Absolute Quantification of sp³ Defects in Semiconducting Single-Wall Carbon Nanotubes by Raman Spectroscopy

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ABSTRACT: The functionalization of semiconducting single-wall carbon nanotubes (SWCNTs) with luminescent sp³ defects creates red-shifted emission features in the near-infrared and boosts their photoluminescence quantum yields (PLQYs). While multiple synthetic routes for the selective introduction of sp³ defects have been developed, a convenient metric to precisely quantify the number of defects on a SWCNT lattice is not available. Here, we present a direct and simple quantification protocol based on a linear correlation of the integrated Raman D/G⁺ signal ratios and defect densities as extracted from PLQY measurements. Corroborated by a statistical analysis of single-nanotube emission spectra at cryogenic temperature, this method enables the quantitative evaluation of sp³ defect densities in (6,5) SWCNTs with an error of ±3 defects per micrometer and the determination of oscillator strengths for different defect types. The developed protocol requires only standard Raman spectroscopy and is independent of the defect configuration, dispersion solvent, and nanotube length.

The chemical modification of semiconducting single-wall carbon nanotubes (SWCNTs) is a versatile tool to tune their properties for various applications such as quantum-light sources,2−5 sensing, or bioimaging.4−7 In particular, covalent functionalization of SWCNTs with luminescent sp³ defects (also referred to as organic color centers) creates red-shifted emissive states in the near-infrared (NIR).8−12 These states exhibit deep optical trap potentials (100−250 meV), which are able to localize the highly mobile excitons9 that would otherwise explore large nanotube segments to encounter quenching sites or decay radiatively by E₁₁ emission (see Figure 1a).13 By preventing excitons from reaching quenching sites and decaying nonradiatively, these sp³ defects can increase the total photoluminescence quantum yield (PLQY) of SWCNTs.8−14 However, precise control of the degree of sp³ functionalization is crucial. The maximum ensemble PLQY is observed at fairly low levels of functionalization, which would be favorable for electrically pumped light-emitting devices.15 In contrast, single-photon emission requires exactly one luminescent defect per SWCNT.1 Hence, accurate control over the degree of functionalization and knowledge of the precise sp³ defect densities are highly desired for further optimization.

The emission wavelengths of functionalized SWCNTs are predominantly determined by the binding configuration of the defects, as two sp² carbon atoms must be converted to sp³ carbon to form one defect state. In chiral SWCNTs there are six possible relative positions of the involved carbon atoms, all of which lead to different optical trap depths and photoluminescence (PL) peak wavelengths.16,17 However, only two of them are commonly found in functionalized (6,5) SWCNTs and give rise to separate NIR emission peaks termed E₁₁,8 and E₁₁*,8,18 the latter being more red-shifted and exhibiting a longer fluorescence lifetime than the former.19,18

Various synthetic methods have been developed in an attempt to control the degree and type of sp³ functionalization of nanotube dispersions in water or organic solvents.14,18−20 However, comparing different reports on functionalized SWCNTs and their properties is difficult because of the use of indirect metrics for their quantification. For example, PL peak intensity ratios strongly depend on the specific experimental setup and excitation power. They only provide a relative but not an absolute defect density.21 Currently, the most reliable technique to determine the number of luminescent defects on individual SWCNTs is to count distinct emission peaks at cryogenic temperatures.5,22 However, this method requires substantial experimental effort and tedious statistical analysis.

For graphene, a simple approach to quantify lattice defect densities using Raman spectroscopy is already well-established.23,24 The introduction of point-like defects into the planar sp² carbon lattice leads to the activation of the Raman D mode. Its relative intensity compared to the G mode can be
used as a direct metric for the areal defect density. The corresponding equation has been applied as a means of quality control in graphene samples and to monitor the degree of chemical functionalization. It was recently modified and extended to include line defects in graphene. Although the Raman D mode of SWCNTs also reflects the degree of structural disorder and number of defects, no quantitative relation to the absolute density of defects, especially at low defect densities, has been reported so far.

Here, we present a robust empirical metric for the absolute quantification of sp³ defects in the most commonly used (6,5) SWCNTs. Our method is based on a cross-correlation of Raman spectra, PLQY data, and statistics of low-temperature single-nanotube PL measurements. The final protocol only requires resonant Raman spectroscopy of drop-cast SWCNT films. That way, we are able to extract the absolute sp³ defect density, independent of type, within an error of ±3 defects per micrometer.

To produce nanotube samples with a controlled number of defects per nanotube length, polymer-sorted (6,5) SWCNTs were functionalized using two different procedures (see Methods, Supporting Information). E₁₁⁺ defects (emission at ~1170 nm) were introduced by treatment with 4-nitrobenzenediazonium tetrafluoroborate (DzNO₂) in a mixture of toluene/acetonitrile employing a phase-transfer agent. More red-shifted E₁₁⁻⁻ defects (emission at ~1250 nm) were created by reaction with 2-iodoaniline in the presence of the organic base potassium tert-butoxide (KOᵗBu). The degree of sp³ functionalization was controlled by variation of the DzNO₂ concentration or by adjusting the reaction time with 2-iodoaniline. Figure 1b,c shows the corresponding normalized PL spectra of selectively functionalized (6,5) SWCNT dispersions collected under pulsed excitation at the E₂₂ transition (575 nm). Furthermore, we employed a sequential reaction scheme to create (6,5) SWCNTs with controlled concentrations of E₁₁⁺ and E₁₁⁻⁻ defects as shown in Figure 1d.

The increasing defect emission intensities in relation to the intrinsic E₁₁ emission (~1000 nm) reflect the rising number of defects, but this ratio strongly depends on excitation power and cannot provide an absolute number. In contrast to that, absolute PLQY values of functionalized SWCNT dispersions can be used to calculate the density of luminescent sp³ defects within the framework of the diffusion-limited contact quenching (DLCQ) model. The DLCQ model assumes that excitonic E₁₁ emission is governed by exciton diffusion and nonradiative decay at stationary quenching sites. Within this model, luminescent sp³ defects represent an additional relaxation pathway competing for mobile excitons and resulting in a lower E₁₁ PLQY of the functionalized SWCNTs (η*) compared to pristine SWCNTs (η) as introduced by Miyauchi et al. The ratio (η/η*) can be used to calculate the density of luminescent defects n_d [μm⁻¹] according to

\[ n_d = \frac{\pi}{2D\tau_{rad}} \left[ \sqrt{\frac{\eta}{\eta^*}} - 1 \right] \]

where D is the exciton diffusion constant and \( \tau_{rad} \) is the radiative lifetime of the E₁₁ exciton. The values for D and \( \tau_{rad} \) were taken from previous experimental studies on (6,5) SWCNTs (for details, see the Supporting Information). Absolute PLQY values of SWCNT dispersions can be obtained from the direct measurement of absorbed and emitted photons in an integrating sphere in comparison to a reference sample (cuvette with solvent, see Figure 1e and Supporting Information for experimental details) as described previously.
The spectral contributions of the intrinsic excitonic E_{11} emission and defect emission (E_{11}*, E_{11}**−) are separated, and the defect density is calculated using eq 1 with only the E_{11} PLQY. Based on the uncertainties of the PLQY measurements and the error margins of the reported D and G relaxed values, a relative uncertainty of the defect density of about 15% can be estimated. Figure 2a shows the E_{11} and E_{11}* contributions to the total PLQY versus the calculated defect densities for (6,5) SWCNTs functionalized with different concentrations of DzNO2. Pristine (6,5) SWCNTs exhibit a total PLQY of ~2% in dispersion. Low levels of luminescent defects (up to ~10 μm^{−1}) increase the total PLQY by a factor of 2 followed by a strong reduction of the total PL yield at higher degrees of functionalization, in agreement with previous studies.14,18

A major drawback of this approach is the necessity of an experimental setup with an integrating sphere for determining the PLQY in combination with precisely defined measurement conditions to prevent distortions due to photon reabsorption.55 In contrast, determining the relative integrated D mode (I_{D} (1200−1400 cm^{−1}) to G mode intensity (I_{G}, 1560−1640 cm^{−1}) from Raman spectra of the corresponding drop-cast nanotube films is straightforward and very reliable. As shown in Figure 2b, the D mode intensity increases with the degree of functionalization, being indicative of the number of sp^{3} carbon atoms. Figure 2c confirms a linear correlation of the integrated Raman signal ratio (I_{D}/I_{G}) with the calculated defect densities obtained from the E_{11} PLQY data in Figure 2a.

The linear correlation in Figure 2c should enable a direct evaluation of the number of sp^{3} defects based only on Raman spectra of functionalized (6,5) SWCNTs. However, this metric does not take into account the variations in initial quality of nanotubes before functionalization and thus the variability of the Raman D/G ratios of the pristine samples. As sp^{3} functionalization adds luminescent defects to a SWCNT lattice that already contains a certain number of defects depending on starting material and processing, the absolute Raman D/G ratios cannot be used to determine the number of introduced sp^{3} defects. Hence, we propose to use the difference between the integrated Raman D/G ratios of the pristine and functionalized sample, i.e., Δ(I_{D}/I_{G}), as a suitable metric for the quantification of defects introduced by functionalization. Note that we use the integrated Raman D/G ratio instead of just the peak intensity ratio because it provides more reliable and reproducible values, especially for small changes in defect density.

This differential integrated Raman D/G ratio enables comparison between different batches of nanotubes and different functionalization methods. Figure 3 shows a summary of different batches of functionalized (6,5) SWCNTs (see Supporting Information, Figures S1−S3 for detailed PLQY data, PL and Raman spectra). The linear correlation of Δ(I_{D}/I_{G}) with the defect density extracted from the PLQY holds for different defect densities, various SWCNT batches, E_{11}*, and E_{11}**− defects as well as sequential functionalization to create both defects.

A linear fit to the compiled data yields the following simple expression for the density of introduced sp^{3} defects in (6,5) SWCNTs:

\[ n_d = (414 \pm 11) \mu m^{-1} \left( \frac{I_D}{I_G} \right) \]

This equation is valid across a wide range of relevant defect densities (2−40 defects μm^{−1}) and, in particular, covers the defect densities associated with maximum total PLQYs (i.e., 4−8 defects μm^{−1}).

To exclude any potential influence of the laser excitation power on the integrated Raman D/G ratios and thus extracted defect densities, Raman spectra of functionalized (6,5) SWCNTs were recorded under identical conditions but at
different excitation power densities (see Figure S4, Supporting Information). No significant changes of the integrated Raman D/G’ ratios were observed. Values obtained at typical laser power densities for Raman spectroscopy of (6,5) SWCNTs should also be comparable between different Raman spectrometers. Thus, this simple metric enables a quick and precise characterization of functionalized SWCNTs, and could be used for a reliable comparison of experiments in different laboratories using different experimental setups. It could also be applied to quickly identify a batch of functionalized nanotubes that is most likely to produce the strongest NIR emission upon excitation.

Note that other possible metrics were also tested, such as the integrated defect-to-E_{11} absorption and emission ratios. In general, absorption ratios are rather unreliable because of the very low absorbance values for E_{11}^* and E_{11}^{-*} transitions at low defect densities even for fairly concentrated dispersions (see Figure S5, Supporting Information). No clear correlation with the calculated defect densities could be identified across different SWCNT batches and defect configurations (see Figure S6, Supporting Information). The more commonly employed defect-to-E_{11} emission ratio, which can assess the relative degree of sp^3 functionalization of SWCNTs, is not applicable across different batches and functionalization methods because of the nonlinear and variable dependence of E_{11} and defect emission on excitation power (see Figure S7, Supporting Information).\(^{18,38}\)

The demonstrated cross-correlation of integrated Raman D/G’ ratios and defect densities calculated from E_{11} PLQY data enables a simple evaluation of sp^3 defect densities. However, even the DLCQ model only quantifies the number of defects indirectly and relies heavily on correct values for the exciton diffusion constant and radiative lifetime. In contrast, PL spectra of individual functionalized SWCNTs at cryogenic temperature (cryo-PL) allow for each luminescent defect to be counted as a separate emission peak,\(^{22,39}\) assuming that each distinguishable peak within the E_{11}^* or E_{11}^{-*} spectral emission range corresponds to precisely one sp^3 defect of the respective binding configuration. Different defect emission intensities only reflect the integrated probability for exciton relaxation in a given defect state (not multiple defects), as previously reported for the intrinsic E_{11} transition.\(^{22}\)

To cross-check the calculated defect densities from PLQY measurements, two samples of (6,5) SWCNTs that were functionalized with low and medium densities of E_{11}^* defects (spectral region 1100–1220 nm) were produced and PL spectra at 4.6 K from a large number of individual nanotubes embedded in a polystyrene matrix were statistically analyzed (see Figure 4). At low calculated defect densities of ~4 \(\mu m^{-1}\), only few defect emission peaks were found in over 50 representative spectra (see Figures 4a and S8, Supporting Information). At medium defect densities (~8 \(\mu m^{-1}\)) significantly more defect PL peaks were identified on more than 40 single SWCNTs (see Figures 4b and S9, Supporting Information). Some E_{11}^{-*} defects (spectral region 1220–1360 nm) were found for these defect densities, which is consistent with literature reports for (6,5) SWCNTs functionalized with DzNO_2.\(^{16,17,40}\) As both defect configurations contribute equally to E_{11} quenching within the DLCQ model, and the developed quantification metric does not depend on the binding configuration, all defect peaks were included in the statistical analysis. The respective histograms for the number of defects per nanotube at low and medium sp^3 defect densities are shown in Figure 4c,d. The defect densities calculated from PLQY data and the average defect densities obtained from histograms are in good agreement. However, while calculated defect densities are given per micrometer of SWCNT, cryo-PL spectra show defects on individual nanotubes with unknown length. Hence, the length distribution of sp^3-functionalized SWCNTs needs to be considered for a thorough comparison. For this purpose, atomic force micrographs of nanotubes from the same dispersion of functionalized SWCNTs as those used

![Figure 4. Low-temperature (4.6 K) single-SWCNT PL spectra of (6,5) SWCNTs in a polystyrene matrix functionalized with (a) low and (b) medium defect densities. Black triangles indicate individual defect emission peaks, spectral regions are highlighted for E_{11} (blue), E_{11}^* (red), and E_{11}^{-*} (orange) emission. Defect peak histograms of (c) 51 functionalized (6,5) SWCNTs with defect density 3.6 \(\mu m^{-1}\) and (d) 43 functionalized (6,5) SWCNTs with defect density 7.9 \(\mu m^{-1}\) as calculated from PLQY data.](https://doi.org/10.1021/acs.jpclett.2c00758)
in cryo-PL spectroscopy were recorded and statistically analyzed (see Figures S8 and S9, Supporting Information). Both pristine and functionalized (6,5) SWCNTs exhibited average lengths of \(~1.6\ \text{μm}\). This length distribution suggests that the number of defects per micrometer obtained via cryo-PL measurements is actually slightly lower than that extracted from PLQY measurements (possibly due to a selection bias toward less bright spots to avoid bundles and not all introduced defects being bright, see Supporting Information) but still within the margin of error \((±3\ \text{μm}^{-1})\) established in eq 2.

Although eq 2 was derived from measurements of long, polymer-wrapped (6,5) SWCNTs functionalized in organic solvents, the method is also applicable to short nanotubes and aqueous dispersions of SWCNTs. We used DzNO₂ to functionalize polymer-sorted (6,5) SWCNTs that were intentionally shortened to average lengths of \(0.46\ \text{μm}\) by tip sonication (Supporting Information, Figures S10 and S11) and (6,5) SWCNTs sorted by aqueous two-phase extraction (ATPE), stabilized by surfactants in water (see Methods and Figure S12, Supporting Information). For both, a linear correlation between the differential Raman \(D/G+\) ratio and calculated defect densities in agreement with eq 2 was found (see Figure 5a). Moreover, nearly monochiral dispersions of polymer-sorted (7,5) SWCNTs, functionalized with DzNO₂ (see Methods and Figure S13, Supporting Information) in a first attempt to expand our approach to other nanotube species. Because of the lower reactivity of (7,5) SWCNTs compared to (6,5) SWCNTs, \(2^\text{a}\) a maximum absolute defect density of \(~20\ \text{μm}^{-1}\) was achieved. Nevertheless, the presented quantification method was also applicable to (7,5) SWCNTs (wrapped with polydioctylfluorene, PFO) as shown in Figure 5b, although with some deviations in the precise slope.

This is particularly interesting as resonant Raman measurements of (7,5) SWCNTs are performed at a different excitation wavelength (633 nm) compared to (6,5) SWCNTs (532 nm). For point-like defects in graphene, Cançado et al. reported a strong dependence of the Raman \(D/G\) intensity ratio on excitation laser wavelength, which was included in the expression for the average defect distance. However, for large defect distances, the influence of the excitation wavelength on the absolute Raman \(D/G\) intensity ratio becomes negligible.\(^{23}\) The mean defect distances in \(sp^3\)-functionalized SWCNTs relevant for most applications and investigated here (20–30 nm, see Figure S14, Supporting Information) are much larger than those considered in studies of defective graphene (5–30 nm).\(^{23}\) Nevertheless, it remains to be tested what impact the Raman laser excitation wavelength has on SWCNTs with larger diameters.

One direct application of the presented quantification method is the experimental determination of the oscillator strengths of \(E_{11}^*\) and \(E_{11}^{-*}\) defects. Integration of the defect peak areas in the NIR absorbance spectra of functionalized SWCNTs with different defect densities yielded the integrated molar absorptivities and absorption cross sections of the \(E_{11}^*\) and \(E_{11}^{-*}\) states (see Table 1 and Figure S15, Supporting Information). The oscillator strength of an optical transition was calculated using

\[
f = 4\varepsilon_0c^2m_e\ln(10) \int \sigma(\nu)d\nu\tag{3}
\]

where \(\varepsilon_0\) denotes the vacuum permittivity, \(c\) is the speed of light, \(m_e\) is the electron mass, \(N_A\) is Avogadro’s number, \(c\) is the elementary charge, \(\varepsilon_0\) is the molar extinction coefficient of the \(E_{11}^*\) or \(E_{11}^{-*}\) transition, and \(\nu\) is the wavenumber.\(^{41}\)

For \(E_{11}^*\) and \(E_{11}^{-*}\) defects, oscillator strengths of \((3.5 ± 0.6)\) and \((1.1 ± 0.3)\) per defect were obtained, respectively. The error margins for the oscillator strengths of \(E_{11}^*\) and \(E_{11}^{-*}\) are mainly due to the low total absorbances of the \(sp^3\) defects and the corresponding uncertainties of the integrated defect absorption (see Figure S5, Supporting Information). While density functional theory calculations predicted larger oscillator strengths (by a factor of \(3–5\)),\(^{16,17}\) they also suggested a reduction of the oscillator strength with a greater red-shift of the defect emission, which is in agreement with our findings. It is important to note that the discussed spectroscopic metrics provided here are given per defect site and are not directly comparable to literature data on the \(E_{11}^*\) oscillator strengths of (6,5) SWCNTs (\(~0.01\) per carbon atom).\(^{42}\) As electron–hole correlation lengths are still on the order of 1 nm despite

![Figure 5. Differential integrated Raman D/G’ ratio versus calculated defect densities and linear fits for (a) aqueous dispersions of ATPE-sorted (6,5) SWCNTs and tip-sonicated, polymer-wrapped (6,5) SWCNTs and for (b) polymer-wrapped (7,5) SWCNTs. All functionalization steps were performed with DzNO₂.](image-url)
localization at defect sites,\textsuperscript{43} \(100\) carbon atoms are presumed to contribute to the sp\(^3\) defect oscillator strength. Although the acquired data is not accurate enough to corroborate an increase of oscillator strength by a factor of 2 upon exciton trapping as proposed by Miyauchi et al.,\textsuperscript{10} our findings suggest that the oscillator strengths of sp\(^3\) defects are at least on the same order of magnitude as those for the E\(_{11}\) transition.

In conclusion, we have developed a straightforward and reliable method to quantify the number of sp\(^3\) defects in (6,5) SWCNTs using resonant Raman spectroscopy. By establishing a linear correlation between the differential integrated Raman D/G‘ ratio and sp\(^3\) defect densities calculated from PLQYs, the number of added defects per micrometer nanotube can be obtained within an error margin of \(\pm 3\) defects \textmu m\(^{-1}\). This method is suitable for SWCNTs functionalized with E\(_{11}\), E\(_{11}\)‘, or both defect configurations, independent of the type of dispersion (polymer-wrapped in organic solvent or surfactant-stabilized in water) and nanotube length of the starting material. A statistical analysis based on PL spectra of individual (6,5) SWCNTs at cryogenic temperature provided direct access to the number of defects per nanotube, which roughly matched the densities calculated from Raman spectra. From these data, the oscillator strengths of the E\(_{11}\)‘ and E\(_{11}\)‘‘ defects were determined experimentally, confirming the predicted decrease in oscillator strength with optical trap depth of the defects. The applicability of the presented quantification method also extends to other nanotube species as demonstrated for (7,5) SWCNTs. However, additional resonant Raman and PLQY data of functionalized SWCNTs with different diameters will be required to obtain a universal expression similar to that for defects in graphene.

**ASSOCIATED CONTENT**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.2c00758.

Experimental details, characterization methods, calculation of sp\(^3\) defect densities, additional data for functionalized SWCNTs (PLQY; PL, Raman, absorption spectra), Raman laser power density dependence of integrated D/G’ ratios, low-temperature PL spectra of individual nanotubes, AFM length statistics, calculation of integrated molar absorbivities (PDF)

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**Notes**

The authors declare no competing financial interest.

**REFERENCES**

1. He, X.; Htoon, H.; Doorn, S. K.; Pernice, W. H. P.; Pyatkov, F.; Krupke, R.; Jeantet, A.; Chassagneux, Y.; Voisin, C. Carbon Nanotubes as Emerging Quantum-Light Sources. Nat. Mater. 2018, 17, 663–670.

2. Luo, Y.; He, X.; Kim, Y.; Blackburn, J. L.; Doorn, S. K.; Htoon, H.; Strauf, S. Carbon Nanotube Color Centers in Plasmonic Nanocavities: A Path to Photon Indistinguishability at Telecom Bands. Nano Lett. 2019, 19, 9037–9044.

3. Zheng, Y.; Kim, Y.; Jones, A. C.; Olinger, G.; Bittner, E. R.; Bachilo, S. M.; Doorn, S. K.; Weisman, R. B.; Piriyatinski, A.; Htoon, H. Quantum Light Emission from Coupled Defect States in DNA-Functionalized Carbon Nanotubes. ACS Nano 2021, 15, 10406–10414.

4. Mandal, A. K.; Wu, X.; Ferreira, J. S.; Kim, M.; Powell, L. R.; Kwon, H.; Groc, L.; Wang, Y.; Cognet, L. Fluorescent sp\(^3\)-Defect-Tailored Carbon Nanotubes Enable NIR-II Single Particle Imaging in Live Brain Slices at Ultra-Low Excitation Doses. Sci. Rep. 2020, 10, 5286.

5. Berger, F. J.; de Sousa, J. A.; Zhao, S.; Zorn, N. F.; El Yumin, A. A.; Quintana Garcia, A.; Settele, S.; Högele, A.; Crivillers, N.; Zaumseil, J. Interaction of Luminescent Defects in Carbon Nanotubes with Covalently Attached Stable Organic Radicals. ACS Nano 2021, 15, 5147–5157.

6. Spreinat, A.; Dohmen, M. M.; Lüttgens, J.; Herrmann, N.; Klempig, L. F.; Nißler, R.; Weber, S.; Mann, F. A.; Lauth, J.; Kruss, S. Quantum Defects in Fluorescent Carbon Nanotubes for Sensing and Mechanistic Studies. J. Phys. Chem. C 2021, 125, 18341–18351.

7. Zaumseil, J. Luminescent Defects in Single-Walled Carbon Nanotubes for Applications. Adv. Optical Mater. 2022, 10, 2101576.

8. Ghosh, S.; Bachilo, S. M.; Simonette, R. A.; Beckham, K. M.; Weisman, R. B. Oxygen Doping Modifies Near-Infrared Band Gaps in Fluorescent Single-Walled Carbon Nanotubes. Science 2010, 330, 1656–1659.

9. Piao, Y.; Meany, B.; Powell, L. R.; Valley, N.; Kwon, H.; Schatz, G. C.; Wang, Y. Brightening of Carbon Nanotube Photoluminescence
through the Incorporation of sp³ Defects. Nat. Chem. 2013, 5, 840–845.

(10) Miyachi, Y.; Iwamura, M.; Mouri, S.; Kawazoe, T.; Ohtsu, M.; Matsuda, K. Brightening of Excitons in Carbon Nanotubes on Dimensionality Modification. Nat. Photonics 2013, 7, 715–719.

(11) Shiraki, T.; Miyachi, Y.; Matsuda, K.; Nakashima, N. Carbon Nanotube Photoluminescence Modulation by Local Chemical and Supramolecular Chemical Functionalization. Acc. Chem. Res. 2020, 53, 1846–1859.

(12) Brozena, A. H.; Kim, M.; Powell, L. R.; Wang, Y. Controlling the Optical Properties of Carbon Nanotubes with Organic Colour-Centre Quantum Defects. Nat. Rev. Chem. 2019, 3, 375–392.

(13) Hertel, T.; Himmelein, S.; Ackermann, T.; Stich, D.; Crochet, J. Diffusion Limited Photoluminescence Quantum Yields in 1-D Semiconductors: Single-Wall Carbon Nanotubes. ACS Nano 2010, 4, 7161–7168.

(14) Berger, F. J.; et al. Brightening of Long, Polymer-Wrapped Carbon Nanotubes by sp³ Functionalization in Organic Solvents. ACS Nano 2019, 13, 9259–9269.

(15) Zorn, N. F.; Berger, F. J.; Zausnig, J. Charge Transport in and Electroluminescence from sp³-Functionalized Carbon Nanotube Networks. ACS Nano 2021, 15, 10451–10463.

(16) Gifford, B. J.; Kilina, S.; Htoon, H.; Doorn, S. K.; Tretiak, S. Exciton Localization and Optical Emission in Aryl-Functionalized Carbon Nanotubes. J. Phys. Chem. C 2018, 122, 1828–1836.

(17) Saha, A.; Gifford, B. J.; He, X.; Ao, G.; Zheng, M.; Katohura, H.; Htoon, H.; Kilina, S.; Tretiak, S.; Doorn, S. K. Narrow-Band Single-Photon Emission through Selective Aryl Functionalization of Zigzag Carbon Nanotubes. Nat. Chem. 2018, 10, 1089–1095.

(18) Settele, S.; Berger, F. J.; Lindenthal, S.; Zhao, S.; El Yumin, A. A.; Zorn, N. F.; Asyuda, A.; Zharnikov, M.; Högele, A.; Zausnig, J. Synthetic Control over the Binding Configuration of Luminescent sp³-Defects in Single-Walled Carbon Nanotubes. Nat. Commun. 2021, 12, 2119.

(19) Kwon, H.; Furmanchuk, A.; Kim, M.; Meany, B.; Guo, Y.; Schatz, G. C.; Wang, Y. Molecule-Tunable Fluorescent Quantum Defects. J. Am. Chem. Soc. 2016, 138, 6878–6885.

(20) Zheng, Y.; Bachilo, S. M.; Weisman, R. B. Photoexcited Aromatic Reactants Give Multicolor Carbon Nanotube Fluorescence from Quantum Defects. ACS Nano 2020, 14, 715–723.

(21) Iwamura, M.; Akizuki, N.; Miyachi, Y.; Mouri, S.; Shaver, J.; Gao, Z.; Cognet, L.; Lounis, B.; Matsuda, K. Nonlinear Photoluminescence Spectroscopy of Carbon Nanotubes with Localized Exciton States. ACS Nano 2014, 8, 11254–11260.

(22) Raynaud, C.; Claude, T.; Borel, A.; Amara, M. R.; Graf, A.; Zausnig, J.; Laurent, J. S.; Chassagneux, Y.; Voisin, C. Super-localization of Excitons in Carbon Nanotubes at Cryogenic Temperature. Nano Lett. 2019, 19, 7210–7216.

(23) Cançado, L. G.; Jorio, A.; Ferreira, E. H.; Stavale, F.; Achete, C. A.; Capaz, R. B.; Jorio, A. Disentangling Contributions of Point and Line Defects in the Raman Spectra of Graphene-Related Materials. 2D Mater. 2017, 4, 025039.

(24) Wang, J.; Shea, M. J.; Flach, J. T.; McDonough, T. J.; Way, A. J.; Zanni, M. T.; Arnold, M. S. Role of Defects as Exciton Quenching Sites in Carbon Nanotube Photovoltaics. J. Phys. Chem. C 2017, 121, 8310–8318.

(25) Dresselhaus, M. S.; Jorio, A.; Souza Filho, A. G.; Saito, R. Defect Characterization in Graphene and Carbon Nanotubes Using Raman Spectroscopy. Philos. Trans. R. Soc. A 2010, 368, 5355–5377.

(26) Abe, K.; et al. Defect Evolution of Ion-Exposed Single-Wall Carbon Nanotubes. J. Phys. Chem. C 2019, 123, 2496–2505.

(27) Ghosh, S.; Wei, F.; Bachilo, S. M.; Hauge, R. H.; Billups, W. E.; Weisman, R. B. Structure-Dependent Thermal Defunctionalization of Single-Walled Carbon Nanotubes. ACS Nano 2015, 9, 6324–6332.

(28) Hoffmann, M. S.; Gluckert, J. T.; Noe, J.; Bourjau, C.; Dehmel, R.; Högele, A. Bright, Long-Lived and Coherent Excitons in Carbon Nanotube Quantum Dots. Nat. Nanotechnol. 2013, 8, 502–505.

(29) Graf, A.; Zakharko, Y.; Schießl, S. P.; Backes, C.; Pfohl, M.; Flavel, B. S.; Zausnig, J. Large Scale, Selective Dispersion of Long Single-Walled Carbon Nanotubes with High Photoluminescence Quantum Yield by Shear Force Mixing. Carbon 2016, 105, 593–599.

(30) Wei, X.; et al. Photoluminescence Quantum Yield of Single-Wall Carbon Nanotubes Corrected for the Photon Reabsorption Effect. Nano Lett. 2020, 20, 410–417.

(31) Hartmann, N. F.; Velizhanin, K. A.; Haroz, E. H.; Kim, M.; Ma, X.; Wang, Y.; Htoon, H.; Doorn, S. K. Photoluminescence Dynamics of Aryl sp³ Defect States in Single-Walled Carbon Nanotubes. ACS Nano 2016, 10, 8355–8365.

(32) Kim, M.; et al. Fluorescent Carbon Nanotube Defects Manifest Substantial Vibrational Reorganization. J. Phys. Chem. C 2016, 120, 11268–11276.

(33) Ma, X.; Adamska, L.; Yamaguchi, H.; Yalcin, S. E.; Tretiak, S.; Doorn, S. K.; Htoon, H. Electronic Structure and Chemical Nature of Oxygen Dopant States in Carbon Nanotubes. ACS Nano 2014, 8, 10782–10789.

(34) Hofmann, M. S.; Noe, J.; Kneer, A.; Crochet, J. J.; Högele, A. Ubiquity of Exciton Localization in Cryogenic Carbon Nanotubes. Nano Lett. 2016, 16, 2958–2962.

(35) Shiraki, T.; Shiraiishi, T.; Juhász, G.; Nakashima, N. Emergence of New Red-Shifted Carbon Nanotube Photoluminescence Based on Proximal Doped-Site Design. Sci. Rep. 2016, 6, 28393.

(36) Schöppler, F.; Mann, C.; Hain, T. C.; Neubauer, F. M.; Privitera, G.; Bonaccorso, F.; Chu, D.; Ferrari, A. C.; Hertel, T. Molar Extinction Coefficient of Single-Wall Carbon Nanotubes. J. Phys. Chem. C 2011, 115, 14682–14686.

(37) Streit, J. K.; Bachilo, S. M.; Ghosh, S.; Lin, C.-W.; Weisman, R. B. Directly Measured Optical Absorption Cross Sections for Structure-Selected Single-Walled Carbon Nanotubes. Nano Lett. 2014, 14, 1530–1536.

(38) Gifford, B. J.; Kilina, S.; Htoon, H.; Doorn, S. K.; Tretiak, S. Controlling Defect-State Photophysics in Covalently Functionalized Single-Walled Carbon Nanotubes. Acc. Chem. Res. 2020, 53, 1791–1801.