

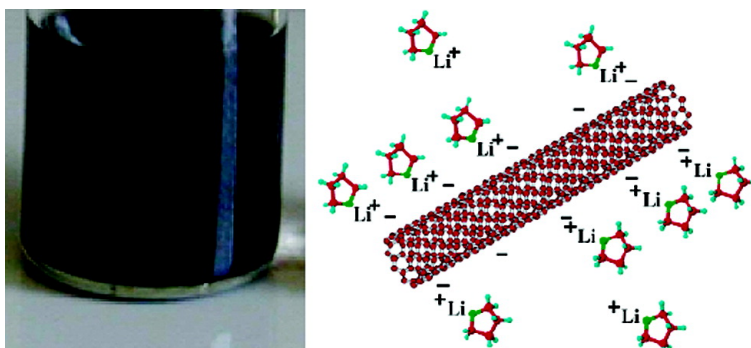
Communication

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Spontaneous Dissolution of a Single-Wall Carbon Nanotube Salt

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In recent years, there has been much interest in preparing homogeneous dispersions of single-wall carbon nanotubes (SWNTs), suitable for processing into thin films and composites exploiting the unrivalled properties of carbon nanotubes. The main routes consist of end¹ and/or sidewall functionalization,² use of surfactants with sonication or high-shear mixing,^{3–6} polymer wrapping of nanotubes,^{7–10} and protonation by superacids.¹¹ Although these methods are quite successful, they often indicate cutting the tubes into smaller pieces (sonication and/or functionalization), thus partly losing the high aspect ratio of SWNTs. All these routes follow one strategy, which consists of intercalating a mediator between the tubes to counterbalance the strong van der Waals energy. This mediator yields metastable dispersions when noncovalently adsorbed, and chemically modified carbon structures when covalently bound. Here we show that, upon reduction with alkali metals, SWNTs form polyelectrolyte salts that are soluble in polar organic solvents without any sonication, use of surfactants, or functionalization whatsoever, thus forming true thermodynamically stable solutions of naked SWNTs that can be processed into composite thin films of unmodified and uncut SWNTs.

Ionic organic or inorganic macromolecules, referred to as polyelectrolytes, dissolve spontaneously in polar solvents upon ionic dissociation. We discovered that carbon nanotube salts can bear a sufficient electrostatic charge to form a new, stiff, conducting polyelectrolyte.

Indeed, SWNTs reduced with Li or Na¹² dissolve spontaneously (Figure 1) in polar aprotic solvents such as sulfolane, dimethyl sulfoxide (DMSO), *N*-methylformamide (NMF), dimethylformamide (DMF), 1-methyl-2-pyrrolidone (NMP), etc. in concentration up to 2.0 mg/g in DMSO and 4.2 mg/g in sulfolane. Being at thermodynamic equilibrium, the nanotube polyelectrolyte solution (Figure S1) is indefinitely stable (at least 1 year) when prepared and kept under inert atmosphere (since the reduced form of SWNTs is air sensitive). Such spontaneous dissolution was obtained for SWNTs synthesized from the electric arc process as well as from the HiPco process, albeit less efficiently in the latter case (0.4 mg/g in DMSO vs 2 mg/g for electric arc SWNTs). The absorption spectrum (Figure S2) shows a monotonic decrease above 260 nm (DMSO absorbs below). In particular, the absorption bands expected at ca. 700, 1000, and 1750 nm, corresponding to transitions between the symmetric van Hove singularities in the density of states, are absent. This is consistent with the fact that the SWNTs are fully doped; hence, discrete electronic transitions disappear.¹² Raman spectra are shown in Figure 2 for a DMSO solution of [Na(THF)]_nNT, before and after air oxidation and, for comparison, the spectrum of a suspension of SWNT with Triton × 100. The solution shows a broadening, an upshift from 1591 to 1596 cm⁻¹ and a loss

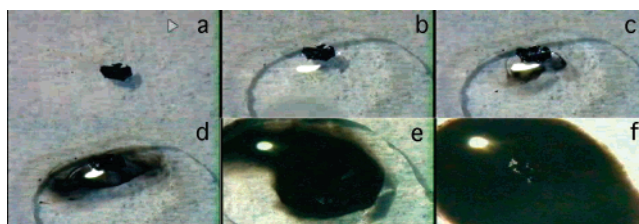


Figure 1. (a–f) Sequential photographs of the spontaneous dissolution of [Na(THF)]_nNT in a drop of DMSO.

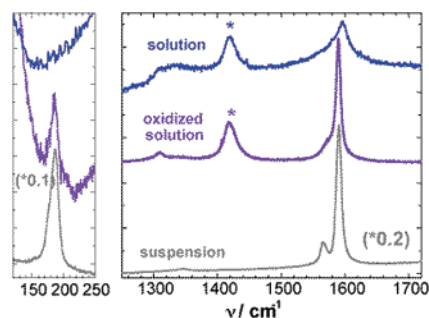


Figure 2. Raman spectra of [Na(THF)]_nNT in DMSO (see text), taken with a 514.5 nm laser excitation. The starred bands come from the solvent.

of intensity of the tangential mode (TM), a broad asymmetric band around 1320 cm⁻¹, and disappearance of the radial breathing mode (RBM) around 190 cm⁻¹, all features characteristic of charged SWNTs^{13,14} while the oxidized solution shows the classical feature of neutral NTs.¹⁵ Raman spectra are thus fully consistent with the existence of SWNTs in solution and the necessary charging of the NTs for dissolution. Atomic force microscopy (AFM) pictures (Figure 3) of diluted solutions deposited on mica reproducibly show micrometer-long nanotubes. Height measurements yield a height of about 1 nm on all nanotubes measured thus far, consistent with the presence of isolated SWNTs in the solution. For such high molecular weight species, it is not straightforward to state that the dispersion is a true solution rather than a metastable suspension.¹⁶ The fact that lithium or sodium salts of SWNTs dissolve spontaneously, i.e., with no supplied energy, and that the solutions are stable confirms true thermodynamic solution character, as expected for a classical polyelectrolyte. Furthermore, the first AFM images pointing to true exfoliation support a dissolution mechanism.

Elemental analysis (see Supporting Information) yields a chemical formula of A(THF)C₁₀ (A = Li, Na), hence, one negative charge per 10 carbon atoms.¹⁷ Taking as hypothesis a carbon–carbon distance of 1.42 Å, as in graphite, one obtains a mean surface area per negative charge of 26 Å² on the nanotube surface, hence a mean distance of ca. 5.1 Å. The Bjerrum length,¹⁸ i.e., the distance between *dissociated* charges set by the competition between electrostatic condensation and thermal energy, is 12 Å at room

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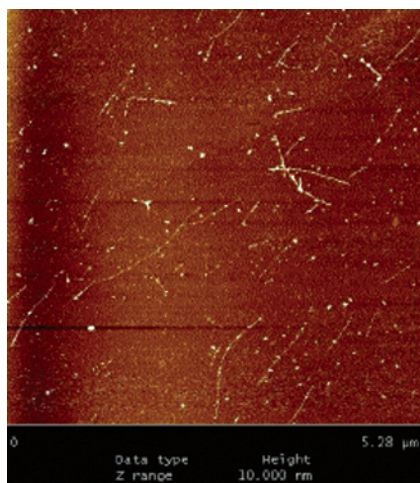


Figure 3. AFM height image of electric arc SWNTs deposited on mica from solution (see text).

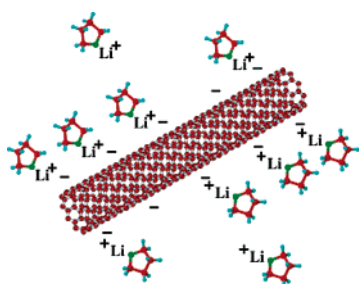


Figure 4. Sketch of a negatively charged nanotube with its surrounding lithium cations and THF molecules (not to scale).

temperature (using the relative dielectric constant of DMSO, 46.45 at 20 °C). This corresponds to a maximum possible surface density of one charge per 144 Å². Hence, only one out of five charges are dissociated, whereas the others are canceled through condensation of alkali cations (Figure 4). Incidentally, this ratio of 20% is often encountered in surfactant micellar suspensions.¹⁹ The important point is that the nanotubes, although reduced to LiC₁₀ or NaC₁₀, bear their maximum allowed surface charge density. Actually, it can even be predicted that a stoichiometry of Na(THF)C₅₀ should be enough to dissolve SWNTs.

Composites and conducting/antistatic coatings are some of the most sought-after applications of carbon nanotubes. Homogeneous, stable, and spontaneously formed solutions of unmodified SWNTs should be a welcome starting material for obtaining such devices. Indeed, preliminary experiments show that PVA composite films can be obtained with improved mechanical properties when compared to pure PVA. Another important development, unique to these SWNT solutions, is the possibility to selectively and stoichiometrically functionalize the nanotube walls in the same way as in the early days of C₆₀ chemistry where C₆₀R_n molecules could be selectively obtained from C₆₀ⁿ⁻ solutions.²⁰ Indeed, by adjusting the charge on the nanotubes, one could precisely monitor the amount

of attached functional groups on the SWNT.^{17,21–22} We are now exploring the possibilities of obtaining such multifunctional materials by coupling the mechanical and electronic properties of the SWNT backbone with specific properties of the attached functional group (polymers, sensors, photochemical devices, etc.).

Acknowledgment. We thank Mathieu Paillet for advice with the AFM sample preparation, Hassan Saadaoui for the AFM experiments, and Brigitte Vigolo for preliminary dissolution experiments and the GDR Nanotubes.

Supporting Information Available: Detailed experimental procedures, photograph of a solution of SWNT (Figure S1), absorption spectrum between 250 and 1800 nm (Figure S2), video showing the spontaneous dissolution of [Na(THF)]_nNT. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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