Carbon Nanodots: Structural and Electronic Insights Using Infrared and Fluorescence Spectroscopy Techniques

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Abstract

Carbon quantum dots were prepared via hydrothermal synthesis by the reaction of a dicarboxylic acid (two stereoisomers, maleic acid (MA) and fumaric acid (FA)) with a diamine (ethylenediamine (EDA) or paraphenylenediamine (PPD)). The acids were combined with varying molar ratios of EDA and PPD with water or deuterium oxide as the solvent. The optical properties of the carbon quantum dots were investigated by fluorescence spectroscopy and showed blue, green, and yellow fluorescence. The FTIR spectra of the samples suggested new amide bonds were formed. Computational methods such as density functional theory, molecular dynamics, and nudged elastic band methods embedded in the quantum chemistry packages, ORCA and Chimera, were used to simulate the IR spectra and to generate possible structures for the carbon quantum dots. These fluorescent quantum dots may have potential in biological imaging.

Introduction

Carbon quantum dots are nanomaterials that have emerged as an alternative to conventional inorganic semiconductor quantum dots. Unlike semiconductor quantum dots, carbon quantum dots are synthesized with biocompatible reagents that are low cost and environmentally friendly. The unique characteristics of the carbon quantum dots, such as photoluminescence, chemical stability, biocompatibility, facile synthesis, and water solubility have potential applications in bioimaging, drug delivery, phototherapy, and biosensing. Despite the extensive research on these materials, little is known about the structures of the carbon dots or how the structures influences the photoluminescence. The objective of this research is to gain insight into the structure of these materials and the inter-molecular interactions by analyzing spectroscopic properties of carbon quantum dots synthesized with two stereoisomers of a dicarboxylic acid and varying concentrations of two diamines.

Synthesis

Samples were synthesized by first dissolving either maleic acid or fumaric acid in water or D_2O, to which varying amounts of EDA or PPD (PPD was dissolved in water as well) were added in 1:1, 1:1.5 or 1.2 ratios. The solutions were placed in Teflon lined autoclaves and heated in an oven at 100°C for 24 hours.

Results

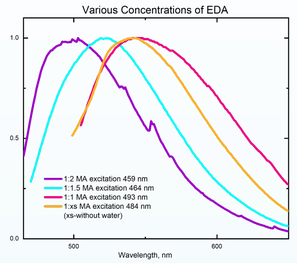

Figure 1

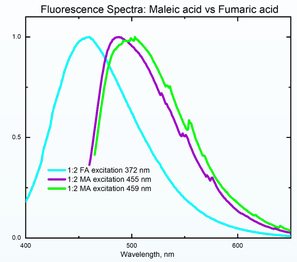

Figure 2

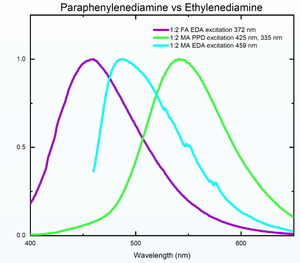

Figure 3

The emission wavelengths of the samples ranged from 460 nm to 548 nm (Fig.1). The emission wavelength increased with higher concentrations of EDA, suggesting the nanodot size can be modulated to yield a specific range in emission wavelength (Fig.1). The carbon quantum dots synthesized with MA showed two emission peaks of a higher wavelength than the same concentration of FA, suggesting that the geometric conformation of the acid influenced the size, the three-dimensional structure, and fluorescence properties of the carbon quantum dots (Fig.2). The carbon quantum dots synthesized with PPD had an emission peak higher than any other sample at 548 nm (Fig.3).

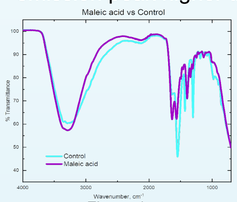

Figure 4

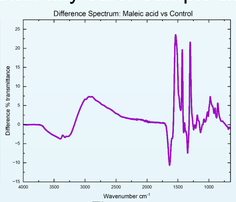

Figure 5

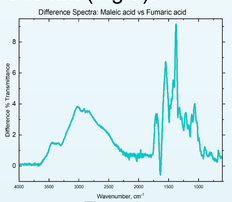

Figure 6

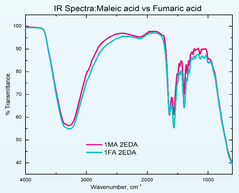

Figure 7

FTIR spectra of the samples were analyzed, and new peaks were observed at 1640 cm^{-1}, 1340 cm^{-1}, and 1128 cm^{-1}, while peaks at 1542 cm^{-1} 1431 cm^{-1}, and 1305 cm^{-1} decreased or were absent with respect to the controls, suggesting new bonds were formed, specifically amide bonds.

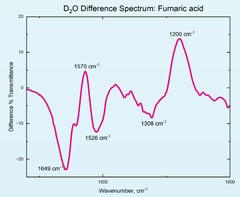

Figure 8

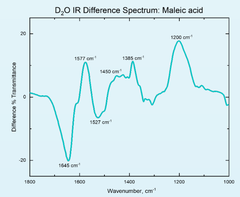

Figure 9

FTIR difference spectra for the deuterated samples FA (Fig. 8) and MA (Fig. 9)

Possible structure modeled in Avogadro showing highest occupied molecular orbital calculated via ORCA (Fig.10). The hydrophobic and hydrophilic regions of the structure are clearly delineated.

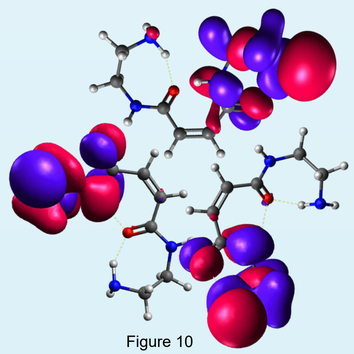
Figure 10

Computational Analysis

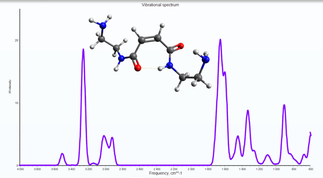
Figure 11

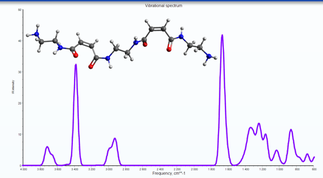
Figure 12

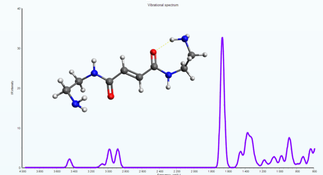
Figure 13

Calculated IR spectra of possible carbon quantum dot units, using CPCM solvent model and def2-SVP basis set in ORCA (Fig.11, 12, and 13).

Conclusion and Future Work

The fluorescence spectra showed increasing emission wavelength with decreasing amounts of EDA. The two stereoisomers showed different optical properties under the same reaction conditions, which suggests the conformation of the reagents influences the emission wavelength. The FTIR results showed that amide bonds were formed, suggesting the carbon quantum dots may have a polyamide-like structure. Our future plans include gaining a greater understanding of the structure and properties of these carbon dots by employing techniques such as Nuclear Magnetic Resonance and Transmission Electron Microscopy and by systematically tweaking the backbone structures of the diamine and the dicarboxylic acid.

References

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Acknowledgments

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