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Electronic Supplementary Information

Mechanically robust crystalline monolayer assemblies of oligosaccharide-based amphiphiles on water surfaces

Yusuke Yataka,[a] Shoki Tanaka,[a] Toshiki Sawada[a,b] and Takeshi Serizawa*[a]

[a] Department of Chemical Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8550, Japan

[b] Precursory Research for Embryonic Science and Technology, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi-shi, Saitama 332-0012, Japan

Fax: +81-3-5734-2128; E-mail: serizawa@polymer.titech.ac.jp

Experimental details

Materials. Alkyl β-cellulosides were enzymatically synthesized following our previous report.[1] Octyl β-D-glucopyranoside (Glc-C_8) was purchased from Dojindo Laboratories. Deuterated water was purchased from Sigma-Aldrich. All other reagents were purchased from Nacalai Tesque. Parafilm® was purchased from Bemis Company. Au substrates were purchased from TANAKA KIKINZOKU KOGYO K.K. Ultrapure water (>18.2 MΩ·cm) was supplied by a Milli-Q system (Merck Millipore) and was used throughout all the experiments.

Critical association concentration (CAC) measurements. The CAC of alkyl β-cellulosides or Glc-C_8 was determined using a pyrene fluorescence method.[2] A pyrene solution dissolved in *N*,*N*-dimethylformamide (DMF) (5 μL) was mixed with aqueous alkyl β-celluloside (0.00001-0.1% (w/v)) or Glc-C_8 (0.001-3.0% (w/v)) (495 μL) solutions to prepare a final pyrene concentration of 500 nM. The emission spectra at 373 nm were recorded on a JASCO FP-6500 at 25 °C in a wavelength range between 300 and 350 nm with a resolution of 0.2 nm, an excitation slit of 5 nm, and an emission slit of 3 nm. The ratios of fluorescence intensities at 337.6 nm and 333.8 nm were plotted against alkyl β-celluloside or Glc-C_8 concentrations on a logarithmic scale and fitted to a sigmoidal curve. The CAC was determined as the intersection of the tangent to low-concentration points and the tangent to the inflection point.

Pendant drop tensiometry. Surface tensions of water droplets were measured with a Kyowa Interface Science Dropmaster DM-300 tensiometer and analysis software (FAMAS, version 5.0.26) by the pendant drop method. A water droplet (10 μL) containing Cell-C_8 or Glc-C_8 was extruded from a 22G needle in a handmade closed system, which was constructed as follows. A disposable polystyrene cuvette (size: 1.2×1.2×4.5 cm) containing 1 mL of water was covered with a silicone cap and incubated for 30 min. Then, the needle was inserted into the air phase of the cuvette through a silicone cap. After 30 min, surface tension measurements were begun.

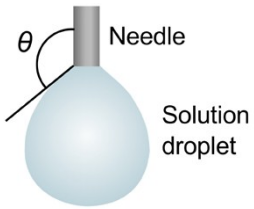
Brewster angle microscopy (BAM). Aqueous Cell-C_8 solution (0.01% (w/v), 26 mL) was spread on a glass petri dish (Φ 4.5 mm). BAM images were taken with a KSV NIMA MicroBAM with a resolution of approximately 12 μm using a 20-30 mW laser at λ = 659 nm under ambient conditions.

Atomic force microscopy (AFM). Aqueous Cell-C_8 solution (0.01% (w/v), 50 μL) was mounted on Parafilm®. After adequate incubation time, a mica substrate was put in contact with the droplet surface. The residual solution was removed by using filter paper, and then the substrate was dried in a desiccator for at least 12 h. The AFM images were taken with a Shimadzu SPM-9600 in tapping mode under ambient conditions using an aluminum reflex-coating cantilever.

Attenuated total reflection-Fourier transform infrared (ATR-FTIR) absorption spectroscopy. Aqueous Cell-C_8 solution (0.01% (w/v), 50 μL) was mounted on Parafilm®. After 10 min of incubation, a gold-sputtered PET substrate was put in contact with the droplet surface. The residual solution was removed by using filter paper, and then the substrate was dried in a desiccator for at least 12 h. For a reference solution of Cell-C_8 in deuterated water, the solvent of Cell-C_8 solution (0.01% (w/v), 1 mL) was exchanged from ultrapure water to deuterated water through three centrifugation/redispersion cycles (20400 rpm using a TOMY MX-301 and MX-305). Then, the wet sample was collected by centrifugation. For another reference Cell-C_8 in the dried state, aqueous Cell-C_8 solution (0.01% (w/v), 20 μL) was mounted on a gold-sputtered PET substrate and dried in a desiccator for 24 h. The ATR-FTIR absorption spectra were obtained on a JASCO FT/IR-4100 spectrometer with a cumulative number of 100 and a resolution of 2.0 cm^{-1} under ambient conditions.

Microscopy for droplet observations. A water droplet (10 μL) containing Cell-C_8 was extruded from a 22G needle in the aforementioned handmade closed system and was observed by using an AS ONE DX-012B digital microscope. The surface area of the droplet was estimated from the digital

image.[3] The surface area at the onset of buckling (S_b) was defined as the surface area of the droplet when the contact angle (Θ) in the following figure sharply increased against a decrease in droplet volume.



Stacking of two droplets. A water droplet (10 μL) containing 0.01% (w/v) Cell-C_8 and 100 μM methylene blue (MB) was extruded from a 22G needle in air. After adequate incubation time, the volume of the droplet was decreased to obtain the buckling state, and the droplet was mounted on a Parafilm®. Then, a water droplet (10 μL) containing 0.01% (w/v) Cell-C_8 without MB was extruded from a 22G needle in air. After adequate incubation time, the volume of the droplet was decreased to obtain the buckling state, and the droplet was stacked on the premounted droplet. After 5 min of incubation, the upper droplet (2 μL) was partially collected for an ultraviolet-visible (UV-vis) absorption spectrum, which was measured on a Thermo Fisher Scientific Nanodrop2000c spectrometer under ambient conditions.

Stacking of multiple droplets. A water droplet (10 μL) containing 0.01% (w/v) Cell-C_8 was extruded from a 22G needle in air. After adequate incubation time, the volume of the droplet was decreased to obtain the buckling state. The droplet was stacked multiply on a Parafilm®.

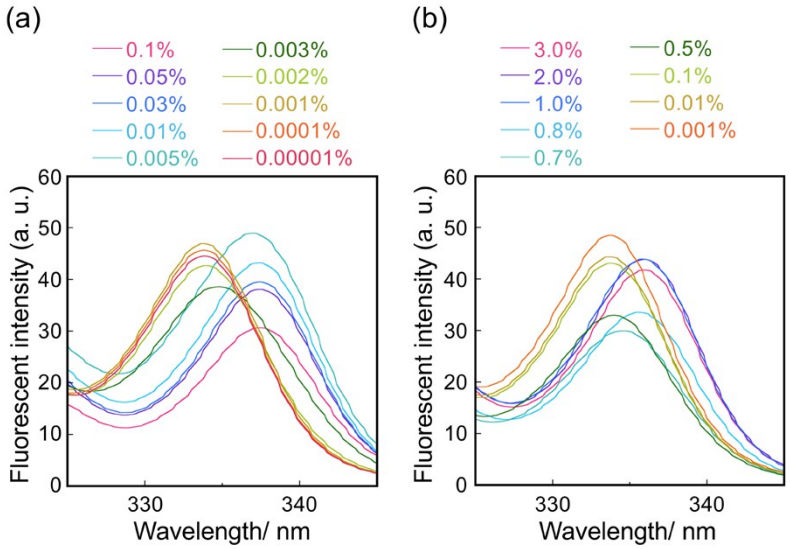


Fig. S1 Excitation spectra of pyrene at different (a) Cell-C_8 and (b) Glc-C_8 concentrations. The fluorescence peak redshifted from approximately 333.8 nm to 337.6 nm above a threshold concentration.

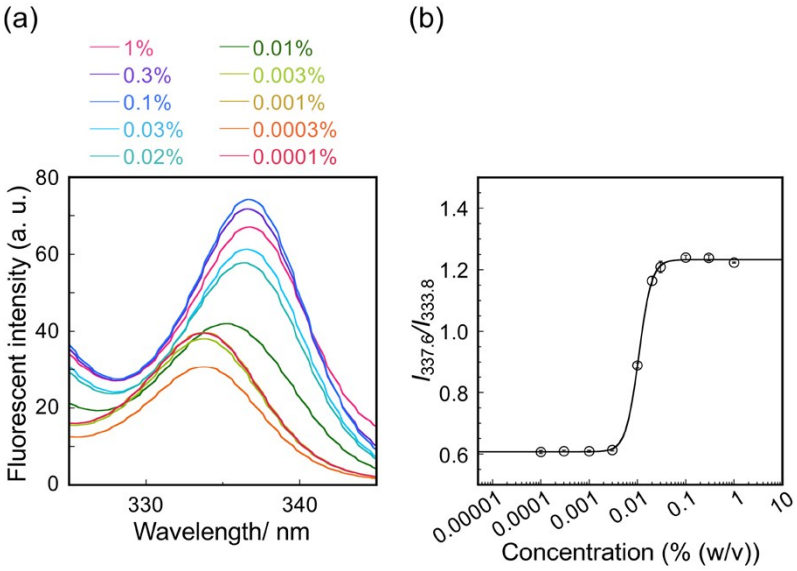


Fig. S2 (a) Excitation spectra of pyrene at different hexyl β-celluloside concentrations. (b) Dependence of $I_{337.6}/I_{333.8}$ for the excitation spectra of pyrene on the hexyl β-celluloside concentration.

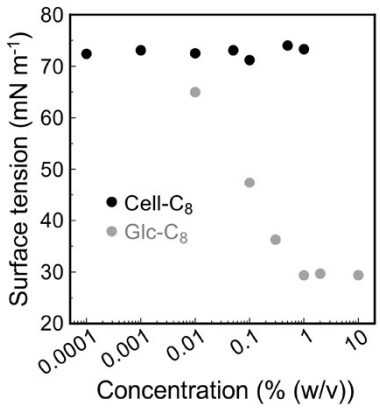


Fig. S3 Dependence of the surface tension of aqueous Cell-C_8 or Glc-C_8 solution on the concentration.

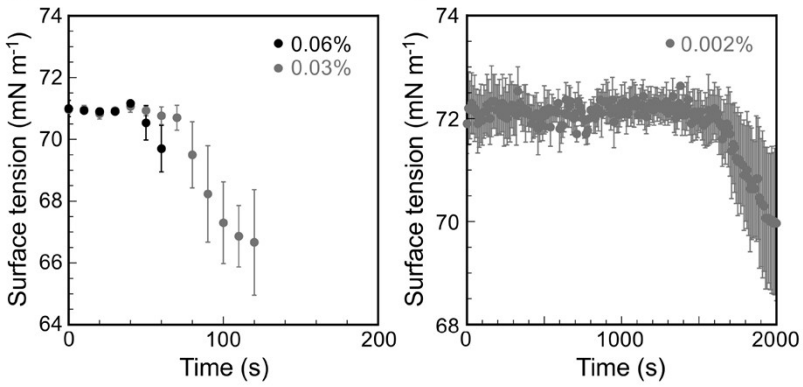


Fig. S4 Time dependence of the surface tension at high and low Cell-C_8 concentrations.

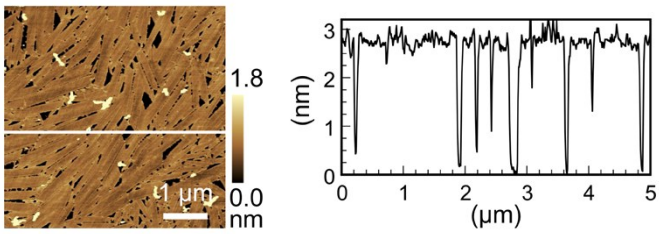


Fig. S5 Cross-sectional AFM image of the 2D objects of Cell-C_8 after 60 sec of incubation.

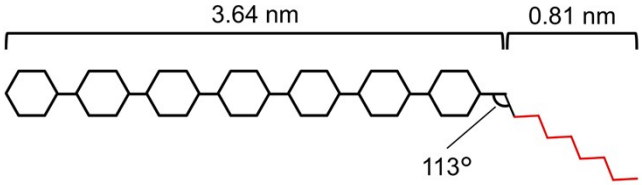


Fig. S6 The estimated molecular length of octyl β-celloheptaose. The molecular length of the celloheptaose moiety was estimated from the structure of the cellulose I allomorph.[4] The bond angle of methyl β-cellotrioside was applied to the bond angle between the cellulose oligomer and alkyl group according to a previous report.[5]

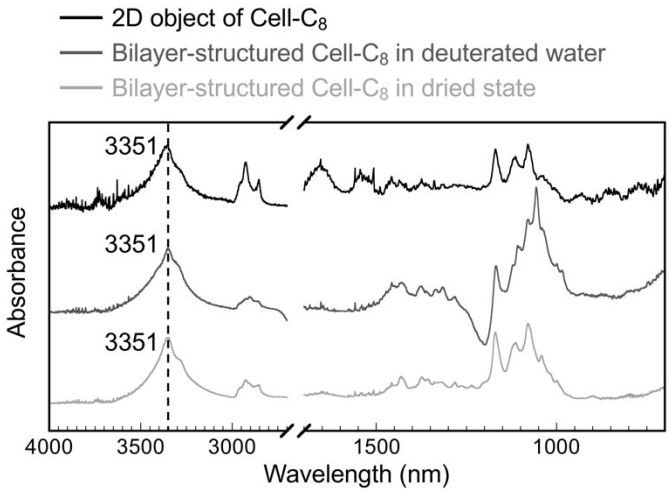


Fig. S7 ATR-FTIR absorption spectra of the 2D objects of Cell-C_8 transferred on a gold-sputtered PET substrate from water surfaces (top) and bilayer-structured Cell-C_8 in deuterated water (middle) or in a dried state (bottom).

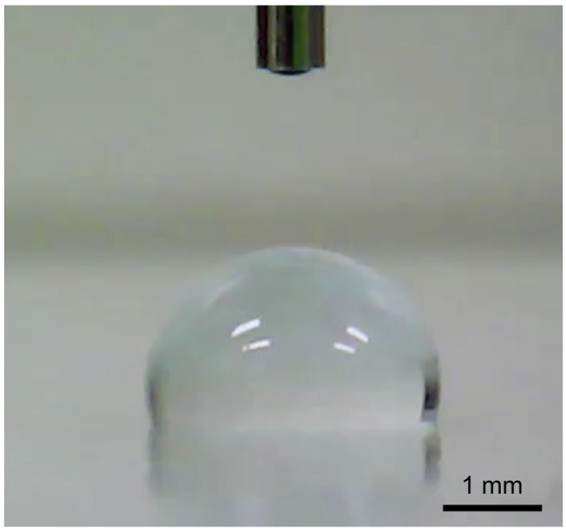


Fig. S8 Microscopic image after the MB-containing water droplet covered with Cell-C_8 monolayers was stacked with a pure water droplet.

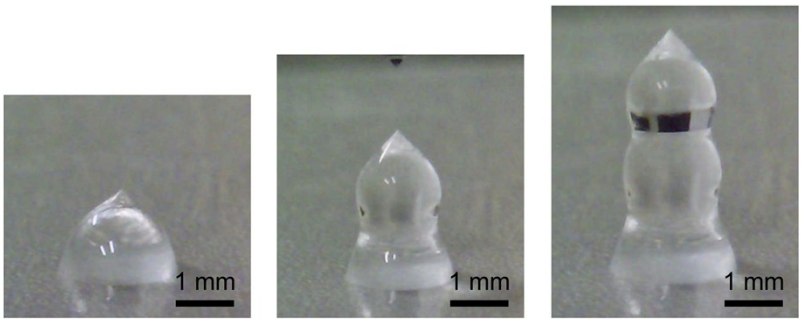


Fig. S9 Microscopic images after stacking of multiple droplets.

References

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