

Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.

Edge Functionalisation of Graphene Nanoribbons with a Boron Dipyrroin Complex

A thesis presented in partial fulfilment of the requirements for the
degree of

Doctor of Philosophy

in

Nanoscience

at Massey University, Manawatū,

New Zealand.

Ashley Jacquelyne Way

2017

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

Acknowledgements

I would like to thank my supervisor Associate Professor Mark Waterland for his guidance throughout this PhD. Thank you for your guidance on computational methods and assistance with Raman measurements.

I also thank my co-supervisors Professors Shane Telfer and Simon Hall for their assistance when needed. I would like to acknowledge Joran Taylor for her assistance and expertise in the microtomy techniques used to prepare the graphene nanoribbons used in this work. I also thank David Lun for his assistance and guidance in the lab, and Dr. Pat Edwards for his assistance with NMR measurements.

I thank Ewan Fisher for acquiring IR spectra, Josiah Cleland for assistance with Raman spectra background removal, and the rest of the Waterland research group for discussions of Raman and optimisation of techniques.

I thank Geoffry Laufersky for calculations of lifetimes from time resolved emission measurements performed at Victoria University, Wellington.

I would like to acknowledge the financial support from Massey University for a Doctoral scholarship, and the Institute of Fundamental Sciences for additional funding. I also thank the New Zealand Institute of Chemistry for assisting with conference funding throughout my studies.

Finally, I thank my family and friends, for their encouragement and support throughout my studies, especially the last 3 and a half years.

Contents

Abstract.....	i
Contributions.....	ii
Acknowledgements.....	iii
Figures.....	ix
Tables.....	xiv
Abbreviations.....	xv
Chapter 1. Introduction.....	1
1.1 Materials.....	2
1.1.1 Graphene.....	2
1.1.2 The chemistry of graphene.....	5
1.1.3 Graphene nanoribbons.....	6
1.1.4 Light-harvesting molecules.....	8
1.1.5 Potential applications.....	10
1.2 Characterisation of Materials.....	10
1.2.1 Raman spectroscopy of graphitic materials.....	10
1.2.2 Infrared spectroscopy of graphene.....	13
1.2.3 Computational studies of graphitic compounds.....	14
1.3 Theory of interaction between dipyrin and graphene.....	14
1.4 Stability of aromatic compounds.....	19

Chapter 2. Synthetic methods.....	23
2.1 Synthesis of dipyrin compounds.....	23
2.1.1 Thioketone dipyrin	23
2.1.2 Ketone dipyrin	24
2.1.3 Cl-BODIPY.....	24
2.2 Functionalisation of small-analogue compounds.....	25
2.2.1 Phenol/BODIPY	25
2.2.2 MeO/BODIPY.....	26
2.2.3 Aniline/BODIPY	27
2.2.4 1-naphthylamine/BODIPY.....	29
2.2.5 2-naphthylamine/BODIPY.....	30
2.2.6 1-naphthol/2xBODIPY	31
2.2.7 2-naphthol/BODIPY	32
2.2.8 2-naphthol/2xBODIPY	33
2.2.9 1-aminoanthracene/BODIPY.....	34
2.2.10 2-aminoanthracene/BODIPY.....	34
2.2.11 9-aminophenanthrene/BODIPY.....	35
2.2.12 9-hydroxyphenanthrene/BODIPY.....	35
2.2.13 2-hydroxytriphenylene/BODIPY.....	36
2.2.14 1-hydroxypyrene/BODIPY	37
2.2.15 HBC(t-Bu) ₅ OH/BODIPY	38

2.2.16	HPB(t-Bu)5OH/BODIPY.....	39
2.2.17	Benzoic acid/BODIPY.....	40
2.3	Functionalisation of graphene nanoribbons.....	40
2.3.1	Calculation of nanoribbon quantity.....	40
2.3.2	General reaction for BODIPY-functionalisation of graphene nanoribbons.....	42
2.3.3	Purification of BODIPY-functionalised graphene nanoribbons.....	43
2.4	Crystallography.....	43
2.4.1	1-naphthylamine/BODIPY.....	45
2.4.2	1-naphthol/2xBODIPY.....	45
2.4.3	2-naphthol/2xBODIPY.....	46
Chapter 3.	Computational studies of graphene nanoribbons.....	47
3.1	Graphene analogue computational studies.....	48
3.1.1	Description of analogues.....	49
3.1.2	Results and discussion.....	55
3.1.3	Analysis of models.....	58
3.2	Graphene nanoribbon studies.....	60
3.2.1	Graphene nanoribbon structures.....	60
3.2.2	Discussion of results.....	61
3.3	Functionalisation studies.....	64

3.4	Reaction mechanism study	70
3.4.1	Calculation of pKa values	72
3.4.2	Thermodynamics.....	76
Chapter 4. Spectroscopy of dipyrins		87
4.1	Quantitative absorption studies.....	88
4.1.1	TD-DFT studies of excitations	90
4.1.2	Solvent dependent excitations	91
4.1.3	Effect of double-substitution on spectra	96
4.1.4	Exciton coupling in multi-chromophore systems.....	101
4.2	Quantitative emission studies.....	104
4.2.1	Determination of Quantum Yields	104
4.2.2	3-Dimensional emission plots	107
4.3	Time-resolved emission	110
4.4	Infrared spectroscopy	116
4.5	Raman spectroscopy.....	124
Chapter 5. Dipyrin-functionalised graphene nanoribbons		127
5.1	Infrared spectroscopy	129
5.2	Raman spectroscopy.....	131

Chapter 6. Summary and Perspectives.....	135
Bibliography.....	139
Appendices	147
Appendix A: NMR Spectra.....	147
Appendix B: Conversion of Raman spectra units	164

Figures

Figure 1.1 - Graphene sheet.....	2
Figure 1.2 - Number of publications with title containing keywords “graphene” (grey) and “nanoribbon” (gold) since 2004	3
Figure 1.3 - Number of graphene publications by field: chemistry (blue) and physics (purple).....	4
Figure 1.4 - Demonstration of zig-zag (blue) and armchair (orange) edges of graphene	4
Figure 1.5 - Potential edge structure combinations of graphene nanostructures (orange: armchair; blue: zig-zag)	6
Figure 1.6 - a) Accumulation of graphene nanoblocks during mechanical fracturing; b) Transfer of graphene nanoblocks	7
Figure 1.7 - Nucleophilic displacement in meso-halogenated BODIPY dyes	9
Figure 1.8 - Raman modes of graphene	11
Figure 1.9 - Jablonski diagram showing photophysical processes.....	15
Figure 1.10 - Illustration of Franck-Condon factors for large and small vibrational mode displacements.....	16
Figure 1.11 - Franck-Condon principle for a radiative transition (absorption)	18
Figure 1.12 - Kekulé (a) and Clar (b) representations of naphthalene	20
Figure 1.13 - Clar structures of: a) anthracene; and b) phenanthrene.....	21
Figure 2.1 - GNR edge "unit cell".....	42
Figure 2.2 – Crystal structure of 1-naphthylamine/BODIPY.....	45
Figure 2.3 – Crystal structure of 1-naphthol/2xBODIPY	45
Figure 2.4 – Crystal structure of 2-naphthol/2xBODIPY	46

Figure 3.1 - Comparison between PBE and B3LYP functionals for frequency calculation for the transition state structure of phenol/BODIPY.....	48
Figure 3.2 - Zig-zag edged structures: a) anthracene; b) pentacene; c) heptacene; and d) nonacene	49
Figure 3.3 - Armchair edged structures: a) phenanthrene; b) picene; c) dibenzopicene; and d) dinaphthopicene.....	50
Figure 3.4 - Ring structures: a) pyrene; b) coronene; c) ovalene; d) hexa-peri-benzocoronene; and e) TBDBPP-ovalene	51
Figure 3.5 - Calculated Raman spectra of zig-zag structures	52
Figure 3.6 - Calculated Raman spectra of armchair structures.....	53
Figure 3.7 - Calculated Raman spectra of ring structures	54
Figure 3.8 - Relative D mode intensity in calculated zig-zag Raman spectra	55
Figure 3.9 - Relative R mode intensity in calculated armchair Raman spectra	56
Figure 3.10 - Vibrational modes of ovalene (left) and hexa-peri-benzocoronene (right).....	59
Figure 3.11 - Comparison of Raman bond parameters for graphene fragments using Hückel and DFT methods; good agreement is observed between low and high levels of theory	60
Figure 3.12 - Skeletal structures of a) armchair and b) zig-zag edged nanoribbon analogues.....	61
Figure 3.13 - Calculated IR spectra for armchair and zig-zag nanoribbon analogues (individual points plotted)	62
Figure 3.14 - Calculated IR spectra for armchair and zig-zag nanoribbon analogues (artificially widened)	63
Figure 3.15 - Calculated and experimental IR spectra for graphene nanoribbons .	63

Figure 3.16 - Crystal structures for basis set optimisation; left: 1-naphthylamine/BODIPY; right: 2-naphthol/2xBODIPY	65
Figure 3.17 - Optimised geometries of 1-naphthylamine/BODIPY	67
Figure 3.18 - Optimised geometries of 2-naphthol/2xBODIPY	69
Figure 3.22 - Molecular orbital diagrams for 1-naphthylamine (left) and 2-naphthylamine (right)	78
Figure 3.23 - Density of states for 2-naphthol with overlaid molecular orbitals	80
Figure 3.24 - Density of states for 2-naphthylamine with overlaid molecular orbitals	80
Figure 3.25 - HOMO for -O-BODIPY compounds with HOMO-LUMO gap stated	82
Figure 3.26 - LUMO for -O-BODIPY compounds	83
Figure 4.1 - Solvatochromism of Cl-BODIPY	87
Figure 4.2 - Beer-Lambert plot for 2-aminoanthracene/BODIPY in toluene	88
Figure 4.3 - Normalised absorption spectra of 1-naphthol/2xBODIPY	92
Figure 4.4 - TD-DFT excitation spectra of 1-naphthol/2xBODIPY; Modes with oscillator strength > 0.1 have been assigned to molecular orbital transitions..	94
Figure 4.5 - Occupied orbitals: 1-naphthol/2xBODIPY	95
Figure 4.6 - Virtual orbitals: 1-naphthol/2xBODIPY	95
Figure 4.7 - Absorption spectra of 2-naphthol/1x and 2xBODIPY	98
Figure 4.8 - TD-DFT excitation spectra of 2-naphthol/1x and 2xBODIPY; Modes with oscillator strength > 0.1 have been assigned to molecular orbital transitions..	98
Figure 4.9 - Occupied (blue and red) and virtual (orange and teal) orbitals: 2-naphthol/1xBODIPY	99
Figure 4.10- Occupied (blue and red) and virtual (orange and teal) orbitals: 2-naphthol/2xBODIPY	99

Figure 4.11 - Absorption spectra of 2-naphthol/2xBODIPY in acetonitrile at different concentrations.....	100
Figure 4.12 - Transition dipole for BODIPY	101
Figure 4.13 - Geometrical parameters used to define the orientation of two transition dipole moments	102
Figure 4.14 - Determination of geometrical parameters for 1-naphthol/2xBODIPY (top) and 2-naphthol/2xBODIPY (bottom) with α and α' (left) and β (right). BODIPY planes (long axis = dipole) are shown for clarity	103
Figure 4.15 - E_T^N scale for selected solvents	107
Figure 4.16 - 3D (left) and contour (right) plots of Cl-BODIPY in: ethyl acetate (top); acetonitrile (centre); and toluene (bottom)	108
Figure 4.17 - 3D (left) and contour (right) plots of Cl-BODIPY in: chloroform (top); chlorobenzene (centre); and isopropyl alcohol (bottom).....	109
Figure 4.18 - Excitation data for Cl-BODIPY in three solvents; Data for $\lambda_{ex} = 500$ nm has been scaled to match λ_{em} at approximately 525 nm.....	111
Figure 4.19 - $\ln k_{nr}$ vs E_{em} for all compounds	114
Figure 4.20 - $\ln k_{nr}$ vs E_{em} for hydroxyl containing compounds; Data has been separated between mono- (1x) and d- (2x) substituted analogues	115
Figure 4.21 - Comparison between calculated and experimental IR spectra of 1-hydroxypyrene.....	117
Figure 4.22 - Comparison between calculated and experimental IR spectra of 1-hydroxypyrene/BODIPY.....	117
Figure 4.23 - Experimental IR spectra of 1-hydroxypyrene and 1-hydroxypyrene/BODIPY.....	119

Figure 4.24 - Calculated IR spectra of 1-hydroxypyrene and 1-hydroxypyrene/BODIPY.....	119
Figure 4.25 - Calculated IR spectra of HBC(t-Bu)5OH and HBC(t-Bu)5OH/BODIPY.....	120
Figure 4.26 - Vibrational modes - BODIPY functionalisation;.....	121
Figure 4.27 - Calculated IR spectrum for 1-hydroxypyrene/BODIPY with assigned vibrational modes.....	123
Figure 4.28 - Calculated IR spectrum for HBC(t-Bu)5OH/BODIPY with assigned vibrational modes.....	124

Tables

Table 2.1 - Crystallography data	44
Table 3.1 - Bonding energies for 1-naphthylamine	67
Table 3.2 - Bonding energies for 2-naphthol/2xBODIPY	68
Table 3.3 - Comparison of experimental and calculated pKa values	73
Table 3.4 - Comparison of experimental and calculated pKa values in water	75
Table 3.5 - Comparison of experimental and calculated pKa values in dichloroethane	75
Table 3.6 - Calculated pKa values for analogues.....	75
Table 3.7 - Thermodynamic information for functionalisation studies.....	77
Table 4.1 – Summary of molar absorptivity coefficients ($\text{mol}^{-1}\text{Lcm}^{-1}$) for Cl-BODIPY and its small-analogue products. Standard errors (rounded to 1 significant figure) are included in brackets	90
Table 4.2 - Geometrical parameters for exciton coupling.....	104
Table 4.3 - Relative quantum yields. * indicates reference standard used is Coumarin 6H; all others calculated with Coumarin 334 as standard	106
Table 4.4 - Lifetimes in ethyl acetate.....	112
Table 4.5 - Lifetimes in acetonitrile	112
Table 4.6 - Lifetimes in toluene	112

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