Supplementary Information

Highly Ordered Superstructures of Single Wall Carbon Nanotube-Liposome Complexes

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Preparation of p-SWNT25

HiPco single wall carbon nanotubes (SWNTs, 2 mg/mL) were mixed with cetyltrimethylammonium 4-vinylbenzoate (CTVB, 5 mg/mL) containing a polymerizable counterion and sodium styrenesulfonate (NaSS) 25 mol % (relative to the CTVB concentration) in heavy water (D_2O) and then sonicated (Cole-Parmer VCX750, 20 kHz, 750 W) for 1 hour at 60 °C. After sonication, the counterions of the CTVB were polymerized using the VA-044 free radical initiator at 60 °C. To separate the individually isolated SWNTs, the suspension was ultracentrifuged at ca. 111,000g for 4 hours (Beckman XL-100) and the upper ca. 70 % of the solution was decanted. From the UV-vis-NIR absorbance at 744 nm, the concentration of SWNT (0.07 mg/mL) in the decanted p-SWNT25 dispersions was estimated by Beer’s law. The concentration of CTVB/NaSS surfactant (1.847 mg/mL) was calculated from thermogravimetric analysis (TGA) and the SWNT concentration estimated from the UV-vis-NIR measurement. The decanted p-SWNT25 dispersion in water was freeze-dried at -55 °C for 3 days, resulting in a black powder of p-SWNT25.
**1H-NMR measurement of p-SWNT25**

To characterize the degree of polymerization of CTVB and NaSS molecules for p-SWNT25, a series of 1H NMR measurements (Bruker FT-500 MHz NMR spectrometer) were performed for the unpolymerized and polymerized SWNT/CTVB/NaSS in D2O. The 1H NMR spectrum of the unpolymerized SWNT/CTVB/NaSS is shown in Fig. S1a. The peaks correspond to the protons in the alkyl chain group (1.0 and 1.39 ppm), the 3 methyl groups coupled with nitrogen (2.93 ppm), residual H2O (4.8 ppm), the vinyl group (5.17, 5.72, and 6.60 ppm), and the aromatic group (7.25 and 7.83 ppm). Since the counterion (SS) of NaSS molecules is composed of the same aromatic and vinyl groups as that (VB) of CTVB molecules, the spectrum of the unpolymerized SWNT/CTVB/NaSS mixture is very similar to that of unpolymerized SWNT/CTVB mixture. The 1H-NMR spectrum of the polymerized SWNT/CTVB/NaSS (p-SWNT25) is shown in Fig. S1b. It should be noted the peaks arising from the vinyl and aromatic groups of the polymerizable counterions (VB` and SS` ions) almost completely disappear upon polymerization. This disappearance of peaks is due to the reduced mobility of VB` and SS` ions upon their polymerization and hence shortened T2-relaxtion time. This clearly indicates that almost all of VB` and SS` ions are polymerized, forming stable p-SWNT25.
Fig. S1 $^1$H-NMR spectra of a) unpolymerized SWNT/CTVB/NaSS and b) $p$-SWNT25 in D$_2$O.
UV-vis-NIR spectra of $p$-SWNT25 after and before freeze drying

The UV-vis-NIR spectra of the $p$-SWNT25 dispersion in water showed a sharp van Hove transition, which is typical for individually isolated SWNT in solution\textsuperscript{2-7} (Fig. S2). The freeze-dried $p$-SWNT25 was easily re-dispersible in water with mild vortexing for a few minutes without forming any visible aggregates. The UV-vis-NIR spectrum of $p$-SWNT25 dispersion as prepared and that of re-dispersed $p$-SWNT25 after freeze drying were essentially identical (Fig. S2), indicating the excellent re-dispersibility of $p$-SWNT25.

**Fig. S2** UV-vis-NIR spectra of $p$-SWNT25 before and after freeze drying. The spectrum of the re-dispersed $p$-SWNT25 is shifted vertically for visual clarity.
Determination of the isoelectric points of $p$-SWNT25-CL complexes

The zeta potentials of $p$-SWNT25-cationic liposome (CL) complexes ($\Phi_{DOPE} = 0.33, 0.5, 0.67, 0.75, 0.8$, and $0.85$) for various CL/$p$-SWNT25 mass ratios (L/S) were measured. As the L/S mass ratio increases, the zeta potential changes its sign from negative to positive, from which the isoelectric points of $p$-SWNT25-CL complexes are determined, as indicated by blue dotted lines in Fig. S3. The dynamic light scattering measurements of the $p$-SWNT25-CL complexes show that they form large aggregates at the isoelectric points (Fig. S4).

![Graphs showing zeta potentials at various L/S mass ratios](image)

**Fig. S3** Zeta potentials of $p$-SWNT25-CL complexes at various L/S mass ratios. $\Phi_{DOPE} = a) 0.33, b) 0.5, c) 0.67, d) 0.75, e) 0.8$, and f) 0.85.
Fig. S4 Hydrodynamic diameters of p-SWNT25-CL complexes at various L/S mass ratios. 

$\Phi_{\text{DOPE}} = $ a) 0.33, b) 0.5, c) 0.67, d) 0.75, e) 0.8, and f) 0.85.
**Structure of p-SWNT25**

The structure of p-SWNT25 was confirmed by atomic force microscopy (AFM) measurements as shown in Fig. S5. The diameter distribution of bare SWNTs (which are obtained by burning the p-SWNT25 for 4 hr at 330 °C to remove CTVB/NaSS layer absorbed on SWNT) is peaked at (1 ± 0.1) nm, and diameters less than 2 nm occupy 90% of the distribution, which indicates that p-SWNT25s are dispersed in an isolated form or in a very small bundle (Fig. S5a). The diameter distribution of p-SWNT25s is peaked at (5 ± 0.1) nm, and 87% of the distribution is in the range of 4.4–5.6 nm (Fig. S5b). The polymerized surfactant shell thickness of the p-SWNT25s, which is determined from the diameter distributions of bare SWNT (ca. 1 nm) and p-SWNT25 (ca. 5 nm), is about 2 nm. The length distribution of the p-SWNT25 is peaked at (500 ± 50) nm with a mean length of ca. 500 nm (Fig. S5c). This result is consistent with the AFM result of p-SWNTs¹ (functionalized SWNTs fabricated in the exactly same procedure as p-SWNT25, except that NaSS was not added.).
Fig. S5 The diameter distributions of a) the bare SWNTs and b) p-SWNT25s. c) The length distribution of p-SWNT25s. The insets are AFM images (1 µm x 1 µm) and sectional analyses of a) bare SWNTs and b) p-SWNT25s.
Reference


