# Supramolecular single-walled carbon nanotubes (SWCNTs) network polymer made by hybrids of SWCNTs and water-soluble calix[8]arenes†

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**We report on hybrids of water-soluble calix[8]arenes and single-walled carbon nanotubes (SWCNTs); the hybrids formed supramolecular SWCNTs network polymer by adding guest dimer.**

Single-walled carbon nanotubes (SWCNTs) have held the promise of nanoscale electronics and machines owing to their unique structural, electrical and mechanical properties.[1] However, their applications have been extremely limited due to their low solubility in solvents. Therefore, solubilization of SWCNTs has been one of hot topics for the past few years. For solubilization of SWCNTs in solvents, chemical modification of SWCNTs[2] and physical adsorption of organic molecules on SWCNT surfaces[3] are useful methods.

Calixarenes, macrocyclic compounds, composed of benzene units, have been of potential interest because they form host–guest complexes with various guest molecules.[4] Especially, calix[8]arenes were found to bind fullerene strongly and were applied for purification of fullerene.[5] Moreover, water-soluble calix[8]arenes were synthesized and able to capture fullerene into their hydrophobic cavities in aqueous media.[6]

In this communication, we first report on solubilization of SWCNTs by using calixarenes. Water-soluble *p*-sulfonatocalix[*n*]arenes [**CXs**: $n = 4$ (**CX4**), $n = 6$ (**CX6**) and $n = 8$ (**CX8**)] and *p*-phenolsulfonic acid, a constituent unit of **CXs**, were used as solubilizers of SWCNTs (Fig. 1(A)). Interestingly, SWCNTs were soluble in aqueous media in the presence of **CX6** and **CX8**, while SWCNTs were insoluble in the presence of *p*-phenolsulfonic acid and **CX4**.

We purchased SWCNTs produced by the method of high-pressure decomposition of carbon monoxide (HiPco Process) from Carbon nanotechnologies, Inc., Texas, USA. The HiPco SWCNTs were purified according to a previous paper.[7] We applied *p*-phenolsulfonic acid, **CX4**, **CX6** and **CX8** as a solubilizing agent. To a suspension of SWCNTs (1.0 mg) in aqueous solution (5 mL), solubilizer (0.0269 mmol) was added. The solution was sonicated for 3 h at room temperature. By using **CX6** or **CX8** as a solubilizer, the aqueous solution changed from colorless to black during the sonication, indicating solubilization of the SWCNTs in aqueous solution. After the sonication, insoluble SWCNTs were removed by centrifugation. By using **CX6** or **CX8**, the supernatant was a homogeneous black solution (Fig. 1(B)(b) and (B)(c)). The supernatant using **CX6** was not stable and a black precipitation appeared after one week while the supernatant using **CX8** was extremely stable for more than a month. In contrast, in the presence of *p*-phenolsulfonic acid or **CX4**, SWCNTs were insoluble (Fig. 1B(a)). Fig. 1(C) shows UV-Vis spectra of the supernatants after centrifugation. Characteristic absorptions were observed around 400–1100 nm in the supernatants with **CX6** and **CX8**. Since no absorptions were observed in the region in cases of **CXs** solubilizer (**CX4**, **CX6** and **CX8**), the absorptions were typical HiPco SWCNT van Hove singularities,[8,9] which were attributable to metallic transitions (M11) in the 500–600 nm region, and semiconducting transitions in the 600–900 nm (S22) and 1000–1100 nm (S11) regions, respectively. The absorption from SWCNTs was not observed in the supernatant of SWCNTs with **CX4**. These data indicate that solubility of SWCNTs in aqueous media with water-soluble calixarenes increases in the approximate order: **CX4** and *p*-phenolsulfonic acid (insoluble) $\ll$ **CX6** $<$ **CX8**. We checked the ability of **CX8** for solubilization of SWCNTs compared to that of typical surfactants (ESI†). Compared to sodium dodecylbenzene sulfonate (**SDBS**) and **Triton X-405** (typical ionic and nonionic surfactants for solubilization of SWCNTs),[8] **CX8** gave the best solubility of SWCNTs. The solubility of SWCNTs using **CX8** was $2.34 \times 10^{-2}$ mg mL$^{-1}$.

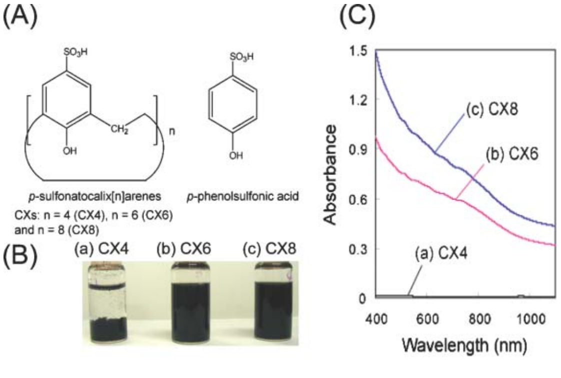

**Fig. 1** (A) Chemical structure of *p*-sulfonatocalix[*n*]arenes [**CXs**: $n = 4$ (**CX4**), $n = 6$ (**CX6**) and $n = 8$ (**CX8**)] and *p*-phenolsulfonic acid. (B) Photos of SWCNTs in aqueous media with (a) **CX4**, (b) **CX6** and (c) **CX8**, after sonication. (C) UV-Vis spectra of aqueous supernatants (5 mL) containing SWCNTs (1 mg) with (a) **CX4**, (b) **CX6** and (c) **CX8** (0.0269 mmol) after sonication.

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† Electronic supplementary information (ESI) available: Experimental section, UV-Vis spectra of SWCNTs suspended in **CX8**, **Triton X-405** and **SDBS**, UV-Vis spectra of **CX8/SWCNT hybrids** upon addition of salts, $^1$H NMR spectra of **CX8** and **CX8/SWCNT hybrids**, **CX8/SWCNT hybrids** with **AdPy** and size distributions of **CX8/SWCNT hybrids** by adding **AdPy** and **Guest Dimer**. See DOI: 10.1039/b711800g

From tapping mode atomic force microscopy (TM-AFM), SWCNTs solubilized by **CX8** (**CX8/SWCNT hybrids**) were observed and the average size of the nanotubes was about 1.0 nm (Fig. 2(a)). Since the average diameter of the HiPco SWCNTs is 1.0–1.2 nm,[10] the nanotubes observed were individual SWCNTs. Nanotubes on the carbon grid were also found by transmission electron microscopy (TEM) (Fig. 2(b)).

To investigate the nanostructure of **CX8/SWCNT hybrids**, we used a guest molecule, 1-adamantane trimethylammonium iodide (**AdTriMe**), which forms a strong complex with **CX8**.[11] SWCNTs were soluble in aqueous solution even with the mixture of **AdTriMe** and **CX8**. Fig. 3 shows $^1$H NMR spectra of **AdTriMe**, a mixture of **AdTriMe** and **CX8**, and **CX8/SWCNT hybrids** with **AdTriMe** in $D_2O$. With **CX8** (Fig. 3(B)), the resonance bands due to methyl, methylene and methine protons of **AdTriMe** exhibited downfield shifts, indicating formation of a host–guest complex between **CX8** and **AdTriMe**. The same resonance bands were found at the same chemical shifts in **CX8/SWCNT hybrids** with **AdTriMe** (Fig. 3(C)). The results indicate that **CX8** forms a complex with **AdTriMe** even in the presence of SWCNTs. Therefore, it was found that the cavity of **CX8** in **CX8/SWCNT hybrids** was vacant.

Upon addition of KCl to **CX8/SWCNT hybrids** in aqueous solution (150 eq. relative to **CX8**), a black suspension was observed. By centrifugation of the solution, a black precipitate formed. In the resulting supernatant, no typical SWCNTs absorptions were observed (ESI†), indicating aggregation of SWCNTs by adding KCl salt. The 'salting out' observation indicates that SWCNTs are dispersed by electrostatic repulsive forces. Furthermore, the black precipitate could be completely dissolved again in aqueous media (ESI†), suggesting that **CX8** molecules strongly interacted with SWCNTs.

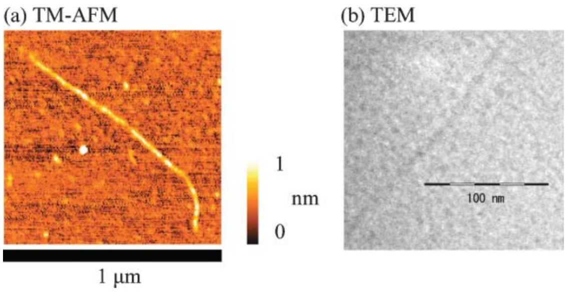


**Fig. 2** (a) TM-AFM and (b) TEM images of water-soluble **CX8/SWCNT hybrids**.

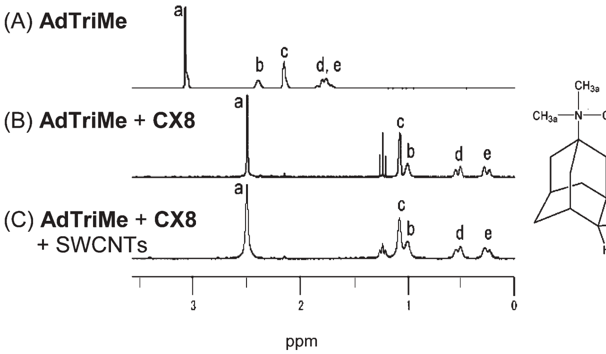
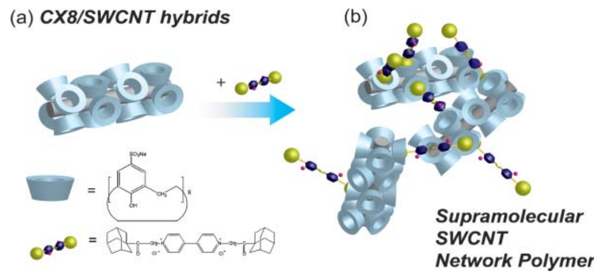


**Fig. 3** 270 MHz $^1$H NMR spectra of (A) **AdTriMe** (2.66 mM), (B) **AdTriMe** (2.66 mM) with **CX8** (2.66 mM) and (C) a supernatant containing SWCNTs solubilized by **CX8** (2.66 mM) with **AdTriMe** (2.66 mM) in $D_2O$ at 25 °C.

From these observations, we can examine the nanostructure of **CX8/SWCNT hybrids**. Since SWCNTs were insoluble with **CX4** and soluble with **CX6** and **CX8**, the cavity size of **CXs** should affect the solubility of SWCNTs in aqueous solution. However, SWCNTs were also soluble even with **AdTriMe**, which formed a complex with **CX8**. Considering that the cavity size of **CX8** is about 0.8 nm[4] and the outer diameter of HiPco SWCNT is about 1.2 nm,[10] the inner cavity of **CX8** is too small to form a pseudo-rotaxane structure between SWCNT as axle and **CX8** as ring. Therefore, SWCNTs are not solubilized by forming pseudo-rotaxane structures. The other solubilization mechanism should be adsorption of CX8 on the SWCNT surface. As illustrated in Scheme 1(a), hydrophobic segments of benzene rings and methylene groups of **CX8** might be adsorbed to the SWCNT surface. The hydrophilic parts of sulfonate anions of **CX8** prevent SWCNTs from undergoing aggregation in aqueous solution. With any type of calixarenes, increasing the macrocycle size usually leads to an increase in conformational flexibility.[4] The conformation of **CX8** is so flexible that the hydrophobic segments of the benzene ring and methylene bridges of **CX8** might be easily adsorbed to the SWCNT surface compared to that of **CX4**. In the $^1$H NMR spectrum of **CX8** (ESI†), proton resonances derived from the methylene bridges and phenyl groups were observed as singlets at 4.10 and 7.55 ppm, respectively. The observation indicates that macrocycle quickly exchanges between several conformations on the NMR time scale. In the $^1$H NMR spectrum of **CX8/SWNCT hybrids**, these proton resonances were also the same. Therefore, conformational exchange was fast on the NMR timescale even with SWCNTs.

To the vacant cavity of **CX8** on SWCNT, guest molecules were added. When **Guest Dimer** (0.5 eq. to **CX8**, 1.33 mM) was added to **CX8/SWCNT hybrids** in aqueous media, black suspensions were found in the solution.[12] The colloidal size of **CX8/SWCNT hybrids** was 505 nm. The size changed to 1864 nm by adding **Guest Dimer** (ESI†). On centrifugation of the solution a black precipitate was formed. In contrast, no change was observed upon addition of 1-adamantane carbomethylpyridinium bromide (**AdPy**, 1 eq. to **CX8**, 2.66 mM).[12] The colloidal size of the **CX8/SWCNT hybrids** exhibited no changes upon addition of **AdPy** (ESI†). Fig. 4 shows UV-Vis spectra of these supernatants. The absorption due to SWCNTs decreased with **Guest Dimer**, while spectral changes were



**Scheme 1** (a) Proposed structure of **CX8/SWCNT hybrids** and (b) supramolecular SWCNTs network polymer made from **CX8/SWCNT hybrids** and **Guest Dimer**.

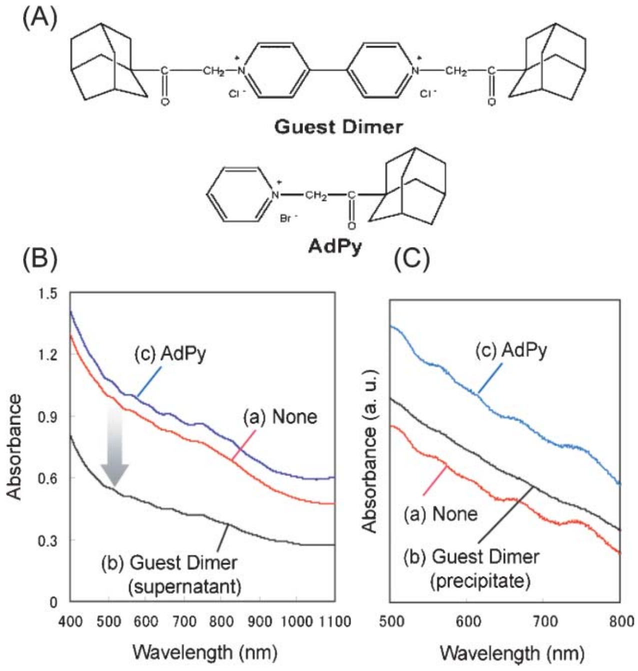


**Fig. 4** (A) Chemical structure of **Guest Dimer** and **AdPy**. (B) UV-Vis spectra of (a) **CX8/SWCNT hybrids**, the supernatant with (b) **AdPy** and (c) **Guest Dimer**. (C) SWCNTs van Hove singularities of (a) **CX8/SWCNT hybrids**, (b) **CX8/SWCNT hybrids** with **AdPy** and (c) the precipitate of **CX8/SWCNT hybrids** with **Guest Dimer**, which was suspended again in water.

not observed with **AdPy**. The data indicate that the black precipitate formed by centrifugation was SWCNTs. Furthermore, in the precipitate of **CX8/SWCNT hybrids** with **Guest Dimer** suspended again in water, the intensity of SWCNT van Hove singularities weakened compared with that of **CX8/SWCNT hybrids** and **CX8/SWCNT hybrids** with **AdPy**, indicating that SWCNTs in the precipitate formed large bundles.[9] From these data, it was found that **CX8/SWCNT hybrids** formed supramolecular SWCNTs network polymer by adding **Guest Dimer** (Scheme 1(b)).

In conclusion, water-soluble calixarene-functionalized SWCNTs have been prepared. Calixarenes wrapped the SWCNTs and their electrostatic repulsion forces inhibited aggregation of the SWCNTs in aqueous solution. To the best of our knowledge, this is the first example of solubilization of SWCNTs with calixarenes. The cavity of the calixarene on binding to SWCNTs was vacant and able to capture guest molecules. Formation of SWCNTs network polymer occurred upon addition of **Guest Dimer**, while no change was observed by adding **AdPy**. There are few examples of supramolecular network polymers composed of SWCNTs, while supramolecular network polymers based on host–guest chemistry have been reported.[13] Detailed nanostructure, electrical and mechanical properties of supramolecular SWCNTs network polymers are now under investigation.

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