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An Unexpected New Optimum in the Structure Space of DNA Solubilizing Single-Walled Carbon Nanotubes

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Abstract: Here we report quantitative data on the amount of single-walled carbon nanotubes that can be suspended with oligodeoxynucleotides in aqueous buffer, together with rate constants for the thermal denaturation of the resulting DNA-nanotube complexes at elevated temperatures. Sequence motifs $d(GT)_n$ and $d(AC)_n$ with $n=2$, 3, 5, 10, 20, or 40 were employed, both individually and as equimolar mixtures of the complementary strands. Unexpectedly, the greatest suspending efficiency was found for the mixture of short, complementary oligonucleotides $d(GT)_3$ and $d(AC)_3$. Unlike the suspending efficiency, the kinetic stability of the nanotube suspensions increases with increasing chain length of the DNA, with half life times of >25 h at 90 °C for the complexes of the longest strands. Our results identify a new, unexpected optimum in DNA sequence space for suspending carbon nanotubes. They also demonstrate that suspending power depends on the presence of complementary strands. Exploratory assays suggest that nanotubes can be deposited site-selectively from suspensions formed with short DNA sequences.

Keywords: carbon · DNA · nanotechnology · nanotubes · noncovalent interactions

Introduction

Single-walled carbon nanotubes (SWCNTs)[1] show high mechanical strength, low density, thermal stability and interesting electrical properties,[2] making them attractive for nanoscale devices and high-performance materials.[3] Due to their long, tubular structure, single-walled carbon nanotubes form bundles of great stability, making it difficult to produce concentrated and stable suspensions.[4] This complicates separation of metallic from semiconducting tubes,[5] and protocols producing pristine carbon nanotubes of a single, defined helicity remain elusive.

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Suspensions of carbon nanotubes can be prepared by treating raw nanotube material with strong, oxidizing acids or other highly reactive reagents to generate shorter and partially modified nanotubes,[6] but the process introduces defects in the π-structure. Carbon nanotubes can also be suspended using superacids,[7] highly charged nanoparticles,[8] or polymers,[9] but the resulting suspensions do not handle like common solutions. Aqueous suspensions of nanotubes form upon sonication with ionic detergents,[6] such as SDS or cholate. The like charges of the detergents apparently prevent the re-association of the tubes kinetically. Relatively high concentrations of detergents are required, however, and removing excess detergents induces re-bundling, complicating chromatographic purification.

Curiously, DNA, the biomacromolecule developed by nature to store genetic information, not only solubilizes SWCNTs well, but has also been reported to facilitate their separation into metallic and semiconducting fractions,[10,11] even though carbon nanotubes are very lipophilic, stiff molecules with strongly curved surfaces, whereas DNA is a very polar, water-soluble compound that prefers complexes formation through hydrogen bonding and base stacking. Noncovalent carbon nanotube–DNA complexes[12] can align spontaneously,[13] facilitate transport of DNA into the nucleus of cancer cells,[14] and allow for the detection of DNA.[15] While theoretical work on the separation by chromatography is emerging,[16] the detailed structure of the

complexes and quantitative data on their strength and sequence and length dependence are lacking. A sequence dependence was initially reported, with poly-d(T) and $d(GT)_{10-45}$ as the sequences with highest suspending efficiency,[10a,b] but a recent report by another group states that nanotubes are dispersed irrespective of the DNA sequence.[17] Either group reports that single-stranded DNA suspends SWCNTs better than double-stranded DNA, even though suspensions have been generated from double-stranded, genomic DNA,[18] and a clear dependence on the nature of the nucleobase was found for individual nucleotides.[19]

Here we show that *short* DNA strands solubilize SWCNT unusually well. Further, mixtures of complementary, (duplex-forming) DNA strands are at least as good as single-stranded (non-selfcomplementary) DNA sequences in producing suspensions of nanotubes. Finally, we provide data on the kinetic stability of carbon nanotube–DNA complexes. These help to develop protocols for site-specific deposition of single-walled carbon nanotubes.

Results and Discussion

In the present study, we sonicated HiPco SWCNTs,[20] known to have diameters of 0.7–1.4 nm, in aqueous buffers containing oligonucleotides $d(GT)_n$ or $d(AC)_n$, with $n=2$, 3, 5, 10, 20, or 40 at a nucleotide concentration of 0.74 mM, which corresponds to approximately 0.22 mg DNA per mL. Additionally, 1:1 mixtures of the complementary sequences were tested for each of the strand lengths. Finally, DNA from salmon sperm was tested as an inexpensive form of initially double-stranded, genomic deoxyribonucleic acid.

The black suspensions resulting from treatment of the slurries with a probe sonicator underwent ultracentrifugation to remove undissolved nanotube aggregates, catalyst, and impurities from the production process. Absorption spectroscopy (UV/Vis/NIR) of the supernatants then showed sharp bands characteristic for pristine nanotubes. Representative spectra are shown in Figure 1.

The amount of nanotubes solubilized was quantified at two wavelengths, 730 and 1130 nm, that is, bands in the visible and NIR range. The absorbances can be converted into microgram quantities of nanotubes, if one assumes an approximated, average extinction coefficient (see Table S1, Supporting Information). As expected,[10] oligomers of the sequence $d(GT)_n$ solubilized slightly more nanotubes than those of $d(AC)_n$, with little length dependence (Figure 2b and c). For the mixture of $d(GT)_n$ and $d(AC)_n$, however, the suspending efficiency *decreased* significantly for the longest strands and increased significantly for shorter strands (Figure 2a). The most concentrated suspensions were obtained for the mixture of hexamers $d(GT)_3$ and $d(AC)_3$ (Figures 1a and 2a). The mixture of tetramers $d(GT)_2$/$d(AC)_2$ gave only 0.7-fold as much suspended nanotube material as the hexamers, and significantly more background signal, indicating that these shorter strands prevent bundling to a lesser

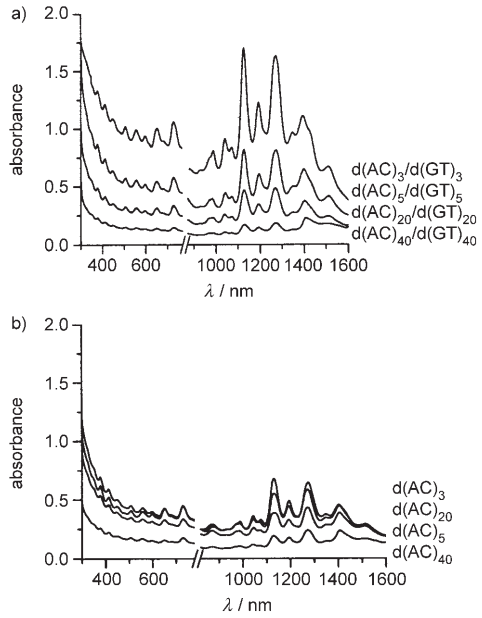

Figure 1. Absorption spectra of suspensions of SWCNTs generated through sonication in the presence of a) mixtures of $d(AC)_n$/$d(GT)_n$ and b) $d(AC)_n$ where $n=3$, 5, 20 and 40, and subsequent ultracentrifugation. The discontinuity at 800 nm is caused by the change of gratings in the spectrophotometer.

extent, and confirming that the hexamers constitute the optimum in the sequence space tested. In fact, to the best of our knowledge, the mixture of complementary hexamers gives the most concentrated suspensions of pristine single-walled carbon nanotubes solubilized with DNA reported to date.

The mixture of the complementary hexamers $d(GT)_3$ and $d(AC)_3$ behaves differently from common double-stranded DNA. At our standard concentration of 0.74 mM nucleotides, the initially double-stranded, genomic DNA from salmon sperm, gave low absorbances readings for carbon nanotubes of 0.085 (730 nm) and 0.095 (1130 nm). When increasing the nucleotide concentration of this DNA to 3 mM, the genomic DNA gave significantly stronger nanotube absorbances of 0.32 (730 nm) and 0.42 (1130 nm). On the other hand, experiments performed with $d(GT)_3$ and $d(AC)_3$ at nucleotide concentrations between 0.37 and 2.22 mM gave almost identical absorbance readings, that are within a factor of two of what was measured at 0.74 mM nucleotides (Figure S2c,d, Supporting Information). So, there does not seem to be a steep concentration dependence in the amount of SWCNTs that can be suspended with the hexamer mixture. Even at low concentrations, the hexamers perform superior to the very long, initially double-stranded DNA as solubilizing agent.

Further evidence for an entirely new, unexpected property of the mixture of hexamer DNA strands as solubilizing agents for carbon nanotubes comes from a comparison of our data with literature values for other DNA. The solubilization of unusually large quantities of nanotubes with the hexamer mixture occurred at a DNA concentration that

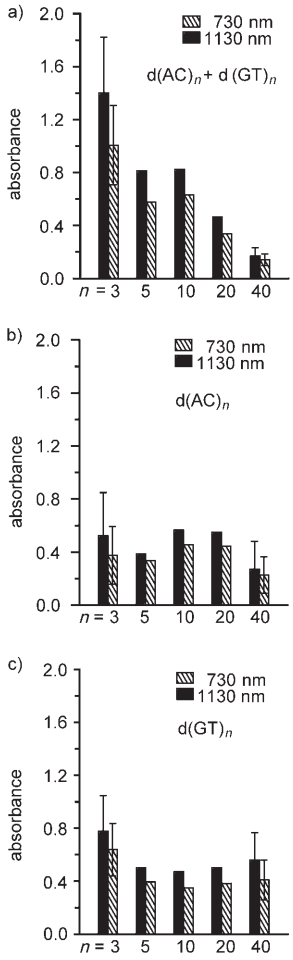

Figure 2. Suspending SWCNTs with a) mixtures of complementary DNA strands, or b), c) single-stranded DNA, as determined by spectrophotometry of suspensions after sonication and ultracentrifugation (representative bands). Assays involving the shortest and longest DNA strands were repeated ≥ 3 times to ensure that trends are represented properly (mean $\pm$ one standard deviation).

should not give stable suspensions of pristine nanotubes at all, according to the phase diagram recently published (compare Figure S13, Supporting Information).[21] As mentioned above, even half the strand concentration for the mixture of hexamers still gave nanotube absorbance readings of up to 0.98 at 1130 nm.

The high solubilizing efficiency of the mixture of short oligonucleotides is counter-intuitive. Single-walled carbon nanotubes of the type employed by us are exceptionally long structures. Longer DNA should bind more tightly to such structures than shorter DNA. To shed some light on our unexpected findings, we performed additional experiments. First, we determined the fraction of DNA actually bound to the nanotubes in the suspension and that of the free DNA. The DNA-nanotube suspensions were applied to microspin filters,[22] and nanotube-free filtrates were then used to quantify the amount of unbound DNA. Additionally, the DNA-wrapped nanotubes on the filters were re-suspended in fresh buffer, free of excess DNA. This process was successful for most preparations, demonstrating that DNA–nanotube complexes are stable enough to survive removal of excess ligand from the liquid phase and condensation into a small volume. While the amount recovered varied for certain sequences, the resuspended preparations lacking excess DNA were long-time stable at room temperature and gave reproducible results in thermal denaturation studies (see below). Once the nanotube–DNA complexes were denatured through heating, the fraction of previously nanotube-bound DNA could be determined from the supernatant by absorption spectroscopy.

Based on the procedure outlined above, the DNA distributions given in Table 1 were obtained. Interestingly, all preparations contained $\leq 10\,\%$ of the DNA bound to the solubilized nanotubes. Much of the DNA (between 29 and 74 %) remained free in solution, and only the remainder was associated with the undissolved (nanotube) material (see Table 1). Unexpectedly, there was no clear trend for shorter or longer strands. The DNA distribution was not dramatically different for either length. This suggests that the differences in solubilizing power for the nanotubes was not simply due to an increase in affinity for the nanotubes.

Table 1. Distribution of free DNA, unincorporated DNA and DNA bound to carbon nanotubes, values are percentages based on the total amount of DNA used to prepare the DNA–SWCNT samples.

DNA used	Free in solution	Precipitate	Bound to SWCNT
$d(AC)_3$	38 ± 24	61 ± 23	2 ± 1
$d(GT)_3$	39 ± 32	51 ± 29	10 ± 4
$d(AC)_3/d(GT)_3$	74 ± 21	23 ± 19	3 ± 2
$d(AC)_5$	60	36	4
$d(GT)_5$	56	41	3
$d(AC)_5/d(GT)_5$	60	38	2
$d(AC)_{10}$	49	49	3
$d(GT)_{10}$	31	67	2
$d(AC)_{10}/d(GT)_{10}$	56	42	1
$d(AC)_{20}$	54	43	4
$d(GT)_{20}$	37	61	2
$d(AC)_{20}/d(GT)_{20}$	45	53	3
$d(AC)_{40}$	32 ± 7	60 ± 5	8 ± 2
$d(GT)_{40}$	29 ± 13	67 ± 13	4 ± 1
$d(AC)_{40}/d(GT)_{40}$	–[a]	–[a]	–[a]

[a] Incomplete passage of unbound DNA through filter.

Next, we asked whether the mixture of DNA hexamers dissolve a specific fraction of carbon nanotubes from the crude HiPco material. Comparison of the UV/Vis/NIR spectra from the different nanotube–DNA preparations suggested that no significant bias towards a certain diameter and/or helicity existed in the suspensions containing the hexamers. Further, AFM images of suspensions generated with the DNA hexamers or sodium cholate (as control) showed similar distributions in terms of length and diameter of the adsorbed carbon nanotubes, again suggesting that the hexamers are not selectively dissolving a specific fraction of nano-

tubes (compare Figure S4 and S5, Supporting Information). The AFM images obtained also demonstrate that the carbon nanotubes solubilized with the hexamers are not aggregated into bundles.

A clear difference in properties was found between the suspensions prepared with different DNA species when the kinetic stability of nanotube suspensions was determined. For this, we heated the DNA–nanotube complexes obtained through spin filtration and re-suspending in fresh buffer to 90 °C. This led to flocculation and eventual precipitation of carbon nanotube bundles. Figure 3 shows an overlay of UV/Vis/NIR spectra after different incubation times at 90 °C. It can be discerned how similar the decline in intensity is for the different absorption bands. This allowed us to monitor the loss of solubilized nanotubes from the suspensions at a single wavelength. We chose 730 nm, a wavelength accessible with common UV/Vis spectrophotometers.

The $t_{1/2}$ values obtained through absorbance readings at this wavelength (Table 2), where only the nanotubes, but not the DNA, absorb, range from two hours to days, and *increase* with the length of the oligonucleotides, as expected, if one assumes that the longer DNA chains engage in more multivalent interactions. Heating the different nanotube–DNA suspensions also led to bathochromic shifts in the absorbance peaks (see Figure S12 of the Supporting Information for representative data). The complexes with shorter DNA show a stronger shift, suggesting that they more readily allow access of the solvent to the nanotube surface.

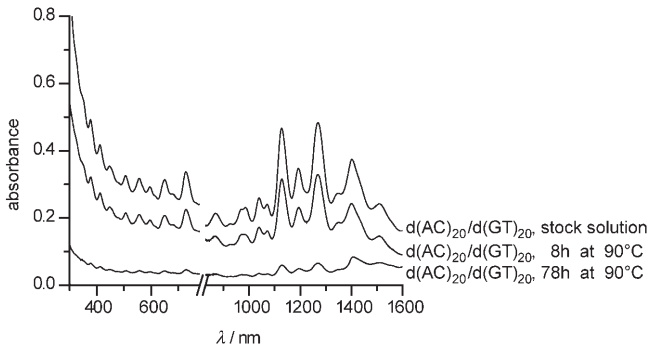

Figure 3. Representative absorption spectra of a SWCNT–DNA suspension prior to, during, and after thermal denaturation.

The heterogeneity of the slurry produced upon flocculation leads to substantial scattering of the absorbance readings when nanotubes are solubilized with short DNA. This leads to smaller R^2 values for the resulting fits, since the denaturation process is now accelerated to a time scale rivaling that of precipitation of aggregating nanotubes in the (macroscopic) set-up for spectrophotometric monitoring. As nanotube bundles and flakes diffuse through the light path of the spectrometer, spikes in the absorbance appear under these circumstances. Despite the unavoidable scattering in these special cases, the half-life times obtained are reasonably well reproducible. For example, repeating the same denaturation experiment with two different nanotube preparations generated with hexamer $d(GT)_3$ gave $t_{1/2}$ values of 3.9 h ($R^2=0.72$) and 3.4 h ($R^2=0.93$). An overlay of data points obtained for two different samples of $d(AC)_3/d(GT)_3$ is shown in Figure S11 (Supporting Information).

Table 2. Half life times of flocculation of SWCNT–DNA complexes in D_2O buffer, freed of excess DNA, induced by heating to 90 °C.

DNA sequence	$t_{1/2}$ [h][a]	R^2[b]
$d(AC)_3$	–	–
$d(GT)_3$	3.9	0.716
$d(AC)_3/d(GT)_3$	2.0	0.521
$d(AC)_{10}$	7.6	0.983
$d(GT)_{10}$	13.8	0.990
$d(AC)_{10}/d(GT)_{10}$	23.8	0.662
$d(AC)_{20}$	13.1	0.969
$d(GT)_{20}$	17.0	0.992
$d(AC)_{20}/d(GT)_{20}$	20.5	0.965
$d(AC)_{40}$	15.6	0.992
$d(GT)_{40}$	22.9	0.992
$d(AC)_{40}/d(GT)_{40}$	25.8	0.986

[a] As determined by fitting a monoexponential decay to the absorbance at 730 nm. [b] For fit to experimental data in non-linear regression.

Our results show that most of the DNA in the SWCNT preparations remains unbound, probably because of electrostatic repulsion between the polyanions. Further, the data demonstrates that DNA–SWCNT complexes are kinetically quite stable. Longer oligonucleotides may, in fact, be trapped on those nanotube patches that they happen to associate with, immediately after sonication, whereas shorter DNA strands may be more mobile, producing a more even coverage, and leaving fewer surface areas exposed. Any naked patches of nanotubes may induce bundling.

But, long, complementary DNA strands, particularly when partially dangling off nanotubes, may also cross-link tubes, leading to removal during ultracentrifugation as aggregates. This form of cross-linking becomes increasingly unlikely as the DNA chains get shorter, as a minimum length of 4–6 base pairs is required for stable DNA duplexes. Unless long DNA is used, the ability to form DNA:DNA duplexes does not seem to compete successfully with the kinetically metastable adsorption on nanotubes. The melting point of the duplex $d(GT)_3$:$d(AC)_3$, for example, is 17 °C, that is, well below the 90 °C required for flocculation of the nanotube complexes within hours. For short strands, the presence of a base pairing partner seems to aid solubilization of nanotubes. The two sequence motifs, when combined, dissolve nanotubes particularly well, either through their direct structural complementarity or through complementary properties of a more general sense.

Conclusions

The results presented here demonstrate that the chemistry of DNA–nanotube complexes is still full of surprises. But,

the more quantitative understanding of SWCNT–DNA interactions also provides immediate opportunities. For example, knowing that fairly concentrated, but thermally labile suspensions can be generated with minute amounts of DNA allows one to develop improved protocols for suspending *and* depositing SWCNTs, a process critical for practical applications in molecular electronics. A first, strictly exploratory experiment performed with SWCNTs solubilized with the aid of tetramers $d(GT)_2$ and $d(AC)_2$ demonstrates that local heating leads to site-selective flocculation of nanotubes in a capillary (see Figure S15, Supporting Information). We are now developing methods for a deposition with greater spatial resolution, using lasers.

Experimental Section

General information: Oligonucleotides of 6, 10, 20, and 80 nucleotides in length were purchased from Operon Biotechnologies GmbH (Cologne, Germany), tetramers were from BioSpring GmbH (Frankfurt/Main, Germany). Oligonucleotides of 40 nucleotides in length were synthesized with standard β-cyanoethyl phosphoramidites of all four protected 2′-deoxynucleosides (A^{Bz}, C^{Bz}, T, G^{dmf}) on a Perseptive Biosystem 8909 Expedite DNA synthesizer, using a modification of the protocol for 3 μmol scale syntheses recommended by the manufacturer. Oligonucleotides were purified on reversed-phase cartridges (RP-C18, Sep-Pak Vac 3cc, Waters, Eschborn, Germany) and characterized via MALDI-TOF MS on a Bruker REFLEX IV mass spectrometer. HiPco SWCNTs were a gift from the research group of Professor Richard E. Smalley at Rice University, obtained through Dr. F. Hennrich at Forschungszentrum Karlsruhe, Germany. Genomic DNA from salmon sperm was from Acros (Geel, Belgium) and was used without modifications. Reagents for buffer salts, namely NaCl, Na_2HPO_4 and NaH_2PO_4 were the best available grade from Acros (Geel, Belgium) or Aldrich/Fluka/Sigma (Deisenhofen, Germany), whereas D_2O was purchased from EURISO-TOP GmbH (Saarbrücken, Germany) in 99.92% quality. The UV/Vis and UV/Vis/NIR spectra were measured on a Perkin Elmer Lambda 10, a NanoDrop ND-1000 spectrophotometer (UV/Vis), or a Varian Carey 500 spectrophotometer (UV/Vis/NIR). Sonications were performed with a probe sonicator HD 2070 (Bandeline, 200 W, 20 kHz) and ultracentrifugations involved a Beckman, 50 Ti rotor instrument. Spin filters for filtration of DNA–SWCNT suspensions were Microcon YM-100 filters (Millipore GmbH, Schwalbach, Germany) and were employed in a conventional microcentrifuge Hermle Z 100-M (Hermle Labortechnik, Wehingen, Germany).

Preparation of DNA–SWCNT suspensions: Suspensions of DNA-solubilized single-walled carbon nanotubes were prepared by mixing the appropriate amount of each oligonucleotide with HiPco material (0.5 mg) in D_2O buffer (1 mL, 0.1 M NaCl, 10 mM phosphate buffer, pH 7.0, uncorrected for deuterium effect). The nucleotide concentration was kept constant (744 μM for individual oligonucleotides and 2x 744 μM or 2x 372 μM for mixtures of oligonucleotides; the latter value for half-concentrated suspension, or 2x 2.232 mM for mixtures of oligonucleotides at tripled concentration) and the molar concentrations of DNA strands were adjusted according to the length of the oligonucleotides used. The slurries were sonicated with the probe sonicator for 10 min while cooling with an ice/water bath, using the set-up shown in Figure S1 (Supporting Information). The sonication mode was one pulse per second at 10% of the maximum power (200 W, 20 kHz). The resulting black suspensions were subjected to ultracentrifugation for 1 h at 20 °C and 90000 g. The gray supernatants were carefully aspired to give the DNA–SWCNT suspensions, leaving behind undissolved material as a black precipitate. Aspiring of the supernatant from the precipitate is known to be a delicate process,[3] as accidental agitation of spun-down material can lead to variations in the absorbance, so the most critical assays were run in triplicate to ensure reproducibility. The suspensions thus prepared gave absorption spectra such as those shown in Figure 1 and Figure S2 (Supporting Information). We have shown earlier that suspensions of single-walled carbon nanotubes prepared by the same sonication procedure, including the same sonicator, do not show signs of defects in the side walls of the nanotubes, as evidenced by Raman spectra (D-band intensity).[23]

Removal of unbound DNA via filtration and resuspension of nanotubes that are free of excess DNA: Figure S3 (Supporting Information) shows the steps of the assay employed in cartoon format. For the removal of free, unbound oligonucleotides from as-prepared DNA–SWCNT suspensions, Microcon centrifugal filter devices with nucleotide cut-off for double-stranded DNA of 125 and a pore size of 6–7 nm were used. Control experiments demonstrated that the membranes of these spin filters do not retain significant amounts of the DNA strands chosen, but prevent the passage of carbon nanotubes. Only the mixture of the very longest oligonucleotides ($d(GT)_{40}$ and $d(AC)_{40}$) did not pass through the membranes with near-quantitative efficiency, most probably because of the formation of long helices between overlapping stretches of DNA. Prior to filtration, the filter membrane was washed with D_2O (500 μL) by spinning down the liquid once at 14000 g for ten minutes. Then, the as-prepared DNA–SWCNT suspension (500 μL) was applied, followed by centrifugation at 14000 g for 10 min. To free the nanotubes retained on the filter membrane of any unbound DNA, fresh D_2O buffer (500 μL) was applied, followed by centrifugation at 14000 g for 10 min. The DNA-wrapped nanotubes retained on the spin filters were recovered by inverting the filters and eluting the concentrate by spinning at 1000 g for three minutes with fresh D_2O buffer (500 μL). For some nanotube preparations, this yielded only part of the DNA-wrapped nanotubes. Shorter DNA tended to give lower recovery values. Incomplete recovery of nanotube complexes from spin columns, as measured by the relative intensity of nanotube absorption bands prior to and after filtration, was accounted for in the calculation of DNA distribution.

Distribution of DNA between solution, precipitated material and suspended SWCNTs: The amount of unbound DNA was determined by UV/Vis measurements of the combined filtrate and wash solutions after spin filtration. Even extensive washing of the nanotube material separated from the solution did not set free any additional DNA, as monitored by UV absorbance. Determination of DNA amounts in suspension of excess-free SWCNT–DNA complexes is complicated by the strong absorbance of the single-walled carbon nanotubes. Therefore, the DNA initially bound to the nanotubes was determined from the supernatant after re-suspended nanotube preparations were denatured through heating to 90 °C, resulting in the dissociation of DNA–nanotube complexes and precipitation of nanotubes. Data are uncorrected for residual DNA bound to precipitates. Incomplete recovery of nanotube complexes during spin filtration was compensated mathematically, where encountered. As mentioned in the legend to Figure 2, experiments were repeated ≥ 3 times for the longest DNA strands and the hexamers.

Thermal denaturation of SWCNT–DNA complexes as determined through absorption changes induced by flocculation: After the removal of unbound oligonucleotides, the DNA–SWCNT suspensions were subjected to thermal denaturation by heating the buffered solution to 90 °C in cuvettes placed in a spectrophotometer with thermostatable cuvette holder and internal thermosensor. An optimization study involving SWCNT suspensions prepared with $d(GT)_{20}$ had identified the temperature most suitable for denaturation studies, based on assays performed at 30, 40, 50, 60, 70, and 80 °C, monitored at 555, 650 and 730 nm. Heating to 70 °C gave little change after short periods of time and precipitated less than 50% after 5 h. Heating to 80 °C gave 13% absorbance loss after 1 h and required approx. 1 d for 90% denaturation. Only 90 °C gave sufficiently fast kinetics of flocculation. Absorbance changes induced by heat-induced flocculation (and eventual precipitation) of the nanotubes at 90 °C (Figure S7, Supporting Information) for a representative band were measured over time. Bundles are known to give broader bands than those of the monomeric nanotubes,[24] so that the gradual change in absorbance is the consequence of a multi-step process. The decrease in absorbance was monitored at 730 nm, a wavelength accessible with common UV/Vis spectrophotometers. In some cases, particularly for short DNA strands, the onset of flocculation was accompanied by forma-

tion of aggregates of nanotubes that diffuse in irregular intervals through the light path, leading to an increase in noise in the absorbance data. Half-life times for the different SWCNT–DNA preparations were reproducible within an error of 10–40%.

Acknowledgements

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