

RH_LP_002; 22 Aug. 2018, Ian N. Stanton, Ph. D.

Introduction

Interrogating photophysical properties of novel nanoscale materials is fundamental to designing and developing new devices to advance and pioneer new technologies ranging from medical imaging to printable solar-cells. Single-walled carbon nanotubes feature immense tensile and thermal strength with advantageous 1-dimensional molecular wire electronic properties. The Edinburgh Instruments LP980 Transient Absorption Spectrometer is well suited to study these photo-generated excited states, especially with the capability to add near-infrared (NIR) detectors needed to capture the transient species in these materials.



Figure 1: The Edinburgh Instruments LP980 Spectrometer.

Research

Researchers at Duke University, in the lab of Prof. Michael Therien, have utilised an Edinburgh Instruments LP980 laser flash photolysis spectrometer equipped with an InGaAs near-infrared (NIR) detector to experimentally observe excited triplet states of individualized single-wall carbon nanotubes (SWNTs) for the first time (*J. Am. Chem. Soc.* 2011, 133, 17156–17159).

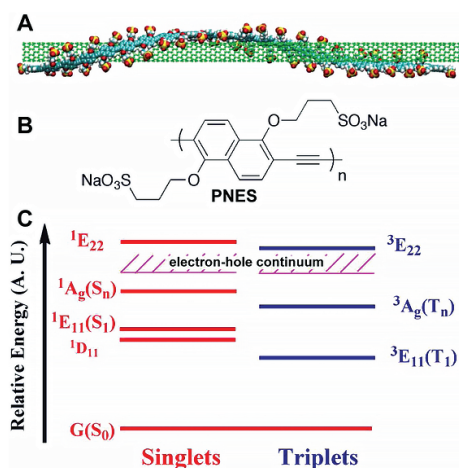


Figure 2: (A) Rendering of PNES-Wrapped SWNTs (PNES-SWNTs), (B) PNES Molecular Structure and (C) the relative excited state energy levels for Semiconducting SWNTs.

In this study, (6,5)-chirality enriched semiconducting SWNTs that were helically wrapped by an aryleneethynylene polymer monolayer at periodic and constant morphology, were utilized. These polymer-wrapped SWNTs maintain uniform structure morphology in both D₂O and DMSO solvents, and provide versatile constructs in which to probe nanotube triplet excited states.

These SWNT triplet states have lifetimes in the order of microseconds, differing vastly from the picosecond lifetimes characteristic of the well-known SWNT singlet states in these unique of 1-dimensional carbon-based nanostructures.

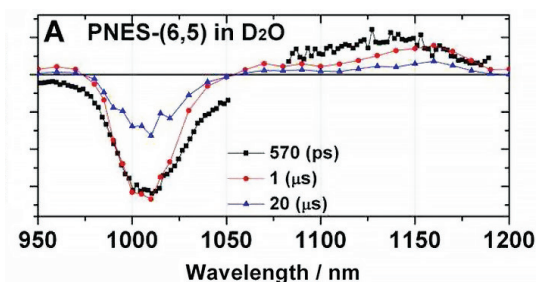


Figure 3: Near-Infrared (NIR) transient absorption spectra of PNES-SWNTs in deoxygenated D₂O. These spectra were generated from single channel kinetics recorded on an InGaAs detector with sensitivity to 2050 nm.

A previously unidentified transient absorption band at 1150 nm is shown to correspond to a SWNT T₁→T_n transition; the lifetime of the SWNT triplet excited state was found to be 17.4 μs and 6.5 μs, respectively, in D₂O and DMSO solvents when deaerated by Argon. Air saturated samples displayed much faster lifetimes in the presence of oxygen, a common indicator of a triplet state formation.

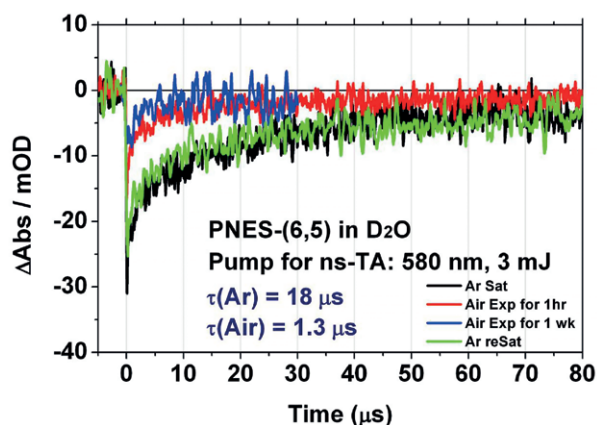


Figure 4: Triplet excited state emission lifetimes as a function of Argon or air saturation at 1000 nm for PNES-SWNTs in D₂O.

Conclusion

The supramolecular PNES-SWNT constructs, along with sensitive NIR transient absorption detection of the Edinburgh Instruments LP980, allowed for the first measurements of the photogenerated carbon nanotube triplet state. SWNTs facilitate ballistic charge transport and fast singlet exciton migration over long distances and the experimental identification of the SWNT triplet excitation state significantly expands the scope of nanotube electron and energy migration reactions that can be exploited for electronic and photonic devices.

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EDINBURGH INSTRUMENTS

2 Bain Square,
Kirkton Campus,
Livingston, EH54 7DQ
United Kingdom

Tel: +44 (0)1506 425 300
Fax: +44 (0)1506 425 320

sales@edinst.com

U.S. SUPPORT

Tel: +1 800 323 6115
Fax: +44 (0)1506 425 320

ussales@edinst.com



Customer support is
available worldwide

edinst.com

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