

Supporting information

Thermogravimetric analysis (TGA)

To determine the stability of the samples to oxidation, thermogravimetric analyses of as-produced and $\text{HNO}_3/\text{H}_2\text{SO}_4$ (acid) purified MWCNTs were performed, using a PerkinElmer (Pyris 6) thermogravimetric analyzer (heat rate: $10^\circ\text{C}/\text{min.}$; air flow rate: $20\text{ ml}/\text{min.}$). (Figure S1) A faster loss of the material in the case of the acid treated sample could be related with the loss of the residual physisorbed water/acids. As one can notice, the differential TGA curves are almost perfectly superimposed, suggesting that the acid treatment did not result in the damage or destroying of MWCNTs.(Figure S1)

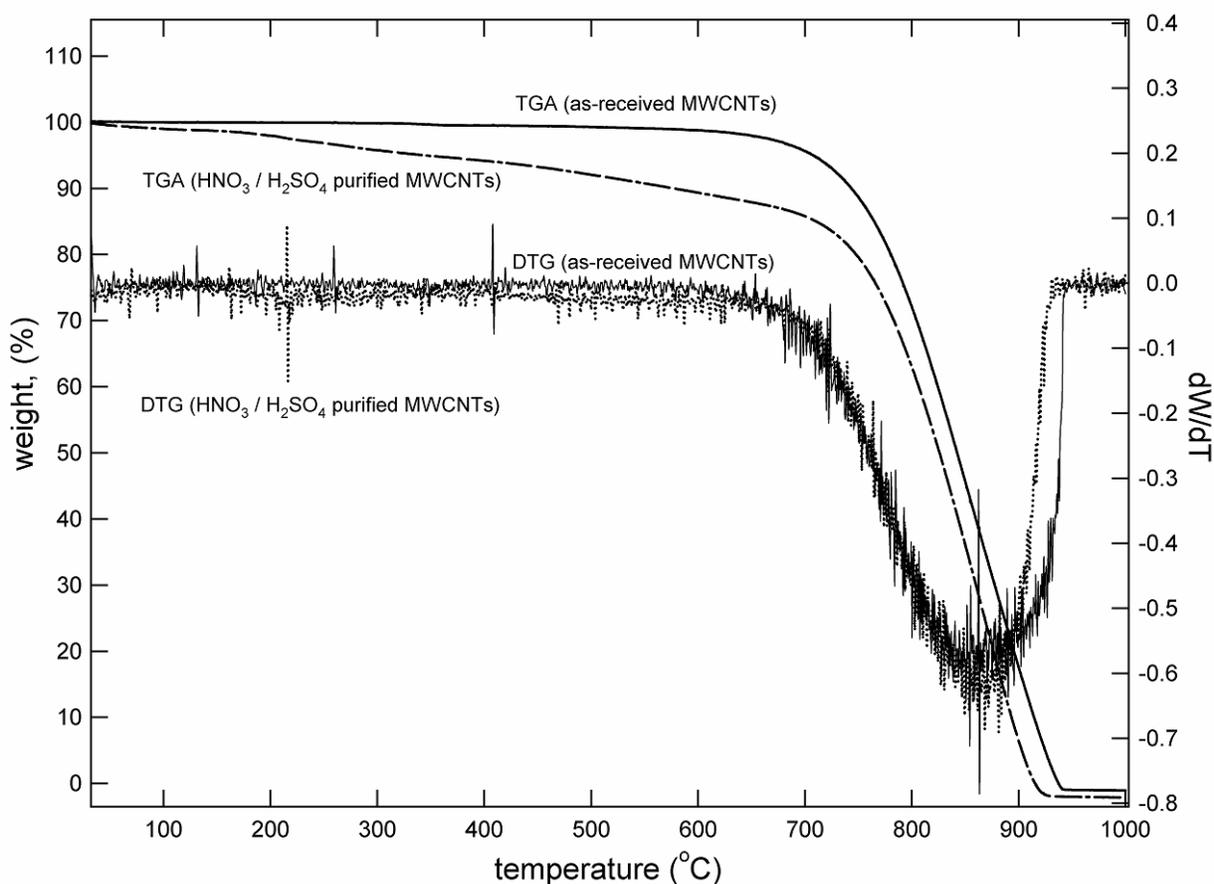


Figure S1. Thermogravimetric (TGA, as-received MWCNTs: thick solid line; acid purified MWCNTs: double dash / dotted line) and differential TGA curve (DTG, as-received MWCNTs: thin solid line; acid purified MWCNTs: dotted line)

Purification of multi-walled carbon nanotubes

To study the effect of the acid treatment on the composition/content of surface functionalities, as-produced MWCNTs were purified with a mixture of nitric and sulfuric acids, following the protocol described elsewhere [1, 2]. Typically, ~ 500 mg of as-produced MWCNTs were sonicated with 100 ml of 96% H₂SO₄ and 100 ml of 50-70% HNO₃ in a 500 ml beaker for ~5 min. to form a homogeneous mixture. The mixture was then refluxed (105 -110°C) while stirring (magnetic Teflon coated stir bar) for 5 hours, after which the heating was stopped and the mixture was allowed to cool down to room temperature for 12-18 hours. The mixture was added to ~600 ml of deionized (DI) water in a 1L beaker and then vacuum filtrated through a cotton filter (Whatman #2). Wet purified MWCNTs were washed with DI water on the filter until the pH of the filtrate was neutral. After heating the filter covered with wet MWCNTs in an oven at ~ 100-110°C for ~30 min., long enough to forma a “cake” of MWCNTs which was then separated from the filter with a spatula and transferred into a beaker and heated in the oven (at ~110⁰C) until constant weight was reached. The purification was run 3 more times, each time for ~500 mg of as-produced MWCNTs to collect sufficient amount of the purified material to run labeling reactions. Yields of the purification were typically 30-40 % wt.. Purified nanotubes after each purification treatment were collected, mixed together, and used as a one sample in further labeling reactions.

Labeling and quantification of carboxylic groups

A stock solution for the labeling (250 ml) was prepared in the dark, containing 0.218 mM of panacyl bromide (PB) and 0.1 mM of dibenzo-18-crown-6 (D18C6) (Aldrich) (used as a catalyst) with acetone (Fisher) as a solvent. Two samples of as-produced MWCNTs (46.1 mg and 41.9 mg) and two samples of acid treated MWCNTs (46.1 mg and 44.7 mg) were reacted in the dark. Each sample was in a separate 50 ml glass beaker with 30 ml of the stock solution

for ~ 4 hrs at ~ 50⁰C (hot plate) while stirring (Teflon coated magnetic stir bar). After the reaction, ~20 ml of supernatant over the labeled MWCNTs was collected into a separate 200 ml volumetric flask for each of the samples. Each of the samples was washed, in its corresponding beaker, with neat acetone several times (4-5 times) and the supernatants after the washings were also collected in the same corresponding flasks as well. The collected supernatants for each of the samples were diluted up to 200 ml with neat acetone. Subsequent dilution of each of the solutions by a factor of 500 (100 µl up to 50ml) with neat acetone, resulted in the solutions used for the fluorescence measurements (excitation at 362 nm).(Figures 2, 3)

Labeling and quantification of carbonyl groups

A stock solution for the labeling (250 ml) was prepared in the dark, containing 0.145 mM of dansyl hydrazine (DH) with methanol (JT Baker) as a solvent. Two samples of as-produced MWCNTs (44.9 mg and 56.2 mg) and two samples of acid treated MWCNTs (54.8 mg and 55.4 mg) were reacted in the dark. Each sample was placed in a separate 50 ml glass beaker, with 30 ml of the stock solution for ~ 70 hrs at room temperature in the presence of a catalytic amount of HCl (1 ml of 0.1 M solution of HCl in methanol for each beaker) while stirring (Teflon coated magnetic stir bar). After the reaction, ~20 ml of supernatant over the labeled MWCNTs was collected into a separate 200 ml volumetric flask for each of the samples. Each of the samples was washed, in its corresponding beaker, with neat methanol several times (4-5 times) and the supernatants after the washings were also collected in the same corresponding flasks as well. The collected supernatants for each of the samples were diluted up to 200 ml with neat acetone. Subsequent dilution of each of the solutions by a factor of ~70 (700 µl up to 50ml) with acetone and catalytic amount of HCl, resulted in the solutions used for the fluorescence measurements (excitation at 350 nm).(Figures S2-S4) The rationale in using acetone as a solvent in the final dilutions was stipulated by the fact that DH fluoresces more

brightly upon the reaction with carbonyls. Fluorescence measurements were performed at least 12 hrs after the final dilutions with acetone were done to make sure that all DH reacted.

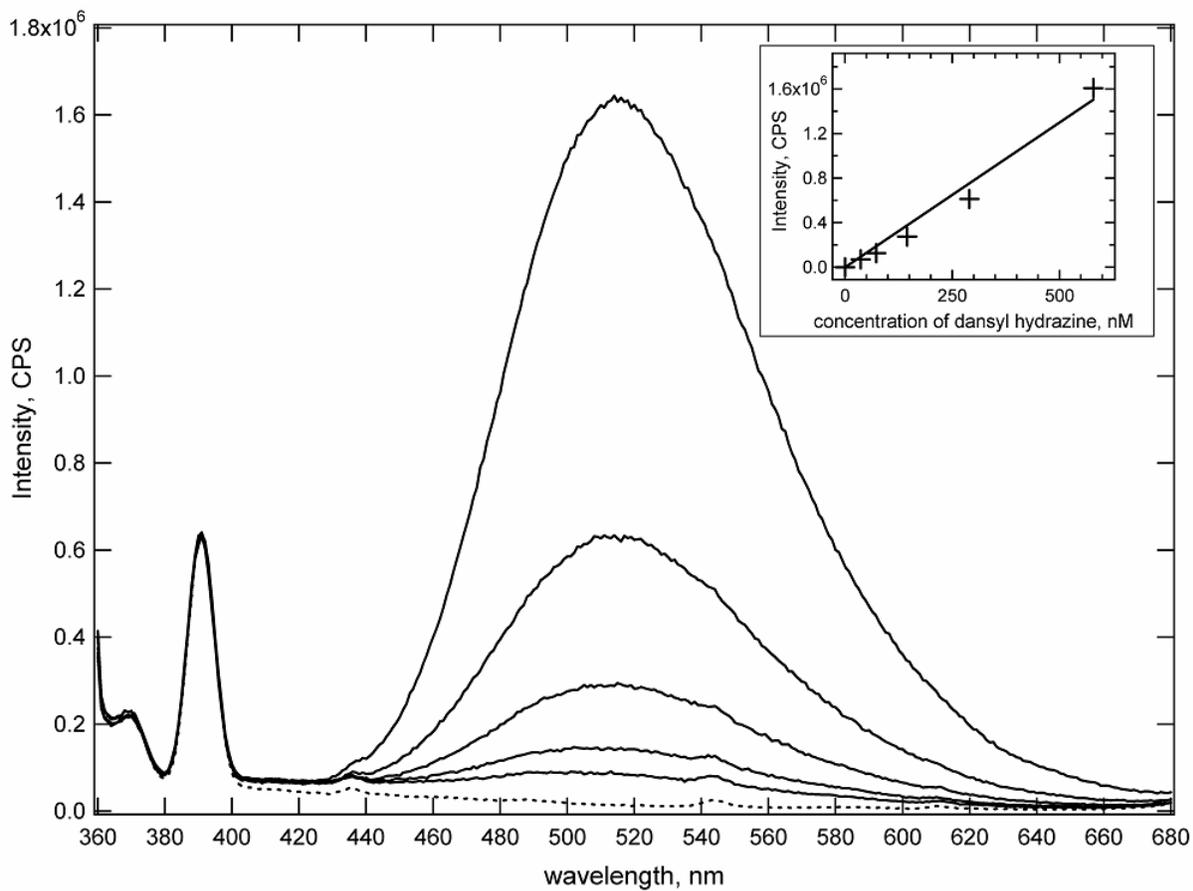


Figure S2. Emission spectra of dansyl hydrazine (DH) of different concentrations (from top to bottom): 579 nM, 289 nM, 145 nM, 72 nM, 36 nM; neat acetone+HCl (dotted line) excited at 350 nm. (Inset: calibration plot of fluorescence intensity at 510 nm vs. DH concentration)

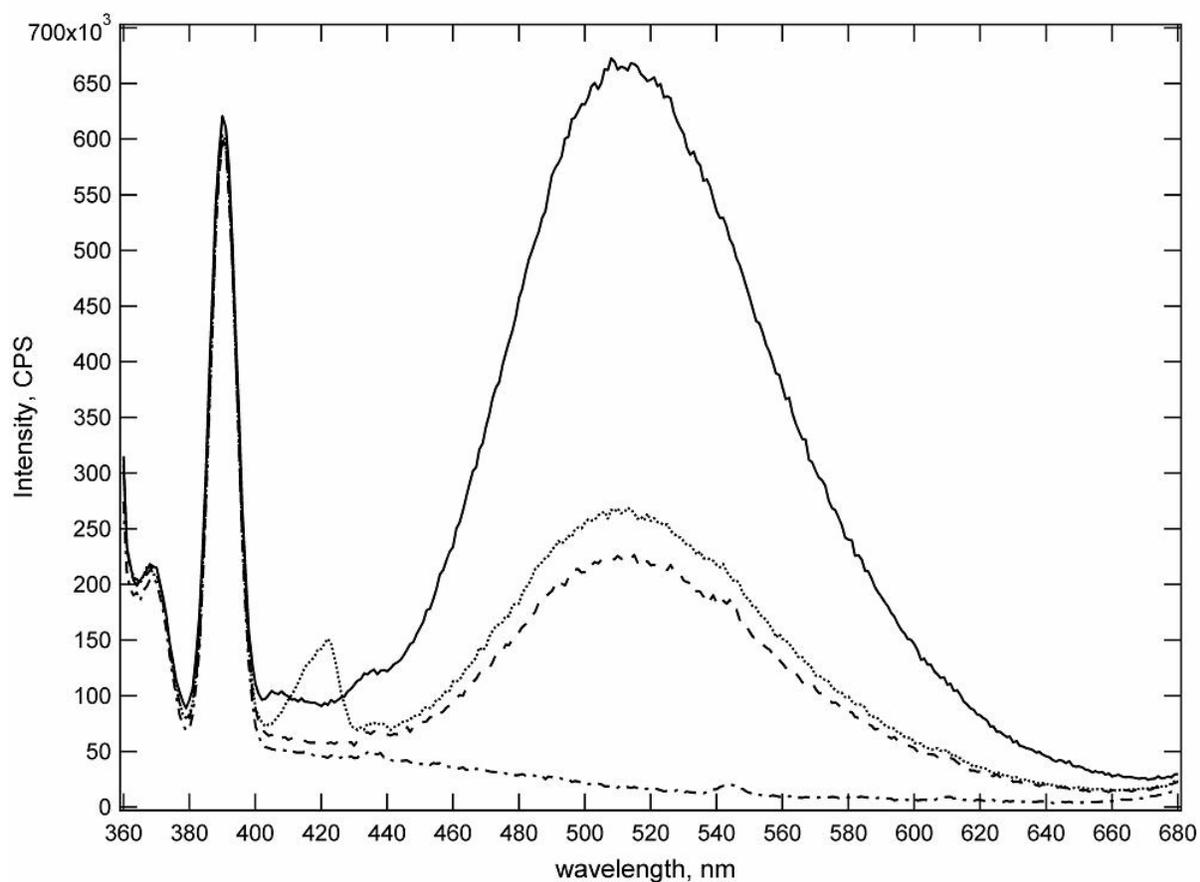


Figure S3. Emission spectra of dansyl hydrazine reacted with carbonyls of as-produced MWCNTs: control experiment without MWCNTs (solid line at the top), after reaction with 44.9 mg MWCNTs (dotted line), after reaction with 56.2 mg MWCNTs (dashed line); neat acetone (dash-dotted line at the bottom). Excitation at 350 nm.

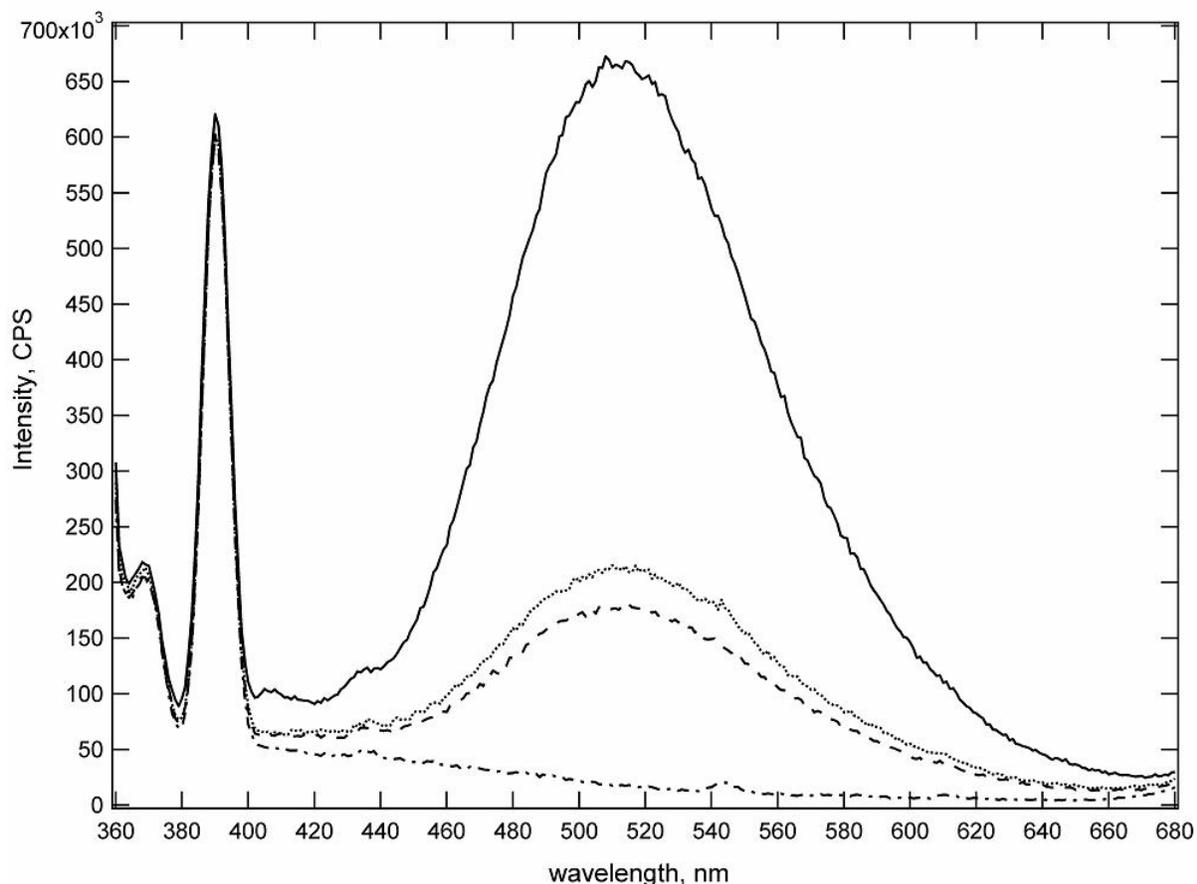


Figure S4. Emission spectra of dansyl hydrazine reacted with carbonyls of $\text{HNO}_3 / \text{H}_2\text{SO}_4$ purified MWCNTs: control experiment without MWCNTs (solid line at the top), after reaction with 54.8 mg MWCNTs (dotted line), after reaction with 55.4 mg MWCNTs (dashed line); neat acetone (dash-dotted line at the bottom). Excitation at 350 nm.

Labeling and quantification of alcohol groups

To prevent 5-DTAF from reacting with hydroxyls of water, which are inevitably present in the air moisture and to some extent physisorbed on MWCNTs, an aqueous solution of Na_2CO_3 (Fisher) of pH ~11 (~20 g of Na_2CO_3 for 1 L of water) was prepared and used as a solvent to prepare (in the dark) 0.096 mM stock solution (250 ml) of 5-DTAF for the labeling. According to the manufacturer (Molecular Probes) 5-DTAF reacts only with alcohol $-\text{OH}$, not $-\text{OH}$ of water, provided that pH~9-11. Two samples of as-produced MWCNTs (50.5 mg and 50.6 mg) and two samples of acid treated MWCNTs (48.9 mg and 52.1 mg) were reacted in the dark. Each sample was in a separate 50 ml glass beaker, with 30 ml of the stock solution for ~ 24 hrs

at room temperature, while stirring (Teflon coated magnetic stir bar). After the reaction, ~20 ml of supernatant over the labeled MWCNTs was collected into a separate 200 ml volumetric flask, separate for each of the samples. Each of the samples was washed, in its corresponding beakers, with aqueous solution of Na_2CO_3 (pH ~11) several times (4-5 times) and the supernatants after the washings were also collected in the same corresponding flasks as well. The collected supernatants for each of the samples were diluted up to 200 ml with neat acetone. Subsequent dilution of each of the solutions by a factor of 5000 (10 μl up to 50ml) with aqueous solution of Na_2CO_3 (pH ~11), resulted in the solutions, used for the fluorescence measurements (excitation at 490 nm).(Figures S5, S6)

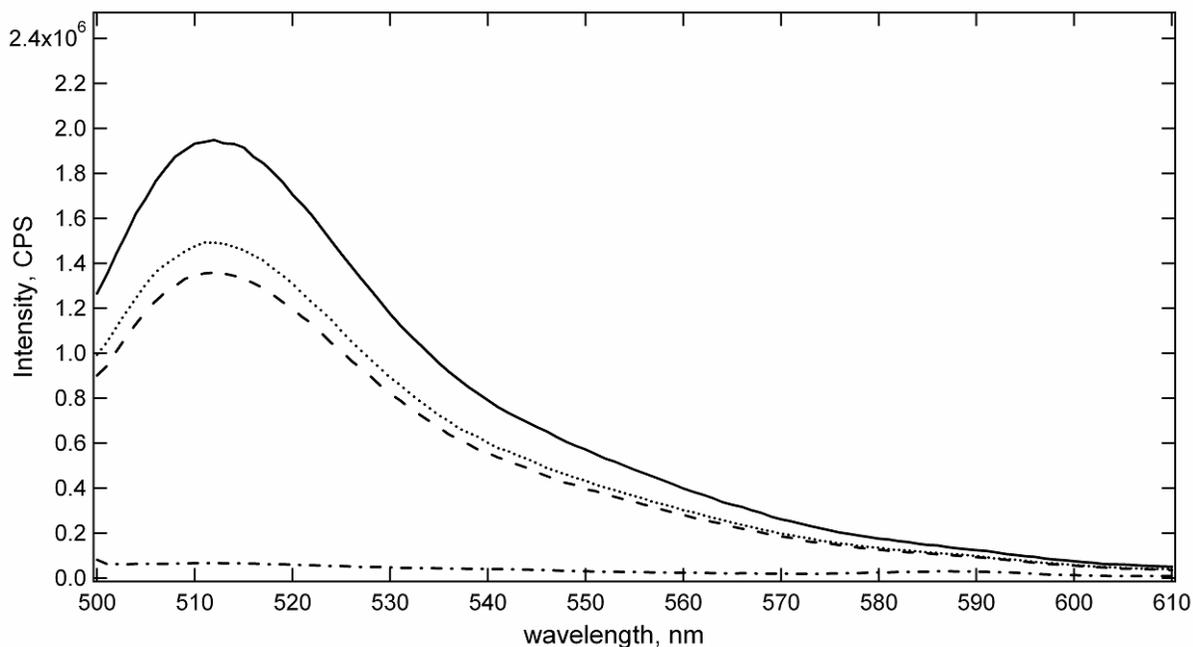


Figure S5. Emission spectra of 5-DTAF reacted with hydroxyls of as-received MWCNTs: control experiment without MWCNTs (solid line at the top), after reaction with 50.5 mg MWCNTs (dotted line), after reaction with 50.6 mg MWCNTs (dashed line); $\text{Na}_2\text{CO}_3+\text{H}_2\text{O}$ (pH~11) (dash-dotted line at the bottom). Excitation at 490 nm.

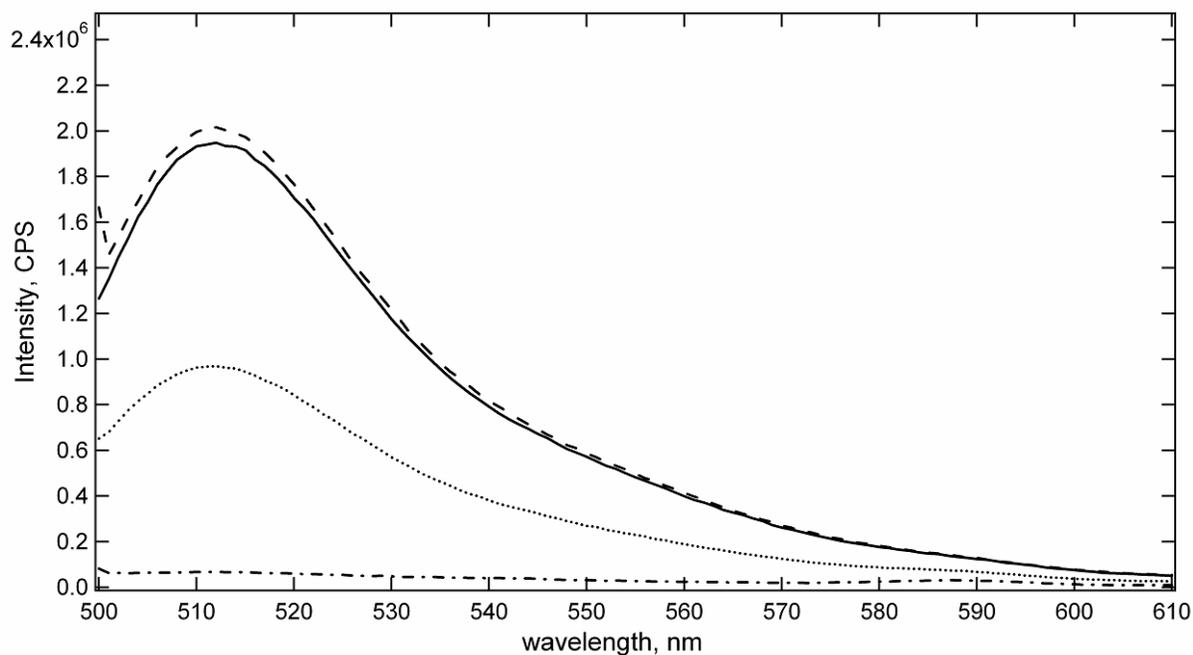


Figure S6. Emission spectra of 5-DTAF reacted with hydroxyls of HNO₃/H₂SO₄ purified MWCNTs: control experiment without MWCNTs (solid line at the top), after reaction with 48.9 mg MWCNTs (dotted line), after reaction with 52.1 mg MWCNTs (dashed line); Na₂CO₃+H₂O (pH~11) (dash-dotted line at the bottom). Excitation at 490 nm.

Control experiments

Dye physisorption control experiments

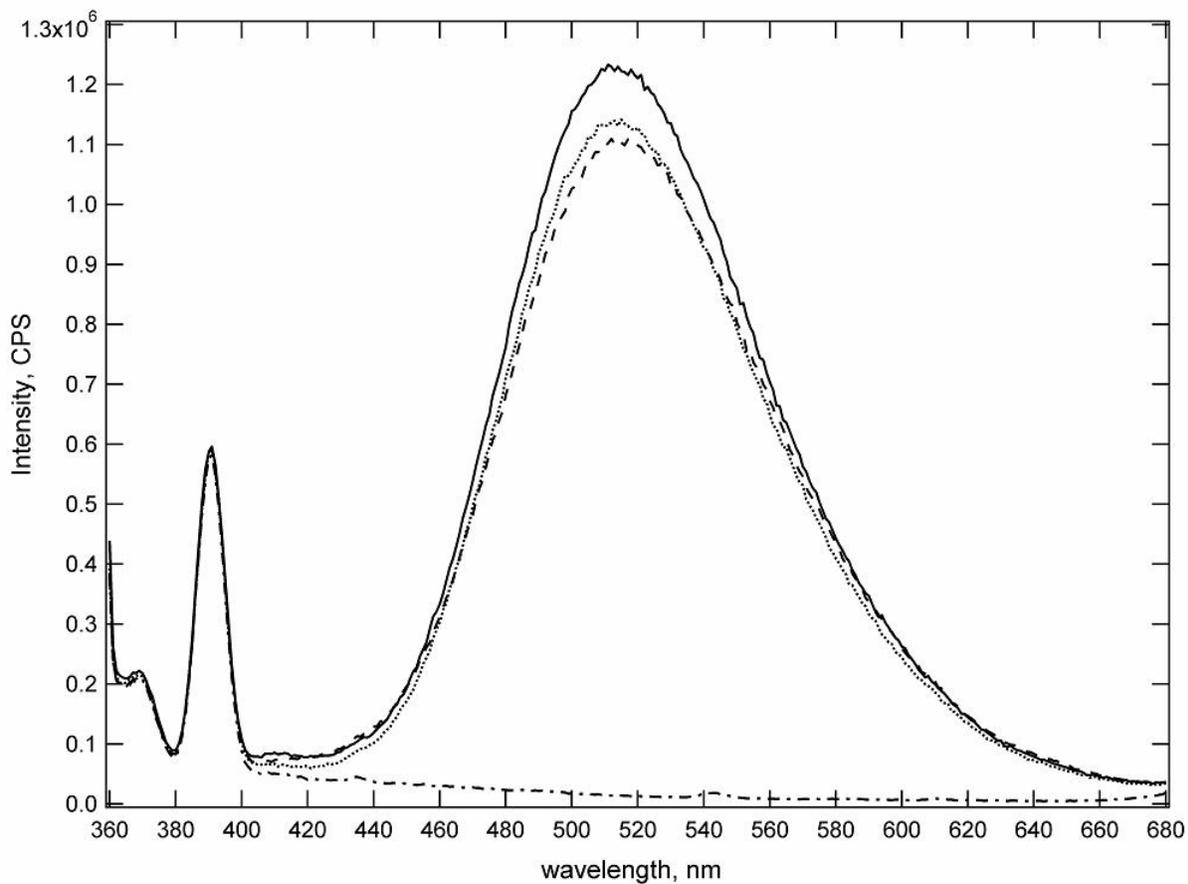


Figure S7. Emission spectra of deactivated dansyl hydrazine after contact (~ 70 hr.) with 46.6 mg as-received (dotted line) and 42.7 mg HNO₃/H₂SO₄ purified (dashed line) MWCNTs; control experiment without MWCNTs (solid line at the top), acetone (dash-dotted line at the bottom). Excitation at 350 nm.

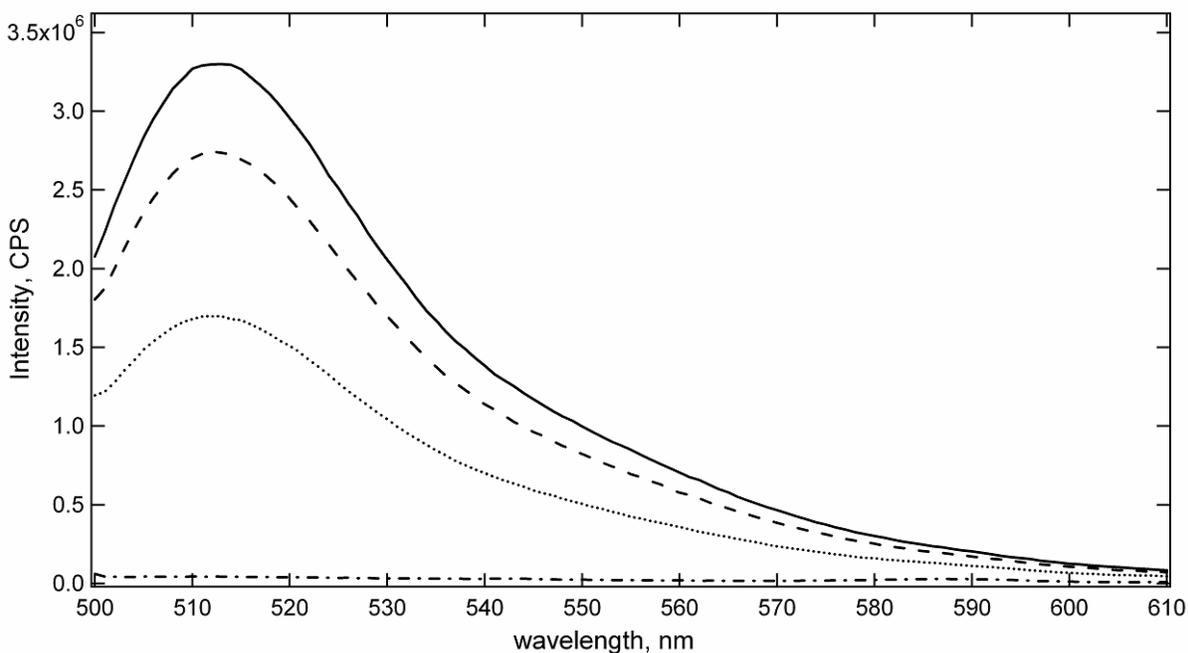


Figure S8. Emission spectra of deactivated 5-DTAF after contact (24 hrs) with as-received MWCNTs: control experiment without MWCNTs (solid line at the top), after contact with 49.4 mg MWCNTs (dotted line), after contact with 48.4 mg MWCNTs (dashed line); $\text{Na}_2\text{CO}_3+\text{H}_2\text{O}$ (pH~11) (dash-dotted line at the bottom). Excitation at 490 nm.

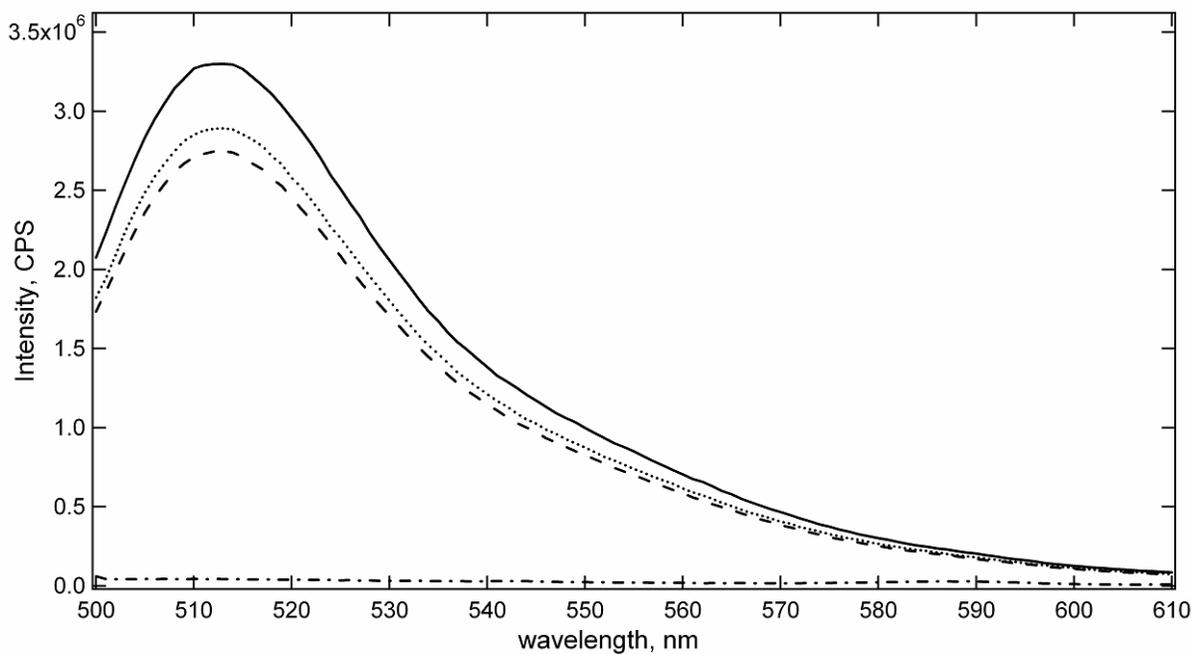


Figure S9. Emission spectra of deactivated 5-DTAF after contact (24 hrs) with $\text{HNO}_3/\text{H}_2\text{SO}_4$ purified MWCNTs: control experiment without MWCNTs (solid line at the top), after contact with 50.1 mg MWCNTs (dotted line), after contact with 51.9 mg MWCNTs (dashed line); $\text{Na}_2\text{CO}_3+\text{H}_2\text{O}$ (pH~11) (dash-dotted line at the bottom). Excitation at 490 nm.

Reaction time control experiments

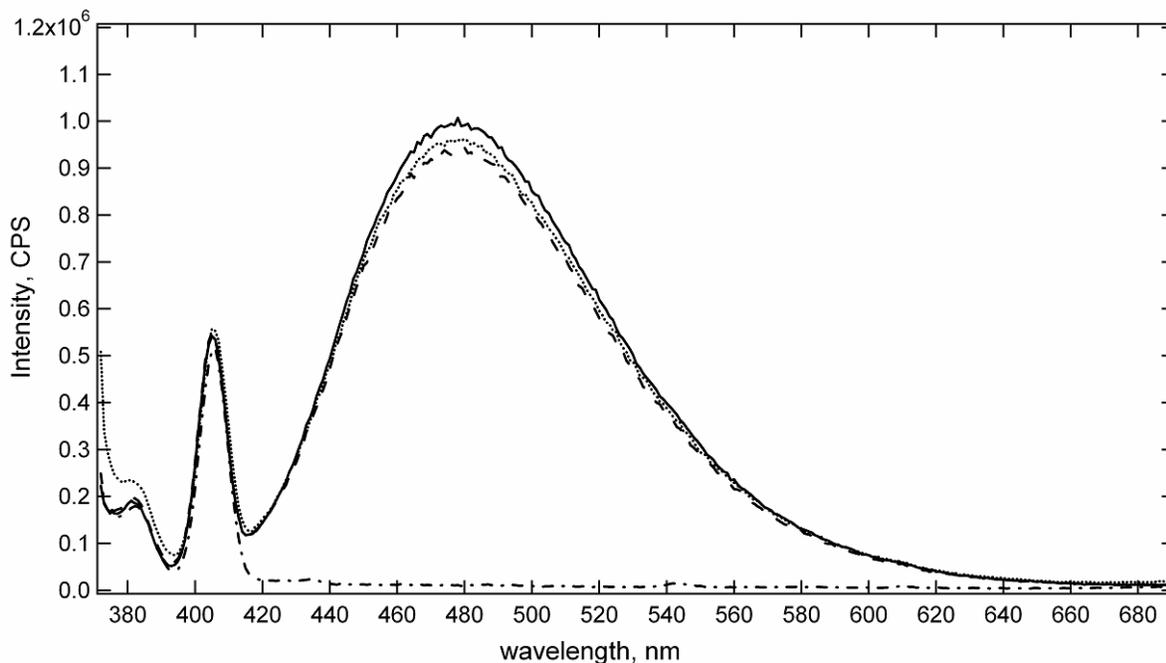


Figure S10. Emission spectra of Panacyl Bromide after first run of the reaction with 46.1 mg of non-labeled HNO₃ / H₂SO₄ purified MWCNTs for 3.5 hrs. (dashed line) and second run with 46.1 mg of labeled HNO₃ / H₂SO₄ purified MWCNTs for 26 hrs. (dotted line); control experiment without MWCNTs (solid line at the top), acetone (dash-dotted line at the bottom). Excitation at 362 nm.

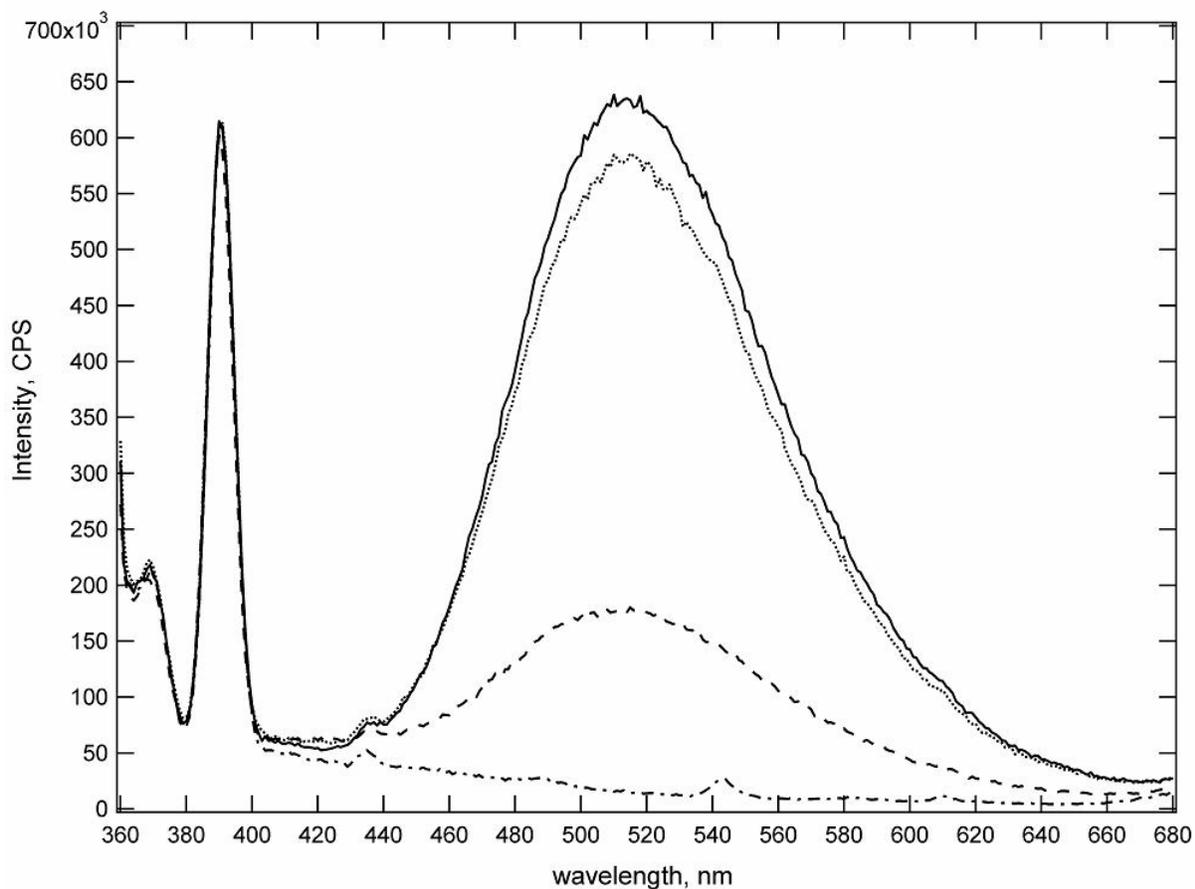


Figure S11. Emission spectra of dansyl hydrazine after first run of the reaction with 54.8 mg of non-labeled $\text{HNO}_3/\text{H}_2\text{SO}_4$ purified MWCNTs for 62 hrs. (dashed line) and second run with 54.8 mg of labeled $\text{HNO}_3/\text{H}_2\text{SO}_4$ purified MWCNTs for 72 hrs. (dotted line); control experiment without MWCNTs (solid line at the top), acetone (dash-dotted line at the bottom). Excitation at 350 nm.

References

- [1] H. Hiura, T. Ebbesen, Process for purifying, uncapping and chemically modifying carbon nanotubes, US patent 5698175 (1997).
- [2] H. Hiura, T.W. Ebbesen, K. Tanigaki, Opening And Purification Of Carbon Nanotubes In High Yields, *Advanced Materials*, 7 (1995) 275-276.