Enantiomers of Single-Wall Carbon Nanotubes Show Distinct Coating Displacement Kinetics

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ABSTRACT: It is known that specific oligomers of single-stranded DNA (ssDNA) can show remarkable selectivity when coating different structural species of single-wall carbon nanotubes (SWCNTs). We report that (ATT)₄ ssDNA coatings strongly distinguish between the two optical isomers of (7,5) SWCNTs. This causes resolvable shifts in their fluorescence spectra and differences of two orders of magnitude in the room temperature rates of coating displacement, as monitored through changes in nanotube fluorescence wavelength and intensity on exposure to sodium deoxycholate. During coating displacement, the enantiomer with high affinity for the ssDNA oligomer is deduced to form an intermediate hybrid that is not observed for the low affinity enantiomer. These results reveal that enantiomeric differences in SWCNTs complexed with ssDNA are more diverse and dramatic than previously recognized.

Single-wall carbon nanotubes (SWCNTs) are a family of tubular nanomaterials that resemble rolled-up sections of graphene sheets. A variety of possible SWCNT structures exist. Each of these is designated by a pair of integers, (n,m) , and has long-range crystalline order with a well-defined diameter and roll-up angle.^{1,2} Because the π -electron bands depend on SWCNT transverse structure, each (n,m) species also has a distinct electronic character. Most are semiconducting and emit characteristic short-wave infrared fluorescence corresponding to their structure-specific band gaps.^{3,4} Nearly all (n,m) species are also chiral because they comprise two non-superimposable mirror image forms corresponding to right- and left-handed helices (termed P and M).⁵⁻⁷ Although these enantiomers have identical intrinsic electronic properties, they may be physically separated through their differing interactions with chiral materials.⁸⁻¹⁰ Recently, Zheng and coworkers have efficiently sorted SWCNT enantiomers coated with single-stranded DNA (ssDNA) using aqueous two-phase partitioning.¹¹ We find that ssDNA coatings can also greatly assist the separation of SWCNT enantiomers in nonlinear density-gradient ultracentrifugation. The major new finding reported here is that the structure-specific noncovalent interactions in a particular ssDNA-SWCNT hybrid show strong enough enantiomeric differences to cause resolvable spectral shifts in SWCNT fluorescence and dramatic kinetic differences in coating displacement.

According to the ssDNA-assisted sorting report of Zheng and co-workers and our recent discovery of selective fluorescence quenching by dissolved O_2 in ssDNA-coated SWCNTs, (7,5) SWCNTs show specific recognition by ssDNA oligos with the sequence (ATT)₄.¹¹⁻¹⁴ To further explore this unusual interaction, we suspended HiPco SWCNTs in aqueous (ATT)₄ solution with the pH stabilized at 7.4 by buffering. Figure 1a shows the fluorescence spectrum of this sample. It contains a familiar superposition of emission features from a variety of semiconducting (n,m) species whose peak wavelengths, spectral widths, and shapes differ slightly from those found in prior studies with more common surfactants. Using the approach developed previously,¹⁵ we

analyzed the sample's emission spectrum to obtain the accurate simulation plotted as the red curve in Figure 1a. The underlying components deduced in this fitting showed one anomaly: a surprisingly large full-width at half-maximum of more than 30 nm for the (7,5) feature, as compared to widths of 22.5 to 28.5 nm for other (n,m) peaks in the spectrum. We found that an accurate spectral fit was also possible assuming two distinct (7,5) emission features with plausible widths of 26 and 25 nm and peaks at 1044 and 1055 nm.

Such a splitting of the (7,5) emission might arise if the (ATT)₄ ss-DNA coatings led to significantly different dielectric environments for the two enantiomers. In this view, the (ATT)₄ ssDNA oligos more effectively coat the high affinity (7,5) enantiomer, denoted as (7,5)_{HA}, than the lower affinity enantiomer, denoted as (7,5)_{LA}. This effect should also lead to different buoyant densities of DNA-(7,5)_{HA} and DNA-(7,5)_{LA}. To test this, we applied nonlinear density-gradient ultracentrifugation to the (ATT)₄-suspended sample and successfully extracted one (7,5) band, which appeared as a distinct green layer in the upper part of the ultracentrifuge tube (see Figure S1).¹⁶ That component, termed DNA-(7,5)_{HA}, was thus found to have a significantly lower buoyant density than the other species. Figure 1b shows the fluorescence spectrum of the extracted DNA-(7,5)_{HA}. The main feature is a peak at 1055 nm whose position and width closely match the longer wavelength (7,5) emission component deduced by analyzing the spectrum of unsorted SWCNTs suspended in (ATT)₄ (Figure 1a). This agreement confirms that the unusual (7,5) emission in that spectrum arises from two (7,5) subspecies. We assign these to the nanotube enantiomers, with emission peaks of 1055 nm and 1044 nm (DNA-(7,5)_{HA} and DNA-(7,5)_{LA}, respectively).

Further experiments revealed that the difference in coating environment that causes the 11 nm (100 cm⁻¹) spectral splitting gives an even more dramatic difference in coating displacement kinetics. We measured time-sequenced fluorescence spectra after adding a solution of sodium deoxycholate (SDC), a strong nanotube surfactant, to the unsorted (ATT)₄-suspended SWCNT

mixture. Figure 2 plots the results, which are more complex than reported from prior kinetic spectroscopy studies of ssDNA displacement from SWCNTs.¹⁷⁻²⁰ Within ca. 100 s, most (n,m) emission peaks had shifted to shorter wavelengths and intensified, an expected consequence when SDC displaces ssDNA on the nanotube surface. However, the spectral region near the (7,5) emission feature (shown expanded in the figure inset) displayed much more complex changes over a range of time scales.

To investigate these changes, we analyzed kinetic spectra in the region of (7,5) emission by careful deconvolution to find the underlying components and their magnitudes as a function of time. Figure 3 shows such deconvolutions at four time points during the first 100 s of coating displacement. As listed in Table 1, we found spectral components centered at 1035, 1044, and approximately 1054 nm. Figure 4 plots the time dependence of these three emission spectra (note that the time scale of the top frame is 100 times shorter than the other two frames). The rapid decrease of the 1044 nm feature (top frame) is interpreted as the loss of the DNA-coated lower affinity enantiomer as its coating is displaced by SDC. The 1035 nm feature (bottom frame) appears within 3 seconds and grows with both rapid and slow components. We assign this feature to SDC-coated (7,5) SWCNTs of both subspecies (although SDC is a chiral surfactant, it does not cause a resolvable shift between emission peaks of the enantiomers). We hypothesize that the rapid 1035 nm kinetic component corresponds to displacement of ssDNA from the lower affinity enantiomer. Emission near 1054 nm, plotted in the center frame, also shows bimodal behavior. It quickly increases in intensity by ca. 20% during the first 15 seconds and then decreases slowly to an asymptotic level as the peak wavelength shifts slightly from 1055 to 1053 nm. We assign this feature to the high affinity (7,5) enantiomer, which is coated initially with (ATT)₄ ssDNA. In our model, the rapid increase in its emission intensity reflects the formation of a secondary coating of SDC, which may fill some of the gaps in the DNA surface coverage or adsorb as an additional layer. The subsequent intensity decrease near 1054 nm is caused by a

blue shift of the emission peak to 1035 nm as SDC becomes the inner coating in a reversible displacement that leaves DNA in an outer layer (see step with k_3 in the scheme below).

These processes are summarized in the following proposed kinetic scheme:

Here, k_1 and k_2 are pseudo-first order rate constants that depend on the concentration of free SDC, and k_3 and k_{-3} describe the reversible reorganization of mixed coatings of SDC and DNA on the high affinity (7,5) nanotubes. Note that because our SWCNT samples likely contain a variety of specific surface coating structures for each species in the scheme above, the use of simple kinetic models with precisely defined rate constants will be less successful than for homogenous molecular systems. Nevertheless, the model shown above allows adequate kinetic fits to the data. These are shown as the computed solid curves in Figure 4. The deduced rate constant values are 0.067 s^{-1} for k_1 , 0.30 s^{-1} for k_2 , $5.8 \times 10^{-4} \text{ s}^{-1}$ for k_3 , and $4.6 \times 10^{-4} \text{ s}^{-1}$ for k_{-3} . Our simulations also use a value of 1.3 (determined from the peak in Figure 4b) for the emissive quantum yield ratio of SDC/DNA-(7,5)_{HA} compared to DNA-(7,5)_{HA}, and a value of 0.38 for the initial concentration

ratio $\frac{[\text{DNA-(7,5)}_{\text{LA}}]_0}{[\text{DNA-(7,5)}_{\text{HA}}]_0}$. The spectral deconvolution shown in Figure 1a indicates that the

product of initial concentration and emissive quantum yield is greater for the high affinity than for the low affinity species in our ATT₄-dispersed sample, although we do not know the separate roles of these factors. In our ambient temperature measurements, the ratio of time scales for displacement, corresponding to k_1 / k_3 , is approximately 115. Assuming similar kinetic pre-factors, this suggests an activation energy difference of ca. 12 kJ/mol ($5 k_{\text{B}}T$) between enantiomers. This result may aid computational efforts to clarify the energetic factors controlling SWCNT enantiomer recognition by ssDNA.^{18,21,22}

The pseudo-first order rate constants k_1 and k_2 given above were deduced for an initial SDC concentration of 4.8×10^{-4} M. Surprisingly, we observed a highly nonlinear dependence of these rate constants on SDC concentration, with a kinetic partial order estimated as approximately 5 (see Supporting Information). We suggest that this reflects the dominant role of small molecular clusters of SDC, rather than individual molecules, in the coating displacement mechanism. Although it is not included in the kinetic scheme, higher SDC concentrations (such as used for the run of Figure 2) or longer incubations lead to the irreversible conversion of DNA-(7,5)_{HA} into SDC-(7,5)_{HA}.

We have previously reported that dissolved O₂ can partially quench the fluorescence of SWCNTs in aqueous ssDNA dispersions, and that the extent of this quenching reveals selective affinities between specific ssDNA oligos and specific (n,m) species.¹⁴ Consistent with the kinetic findings described above, we observe large differences in dissolved oxygen fluorescence quenching of DNA-(7,5)_{LA} compared to DNA-(7,5)_{HA}. The quenching is much stronger for the DNA-(7,5)_{LA} enantiomer, as expected for less complete coverage of the nanotube surface and greater exposure to dissolved species. Details of enantiomer-specific O₂ quenching will be reported separately.

In summary, we have used fluorescence spectroscopy to uncover strongly enantiomer-specific coating displacement kinetics for (7,5) SWCNTs suspended by ssDNA oligos with the structure (ATT)₄. The enantiomeric selectivity of this ssDNA coating creates two sub-populations with distinct emission wavelengths and buoyant densities, in addition to dramatically different rates and mechanisms of displacement by added SDC. While the lower affinity enantiomer is displaced in seconds by ca. 5×10^{-4} M SDC, the higher affinity enantiomer is deduced to quickly acquire a secondary coating of SDC that dislodges the ssDNA layer on a time scale approximately 100 times longer than displacement from the lower affinity form. This study

shows that the wide range of physicochemical properties displayed by single-wall carbon nanotubes is significantly expanded by distinguishing their left- and right-handed enantiomers.

ASSOCIATED CONTENT

Supporting Information

Details of materials and sample preparation; nonlinear DGU sorting; photoluminescence measurements; and effect of SDC concentration on displacement kinetics. The Supporting Information is available free of charge on the ACS Publications website.

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Notes

The authors declare the following competing financial interest: R.B.W. has a financial interest in Applied NanoFluorescence, LLC, which manufactures one of the instruments used in this study.

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Table 1. (7,5) SWCNT Species Involved in the Coating Displacement Study

species	symbol	emission peak (nm)	relative quantum yield	kinetics	notes
(7,5) enantiomer 1 in (ATT) ₄ ssDNA	DNA-(7,5) _{LA}	1044	low	fast decay	low affinity hybrid
(7,5) enantiomer 2 in (ATT) ₄ ssDNA	DNA-(7,5) _{HA}	1055	low	complex	high affinity hybrid
(7,5) enantiomer 1 in SDC	SDC-(7,5) _{LA}	1035	high	fast rise	enantiomer 2 in sodium deoxycholate
(7,5) enantiomer 2 in SDC and (ATT) ₄	DNA/SDC-(7,5) _{HA}	1035	high	slow rise	enantiomer 1 with primary coating of sodium deoxycholate, secondary of DNA
(7,5) enantiomer 2 in (ATT) ₄ and SDC	SDC/DNA-(7,5) _{HA}	1053	medium	fast rise	enantiomer 1 with primary coating of DNA, secondary of sodium deoxycholate

Figure 1. (a) Measured (symbols) and simulated (solid red curve) fluorescence spectrum of an unsorted bulk SWCNT sample suspended in (ATT)₄ ssDNA solution (642 nm excitation). Thin black curves show the deduced emission components from different (*n,m*) species. Components between 900 and 1200 nm represent specific known (*n,m*) species, but those between 1200 and 1400 nm do not. Deduced emission spectra assigned to the two (7,5) enantiomers are drawn in pink and blue. (b) Fluorescence spectrum of a (7,5)-enriched SWCNT sample suspended in (ATT)₄ solution. The spectrum is dominated by the component shown as a blue trace (DNA-(7,5)_{HA}).

Figure 2. Time-resolved fluorescence spectra for SWCNTs dispersed in (ATT)₄ during displacement by SDC. The traces were measured at 0, 1, 2, 3, 4, 5, 10, 30, 150, 390, and 800 minutes after exposure to 6.3×10^{-4} M SDC. The inset shows spectral changes in the region of (7,5) emission.

Figure 3. Measured (symbols) and simulated (solid red curves) fluorescence spectra of a bulk SWCNT sample in the range of (7,5) emission. The green curve represents the emission from low affinity DNA-(7,5)_{LA}; the blue curve represents the emission from high affinity DNA-(7,5)_{HA}; the orange curve represents the emission from SDC-(7,5). (a) Emission from SWCNTs suspended in (ATT)₄ solution just before SDC addition, (b) at 3 s after addition, (c) at 7 s, (d) at 100 s.

Figure 4. Deduced species-resolved fluorescence kinetics during displacement of ssDNA coating by SDC. (a) species with emission peak at 1044 nm, assigned as DNA-(7,5)_{LA}; (b) species with emission peak near 1054 nm; (c) species with emission peak at 1035 nm, assigned as SDC-(7,5). Note that the time scale in (a) is 100 times shorter than in (b) and (c). Symbols are experimental points and solid curves show kinetic simulations using parameters given in the text.