

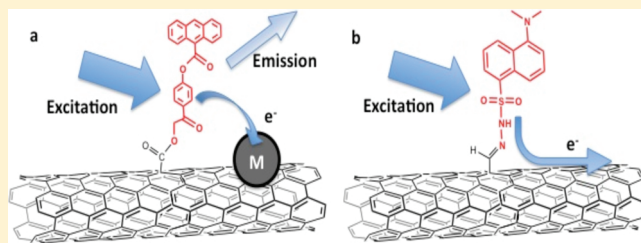
Fluorescence Quenching of Dyes Covalently Attached to Single-Walled Carbon Nanotubes

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Supporting Information

ABSTRACT: The development of chromophore-carbon nanotube hybrids requires efficient and accurate methods to investigate their photophysical properties. Using the ability of the fluorescence labeling of surface species (FLOSS) technique to determine the density of covalently attached dyes to the surface of single-walled carbon nanotubes (SWCNTs), the luminescence of dye-SWCNT hybrids was quantitatively studied with two chromophores: dansyl hydrazine (DH) and panacyl bromide (PB). The fluorescence intensity of PB-SWCNT hybrids was reduced by 20–80% compared to that of free PB. A strong positive correlation between the degree of quenching and the residual metal impurity content in the SWCNT sample suggests that quenching of fluorescence of PB in PB-SWCNTs may be caused by the metal impurities and not by SWCNTs. On the contrary, the intensity of fluorescence of DH-SWCNT hybrids was reduced by almost 2 orders of magnitude compared to free DH, independent of the residual metal content in the SWCNT sample, suggesting that quenching of fluorescence in DH-SWCNT hybrids might occur via charge transfer from DH chromophores to SWCNTs, and revealing the potential of DH-SWCNT hybrids for solar light harvesting applications.



INTRODUCTION

Carbon nanotubes (CNTs) have unique mechanical and electronic properties, and have attracted interest for many years because of potential applications in sensors, scanning probe tips, and electronic devices.^{1,2} Recent studies have used CNTs as nanoplatoms to attach molecules, providing hybrid systems that can be designed for specific tasks, including sensors,^{3–5} drug delivery⁶ and possible light-harvesting devices.⁷

Despite these potential applications of CNTs, one of the major drawbacks is that nanotubes are often produced with metal catalyst and carbon impurities. These impurities need to be removed as they can obscure the properties of CNTs. Nitric acid treatment and Air/HCl treatment are the most commonly used purification procedures.^{8,9} These treatments have been shown to create oxygen-containing functional groups on the CNT surfaces^{8,10} that can be used as reaction sites for the further chemical derivatization of CNTs.^{11,12} The covalent attachment of molecules to CNTs broadens the range of potential applications of CNT systems and allows one to tailor the properties of modified CNTs.^{11,12}

Investigations of the photophysical properties of photosensitive molecules on CNTs are of interest as they provide the scientific basis for hybrid materials with potential applications as optical sensors^{4,5} and light harvesting devices.⁷ For example, Cho et al. developed a CNT-chromophore based pH sensor in which a fluorescent dye (pyrene) was attached to the surface of CNT by a pH sensitive polymeric linker that coils up at low pH and causes quenching of the dyes.⁴ CNTs have been used as substrates in immunoassays.^{13,14} CNT electrodes were decorated

with antibodies that can bind antigens, allowing an electrochemiluminescence-active second antibody to bind, thereby enabling detection of the antigen.^{13,14} CNT-polymer hybrids¹⁵ and CNT-phthalocyanine¹⁶ hybrids have been developed as light-harvesting devices.

Common approaches to study the photophysics of CNT-dye hybrids conventionally include UV-vis spectroscopy, as well as steady-state and time-resolved fluorescence spectroscopy.^{17–20} In general, CNTs are reported to reduce the fluorescence of the attached molecules.^{17–20} In most cases, dye and dye-substrate hybrids are dispersed in solutions, and their concentrations are adjusted in such a way as to provide the same ultraviolet-visible-near-infrared (UV-vis-NIR) absorbance for each of the samples. The luminescence of free dye and dye-substrate hybrid solutions is analyzed by taking their steady-state fluorescence spectra.^{19,20} The decrease in fluorescence intensity of the dye-substrate samples compared to the free dye solutions is conventionally attributed to the quenching of the fluorescence by a substrate. This approach can be applied to situations where the absorption wavelengths of the substrate and dye do not overlap. However, when there is overlap, the decrease in the fluorescence intensity of dye in the hybrids might simply be caused by the smaller concentration of dye on hybrids compared to that of a

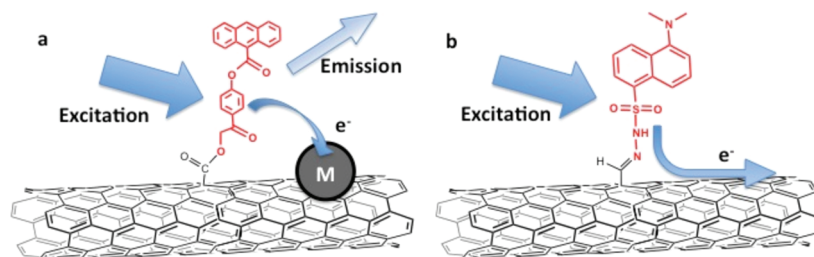
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Scheme 1. (a) PB Covalently Attached to SWCNTs; (b) DH Covalently Attached to SWCNTs



free dye. That being said, absorption is not as sensitive as emission, especially at low concentrations. Since the conventional approaches described above do not allow the precise determination of the dye concentrations on the CNTs, the results and interpretation of the changes of fluorescence intensity can be ambiguous. What is needed for quantitative studies is a precise determination of the concentration of dyes on the CNTs.

In this work, we studied the photophysics of two chromophores, 5-dimethylaminonaphthalene-1-sulfonyl hydrazine (dansyl hydrazine or DH) and 4-(9-anthroyloxy)-2-bromoacetophenone (panacyl bromide or PB), upon covalent attachment to the surface of single-walled CNTs (SWCNTs; Scheme 1). DH and PB are dyes for the detection of aldehyde/ketone groups^{21–24} and fatty acids,^{25,26} respectively. These dyes are known to fluoresce upon attachment to analytes, and are often used as labeling tags in liquid chromatography. The dyes have solvatochromic shifts of ~ 50 nm.^{21–26} We build on our previous work on the detection, identification, and quantification of carbonyls and carboxyls on the surface of SWCNTs via fluorescence labeling of surface species (FLOSS) with DH and PB, respectively.^{27–29} The results of the FLOSS experiments provided us with quantitative information about the concentration of DH and PB on the surface of DH–SWCNTs and PB–SWCNTs.²⁹ Hence, the FLOSS information allowed us to control the concentration of dye in bulk dispersions of dye–SWCNT hybrids, providing a precise quantitative comparison with fluorescence of solutions containing free dye of the same concentrations.

Our results show that the luminescence of PB is somewhat attenuated upon attachment to SWCNT surfaces. The variations in luminescence intensities might be attributed to the amount of metal impurities present in the SWCNT samples. However, the luminescence of DH is dramatically quenched upon attachment to SWCNTs regardless of the CNT purification methods. Experiments, described below, show that metal impurities are not the primary factor for the quenching of fluorescence of DH–SWCNTs, which might happen via a charge transfer from DH to SWCNTs, thus making DH–SWCNT hybrids a candidate for possible use in light harvesting devices where solar photons could be converted into electrical charge that can be used to do useful work.

EXPERIMENT

Materials and Instruments. As-produced, air/HCl-treated, and nitric acid-purified arc-produced SWCNTs were purchased from Carbon Solutions, Inc. DH and PB were purchased from Molecular Probes. Analytical-grade acetone was purchased from J.T. Baker.

Chromophores were attached to CNTs as described elsewhere.²⁹ Briefly, an excess amount of chromophores was added to CNTs suspended in solvent (methanol for DH and acetone for PB). After the reactions, the chromophore-attached CNTs (dye–SWCNTs) were separated from the solutions and washed with the solvents to remove physisorbed fluorophores from the material. The washing process was repeated 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.²⁹ The dye–SWCNTs were collected by evaporating the solvent. The resulting samples were labeled with the name of the dye and the treatments of the SWCNTs underwent. For example, PB attachment to SWCNTs purified via nitric acid treatment was labeled as PB–SWCNTs–HNO₃. Excitation and emission spectra were obtained using a Jobin-Yvon Spex FluoroMax-2 spectrofluorimeter with square quartz cuvettes (10 mm path length). The excitation wavelength was set to be 362 nm for PB³⁰ and 350 nm for DH.³¹ The observed emission maxima were 475 nm for PB and 510 nm for DH.³⁰ The spectra of free chromophores, dye–CNT hybrids, and bare CNTs were obtained in solutions with acetone as a solvent. UV–vis absorption spectra were obtained using a JASCO V680 spectrometer with 10 mm path length square quartz cuvettes. All measurements were performed at room temperature.

RESULTS AND DISCUSSION

The results of FLOSS on SWCNTs provided us with quantitative information about surface concentrations of PB and DH on PB–SWCNT and DH–SWCNT hybrids, respectively.²⁹ FLOSS results together with the knowledge of the specific surface areas of SWCNTs (Brunauer–Emmett–Teller (BET) analysis)²⁹ allowed us to prepare bulk dispersions of PB–SWCNTs and DH–SWCNTs in acetone (mild sonication, Branson S210) with known bulk concentrations of PB and DH. Fluorescence spectra were taken for the solutions of different concentrations of PB and DH, prepared by dilution of the bulk solutions of PB–SWCNTs and DH–SWCNTs with acetone. (Figures 1 and S2–S7 (Supporting Information))

DH in DH–SWCNTs is connected to SWCNTs via a hydrazone linkage. Previous studies had shown that the reacted DH has a slightly higher quantum yield compared to that of a nonreacted DH.^{32,33} The fluorescence intensity of a free DH, prereacted with acetone, was used as a reference to exclude the aforementioned effect of the linkage.³³ The comparison between the reacted DH and DH–SWCNTs should reveal the difference in luminescence intensity with or without the influence of SWCNT substrate.

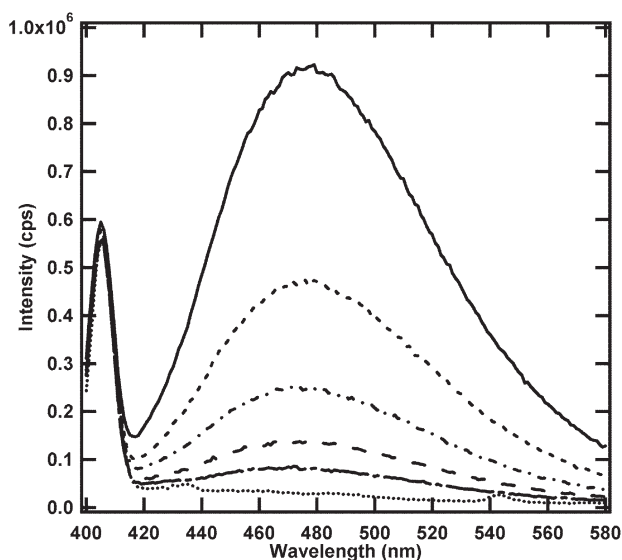


Figure 1. Emission spectra of PB covalently attached to air/HCl-treated SWCNT (PB-SWCNT-air/HCl) hybrids of different PB concentrations (from top to bottom: 85, 43, 21, 11, 5.3 nM) dissolved in acetone together with neat acetone (dotted line at the bottom). Excitation at 362 nm.

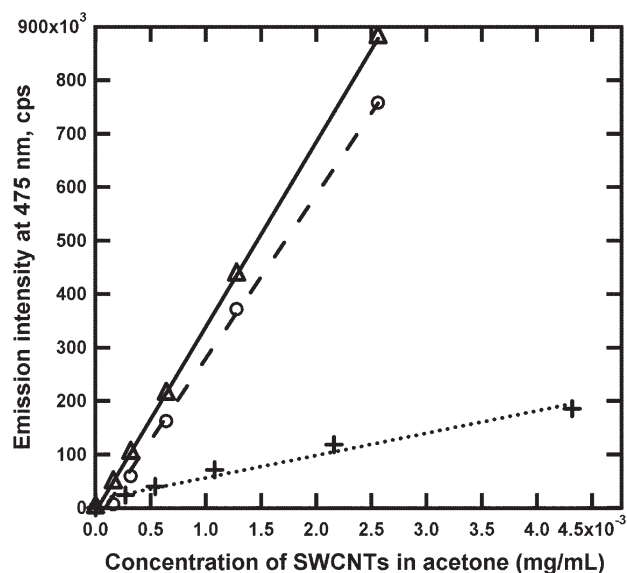


Figure 2. Fluorescence plot, corrected for background scattering. Dye fluorescence of PB attached on air/HCl-treated SWCNTs (PB-SWCNT-air/HCl) (dashed line, circles) obtained by subtracting the fluorescence plot of bare air/HCl-treated SWCNTs (dotted line, crosses) from the fluorescence plot of PB-SWCNTs hybrids (solid line, triangles). Excitation at 362 nm.

To compare and interpret the fluorescence intensity of free and SWCNT-bound dye solutions, it is necessary to make a correction for the background signal caused by light scattering from SWCNTs in solution. To achieve this, we prepared dye-SWCNT and SWCNT solutions of controlled nanotube concentration and recorded their emission spectra. The fluorescence signals from dye-SWCNT hybrid solutions were corrected in such a way that the signals of bare SWCNTs were subtracted from that of the dye-SWCNTs to obtain the

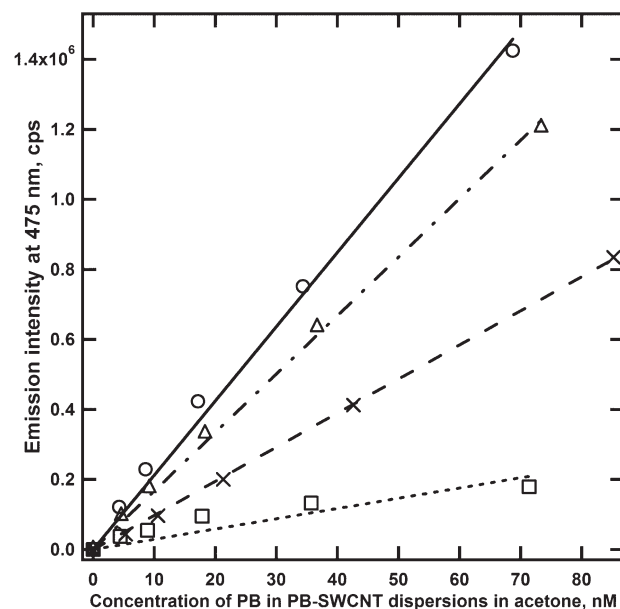


Figure 3. Background corrected fluorescence intensity of PB for free PB (solid line, circles), PB-SWCNTs-HNO₃ hybrid (dash-dotted line, triangles), PB-SWCNT-air/HCl hybrid, (dashed line, crosses), and PB-SWCNT-as-produced hybrid (dotted line, squares). Acetone was used as the solvent for each of the solutions.

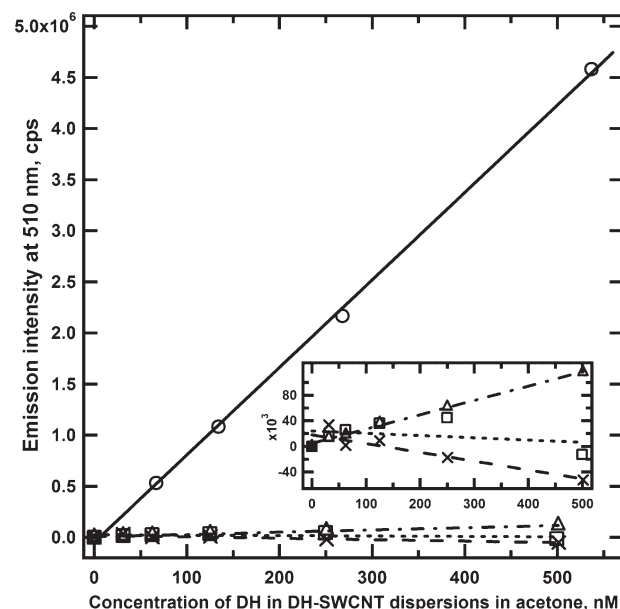


Figure 4. Background corrected fluorescence intensity of DH for free DH (solid line, circles), DH-SWCNT-HNO₃ hybrid (dash-dotted line, triangles), DH-SWCNT-air/HCl hybrid, (dashed line, crosses), and DH-SWCNT-as-produced hybrid (dotted line, squares). Inset: zoom-in of emission intensity of the three hybrids.

background scattering corrected fluorescence intensity of the dyes in dye-SWCNT hybrid solutions. (Figures 2 and S8-S12) The corrected intensity plots of dye-SWCNT hybrids compared to that of free dye are shown above in Figures 3 and 4.

As one can see from Figure 3, the fluorescence intensity of PB significantly depends on the treatment the SWCNTs underwent prior to the labeling. The PB-SWCNT-as-produced hybrid

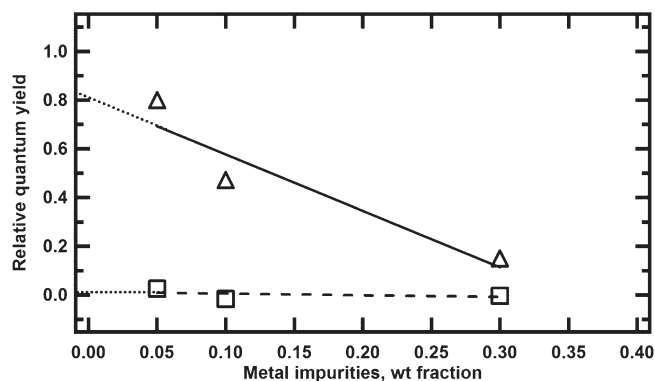


Figure 5. Quantum yield of covalently attached dye to free dye versus metal impurities in CNT samples for DH-SWCNT hybrids (dashed line, squares) and PB-SWCNT hybrids (solid line, triangles).

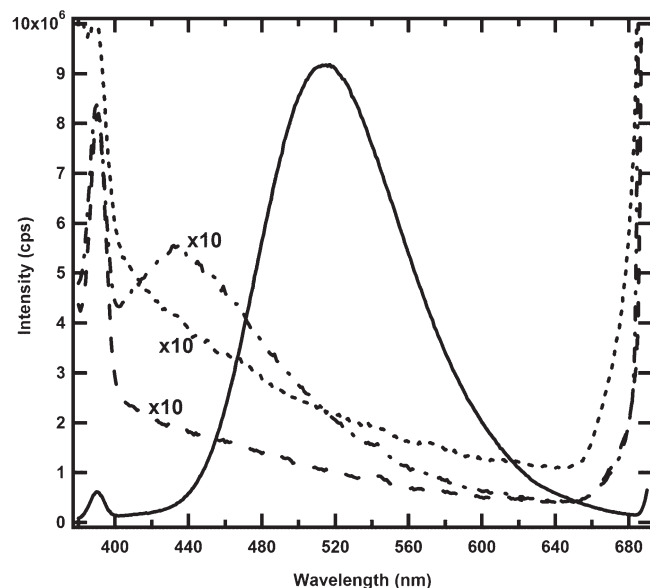


Figure 6. Emission spectra of DH at ~ 500 nM concentration as free DH (solid line), DH-SWCNTs-HNO₃ hybrid (dash-dotted line), DH-SWCNT-air/HCl hybrid, (dashed line), and DH-SWCNT-as-produced hybrid (dotted line). Intensity signals for DH hybrids are magnified 10-fold. Excitation at 350 nm.

exhibits the highest fluorescence quenching, while for the PB-SWCNT-HNO₃ hybrid the quenching is the lowest (Figure 3). Thermogravimetric analysis (TGA) of SWCNTs²⁹ showed that the amount of residual metal catalyst depends on the acid purification of the SWCNTs²⁹ (Table 1 SI, Supporting Information.) To analyze the effect of metal impurities on the quantum efficiency of the chromophores, we normalized the slope of emission intensity versus the concentration of dyes (Figures 3 and 4) against the slope of the free dye and plotted the normalized slope against the weight fraction of metal impurities (Figure 5). The intercept on the Y-axis, obtained by extrapolation of the graph (Figure 5) to 0 wt % of the metal content, allowed us to estimate the relative quantum yield of the chromophores in the absence of the metal impurities. As one can see from Figure 5, the relative quantum yield of DH is close to zero in the absence of metal impurities, with no correlation with metal content, suggesting that the quenching of DH in DH-SWCNTs hybrids

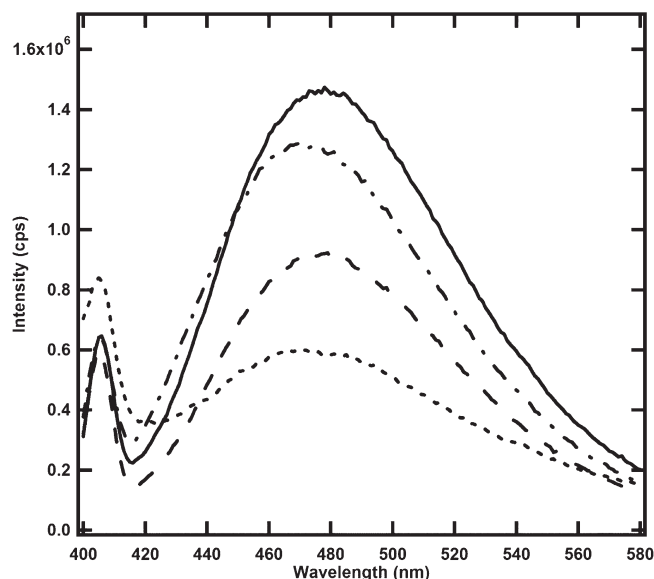


Figure 7. Emission spectra of PB at ~ 80 nM concentration as free PB (solid line), PB-SWCNTs-HNO₃ hybrid (dash-dotted line), PB-SWCNT-air/HCl hybrid, (dashed line), and PB-SWCNT-as-produced hybrid (dotted line). Excitation at 362 nm.

was predominantly caused by attachment to the SWCNTs. For PB, in the absence of metal impurities, the relative quantum yield upon attachment is ~ 0.8 compared to that of the free dye. This suggests that the attachment to nanotube contributes to $\sim 20\%$ (i.e., $1.0 - 0.8$) of intensity quenching. The quenching mechanism of the dye-CNT hybrids could occur via various possible pathways. These processes could include, but are not limited to, a direct energy transfer from dye to substrate through space^{4,34} or through the chemical bond linkage,^{35,36} alteration of dye property due to the formation of a chemical bond,³² or dye quenching by proximity to a conducting surface, e.g., metallic SWCNTs in our case.³⁷

While Cho et al. demonstrated that the through-space quenching between pyrene and surface of nanotube occurred in pH sensing hybrids,⁴ control experiments with deactivated PB and DH on SWCNT²⁹ suggest that π - π interaction through space has little effect on the quenching of the luminescence of the chromophores used in this study. The formation of a chemical bond may eliminate a molecular functional group that is critical to the light emitting property of the molecule.³² To check whether the attachment of chromophores would alter their photoactivities, we have compared the emission spectra of the covalently attached chromophores on the CNT surface as described above. Figures 6 and 7 show the overlapped emission spectra of DH and PB solutions at their highest concentration. The luminescence intensities for CNT-attached DH were magnified 10-fold. There is a small peak at ~ 440 nm for DH-SWCNT-HNO₃, suggesting that there could be an alteration of chromophore structure due to the covalent attachment to nitric acid-treated SWCNT surfaces. This peak was not observed in DH-SWCNT-as-produced and DH-SWCNT-air/HCl, possibly due to the strong quenching in these systems. Meanwhile, the emission peaks for PB upon attachment were not shifted significantly, showing that the chromophore retained much of its optical properties (Figure 7).

Quenching can also occur by the proximity of dye to a conducting surface.³⁷ The excited state energy of the dye is

transferred to the conducting surface by the generation of electron–hole pairs. We attribute the quenching of PB to this process as we observed a correlation between the relative quenching and the concentration of metal.

DH–SWCNT hybrids show the type of results we expect from a potential solar cell material. First of all, the fluorescence of the dye–SWCNT hybrids should be quenched with respect to free dye; useful, harnessable energy conversion will not occur if the absorbed photon energy is simply reradiated. In this respect, PB does not appear promising, as it retains its fluorescing ability to a large extent even when bound in a dye–SWCNT hybrid. In comparison, DH–SWCNT hybrids are more promising, as the quenching of the luminescence was more than 1 order of magnitude, and it appeared to not correlate with the presence of metal impurities that can be challenging to remove entirely.

CONCLUSIONS

In conclusion, we have demonstrated that the results of quantitative fluorescence labeling (FLOSS) can be used for precise evaluation of the luminescence signal from dye–SWCNT hybrids in solution. In the case of PB, the luminescence is reduced by 20–80% depending on the content of metal impurities in the SWCNTs. Our result indicates that the decrease of fluorescence signal from dye–hybrids can be compromised by the presence of metal impurities. In the case of DH, the luminescence is quenched by almost 2 orders of magnitude. These results show that light harvesting hybrid materials based on DH and CNTs can be considered.

To the best of our knowledge, this is the first report in which concentrations of a free dye and the dye in dye–SWCNT hybrid solutions were both quantitatively determined for absolute comparison of fluorescence measurements. As a result, this study provides insight into the mechanisms of fluorescence quenching, allowing unambiguous studies of the fluorescence quenching effects caused by SWCNTs, and provides a means to screen potential fluorophores for possible use in dye–SWCNT light harvesting devices.

ASSOCIATED CONTENT

S Supporting Information. Additional details as described in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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