

# Fluorescence quenching of dyes covalently attached to single-walled carbon nanotubes

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## Supplementary Information

Table. 1 SI. Surface concentration of dyes on dye-SWCNTs hybrids. Taken from<sup>[1]</sup>

Material SWCNT	Panacyl Bromide		Dansyl Hydrazine		Specific Surface Area
As-received	$< 10^{12}$ chrophores/cm <sup>2</sup>	$< 0.03\%$	$1.1 \times 10^{13}$ ( $\pm 0.07 \times 10^{13}$ ) chrophores/cm <sup>2</sup>	0.3%	307 m <sup>2</sup> /g ( $\pm 21$ m <sup>2</sup> /g)
Air/HCl treated	$1.5 \times 10^{13}$ ( $\pm 0.2 \times 10^{13}$ ) chrophores/cm <sup>2</sup>	0.4%	$1.9 \times 10^{13}$ ( $\pm 0.1 \times 10^{13}$ ) chrophores/cm <sup>2</sup>	0.5%	369 m <sup>2</sup> /g ( $\pm 31$ m <sup>2</sup> /g)
HNO <sub>3</sub> treated	$7.3 \times 10^{13}$ ( $\pm 0.07 \times 10^{13}$ ) chrophores/cm <sup>2</sup>	1.9%	$1.1 \times 10^{14}$ ( $\pm 0.1 \times 10^{14}$ ) chrophores/cm <sup>2</sup>	2.9%	21 m <sup>2</sup> /g ( $\pm 4$ m <sup>2</sup> /g)

The calibration plots of free dye in solutions were produced as described below. 5-dimethylaminonaphthalene-1-sulfonyl hydrazine (dansyl hydrazine) was dispersed in acetone at concentrations up to ~500 nM (537, 268, 134 and 67 nM). 4-(9-anthroyloxy)-2-bromoacetophenone (panacyl bromide) was dispersed in acetone at concentrations

between up to ~75 nM (69, 34, 17, 8.6 and 4.3 nM). The solutions were bath-sonicated for 1 hr using a Branson 5210 sonicator. Fluorescence emission spectra of these solutions were recorded immediately after sonication.

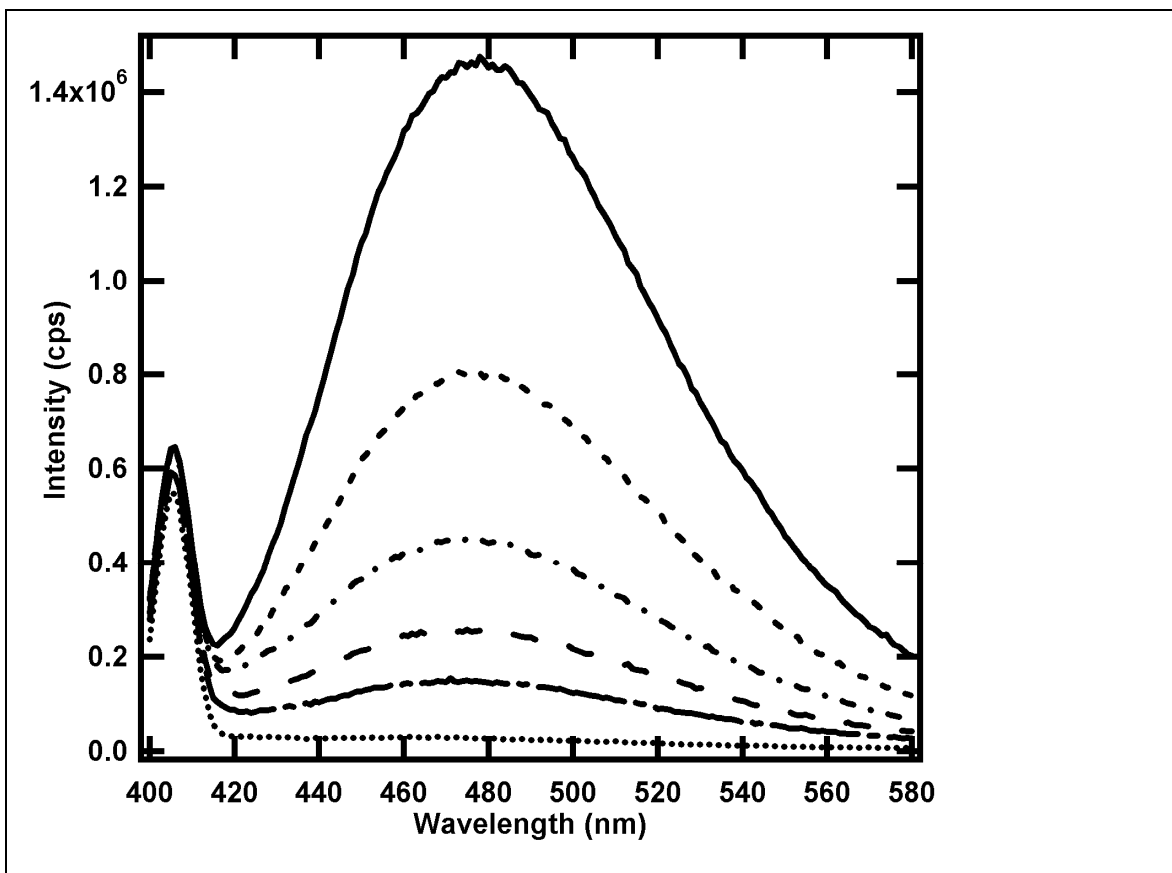
Chromophores were attached to carbon nanotubes as described elsewhere.<sup>[1]</sup> Briefly, an excess amount of chromophores was added to carbon nanotubes suspended in solvent (methanol for dansyl hydrazine and acetone for panacyl bromide). After the reactions, the chromophore-attached carbon nanotubes (dye-SWCNTs) were separated from the solutions and washed with the solvents to remove physisorbed fluorophores from the material. The washing process was repeated for several times. Fluorescence spectra of the supernatants were taken to ensure all physisorbed dyes were removed. Control experiments with deactivated dyes showed that physisorption was not significant after these procedures.<sup>[1]</sup> The dye-SWCNTs were collected by evaporating the solvent.

The dye-SWCNT solutions were prepared by dispersing dye-SWCNT material in acetone. To calculate the amount of dye-labeled SWCNTs needed in this experiment, we calculate the weight of dye-CNT material which would provide ~80 nM of panacyl bromide or ~500 nM of dansyl hydrazine in solutions, similar to the concentrations in the free dye solutions. For each dye attached to a single functional site, there is a one to one ratio between the number of chromophores and the number of functional groups needed. The value of required functional sites was then converted to the mass of the CNT using the density of functional groups on CNT surfaces and the surface area per gram coefficient determined by Dementev et al.<sup>[1]</sup>

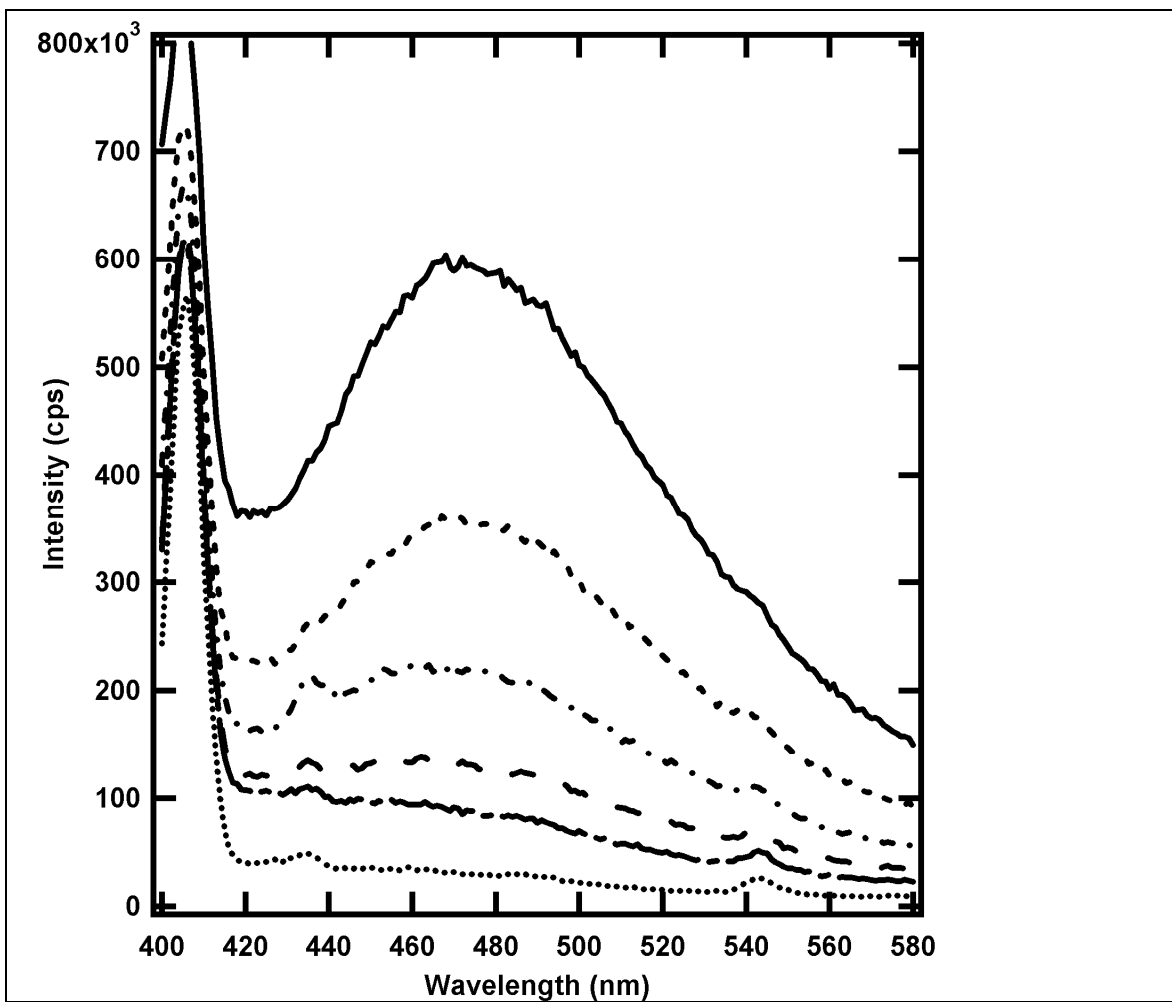
In the experiment with panacyl bromide, 1.8 mg of panacyl-bromide-attached nitric-acid-treated SWCNTs (PB-SWCNTs-HNO<sub>3</sub>) was dispersed in 50 mL of acetone

using mild sonication with a Branson 5210 sonicator for 1 hr. The solution was further diluted with acetone to the concentration of 2.88  $\mu\text{g/mL}$ , which is equivalent to 73 nM of panacyl bromide in solution. This bulk solution was diluted by a factor of 2 to concentrations similar to the free dye solutions. 1.6 mg of panacyl-bromide-attached air/HCL-treated SWCNTs and 1.0 mg panacyl-bromide-attached as-produced SWCNTs were dispersed in acetone and diluted to 2.56  $\mu\text{g/mL}$  and 1.60  $\mu\text{g/mL}$  respectively under the same procedure. SWCNTs with no chromophores were also dispersed in acetone and diluted to the same SWCNTs concentrations as the hybrid samples. These reference samples provide the SWCNT baseline signals attributed to the presence of SWCNTs alone and the calibration plots of the bare-SWCNTs were used for signal collection as mentioned in the paper.

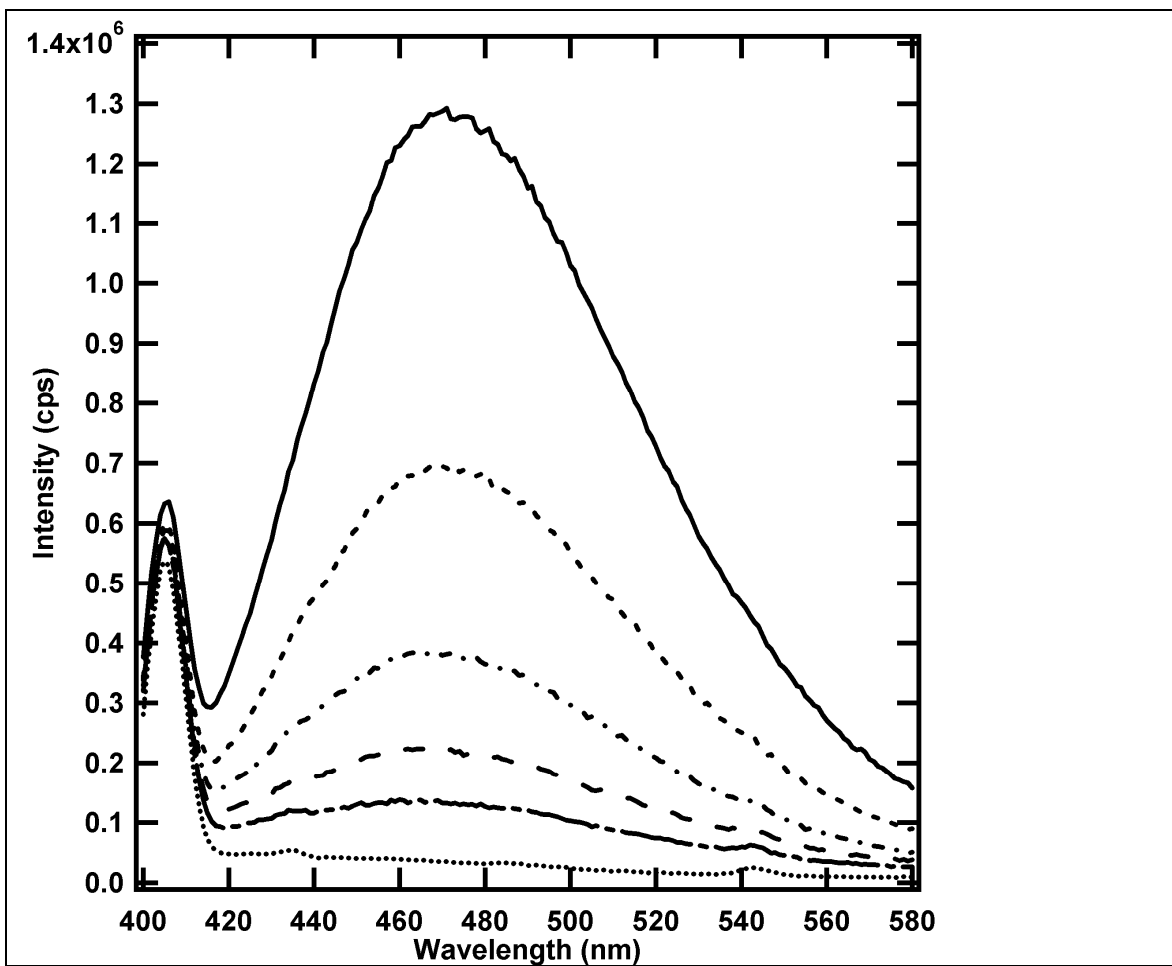
In the experiment with dansyl hydrazine, 1.8 mg as-received SWCNTs-dye hybrids, 1.1 mg of air / HCl treated SWCNT-dye hybrids and 1.6 mg nitric acid treated SWCNT-dye hybrids were dispersed in acetone, sonicated and diluted to 9.36 $\mu\text{g/mL}$ , 13.1 $\mu\text{g/mL}$  and 4.3 $\mu\text{g/mL}$  respectively. All these solutions contain ~500 nM of dansyl hydrazine, similar to the concentration used in the free dye calibrations. Dye-SWCNT hybrid solutions were diluted by a factor of 2 to produced hybrid solutions with dansyl hydrazine concentrations at 250 nM, 125 nM, 62.5 nM and 31.25 nM. Bare-SWCNTs were dispersed in acetone at the same SWCNT concentrations to provide samples for baseline corrections.



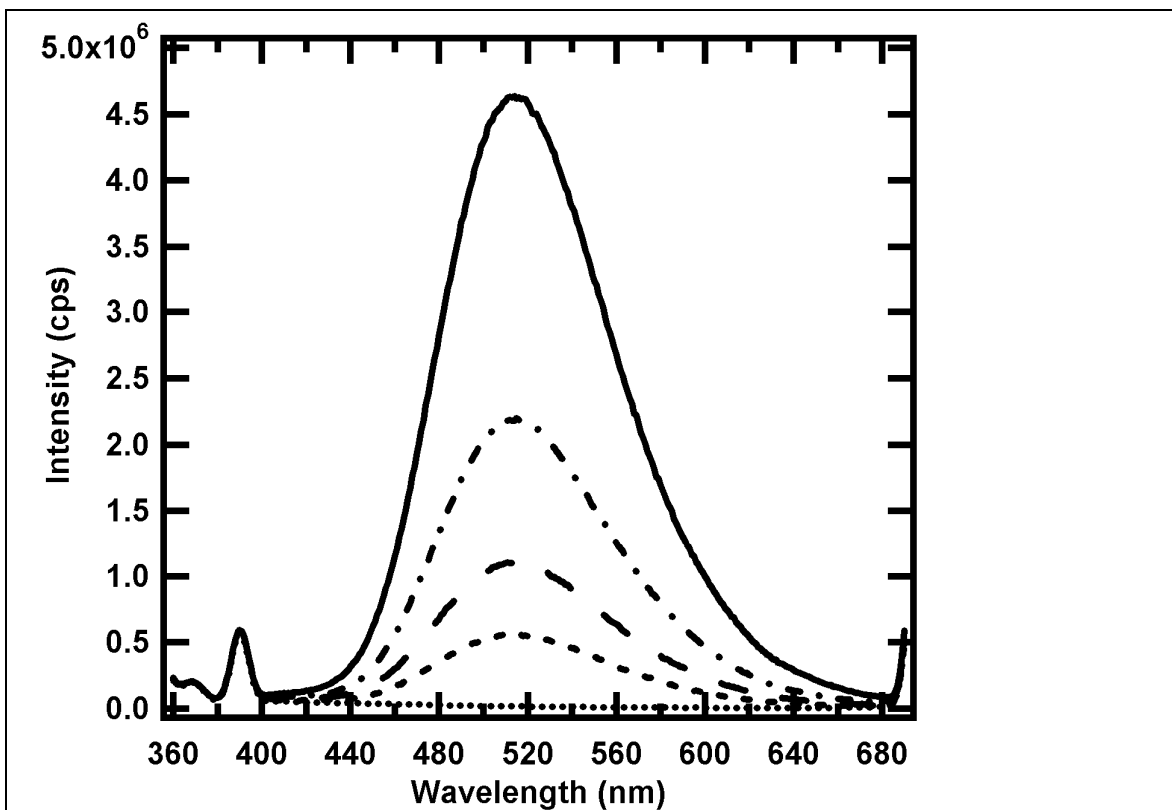
**Figure S1.** Emission spectra of panacyl bromide in acetone. Panacyl bromide concentrations from top to bottom: 69, 34, 17, 8.6, 4.3 nM and neat acetone. Excitation at 362 nm.



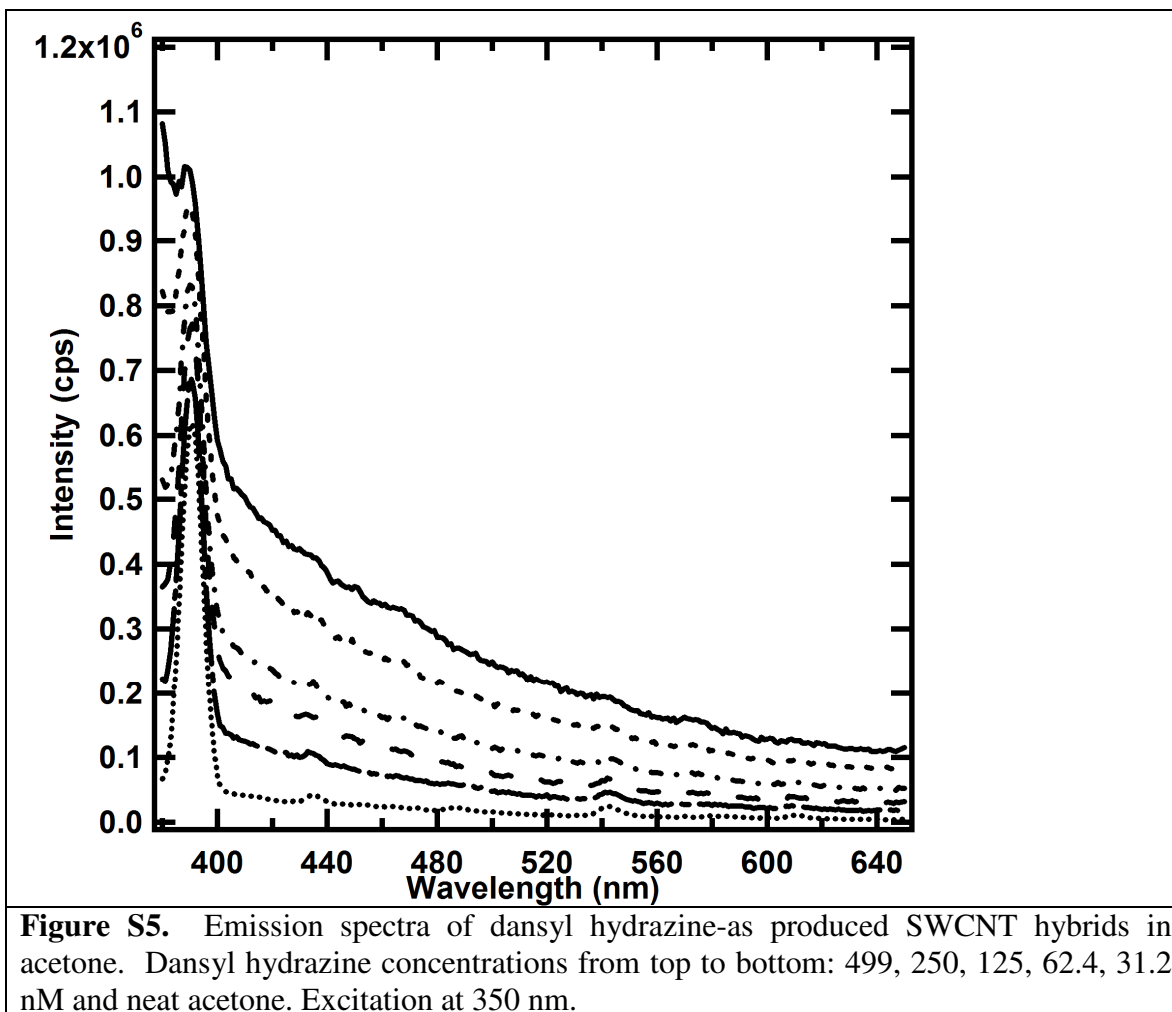
**Figure S2.** Emission spectra of panacyl bromide-as produced SWCNT hybrids in acetone. Panacyl bromide concentrations from top to bottom: 71, 36, 18, 8.9, 4.5 nM and neat acetone. Excitation at 362 nm.



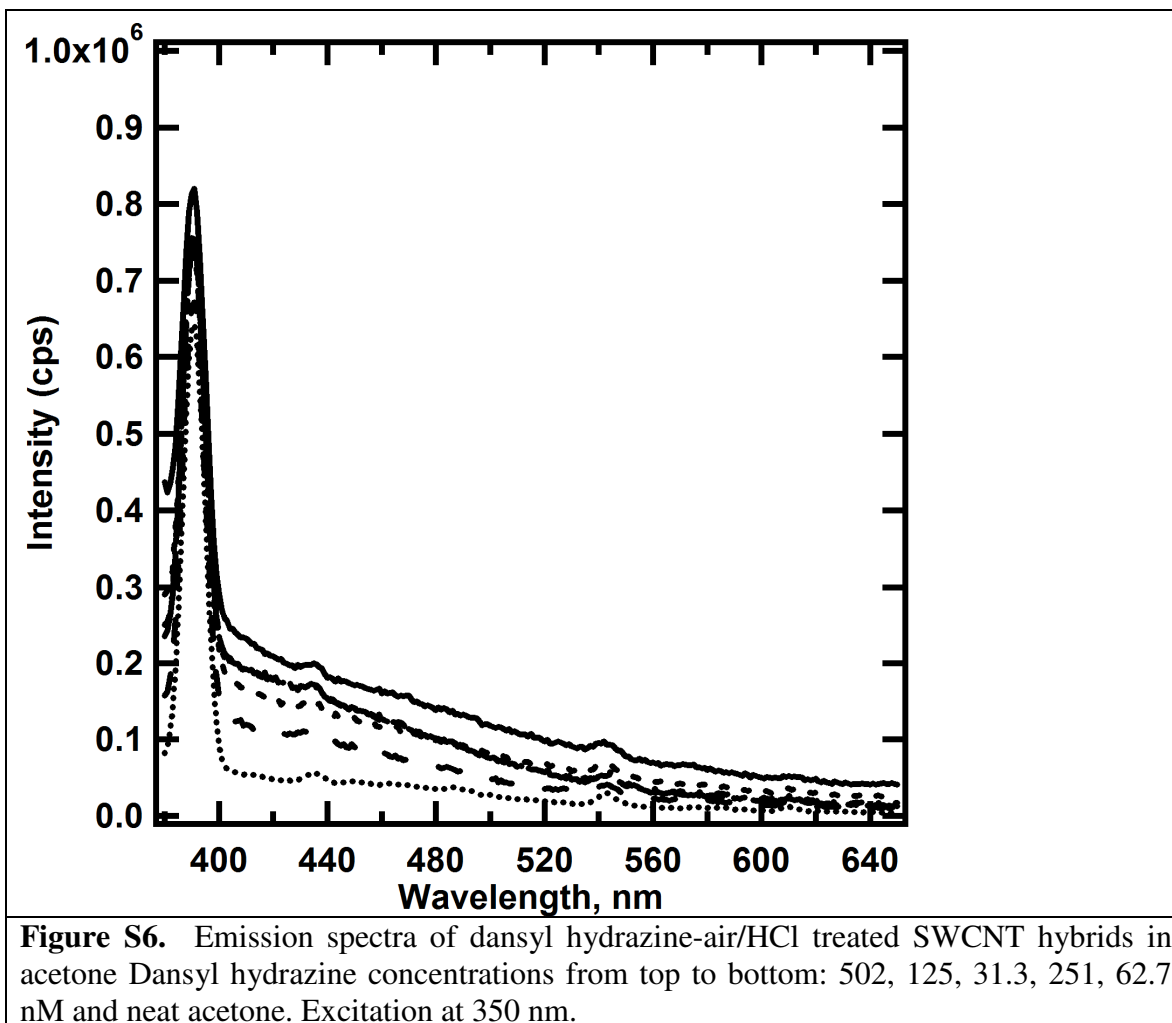
**Figure S3.** Emission spectra of panacyl bromide-nitric acid treated SWCNT hybrids in acetone Panacyl bromide concentrations from top to bottom: 73, 37, 18, 9.1, 4.6 nM and neat acetone. Excitation at 362 nm.

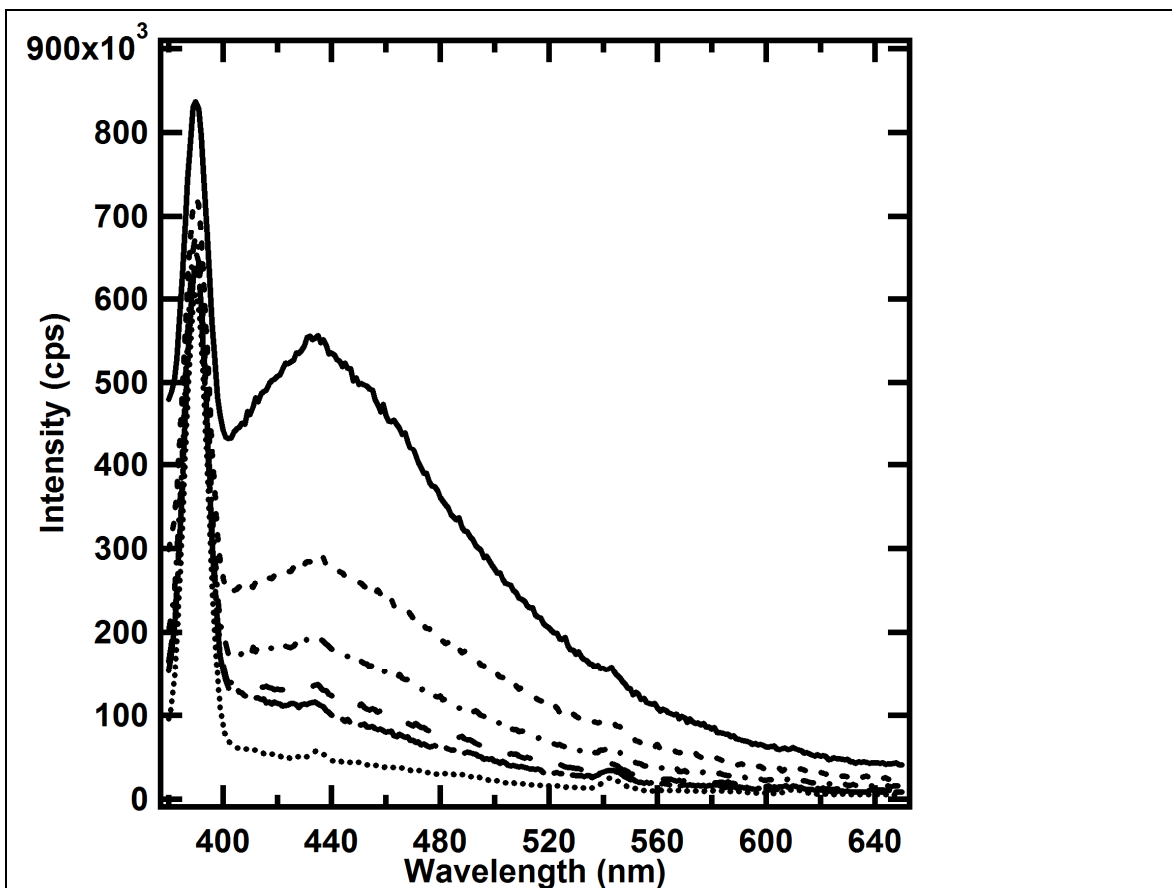


**Figure S4.** Emission spectra of dansyl hydrazine in acetone. Dansyl hydrazine concentrations from top to bottom: 537, 268, 134, 67 nM and neat acetone. Excitation at 350 nm.

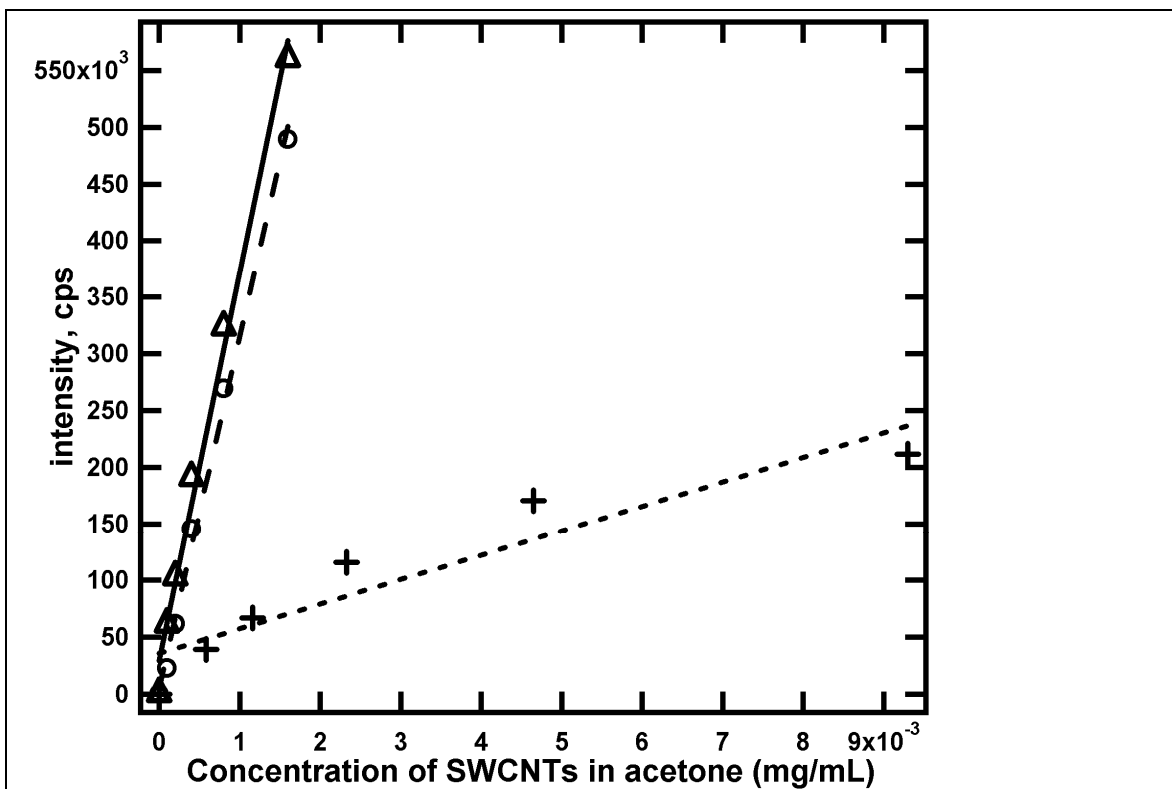




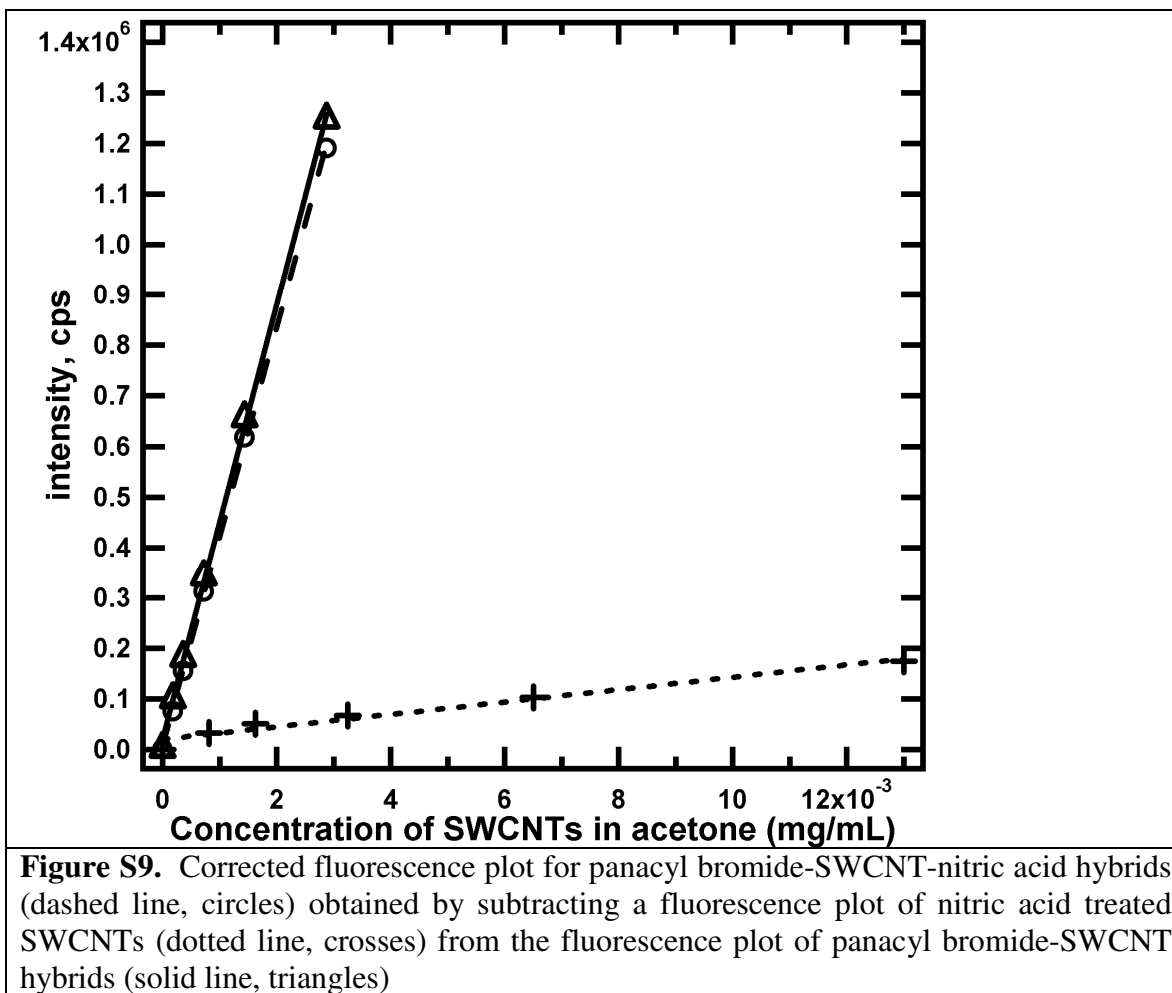


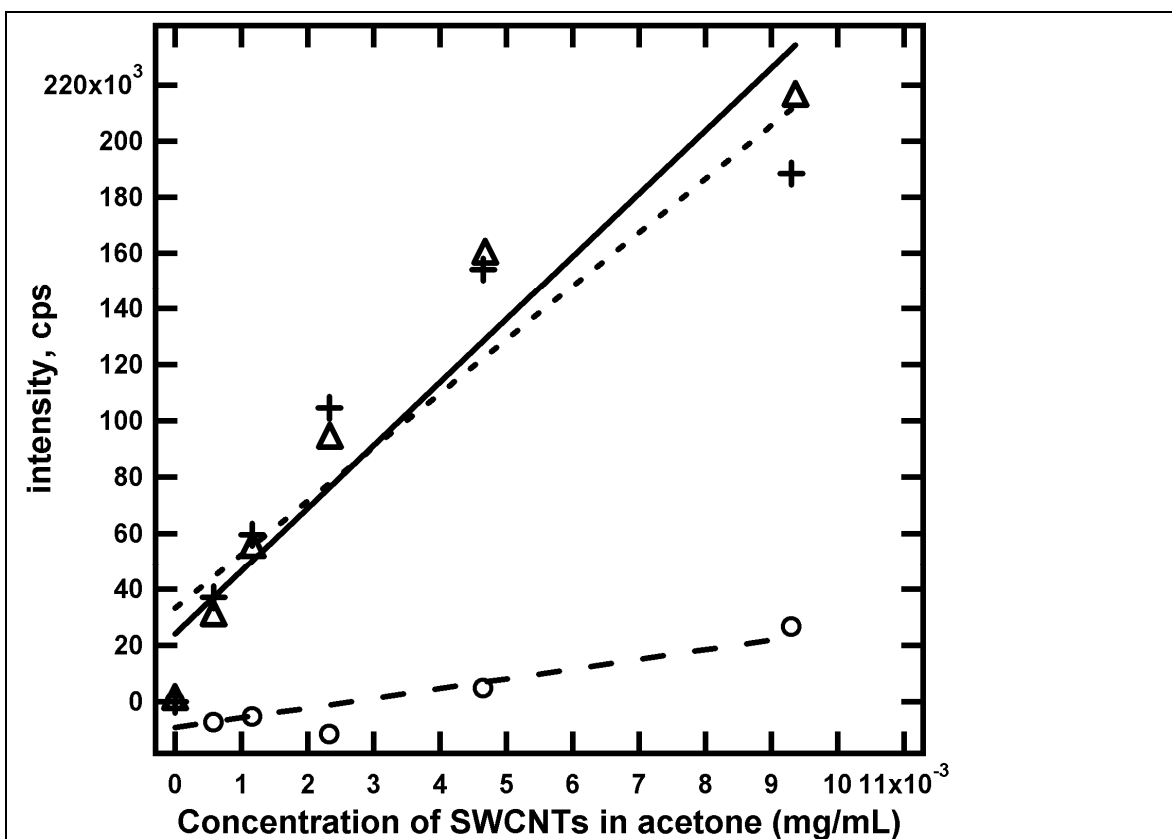


**Figure S7.** Emission spectra of dansyl hydrazine-nitric acid treated SWCNT hybrids in acetone. Dansyl hydrazine concentrations from top to bottom: 501, 250, 125, 62.6, 31.3 nM and neat acetone. Excitation at 350 nm.

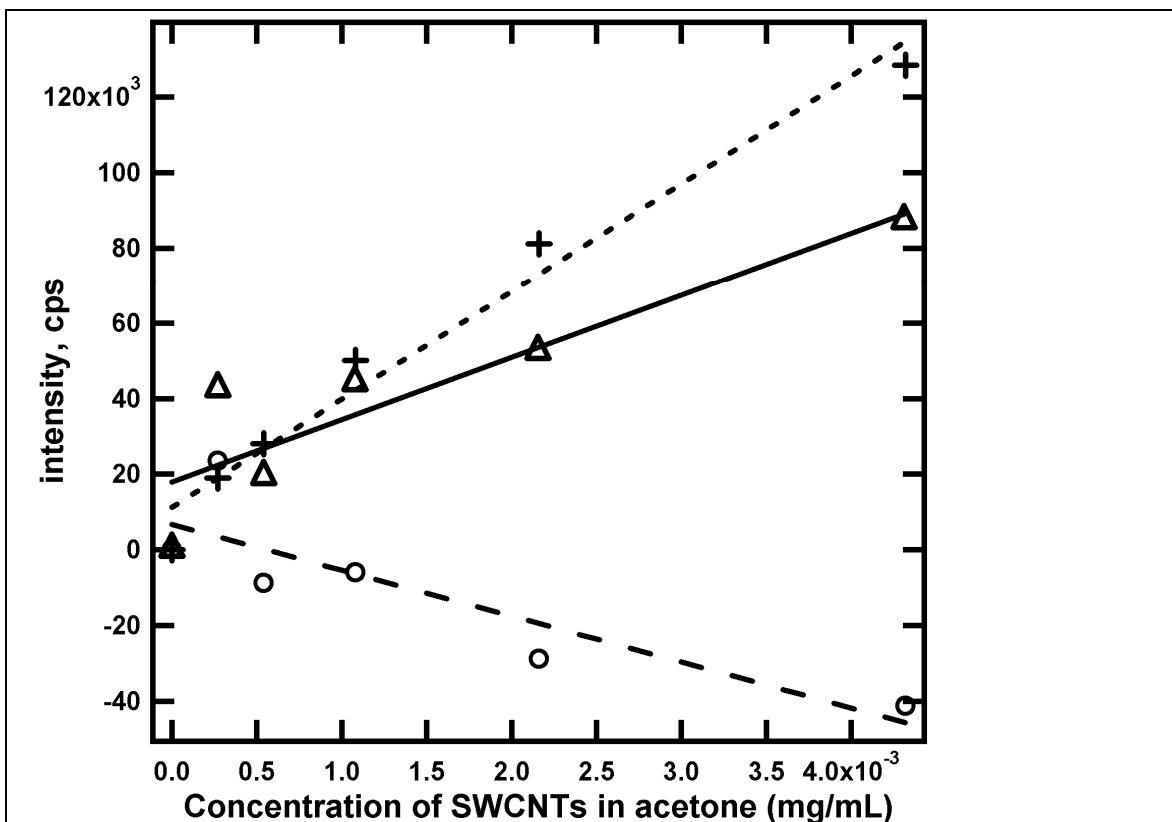


**Figure S8.** Corrected fluorescence plot for panacyl bromide-SWCNT-as produced hybrids (dashed line, circles) obtained by subtracting a fluorescence plot of as produced SWCNTs (dotted line, crosses) from the fluorescence plot of panacyl bromide-SWCNT hybrids (solid line, triangles)

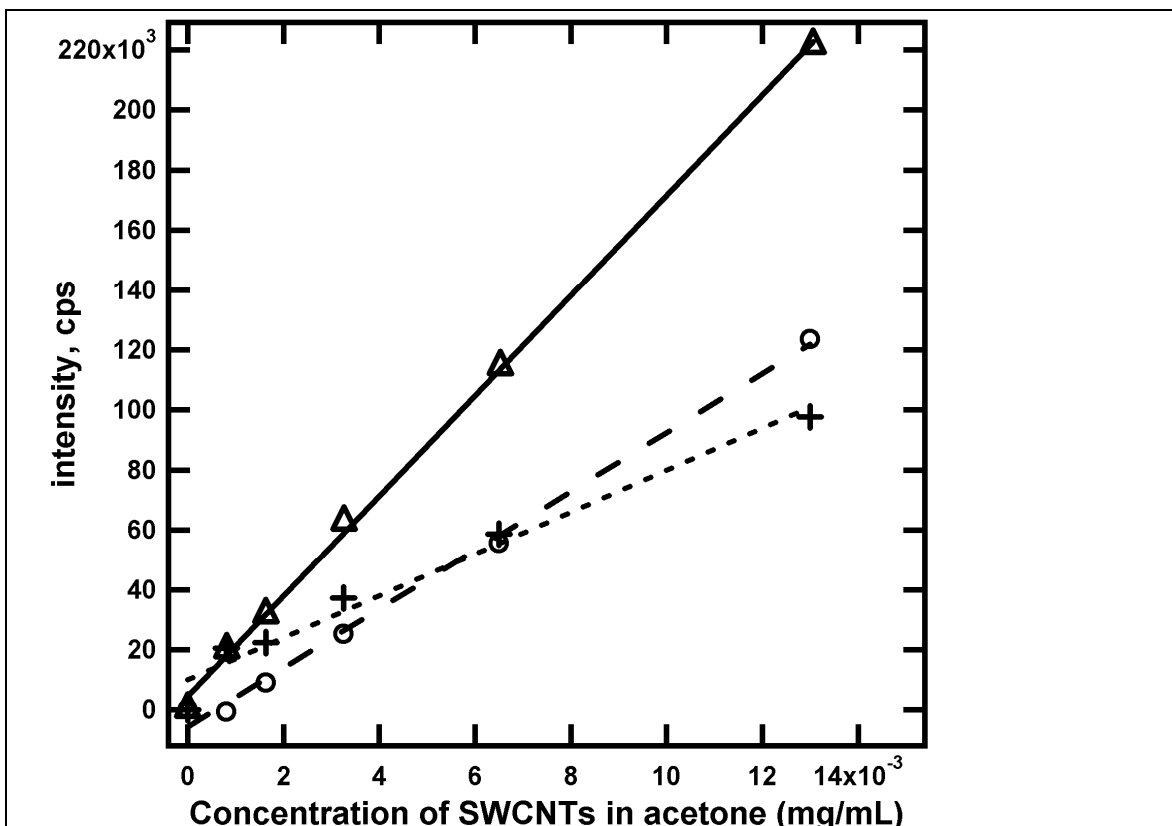




**Figure S10.** Corrected fluorescence plot for dansyl hydrazine-SWCNT-as produced hybrids (dashed line, circles) obtained by subtracting a fluorescence plot of as produced SWCNTs (dotted line, crosses) from the fluorescence plot of dansyl hydrazine-SWCNT hybrids (solid line, triangles)



**Figure S11.** Corrected fluorescence plot for dansyl hydrazine-SWCNT-air/HCl hybrids (dashed line, circles) obtained by subtracting a fluorescence plot of as produced SWCNTs (dotted line, crosses) from the fluorescence plot of dansyl hydrazine-SWCNT hybrids (solid line, triangles)



**Figure S12.** Corrected fluorescence plot for dansyl hydrazine-SWCNT-nitric acid hybrids (dashed line, circles) obtained by subtracting a fluorescence plot of as produced SWCNTs (dotted line, crosses) from the fluorescence plot of dansyl hydrazine-SWCNT hybrids (solid line, triangles)

**Table. 2 SI.** Degree of quenching of panacyl bromide luminescence and metal catalyst impurities left in the carbon nanotubes

Sample	Abbreviation	Degree of quenching	Metal Impurities <sup>[1]</sup>
Panacyl Bromide on nitric acid treated SWCNTs	PB -SWCNT- HNO <sub>3</sub> hybrids	21.3 %	5 %wt
Panacyl Bromide on air / HCl treated SWCNTs	PB-SWCNT- air/HCl hybrids	54.1 %	10 %wt
Panacyl Bromide on as-produced SWCNTs	PB-SWCNT-as-produced hybrids	86.2 %	30 %wt

1. Dementev, N., X. Feng and E. Borguet, *Fluorescence Labeling and Quantification of Oxygen-Containing Functionalities on the Surface of Single-Walled Carbon Nanotubes*. Langmuir, 2009. **25**(13): p. 7573-7577.