Interaction of Luminescent Defects in Carbon Nanotubes with Covalently Attached Stable Organic Radicals

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Cite This: ACS Nano 2021, 15, 5147−5157

ABSTRACT: The functionalization of single-walled carbon nanotubes (SWCNTs) with luminescent sp³ defects has greatly improved their performance in applications such as quantum light sources and bioimaging. Here, we report the covalent functionalization of purified semiconducting SWCNTs with stable organic radicals (perchlorotriphenylmethyl, PTM) carrying a net spin. This model system allows us to use the near-infrared photoluminescence arising from the defect-localized exciton as a highly sensitive probe for the short-range interaction between the PTM radical and the SWCNT. Our results point toward an increased triplet exciton population due to radical-enhanced intersystem crossing, which could provide access to the elusive triplet manifold in SWCNTs. Furthermore, this simple synthetic route to spin-labeled defects could enable magnetic resonance studies complementary to in vivo fluorescence imaging with functionalized SWCNTs and facilitate the scalable fabrication of spintronic devices with magnetically switchable charge transport.

KEYWORDS: single-walled carbon nanotube, sp³ defect, stable organic radical, photoluminescence, triplet, magnetic field

The controlled covalent modification of single-walled carbon nanotubes (SWCNTs) has boosted their potential for a broad range of applications including quantum light emission,1 bioimaging,2 and sensing.3 The one-dimensional structure of SWCNTs, their large charge carrier mobilities,4 and high exciton diffusivity5 make them ideal for efficient interaction of charges and excitations with lattice defects, thus further expanding the nanotubes’ properties. In recent years, the low-density functionalization of semiconducting SWCNTs with luminescent sp³ defects, sometimes referred to as organic color centers or quantum defects, has received particular attention.6−8 The deep optical trap potentials (∼100 meV) of these defects created by binding of oxygen,9 aryl,10 or alkyl11 substituents lead to efficient exciton localization. These trapped excitons give rise to red-shifted photoluminescence (PL) with long lifetimes and even enable room-temperature single-photon emission at telecommunication wavelengths.12

As the defect states arise from the perturbation of the SWCNT’s electronic structure, their properties are dominated by the precise binding pattern with respect to the SWCNT lattice rather than the molecular structure of the substituents.13 Hence, the molecular groups that are bound to the nanotube surface are often structurally simple, and only few examples are known, in which the attached group contributes and performs a function itself, such as sensing14−16 or anchoring of biomolecules.17

A highly desirable property for functional groups attached to SWCNTs is a net spin, as carried by unpaired electrons. Previously, mixed-chirality samples of SWCNTs and multi-walled carbon nanotubes were decorated with open-shell transition metal18 or lanthanide19,20 complexes, and charge transport measurements at cryogenic temperatures revealed spin valve switching behavior without the need for ferromagnetic contacts.19,20 Another class of spin-bearing compounds are stable organic radicals, i.e., charge-neutral molecules with an unpaired electron.21,22 One of the most prominent examples is the perchlorinated triphenylmethyl (PTM) radical, in which a propeller-shaped arrangement of phenyl rings protects the carbon-centered radical, resulting in a half-life of ∼100 years.23 The interaction of SWCNTs with the...
unpaired spin of the radical via a luminescent sp³ defect may result in spin-dependent properties and provide optical means for probing them. However, up to now there are no reports of stable organic radicals bound to carbon nanotubes or chirality-sorted SWCNTs with any covalent spin label.

In this work, we functionalize purely semiconducting (6,5) SWCNTs with aryl defects linked to PTM radicals and use the PL arising from the defect-localized exciton as a highly sensitive probe for the short-range interaction between the radical and the SWCNT. By comparing them to aryl defects with closed-shell substituents, we observe PL quenching associated with the radical. Based on the PL decay dynamics, we propose partial transfer of the exciton population to triplet states via radical-enhanced intersystem crossing as the dominant quenching mechanism, while a smaller portion may be attributed to a photoinduced electron transfer process.

In addition to providing a simple route to spin-labeled defects for magnetic resonance studies and spintronics, radical functionalization could improve the accessibility of the elusive triplet states in carbon nanotubes.

RESULTS AND DISCUSSION

SWCNT Functionalization and Characterization. Highly purified (6,5) SWCNTs (diameter ~0.76 nm, average length 1.0–1.5 µm) wrapped with the fluorene–bipyridine copolymer PFO-BPy (see the Methods and Figure 1 for molecular structure) serve as a robust model system for sp³ functionalization. As shown in Figure 1, diazonium (Dz) chemistry was used to introduce aryl defects bearing charge-neutral substituents with either radical (open-shell) or closed-shell character. Reacting (6,5) SWCNTs with the tailored diazonium salt PTM-Dz produced aryl defects on the nanotube lattice that act as covalent linkers to PTM radicals.

Figure 1. Reaction scheme depicting the functionalization of polymer-wrapped (6,5) SWCNTs with aryl defects bearing radical (PTM, red) or closed-shell (PTMH, ArBr, blue) substituents.

Figure 2. (a) Normalized PL spectra recorded for dispersions of pristine and PTM- and PTMH-functionalized (6,5) SWCNTs in toluene. (b) EPR spectra (at room temperature) of these dispersions in addition to a dispersion of (6,5) SWCNTs with a high density of ArBr defects (h.f.) and a solution of the PTM-Dz precursor in tetrahydrofuran.
dispersions of the nanotubes at room temperature (Figure 2).

magnetic resonance (EPR) spectra were recorded for toluene with PTM radicals, photoluminescence and electron para-

pristine lattice segments (E₁₁ transition). In addition, both sp³ functionalized SWCNTs and the corresponding closed-shell PTMH-functionalized SWCNTs as well as pristine SWCNTs. Here, we focus on a comparison between PTM radical-functionalized nanotubes without the need for any solubilizing agents. Nanotube functionalization was always performed in the dark and completed within 16 h at room temperature. Subsequently, the functionalized SWCNTs were collected by vacuum filtration, carefully washed with pure solvent to remove unreacted diazonium salt and byproducts, and finally redispersed in fresh toluene for characterization.

To confirm the covalent functionalization of (6,5) SWCNTs with PTM radicals, photoluminescence and electron paramagnetic resonance (EPR) spectra were recorded for toluene dispersions of the nanotubes at room temperature (Figure 2). Here, we focus on a comparison between PTM radical-functionalized SWCNTs and the corresponding closed-shell PTMH-functionalized SWCNTs as well as pristine SWCNTs. All (6,5) SWCNT dispersions exhibit photoluminescence at 1006 nm originating from mobile excitons recombining on pristine lattice segments (Eₙ transition). In addition, both sp³ functionalized nanotubes show emission at ~1165 nm, which is characteristic of defect-localized excitons (E₁₁*) and strong evidence for the covalent attachment of molecular groups to the nanotube lattice (Figure 2a). To analyze the influence of the radical substituent on the defect state energy, the optical trap depth of PTM- and PTMH-functionalized SWCNTs (Supporting Information Figure S1). The optical trap depth of PTM defects (172 meV) was slightly larger than that of PTMH defects (168 meV), which is in agreement with the stronger electron-withdrawing character of the PTM group. However, the difference is small, presumably due to the relatively long distance between the central carbon of the PTM moiety and the SWCNT lattice. We can conclude that the optical trap depth should only play a minor role with regard to any differences observed between PTM and PTMH defects.

While the presence of an E₁₁* emission feature clearly indicates covalent functionalization, it is relatively insensitive to the precise molecular structure of the attached group. Hence, EPR measurements were performed to ascertain that the substituent was indeed the desired PTM-styryl unit and the radical character was preserved after the reaction. Figure 2b shows that the pristine (6,5) SWCNTs do not display any EPR signal, as expected for highly purified semiconducting SWCNTs. Likewise, closed-shell PTMH-functionalized SWCNTs show no EPR intensity at room temperature. To make sure that this result was not compromised by the low density of PTMH defects, a second control experiment was performed on (6,5) SWCNTs that were highly functionalized with closed-shell ArBr defects, which also did not give rise to any EPR signal (see Supporting Information Figure S2 for additional characterization). The PTM-functionalized SWCNTs, on the other hand, show the clear EPR signature of the PTM-styryl unit with a g factor of 2.0024, which is characteristic for PTM radicals, and a peak splitting due to hyperfine coupling between the PTM radical and the vinylene proton with appropriate symmetry (for more details on the fine structure see the Supporting Information Figure S3).

Furthermore, the EPR signal of the PTM radical attached to the SWCNT is broadened compared to that of the molecular precursor PTM-Dz (line widths of 1.4 and 1.1 G, respectively; see Supporting Information Figure S4). This broadening may be attributed to the slow tumbling of the micrometer-long nanotube in dispersion with a rotational correlation time of ~10 ms rad⁻¹ G⁻¹ which is much longer than that of the unbound PTM-Dz molecule. Consequently, the line broadening further corroborates the successful decoration of SWCNTs with stable organic radicals.

These results clearly indicate that the room-temperature EPR response of PTM-tailored SWCNTs originates from an unpaired spin localized on the PTM moiety and not on the nanotube itself. In contrast to that, Lohmann et al. recently reported that aryl-functionalization of SWCNTs with closed-shell substituents in aqueous dispersions may give rise to an EPR signal at low temperatures. The authors assigned this signal to a nanotube-centered radical, which might be formed upon addition of an odd number of sp³ defects to the lattice. Since the intensity of this EPR signal decreased strongly with increasing temperature and became undetectable above 200 K, such a feature is not expected to appear in our room-temperature EPR measurements.

Impact of Radical on Defect PL. The unusual observation of a pronounced absorption band accompanied
by relatively weak PL from the PTM defects (compare Figure 2 and Supporting Information Figure S2) prompted a more detailed investigation of their PL efficiency in relation to a reference sample of closed-shell ArBr-functionalized SWCNTs with similar defect density, as indicated by the E11*/E11 absorbance ratio (Figure 3a). As shown in Figure 3b, the radical-functionalized defects exhibit a significantly lower E11*/E11 PL intensity ratio than the closed-shell reference despite having a similar defect density. This picture is complemented by PL lifetime measurements via time-correlated single-photon counting (TCSPC) for the E11* PL from different defect types. The data indicate a substantially shorter decay time for the radical-functionalized defects compared to both closed-shell references (Figure 3c). It should be noted that the emission from all samples was filtered by a grating spectrophotograph to pass only the intensity from a narrow wavelength band around 1165 nm to the single-photon detector. Thereby, we rule out the wavelength-dependence of defect state lifetime as a possible cause for the observed differences.33 Combined with the reduced defect emission intensity, the shortened PL lifetime of PTM-functionalized SWCNTs points toward a nonradiative relaxation pathway associated with the radical in close proximity to the defect. Notably, the E11* PL decay of the radical-functionalized SWCNTs can still be described by the biexponential model typical for localized exciton decay dynamics at room temperature.33,34

If the observed E11* PL quenching results from the presence of the radical substituent on the aryl defect, the in situ conversion of open-shell to closed-shell substituents on the sp3 defects will be the most direct way to confirm and quantify this effect. For this purpose, we exploited the fact that PTM radicals are sensitive to UV and blue light (in the range of their absorption maximum around 385 nm). It is well-established that irradiation in this spectral range induces chlorine atom elimination from the PTM followed by ring closure to the perchlorophenylfluorenyl (PPF) radical.35,36 Due to the planar structure of the fluorene unit hosting the radical, the PPF radical is much more susceptible to chemical attack than the PTM radical. Hence, we consider hydrogen atom abstraction from the solvent and formation of the closed-shell PPFH species as a plausible decomposition pathway, as shown schematically in Supporting Information Figure S5. In practice, degradation of the PPF radical yields a mixture of closed-shell products. Although the extremely low defect concentrations (estimated to be in the range of nmol/L) did not allow us to determine the molecular structure of any photolysis products, we confirmed experimentally that all of them were of closed-shell nature (see below). As noted in the discussion of optical trap depths of PTM versus PTMH defects, minor changes in substituent molecular structure far away from the SWCNT do not impact the E11* PL properties significantly;13 thus the PPFH substituent is a good closed-shell reference system for the open-shell PTM.

For in situ conversion, a dispersion of PTM-functionalized SWCNTs was exposed to UV light (365 nm, 0.2 W cm−2) for 40 min and PL spectra as well as PL decay traces were recorded under identical conditions before and after irradiation. As expected, the E11* PL intensity strongly increased due to light-induced radical degradation, whereas the E11 intensity remained constant (Figure 4a, note that absolute PL intensities are compared). Hence, the creation of additional sp3 defects as the origin of increased E11* intensity can be ruled out. In that case, the E11 intensity would be reduced due to the higher density of exciton trapping sites. The unchanged E11 emission confirms that the interaction between the radical and the SWCNT is confined to the sp3 defect. To exclude that these changes are related to photochemical reactions on the SWCNT lattice itself, e.g., rearrangement of sp3 defects, the experiment was repeated with a dispersion of ArBr-functionalized SWCNTs. As shown in Figure 4b, these defects did not respond to UV irradiation. The minor drop of PL intensity is likely due to slight SWCNT aggregation over the course of irradiation, and the normalized spectra in Supporting Information Figure S6 illustrate that the PL spectral shape does not change at all. Hence, the E11* brightening observed in Figure 4a can be attributed unambiguously to the photochemical transformation of the PTM radical to a closed-shell system.

The marked increase in E11* emission efficiency can be understood by considering the prolonged PL lifetime of the defect-localized exciton following the open-shell to closed-shell conversion (Figure 4c). Upon irradiation, the initially short PL lifetime of the PTM defects rises to the level of the closed-shell references (PTMH and ArBr). By comparing EPR spectra of the PTM-functionalized SWCNT dispersion before and after irradiation (Figure 4d), we can conclude that the PTM radical was indeed converted to a closed-shell species. Consequently, the mechanism responsible for E11* PL quenching in PTM-functionalized SWCNTs must be directly linked to the presence of the radical on the substituent of the aryl defect. The PL quenching effect can be quantified based on the PL spectral and lifetime data. Table 1 details the extracted lifetime components and amplitudes together with the integrated E11* to E11 PL intensities for each defect type. We find that the amplitude-averaged E11* lifetime (τamp−av) of PTM defects increases by a factor of 2.4 upon radical decomposition, which is in excellent agreement with the 2.5-fold enhancement of the E11*/E11 PL intensity ratio.

Figure 4. (a) PL spectra of PTM-functionalized and (b) ArBr-functionalized (6,5) SWCNTs before and after irradiation. (c) PL lifetime components extracted from biexponential fits to the decay traces. (d) EPR spectra recorded for the dispersions used in the PL experiments before and after irradiation. Note that the initial EPR signal intensity is relatively low, because dilute dispersions were employed for the optical characterization.
**Table 1. PL Lifetime Components (Long: $\tau_l$, Short: $\tau_s$) with Corresponding Amplitudes ($A_l$ and $A_s$), Amplitude-Averaged Lifetimes ($\tau_{\text{amp-\text{av}}}$), and Integrated Defect-to-E11 Intensity Ratio $\text{PL}(E_{11}^\text{red}/E_{11}^\text{red})$**

| defect     | $A_l$ (%) | $\tau_l$ (ps) | $A_s$ (%) | $\tau_s$ (ps) | $\tau_{\text{amp-\text{av}}}$ (ps) | $\text{PL}(E_{11}^\text{red}/E_{11}^\text{red})$ |
|------------|-----------|---------------|-----------|---------------|-----------------------------------|---------------------------------------------|
| PTM        | 16        | 162           | 84        | 30            | 51                                 | 2.6                                         |
| PTM irrad. | 30        | 245           | 70        | 68            | 121                                | 6.5                                         |
| PTMH       | 29        | 239           | 71        | 81            | 127                                | 0.6                                         |
| ArBr       | 31        | 275           | 69        | 95            | 150                                | 3.7                                         |

**PL Quenching Mechanism.** In the following, we discuss the possible underlying mechanisms of quenching of the defect-localized exciton by the radical substituent on the aryl defect. Three mechanisms must be considered: resonant excitation energy transfer, photoinduced electron transfer, and enhanced intersystem crossing. First, the possibility of energy transfer from the sp$^3$ defect state to the PTM radical can be ruled out based on the much smaller optical gap of the defect compared to the PTM and negligible spectral overlap between the two partners, as shown in Supporting Information Figure S7.

Second, in order to assess the potential for photoinduced electron transfer (PET), the redox potentials of all involved species and their optical transition energies must be considered (see Table 2). From these data, the Gibbs free energy for PET from pristine or sp$^3$-functionalized regions of the SWCNT (donor D) to the PTM (acceptor A) was evaluated according to

$$\Delta G_{\text{PET}} = eE_{\text{red}}(D^+/D) - eE_{\text{red}}(A/A^-) - \Delta G_{00} = \frac{e^2}{4\pi\epsilon\epsilon_0 d}$$

where $E_{\text{red}}$ denotes the reduction potential, $\Delta G_{00}$ is the optical transition energy, and the electrostatic work term amounts to 0.5 eV for the relative permittivity of toluene ($\epsilon_r = 2.38$) and an ion pair separation $d \sim 1.2$ nm. After PET to the functional group, the electron is back-transferred to the ground state of the defect/SWCNT, thereby resulting in nonradiative recombination. As indicated by a large negative $\Delta G_{\text{PET}}$ in Table 2, PET is thermodynamically highly favorable and could potentially quench both $E_{11}$ and $E_{11}^*$ emission. However, since the rate of electron transfer reactions decreases exponentially on a length scale of $\sim 0.1$ nm, the quenching of mobile $E_{11}$ excitons can be excluded due to their long average distance to the radical, in agreement with negligible $E_{11}$ brightening in Figure 4a. The defect-localized exciton, on the other hand, is sufficiently close to the PTM to be quenched via PET, even though the separation of $\sim 1$ nm is likely to limit the rate of this process. For the sake of completeness, it is worth noting that the redox potentials in Table 2 permit ground state charge transfer from the SWCNT/defect to the PTM as well, but such a permanent ion pair formation at the defect site is irreconcilable with the observation of the EPR signature from the PTM defect and the PL lifetime shortening, which indicates dynamic rather than static quenching.

As another potential mechanism, covalently bound radicals have been shown to substantially speed up intersystem crossing in organic fluorophores. This effect can be modeled by treating the electronic exchange interaction as a perturbation that promotes spin flips of the unpaired electron on the radical and the photoexcited electron on the chromophore.

The intersystem crossing rate thus depends sensitively on the degree of wave function overlap between the singly occupied molecular orbital (SOMO) on the radical and the singlet exciton. It can reach time scales of $\sim 100$ ps for not too distant radicals. Hence, this mechanism is similarly short-ranged to PET and could affect defect-localized excitons close to the PTM radical. As discussed below, such radical-enhanced intersystem crossing (EISC) would allow triplet states to

**Table 2. Redox Potentials ($E_{\text{ox}}$, $E_{\text{red}}$), Optical Transition Energies ($\Delta G_{00}$), and Gibbs Free Energies for Photoinduced Electron Transfer ($\Delta G_{\text{PET}}$)**

| species      | $E_{\text{ox}}$ (V) | $E_{\text{red}}$ (V) | $\Delta G_{00}$ (eV) | $\Delta G_{\text{PET}}$ (eV) |
|--------------|----------------------|----------------------|----------------------|-----------------------------|
| (6,5) pristine | 0.615                | −0.420               | 1.24                 | −2.17                       |
| (6,5) sp$^3$ defect | 0.584                | −0.398               | 1.06                 | −1.95                       |
| PTMH         | 1.61                 | −0.19                |                      |                             |

“Potentials from Shiraishi et al. and Souto et al. measured versus a Ag/AgCl reference electrode. Data from Shiraishi et al. for ArBr defects were used as an approximation to PTM-substituted aryl defects because of their near-identical optical trap depths. Energy of the $E_{11}$ and $E_{11}^*$ PL transition, respectively. Including an electrostatic work term of $\sim 0.5$ eV. For the reaction: SWCNT + PTM → SWCNT$^\pi$ + PTM. For the reaction: defect + PTM → defect$^\pi$ + PTM$^\pi$.”

**Figure 5. Model of exciton dynamics in SWCNTs with sp$^3$ defects with (a) closed-shell or (b) open-shell functional groups.** The energy level diagrams include the ground state (GS), the defect-localized bright (B) and dark (D) singlet states, and a triplet (T) state with energy gaps $\Delta_{BD}$ and $\Delta_{BT}$. The relevant rate constants are indicated as follows: $k$, radiative and nonradiative recombination; $k_{\text{PET}}$, photoinduced electron transfer (PET); $k_{\text{ISR}}$, intersystem crossing between B and D state population; $k_{\text{RISC}}$, relaxation of the triplet state; $k_{\text{EISC}}$, exciton quenching by the radical via EISC and thermally activated reverse intersystem crossing (RISC). Note that $k_{\text{ISR}}$ and $k_{\text{RISC}}$ are not the transition rates between states, but represent the relaxation rates at which the involved populations approach their equilibrium value. The rate of this relaxation process depends on the elementary transition rates. Gray color marks states with small population or rates that are not competitive. (c) Schematic illustration of PET and EISC as the PL quenching processes in open-shell PTM defects.
participate in the fast population redistribution process between bright and dark defect states following exciton trapping.\textsuperscript{33,34,47} In this case, the radical-induced PL quenching may be explained by exciton population transfer from the bright singlet to a dark triplet state.

Both the PET and the EISC mechanisms are likely to occur for PTM defects based on thermodynamic considerations and previous work on structurally similar molecular systems. To further corroborate or exclude the involvement of either quenching mechanism, we now discuss the $E_{11}^\ast$ PL decay in more detail, as it is rich in information and data are available for both radical-functionalized and reference defects (Table 1). Hartmann et al.\textsuperscript{34} and He et al.\textsuperscript{33} developed a model for the biexponential decay of excitons localized at defects with closed-shell substituents at room temperature. Since the $E_{11}^\ast$ PL decay of radical-functionalized defects remains biexponential with well-separated long and short time scales, we assume that the dynamics in such defects are still similar to the existing model but should be modified by introducing PET or EISC. With these assumptions, the observed radical-induced changes in the long and short decay components can only be explained by a combination of PET and reversible EISC to a triplet state that is energetically below the bright state, as discussed in detail in the Supporting Information.

Figure 5 illustrates our proposed model for defects with open-shell substituents and compares it with the model that is generally applied for defects with closed-shell substituents.\textsuperscript{33,34,47} The involved states are the defect-localized bright singlet exciton (B) and parity-forbidden dark singlet exciton (D), as well as a triplet exciton (T), which could be either mobile or defect-localized. These states are assumed to reversibly exchange population at room temperature as the energy gaps between them are either smaller ($\Delta_G \approx 9$ meV as found by Kim et al.\textsuperscript{47}) or not much larger than 25 meV (an upper boundary of $\Delta_{BT}$ = 38 meV will be estimated below). In general, the fast decay component is attributed to the redistribution of exciton population among these bright and dark states, which is followed by the slow recombination of trapped excitons via radiative and nonradiative channels. More specifically, as intersystem crossing is slow in the absence of the radical (Figure 5a); only the D state accepts population from the B state with the redistribution rate $k_{BD}$. Subsequently, trapped excitons recombine via multiphonon decay and other pathways with the cumulative rate $k = \tau_1^{-1}$, while the ratio of B and D state populations retains its equilibrium value. Since recombination can occur at any time after the trapping event, the short decay component is given by $\tau_1^{-1} = k_{BD} + \tau_{e1}^{-1}$. In contrast to that, we propose that radical functionalization (Figure 5b) enables fast EISC and thermally activated reverse intersystem crossing (RISC) between the B state and an energetically low-lying T state. As a result, this T state dominates the population redistribution process among bright and dark states (for details see Supporting Information). Simultaneously, PET is responsible for enhanced nonradiative recombination, resulting in $\tau_1 = k + k_{PET}$ and $\tau_e^{-1} = k_{BT} + \tau_{e1}^{-1}$ for radical-substituted defects.

A quantitative analysis of the data in Table 1 further supports this picture. Assuming that PET is responsible for changes in the decay rates $\tau_1^{-1}$, a PET rate of $\tau_1^{-1}(PTM) - \tau_1^{-1}(PTM \ irr.) = (500 \text{ ps})^{-1}$ is extracted. This moderately fast electron transfer rate is rationalized by the trade-off between the large thermodynamic driving force for the process ($\Delta G_{PET} = -1.95 \text{ eV}$) and the relatively long distance (~1.2 nm) between the SWCNT surface and the radical center. Further, the term ($\tau_1^{-1} - \tau_{e1}^{-1}$) yields the population redistribution rates $k_{BD} = (91 \text{ ps})^{-1}$ and $k_{BT} = (37 \text{ ps})^{-1}$ for the closed- and open-shell case, respectively. Note that the calculated $k_{BT}$ is in good agreement with EISC rates\textsuperscript{33,45} for chromophore–radical distances of 1 nm as present in PTM defects. As pointed out by He et al.,\textsuperscript{33} the normalized amplitude of the long decay component may be used as a measure of bright state population in equilibrium with respect to its initial population immediately after trapping (Supporting Information). For radical-functionalized defects $A_1$ is 16%, whereas $A_1$ is about 30% across all reference defects, in good agreement with previous reports.\textsuperscript{33} This reduction of $A_1$ further supports EISC-mediated population transfer from the B to the T state as a contribution to $E_{11}^\ast$ PL quenching. Moreover, because the equilibrium populations of the B, D, and T states should simply reflect the Boltzmann distribution, we can use the information that $A_1 = 16\%$ together with $\Delta_{BD} \approx 9$ meV for $E_{11}^\ast$ defects in (6,5) SWCNTs\textsuperscript{48} to obtain a rough estimate of $\Delta_{BT} \approx 38$ meV. So far, we assumed a single triplet state to be involved, although several triplet states are predicted\textsuperscript{48} within a few 10 meV of the bright $E_{11}^\ast$ singlet. Including a second triplet state will further reduce $\Delta_{BT}$, so 38 meV should be regarded as an upper boundary, which justifies the earlier assumption of RISC at room temperature. Finally, we note that within this model about ~1/3 of the defect PL intensity drop results from PET, whereas ~2/3 are a consequence of EISC (Supporting Information). It is important to emphasize that our description of the decay dynamics of radical-functionalized
defects and the extracted physical parameters only apply as long as the underlying model for closed-shell defects is valid. For example, if the biexponential decay instead resulted from shelving into dark states, similar to the case of E₁₁ excitors, other quenching mechanisms might match the data more closely.

As long lifetimes (> 1 μs) are a hallmark of triplet states in organic materials, we also looked for delayed fluorescence at room temperature. To this end, the PL decay of PTM-functionalized SWCNTs was monitored at the E₁₁ or E₁₁⁎ peak emission wavelength by TCSPC over a time window of 0.3 μs. However, in neither case was a component with μs lifetime detectable. While it is possible that the delayed fluorescence signal is simply too weak to be detected in our setup, it is important to keep in mind that RISC (from the T to the B state) is enhanced by the same factor as the forward process. Thus, their efficient coupling via EISC and RISC should lead to simultaneous depopulation of the B and the T state on the time scale of ∼100 ps. Hence, the effective triplet state lifetime is strongly reduced and delayed fluorescence is no longer expected.

**Magneto-photoluminescence Spectroscopy.** Given the clear evidence for interaction of the radical with the trapped exciton, we explored how the paramagnetic PTM substituent influences the PL of sp³ defects in magnetic fields. Low-temperature magneto-PL experiments were performed on individual, PTM-functionalized (6,5) SWCNTs embedded in a polystyrene layer (see Supporting Information Figure S8) for a scanning confocal PL image. As illustrated in Figure 6a, the sample was mounted such that PL could be collected while scanning confocal PL image. As illustrated in Figure 6a, the sample was mounted such that PL could be collected while scanning confocal PL image. As illustrated in Figure 6a, the sample was mounted such that PL could be collected while scanning confocal PL image. Thus, their efficient coupling via EISC and RISC should lead to simultaneous depopulation of the B and the T state on the time scale of ∼100 ps. Hence, the effective triplet state lifetime is strongly reduced and delayed fluorescence is no longer expected.

In summary, we have demonstrated the functionalization of achiral semiconducting SWCNTs with stable organic radicals via simple diazonium chemistry. The presence of the radical leads to partial quenching of defect PL, which is likely due to a combination of a photoinduced electron transfer process and population transfer to triplet states enabled by radical-enhanced intersystem crossing. Consequently, radical-functionalized sp³ defects are an interesting platform for future studies of the elusive triplet exciton manifold in carbon nanotubes employing spin-sensitive methods such as optically detected magnetic resonance. Moreover, as pulsed EPR techniques can probe the distances between spin labels on the length scale of a few nanometers, such defects could be a model system for investigating clustering, which is suspected to play an important part in both synthetic and optical features of luminescent defects. Beyond that, the encapsulation of such radical-tailored SWCNTs in biocompatible surfactants might even enable their use as metal-free contrast agents for magnetic resonance imaging (MRI) and optical imaging, complementary to in vivo near-infrared fluorescence imaging. Finally, our functionalization approach should be easily transferable to metallic SWCNTs, which show even higher reactivity toward diazonium reagents and are commonly used in spin valves. In order to maximize the coupling between the radical and the itinerant electrons in such a system, the covalent linker should
be as short as possible to place the radical close to the conducting channel.

**METHODS**

Selective Dispersion of (6,5) SWCNTs. As described previously,
(6,5) SWCNTs were extracted from CoMoCAT raw material (Chasix Advanced Materials, SGE6S-L63, 0.38 g L\(^{-1}\)) by selective wrapping with poly-[\(\text{-(9,9-diocetylfluorenyl-2,7-diyl)-alt-(6,6')-(2,2'-bipyridine)}\)] (PFO-BPy, American Dye Source, \(\text{Mr} = 40 \text{ kg mol}^{-1}\), 0.5 g L\(^{-1}\)) under shear force mixing (Silverstone L2/Air, 10 230 rpm, 72 h) in toluene. Aggregates and impurities were removed by two centrifugation steps \((6000 \times g \text{ for 45 min each})\) and subsequent filtration (poly(tetrafluoroethylene) (PTFE) syringe filter, 5 \(\mu\)m pore size).

**SWCNT Functionalization.** (6,5) SWCNTs were reacted with a series of diazonium compounds to introduce sp\(^3\) aryl defects with either radical (PTM) or closed-shell substituents (PTMH, Br). Since the employed diazonium salts displayed different solubility characteristics, the functionalization procedure was adapted to this. The reactions between (6,5) SWCNTs and the tailored diazonium salts PTM-Dz and PTMH-Dz (see the Supporting Information for the synthesis and characterization) were performed in THF, which was freshly distilled to remove water and any peroxide contaminations. First, the PFO-BPy-wrapped (6,5) SWCNTs were transferred to THF by passing the toluene dispersion through a PTFE membrane filter (Merck Millipore, JWP, 0.1 \(\mu\)m pore size) to collect the SWCNTs, which were subsequently redispersed in a small volume of THF by bath sonication. To this dispersion was added a solution of the diazonium salt (PTM-Dz or PTMH-Dz) in THF such that the (6,5) SWCNT concentration in the reaction mixture was 0.72 mg L\(^{-1}\) (optical density of 0.4 cm\(^{-1}\) at the E\(_{11}\) transition) and the diazonium salt concentration 0.15 mmol L\(^{-1}\). In contrast to that, the reaction with the commercial 4-bromobenzenediazonium tetrاعfluoroborate (Br-Dz, Sigma-Aldrich) was carried out according to our previously reported procedure\(^{26}\) using 18-crown-6 as a phase transfer agent in an 80:20 vol % toluene/acetonitrile mixture, but without the addition of potassium acetate. The (6,5) SWCNT concentration was adjusted to 0.72 mg L\(^{-1}\) and the Br-Dz concentration to 0.37 mmol L\(^{-1}\) for moderate- or 1.85 mmol L\(^{-1}\) for high-density functionalization. All reactions proceeded in air at room temperature under dark conditions. After 16 h, the functionalized SWCNTs were collected by vacuum filtration through a PTFE membrane filter (Merck Millipore, JWP, 0.1 \(\mu\)m pore size) and washed with either THF (3 \(\times\) 7 mL) or acetonitrile (10 mL) followed by toluene (5 mL), but without the addition of potassium acetate. The (6,5) SWCNTs were then dried under ambient conditions before the subsequent functionalization realised through microwave power saturation interaction (MPSI) and functionalization by direct exposure to the diazonium salt (PTM-Dz or PTMH-Dz) in THF such that the (6,5) SWCNT concentration in the reaction mixture was 0.15 mmol L\(^{-1}\) at the E\(_{11}\) transition) and the diazonium salt concentration 0.37 mmol L\(^{-1}\).

Precautions to avoid undesirable spectral distortion and line broadening, such as those arising from microwave power saturation interaction (MPSI) and functionalization by direct exposure to the diazonium salt (PTM-Dz or PTMH-Dz) in THF such that the (6,5) SWCNT concentration in the reaction mixture was 0.15 mmol L\(^{-1}\) at the E\(_{11}\) transition) and the diazonium salt concentration 0.37 mmol L\(^{-1}\).

Low-Temperature Magneto-spectroscopy. For PL microscopy on the single-defect level, a low concentration of functionalized (6,5) SWCNTs (optical density of 0.005 cm\(^{-1}\) at the E\(_{11}\) transition) was blended into a solution of polystyrene (20 kg L\(^{-1}\)) in toluene and spin-coated at 2000 rpm onto glass slides coated with 150 nm of gold. The sample was loaded into a home-built confocal microscope setup inside a closed-cycle magneto-cryostat (attoDRY1000, attocube systems AG) with a base temperature of 3.2 K and magnetic fields of up to 9 T. A customized holder was used to mount the sample in Voigt geometry with the magnetic field parallel and light propagation orthogonal to the sample surface. A wavelength-tunable Ti:sapphire laser (Coherent Mira) served as the excitation source and was tuned to 995 nm (continuous wave, 6 \(\mu\)W) to be in resonance with the E\(_{11}\) transition of (6,5) SWCNTs. The PL from individual nanotubes was collected by an aspheric lens (Thorlabs TSL33x10-B, NA = 0.68), dispersed by a grating spectograph (Acton SpectroPro SP2388, 150 lines mm\(^{-1}\)) and recorded by a liquid nitrogen cooled InGaAs line camera (Princeton Instruments OMA V:1024-1.7 LN). For TCSPC, nanotubes were excited in pulsed mode (\(\sim 2 \times 10^{14} \text{ photons cm}^{-2} \text{ pulse}^{-1}\)) and the PL was directed to a superconducting single-photon detector (TCORPS-CCR-SW-85, Scontent). The IRF was measured on the attenuated laser signal.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.0c10341.

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Notes
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ACKNOWLEDGMENTS
The authors thank Dr. Vega Lloveras for performing electron paramagnetic resonance measurements. This project has received funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (grant agreement no. 817494 “TRIFECTs”). S.Z. acknowledges funding from the Alexander von Humboldt Foundation, and A.H. from the European Research Council (ERC) under the grant agreement no. 772195 and the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany’s Excellence Strategy EXC-2111-390814868. This work was also supported by the MICIU of Spain (PID2019-116822RB-I00), the Generalitat de Catalunya (2017-SGR-918), and the Severo Ochoa FUNDUTERE (CEX2019-000917-S). J.A.d.S. is enrolled in the Materials Science Ph.D. program of UAB. J.A.d.S. thanks the FPI fellowship.

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