could be measured with and without calixarene present. A ratio of the rates was taken (Rate with calixarene/Rate without calixarene) as a means of normalisation. A low S value of 5 was used in the AFM work since higher S values (7-10) lead to rates too fast to be captured by the imaging software and higher S values still (>10-12) result in homogenous nucleation.

X-ray diffraction (XRD)

For calixarene concentrations that resulted in a barium sulfate morphology of interest, the conductivity experiment conditions were replicated but up-scaled to 4 L. The filtered, washed and dried solids obtained from these batches were used for X-ray diffraction analysis. The XRD patterns were collected on a Bruker D8 Advance instrument using Cu K α radiation. A low background holder spinning at 30 rpm was used and the 2 theta range was 15-50 degrees with a step size of 0.001 $^\circ$ and a divergence slit of 0.3 $^\circ$.

Thermal gravimetric analysis (TGA)

Approximately 15 mg of sample was heated in a platinum pan in a TA Instruments SDT 2960 simultaneous DSC-TGA from ambient to 800 $^\circ\text{C}$ at 5 $^\circ\text{C}$ per minute in air at a flow rate of 40 ml/min.

The temperature of the instrument was calibrated against the melting points of indium, zinc, tin, silver and gold. The balance was calibrated over the temperature range with standard alumina weights as provided by the vendor.

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Results

Fig S1. XRD pattern for barium sulfate formed in the presence of 10 *p*-sulfonated calix[4]arene at 0.0145 mmol L⁻¹ mM

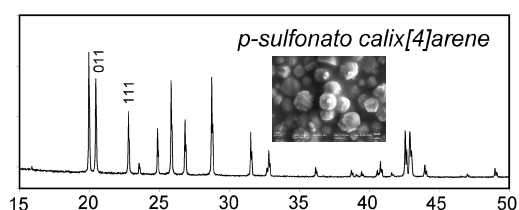
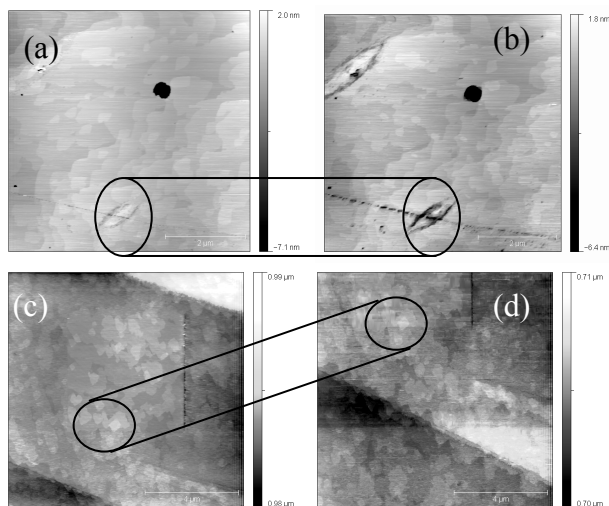


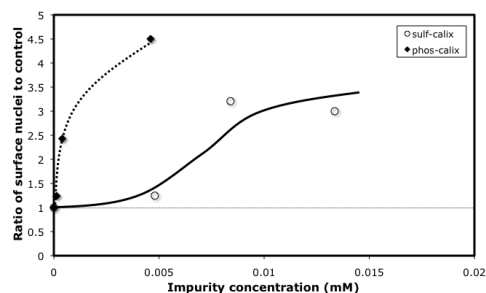
Fig. S2. AFM images of the barium sulfate (001) face after several hours of crystalline growth and subsequent flushing with pure water. Barium sulfate deposited in the presence of *p*-phosphonato calix[4]arene, (a) and (b) taken 15 minutes apart, and *p*-sulfonato calix[4]arene (c) and (d) taken 1 hour apart (circles highlight features that are either dissolving in the case of *p*-phosphonato calixarene or not dissolving in the case of the sulfonato analogue). Concentration of *p*-phosphonato calix[4]arene is 0.002 and *p*-sulfonato calix[4]arene is 0.015 mM.



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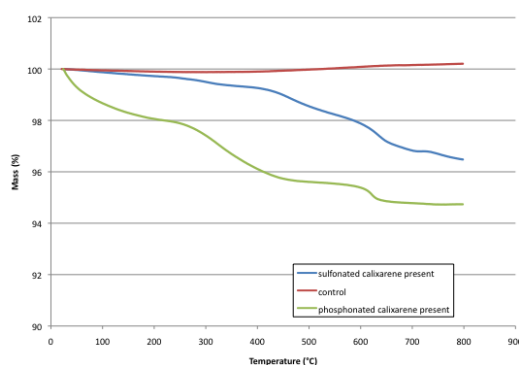
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Fig S3. 2D nucleation rates normalized to control, for 5x5 μm scan area, 253 s scan time (lines drawn to aid reader only).



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Fig. S4. Thermal gravimetry result of barium sulfate control versus barium sulfate formed in the presence of 0.42 mM *p*-sulfonato calix[4]arene.



45 References

- R1. A. Baynton, T. Radomirovic, M. I. Ogden, C. L. Raston, W. R. Richmond, F Jones (2011), *CrystEngComm.*, 13 109–112.