Supporting Information

Resonance Raman Optical Activity Spectra of Single-Walled Carbon Nanotube Enantiomers

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S1. Density gradient ultracentrifugation (DGU) of (6,5) SWCNTs

Figure S1. Enantiomers of (6,5) SWCNTs separated by nonlinear DGU. Left: photo of centrifuge tube before fractionation of the two distinct colored layers. Right: Normalized fluorescence spectra of the two extracted fractions, along with a photo showing samples accumulated from 8 centrifuge tubes.
S2. Radial Breathing Modes (RBMs) in DGU-separated (6,5) SWCNTs

In addition to UV/Vis, electronic circular dichroism (ECD) and 2D Emission/Excitation plots (Figure 2), we also used the RBM in Raman spectra to characterize impurities in the prepared SWCNT samples (Figure S2).\(^1\) Figure S2a shows the RBM region for excitation at 2.33 eV (532 nm). Three RBM features can be identified, originating from (6,5), (10,0) and (9,3) SWCNTs. We assign the signals at 309 cm\(^{-1}\) to (6,5) SWCNTs. The weak RBM signal at first seems inconsistent with the PL excitation-emission plots, which show strong enrichment in (6,5) SWCNTs (Figure 2c). However, the intensity pattern of RBM features reflects the fact that our 532 nm Raman laser is off-resonance for the (6,5) species but very near resonance for the (9,3) and (10,0) species, greatly intensifying their RBM signals. In addition, the RBM intensity is predicted to be 5 times larger for (10,0) SWCNTs than for (6,5) adding to the comparably large RBM intensity of this species.\(^2\) Using 1.96 eV (633 nm) Raman excitation wavelength, the (7,5) and (7,6) species can be resonantly excited, giving rise to RBM peaks at 282 and 263 cm\(^{-1}\) (Figure S2b and Figure S2c). Spectral signatures for (7,5) and (7,6) are also detectable in the PL excitation-emission plots at 633 nm excitation wavelength, although they are about \(10^2\) times the intensity of the corresponding (6,5) peak.
Figure S2. Raman spectra of our samples in the RBM region for different laser sources. a) 2.33 eV (532 nm) laser with 48 mW power, measured on bulk suspensions for 240 min. b) and c) 1.96 eV (633 nm) laser, measured using a Raman microscope on films deposited on glass slides for 2 s.
S3. Raman raw data

For further analysis we removed the emissive background in the raw Raman spectra. We fitted the baseline with spectral regions without SWCNT Raman bands using a 5th order polynomial function. This baseline was then subtracted from the raw data as shown in Figure S3.

Figure S3. Raw and baseline-subtracted Raman spectra of DGU-separated SWCNT samples. Experimental conditions were 2.33 eV excitation, 48 mW laser power, and 240 min accumulation time.
S4. Effect of surfactants SDS and SC on Raman spectra

Figure S4 shows Raman spectra of DGU-separated (6,5) SWCNTs as well as Raman spectra of surfactant dispersed CoMoCAT SWCNTs which also contain (6,5) SWCNTs as an abundant species. Sodium dodecyle sulfate (SDS, 2 wt%) and sodium cholate (SC, 2wt%) were used as surfactants. The intensity scale for DGU-separated SWCNTs is shown on the right hand side and is in the order of $10^3$ larger compared to the intensity of SDS and SC dispersed CoMoCAT SWCNTs. The RBM, IMF, D-band and iTOLA features are highlighted. For comparison the Raman spectra of a 10 wt% solution of SC in water are also shown. The effect of the surfactant on the Raman spectra is only minor with two SC traces highlighted at 473 cm$^{-1}$ and 1455 cm$^{-1}$.

Figure S4. Surfactant effect on Raman spectra of DGU-separated as well as surfactant-dispersed SWCNTs. Spectra have been normalized with regard to accumulation time and laser power. Note that the Raman intensity for DGU separated SWCNTs is shown on the right and is in the order of $10^3$ larger than for surfactant-dispersed spectra. For all other spectra, the Raman intensity is shown on the left.
S5. Calculation of anisotropy factor and ROA-to-Raman ratios

The anisotropy factor $g_{ECD}$ for the $E_{22}^S$ absorption at 570 nm was calculated using eq S1, in which $A$ represents the maximum absorption taken from UV/Vis and $A_L - A_R$ is the maximum absorption taken from ECD spectra.

$$g_{ECD} = \frac{A_L - A_R}{A} = \frac{[mdeg]}{32980\times A}$$  \hspace{1cm} \text{(S1)}

We determined $g_{ECD}$ to be $-1.4 \times 10^{-3}$ and $9.7 \times 10^{-4}$ for the (-)-(6,5) and (+)-(6,5) SWCNTs sample. ROA-to-Raman ratios $\Delta$ were calculated for both enantiomers of (6,5) SWCNTs using the band integral in the RROA spectrum ($g_\omega$) and Raman spectrum ($f_\omega$) as shown in eq S2.

$$\Delta = \frac{I_R - I_L}{I_R + I_L} = \frac{\int g_\omega d\omega}{\int f_\omega d\omega}$$  \hspace{1cm} \text{(S2)}

Table S1. SCP-RROA to RR ratios ($\Delta$) obtained for DGU-separated (6,5)-SWCNT enantiomers at 2.33 eV laser excitation energy.

<table>
<thead>
<tr>
<th>Mode</th>
<th>(-)-(6,5)-SWCNT$^a$</th>
<th>(+)-(6,5)-SWCNT$^{a,b}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RBM</td>
<td>$9.8 \times 10^{-4}$</td>
<td>$-3.2 \times 10^{-4}$</td>
</tr>
<tr>
<td>IMF</td>
<td>$9.6 \times 10^{-4}$</td>
<td>$-1.6 \times 10^{-4}$</td>
</tr>
<tr>
<td>$G^+$</td>
<td>$7.3 \times 10^{-4}$</td>
<td>$-4.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>$G^-$</td>
<td>$5.5 \times 10^{-4}$</td>
<td>$-4.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>iTol</td>
<td>$11 \times 10^{-4}$</td>
<td>$-10 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

$^a$ after removal of background in Raman spectra  
$^b$ corrected for offset in SCP-RROA between 900-1500 cm$^{-1}$

Table S1 summarizes the results for selected Raman modes in the SWCNT spectra.
S6. SCP-ROA spectra of chiral sodium cholate (SC)

Figure S5 shows SCP-ROA spectra of the chiral surfactant SC. SCP-ROA signals in 10 wt% solution of SC surfactant (0.24 M) are in the order of $10^{-5}$ compared to SCP-RROA spectra of the SWCNT enantiomers. On the other hand this illustrates the strong resonance enhancement of SWCNT SCP-RROA spectra.

**Figure S5.** SCP-ROA of the chiral SC surfactant. All spectra have been normalized with regard to accumulation time and laser power. Bottom and middle spectra show Raman and SCP-ROA of a 10 wt% solution of SC (2.33 eV, 100 mW, 200 min). Top: SCP-ROA for a 2 wt% SC CoMoCAT suspension (2.33 eV, 48 mW, 240 min). The top spectrum is offset for clarity.

**References**
