Supplementary Information for

Static and Dynamic Raman Excitation Mapping of Chirality-Pure Carbon Nanotube Films

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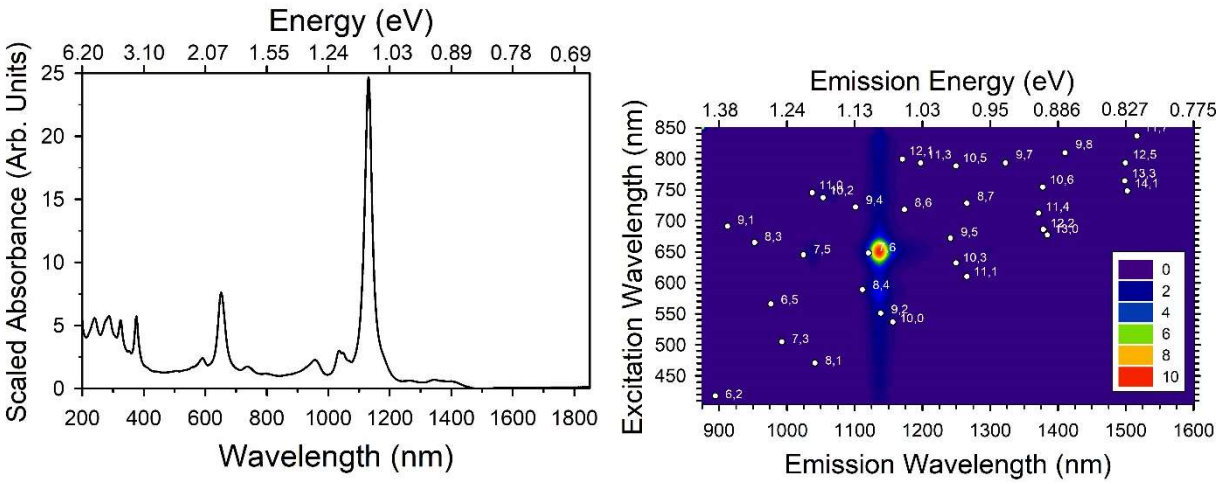
Acronyms:

highly-ordered pyrolytic graphite (HOPG)

Raman excitation mapping (REM)

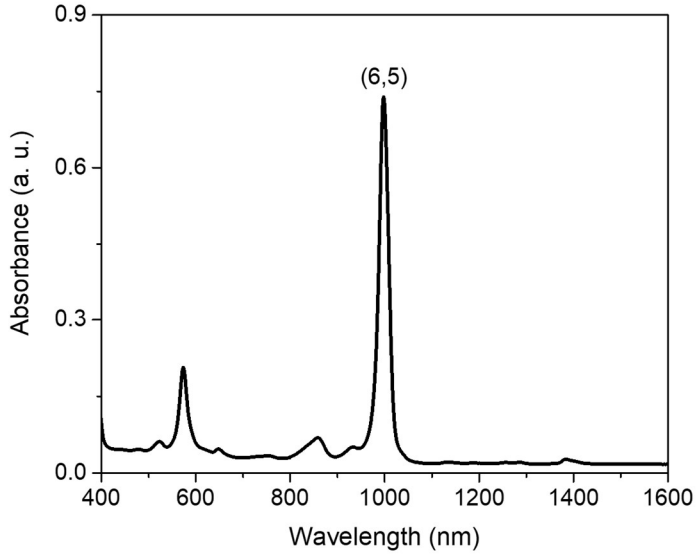
single-wall carbon nanotube (SWCNT)

poly[(9,9-dioctylfluorenyl-2,7-diyl)-alt-co-(6,6'-{2,2'-bipyridine})] (PFO-BPy)



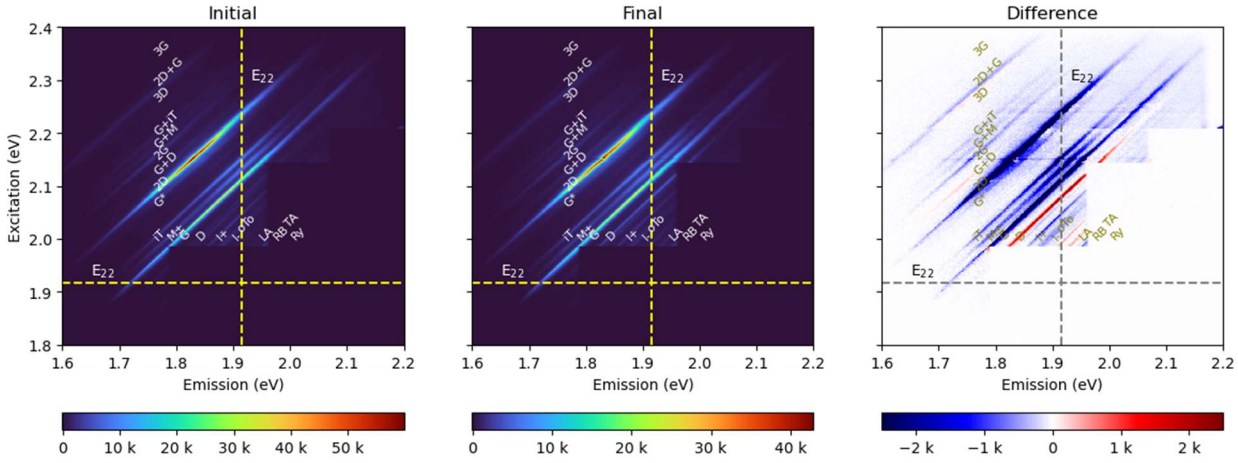
Supplementary Figure 1: Absorbance and Photoluminescence Spectroscopy of (7,6) sample

Absorbance spectrum (left) and photoluminescence excitation-emission contour plot (right) for the heavily enriched (7,6) species SWCNT sample. Measurements were made on the dispersion prior to deposition for REM measurements. The contour plot is scaled to equal 10 arbitrary units at the (7,6) emission peak. The dominant peaks in both spectroscopy methods are indicative of very high enrichment of the (7,6) and few remaining other SWCNT species. An estimate of the (7,6) chiral purity of 90% is deduced from the integrated area of the (7,6) E11 peak absorption area compared to any minor features. The PLE map indicates minor impurities of the remainder are (7,5), (11,0) and (10,2).



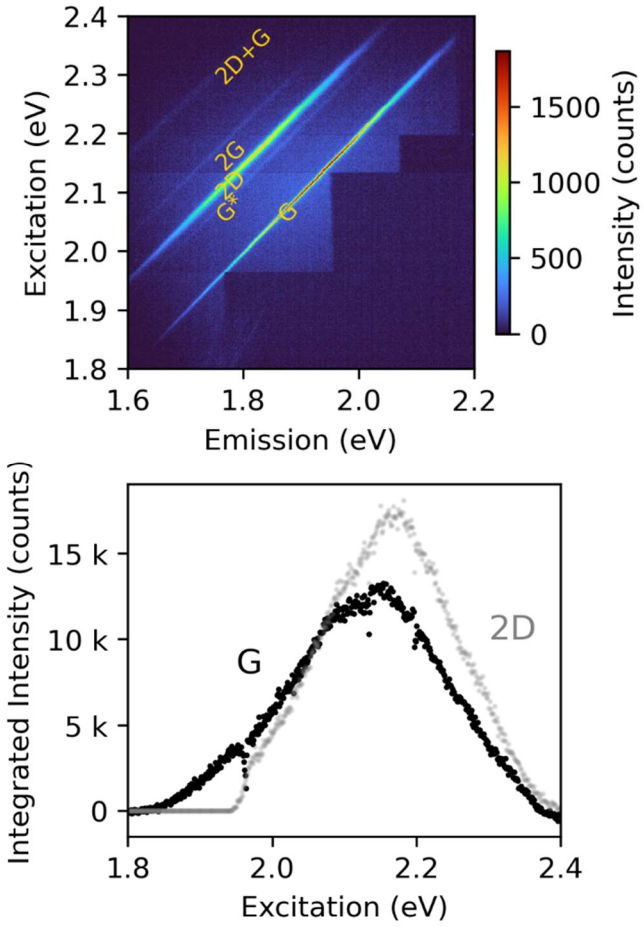
Supplementary Figure 2: Absorbance Spectroscopy of (6,5) sample

The absorption of (6,5) material dispersed in toluene using an optical path of 4 mm. An estimate of the (6,5) chiral purity of 97% was calculated based on the ratio of the integrated E_{11} peak area (from 946 nm to 1100 nm) to the total absorption above the baseline over the range 946 to 1450 nm. That purity uses the simplifying assumption that all SWCNTs absorb equally efficiently.



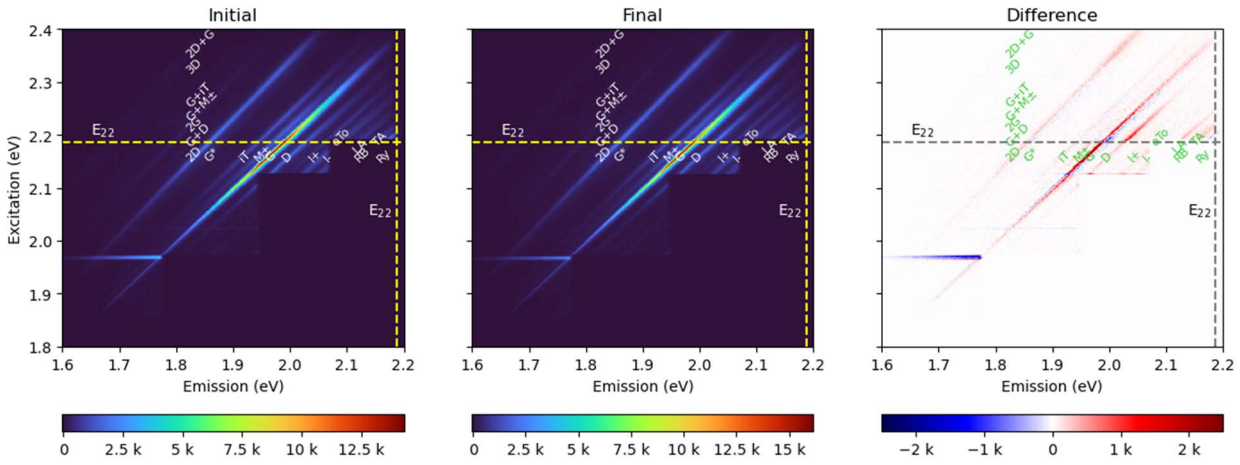
Supplementary Figure 3: **Raman Excitation Mapping of SWCNTs and Map Evolution on a Wide Scale**

Wider scale versions of the Raman excitation mapping panels presented in the main text of Figure 1. These versions are also presented on the full dynamic range scale, ≈ (0 – 60) kcounts; in the main text they are presented at a zoomed-in excitation axis (*y*-axis) and emission axis (*x*-axis) scale and a reduced intensity (color, *z*-axis) scale to better display contributions from weaker Raman scattering features.



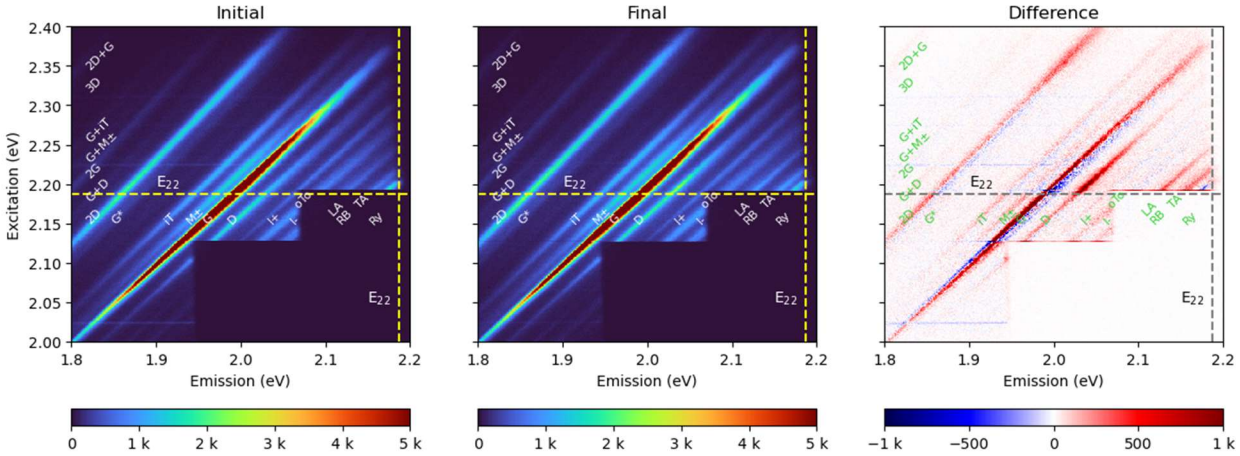
Supplementary Figure 4: Raman Excitation Map and Extracted Raman Excitation Profiles for HOPG Graphite

This mapping data is obtained from a highly-ordered pyrolytic graphite (HOPG) sample with the default instrumental configuration used for the data in Figures 1, 2, 3 and 4 of the main text and Supplementary Figures 3, 4, 5, 6 and 7. This is the integrated signal from a sum of six 10 second exposures. Its intensity can be used as reference for the system response alone. HOPG lacks the electronic and excitonic resonances which come from quantum confinement in SWCNTs so it should not show any resonances. That is, any structure is instrumental, and this is non-resonant Raman scattering. The collected intensity for HOPG is ≈ 1/1200 that of the (7,6) sample at the G band peak; see main text for details. That is a measure of the resonance enhancement in SWCNTs.



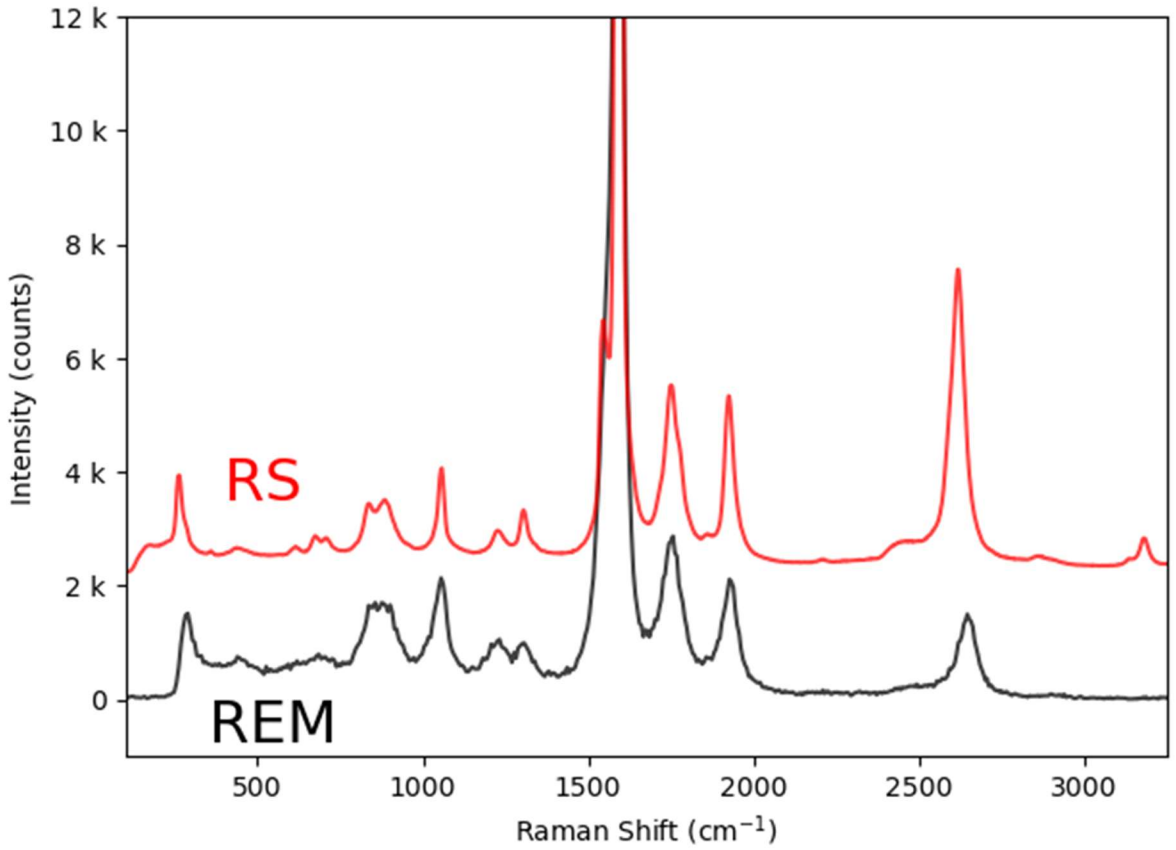
Supplementary Figure 5: Raman Excitation Mapping of (6,5) SWCNTs and Map Evolution on a Wide Scale

Unsaturated, wide scale REMs for the (6,5) SWCNT sample before (left) and after (middle) exposure as described in the main text. The difference (final – initial) of the two is shown on the right. Band labels are as described in the main text.



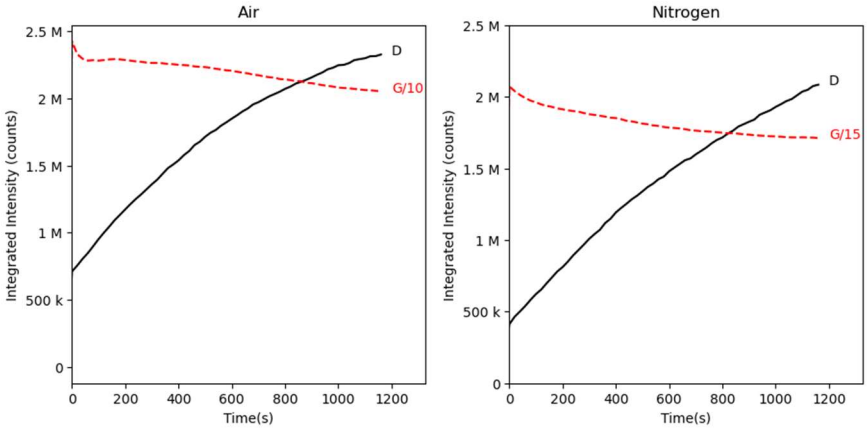
Supplementary Figure 6: Raman Excitation Mapping of (6,5) SWCNTs and Map Evolution on an Enhanced Scale

The same REMs for the (6,5) SWCNT sample as in Figure S5, but zooming in slightly in the emission axis and the excitation axis, and saturating the (*z*-axis) color scale to better reveal details from lower intensity features. Band labels are as described in the main text.



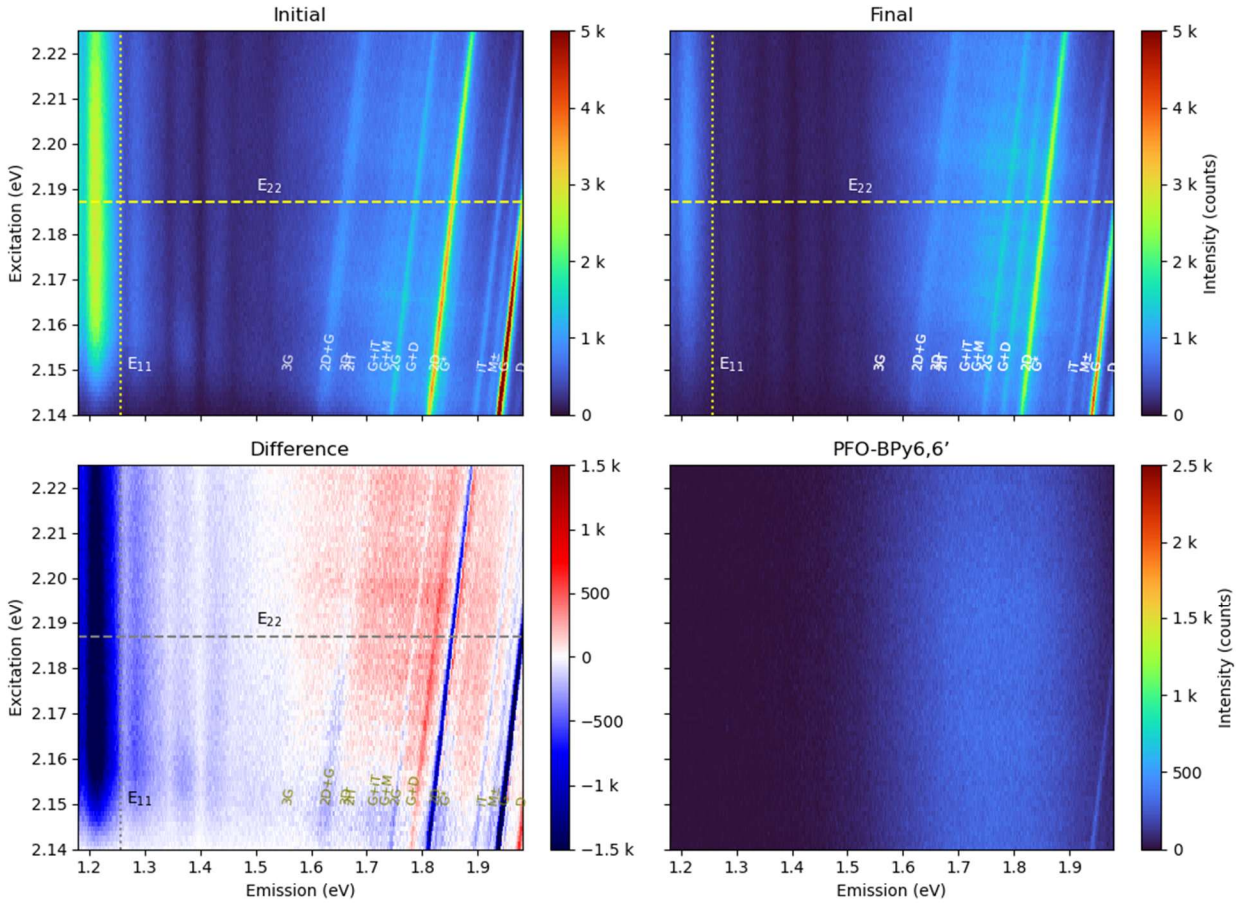
Supplementary Figure 7: Raman Spectra extracted from a Raman Excitation Map compared to Fixed Wavelength Raman Spectrum

This is a direct comparison between a Raman spectrum extracted from the Raman Excitation Map (black curve, labelled REM) in Fig. 1a, and the fixed wavelength Raman spectrum from a 632.8 nm laser (red curve, labelled RS) shown in Fig. 2 for a (7,6) nanotube film. The REM slice was taken at 621.5 nm since some peaks are obscured by filters at 632.8 nm. The red curve has been offset by adding 2000 counts. The comparison is overall excellent. The REM slice is somewhat lower resolution than the fixed wavelength RS. The quantum efficiency of the detector used in the fixed wavelength system is higher at long wavelength relative to the detector in the REM system, leading to a decrease in intensity at large Raman shift for the REM-derived spectrum. The Raman shift is calibrated precisely for the fixed wavelength RS following ASTM E1840-96 (Reapproved 2014) standards. The Raman shift for the REM is less precise, leading to small shifts along the x-axis.



Supplementary Figure 8: Integrated Peak Intensities for D and G Bands in Air and in N_2 Atmosphere.

Measured change in integrated Raman scattering intensity from the D and G bands in air (left) and in nitrogen gas (right) from (7,6) SWCNT film samples. The overall evolution was qualitatively similar in rate and in magnitude. The G bands have been divided by a constant factor of 10 (left) and 15 (right) to bring them into the same scale as the D band.



Supplementary Figure 9: Extended Emission Range Configuration Measurements

REMs for (6,5) SWNCT samples: Initial (top left), after light exposure (Final, top right), and a difference plot of the two (bottom left). The bottom right panel is a REM of a neat film of dropcast PFO-BPy without SWCNTs. Peaks are labelled in the same manner as other figures. While the emission energy calibration is highly accurate toward the right-hand side of each panel (greater energy), it is less so at the left. For these panels this results in the observed position of the E_{11} emission being slightly offset from the labelled position.

File: “M1-movie76.mp4”

Supplementary Movie 1 Time Evolution of the (7,6) Nanotube Sample Raman Excitation Map

This movie shows the photo-evolution of the (7,6) SWCNT sample Raman Excitation Map that takes place in Figure 1. Each frame is taken 20 seconds apart. The color scale is as in Fig. 1(c), (d) but with a range from 0 to 10k counts.

File: “M2-diffmovie76.mp4”

Supplementary Movie 2 Difference Plot of the Evolution of the (7,6) Sample Nanotube Raman Excitation Map

This movie shows a difference plot movie for the photo-evolution of the (7,6) SWCNT sample Raman Excitation Map that takes place in Figure 1. The first frame (t=0) is subtracted from all subsequent frames. Each frame is taken 20 seconds apart. The color scale is the same as in Fig. 1(e).

File: “M3-movie65poly.mp4”

Supplementary Movie 3 Time Evolution of the (6,5) Nanotube Sample Raman Excitation Map

This movie shows the photo-evolution of the (6,5) SWCNT sample Raman Excitation Map which takes place in Figure 5. Each frame is taken 20 seconds apart. The color scale is the same as in Fig. 5(a), (b).

File: “M4-diffmovie65poly.mp4”

Supplementary Movie 4 Difference Plot of the Evolution of the (7,6) Sample Nanotube Raman Excitation Map

This movie shows a difference plot movie for the photo-evolution of the (7,6) SWCNT sample Raman Excitation Map that takes place in Figure 5. The first frame (t=0) is subtracted from all subsequent frames. Each frame is taken 20 seconds apart. The color scale is the same as in Fig. 5(c). This movie runs past the frame in Figure 5b.

File: “M5-rolldiffmovie76.mp4”

Supplementary Movie 5 Rolling Difference Plot of the Evolution of the (7,6) Sample Nanotube Raman Excitation Map

This movie shows the rolling difference between frames as a function of time. That is, it shows the difference between the $(n+1)^{th}$ frame and the n^{th} frame. The purpose of this plot is to show a more step-by-step view of the differences than is captured in the difference movie of Movie M2. This is for the photo-evolution of the (7,6) SWCNT sample Raman Excitation Map that takes place in Figure 1. Each frame is taken 20 seconds apart. The color scale is the same as in Fig. 1(e).

Supplementary Note 1: Raman Scattering Matrix Element

$$I = \left| \frac{m}{E_L - E_{eh} + i\Gamma} + \frac{M}{E_L - \left(E_{eh} + E_p\right) + i\Gamma} \right|^2$$

A simple model of the resonance Raman scattering intensity I for laser of energy E_{L} on an electronic/excitonic resonance E_{eh} for a phonon of energy E_{p} and a lifetime Γ where m is the matrix element for the excitation resonance and M is the matrix element for the emission resonance. After Supplementary Reference [1].

Supplementary Reference

Duque, J. G. *et al.* Violation of the Condon approximation in semiconducting carbon nanotubes. *ACS Nano*. **5**, 5233 – 5241 (2011).