Water-Soluble Single-Walled Carbon Nanotubes via Noncovalent Sidewall-Functionalization with a Pyrene-Carrying Ammonium Ion

Naotoshi Nakashima,* Yasuhiko Tomonari, and Hiroto Murakami†
Department of Materials Science, Graduate School of Science and Technology, Nagasaki University, Bunkyo, Nagasaki 852-8521
†*Institute for Fundamental Research of Organic Chemistry, Kyushu University, Fukuoka 812-8581*

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In this communication, we describe the finding that sonication of solid single-walled carbon nanotubes (p-SWNT) in an aqueous solution of a pyrene-carrying ammonium ion **1** gave a transparent dispersion/solution of the nanotubes, which was characterized by transmission electron microscopy, UV-vis absorption, fluorescence and ^{1}H NMR spectroscopies. We showed evidence for the interaction of the nanotube sidewall and the pyrene moiety in the aqueous dispersion/solution.

Since the discovery in 1991,[1] carbon nanotubes have been in the forefront of nanoscience and nanotechnology because of their many unique properties.[2] Very recently, considerable attention has focused on the preparation of soluble carbon nanotubes[3] that would find many chemical applications in fundamental and practical research fields. Shortened SWNTs have been reported to be soluble in the organic solvents by derivatization with thionyl chloride and octadecylamine.[3] Full-length SWNTs were rendered soluble in common organic solvents by ionic complexation with the terminal carboxylic acid in the SWNTs and octadecylamine.[4] Carbon nanotubes have been reported to be soluble in the aqueous micellar solution of some detergents[5] and in the aqueous solutions of poly(vinyl pyrrolidone) and poly(styrene sulfonate).[6] We describe in this paper the first preparation of sidewall-functionalized water-soluble single-walled carbon nanotubes (SWNTs). Here, a pyrene-carrying ammonium ion, trimethyl-(2-oxo-2-pyren-1-yl-ethyl)-ammonium bromide (**1**, Chart 1) was designed and synthesized as a solubilizer, since the pyrene moiety has been reported to have affinity with carbon nanotubes.[7]

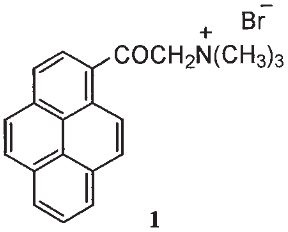

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Chart 1.

SWNTs (HiPco^{TM}),[8] length obtained from Carbon Nanotechnologies Incorporated were placed in a ceramic boat and heated in a furnace for 18 h at 225 °C in humid synthetic air, and then sonicated in concentrated HCl for 15 min. The tubes were collected by a filter (pore size, 100 nm), and then washed with sodium hydrogencarbonate. The nanotubes were collected by a filter (pore size, 100 nm), and then heated at 50 °C to obtain the purified SWNTs (p-SWNTs). The XPS measurements revealed that for the p-SWNTs, $Fe2p_{3/2}$ did not appear in the region of 706–714 eV. This is indicating that Fe from the catalyst for the synthesis of the SWNTs was almost removed by the purification procedure. The reaction of 1-(bromoacetyl)pyrene with trimethylamine in THF gave a precipitate, which was recrystallized from chloroform to give a compound **1** that was identified by ^{1}H NMR, IR and elemental analysis.[9]

The maximum solubility of **1** in water was ca. 2 mM ($1\,M = 1\,mol\,dm^{-3}$). It was found that **1** does not form a micelle in water since the surface tension of **1** on water was almost constant at 69 ± 1 mN/m for concentrations below 2 mM.

About 1 mg of the solid p-SWNTs and compound **1** was sonicated with a bath-type sonicator (Branson 2210) in water (**1** = 1 mM) for 1 h. Centrifugation of the suspension for 1 h gave a black-colored transparent supernatant aqueous dispersion/solution (Figure 1). TEM measurements for the aqueous dispersion of p-SWNTs-**1** were conducted on a Jeol JEM-100S electron microscope. A carbon-coated TEM grid (Ouken-Shoji, 200-A mesh) was immersed in the dispersion/solution for 0.5 h, followed by air-drying. In Figure 2, we demonstrate a typical TEM image, in which dispersed bundled SWNTs with molecular length of ~0.7–~3 μm are observed. It is in fact that the water solution/dispersion contains the nanotubes.

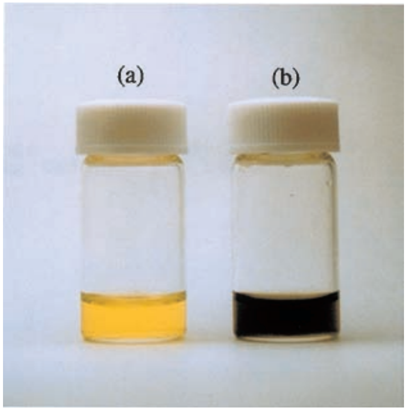

Figure 1. Aqueous solutions of (a) **1** (1.0 mM) and (b) p-SWNT-**1** (**1**, ca. 1 mM).

The UV-vis absorption and fluorescence spectra of the aqueous dispersion/solution of **1** and p-SWNT-**1** were measured. The absorption maxima of the UV-vis spectra for p-SWMT-**1** appeared at 234, 288, and 368 nm together with a shoulder at 400 nm, which were almost identical with those for **1**-soley aqueous solution.[10] The fluorescence behavior for the aqueous solutions of **1** and p-SWNT-**1** were similar.[11] As stated, the UV-vis absorption and fluorescence spectra did not give direct evidence for the interaction of the pyrene moiety with the sidewall of the nanotubes. On the contrary, we could obtain direct evidence

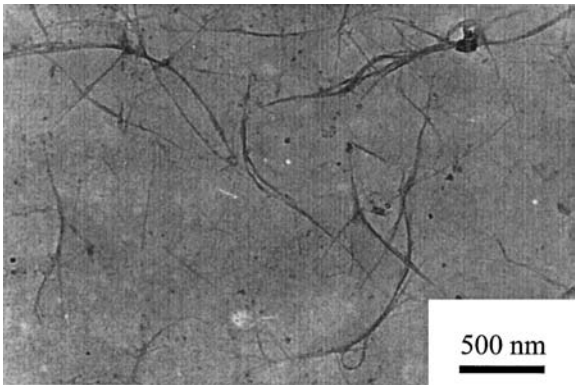

Figure 2. A typical TEM image for an aqueous solution of p-SWNTs-**1**.

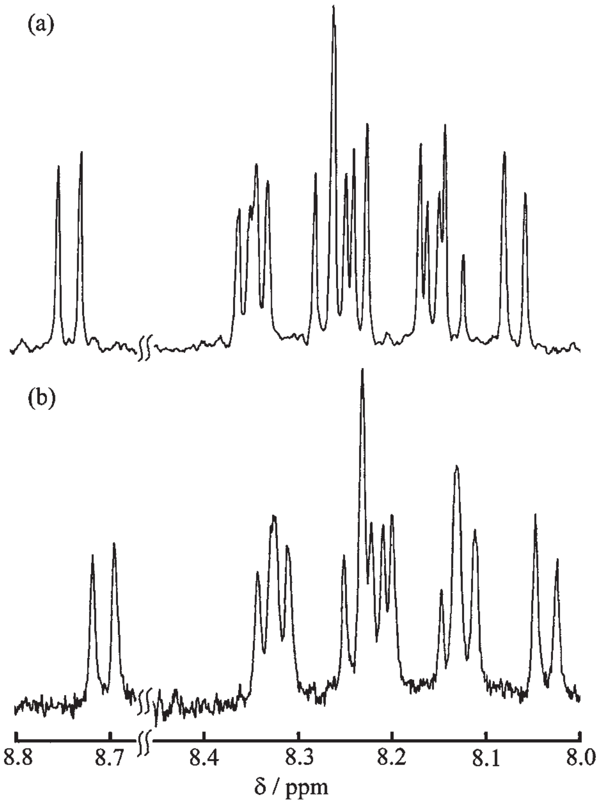

Figure 3. ^{1}H NMR spectra (400 MHz, D_2O, DSS) in the range of 8.0–8.8 ppm for aqueous solutions of (a) **1** (1.0 mM) and (b) p-SWNTs-**1** (1, ca. 1 mM).

for the interaction of the nanotube sidewall with the pyrene moiety by means of ^{1}H NMR spectral measurements. The result is shown in Figure 3.[12] The chemical shifts for the pyrene-protons in the p-SWNT-**1** solution shifted to the higher magnetic field by ca. 0.017–0.034 ppm compared to those for the **1** solution. The shift is derived from the effect of the ring current in the pyrene π-systems. This is the direct evidence showing the interaction between the nanotube sidewall and the pyrene chromophore in the aqueous dispersion/solution.

In conclusion, pyrene-functionalized water-soluble single-walled carbon nanotubes were prepared. We obtained direct interaction of the nanotube sidewall and the pyrene moiety in water. The importance of π-stacking of the pyrene moiety with the sidewall of the nanotube is suggested for the solubilization of the nanotubes in water. The carbon nanotube aqueous dispersion/solution prepared by the present method would be useful for many research fields both for fundamental and practical applications. The present study opens the door for chemical design to create functional carbon nantubes in aqueous systems.

References and Notes

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8 Length and diameter of pristine SWNTs are ~1–10 μm and ~0.8–1.2 nm, respectively. The purity of the material is about 99%.

9 Anal. Found: C, 62.16; H, 5.21; N, 3.06%. Calcd for $C_{21}H_{20}NOBr + 1.2H_2O$: C, 62.45; H, 5.59; N, 3.47%. ^{1}H NMR (300 MHz, CD_3OD, TMS); d 8.1–9.1 (m, 9H, PyH), 4.1 (s, 2H, CH_2N^+), 3.6 (s, 9H, $(CH_3)_3N^+$). IR (KBr): 3045 and 3012 cm^{-1} ($\upsilon_{C\text{–}H}$, Ar) and 1674 ($\upsilon_{C=O}$) cm^{-1}.

10 The peak maxima for the aqueous solutions of **1** and p-SWNT-**1** were almost the same in the concentration range of 5×10^{-6}–1×10^{-3} M.

11 The peak maxima of the monomer and excimer emission for the aqueous solution of p-SWNT-**1** appeared around 420–422 and 490–502 nm, respectively, which were close to those for the **1** aqueous solution.

12 The chemical shift of N-(CH_3) for a p-SWNT-**1** D_2O solution appeared at $\delta = 3.523$, which is almost identical with that for a **1** D_2O solution ($\delta = 3.519$).