Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information for

Switching of Carbohydrate Nanofibers for Regulating Cell Proliferation

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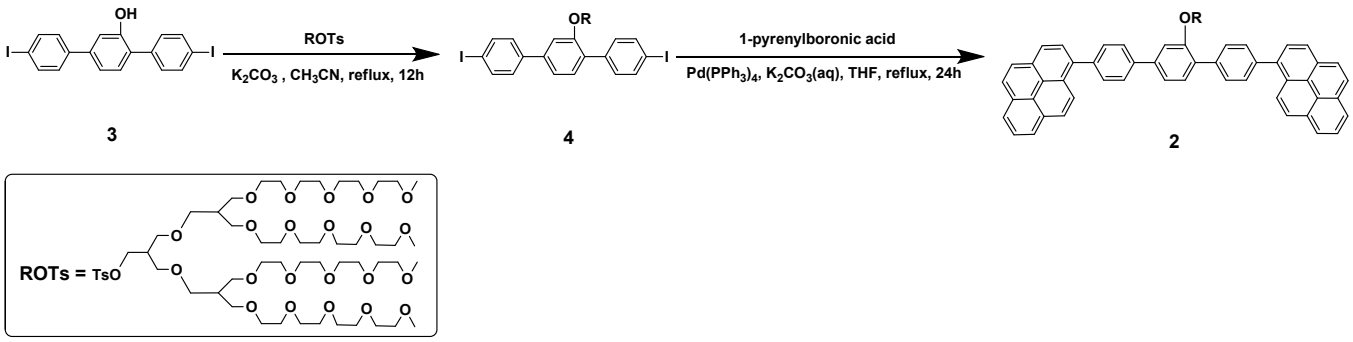
1. Materials

Tetrakis(triphenylphosphine) palladium(0) (99 %), NaH (60 %), and *p*-toluenesulfonyl chloride (98 %) from TCI and Tokyo Kasei were used as received. 2,6-dibromophenol, Pyrene-1-boronic acid, iodine monochloride (1.0 M solution in dichloromethane), boron tribromide (1.0 M solution in dichloromethane) from Aldrich were used as received. Unless otherwise indicated, all starting materials were obtained from commercial suppliers (Aldrich, Lancaster, and TCI, etc.) and were used without purification. Methylene chloride, hexane, Acetonitrile, DMF, and THF were distilled before use. Visualization was accomplished with UV light and iodine vapor. Flash chromatography was carried out with Silica Gel 60 (230-400 mesh) from EM Science. Amphiphile **1** was prepared according to the procedures described previously.[S1]

2. Techniques

^{1}H-NMR was recorded from $CDCl_3$ solutions on a Bruker AM 500 spectrometer. The purity of the products was checked by thin layer chromatography (TLC; Merck, silica gel 60). The UV/vis spectra were obtained from Hitachi U-2900. The fluorescence spectra were obtained from a Hithachi F-7000 Fluoresence Spectrophotometer. MALDI TOF-MS spectroscopy was performed on a Bruker Autoflex TOF/TOF using α-cyano- 4-hydroxy cinnamic acid and 2,5-dihydroxy benzoic acid matrix. The bacteria agglutination was observed with a Nikon Eclipse TE2000-U inverted fluorescence microscope equipped with a DXM1200C digital camera. Compounds were synthesized according to the procedure described in scheme 1 and then purified by silica gel column chromatography and prep HPLC (Japan Analytical Instrument).

3. Synthetic Method



Scheme 1: The synthetic procedure of amphiphile **2**

Compound 4. Compounds **3**[S2] (45 mg, 0.09 mmol), TsOR (130 mg, 0.11 mmol) and excess K_2CO_3 (64 mg, 0.46 mmol) were dissolved in 1.1 ml of distilled acetonitrile. The mixture was heated at reflux for 12 hrs and then cooled to room temperature. After solvents was removed in a rotary evaporator, the mixture was extracted with ethyl acetate and water and then dried over anhydrous magnesium sulfate, and filtered. After the solvent was removed in a rotary evaporator, the crude products were purified by column chromatography (silica gel) using methyl alcohol : ethyl acetate (1 : 20 v/v) to yield 110 mg (67 %).

^{1}H-NMR (500MHz, $CDCl_3$) δ 7.79-7.72 (m, 4H), 7.38-7.32 (m, 4H), 7.28 (s, 2H), 7.18 (s, 1H), 4.26 (d, 2H), 3.59–3.55 (m, 25H), 3.55–3.44 (m, 55H), 3.33 (s, 12H), 2.49–2.42 (m, 1H); MALDI-TOF-mass (m/z): $[M + H]^+$ calcd. for $C_{66}H_{108}I_2O_{23}$, 1522.54; Found: 1545.53 $[M + Na]^+$.

Compound 2. Compound **4** (110 mg, 0.07 mmol) and 1-pyrenylboronic acid (52 mg, 0.21 mmol) were dissolved in 0.7 ml THF and added 0.3 ml of degassed 2.0 M Na_2CO_3 aqueous solution . Then tetrakis(triphenylphosphine) palladium(0) (6 mg, 0.005 mmol) was added. The mixture was heated at reflux for 24 hrs with vigorous stirring under nitrogen. Cooled to room temperature, the layers were separated, and the aqueous layer was then washed twice with ethyl acetate. The combined organic layer was dried over anhydrous magnesium sulfate and filtered. The solvent was removed in a rotary evaporator, and the crude product was purified by column chromatography (silica gel) using methyl alcohol : ethyl acetate (1 : 10, v/v) as eluent to yield 55 mg (47 %).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (t, *J* = 9.5 Hz, 2H), 8.27 (d, *J* = 7.8 Hz, 2H), 8.23 – 8.19 (m, 4H), 8.12 (d, *J* = 2.7 Hz, 3H), 8.10–8.07 (m, 3H), 8.06 – 8.01 (m, 3H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.43 (s, 1H), 4.26 (d, *J* = 5.3 Hz, 2H), 3.59–3.55 (m, 25H), 3.55–3.44 (m, 55H), 3.33 (s, 12H), 2.49–2.42 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 156.72, 154.89, 141.71, 141.16, 140.63, 140.01, 139.85, 138.90, 137.82, 137.45, 137.42, 136.74, 131.70, 131.32, 131.24, 131.21, 130.87, 130.77, 130.28, 129.79, 129.15, 128.73, 127.86, 127.75, 127.68, 127.65, 127.60, 127.58, 127.26, 126.20, 125.53, 125.42, 125.32, 125.26, 125.21, 125.04, 124.99, 124.87, 120.76, 119.93, 116.52, 111.50, 77.41, 77.16, 76.91, 72.06, 70.69, 70.66, 70.60, 70.55, 69.86, 69.77, 69.53, 66.87, 59.08, 40.40, 40.25, 29.82; MALDI-TOF mass (m/z): $[M + H]^+$ calcd. for $C_{98}H_{126}O_{13}$, 1670.87; Found: 1693.86 $[M + Na]^+$.

4. Experimental Sections

TEM experiments. The transmission electron microscope (TEM) was performed at 120 kV using JEOL-JEM HR2100. 60 μM of amphiphiles was dissolved in 1 ml pure water in 3 ml vial and placed in a water bath at room temperature with mild sonication. After 2 hours, the aqueous solutions was slowly dropped on a carbon-coated copper grid and the solution was allowed to evaporate under under ambient conditions. These samples were stained by depositing a drop of uranyl acetate aqueous solution (0.2 wt%) onto the surface of the sample-loaded grid. For the preparation of the heated sample, the sample solution, carbon-coated copper grid, and uranyl acetate aqueous solution were incubated in 37 °C oven for 1 h. Then, the sample solution was cast on the grid and the solvent was evaporated in 37 °C oven for 30 min. The thin film sample was stained by 37 °C uranyl acetate aqueous solution for 1 min in 37 °C oven. The dried specimen was observed by using a JEOL-JEM HR2100 instrument operating at 120 kV.

Microscopy Experiment for the agglutination of *E. coli*. 0.2 ml frozen culture of *E. coli* stain ORN 178-GFP were grown overnight in 5 ml LB media with tetracycline (4 mg/ml) and ampicilin (0.1 mg/ml) in an incubater (37 ℃) with shaking. The *E. coli* culture was diluted to reach an OD_{600} to 1. The bacterial culture was centrifuged for 3 min at 13000 rpm. The liquid was removed and the bacteria pellet re-suspended in 1 ml of PBS buffer and washed two times with same buffer. Finally,

the bacterial pellet was re-suspended in 1 ml PBS buffer and added (20 μl) amphiphile **1**, **2** and one of co-assembled samples which was dissolved in PBS buffer. This mixture solution was incubated for 2h at (37 ℃) and this suspension was fixed on microscope slides, covered with glass slides for checking fluorescence co-localization studies of the bacteria with compounds.

***E. coli* proliferation assay**. The OD_{600} was measured and diluted with LB media to reach an OD_{600} of 1.1~1.2. After taking 1 ml of bacterial culture to eppendorf tube, centrifuged for 3min at 13000 rpm. The LB media liquid was removed and white bacteria pellet was resuspended in 1 ml PBS buffer solution. This solution (10 μl) was added to each co-assembled amphiphies solution (1 mg + 490 μl LB media) and all samples were put into incubater with mild shaking. The OD_{600} of each samples was measured at every one hour.

Fluorescence Resonance Energy Transfer Experiments (FRET). Stock solutions of Fluorescein labeled Con A were resuspended in PBS to 0.1 mg per μl. Each solution of amphiphile **1** and **2** were diluted in PBS, pH 7.4 buffer to 0.02 mg per ml. Aliquots of Fluorescein labeled Con A (50 μl) were added to solution of amphiphile **1** and **2** (450 ul). After each addition, the sample was allowed to equilibrate for 1 h prior to recording a spectrum. Fluorescein emission was measured on a Hithachi F-7000 Fluoresence Spectrophotometer using 5 nm slit widths, a PMT voltage of 400 V, excitation wavelength of 357, and an emission scan was from 390 ~ 720 nm.

5. Supplementary Figure

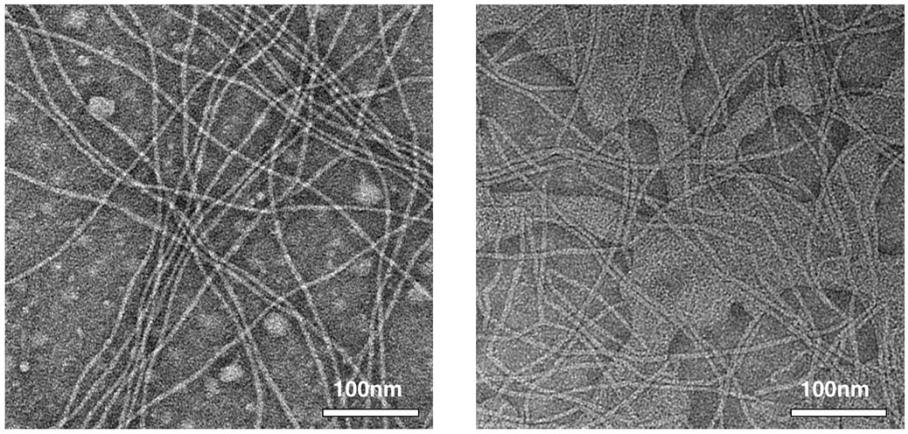


Figure S1. TEM images of 0.02 wt% aqueous solution from **1** (left) and **2** (right), respectively, at room temperature.

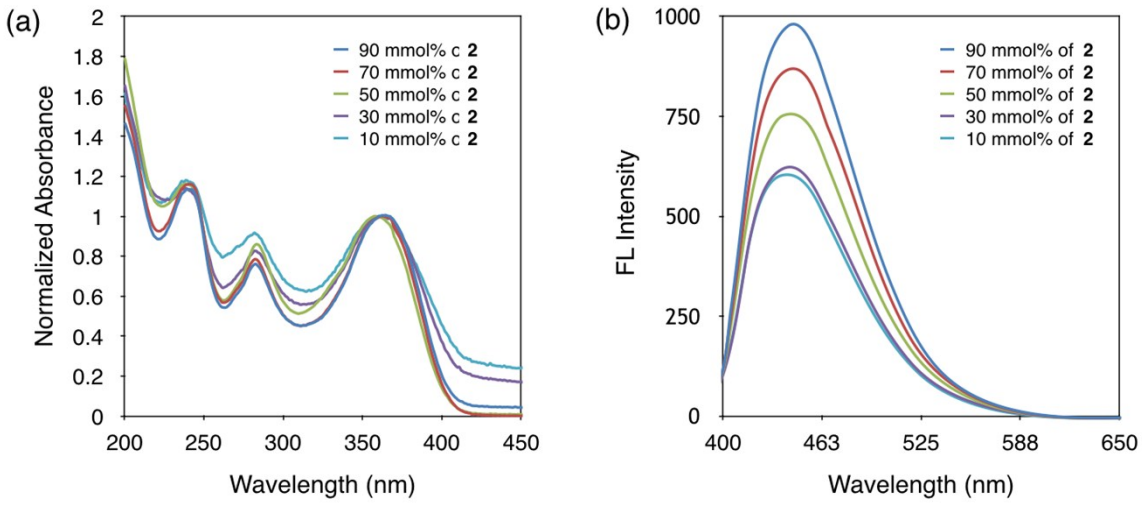


Figure S2. (a) Absorption and (b) emission spectra of co-assembled nanofibers from 0.04 wt% aqueous solution with different ratio between amphiphile **1** and **2**. For a comparison, absorption spectra was normalized at 357 nm.

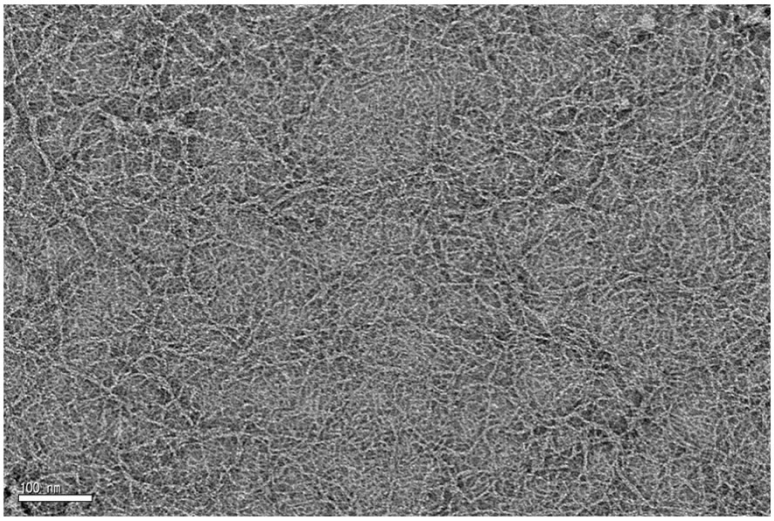


Figure S3. TEM image of the coassembled nanofibers (50 mol% of **2**) at 37 °C demonstrates that the nanofibers are stable without further aggregation even after dehydration of the oligoether chains and the size decreases from 6 nm to 5 nm in diameter.

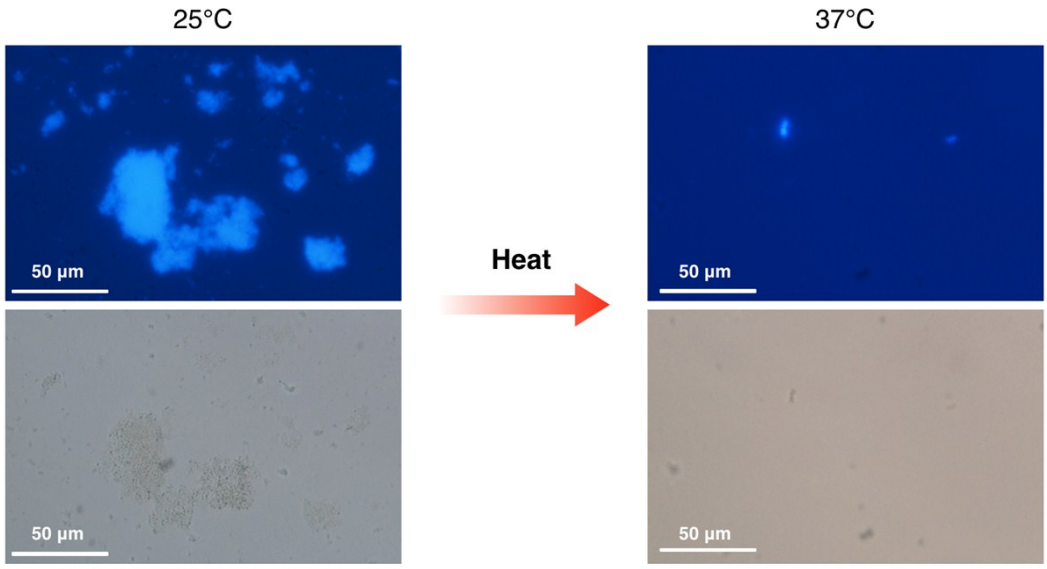


Figure S4. Microscopy images from fluorescence colocalization studies of *E. coli* with nanofibers (50 mol% of **2**) in different temperature under excitation filter at λ_{ex} = 340−380 nm (up) and bright field (down).

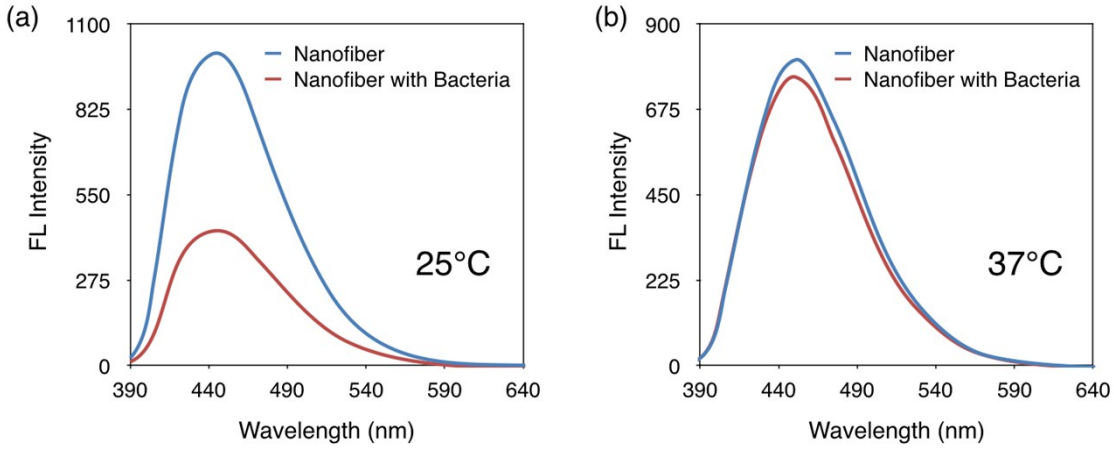


Figure S5. Emission spectra of the coassembled nanofibers (50 mol% of **2**) without and with bateria at (a) 25 °C and (b) 37 °C, demonstrating that the binding activity of the coassembled nanofibers to the bacterial cells is lost upon heating.

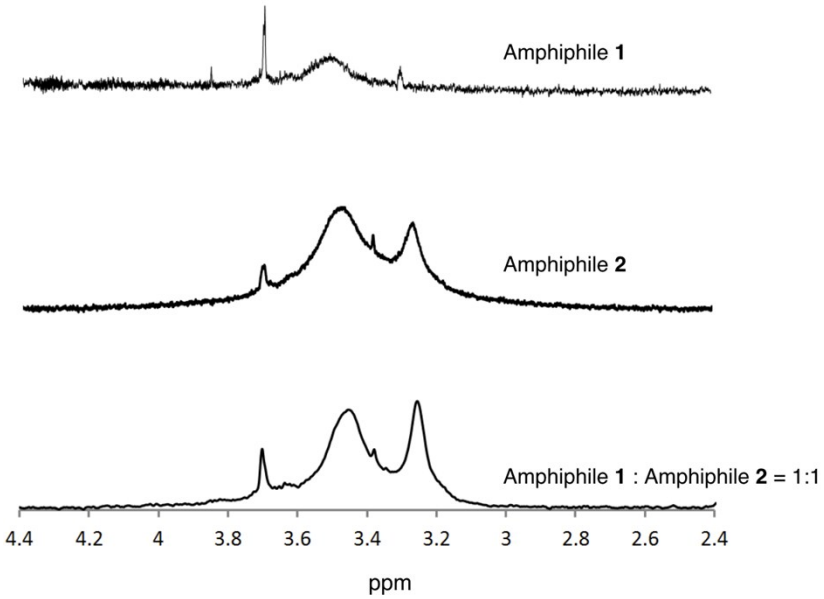


Figure S6. ^{1}H-NMR spectra of 0.1 wt% amphiphile **1**, **2**, or coassembly from 50 mol% of **2** in D_2O.

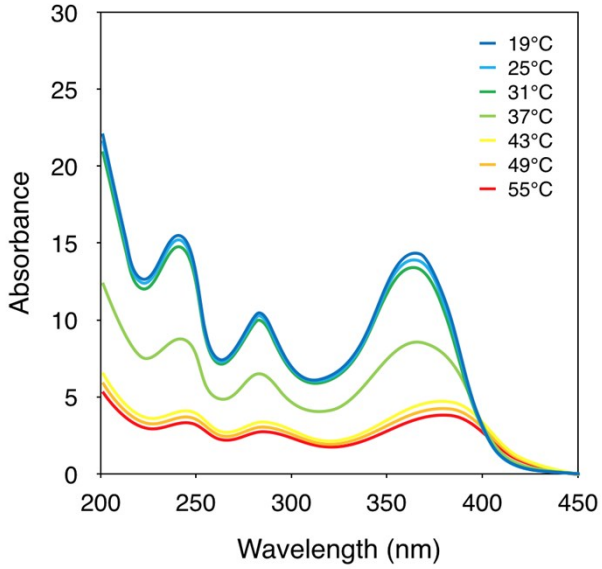


Figure S7. Absorption spectra in a series of temperature from 0.04 wt% aqueous solution based on 50 mol% of **2**.

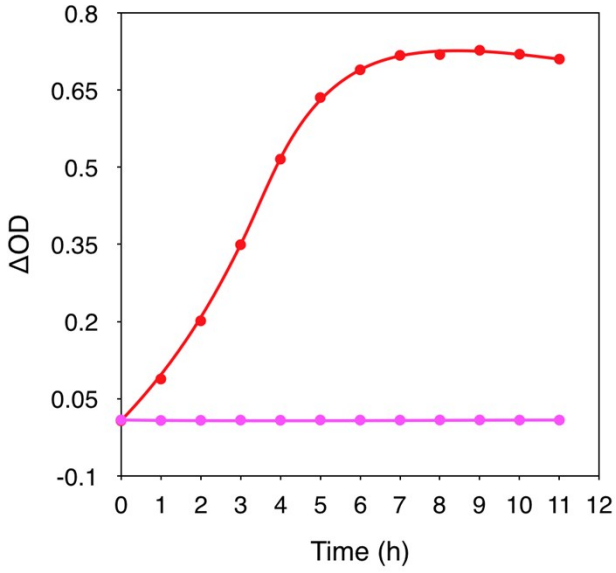


Figure S8. Growth curves based on the optical density (OD) at 600 nm for *E. coli* grown in the presence of coassembled amphiphiles (50 mol% of **2**, red line) and pure amphiphile **1** (magenta line) for 11 h at 37 °C.

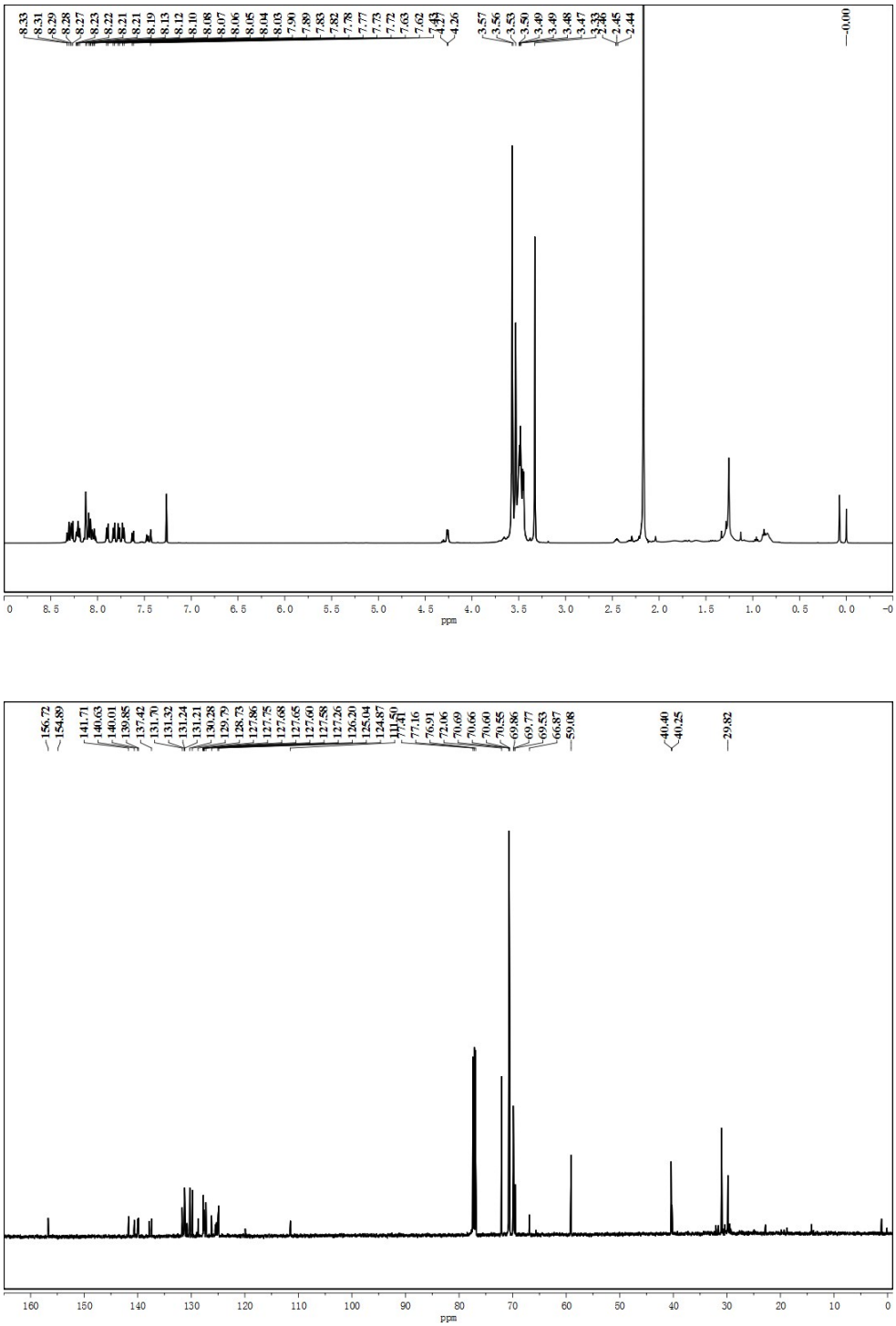


Figure S9. ^{1}H / ^{13}C-NMR spectra of amphiphile **2** in $CDCl_3$.

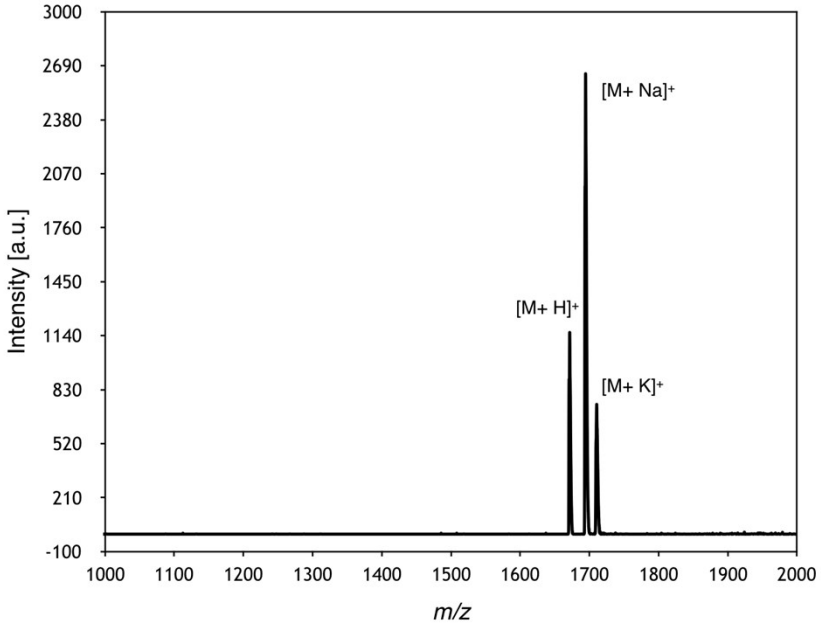


Figure S10. MALDI-TOF mass spectrum of amphiphile **2**

Reference

S1) D.-W. Lee, T. Kim, I.-S. Park, Z. Huang, M. Lee, *J. Am. Chem. Soc.* **2012**, *134*, 14722

S2) D.-W. Lee, Taehoon, Kim, M. Lee. *Chem. Commun*. **2011**, *47*, 8529