

Racemic Single-Walled Carbon Nanotubes Exhibit Circular Dichroism When Wrapped with DNA

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Single-walled carbon nanotube (SWNT) structure is defined by diameter and chiral angle, that is, the degree of helical twist of the graphene lattice along the nanotube axis.¹ With the exception of structures with high symmetry (the so-called armchair and zigzag tubes), all nanotubes are chiral, that is, the tubes of right- and left-handed helicity are enantiomers of each other.¹ The chiralities of the (6,5) nanotube and its enantiomer are illustrated in Figure 1. It has been predicted that pure SWNT enantiomers should exhibit circular dichroism (CD).^{2–5} However, measurement of the CD of carbon nanotubes has not been reported to date.

DNA, both in natural polymeric form and in synthetic oligomeric form, is an excellent surfactant for solubilization of SWNTs in water.^{7–9} Here we show that a *racemic* mixture of nanotubes exhibits CD when the SWNTs are wrapped with DNA. We attribute the observed CD signal to quantum mechanical coupling of the transition dipole moments of nanotubes and DNA, a phenomenon known as induced CD.

In this study, we used a solution of mostly (6,5) semiconducting nanotubes wrapped with the DNA oligomer d(GT)₂₀ in D₂O (see Supporting Information for sample preparation). Interaction between d(GT)₂₀ and SWNTs is very robust, and excess DNA can be removed without nanotube precipitation, indicating that the nanotube forms a stable complex with the DNA. AFM images of dry DNA–SWNT complexes suggest that the DNA wraps in a helical fashion.^{9,10}

Absorption and CD spectra of DNA-wrapped SWNTs are shown in Figure 1c. The three prominent sharp peaks in the absorption spectrum correspond to the excitonic transitions of the (6,5) SWNT: E₁₁ (associated with the fundamental band gap) at 994 nm, E₂₂ at 574 nm, and E₃₃ at 350 nm. The spectral region between 200 and 300 nm contains the E₄₄ and higher nanotube transitions as well as the electronic transitions of the DNA bases G and T. Smaller peaks at 850 and 520 nm correspond to the vibronic transitions of the G-mode phonon in E₁₁ and E₂₂.^{11,12} Very weak peaks assigned to the excitonic transitions of the minority nanotube species (8,3) and (9,1) are also present.

In the corresponding CD spectrum, peaks associated with the E₃₃, E₂₂, and E₁₁ transitions of the (6,5) nanotube are clearly evident. The signs of the CD peaks alternate (negative at 350 nm, positive at 574 nm, and negative at 994 nm), and the signal strength decreases with increasing wavelength. These features (sign alternation and increasing intensity toward higher energy) are consistent with the theoretical prediction for the CD spectrum of one SWNT enantiomer.⁵ Below 300 nm, the spectrum is more complicated, consisting of intense CD associated with electronic transitions of both nanotubes and DNA bases. Weak CD signal is also observed

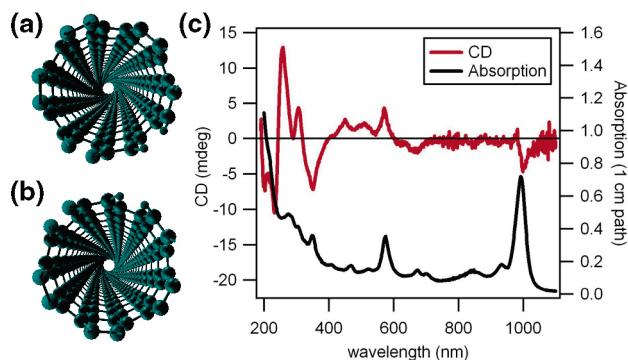


Figure 1. View along nanotube axis of (a) (6,5) and (b) (5,6) SWNT. The two structures are enantiomers with clockwise (a) and counterclockwise (b) helical direction.⁶ (c) CD and absorption spectra of a solution containing mostly (6,5) SWNTs complexed with d(GT)₂₀.

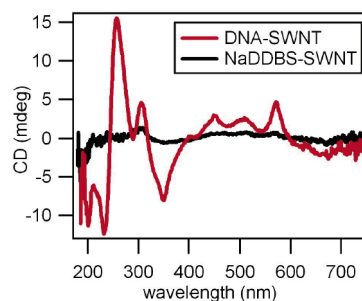


Figure 2. Comparison of CD spectra of SWNTs before (DNA–SWNT) and after (NaDDBS–SWNT) the replacement of d(GT)₂₀ with NaDDBS. The estimated degree of replacement was at least 70%.

from the minority (8,3) species (E₁₁ = 972 nm, positive; E₂₂ = 674 nm, negative). Note that the sign of CD for this species is opposite of that for (6,5).

Unlike DNA-wrapped SWNTs, nanotubes solubilized with sodium dodecyl benzenesulfonate (NaDDBS), a nonchiral surfactant, do not exhibit CD. This suggests that either (i) wrapping with d(GT)₂₀ selects one nanotube enantiomer over the other, resulting in observation of CD signal inherent to a chiral nanotube, or (ii) the inherent chirality of DNA induces the CD signal in a racemic mixture of SWNTs. The key experiment to evaluate these possibilities is to replace the d(GT)₂₀ with a nonchiral surfactant, such as NaDDBS (See Supporting Information). Figure 2 shows that replacement of DNA with NaDDBS (at least 70% of the DNA removed) results in the disappearance of the nanotube CD in a sample with similar nanotube concentration. This means that the two enantiomers are present in approximately equal amounts such that their CD signals cancel out. We cannot completely discount the possibility that one enantiomer is prevalent, but with a weak, undetectable CD signal. However, this would contradict the

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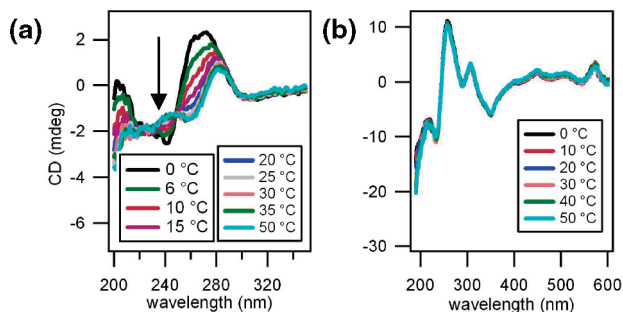


Figure 3. Temperature dependence of the CD spectra of (a) d(GT)₂₀ and (b) SWNTs wrapped with d(GT)₂₀.

theoretical prediction that the CD signal of a single nanotube enantiomer should be quite strong for the higher-energy transitions.⁵ This experiment proves that the observed CD signal is due to nanotube–DNA interaction and likely means that DNA-wrapping does not select one enantiomer over another.

We propose that the CD spectrum of the DNA–SWNT complex originates from induced circular dichroism (ICD). ICD occurs when transition dipole moments of optically active electronic transitions in a chiral molecule couple to transition dipole moments of a nearby molecule, which may or may not be chiral.¹³ The coupling can involve electronic or magnetic transition dipole moments.¹⁴ ICD has been used to elucidate the binding of host–guest complexes, including those consisting of nonchiral drug molecules and DNA.¹⁵ The theory of ICD predicts an increase in CD signal intensity as the energies of the interacting transitions approach each other.¹³ The observed increasing nanotube CD signal intensity with increasing proximity to DNA transition energy is consistent with this prediction. In principle, the ICD spectrum could provide insight into the binding geometry of the DNA–SWNT complex. However, the theoretical issues involved in extracting this information are complex and are beyond the scope of this Communication.

How do we explain the observation of nanotube CD signal when they are present as a racemic mixture? We propose that the asymmetry necessary to observe CD arises from the inherent chirality of the DNA, which causes it to wrap with a preferred chiral secondary structure on both SWNT enantiomers. This wrapping functions as an external chiral perturbation on the SWNT electrons that strengthens the intrinsic CD signal of one SWNT enantiomer relative to that of the other. The difference in coupling strength for the two enantiomers results in an overall CD signal.

Temperature-dependence of the CD spectra, shown in Figure 3, provides insight into the strength of interaction between SWNTs and the d(GT)₂₀ oligomer. Over the temperature range of 0–50 °C, the CD spectrum of d(GT)₂₀ in D₂O (Figure 3a) changes drastically, whereas the spectrum of the DNA–SWNT (Figure 3b) remains constant. In the case of d(GT)₂₀ in D₂O, the CD intensity decreases with increasing temperature, consistent with the melting of an organized secondary structure (denaturation). Although d(GT)₂₀ consists of noncomplementary bases (and, therefore, does not form a Watson–Crick double helix), CD spectra similar to those in Figure 3 have been attributed to denaturation of noncanonical double-stranded poly(GT) structures formed at high Na⁺ concentrations by hydrogen bonding via so-called wobble base pairing.^{16,17}

In contrast, the temperature-independent CD spectra of the DNA–SWNT complex point to a more strongly bound rigid DNA structure formed by π – π stacking between the bases and the nanotube sidewall. It has been suggested that d(GT)₂₀ forms a double-stranded ribbonlike structure, where the aromatic bases lie on the nanotube sidewall and the phosphate backbone interfaces with water.¹⁰

In this work, we have shown that the chiral DNA induces CD in SWNTs, which are themselves chiral but present as a racemic mixture. We attribute the nanotube CD signal to the differences in DNA–SWNT transition moment coupling for the two enantiomers, which arises from the inherent DNA chirality. We expect that further theoretical and experimental work will provide more detailed understanding of the DNA–SWNT interaction responsible for the induced CD. In addition to these fundamental considerations, our work also¹⁸ identifies CD spectroscopy as a tool for the characterization of DNA–SWNT wrapping.

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Supporting Information Available: Sample preparation and supporting absorption and CD spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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