Supplementary Material (ESI) for CrystEngComm

Supporting Information for

Gel incorporation inside of organic single crystals grown in agarose hydrogels

Hanying Li,[a] Yuzo Fujiki,[b] Kazuki Sada[b] and Lara A. Estroff*[a]

[a] Department of Materials Science and Engineering, Cornell University, Ithaca, NY 14853, USA; E-mail: lae37@cornell.edu

[b] Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Nishi Ku, Fukuoka 819039, Japan.

Experimental section:

Glycine crystallization:

Agarose solutions (1 w/v %) were prepared by dissolving agarose powder (Type IB, Sigma) in a hot solution of glycine (60 mg/mL, J.T.Baker). The agarose solution (3 mL) was then filtered (syringe filter; 0.2 μm, Nylon, Millipore) into a 20 mL vial. After gelation (about 30 minutes), ethanol (6 mL) was filtered into the vial that was then sealed and laid upside down immediately. After 3 days, crystals form in the gel, and 10 days later, crystals were manually removed using tweezers.

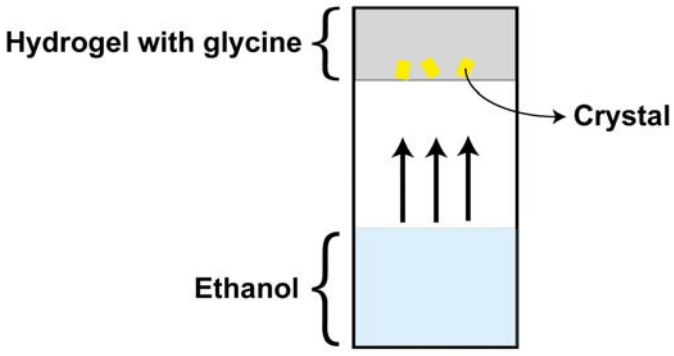

Fig. S1 A schematic representation of the crystallization of glycine in an agarose hydrogel. An agarose hydrogel containing glycine solution was formed on the bottom of a vial. After ethanol

was filtered in, the vial was sealed and laid upside down immediately to separate the gel and ethanol. The slow diffusion of ethanol (g) into the hydrogel resulted in the crystallization of glycine. Due to the syneresis (exudation) of glycine solution from the hydrogels, some precipitate also formed on the wall of the vial. Only the crystals grown in the hydrogel were used for this study. (The drawing is not to scale.)

Calcium tartrate tetrahydrate (CTT) crystallization:

Agarose solutions (1 w/v %) were prepared by dissolving agarose powder (Type IB, Sigma) in a hot solution of 40 mM $CaCl_2 \cdot 2H_2O$ (99+%, Sigma-Aldrich). The agarose solution (5 mL) was then filtered (syringe filter; 0.2 μm, Nylon, Millipore) into a 15 mL centrifuge tube. After gelation (about 30 minutes), 5 mL of 40 mM sodium tartrate solution was filtered into the tube. After 2-3 days, crystals form at the solution/gel interface, and 15 days later, crystals were taken out using tweezers. The half of the crystal that grew into the gel (Fig. 2a, right) is more opaque than the part of the crystal that grew into solution (Fig. 2a, left).

Etching:

In order to observe the incorporated gel fibers, the crystals were etched. Glycine crystals were etched in ethanol for four days. The half of the CTT crystal that grew into the gel was cut with a clean razor and a block of the cut crystal was then etched in DI water for two days. After etching, the etched crystals were air-dried for characterization. CTT crystals were also etched in 0.1 M HCl solution and observed in-situ by optical microscopy.

Single-crystal X-ray diffraction:

A small block of crystal was cut and transferred to the goniometer head of a Bruker X8 APEX2 diffractometer equipped with a molybdenum X-ray tube (λ = 0.71073 Å). Diffraction points (155 points in 60 frames for glycine crystal; 707 points in 120 frames for calcium tartrate tetrahydrate crystal) were collected in frames with 0.5^{o}/frame. The unit cell was obtained using Apex V2.1 program.

Microscopies:

The as-grown crystals were imaged by optical microscopy (Olympus SZ) equipped with a digital camera (Olympus C-7070). The CTT crystals during HCl etching were imaged by optical microscopy (Leica DM EP) equipped with a digital camera (Leica DFC 290). The morphologies of the etched crystals were investigated by field emission scanning electron microscopy (Hitachi S4500, 5 kV for glycine, 10 kV for CTT) after being sputter-coated with Pd-Au.