Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Electronic Supplemental Information (ESI)

Title

A supramolecular nanotube used as a water-degradable template for the production of protein nanotubes with high thermal/chemical stabilities

Authors

N. Kameta,* and W. Ding

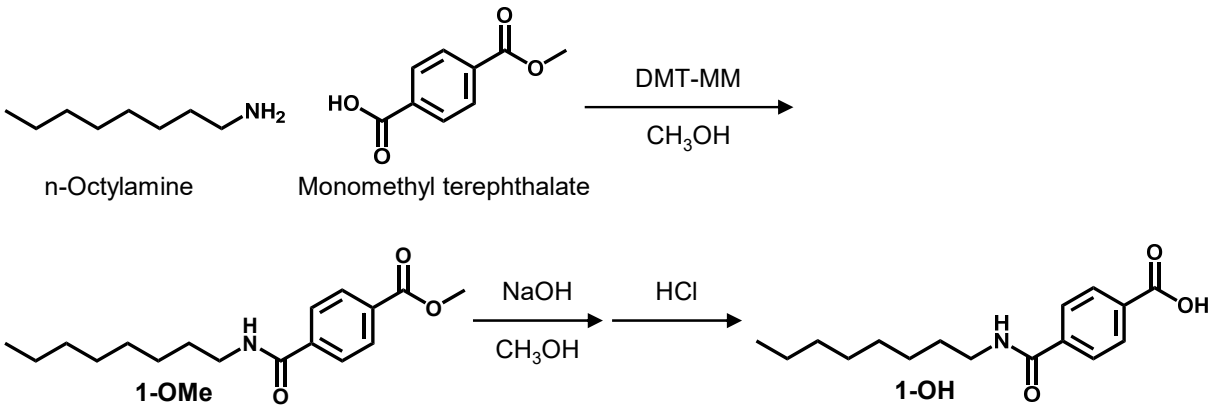

Fig. S1 Synthetic scheme of an amphiphile **1-OH**.

n-Octylamine (0.72 g, 5.55 mmol, TCI) and monomethyl terephthalate (1.00 g, 5.55 mmol, TCI) were dispersed in methanol (50 mL) in the presence of 4-(4,6-Dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMT-MM, 1.54 g, 5.55 mmol, Wako). The mixture was stirred for 12 h at a room temperature. After evaporation of the solvent, the residual solid was washed with 10% $NaHCO_3$ solution, 5% citric acid solution and water. The resultant white solid corresponding to an intermediate, 1-OMe, was dissolved in a mixing solution of methanol (50 mL) and NaOH (0.33 g, 8.33 mmol) solution (9 mL). After stirring the solution for 12 h, conc. HCl was added to the solution to precipitate 1-OH as a white solid. 1-OH was corrected by a paper filtration and dried in vacuum desiccator (1.28 g, 4.62 mmol, 83% yield).

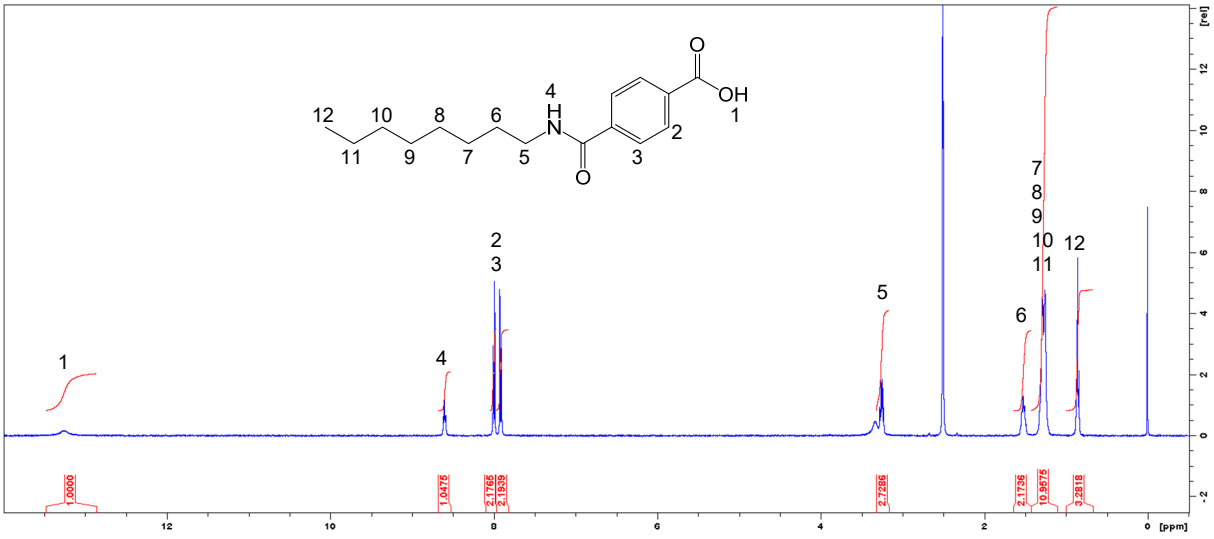

Fig. S2 ^{1}H NMR spectra of **1-OH** in DMSO-d_6.

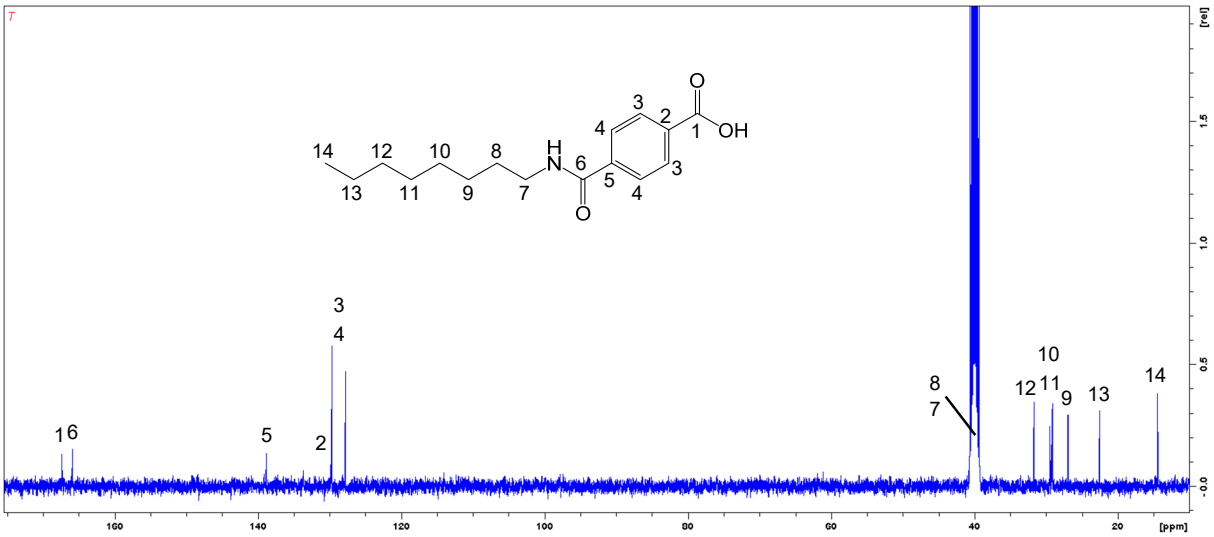

Fig. S3 ^{13}C NMR spectra of **1-OH** in DMSO-d_6.

1-OH: ^{1}H NMR (400 MHz, in DMSO-d_6): δ 13.25 (br, 1H, OH), 8.60 (t, 1H, J = 5.5 Hz, NH), 8.00 (d, 2H, J = 8.4 Hz, aromatic ring), 7.91 (d, 2H, J = 8.4 Hz, aromatic ring), 3.25 (dd, 2H, J = 13.0 and 6.7 Hz, -CH_2-NH-C=O), 1.52 (m, 2H, -CH_2-CH$_2$-NH-C=O), 1.27 (m, 10H, -CH$_2$-), 0.86 (t, 3H, J = 6.8, CH$_3$). ^{13}C NMR (400 MHz, in DMSO-d_6): 167.3 (C=O), 165.8 (C=O), 138.8 (aromatic ring), 129.8 (aromatic ring), 129.7 (aromatic ring), 127.8 (aromatic ring), 39.8 (CH$_2$, overlapped with the solvent), 31.7 (CH$_2$), 29.5 (CH$_2$), 29.2 (CH$_2$), 26.9 (CH$_2$), 22.5 (CH$_2$), 14.4 (CH$_3$). ESI-MS (anionic mode) m/z: 276.1 [M – H]$^-$. Anal. calcd for C$_{16}$H$_{23}$NO$_3$: C 69.29, H 8.36, N 5.05; found C69.25, H 8.39, N 5.03.

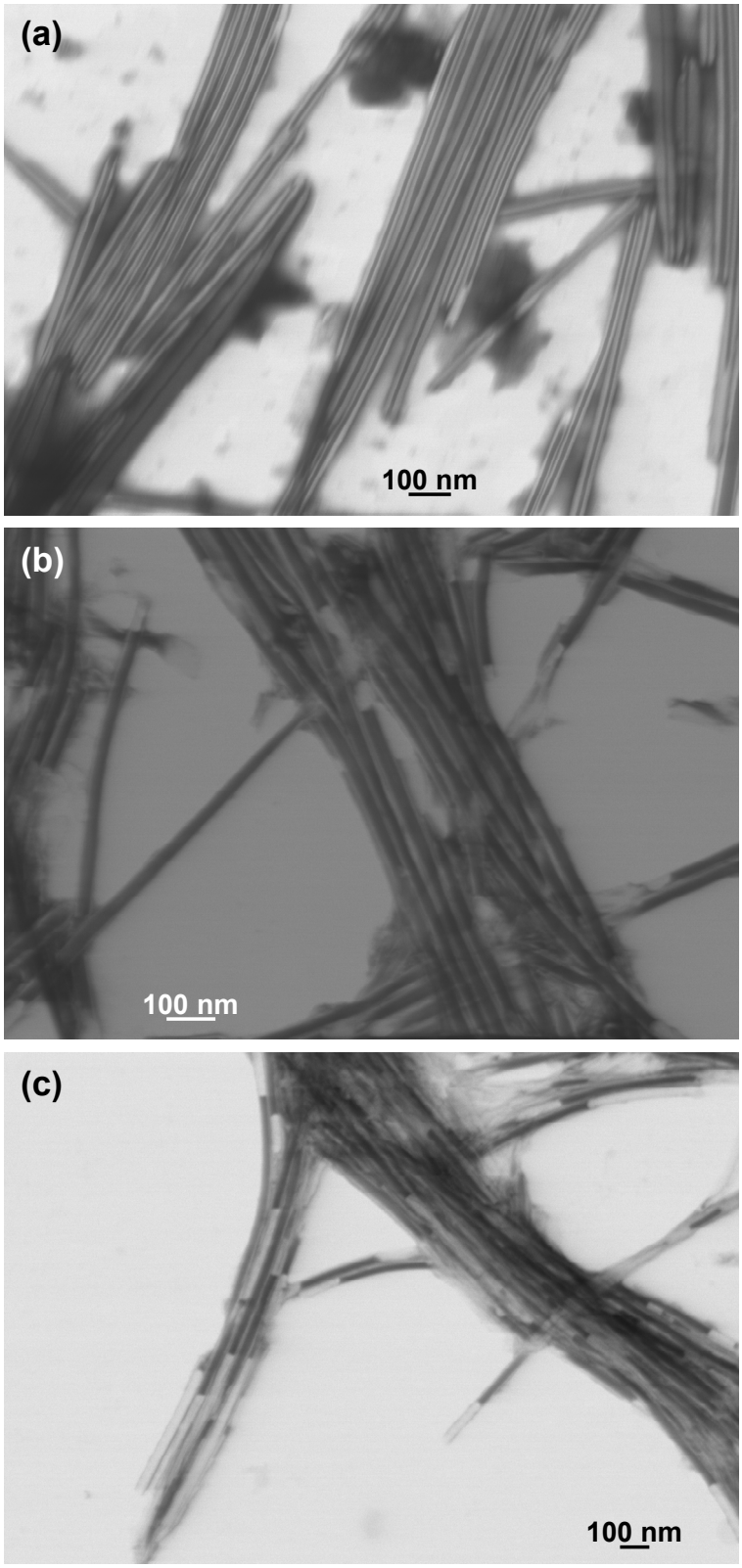

Fig. S4 Scanning transmission electron micrographs of (a) 1-ONa nanotubes, (b) lysozyme nanotubes and (c) cytochrome-*c* nanotubes. Nanochannels were visualized by means of negative staining with 2 wt% phosphotungstate.

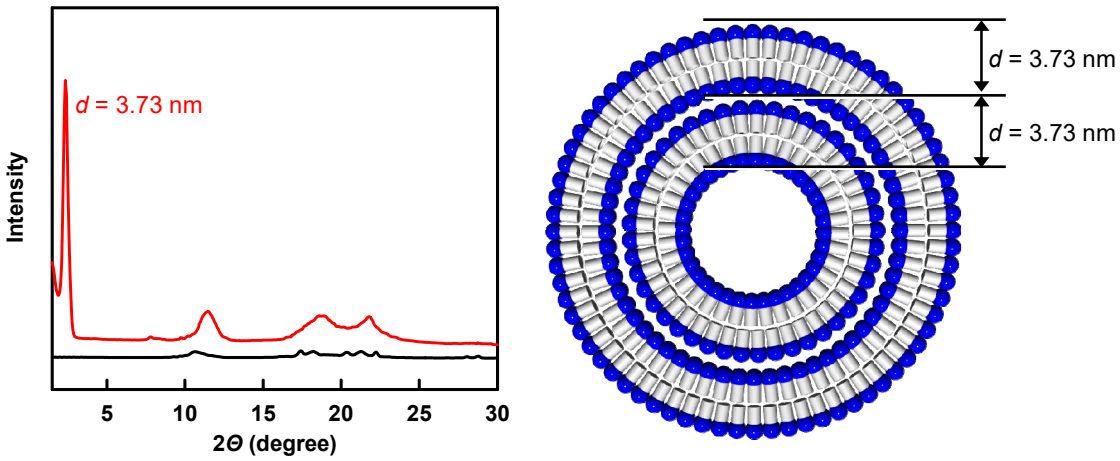

Fig. S5 (left panel) Powder X-ray diffraction patterns of 1-ONa nanotube (a red spectrum) and a decomposition product of 1-ONa nanotube (a black spectrum). (Right panel) Schematic image of 1-ONa nanotube consisting of bilayer membranes with the stacking periodicity. Although the structure here is presented as double bilayer membranes for simplicity, in reality the nanotube was formed by the stacking of four bilayer membranes.

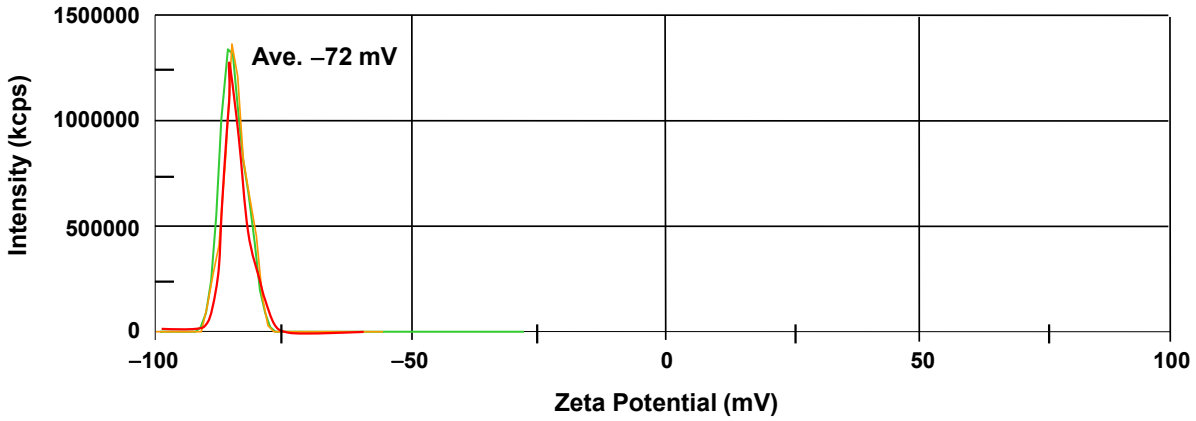

Fig. S6 Zeta potential distributions of 1-ONa nanotube dispersed in water at pH 8.1.

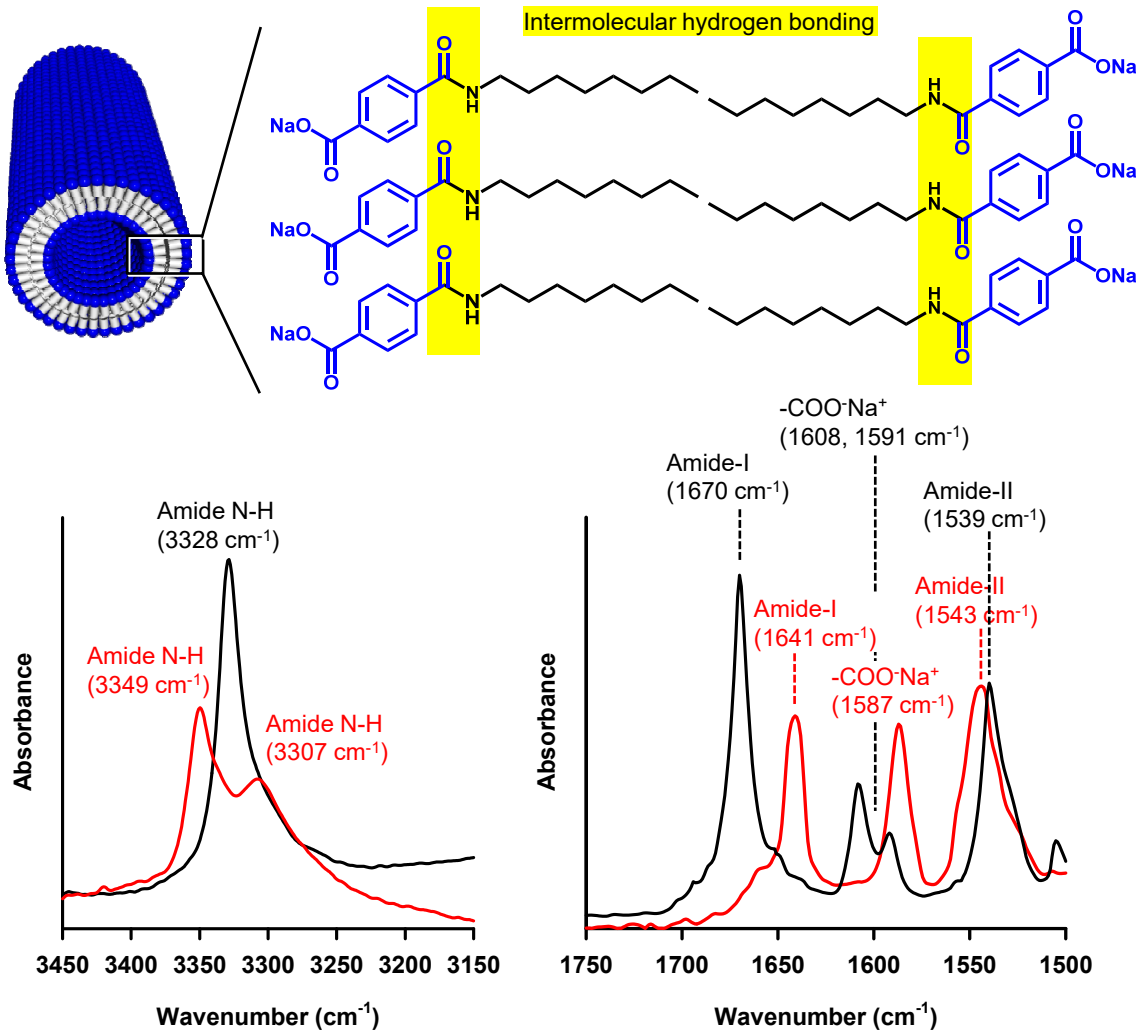

Fig. S7 (Upper panel) Schematic image of 1-ONa nanotube consisting of a bilayer membrane stabilized by intermolecular hydrogen bonds among amide bonds in **1-ONa**. (Lower panel) Infrared spectra of an amide N-H, amide-I and amide-II bands of 1-ONa nanotube (a red spectrum) and a decomposition product of 1-ONa nanotube (a black spectrum).

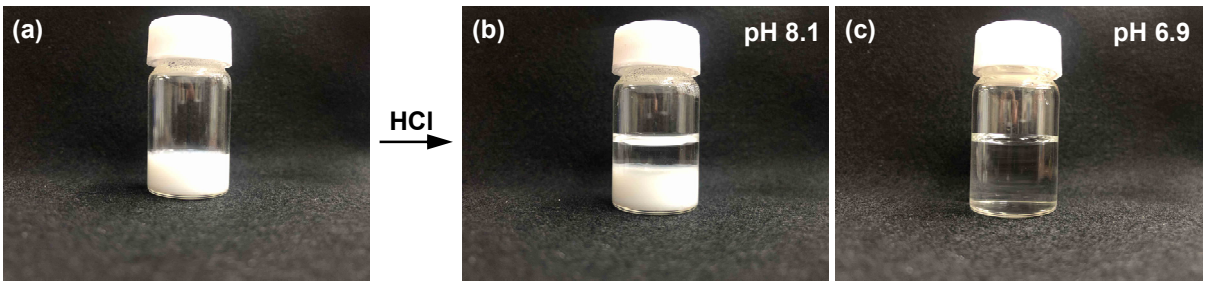

Fig. S8 Photographs of (a) 1-ONa nanotube hydrogel, (b) survival of the hydrogel at pH 8.1 and (c) disappearance and decomposition of the hydrogel at pH 6.9.

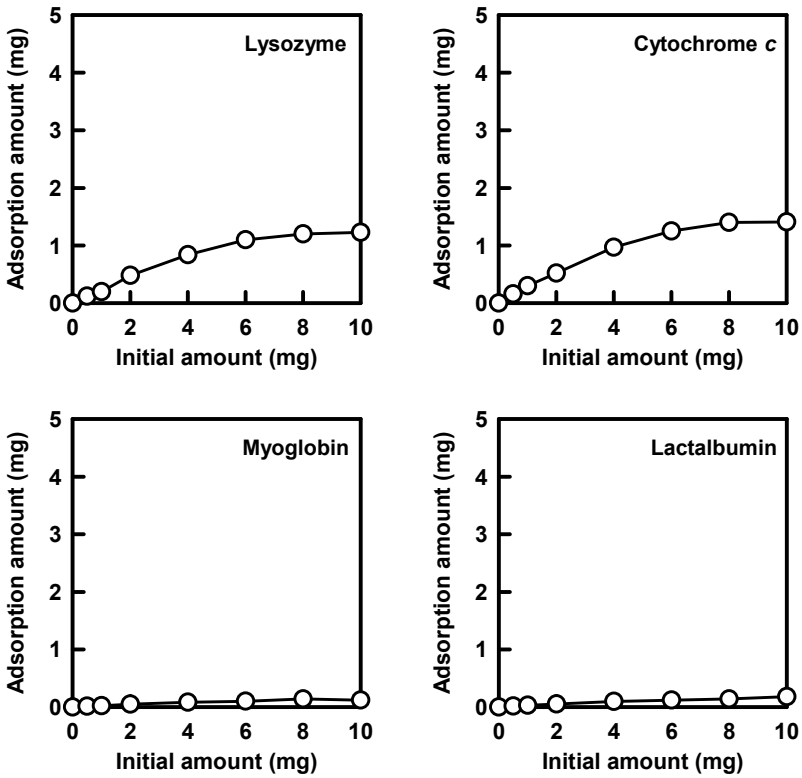

Fig. S9 Relationship between initial amounts of proteins and adsorption amounts of proteins on 1-ONa nanotube.

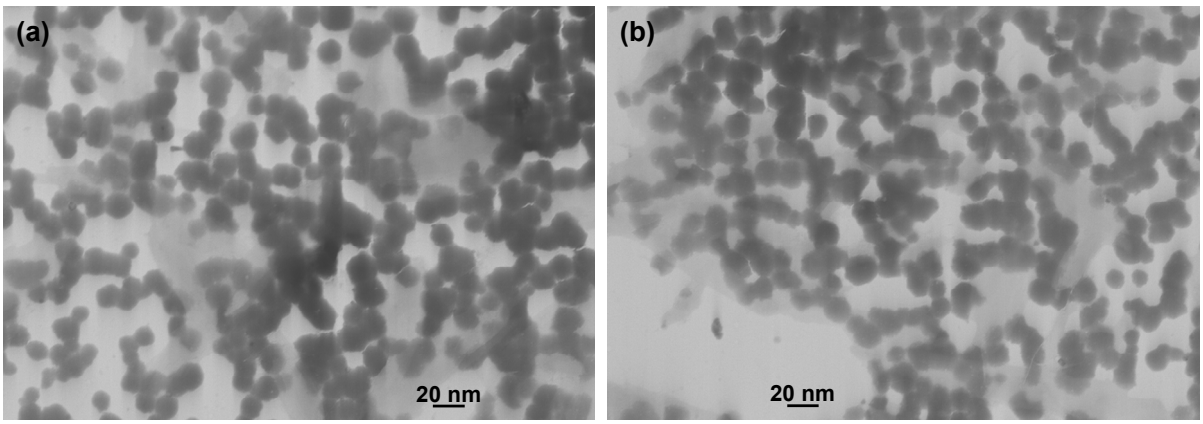

Fig. S10 Scanning transmission electron micrographs of (a) lysozyme nanoparticles and (b) cytochrome-*c* nanoparticles. The protein nanoparticles were prepared as follows: An aqueous solution (100 μL) of glutaraldehyde (90 nmol or 120 nmol) as a cross linker was added to lysozyme (1.2 mg, 85 nmol) or cytochrome c (1.4 mg, 117 nmol), respectively (Fig. 1b). The mixtures were aged for 10 min at pH 8.1. After centrifugation (3000 rpm, 15 min, 15 °C), the precipitated protein nanoparticles were washed with water several times.

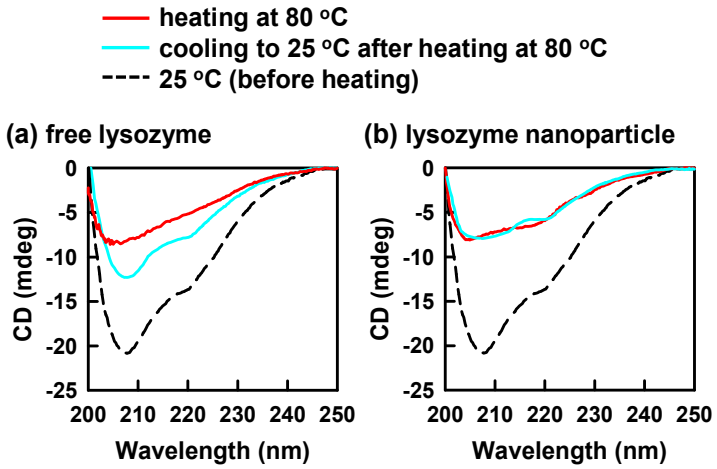

Fig. S11 Circular dichroism spectra of aqueous dispersions of (a) free lysozyme and (b) lysozyme nanoparticle at different temperatures. [lysozyme] = 0.02 mmolL^{-1}

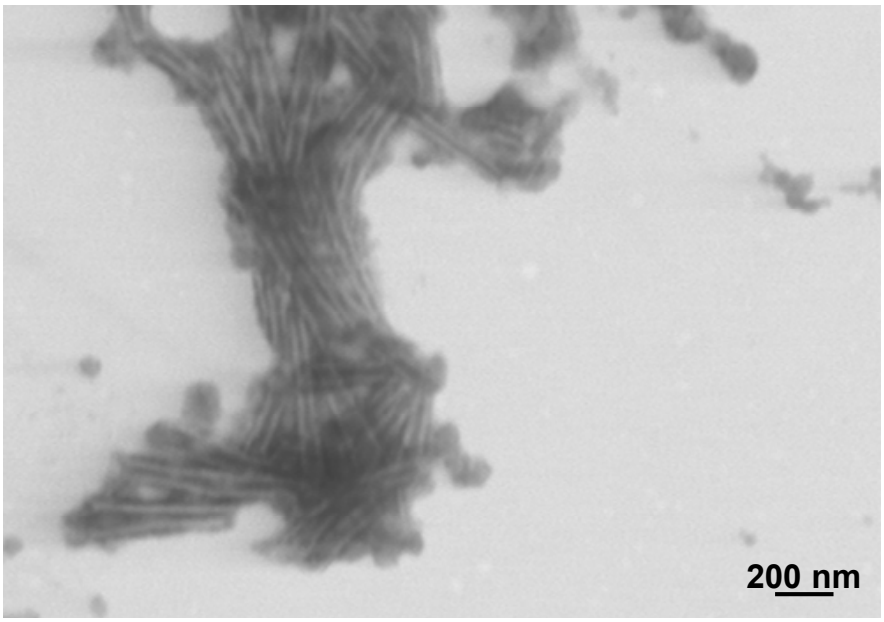

Fig. S12 Scanning transmission electron micrographs of cytochrome-*c* nanotubes shortened by aging with trypsin for 24 h. Nanochannels were visualized by means of negative staining with 2 wt% phosphotungstate.