Electronic Supplementary Material (ESI) for Chemical Communications.
This journal is © The Royal Society of Chemistry 2020

Electronic Supplemental Information (ESI)

Title

Glycolipid nanotube templates for the production of hydrophilic/hydrophobic and left/right-handed helical polydiacetylene nanotubes

Authors

N. Kameta,* W. Ding and M. Masuda

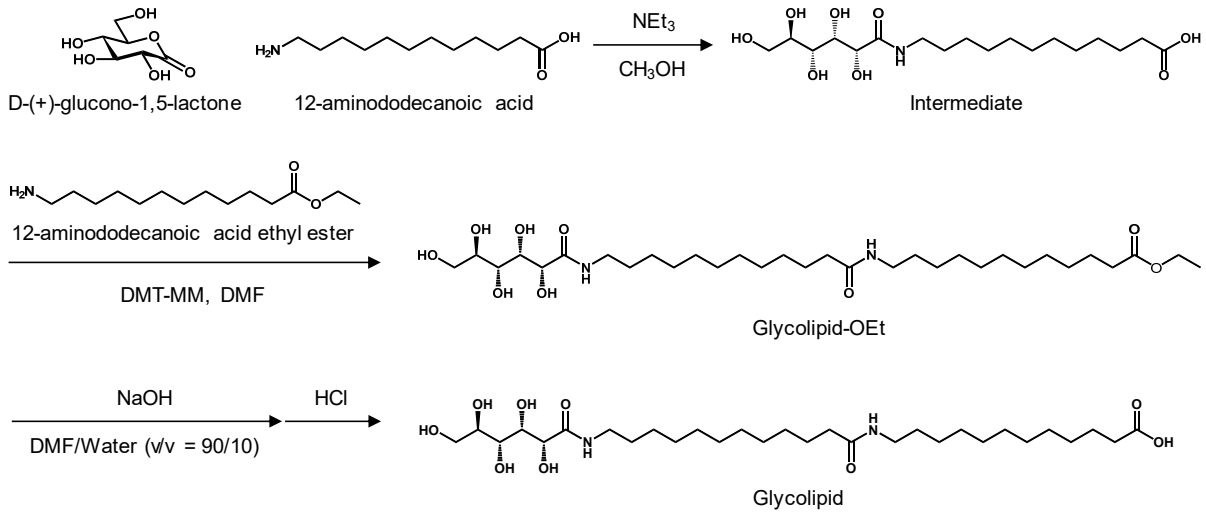

Fig. S1 Synthetic scheme of glycolipids.

12-aminododecanoic acid (22.0 g, 0.102 mol) and D-(+)-glucono-1,5-lactone (18.0 g, 0.101 mol) were dispersed in triethylamine (10.6 g, 0.114 mol) / methanol (195 mL) solution. After 4 h refluxing, the dispersion became almost clear, and solvent was condensed. The residual solid was dried under vacuum to give an intermediate as a white solid (40.1 g, 99%).

The intermediate (3.93 g, 0.010 mol) and 12-aminododecanoic acid ethyl ester (2.43 g, 0.010 mol) were dissolved in dimethylformamide (DMF, 150 mL) at 60 ºC. As a condensation reagent, 4-(4,6-Dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMT-MM) was added to the solution. The solution turned into a whitish gel within 30 min. The gel was filtrated and washed by methanol (50 mL), water (50 mL) and methanol (50 mL). The resultant solid was further purified by reprecipitation from hot solution of a mixed solvent consisted of ethanol, methanol and water (360 mL/130 mL/40 mL, respectively) to give Glycolipid-OEt as a white solid (5.82 g, 94%).

An aqueous solution of NaOH (4 N, 1.5 mL) was added dropwise over 4 h to a DMF solution (100 mL) of Glycolipid-OEt (3.04 g, 0.0049 mol) at 70 ºC. After stirring for 6h, the solution was neutralized by hydrochloric acid (4 N, 4.5 mL), and condensed under vacuum. The resultant solid was redispersed in water, filtered, washed by water, and dried under vacuum to give Glycolipid as a white solid (2.32 g, 88%):

Intermediate: ^{1}H NMR (500 MHz, in DMSO-d_6): δ 7.58 (t, 1H, J = 7.3 Hz, NH), 5.32 (Br, 1H, 2-OH), 4.44 (Br, 4H, 3-OH, 4-OH, 5-OH, 6-OH), 3.97 (d, 1H, J = 4.7 Hz, Glc-2), 3.89 (m, 1H, Glc-3), 3.57 (dd, 1H, J = 13.5 and 3.5 Hz, Glc-6), 3.46 (m, 2H, Glc-4, Glc-5), 3.37 (dd, 1H, J = 13.5 and 6.7 Hz, Glc-6), 3.06 (m, 2H, C(=O)NHCH_2-), 2.18 (t, 2H, J = 9.2 Hz, -CH_2COOH), 1.48 (t, 2H, J = 8.7 Hz, -CH_2-), 1.40 (t, 2H, J = 7.8 Hz, -CH_2-), 1.24 (m, 14H, -CH_2-).

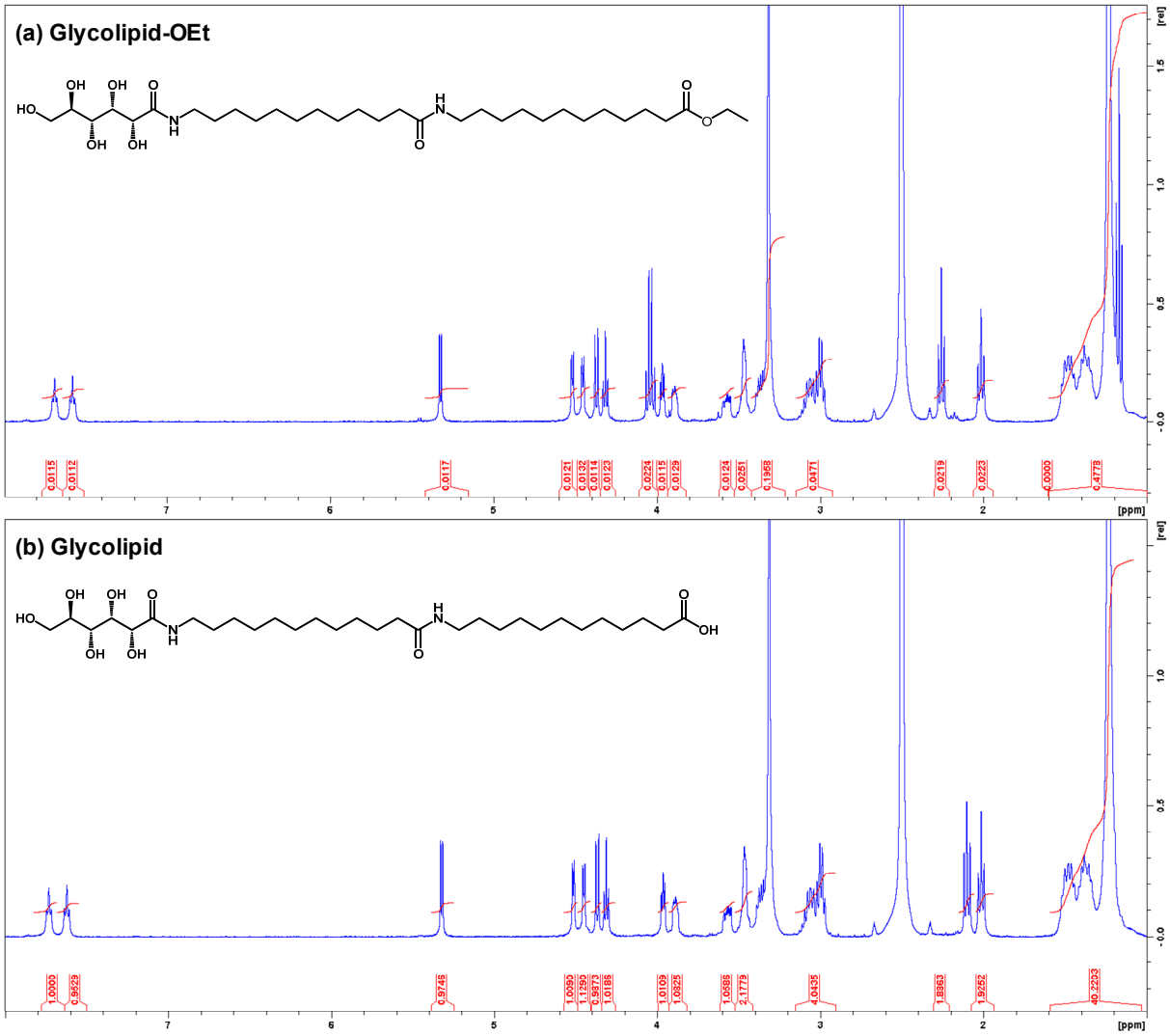

Fig. S2 ^{1}H NMR spectra of (a) Glycolipid-OEt and (b) Glycolipid in DMSO-d_6.

Glycolipid-OEt: ^{1}H NMR (500 MHz, in DMSO-d_6): δ 7.69 (t, 1H, J = 6.9 Hz, NH), 7.58 (t, 1H, J = 7.3 Hz, NH), 5.32 (d, 1H, J = 6.4 Hz, 2-OH), 4.52 (d, 1H, J = 6.3 Hz, 4-OH or 5-OH), 4.45 (d, 1H, J = 6.7 Hz, 4-OH or 5-OH), 4.37 (d, 1H, J = 9.0 Hz, 3-OH), 4.31 (t, 1H, J = 7.1 Hz, 6-OH), 4.04 (q, 2H, J = 8.9 Hz, -OCH_2CH$_3$), 3.97 (m, 1H, Glc-2), 3.88 (m, 1H, Glc-3), 3.57 (m, 1H, Glc-6), 3.47 (m, 2H, Glc-4 and Glc-5), 3.36 (m, 1H, Glc-6), 3.06 (m, 2H, C(=O)NHCH_2-), 3.01 (m, 2H, C(=O)NHCH_2-), 2.26 (t, 2H, J = 9.2 Hz, -CH$_2$C=O), 2.01 (t, 2H, J = 9.2 Hz, -CH$_2$C=O), 1.47 (m, 4H, -CH$_2$-), 1.35 (m, 4H, -CH$_2$-), 1.23 (m, 28H, -CH$_2$-), 1.68 (t, 3H, J = 8.9 Hz, -OCH$_2$CH_3); ESI-MS (anionic mode): m/z = 617.44 (-H$^+$).

Glycolipid: ^{1}H NMR (500 MHz, in DMSO-d_6): δ 7.71 (t, 1H, J = 6.8 Hz, NH), 7.64 (t, 1H, J = 7.2 Hz, NH), 5.33 (d, 1H, J = 6.4 Hz, 2-OH), 4.51 (d, 1H, J = 6.2 Hz, 4-OH or 5-OH), 4.46 (d, 1H, J = 6.7 Hz, 4-OH or 5-OH), 4.36 (d, 1H, J = 9.0 Hz, 3-OH), 4.31 (t, 1H, J = 7.2 Hz, 6-OH), 3.96 (m, 1H, Glc-2), 3.89 (m, 1H, Glc-3), 3.58 (m, 1H, Glc-6), 3.46 (m, 2H, Glc-4

and Glc-5), 3.35 (m, 1H, Glc-6), 3.08 (m, 2H, C(=O)NHCH_2-), 3.00 (m, 2H, C(=O)NHCH_2-), 2.13 (t, 2H, J = 9.2 Hz, -CH_2C=O), 2.02 (t, 2H, J = 9.2 Hz, -CH_2C=O), 1.46 (m, 4H, -CH_2-), 1.37 (m, 4H, -CH_2-), 1.23 (m, 28H, -CH_2-); ESI-MS (anionic mode): m/z = 589.40 (-H^+).

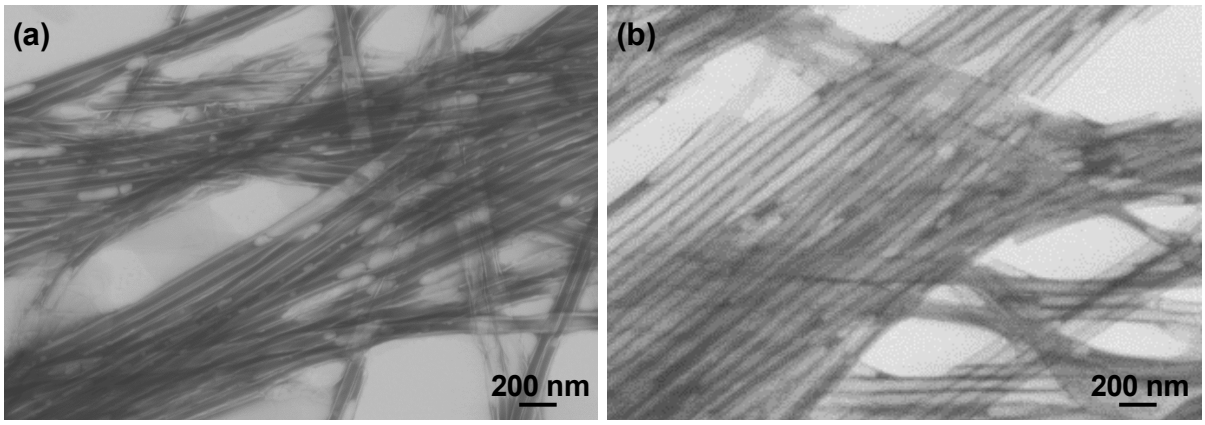

Fig. S3 S-TEM images of (a) Glyco-NTs formed by self-assembly of Glycolipid and (b) GlycoOEt-NTs formed by self-assembly of Glycolipid-OEt. Nanochannels were visualized by means of negative staining with 2 wt% phosphotungstate.

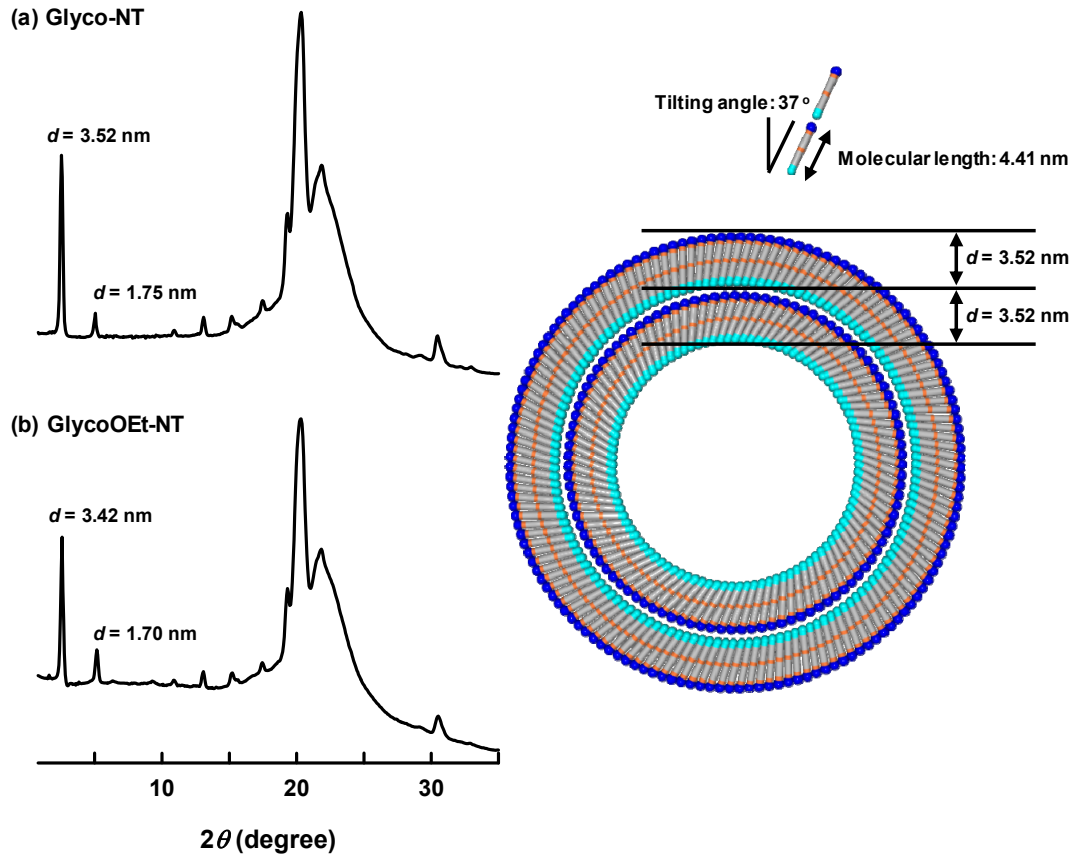

Fig. S4 XRD patterns of the Glyco-NT and GlycoOEt-NT. Schematic image of the Glyco-NT consisting of the monolayer membranes with the stacking periodicity.

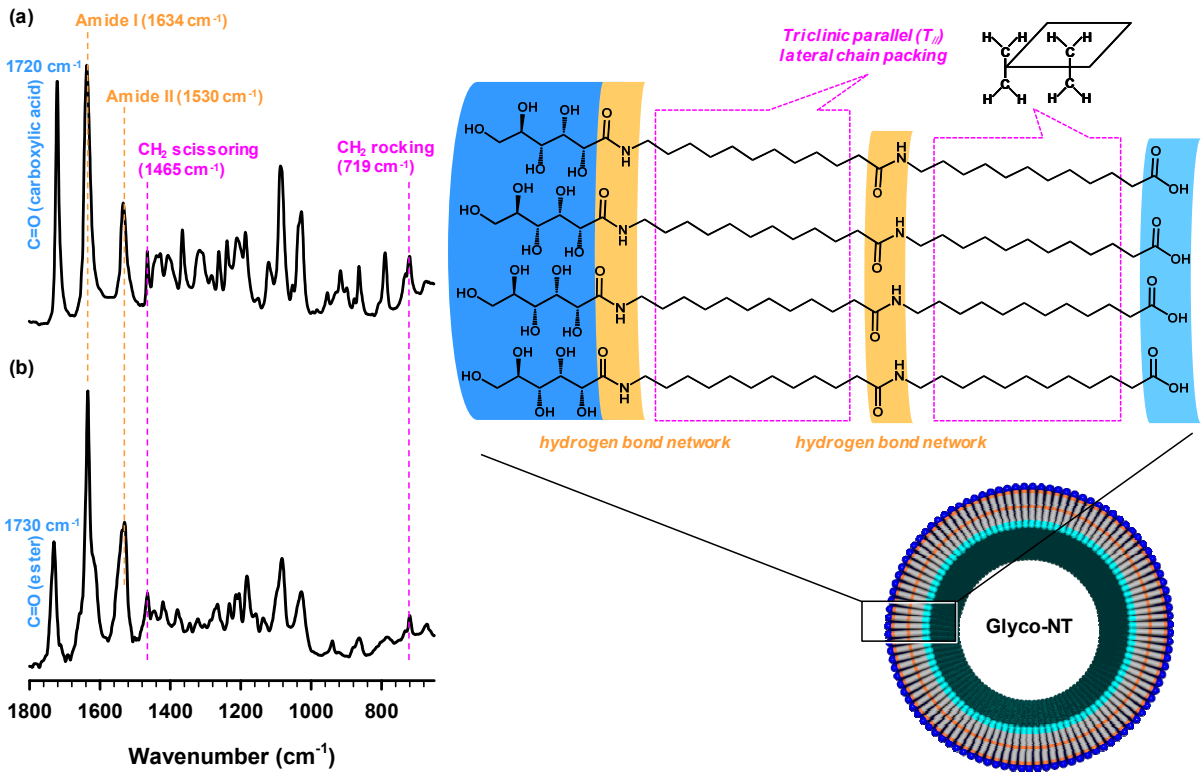

Fig. S5 IR spectra of (a) the Glyco-NT and (b) GlycoOEt-NT. The single sharp peaks of the CH_2 scissoring and CH_2 rocking bands indicate that the subcell structure (lateral chain packing) of the oligomethylene spacer of Glycolipid and Glycolipid-OEt in the nanotubes is the triclinic parallel. The amide-I and -II bands are assignable to intermolecular hydrogen bonding among the glycolipids packed in parallel within the monolayer membrane.

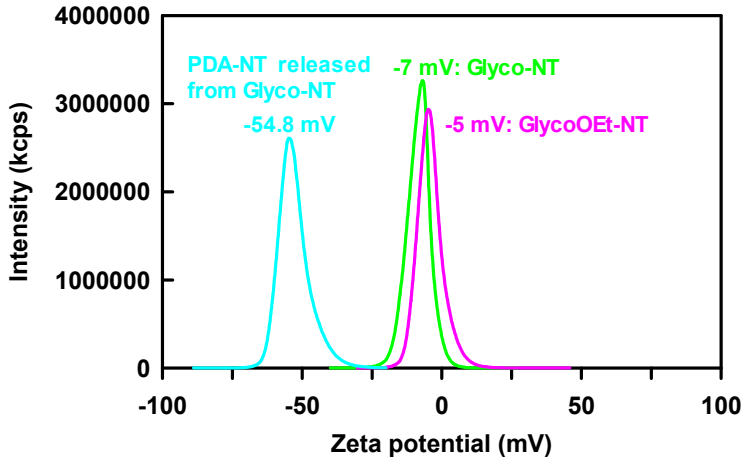

Fig. S6 Zeta potential distribution of the Glyco-NT, GlycoOEt-NT and PDA-NT (formed in the Glyco-NT) dispersed in pure water.

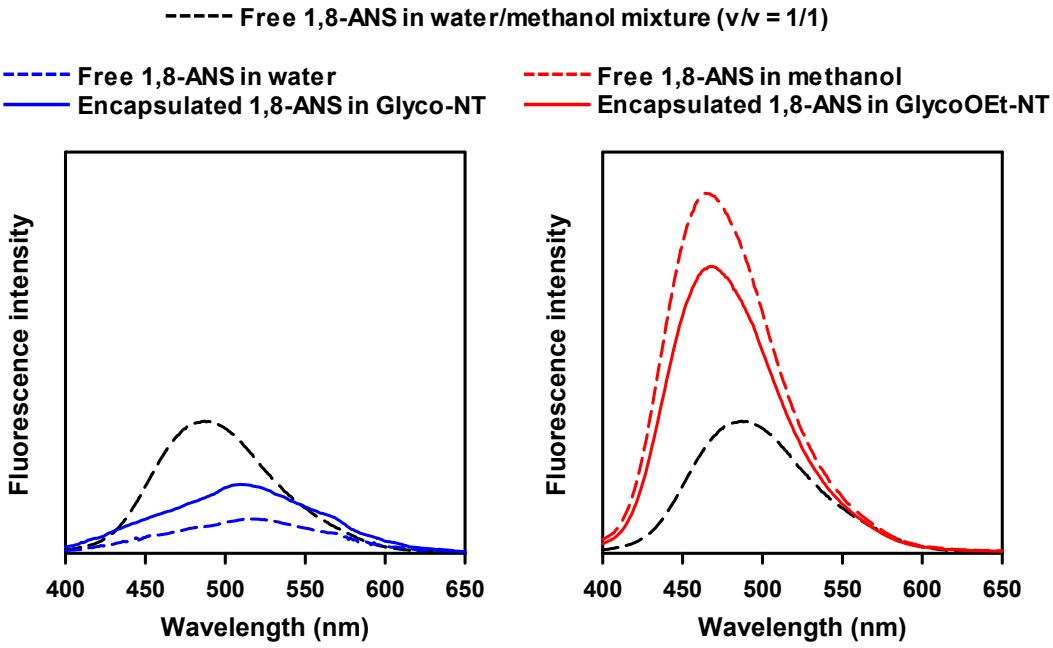

Fig. S7 Fluorescence spectra of the encapsulated 8-anilinonaphthalene-1-sulfonate (1,8-ANS) in the indicated nanotubes dispersed in water/methanol mixture (v/v = 1/1), free 1,8-ANS in water and methanol. [1,8-ANS] = 1.0×10^{-7} molL^{-1}

The Glyco-NT or GlycoOEt-NT encapsulating 1,8-ANS were prepared by addition of the lyophilized nanotubes to a water/methanol mixture (v/v = 1/1) of 1,8-ANS. The fluorescence band of 1,8-ANS encapsulated in the Glyco-NT was red-shifted, smaller, and wider than that of free 1,8-ANS in the water/methanol mixture, and was relatively similar to that of free 1,8-ANS in water. In contrast, the fluorescence band of 1,8-ANS encapsulated in the GlycoOEt-NT was blue-shifted, larger, and narrower than that of the free 1,8-ANS in the water/methanol mixture, and was relatively similar to that of free 1,8-ANS in methanol. The results suggest that the Glyco-NTs have rich water nanochannels, while the GlycoOEt-NT have rich methanol nanochannels, even though the water/methanol mixture was used for the encapsulation procedure. This supports the hydrophilic and hydrophobic features of the both nanotubes.

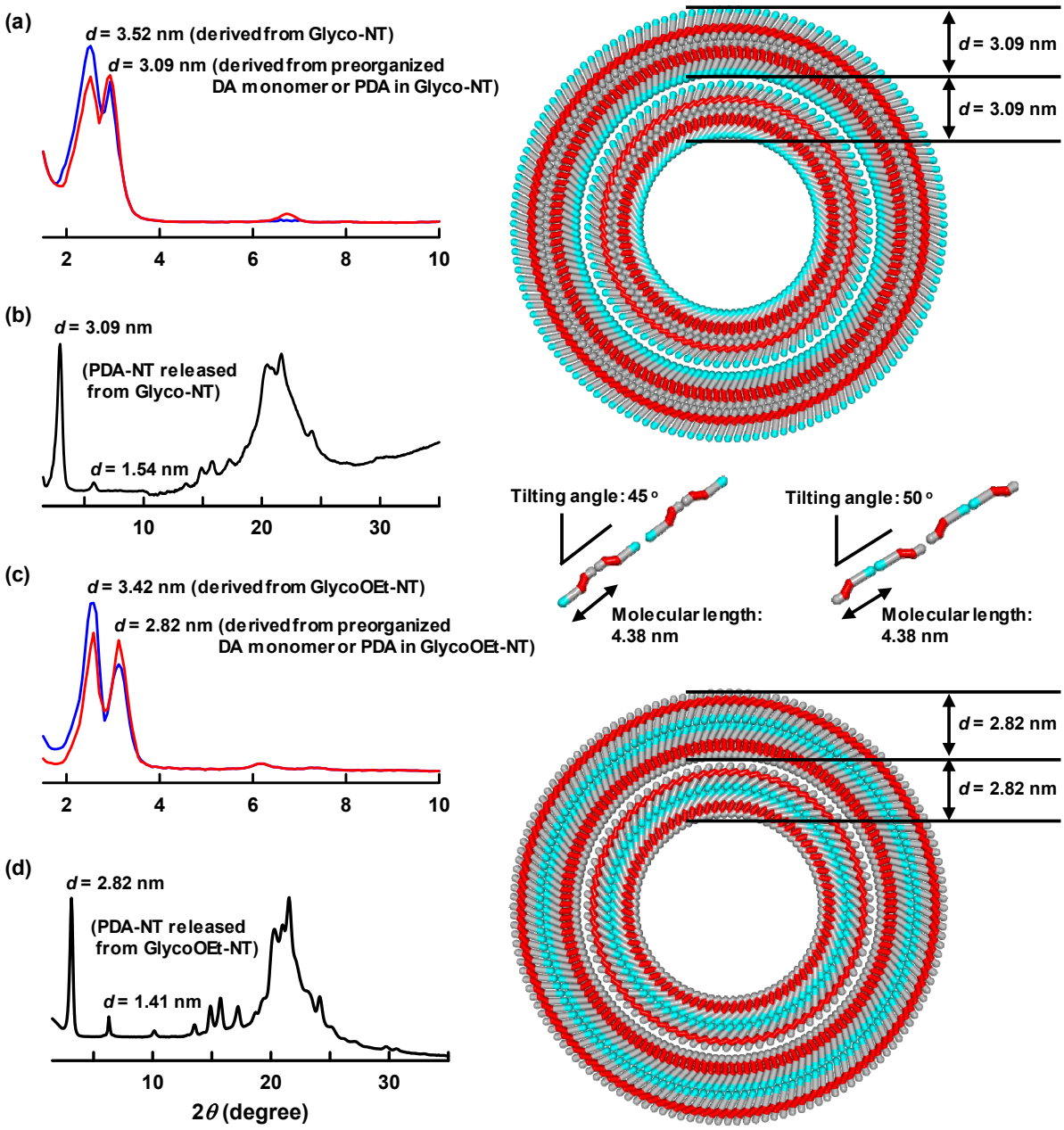

Fig. S8 (a) XRD patterns of the Glyco-NT encapsulating the DA monomers (a blue line) and Glyco-NT encapsulating PDA (a red line). (b) XRD patterns of the PDA-NT released from the Glyco-NT. (c) XRD patterns of the GlycoOEt-NT encapsulating the DA monomers (a blue line) and GlycoOEt-NT encapsulating PDA (a red line). (d) XRD patterns of the PDA-NT released from the GlycoOEt-NT. Schematic images of the PDA-NT consisting of the bilayer membranes with the stacking periodicity. The upper PDA-NT, which is formed in the Glyo-NT, has hydrophilic inner and outer surfaces covered with the carboxyl groups. The lower PDA-NT, which is formed in the GlyoOEt-NT, has hydrophobic inner and outer surfaces covered with the alkyl groups.

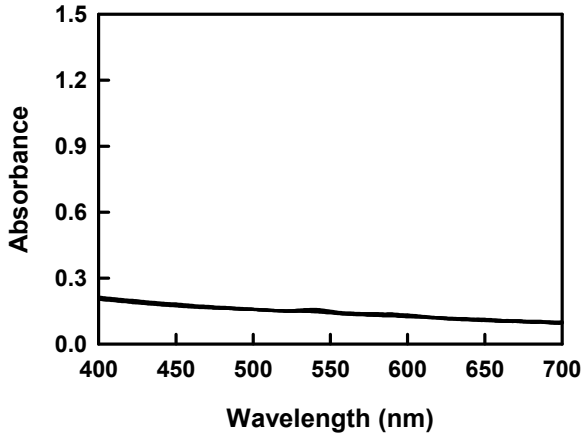

Fig. S9 Absorption spectra of the DA monomer in water/methanol (v/v = 50/50) upon UV light irradiation.

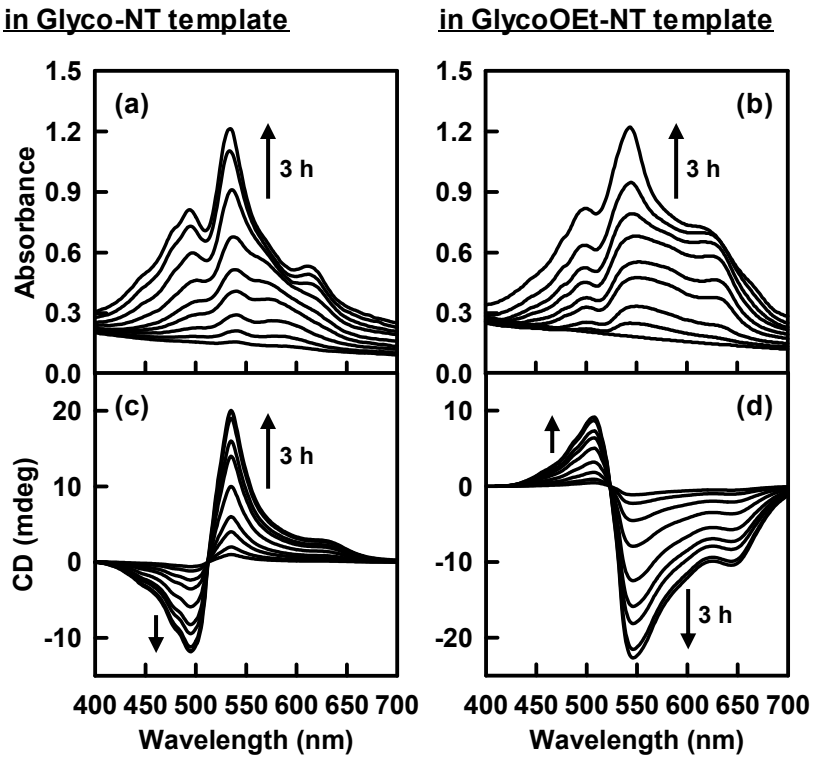

Fig. S10 Changes in the absorption (a, b) and circular dichroism (CD) (c, d) spectra of diacetylene monomers encapsulated in nanotube channels during ultraviolet irradiation for 0–3 h.

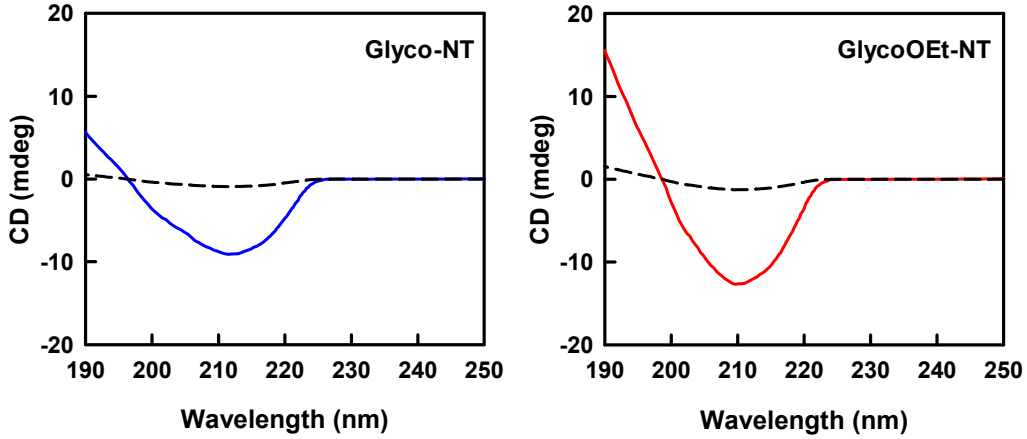

Fig. S11 (Solid line) CD spectra of the Glyco-NT and GlycoOEt-NT dispersed in pure water at 25 ºC. (Dotted lines) CD spectra of Glycolipid and Glycolipid-OEt existing as molecules obtained from thermal destruction of the corresponding nanotubes at 90 ºC.

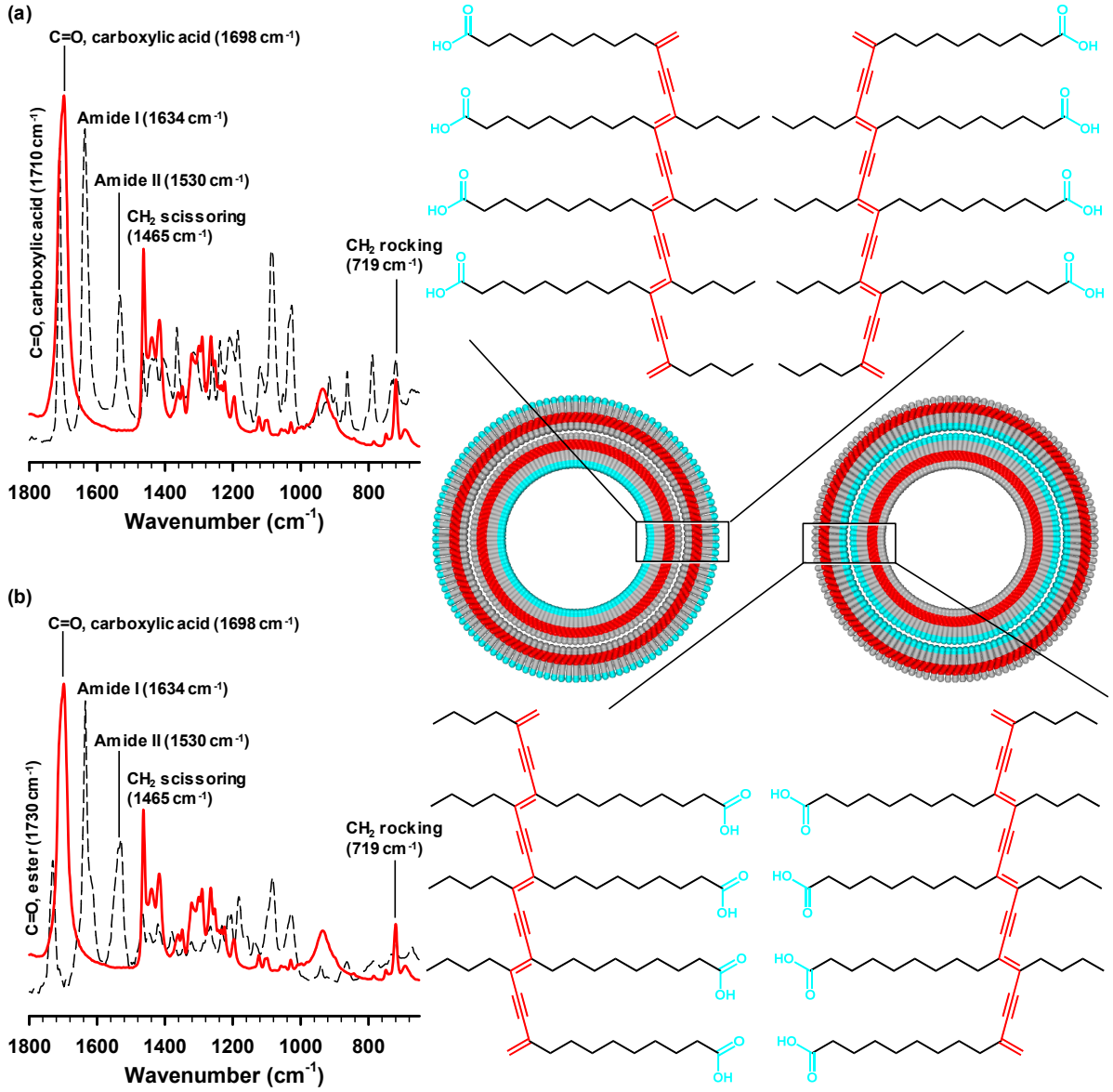

Fig. S12 (a) IR spectra of the Glyco-NT template (a black dotted line) and PDA-NT released from the Glyco-NT template (a red solid line). (b) IR spectra of the GlycoOEt-NT template (a black dotted line) and PDA-NT released from the GlycoOEt-NT template (a red solid line). The single sharp peaks of the CH_2 scissoring bands at 1465 cm^{-1} and CH_2 rocking bands at 719 cm^{-1} indicate that the oligomethylene spacer moieties never have an interdigitated fashion. Schematic images of the molecular packing within the bilayer membrane of the PDA-NTs.

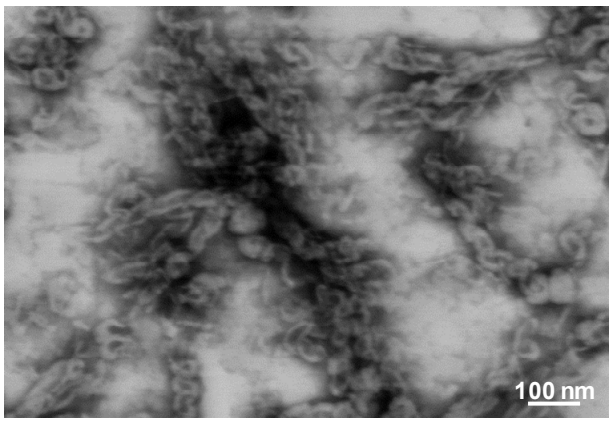

Fig. S13 Scanning-TEM image of the solids obtained by evaporation of the DA solution.

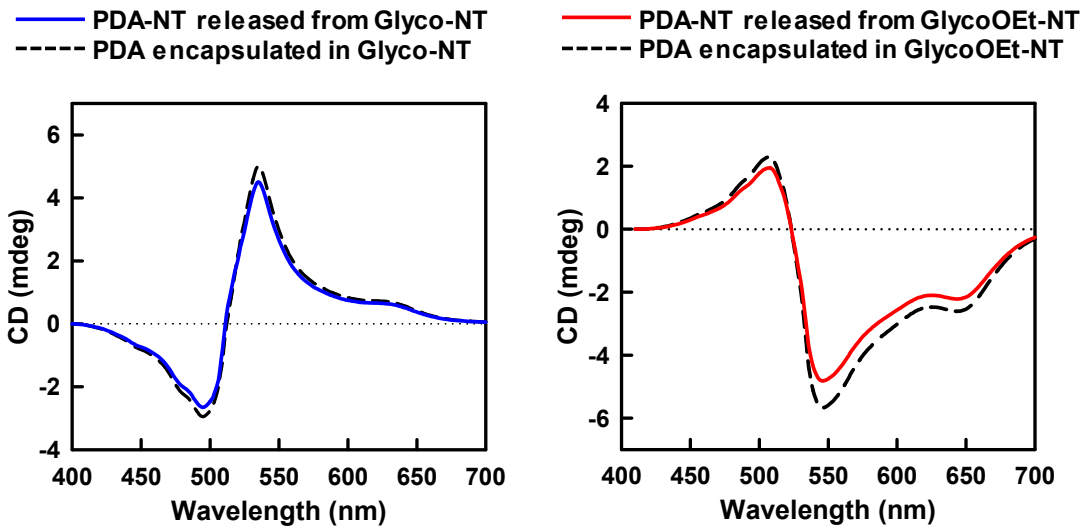

Fig. S14 (left) CD spectra of the water/methanol (v/v = 50/50) solutions of the PDA-NT released from the Glyco-NT and PDA encapsulated in the Glyco-NT. (right) CD spectra of the water/methanol (v/v = 50/50) solutions of the PDA-NT released from the GlycoOEt-NT and PDA encapsulated in the GlycoOEt-NT.