Molecular and Polymeric Materials Based On Asymmetrically Substituted BF2 3-Cyanoformazanates

Samantha Novoa
The University of Western Ontario

Supervisor
Dr. Joe Gilroy
The University of Western Ontario

Graduate Program in Chemistry

A thesis submitted in partial fulfillment of the requirements for the degree in Master of Science

© Samantha Novoa 2017

Follow this and additional works at: https://ir.lib.uwo.ca/etd
Part of the Polymer Chemistry Commons

Recommended Citation
https://ir.lib.uwo.ca/etd/4585

This Dissertation/Thesis is brought to you for free and open access by Scholarship@Western. It has been accepted for inclusion in Electronic Thesis and Dissertation Repository by an authorized administrator of Scholarship@Western. For more information, please contact tadam@uwo.ca, wlswadmin@uwo.ca.
Abstract

This thesis outlines the synthesis and characterization of asymmetric and symmetric 3-cyanoformazanate BF$_2$ complexes and their incorporation into polymers. CuAAC chemistry was used to synthesize two additional asymmetric BF$_2$ complexes and a side product that was identified as a symmetric dimer. Spectroscopic and electrochemical properties of these compounds are described.

Incorporation of an asymmetric 3-cyanoformazanate BF$_2$ complex into polymers was done by ROMP. This reaction was used to make homo, block, and random copolymers, where the comonomer was an organic norbornene derivative. Spectroscopic studies of these polymers revealed that, as the mole fraction of BF$_2$ ($f_{BF2}$) in random copolymers decreased, the quantum yield of fluorescence increased; this was due to less quenching/self-absorption from nearby chromophores. Thermal and electrochemical properties of all polymers are described.

Keywords

Formazanate ligands, Copper (I)-assisted alkyne-azide cycloaddition, Ring-Opening Metathesis Polymerization, Absorption/Emission Spectroscopy, Redox-active polymers.
Co-Authorship Statement

The work described in this thesis contains contributions from the author as well as my co-worker Stephanie Barbon and my supervisor Prof. Joe B. Gilroy. The contributions of each are described below.

Chapter 1 was written by the author and edited by Prof. Gilroy.

Chapter 2 describes various small molecule syntheses that were completed by the author. All X-ray crystallographic studies described were done by Stephanie Barbon. The chapter was written by the author and edited by Prof. Gilroy.

Chapter 3 describes a project where all the experimental work and characterization was performed by the author. The chapter was written by the author and edited by Prof. Gilroy.

Chapter 4 was written by the author and edited by Prof. Gilroy.
Acknowledgments

First and foremost, I would like to thank Professor Joe Gilroy for his immeasurable mentorship and support; thank you for giving me the opportunity to work in your group and for always pushing me to do my best. I can say that, through your guidance, I have become a better chemist, presenter, mentor, and an overall professional that is ready for the real world. Your dedication to all your students is admirable and has been an essential part of the completion of my degree. Thank you.

I would also like to thank my amazing lab mates for always lending a helping hand and for being the kindest people I could have asked to work with. More specifically, I would like to thank Dr. Rabiee Kenaree for always being available for real life-talk and venting; I’m also glad you can use Snapchat now. Dr. Paquette, thank you for all the laughs, jokes, and for providing me with great interview question examples— you’re the best. Ryan Maar, thanks for being my competitive twin; your passion and dedication for research really pushed me to put in 110%. Alex Van Belois, thanks for teaching me how to play squash and for laughing at my jokes. And last, but certainly not least, Stephanie Barbon; you started off as a mentor and have become a close friend. Thank you for always being there whether it was to joke around or to discuss research, grad school would not have been the same without you! I would also like to thank the rest of the graduate students I have had the pleasure of working with and meeting specifically all the members of the baseball, soccer, and ultimate Frisbee teams, it was super fun getting to know you all!

The Department of Chemistry has been essential in the completion of this degree, and I would also like to express my gratitude. Thank you to Aneta Borecki for running all of my GPC samples, Mat Willans for his advice and support in the NMR spectroscopy field, Doug Harsine for running mass spectrometry experiments, and Steph for crystallography studies. I would also like to thank the office staff, especially Darlene who was always available to answer my questions and help with all the paperwork needed to graduate. Also, thank you to ChemBio Stores for all your help throughout the years.

Finally, I would like to thank my family and friends. To my parents, Pedro and Nubia, I want to thank you for always supporting me in everything that I do. Thank you for sacrificing so
much for my sister and me; your immense courage and perseverance have founded my core. I would not be the same person without you, I love you both immensely. To my sister, Stefania, I want to tell you that I thank God every day for providing me with my best friend. Thank you for always being with me through thick and thin, I love you so much, and I'm so excited to see where life will take us. To all my friends and family, you know who you are, I just want to say thank you for your support and friendship throughout my life. I love you all.
# Table of Contents

Abstract ............................................................................................................................... i
Co-Authorship Statement...................................................................................................... ii
Acknowledgments ................................................................................................................ iii
Table of Contents .................................................................................................................. v
List of Tables ........................................................................................................................ viii
List of Figures ......................................................................................................................... ix
List of Schemes ....................................................................................................................... xiii
List of Appendices ................................................................................................................ xvi
List of Abbreviations .............................................................................................................. xvi
Chapter 1 .................................................................................................................................. 1
1 Introduction ........................................................................................................................... 1
1.1 Polymers Containing Quinoline Derivatives ................................................................. 1
1.2 Polymers Containing Naphthalene and Anthracene Derivatives ................................. 5
1.3 Polymers Containing Fluorene Derivatives ................................................................... 10
1.4 Boron Containing Fluorophores and Polymers ............................................................ 14
1.5 Scope of Thesis ............................................................................................................... 19
1.6 References ....................................................................................................................... 20
Chapter 2 .................................................................................................................................. 25
2 Asymmetric 3-Cyanoformazanate BF$_2$ Complexes ....................................................... 25
2.1 Introduction ..................................................................................................................... 25
2.2 Results and Discussion ................................................................................................. 27
2.2.1 Synthesis of Asymmetric 3-Cyanoformazans .......................................................... 27
2.2.2 Synthesis of BF$_2$ 3-Cyanoformazanate Complexes ................................................ 28
2.2.3 X-ray Crystallography .............................................................................................. 32
3.5 References............................................................................................................. 78
Chapter 4 ....................................................................................................................... 81
4   Conclusions and Future Work .............................................................................. 81
4.1 Conclusions.............................................................................................................. 81
4.2 Future Work ........................................................................................................... 84
4.3 References.............................................................................................................. 85
Appendices.................................................................................................................... 86
Appendix 1 – Supporting Information for Chapter 2.................................................. 86
Appendix 2 – Supporting Information for Chapter 3.................................................. 97
Curriculum Vitae.......................................................................................................... 106
List of Tables

Table 2.1 Experimental yields for asymmetric syntheses .......................................................... 28

Table 2.2. Selected bond lengths (Å) and angles (degrees) for 2.13 BF$_2$ complex.............. 33

Table 2.3. Selected bond lengths (Å) and angles (degrees) for 2.18 BF$_2$ complex.............. 34

Table 2.4. Spectroscopic properties of BF$_2$ complex 2.13, benzyl-substituted BF$_2$ complex 2.14, monomer 2.17, and dimer 2.18 ................................................................................................. 36

Table 2.5. Electrochemical properties of BF$_2$ complex 2.13, benzyl-substituted BF$_2$ complex 2.14, monomer 2.17, and dimer 2.18 ................................................................................................. 38

Table 2.6 Crystallographic data for compounds 2.13 and 2.18.............................................. 41

Table 3.1. Summary of molecular weight data determined by GPC for PBF$_2$N polymers ... 52

Table 3.2. Summary of molecular weight data determined by GPC for PDND ................. 56

Table 3.3. Summary of molecular weight data determined for the first block and diblock copolymers (PDND)$_{276}$-b-(PBF$_2$N)$_{255}$ ($f_{BF2} = 0.48$), (PDND)$_{355}$-b-(PBF$_2$N)$_{53}$ ($f_{BF2} = 0.13$) and (PDND)$_{266}$-b-(PBF$_2$N)$_{20}$ ($f_{BF2} = 0.07$) ............................................................................................................. 61

Table 3.4. Summary of molecular weight data for random copolymers (PDND)$_{316}$-r-(PBF$_2$)$_{316}$ ($f_{BF2} = 0.50$), (PDND)$_{292}$-r-(PBF$_2$N)$_{52}$ ($f_{BF2} = 0.15$) and (PDND)$_{298}$-r-(PBF$_2$N)$_{26}$ ($f_{BF2} = 0.08$) .......................................................................................................................... 63

Table 3.5. Spectroscopic properties of BF$_2$N, PBF$_2$N, and all block copolymers (PDND)$_m$-b-(PBF$_2$N)$_n$ and random copolymers (PDND)$_m$-r-(PBF$_2$N)$_n$ .......................................................... 67
List of Figures

Figure 2.1. Overlay of $^1$H NMR spectra of compounds 2.13 (red) and 2.14 (black) in CDCl$_3$. The triangle represents the ≡CH proton and the circle represents ≡CH peak of the triazole ring. .......................................................................................................................................................................................... 30

Figure 2.2. Solid-state structure of BF$_2$ complex 2.13 (top and side views). Hydrogen atoms have been omitted for clarity. Thermal displacement ellipsoids are shown at 50% probability .................................................................................................................................................................................. 32

Figure 2.3. Solid-state structure of dimer 2.18 (top and side views). Hydrogen atoms have been omitted for clarity. Thermal displacement ellipsoids are shown at 50% probability .... 34

Figure 2.4. Normalized absorption (a) and emission (b) spectra for BF$_2$ complex 2.13 (black), benzyl-substituted BF$_2$ complex 2.14 (blue), monomer 2.17 (green), and dimer 2.18 (red) recorded in CH$_2$Cl$_2$ ................................................................................................................................................................................................. 35

Figure 2.5. Normalized absorption (solid line) and emission (dashed line) spectra for monomer 2.17 recorded in CH$_2$Cl$_2$ ................................................................................................................................................................................................. 35

Figure 2.6. Cyclic voltammograms for BF$_2$ complex 2.13 (black), benzyl-substituted BF$_2$ complex 2.14 (blue), monomer 2.17 (green), and dimer 2.18 (red), were recorded at a scan rate of 250 mV s$^{-1}$ for 1 mM analyte solutions in CH$_2$Cl$_2$ containing 0.1 M [nBu$_4$N][PF$_6$] as the supporting electrolyte. All voltammograms were referenced internally against the ferrocence/ferrocenium redox couple .................................................................................................................................................................................. 38

Figure 3.1. Overlay of $^1$H NMR spectra for BF$_2$N monomer (red) and PBF$_2$N (black) in CDCl$_3$. The triangles represent the norbornene alkene protons on BF$_2$N and the circles represents the new alkene protons found in the backbone of PBF$_2$N ................................................................. 51

Figure 3.2. Relationship between $M_n$ of PBF$_2$N as a function of time (a), and corresponding GPC traces (b). Dark blue dot at zero 0 min in (a) represents the $M_n$ value determined for the BF$_2$N monomer. GPC traces in (b) are colour coded: 1 min (light blue), 3 min (red), 5 min (black), 10 min (dark yellow), 20 min (green), 30 min (purple), 60 min (grey) ..................................................................... 52
Figure 3.3. Overlay of the $^1$H NMR spectra of compound PDND (red) and PDND (black) in CDCl$_3$. The triangle represents the norbornene alkene protons and the circles represent the new alkene protons found in the backbone of PDND........................................................................... 55

Figure 3.4. Relationship between the $M_n$ of PDND as a function of time (a), and corresponding GPC traces (b). GPC traces in (b) are colour coded: 0.5 min (light blue), 1 min (red), 3 min (black), 5 min (dark yellow), 7 min (green), 9 min (purple) ........................................................................... 56

Figure 3.5. GPC traces (in DMF) of polymer PDND ($f_{BF2} = 0.0$, dark yellow) and block copolymers (PDND)$_{276}$-b-(PBF$_2$N)$_{285}$ ($f_{BF2} = 0.48$, blue), (PDND)$_{355}$-b-(PBF$_2$N)$_{53}$ ($f_{BF2} = 0.13$, purple) and (PDND)$_{266}$-b-(PBF$_2$N)$_{20}$ ($f_{BF2} = 0.07$, red) ........................................................................... 58

Figure 3.6. Overlay of $^1$H NMR spectra of compound PDND (green), PBF$_2$N (red) and polymer (PDND)$_{276}$-b-(PBF$_2$N)$_{285}$ (black) in CDCl$_3$. The circles represent the new alkene protons found in the backbone of (PDND)$_{276}$-b-(PBF$_2$N)$_{285}$, the triangle represents the protons on the methoxy substituent of PBF$_2$N, the square represents the methyl groups on PDND, and the star represents two aryl protons on the PBF$_2$N subunit........................................................................... 59

Figure 3.7. $^1$H NMR spectra of (PDND)$_{316}$-r-(PBF$_2$N)$_{316}$ in CDCl$_3$. The circles represent the alkene protons found in the backbone of the polymer, the triangle represents the protons on the methoxy group on the PBF$_2$N subunit, and the square represents the methyl groups on the DND subunit. The star represents two aryl protons on the PBF$_2$N subunit ...................... 63

Figure 3.8. GPC traces (in DMF) of polymer PDND ($f_{BF2} = 0.0$, dark yellow) and random copolymers (PDND)$_{316}$-r-(PBF$_2$N)$_{316}$ ($f_{BF2} = 0.50$), (PDND)$_{292}$-r-(PBF$_2$N)$_{52}$ ($f_{BF2} = 0.15$) and (PDND)$_{298}$-r-(PBF$_2$N)$_{26}$ ($f_{BF2} = 0.08$) ........................................................................... 64

Figure 3.9. TGA graphs of PBF$_2$N ($f_{BF2} = 1.0$, black), (PDND)$_{276}$-b-(PBF$_2$N)$_{285}$ ($f_{BF2} = 0.48$, blue), (PDND)$_{355}$-b-(PBF$_2$N)$_{53}$ ($f_{BF2} = 0.13$, purple), (PDND)$_{266}$-b-(PBF$_2$N)$_{20}$ ($f_{BF2} = 0.07$, red), and PDND ($f_{BF2} = 0.0$, dark yellow) ........................................................................... 65

Figure 3.10. TGA graphs of PBF$_2$N ($f_{BF2} = 1.0$, black), (PDND)$_{316}$-r-(PBF$_2$N)$_{316}$ ($f_{BF2} = 0.50$, blue), (PDND)$_{292}$-r-(PBF$_2$N)$_{52}$ ($f_{BF2} = 0.15$, purple), (PDND)$_{298}$-r-(PBF$_2$N)$_{26}$ ($f_{BF2} = 0.08$, red), and PDND ($f_{BF2} = 0.0$, dark yellow) ........................................................................... 65
Figure 3.11. DSC traces (a) and first derivative traces (b) for polymer PDND ($f_{\text{BF}_2} = 0.0$, dark yellow), PBF$_2$N ($f_{\text{BF}_2} = 1.0$, black), and block copolymers (PDND)$_{276}$-$b$-(PBF$_2$N)$_{255}$ ($f_{\text{BF}_2} = 0.48$, blue), (PDND)$_{355}$-$b$-(PBF$_2$N)$_{53}$ ($f_{\text{BF}_2} = 0.13$, purple) and (PDND)$_{266}$-$b$-(PBF$_2$N)$_{20}$ ($f_{\text{BF}_2} = 0.07$, red). Decomposition point of PDND was lower than the other polymers, and thus DSC could only be done up to 130 °C.

Figure 3.12. DSC traces (a) and first derivative traces (b) for polymer PDND ($f_{\text{BF}_2} = 0.0$, dark yellow), PBF$_2$N ($f_{\text{BF}_2} = 1.0$, black), and random copolymers (PDND)$_{316}$-$r$-(PBF$_2$N)$_{316}$ ($f_{\text{BF}_2} = 0.50$, blue), (PDND)$_{292}$-$r$-(PBF$_2$N)$_{52}$ ($f_{\text{BF}_2} = 0.15$, purple) and (PDND)$_{298}$-$r$-(PBF$_2$N)$_{26}$ ($f_{\text{BF}_2} = 0.08$, red).

Figure 3.13. UV-vis absorption spectra of BF$_2$N (dark yellow) and PBF$_2$N ($f_{\text{BF}_2} = 1.0$, black) (a, b), and block copolymers (PDND)$_m$-$b$-(PBF$_2$N)$_n$ (a), and random copolymers (PDND)$_m$-$r$-(PBF$_2$N)$_n$ (b). All spectra were recorded in CH$_2$Cl$_2$ using 0.00005 g mL$^{-1}$ solutions.

Figure 3.14. Emission spectra for BF$_2$N (dark yellow), PBF$_2$N ($f_{\text{BF}_2} = 1.0$, black) and random copolymers (PDND)$_{316}$-$r$-(PBF$_2$N)$_{316}$ ($f_{\text{BF}_2} = 0.50$, blue), (PDND)$_{292}$-$r$-(PBF$_2$N)$_{52}$ ($f_{\text{BF}_2} = 0.15$, purple) and (PDND)$_{298}$-$r$-(PBF$_2$N)$_{26}$ ($f_{\text{BF}_2} = 0.08$, red) (b). All spectra were recorded in CH$_2$Cl$_2$ and their absorbance in the UV-vis region was approximately 0.1.

Figure 3.15. Summary of the quantum yields of fluorescence (red dots) for the random copolymers (PDND)$_m$-$r$-(PBF$_2$N)$_n$, as well as for BF$_2$N (defined as $f_{\text{BF}_2} = 1.0$), and PBF$_2$N ($f_{\text{BF}_2} = 1.0$). Errors bars associated with the quantum yields calculated were placed by using the standard deviation for three repeated experiments of each. Spectra were recorded in CH$_2$Cl$_2$ and their maximum absorbance in solution was approximately 0.1.

Figure 4.1. BF$_2$ complexes studied in Chapter 2.

Figure 4.2. Block and random copolymers of PBF$_2$N and PDND studied in Chapter 3.

Figure 4.3. Block copolymers 4.1 and 4.2. The cartoon is a representation of the block copolymer where the blue represents the first block (BF$_2$ containing random copolymer) and the black represents the non-fluorescent organic block.
Figure 4.4. Visual representation of micelle formation of block copolymers 4.1 and 4.2.
Yellow cartoon around the micelle on the right represents fluorescence ............................. 85
List of Schemes

**Scheme 1.1.** Synthesis of quinoline containing monomer 1.3 and polymer 1.4 .................. 2

**Scheme 1.2.** Synthesis of monomer 1.12 and 1.13 for subsequent Suzuki coupling to afford polymers 1.14 .......................................................... 4

**Scheme 1.3.** Free radical copolymerization of 1.15 and 1.16 for the synthesis of 1.17 ........ 5

**Scheme 1.4.** Synthesis of linear polymer 1.23 and cyclic polymer 1.25 .......................... 7

**Scheme 1.5.** Synthesis of monomer 1.28 and polymers 1.31 and 1.32 .......................... 8

**Scheme 1.6.** Synthesis of monomer 1.35 ................................................................. 9

**Scheme 1.7.** Synthesis of monomer 1.37 ................................................................. 9

**Scheme 1.8.** Synthesis of polymer 1.39 ....................................................................... 10

**Scheme 1.9.** Synthesis of polymer 1.41 ....................................................................... 10

**Scheme 1.10.** Synthesis of polymers 1.47 and 1.48 .................................................... 11

**Scheme 1.11.** Synthesis of polymer 1.51 ...................................................................... 12

**Scheme 1.12.** Synthesis of polymer 1.57 ...................................................................... 13

**Scheme 1.13.** Isomerization of trans-1.57 to cis-1.58 using visible light ......................... 14

**Scheme 1.14.** Synthesis of monomers 1.68–1.70 and polymers 1.72–1.74 ................. 17

**Scheme 1.15.** ROMP of monomer 1.76 to yield homopolymer 1.77 ............................ 19

**Scheme 1.16.** ROMP of monomer 1.78 and monomer 1.76 to yield block copolymer 1.79 . 19

**Scheme 2.1.** Benzoid (2.4) to quinoid (2.5) resonance structures .............................. 26

**Scheme 2.2.** Stolarski synthesis of asymmetric 3-cyanoformazans ............................. 27
Scheme 2.3. Elnagdi synthesis for asymmetric 3-cyanoformazans ........................................ 27

Scheme 2.4. “Statistical” synthesis of asymmetric 3-cyanoformazan 2.12 ....................... 28

Scheme 2.5. Synthesis of asymmetric BF₂ formazanate complex 2.13 .......................... 29

Scheme 2.6. CuAAC reaction for the synthesis of benzyl-substituted BF₂ complex 2.14..... 29

Scheme 2.7. DCC coupling for the synthesis of azide-substituted norbornene 2.16 ........... 31

Scheme 2.8. Synthesis of monomer 2.17 by CuAAC ...................................................... 31

Scheme 2.9. Redox reactions of a BF₂ formazanate complex (2.19a) to afford a radical anion (2.19b) and dianion (2.19c) ........................................................................................................ 37

Scheme 3.1. ROMP of BF₂N monomer ........................................................................... 51

Scheme 3.2. Synthesis of monomer exo-NDCA ................................................................ 53

Scheme 3.3. Polymerization of monomer exo-NDCA ..................................................... 53

Scheme 3.4. Synthesis of monomer DND ...................................................................... 54

Scheme 3.5. ROMP of DND .......................................................................................... 55

Scheme 3.6. Representative synthesis of (PDND)ₘ₋ₘ₋ₙ₋ₙ polymers using ROMP .... 57

Scheme 3.7. Synthesis for random block copolymers (PDND)ₘ₋ₘ₋ₙ₋ₙ. M represents the DPₘ for the DND subunit, and n represents the DPₙ for the BF₂N subunit ......................... 62
List of Appendices

Appendix 1 – Supporting Information for Chapter 2.......................................................... 86

Appendix 2 – Supporting Information for Chapter 3.......................................................... 97
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>°</td>
<td>degree</td>
</tr>
<tr>
<td>°C</td>
<td>degrees Celsius</td>
</tr>
<tr>
<td>( ^{11}\text{B} )</td>
<td>boron-eleven</td>
</tr>
<tr>
<td>( ^{13}\text{C} )</td>
<td>carbon-thirteen</td>
</tr>
<tr>
<td>( ^{1}\text{H} )</td>
<td>proton</td>
</tr>
<tr>
<td>( ^{19}\text{F} )</td>
<td>fluorine-nineteen</td>
</tr>
<tr>
<td>+ve</td>
<td>positive</td>
</tr>
<tr>
<td>A</td>
<td>absorbance</td>
</tr>
<tr>
<td>Å</td>
<td>angstrom</td>
</tr>
<tr>
<td>a. u.</td>
<td>arbitrary units</td>
</tr>
<tr>
<td>AcOH</td>
<td>acetic acid</td>
</tr>
<tr>
<td>AIBN</td>
<td>2,2’-azo-bis(2-methylpropionitrile)</td>
</tr>
<tr>
<td>AIE</td>
<td>aggregation-induced emission</td>
</tr>
<tr>
<td>ATR</td>
<td>attenuated total reflectance</td>
</tr>
<tr>
<td>ATRP</td>
<td>atom transfer radical polymerization</td>
</tr>
<tr>
<td>BASi</td>
<td>Bioanalytical Systems Inc.</td>
</tr>
<tr>
<td>BOIMPY</td>
<td>boron complexes of iminopyrrolide ligands</td>
</tr>
<tr>
<td>BODIPY</td>
<td>boron dipyrrromethene</td>
</tr>
<tr>
<td>bpy</td>
<td>bispyridine</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>br</td>
<td>broad</td>
</tr>
<tr>
<td>Bu</td>
<td>butyl</td>
</tr>
<tr>
<td>CCDC</td>
<td>Cambridge crystallographic data centre</td>
</tr>
<tr>
<td>cm</td>
<td>centimeter</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>change</td>
</tr>
<tr>
<td>cm$^{-1}$</td>
<td>wavenumber</td>
</tr>
<tr>
<td>CMPB</td>
<td>2-(4-chloromethyl-phenyl)-benzoxazole</td>
</tr>
<tr>
<td>CuAAC</td>
<td>copper (I)-assisted alkyne-azide cycloaddition</td>
</tr>
<tr>
<td>$D$</td>
<td>dispersity</td>
</tr>
<tr>
<td>d</td>
<td>doublet</td>
</tr>
<tr>
<td>DCC</td>
<td>$N,N'$-dicyclohexylcarbodiimide</td>
</tr>
<tr>
<td>DLS</td>
<td>dynamic light scattering</td>
</tr>
<tr>
<td>DMA</td>
<td>dimethylacetamide</td>
</tr>
<tr>
<td>dd</td>
<td>doublet of doublets</td>
</tr>
<tr>
<td>DMAP</td>
<td>dimethylaminopyridine</td>
</tr>
<tr>
<td>DMF</td>
<td>dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethylsulfoxide</td>
</tr>
<tr>
<td>DMSO-$d_6$</td>
<td>deuterated dimethylsulfoxide</td>
</tr>
<tr>
<td>DNA</td>
<td>deoxyribonucleic acid</td>
</tr>
<tr>
<td>DP$_n$</td>
<td>degree of polymerization</td>
</tr>
<tr>
<td>Symbol</td>
<td>Term</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>DSC</td>
<td>differential scanning calorimetry</td>
</tr>
<tr>
<td>E</td>
<td>potential</td>
</tr>
<tr>
<td>EDX</td>
<td>energy dispersive X-ray</td>
</tr>
<tr>
<td>EI</td>
<td>electron-impact ionization</td>
</tr>
<tr>
<td>Et</td>
<td>ethyl</td>
</tr>
<tr>
<td>Et₂O</td>
<td>diethyl ether</td>
</tr>
<tr>
<td>Et₃N</td>
<td>triethylamine</td>
</tr>
<tr>
<td>EtOAc</td>
<td>ethyl acetate</td>
</tr>
<tr>
<td>EtOH</td>
<td>ethanol</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier transform infra-red spectroscopy</td>
</tr>
<tr>
<td>$f_{BF_2}$</td>
<td>mole fraction of BF₂N</td>
</tr>
<tr>
<td>g</td>
<td>gram</td>
</tr>
<tr>
<td>GIII</td>
<td>3-bromo pyridine derivative of Grubb’s third generation catalyst</td>
</tr>
<tr>
<td>GPC</td>
<td>gel permeation chromatography</td>
</tr>
<tr>
<td>GOF</td>
<td>goodness of fit</td>
</tr>
<tr>
<td>h</td>
<td>hours</td>
</tr>
<tr>
<td>hex</td>
<td>hexanes</td>
</tr>
<tr>
<td>Hz</td>
<td>hertz</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>$J$</td>
<td>NMR coupling constant</td>
</tr>
</tbody>
</table>
K Kelvin

LED light emitting diode

\([M]_0\) initial monomer concentration

\([M]\) monomer concentration

M molar

\(\mu M\) micromolar

m multiplet

mA milliamps

max maximum

Me methyl

MeOH methanol

mg milligram

MHz megahertz

min minute/minutes

mL milliliter

mm millimeter

mM millimolar

mmol millimoles

\(M_n\) number average molecular weight

mol moles
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>mV</td>
<td>millivolts</td>
</tr>
<tr>
<td>MW</td>
<td>molecular weight</td>
</tr>
<tr>
<td>$M_w$</td>
<td>weight average molecular weight</td>
</tr>
<tr>
<td>nm</td>
<td>nanometers</td>
</tr>
<tr>
<td>NMP</td>
<td>1-methyl-2-pyrrolidinone</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>O. D.</td>
<td>onset of decomposition</td>
</tr>
<tr>
<td>OAc</td>
<td>acetate</td>
</tr>
<tr>
<td>OLED</td>
<td>organic light-emitting diode</td>
</tr>
<tr>
<td>$p$</td>
<td>para</td>
</tr>
<tr>
<td>PBB</td>
<td>propargyl-2-bromoisobutyrate</td>
</tr>
<tr>
<td>Pd(dppf)Cl$_2$</td>
<td>[1,1′-Bis(diphenylphosphino)ferrocene]dichloropalladium(II)</td>
</tr>
<tr>
<td>PLA</td>
<td>polylactic acid</td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl</td>
</tr>
<tr>
<td>PMDETA</td>
<td>$N,N,N',N'' ,N'''$-pentamethyldiethylenetriamine</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>$\pi$</td>
<td>pi</td>
</tr>
<tr>
<td>py</td>
<td>pyridine</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>$\Phi_F$</td>
<td>fluorescence quantum yield</td>
</tr>
<tr>
<td>Symbol</td>
<td>Term</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>q</td>
<td>quartet</td>
</tr>
<tr>
<td>R&lt;sub&gt;1&lt;/sub&gt;</td>
<td>residual factor</td>
</tr>
<tr>
<td>r.t.</td>
<td>room temperature</td>
</tr>
<tr>
<td>RI</td>
<td>refractive index</td>
</tr>
<tr>
<td>RAFT</td>
<td>reversible addition-fragmentation chain transfer</td>
</tr>
<tr>
<td>ROMP</td>
<td>ring-opening metathesis polymerization</td>
</tr>
<tr>
<td>s</td>
<td>singlet</td>
</tr>
<tr>
<td>t</td>
<td>triplet</td>
</tr>
<tr>
<td>t&lt;sub&gt;-BuOK&lt;/sub&gt;</td>
<td>potassium tert-butoxide</td>
</tr>
<tr>
<td>T&lt;sub&gt;g&lt;/sub&gt;</td>
<td>glass transition temperature</td>
</tr>
<tr>
<td>TGA</td>
<td>thermal gravimetric analysis</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TBAI</td>
<td>tetrabutylammonium iodide</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>UV-vis</td>
<td>ultraviolet-visible</td>
</tr>
<tr>
<td>v/v</td>
<td>volume to volume ratio</td>
</tr>
<tr>
<td>w</td>
<td>weak</td>
</tr>
<tr>
<td>vs.</td>
<td>versus</td>
</tr>
<tr>
<td>x</td>
<td>Cartesian axis</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>
$y$ Cartesian axis

$z$ Cartesian axis

$\alpha$ crystallographic lattice constant, torsional angle

$\beta$ crystallographic lattice constant, torsional angle

$\gamma$ crystallographic lattice constant, torsional angle

$\delta$ chemical shift, partial charge

$\varepsilon$ molar absorptivity

$v_{ST}$ Stoke’s shift

$\theta$ theta (range for crystallographic data collection)

$\lambda$ wavelength

$\lambda_{\text{max}}$ wavelength of maximum absorption

$\lambda_{\text{em}}$ wavelength of maximum emission
Chapter 1

1 Introduction

Polymers have been synthesized for over 100 years due to the observation that molecular properties change dramatically once molecules are incorporated into long chains. Polymers are essential on a day to day basis whether they are found in plastic containers (polystyrene), batteries (polyethylene and polypropylene), or as the genetic code needed for human function and growth (DNA). Furthermore, π-conjugated polymers that have luminescent properties have been researched for their potential use in biological sensors, semiconductors and LED applications.\(^1\) \(^2\) Below, several classes of emissive polymers are highlighted.

1.1 Polymers Containing Quinoline Derivatives

Polymers containing quinoline chromophores (1.1) (or derivatives of) have been studied for their use in applications such as LEDs, \(^3\) \(^4\) \(^5\) electronic optical materials, \(^6\) \(^7\) and optical sensors. \(^8\) \(^9\) These polymers can be synthesized in different ways so that the quinoline chromophores appear in the side- or main-chain of polymers. For example, Wen and co-workers synthesized a novel polymer that contained a quinoline derivative in the side-chain (1.4) (Scheme 1.1). The synthesis of monomer 1.3 was carried out by dissolving previously synthesized molecule 1.2 \(^10\) in THF and Et\(_3\)N, cooling the solution down, and then adding methacryloyl chloride. Monomer 1.3 was then polymerized by using atom transfer radical polymerization (ATRP) where CMPB was used as the initiator, and CuCl/PMDETA as the catalyst/ligand system. A plot of \(\ln([M]_0/[M])\) vs. time was plotted where \([M]_0\) corresponds to the initial monomer concentration, and \([M]\) corresponds to the monomer concentration at a certain time interval. This relationship was found to be linear, which showed the controlled polymerization of monomer 1.3, along with the fact that the polymers had low dispersity (\(D\)) values. The spectroscopic properties of monomer 1.3 and polymer 1.4 were studied, and it was found that the emission of the polymer was significantly higher than that of the monomer. This was attributed to a phenomenon known as “fluorescence structural self-quenching”\(^11\) whereby intra- or intermolecular excimer formation occurs. In this case, the alkene of the methacrylate group on monomer 1.3 is electron-accepting and will quench fluorescence from the quinoline portion of the monomer (excimer formation). However, the absence of alkene group in polymer
1.4 allows for emission from the chromophore without quenching. These polymers emitted at 424 nm in the solution state (DMF) and 432 nm in the solid state.

![Scheme 1.1. Synthesis of quinoline containing monomer 1.3 and polymer 1.4.](image)

The effect of quenching or enhancing the fluorescence of quinoline based polymers due to the presence of other molecules in the structure or in solution has been explored as a means of using these molecules in sensing applications. For example, quinoline-containing conjugated polymers 1.5, 1.6 and 1.7 were studied for their potential use in sensing Cu$^{2+}$ ions and amino acids.\textsuperscript{12} It was observed that when 1.6 was dissolved in THF it had a wavelength of maximum absorption ($\lambda_{\text{max}}$) of 410 nm, and a wavelength of maximum emission ($\lambda_{\text{em}}$) of 460 nm. This emission was quenched to 10% of its initial value when 1.6 μM concentrations of Cu$^{2+}$ were added. The same response was observed for 1.7, but the emission of 1.5 was not affected. This was attributed to the fact that functional groups on 1.5 do not have a specific affinity to Cu$^{2+}$ ions, and thus no quenching was observed. However, 1.6 contains an imidazole functional group and 1.7 contains an 8-hydroxyquinoline group which can chelate Cu$^{2+}$ and result in quenched emission. The emission of 1.6 was recovered by adding amino acid glycine (1.8); this was rationalized by the fact that glycine is a stronger chelate to Cu$^{2+}$ than the imidazole functional group on 1.6. Conversely, no change of the emission of 1.7 was observed upon addition of glycine because 8-hydroxyquinoline is a stronger chelate than glycine.
The Liu group synthesized copolymers 1.14 containing derivatives of quinoline, thiophene and benzothiazole and studied their potential use in metal ion sensing. The synthesis of these copolymers began by the addition of sulfonyl chloride to compound 1.9 in a NaOH/THF solution. This reaction afforded compound 1.10 in 70% yield, which was then reacted with 8-hydroxyquinoline in a K₂CO₃/DMF solution to afford 1.11 in 66% yield (Scheme 1.2). Monomer 1.12 was then synthesized by reacting 1.11 with bis(pinacolato)diboron, Pd(dppf)Cl₂ and Na₂CO₃ in DMSO for 12 h at 100 °C. Suzuki coupling was then employed as a means to synthesize polymer 1.14. First, monomer 1.12 and monomer 1.13 were dissolved in a solution of Na₂CO₃/toluene and then catalyst Pd(PPh₃)₄ was added. The reaction proceeded for 48 h at 110 °C and the polymer was isolated in 65% yield. Spectroscopic studies for the polymer revealed that it had a λ_max at 490 nm, and a λ_em at 610 nm (in DMSO), although its emission was rather weak. However, a 12 fold enhancement of the emission was observed when a 5.0 x 10⁻⁵ M Hg(II) ion solution was added, along with a 10 nm blue shift in the λ_max. Therefore, polymers 1.14 are effective as sensors for Hg(II) ions.

Water-soluble copolymers containing quinoline units (e.g., 1.17) have also been synthesized and studied for their pH tunable fluorescence response. These polymers were made by free radical copolymerization of \( N,N \)-dimethylacrylamide (1.15) and quinoline containing monomer 1.16 using AIBN as the free radical initiator (Scheme 1.3). The resulting polymers contained approximately 3.5 mol % of quinoline units; this was done to avoid excimer formation between quinoline units which would result in the quenching of their emission. The polymers’ \( \lambda_{em} \) was observed to shift from 411 nm to 484 nm as the pH of the solution decreased, and its emission intensity changed linearly. This shift in \( \lambda_{em} \) was attributed to the protonation of the quinoline group in the polymer. A second copolymer containing an anionic backbone and quinoline units was synthesized (1.18). It was found that this polymer was more readily protonated than neutral polymer 1.17, due to the electrostatic attraction between the protonated quinoline unit and the negatively charged chain. This phenomenon was demonstrated by looking at the fluorescence quantum yields (\( \Phi_F \)) at 411 nm (free quinoline) and 485 nm (protonated quinoline). For polymer 1.17, the \( \Phi_F \) at pH 7 and pH 2 were 85% and 38%, respectively. Conversely, the \( \Phi_F \) for polymer 1.18 at pH 7 and pH 2 were 84% and 55%, respectively. This difference in \( \Phi_F \) at 485 nm was attributed to the shift in equilibrium for the protonation of quinoline whereby polymer 1.18 was more easily protonated due to electrostatic
interactions of the protonated quinoline group with the polymer backbone. These properties highlight the use of these polymers as pH indicators.

**Scheme 1.3.** Free radical copolymerization of 1.15 and 1.16 for the synthesis of 1.17.

1.2 Polymers Containing Naphthalene and Anthracene Derivatives

Naphthalenes have been incorporated into various types of polymers due to their interesting spectroscopic properties. For example, the Zhu group synthesized linear and cyclic side-chain phenylazo naphthalene polymers and studied their photoisomerization as well as their fluorescence. Synthesis of these polymers began by the addition of the diazonium salt of 4-methoxy aniline to a solution of 1-naphthol (1.19) in NaHCO₃ and NaOH to afford 1.20 which contains both a naphthalene group and an azo-benzene group (Scheme 1.4). This molecule was then reacted with 6-bromohexanol in a DMF solution containing K₂CO₃ and catalytic amounts of KI to obtain 1.21. A polymerizable group (methyl methacrylate) was then attached
to 1.21 by adding methacryloyl chloride into a solution of 1.21 and Et₃N in THF; this resulted in the synthesis of monomer 1.22. This monomer was polymerized by using ATRP where propargyl-2-bromoisobutyrate (PBB) was the initiator, and CuBr (with PMDETA as the ligand) was the catalyst. Post-polymerization functionalization of linear polymer 1.23 was then used to attach an azide group at the chain end (1.24). CuAAC was employed in order to convert linear polymer 1.24 into cyclic polymer 1.25. Both linear and cyclic polymer 1.23 and 1.25 have azo-benzene groups as part of their side-chain and thus these polymers could undergo photoisomerization. Studies of the rate of photoisomerization of the azobenzene unit from trans to cis revealed that cyclic polymers 1.25 had a faster rate of conversion from trans to cis than that of the linear polymers 1.23. This was attributed to the fact that there is less resistance upon conversion due to minimal entanglement in the cyclic polymers vs. the linear polymers. The naphthalene unit is also found in the side-chain of both the linear (1.23) and cyclic (1.25) polymers and thus the fluorescence of these polymers was investigated. It was found that the linear polymers exhibited weak fluorescence at 430 nm, but cyclic polymers showed an enhancement in fluorescence intensity, which was more obvious when looking at polymers with lower weight average molecular weights (Mₘ). Although this phenomenon is not completely understood, it was suggested that there is more rigidity in the cyclic polymers vs. the linear ones, reducing both aggregation-caused self-quenching in solution, and vibrational non-radiative relaxation pathways.
Copolymers containing naphthalene and a second fluorescent molecule known as oxadizole, were synthesized by the Bruma group. Polycondensation was used to synthesize these polymers from monomers 1.29 and 1.30. Synthesis of monomer 1.28 began by stirring 5-amino-naphthol 1.26 with fluorophenyl-oxadiazole derivative 1.27 in K₂CO₃ and 1-methyl-2-pyrrolidinone (NMP) for 40 h at 180 °C. Polymers 1.31 and 1.32 were prepared through low temperature (−10 °C) polycondensation reaction of monomer 1.28 with diacid chloride monomer 1.29 or 1.30 in NMP and pyridine. After 15 min of stirring, the reaction was warmed to room temperature and stirred for an addition 6 h. Polymer films were made by drop casting solutions (in NMP) of these polymers into glass plates. The spectroscopic properties of the polymers in solution and in the solid state were investigated. It was found that in solution, both polymers absorbed in the UV-vis region at a \( \lambda_{\text{max}} \) of 312 nm, however, as films, these absorptions red-shifted to 343–350 nm. This shift in absorbance was attributed to an increase in intermolecular interactions of the bulk polymer, leading to differences in the conformational state of the polymer in the solid state vs. in solution. The polymers were also emissive in solution and in the solid state. In solution, \( \lambda_{\text{em}} \) was at 420 nm and in the solid state (films) emission occurred at 413–420 nm and at 445–465 nm. The first peak was concluded to arise from the phenyl-oxadiazole portion of the polymers, whereas the second was due to the naphthalene-containing portion of the polymers. Polymer 1.31 also gave rise to an emission
shoulder at 433 nm and polymer 1.32 had an emission shoulder at 498 nm; these emissions were due to aggregation and excimer formation which led to a red-shift in the emission as well as quenching. It is noteworthy that the emission of these polymers in the solid state were blue-shifted from that in the solution phase. This led to the conclusion that there was no extended π-conjugation in the polymers in the solid state, but rather there is organization of the chains that causes their emission to shift. This makes these polymers excellent candidates for blue light-emitting devices.

Scheme 1.5. Synthesis of monomer 1.28 and polymers 1.31 and 1.32.

Anthracenes (1.33) are another class of aromatic molecules that have found use as functional materials in organic light-emitting diodes (OLEDs), transistors and photovoltaic cells; they are fluorescent and have been incorporated into semiconducting polymers. The Majdoub group synthesized two anthracene containing copolymers (1.39 and 1.41) whose properties differed greatly as a result of the nature of the comonomer. Synthesis of polymer 1.39 began by the direct bischloromethylation of anthracene (1.33) with paraformaldehyde ((H₂CO)n) and HCl in acetic acid (AcOH) to afford 1.34. The next step was the synthesis of comonomer 1.35 which was carried out by reacting 1.34 with PPh₃ in toluene (Scheme 1.6). Dialdehyde 1.37 was then synthesized by reacting vanillin (1.36) with K₂CO₃ in DMF and adding dibromodecane dropwise (Scheme 1.7). Once the monomers had been prepared, polymers 1.39 and 1.41 were synthesized by using Wittig polycondensation whereby monomer
1.37 or 1.39 were stirred with 1.35 in THF and 0.5 M t-BuOK solution was added (Scheme 1.8 and 1.9). UV-vis absorption spectra for both polymers revealed three maxima in solution; these maxima were consistent with UV-vis absorptions of anthracene molecules.\(^{27}\) Polymers 1.39 had a \(\lambda_{\text{max}}\) at 365, 385, and 408 nm, while polymers 1.41 had a \(\lambda_{\text{max}}\) at 357, 383, and 406 nm, pertaining to \(\pi \rightarrow \pi^*\) electronic transitions in the anthracene group. Both polymers were fluorescent in solution, 1.39 had \(\lambda_{\text{em}}\) at 410, 432, and 458 nm (\(\Phi_F = 37\%\)), whereas polymer 1.41 had \(\lambda_{\text{em}}\) at 420 and 443 nm (\(\Phi_F = 72\%\)). The difference in \(\Phi_F\) between the two polymers was attributed to the fact that in polymer 1.41 the isosorbide groups (functional group on comonomer 1.40) increased the rigidity of the polymer, which in turn decreased the vibrational and rotational degrees of freedom of the chain, making vibrational relaxation less likely, and relaxation through emission more likely. Films of both polymers were also made and their \(\lambda_{\text{em}}\) were found to be at 570 nm and 562 nm for 1.39 and 1.41, respectively. The shift of the \(\lambda_{\text{em}}\) in the solid state versus that in solution was due to \(\pi \rightarrow \pi\) interactions of the conjugated fluorophores which lead to excimer formation.\(^{28}\)

**Scheme 1.6.** Synthesis of monomer 1.35.

**Scheme 1.7.** Synthesis of monomer 1.37.
1.3 Polymers Containing Fluorene Derivatives

Polyfluorenes are a class of conjugated fluorescent polymers that benefit from high Φ_F, and impressive thermal and chemical stability.\textsuperscript{29-31} Polyfluorenes containing phosphonate groups in the side-chain (e.g., 1.47 and 1.48) have been synthesized and their use as chemosensors has been explored.\textsuperscript{32} Synthesis of these polymers began by reacting 2,7-dibromofluorene (1.42) with 1,3-dibromopropane (Br(CH\textsubscript{2})\textsubscript{3}Br) or 1,6-dibromohexane (Br(CH\textsubscript{2})\textsubscript{6}Br) in an aqueous solution containing NaOH to afford 1.43 and 1.44. These molecules were then refluxed in the presence of P(C\textsubscript{2}H\textsubscript{5})\textsubscript{3} to obtain monomers 1.45 and 1.46. Polymerization was then performed by Yamamoto polycondensation where monomers were reacted with nickle (0) catalyst (Scheme 1.10). The spectroscopic properties of these polymers were investigated, and it was found that their absorption depends on the solvent being used. For example, 1.47 has λ\textsubscript{max} at 382 nm in CHCl\textsubscript{3}, but 338 nm in EtOH, and 1.48 has an λ\textsubscript{max} at 392 nm in CHCl\textsubscript{3} and 401 nm.
in EtOH. The emission spectra were also solvent dependent. Polymers 1.47 and 1.48 emit at 418 nm in CHCl₃ and 422 nm in EtOH. The Φᵢ for both polymers in EtOH was found to be 74%, suggesting that there is no aggregation in solution since little to no quenching was observed. Furthermore, the sensing properties of these polymers to metal ions was investigated. This was done by adding various metal ions (Li⁺, Na⁺, K²⁺, Mg²⁺, Ca²⁺, Cd²⁺, Zn²⁺, Fe³⁺) to a solution of polymers 1.47 or 1.48 in CHCl₃. No significant changes to the emission of these solutions was observed for any of the ions, except for when Fe³⁺ was added. Addition of Fe³⁺ resulted in dramatic quenching of the emission intensity by 210 fold for 1.47 and 130 fold for 1.48. These results demonstrate the efficacy of these polymer as sensitive and selective chemosensors of Fe³⁺.

Scheme 1.10. Synthesis of polymers 1.47 and 1.48.

Imidazole-functionalized polyfluorenes 1.51 have also been synthesized and investigated for their use as chemosensors. The design of these polymers was based on the fact that the imidazole has been demonstrated to have ion coordinating abilities to various ions, and the fluorene portion would have strong luminescence properties. Synthesis of this copolymer began by reacting 1.44 with imidazole in THF and NaH using TBAI. This resulted in the synthesis of monomer 1.49, which was then copolymerized with 1.50 using Suzuki coupling.
polymerization (Pd(PPh$_3$)$_4$ as the catalyst) to obtain polymer 1.51. This polymer was shown to absorb in the UV-vis region, specifically having a $\lambda_{\text{max}}$ at 390 nm. It was also emissive, with a $\lambda_{\text{em}}$ at 404 nm, and a shoulder at 425 nm. Their use as chemosensors was explored by adding various metals (e.g., Fe$^{2+}$, Ni$^{2+}$, Cd$^{2+}$, Mn$^{2+}$, Al$^{3+}$) to polymer solutions in THF; however, no change in the absorbance of the polymers or their emission was detected. Nevertheless, when Cu$^{2+}$ was added, a blue-shift in the $\lambda_{\text{max}}$ of the polymer solution was detected ($\Delta\lambda = 7$ nm); this was due to the change in the electronic structure of the backbone upon metal binding. The emission properties of the polymers were affected more dramatically, whereby addition of 1–2 ppm Cu$^{2+}$ solutions completely quenched the fluorescence. Films of these polymers were made, and placed into an aqueous solution of CuCl$_2$ where the same blue-shift in the $\lambda_{\text{max}}$, and quenching of the fluorescence was observed. Furthermore, when the films were placed into an ammonia solution, the fluorescence was rejuvenated. These properties showed the potential use of these polymers for applications as fluorescent chemosensors.

Scheme 1.11. Synthesis of polymer 1.51.

Polymers containing derivatives of fluorene (1.52, 1.53), benzothiadiazole (1.54) and bisthiophenylbenzothiadiazole (1.55) have also been synthesized, and their use as white-light-emitting polymers has been demonstrated.$^{35}$ These polymers (1.57) were made by using Suzuki polycondensation of monomers containing oxidiazole (1.52), triphenylamine (1.53), 4,7-dibromo2,1,3-benzothiadiazole (1.54), 4,7-bis(5-bromothiophen-2-yl)-2,1,3benzothiaadiazole
(1.55), and the diborane (1.56), where Pd(PPh₃)₄ was used as the catalyst, and aliquat 336 was used as the phase-transfer reagent as this polymerization took place in a mixture of toluene and aqueous K₂CO₃ (2M) solution (Scheme 1.52). These polymers possessed $D$ of 2.0, typical for condensation polymerizations, and $\lambda_{\text{max}}$ at around 300 and 380 nm in CHCl₃. Emission spectra collected for these polymers in CHCl₃ showed two $\lambda_{\text{em}}$ at approximately 430 and 460 nm. Thin film fabricated devices of these polymers were also made, and emission from these films ranged from 400–700 nm, having $\lambda_{\text{em}}$ peaks at 430, 460, 518, and 602 nm (each pertaining to one of the chromophores in the polymer). The combination of these specific emission wavelengths led to the devices emitting white light when an electric field was applied. Furthermore, the different emissions from this polymer was concluded to be due to partial energy transfer from the blue-fluorescent polyfluorene backbone to the other chromophores. Controlling the contribution of light from each chromophores (by controlling the number of chromophores within the polymer) led to the emission of white light.

1.4 Boron Containing Fluorophores and Polymers

BF$_2$ complexes of chelating $N,N$- and $N,O$- ligands have received a lot of interest and have been extensively researched due to their unique properties, which include: large absorption coefficients, high $\Phi_F$, redox activity, and excellent stability. These compounds have found use as photosensitizers, fluorescent imaging agents, OLEDs, and as the functional component of sensors.$^{36-42}$

The ability to synthesize asymmetric BF$_2$ complexes has allowed for versatility in their applications as well as in their properties. For example, the Aprahamian group was able to synthesize $N,N$-chelated asymmetric BF$_2$ molecules containing an azo group (e.g., 1.58) by reacting BF$_3$·OEt$_2$ boron trifluoride etherate with the corresponding hydrazone at room temperature.$^{43}$ Isomerization of this molecule from its trans (1.58) to cis (1.59) confirmation was induced by visible light (570 nm) (Scheme 1.13), and their photoisomerization properties could be studied using UV/vis spectroscopy thanks to their very distinct $\lambda_{\text{max}}$ at 530 nm and 480 nm, respectively. Furthermore, they were able to obtain a red-shift in the activation wavelength of these complexes by the addition of an electron donating group in the $R^1$ position such as a methoxy or dimethyl amine group.$^{44}$ The activation wavelength of these complexes was shifted to the near-IR region of the spectrum (630 nm and 710 nm, respectively).

![Scheme 1.13. Isomerization of trans-1.57 to cis-1.58 using visible light.](image)

Besides being able to introduce interesting functional groups to BF$_2$ complexes, asymmetric synthesis can also be used as a means to create rigid BF$_2$ complexes so that fluorescence in the solid state can be obtained. For example, phenanthro[9,10-$d$]imidazole-quinoline BF$_2$ 1.59 was synthesized in hopes of obtaining solid-state fluorescence.$^{45}$ This approach was taken due to the fact that phenanthro[9,10-$d$]imidazole-quinoline dyes display large Stokes’ shifts, which
aid in minimizing reabsorption and self-quenching in the solid state.\textsuperscript{46} They found that compound 1.59 had strong absorbance in solution at 476 nm, and bright luminescence at 585 nm in solution with a $\Phi_F$ of 90\% and also possessed emission in the solid state at 622 nm with a $\Phi_F$ of 18\%.

![Chemical structure of 1.59](image1.png)

Emission in the solid state can also be realized by synthesizing molecules that undergo aggregation-induced emission (AIE), which is a phenomenon whereby the structure of the molecule becomes restricted in the solid state, thereby enhancing the emission of the chromophores.\textsuperscript{47} For example, BF$_2$ complexes of quinoxaline-$\beta$-ketoiminates (e.g., 1.60 and 1.61) have strong absorption and emission properties in solution.\textsuperscript{48} However, in the solid state, 1.60 was essentially non-emissive ($\Phi_F = 2\%$) whereas 1.61 had a solid-state $\Phi_F$ of 22\%. The difference in their behaviour was attributed to the phenyl group introduced at the R$^1$ position in 1.61. This phenyl group was observed to be twisted in the solid-state structure, which in turn increased the $\pi$-$\pi$ distance between adjacent molecules, decreased $\pi$-$\pi$ stacking, and resulted in the impediment of intermolecular quenching, allowing the molecule to fluoresce in the solid state.

![Chemical structures of 1.60 and 1.61](image2.png)

Another class of BF$_2$ dyes that have been extensively studied are those of chelating dipyrromethene ligands (e.g., 1.62).\textsuperscript{49} These molecules, known as boron dipyrromethenes (BODIPYs), benefit from tunable optical and chemical properties as well as high $\Phi_F$. Recently, the first example of zwitterionic BODIPYs was described (1.63 and 1.64).\textsuperscript{50} These asymmetric BODIPYs possessed large Stokes’ shifts, intense emission, and were water soluble. Their absorption bands (in MeOH) were quite broad and ranged from 390–405 nm for compound
1.63 and 414–434 nm for compound 1.64. Moreover, they displayed λ_{em} in EtOH at 461 nm with a Φ_{F} of 95% for 1.63, and 506 nm with a Φ_{F} of 68% for 1.64. Thanks to their solubility in water, their use as live cell imaging agents was demonstrated by subjecting both dyes to yeast cells and observing the specific staining of the cells in the granules of the yeast.

The Liu group synthesized copolymers of BODIPYs and fluorenes in order to take advantage of their interesting properties. The idea was to make three separate copolymers bearing fluorene units and BODIPY units; these copolymers would differ based on the BODIPY derivative used. Different functional groups on the BODIPYs would tune their spectroscopic properties, and thus the polymers would benefit from these differences. Synthesis began by the iodization of BODIPYs 1.65, 1.66, 1.67 by dissolving each BODIPY in an EtOH/water solution containing I\(_2\) and HIO\(_3\), stirred at 60 °C for 30 min. This yielded monomers 1.68, 1.69, 1.70 which were then copolymerized with fluorene 1.71 using palladium-catalyzed Suzuki polymerization to yield polymers 1.72, 1.73, 1.74 where both fluorenes and BODIPYs are found in the main chain. The spectroscopic properties of molecules 1.65, 1.66, 1.67 were studied, and it was found that they all had λ_{max} in CHCl\(_3\) at approximately 500 nm, and emission at approximately 510 nm, with Φ_{F} ranging from 72% for compound 1.65 to 87% for compound 1.67. Once iodine was installed, all compounds experienced a red-shift in the absorbance and emission spectra by 33–38 nm. The Φ_{F} decreased, now ranging from 6% for compound 1.69 to 9% for compound 1.70; this was attributed to quenching by the heavy atom effect. Once the monomers were copolymerized with fluorene, their absorbance and emission spectra were further red-shifted by 14–22 nm for the absorbance spectra, and 37–39 nm for the emission spectra. The Φ_{F} also increased, ranging from 56% for 1.73 to 85% for 1.74. This red-shift in the λ_{max} and λ_{em} for polymers 1.72, 1.73, 1.74 was attributed to the extended π-conjugation in the polymers. It was also observed that emission from the fluorene moiety in the backbone was no longer observed once it had been incorporated into the polymers; this was
due to efficient photoinduced energy transfer from the fluorene moiety to the BODIPY moiety. Fluorescence quenching was observed for all polymers when titrated with fluoride or cyanide ions; this demonstrated their potential use in chemical and biological sensing applications.

Scheme 1.14. Synthesis of monomers 1.68–1.70 and polymers 1.72–1.74.

The Jäkle group incorporated boron-containing molecules 1.76 into polymers 1.77 and block copolymers 1.79 in order to study their potential metal complexation properties. Molecule 1.76 was chosen since this polydentate ligand has been previously studied for its potential metal complexation properties with various metals (e.g., Mg$^{2+}$, Fe$^{2+}$, Mn$^{2+}$).$^{52-54}$ Synthesis of these polymers was achieved using ring-opening metathesis polymerization (ROMP) of the pendant norbornene group found in monomer 1.76 and the pendant oxabicycloheptene group on 1.78. Monomer 1.77 was dissolved in CHCl$_3$ and the 3-bromo pyridine derivative of Grubbs’ third generation catalyst (GIII, 1.75) was added and the reaction was stirred for 1 h, yielding homo polymer 1.77. Block copolymer 1.79 was synthesized by dissolving monomer 1.78 in CHCl$_3$, adding GIII (1.75) and stirring for 1 h; then 1.77 was added and the reaction mixture was stirred...
for an additional 4 h. The polymerization for both polymers was terminated using ethyl vinyl ether. Homopolymer 1.77 had $D$ of 1.29, while block copolymer 1.79 had $D$ of 1.16, which are within the range of living / step-growth polymerizations.\textsuperscript{55} Monomer 1.76 was tested for its metal ion complexation properties. This was done by treating 1.76 with Cu(ClO$_4$)$_2$·6H$_2$O or FeCl$_2$, in the presence of Et$_3$N. Once complexation was done, the UV-vis absorption spectra of the complexes were studied in CH$_2$Cl$_2$ and it was found that for the Fe$^{2+}$ complexes, $\lambda_{\text{max}}$ were found at 425 and 480 nm, whereas for complexes with Cu$^{2+}$, the $\lambda_{\text{max}}$ was at 600 nm. Successful complexation of metals to the polydentate ligands led the group to test whether or not aggregates of block copolymers 1.79 would also form complexes with these metal ions which would lead to crosslinking of the polymers. First, aggregates of the blocks were made by taking advantage of their amphiphilic properties, where the borate containing block is soluble in EtOH, but the oxabicyclo dicarboxylate portion is not. Thus, a solution of these polymers in DMF was placed in a dialysis tube and allowed to stir in EtOH for 3 h; dynamic light scattering (DLS) of this solution concluded that the block copolymers had formed aggregates in solution. FeCl$_2$ was then added to the aggregate solution followed by addition of Et$_3$N. It was observed that a red precipitate began to form over time. Energy-dispersive X-ray (EDX) spectroscopy measurements proved that Fe(II) had successfully complexed with the aggregate molecules, and thus caused the polymers to crosslink and precipitate out of solution. Furthermore, metal exchange reactions could also be achieved by first complexing homo polymer 1.77 with Cu(ClO$_4$)$_2$·6H$_2$O in EtOH, yielding a green precipitate, and then adding FeCl$_2$. Over a span of 2 days the colour of the precipitate began to change to beige; and EDX showed successful metal ion exchange. The complexation of these metal ions resulted in metal-rich cross-linked polymer networks.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{1.75}
\caption{Structure of 1.75}
\end{figure}
Scheme 1.15. ROMP of monomer 1.76 to yield homopolymer 1.77.

Scheme 1.16. ROMP of monomer 1.78 and monomer 1.76 to yield block copolymer 1.79.

1.5 Scope of Thesis

This thesis will focus on the synthesis of various novel asymmetric and symmetric 3-cyanoformazanate BF$_2$ complexes and the incorporation of these molecules into homo, block, and random copolymers by the use of ROMP. The interest in these studies lies in the observation that BF$_2$ formazanate complexes have low energy absorption/emission, which is advantageous in various applications such as cell imaging, as well as the fact that polymers are easier to solution process which is important in applications that would require formation of films, such as in OLEDs. These complexes also have similar properties to that of the widely researched BODIPYs, yet their synthesis is easier and yields of these complexes are much higher making them cost effective. Thus, my goal was to make fluorescent BF$_2$ cyanoformazanate containing polymers that can be used as cell imaging agents, as functional thin films, and to track block copolymer self-assembly.
Chapter 2 will focus on the synthesis of an asymmetric 3-cyanoformazan along with its corresponding BF$_2$ complex. Synthesis of other 3-cyanoformazanate BF$_2$ complexes will also be outlined, and a detailed comparison of their spectroscopic and electrochemical properties described. Furthermore, X-ray crystallographic studies of two specific BF$_2$ complexes will also be discussed.

Chapter 3 will outline the use of ROMP in order to synthesize various polymers that contain 3-cyanoformazanate BF$_2$ complexes. Block and random copolymer synthesis for these 3-cyanoformazanate BF$_2$ complexes with a second organic monomer will also be described. Spectroscopic, thermal and electrochemical properties of the polymers will be studied in detail.

Chapter 4 will summarize the work in this thesis as well as describe future work involving the synthesis of new BF$_2$ containing block copolymers that can self-assemble into fluorescent micelles.

1.6 References


Chapter 2

2 Asymmetric 3-Cyanoformazanate BF$_2$ Complexes

2.1 Introduction

Extensive research has been done on BF$_2$ containing complexes due to their interesting properties which include high molar extinction coefficients, high emission quantum yields, and redox activity.$^{1-3}$ One specific family of BF$_2$ molecules that has garnered a lot of attention are BODIPYs (2.1).$^4$ Although BODIPYs possess a lot of the interesting properties described, they generally suffer from small Stokes’ shifts which results in low $\Phi_F$ in concentrated solutions and in the solid state due to self-quenching. One way to increase the Stokes’ shifts, is to break the pseudo-$C_2$-symmetry often found in symmetrical BODIPYs. Breaking the symmetry allows for a large distribution of charge upon excitation of the molecule thereby making the ground and excited states more energetically different and thus increasing Stokes’ shifts.$^5$ In an attempt to address this issue, boron complexes of iminopyrrolide ligands (BOIMPYs) were synthesized (e.g., 2.2) as an asymmetric mimic to BODIPYs.$^6$ BOIMPYs retained the interesting spectroscopic properties found in BODIPYs, such as high absorption coefficients and fluorescence, but possessed higher Stokes’ shifts. It was also found that the de-excitation mechanism for these complexes relied on the substituents attached on the para position of Ar. For example, addition of a dimethylamino substituent in the para position (2.4) allowed the molecule to possess quinoid type resonance (2.5) that promoted charge separated character resulting in large Stokes’ shifts (192 nm) and also solvatochromism (Scheme 2.1). Solvatochromism supported the idea that by obtaining such charge separated character, this complex had begun to develop charge transfer character. Conversely, having a tert-buty group in the para position (2.3) also resulted in large Stokes’ shifts (105 nm), but its emission was not solvent dependent, and thus relaxation most likely occurred from locally excited states and charge transfer.

![Diagram](2.1)
Another class of BF$_2$ dyes that has shown potential as alternatives to BODIPYs are those of chelating nitrogen ligands from a formazanate backbone (2.6‒2.8). These BF$_2$ complexes exhibit tunable absorption, emission and electrochemical properties, as well as good $\Phi_F$ and high yielding syntheses.$^7,8$ Triaryl BF$_2$ formazanate complexes (2.7) possess the largest Stokes’ shifts (>100 nm) out of the three. Breaking the symmetry in these BF$_2$ complexes (e.g., 2.9) has been shown to improve their $\Phi_F$ due to the push-pull electronics of the varying substituents in the Ar$^1$ and Ar$^5$ positions. Conversely, BF$_2$ complexes of 3-cyanoformazans (2.6) possess the highest $\Phi_F$ in comparison to those with phenyl or nitro groups at the R$^3$ position (2.7, 2.8).$^8$ These properties paved the way to pursue asymmetric 3-cyanoformazans, where the corresponding BF$_2$ complexes would benefit from an increase in emission intensity due to a combination of the presence of a cyano group in the R$^3$ position, and asymmetry. Moreover, synthesis of an asymmetric BF$_2$ complex would allow for functionalization of one of the N-aryl substituents with a polymerizable group. This would make it possible to synthesize polymers bearing BF$_2$ formazanate units appended to the polymer backbone.
This chapter describes the synthesis and characterization of various asymmetrically substituted BF$_2$ formazanate complexes. It also outlines the synthesis of the first reported asymmetric 3-cyanoformazan and its corresponding BF$_2$ complex. The use of CuAAC chemistry as a means of attaching a polymerizable group to one of the N-aryl substituents in the corresponding BF$_2$ complex is also described. The effect on the spectroscopic and electrochemical properties upon adding a triazole ring or coupling an alkyne group to one of the N-aryl substituents in the formazanate backbone was also investigated.

2.2 Results and Discussion

2.2.1 Synthesis of Asymmetric 3-Cyanoformazans

Two different methods were used in order to synthesize asymmetric 3-cyanoformazans (Scheme 2.2 and 2.3).\textsuperscript{9,10} Both of these methods were unsuccessful as yields and purification of the target formazans were low (Table 1). During optimization of both methods, it was observed that when the diazoniums of p-anisidine and p-toluidine were used in order to make either the hydrazone or the asymmetric formazan, a scrambling of aryl groups occurred where the symmetric formazans of the diazoniums used were observed along with the asymmetric formazan intended.

![Scheme 2.2. Stolarski synthesis of asymmetric 3-cyanoformazans.\textsuperscript{9}](image)

![Scheme 2.3. Elnagdi synthesis for asymmetric 3-cyanoformazans.\textsuperscript{10}](image)
Table 2.1. Experimental yields for asymmetric syntheses.

<table>
<thead>
<tr>
<th>Route</th>
<th>R&lt;sup&gt;1&lt;/sup&gt;</th>
<th>R&lt;sup&gt;2&lt;/sup&gt;</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stolarski</td>
<td>H</td>
<td>Br</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>OH</td>
<td>23*</td>
</tr>
<tr>
<td></td>
<td>Br</td>
<td>OCH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>65*</td>
</tr>
<tr>
<td>Elnagdi&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Br</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>9*</td>
</tr>
<tr>
<td></td>
<td>Cl</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>OCH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>26*</td>
</tr>
</tbody>
</table>

<sup>a</sup>Yield stated does not include the yield for the synthesis of enaminonitrile (37%).<sup>b</sup> Asterisk denotes crude yield (due to failed purification).

After this discovery, the need to find a route that involved fewer steps and produced asymmetric formazans in a higher yield was necessary. Therefore, a different method for obtaining asymmetric 3-cyanoformazan 2.12 was employed (Scheme 2.4), whereby the asymmetric formazan desired was separated from the two corresponding symmetric formazans via column chromatography. This route has been previously reported for the synthesis of symmetric 3-cyanoformazans,<sup>11</sup> and although its use for asymmetric formazans is not elegant, it involves only one step and produces the same yields as the time-consuming methods mentioned above.

Scheme 2.4. Synthesis of asymmetric 3-cyanoformazan 2.12.

2.2.2 Synthesis of BF<sub>2</sub> 3-Cyanoformazanate Complexes

Formazan 2.12 was dissolved in toluene and excess Et<sub>3</sub>N and BF<sub>3</sub>•OEt<sub>2</sub> were added under an inert atmosphere. The solution was stirred overnight at 80 °C (Scheme 2.5). After aqueous work-up and column chromatography, <sup>1</sup>H NMR spectroscopy revealed the disappearance of the characteristic NH peak of the formazan seen at 12.5 ppm upon insertion of the BF<sub>2</sub> moiety. The introduction of the BF<sub>2</sub> moiety was also verified by a distinctive 1:1:1:1 quartet and a 1:2:1 triplet in the <sup>19</sup>F NMR and <sup>11</sup>B NMR spectra, respectively.
In order to explore the possibility of using CuAAC chemistry to attach polymerizable groups to BF$_2$ complex 2.13, benzyl azide was used to test the reaction. Copper (I) coordinated by PMDETA was the catalyst of choice. Benzyl azide and BF$_2$ complex 2.13 were added to the catalyst solution in dry and degassed THF and stirred at 23 °C for 16 h (Scheme 2.6). $^1$H NMR spectroscopy (Figure 2.1) revealed the disappearance of the $\equiv$CH peak at 3.28 ppm (triangle) and the appearance of the $=$CH peak of the triazole ring at 7.76 ppm (circle). Further confirmation for the successful CuAAC reaction was evident when comparing the IR spectra of BF$_2$ complex 2.13 and benzyl-substituted BF$_2$ complex 2.14. The IR spectrum for BF$_2$ complex 2.13 reveals the $\equiv$CH stretch at 3282 cm$^{-1}$, while the IR spectrum of benzyl-substituted BF$_2$ complex 2.14 does not show the $\equiv$CH stretch or the strong R-N$_3$ stretch of an azide which usually appears around 2170–2180 cm$^{-1}$.$^{12}$ The unique 1:1:1:1 quartet in the $^{19}$F NMR spectrum and 1:2:1 triplet in the $^{11}$B NMR spectrum along with the persistent purple colour of the compound indicated the tolerance of the BF$_2$ moiety to the conditions for the CuAAC reaction. The synthesis of this compound also allowed for the study of the effects a triazole ring has on the spectroscopic and electrochemical properties of BF$_2$ complexes.

**Scheme 2.5.** Synthesis of asymmetric BF$_2$ formazanate complex 2.13.

**Scheme 2.6.** CuAAC reaction for the synthesis of benzyl-substituted BF$_2$ complex 2.14.
Figure 2.1. Overlay of $^1$H NMR spectra of compounds 2.13 (red) and 2.14 (black) in CDCl$_3$. The triangle represents the ≡CH proton and the circle represents =CH peak of the triazole ring.

In pursuit of side-chain BF$_2$ formazanate polymers, azide-substituted norbornene 2.16 was synthesized (Scheme 2.7). This compound contains a polymerizable norbornene suitable for ROMP, along with an azide group that could be useful for clicking onto BF$_2$ complex 2.13. Previously reported 3-azido-1-propanol 2.15$^{13}$ was added to a solution of 5-norbornene-endo-2-carboxylic acid, DCC, DMAP, and dry CH$_2$Cl$_2$ and stirred at 23 °C for 2 h. The reagent 5-norbornene-endo-2-carboxylic acid was separated from the endo/exo mixture purchased by reacting it with KI and I$_2$ in a basic solution, which resulted in the iodolactone formation of the endo isomer. The iodolactone was then isolated through an aqueous workup, and converted back to the endo isomer by stirring it in a solution of AcOH and zinc powder to afford pure 5-norbornene-endo-2-carboxylic acid.$^{14}$

$^1$H NMR spectroscopy revealed the success of the coupling reaction, and the alkene protons corresponding to the endo isomer were found at 6.22 ppm and 5.93 ppm. The IR spectrum verified the presence of the azide functionality due to the strong R-N$_3$ stretch at 2095 cm$^{-1}$. 
Scheme 2.7. DCC coupling for the synthesis of azide-substituted norbornene 2.16.

Azide-alkyne cycloaddition chemistry was then employed as a means of synthesizing a BF₂ containing monomer for future polymerization. Again, copper(I) coordinated by PMDETA was the catalyst of choice. BF₂ complex 2.13 was added to a solution of azide-substituted norbornene 2.16, copper catalyst, and dry and degassed THF and stirred at 23 °C for 2 h (Scheme 2.8). ¹H NMR spectroscopy revealed the disappearance of the ≡CH peak at 3.28 ppm and the appearance of the =CH peak of the triazole ring at 7.90 ppm. The IR spectrum of monomer 2.17 also verified the absence of ≡CH stretch at 3282 cm⁻¹ from BF₂ complex 2.13. ¹⁹F and ¹¹B NMR spectroscopy revealed the unique 1:1:1:1 quartet and 1:2:1 triplet respectively, again verifying the stability of the BF₂ moiety under the conditions employed.

Scheme 2.8. Synthesis of monomer 2.17 by CuAAC.

During optimization experiments for the synthesis of monomer 2.17, it was observed that when the reaction was left overnight, additional products formed. These products were isolated by column chromatography. One of the fractions was isolated in 7 % yield and was blue in colour. Its ¹⁹F NMR and ¹¹B NMR spectra revealed the presence of a BF₂ moiety. Crystals of this compound (2.18) suitable for X-ray diffraction studies were grown (see below), and it was discovered that the compound was a dimer of BF₂ complex 2.13. This structure was confirmed by ¹H NMR spectroscopy and mass spectrometry. Literature precedence confirmed that Cu(II) can catalyze the oxidative dimerization of alkynes,¹⁵⁻¹⁹ supporting the hypothesis that this side
product forms as a result of the gradual oxidation of Cu(I) in the reaction mixture to yield catalytic Cu(II).

![Chemical structure](image)

### 2.2.3 X-ray Crystallography

Single crystals of BF₂ complex 2.13 were grown by slow diffusion of hexanes into a saturated solution of BF₂ complex 2.13 in slow evaporating CH₂Cl₂. The crystal displayed disorder at the alkyne and methoxy substituents as a result of a two-fold rotation axis. The solid-state structure revealed the boron centre to be found in a distorted tetrahedral geometry when looking at angles (°): F1’–B1–F1 112.01(15), F1’–B1–N1 108.75(5), F1’–B1–N1’ 110.42(5), N1–B1–N1’ 106.34(13). Furthermore, the structure is relatively planar with a torsion angle of 7.2° between the N1–N2–C1–N2–N1 plane of the formazanate backbone, and the C3–C8 plane of the N-aryl substituents.

**Figure 2.2.** Solid-state structure of BF₂ complex 2.13 (top and side views). Hydrogen atoms have been omitted for clarity. Thermal displacement ellipsoids are shown at 50% probability.
Table 2.2. Selected bond lengths (Å) and angles (degrees) for 2.13 BF₂ complex.

<table>
<thead>
<tr>
<th>Bond/Distance</th>
<th>Length/Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1-F1</td>
<td>1.3732(14)</td>
</tr>
<tr>
<td>B1-N1</td>
<td>1.5759(15)</td>
</tr>
<tr>
<td>N1-N2</td>
<td>1.3023(15)</td>
</tr>
<tr>
<td>N2-C1</td>
<td>1.3351(13)</td>
</tr>
<tr>
<td>N3-C2</td>
<td>1.146(2)</td>
</tr>
<tr>
<td>C9'-C10'</td>
<td>1.191(7)</td>
</tr>
<tr>
<td>O1-C10</td>
<td>1.418(5)</td>
</tr>
<tr>
<td>N1-N2-C1</td>
<td>117.24(11)</td>
</tr>
<tr>
<td>N2-N1-C1-N2</td>
<td>130.03(16)</td>
</tr>
<tr>
<td>N2-C1-C2</td>
<td>114.99(8)</td>
</tr>
<tr>
<td>C10'-C9'-C6</td>
<td>174.8(6)</td>
</tr>
<tr>
<td>C10-O1-C6</td>
<td>112.7(3)</td>
</tr>
<tr>
<td>F1-B1-N1-N2</td>
<td>118.09(12)</td>
</tr>
<tr>
<td>N2-N1-C3-C8</td>
<td>6.26(16)</td>
</tr>
<tr>
<td>C7-C6-O1-C10</td>
<td>-1.3(5)</td>
</tr>
<tr>
<td>C5-C6-O1-C10</td>
<td>178.2(3)</td>
</tr>
</tbody>
</table>

Single crystals of dimer 2.18 were grown by slow evaporation of hexanes into a saturated solution of dimer 2.18 in benzene. The solid-state structure revealed the planar confirmation of this molecule with a torsion angle of 9.7° between the N1–N2–C1–N4–N3 plane of the formazanate backbone and the C10–C15 plane, and a torsion angle of 0.07° between the C10–C15 plane and the C10’–C15’ plane. The boron centre is also found in a distorted tetrahedron geometry when looking at angles (°): F1–B1–F2 112.59(11), F1–B1–N3 111.12(11), F2–B1–N1 109.58(10), N3–B1–N1 106.52(9). The delocalized nature of the formazanate backbone is apparent when looking at the bond lengths (Å): N1–N2 1.3007(14), N3–N4 1.3066(14), N2–C1 1.3409(16), and N4–C1 1.3354(14), since these bond lengths are in between those expected for single and double bonds of the same atoms. The torsion angle between the N1–N2–C1–N4–N3 plane of the formazanate backbone and the C3–C8 plane is 17.1°.
Figure 2.3. Solid-state structure of dimer 2.18 (top and side views). Hydrogen atoms have been omitted for clarity. Thermal displacement ellipsoids are shown at 50% probability.

Table 2.3. Selected bond lengths (Å) and angles (degrees) for 2.18 BF₂ complex.

<table>
<thead>
<tr>
<th>2.18</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>B1-F1</td>
<td>1.3671(17)</td>
</tr>
<tr>
<td>B1-F2</td>
<td>1.3736(15)</td>
</tr>
<tr>
<td>B1-N3</td>
<td>1.5648(18)</td>
</tr>
<tr>
<td>B1-N1</td>
<td>1.5793(16)</td>
</tr>
<tr>
<td>N5-C2</td>
<td>1.1453(16)</td>
</tr>
<tr>
<td>O1-C9</td>
<td>1.4344(15)</td>
</tr>
<tr>
<td>C16-C17</td>
<td>1.2063(16)</td>
</tr>
<tr>
<td>C17-C17₁</td>
<td>1.369(2)</td>
</tr>
<tr>
<td>N1-N2-C1</td>
<td>117.24(9)</td>
</tr>
<tr>
<td>N3-N4-C1</td>
<td>117.01(10)</td>
</tr>
<tr>
<td>N4-C1-N2</td>
<td>129.89(11)</td>
</tr>
<tr>
<td>N2-C1-C2</td>
<td>114.68(10)</td>
</tr>
<tr>
<td>C17-C16-C13</td>
<td>178.73(14)</td>
</tr>
<tr>
<td>C16-C17-C17₁</td>
<td>179.48(19)</td>
</tr>
<tr>
<td>N4-N3-C10-C15</td>
<td>5.74(16)</td>
</tr>
<tr>
<td>N2-N1-C3-C8</td>
<td>16.06(16)</td>
</tr>
<tr>
<td>C9-O1-C6-C5</td>
<td>-175.67(11)</td>
</tr>
</tbody>
</table>
2.2.4 Absorption/Emission Properties of BF$_2$ 3-Cyanofomazanate Complexes

The spectroscopic properties of the BF$_2$ formazanate complexes that were synthesized are summarized in Table 2.4. Figures 2.4a and 2.4b display the UV-vis absorption and emission spectra for selected compounds.

![Figure 2.4](image)

**Figure 2.4.** Normalized absorption (a) and emission (b) spectra for BF$_2$ complex 2.13 (black), benzyl-substituted BF$_2$ complex 2.14 (blue), monomer 2.17 (green), and dimer 2.18 (red) recorded in CH$_2$Cl$_2$.

![Figure 2.5](image)

**Figure 2.5.** Normalized absorption (solid line) and emission (dashed line) spectra for monomer 2.17 recorded in CH$_2$Cl$_2$. 
Table 2.4. Spectroscopic properties of BF$_2$ complex \textit{2.13}, benzyl-substituted BF$_2$ complex \textit{2.14}, monomer \textit{2.17}, and dimer \textit{2.18}.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon$ (M$^{-1}$ cm$^{-1}$)</th>
<th>$\lambda_{\text{em}}$ (nm)</th>
<th>$\Phi_F$ (%)$^a$</th>
<th>$\upsilon_{\text{ST}}$ (nm)</th>
<th>$\upsilon_{\text{ST}}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textit{2.13}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>552</td>
<td>30,400</td>
<td>647</td>
<td>30</td>
<td>95</td>
<td>2660</td>
</tr>
<tr>
<td>THF</td>
<td>550</td>
<td>32,500</td>
<td>650</td>
<td>27</td>
<td>100</td>
<td>2797</td>
</tr>
<tr>
<td>Toluene</td>
<td>569</td>
<td>26,800</td>
<td>647</td>
<td>36</td>
<td>78</td>
<td>2119</td>
</tr>
<tr>
<td>\textit{2.14}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>560</td>
<td>31,000</td>
<td>660</td>
<td>30</td>
<td>100</td>
<td>2706</td>
</tr>
<tr>
<td>THF</td>
<td>560</td>
<td>33,900</td>
<td>671</td>
<td>25</td>
<td>111</td>
<td>2954</td>
</tr>
<tr>
<td>Toluene</td>
<td>579</td>
<td>37,400</td>
<td>661</td>
<td>37</td>
<td>82</td>
<td>2143</td>
</tr>
<tr>
<td>\textit{2.17}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>561</td>
<td>35,300</td>
<td>663</td>
<td>29</td>
<td>102</td>
<td>2742</td>
</tr>
<tr>
<td>THF</td>
<td>560</td>
<td>23,100</td>
<td>668</td>
<td>20</td>
<td>108</td>
<td>2887</td>
</tr>
<tr>
<td>Toluene</td>
<td>578</td>
<td>30,100</td>
<td>661</td>
<td>33</td>
<td>83</td>
<td>2172</td>
</tr>
<tr>
<td>\textit{2.18}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>597</td>
<td>78,500</td>
<td>687</td>
<td>&lt;1</td>
<td>90</td>
<td>2194</td>
</tr>
<tr>
<td>THF</td>
<td>592</td>
<td>77,400</td>
<td>685</td>
<td>&lt;1</td>
<td>93</td>
<td>2293</td>
</tr>
<tr>
<td>Toluene</td>
<td>605</td>
<td>62,500</td>
<td>688</td>
<td>&lt;1</td>
<td>83</td>
<td>1994</td>
</tr>
</tbody>
</table>

$^a$Quantum yields were measured according to published protocol using ruthenium tris(bipyridine) hexafluorophosphate as a relative standard$^{21,22}$ and corrected for wavelength-dependent detector sensitivity (Figure A2.21). Due to error associated with the integration of the fluorescence spectra, we estimate that the quantum yields determined for dimer \textit{2.18} are less than 1%.

These results reveal that, upon introduction of a triazole ring, the maximum absorption ($\lambda_{\text{max}}$) and emission ($\lambda_{\text{em}}$) associated with the BF$_2$ formazanates red-shift by approximately 10 nm when comparing BF$_2$ complex \textit{2.13} with benzyl-substituted BF$_2$ complex \textit{2.14} and monomer \textit{2.17}. This is likely a result of extended electronic conjugation. Furthermore, the oxidative dimerization of alkynes to yield dimer \textit{2.18} also resulted in a red-shift of $\lambda_{\text{max}}$ and $\lambda_{\text{em}}$ by approximately 45 nm and 40 nm, respectively. A larger red-shift can be attributed to the planarity of the two chromophores with respect to one another which results in an extent of conjugation along both chromophores as opposed to just the triazole ring in the previous examples.

BF$_2$ complex \textit{2.13}, benzyl-substituted BF$_2$ complex \textit{2.14} and monomer \textit{2.17} all have moderate $\Phi_F$ (29–30% in CH$_2$Cl$_2$). It is worth noting that, upon introduction of a triazole ring, the quantum yields were not increased, which is opposite to a phenomenon often reported.$^{23}$ This can be rationalized by the fact that formation of a triazole ring causes the compound to no longer possess the push-pull electronics which has been shown to increase $\Phi_F$.$^8$ Dimer \textit{2.18} is essentially non-emissive, which can be attributed to possible intramolecular quenching due to the proximity of both chromophores. The Stokes’ shifts observed provide a range of values for these compounds that are within the range of typical Stokes’ shifts found in other BF$_2$ formazanate complexes.$^7$
2.2.5 Electrochemical Properties of BF₂

3-Cyanoformazanates Complexes

The redox properties of the BF₂ formazanate complexes that were synthesized were studied using cyclic voltammetry and are summarized in Table 2.5. Experiments were performed in CH₂Cl₂, and the cyclic voltammograms for all compounds are shown in Figure 2.6. BF₂ complex 2.13, benzyl-substituted BF₂ complex 2.14 and monomer 2.17 exhibited two reversible one-electron reduction waves (Scheme 2.9). Each BF₂ formazanate in dimer 2.18 can also be reversibly reduced twice. The first reduction event, centred at −0.65 mV, corresponds to the formation of a radical anion on one of the BF₂ formazanate units. This reduction wave overlapped a second one electron reduction for the remaining BF₂ formazanate unit in the dimer. The second reduction event, centred at −1.65 mV, was also comprised of two overlapping one-electron reduction waves. The observed behaviour is a demonstration of electronic communication between the BF₂ formazanates in dimer 2.18. No oxidation events were observed within the solvent window. It was observed that, when a triazole moiety was introduced, reduction of the molecule was made more difficult; this is due to the stronger electron donating effects of the triazole ring versus the alkyne. Furthermore, when comparing the potential required to reduce dimer 2.18, it was observed that it was easier to reduce than BF₂ complex 2.13 due to the increase in conjugation and the BF₂ complex-substituted alkyne’s electron withdrawing effects.

Scheme 2.9. Redox reactions of a BF₂ formazanate complex (2.19a) to afford a radical anion (2.19b) and dianion (2.19c).
Table 2.5. Electrochemical properties of BF$_2$ complex 2.13, benzyl-substituted BF$_2$ complex 2.14, monomer 2.17, and dimer 2.18.

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{red1}}$(V)</th>
<th>$E_{\text{red2}}$(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.13</td>
<td>-0.67</td>
<td>-1.69</td>
</tr>
<tr>
<td>2.14</td>
<td>-0.69</td>
<td>-1.73</td>
</tr>
<tr>
<td>2.17</td>
<td>-0.69</td>
<td>-1.75</td>
</tr>
<tr>
<td>2.18$^a$</td>
<td>-0.65</td>
<td>-1.65</td>
</tr>
</tbody>
</table>

$^a$Potentials reported as the mid-point of two consecutive one-electron reduction processes.

Figure 2.6. Cyclic voltammograms for BF$_2$ complex 2.13 (black), benzyl-substituted BF$_2$ complex 2.14 (blue), monomer 2.17 (green), and dimer 2.18 (red), were recorded at a scan rate of 250 mV s$^{-1}$ for 1 mM analyte solutions in CH$_2$Cl$_2$ containing 0.1 M [nBu$_4$N][PF$_6$] as the supporting electrolyte. All voltammograms were referenced internally against the ferrocene/ferrocenium redox couple.

2.3 Conclusion

Attempts to synthesize asymmetric 3-cyanoformazans using literature procedures was unsuccessful in giving high yields and pure formazans. Thus, a different method was employed that allowed for the synthesis of the first reported asymmetric 3-cyanoformazan 2.12, which was then converted to the corresponding BF$_2$ complex 2.13. CuAAC chemistry was used as a method for synthesizing various types of BF$_2$ complexes. All compounds showed strong $\lambda_{\text{max}}$ ranging from 552–597 nm in CH$_2$Cl$_2$ and $\lambda_{\text{em}}$ from 647–687 nm. The introduction of triazole rings was shown to red-shift the $\lambda_{\text{max}}$ and $\lambda_{\text{em}}$ by about 10 nm, and the oxidative coupling of alkynes caused a red-shift in the $\lambda_{\text{max}}$ and $\lambda_{\text{em}}$ by approximately 45 and 40 nm, respectively. All compounds were redox active, and had cyclic voltammograms comprised of two reversible
one-electron (2.13, 2.14 and 2.17) or two sets of overlapping reversible one-electron reduction waves (2.18). Introduction of a triazole ring made it more difficult to reduce the BF$_2$ formazanate due to its electron donating character, while alkyne coupling caused reduction to be easier due to the increase in conjugation and the BF$_2$ complex-substituted alkyne’s withdrawing effects. The next chapter will focus on the polymerization of monomer 2.17 by using ROMP of its pendant norbornene group.

2.4 Experimental

2.4.1 General Considerations

Reactions and manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques unless otherwise stated. Solvents were obtained from Caledon Laboratories, dried using an Innovative Technologies Inc. solvent purification system, collected under vacuum, and stored under a nitrogen atmosphere over 4 Å molecular sieves. Endo-5-norbornene-2-carboxylic acid was separated from the endo/exo mixture using a published procedure.$^{14}$ All other reagents were purchased from Sigma Aldrich, Alfa Aesar or TCI America and used as received.

NMR spectra were recorded on a 400 MHz ($^1$H: 399.8 MHz, $^{11}$B: 128.3 MHz, $^{19}$F: 376.1 MHz, $^{13}$C: 100.5 MHz), or a 600 MHz ($^{13}$C: 150.7 MHz) Varian INOVA instruments. $^1$H NMR spectra were referenced to residual CHCl$_3$ at 7.27 ppm and $^{13}$C{$^1$H} NMR spectra were referenced to CDCl$_3$ at 77.00 ppm. $^{11}$B NMR spectra were referenced internally to BF$_3$•OEt$_2$ at 0 ppm. $^{19}$F NMR spectra were referenced internally to CFCl$_3$ at 0 ppm. Mass spectrometry data were recorded in positive-ion mode using a high-resolution Finnigan MAT 8200 spectrometer using electron impact ionization. UV-vis absorption spectra were recorded using a Cary 5000 Scan instrument using standard quartz cells (1 cm path length) with a scan range of 200 to 800 nm. Four separate concentrations were run for each sample, and molar extinction coefficients were determined from the slope of a plot of absorbance against concentration. Emission spectra were recorded using a Photon Technology Internation QM–4 SE spectrofluorometer. Emission quantum yields were estimated relative to [Ru(bpy)$_3$][PF$_6$]$_2$ and corrected for wavelength dependent detector sensitivity (Figure A2.21).$^{21}$ FT-IR spectra were
recorded using a PerkinElmer Spectrum Two FT-IR spectrometer using an attenuated total reflectance (ATR) accessory.

2.4.2. X-ray Crystallography Methods

Single crystals for X-ray diffraction studies of BF₂ complex 2.13 and dimer 2.18 were grown by slow vapour diffusion of hexanes into a saturated solution of BF₂ complex 2.13 in CH₂Cl₂ and dimer 2.18 in benzene; these crystals were analyzed by Stephanie Barbon. The samples were mounted on a MiTeGen polyimide micromount with a small amount of Paratone N oil. All X-ray measurements were made on a Bruker Kappa Axis Apex2 diffractometer at a temperature of 110 K. The data collection strategy was a number of ω and φ scans which collected data over a range of angles, 2θ. The frame integration was performed using SAINT program. The resulting data was scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using SADABS. The structures were solved by dual space methodology using the SHELXT program. All non-hydrogen atoms were obtained from the initial solution. The hydrogen atoms were introduced at idealized positions and were allowed to refine isotropically for BF₂ complex 2.13, but for dimer 2.18 the hydrogen atoms were introduced at idealized positions and the positional parameters but not the displacement parameters were allowed to refine. The structural model was fit to the data using full matrix least-squares based on $F^2$. The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. The structure was refined using the SHELXL-2014 program from the SHELX suite of crystallographic software. Graphic plots were produced using the Mercury software. See Table 2.6 for crystallographic data.
Table 2.6. Crystallographic data for compounds 2.13 and 2.18.

<table>
<thead>
<tr>
<th></th>
<th>2.13</th>
<th>2.18</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C₁₁₂H₁₂BF₂N₅O</td>
<td>C₆₆H₃₂B₄F₄N₁₀O₂</td>
</tr>
<tr>
<td>Formula Weight (g/mol)</td>
<td>351.13</td>
<td>856.45</td>
</tr>
<tr>
<td>Crystal Dimensions (mm)</td>
<td>0.188 x 0.107 x 0.104</td>
<td>0.509 x 0.244 x 0.074</td>
</tr>
<tr>
<td>Crystal Color and Habit</td>
<td>purple prism</td>
<td>blue plate</td>
</tr>
<tr>
<td>Crystal System</td>
<td>monoclinic</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space Group</td>
<td>C 2/c</td>
<td>P ̅ 1</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>110</td>
<td>110</td>
</tr>
<tr>
<td>a (Å)</td>
<td>10.248(6)</td>
<td>6.917(2)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>14.634(7)</td>
<td>10.231(4)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>11.146(5)</td>
<td>15.408(9)</td>
</tr>
<tr>
<td>α (°)</td>
<td>90</td>
<td>101.670(11)</td>
</tr>
<tr>
<td>β (°)</td>
<td>107.352(18)</td>
<td>92.500(12)</td>
</tr>
<tr>
<td>γ(°)</td>
<td>90</td>
<td>107.13(2)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>1595.5(14)</td>
<td>1014.3(8)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>ρ (g/cm)</td>
<td>1.462</td>
<td>1.402</td>
</tr>
<tr>
<td>λ, Å, (Mo Kα)</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>μ, (cm⁻¹)</td>
<td>0.111</td>
<td>0.102</td>
</tr>
<tr>
<td>Diffractometer Type</td>
<td>Bruker Kappa Axis Apex2</td>
<td>Bruker Kappa Axis Apex2</td>
</tr>
<tr>
<td>Rmerge</td>
<td>0.0406</td>
<td>0.0425</td>
</tr>
<tr>
<td>aR₁[2σI &gt; 2]</td>
<td>0.0428</td>
<td>0.054</td>
</tr>
<tr>
<td>bwr₂[2σI &gt; 2]</td>
<td>0.0963</td>
<td>0.1153</td>
</tr>
<tr>
<td>R₁ (all data)</td>
<td>0.077</td>
<td>0.1232</td>
</tr>
<tr>
<td>wR₂ (all data)</td>
<td>0.1107</td>
<td>0.1399</td>
</tr>
<tr>
<td>GOF</td>
<td>1.038</td>
<td>1.013</td>
</tr>
</tbody>
</table>

*aR₁ = Σ(|Fₒ| - |Fₐ|) / Σ|Fₒ|

*bwr₂ = [ Σ( w( Fₐ² - Fₖ²)² ) / Σ( w Fₐ⁴ ) ]^½

GOF = [ Σ( w( Fₐ² - Fₖ²)² ) / (No. of reflns. - No. of params.) ]^½

2.4.3 Electrochemical Methods

Cyclic voltammetry experiments were performed with a Bioanalytical Systems Inc. (BASi) Epsilon potentiostat and analyzed using BASi Epsilon software. Typical electrochemical cells consisted of a three-electrode setup including a glassy carbon working electrode, platinum counter electrode, and silver pseudo reference electrode. Experiments were run at 250 mV s⁻¹ in degassed CH₂Cl₂ solutions of the analyte (~1 mM) and electrolyte (0.1 M [nBu₄N][PF₆]). Cyclic voltammograms were internally referenced against the ferrocene/ferrocenium redox couple (~1 mM internal standard) and corrected for internal cell resistance using the BASi Epsilon software.
2.4.4. Synthetic Procedures

3-Cyanoformazan 2.12

In air, cyanoacetic acid (1.00 g, 11.7 mmol) and NaOH (4.70 g, 11.7 mmol) were mixed with deionized H₂O (60 mL) and the solution was stirred in an ice bath for 20 min. Meanwhile, in a separate flask, 4-ethynylaniline (1.10 g, 9.39 mmol) was mixed with 12 M HCl (2.35 mL, 28.2 mmol) in deionized H₂O (2.3 mL). The solution was cooled in an ice bath for 15 min before a cooled solution of sodium nitrite (0.75 g, 11 mmol) in deionized H₂O (5 mL) was added dropwise. The resulting reaction mixture, which contained diazoniunm salt, was stirred in an ice bath for an additional 20 min. In the meantime, in a separate flask, p-anisidine (1.44 g, 11.7 mmol) was mixed with 12 M HCl (2.94 mL, 35.3 mmol) in deionized H₂O (2.9 mL). The solution was cooled in an ice bath for 15 min before a cooled solution of sodium nitrite (0.93 g, 13 mmol) in deionized H₂O (5 mL) was added dropwise. The resulting reaction mixture, which contained diazonium salt, was stirred in an ice bath for an additional 20 min. The diazonium salt solutions were then mixed together and stirred in an ice bath for 10 min. The diazonium-containing solution was then added dropwise to the cyanoacetic acid solution. The solution turned dark red after approximately 2 min. After complete addition, the mixture was stirred in an ice bath for an additional 60 min before being neutralized with 1 M HCl. The resulting red-brown solid was filtered off and purified by flash chromatography using a gradient strategy (starting at 1:1 n-hexanes: CH₂Cl₂ and ending with 2:8 n-hexanes: CH₂Cl₂) where the second coloured fraction contained the desired product. Removal of the solvent *in vacuo* afforded 3-cyanoformazan 2.12 as a dark red microcrystalline solid. Yield = 1.18 g, 33%. M.p 212–213 °C. ¹H NMR (400.1 MHz, DMSO-d₆): δ 12.49 (br s, 1H, NH), 8.08 (d, 3J_HH = 9 Hz, 2H, aryl CH), 7.54 (br d, 4H, aryl CH), 7.18 (d, 3J_HH = 9 Hz, 2H, aryl CH), 4.19 (s, 1H, =CH), 3.91 (s, 3H, OCH₃). ¹³C{¹H} NMR (100.6 MHz, DMSO-d₆): δ 163.4, 146.1, 142.7, 133.0, 127.0, 126.4, 116.8, 115.7, 115.0, 112.8, 83.5, 80.7, 55.9. FT-IR (ATR): 3308 (m), 3230 (m), 2942 (s), 2837 (s), 2224 (m), 2099 (m), 1605 (m), 1579 (m), 1514 (s), 1249 (s), 1183 (s), 1164 (s), 1140 (s), 1110 (m), 1028 (m) cm⁻¹. UV-vis (CH₂Cl₂): λ_max 444 nm (ε = 26,400 M⁻¹cm⁻¹). Mass Spec. (EI, +ve mode): exact mass calculated for C₁₇H₁₃N₅O: 303.1120; exact mass found: 303.1111; difference: −3.0 ppm.
Asymmetric 3-cyanoformazanate BF$_2$ complex 2.13

Asymmetric formazan 2.12 (0.40 g, 1.3 mmol) was dissolved in dry toluene (75 mL). Et$_3$N (0.40 g, 0.55 mL, 3.9 mmol) was then added slowly, and the solution was stirred for 10 min before BF$_3$•OEt$_2$ (0.94 g, 0.81 mL, 6.6 mmol) was added, and the solution was heated to 80 °C with stirring for 16 h. The solution became dark purple during this time and after cooling to 23 °C, deionized H$_2$O (10 mL) was added to quench any excess boron-containing compounds. The toluene solution was then washed with deionized H$_2$O (3 × 20 mL), dried over MgSO$_4$, gravity filtered, and concentrated in vacuo. The resulting compound was purified by flash chromatography (THF, neutral alumina) to afford BF$_2$ complex 2.13 as a dark-purple solid. Yield = 0.31 g, 68%. M.p 199–200 °C. $^1$H NMR (399.8 MHz, CDCl$_3$): δ 7.97 (d, 3$^3$J$_{HH}$ = 9 Hz, 2H, aryl CH), 7.87 (d, 3$^3$J$_{HH}$ = 9 Hz, 2H, aryl CH), 7.60 (d, 3$^3$J$_{HH}$ = 9 Hz, 2H, aryl CH), 7.01 (d, 3$^3$J$_{HH}$ = 9 Hz, 2H, aryl CH), 3.92 (br s, 3H, OCH$_3$), 3.28 (br s, 1H, $\equiv$CH). $^{13}$C{$^1$H} NMR (150.7 MHz, CDCl$_3$): δ 163.6, 142.9, 136.8, 133.1, 125.4, 124.5, 122.5, 115.0, 114.1, 110.0, 82.6, 80.8, 55.9. $^{11}$B NMR (128.3 MHz, CDCl$_3$): δ –0.7 (t, $^1$J$_{BF}$ = 31 Hz). $^{19}$F NMR (376.1 MHz, CDCl$_3$): δ –133.7 (q, $^1$J$_{FB}$ = 31 Hz). FT-IR (ATR): 3282 (m), 2928 (s), 2840 (s), 2240 (m), 1593 (s), 1505 (m), 1407 (s), 1343 (s), 1328 (s), 1307 (s), 1262 (s), 1166 (s), 1138 (s) cm$^{-1}$. UV-vis (CH$_2$Cl$_2$): $\lambda_{max}$ 552 nm ($\varepsilon$ = 30,400 M$^{-1}$ cm$^{-1}$). Mass Spec. (EI, +ve mode): exact mass calculated for C$_{17}$H$_{12}$BF$_2$N$_3$O: 351.1103; exact mass found: 351.1108; difference: +1.4 ppm.

Benzyl-substituted BF$_2$ complex 2.14

PMDETA (0.002 g, 0.003 mL, 0.01 mmol) was dissolved in dry THF (2 mL) and the solution was degassed via three freeze-pump-thaw cycles, before CuI (0.003 g, 0.01 mmol) was added and the resulting mixture was stirred for 15 min at 23 °C. Benzyl azide (0.045 g, 0.043 mL, 0.34 mmol) and BF$_2$ complex 2.13 (0.100 g, 0.285 mmol) were then added and the reaction mixture was stirred at 23 °C for 16 h. Upon cooling, the THF solution was purified by flash chromatography (THF, neutral alumina) and recrystallized from MeOH to afford benzyl-substituted BF$_2$ complex 2.14 as a dark-purple microcrystalline solid. Yield = 0.14 g, 51%. M.p 188–189 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.95–7.93 (m, 6H, aryl CH),
7.76 (br s, 1H, =CH), 7.42–7.40 (m, 3H, aryl CH), 7.34–7.32 (m, 2H, aryl CH), 7.00 (d, \(^3J_{HH} = 9\) Hz, 2H, aryl CH), 5.61 (br s, 2H, CH\(_2\)), 3.91 (br s, 3H, OCH\(_3\)). \(^1^3\)C\{\(^1\)H\} NMR (150.7 MHz, CDCl\(_3\)): \(\delta\) 162.7, 146.6, 142.6, 136.8, 134.3, 132.9, 129.2, 128.9, 128.1, 126.4, 125.2, 123.3, 120.4, 114.9, 114.2, 110.0, 55.8, 54.3. \(^1^1\)B NMR (128.3 MHz, CDCl\(_3\)): \(\delta\) –0.7 (t, \(^1J_{BF} = 29\) Hz). \(^1^9\)F NMR (376.1 MHz, CDCl\(_3\)): \(\delta\) –134.2 (q, \(^1J_{FB} = 29\) Hz). FT-IR (ATR): 3123 (m), 2849 (m), 2250 (m), 1603 (s), 1375 (s), 1344 (s), 1326 (s), 1308 (s) cm\(^–1\). UV-vis (CH\(_2\)Cl\(_2\)): \(\lambda_{max}\) 560 nm (\(\varepsilon = 31,000\) M\(^–1\) cm\(^–1\)). Mass Spec. (EI, +ve mode): exact mass calculated for C\(_{24}\)H\(_{19}\)BF\(_2\)N\(_8\)O: 484.1743; exact mass found: 484.1759; difference: +3.3 ppm.

**Azide-substituted norbornene 2.16**

As previously reported,\(^2^7\) endo-5-norbornene-2-carboxylic acid (1.52 g, 11.0 mmol), DCC (2.47 g, 12.0 mmol) and DMAP (1.46 g, 12.0 mmol) were dissolved in dry CH\(_2\)Cl\(_2\) (110 mL) and the solution was stirred for 15 min at 23°C. 3-azido-1-propanol (1.01 g, 10.0 mmol) was then added to the reaction mixture and stirred at 23°C for 2 h. The solvent was then removed in vacuo and the crude mixture was purified by flash chromatography (3:1 \(n\)-hexanes:EtOAc, silica) to afford azide-substituted norbornene 2.16 as a clear and colourless liquid. Yield = 1.88 g, 85%.

\(^1\)H NMR (399.8 MHz, CDCl\(_3\)): \(\delta\) 6.21 (dd, 1H, \(^3J_{HH} = 6\), \(^3J_{HH} = 3\) Hz, =CH), 5.93 (dd, 1H, \(^3J_{HH} = 6\), \(^3J_{HH} = 3\) Hz, =CH), 4.12 (t, 2H, \(^3J_{HH} = 6\) Hz, CH\(_2\)), 3.40 (t, 2H, \(^3J_{HH} = 7\) Hz, CH\(_2\)), 3.22 (br s, 1H, CH), 2.99–2.95 (m, 1H, CH), 2.92 (br s, 1H, CH), 1.95–1.87 \{m, 3H, CH\(_2\)(2H) and diastereotopic CH\(_2\)(1H)\}, 1.47–1.41 (m, 2H, 2 x diastereotopic CH\(_2\)), 1.29 (d, 1H, \(J_{HH} = 8\) Hz, diastereotopic CH\(_2\)). \(^1^3\)C\{\(^1\)H\} NMR (150.7 MHz, CDCl\(_3\)): \(\delta\) 174.6, 137.9, 132.2, 61.0, 49.6, 48.3, 45.7, 43.3, 42.5, 29.2, 28.2. FT-IR (ATR): 3064 (w), 2968 (m), 2876 (m), 2905 (s), 1730 (s), 1455 (m), 1336 (m), 1270 (m), 1172 (s) cm\(^–1\). Mass Spec. (EI, +ve mode): exact mass calculated for C\(_{11}\)H\(_{15}\)N\(_3\)O\(_2\): 221.1164; exact mass found: 221.1158; difference: –2.7 ppm.
Monomer 2.17

PMDETA (0.005 g, 0.006 mL, 0.03 mmol) and azide-substituted norbornene 2.16 (0.162 g, 0.732 mmol) were dissolved in dry THF (4 mL) and the solvent was degassed via three freeze-pump-thaw cycles. Cul (0.006 g, 0.03 mmol) was then added and the mixture was stirred for 15 min at 23 °C. BF$_2$ complex 2.13 (0.214 g, 0.610 mmol) was then added and the reaction mixture was stirred at 23 °C for 2 h. The solvent was removed in vacuo and the mixture purified by flash chromatography; first a toluene/silica column was employed to remove purple and blue side products, then 1:1 toluene:EtOAc was added and the third coloured fraction contained the desired product. Removal of the solvent in vacuo afforded monomer 2.17 as a dark-purple microcrystalline solid. Yield = 0.27 g, 77%. M.p 75–76 °C. $^1$H NMR (399.8 MHz, CDCl$_3$): $\delta$ 7.97–7.95 (m, 6H, aryl CH), 7.90 (br s, 1H, triazole =CH), 7.02–7.00 (m, 2H, aryl CH), 6.23 (dd, 1H, $^3$J$_{HH}$ = 6, $^3$J$_{HH}$ = 3 Hz, =CH), 5.95 (dd, 1H, $^3$J$_{HH}$ = 6, $^3$J$_{HH}$ = 3 Hz, =CH), 4.53 (t, $^3$J$_{HH}$ = 7 Hz, 2H, CH$_2$), 4.15–4.11 (m, 2H, CH$_2$), 3.92 (s, 3H, OCH$_3$), 3.22 (br s, 1H, CH), 2.99–2.94 (m, 2H, 2CH), 2.35–2.29 (m, 2H, CH$_2$), 1.96–1.90 (m, 1H, diastereotopic CH$_2$), 1.48–1.41 (m, 2H, 2 × diastereotopic CH$_2$), 1.30–1.28 (m, 1H, diastereotopic CH$_2$). $^{13}$C{[H]} NMR (150.7 MHz, CDCl$_3$): $\delta$ 174.6, 162.7, 146.3, 142.7, 138.1, 138.0, 136.8, 132.9, 132.1, 126.4, 125.2, 123.4, 120.7, 114.9, 114.2, 60.6, 55.9, 49.7, 47.4, 45.8, 43.3, 42.5, 29.6, 29.2. $^{11}$B NMR (128.3 MHz, CDCl$_3$): $\delta$ –0.7 (t, $^1$J$_{BF}$ = 30 Hz). $^{19}$F NMR (376.1 MHz, CDCl$_3$): $\delta$ –134.1 (q, $^1$J$_{FB}$ = 30 Hz). FT-IR (ATR): 3138 (w), 2933 (m), 2857 (m), 2241 (m), 1726 (s), 1597 (s), 1505 (m), 1334 (s), 1261 (s) cm$^{-1}$. UV-vis (CH$_2$Cl$_2$): $\lambda_{max}$ 561 nm ($\varepsilon$ = 35,300 M$^{-1}$ cm$^{-1}$). Mass Spec. (EI, +ve mode): exact mass calculated for C$_{28}$H$_{27}$BF$_2$N$_8$O$_3$: 572.2267; exact mass found: 572.2256; difference: –1.9 ppm.
Dimer 2.18

This product appeared when the synthesis for monomer 2.17 was left overnight. The dimer was purified by flash chromatography (silica gel, toluene), where the second blue coloured fraction contained the dimer. Yield = 0.02 g, 7%. M.p 249–250 °C. $^1$H NMR (399.8 MHz, CD$_2$Cl$_2$): δ 7.96 (d, $^3$J$_{HH} = 9$ Hz 4H, aryl CH), 7.88 (d, $^3$J$_{HH} = 9$ Hz 4H, aryl CH), 7.66 (d, $^3$J$_{HH} = 9$ Hz 4H, aryl CH), 7.04 (d, $^3$J$_{HH} = 9$ Hz 4H, aryl CH), 3.91 (s, 6H, OCH$_3$). $^{13}$C($^1$H) NMR (150.7 MHz, CD$_2$Cl$_2$): δ 164.0, 144.1, 137.5, 134.2, 128.7, 126.1, 124.2, 123.3, 115.7, 114.7, 83.0, 77.5, 56.6. $^{11}$B NMR (128.3 MHz, CD$_2$Cl$_2$): δ −0.7 (t, $^1$J$_{BF} = 31$ Hz). $^1$F NMR (376.1 MHz, CD$_2$Cl$_2$): δ −134.3 (q, $^1$J$_{FB} = 31$ Hz). FT-IR (ATR): 3011 (w), 2936 (w), 2843 (w), 2247 (m), 1731 (w), 1599 (s), 1507 (m), 1406 (m) cm$^{-1}$. UV-vis (CH$_2$Cl$_2$): $\lambda_{max}$ 597 nm ($\varepsilon = 78,500$ M$^{-1}$ cm$^{-1}$). Mass Spec. (EI, +ve mode): exact mass calculated for C$_{34}$H$_{22}$B$_2$F$_4$N$_{10}$O$_2$: 700.2049; exact mass found: 700.2061; difference: +1.7 ppm.

2.5 References


Chapter 3

3 Fluorescent BF2 3-Cyanoformazanate Polymers

3.1 Introduction

Fluorescent, boron-containing molecules have been incorporated into polymers that have shown potential use in various areas such as: spectroscopic sensing, fluorescence imaging, gene and drug delivery, and light-harvesting materials.\textsuperscript{1-3,17} For example, the Fraser group was able to modulate solid-state fluorescence and phosphorescence of polymer 1 by varying the length of appended polylactic acid (PLA) chains and using heavy atoms.\textsuperscript{18} Furthermore, they showed that low molecular-weight polymers had weak fluorescence but strong phosphorescence spectra in anaerobic/low-oxygen conditions. These properties allowed the group to carry out \textit{in vivo} imaging of breast cancer mammary carcinoma tumour regions in mice, thereby demonstrating their use as tumour hypoxia imaging agents.

Chujo and coworkers synthesized a methacrylate derivative with a pendant BODIPY unit which was copolymerized with polystyrene using reversible addition-fragmentation chain transfer (RAFT) polymerization to yield polymer 2.\textsuperscript{19} This polymer self-assembled into nanosized particles that exhibited absorption and emission properties similar to that of the free BODIPY monomer unit. The $\Phi_F$ of the particles was much higher than that of the monomer which was due to the fact that polystyrene units inhibited the $\pi-\pi$ stacking of the BODIPY units, which would otherwise cause collision quenching of the fluorescence.

The controlled ROMP of side-chain BF\textsubscript{2} formazanate containing polymers 3 has been reported previously.\textsuperscript{20} These polymers retained the properties of the BF\textsubscript{2} monomer such as high molar extinction coefficients, fluorescence, and redox activity. However, the $\Phi_F$ for both the monomer and polymer were rather low ($\Phi_F = 1.5\%$ and 2.5\%, respectively). These results
revealed the need to make a monomer with higher $\Phi_F$, so that the corresponding polymer may also benefit from this property. This chapter describes the polymerization of monomer 2.21 ($\text{BF}_2\text{N}$) using ROMP. The synthesis of various block and random copolymers of $\text{BF}_2\text{N}$ is also described, along with their thermal and spectroscopic properties.

3.2 Results and Discussion

3.2.1 Synthesis of Side-Chain Polymers

Attempts to polymerize monomer $\text{BF}_2\text{N}$ using ROMP began by dissolving the monomer in dry and degassed $\text{CH}_2\text{Cl}_2$ at 50 mg mL$^{-1}$ concentrations, at 23 °C, using the 3-bromo pyridine derivative of Grubbs’ third generation catalyst (GIII). However, after various attempts to optimize the conditions of the polymerization (such as temperature and time), there was no evidence of polymer formation using $^1\text{H}$ NMR spectroscopy. It was concluded that the polymer was likely not very soluble in $\text{CH}_2\text{Cl}_2$ and that short oligomers were crashing out of solution upon formation. Thus, dimethyacetamide (DMA) was used as a solvent since it solubilized the $\text{BF}_2\text{N}$ monomer better than $\text{CH}_2\text{Cl}_2$. The reactions were carried out in dry and degassed DMA at 50 mg mL$^{-1}$ concentrations, at 23 °C, using GIII. Ethyl vinyl ether was used as the terminating agent, and the polymer was purified by precipitation from pentane and isolated by centrifugation (Scheme 3.1). $^1\text{H}$ NMR spectroscopy of the $\text{BF}_2$ polymer ($\text{PBF}_2\text{N}$) revealed the disappearance of the alkene protons of the norbornene group on $\text{BF}_2\text{N}$ monomer, which appeared at 6.22 ppm and 5.93 ppm (triangles), and the appearance of broad signals between 5.25 and 5.35 ppm (circles) which are from the alkene protons found in the backbone of $\text{PBF}_2\text{N}$ (Figure 3.1). Furthermore, all signals in the $^1\text{H}$ NMR spectrum were broad, which is often an indication of polymer formation. The $\text{BF}_2$ moiety remained intact, which was evident by looking at the broad signal at $-133.4$ ppm in the $^{19}\text{F}$ NMR spectrum, and a 1:2:1 triplet at $-0.8$ ppm in the $^{11}\text{B}$ NMR spectrum (Figure A.3.9.). Cyclic voltammetry experiments were performed in $\text{CH}_2\text{Cl}_2$ and showed that the polymers exhibited two reversible one-electron reduction waves to yield first the poly radical anion, and then the poly dianion (Figure A.3.17.).
In order to determine the time at which the ROMP reaction was finished, it was monitored by taking aliquots of a reaction solution at different time intervals and terminating the polymerization with ethyl vinyl ether. Monitoring the reaction revealed that the polymerization was complete after approximately 10 min (Figure 3.2). The number average molecular weight ($M_n$), weight average molecular weight ($M_w$) and dispersity ($D$) for each of the aliquots of PBF$_2$N was then determined by gel permeation chromatography (GPC) relative to polystyrene standards and summarized in Table 3.1. $^1$H NMR spectroscopy could not be used to determine the molecular weight of the PBF$_2$N since resonances associated with the phenyl end group...
overlapped with those of the polymer repeating unit. Furthermore, the polymer absorbs at 630 nm, impeding the use of triple-detection GPC as a means for determining absolute molecular weight. Dispersity values ranged from 1.10–1.31 demonstrating the controlled polymerization of monomer BF$_2$N using ROMP, which is an important trait for future block and random copolymer synthesis. Molecular weight data for the BF$_2$N monomer was also collected. It is worth noting that the molecular weight of the monomer (572.37 g mol$^{-1}$) has been overestimated by GPC ($M_n = 4,140$ g mol$^{-1}$), and thus we postulate that all the molecular weights found for the polymers are also overestimated.

**Table 3.1.** Summary of molecular weight data determined by GPC for PBF$_2$N polymers.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>$D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF$_2$N</td>
<td>4,140</td>
<td>4,869</td>
<td>1.18</td>
</tr>
<tr>
<td>1</td>
<td>109,200</td>
<td>126,500</td>
<td>1.16</td>
</tr>
<tr>
<td>3</td>
<td>151,400</td>
<td>189,200</td>
<td>1.25</td>
</tr>
<tr>
<td>5</td>
<td>164,500</td>
<td>210,400</td>
<td>1.28</td>
</tr>
<tr>
<td>10</td>
<td>182,100</td>
<td>226,400</td>
<td>1.24</td>
</tr>
<tr>
<td>20</td>
<td>185,600</td>
<td>241,400</td>
<td>1.30</td>
</tr>
<tr>
<td>30</td>
<td>193,100</td>
<td>241,400</td>
<td>1.25</td>
</tr>
<tr>
<td>60</td>
<td>201,500</td>
<td>264,300</td>
<td>1.31</td>
</tr>
</tbody>
</table>

**Figure 3.2.** Relationship between $M_n$ of PBF$_2$N as a function of time (a), and corresponding GPC traces (b). Dark blue dot at zero 0 min in (a) represents the $M_n$ value determined for the BF$_2$N monomer. GPC traces in (b) are colour coded: 1 min (light blue), 3 min (red), 5 min (black), 10 min (dark yellow), 20 min (green), 30 min (purple), 60 min (grey).

In order to synthesize copolymers containing BF$_2$N subunits, a second monomer containing a polymerizable norbornene group was synthesized according to a modified procedure developed by Alfred *et al.* (Scheme 3.2). First, cis-5-norbornene-exo-2,3-dicarboxylic
anhydride (exo-NDCAn) was synthesized by heating cis-5-norbornene-endo-2,3-dicarboxylic anhydride (endo-NDCAn) at 200 °C for 2 h, and separating exo-NDCAn from the remaining starting material (endo-NDCAn) by the use of column chromatography (1:1 n-hexanes:EtOAc). Cis-5-norbornene-endo-2,3-dicarboxylic acid (exo-NDCA) was then synthesized by stirring exo-NDCAn in a 1.4 M solution of KOH for 45 min. 1H NMR spectroscopy confirmed the synthesis of solely the exo isomer for both exo-NDCAn and exo-NDCA (Figure A.3.1 and Figure A.3.2).

Scheme 3.2. Synthesis of monomer exo-NDCA.

Polymerization of exo-NDCA was carried out according to a modified procedure,21 where monomer exo-NDCA was dissolved in dry and degassed DMA at 50 mg mL⁻¹ concentrations, at 23 °C, using GIII; ethyl vinyl ether was once again used as the terminating agent (Scheme 3.3).

Scheme 3.3. Polymerization of monomer exo-NDCA.

1H NMR spectroscopy revealed the disappearance of the alkene protons of the norbornene group on exo-NDCA which appeared as a multiplet at 6.24 ppm, and the appearance two broad signals at 5.25 and 5.43 ppm which are from the alkene protons found in the backbone of the cis-5-norbornene-endo-2,3-dicarboxylic acid polymer (P-exo-NDCA) (Figure A.3.3.). The polymerization of exo-NDCA was monitored as a function of time by taking aliquots of the reaction solution and terminating the polymerization with ethyl vinyl ether. The $M_n$, $M_w$ and $Đ$ for each of the aliquots of polymers was determined by GPC relative to polystyrene
standards and summarized in Table A.3.1. Prior to GPC analysis, the polymers were methylated by stirring in dry DMF with excess K$_2$CO$_3$ and CH$_3$I overnight. This was done to prevent any irreversible adsorption of the polymer to the GPC column due to the presence of the carboxylic acid groups in the P-exo-NDCA. Monitoring the reaction mechanism revealed that the polymerization was complete after approximately 6 min (Figure A.3.4). Dispersity values ranged from 1.07–1.38 showing controlled polymerization of monomer exo-NDCA.

Initial attempts to synthesize block copolymers containing BF$_2$N and exo-NDCA subunits using ROMP were met with difficulties when trying to obtain a $^1$H NMR spectrum. Although various solvents were used (e.g., CDCl$_3$, DMSO-$d_6$, or both) and variable temperature experiments were carried out (up to 125 °C in DMSO-$d_6$), all experiments were unsuccessful in revealing peaks pertaining to both polymers. This difficulty was most likely due to a difference in the solubility of both blocks rather than failed polymerization, since GPC traces suggest block copolymer synthesis was successful based on an increase in molecular weight of (PBF$_2$N)-b-(P-exo-NDCA) vs. solely the first block (PBF$_2$N) (Figure A.3.5). These difficulties, along with the inconvenience of having to methylate each polymer before GPC analysis, prompted the synthesis of a new monomer for block copolymer and random copolymer synthesis with BF$_2$N. Cis-dimethyl-5-norbornene-exo-2,3-dicarboxylate (DND) was synthesized by a modified procedure from Hennis et al.$^{22}$ where sulfuric acid was substituted for hydrochloric acid (Scheme 3.4). $^1$H NMR spectroscopy confirmed the synthesis of solely DND as the exo isomer (Figure 3.3).

Scheme 3.4. Synthesis of monomer DND.

Polymerization of DND was performed in the same manner as exo-NDCA, where DND was dissolved in dry and degassed DMA at 50 mg mL$^{-1}$ concentrations, at 23 °C, using GIII; ethyl vinyl ether was used as the terminating agent (Scheme 3.5). $^1$H NMR spectroscopy revealed the disappearance of the alkene protons of the norbornene group of DND (triangle) which appeared as a broad singlet at 6.21 ppm, and the appearance of two
broad signals at 5.24 and 5.42 ppm (circles) due to the presence of the alkene protons found in the backbone of poly(cis-dimethyl-5-norbornene-exo-2,3-dicarboxylate) (PDND) (Figure 3.3).

Scheme 3.5. ROMP of DND.

Figure 3.3. Overlay of the $^1$H NMR spectra of compound DND (red) and PDND (black) in CDCl$_3$. The triangle represents the norbornene alkene protons and the circles represent the new alkene protons found in the backbone of PDND.

The polymerization of DND was monitored over time by taking aliquots of the reaction solution at 0.5, 1, 3, 5, 7 and 9 min, prior to termination with ethyl vinyl ether. The $M_n$, $M_w$ and $D$ for each of the aliquots of polymers was determined by GPC (vs. polystyrene standards) (without the need of post-polymerization modification) and summarized in Table 3.2. Monitoring the reaction mechanism revealed that the polymerization was complete after approximately 3 min due to a plateauing of the $M_n$ (Figure 3.4a), which is also seen by the overlap of GPC traces of 3, 5, 7, and 9 min seen in Figure 3.4b. The dispersity for all aliquots ranged from 1.12–1.14 which shows the controlled polymerization of DND, an important trait for future block and random copolymer synthesis.
Table 3.2. Summary of molecular weight data determined by GPC for PDND.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>$D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>36,900</td>
<td>41,250</td>
<td>1.12</td>
</tr>
<tr>
<td>1</td>
<td>39,510</td>
<td>44,360</td>
<td>1.12</td>
</tr>
<tr>
<td>3</td>
<td>43,680</td>
<td>49,280</td>
<td>1.13</td>
</tr>
<tr>
<td>5</td>
<td>42,520</td>
<td>48,510</td>
<td>1.14</td>
</tr>
<tr>
<td>7</td>
<td>43,060</td>
<td>48,730</td>
<td>1.13</td>
</tr>
<tr>
<td>9</td>
<td>43,190</td>
<td>48,910</td>
<td>1.13</td>
</tr>
</tbody>
</table>

Figure 3.4. Relationship between the $M_n$ of PDND as a function of time (a), and corresponding GPC traces (b). GPC traces in (b) are colour coded: 0.5 min (light blue), 1 min (red), 3 min (black), 5 min (dark yellow), 7 min (green), 9 min (purple).

3.2.2 Synthesis of Block Copolymers Containing BF$_2$ Complexes

A representative block copolymer (PDND)$_m$-b-(BF$_2$N)$_n$ containing subunits of DND and BF$_2$N was synthesized by first dissolving DND in dry degassed DMA at a concentration of 50 mg mL$^{-1}$, at 23 °C, and 1 mol % of GIII catalyst was added. The reaction mixture was stirred for 6 min. At this time, an aliquot of the first block (PDND) was removed and added to a solution containing ethyl vinyl ether; this was done so that the $M_n$ of the first block could be found using GPC. A solution of monomer BF$_2$N was then added to the PDND reaction solution and the second monomer was allowed to polymerize from the active end of PDND for an additional 12 min and then quenched with ethyl vinyl ether (Scheme 3.6).
Scheme 3.6. Representative synthesis of (PDND)$_m$-$b$-(PBF$_2$N)$_n$ polymers using ROMP.

As described, the synthesis of all block copolymers began by targeting 100 units of DND in PDND (1 mol% of GIII to DND). This method was used to synthesize three block copolymers that differed by the amount of BF$_2$ subunit allowed to grow off of the active PDND chain. The more BF$_2$N subunits allowed to grow off of the PDND live chain end, the greater the mole fraction of BF$_2$N subunit ($f_{BF2}$) in each block copolymer, and thus a greater $M_n$ for the block polymer (Table 3.3). This was also made evident by comparing the GPC traces for polymers (PDND)$_{276}$-$b$-(PBF$_2$N)$_{255}$, (PDND)$_{355}$-$b$-(PBF$_2$N)$_{53}$, (PDND)$_{266}$-$b$-(PBF$_2$N)$_{20}$, and PDND (Figure 3.5). As the $f_{BF2}$ increased, the $M_n$ of the block copolymers also increased. $D$ values for the first blocks of all block copolymers ranged from 1.11–1.16, and $D$ from the block copolymers ranged from 1.16–1.45, consistent with controlled ROMP. 23
Figure 3.5. GPC traces (in DMF) of polymer PDND ($f_{BF2} = 0.0$, dark yellow) and block copolymers (PDND)$_{276-b-}$-(PBF$_2$N)$_{255}$ ($f_{BF2} = 0.48$, blue), (PDND)$_{355-b-}$-(PBF$_2$N)$_{53}$ ($f_{BF2} = 0.13$, purple) and (PDND)$_{266-b-}$-(PBF$_2$N)$_{20}$ ($f_{BF2} = 0.07$, red).

$^1$H NMR spectroscopy confirmed the synthesis of the block copolymers described above, along with the $f_{BF2}$ in each polymer (Figure A.3.10. – A.3.12.). Figure 3.6 shows the $^1$H NMR spectrum of block copolymer (PDND)$_{276-b-}$-(PBF$_2$N)$_{255}$, PBF$_2$N and PDND. The alkene protons of the norbornene group on BF$_2$N which appear between 5.94–5.96 and 6.22–6.24 ppm and the alkene protons of DND which appear as a broad singlet at 6.21 ppm have disappeared and new alkene protons that pertain to the backbone of (PDND)$_{276-b-}$-(PBF$_2$N)$_{255}$ have appeared as two broad signals at 5.25 and 5.43 ppm (circles). Integration of these signals with respect to the broad singlet at 6.92 ppm (star), which pertains to two aryl protons on the BF$_2$N containing block, was used in order to determine the block ratio of these polymers. In the case of block copolymer (PDND)$_{276-b-}$-(PBF$_2$N)$_{255}$, the integrations of these signals is 2.00 to 4.20. As the signal that integrates to 4.20 contains two protons from PBF$_2$N, the remaining integration is attributed to PDND (2.20), thus the mole ratio of BF$_2$N subunit to DND subunits is 1:1.1, and thus (PDND)$_{276-b-}$-(PBF$_2$N)$_{255}$ contains $f_{BF2} = 0.48$. Signals pertaining to the methoxy substituent on PBF$_2$N (triangle) and methyl ester groups on PDND (squares) are found at 3.83 ppm and 3.64 ppm, respectively. These signals are found in the $^1$H NMR spectrum of (PDND)$_{276-b-}$-(PBF$_2$N)$_{255}$ as well; the $^1$H NMR spectrum of (PDND)$_{276-b-}$-(PBF$_2$N)$_{255}$ is essentially an overlay of $^1$H NMR spectrum of PBF$_2$N and PDND. All signals in the $^1$H NMR spectrum were broad, which is an indication of polymer formation, and the BF$_2$
moiety remained intact, as evidenced by looking at the broad signal at $-133.4$ ppm in the $^{19}$F NMR spectrum, and the broad 1:2:1 triplet at $-0.75$ ppm in the $^{11}$B NMR spectrum (Figure A.3.16.). Cyclic voltammetry experiments were performed in CH$_2$Cl$_2$ and showed that the copolymers exhibited two reversible one-electron reduction waves to yield the poly radical anion and the poly dianion (Figure A.3.17).

**Figure 3.6.** Overlay of $^1$H NMR spectra of compound PDND (green), PBF$_2$N (red) and polymer (PDND)$_{276}$-$b$-(PBF$_2$N)$_{255}$, (black) in CDCl$_3$. The circles represent the new alkene protons found in the backbone of (PDND)$_{276}$-$b$-(PBF$_2$N)$_{255}$, the triangle represents the protons on the methoxy substituent of PBF$_2$N, the square represents the methyl groups on PDND, and the star represents two aryl protons on the PBF$_2$N subunit.

The number of repeating units for each block of (PDND)$_m$-$b$-(PBF$_2$N)$_n$ were determined in two ways using GPC analysis in DMF (vs. polystyrene) and $^1$H NMR spectroscopy. Method 1 involved the use $f_{BF2}$ found using $^1$H NMR spectroscopy, and the $M_n$ value found using GPC analysis. The following formula was used:

**Block copolymer** (PDND)$_{276}$-$b$-(PBF$_2$N)$_{255}$

$$M_n = 204,300 \text{ g mol}^{-1} \text{ (determined by GPC)}$$
n is mole fraction of $\text{BF}_2\text{N}$ subunit =

$$\frac{n}{n+m} = 0.48 \text{ (based on } ^1\text{H NMR spectroscopy)}$$

3.1

m is mole fraction of $\text{DND}$ subunit =

$$\frac{m}{n+m} = 0.52 \text{ (based on } ^1\text{H NMR spectroscopy)}$$

3.2

$m\text{MM}_{\text{DND}} + n\text{MM}_{\text{BF}_2} = 204,300 \text{ g mol}^{-1}$

3.3

where: $\text{MM}_{\text{DND}} = 210.2265 \text{ g mol}^{-1}$ and $\text{MM}_{\text{BF}_2} = 572.3736 \text{ g mol}^{-1}$

Thus, using Equation 3.1 and 3.2 we know:

$$m = \frac{0.52}{0.48} n$$

3.4

Substituting Equation 3.4 into Equation 3.3:

$$\frac{0.52}{0.48} n \text{MM}_{\text{DND}} + n\text{MM}_{\text{BF}_2} = 204,300 \text{ g mol}^{-1}$$

3.5

$$n = \frac{204,300 \text{ g mol}^{-1}}{\left(\frac{0.52}{0.48}\right)\text{MM}_{\text{DND}} + \text{MM}_{\text{BF}_2}}$$

3.6

Therefore:

$$n = 255$$

Substituting n into Equation 3.4 results in:

$$m = 276$$

Therefore, the degree of polymerization ($\text{DP}_n$) for each subunit within block copolymer ($\text{PDND})_{276-b-(\text{PBF}_2\text{N})_{255}}$ is 276 units for the $\text{DND}$ portion, and 255 for the $\text{BF}_2$ portion.

Method 2 is more common, and involves finding the $\text{DP}_n$ of the $\text{DND}$ portion of the block copolymer by determining the $M_n$ for an aliquot of the first block ($\text{PDND}$), and dividing it by the molar mass of $\text{DND}$ ($38,820 \text{ g mol}^{-1}/210.23 \text{ g mol}^{-1}$). This resulted in a number average $\text{DP}_n$ of 185 units of $\text{DND}$ in $\text{PDND}$. As previously discussed, $^1\text{H}$ NMR spectroscopy revealed
that the ratio of DND subunit to BF2N subunit in the block copolymer was 1.1 to 1. Using this information, the number of subunits of BF2N in the second block (PBF2N) was found to be 168. The Mn of the second block (PBF2N) can then be found by multiplying the DPn by the molar mass of BF2N (168 * 572.3736 g mol⁻¹), which resulted in a molar mass of 96,159 g mol⁻¹. Using this information, the Mn of (PDND)276-b-(PBF2N)255 was found to be 134,979 g mol⁻¹ (38,820 g mol⁻¹ + 96,159 g mol⁻¹). The results for both methods are summarized in Table 3.3. Although Method 2 is the most widely used, Method 1 was the only way the degree of polymerization for the random copolymers could be calculated. Therefore, for consistency, the DPn for both block and random copolymers will be reported using Method 1.

Table 3.3. Summary of molecular weight data determined for the first block and diblock copolymers (PDND)276-b-(PBF2N)255 (fBF2 = 0.48), (PDND)355-b-(PBF2N)53 (fBF2 = 0.13) and (PDND)266-b-(PBF2N)20 (fBF2 = 0.07).

<table>
<thead>
<tr>
<th>fBF2a</th>
<th>Method 1</th>
<th>Method 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(PDND)m-b-(PBF2N)n</td>
<td>PDNDm</td>
</tr>
<tr>
<td></td>
<td>Mₙ b</td>
<td>m¹b</td>
</tr>
<tr>
<td>0.48</td>
<td>204,300</td>
<td>276</td>
</tr>
<tr>
<td>0.13</td>
<td>104,000</td>
<td>355</td>
</tr>
<tr>
<td>0.07</td>
<td>66,040</td>
<td>266</td>
</tr>
</tbody>
</table>

a Determined from the relative integrations of unique ¹H NMR spectroscopic signals. b Determined by GPC analysis (vs. polystyrene standards).

3.2.3 Synthesis of Random Copolymers Containing BF2 Complexes

Random copolymers of monomers DND and BF2N were synthesized by dissolving DND and BF2N in dry, degassed DMA at a total monomer concentration of 50 mg mL⁻¹, at 23 °C, and adding 1 mol % of GIII catalyst. The reaction mixture was stirred for 12 min and then quenched with ethyl vinyl ether (Scheme 3.7). The targeted DPn of the three random copolymers that were synthesized was 100 (1 mol% GIII). Each random copolymer differed by the fBF2 within the polymer, and this was calculated using the ¹H NMR methods described above for the block copolymers. ¹H NMR spectroscopy confirmed the synthesis of the copolymers (e.g., Figure 3.7). Two broad signals pertaining to the alkene protons found in the backbone of the random copolymers were found in the range of 5.40–5.23 ppm (circles). The methoxy group of the
BF$_2$N unit of the polymer was found as a broad singlet at 3.88 ppm (triangle), and the methyl groups pertaining to the DND portion of the polymer were found as one broad singlet at 3.62 ppm (square). For random copolymer (PDND)$_{316}$-r-(PBF$_2$)$_{316}$ the ratio of BF$_2$N subunit to DND subunit was 1.0:1.0, and thus $f_{BF2} = 0.50$. The BF$_2$ moiety remained intact, which was made evident by looking at the broad signal at −133.8 ppm in the $^{19}$F NMR spectrum, and the broad 1:2:1 triplet at −0.7 ppm in the $^{11}$B NMR spectrum (Figure A.3.16). GPC (vs. polystyrene standards) was used to find the $M_n$, $M_w$, and $D$ of the remaining random copolymers, and Method 1 was used to find the $D_P n$. Cyclic voltammetry experiments were performed in CH$_2$Cl$_2$ and showed that the polymers exhibited two reversible one-electron reduction waves to yield first the poly radical anion, and then the poly dianion (Figure A.3.17).

Scheme 3.7. Synthesis for random block copolymers (PDND)$_{m}$-r-(PBF$_2$N)$_{n}$. $m$ represents the DP$_n$ for the DND subunit, and $n$ represents the DP$_n$ for the BF$_2$N subunit.
**Figure 3.7.** $^1$H NMR spectra of $(\text{PDND})_{n-16^{-}}-(\text{PBF}_2\text{N})_{316}$ in CDCl$_3$. The circles represent the alkene protons found in the backbone of the polymer, the triangle represents the protons on the methoxy group on the PBF$_2$N subunit, and the square represents the methyl groups on the DND subunit. The star represents two aryl protons on the PBF$_2$N subunit.

**Table 3.4.** Summary of molecular weight data for random copolymers $(\text{PDND})_{316-}r-(\text{PBF}_2\text{N})_{316}$ $(f_{\text{BF}_2} = 0.50)$, $(\text{PDND})_{292-}r-(\text{PBF}_2\text{N})_{52}$ $(f_{\text{BF}_2} = 0.15)$ and $(\text{PDND})_{298-}r-(\text{PBF}_2\text{N})_{26}$ $(f_{\text{BF}_2} = 0.08)$.

<table>
<thead>
<tr>
<th>$f_{\text{BF}_2}$</th>
<th>$(\text{PDND})_{m-}r-(\text{PBF}_2\text{N})_n$</th>
<th>$(\text{PDND})_{m-}r-(\text{PBF}_2\text{N})_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>$M_n$ = 247,300, $M_w$ = 335,200, $D$ = 1.36</td>
<td>$m^c$ = 316, $n^c$ = 316</td>
</tr>
<tr>
<td>0.15</td>
<td>90,890, 107,000, 1.18</td>
<td>292, 52</td>
</tr>
<tr>
<td>0.08</td>
<td>77,490, 88,820, 1.15</td>
<td>298, 26</td>
</tr>
</tbody>
</table>

$^a$Determined by relative integrations of $^1$H NMR spectroscopic signals. $^b$Determined by GPC analysis (vs. polystyrene standards). $^c$Determined by relative integrations of $^1$H NMR spectroscopic signals and $M_n$ from GPC.

The GPC data shows that as the $f_{\text{BF}_2}$ increases the $M_n$ of the polymer will also increase which makes sense since the BF$_2$N subunit has a molar mass that is 2.7 times greater than that of the DND subunit. Comparison of the GPC traces of all three random copolymers and PDND $(f_{\text{BF}_2} = 0.0)$ also displays this trend (Figure 3.8). The dispersity values for the all three random copolymers range from 1.15–1.36, owing to the controlled polymerization of these polymers.
3.2.4 Thermal Properties

Thermal gravimetric analysis (TGA) of the block and random copolymers, along with PBF$_2$N and PDND was used to determine the temperature corresponding to the onset of decomposition (2% mass loss, O.D.) for each polymer as well as to study their degradation over a range of temperatures (25 – 1000 °C). In general, PDND was found to be more thermally stable (O.D. = 155 °C) than PBF$_2$N (O.D. = 136 °C) as it survives a higher temperature range before losing a significant amount of its mass (Figure 3.9 and 3.10). The block (Figure 3.9) and random (Figure 3.10) copolymers followed a similar trend whereby thermal stability increased as $f_{BF2}$ decreased.
Differential scanning calorimetry (DSC) studies of all of the polymers described in this work revealed their glass transition temperatures ($T_g$). PDND ($f_{BF2} = 0.0$) was found to have a $T_g$ of 83 °C while PBF$_2$N ($f_{BF2} = 1.0$) had a $T_g$ of 136 °C. When looking at the DSC traces for the block copolymers they revealed two $T_g$s, which proves we have made block copolymers (except for (PDND)$_{266}$-$b$-(PBF$_2$N)$_{20}$ ($f_{BF2} = 0.07$) (Figure 3.11). This behaviour is likely due to the small percentage of the PBF$_2$N block, making the transition difficult to observe. The first $T_g$ corresponds to the transition from the glassy state to the rubbery state of the PDND.
portion of the block copolymer. The temperatures at which this transition occurs ranged from 81–85 °C. The second \( T_g \) corresponds to the change in state from glassy to rubbery for the \( \text{PBF}_2\text{N} \) block portion. As the \( f_{\text{BF}_2} \) increases the temperature at which this transition occurred also increased. This second transition was not observed for \((\text{PDND})_{266-b-(\text{PBF}_2\text{N})_{20}} \) (\( f_{\text{BF}_2} = 0.07 \)) since the fraction of \( \text{BF}_2\text{N} \) units was small. DSC traces for the random copolymers reveal only one \( T_g \), which suggests that we have synthesized random copolymers, and also supports the idea that polymerization of both monomers occurs at the same rate (Figure 3.12). It was observed that as the \( f_{\text{BF}_2} \) increases, the \( T_g \) also increased. The first derivative of all DSC traces was also plotted so that the transitions could be seen more clearly (Figure 3.11b and Figure 3.12b). No melt or crystallization events were observed.

**Figure 3.11.** DSC traces (a) and first derivative traces (b) for polymer \( \text{PDND} \) (\( f_{\text{BF}_2} = 0.0, \text{dark yellow} \)), \( \text{PBF}_2\text{N} \) (\( f_{\text{BF}_2} = 1.0, \text{black} \)), and block copolymers \((\text{PDND})_{276-b-(\text{PBF}_2\text{N})_{255}} \) (\( f_{\text{BF}_2} = 0.48, \text{blue} \)), \((\text{PDND})_{355-b-(\text{PBF}_2\text{N})_{353}} \) (\( f_{\text{BF}_2} = 0.13, \text{purple} \)) and \((\text{PDND})_{266-b-(\text{PBF}_2\text{N})_{20}} \) (\( f_{\text{BF}_2} = 0.07, \text{red} \)). Decomposition point of \( \text{PDND} \) was lower than the other polymers, and thus DSC could only be done up to 130 °C.

**Figure 3.12.** DSC traces (a) and first derivative traces (b) for polymer \( \text{PDND} \) (\( f_{\text{BF}_2} = 0.0, \text{dark yellow} \)), \( \text{PBF}_2\text{N} \) (\( f_{\text{BF}_2} = 1.0, \text{black} \)), and random copolymers \((\text{PDND})_{316-r-(\text{PBF}_2\text{N})_{316}} \) (\( f_{\text{BF}_2} = 0.50, \text{blue} \)), \((\text{PDND})_{292-r-(\text{PBF}_2\text{N})_{52}} \) (\( f_{\text{BF}_2} = 0.15, \text{purple} \)) and \((\text{PDND})_{298-r-(\text{PBF}_2\text{N})_{26}} \) (\( f_{\text{BF}_2} = 0.08, \text{red} \)).
3.2.5 Spectroscopic Properties

The spectroscopic properties of BF$_2$N and all of the polymers synthesized in this study are summarized in Table 3.5. Figure 3.13 and 3.14 display the UV-vis absorption and emission spectra for selected compounds. Figure 3.15 displays the $\Phi_F$ for the random copolymers, BF$_2$N and PBF$_2$N. All of the spectroscopic data were collected in CH$_2$Cl$_2$.

Table 3.5. Spectroscopic properties of BF$_2$N, PBF$_2$N, and all block copolymers (PDND)$_m$-$b$-(PBF$_2$N)$_n$ and random copolymers (PDND)$_m$-$r$-(PBF$_2$N)$_n$.

<table>
<thead>
<tr>
<th></th>
<th>$f_{BF2}$</th>
<th>$\lambda_{max}$ (nm)</th>
<th>$\epsilon$ (M$^{-1}$ cm$^{-1}$)</th>
<th>$\lambda_{em}$ (nm)</th>
<th>$\Phi_F$ (%)$^a$</th>
<th>$\nu_{ST}$ (nm)</th>
<th>$\nu_{ST}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF$_2$N</td>
<td>1</td>
<td>561</td>
<td>35,300</td>
<td>663</td>
<td>35</td>
<td>102</td>
<td>2742</td>
</tr>
<tr>
<td>PBF$_2$N</td>
<td>1</td>
<td>559</td>
<td>27,500</td>
<td>663</td>
<td>12</td>
<td>104</td>
<td>2806</td>
</tr>
<tr>
<td>(PDND)$_m$-</td>
<td>0.48</td>
<td>559</td>
<td>-</td>
<td>667</td>
<td>2</td>
<td>108</td>
<td>2897</td>
</tr>
<tr>
<td>$b$-</td>
<td>0.13</td>
<td>559</td>
<td>-</td>
<td>665</td>
<td>3</td>
<td>106</td>
<td>2851</td>
</tr>
<tr>
<td>(PBF$_2$N)$_n$</td>
<td>0.07</td>
<td>559</td>
<td>-</td>
<td>665</td>
<td>1</td>
<td>106</td>
<td>2851</td>
</tr>
<tr>
<td>(PDND)$_m$-</td>
<td>0.50</td>
<td>558</td>
<td>-</td>
<td>664</td>
<td>8</td>
<td>106</td>
<td>2861</td>
</tr>
<tr>
<td>$r$-</td>
<td>0.15</td>
<td>560</td>
<td>-</td>
<td>664</td>
<td>19</td>
<td>104</td>
<td>2797</td>
</tr>
<tr>
<td>(PBF$_2$N)$_n$</td>
<td>0.08</td>
<td>561</td>
<td>-</td>
<td>664</td>
<td>26</td>
<td>103</td>
<td>2765</td>
</tr>
</tbody>
</table>

$^a$Quantum yields were measured according to published protocol$^{25}$ using ruthenium tris(bipyridine) hexafluorophosphate as a relative standard$^{26}$ and corrected for wavelength-dependent detector sensitivity (Figure A2.21).

Figure 3.13. UV-vis absorption spectra of BF$_2$N (dark yellow) and PBF$_2$N ($f_{BF2} = 1.0$, black) (a, b), and block copolymers (PDND)$_m$-$b$-(PBF$_2$N)$_n$ (a), and random copolymers (PDND)$_m$-$r$-(PBF$_2$N)$_n$ (b). All spectra were recorded in CH$_2$Cl$_2$ using 0.00005 g mL$^{-1}$ solutions.
Figure 3.14. Emission spectra for BF$_2$N (dark yellow), PBF$_2$N ($f_{BF2} = 1.0$, black) and random copolymers (PDND)$_{316}$-r-(PBF$_2$N)$_{316}$ ($f_{BF2} = 0.50$, blue), (PDND)$_{292}$-r-(PBF$_2$N)$_{52}$ ($f_{BF2} = 0.15$, purple) and (PDND)$_{298}$-r-(PBF$_2$N)$_{26}$ ($f_{BF2} = 0.08$, red) (b). All spectra were recorded in CH$_2$Cl$_2$ and their absorbance in the UV-vis region was approximately 0.1.

Figure 3.15. Summary of the quantum yields of fluorescence (red dots) for the random copolymers (PDND)$_{m}$-r-(PBF$_2$N)$_{n}$, as well as for BF$_2$N (defined as $f_{BF2} = 1.0$), and PBF$_2$N ($f_{BF2} = 1.0$). Errors bars associated with the quantum yields calculated were placed by using the standard deviation for three repeated experiments of each. Spectra were recorded in CH$_2$Cl$_2$ and their maximum absorbance in solution was approximately 0.1.

These results reveal that the polymers have a $\lambda_{max}$ from 558–561 nm and a $\lambda_{em}$ from 663–667 nm. The UV-vis absorption spectra were recorded in 0.00005 g mL$^{-1}$ solutions in CH$_2$Cl$_2$ and show that as the $f_{BF2}$ in the polymer increases, the $\lambda_{max}$ at approximately 560 nm also increases (Figure 3.13). The Stokes’ shifts for all polymers ranged from 103–106 nm. The $\Phi_F$ for the
block copolymers ranged from 1–3%, and were essentially non-emissive. In the case of the random copolymers, it was observed that as the $f_{BF2}$ decreased, the $\Phi_F$ increased. Figure 3.15 summarizes the average of the $\Phi_F$ found for three separate runs; error bars were included and calculated using the standard deviation from three unique measurements. Examining this graph reveals a clear correlation between the $\Phi_F$ and the average distance between BF$_2$N subunits in the polymer. For PBF$_2$N, for example, the quantum yield is low (12%) compared to BF$_2$N monomer (35%) and this is most likely due to the close proximity of the BF$_2$N units within the polymer resulting in reabsorption of emitted photons, due to the overlap between the absorption and emission spectra. However, as the $f_{BF2}$ decreases in the polymer, the average distance between each BF$_2$N subunit increases, and thus reabsorption from nearby BF$_2$N units is less likely. This results in an increase in $\Phi_F$, with (PDND)$_{298}$-r-(PBF$_2$N)$_{26}$ ($f_{BF2} = 0.08$) having the highest $\Phi_F$ of 26%. Another argument for the decrease in $\Phi_F$ of polymers relative to monomer BF$_2$N could be π-stacking of BF$_2$N subunits in the polymer solution.$^{27}$ However, solutions were prepared to have absorbance values of approximately 0.1, and thus the amount of BF$_2$N in solution was approximately the same for all. Also, π-stacking in solution is usually accompanied by a red-shift in the absorbance and emission maxima, which was not observed for these systems.$^{28-29}$ Thus, π-stacking is likely not occurring. Similar approaches have been employed in order to increase the quantum yield of fluorescence of polymers.$^{19,30-31}$

### 3.3. Conclusions

ROMP was used to synthesize a variety of polymers containing 3-cyanoformazanate BF$_2$ complexes (PBF$_2$N) and cis-dimethyl-5-norbornene-exo-2,3-dicarboxylate polymer (PDND). Homopolymers, block copolymers and random copolymers were characterized using $^1$H NMR, $^{19}$F NMR, and $^{11}$B NMR spectroscopy, UV-vis absorption/emission spectroscopy, IR spectroscopy, GPC, TGA, and DSC. In order to find the ratio of BF$_2$N and DND subunit in the copolymers, $^1$H NMR spectroscopy was used where integrations of the backbone alkene protons and 2 aryl protons on the BF$_2$N subunit were used. GPC was used in order to determine the time at which the polymerizations of PBF$_2$N and PDND were finished, as well as to find $M_n$, $M_w$, and $D$ values for all polymers. For the block copolymers, it was found that the $M_n$ increased as the $f_{BF2}$ increased since more BF$_2$N was allowed to grow off of the initial PDND chain. For the random copolymers, it was found that as the $f_{BF2}$ increased the $M_n$ also increased;
this is because the BF$_2$ portion of the polymer is much heavier than the DND. TGA was used to determine the decomposition point of all polymers. DSC was used to find the $T_g$ of all polymers, and it was found that the block copolymers possessed two distinct $T_g$s, one for the PDND block, and the other for the PBF$_2$N block. The random copolymers possessed only one $T_g$; this $T_g$ increased as $f_{BF2}$ increased. All polymers showed strong $\lambda_{max}$ ranging from 558–561 nm in CH$_2$Cl$_2$ and $\lambda_{em}$ from 663–667 nm. The absorbance of all the polymers increased as the $f_{BF2}$ increased. The $\Phi_F$ for the random copolymers increased as $f_{BF2}$ decreased; this was attributed to the fact that in the chain with less BF$_2$N subunits, each BF$_2$N subunit would be further apart from the other, minimizing self-absorption. In developing this random copolymerization process, we have also created a dilution strategy allowing for emission intensity of BF$_2$ formazanate polymers to be maximized. It was also concluded that no $\pi$-stacking was occurring due to the absence of a red-shift in the absorbance and/or emission spectra. The block copolymers had a low $\Phi_F$ and were essentially non-emissive. PBF$_2$N, (PDND)$_{276}$-b-(PBF$_2$N)$_{255}$, and (PDND)$_{316}$-r-(PBF$_2$N)$_{316}$ were found to be redox active, and exhibited two reversible one-electron reduction waves.

3.4. Experimental

3.4.1 General Considerations

Reactions and manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques unless otherwise stated. Solvents were obtained from Caledon Laboratories, dried using an Innovative Technologies Inc. solvent purification system, collected under vacuum, and stored under a nitrogen atmosphere over 4 Å molecular sieves. All other reagents were purchased from Sigma Aldrich, Alfa Aesar or TCI America and used as received.

NMR spectra were recorded on a 400 MHz ($^1$H: 399.8 MHz, $^{11}$B: 128.3 MHz, $^{19}$F: 376.1 MHz, $^{13}$C: 100.5 MHz) or 600 MHz ($^{13}$C: 150.7 MHz) Varian INOVA instruments. $^1$H NMR spectra were referenced to residual CHCl$_3$ at 7.27 ppm and $^{13}$C NMR spectra were referenced to CDCl$_3$ at 77.00 ppm. $^{11}$B NMR spectra were referenced internally to BF$_3$•OEt$_2$ at 0 ppm. $^{19}$F NMR spectra were referenced internally to CFCl$_3$ at 0 ppm. UV-vis absorption spectra were recorded using a Cary 5000 Scan instrument using standard quartz cells (1 cm path length) with a scan
range of 200 to 800 nm. Emission spectra were recorded using a Photon Technology Internation QM–4 SE spectrofluorometer. Emission quantum yields were estimated relative to \([\text{Ru(bpy)}_3][\text{PF}_6]_2\) and corrected for wavelength dependent detector sensitivity (Figure C1). FT-IR spectra were recorded using a Perkin Elmer Spectrum Two FT-IR spectrometer.

### 3.4.2 Electrochemical Methods

Cyclic voltammetry experiments were performed with a Bioanalytical Systems Inc. (BASi) Epsilon potentiostat and analyzed using BASi Epsilon software. Typical electrochemical cells consisted of a three-electrode setup including a glassy carbon working electrode, platinum counter electrode, and silver pseudo reference electrode. Experiments were run at 250 mV s\(^{-1}\) in degassed CH\(_2\)Cl\(_2\) solutions of the analyte (~1 mM) and electrolyte (0.1 M [\(n\text{Bu}_4\text{N}\)][PF\(_6\)]). Cyclic voltammograms were internally referenced against the ferrocene/ferrocenium redox couple (~1 mM internal standard) and corrected for internal cell resistance using the BASi Epsilon software.

### 3.4.3 Gel Permeation Chromatography

GPC was carried out at a flow rate of 1 mL min\(^{-1}\) in DMF with 10 mM LiBr and 1% (v/v) Et\(_3\)N added at a regulated temperature of 85 °C using a Waters 515 pump, equipped with a Wyatt Optilab REx detector and two PLgel 5 μm mixed-D (300 mm × 7.5 mm) columns from Polymer Laboratories connected in series. Calibration was performed using monodisperse polystyrene standards supplied by Polymer Lab.

### 3.4.4 Thermal Analysis

Thermal degradation studies were performed using a TA Instruments Q50 TGA. The samples were placed in a platinum pan and heated at a rate of 10 °C min\(^{-1}\) from 25 °C to 1000 °C under a flow of nitrogen (100 mL min\(^{-1}\)). Glass transition temperatures (\(T_g\)s) were determined using Differential Scanning Calorimetry (DSC) on a TA Instruments DSC Q2000. The polymer samples were placed in an aluminum Tzero pan and heated to varying temperature ranges at 10 °C min\(^{-1}\) under a flow of nitrogen (50 mL min\(^{-1}\)) and cooled down to −75 °C at 10 °C min\(^{-1}\), before the sample underwent two more heating/cooling cycles. \(T_g\)s were determined from the third heating/cooling cycle.
3.4.5 Synthetic Procedures

*Synthetic Procedures*

**Cis-5-norbornene-exo-2,3-dicarboxylic anhydride (exo-NDCAn)**

*exo-NDCAn* was synthesized according to a modified version of a procedure previously reported by Alfred et al.\textsuperscript{21} Cis-5-norbornene-endo-2,3-dicarboxylic anhydride *endo-NDCAn* (20.0 g, 122 mmol) was stirred at 210 °C for 2 h. The solution was cooled to 80 °C and 20 mL of toluene were added, which allowed white crystals to crash out. The resulting white crystals were isolated by vacuum filtration and purified by flash chromatography (1:1 *n*-hexanes:EtOAc, silica gel) where the first fraction contained the desired product. Removal of the solvent *in vacuo* yielded *exo-NDCAn* as a white solid. Yield = 3.11 g, 15%. \textsuperscript{1}H NMR (399.8 MHz, CDCl$_3$): δ 6.34 (br s, 2H, =CH), 3.46 (br s, 2H, CH), 3.00 (br s, 2H, CH), 1.67 (d, \textsuperscript{3}J$_{HH}$ = 10 Hz, 1H, CH$_2$), 1.45 (d, \textsuperscript{3}J$_{HH}$ = 10 Hz, 1H, CH$_2$). These data are consistent with previous reports.\textsuperscript{21}

**Cis-dimethyl-5-norbornene-exo-2,3-dicarboxylate (DND)**

*Cis-dimethyl-5-norbornene-exo-2,3-dicarboxylate (DND)* was synthesized by a modified version of a procedure reported by Hennis et al.\textsuperscript{22} In air, *exo-NDCAn* (2.47 g, 15.0 mmol) was dissolved in 5.5 mL of MeOH and 0.25 mL of 12 M HCl. This solution was refluxed for 2 h. After cooling to room temperature, the solution was concentrated *in vacuo* and then washed with 2 x 25 mL of a saturated solution of NaHCO$_3$ and 1 x 25 mL of H$_2$O and dried over MgSO$_4$, gravity filtered and concentrated *in vacuo* to afford monomer *DND* as a white solid. Yield = 1.83 g, 58%. \textsuperscript{1}H NMR (399.8 MHz, CDCl$_3$): δ 6.21 (br s, 2H, =CH), 3.66 (br s, 6H, CH$_3$), 3.10 (m, 2H, CH), 2.63 (m, 2H, CH), 2.12 (d, \textsuperscript{3}J$_{HH}$ = 9 Hz, 1H, diastereotopic CH$_2$), 1.51 (d, \textsuperscript{3}J$_{HH}$ = 9 Hz, 1H, diastereotopic CH$_2$). These data are consistent with previous reports.\textsuperscript{22}

*Representative ROMP of DND*

Monomer *DND* (0.100 g, 0.476 mmol) was dissolved in 1.9 mL of dry and degassed (*via* three freeze-pump-thaw cycles) DMA, and the solution was stirred at 23 °C for 15 min. Meanwhile, GIII (0.0126 g, 0.0142 mmol) was dissolved in 0.3 mL of dry and degassed (*via* three freeze-pump-thaw cycles) DMA. A 0.1 mL
portion of the solution of GIII (0.0042 g, 1 mol %) was then added to the solution of monomer DND and stirred at 23 °C for 6 min. After 6 min, ethyl vinyl ether (0.857 g, 0.62 mL, 11.9 mmol) was added and the solution was stirred at 23 °C for 30 min. The product was precipitated from pentane, isolated by centrifugation, and dried at 23 °C in vacuo for 16 h to afford PDND as a white solid. Yield = 0.075 g, 75%. \[^{1}\]H NMR (399.8 MHz, CDCl\(_3\)): \(\delta 5.42\) and \(5.24\) (br m, 2H, =CH), \(3.64\) (br s, 6H, 2 x OCH\(_3\)), \(3.38\) (br s, 1H, CH), \(2.98\) (br m, 1H, CH), \(2.85\) (br m, 2H, 2 x CH), \(2.07\) (br m, 1H, diastereotopic CH\(_2\)), \(1.23\) (br m, 1H, diastereotopic CH\(_2\)). GPC: \(M_n = 38820\) g mol\(^{-1}\), \(M_w = 43070\) g mol\(^{-1}\), \(D = 1.11\). These data are consistent with previous reports.\(^{27}\)

**Representative polymerization of BF\(_2\)N**

Monomer BF\(_2\)N (0.050 g, 0.087 mmol) was dissolved in 1.9 mL of dry and degassed (via three freeze-pump-thaw cycles) DMA, and the solution was stirred at 23 °C for 15 min. Meanwhile, GIII (0.003 g, 1 mol %) was dissolved in 0.3 mL of dry and degassed (via three freeze-pump-thaw cycles) DMA. A 0.1 mL portion of the solution of GIII (0.001 g, 1 mol %) was then added to the solution of monomer BF\(_2\)N and stirred at 23 °C for exactly 1 h. After 1 h, ethyl vinyl ether (0.157 g, 2.18 mmol) was added and the solution was stirred at 23 °C for 30 min. The resulting dark-purple solution was purified by flash chromatography (THF, neutral alumina), and the product was precipitated from pentane, isolated by centrifugation, and dried at 23 °C in vacuo for 16 h to afford polymer PBF\(_2\)N as a purple solid. Yield = 0.030 g, 66%. \[^{1}\]H NMR (399.8 MHz, CDCl\(_3\)): \(\delta 7.97\) (br s, 1 H, triazole CH), \(7.84\) (br s, 6 H, aryl CH), \(6.92\) (br s, 2 H, aryl CH), \(5.35\)–\(5.25\) (2 x br m, 2H, =CH), \(4.45\) (br s, 2H, CH\(_2\)), \(4.07\) (br s, 2H, CH\(_2\)), \(3.84\) (br s, 3H, OCH\(_3\)), \(3.13\) (br s, 1H, CH), \(2.84\) (br m, 2H, 2CH), \(2.24\) (br s, 2H, CH\(_2\)), \(1.90\) (br m, 2H, diastereotopic CH\(_2\)), \(1.71\) (br m, 1H, diastereotopic CH\(_2\)), \(1.30\) (br m, 1H, diastereotopic CH\(_2\)). \[^{11}\]B NMR (128.3 MHz, CDCl\(_3\)): \(\delta -0.8\) (t, \(J_{BF} = 30\) Hz). \[^{19}\]F NMR (376.1 MHz, CDCl\(_3\)): \(\delta -133.4\) (br s). FT-IR (ATR): 3153 (w), 2952 (m), 2843 (m), 2243 (m), 1729 (s), 1598 (s), 1506 (m), 1343 (s), 1263 (s) cm\(^{-1}\). UV-vis (CH\(_2\)Cl\(_2\)): \(\lambda_{max} = 555\) nm (\(\varepsilon = 27,500\) M\(^{-1}\) cm\(^{-1}\)). GPC: \(M_n = 201,500\) g mol\(^{-1}\), \(M_w = 264,300\) g mol\(^{-1}\), \(D = 1.31\).
Block Copolymers:

Representative procedure for the preparation of block copolymers (PDND)$_m$-$b$-(PBF$_2$N)$_n$

(PDND)$_{276}$-$b$-(PBF$_2$N)$_{255}$ ($f_{BF_2} = 0.48$)

Monomer DND (0.150 g, 0.713 mmol) was dissolved in 2.9 mL of dry and degassed (*via* three freeze-pump-thaw cycles) DMA, and the solution was stirred at 23 °C for 15 min. Meanwhile, GIII (0.019 g, 0.021 mmol) was dissolved in 0.3 mL of dry and degassed (*via* three freeze-pump-thaw cycles) DMA, and BF$_2$N (0.272 g, 0.475 mmol) was dissolved in 0.64 mL of dry and degassed (*via* three freeze-pump-thaw cycles) DMA. A 0.1 mL portion of the solution of GIII (0.0063 g, 1 mol %) was then added to the solution of monomer DND and stirred at 23 °C for 6 min. After 6 min, 1 mL of the reaction solution was removed and added to ethyl vinyl ether (0.429 g, 0.31 mL, 5.95 mmol) and stirred at 23 °C for 30 min. After removal of the 1 mL aliquot of the reactant solution, the BF$_2$N solution was added and stirred at 23 °C for 12 min. After 12 min, ethyl vinyl ether (0.857 g, 0.62 mL, 11.9 mmol) was added and the solution was stirred at 23 °C for 30 min. The aliquot removed after 6 min was clear and the product colourless and was precipitated from pentane, isolated by centrifugation, and dried *in vacuo* for 16 h to afford polymer PDND as a white solid. GPC: $M_n = 38,820$ g mol$^{-1}$, $M_w = 43,070$ g mol$^{-1}$, $D = 1.11$. The second solution was dark-purple, and the product was purified by precipitation into pentane, isolated by centrifugation and dried at 23 °C *in vacuo* for 16 h to afford polymer (PDND)$_{276}$-$b$-(PBF$_2$N)$_{255}$ as a purple solid in quantitative yield. $^1$H NMR (399.8 MHz, CDCl$_3$): $\delta$ 7.97 (br s, 1H, triazole CH), 7.83 (br m, 6H, aryl CH), 6.91 (br s, 2H, aryl CH), 5.42–5.24 (2 x br m, 4.2H, =CH), 4.44 (br s, 2H, CH$_2$), 4.07 (br s, 2H, CH$_2$), 3.83 (br s, 3H, OCH$_3$), 3.64 (br s, 6.6H, 2 x OCH$_3$), 3.38 (br s, 1H, CH), 3.13 (br s, 1H, CH),
2.98–2.85 (br m, 5H, CH), 2.25 (br s, 2H, CH₂), 2.05 (br m, 1H, diastereotopic CH₂), 1.92 (br m, 2H, diastereotopic CH₂), 1.72 (br m, 1H, diastereotopic CH₂), 1.34–1.16 (br m, 2H, diastereotopic CH₂). ¹¹B NMR (128.3 MHz, CDCl₃): δ −0.8 (t, ¹JBF = 30 Hz). ¹⁹F NMR (376.1 MHz, CDCl₃): δ −133.4 (br s). FT-IR (ATR): 3138 (w), 2955 (m), 2849 (m), 2240 (s), 1733 (s), 1597 (s), 1505 (m), 1343 (s), 1261 (s) cm⁻¹. UV-vis (CH₂Cl₂): λ max = 556 nm. GPC: Mₙ = 204,300 g mol⁻¹, Mₓ = 295,400 g mol⁻¹, D = 1.45.

(PDND)₃₅₅-b-(PBF₂N)₅₃ (f BF₂ = 0.13)

From monomer DND (0.250 g, 1.19 mmol) and BF₂N (0.109 g, 0.190 mmol). The aliquot removed at 6 min yielded polymer PDND. GPC: Mₙ = 54,910 g mol⁻¹, Mₓ = 62,670 g mol⁻¹, D = 1.14. The second solution afforded polymer (PDND)₃₅₅-b-(PBF₂N)₅₃ in quantitative yield. ¹H NMR (399.8 MHz, CDCl₃): δ 7.97 (br s, 1 H, triazole CH), 7.85 (br s, 6 H, aryl CH), 6.93 (br s, 2 H, aryl CH), 5.43–5.24 (2 x br m, 15.8 H, =CH), 4.46 (br s, 2H, CH₂), 4.08 (br s, 2H, CH₂), 3.85 (br s, 3H, OCH₃), 3.64 (br s, 41H, OCH₃), 3.38 (br s, 7H, CH), 3.13 (br s, 1H, CH), 3.02–2.85 (br m, 21H CH), 2.25 (br s, 2H, CH₂), 2.07 (br m, 7H, diastereotopic CH₂), 1.91 (br m, 2H, diastereotopic CH₂), 1.70 (br m, 1H, diastereotopic CH₂), 1.33–1.14 (br m, 8H, diastereotopic CH₂). ¹¹B NMR (128.3 MHz, CDCl₃): δ −0.8 (t, ¹JBF = 30 Hz). ¹⁹F NMR (376.1 MHz, CDCl₃): δ −133.5 (br s). FT-IR (ATR): 2989 (w), 2950 (m), 2849 (w), 2240 (s), 1733 (s), 1599 (s), 1436 (m), 1345 (s), 1263 (s) cm⁻¹. UV-vis (CH₂Cl₂): λ max = 556 nm. GPC: Mₙ = 104,000 g mol⁻¹, Mₓ = 126,300 g mol⁻¹, D = 1.21.

(PDND)₂₆₆-b-(PBF₂N)₂₀ (f BF₂ = 0.07)

From monomer DND (0.300 g, 1.43 mmol) and BF₂N (0.068 g, 0.119 mmol). The aliquot removed at 6 min yielded polymer PDND. GPC: Mₙ = 42,810 g mol⁻¹, Mₓ = 48,610 g mol⁻¹, D = 1.13. The second solution afforded polymer (PDND)₂₆₆-b-(PBF₂N)₂₀ in quantitative yield. ¹H NMR (399.8 MHz, CDCl₃): δ 7.98 (br s, 1 H, triazole CH), 7.89 (br s, 6 H, aryl CH), 6.96 (br s, 2 H, aryl CH), 5.43–5.24 (2 x br m, 27H, =CH), 4.47 (br s, 2H, CH₂), 4.09 (br s, 2H, CH₂), 3.88 (br s, 3H, OCH₃), 3.64 (br s, 73H, OCH₃), 3.38 (br s, 13H, CH), 3.13 (br s, 1H, CH), 3.02–2.85 (br m, 40 H, CH), 2.27 (br s, 2H, CH₂), 2.07 (br m, 13H, diastereotopic CH₂), 1.91 (br m, 2H, diastereotopic CH₂), 1.70 (br m, 1H, diastereotopic CH₂), 1.30–1.17 (br m, 14H, diastereotopic CH₂). ¹¹B NMR (128.3 MHz, CDCl₃): δ −0.7 (t, ¹JBF = 30 Hz). ¹⁹F NMR
(376.1 MHz, CDCl$_3$): $\delta$ –134.0 (br s). FT-IR (ATR): 3000 (w), 2951 (m), 2848 (m), 1733 (s), 1599 (m), 1436 (s), 1362 (m), 1264 (s) cm$^{-1}$. UV-vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ = 558 nm. GPC: $M_n$ = 66,040 g mol$^{-1}$, $M_w$ = 76,370 g mol$^{-1}$, $D$ = 1.16.

Random Copolymers:

Representative procedure for the preparation of random copolymers (PDND)$_m$-$(PBF_2N)_n$

(PDND)$_{316}$-$r$-(PBF$_2$N)$_{316}$ ($f_{BF_2} = 0.50$)

Monomer BF$_2$N (0.150 g, 0.262 mmol) and DND (0.055 g, 0.262 mmol) was dissolved in 3.9 mL of dry and degassed (via three freeze-pump-thaw cycles) DMA, and the solution was stirred at 23 °C for 15 min. Meanwhile, GIII (0.0092 g, 0.0104 mmol) was dissolved in 0.4 mL of dry and degassed (via three freeze-pump-thaw cycles) DMA. A 0.2 mL portion of the solution of GIII (0.0046 g, 1 mol %) was then added to the solution of monomer BF$_2$N and DND and stirred at 23 °C for exactly 12 min. After 12 min, ethyl vinyl ether (0.945 g, 0.69 mL, 13.1 mmol) was added and the solution was stirred at 23 °C for 30 min. The resulting dark-purple solution was purified by precipitation from pentane, isolated by centrifugation, and dried at 23 °C in vacuo for 16 h to afford (PDND)$_{316}$-$r$-(PBF$_2$N)$_{316}$ as a purple solid. Yield = 0.248 g, 60%. $^1$H NMR (399.8 MHz, CDCl$_3$): $\delta$ 7.90 (br m, 7 H, triazole CH + aryl CH), 6.97 (br s, 2 H, aryl CH), 5.41–5.23 (2 x br m, 4H, =C CH), 4.49 (br s, 2H, CH$_2$), 4.11 (br s, 2H, CH$_2$), 3.88 (br s, 3H, OCH$_3$), 3.63 (br s, 3H, OCH$_3$), 3.35 (br s, 1H, CH), 3.13 (br s, 1H, CH), 2.98–2.85 (br m, 5H, CH), 2.29 (br s, 2H, CH$_2$), 2.07–1.91 (br m, 3H, diastereotopic CH$_2$), 1.72 (br m, 1H, diastereotopic CH$_2$), 1.36–1.20 (br m, 2H, diastereotopic CH$_2$). $^{11}$B NMR
(128.4 MHz, CDCl₃): δ –0.7 (t, JBF = 30 Hz). ¹⁹F NMR (376.4 MHz, CDCl₃): δ –133.8 (br s).
FT-IR (ATR): 2980 (w), 2951 (m), 2845 (m), 2240 (m), 1736 (s), 1604 (s), 1505 (m), 1348 (s), 1263 (s) cm⁻¹. UV-vis (CH₂Cl₂): λ_max = 558 nm. GPC: M_n = 247,300 g mol⁻¹, M_w = 335,200 g mol⁻¹, D = 1.36.

(PDND)₂⁹²₋ᵣ₋(PBF₂N)₅₂ (f_{BF²} = 0.15)

From monomer BF₂N (0.030 g, 0.053 mmol) and DND (0.056 g, 0.265 mmol). Yield = 0.81 g, 94%. ¹H NMR (399.8 MHz, CDCl₃): δ 8.04 (br s, 1 H, triazole CH), 7.95 (br s, 6 H, aryl CH), 7.00 (br s, 2 H, aryl CH), 5.42–5.24 (2 x br m, 13H, =CCH), 4.51 (br s, 2H, CH₂), 4.14 (br s, 2H, CH₂), 3.91 (br s, 3H, OCH₃), 3.63 (br s, 3H, OCH₃), 3.37 (br s, 3H, CH), 3.13 (br s, 1H, CH), 2.98–2.85 (br m, 19 H, CH₂), 2.29 (br s, 2H, CH₂), 2.06 (br m, 6H, diastereotopic CH₂), 1.90 (br m, 2H, diastereotopic CH₂), 1.72 (br m, 1H, diastereotopic CH₂), 1.38 (br m, 1H, diastereotopic CH₂), 1.30–1.16 (br m, 5.5 H, diastereotopic CH₂). ¹¹B NMR (128.3 MHz, CDCl₃): δ –0.7 (t, JBF = 31 Hz). ¹⁹F NMR (376.1 MHz, CDCl₃): δ –134.0 (br s). FT-IR (ATR): 2998 (m), 2952 (m), 2850 (m), 1733 (s), 1599 (w), 1436 (m), 1364 (m), 1267 (s) cm⁻¹. UV-vis (CH₂Cl₂): λ_max = 560 nm. GPC: M_n = 90,890 g mol⁻¹, M_w = 107,000 g mol⁻¹, D = 1.18.

(PDND)₂⁹⁸₋ᵣ₋(PBF₂N)₂⁶ (f_{BF²} = 0.08)

From monomer BF₂N (0.021 g, 0.036 mmol) and DND (0.076 g, 0.362 mmol). Yield = 0.85 g, 88%. ¹H NMR (399.8 MHz, CDCl₃): δ 8.05 (br s, 1 H, triazole CH), 7.94 (br s, 6 H, aryl CH), 7.01 (br m, 2 H, aryl CH), 5.42–5.24 (2 x br m, 13H, =CCH), 4.51 (br s, 2H, CH₂), 4.14 (br s, 2H, CH₂), 3.91 (br s, 3H, OCH₃), 3.63 (br s, 3H, OCH₃), 3.37 (br s, 12H, CH), 3.14 (br s, 1H, CH), 3.02–2.84 (br m, 36 H, CH), 2.28 (br s, 2H, CH₂), 2.07 (br m, 12H, diastereotopic CH₂), 1.90 (br m, 2H, diastereotopic CH₂), 1.73 (br m, 1H, diastereotopic CH₂), 1.33–1.19 (br m, 13 H, diastereotopic CH₂). ¹¹B NMR (128.3 MHz, CDCl₃): δ –0.7 (t, JBF = 33 Hz). ¹⁹F NMR (376.1 MHz, CDCl₃): δ –134.0 (br s). FT-IR (ATR): 2998 (m), 2952 (m), 2850 (m), 1733 (s), 1599 (w), 1436 (m), 1364 (m), 1264 (m) cm⁻¹. UV-vis (CH₂Cl₂): λ_max = 561 nm. GPC: M_n = 77,490 g mol⁻¹, M_w = 88,820 g mol⁻¹, D = 1.15.
3.5 References


Chapter 4

4  Conclusions and Future Work

4.1  Conclusions

This thesis describes the development of synthetic procedures required to produce asymmetric and symmetric 3-cyanoformazanate BF$_2$ complexes and the incorporation of the first reported asymmetric 3-cyanoformazanate BF$_2$ complex (2.13) into polymers using ROMP. The work began by synthesizing asymmetric 3-cyanoformazans using a different whereby the asymmetric formazan was isolated from a mixture containing symmetric derivatives through column chromatography. The BF$_2$ complex of this formazan was then synthesized by stirring it in a solution of toluene and excess Et$_3$N and BF$_3$•OEt$_2$ under an inert atmosphere at 80 °C overnight. Using CuAAC chemistry two additional BF$_2$ complexes were synthesized, one containing a benzyl group (2.14) and the other a polymerizable norbornene group (2.17); the latter would become the monomer used for future polymerization studies. The reaction used to make the monomer yielded a side product which was identified to be a dimer (2.18) of BF$_2$ complex 2.13; connectivity of both of these structures was determined through X-ray crystallographic studies. Spectroscopic properties of all the BF$_2$ complexes synthesized revealed strong $\lambda_{\text{max}}$ ranging from 552–597 nm in CH$_2$Cl$_2$ and $\lambda_{\text{em}}$ from 647–687 nm. It was observed that the introduction of a triazole ring in compound 2.14 and monomer 2.17 caused a red-shift in the $\lambda_{\text{max}}$ and $\lambda_{\text{em}}$ (relative to 2.13). This was attributed to an increase in the extent in electronic conjugation. A greater red-shift was observed for dimer 2.18; this was concluded to be due to the extent of conjugation along both chromophores. Quantum yields of fluorescence for compounds 2.13, 2.14 and 2.17 ranged from 29–30% in CH$_2$Cl$_2$. Dimer 2.18 was found to be non-emissive, most likely due to intramolecular quenching of the adjacent chromophores. All compounds were redox active and possessed two reversible reduction processes in their cyclic voltammograms that yielded a radical anion, and dianion. Introduction of a triazole ring resulted in the need for a more negative potential to be attained before reduction occurred (relative to 2.13); this was due to the electron donating character of this group. Conversely, dimer 2.18 could be reduced at a lower potential (relative to 2.13); this was
attributed to the increase in conjugation and the BF\textsubscript{2} complex-substituted alkyne’s withdrawing effects.

![Chemical structures](image)

**Figure 4.1.** BF\textsubscript{2} complexes studied in Chapter 2.

Polymers containing 3-cyanoformazanate BF\textsubscript{2} complex (\textbf{2.13}/BF\textsubscript{2}N) in the side chain were synthesised using ROMP. Homopolymers (PBF\textsubscript{2}N) were synthesized by using GIII; the DP\textsubscript{n} per polymer chain was targeted to be 100 (1 mol % catalyst). Block and random copolymers of BF\textsubscript{2}N and \textit{cis}-dimethyl-5-norbornene-	extit{exo}-2,3-dicarboxylate (DND) were also synthesized. For block copolymers (PDND)\textsubscript{m-b-(PBF\textsubscript{2}N)}\textsubscript{n}, the first block (PDND) was targeted to have a DP\textsubscript{n} of 100, whereas the second block (PBF\textsubscript{2}N) differed in length based on the mole ratio of BF\textsubscript{2}N added to the living end of the first block. This difference gave rise to three separate block copolymers that differed in the \(f_{BF2}\). In the case of the random copolymers (PDND)\textsubscript{m-r-}
(PBF\textsubscript{2}N)\textsubscript{n}, they all had targeted degrees of polymerization of 100 and differing \( f_{BF2} \). \(^1\text{H} \) NMR, \(^{19}\text{F} \) NMR, and \(^{11}\text{B} \) NMR spectroscopy, UV-vis absorption/emission spectroscopy, IR spectroscopy, GPC, TGA, and DSC were used in order to characterize all of the polymers synthesized. GPC data for the block copolymers and PDND revealed that as the \( f_{BF2} \) increased, the \( M_n \) of the polymers also increased. This was also true for the random copolymers. In both cases, molecular weights for polymers containing BF\textsubscript{2}N were over estimated. TGA revealed PDND to be more thermally stable than PBF\textsubscript{2}N, and the block and random copolymers increased in thermal stability as the \( f_{BF2} \) decreased. DSC revealed two \( T_g \) s for the block copolymers, the first one pertaining to the PDND block, and the second to the PBF\textsubscript{2}N block. Random copolymers had one \( T_g \), and it was observed that as the \( f_{BF2} \) increased, the \( T_g \) also increased. All BF\textsubscript{2} containing polymers had strong \( \lambda_{max} \) ranging from 558–561 nm in \( \text{CH}_2\text{Cl}_2 \) and \( \lambda_{em} \) from 663–667 nm. The block copolymers were found to be non-emissive, while the random copolymers showed an increase in the \( \Phi_F \) as the \( f_{BF2} \) decreased (Figure 4.1). This was attributed to the fact that in the random copolymers, BF\textsubscript{2}N subunits would be further apart as the \( f_{BF2} \) decreased, which would lead to less self-absorption and thus a higher \( \Phi_F \). All BF\textsubscript{2} containing polymers were also found to be redox active, and exhibited two reversible one-electron reduction waves.

Synthesis of the first asymmetric BF\textsubscript{2} complex has opened up a way to synthesize various functional fluorescent molecules by using CuAAC chemistry. ROMP was demonstrated to be an efficient way to incorporate these complexes into polymers; these polymers demonstrated interesting properties, which showed their potential use as functional fluorescent materials.

![Figure 4.2](image-url)

**Figure 4.2.** Block and random copolymers of PBF\textsubscript{2}N and PDND studied in Chapter 3.
4.2 Future Work

Future work in this area will involve the synthesis of amphiphilic fluorescent block copolymers (e.g., 4.1 and 4.2) that can self-assemble into micelles. The first block will ideally have very different solubility properties than the second.\textsuperscript{1-2} The second block will be a random copolymer of PBF\textsubscript{2}N and PDND, where the $f_{BF2}$ should be less than 0.10 so that the $\Phi_F$ is high enough to eventually make fluorescent micelles whereby the fluorescence will allow for micelle formation to be followed using laser confocal microscopy. It is hypothesized that when the PBF\textsubscript{2}N / PDND block is found on the outside of micelles (the corona) fluorescence from the subunit will be observed. However, if the PBF\textsubscript{2}N / PDND containing block is found on the inside of the micelles, the close proximity of the PBF\textsubscript{2}N subunits may quench the fluorescence.

![Block copolymers 4.1 and 4.2](image)

\textbf{Figure 4.3.} Block copolymers 4.1 and 4.2. The cartoon is a representation of the block copolymer where the blue represents the first block (BF\textsubscript{2} containing random copolymer) and the black represents the non-fluorescent organic block.
Figure 4.4. Visual representation of micelle formation of block copolymers 4.1 and 4.2. Yellow cartoon around the micelle on the right represents fluorescence.

4.3 References


Appendices

Appendix 1 - Supporting Information for Chapter 2

Figure A2.1. $^1$H NMR spectrum of formazan 2.12 in DMSO-$d_6$.

Figure A2.2. $^{13}$C($^1$H) NMR spectrum of 2.12 in DMSO-$d_6$. The asterisk denotes solvent signals.
Figure A2.3. $^1$H NMR spectrum of BF$_2$ complex 2.13 in CDCl$_3$.

Figure A2.4. $^{13}$C($^1$H) NMR spectrum of BF$_2$ complex 2.13 in CDCl$_3$. 
Figure A2.5. $^{11}$B NMR spectrum of BF$_2$ complex 2.13 in CDCl$_3$.

Figure A2.6. $^{19}$F NMR spectrum of BF$_2$ complex 2.13 in CDCl$_3$. 
Figure A2.7. $^1$H NMR spectrum of benzyl-substituted BF$_2$ complex 2.14 in CDCl$_3$.

Figure A2.8. $^{13}$C/$^1$H NMR spectrum of benzyl-substituted BF$_2$ complex 2.14 in CDCl$_3$. 
Figure A2.9. $^{11}$B NMR spectrum of benzyl-substituted BF$_2$ complex 2.14 in CDCl$_3$.

Figure A2.10. $^{19}$F NMR spectrum of benzyl-substituted BF$_2$ complex 2.14 in CDCl$_3$. 
Figure A2.11. $^1$H NMR spectrum of azide-substituted norbornene 2.16 in CDCl$_3$.

Figure A2.12. $^{13}$C($^1$H) NMR spectrum of azide-substituted norbornene 2.16 in CDCl$_3$. 
Figure A2.13. $^1$H NMR spectrum of monomer 2.17 in CDCl$_3$.

Figure A2.14. $^{13}$C($^1$H) NMR spectrum of monomer 2.17 in CDCl$_3$. 
Figure A2.15. $^{11}$B NMR spectrum of monomer 2.17 in CDCl$_3$.

Figure A2.16. $^{19}$F NMR spectrum of monomer 2.17 in CDCl$_3$. 
Figure A2.17. $^1$H NMR spectrum of dimer 2.18 in CD$_2$Cl$_2$.

Figure A2.18. $^{13}$C NMR spectrum of dimer 2.18 in CD$_2$Cl$_2$. 

H NMR spectrum of dimer 2.18 in CD$_2$Cl$_2$.

C NMR spectrum of dimer 2.18 in CD$_2$Cl$_2$. 

Chemical Shift (ppm)
Figure A2.19. $^{11}$B NMR spectrum of dimer 2.18 in CD$_2$Cl$_2$.

Figure A2.20. $^{19}$F NMR spectrum of dimer 2.18 in CD$_2$Cl$_2$. 
Figure A2.21. Wavelength-dependent emission correction provided by Photon Technology International.
Figure A3.1. $^1$H NMR spectrum of *exo-NDCA* in CDCl$_3$.

Figure A3.2. $^1$H NMR spectrum of *exo-NDCA* in CDCl$_3$.
Figure A3.3. $^1$H NMR spectrum of P-exo-NDCA in DMSO-$d_6$.

Table A3.1. Summary of molecular weight data determined by GPC for P-exo-NDCA.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>$D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>26,740</td>
<td>23,710</td>
<td>1.13</td>
</tr>
<tr>
<td>2</td>
<td>46,300</td>
<td>33,480</td>
<td>1.38</td>
</tr>
<tr>
<td>3</td>
<td>49,830</td>
<td>43,430</td>
<td>1.15</td>
</tr>
<tr>
<td>4</td>
<td>57,120</td>
<td>53,170</td>
<td>1.07</td>
</tr>
<tr>
<td>5</td>
<td>61,590</td>
<td>53,690</td>
<td>1.15</td>
</tr>
<tr>
<td>6</td>
<td>63,970</td>
<td>59,010</td>
<td>1.08</td>
</tr>
</tbody>
</table>
Figure A3.4. Relationship between number average molecular weight ($M_n$) of $\text{P-exo-NDCA}$ as a function of time (min).

Figure A3.5. Corresponding GPC traces for $\text{PBF}_2\text{N}$ and $(\text{PBF}_2\text{N})-b-(\text{P-exo-NDCA})$. 

Figure A3.6. $^1$H NMR spectrum of DND in CDCl$_3$.

Figure A3.7. $^1$H NMR spectrum of PDND in CDCl$_3$. 
Figure A3.8. $^1$H NMR spectrum of PBF$_2$N in CDCl$_3$.

Figure A3.9. $^{19}$F NMR (left) spectrum and $^{11}$B NMR (right) of PBF$_2$N in CDCl$_3$. 
Figure A3.10. $^1$H NMR spectrum of $(PDND)_{276-b-(PBF_2N)_{255}}$ ($f_{BF2} = 0.48$) in CDCl$_3$.

Figure A3.11. $^1$H NMR spectrum of $(PDND)_{355-b-(PBF_2N)_{53}}$ ($f_{BF2} = 0.13$) in CDCl$_3$. 
Figure A3.12. $^1$H NMR spectrum of \((\text{PDND})_{266-b-(PBF}_2\text{N})_{20}\) \((f_{BF2} = 0.07)\) in CDCl$_3$.

Figure A3.13. $^1$H NMR spectrum of \((\text{PDND})_{316-r-(PBF}_2\text{N})_{316}\) \((f_{BF2} = 0.50)\) in CDCl$_3$. 
Figure A3.14. $^1$H NMR spectrum of (PDND)$_{292-r}$-(PBF$_2$N)$_{52}$ ($f_{BF} = 0.15$) in CDCl$_3$.

Figure A3.15. $^1$H NMR spectrum of (PDND)$_{298-r}$-(PBF$_2$N)$_{26}$ ($f_{BF} = 0.08$) in CDCl$_3$. 
**Figure A3.16.** Representative $^{11}$B NMR and $^{19}$F NMR for block and random copolymers in CDCl$_3$.

**Figure A3.17.** Cyclic voltammograms for BF$_2$N (dark yellow), PBF$_2$N (black), (PDND)$_{276}$-$b$-(PBF$_2$N)$_{255}$ (blue), and (PDND)$_{316}$-$r$-(PBF$_2$N)$_{316}$ (red), were recorded at a scan rate of 250 mV s$^{-1}$ for 1 mM analyte solutions (calculated using an average molar mass for blocks and random copolymers from $f_{BF2}$ in each) in CH$_2$Cl$_2$ containing 0.1 M $[n$Bu$_4$N][PF$_6$] as the supporting electrolyte. Voltammograms were referenced internally against the ferrocence/ferrocenium redox couple.
Curriculum Vitae

Name: Samantha Novoa

Post-secondary Education and Degrees:
The University of Western Ontario
London, Ontario, Canada
2010-2015 B. Sc.
The University of Western Ontario
London, Ontario, Canada

Honours and Awards:
Ontario Graduate Scholarship (OGS) 2016–2017 $15,000
Canada Graduate Scholarship – Master’s Program (CGS-M) 2015–2016 $17,500
Ontario Graduate Scholarship (OGS) 2015–2016 (declined) $15,000
2nd Place Poster Prize Inorganic Discussion Weekend 2016 $50

Related Work Experience
Teaching Assistant – CH2271
The University of Western Ontario 2015–2017
Teaching Assistant – CH1302
The University of Western Ontario 2015–2017

Publications:


Conferences:


Training Programs/Volunteer Work:

Teacher Assistant Training Program
The University of Western Ontario, 2015/9

Let’s Talk Science Outreach Program
The University of Western Ontario, 2015–present

Western Chemistry Outreach Program
The University of Western Ontario, 2012/6–present

Fall Preview Day and March Break Open House
The University of Western Ontario, 2011/11–present

National Chemistry Awareness Week
The University of Western Ontario, 2011/10–present