Defection-selective solubilization and chemically-responsive solubility switching of single-walled carbon nanotubes with cucurbit[7]uril

doi: 10.1039/b801546e

Defection-Selective Solubilization and Chemically-Responsive Solubility Switching of Single-Walled Carbon Nanotubes with Cucurbit[7]uril

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***Receipt/Acceptance Data* [DO NOT ALTER/DELETE THIS TEXT]**
***Publication data* [DO NOT ALTER/DELETE THIS TEXT]**
DOI: 10.1039/b000000x [DO NOT ALTER/DELETE THIS TEXT]

Single-walled carbon nanotubes (SWCNTs) were suspended in aqueous media with cucurbit[7]uril (CB7), while SWCNTs were insoluble with cucurbit[5]uril (CB5). Moreover, defection-selective solubilization of SWCNTs with CB7 was demonstrated.

Single-walled carbon nanotubes (SWCNTs) are one-dimensional nanomaterials with unusual properties and potential applications.[1] Especially, for the application of SWCNTs in biology and material science, the preparation of water-soluble SWCNTs has been attractive research target. Solubilization of SWCNTs in aqueous media using amphiphilic polymers[2], DNA[3], peptides[4] and surfactants[5] has been reported. Solubility switching of SWCNTs in response to environmental triggers, such as pH change[6], ions[7], chemicals[8] and light[9], is also intriguing and important for the applications of SWCNT-based sensors, because electrical and optical properties of SWCNTs are extremely sensitive to the dispersion state of SWCNTs. Moreover, solubilization of SWCNTs aimed toward their purification in terms of diameters and defections is technologically important, since there have so far been no methods for selective preparation of SWCNTs with narrow distribution diameters and no defections.

Our current interest is preparation of water-soluble SWCNTs using macrocyclic host molecules.[8,10,11] Because host compounds form host-guest complexes with various guests, host molecules around SWCNT are able to capture guest molecules on SWCNT surface and solubilize the SWCNT simultaneously. Herein, we report on solubilization of SWCNTs in aqueous media by using hosts of cucurbit[n]urils (CBs) as solubilizing agent. Since CBs captured various guests into their cavity[12] and preferably formed 2:1 host-guest complex with C60[13], in the present research, we investigated solubilization of SWCNTs with CBs. CBs [n= 5 (**CB5**) and 7 (**CB7**)] were employed as solubilizing agent of SWCNTs (Fig. 1(A)). Interestingly, by using CBs as solubilizing agent, solubility of SWCNTs in aqueous media clearly depended on cavity size of CBs, addition of guests and salts. Moreover, CBs showed defection-selective solubilization of SWCNTs.

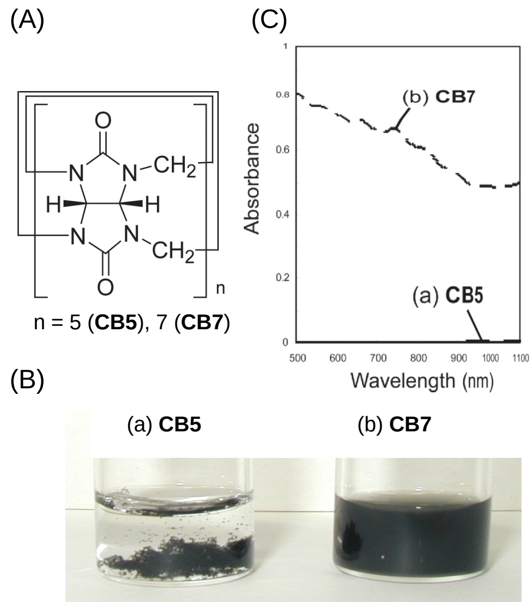

Fig. 1 (A) Chemical structure of cucurbiturils. (B) Photos of Hipco SWCNTs in aqueous media with (a) **CB5** and (b) **CB7** after sonication. (C) UV-Vis spectra of aqueous supernatants (5 mL) containing Hipco SWCNTs (1 mg) with (a) **CB5** (solid line) and (b) **CB7** (dash line) after sonication.

We purchased Hipco SWCNTs from Carbon nanotechnologies, Inc., Texas, USA. The Hipco SWCNTs were purified according to previous paper described.[14] We used **CB5** and **CB7** as solubilizing agent because of high solubility of **CB5** and **CB7** in water (water-solubility is about 20-30 mM). To suspension of Hipco SWCNTs (1.0 mg) in aqueous solution (5.0 mL), solubilizer (20 mg) was added and the resulting solution was sonicated for 3 h at room temperature. In case of **CB7**, during the sonication, the aqueous solution changed from colorless to black, indicating solubilization of Hipco SWCNTs with **CB7** (Fig. 1(B)(b)). After the sonication, insoluble Hipco SWCNTs (ca. 0.80 mg) were removed by centrifugation (12500 g).The supernatant using **CB7** was homogeneous black solution and extremely stable for more than a month. In contrast, in the presence of **CB5**, Hipco SWCNTs were insoluble even after sonication

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† Electronic Supplementary Information (ESI) available: Experimental section, UV-Vis spectra of soluble Hipco SWCNTs with the increasing of **CB7** concentration, UV-Vis spectra of Hipco SWCNTs suspended in **CB7** and **SDBS**, photo and UV-Vis spectra of **CB7/Hipco SWCNT hybrids** upon addition of $AdNH_2$, ^1H NMR spectra of the supernatant after addition of $AdNH_2$, UV-Vis spectra of the supernatants of CoMoCAT and CarboLex SWCNTs with **CB7**, and Raman spectra of pristine Hipco SWCNTs and SWCNT-COOH.

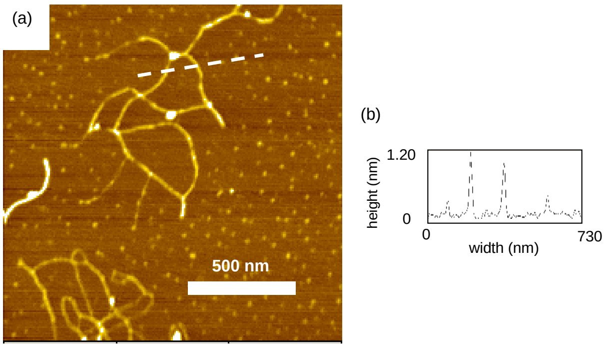

Fig. 2 (a) Tapping mode atomic force microscopic image of **CB7/Hipco SWCNT hybrids**. (b) Height profile along dash line in (a).

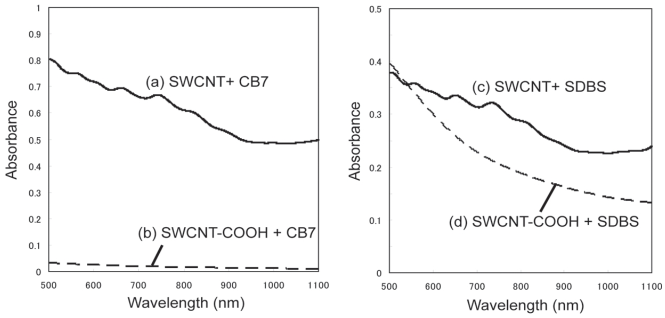

Fig. 3 UV-Vis spectra of the supernatants of (a) pristine Hipco SWCNTs with **CB7** (solid line), (b) SWCNT-COOH with **CB7** (dash line), (c) pristine Hipco SWCNTs with **SDBS** (solid line) and (d) SWCNT-COOH with **SDBS** (dash line) after sonication.

(Fig. 1(B)(a)). Fig. 1(C) shows UV-Vis spectra of the supernatants after centrifugation. In the region of 500 – 900 nm, typical Hipco SWCNT van Hove singularities were observed in the presence of **CB7** (Fig. 1(C)(b)), while no absorption bands were found in the presence of **CB5** (Fig. 1(C)(a)). From these data, Hipco SWCNTs were soluble in aqueous solution with **CB7** and insoluble with **CB5**. Solubilization ability of **CB7** was compared to that of conventional solubilizer of sodium dodecylbenzenesulfonate (**SDBS**).[5] Solubility of Hipco SWCNTs with **CB7** was higher than that with **SDBS** (ESI). Solubility of Hipco SWCNTs with **CB7** (4 mg mL^{-1}) was 3.42 x 10^{-2} mg mL^{-1}. We examined effect of the concentration of **CB7** on solubility of Hipco SWCNTs in aqueous media. As the concentration of **CB7** increased, solubility of Hipco SWCNTs also increased (ESI).

From tapping mode atomic force microscopic (TM-AFM) image of Hipco SWCNTs solubilized by **CB7** (**CB7/Hipco SWCNT hybrids**), nanotubes were observed (Fig. 2(a)) and average size of the tubes was about 1.1 - 1.2 nm (Fig. 2(b)). Since the average diameter of Hipco SWCNT is 0.8 - 1.2 nm[15], the nanotube observed is individual SWCNT.

Solubilization of Hipco SWCNTs with host-guest complex was carried out. 1-Adamantanamine ($AdNH_2$) was used as guest. With the mixture of **CB7** and $AdNH_2$, Hipco SWCNTs were insoluble in aqueous solution. When $AdNH_2$ was added to **CB7/Hipco SWCNT hybrids**, aggregation of Hipco SWCNTs was observed (ESI). These observations indicate that Hipco SWCNTs were insoluble by formation of host-guest complex with $AdNH_2$.[16] Furthermore, upon addition of aqueous NaCl or hydrochloric acid solution, precipitation of Hipco SWCNTs was also observed. Because urea groups of **CB7** bind cations *via* ion-dipole interaction[12], **CB7** binds sodium cation and proton as guest. From these data, it was found that complex between **CB7** and Hipco SWCNT was dissociated by formation of **CB7**-guest complexes. The binding of **CB7** with Hipco SWCNT is weaker than that of **CB7**-guest complexes.

From these observations, we examine nanostructure of **CB7/Hipco SWCNT hybrids**. Since Hipco SWCNTs were insoluble with **CB5** and soluble with **CB7**, cavity size of CBs should effect on solubility of Hipco SWCNTs in aqueous solution. Moreover, by adding guests such as $AdNH_2$ and cation, aggregation of Hipco SWCNTs was observed, also indicating that cavity of **CB7** should act as an important role for solubilization of Hipco SWCNTs. However, considering that the portal size of **CB7** cavity is about 0.54 nm[12] and the outer diameter of Hipco SWCNT is about 1.0 nm[15], cavity of **CB7** is too small to form *pseudo*-rotaxane structure between Hipco SWCNT as axle and **CB7** as ring. By using CoMoCAT SWCNTs[17] (average diameter = 0.8 nm) and CarboLex SWCNTs (average diameter = 1.3 nm) instead of Hipco SWCNTs, CoMoCAT and CarboLex SWCNTs were water-soluble with **CB7** (ESI). The data indicate that solubilization of SWCNTs with **CB7** is independent of diameter of SWCNTs. Thus, SWCNTs are not solubilized by forming *pseudo*-rotaxane structure. The other possible solubilization mechanism should be adsorption of **CB7** on SWCNT surface. Amphiphilic urea groups of **CB7** might be adsorbed to SWCNT surface. Generally, amphiphilic polymers such as poly(*N*-vinyl-2-pyrrolidone) and poly(ethylene glycol) are able to solubilize SWCNTs in aqueous media by wrapping.[2] Moreover, for the nonionic surfactants such as Triton X-405, poly(*N*-vinyl-2-pyrrolidone) and poly(ethylene glycol), surfactants with high molecular weight were able to suspend more SWCNTs.[5] Therefore, in the same way as amphiphilic polymers, **CB7** might be easily adsorbed to SWCNT surface compared to **CB5**. The same trends were also observed in solubilization of SWCNTs with water-soluble amphiphilic calixarenes.[10]

By using **CB7** as solubilizing agent, solubilization of Hipco SWCNTs with defection sites on graphitic surface and at ends was examined. By treating with boiling diluted 2 M nitric acid for 24 h, acid cut SWCNT (SWCNT-COOH) was obtained.[18] SWCNT-COOH was insoluble in aqueous solution by using **CB7** as solubilizer, while pristine nondefective Hipco SWCNTs were soluble with **CB7**. In contrast, by using **SDBS**, both Hipco SWCNTs and SWCNT-COOH were soluble in aqueous media. UV-Vis spectra of these supernatants are shown in Fig. 3. The absorption of SWCNT-COOH was not observed in the supernatant of SWCNT-COOH with **CB7** (Fig. 3(b)), while typical Hipco van Hove singularities were observed in Hipco SWCNTs with **CB7** (Fig. 3(a)). In the supernatant containing SWCNT-COOH suspended with **SDBS**, absorption band in the region of 500 - 1100 nm was observed (Fig. 3(d)), indicating solubilization of SWCNT-COOH with **SDBS**. The absorption displayed a loss of features compared to typical Hipco SWCNT van Hove singularities (Fig. 3(c)), suggesting a disruption in the electron structure due to oxidation of Hipco SWCNTs.[19] From these observations, by using **CB7** as a solubilizer, Hipco SWCNTs were water-soluble but defected SWCNT-COOH was insoluble in water. Since typical surfactant of **SDBS** solubilizes both Hipco SWCNTs and defected SWCNT-COOH and solubility of SWCNTs generally increases with increasing number of oxidation sites on SWCNT[18], **CB7** is able to selectively solubilize nondefective SWCNTs. Formation of host-guest complex between **CB7** and proton of carboxylic acid from SWCNT-COOH should result in the defection-selective insolubilization of SWCNTs.

In conclusion, by using **CB7**, water-soluble SWCNTs were successfully prepared. To the best of our knowledge, it is the first example of solubilization of SWCNTs with CBs. **CB7** wrapped SWCNT and solubility of SWCNTs clearly changed by adding guests. Moreover, **CB7** was able to selectively solubilize nondefective SWCNTs in aqueous media. There are few examples of defection-selective solubilization of SWCNTs, while diameter selective solubilization of SWCNTs has been reported.[20] Since oxidation damages of nanotubes lose valuable material property, selective ablation of defective SWCNTs is technologically important. Thus, **CB7** will be used not only for solubilizer of SWCNTs but also for purification of defected SWCNTs.

We thank Prof. Kohshin Takahashi (Kanazawa University) for TM-AFM measurements and Dr. Tomokazu Umeyama (Kyoto University) for many useful discussions. This work was supported by the Kinki Invention Center and a Grant-in-Aid for Young Scientists (WAKATE B-1975011) from the ministry of Education, Culture, Sports, Science and Technology, Japan.

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