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Communications to the Editor

High Dissolution and Strong Light Emission of Carbon Nanotubes in Aromatic Amine Solvents

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Carbon nanotubes (NT) have been the subject of much research in recent years because of their unique electronic, mechanical, and physical properties.[1,2] Some solution properties of carbon nanotubes have also been studied, aimed at their chemical modification and functionalization.[3−6] However, the low solubility of NT in most organic solvents limits their chemical manipulation, quantitative characterization, and wide application. Several methods have been reported to make solubilized NT, including attachment of long alkyl chains[3] and admixture with polymers.[4,5] Despite those attempts, the dissolution of pristine carbon nanotubes, to our knowledge, has not been realized. In this paper, we report here the high dissolution of pristine single-walled carbon nanotubes in aromatic amines, and the strong fluorescence of these NT-aniline solutions. Similar results have been obtained with multiwalled NT as well.

Purified single-walled carbon nanotubes (SWNT) were purchased from Rice University (http://cnst.rice.edu) in toluene suspension. SWNT were filtered through a 0.2 μm PTFE filter membrane to produce so-called “bucky paper”.[2] Multiwalled nanotubes were purchased from Nanocs Inc., New York (http://www.nanocs.com). In a typical experiment, 40 mg of accurately weighed NT were added to 5 mL of aniline and the mixture was heated at reflux for 3 h in the dark. Dissolution of carbon nanotubes in aniline can be observed by the color change of the solution after reflux for a short time. Thus, with continuous heating, the original colorless aniline solution first became brownish and then turned dark red. After being cooled to room temperature, a NT solution was obtained by filtration through a 0.2 PTFE membrane. An SEM picture of carbon nanotubes dissolved in aniline (see Figure 1) showed similar structural features to that before dissolution,[9] suggesting no damage had occurred to the NT (of course, SEM would not reveal evidence of chemical reaction of the NT). The solubility of SWNT in aniline is up to 8 mg/mL. This aniline-nanotube solution can be readily diluted with other organic solvents such as acetone, THF, and DMF.

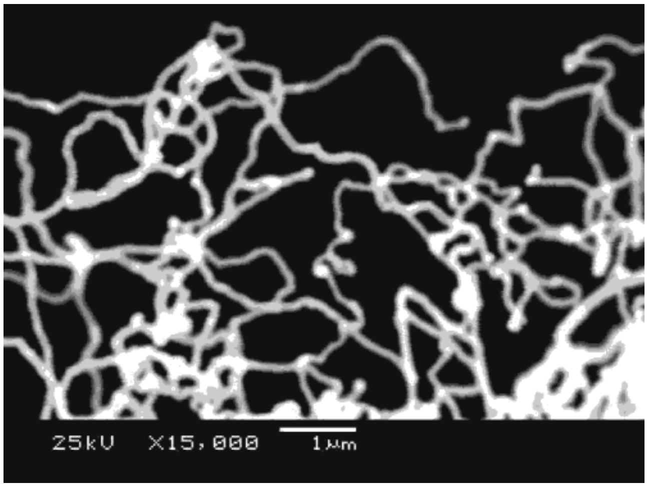

Figure 1. SEM picture of dissolved carbon nanotubes after evaporation of solvent.

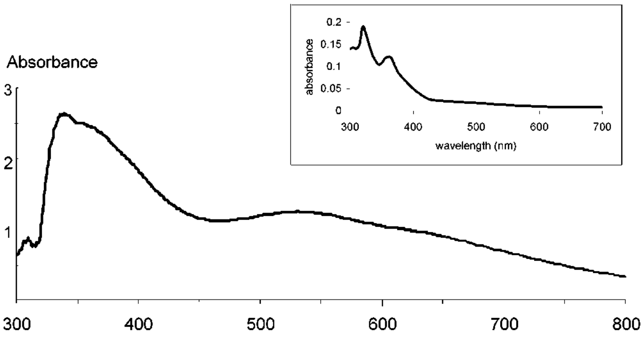

Figure 2. UV−vis absorption spectra of aniline dissolved carbon nanotubes solution. Inset: Carbon nanotube aniline solution diluted with acetone.

Figure 2 shows the UV−vis absorption spectra of the SWNT-aniline diluted with acetone solution. Absorption between 310 and 400 nm is very strong while a new peak at 530 nm suggests the formation of an aniline-SWNT charge-transfer complex. In very dilute solution, the broad peak between 310 and 400 nm can be resolved into two sharp peaks at 325 and 375 nm, respectively, while the peak at 530 nm is no longer observed.

C_{60} has been shown to form donor−acceptor complexes in the liquid state when dissolved in tertiary amines and substituted anilines. The room temperature solubility of C_{60} in aniline, *N*-methylaniline, and *N,N*-dimethylaniline was found to be 1.05, 1.16, and 3.89 mg/mL, respectively.[10−12] Complexation with aniline has also been applied to separate C_{60} from various

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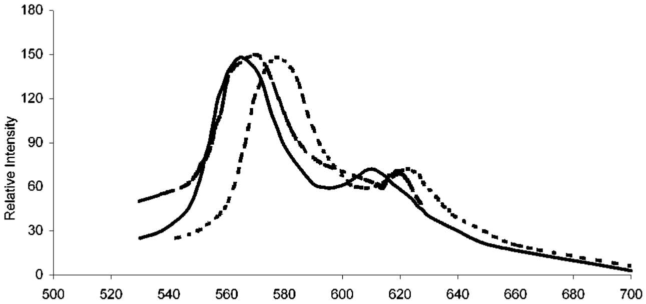
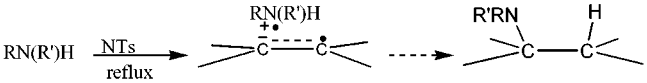


Figure 3. Emission spectra of aniline dissolved carbon nanotubes in different solvents: in acetone (—), in toluene (— • • —), and in methanol (- - -). All samples were excited at 500 nm.

Scheme 1. Proposed Reaction Mechanism between NTs and Aromatic Amines



endohedral complexes.[13] C$_{60}$ also showed reactivity in the ground state with various primary, secondary, and tertiary amines, attributed to electron transfer from the amines to the fullerene.[14] Because of its structural similarity to fullerenes, NT should be a good electron acceptor,[4,7] while aniline is a fairly good electron donor. At elevated temperatures, NT and aniline may form a charge-transfer complex in its ground state, as evidenced by the appearance of new absorption in the visible region (Figure 2). As in the interaction of primary and secondary amines with C$_{60}$,[14] this may be followed by proton transfer from aniline to the fullerene (see Scheme 1). The NT-aniline complex (or adduct) is quite stable, even after three months, as shown by the persistence of the new spectral features. In contrast, no measurable dissolution of carbon nanotubes was observed in nitrobenzene, an electron acceptor. Solubilization was also observed between *N,N*-dimethylaniline (DMA) and NT, but the process may not be the same as with aniline, since adduct formation by proton transfer between DMA and the NT is not possible. The fluorescence of DMA-NT solutions is also much weaker than that of the NT-aniline solutions, indicating a different species is produced. The observation that dissolution of NT in aniline requires higher temperatures than are needed for interaction of amines with fullerenes is reasonable considering not only the difference in molecular size but also the fact that nanotubes have a very strong tendency to aggregate, which is one reason they are insoluble in most common solvents.

Strong fluorescence was observed upon exciting the diluted SWNT-aniline solutions at 500 nm. Figure 3 shows the emission spectra of solutions in acetone, toluene, and methanol, respectively. The maximum emission in acetone was observed at 565 nm with a shoulder at 610 nm. In methanol the emission is red-shifted by 20 nm with no change in intensity. The shift of the emission maximum in polar vs nonpolar solvents is consistent with charge separation in the excited state. The fluorescence excitation spectra are quite different from the absorption spectra of the individual components, indicating the formation of a new light-absorbing species. The quantum yield of fluorescence of SWNT-aniline in acetone is 0.30,[18] considerably higher than that of aromatic molecules such as phenanthrene (0.10) and naphthalene (0.11), but similar to that of anthracene (0.29). Luminescence has been observed[4] at slightly longer wavelengths for polymer-bound NTs (i.e., NT covalently linked to poly(propionylethylenimine-*co*-ethylenimine) but the origin of this fluorescence is controversial. The quantum yields for our NT-aniline solutions are also higher than those for the polymer-bound NTs.[4] As in previous work, precautions were taken to prevent interference from fluorescence of small aromatic species and other impurities.

As indicated above, we believe that a new chemical species is produced on heating SWNT in aniline, and that photoexcitation of this species leads to a luminescent charge separated state (exciplex). In polymer-bound carbon nanotubes, Riggs et al. rationalized that the luminescence might be due to the trapping of the excitation energy at defect sites.[4] Another factor that might enhance the fluorescence efficiency of nanotubes is their large molecular size, which would inhibit deactivation through molecular motion. In this respect, studies with purified NT of different types and sizes would be informative. We expect that there would be differences in the fluorescence efficiency of zigzag, armchair, semiconducting, metallic, and chiral carbon nanotubes.[1a]

In conclusion, dissolution of carbon nanotubes and the study of their properties in solution has been a challenge for chemists. Although some efforts have been made in this direction, most studies to date have involved cutting and chemical functionalization of carbon nanotubes, or attachment to polymers with solubilizing features. This approach has two disadvantages. On one hand, tedious chemical derivatization is often required, while on the other hand, cut carbon nanotube derivatives may have significantly different properties than those of pristine materials. In this work, we showed that carbon nanotubes can be dissolved in aniline without any prior chemical functionalization, and this material is then soluble in a variety of organic solvents. To our knowledge, this represents the first observation of significant dissolution of pristine carbon nanotubes in standard organic solvents. For future work involving the separation, purification, and chemical functionalization of carbon nanotubes, solubilized nanotubes are a distinct advantage. For example, one can envisage NT-aniline solutions for the formation of nanocomposites or thin films, which would solve some of the the practical problems involved in making nanotube-based electronic and field emission display devices.[17] The strong fluorescence emission of carbon nanotubes should also be a useful probe in elucidation of the physical and biological properties of these materials.

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