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

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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 an 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 defects is technologically important, since there have so far been no methods for the selective preparation of SWCNTs with narrow distribution diameters and no defects.

Our current interest is the 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 SWCNTs are able to capture guest molecules on the SWCNT surface and solubilize the SWCNT simultaneously. Herein, we report on solubilization of SWCNTs in aqueous media by using cucurbit[*n*]uril (CB) hosts as solubilizing agents. Since CBs capture various guests into their cavity[12] and preferably form 2 : 1 host–guest complexes with C_{60},[13] in the present research, we investigated solubilization of SWCNTs with CBs. CBs [*n* = 5 (**CB5**) and 7 (**CB7**)] were employed as solubilizing agents of SWCNTs (Fig. 1(A)). Interestingly, by using CBs as solubilizing agents, the solubility of SWCNTs in aqueous media clearly depended on the cavity size of the CBs, and addition of guests and salts. Moreover, CBs showed defect-selective solubilization of SWCNTs.

We purchased Hipco SWCNTs from Carbon nanotechnologies, Inc., TX, USA. The Hipco SWCNTs were purified according to our previous paper.[14] We used **CB5** and **CB7** as solubilizing agents because of the high solubility of **CB5** and **CB7** in water (*ca.* 20–30 mM). To a 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 the 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 (12 500 g). The supernatant using **CB7** was a 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 (Fig. 1(B)(a)). Fig. 1(C) shows UV-Vis spectra of the supernatants after centrifugation. In the region of 500–900 nm,

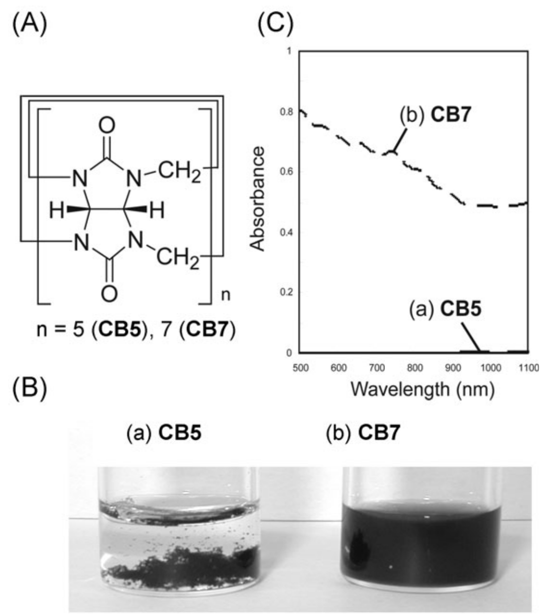

Fig. 1 (A) Chemical structure of cucurbiturils. (B) Photos of Hipco SWCNTs in aqueous media with (a) **CB5** and (b) **CB7** after sonication. (C) UV-Vis spectra of aqueous supernatants (5 mL) containing Hipco SWCNTs (1 mg) with (a) **CB5** (solid line) and (b) **CB7** (dashed line) after sonication.

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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. See DOI: 10.1039/b801546e

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**. The solubilization ability of **CB7** was compared to that of conventional solubilizer of sodium dodecyl benzenesulfonate (**SDBS**).[5] The solubility of Hipco SWCNTs with **CB7** (4 mg mL^{-1}) was 3.42×10^{-2} mg mL^{-1} and was higher than that with **SDBS** (ESI†). We examined the effect of the concentration of **CB7** on solubility of Hipco SWCNTs in aqueous media. As the concentration of **CB7** increased, the solubility of Hipco SWCNTs also increased (ESI†).

From a 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 the average size of these was about 1.1–1.2 nm (Fig. 2(b)). Since the average diameter of Hipco SWCNTs is 0.8–1.2 nm,[15] the observed nanotubes are individual SWCNTs.

Solubilization of Hipco SWCNTs with host–guest complexes 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 and 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 on formation of host–guest complexes with $AdNH_2$.[16] Furthermore, upon addition of aqueous NaCl or hydrochloric acid solution, precipitation of Hipco SWCNTs was also observed. Because the urea groups of **CB7** bind cations *via* ion–dipole interactions,[12] **CB7** binds sodium cations and protons as guests. From these data, it was found that the 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 can examine the nanostructure of **CB7/Hipco SWCNT** hybrids. Since Hipco SWCNTs were insoluble with **CB5** and soluble with **CB7**, the cavity size of CBs should affect the solubility of Hipco SWCNTs in aqueous solution. Moreover, by adding guests such as $AdNH_2$ and cations, aggregation of Hipco SWCNTs was observed, also indicating that the 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] the cavity of **CB7** is too small to form a 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 the diameter of SWCNTs. Thus, SWCNTs are not solubilized by forming pseudo-rotaxane structures. The other possible solubilization mechanism should be adsorption of **CB7** on the SWCNT surface and amphiphilic urea groups of **CB7** might be adsorbed to the 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 nonionic surfactants such as Triton X-405, poly(*N*-vinyl-2-pyrrolidone) and poly(ethylene glycol), surfactants with high molecular weight were able to solubilize more SWCNTs.[5] Therefore, in the same way as amphiphilic polymers, **CB7** might be more easily adsorbed to SWCNT surfaces 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 defect sites on graphitic surface and at ends was examined. By treating with boiling diluted 2 M nitric acid for 24 h, acid cut SWCNTs (SWCNT-COOH) were 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 bands 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 electronic

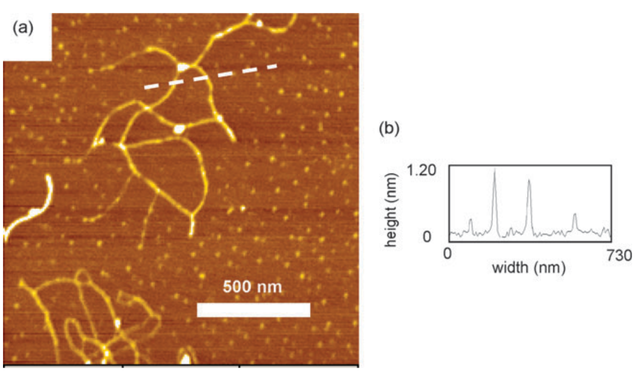

Fig. 2 (a) Tapping mode atomic force microscopic image of **CB7/Hipco SWCNT** hybrids. (b) Height profile along the dash lined in (a).

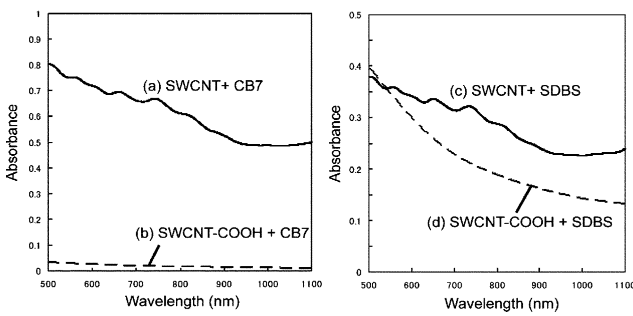

Fig. 3 UV-Vis spectra of the supernatants of (a) pristine Hipco SWCNTs with **CB7** (solid line), (b) SWCNT-COOH with **CB7** (dashed line), (c) pristine Hipco SWCNTs with **SDBS** (solid line) and (d) SWCNT-COOH with **SDBS** (dashed line) after sonication.

structure due to oxidation of Hipco SWCNTs.[19] From these observations, by using **CB7** as a solubilizer, Hipco SWCNTs were water-soluble but defective SWCNT-COOH was insoluble in water. Since typical surfactants for **SDBS** solubilizes both Hipco SWCNTs and defective 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 complexes between **CB7** and the proton of carboxylic acid from SWCNT-COOH should result in the defect-selective nonsolubilization of SWCNTs.

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

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Notes and references

1 D. Tasis, N. Tagmatarchis, A. Bianco and M. Prato, *Chem. Rev.*, 2006, **106**, 1105; N. R. Baughman, A. A. Zakhidov and W. A. de Heer, *Science*, 2002, **297**, 787; J. Chen, M. A. Hamon, H. Hu, Y. S. Chen, A. M. Rao, P. C. Eklund and R. C. Haddon, *Science*, 1998, **282**, 95; J. Liu, A. G. Rinzler, H. J. Dai, J. H. Hafner, R. K. Bradley, P. J. Boul, A. Lu, T. Iverson, K. Shelimov, C. B. Huffman, F. Rodriguez-Macias, Y. S. Shon, T. R. Lee, D. T. Colbert and R. E. Smalley, *Science*, 1998, **280**, 1253; V. Zorbas, A. O. Acevedo, A. B. Daltonm, M. M. Yoshida, G. R. Dieckmann, R. K. Draper, R. H. Baughman, M. J. Yacaman and I. H. Musselman, *J. Am. Chem. Soc.*, 2004, **126**, 7222; N. Nakashima, Y. Tomonari, H. Murakami and K. Yoshinaga, *Chem. Lett.*, 2002, **31**, 638.

2 M. J. O'Connell, P. Boul, L. M. Ericson, C. Huffman, Y. H. Wang, E. Haroz, C. Kuper, J. M. Tour, K. D. Ausman and R. E. Smalley, *Chem. Phys. Lett.*, 2002, **364**, 303; C. Park, Z. Ounaies, K. A. Watson, R. E. Crooks, J. Smith, Jr, S. E. Lowther, J. W. Connell, E. J. Siochi, J. S. Harrison and T. L. St. Chair, *Chem. Phys. Lett.*, 2002, **364**, 303.

3 G. R. Dieckmann, A. B. Dalton, P. A. Johnson, J. Razal, J. Chen, G. M. Giordano, E. Muñoz, I. H. Musselman, R. H. Baughman and R. K. Draper, *J. Am. Chem. Soc.*, 2003, **125**, 1770.

4 A. Ishibashi, Y. Yamaguchi, H. Murakami and N. Nakashima, *Chem. Phys. Lett.*, 2006, **419**, 574.

5 V. C. Moore, M. S. Strano, E. H. Haroz, R. H. Hauge, R. E. Smalley, J. Schmidt and Y. Talmon, *Nano Lett.*, 2003, **3**, 1379.

6 J. C. Grunlan, L. Liu and Y. S. Kim, *Nano Lett.*, 2006, **6**, 911; W. Zhao, C. Song and P. E. Pehrsson, *J. Am. Chem. Soc.*, 2002, **124**, 12418.

7 B. Yu, F. Zhou, G. Liu, Y. Liang, W. T. S. Huck and W. Liu, *Chem. Commun.*, 2006, 2356.

8 T. Ogoshi, Y. Takashima, H. Yamaguchi and A. Harada, *J. Am. Chem. Soc.*, 2007, **129**, 4878.

9 K. Narimitsu, J. Nishioka, H. Murakami and N. Nakashima, *Chem. Lett.*, 2006, **35**, 892.

10 T. Ogoshi, T. Yamagishi and Y. Nakamoto, *Chem. Commun.*, 2007, 4776.

11 T. Ogoshi, T. Yamagishi, Y. Nakamoto and A. Harada, *Chem. Lett.*, 2007, **36**, 1026.

12 J. W. Lee, S. Samal, N. Selvapalam, H. J. Kim and K. Kim, *Acc. Chem. Res.*, 2003, **36**, 621; J. Lagona, P. Mukhopadhyay, S. Chakrabarti and L. Isaacs, *Angew. Chem., Int. Ed.*, 2005, **44**, 4844.

13 F. Constabel and K. E. Geckeler, *Tetrahedron Lett.*, 2004, **45**, 2071.

14 W. Zhou, Y. H. Ooi, R. Russo, P. Papanek, D. E. Luzzi, J. E. Fischer, M. J. Bronikowski, P. A. Willis and R. E. Smalley, *Chem. Phys. Lett.*, 2001, **350**, 6.

15 P. Nikolaev, M. Bronikowski, R. Bradley, F. Rohmund, D. Colbert, K. Smith and R. E. Smalley, *Chem. Phys. Lett.*, 1999, **313**, 91.

16 Formation of the host–guest complex between **CB7** and $AdNH_2$ was checked by ^1H NMR measurements (ESI†).

17 S. M. Bachilo, L. Balzano, J. E. Herrera, F. Pompeo, D. E. Resasco and R. B. Weisman, *J. Am. Chem. Soc.*, 2003, **125**, 11186.

18 M. N. Tchoul, W. T. Ford, G. Lolli, D. E. Resasco and S. Arepalli, *Chem. Mater.*, 2007, **19**, 5765.

19 The defective nature of SWCNT-COOH was checked by Raman measurements (ESI†).

20 S. Banerjee, T. H. Benny and S. S. Wong, *J. Nanosci. Nanotechnol.*, 2005, **5**, 841; S. Banerjee and S. S. Wong, *J. Am. Chem. Soc.*, 2004, **126**, 2073; Z. B. Zhang and S. L. Zhang, *J. Am. Chem. Soc.*, 2007, **129**, 666.