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Edge Functionalisation of Graphene Nanoribbons with a Boron Dipyrin Complex

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Abstract

Chemical modification can be used to tune the properties of graphene and graphene nanoribbons, making them promising candidates for carbon-based electronics. The control of edge chemistry provides a route to controlling the properties of graphene nanoribbons, and their self-assembly into larger structures. Mechanically fractured graphene nanoribbons are assumed to contain oxygen functionalities, which enable chemical modification at the nanoribbon edge.

The development of graphene nanoribbon edge chemistry is difficult using traditional techniques due to limitations on the characterisation of graphene materials. Through the use of a chromophore with well-defined chemistry, the reactivity of the edges has been investigated. Small aromatic systems were used to understand the reactivity of the boron dipyrin Cl-BODIPY, and with the aid of spectroscopic and computational methods, the substitution mechanism and properties of the compounds have been investigated.

The synthetic procedure was then applied to graphene nanoribbons. Results from infrared and Raman spectroscopy studies show that edge-functionalisation of graphene nanoribbons with BODIPY was successful, and no modifications to the basal plane have been observed.

Contributions

All work presented in this thesis was completed by Ashley Way

Except:

- All infrared spectroscopy data was acquired by Ewan Fisher
- NMR spectra utilising the 700 MHz NMR spectrometer were performed by Dr. Pat Edwards
- Mass Spectrometry measurements were performed by David Lun
- Emission lifetime calculations were performed by Geoffry Laufersky at Victoria University, Wellington, using data acquired by Ashley Way
- Raman spectra background removal was performed by Josiah Cleland
- X-ray crystallographic data was acquired by Prof. Shane Telfer and David Perl

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Abbreviations

General

GNR	Graphene nanoribbon
HOPG	Highly-oriented pyrolytic graphite
kT	Energy equal to 4.11×10^{-21} J at 298 K

Molecular orbitals

HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital

Computational terms

STO	Slater-type orbital	
GTO	Gaussian-type orbital	
B3LYP	Becke, 3-parameter, Lee-Yang-Parr	(functional)
PBE	Perdew-Burke-Ernzerhof	(functional)
MO6	Minnesota-06	(functional)
MO6-2X	Minnesota-06, Hartree-Fock exchange	(functional)
DZP	Double-zeta, 1 polarisation (STO)	(basis set)

Notation for computational terms

(functional)/(basis set) Example: B3LYP/DZP

Notation for analogue compounds

analogue/BODIPY

Example: phenol/BODIPY

Solvents

DCM

Dichloromethane

IPA

Isopropyl alcohol / propan-2-ol

DCE

1,2-dichloroethane

EtOAc

Ethyl acetate

MeCN

Acetonitrile