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Surface Functionalization of Pure-Chirality Carbon Nanotubes by Covalent and Noncovalent Chemistry

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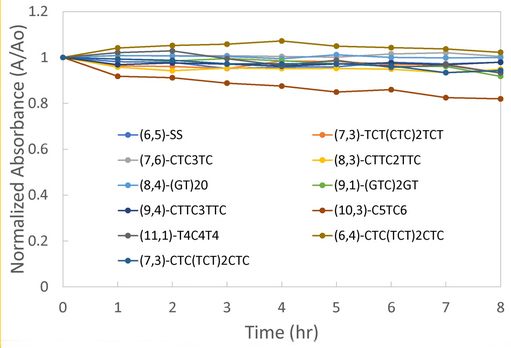
Abstract

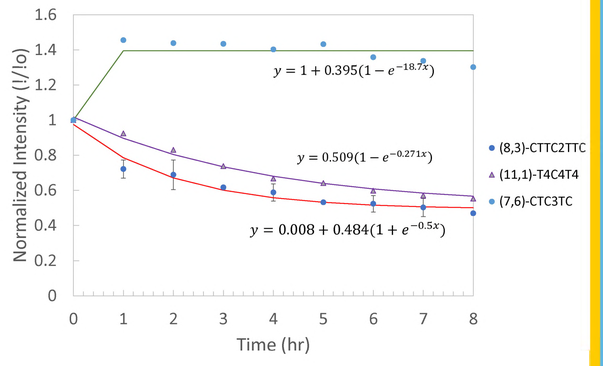
Single-wall carbon nanotubes (SWCNTs) are one-dimensional cylindrical nanostructures with distinct electronic and optical properties. With all its atoms on the surface, SWCNTs have been widely explored for chemical modification through noncovalent and covalent chemistry, which can provide promising applications in bioimaging and sensing. Here we investigated surface functionalization of pure-chirality SWCNTs with various glycopolymers, surfactants, and RPMI cell culture media with and without fetal bovine serum (FBS). Raman, vis-NIR absorption, and vis-NIR fluorescence spectra of SWCNTs in various solvent environments were monitored over time. While nanotube aggregation was not observed for incubation in FBS containing RPMI for 8 hours, interactions of DNA-SWCNTs with biological media resulted in a PL intensity increase for (7,6) and (8,4), decrease for (10,3), (7,3), (8,3), (11,1), (9,1) and (6,4), and relatively stable for (6,5), and (9,4). Photochemistry with aryl azide chain-end functionalized glycopolymers introduces sp^3 defect sites into the carbon lattice of SWCNTs. This defect-induced E_{11}^- emits light at a lower energy peak than the original E_{11} in the NIR region. Interestingly, an E_{11}^- peak formation was observed for (6,5) SWCNTs upon photo reaction with N-lactosyl, and N-mannosyl polymers.

Pure-Chirality SWCNTs remain uniformly dispersed in 10% FBS-RPMI over a period of 8 hours

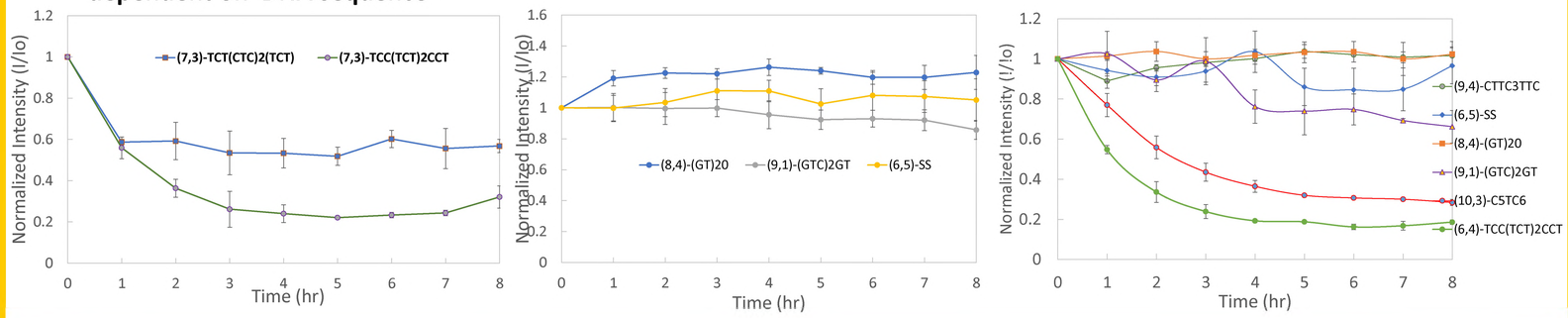


- The dynamic behavior of DNA-SWCNT hybrids with biological molecules depends on the DNA sequence and chirality of SWCNTs.
- All DNA-SWCNT hybrids are stable in serum containing RPMI cell culture media..
- Most DNA-SWCNTs aggregated in serum-free RPMI.

PL Intensity at E11 peak of various SWCNTs in 10% FBS-RPMI



Interaction of DNA-SWCNT with biological environment is strongly dependent on DNA sequence



PL Intensity of Pure-Chirality SWCNTs in RPMI

Materials and Methods

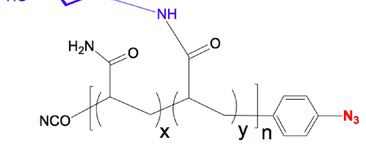
Cell Culture:

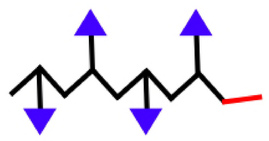
- Roswell Park Memorial Institute (RPMI) medium with 10% fetal bovine serum (FBS), and serum-free RPMI media were used as solvent environments.
- 120uL DNA-SWCNT samples prepared with E11 absorbance ~0.3 OD.
- Monitor UV-vis-NIR Absorption, Vis-NIR Fluorescence at 1hr intervals for 8 hours.
- *Samples were incubated in quartz cuvettes.

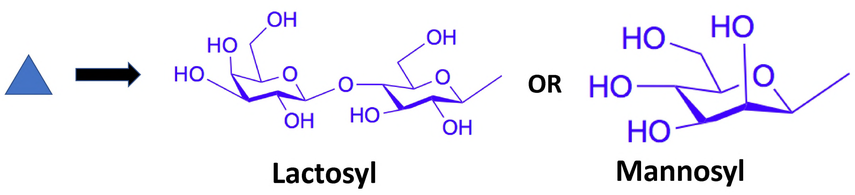
Photochemistry:

- Samples were diluted with DI H2O to ~0.12 OD E_{11} absorbance.
- 6:1 mass ratio of Glycopolymer to SWCNT.
- Expose to UV light ~1 hour.
- *Samples were kept incubated in quartz cuvettes and protected from environment light at all times except when exposed to UV light.

N-Glycan Polymers:

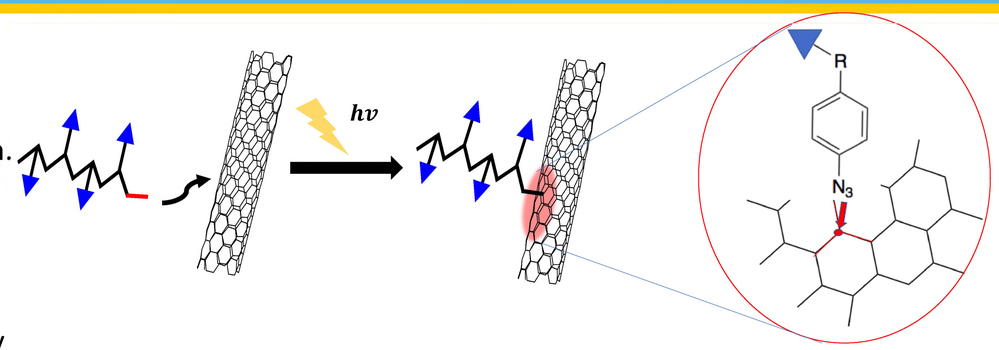




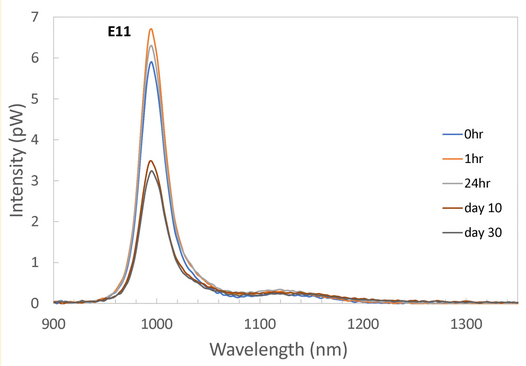


Photochemistry

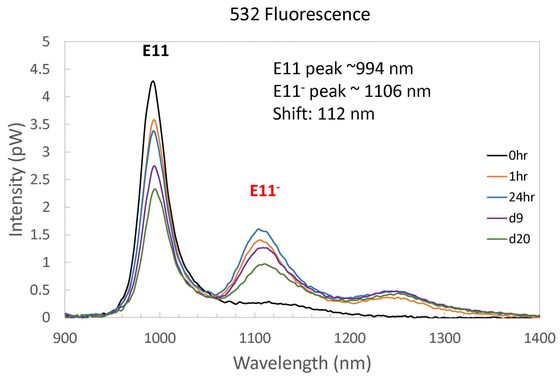
- Covalent attachment to the nanotubes produces E_{11}^- bright defect PL at ~1150 nm.
- E_{11}^- originates from sp^3 defect due to covalent attachment of aryl functional groups to sp^2 carbon lattice of SWCNTs.
- *sp^3 defect creates a local energy minimum from where the exciton optically emits as E_{11}^-.



(6,5)-SS N-Lactosyl
532 Fluorescence Spectra



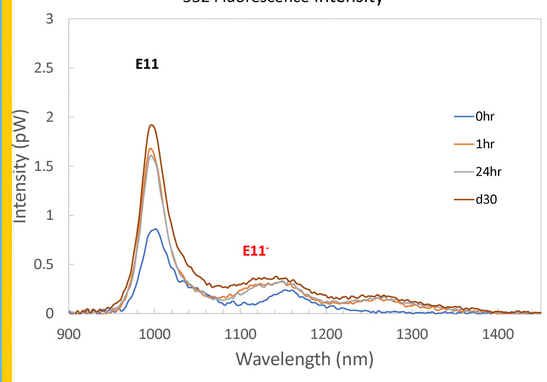
(6,5)-SDBS N-Lactosyl
532 Fluorescence



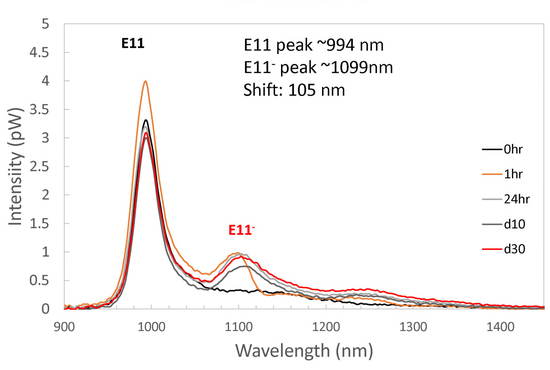
- UV light excites N_3 allowing it to attach to the carbon in the surface of SWCNTs.
- "R" is the backbone.
- ▲ can be lactosyl, or mannosyl.

- Formation of covalent N-C bond between SWCNT surface and functional group: rise of defect "D" peak Raman scattering ~1330 cm^{-1}.

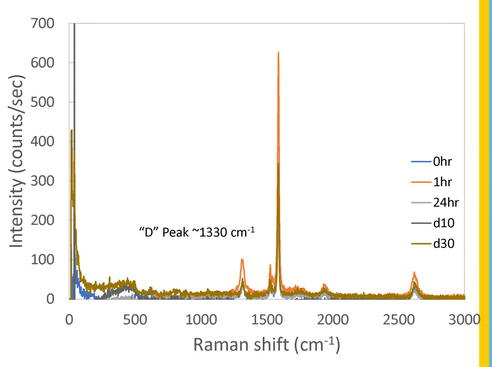
(6,5)-SC N-Lactosyl
532 Fluorescence Intensity



(6,5)-SDBS N-Mannosyl
532 Fluorescence



(6,5)-SDBS N-Mannosyl
Raman



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Acknowledgments

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Summary and Future Perspective

★The distinct surface structure of SWCNTS allows for its chemical modification through covalent and noncovalent chemistry, which can very promising for biomedical applications.

★ Our work provides a better understanding of the interaction mechanisms for DNA-SWCNTs in biological media, and finding the most stable hybrid is crucial for their application in bioimaging and sensing.

★ Further investigation of structure-property relationship of novel glycopolymer-SWCNTs materials will be performed, focusing on their targeted interactions with proteins and cell types, and developments of carbon-based NIR fluorescent probes for biological sensing and imaging applications.