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Single-Walled Carbon Nanotubes Template the One-Dimensional Ordering of a Polythiophene Derivative

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ABSTRACT

We have used a mechanochemical high-speed vibration milling (HSVM) technique to solubilize single-walled carbon nanotubes (SWNTs) in organic solvents through the formation of complexes between the SWNTs and a polythiophene (PT) derivative. This HSVM approach is superior to the conventional sonication method used to solubilize SWNTs in organic solvents. Moreover, we found that in these supramolecular complexes the PT chains were ordered one-dimensionally on the SWNT surfaces in organic solvents.

Single-walled carbon nanotubes (SWNTs) are novel one-dimensional cylindrical nanostructures that have a number of promising applications.[1−2] Unfortunately, pristine SWNTs are insoluble in all solvents, and therefore, they are difficult to process.[3] Much research has been devoted to overcoming this problem.[4−7] For example, SWNTs have been solubilized in water through complex formation with a solubilizing agent (e.g., a cyclodextrin and nucleotide)[8] while using the mechanochemical technique of high-speed vibrational milling (HSVM).[9] This approach is superior to that of conventional sonication for preparing water-soluble SWNTs.

Because of our interest in the chemistry of fullerenes and carbon nanotubes,[8,10] we continue to seek efficient methods for solubilizing SWNTs in organic solvents. In this paper, we report a process for the solubilization of SWNTs in organic solvents that results in the first example of the formation of a one-dimensionally ordered conjugated poly-

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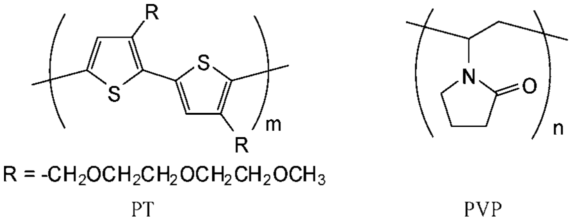
mer, by self-assembly, which was templated by the SWNTs in organic solvents.[11,12] We selected the regioregular conjugated polymer, poly[3-(2-methoxyethoxy)ethoxymethylthiophene-2,5-diyl] (PT), to be the solubilizing agent (Scheme 1) because it is commercially available and highly soluble in organic solvents. This approach may open up a broad range of applications for SWNTs in molecular electronics (including molecular wires and switches)[13] and for the preparation of conducting hybrid materials composed of polymers and carbon nanotubes.[14]

Scheme 1. Solubilizing Agents



Pristine SWNTs (1.00 mg)[15] and PT (5.00 mg; M_n = 11 000; M_w/M_n = 1.6)[15] were placed in an agate capsule together with two agate mixing balls. The mixture was mixed vigorously at 1800 rpm for 20 min using a high-speed vibration mill (MM 200; Retsch Co. Ltd.). The solid mixture was suspended in an organic solvent [chloroform, 1-methyl-2-pyrrolidone (NMP), *N*,*N*-dimethylformamide (DMF), or dimethyl sulfoxide (DMSO); 10 mL] to produce a black emulsion. After centrifugation (18 000 rpm, 20 °C, 20 min), the small amount of suspended SWNTs was removed through decantation. The residual solid was dispersed into the respective solvent (1 mL) through sonication (5 min). After centrifugation (18 000 rpm, 20 °C, 60 min), the nondispersed SWNTs were removed from the solution (Supporting Information, Figure S1). As a reference sample, we used a simpler approach to prepare a complex between the SWNTs and polyvinylpyrrolidone (PVP; M_w = 360 000; 5.00 mg)[15] in NMP.

The UV−vis absorption spectrum of PT in NMP at 25 °C (red line in Figure 1A) displays an absorption maximum (λ_{max}) at 449 nm, which we attribute to the random coil structure of the PT backbone. The SWNT−PVP complex in NMP (orange line in Figure 1B) exhibits a broadened absorption in the range 300−800 nm that results from the presence of the SWNTs. In contrast, in the spectrum of the SWNT−PT complex in NMP (red line in Figure 1B), we observe an additional broad and strong peak at 350−650 nm, which we assign to the bathochromic shift of the absorption of PT that arises from its interaction with the SWNT surface. We obtained similar spectra for the SWNT−PT complexes formed in chloroform and DMF (black and green lines, respectively, in Figure 1B). Presumably, these large bathochromic shifts occur through the synergistic effects of (i) $\pi-\pi$ stacking interactions between the SWNT surface and the thiophene units and (ii) the increased effective conjugation length of PT arising from the more planar structure of its backbone after it has interacted with the SWNT surface (Supporting Information, Scheme S1). Evidence supporting this synergistic effect is that $\pi-\pi$ stacking usually causes very small bathochromic shifts[16] and that greater planarity in PT derivatives engenders bathochromic shifts as a result of increased effective conjugation length of the PT backbone.[11,12]

Next, we used UV−vis absorption spectra to examine the solubilities of the SWNT−PT complexes in various solvents (Figure 1B); i.e., we measured their absorbances in solution at 700 nm and used a specific extinction coefficient (ϵ_{700}) for SWNTs of 2.35×10^4 cm^2 g^{-1}.[17] Table 1 summarizes these results. The SWNT−PT complex was poorly soluble in DMSO (solubility: 0.04 mg mL^{-1}); because the peak at ca. 400 nm (i.e., that of free PT) essentially disappeared, we attribute this low solubility to the physical adsorption of PT onto the surfaces of the solid SWNTs (Figure 1B).[18] The SWNT−PT complexes exhibited moderate solubilities in

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(18) The reason for the poor solubility of SWNT in DMSO remains unclear. We expect that the reason is the low solubility of the SWNT−PT complex or few SWNTs debundled by PT in DMSO.

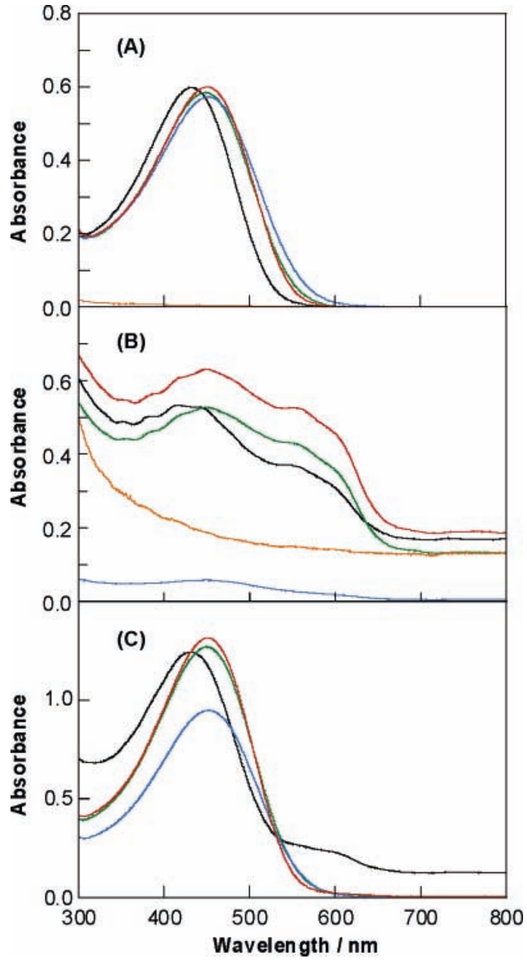

Figure 1. UV−vis absorption spectra of (A) PT (0.20 mg mL^{-1}), (B) the SWNT−PT complex prepared using HSVM, and (C) the SWNT−PT complex prepared using sonication methods in (a) NMP (red line), (b) chloroform (black line), (c) DMF (green line), and (d) DMSO (blue line). For comparison, the spectra of PVP and the SWNT−PVP complex in NMP (orange line) are also presented [N.B.: the spectrum of the SWNT−PVP complex has been expanded (×10)]. All spectra were measured at 25 °C (1 mm cell). All saturated solutions were diluted to 1:10.

chloroform, NMP, and DMF (0.072, 0.081, and 0.060 mg mL^{-1}, respectively, Table 1); e.g., the solubility in NMP was 20 times higher than that in DMSO. In contrast, the UV−vis absorption spectra of the SWNT−PT complex prepared using the sonication method (Figure 1C) indicate that no SWNT−PT complex—instead only free PT—was extracted into DMSO, DMF, or NMP. Although a considerable amount of the SWNT−PT complex (prepared using the sonication method) was extracted into chloroform (solubility: 0.055 mg mL^{-1}), the solution contained a large amount of free PT and its purification was extremely difficult.

In the near-IR spectra (Supporting Information, Figure S2) of the SWNT−PT complexes formed in each solvent—as well as that of the SWNT−PVP complex in NMP—we observe characteristic absorption bands corresponding to the van Hove singularities, in both the 800 and 1400 nm regions, which closely resemble those reported previously.[5h−j]

Table 1. Absorbance and Solubility (mg mL^{-1}) of SWNT−PT Complexes by HSVM and Sonication Methods in Each Solvent

solvent	method	$A_{700}{}^a$	SWNTs solubility^b (mg mL^{-1})	(extractability)
NMP	HSVM	0.19	0.081	(81%)
	sonication	0.00	0.000	(0%)
chloroform	HSVM	0.17	0.072	(72%)
	sonication	0.13	0.055	(55%)
DMF	HSVM	0.14	0.060	(60%)
	sonication	0.00	0.000	(0%)
DMSO	HSVM	0.01	0.004	(4%)
	sonication	0.00	0.000	(0%)

[a] 1-mm cell, saturated solution, 25 °C. [b] Concentrations of SWNTs were determined using a specific extinction coefficient for pristine SWNTs of $\epsilon_{700} = 2.35 \times 10^4$ cm^2 g^{-1}.[17]

The ^{1}H NMR spectrum (Supporting Information, Figure S3) of the SWNT−PT complex in chloroform provided no useful information because of extensive broadening of all of the signals.

We used transmission electron microscopy (TEM) to observe the morphology of the SWNT−PT complexes (Figure 2). A TEM micrograph of the SWNT−PT complex prepared using NMP revealed that it formed structures having a mean diameter of ca. 3 nm and that the SWNT surface was coated by several PT chains (Figure 2A). On the other hand, the SWNT−PT complex prepared using chloroform existed in the form of debundled SWNTs having diameters in the range 1−2 nm and part of the SWNT surface was cropped out (Figure 2B), indicating that these SWNTs were well dispersed in chloroform. These complexes suggested that several or a few PT chains were entwisted around the cylindrical skeletons of the SWNTs as shown in Supporting Information Scheme S1.

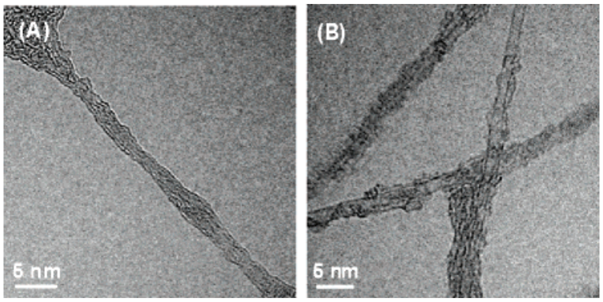

Figure 2. TEM images of the SWNT−PT complexes prepared using (A) NMP and (B) chloroform.

We also used atomic force microscopy (AFM) to investigate the SWNT−PT complexes formed after evaporation of single drops of their NMP and chloroform solutions on mica (Figures 3A and 3B). Height profiles (1.4−3.9 and 1.0−

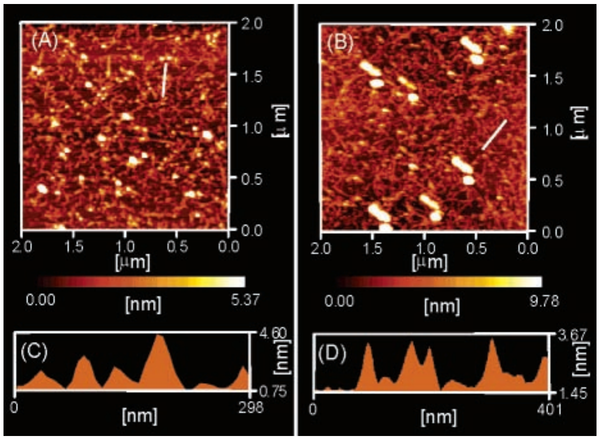

Figure 3. AFM images of SWNT−PT complexes prepared using (A) NMP and (B) chloroform by HSVM on mica. Height profiles of SWNT−PT complexes prepared using (C) NMP and (D) chloroform.

2.2 nm, respectively) of these images indicate almost the existence of individual, nonaggregated SWNTs (Figures 3C and 3D). These values are comparable to the diameters that we estimated from the TEM images.

In summary, we have prepared one-dimensional ordered PT structures on SWNT surfaces in organic solvents through the formation of supramolecular complexes. We are now examining the feasibility of applying this technique to other conjugated polymers, not only to elucidate the mechanistic details of this process but also to explore the practicality of this method as a general means for preparing one-dimensional ordered polymers.

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Supporting Information Available: Supporting Figures (S1−S3) and a Scheme (S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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