

## Oriented Attachment by Enantioselective Facet Recognition in Millimeter-sized Gypsum Crystals†

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### Supplementary information

#### EXPERIMENTAL SECTION

##### Chemicals

Anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) and calcium chloride dihydrate ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ) were purchased from Sigma and used as received without further purification. Distilled water used throughout all experiments was purified using a Milli-Q system.

##### Instrumentation

Polarized light microscopy (PLM) was carried out with a Nikon petrographic microscope. Samples were taken from the reaction solutions at different times and dried at room temperature. Together with representative figures shown in the main text, additional PLM images are shown in Figures S1-S7.

SEM samples were stored in a desiccator with silica gel until dry and imaged using a JEOL JSM-820 microscope, with typical beam settings of 1.5 kV. SEM images of the aggregated gypsum crystals are shown in Figures S8-S9.

PXRD was performed using a Siemens diffractometer with X-ray source emitting Cu  $K\alpha$  radiation. Samples were ground and placed on a piece of silicon wafer. X-ray data were collected between  $10^\circ$  and  $60^\circ$  with a scan rate of  $1^\circ/\text{min}$  (Figures S10-S11).

## Experimental procedures

### Protocol A

Calcium sulfate was precipitated as follows: A stock solution of anhydrous sodium sulfate (200 mL, 1M) was added to a flask containing distilled water (500 mL) under continuous stirring. Then, a stock solution of calcium chloride dihydrate (200 mL, 1.5M) was added. The resulting suspension containing acicular gypsum crystals was heated at 70-80 °C under stirring. Gypsum aggregates could be detected by polarizing light analysis at times between 24 and 48 h (See Figure S1). To keep the solution supersaturated it is necessary to add 10 mL of each solution after a few days (no new crystals are generated).

### Protocol B

Initial crystals of the bassanite form ( $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ) were obtained by adding a boiling aqueous solution of calcium chloride dihydrate (200 mL, 1.5M) to a boiling aqueous solution of sodium sulfate (200 mL, 1M) under stirring (Figure S10). The hemihydrate form converts into gypsum after a few minutes (Figure S11), while further stirring for 24 h gave rise to larger aggregates (Figure S2). To keep the solution supersaturated it is necessary to add 10 mL of each solution after a few days (no new crystals are generated).

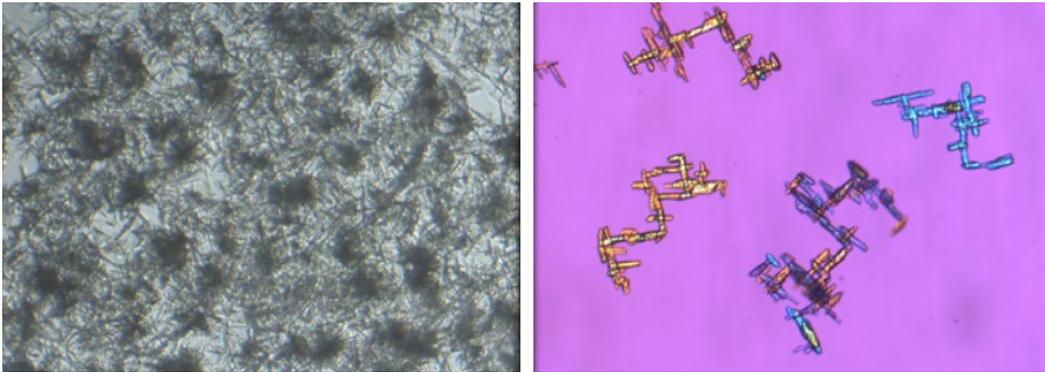
### Protocol C

Gypsum twins were obtained in supersaturated solutions as follows: An aqueous solution of  $\text{Na}_2\text{SO}_4$  (3 mL, 1M) was added under boiling to a brine solution (20 mL, 2.5M). The flask was then removed from the heater and an aqueous solution of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  (3 mL, 1.5M) was added under stirring. The bassanite form initially detected converted rapidly into gypsum twinned crystals (Figures S3).

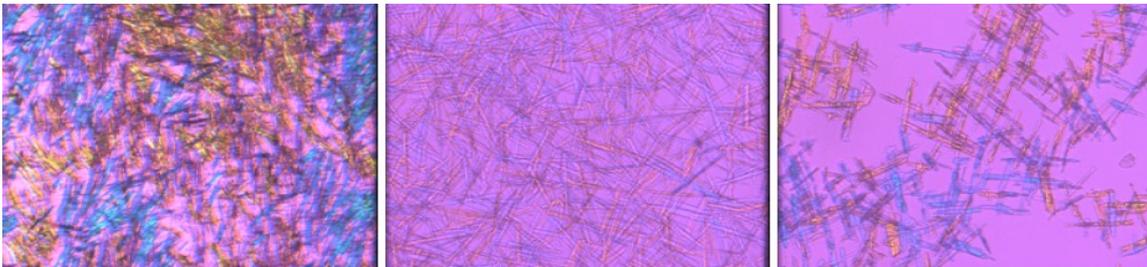
### Protocol D

As above, the protocol unravels the generation of new aggregates from gypsum twins and/or incorporation of twins into previous aggregates, so long as the system is kept supersaturated (adding 10 mL of both solutions, but no new crystals are generated). By combining a suspension of gypsum aggregates (Protocol A, after 24 h) and the final stage of Protocol C, further aggregation takes place after 24 h-monitoring (Figure S4).

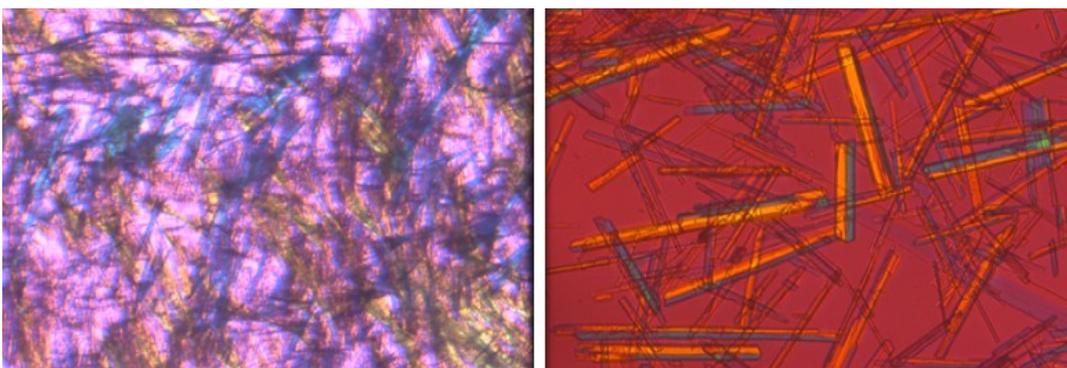
## Figures



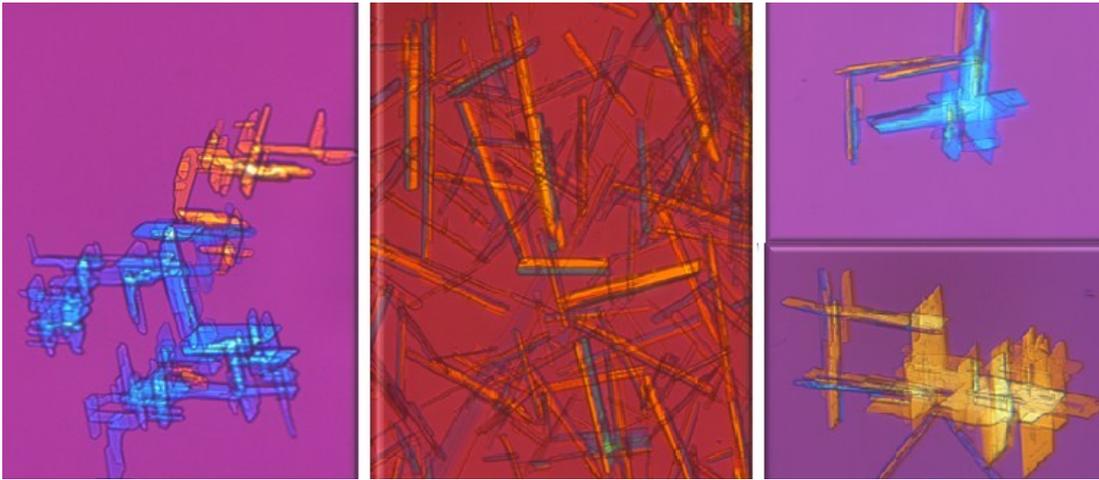
**Figure S1.**  $\text{CaSO}_4$  solution at ambient conditions after *ca.* 24 h with formation of acicular gypsum crystals (left) and subsequent formation of aggregates after 2-5 days (right) viewed between crossed polarizers with the introduction of a first order red wave plate (Protocol A).



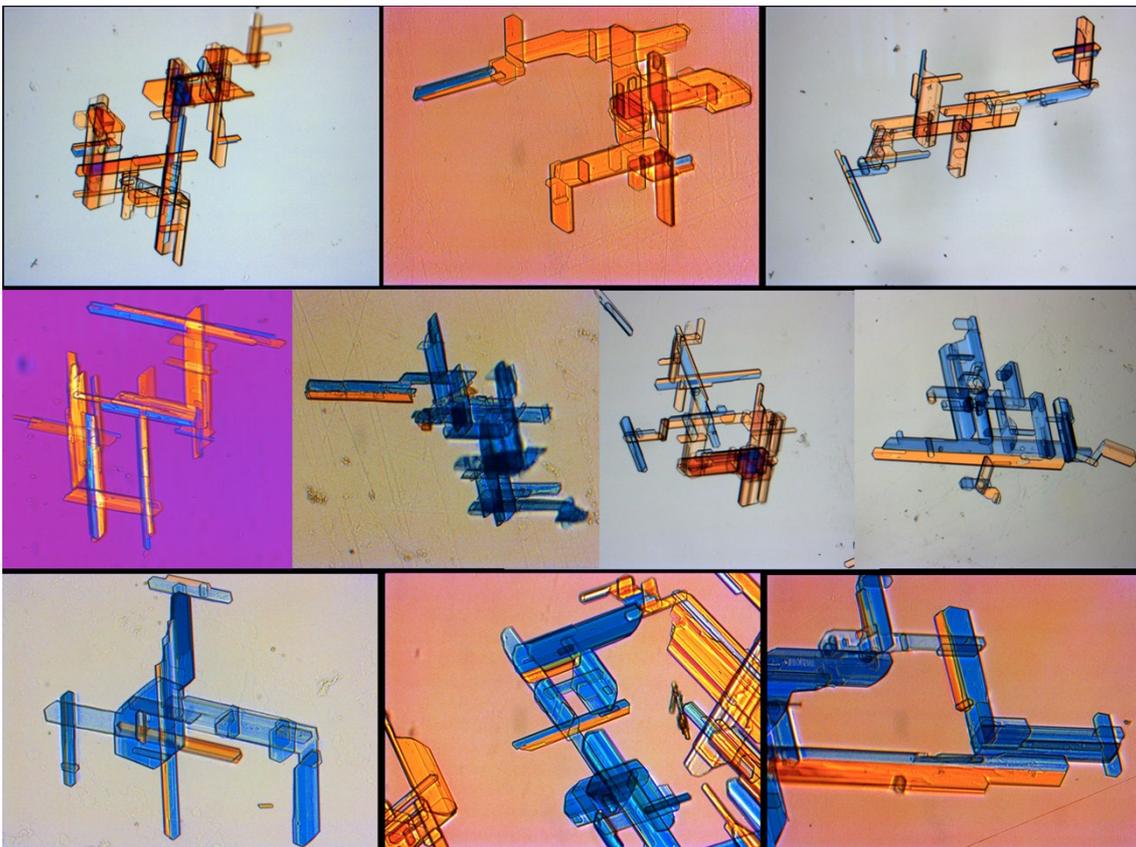
**Figure S2.** Sequential transformation of bassanite (left) to gypsum crystals (middle) and their subsequent aggregation (right) as viewed between crossed polarizers with the introduction of a first order red wave plate (Protocol B).



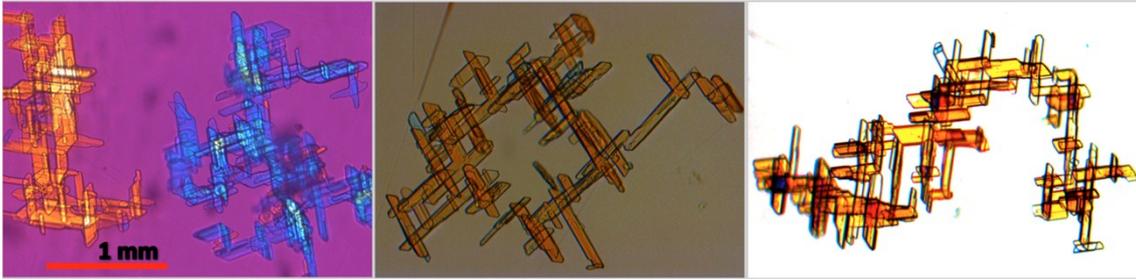
**Figure S3.** Gypsum crystals (commonly twinned on the  $\{100\}$  plane) from supersaturated solutions starting from the bassanite form, as viewed between crossed polarizers with the introduction of a first order red wave plate (Protocol C).



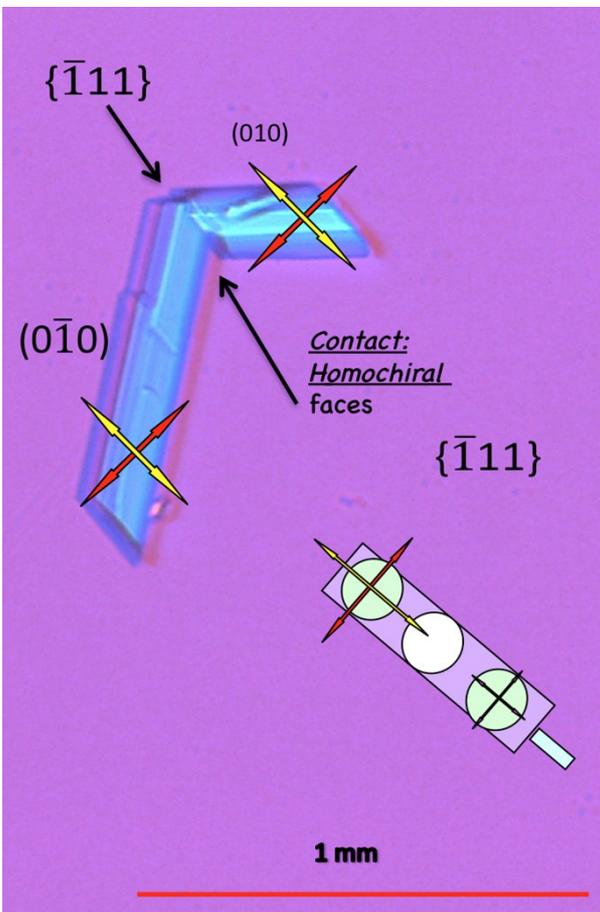
**Figure S4.** Incorporation of cruciform twins (middle) into untwinned aggregates (left) leading to new aggregates (right) as viewed between crossed polarizers with the introduction of a first order red wave plate (Protocol D).



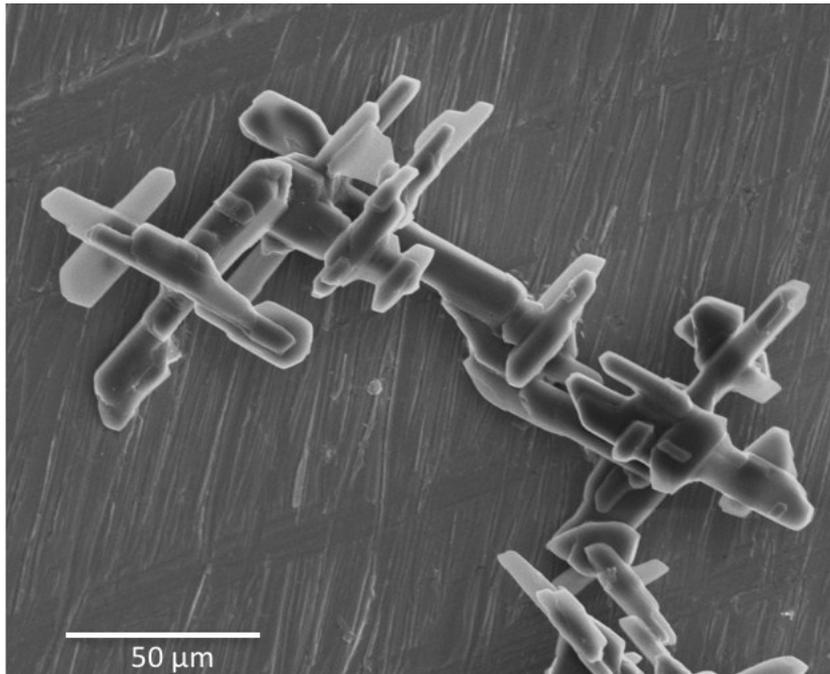
**Figure S5.** Incorporation of twins into untwinned aggregates as viewed between crossed polarizers with the introduction of a first order red wave plate.



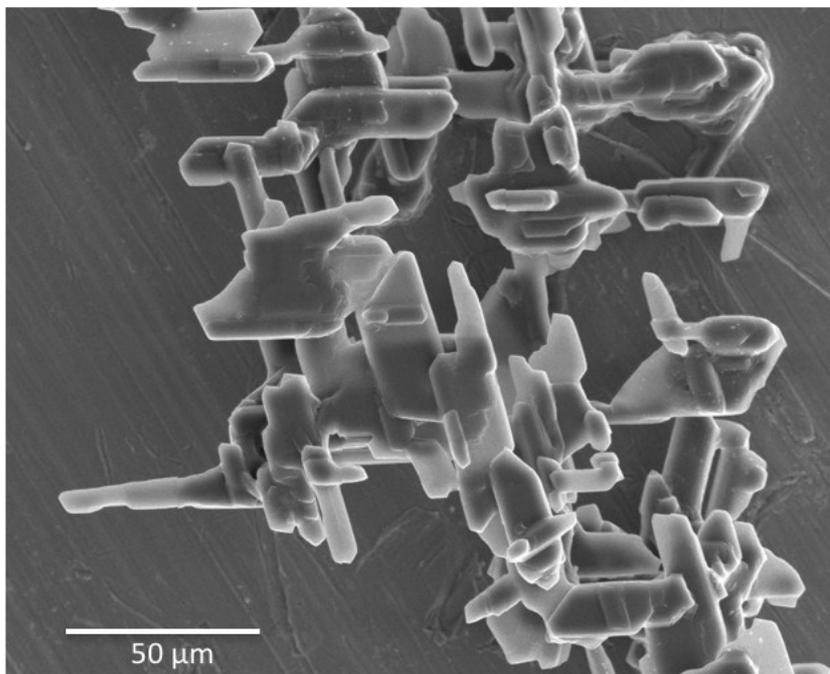
**Figure S6.** A group of aggregates as viewed between crossed polarizers with the introduction of a first order red wave plate.



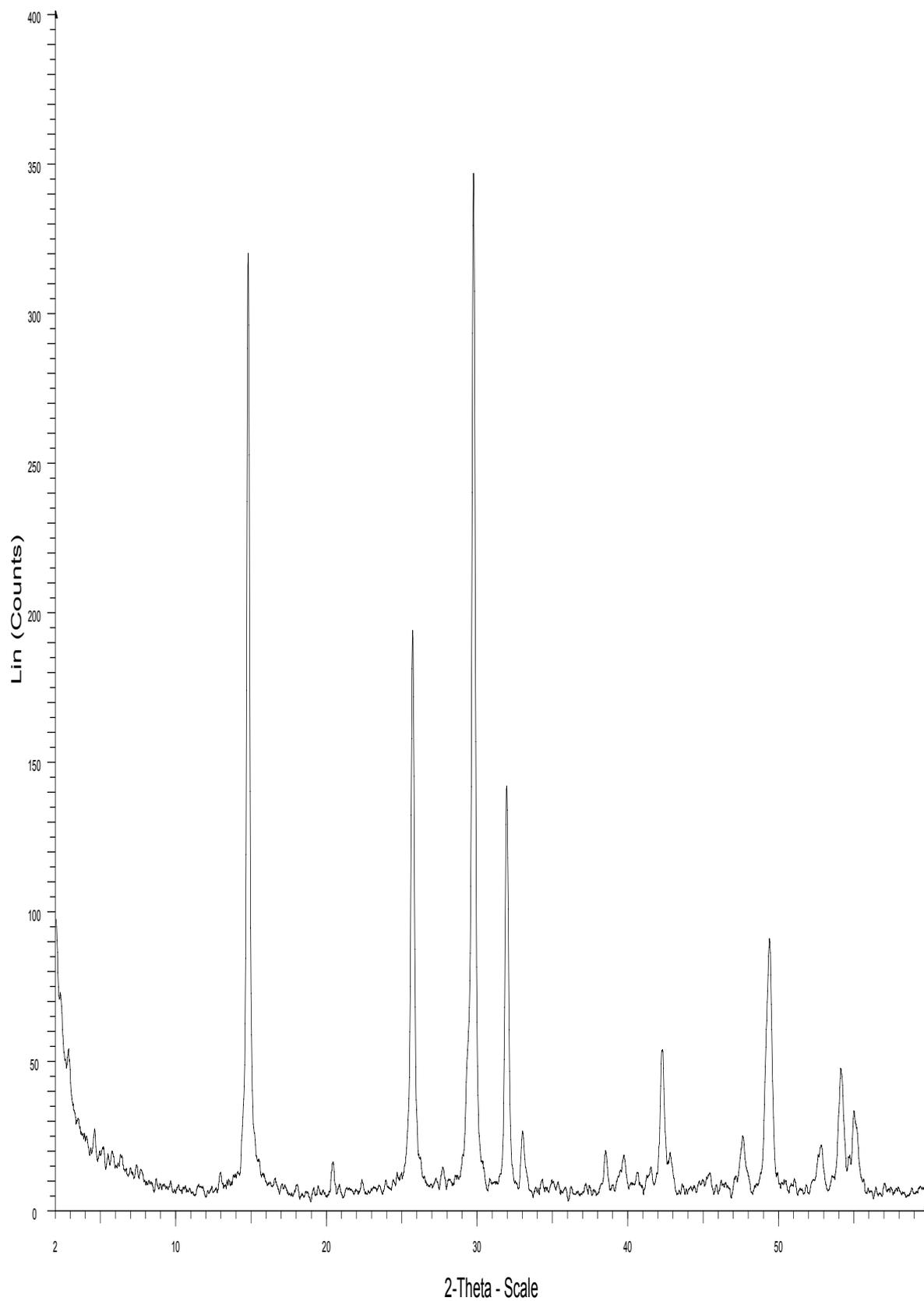
**Figure S7.** Initial gypsum aggregate with arrows highlighting the homochiral  $\{111\}$  contact as viewed between crossed polarizers with the introduction of a first order red wave plate with fast and slow axes indicated. A crystal can only achieve homochiral contacts between two such surfaces if one of the crystals has been turned over.



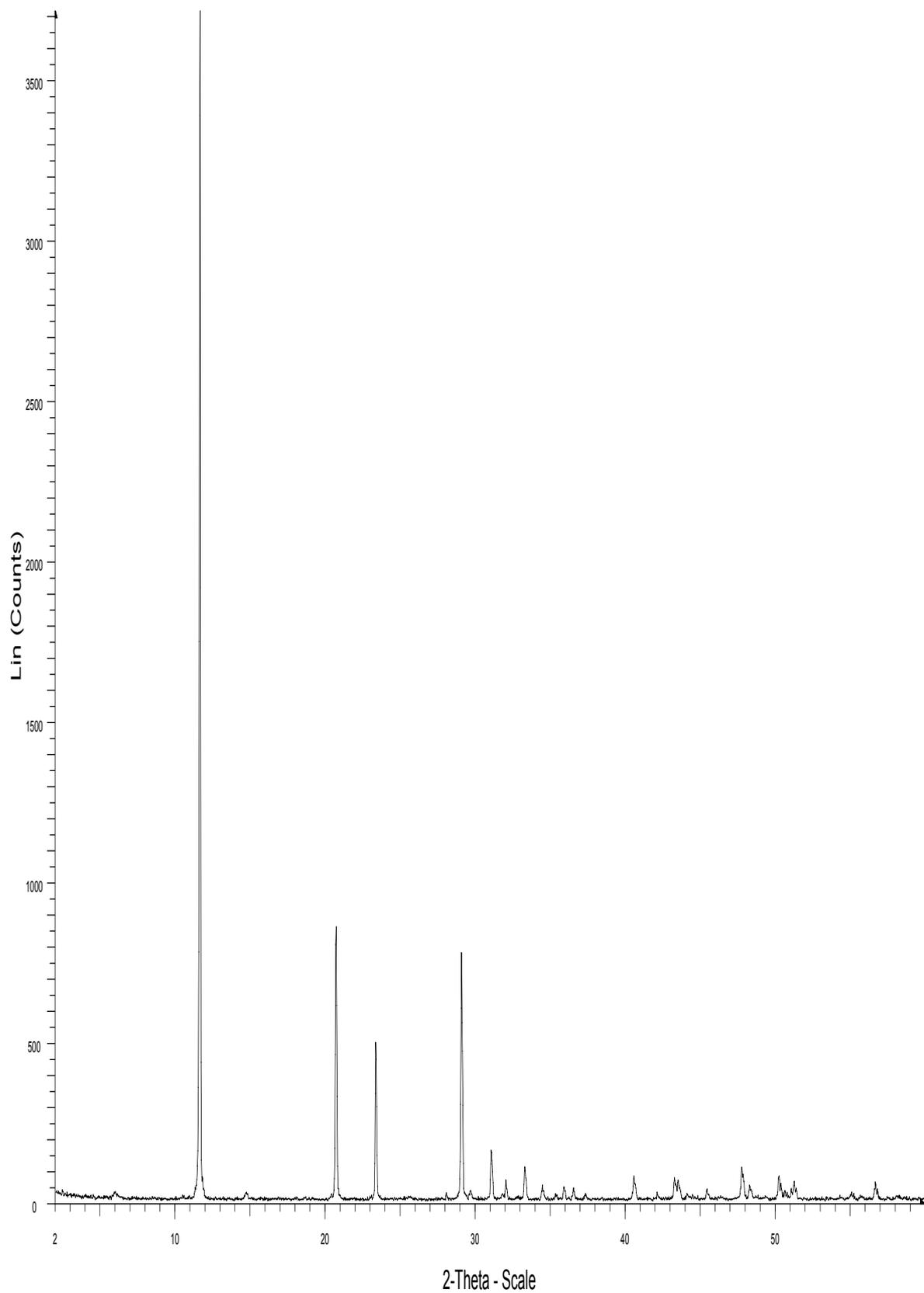
**Figure S8.** SEM image of initial precipitates of gypsum (dihydrate  $\text{CaSO}_4$  particles) from almost equimolar mixtures of  $\text{Na}_2\text{SO}_4$  and  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  solutions.



**Figure S9.** SEM image of gypsum aggregates (after *ca.* 24 h precipitation).



**Figure S10.** XRPD diffractogram of initial powder obtained in experiments with protocol B that corresponds to bassanite.



**Figure S11.** Representative XRPD diffractogram of initial powder obtained in experiments with protocol A or after a few hours with protocol B, that correspond to gypsum.