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Channeling Excitons to Emissive Defect Sites in Carbon Nanotube Semiconductors beyond the Dilute Regime

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Abstract

The exciton photoluminescence of carbon nanotube semiconductors has been intensively exploited for bioimaging, anticounterfeiting, photodetection, and quantum information science. However, at high concentrations, photoluminescence is lost to self-quenching because of the nearly complete overlap of the absorption and emissive states (~10 meV Stokes shift). Here we show that by introducing sparse fluorescent quantum defects via covalent chemistry, self-quenching can be efficiently bypassed by means of the new emission route. The defect photoluminescence is significantly red-shifted by 190 meV for *p*-nitroaryl tailored (6,5)-single-walled carbon nanotubes (SWCNTs) from the native emission of the nanotube. Notably, the defect photoluminescence is more than 34 times brighter than the native photoluminescence of unfunctionalized SWCNTs in the most concentrated nanotube solution tested (2.7×10^{14} nanotubes/mL). Moreover, we show that defect photoluminescence is more resistant to self-quenching than the native state in a dense film, which is the upper limit of concentration. Our findings open opportunities to harness nanotube excitons in highly concentrated systems for applications where photoluminescence brightness and light-collecting efficiency are mutually important.

Graphical Abstract

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Notes

The authors declare no competing financial interest.

Supporting Information

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Semiconducting single-walled carbon nanotubes (SWCNTs) have been proposed for applications as bioimaging fluorophores,¹ fluorescent inks,² photodetectors,³ exciton–polariton devices,⁴ and quantum light sources,^{5,6} where high concentrations and thin films are typically required. While methods have been developed for dispersing SWCNTs in aqueous solutions at high concentrations for use as near-infrared emitters,² application of photoluminescence (PL) at such high concentrations is challenging because of self-quenching effects. When left unaddressed, self-quenching adversely affects the resolution, sensitivity, and reliability of PL from SWCNTs at high concentrations,⁷ which leads to significant distortions in spectral analysis and decreased quantum yields.⁸ These effects are especially significant when quantitative measurements are required, particularly in the case of SWCNTs.⁹ Because of this limitation, concentrations of SWCNTs are typically kept within the millimolar range to prevent self-quenching. However, this is not a feasible solution in the many instances where dense systems of the nanomaterials are needed.

While quenching of SWCNT PL in solution may occur because of a variety of both radiative and nonradiative energy-transfer mechanisms, inner filter effects, or interactions of SWCNTs with the environment,^{10,11} in this work we specifically address collisional self-quenching of PL that becomes significant at high concentrations.¹² The increased collisions at high concentrations cause the excitation energy to be transferred to neighboring nanotubes and effectively lost to the dark states.¹³ The effects of these collisions are made even more significant for SWCNTs because of the small Stokes shift (~ 10 meV) between the emissive state, E_{11} , and the corresponding absorption peak (Figure 1a,b). Because of the significant overlap of the two states, undesirable nonradiative energy transfer occurs efficiently between SWCNTs.

In this work, we present a strategy to bypass self-quenching by channeling excitons to a new emissive state that is chemically introduced into the SWCNTs. As a proof of concept, we chemically modified (6,5)-SWCNTs with *p*-nitroaryl functional groups to generate (6,5)-SWCNT- $C_6H_4NO_2$ through aryldiazonium chemistry (see Experimental Methods in the

Supporting Information). The nitroaryl functional group introduces a fluorescent quantum defect that produces a new emissive state (E_{11}^-) that is distinctly different from the semiconductor host.¹⁴ This new state not only is significantly brighter than the nanotube's intrinsic PL state (E_{11}) but also lies considerably red-shifted (190 meV) from that of the absorption peak state (Figure 1c,d), bypassing the self-quenching route to which excitons are typical lost at E_{11} , even at high concentrations of SWCNTs.

Duggal et al.¹⁵ described the concentration boundary below which surfactant-wrapped SWCNTs are able to rotate freely in a solution. SWCNTs that are monodispersed in water behave as Brownian rigid rods because of their high aspect ratio. The Debye equation describes the rotational diffusion of an ensemble of Brownian rigid rods, and this equation can be related to the length of the rods, in this case the length of the SWCNTs (L), and used to define the theoretical boundary between the dilute and concentrated regimes. In this work, we define the boundary as the critical concentration, c^* (Figure 2). At concentrations above c^* , it is predicted that interactions between SWCNTs become significant as they are no longer able to freely rotate in solution,¹⁵ which will have a destructive effect on their PL. The transition between the two regimes is described by eq 1.

$$c^* = 2/\langle L^3 \rangle \quad (1)$$

in which $\langle L^3 \rangle$ is the third moment of the length distribution of the SWCNTs in solution. The third moment describes a distribution's skewness, or asymmetry about the mean. In the case of a solution of SWCNTs, $\langle L^3 \rangle$ is related to the volume occupied by a freely rotating nanotube.

We used this equation to predict the boundary beyond which we expect to observe PL self-quenching of the native E_{11} PL due to collisions of SWCNTs. Using atomic force microscopy (AFM), we determined the cube root of the third moment ($\langle L^3 \rangle^{1/3}$) of the (6,5)-SWCNTs in our solution to be 346 nm (Figure 3a). By applying this value for $\langle L^3 \rangle$ to eq 1, we calculated c^* to be $(2.8 \pm 0.1) \times 10^{13}$ SWCNTs mL⁻¹.

We performed a concentration-dependent spectroscopic study measuring the optical absorption and PL of both the chemically modified (6,5)-SWCNT-C₆H₄NO₂ and unmodified (6,5)-SWCNTs. Upon functionalization of the most concentrated solution of (6,5)-SWCNT, $(27 \pm 1) \times 10^{13}$ SWCNTs mL⁻¹, the absorbance of the E_{11} peak decreased by only 18% without significant peak broadening (Figure S1). The only partial quenching of E_{11} absorption reflects the sparse nature of the aryl groups with respect to the carbon lattice of the SWCNT. The low concentration of defects, approximately 1 defect per 20 nm of SWCNT length,¹⁴ is also reflected in the low absorbance of the defect state (E_{11}). Several sequential dilutions of stock solutions of (6,5)-SWCNTs and (6,5)-SWCNT-C₆H₄NO₂ were made, spanning the range of the theoretically predicted dilute regime and up to nearly 10 times the calculated c^* . The absorbance at the E_{11} and E_{22} features of both the functionalized and unfunctionalized SWCNTs maintained linearity with nanotube

concentration throughout the range of SWCNT concentrations tested, from (2.8 ± 0.1) to $(27 \pm 1) \times 10^{13}$ SWCNTs mL^{-1} (Figure 3b).

In contrast to the optical absorption study, PL from the two emissive states, E_{11} and E_{11}^- , of the unfunctionalized (6,5)-SWCNTs and (6,5)-SWCNT- $\text{C}_6\text{H}_4\text{NO}_2$, respectively, evolved differently as a function of SWCNT concentration (Figures 3c,d and S2). In the case of the unmodified (6,5)-SWCNTs, the PL from the native PL state, E_{11} (980 nm), is positively correlated with the SWCNT concentration up to $\sim(2.7 \pm 0.1) \times 10^{13}$ SWCNTs mL^{-1} , which is in good agreement with the predicted c^* , $(2.8 \pm 0.1) \times 10^{13}$ SWCNTs mL^{-1} (Figure 3e). Beyond this concentration, PL becomes negatively correlated with concentration. The E_{11} PL of the (6,5)-SWCNT- $\text{C}_6\text{H}_4\text{NO}_2$ sample was even more significantly quenched with concentration than that of the (6,5)-SWCNT sample (Figure S3). It is important to note that the initial intensity of PL from E_{11} in (6,5)-SWCNT- $\text{C}_6\text{H}_4\text{NO}_2$ is lower than that of (6,5)-SWCNT (Table S1) because of partial quenching of mobile E_{11} excitons due to functionalization of SWCNTs with *p*-nitroaryl groups, which is also reflected in the corresponding absorption spectra for each concentration (Figure 3b).

On the other hand, E_{11}^- in (6,5)-SWCNT- $\text{C}_6\text{H}_4\text{NO}_2$ was positively correlated with the SWCNT concentration beyond the dilute regime and throughout the entire range tested (Figure 3f). It appears that the chemical modification of the SWCNTs extended the onset of self-quenching (the region where PL evolves linearly with SWCNT concentration) 2-fold. The difference in the trends of the E_{11} PL in the two systems may reflect the efficient channeling of excitons to emissive defect sites in (6,5)-SWCNT- $\text{C}_6\text{H}_4\text{NO}_2$, in the case where there are sufficient numbers of defects such that the diffusional transport of E_{11} excitons can outrun collisional self-quenching. Provided this rationale, the results presented here may underestimate the effectiveness of E_{11}^- as a means of bypassing the self-quenching route of E_{11} excitons. Further optimization of the defect density of SWCNTs could enhance the PL even further.

Further analysis of the PL emission spectra of (6,5)-SWCNT samples reveals not only that the PL from E_{11} was quenched with increasing concentrations of SWCNTs but also that the PL feature is significantly broadened (Table 1). We found that the full width at half-maximum (fwhm) of the E_{11} PL for the (6,5)-SWCNTs increased by 62% (from 37 to 60 meV), within the range of concentrations tested. This spectral broadening effect at high concentrations is evidence of strong electronic interactions among SWCNTs in dense systems. Interestingly, this peak broadening was not observed in the case of the chemically modified (6,5)-SWCNT- $\text{C}_6\text{H}_4\text{NO}_2$ sample for either PL state (E_{11} and E_{11}^-). The lack of broadening suggests that the electronic coupling between neighboring nanotubes is effectively minimized because of the presence of quantum defects, which trap the excitons that would be otherwise lost to collisional quenching. Notably, we did not observe any red-shifts in the emission spectra in our concentration-dependent study, the absence of which suggests that the inner filter effect¹² does not contribute significantly to the concentration-dependent trends of E_{11}^- PL described in this work. However, given that the Stokes shift of the native SWCNT emission is very small (10 meV), such red-shifts would be difficult to resolve. PL lifetime studies may provide further insight into the mechanism of the quenching.

PL brightness is an important property for quantum emitters, and our previous work¹⁴ outlined that fluorescent quantum defects can brighten carbon nanotube PL substantially through defect PL, E_{11} . However, it is not well-understood how the defect PL evolves with concentration, beyond the dilute regime, which is vital for obtaining bright emission for application of fluorescent quantum defects. We compared the PL brightness of the (6,5)-SWCNT and (6,5)-SWCNT- $C_6H_4NO_2$ systems (Table S1) by calculating the relative efficiency (ϕ_{rel}) of converting absorbed photons to observed emission using eq 2.

$$\phi_{rel} = C \times \frac{A_{E_{11}}^-}{A_{E_{11}}} \quad (2)$$

in which $A_{E_{11}}^-$ and $A_{E_{11}}$ are the integrated areas of the PL peaks at E_{11} in (6,5)-SWCNT- $C_6H_4NO_2$ and E_{11} of (6,5)-SWCNT, respectively. C takes into account the difference in the absorbance at E_{22} between the (6,5)-SWCNT and the (6,5)-SWCNT- $C_6H_4NO_2$ samples and is given by eq 3.

$$C = \frac{OD_{E_{22}}(p)}{OD_{E_{22}}(d)} \quad (3)$$

in which $OD_{E_{22}}(p)$ and $OD_{E_{22}}(d)$ are equal to the amplitudes of the absorption peaks at E_{22} (565 nm) for the unmodified (6,5)-SWCNTs and chemically modified (6,5)-SWCNT- $C_6H_4NO_2$, respectively.

ϕ_{rel} values were calculated for a range of SWCNT concentrations, spanning the dilute and into the concentrated regime. ϕ_{rel} is positively correlated with SWCNT concentration throughout the concentration range tested (Figure 4a). In fact, E_{11}^- from the most concentrated solution of (6,5)-SWCNT- $C_6H_4NO_2$, $(27 \pm 1) \times 10^{13}$ SWCNT mL^{-1} , is 34 times brighter (ϕ_{rel}) than the native E_{11} exciton of (6,5)-SWCNT at the same concentration. The PL enhancement with functionalization of the SWCNTs becomes most significant at high nanotube concentrations because E_{11} PL becomes increasingly quenched with concentration. The positive trend of ϕ_{rel} with SWCNT concentration may be reflective of the channeling of E_{11} excitons, that would otherwise be lost to quenching, to defect sites where they can emit via E_{11}^- PL.

To probe the effectiveness of our strategy at the upper concentration limit, we measured the PL of solid-state films composed of (6,5)-SWCNT- $C_6H_4NO_2$ of different densities of SWCNTs (Figure 4b). AFM imaging of the films revealed that the SWCNTs are in a densely packed, concentrated system (Figure S4). Because the SWCNTs are in a system where they are interconnected (experiencing the maximum number of interactions with each other), it was expected that their direct proximity to one another would result in dramatically quenched E_{11} PL.¹⁶ As expected, upon doubling the film density, from 0.18 to 0.36 μg of

carbon cm^{-2} , emission from E_{11} was nearly completely lost. However, when the film density was doubled, the E_{11}^- PL retained 80% of its integral peak area. This suggests that E_{11} is more resistant to self-quenching than E_{11}^- , even in the case of the densely packed solid phase system. While the difference in PL intensities with concentration could be due to the presence of other semiconducting chiralities of SWCNTs which could quench SWCNT PL on contact, the concentrations of these other chiralities is relatively low as evident from the absorption spectrum of (6,5)-SWCNTs in Figure S5.

In addition, with respect to the less dense film, both the E_{11} and E_{11}^- PL suffer from significant red-shifting of the apparent excitonic peak energies. Notably, the emission from E_{11}^- shifts more (20 meV vs 12 meV) despite the defect state's smaller absorbance. The apparent red-shift in the energies of E_{11} and E_{11}^- could be the result of the inner filter effect, which causes selective absorption of the higher-energy regions of the spectrum.⁸ However, the presence of SWCNT bundles is more likely the cause of the differences in apparent peak energies.¹⁷

The results of our concentration-dependent studies suggest that sparse quantum defects on SWCNTs trap excitons at localized emission centers where they can emit photons that can bypass the self-quenching route to which E_{11} photons are typically lost at high concentrations. By implanting the quantum defects into the carbon lattice at low densities, we ensured that the (6,5)-SWCNT was nearly transparent to E_{11} (190 meV Stokes shift) and that the chances for destructive defect-defect collisions were minimized. Unmodified SWCNTs, lacking such emission outlets, emit primarily from E_{11} , which is readily quenched by neighboring SWCNTs at high concentrations because of the nearly complete spectral overlap with the corresponding absorption peak at this position (10 meV Stokes shift).

In summary, we showed that nanotube excitons can be efficiently channeled to emissive defect sites in highly concentrated systems of SWCNTs. Using a nanotube rotational diffusion model, we experimentally determined that $(2.8 \pm 0.1) \times 10^{13}$ SWCNTs mL^{-1} was the critical concentration at which collisional self-quenching becomes dominate for nanotubes with an average length of 346 ± 148 nm. We studied a range of SWCNT concentrations that spanned the dilute regime and up to nearly 10 times the calculated c^* value. The c^* is in good agreement with our measurements of concentration-dependent native E_{11} PL emission from unmodified (6,5)-SWCNTs. Through the covalent introduction of sparse aryl groups onto the nanotubes, we extended the onset of self-quenching 2-fold via the red-shifted emission from the defect-induced PL state. We observed that emission from E_{11}^- maintained a positive correlation with concentration, even in the case of the most concentrated solution tested, $(27 \pm 1) \times 10^{13}$ SWCNTs mL^{-1} . In fact, at this highest concentration, the E_{11} PL from the (6,5)-SWCNT- $\text{C}_6\text{H}_4\text{NO}_2$ was still 34 times brighter than the E_{11} PL from the unmodified (6,5)-SWCNTs at the same concentration. We also explored the self-quenching effect at the upper concentration limit by using a film of (6,5)-SWCNT- $\text{C}_6\text{H}_4\text{NO}_2$ and found that the E_{11}^- PL was still more resistant to self-quenching than that of the native nanotube PL, E_{11} . We attribute these observations to the energy mismatch of E_{11}^- PL with the absorption of the bulk carbon lattice and the channeling of excitons to sparse emissive defect sites on the SWCNTs, which are less likely to interact with each other.

Further investigation may reveal insights into the mechanism of energy transfer. Our study demonstrates that the E_{11}^- PL can be used to dramatically improve the optical performance of SWCNTs at high concentrations and extend the range of nanotube concentrations that exhibit bright emission.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

Quantum defects channel excitons to emissive defect sites, opening an efficient emission outlet in concentrated SWCNTs. (a, c) Schematics and energy level diagrams illustrate the distinct electronic systems present in (a) (6,5)-SWCNTs and (c) (6,5)-SWCNT- $C_6H_4NO_2$. (b, d) The normalized absorbance (black line) and PL emission ($\lambda_{ex} = 565$ nm) of (b) (6,5)-SWCNTs (blue line) and (d) (6,5)-SWCNT- $C_6H_4NO_2$ (red line) highlight the dramatic difference in the Stokes shifts to the prevailing emission peaks existing in each of the two systems, E_{11} at 980 nm and E_{11} at 1141 nm.

Figure 2.

Theoretical limit for collisional self-quenching of surfactant-wrapped SWCNTs in solution. The interactions between neighboring SWCNTs are predicted by inequalities related to the concentration (c) of the SWCNT solutions, ranging from the dilute regime, where collisions are rare, to the concentrated regime, where interactions become significant. L is the length of the SWCNT (blue cylinders).

Figure 3.

Fluorescent quantum defects provide an emissive outlet for excitons which would otherwise be lost to self-quenching beyond the dilute concentration limit, c^* . (a) The length distribution of 200 individual (6,5)-SWCNTs was determined by AFM. (b) Absorbance at E_{11} of (6,5)-SWCNTs (blue open squares) and (6,5)-SWCNT- $C_6H_4NO_2$ (red open squares) has a strong linear (solid lines) relationship with SWCNT concentration (conc.). The values of R^2 are 0.998 and 0.981 for the (6,5)-SWCNT and (6,5)-SWCNT- $C_6H_4NO_2$ samples, respectively. (c, d) The major emission peaks were isolated from the PL emission spectra ($\lambda_{ex} = 565$ nm) of solutions of different concentrations of (c) (6,5)-SWCNT and (d) (6,5)-SWCNT- $C_6H_4NO_2$. (e) E_{11} PL from solutions of (6,5)-SWCNTs (blue, inset has y-axis scaled) and (f) E_{11}^- PL from (6,5)-SWCNT- $C_6H_4NO_2$ (red) evolves as a function of SWCNT concentration. The dilute regime is indicated by the gray, shaded region in panels b, e, and f. The error bars in panels b, e, and f reflect the error in calculation of concentration (see the Supporting Information).

Figure 4.

Bright defect PL in concentrated solutions and films of (6,5)-SWCNT- $\text{C}_6\text{H}_5\text{NO}_2$. (a) The relative brightness of the defect PL state of (6,5)-SWCNT- $\text{C}_6\text{H}_4\text{NO}_2$ with respect to the brightness of the native PL state, ϕ_{rel} , increases substantially with concentration in solution. (b) PL spectra (circles) and deconvoluted E_{11} and E_{11}^- peaks (filled areas) of the $0.18 \mu\text{g}$ of carbon cm^{-2} (red) and $0.36 \mu\text{g}$ of carbon cm^{-2} (black) films of (6,5)-SWCNT- $\text{C}_6\text{H}_5\text{NO}_2$ ($\lambda_{\text{ex}} = 565 \text{ nm}$).

Table 1Spectral Broadening of the Emissive States of (6,5)-SWCNTs versus (6,5)-SWCNT- $C_6H_4NO_2$ with Increasing SWCNT Concentration^a

concentration ($\times 10^3$ SWCNTs mL^{-1})	(6,5)-SWCNT		(6,5)-SWCNT- $C_6H_4NO_2$			
	E_{11} (nm)	fwhm (meV)	E_{11} (nm)	fwhm (meV)	E_{11} (nm)	fwhm (meV)
1.40 ± 0.06	980	37	980	36	1141	59
2.7 ± 0.1	980	41	980	35	1141	56
6.8 ± 0.3	980	45	980	34	1141	55
13.5 ± 0.5	980	48	980	37	1141	56
27 ± 1	980	60	980	33	1141	53

^aThe values in this table were obtained by the spectral fitting method described in the Supporting Information.