

**Electronic Supplementary Information (ESI) for**

**Oriented Attachment and Aggregation as a Viable Pathway**

**to Self-Assembled Organic/Inorganic Hybrid Materials**

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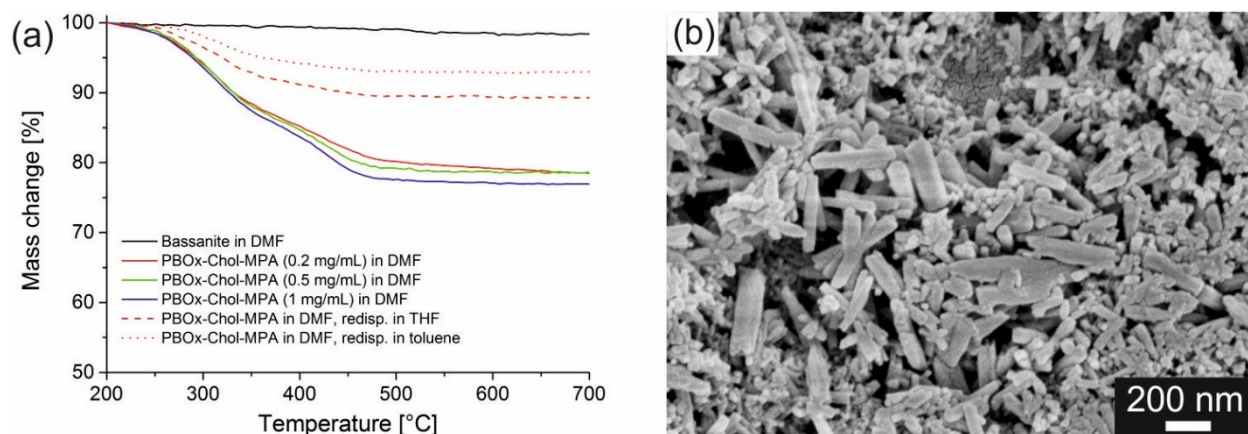
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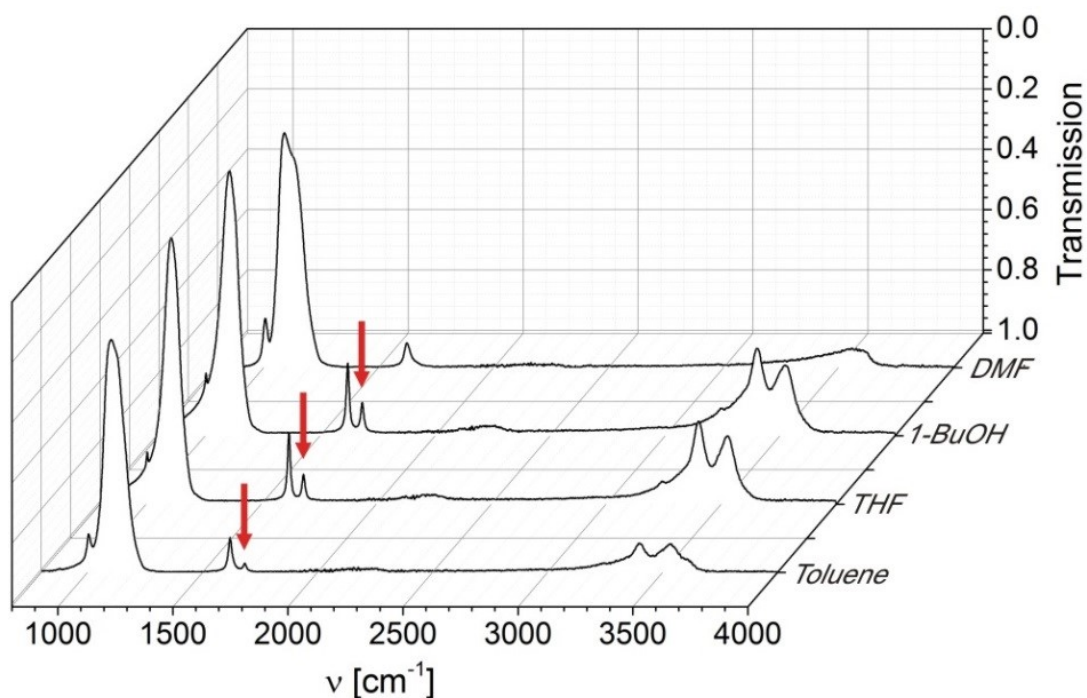
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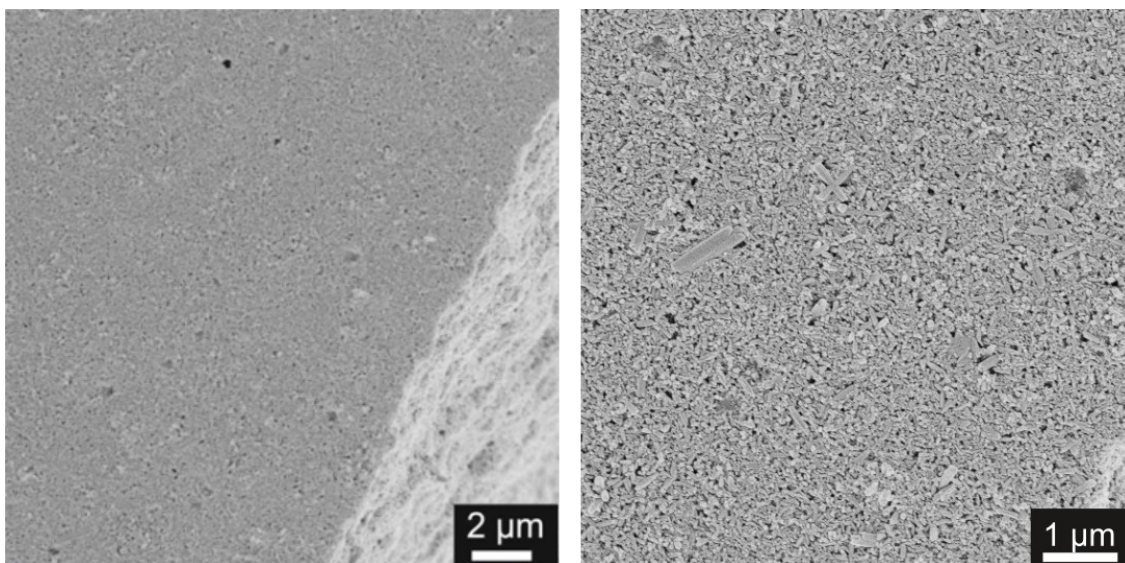
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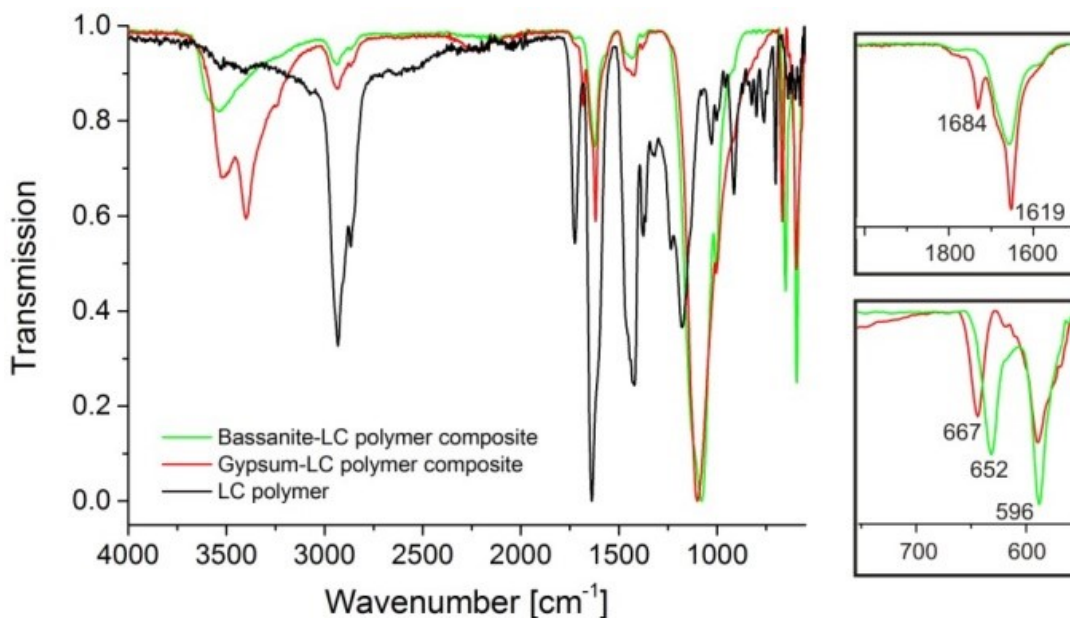
**Figure S1.** (a) TGA data (acquired under  $O_2$  atmosphere) of bassanite (black) and polymer/bassanite particles manufactured by quenching aqueous  $CaSO_4$  solutions in DMF containing 0.2 (red), 0.5 (green) and 1 mg/mL (blue) PBOx-Chol-COOH. Solvent exchange from DMF to THF or toluene produced hybrid materials with reduced fractions of polymer (dashed and dotted red lines). (b) SEM image of polymer/bassanite particles (bassanite:polymer ratio: 4:1 (w/w), LC polymer: PBOx-Chol-COOH).



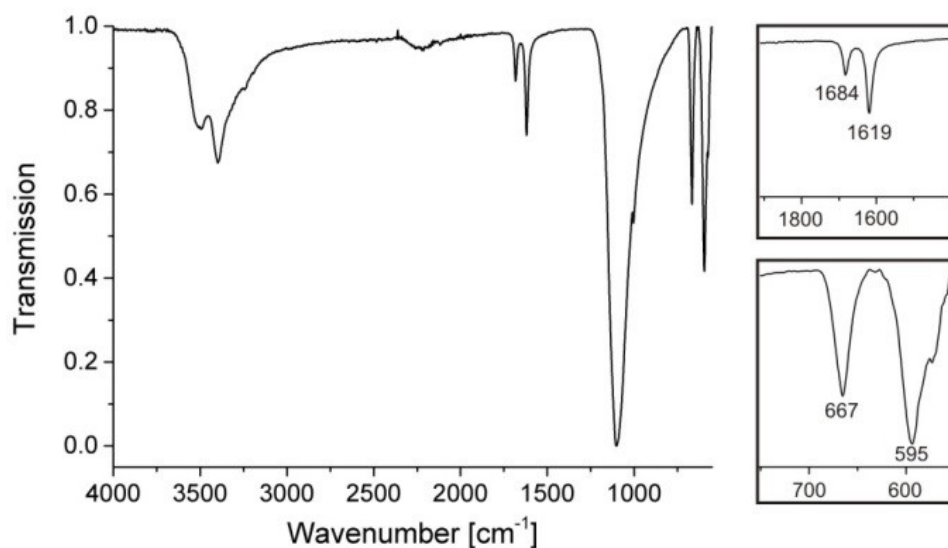
**Figure S2.** IR spectra of solids produced by quenching of 2 mL 50 mM  $CaSO_{4(aq)}$  into 20 mL organic solvent (DMF, 1-BuOH, THF or toluene, as indicated). Phase-pure bassanite was only obtained with DMF as solvent. The band at  $1684\text{ cm}^{-1}$  (marked with a red arrow) is characteristic for gypsum and absent in the case of pure bassanite.



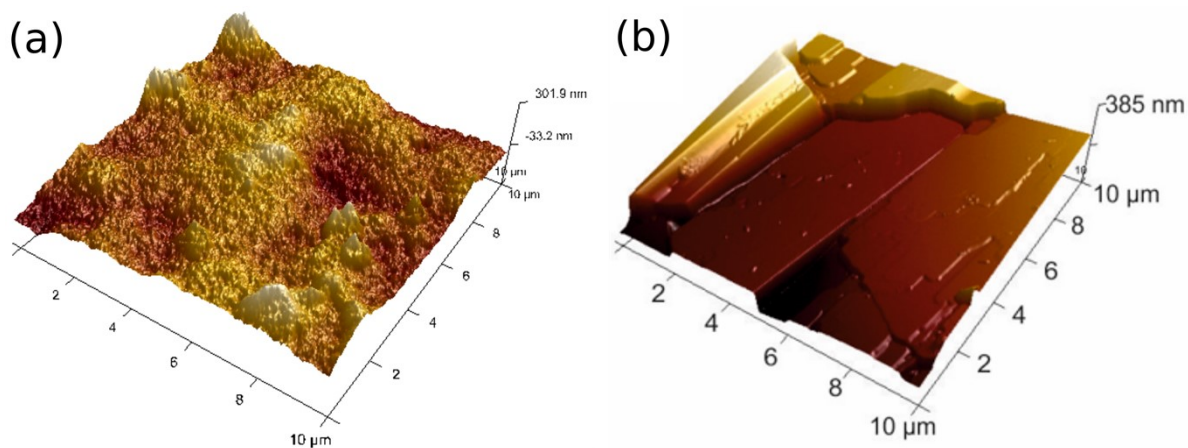
**Figure S3.** Representative SEM images (top view) of polymer/bassanite composites obtained after rotational shearing of particle dispersions prepared via quenching of aqueous calcium sulfate solutions into DMF containing pre-dissolved LC polymer PBOx-Chol-COOH (bassanite:polymer ratio: 4:1 (w/w)).



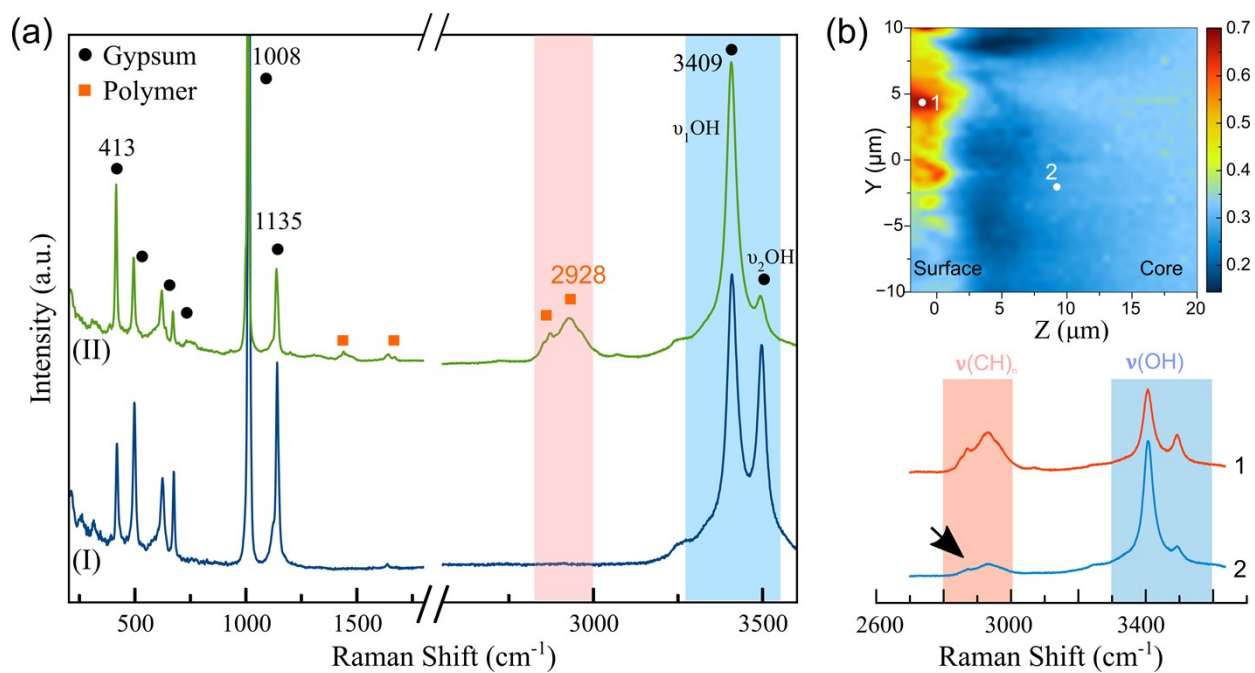
**Figure S4.** IR spectra of a polymer/gypsum hybrid material (red) obtained by transforming corresponding bassanite aggregates (green, bassanite:polymer ratio: 4:1 (w/w), with PBOx-Chol-COOH as LC polymer) via storage in a closed desiccator at 100 % RH at room temperature for 20 h. The spectrum for the neat PBOx-Chol-COOH polymer is also shown as a reference (black). Insets: zooms into spectral regions of 1500-2000  $\text{cm}^{-1}$  and 550-750  $\text{cm}^{-1}$ , both confirming the presence of pure bassanite (green) before and pure gypsum (red) after transformation (cf. Fig. S5).



**Figure S5.** IR spectrum of phase-pure gypsum material produced upon storage of pure bassanite in a closed desiccator at 100 % RH for 20 h at room temperature. Insets: zooms into spectral regions of 550-750 and 1400-1900  $\text{cm}^{-1}$ , where characteristic bands of gypsum occur.

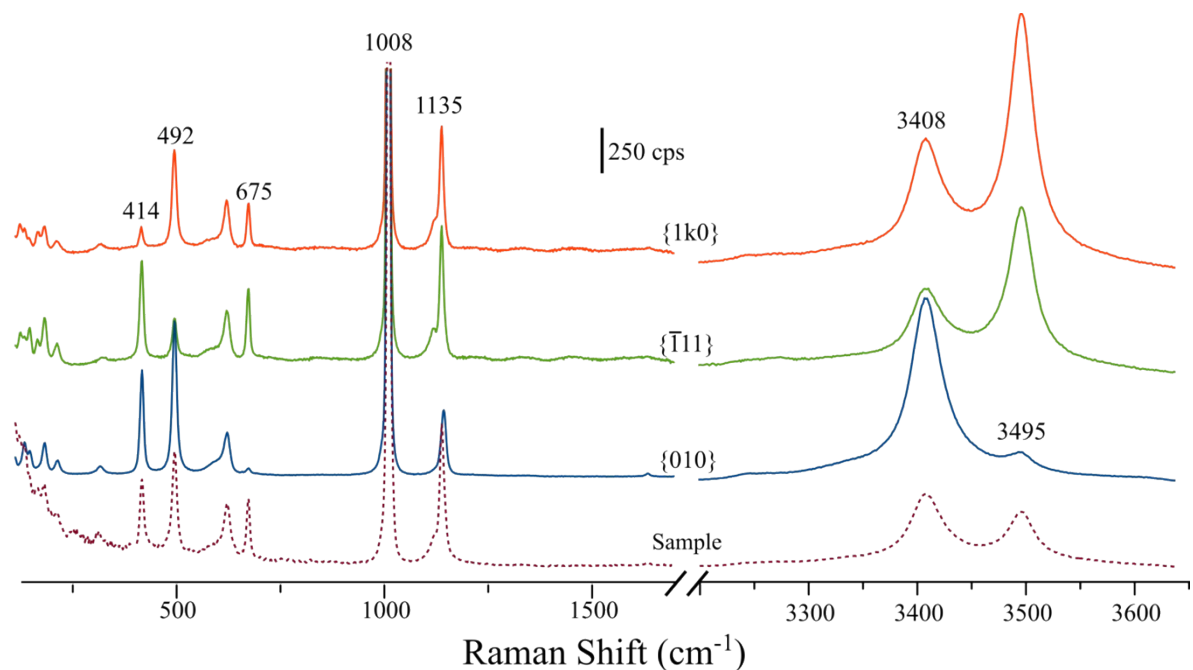


**Figure S6.** AFM images of the surface of (a) polymer/gypsum hybrids (obtained by transforming polymer/bassanite aggregates (bassanite:polymer ratio of 4:1 (w/w), with PBOx-Chol-COOH as LC polymer) and (b) pure gypsum, which was obtained by exposing pure bassanite to humid air.

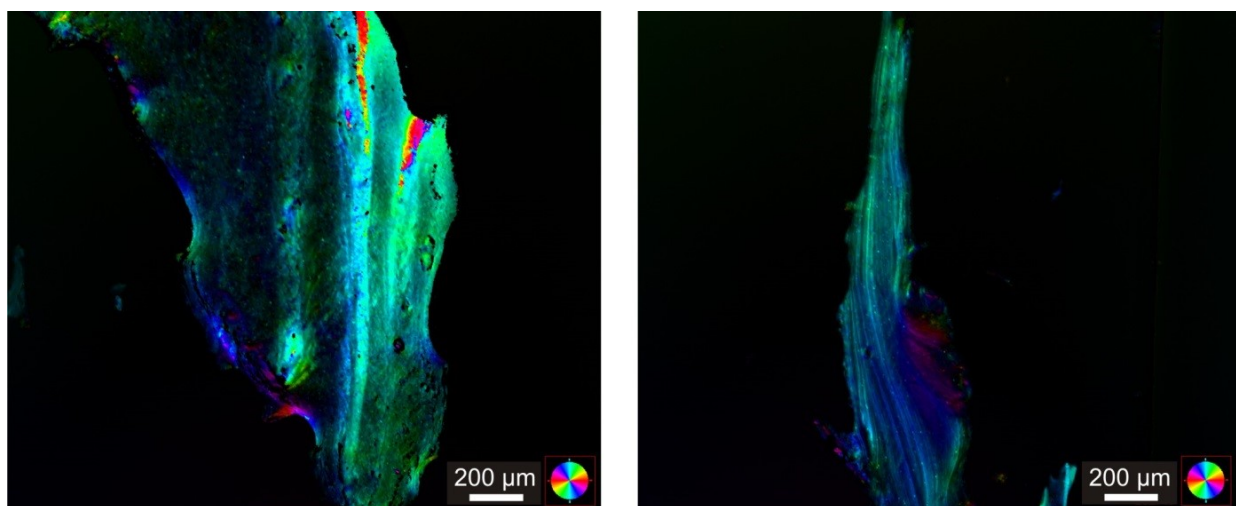


**Figure S7.** (a) Raman spectra of pure gypsum (blue) and polymer/gypsum hybrids (green) obtained by hydration of corresponding bassanite precursor materials (bassanite:polymer ratio of 4:1 (w/w), with PBOx-Chol-COOH as LC polymer). Black circles and orange squares assign the observed peaks to the inorganic and organic phase, respectively. Red- and blue-shaded areas indicate regions where, respectively, aliphatic  $\nu(\text{CH}_n)$  vibrations of the polymer (2800-3000  $\text{cm}^{-1}$ ) and  $\nu(\text{OH})$  vibrations of the structural water in gypsum (3300-3600  $\text{cm}^{-1}$ ) occur. These bands were used to quantify local compositions in the form of 2D maps (as described in the main text). (b) Colour-coded Raman image (XZ section) illustrating the distribution of organic (red) and inorganic (blue) phases in the hybrid structure. (c) Individual Raman spectra collected on the surface (1) and in the core (2) of the composite shown in Fig. 4a (main text). Spectrum 2 reveals that significant amounts of polymers are occluded in the bulk of the mesocrystals (relevant bands indicated by black arrow). The colour code of the shaded areas is the same as in (a).





**Figure S8.** Raman spectra acquired on different faces (orange: {1k0}, green: {-111}, blue: {010}) of natural single gypsum crystals, in comparison to the spectrum of a gypsum reference sample prepared by hydration of bassanite particles in the absence of polymer. Note the strong differences in the relative intensities of structural water bands (3300-3600 cm<sup>-1</sup>) as depending on crystal orientation.



**Figure S9.** Quantitative birefringence optical micrographs of the shear-induced LC polymer phase (PBOx-Chol-COOH), which was obtained by exposing a dried polymer film to humid air at room temperature for 20 h.