Supporting Information:

Confirmation of K-Momentum Dark Exciton Vibronic Sidebands Using ^{13}C-labeled, Highly Enriched (6,5) Single-walled Carbon Nanotubes

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Experimental Details

Two types of SWCNTs were prepared by the CoMoCAT® process. One sample, hereafter denoted "12C", was prepared by the typical CoMoCAT® process,[26] using ultra-high purity ^{12}CO. The other sample, "13C", was prepared using 100% ^{13}CO (Cambridge Isotope Laboratories). Briefly, one gram of calcined catalyst was set into a vertical quartz reactor of ½ inch diameter and pre-reduced under H_2 (300 sccm) for 30 minutes at 545 °C. Subsequently the temperature was raised to 680 °C under He (300 sccm). Carbon monoxide (300 sccm) was finally fed at 680 °C for 30 minutes.

The raw 12C and 13C samples were dispersed into aqueous solution using 1% (by weight) sodium cholate as a surfactant. The absorbance spectra of the un-enriched 12C and 13C samples appeared identical, and indicated that both samples contained a poly-disperse mixture of semiconducting and metallic SWCNTs, with a range of diameters. Raman spectra of the un-enriched samples (not shown) indicate a mixture of s- and m-SWCNTs, with diameters in the range of ~0.7 to 1.0 nm.

To produce highly enriched (6,5) SWCNT samples, we subjected the 12C and 13C samples to density gradient ultracentrifugation (DGU). The 1% sodium cholate dispersions were diluted with a sodium cholate solution and iodixanol density gradient to produce solutions with 2% sodium cholate solution and 25% iodixanol. The DGU conditions were identical to those described previously for enrichment by diameter.[14] The centrifuge tube was prepared with an iodixanol concentration ranging from 7.5% to 22.5%, and the SWCNT dispersions were loaded into the tube at the bottom of the density gradient. After centrifugation at 140,000 rpm in an SW41 swing-bucket rotor (207,570 x g avg. RCF), a purple band enriched in (6,5) SWCNTs was isolated at low density, at around half-height of the centrifuge tube. The 12C and 13C samples studied here were extracted just above this purple band, and appeared clear to the eye when placed into a 1 cm cuvette.

Raman spectroscopy was performed in a back-scattering configuration on the enriched samples after separation, using an excitation wavelength of 532 nm. Samples were excited in solution, and the excitation power was held to ≤ 50 mW. The slit width was 0.1 mm, allowing for a resolution of 2 – 4 cm^{-1} across the measured spectrum.

Steady-state absorbance measurements were made using a Cary 500 double beam spectrometer at a spectral resolution of 1 nm. Photoluminescence spectra were obtained in front-face configuration using a modified Fourier transform instrument with excitation provided by a tungsten lamp coupled to a monochromator. The photoluminescence excitation (PLE) map of the un-enriched 12C sample (Supporting Information) indicates a diameter range from ~0.69 – 1.05 nm. The population distriubtions are determined by creating a histogram of the integrated intensity of each peak in a particular PLE spectrum. The given percentage of a particular SWCNT is calculated as the integrated intensity of that particular SWCNT divided by the total integrated intensity of all SWCNTs within the population. A PLE intensity histogram allows us to estimate the average diameter as 0.82 +/- 0.068 nm for the un-enriched 12C sample and 0.77 +/- 0.037 nm for the enriched samples. The population distribution for the enriched 12C and 13C samples are nearly identical.

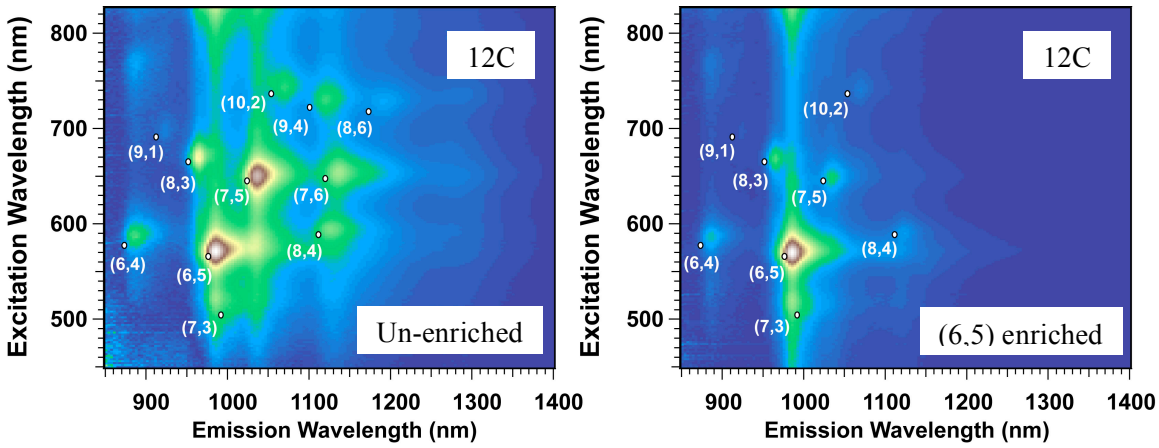

Figure S1. Photoluminescence excitation (PLE) maps of un-enriched 12C sample, compared to (6,5)-enriched 12C sample.

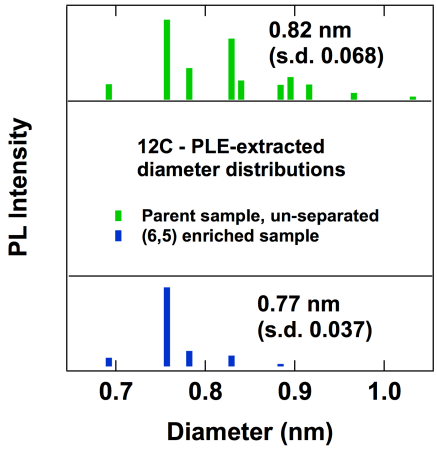

Figure S2. Diameter distributions extracted from PLE spectra of un-enriched or (6,5)-enriched 12C samples.