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Electronic Supplementary Information

Oriented crystal growth of phenylalanine and dipeptide by solution shearing

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Figure S1. Schematic of solution shearing system.

Solution shearing coater

The coater consists of a motorized stage, hot plate and glass slide. A hole was made in a slide glass to provide solution during the process. The slide glass was used as a blade. The substrate and blade were placed on a heater to control temperature of the system. Pattern of optical interference was monitored to control the angle of the blade against the substrate. The interval of fringes was controlled to be maximized using a micrometer, which allow us to place the blade to the substrate in parallel. An aluminum weight was placed on the blade surface to make it tightly contact with the substrate. The gap between the slide glass and the Si wafer was in the range from 200 to 400nm estimated from the optical fringes. 10-µL solution was dropped into the hole, then solution shearing was conducted by moving the motorized stage with a stepping motor, which was remotely controlled by the LabVIEW software. The solution covered the area between the blade and substrate completely during the coating process.



Figure S2. (a) Optical image of thin film of F fabricated by the solution shearing with 100 μ m/s at 70 °C. (b) Height image of atomic force microscopy (AFM) of (a). (c) Phase image of (b). (d) Height profile of (a) as indicated with the red dotted line.

Microscopic morphology of thin film made by solution shearing

Figure S2 shows optical and atomic force microscope images of the thin film of phenylalanine made by the solution shearing. The height image and its height profile show that the thickness of the thin film was 300 nm. Furthermore, the phase image indicates flat faces of the crystal with multiple steps.



Figure S3. (a) Optical images of thin films of F and DF-OMe fabricated by solution shearing with 100 μ m/s at 70 °C. The y-axis shows the position of films grown by solution shearing. Zero is the starting point of shearing. (b) Estimation of coverage by image processing: original image (left) and processed image (right) (c) Estimation of crystal orientations from a binary image.

Estimation of coverage and orientation parameter

The coverage and orientation parameter of thin films were evaluated using an image analysis software, Image J (https://imagej.nih.gov/ij/). The original images are shown in Fig. S3(a). In the first step to estimate the coverage, optical microscope images were converted from RGB images to binary images using the color of the Si substrate as a threshold. A representative processed image is shown in Fig. S3(b). Next, the coverage of F and DF-OMe on Si wafer were estimated by the binary images. Orientation of the crystals was estimated by the direction of crystal edges.

These edges were detected by the Image J, and binary images showing edges with black color were produced. The distribution of the edge orientation was evaluated by Image J plugin (orientation J). The result is shown in Fig. S3(c).

Herman's orientation factor

Using the angle distribution of the edges, we evaluated the distribution of orientation by Herman's orientation factor (O.P.)^{1,2},

$$O.P. = \frac{3 < \cos\theta > ^2 - 1}{2}$$

where θ is the angle between the shearing direction and direction of an edge. In principle, O.P. has a range from 1 to -0.5. O.P.=1 corresponds to perfectly aligned structure. O.P. = 0 corresponds to randomly oriented structure. O.P.=-0.5 corresponds to perfectly aligned structure in perpendicular direction to the shearing direction.

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Figure S4. Schematic of the setup for micro polarized Raman spectroscopy.

Raman spectrum measurement

Raman spectra were obtained by a handmade micro-optical system with a spectrometer Isoplane 320 (Princeton instruments). A 532-nm laser was used for the excitation. Samples were monitored by an optical microscope and the excitation laser was focused lineally on the sample using cylindrical lens. For angle resolved polarized Raman spectroscopy, a Glan-Thompson prism was placed as an analyzer on the laser path. A Fresnel rhomb \Box 1/2 waveplate was also placed on laser path to select a polarization angle of laser before the spectrometer. A 1/4 waveplate was placed in front of the slit of the spectrometer to eliminate the effect of polarization dependence of the spectrometer.

	Peak position (cm ⁻¹)	Vibrational mode	$Int_{\prime\prime\prime}/Int_{\perp}$	Reference
F	1213	$\gamma(C-H), \delta_{ring}$	1.77	[21]
F	1310	v_{ring}	9.41	[21]
F	3055	$[\mathrm{NH}_3]^+$ asym. str.	1.64	[22]
DF-OMe	1204	Phenyl C-C _{β} str	3.23	[23]
DF-OMe	1667	Amide I	0.836	[23]

Table.S1 Summary of Raman spectra with peak position, assignment of the vibrational mode, and intensity ratio between parallel and perpendicular polarization.

Polarization dependence of Raman spectra

The polarization dependence of Raman spectra is shown in Fig. S5(a). The intensity at 3055 cm⁻¹ exhibited a anisotropic feature depending on the polarization orientation of excitation laser (Fig. S5(b) and (c)). The blue curve in Fig. S5(c) is a fitting curve with the following equation.

$I(\theta) = A\cos^2\theta_{+B}$

where *I* is the intensity of Raman peak, A and B are fitting parameters. A and B represent intensities in longitudinal and transverse direction of the anisotropic feature, respectively. We assumed here that the peak intensity ratio, A/B, is unique for the crystal domain grown by solution shearing. The ratio probably arises from a Raman tensor of a vibrational mode in the molecular crystal. When the crystal domain oriented in a direction with an offset angle ϕ from the shearing direction, an intensity ratio between intensities measured with excitation polarization of 0 and 90-dgree along the shearing direction have a dependence on angle ϕ shown as a red curve in Fig. S5(d). The inset represent the orientation of the crystal domain and the excitation polarization. In fact, Fig. 4(c) shows a clear change of the intensity ratio depending on the position, which is probably due to the variation of the orientation of crystal domain. The pink region corresponds to the range of the observed intensity ratio in Fig. 4(c). Based on the observation, we can guess that the range of angle ϕ indicated by the blue lines represents the possible range of the orientation distribution.



Figure S5. (a) Polarization dependence of Raman spectra of F in the range from 2800 to 3200 cm⁻¹. These spectra were measured at a same location of a crystal domain. (b) Polar plot of Raman peak intensity at 3055 cm⁻¹ depending on the polarization angle. (c) Polarization dependence of the Raman intensity same as (b) with a fitting curve. (d) Raman Intensity ratio between 0- and 90-degree polarization for the peak at 3055 cm⁻¹ depending on the polarization angle.



Crystal structures with unit cell were shown by the VESTA software using single crystal XRD data of phenylalanine (F) and aspartame (DF-OMe) crystals from the Cambridge Structural Database (CSD).

Reference code of each structure is F(I) SIMPEJ,F(II) QQQAUJ04,F(III) QQQAUJ003,F(IV) GOFWOP01,DF-Me(I) DAWGOX,DF-OMe(II) EFIFOO01,DF-OMe(III) KETXIR,DF-OMe(IV) ODOBAK.

Polymorphism of F and DF-OMe

The crystal structures of phenylalanine, F, have a structure with hydrophobic region of aromatic ring and hydrophilic region of carboxlic group and amino group. F(I) and F(III) have a similar structure but sligtly different in the angle of aromatic rings. F(II) and F(IV) also have a similar structure. These crystals contain water molecules inside the unit cell.

The crystal structures of aspartame, DF-OMe have a hydrogen network formed by amide bonds along the perpendicular direction to the page. While DF-OMe(I) and DF-OMe(III) have hydrophobic region with 4 aromatic rings, DF-OMe(II) and DF-OMe(IV) have hydrophobic region with 3 aromatic rings.

XRD pattern analysis

Prediction of powder XRD peaks was performed by the VESTA software using single crystal XRD data of phenylalanine (F) and aspartame (DF-OMe) crystals from the Cambridge Structural Database (CSD). The predictive spectra were compared with the observed spectra in Fig. S8-S11.

The crystals grown by the solution shearing at 70 $^{\circ}$ C showed peaks of F(I) and F(II). In addition, the solution shearing at room temperature showed mainly peaks of F(II).



Figure S8. XRD spectra of F thin film by solution shearing with shearing speed of 100 μ m/s (black line) at 70 °C. Calculated spectra from single crystal structure of F(I), F(II), F(III), and F(IV) were plotted with red, blue, pink and green, respectively.



Figure S9. XRD spectra of F thin film by solution shearing with shearing speed of 100 μm/s (black line) at room temperature. Calculated spectra from single crystal structure of F(I), F(II), F(III), and F(IV) were plotted with red, blue, pink and green, respectively.

The sample made by the solution shearing at room temperature showed a clear matching with peaks of DF-OMe(IV). Meanwhile, the sample produced at 70 °C shows a good matching with DF-OMe(I).



 2θ (degree)

Figure S10. XRD spectra of DF-OMe thin film by solution shearing with shearing speed of 100 μ m/s (black line) at 70 °C. Calculated spectra from single crystal structure of DF-OMe(I), DF-OMe(II), DF-OMe(III), and DF-OMe(IV) were plotted with red, blue, pink and green, respectively.



Figure S11. XRD spectra of DF-OMe thin film by solution shearing with shearing speed of 100 μ m/s (black line) at room temperature. Calculated spectra from single crystal structure of DF-OMe(I), DF-OMe(II), DF-OMe(III), and DF-OMe(IV) were plotted with red, blue, pink and green, respectively.

Supplementary movie

The movie was taken under the following condition for the solution shearing: Phenylalanine solution was used with the shearing speed of 100 μ m/s at the stage temparature of 70 °C. The movie plays in real time. The size of the frame is 400 μ m in the horizontal direction.