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Carbon Nanotubes

Reversible Solubilization and Precipitation of Carbon Nanotubes through Oxidation–Reduction Reactions of a Solubilizing Agent**

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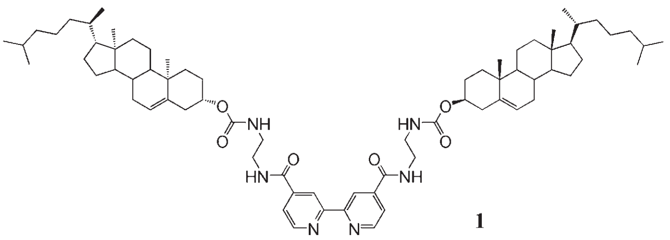
Single-walled carbon nanotubes (SWNTs) have been of great interest to research scientists over the past decade because of their unique structural, mechanical, and electrical properties.[1,2] To exploit these unique properties, a supramolecular approach has been used to dissolve SWNTs in aqueous and organic solvents by using solubilizing agents.[3–14] This approach has the advantage of noncovalent modification of the SWNTs while incurring little damage. The use of large planar π systems as solubilizing agents are expected to result in the SWNTs becoming highly soluble. We have already reported that the planar supramolecular complexes formed between barbituric acid and triaminopyrimidine derivatives, through generation of a hydrogen-bonding network, act as good solubilizing agents.[15] If a planar metal complex was used as the solubilizing agent, we expect the metal complex to solubilize SWNTs. Furthermore, a change from a planar to a nonplanar structure by reduction of the central metal atoms might precipitate the SWNTs because of the disappearance of π–π stacking interactions between the π-conjugated planar molecule and the SWNT surfaces. Therefore, we chose a Cu^{II} complex in which the ligand (**1**) is a 2,2′-bipyridine derivative bearing two cholesteryl groups. The Cu complex shows a reversible sol-gel phase transition on changing the redox state of the Cu^I/Cu^{II} complexes by chemical oxidation and reduction.[16] We report herein that the solubilization and precipitation of CoMoCAT SWNTs,[13,14] which have a uniquely narrow distribution of (n,m) and small diameter (< 1 nm), can be controlled reversibly by changing the redox state of the Cu^I/Cu^{II} complexes by chemical oxidation and reduction.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We have already reported the greater solubilization and debundling of purified and pristine SWNTs through the formation of complexes with a solubilizing agent by using a mechanochemical high-speed vibration milling (HSVM) technique.[15,17–19] The preparation of a solution of $[Cu^{II}(\mathbf{1})_2]$-SWNT in chloroform by the HSVM method is described in detail in the Experimental Section. We introduced two cholesteryl moieties into **1** to form $[Cu(\mathbf{1})_2]$ complexes that had excellent solubility in organic solvents.

Figure 1 shows photographs of a solution of a $[Cu^{II}(\mathbf{1})_2]$-SWNT mixture in chloroform and the precipitate of $[Cu^I(\mathbf{1})_2]$-SWNT prepared by addition of ascorbic acid (AsA) to the mixture. The photograph of a solution obtained by bubbling air into the $[Cu^I(\mathbf{1})_2]$-SWNT mixture was identical to that of the initial solution of the $[Cu^{II}(\mathbf{1})_2]$-SWNT mixture. Furthermore, Vis-NIR absorption spectroscopic measurements showed the presence of SWNTs in chloroform (Figure 2). The mixed solubilizing agent consisting of $\mathbf{1}/Cu(OTf)_2$ at a ratio of 2:1, namely $[Cu^{II}(\mathbf{1})_2]$ (0.33 mM), resulted in a moderately high solubility of the SWNTs (Figure 1a and 2c). In contrast, the SWNTs were not appreciably solubilized in the presence of **1** (0.67 mM) only (Figure 2a). The greatly different solubilities of the SWNTs in the presence of **1** and $[Cu^{II}(\mathbf{1})_2]$ are attributed to the different face-to-face π–π stacking abilities of the two π systems. To obtain additional information on the π–π interaction and the stoichiometry of

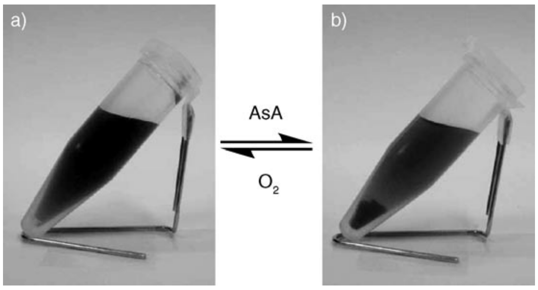

Figure 1. Photographs of chloroform solutions of the: a) $[Cu^{II}(\mathbf{1})_2]$-SWNTs mixture and b) $[Cu^{I}(\mathbf{1})_2]$-SWNTs mixture prepared from the $[Cu^{II}(\mathbf{1})_2]$-SWNTs mixture by the addition of ascorbic acid (AsA).

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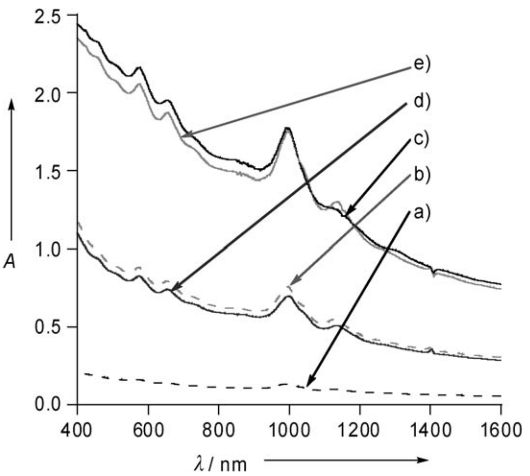
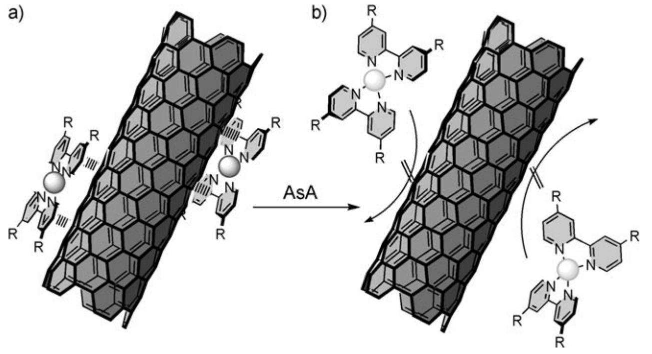


Figure 2. Vis-NIR absorption spectra of SWNTs in chloroform after HSVM in the presence of: a) **1**, b) $[\mathrm{Cu^{II}}(\mathbf{1})_2]$ ($[\mathrm{Cu^{II}}]/[\mathbf{1}]=1{:}4$), c) $[\mathrm{Cu^{II}}(\mathbf{1})_2]$ ($[\mathrm{Cu^{II}}]/[\mathbf{1}]=1{:}2$), d) $[\mathrm{Cu^{II}}(\mathbf{1})_2]$ + AsA, and e) $[\mathrm{Cu^{II}}(\mathbf{1})_2]$ + AsA + bubbling air at 25 °C ($[\mathbf{1}]=0.67$ mM, 1 cm cell).



Scheme 1. Schematic illustration of a) the presence of the π–π stacking interaction between $[\mathrm{Cu^{II}}(\mathbf{1})_2]$ and the SWNTs and b) the absence of the π–π stacking interaction between $[\mathrm{Cu^{I}}(\mathbf{1})_2]$ and the SWNTs.

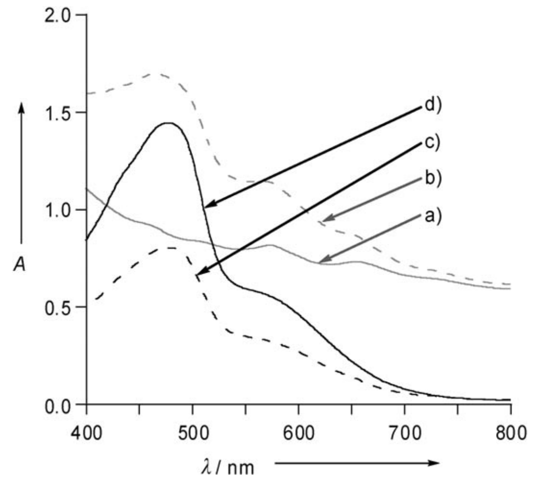


Figure 3. UV/Vis absorption spectra of: a) $[\mathrm{Cu^{II}}(\mathbf{1})_2]$ + SWNTs, b) $[\mathrm{Cu^{II}}(\mathbf{1})_2]$ + SWNTs + AsA, c) difference spectrum between (b) and (a), and d) $[\mathrm{Cu^{II}}(\mathbf{1})_2]$ + AsA at 25 °C ($[\mathbf{1}]=0.67$ mM, 1 cm cell).

the $[\mathrm{Cu^{II}}(\mathbf{1})_2]$-SWNT complex, thermogravimetric analysis (TGA) was performed. A black product was separated from the free $[\mathrm{Cu^{II}}(\mathbf{1})_2]$ complex by filtration through a polytetrafluoroethylene filter of 0.10 μm pore size and dried under vacuum, then subjected to TGA under a nitrogen atmosphere. As shown in Figure S1 in the Supporting Information, the weight loss from the $[\mathrm{Cu^{II}}(\mathbf{1})_2]$-SWNT mixture was 44 % at 500 °C, whereas the weight loss from the $[\mathrm{Cu^{II}}(\mathbf{1})_2]$ complex and the SWNTs under the same experimental conditions were approximately 81 and 4 %, respectively. Consequently, from extrapolation, the amount of $[\mathrm{Cu^{II}}(\mathbf{1})_2]$ complex in the $[\mathrm{Cu^{II}}(\mathbf{1})_2]$-SWNT mixture is about 53 wt %, which indicates there were π–π stacking interactions between the $[\mathrm{Cu^{II}}(\mathbf{1})_2]$ complexes and the SWNT surfaces at a $[\mathrm{Cu^{II}}(\mathbf{1})_2]$/SWNT ratio of about 1:1 (wt/wt). Furthermore, when the **1**/$\mathrm{Cu(OTf)_2}$ solubilizing agent was used at a ratio of 4:1, the SWNTs had a far lower solubility (Figure 2 b), thus indicating the importance of the formation of a 1:2 $[\mathrm{Cu^{II}}(\mathbf{1})_2]$ complex. A solution of the $[\mathrm{Cu^{II}}(\mathbf{1})_2]$-SWNT mixture mixed with **1**/$\mathrm{Cu(OTf)_2}$ at a ratio of 2:1 was stable for one week, while the solutions of the **1**-SWNT mixture and the $[\mathrm{Cu^{II}}(\mathbf{1})_2]$-SWNT mixture mixed with **1**/$\mathrm{Cu(OTf)_2}$ at a ratio of 4:1 were not stable (see Figure S2 in the Supporting Information). On the other hand, when the solution of AsA (3 equiv of $[\mathrm{Cu^{II}}(\mathbf{1})_2]$) in methanol (7.5 μL, 422 mM) was added to the solution of the $[\mathrm{Cu^{II}}(\mathbf{1})_2]$-SWNT mixture in chloroform (3 mL), to obtain the $[\mathrm{Cu^{I}}(\mathbf{1})_2]$ complex by reduction of the $\mathrm{Cu^{II}}$ state, the mixing immediately resulted in the precipitation of the SWNTs from the chloroform solution (Figures 1 b and 2 d). We confirmed that the $[\mathrm{Cu^{II}}(\mathbf{1})_2]$-SWNT mixture did not precipitate on addition of methanol (7.5 μL). These results indicate that the conformational change from the planar structure of the $[\mathrm{Cu^{II}}(\mathbf{1})_2]$ complex to the tetrahedral structure of the $[\mathrm{Cu^{I}}(\mathbf{1})_2]$ complex makes the formation of the π–π stacking interactions between the $[\mathrm{Cu^{I}}(\mathbf{1})_2]$ complexes and the SWNT surface impossible (Scheme 1). However, from the absorbance band at 800 nm, 37 % of the SWNTs remained in solution (Figure 2 c,d). Figure 3 shows the UV/Vis absorption spectra of the $[\mathrm{Cu^{I}}(\mathbf{1})_2]$ complex in the absence and presence of SWNTs after the addition of AsA. From the absorbance at 478 nm, the concentration of the $[\mathrm{Cu^{I}}(\mathbf{1})_2]$ complex in the presence of SWNTs was estimated to be 56 % of that in the absence of SWNTs (Figure 3 c,d). Presumably the lower concentration of the $[\mathrm{Cu^{I}}(\mathbf{1})_2]$ complex in the presence of the SWNTs arises because: 1) a conformational change from the $[\mathrm{Cu^{II}}(\mathbf{1})_2]$ complex to the $[\mathrm{Cu^{I}}(\mathbf{1})_2]$ complex was inhibited by the interaction with the SWNT surface, or 2) a rapid electron transfer from the $[\mathrm{Cu^{I}}(\mathbf{1})_2]$ complex to the SWNTs resulted in oxidation to yield the $[\mathrm{Cu^{II}}(\mathbf{1})_2]$ complex on the SWNT surface. Moreover, bubbling air through the solution for 20 minutes resulted in the precipitate completely redissolving on sonication (ultrasonic bath: 135 W, 42 kHz, 10 min), thus indicating that the $[\mathrm{Cu^{II}}(\mathbf{1})_2]$ complex formed by oxidization of $\mathrm{Cu^{I}}$ by O_2 could again interact with the SWNT surfaces (Figure 1 a). The solubilization and precipitation of the SWNTs was repeated three more times (see Figure S3 in the Supporting Information). However, after the second addition of AsA, an excess of AsA and the oxide were precipitated with the SWNTs, although the precipitated AsA and oxide could be easily removed with methanol. Furthermore, Figure 2 c,e show that similar absorption spectra were observed for the initial and redispersion states, which indicates that the precipitated SWNTs were redissolved in a similar debundled state as present in the initial [Cu^{II}(**1**)$_2$]-SWNT complex.

The [Cu^{II}(**1**)$_2$]-SWNT mixture has pronounced absorption bands at 576 and 993 nm, which correspond to the E22 and E11 transitions of the (6,5) nanotubes, and at 654 and 1136 nm, which correspond to those of the (7,6) nanotubes.[13,14] These sharp van Hove peaks are a characteristic feature of debundled, individually dispersed SWNTs, and indicate that the [Cu^{II}(**1**)$_2$]-SWNTs mixture has a high ability to debundle SWNTs in chloroform. The characteristic absorption bands are apparent between 550 and 1200 nm, which are similar to those of the reported spectra.[12] Moreover, the Raman spectra of these samples have nearly identical sharp peaks, with a shoulder near the high frequency band of 1581 cm^{-1}. They are assigned to the tangential modes of graphite (see Figure S4 in the Supporting Information).[12] The low-frequency range between 230 and 290 cm^{-1} belongs to the radial breathing modes,[12] for which frequencies are dependent on the diameter of the tubes.

A contour plot for the sodium dodecyle sulfate (SDS) CoMoCAT SWNT mixture (see Figure S5a in the Supporting Information) shows the existence of (6,5), (7,6), and (8,3) SWNTs, in agreement with a previous report.[20] On the other hand, no band was evident in the fluorescence spectra for the [Cu^{II}(**1**)$_2$]-SWNT mixture (see Figure S5b in the Supporting Information). The result implies the fluorescence was quenched by the heavy atom effect of the Cu^{II} centers in the [Cu^{II}(**1**)$_2$] complex interacting with the SWNT surfaces.

The morphology of the SWNTs was observed by transmission electron microscopy (TEM; Figure 4). The TEM micrographs show that the [Cu^{II}(**1**)$_2$]-SWNT complex appears in both bundles with diameters in the range of 2 to 10 nm and individual tubes with a mean diameter in the range of 1 to 2 nm (Figure 4 a), thus indicating that a SWNT with a diameter of around 1–2 nm was partially debundled. Figure 4 b shows that the TEM image of the [Cu^{II}(**1**)$_2$]-SWNT complex after redispersion was similar to that in Figure 4 a, which indicates that after redispersion the SWNTs exist in a similar debundled state to that of the initial [Cu^{II}(**1**)$_2$]-SWNT complex. These results are consistent with those obtained using Vis-NIR absorption spectroscopy (Figure 2 c,e).

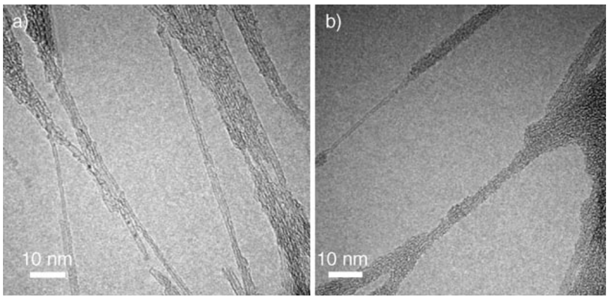


Figure 4. TEM images of the: a) [Cu^{II}(**1**)$_2$]-SWNT complex prepared by the HSVM method and b) [Cu^{II}(**1**)$_2$]-SWNT complex after redispersion.

In conclusion, we have succeeded in solubilizing SWNTs in chloroform by using a [Cu^{II}(**1**)$_2$]-SWNT mixture. However, **1** alone has only a low ability to solubilize SWNTs. These results confirm the importance of the expansion of the π-conjugated planar structure. Furthermore, the addition of a solution of AsA in methanol to the [Cu^{II}(**1**)$_2$]-SWNT mixture immediately resulted in the precipitation of the SWNTs from the chloroform solution, although the precipitate could be redissolved by bubbling air through it. Controlling the solubilization of SWNTs using the redox properties of the solubilizing agents would be useful for the purification of metallic and semiconducting SWNTs and for the electrodeposition of SWNTs on electrode surfaces.

Experimental Section

A solid mixture of **1**[21] (11.21 mg, 9.72 μmol) and Cu(OTf)$_2$ (1.76 mg, 4.87 μmol) was prepared by evaporation from a THF solution. Mixtures of pristine SWNTs (1.00 mg)[21] and the **1**/Cu(OTf)$_2$ mixture (8.89 mg) obtained above were placed in an agate capsule together with two agate mixing balls and mixed vigorously at 1800 rpm for 20 min using a high-speed vibration mill (MM200, Retsch Co. Ltd.). The solid mixtures were dissolved in chloroform (10.0 mL) through sonication (135 W, 20 min). After centrifugation (14000 rpm, 20 min, 20 °C), all nondispersed SWNTs were removed from the solutions and a solution of [Cu^{II}(**1**)$_2$]-SWNT was obtained. A solution of [Cu^{I}(**1**)$_2$]-SWNT was prepared from the [Cu^{II}(**1**)$_2$]-SWNT solution (3.0 mL) by the addition of a solution of AsA in methanol (422 mM, 7.5 μL). As a reference sample, a similar approach was used to prepare a complex of SWNTs (1.00 mg) and **1** (7.68 mg, 6.66 μmol) in chloroform.

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