Electronic Supplementary Information for

One-dimensional supramolecular hybrids: self-assembled nanofibrous materials based on a sugar gelator and calcite developed along an unusual axis

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## **Experimental Section**

**Materials and Syntheses.** All reagents and solvents were purchased from Aldrich, Tokyo Kasei, Kanto Chemical, or Wako, and used as received without further purification. The synthesis of N-octyl-D-gluconamide-6-benzoate was conducted according to the previous litereature.<sup>1</sup> The synthesized organic compounds was characterized with <sup>1</sup>H NMR (JEOL, JNM-ECX400) in dimethyl sulfoxide- $d_6$  (DMSO- $d_6$ ) solution and MALDI-TOF mass (Bruker, Autoflex Speed)

## *N*-octyl-D-gluconamide

D-glucono-1,5-lactone (2.00 g, 11.2 mmol) was dissolved by refluxing in 40 ml methanol and then noctylamine (2.25 g, 17.4 mmol) was added. The reaction was carried out in a dry argon atmosphere. The mixture was stirred for 95 minutes at 80°C. The precipitate was purified by recrystallization from methanol, yield 2.71 g (8.81 mmol, 79%): <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  7.56 (t, 1H), 5.31 (d, 1H), 4.42-4.50 (dd, 2H), 4.34 (d, 1H), 4.29 (t, 1H), 3.93 (t, 1H), 3.85 (t, 1H), 3.53 (m, 1H), 3.43 (m, 2H), 3.33 (overlap with the water signal in DMSO- $d_6$ ), 3.03 (m, 2H), 1.37 (t, 2H), 1.21 (s, 10H), 0.83 (t, 3H)

Scheme S1. Syntheses of N-octyl-D-gluconamide



*N*-octyl-D-gluconamide-6-benzoate (**1**)

Benzoyl chloride (0.915 g, 7.00 mmol) dissolved in 5 ml of THF was added dropwise to a stirred solution of *N*-octyl-D-gluconamide (0.9841 g, 3.20 mmol) in 10 ml of pyridine which was cooled in ice bath. The apparatus was purged with dry argon. The temperature was raised from 0 to 50°C for 45 minutes, then solution was stirred at 60°C for 2 h. The resulting mixture was poured into 400 ml of saturated NaHCO<sub>3</sub> aqueous solution. The precipitate was purified by recrystallization from ethyl acetate, yield 0.291 g (0.707 mmol, 22%): <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.00 (d, 2H), 7.63 (dd, 2H), 7.51 (t, 2H), 5.39 (d, 1H), 5.08 (d, 1H), 4.65(d, 1H), 4.42(m, 2H), 4.20(dd, 1H), 3.99(t, 1H), 3.93(m, 1H), 3.84(m, 1H), 3.57(m, 1H), 3.04(m, 2H), 1.38(t, 2H), 1.22(broad s, 10H), 0.83(t, 3H)

MS (MALDI-TOF): calcd, 434.49 [M+Na]<sup>+</sup>; found, 434.75 [M+Na]<sup>+</sup>

Scheme S2. Syntheses of *N*-octyl-D-gluconamide-6-benzoate.



## Preparation of gel fibers/CaCO<sub>3</sub> hybrids

Compound **1** shows a gel behavior in the solvents as shown in Table S1. To prepare the crystallization template of calcium carbonate, compound **1** (1.0 mg) in 200 µl of mixed solution of THF and water (1:2 by volume) was heated to 50°C and dissolved. The gel of **1** was obtained after cooling at room temperature. The gel was immersed in water to remove THF from the gel. . Obtained hydrogel was used as insoluble matrices of CaCO<sub>3</sub> crystallization. An aqueous solution for the CaCO<sub>3</sub> crystallization was prepared as previously reported.<sup>2</sup> The final concentration of CaCl<sub>2</sub> (Wako) and Na<sub>2</sub>CO<sub>3</sub> (Kanto) was 20 mM and that of PAA (Aldrich,  $Mw = 1.8 \times 10^3$ ) was  $1.1 \times 10^{-1}$  wt%. Gel matrices were soaked in 100 ml of the crystallization solution for 7 days at room temperature. After crystallization, the samples were washed with purified water then freeze dried.

Solvent	State
THF	Solution
THF and water (2:1 by volume)	Solution
THF and water (1:2 by volume)	Gel
Chloroform	Gel
Ethyl acetate	Gel

Table S1. Gel behavior of compound 1	١.
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**Characterization.** The morphologies of the hybrids were observed with a polarized optical microscope (POM) (OLYMPUS, BX-53), a scanning electron microscope (SEM) (Hitachi, S-4700, operated at 5.0 kV) and a transmission electron microscope (TEM) (JEOL, JEM-2000EX, operated at 200 kV). Polymorphs of the CaCO<sub>3</sub> crystals in hybrids were analyzed by X-ray diffraction (XRD) measurements (Rigaku, Smartlab) and FTIR (JASCO/FTIR-660 Plus) measurements with a KBr method. The amount of inorganic crystals in the hybrids were estimated with thermogravimetric (TG) (Rigaku, TG-8120) measurements under a flow of air up to 1000°C with a heating rate of 10°C/min.



Figure S1. (a) SEM and (b) POM images of obtained  $1/CaCO_3$  composites after crystallization in the absence of PAA.



Figure S2. Difference of crystallographic orientations in calcite structures between aligned 2D liquidcrystalline matrices of chitin<sup>3</sup> and self-assembled fiber of compound **1** in the present study.



Figure S3. IR spectra of the fiber of **1** prepared in the THF/water mixture solvent, and  $1/CaCO_3$  hybrids obtained after crystallization for 1, 3 and 7 days.



Figure S4. Thermogravimetric curve of  $1/CaCO_3$  hybrids obtained after crystallization for 1 day. The weight loss until 200°C is attributed to the evaporation of water included in the matrix. The weight loss between 200-400°C originates from the decomposition of organic components and the sudden decrease at 600°C is attributed to the removal of CO<sub>2</sub> from CaCO<sub>3</sub>.

## References

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