Surfactant-Stabilized Single-Walled Carbon Nanotubes Using Triphenylene Derivatives Remain Individually Dispersion in Both Liquid and Dried Solid States

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Abstract

An easy and simple preparation method for individually dispersed single-walled carbon nanotubes (SWNTs) in both liquid and dried solid states was developed using triphenylene derivatives. Furthermore, highly concentrated solution of SWNTs (0.7-0.8 %) was successfully prepared, and also the SWNTs were dispersed well after the addition of methanol (up to 70 %) for a long time. These properties (redispersion ability and dispersion to organic solvent) were not observed in typical dispersing surfactants, such as sodium dodecylbenzensulfonate and sodium cholate. These unique features of the surfactant-stabilized SWNTs promised to be highly useful for practical applications of SWNTs.

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Single-walled carbon nanotubes (SWNTs) are regarded as one of the ultimate nanomaterials owing to their extraordinary strength and unique electrical properties (metallic and semiconductive).[1] These properties are sensitive to the surrounding environment of SWNTs and they cause a big influence on the performance of the application formats of SWNTs, such as nanocomposites, nanoscale electronics, and nanoscale optics.[2,3] To utilize these excellent properties of SWNTs, a mild and nondestructive dispersion method for SWNTs individually and stably into solutions is indispensable. Untill now good dispersants: such as surfactants, polyaromatic hydrocarbons, bio(macro)molecules, and polymers, have been reported by many researchers.[4-8] Most of the dispersants have alkyl chain or aromatic groups that show strong affinity for SWNTs. These functional groups are thought to be adsorbed onto the surface of SWNTs by hydrophobic or π-π interactions, and stabilize the complex of the dispersant and SWNTs in aqueous solutions. The dispersion, however, is a laborious work and dispersed SWNTs are prone to re-bundle gradually with progress of time by their strong van der Waals forces.[7] Therefore, at present SWNTs must be dispersed in solution just prior to use. If SWNTs remained isolated in both the liquid and the dried solid states, and the redispersion was easy, the above-mentioned problems could be solved. Furthermore, such isolation of SWNTs would permit their use in new applications: such as solid–solid reactions and kneading processes.[9, 10] We previously reported an efficient dispersion technique for SWNTs that yields individually dispersed HiPco SWNTs by dispersion with a new surfactant, C10 （2,3,6,7,10,11-hexakis(10-carboxydecyloxy)triphenylene）, which is an amphiphilic compound with a π-conjugated triphenylene skeleton having six undecanoic acid groups (Fig. 1).[11] Herein, we report an easy method using C10 to prepare individually dispersed SWNTs in liquid (water or a mixture of water and methanol) and solid states. The observed properties of the resulting dispersions are unique and different from those of dispersions prepared with conventional surfactants.

SWNTs were dispersed in water with C10 under mild conditions with a bath sonicator and were then freeze-dried. White fibrous structures were obtained after the freeze-drying process, but these fibers could be redispersed by simply adding water and shaking the dispersion; no sonication or vortexing was required for the redispersion. Although the preparation of the initial SWNT dispersion with C10 was laborious work, the redispersion was very easy, indicating that the dispersibility of the SWNTs was changed by the formation of the complex with C10. For the evaluation of the dispersed state of SWNTs (individually dispersed or bundling), we measured the visible–near-infrared (Vis–NIR) spectrum. The spectrum of SWNTs is affected easily by a surrounding environments: such as bundle forming or removal of water by drying.[12, 13] Therefore, we compared the spectrum of the dispersed solution before and afetr drying, because the redispersed procedure was simple (just mixing) and it was expected that the process did not change the dispersed state of SWNTs (Fig. 2). In general, strong van der Waals interactions between SWNTs cause them to bundle when they are dried, and these bundled SWNTs are difficult to redisperse into isolated SWNTs. The spectra of the solution dispersed with C10 exhibited almost no difference after redispersion. Our results show that SWNTs complexed with C10 did not form bundled structures upon drying and instead remained isolated during the drying and redispersion processes. In contrast, the absorption spectra of SWNT solutions prepared with sodium cholate [SC, Fig. 2(b)] and sodium dodecylbenzenesulfonate [SDBS, Fig. 2(c)], which are typical dispersing surfactants for SWNTs, differed markedly upon drying and redispersion of the SWNTs. In particular, a large red shift and decreased absorption around 1120 nm were observed for the solution with SDBS. These results show that the SWNTs in these surfactants probably rebundled during drying. Thus, these results indicated that C10 is a promising surfactant for maintaining an individually dispersed state of SWNTs regardless of drying and that the resulting SWNT complex appeared stable. Therefore, SWNTs dispersed with C10 might be dried and stored without forming bundles and thus changing the SWNTs' properties. Notably, the volume and weight of SWNTs dispersed in C10 were very small after drying, and the SWNTs could be redispersed in water just before use. These features are considered to be highly convenient for the handling and storage of SWNT samples.

Since the dispersions of SWNTs prepared with C10 remained isolated throughout the drying process, we expected that even higher concentrations of SWNT could be prepared, by drying and redispersing SWNTs into smaller volumes of solution, and that these higher concentrations of SWNTs would not affect the SWNTs' properties. Figure 2d depicts the absorption spectra of a 10-times concentrated SWNT sample. Interestingly, no significant change was observed between before and after concentration solutions. Higher concentration solutions of SWNTs were prepared by drying and subsequently redispersing the SWNTs, and a concentration of 0.7-0.8 wt% SWNTs in water was obtained. Although the solution was black and opaque, the solution was not viscous and was easy to handle. The concentration of the obtained solution was very high, considering that the maximum concentrations of SWNTs prepared with other reported surfactants are about 2 wt%.[14] For SWNTs dispersed with C10, the concentration could be easily adjusted by simply adjusting the volume of water used to redisperse dried SWNTs.

Furthermore, we investigated the effect of added methanol on the dispersed state of SWNTs. The absorption spectra of the original aqueous solution (0% methanol) and of solutions containing 50 and 70 vol% methanol are shown in Fig. 3(a). Notably, the strong absorption at 1120 nm was observed without any noticeable peak shift for the dispersed solution with C10, even when the proportion of methanol reached 70 vol%. This result clearly demonstrates that C10 formed a very stable complex. In contrast, when 50% methanol was added to dispersed solutions with SC and SDBS, the SWNTs precipitated from solution, and the peaks characteristic of isolated SWNTs almost completely disappeared [Figs. 3(b) and 3(c)]. These results indicate that the interaction between these surfactants and the SWNTs were weaker than the interactions between the SWNTs and C10, and that the SWNT–surfactant complex collapsed as a result of the addition of the methanol, causing SWNT precipitation.

We hypothesized that C10 formed a complex with SWNTs by means of two coordinated interactions: 1) π–π interaction between the SWNT surface and triphenylene skelton, and this kind of interaction between the SWNT surface and polyaromatic group was also indicated by other manuscripts[7,15,16] and 2) hydrophobic interaction between the SWNT surface and the alkyl chain of the surfactants, which coil around the SWNT as shown in Fig. 4. To test this hypothesis, we newly synthesized two surfactants with different alkyl chain lengths (C6 and C8, Fig. 1), and we dispersed SWNTs in water with these surfactants. The photoluminescence (PL) maps of the resulting dispersed solutions were measured to identify the chiral index distribution of the SWNTs. Although the chiral index distribution of each dispersions were similar [Fig. 5(a)], the intensity ratios of each PL showed small difference. Figure 5(b) shows the ratio of (9,4) / (7,6) for SWNTs dispersed in D_2O with C6, C8, and C10. In the solution with C10, the ratio of thick SWNTs [(9,4); diameter: 0.92 nm] was higher than that of thin SWNTs [(7,6); diameter: 0.90 nm]. For C8, the ratios of these two types of SWNTs were almost the same. However, for C6, which has the shortest alkyl chain among the tested surfactants, the ratios were inverted: the PL intensity of (7,6) was greater than that of (9,4). Thus, the larger diameter SWNTs apparently were better dispersed with C10, which has a longer alkyl chain, and the smaller diameter SWNTs were better dispersed with C6, which has a shorter alkyl chain. Remarkably, this diameter selectivity was observed for a difference in alkyl chain length of only two carbon atoms, implying that the chain length of the surfactant is important for the diameter selectivity of dispersed SWNTs.

Some dispersants form micelle which improved the dispersion ability of SWNTs by taking the SWNTs into the inside of the micelle. The micelle was supontaneously formed more than a certain concentrarion, which was called as critical micelle concentration (cmc). The cmc of C10 was 0.4 mM from spectroscopy and current analyses. [17] Then, to confirm whether C10 formed the micelle, we prepared the dispersion of SWNTs using 0.14 mM C10, which was lower than cmc. The clear PL map of dispersions of SWNTs was obtained after ultracentrifugation, even if the concentration of C10 was lower than cmc [Fig. 5(c)]. Therefore, it was expected that the formation of micelle was not required for the making a complex with SWNTs in case of C10. From these results, we speculate that the C6, C8, and C10 surfactants and the SWNTs formed a complex by the two coordinated interactions described above [Fig. 4(a)].

In this report, we found promising and interesting properties of the triphenylene-based surfactant C10. These properties have not been reported by other researchers. SWNTs that were dispersed in D_2O or D_2O/methanol solutions by means of C10 remained isolated, regardless of drying or addition of methanol. We consider these novel properties of C10 to be highly useful for practical applications of SWNTs.

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Legends

Fig. 1 Chemical structure of the triphenylene derivatives.

Fig. 2 Vis–NIR spectra of SWNTs dispersed in D_2O with (a) C10, (b) SC, and (c) SDBS before (black lines) and after (red lines) drying and subsequent redispersion in D_2O. (d) Vis–NIR spectra of SWNTs dispersed in D_2O before (black line) and after (red line) concentration. The concentrated solution was measured in a 1/10 optical path length cell (1 mm).

Fig. 3 Vis–NIR spectra of SWNTs dispersed in D_2Ocontaining 0, 50, or 70% methanol, as noted in the figure labels. The surfactants used were (a) C10, (b) SC, and (c) SDBS. The spectra for SC and SDBS dispersions in 50% methanol are shown at 2x magnification for clarity.

Fig. 4 A proposed complex between a SWNT and a C10 molecule.

Fig. 5 (a) The PL map of dispersions of SWNTs with 1.4 mM C10 (higher concentration than cmc). (b) The PL intensity ratio of (9,4) / (7,6) for SWNTs dispersed in D_2O with C6, C8, and C10 surfactants. (c) The PL map of dispersions of SWNTs with 0.14 mM C10 (lower concentration than cmc).

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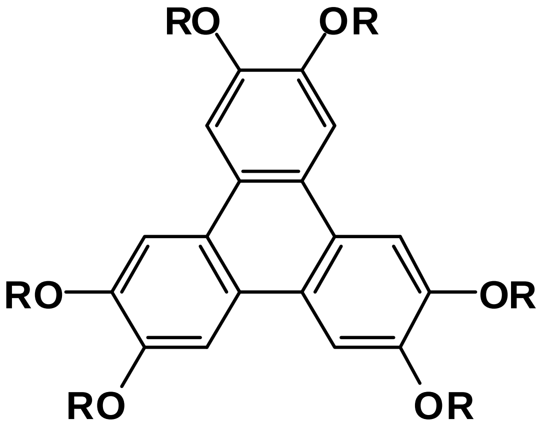
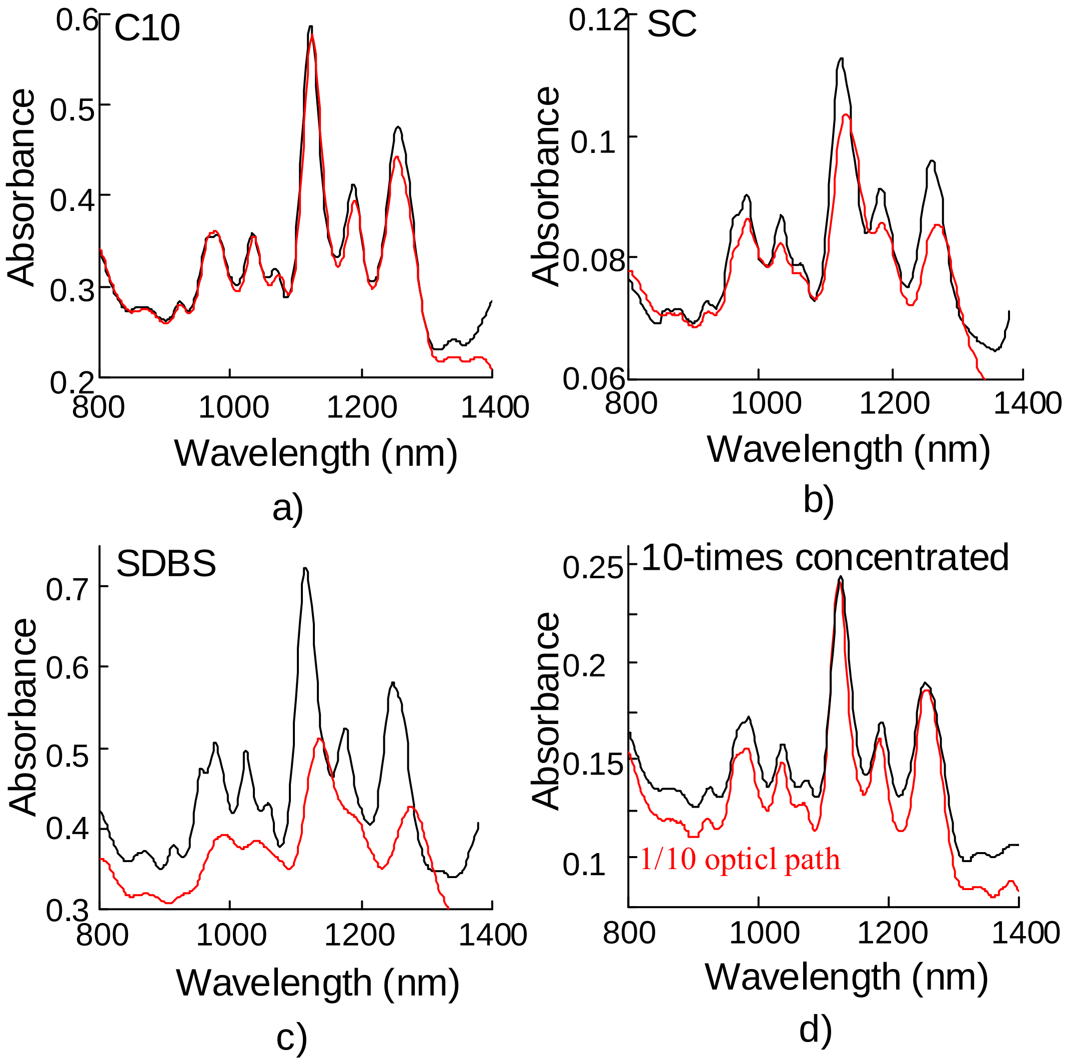


C6: R = $(CH_2)_6CO_2H$

C8: R = $(CH_2)_8CO_2H$

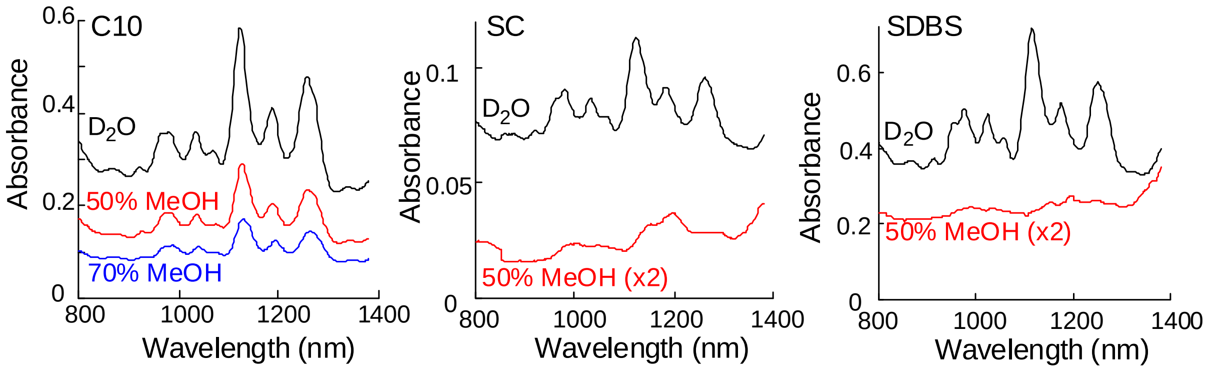
C10: R = $(CH_2)_{10}CO_2H$

Fig. 1


C10
Absorbance
0.6
0.5
0.4
0.3
0.2
800
1000
1200
1400
Wavelength (nm)
SC
0.12
0.1
0.08
0.06
SDBS
0.7
0.6
0.5
0.4
0.3
10-times concentrated
0.25
0.2
0.15
0.1
1/10 opticl path

a) b) c) d)

Fig. 2


C10
SC
SDBS
Absorbance
Wavelength (nm)
D$_2$O
50% MeOH
70% MeOH
50% MeOH (x2)
0
0.2
0.4
0.6
0.05
0.1
800
1000
1200
1400

a) b) c)

Fig. 3

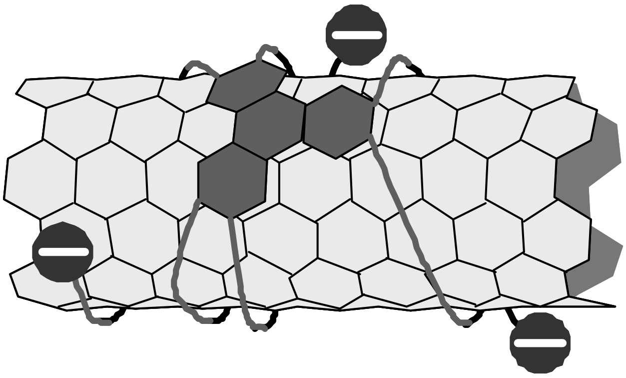
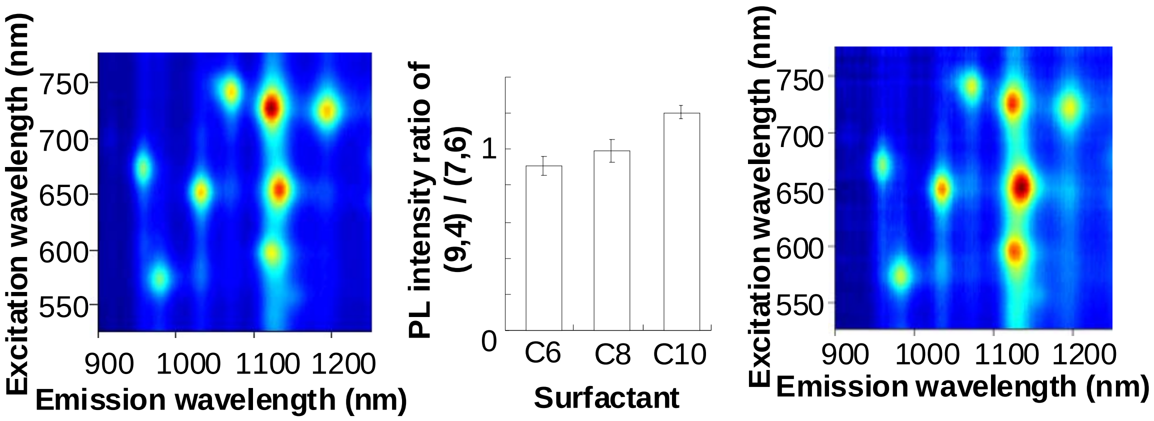


Fig. 4


Excitation wavelength (nm)
750
700
650
600
550
900
1000
1100
1200
Emission wavelength (nm)
PL intensity ratio of (9,4) / (7,6)
1
0
C6
C8
C10
Surfactant
Excitation wavelength (nm)
750
700
650
600
550
900
1000
1100
1200
Emission wavelength (nm)

a) **b)** **c)**

Fig. 5