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Electronic Supplemental Information (ESI)

<u>Title</u>

PEG-nanotube liquid crystals as templates for construction of surfactant-free gold nanorods

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This Supplementary Information file replaces that originally published on 17 April 2018, in which an incorrect photograph was included in Fig. S6. This error did not affect any of the results or conclusions in the article.



Scheme S1 Synthetic scheme of 1(n).

1(2): 1H NMR (400 MHz, DMSO- d_6 , δ): 8.05 (d, 1H: NH), 7.70 (t, 1H: NH), 7.60 (t, 1H: NH), 4.98 (d, 1H: OH), 4.85 (d, 1H: OH), 4.80 (d, 1H: OH), 4.68 (t, 1H: H-1), 4.63 (br, 1H: OH), 4.44 (t, 1H: OH-6), 3.68 (m, 1H: H-6), 3.40 (m, 1H: H-6), 3.35 (q, 2H: $-CH_2CH_2OH$), 3.18 (m, 1H; H-4), 3.13 (q, 2H: $-CH_2CH_2OH$), 3.05 (m, 2H: $-CH_2NHC=O$), 3.02 (m, 2H: $-CH_2NHC=O$), 3.0 (m, 3H: H-2, H-3, H-5), 2.24 (t, 2H: $-CH_2C=O$), 2.01 (t, 2H: $-CH_2C=O$), 1.93 (m, 2H: $-CH_2-$), 1.85 (m, 2H: $-CH_2-$). ESI-MS (cationic mode) m/z: 422.2 [M + H]+. Anal. Calcd for C17H31N3O9: C 48.45, H 7.41, N 9.97; found: C 48.48, H 7.52, N 9.90.

1(6): 1H NMR (400 MHz, DMSO- d_6 , δ): 8.08 (d, 1H: NH), 7.71 (t, 1H: NH), 7.60 (t, 1H: NH), 4.95 (d, 1H: OH), 4.87 (d, 1H: OH), 4.81 (d, 1H: OH), 4.67 (t, 1H: H-1), 4.60 (br, 1H: OH), 4.45 (t, 1H: OH-6), 3.67 (m, 1H: H-6), 3.41 (m, 1H: H-6), 3.36 (q, 2H: $-CH_2CH_2OH$), 3.16 (m, 1H; H-4), 3.14 (q, 2H: $-CH_2CH_2OH$), 3.06 (m, 2H: $-CH_2NHC=O$), 3.03 (m, 2H: $-CH_2NHC=O$), 3.0 (m, 3H: H-2, H-3, H-5), 2.24 (t, 2H: $-CH_2C=O$), 2.01 (t, 2H: $-CH_2C=O$), 1.46 (m, 4H: $-CH_2-$), 1.35 (m, 4H: $-CH_2-$), 1.23 (m, 12H: $-CH_2-$). ESI-MS (cationic mode) m/z: 534.3 [M + H]+. Anal. Calcd for C25H47N3O9: C 56.27, H 8.88, N 7.87; found: C 56.28, H 8.90, N 7.80.

1(10): 1H NMR (400 MHz, DMSO- d_6 , δ): 8.09 (d, 1H: NH), 7.70 (t, 1H: NH), 7.60 (t, 1H: NH), 4.96 (d, 1H: OH), 4.87 (d, 1H: OH), 4.81 (d, 1H: OH), 4.69 (t, 1H: H-1), 4.66 (br, 1H: OH), 4.47 (t, 1H: OH-6), 3.63 (m, 1H: H-6), 3.40 (m, 1H: H-6), 3.39 (q, 2H: $-CH_2CH_2OH$), 3.16 (m, 1H; H-4), 3.13 (q, 2H: $-CH_2CH_2OH$), 3.05 (m, 2H: $-CH_2NHC=O$), 3.02 (m, 2H: $-CH_2NHC=O$), 3.0 (m, 3H: H-2, H-3, H-5), 2.28 (t, 2H: $-CH_2C=O$), 2.01 (t, 2H: $-CH_2C=O$), 1.46 (m, 4H: $-CH_2-$), 1.35 (m, 4H: $-CH_2-$), 1.23 (m, 28H: $-CH_2-$). ESI-MS (cationic mode)

m/z: 646.5 [M + H]+. Anal. Calcd for C33H63N3O9: C 61.37, H 9.83, N 6.51; found: C 61.48, H 9.90, N 6.57.



Scheme S1 Synthetic scheme of 2(n).

2(2): 1H NMR (400 MHz, DMSO- d_6 , δ): 7.96 (t, 1H: NH), 7.70 (t, 1H: NH), 7.61 (t, 1H: NH), 3.58 (m, 24H: -OCH₂CH₂O–), 3.48 (m, 2H: -CH₂–), 3.4 (m, 4H: -CH₂–, -CH₂CH₂OH), 3.19 (m, 2H: -CH₂–), 3.1 (m, 4H: -CH₂–, -CH₂CH₂OH), 3.06 (m, 2H: -CH₂NHC=O), 3.03 (m, 2H: -CH₂NHC=O), 2.34 (m, 2H: -CH₂C=O), 2.27 (m, 2H: -CH₂C=O), 1.95 (m, 2H: -CH₂–), 1.90 (m, 2H: -CH₂–). ESI-MS (anionic mode) m/z: 610.3 [M – H]⁻. Anal. Calcd for C27H53N3O12: C 53.01, H 8.73, N 6.87; found: C 52.95, H 8.71, N 6.87.

2(6): 1H NMR (400 MHz, DMSO-*d*₆, δ): 7.86 (t, 1H: NH), 7.70 (t, 1H: NH), 7.62 (t, 1H: NH), 3.58 (m, 24H: –OCH₂CH₂O–), 3.48 (m, 2H: –CH₂–), 3.3 (m, 4H: –CH₂–, –CH₂CH₂OH), 3.19 (m, 2H: –CH₂–), 3.1 (m, 4H: –CH₂–, –CH₂CH₂OH), 3.06 (m, 2H: –CH₂NHC=O), 3.03 (m, 2H: –CH₂NHC=O), 2.27 (m, 2H: –CH₂C=O), 2.04 (m, 2H: –CH₂C=O), 1.45 (m, 4H: –CH₂–), 1.35 (m, 4H: –CH₂–), 1.23 (m, 12H: –CH₂–). ESI-MS (anionic mode) m/z: 722.5 [M – H]⁻. Anal. Calcd for C35H69N3O12: C 58.07, H 9.61, N 5.80; found: C 57.95, H 9.71, N 5.87.

2(10): 1H NMR (400 MHz, DMSO- d_6 , δ): 7.88 (t, 1H: NH), 7.72 (t, 1H: NH), 7.61 (t, 1H: NH), 3.59 (m, 24H: $-\text{OCH}_2\text{CH}_2\text{O}-$), 3.47 (m, 2H: $-\text{CH}_2-$), 3.4 (m, 4H: $-\text{CH}_2-$, $-\text{CH}_2\text{C}H_2\text{O}\text{H}$), 3.18 (m, 2H: $-\text{CH}_2-$), 3.1 (m, 4H: $-\text{CH}_2-$, $-\text{C}H_2\text{C}H_2\text{O}\text{H}$), 3.05 (m, 2H: $-\text{C}H_2\text{NHC}=\text{O}$), 3.02 (m, 2H: $-\text{C}H_2\text{NHC}=\text{O}$), 2.25 (m, 2H: $-\text{C}H_2\text{C}=\text{O}$), 2.04 (m, 2H: $-\text{C}H_2\text{C}=\text{O}$), 1.46 (m, 4H: $-\text{C}H_2-$), 1.35 (m, 4H: $-\text{C}H_2-$), 1.23 (m, 28H: $-\text{C}H_2-$). ESI-MS (anionic mode) m/z: 834.6 [M

– H]⁻. Anal. Calcd for C43H85N3O12: C 61.77, H 10.25, N 5.03; found: C 60.95, H 10.41, N 5.07.

2-[(6-mercaptohexyl)oxy]methyl-12-crown-4 (3) and 2-[(6-mercaptohexyl)oxy]methyl-15 -crown-5 (4) were synthesized as reported previously (S. Flink et al., *J. Am. Chem. Soc.*, 1998, **120**, 4652).

Construction of nanotubes by binary self-assembly

The mixtures of 1(2) (2.1 g, 5 mmol) and 2(2) (3.0 g, 5 mmol), 1(6) (2.2 g, 4.1 mmol) and 2(6) (3.0 g, 4.1 mmol), 1(10) (2.2 g, 2.6 mmol) and 2(10) (2.8 g, 2.6 mmol), were dispersed in pure water (100 ml) under reflux conditions. The resultant hot solutions were gradually cooled to room temperature.

Preparation of gold seed particles

According to a previously reported method (B. D. Busbee et al., *Adv. Mater.*, 2003, **15**, 414.), An aqueous solution (0.5 ml) of 0.01 M HAuCl₄ and an aqueous solution (0.5 ml) of 0.01 M sodium citrate were mixed in pure water (18 ml). An aqueous solution (0.5 ml) of 0.1 M NaBH₄ was added into the mixtures. The obtained gold seed particles were purified by centrifugation and decantation with pure water. The size of the obtained gold seed particles was estimated to be 3.5 nm by TEM observation and dynamic light scattering measurement (data not shown).

Construction of GNRs by using NT-LC templates

The aqueous dispersion (1 ml) of the gold seeds ([Au] = 0.26 mM) was mixed with the NT-LC templates (100 ml) composed of **1(n)** and **2(n)** ([1(2)] = [2(2)] = 50 mM, [1(6)] = [2(6)] = 41 mM, [1(10)] = [2(10)] = 26 mM). An aqueous solution (2.5 ml) of 0.01 M HAuCl₄ and then an aqueous solution (0.5 ml) of 0.1 M ascorbic acid were added into the resultant mixtures. After standing for 12 h, an aqueous solution (2.5 ml) of 100 mM the thiol-crown ether compounds **3** or **4** was poured to the GNRs grew on the NT-LC template. Near infrared irradiation (Nd-YAG laser, Wavelength: 1064 nm, Pulse width: 7 ns, Frequency: 20 Hz, Power: 0.7 W) was performed to release the GNRs functionalized with **3** or **4** from the NT-LC template. The supernatant containing the GNRs was separated from the nanotube aggregates as the precipitates, and was purified by centrifugation and decantation with pure water.



Fig. S1 TEM images of the self-assembled structures. The nanochannels of the nanotubes were visualized with phosphotungstate as a negative staining reagent.



Fig. S2 Differential scanning calorimetry profiles of the lyophilized self-assembled structures. The endothermic peaks correspond to the isotropic melting points.

Nanotube composed of 1(10) and 2(10)



Fig. S3 (Left) Infrared spectra for the amide-I (green), amide-II (blue), CH_2 scissoring (red) bands of the nanotubes. The lower wavenumber of the amide-I band and the higher wavenumber of the amide-II band indicated the stronger intermolecular hydrogen bonds among **1(n)** and **2(n)**. The single sharp peak of the CH_2 scissoring band indicated that the lateral chain packing (subcell structure) of the oligomethylene spacer of **1(n)** and **2(n)** has a triclinic parallel ($T_{1/1}$) type structure. (Right) powder X-ray diffraction patterns of the nanotubes. The three peaks in the wide angle region support the subcell structure.



Fig. S4 (Upper) TEM image of the nanotubes composed of **1(2)** and **2(2)** after the sonication treatment. (Lower) The length distributions of the indicated nanotubes.



Fig. S5 Photographs of the aqueous dispersion (left), nematic liquid crystal (middle) and hydrogel (right) of the nanotubes composed of **1(2)** and **2(2)** at different concentrations.



Fig. S6 (Left) Representative photographs showing the appearance of the NT-LC composed of 1(2) and 2(2) at the indicated temperatures. (Right) Temperature dependence of the turbidity of the NT-LC upon heating and cooling. T_{-H2O} and T_{+H2O} of the NT-LCs were estimated to be 55–60 °C and 40–45 °C, respectively, by monitoring the change in turbidity.



Fig. S7 (Left) TEM image of the nanotube hydrogel composed of **1(2)** and **2(2)** after addition of the gold seed particles with 3.5 nm size. The black dots corresponding to the gold seed particles were randomly observed around the network structures of the nanotubes. (Right) SEM image of the gold nanoparticles prepared in the presence of the nanotube hydrogel.



Fig. S8 Release profiles of the GNRs from the NT-LC template composed of **1(2)** and **2(2)** upon near infrared irradiation (Nd-YAG laser, 1064 nm, 0.7 W) or heating for indicated times.



Fig. S9 (Left) TEM image of the 12crown4-GNRs prepared by using the NT-LC template composed of **1(6)** and **2(6)**. (Right) TEM image of the 12crown4-GNRs prepared by using the NT-LC template composed of **1(10)** and **2(10)**.



Fig. S10 ScSchematic representation of the relationship between GNR diameter and nanotube diameter.



Fig. S11 (a) Absorption spectra of 12crown4-GNRs ($[3] = 7.2 \times 10^{-4}$ M) in water in the absence and presence of 1.4×10^{-6} M Li⁺ (pink), Na⁺ (blue), and K⁺ (yellow). Inset: Plot of absorbance at 970 nm versus initial ion concentration. The 12crown4-GNRs were prepared by using a NT-LC template composed of **1(10)** and **2(10)**. The diameters and lengths of the 12crown4-GNRs are shown in blue in Fig. 4b,c. (b, c) Plots of absorbance at 970 nm of 15crown5-GNRs ($[4] = 6.5 \times 10^{-4}$ M) versus initial concentration of D- and L-alaninols. The 15crown5-GNRs in panel (b) were prepared by using a NT-LC template composed of **1(10)** and the GNRs in panel (c) were prepared by using a template composed of an enantiomer (with an L-glucose headgroup) of **1(10)** and **2(10)**.

Present system

1:1 host-guest interaction between Li ions and 12crown-4 ether moieties on the surface of GNR



Previous system*

Sandwich type 1:2 host-guest interaction between Na ions and 12-crown-4 ether moieties on the surface of GNR



Aggregation of 12crown4-GNRs



No aggregation

Fig. S12 Schematic images of complexation between 12crown4-GNRs and alkaline metal ions. *H. Nakashima et al., *Chem. Commun.*, 2007, **43**, 1080.



Fig. S13 Circular dichroism spectra of the aqueous dispersions of pyrene-15crown5-GNRs.