

Angle-controlled arrangement of single-walled carbon nanotubes solubilised by 8-quinolinol metal chelate derivatives on mica†

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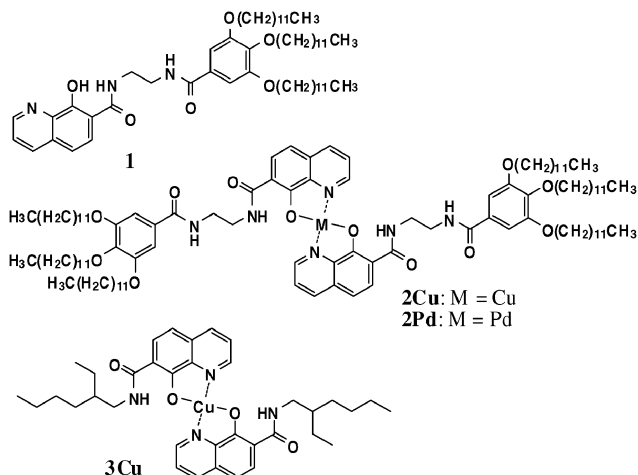
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We solubilised SWNTs of short length using a mechanochemical high-speed vibration milling (HSVM) through formation of complexes between the SWNTs and chelate complexes; the mixture formed a network structure on mica.

Single-walled carbon nanotubes (SWNTs) exhibit characteristic structural, mechanical, and electrical properties. They have been of great interest to researchers over the past decades.^{1,2} One drawback, if any, is their poor solubility. To exploit their unique properties, many researchers have attempted to dissolve SWNTs in aqueous and organic solvents using a supramolecular approach with solubilising agents^{3–5} because this approach involves noncovalent modification with little damage to SWNTs. Although larger π -systems promise high solubilising ability of SWNTs, it is difficult to extend their molecular π -systems using covalent bonds. We examined metal chelates such as 8-quinolinol-copper(II) or -palladium(II) as solubilising agents. These chelates have an extended planar structure with two quinolinols connected with the copper or palladium ion. The square planar chelate structure is known to be greatly advantageous for gel formation for appropriate solvents because of their π - π interactions.^{6,7} We expected that the chelate derivative-SWNTs mixtures might dissolve by π - π interactions between the planar molecule and SWNTs surface. On the other hand, we have already reported higher solubilisation and debundling of purified and pristine SWNTs from formation of SWNT-solubilising agent complexes using a mechanochemical high-speed vibration milling (HSVM) technique.⁸ Although SWNTs prepared using the HSVM method are not long, SWNTs in the length range 10–300 nm might provide connectors and components for molecular electronic devices. Consequently, it is very important to form highly ordered structures on substrates for preparation of such devices. We here report that chelate-SWNTs mixtures formed several different types of unique network structures.



Mixtures of pristine SWNTs (1.00 mg)^{5,9} and 1–3 (1: 6.66 μ mol and 2 and 3: 3.33 μ mol)⁹ were placed in an agate capsule together with two agate mixing balls. They were mixed vigorously at 1800 rpm for 20 min using a high-speed vibration mill (MM200; Retsch Co. Ltd.). The solid mixtures were dissolved in 10.0 mL of chloroform through sonication (40 W, 20 min). After centrifugation (14000 rpm, 20 min, 20 °C), all nondispersed SWNTs were removed from the solutions. On the other hand, dispersion by a sonication method was carried out by adding pristine SWNTs (1.00 mg), 2Cu (3.33 μ mol) and 10.0 mL of a chloroform solution to a 20 mL glass vial. The solution was sonicated using an ultrasonic bath (135 W, 42 kHz, 5510J-DTH Branson Ultrasonic Corp.) for 5 h. After centrifugation (14000 rpm, 20 min, 20 °C), all non-dispersed SWNTs were removed from the solution. Measurements using Vis-NIR absorption spectroscopy evidenced the presence of SWNTs in chloroform (Fig. 1). The 2Cu-SWNTs mixture has pronounced absorption bands at 576 and 993 nm, corresponding to the E22 and E11 transitions of the (6,5) nanotubes.⁵ Because these sharp van Hove peaks are a characteristic of debundled, individually dispersed SWNTs, these results indicate that the 2Cu-SWNTs and 2Pd-SWNTs mixtures have high ability to debundle SWNTs in chloroform. The characteristic absorption bands are apparent between 550 and 1200 nm and are fundamentally identical to those of the reported spectra.⁵ Moreover, in the Raman spectra, these samples have nearly identical sharp peaks with a shoulder near the high frequency of 1581 cm^{-1} . These peaks are assigned to the tangential modes of the graphite (Fig. S1, ESI†).¹⁰ The low-frequency

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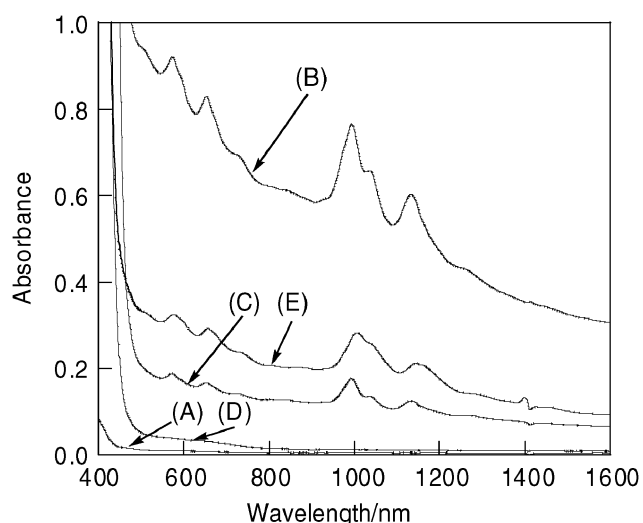


Fig. 1 Vis-NIR absorption spectra of (A) the **1**-SWNTs mixture, (B) the **2Cu**-SWNTs mixture, (C) the **2Pd**-SWNTs mixture and (D) the **3Cu**-SWNTs mixture prepared using the HSVM method; (E) the **2Cu**-SWNTs mixture prepared using the sonication method in chloroform. All spectra were measured at 25 °C.

range of 230–290 cm^{-1} corresponds to radial breathing modes,¹⁰ whose frequencies are dependent on the tube diameter. First, **1**, **2Cu**, and **2Pd** were chosen as solubilising agents to estimate the effects of the central metals of the chelates on SWNT solubility. The order of SWNTs solubility is **2Cu**-SWNTs mixture > **2Pd**-SWNTs mixture, as judged from absorbance intensity depicted in Fig. 1(B) and (C). Although the reason remains unclear, association constants of metalloporphyrins with [60]fullerenes are known to depend on the central metal ions.¹¹ In contrast, SWNTs were extracted only slightly in the experiment using **1** (Fig. 1(A): at a concentration of **1** double that of **2Cu** or **2Pd**). The great difference of solubilities of SWNTs between **1** and **2Cu** is attributable to the relative ability of the face-to-face π - π stacking of their π -systems. On the other hand, the Vis-NIR absorption spectra of the **2Cu**-SWNT mixture indicate that the solubility of SWNTs using the HSVM method is higher than that using sonication (Fig. 1(B) and (E)).

Secondly, **2Cu** and **3Cu** were chosen as solubilising agents to estimate the effects of different substituents on SWNT solubility. The solubilising ability of **2Cu**, which has long chains of 3,4,5-tris(alkoxy)phenyl substituents, was much higher than that of **3Cu** with a 2-ethylhexyl moiety (Fig. 1(B) and (D)).

Finally, we used atomic force microscopy (AFM) to investigate the structures of **2Cu**, the **2Cu**-SWNT mixture, prepared by the HSVM or sonication methods, and the **2Pd**-SWNT mixture formed after evaporation of a droplet of chloroform solutions on mica (Fig. 2 and S2, ESI†). Irrespective of the gelator,⁷ in the absence of the SWNTs **2Cu** does not arrange in any noticeable pattern (Fig. 2(A)). In contrast, linear SWNTs align 120° to one another along directions of the mica surface¹² and are mutually connected (Fig. 2(B)). The height profile (0.8–1.2 nm) of the image indicates the existence of individual, non-aggregated SWNTs (Fig. 2(C)). Fig. 3 shows the AFM images of other areas where SWNTs are condensed. In those areas, it was clarified that more and shorter SWNTs

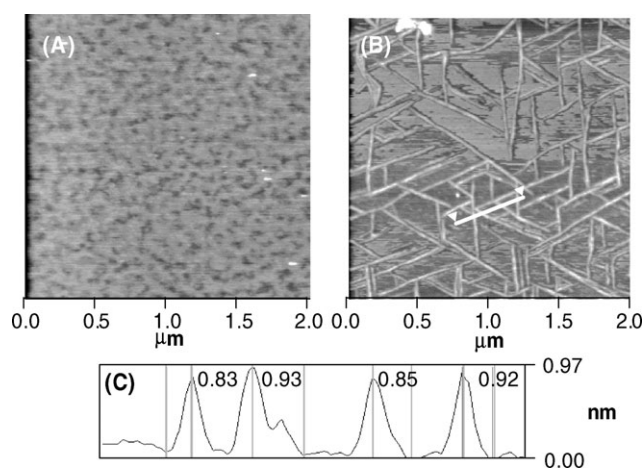


Fig. 2 Tapping mode AFM images of (A) **2Cu** and (B) the **2Cu**-SWNT mixture prepared using the HSVM method on mica. (C) The height profile of the **2Cu**-SWNT mixture is measured along the white line in (B).

align. On the other hand, in the **2Cu**-SWNT mixture prepared by the sonication method, longer SWNTs (> 1 μm) curved and did not align (Fig. S2A, ESI†). Therefore, this study, together with previous references,¹² indicates that alignment of SWNTs onto a substrate requires SWNTs shorter than 1 μm . Do SWNTs interact with a mica surface directly or with **2Cu** on mica? That is, is **2Cu** needed to align SWNTs onto mica? To address the question, we prepared a substrate in which an aqueous solution of chemical-cut SWNTs¹³ was dropped on mica previously deposited by **2Cu** using a spin-coated method. As shown in Fig. S3, because SWNTs aligned onto the film of **2Cu**, the importance of interactions between SWNTs and **2Cu** on the mica surface can be inferred; *i.e.* the SWNTs alignment occurred onto an oriented **2Cu** film on mica(001).¹⁴ This conclusion was supported by AFM examinations of other solubilising agents [*e.g.*, **2Pd** (Fig. S2B, ESI†), polythiophene and nucleotide]⁸ that did not show SWNT alignment. On the other hand, other substrates [highly oriented pyrolytic graphite (HOPG) and silicon wafer] did not show SWNTs alignment.

In summary, we solubilised SWNTs in chloroform using **2Cu**-SWNT and **2Pd**-SWNT mixtures. In contrast, **1** itself shows no ability as an SWNT solubilising agent. These results confirm the importance of the expansion of the planar

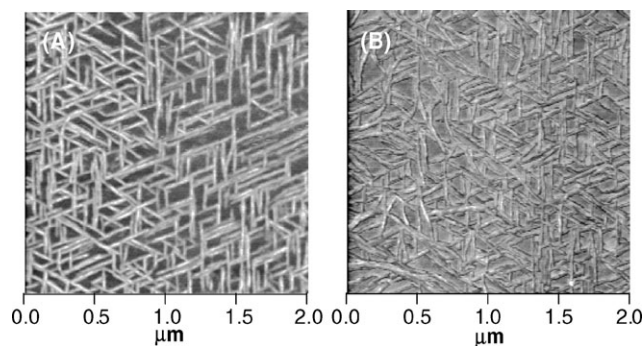


Fig. 3 Tapping mode AFM images of the **2Cu**-SWNTs mixture prepared using the HSVM method on other areas of mica in Fig. 2(B).

structure. Furthermore, SWNTs with shorter length prepared using the HSVM method formed a network structure on mica. The findings imply that the control of SWNT length can produce diverse orientation and morphology.

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