

# Induced chiral Dichroism in Carbon Nanotubes through Surface Functionalization

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Chiroptical properties of confined nanostructures are of great interest in various applications for extending their favorable optoelectronic properties towards polarized photoluminescence, polarized nanosensors, polarized photodetectors. Chiral and non-chiral single wall carbon nanotubes (SWCNTs) have presented excellent enantiomer separation performance of pharmaceuticals, biologics, and chemicals. Moreover, functionalized SWCNTs have been applied in separation science by enhancing the enantioseparation of different chiral selectors.

It is difficult to directly create confined semiconductors with chiral signatures, but it is possible to induce chiroptical activity through manipulation of their surface properties (i.e., chirality transfer). Meanwhile, adsorption of chiral molecules as ligand for nanostructures is a promising approach to induce and enhance overall chirality of nanomaterials. Here we utilize atomistic modeling approach using time-dependent density functional theory (TD-DFT) to explore chirality performance in SWCNTs with hydrogen capped edges and different (n, m) indices i.e. (6,5) (9,1) (11,0) (10,0) (14,0). We covalently functionalized SWCNTs with two phenylalanine (C<sub>6</sub>H<sub>11</sub>NO<sub>2</sub>) enantiomers (D, L) at three ortho positions (O<sup>++</sup>, O<sup>+</sup>, O<sup>-</sup>) to observe enhancement of their chiroptical signatures based on their binding configurations. There are two bonding points for ligand itself and hydrogen at three ortho positions, but the pair has different orientation on surface of SWCNTs. CAM-B3LYP functional was used for all calculations with varying basis set because computed circular dichroism (CD) spectra are sensitive to basis set. We have observed that both chiral and non-chiral pristine SWCNTs exhibit CD spectra but chiral SWCNTs exhibit stronger degree of CD spectra. Two enantiomers of same (6,5) (9,1) (11,0) (10,0) (14,0) SWCNTs with opposite chirality provide opposite sign of CD spectra due to their mirror image geometries. When chiral enantiomers are bound to SWCNTs, the optical transition gains intense chiral signatures in comparison to pristine tubes and chiral ligand. Compared with the CD spectra of the pristine nanotubes, they are shifted to the red toward the main absorption bands of the tubes. The observed chirality is induced through the coupling of the static dipole of the chiral ligands on the surface of nanotube to the transition dipole moment of the nanotubes, as opposed to structural distortions and charge-transfer excitation mechanisms. We observed the CD spectra and thus the chirality induction depend on a specific binding configuration. With site-specific phenylalanine bound to SWCNTs at different positions, anisotropy factors are found to deviate based on different sites, providing mechanistic insight toward improving chiroptical functionality in confined nanomaterials.<sup>1</sup>

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## References

- 1) Forde, A., Ghosh, D., Kilin, D., Evans, A. C., Tretiak, S., & Neukirch, A. J. (2022). Induced Chirality in Halide Perovskite Clusters through Surface Chemistry. *The Journal of Physical Chemistry Letters*, 13(2), 686-693.