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Dynamics and Transient Absorption Spectral Signatures of the Single-Wall Carbon Nanotube Electronically Excited Triplet State

Jaehong Park,^{†,‡} Pravas Deria,[‡] and Michael J. Therien^{*,‡}

[†]Department of Chemistry, University of Pennsylvania, 231 South 34th Street, Philadelphia, Pennsylvania 19104-6323, United States

[‡]Department of Chemistry, French Family Science Center, 124 Science Drive, Duke University, Durham, North Carolina 27708-0346, United States

S Supporting Information

ABSTRACT: We utilize femtosecond-to-microsecond time domain pump–probe transient absorption spectroscopy to interrogate for the first time the electronically excited triplet state of individualized single-wall carbon nanotubes (SWNTs). These studies exploit (6,5) chirality-enriched SWNT samples and poly[2,6- $\{1,5\}$ -bis(3-propoxy-sulfonic acid sodium salt)}naphthylene]ethynylene (PNES), which helically wraps the nanotube surface with periodic and constant morphology (pitch length = 10 ± 2 nm), providing a self-assembled superstructure that maintains structural homogeneity in multiple solvents. Spectroscopic interrogation of such PNES-SWNT samples in aqueous and DMSO solvents using E_{22} excitation and a white-light continuum probe enables E_{11} and E_{22} spectral evolution to be monitored concomitantly. Such experiments not only reveal classic SWNT singlet exciton relaxation dynamics and transient absorption signatures but also demonstrate spectral evolution consistent with formation of a triplet exciton state. Transient dynamical studies evince that (6,5) SWNTs exhibit rapid $S_1 \rightarrow T_1$ intersystem crossing (ISC) ($\tau_{ISC} \sim 20$ ps), a sharp $T_1 \rightarrow T_n$ transient absorption signal ($\lambda_{\max}(T_1 \rightarrow T_n) = 1150$ nm; full width at half-maximum ≈ 350 cm⁻¹), and a substantial T_1 excited-state lifetime ($\tau_{es} \approx 15$ μ s). Consistent with expectations for a triplet exciton state, T_1 -state spectral signatures and T_1 -state formation and decay dynamics for PNES-SWNTs in aqueous and DMSO solvents, as well as those determined for benchmark sodium cholate suspensions of (6,5) SWNTs, are similar; likewise, studies that probe the $^3[(6,5) \text{ SWNT}]^*$ state in air-saturated solutions demonstrate $^3\text{O}_2$ quenching dynamics reminiscent of those determined for conjugated aromatic hydrocarbon excited triplet states.

Single-wall carbon nanotubes (SWNTs) possess a number of compelling optical properties.^{1–6} While SWNT electronic transitions span the visible and NIR spectral regions, the optical absorptions of an individual tube are dominated by sharp singlet exciton interband (van Hove, E_{ii}) transitions at energies fixed by tube diameter and chirality.⁷ Fundamental studies that have examined SWNT excited states interrogate exclusively singlet excitons.^{1–19} Any excited-state dynamical roles played by SWNT triplet excitons are at present obscure;^{20–23} this is perhaps

somewhat surprising, given the prominent role played by electronically excited triplet states in the photophysics of fullerenes, graphenes, and semiconducting polymers.

In this study, we exploit noncovalently modified SWNTs in which an arylenethynylene polymer monolayer helically wraps the nanotube surface at periodic and constant morphology²⁴ as versatile constructs in which to probe nanotube triplet exciton states. Previous work has shown that ionic poly[2,6- $\{1,5\}$ -bis(3-propoxysulfonic acid sodium salt)}naphthylene]ethynylene (PNES) exfoliates and individualizes SWNTs in water and multiple organic solvents via single-chain wrapping (Chart 1A,B); AFM and TEM data demonstrate that PNES-SWNTs manifest a helix pitch length of 10 ± 2 nm, regardless of solvent.²⁵ We demonstrate that PNES wrapping of single-chirality enriched SWNT samples enables a battery of spectroscopic experiments that elucidate SWNT T_1 -state transitions and dynamics.

Pioneering theoretical studies have computed the energy of the lowest energy SWNT triplet exciton state;^{11,26} while these studies predict the existence of low-lying SWNT triplet states and S_1 – T_1 energy gaps significantly smaller than those reported typically for conjugated polymers,²⁷ computations based on the Bethe–Salpeter model indicate that the $^3E_{11}$ state lies ~ 0.03 eV below the $^1E_{11}$ state for (6,5) tubes,¹¹ whereas those relying on TDDFT methods suggest that the $^3E_{11}$ state is more substantially stabilized (~ 0.3 eV) relative to $^1E_{11}$ for (7,6) tubes.²⁶ In this context, it is important to note that SWNT singlet excited-state manifolds possess a lowest energy dark exciton state ($^1D_{11}$); congruently, electronically excited SWNTs are characterized by short picosecond time scale photoluminescence lifetimes and fast ground-state recovery dynamics. These theoretical studies that have examined the SWNT T_1 ($^3E_{11}$) state have important practical implications, as T_1 is predicted to lie below $^1D_{11}$ (Chart 1C). Provided sufficient S_1 – T_1 electronic coupling and Franck–Condon overlap are manifest, optical excitation of a highly individualized, well-dispersed SWNT sample should give rise to a T_1 -state SWNT population; strategies that either augment SWNT S_1 – T_1 electronic mixing or facilitate selective funneling of excitation into the SWNT triplet manifold thus define viable routes to high quantum yield preparation of electronically excited SWNTs having substantial excited-state lifetimes.

Because standard SWNT samples feature heterogeneous distributions of nanotube chiralities and length scales, SWNT pump–probe transient absorption data are characterized by

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Chart 1. (A) Structural Schematic of PNES-Wrapped SWNTs (PNES-SWNTs),²⁵ (B) Molecular Structure of PNES, and (C) Jablonski Diagram Illustrating the Relative Energetics of the Singlet and Triplet Exciton States for Semiconducting SWNTs²⁶

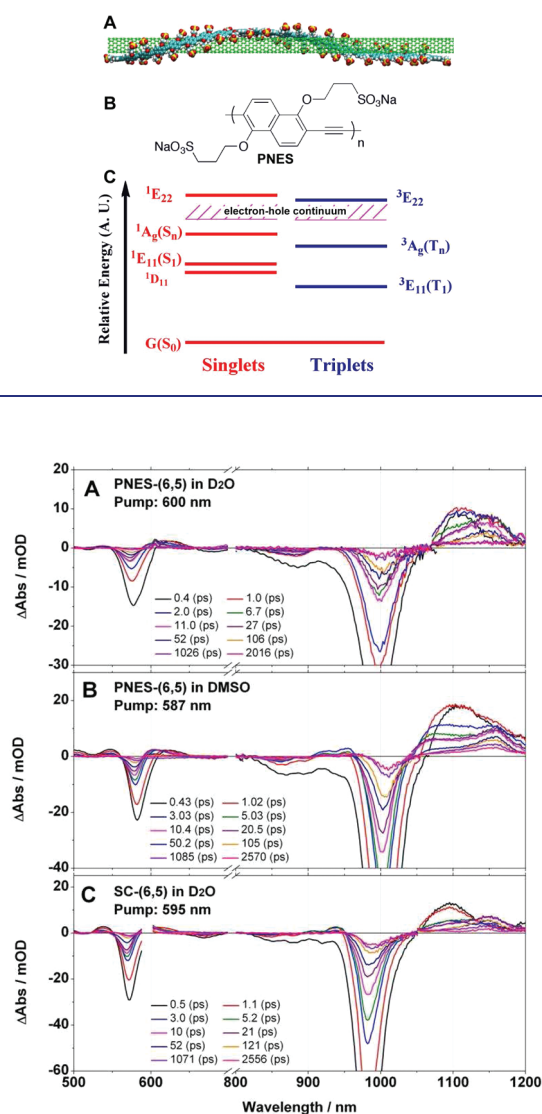


Figure 1. Representative transient absorption spectra obtained for (A) PNES-[(6,5) SWNTs] in D₂O, (B) PNES-[(6,5) SWNTs] in DMSO solvent, and (C) (6,5) SWNTs suspended in D₂O utilizing sodium cholate surfactant at the time delays noted. Experimental conditions: (A) λ_{ex} = 600 nm, (B) λ_{ex} = 587 nm, and (C) λ_{ex} = 595 nm; pulse energy = 300–350 nJ/pulse; temperature = 20 °C; magic angle polarization.

multiple bleaching bands that broadly span the visible and NIR spectral windows, thereby making the identification of excited-state absorptive transitions difficult.²⁸ To circumvent such complications, we utilized recently reported SWNT purification methods that exploit linear and nonlinear density gradient ultracentrifugation^{29,30} to isolate (6,5) SWNTs in >85% purity (Figure S1). Employing established methods, (6,5) SWNTs were single-chain helically wrapped by PNES (Supporting Information);²⁵ transient dynamical experiments that utilized these (6,5) SWNT samples, E₂₂ excitation, and a white continuum probe beam

allowed E₁₁ and E₂₂ spectral evolution to be monitored concomitantly in multiple solvents.

Figure 1A,B displays representative transient absorption spectral data obtained for PNES-[(6,5) SWNTs] following E₂₂ excitation in D₂O and DMSO solvents over the 400 fs-to-2 ns time domain. Congruent with previous data,³¹ these spectral features are dominated by ground-state bleaching bands in both the E₁₁ and E₂₂ spectral regions. Global analysis of the PNES-[(6,5) SWNT] E₁₁ region transient decay dynamics reveals three bleaching recovery time constants: 1.2 ps, 56 ps, and a third that exceeds the delay limit (>3 ns) of our femtosecond pump–probe instrument (Figure S3). While the ~1 and 100 ps time constants have been respectively assigned to exciton–exciton annihilation and singlet exciton recombination dynamics,^{15,25,28,31,32} this long (>3 ns)-lifetime component has not been previously reported. In addition to these dominant spectral features, transient absorption (TA) bands are also observed at the higher and lower energy sides of each E₁₁ and E₂₂ bleaching band. Note that these TA bands lying at the blue and red edges of the E₁₁ and E₂₂ bleaches are evident at t_{delay} = 400 fs; these signals have been previously assigned to biexciton or lowest-lying dark-state absorptions.^{15,31–33} Strikingly, a previously unidentified TA band at ~1150 nm is evident at the earliest t_{delay} values chronicled in these experiments; the Figure 1A,B data indicate that the lifetime of the electronic state that gives rise to this transition exceeds several nanoseconds and displays decay dynamics identical to those of the long time scale bleaching recovery process noted above. Figure 2A,B depicts the spectral evolution of this 1150 nm band following electronic excitation of PNES-[(6,5) SWNTs] in D₂O and DMSO solvents (400 fs < t_{delay} < 50 ps); note that these data preclude the possibility that the 1150 nm signal derives from a spectral shift of the long-wavelength transient absorption observed at t_{delay} = 400 fs and highlight a rise time of ~20 ps for the 1150 nm transient.

Nanosecond pump–probe transient absorption spectroscopic experiments were employed to determine the lifetime of this long-lived (6,5) SWNT excited state produced following E₂₂ excitation. Figure 3A,B displays transient absorption spectral data obtained for PNES-[(6,5) SWNTs] in D₂O and DMSO solvents at time delays of 1 and 20 μ s. Note that the displayed normalized spectra acquired at a sub-nanosecond time delay of ~500 ps match the spectrum acquired at t_{delay} = 1 μ s; furthermore, comparison of the spectra acquired at 1 and 20 μ s reveals no observable spectral shifts over this time domain. These time-resolved spectral data establish single-exponential lifetimes of 17.4 and 6.5 μ s, respectively, for the long-lived PNES-[(6,5) SWNTs] excited state generated in D₂O and DMSO solvents. While femtosecond and picosecond time scale excited-state dynamical processes are well documented for nanotubes, microsecond time scale excited-state SWNT dynamical processes are without precedent. As highlighted by these data, observation of such long-lived excited states in the condensed phase requires (i) SWNT samples that are largely devoid of bundles, (ii) narrow distributions of nanotube chiralities and length scales, and (iii) excitation conditions that do not cause annihilation or biexciton formation/decay processes to dominate the observed dynamics.

Further insight into the nature of this long-lived excited state can be gleaned from experiments that probe SWNT excited-state dynamics in oxygenated solvents. Figure S4 summarizes such experiments, highlighting that this long-lived SWNT excited state exhibits ³O₂ quenching dynamics reminiscent of those determined for conjugated aromatic hydrocarbon electronically

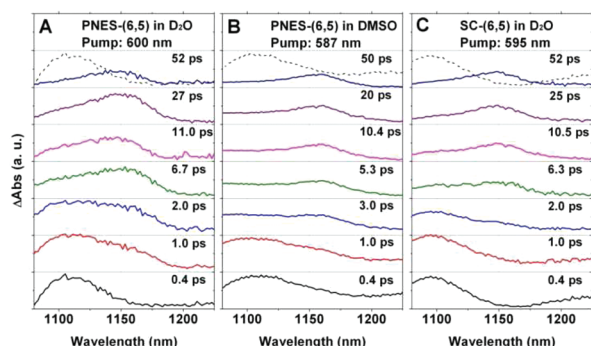


Figure 2. Representative NIR transient absorption spectra obtained for (A) PNES-[(6,5) SWNTs] in D₂O, (B) PNES-[(6,5) SWNTs] in DMSO solvent, and (C) (6,5) SWNTs suspended in D₂O utilizing sodium cholate surfactant at the time delays noted. Experimental conditions: (A) $\lambda_{\text{ex}} = 600$ nm, (B) $\lambda_{\text{ex}} = 587$ nm, and (C) $\lambda_{\text{ex}} = 595$ nm; pulse energy ≈ 300 – 350 nJ/pulse; temperature = 20 °C; magic angle polarization. For comparative purposes, the transient absorption spectrum recorded at $t_{\text{delay}} = 0.4$ ps is overlapped with that recorded at a time delay of ~ 50 ps.

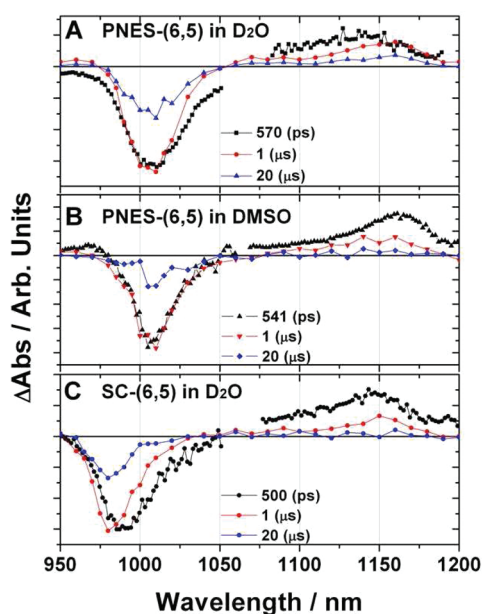


Figure 3. Nanosecond time domain transient absorption spectra obtained for (A) PNES-[(6,5) SWNTs] in D₂O, (B) PNES-[(6,5) SWNTs] in DMSO solvent, and (C) (6,5) SWNTs suspended in D₂O utilizing sodium cholate surfactant at the time delays noted. Experimental conditions: (A) $\lambda_{\text{ex}} = 580$ nm, (B) $\lambda_{\text{ex}} = 580$ nm, (C) $\lambda_{\text{ex}} = 570$ nm; pulse energy = 3.0 mJ/pulse; temperature = 20 °C; deoxygenated solvent. For comparative purposes, a transient absorption spectrum recorded at $t_{\text{delay}} \approx 0.5$ ns is displayed normalized relative to the transient absorption spectrum recorded at $t_{\text{delay}} = 1$ μ s.

excited triplet states.³⁴ Collectively, these data confirm that the microsecond lifetime PNES-[(6,5) SWNT] excited state possesses triplet character, and that the 1150 nm TA band corresponds to a $T_1 \rightarrow T_n$ ($^3E_{11} \rightarrow ^3E_{nn}$) transition. Finally in this regard, while aqueous surfactant solutions do not support the broad range of spectroscopic experiments that can be carried out with PNES-wrapped SWNTs, note that Figures 1C, 2C, and 3C

detail identical femtosecond-through-microsecond time domain transient absorption experiments carried out with the same (6,5) SWNTs utilized in the preceding experiments, but suspended in D₂O via the agency of sodium cholate surfactant. Note that the data from Figures 1–3 are virtually indistinguishable: these experiments establish a $^3[(6,5) \text{ SWNT}]^*$ lifetime of 25.4 μ s in sodium cholate surfactant and underscore that the solubilizing PNES polymer plays no role in this newly identified SWNT electronic state nor impacts intrinsic SWNT intersystem crossing (ISC) dynamics.

In conclusion, femtosecond-to-microsecond time domain pump–probe transient absorption spectroscopic experiments that interrogate (6,5) chirality-enriched single-wall carbon nanotube samples helically wrapped by the semiconducting polymer poly[2,6-{1,5-bis(3-propoxysulfonic acid sodium salt)}-naphthylene]ethynylene (PNES) elucidate for the first time the dynamics and spectroscopic signature of the electronically excited triplet state of individualized SWNTs. Examination of such PNES-SWNT samples in aqueous and DMSO solvents using E_{22} excitation and a white-light continuum probe enables E_{11} and E_{22} spectral evolution to be monitored concomitantly and reveals not only classic SWNT singlet exciton relaxation dynamics and transient absorption signatures but also spectral evolution consistent with formation of a triplet exciton state. Transient dynamical studies show that (6,5) SWNTs exhibit rapid $S_1 \rightarrow T_1$ ISC [$\tau_{\text{ISC}} \approx 20$ ps; $\phi_{\text{ISC}} \approx 3$ – 5% (Supporting Information)], a sharp $T_1 \rightarrow T_n$ transient absorption signal ($\lambda_{\text{max}}(T_1 \rightarrow T_n) = 1150$ nm; full width at half-maximum ≈ 350 cm^{-1}), and a substantial T_1 excited-state lifetime ($\tau_{\text{es}} \approx 15$ μ s). Consistent with expectations for a triplet exciton state, T_1 -state spectral signatures and dynamics of T_1 -state formation and decay for PNES-SWNTs in aqueous and DMSO solvents, and those determined for benchmark sodium cholate suspensions of (6,5) SWNTs, are similar; likewise, studies that probe the $^3[(6,5) \text{ SWNT}]^*$ state in air-saturated solutions demonstrate $^3\text{O}_2$ quenching dynamics reminiscent of those determined for conjugated aromatic hydrocarbon electronically excited triplet states. In sum, these studies establish that the combination of chirality-enriched SWNTs wrapped with solubilizing agents that maintain uniform structural morphology in multiple solvents^{24,25} enables characterization and investigation of a new low-energy SWNT excited state that can be utilized to generate singlet oxygen. Not only do identification of the $^3[(6,5) \text{ SWNT}]^*$ state and elucidation of its corresponding dynamics expand the scope of energy and electron-transfer reactions involving SWNTs that can be mechanistically probed: as the SWNT T_1 state lies lower in energy than the SWNT $^1E_{22}$, $^1E_{11}$, and $^1D_{11}$ states, this work opens up new possibilities for generating long-lived SWNT excited states at high quantum yield via mechanisms that bypass singlet exciton generation.

■ ASSOCIATED CONTENT

S Supporting Information. Experimental methods, electronic absorption spectra, excited-state dynamical data, and oxygen quenching experimental data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

michael.therien@duke.edu

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