Supporting Information for "The Unique Origin of Colors of Armchair Carbon Nanotubes"

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METHODS

Sample Preparation:

Samples enriched in armchair SWCNTs were produced by the density gradient ultracentrifugation (DGU) technique employing a three-surfactant system as previously described (S1). SWCNTs (#1: CoMoCAT- SG65 grade, SouthWest NanoTechnologies Inc.; #2, #3, #4: HiPco- batches HPR189.2, HPR188.2 & HPR107, respectively, Rice University; #5: Laser ablation- batch JSC-385, Johnson Space Center, NASA; and #6: Arc-discharge- P2-SWNT grade, Carbon Solutions Inc.) were initially dispersed in 1% (wt./vol.) sodium deoxycholate (DOC) (sodium deoxycholate monohydrate, Aldrich, 97% purity) by bath sonication (Cole-Parmer 60W ultrasonic cleaner, model #08849-00) for 30 minutes at a starting concentration of SWCNTs of 1 g/L. The suspension was then further sonicated by probe ultrasonicator (Cole-Parmer 500 W ultrasonic processor, model # CPX-600, ¼" probe, 35% amplitude) for 6 hours while being cooled in a water bath maintained at 10°C. Lastly, the suspension was then centrifuged for 1 hour at 208,400 g average (Sorvall Discovery 100SE Ultracentrifuge using a Beckman SW-41 Ti swing bucket rotor) to remove large bundles of SWCNTs. After centrifugation, the upper 80% of the supernatant was removed for use in DGU.

For DGU, the SWCNTs were inserted into a mass density gradient composed of 1.5% (wt./vol.) sodium dodecyl sulfate (SDS) (sodium dodecyl sulfate- molecular biology or electrophoresis grade, Sigma, 99% purity), 1.5 % (wt./vol.) sodium cholate (SC) (sodium cholate hydrate, Aldrich, 98% purity), and varying amounts of iodixanol (Opti-Prep density gradient medium, Sigma, 60% (wt./vol.) solution in water) as indicated in Table S1. Each gradient layer per centrifuge tube is 2 mL in volume, starting with the highest iodixanol concentration layered first at the bottom of the centrifuge tube followed by the next highest concentration layered on top of the previous. This is repeated with each concentration of iodixanol until the entire gradient is formed.

Sample #	SWCNT Material	Iodixanol Gradient	30% Layer Composition	40% Layer Composition
1	CoMoCAT SG65	20-30% in 2.5% steps; 40% bottom layer	30% iodixanol, 1.5% SDS, 1.5% SC	SWCNTs, 40% iodixanol, 1.0% SDS, 1.0% SC, 0.33% DOC
2	HiPco HPR 189.2	20-30% in 2.5% steps; 40% bottom layer	30% iodixanol, 1.5% SDS, 1.5% SC	SWCNTs, 40% iodixanol, 1.0% SDS, 1.0% SC, 0.33% DOC
3	HiPco HPR 188.2	20-30% in 2.5% steps; 40% bottom layer	SWCNTs, 30% iodixanol, 1.0% SDS, 1.0% SC, 0.50% DOC	40% iodixanol, 1.5% SDS, 1.5% SC
4	HiPco HPR 107	20-30% in 2.5% steps; 40% bottom layer	SWCNTs, 30% iodixanol, 1.0% SDS, 1.0% SC, 0.50% DOC	40% iodixanol, 1.5% SDS, 1.5% SC
5	Laser ablation JSC-385	20-30% in 2.5% steps; 40% bottom layer	SWCNTs, 30% iodixanol, 1.0% SDS, 1.0% SC, 0.50% DOC	40% iodixanol, 1.5% SDS, 1.5% SC
6	Arc-discharge P2	20-30% in 2.5% steps; 40% bottom layer	30% iodixanol, 1.5% SDS, 1.5% SC	SWCNTs, 40% iodixanol, 2.4% SDS, 0.6% SC, 0.33% DOC

Table S1 | List of density gradient parameters used to produce samples # 1-6.

The gradient was then centrifuged for 18 hours at 208,400 g average (Beckman SW-41 Ti swing bucket rotor). The resulting separated material was then removed by hand pipetting in 200 μL fractions with the most armchair-enriched material appearing at the top of the resulting colored band. The topmost 200 μL fractions from the colored band of each centrifuge tube were combined together and then dialyzed into a 1% DOC (water) solution (Pierce, 20000 Da MW dialysis cassette). The resulting suspensions were used for all optical measurements.

Optical Measurements:

Optical absorption spectroscopy was performed in the 400-1350 nm range in 1 nm steps on an ultraviolet-visible-near-infrared, double beam spectrophotometer (Shimadzu UV-3101PC scanning spectrophotometer) through a 10 mm path length quartz cuvette using a 1% (wt./vol.) DOC (water) reference.

Resonant Raman spectroscopy was performed on all samples, except sample # 6, in a backscattering configuration with tunable dye laser excitation using Kiton Red (655 nm) & Rhodamine 6G dyes (552 nm), and frequency-doubled cw Ti:Sapphire laser (407, 455, and 500 nm) excitation. Excitation power was maintained at 25 mW. Individual Stokes-shift spectra were obtained as 5 min integrations using a charge coupled device camera mounted on a SPEX triple monochromator. The frequency of each carbon nanotube spectrum was calibrated at each excitation wavelength with the non-resonant Raman spectrum of 4-acetamidophenol. Resonant Raman spectroscopy on sample #6 was performed on a Raman microscope system (Renishaw *inVia* Raman Microscope) fitted with liquid cell holder. Excitation was performed using a diode laser (785 nm) at 60 mW excitation power. The Stokes-shift spectrum was obtained at a 1 min integration using a charge coupled device camera mounted on a single monochromator. The frequency of the carbon nanotube spectrum for sample #6 was calibrated with the

non-resonant Raman spectrum of silicon dioxide. All Raman spectra were taken at room temperature and ambient pressure.

(*n*,*m*)-composition of sample #3 via resonant Raman mapping

To further illustrate the armchair enrichment present in our samples, we display here two-dimensional contour plots of Raman intensity as a function of Raman shift in the radial breathing mode (RBM) region and excitation wavelength for sample #3 (HiPco batch 188.2). As can be clearly seen, strong enrichment occurred particularly for (7,7), (8,8), and (9,9) species as is observed in absorption measurements in Fig. 2a. Additionally, a correspondence between the most intense armchair species in Raman measurements and that in optical absorption displayed in Fig. 2a is observed with the (8,8) species dominating both followed by the (7,7) and then (9,9) species. Resonant Raman spectroscopy was performed in a backscattering configuration with tunable dye laser excitation using Kiton Red and Rhodamine 6G dyes, and frequency-doubled cw Ti:Sapphire laser excitation scanned from 680-610 nm, 615-552 nm, and 500-440 nm, respectively. Excitation power was maintained at 25 mW. Individual Stokes-shift spectra were obtained as 5 min integrations using a charge coupled device camera mounted on a SPEX triple monochromator. The frequency of each carbon nanotube spectrum was calibrated at each excitation wavelength with the non-resonant Raman spectrum of 4-acetamidophenol. Intensities were corrected for instrument response using fits to the intensities of peaks of 4-acetamidophenol and scaling the nanotube radial breathing mode spectra by the average intensity value at each excitation wavelength. All Raman spectra were taken at room temperature and ambient pressure.

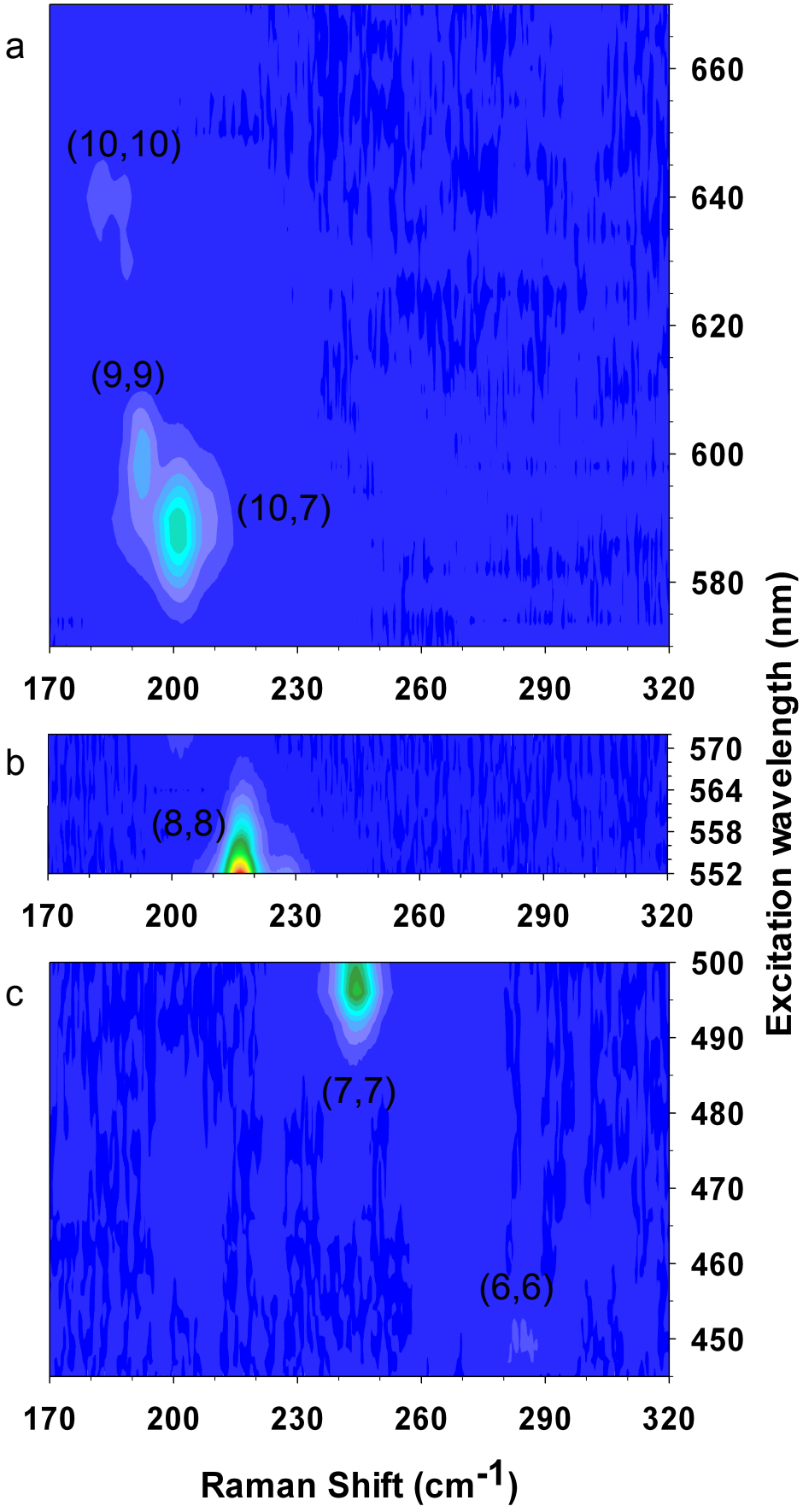

a
(10,10)
(9,9)
(10,7)
660
640
620
600
580
170
200
230
260
290
320
b
(8,8)
570
564
558
552
c
(7,7)
(6,6)
500
490
480
470
460
450
Excitation wavelength (nm)
Raman Shift (cm-1)

Figure S1. Resonant Raman scattering contour plots taken over an excitation range of (a) 572-680 nm, (b) 552-572 nm, and (c) 440-500 nm.

Additional Lorentzian fitting examples of absorption spectra for samples #3 and 4

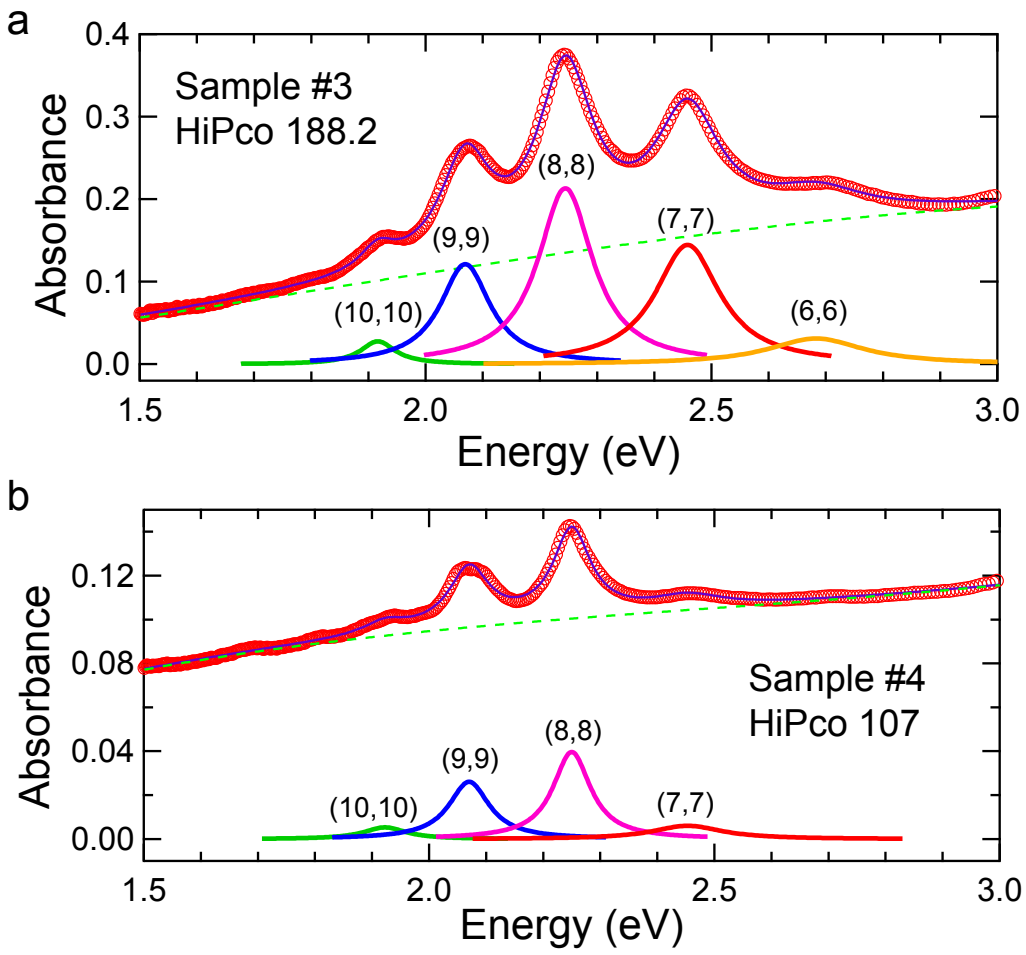
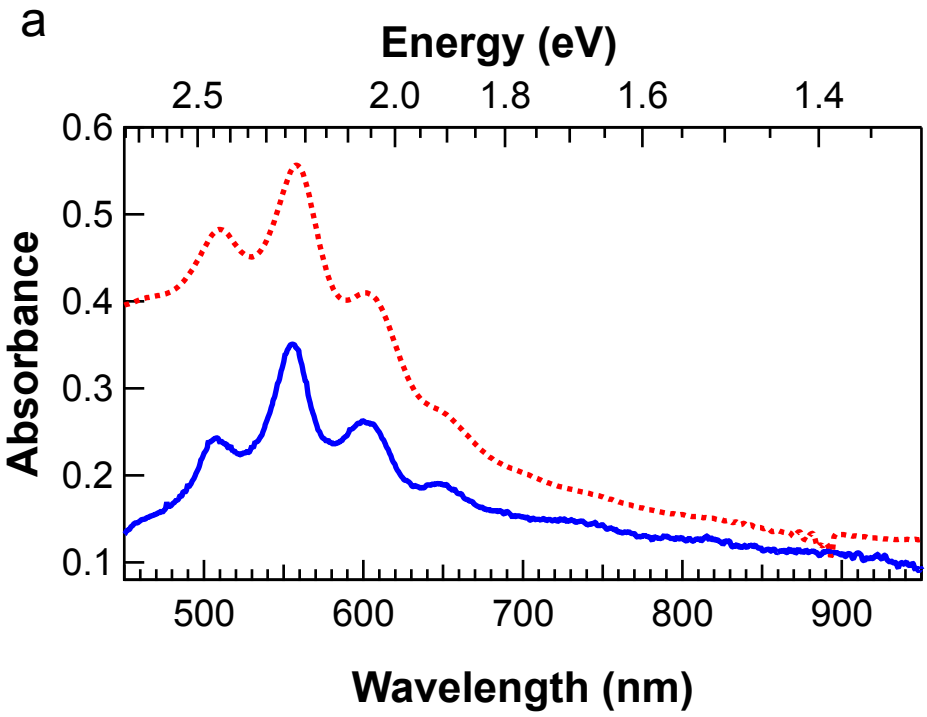


Figure S2. Additional examples of Lorentzian fitting to absorption spectra for (a) sample #3 (HiPco batch 188.2) and (b) sample #4 (HiPco batch 107).

Dependence of Armchair SWCNT Ensemble Color on Aggregate Size

Figure S3a shows optical absorption spectra for a sample similar to sample #3 of the main text (HiPco batch 188.2, prepared as described above) in both its aqueous suspension form and in a thin film form, prepared by vacuum filtration of the same aqueous suspension measured in Fig. S3, as described in Wu *et al.*[S2] It can clearly be seen that despite the large difference in aggregate size (aqueous suspensions contain individualized armchair SWCNTs whereas films contain large aggregates of SWCNTs-see supplementary fig. S3b), there is very little difference in the absorption spectra with the film spectrum showing only a very small red shift (~ 8 meV) and a slight broadening relative to the suspension spectrum. As a result, we do not believe that aggregate size can be responsible for the color mechanism in armchair carbon nanotubes but rather their diameter-dependent optical transitions.



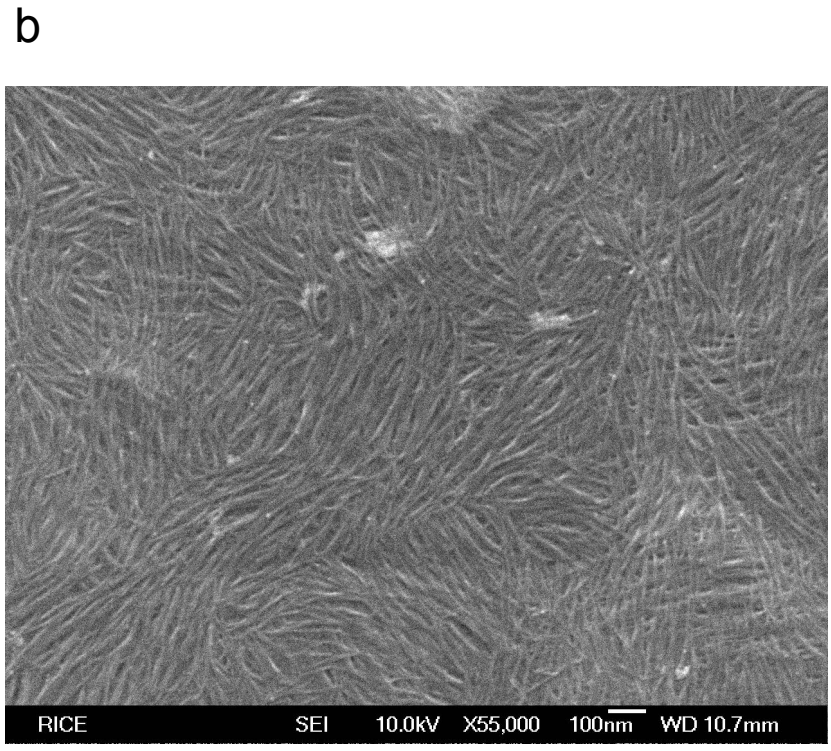


Figure S3. Optical absorption spectra for armchair SWCNTs in aqueous suspension and thin-film forms. (a) Optical absorption spectra of a sample similar to sample #3 (HiPco batch 188.2) in its aqueous suspension form (solid, blue trace) and its thin-film form

(dotted, red trace). (b) An scanning electron microscopy image of the thin-film measured in (a). Scale bar is 100-nm. (Image courtesy of Dr. Budhadipta Dan, Rice University).

Supplementary references

S1. Hároz, E. H.; Rice, W. D.; Lu, B. Y.; Ghosh, S.; Hauge, R. H.; Weisman, R. B.; Doorn, S. K.; Kono, J. *ACS Nano* **2010**, *4*, 1955-1962.

S2. Wu, Z.; Chen, Z.; Du, X.; Logan, J. M.; Sippel, J.; Nikolou, M.; Kamaras, K.; Reynolds, J. R.; Tanner, D. B.; Hebard, A. F.; Rinzler, A. G. *Science* **2004**, *305*, 1273.