

Supporting Information

Construction of Supramolecular Helical Nanofibers Using Renewable Biomaterials: Self-Assembly of Cytidylic Acid-Appended Bolaamphiphile in Lemon Juice

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Materials

Cytidilic acid-appended bolaamphiphile was synthesized in a manner similar to that described in a previous report (R. Iwaura et al, *Small*, **2010**, *6*, 1131.). Oxalic, malonic, succinic, glutaric, adipic, pimelic, and citric acids were purchased from Tokyo Chemical Industry Co. (Tokyo, Japan) and used without further purification. ^1H NMR was recorded on a Bruker Avance model 400 spectrometer (Bruker BioSpin; Billerica, MA).

Preparation of self-assemblies

The pH of the aqueous solutions containing each di-carboxylic acid or citric acid were adjusted with aqueous solutions of 0.1 N NaOH. The final concentrations of the di-carboxylic acids and citric acid were 2×10^{-2} M to $\sim 3 \times 10^{-2}$ M. One mg of C18C was added to aqueous solutions of the di-carboxylic acid or citric acid (100 μl), heated at 90 °C, sonicated for 60 min (Branson ultrasonicator model 1200), and gradually allowed to cool to room temperature. The final concentration of C18C was 1×10^{-2} M. The self-assemblies were kept at room temperature overnight and subjected to microscopic observations and spectroscopic measurements.

ATR-FTIR spectroscopy

For the ATR-FTIR spectroscopic measurements, a Spectrum 100 (Perkin-Elmer Corp.) instrument with a 4-cm^{-1} resolution at 20 °C was used. The binary self-assembly of C18C and CA was prepared as described above at pH 4.7. For comparison, we prepared

the single-component self-assembly of C18C in aqueous HCl at pH 4.7. All the samples were freeze-dried prior to the ATR-FTIR measurements.

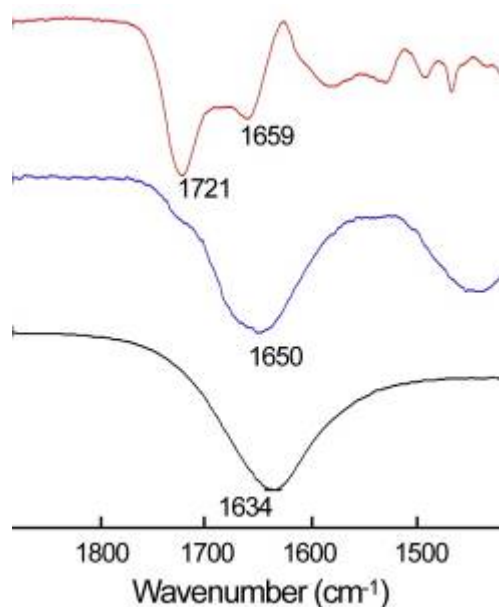


Figure S1 ATR-FTIR spectra for the freeze-dried binary self-assembly of C18C and CA (red), single-component of C18C (blue), and single-component CA (black).

CD and UV-Vis spectroscopies

For CD spectroscopy, self-assemblies were diluted by a factor of 10 with Milli-Q water. CD spectra were measured using a Jasco J-810 spectropolarimeter operating between 200 and 400 nm (scan rate 1 nm/s, sensitivity 0.01°, cell length = 0.01 cm). The UV-Vis spectrum for the aqueous solution of C18C (1×10^{-3} M) was recorded on a Shimadzu TMSPEC-8 spectrometer (cell length = 0.1 cm).

AFM observations

One microliter of each aqueous solution was placed on highly oriented pyrolytic

graphite (HOPG) and dried at room temperature for 30 minutes. The specimen was washed with a little water, dried again overnight, and then subjected to AFM observation on an S-image (SII Nanotechnology Inc.) with a silicon-microcantilever (spring constant 2 N m^{-1} , Olympus) in a tapping mode.

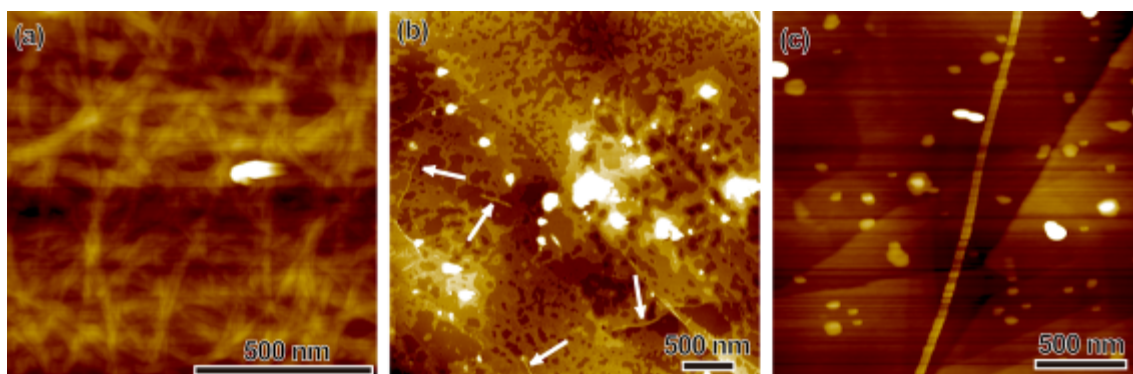


Figure S2 AFM images for the binary self-assembly of C18C and (a) malonic acid, (b) succinic acid, and (c) glutaric acid. The arrows in (b) indicate fiber structures.

pH Titration

For the pH titration of C18C, aqueous solution (2 ml) was prepared by addition of degassed distilled water to C18C and subsequent sonication at $25 \text{ }^{\circ}\text{C}$. The resultant aqueous solution (10 mM) was then titrated with 0.1 N NaOH. The pH titration was carried out using an MP225 pH meter (Mettler Toledo).