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Complete List of Authors:	Hou, Zhentao; University of Rochester, Chemistry Krauss, Todd; University of Rochester, Chemistry

Photoluminescence Brightening of Isolated Single-Walled Carbon Nanotubes

*Zhentao Hou[1] and Todd D. Krauss[1, 2, *]*

[1]Department of Chemistry and [2]The Institute of Optics, University of Rochester,

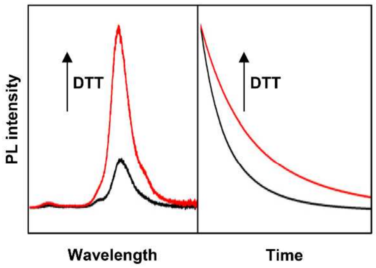
120 Trustee Road, Rochester, New York 14627-0216

***Corresponding Author:** todd.krauss@rochester.edu

ABSTRACT

Addition of dithiothreitol (DTT) to a suspension consisting of either DNA or sodium dodecyl sulfate (SDS) wrapped single-walled carbon nanotubes (SWCNTs) caused significant photoluminescence (PL) brightening from the SWCNTs, while PL quenching to different extents was observed for other surfactant-SWCNT suspensions. PL lifetime studies with high temporal resolution show that addition of DTT mitigates non-radiative decay processes, but also surprisingly increases the radiative decay rate for DNA- and SDS-SWCNTs. Completely opposite effects on the decay rates are found for the other surfactant-SWCNTs that show PL quenching. We propose that the PL brightening results from a surfactant reorganization upon DTT addition.

TOC



KEYWORDS: single-walled carbon nanotubes; photoluminescence brightening; surfactant reorganization; lifetime; exciton dynamics

Single-walled carbon nanotubes (SWCNTs) have unique photophysical properties due to their quasi-one-dimensional nature, which imparts cylindrical quantum confinement onto a strongly bound exciton state.[1-3] Although SWCNTs display stable and robust excitonic photoluminescence (PL) in the near infrared (NIR),[4-6] they have extremely low PL quantum yields (QYs) compared to other NIR emissive semiconductor nanoparticles, such as colloidal quantum dots.[7] For SWCNTs suspended in water, the QY varies between 0.01% and 1%,[4, 8-10] while in organic solvents, the QY approaches a few percent,[11-12] with one study reporting a QY as high as 20%.[13] Individual nanotubes (NTs) generally have QYs an order of magnitude larger than the ensemble,[14-15] which is still unexpectedly low.

Previously we found that the PL from DNA-wrapped SWCNTs can be enhanced by up to an order of magnitude upon addition of small molecular reducing agents such as Trolox, dithiothreitol (DTT) and β-mercaptoethanol (BME) to the SWCNT suspension.[16] This finding is unusual because adding small molecules to a NT suspension generally quenches exciton PL[17-20] or causes spectral shifts.[20-23] After brightening, the QYs of the brightest individual NTs were between 15 and 40%, while removal of the reducing agents caused the QY to return to previous levels. This surprising PL enhancement suggests that under some conditions suspensions of SWCNTs can be rendered highly emissive, which would have important implications for use of SWCNTs as biological imaging agents.[21, 24-25] However, important aspects of the brightening mechanism have not yet been addressed. It is unclear how the reducing agents interact with the SWCNT, and whether the brightening effect could be more generally applied.

Here we report studies of the photophysical properties of isolated SWCNTs upon addition of DTT for various aqueous surfactant-SWCNT suspensions. Like DNA-wrapped SWCNTs, sodium dodecyl sulfate (SDS) wrapped SWCNTs also exhibit significant PL brightening upon addition of DTT. By contrast, SWCNTs dispersed in sodium dodecylbenzenesulfonate (SDBS), sodium cholate (SC) and sodium deoxycholate (DOC) solutions display PL quenching to different extents, with SC-SWCNTs showing the largest PL QY decrease. State-of-the-art time-resolved PL lifetime studies in the NIR clearly show that addition of DTT not only mitigates non-radiative decay processes, but also surprisingly increases the radiative decay rate for DNA- and SDS-SWCNTs. This combination is responsible for the increase of the PL QY upon DTT addition. The opposite effects on radiative and non-radiative rates are found for other surfactant-SWCNTs that show PL quenching. The PL brightening (or quenching) is consistent with changes in the local dielectric environment as well as in SWCNT surfactant coverage, which we propose comes from a surfactant reorganization upon addition of DTT.

The PL spectra of various aqueous surfactant-SWCNT suspensions before and after the addition of DTT are shown in Figure 1 and Figure S1 (Supporting Information). Similar to DNA-wrapped SWCNTs, SDS-SWCNTs exhibited significant PL brightening of the S_1 transition, with an average three-fold enhancement. PL brightening was observed for all the SWCNT chiralities within our detection limit: the PL intensity increased by ~ 4-fold for (6,5) and (7,5) SWCNTs, ~ 3-fold for (8,3) SWCNTs and doubled for (6,4) SWCNTs. The PL intensity of DNA-SWCNTs almost doubled with addition of DTT, which was a slightly smaller increase compared to what we found previously.[16] We attribute this difference to the natural variations in sample preparation, and/or different batches of CoMoCAT SWCNTs.

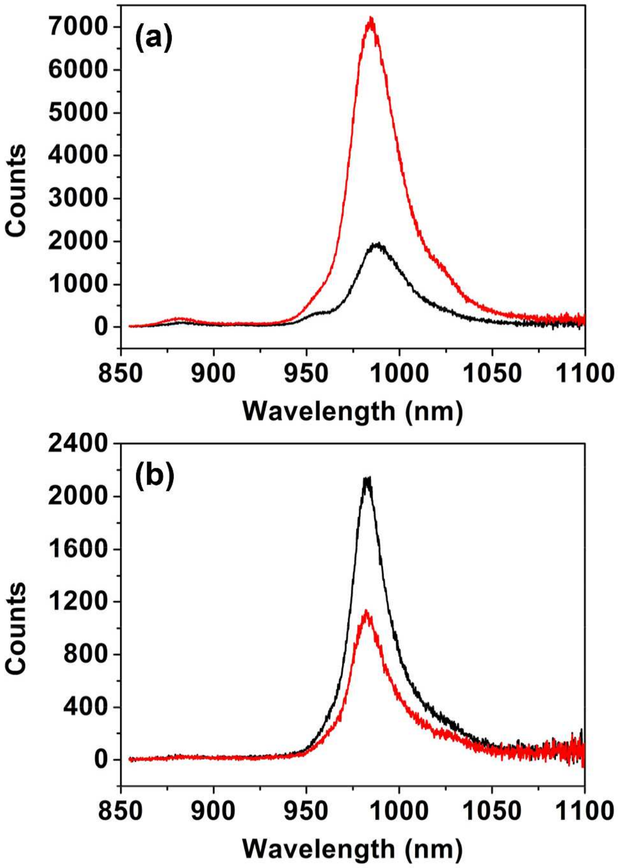


Figure 1. Photoluminescence spectra of SWCNTs suspended in 1% SDS (a) and 1% SC (b) aqueous solutions before (black) and after (red) the addition of DTT.

SDBS, SC and DOC dispersed SWCNTs showed different qualitative behavior compared to DNA and SDS dispersed SWCNTs. A minor PL intensity decrease was observed for SDBS and DOC dispersed SWCNTs, whereby the PL QY dropped by less than 20%. Unexpectedly, SC-SWCNTs showed substantial PL quenching by approximately 40% upon addition of DTT. The PL intensity decreased by ~ 50% for (8,3) SWCNTs and ~ 40% for (6,5) and (7,5) SWCNTs, while the PL from (6,4) SWCNTs was almost completely quenched.

As opposed to relative PL QY changes, knowing the absolute value of the PL QY is important for obtaining a fundamental understanding of the brightening phenomenon, and also for potential photoluminescence based applications. Figure S2 displays the PL QYs for various surfactant-SWCNT suspensions before and after the addition of DTT. Initially, SDS-SWCNTs had the lowest QY (QY ~ 0.12%) while the QY for DOC-SWCNTs was the highest (QY ~ 0.37%). These results are consistent with previous reports that show SWCNTs suspended with SDBS, SC and DOC have higher average QYs than DNA and SDS wrapped SWCNTs.[26-29] The QYs after the addition of DTT were determined using the following relation: $\frac{QY\ (after)}{QY\ (before)} = \frac{Integrated\ PL\ intensity\ (after)}{Integrated\ PL\ intensity\ (before)}$, where the integrated PL intensity was determined from PL spectra taken on the microscope (Figure 1 and Figure S1) and QY (before) is simply the QY measured on a standard fluorometer. The above relationship is accurate under the condition that the addition of DTT causes negligible absorbance change at the excitation wavelength, which we confirmed directly (see Figure S3). Upon addition of DTT, the PL QYs for DNA- and SDS-SWCNTs increased to ~ 0.30 ± 0.02%, while SC-SWCNTs showed a significant QY decrease to a QY value of 0.19 ± 0.01%. SDBS- and DOC-SWCNTs had a QY decrease of less than 20% to QY values of 0.19 ± 0.01% and 0.30 ± 0.01% respectively. Interestingly, despite the large spread in initial QY values, addition of DTT brings the final QYs for all samples to within a similar range of 0.2 to 0.3%.

A change in PL QY can arise from changes in the radiative or non-radiative decay rate of the S_1 exciton, and for a simple molecular system these rates can be determined from measurements of both the QY and the PL lifetime.[30] We measured the PL lifetimes for the various SWCNT samples using time-correlated single photon counting (TCSPC).

Importantly, a state-of-the-art InGaAs/InP avalanche photodiode (APD) detector allowed for determination of PL lifetimes in the NIR to below 7 ps. The photon flux of the excitation beam was kept low enough so that there was less than 0.1 photoexcited excitons per SWCNT per pulse. Two examples of the PL decay curves as well as the instrument response function (IRF) are shown for SDS- (Figure 2a) and SC-SWCNT (Figure 2b) suspensions before and after the addition of DTT. Clearly, addition of DTT has significant impacts on the exciton dynamics, and in particular seems to increase the PL lifetime considerably for the case of SDS-SWCNTs (Figure 2a).

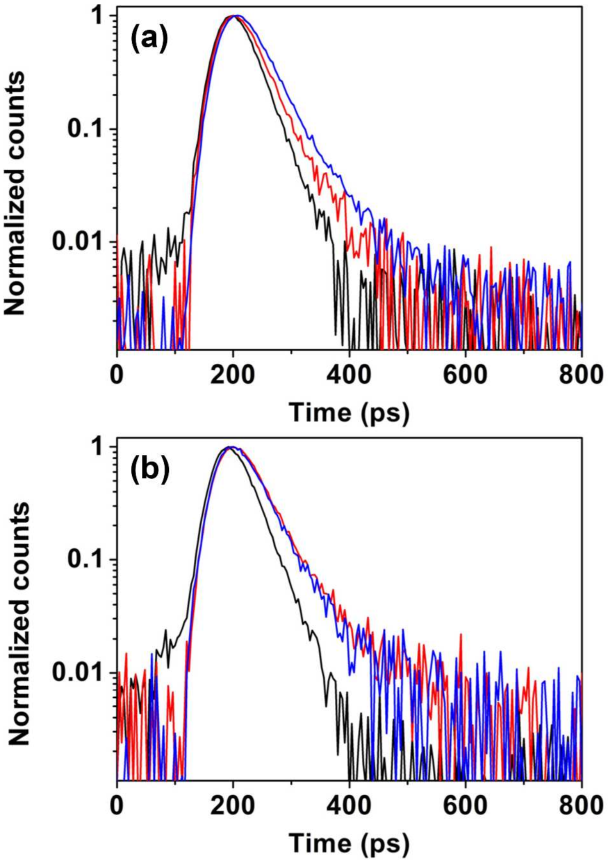


Figure 2. PL decay curves for SDS- (a) and SC-SWCNT (b) suspensions before (red) and after (blue) the addition of DTT as well as the IRF (black).

To better understand the effects of DTT addition, PL decay curves were fit by iterative reconvolution using commercial software (FluoFit), which convolutes an exponential decay function with the measured IRF and achieves the best fit while minimizing the weighted-sum of the residuals. This technique is able to resolve time constants about 5-10% of the width of the IRF[31] and allows for outstanding temporal resolution in determining PL lifetimes of SWCNTs. Satisfactory fits were obtained with a biexponential decay of the form $I(t) = A_1 e\left(-\frac{t}{\tau_1}\right) + A_2 e(-\frac{t}{\tau_2})$, consistent with previous reports on the decay dynamics of SWCNTs.[9, 32-33]

Among all the surfactant-SWCNT suspensions studied, the short time component (τ_1) ranged between 9 and 20 ps while the long time component (τ_2) ranged between 60 and 180 ps. The short and long time components have previously been assigned to the lifetimes of bright and dark excitons.[33-35] Although the amplitude of the long time component (A_2) was less than 5%, it was necessary to include it to accurately model all aspects of the PL decay. Table 1 lists the PL lifetime fitting results for SDS- and SC-SWCNT suspensions where the largest PL changes were observed (see Table S1, Supporting Information for complete fitting results for all samples). For SDS-SWCNTs, addition of DTT results in significant increases in τ_1 and τ_2. However, the opposite happens for SC-SWCNTs, whereby addition of DTT causes τ_1 and τ_2 to decrease.

Table 1. PL lifetimes for SDS- and SC-SWCNT suspensions with DTT addition

Surfactant		A_1 (%)	τ_1 (ps)	A_2 (%)	τ_2 (ps)	τ (ps)
SDS	before	99.2 ± 0.1	8.5 ± 0.6	0.8 ± 0.1	93.3 ± 12.0	9.2 ± 0.7
	After	98.1 ± 0.1	15.4 ± 0.4	1.9 ± 0.1	118.7 ± 8.4	17.3 ± 0.4

SC	before	96.5 ± 0.8	13.8 ± 0.5	3.5 ± 0.8	87.7 ± 14.7	16.0 ± 0.5
	After	96.7 ± 0.6	11.0 ± 0.4	3.3 ± 0.6	73.3 ± 8.7	12.8 ± 0.3

The amplitude-weighted PL lifetime was calculated using $\tau = A_1\tau_1 + A_2\tau_2$[30] for facile comparison among the surfactant-SWCNT suspensions (Figure 3). In general, the nature of the PL QY change upon addition of DTT determined the change in PL lifetime: SWCNTs that brightened showed increases in PL lifetime while those that were quenched showed decreases in lifetime. Knowing the PL QY and the amplitude-weighted lifetime τ, the effect of DTT addition on the radiative (k_r) and non-radiative (k_{nr}) decay rates can be calculated using the following: $k_r = \frac{QY}{\tau}$ and $k_{nr} = \frac{1-QY}{\tau}$,[30] as shown in Figure 4. We found that the radiative decay rate for the as-synthesized SWCNT samples is ~ 0.1 ns^{-1}, in good agreement with both theoretical predictions[36-37] and experiments.[9, 33, 35, 38] Non-radiative decay processes are much faster (rates of tens to hundreds of ns^{-1}) than radiative decay, as expected given the low PL QYs of SWCNTs, and thus non-radiative decay rates primarily determine the PL lifetime.

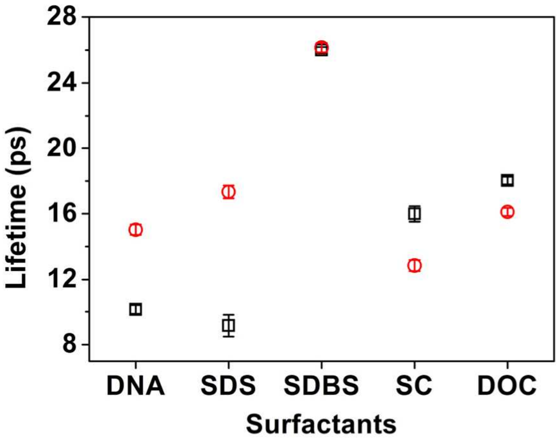


Figure 3. Amplitude-weighted PL lifetime for various surfactant-SWCNT suspensions before (black square) and after (red circle) the addition of DTT.

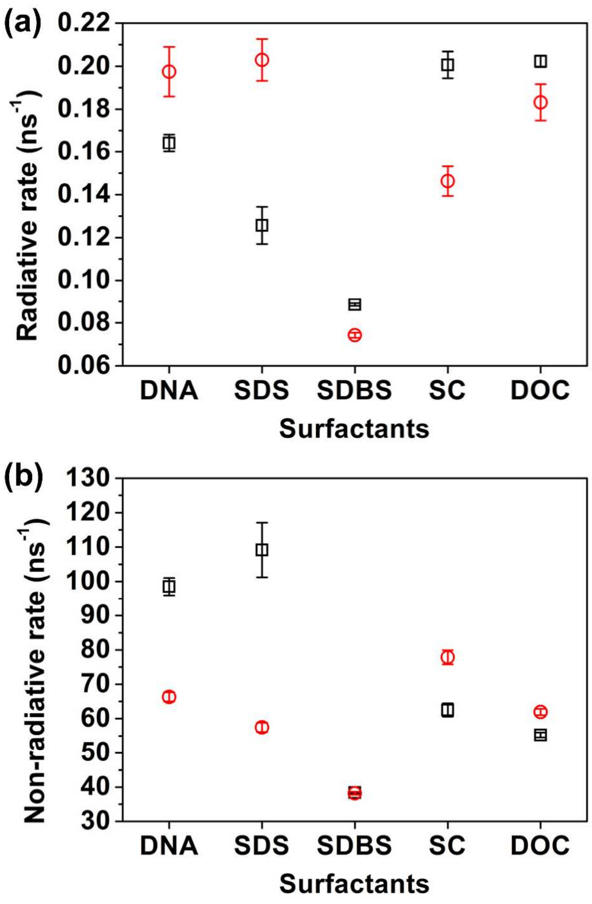


Figure 4. Radiative (a) and non-radiative (b) decay rates for various surfactant-SWCNT suspensions before (black square) and after (red circle) the addition of DTT.

Somewhat unexpectedly, we found that the addition of DTT has substantial effects on both radiative and non-radiative decay processes. For SDS-SWCNTs, the radiative decay rate increases by ~ 60% while the non-radiative decay rate decreases by ~ 50%. DNA-SWCNTs exhibit smaller changes in both rates, which is reasonable considering DNA-SWCNTs showed lower levels of brightening compared to SDS-SWCNTs. The opposite changes were observed for SC- and DOC-SWCNTs. In these two cases, radiative decay becomes slower while non-radiative decay gets faster. SDBS-SWCNTs show a small decrease in the radiative decay rate, but no change in the non-radiative decay rate, indicating that the exciton dynamics is not affected significantly by the DTT addition.

A straightforward explanation for the differences in SWCNT photophysics upon addition of DTT would involve changes in local dielectric constant. It has been previously proposed that the radiative decay rate of SWCNTs can be affected by the dielectric environment.[39] A decrease in dielectric constant causes the exciton size to shrink, giving rise to a larger oscillator strength.[39] In addition, the PL QY increases as the dielectric constant of the solvent decreases.[40-44] Thus, it is possible that the addition of DTT could modify the local dielectric environment, causing the observed changes in the radiative decay and QY. However, the differences in dielectric constant between DTT and the other surfactants are likely to be small, and thus this effect should be minor. Further, simple changes in dielectric constant cannot explain the variations in the non-radiative decay rates with DTT addition for the different surfactants.

The completely opposite effects of DTT on SWCNT PL for SC versus SDS suggest that details of how the surfactants interact with the SWCNT play an important role. A recent study on oxygen-induced PL quenching of SWCNTs also reported the observation of a similar surfactant dependence as we observed here:[45] DNA- and SDS-SWCNTs showed O_2 induced quenching while SDBS and DOC suspended SWCNTs generally exhibited little or no O_2 dependent quenching. DTT, being a mild reducing agent, could react with O_2 to lower its concentration in solution and thus its relative adsorption on the SWCNT. However, were this happening, it would not explain the magnitude of the PL enhancement for SDS-SWCNTs, nor the observation of PL quenching for SC-SWCNTs. Instead, we propose that upon addition of DTT the surfactant reorganizes, causing the changes in the SWCNT PL. Surfactant reorganization on SWCNTs in the presence of molecular additives is not an unreasonable concept. For example, the addition of small amount of electrolyte to SDS-SWCNTs leads to an increase in the PL intensity, attributed to reorganization of SDS molecules adsorbed on the SWCNT surface via electrostatic interactions.[46-48] Similarly, the addition of redox active molecules to SWCNTs triggers a surfactant reorganization, thus altering how SWCNTs are sorted in an aqueous two-phase (ATP) separation process.[49] Surfactant reorganization is also responsible for the differences observed in the absorption and PL of aqueous surfactant-SWCNT suspensions when mixed with immiscible organic solvents.[40] DNA wraps SWCNTs helically[50] and SDS has a relatively small binding energy to SWCNTs,[51] both of which leave significant NT surface exposed. It is possible that since DTT is a mild reducing agent, that addition of DTT slightly modifies the electronic wave function of electrons or holes in SWCNTs, causing changes in the binding affinity between surfactants and SWCNTs, or triggering the rearrangement of DNA or SDS molecules.[49] Alternatively, being more hydrophobic than water, DTT could weakly bind to the SWCNT thus making the environment around the SWCNT more hydrophobic and causing a change in the structure of the layer of surfactant around the SWCNT. The response would be similar to when organic solvent is added into aqueous SWCNT suspensions, whereby a layer of organic solvent molecules forms on the SWCNT and leads to surfactant reorganization.[40]

Surfactant rearrangement providing a more stable and local hydrophobic environment around the SWCNT is consistent with the total of our photophysical observations. A decreased local dielectric constant due to a more hydrophobic local environment would explain increase in the radiative decay rate.[39] Also consistent with this hypothesis is a small blue-shift (~ 4 meV) observed in the absorption and PL of SDS-SWCNTs upon addition of DTT (Figure 1a and Figure S3b), corresponding to a 1% relative decrease in dielectric constant.[39] Non-radiative decay paths such as from protonation and/or oxygen adsorption are also mitigated after surfactant reorganization because of better protection and isolation from the water solvent. In contrast to DNA and SDS, SC and DOC molecules bind very tightly to SWCNTs.[27-28, 51] DTT would likely act to weaken the binding between NTs and SC (or DOC) molecules, in agreement with the previous observation that DOC-SWCNTs showed limited or no response to the addition of electrolyte.[47] Consequently, addition of DTT causes the completely opposite behavior on the PL. Finally, increasing the concentration of DTT increases the magnitude of the PL increase (Figure S4), consistent with increased interactions with the local environment around the SWCNTs.

A final consideration for the cause of the PL changes is passivation of defect sites (*i.e.* hole traps) along the NT sidewall through electron donation from DTT.[16] The dependence of PL enhancement on (*n,m*) chiral structure is interesting in this regard, because within our limited range of chiral indices, the NTs with more negative reduction potentials ((6,4) and (8,3)) show less enhancement than those NTs that are easier to reduce ((6,5) and (7,5)).[52] However, the reduction potential of SWCNT structural and chemical defects is more positive than that of DTT,[18, 53] so DTT should reduce these defects equally for all SWCNT chiralities. Further, if passivation of hole traps with electrons were solely responsible for the brightening effect, we would expect that the non-radiative decay rate would decrease for all surfactant-SWCNTs. However, this is inconsistent with our observations that the non-radiative decay rate increases for SC- and DOC-SWCNTs. Thus, defect passivation is not likely to be a major contributor to the PL brightening effect.

In summary, the PL efficiency of DNA- and SDS-SWCNTs increased substantially upon addition of DTT to the SWCNT suspension, while PL quenching to different extents was observed for SDBS-, SC- and DOC-SWCNTs. The effect of DTT addition on radiative and non-radiative decay rates was determined through measurements of the PL QY and the PL lifetime. Changes in these rates in the presence of DTT are attributed to surfactant reorganization on the SWCNTs. In the case of PL brightening for DNA- and SDS-SWCNTs, the binding and/or surfactant coverage between surfactant molecules and NTs increases upon addition of DTT, which modifies the local dielectric environment in a more non-polar fashion while also mitigating exciton quenching. However, the presence of DTT weakens the interaction between SC (or DOC) molecules and SWCNTs, resulting in completely opposite effects. Our results suggest that the photophysical properties of suspensions of SWCNTs are an unexpectedly strong function of specific molecular properties of the surfactants used to create the suspension, and future studies will explore this relationship further through studies of exciton dynamics.

EXPERIMENTAL METHODS

CoMoCAT-manufactured SWCNT suspensions were prepared using probe sonication following the procedures by O'Connell *et al.*[4] with minor modifications. PL spectra and QY data were acquired on a home-built fluorometer system using IR-140 dye in ethanol

(QY ~ 16.7%)[54] as a standard. PL brightening and PL lifetime experiments were conducted on an inverted microscope, with SWCNT suspensions placed in silicone perfusion chambers adhered to glass coverslips. Samples were photoexcited with few ps pulses at 568 nm using a Ti:sapphire pumped optical parametric oscillator. SWCNT PL was detected by a gated InGaAs/InP APD, with an IRF of ~ 72 ps. See Supporting Information for a full experimental procedure.

ASSOCIATED CONTENT

*Supporting Information

Detailed experimental methods (sample preparation, optical characterization, PL brightening and lifetime measurements), additional PL spectra, PL QY data, absorption spectra, PL enhancement as a function of DTT concentration and complete lifetime fitting results. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Email: todd.krauss@rochester.edu

Notes

The authors declare no competing financial interest.

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