DEVELOPMENT OF ORGANIC PI-CONJUGATED MATERIALS: BONDING AND

STRUCTURAL MORPHOLOGY

by

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B.Sc., Western University, 2015

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

in

THE FACULTY OF GRADUATE AND POSTDOCTORAL STUDIES

(Chemistry)

THE UNIVERSITY OF BRITISH COLUMBIA

(Vancouver)

June 2019

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Abstract

Organic semiconductors, which commonly contain π -conjugated systems, have many advantages over inorganic semiconductors. These advantages have generated significant research interest and have allowed for their successful use in a variety of electronic and optoelectronic devices, such as organic light emitting diodes. Herein, we demonstrate a novel method for the synthesis of nitrogencontaining π -conjugated luminescent materials. The typical synthetic methods suffer from disadvantages such as harsh reaction conditions, expensive metal catalysts, and stoichiometric reagents. By using hydroamination, an atom-economic catalytic route to amine-containing compounds, we demonstrate an alternative synthetic method which circumvents these limitations. We also demonstrate a novel synthetic route to polymeric organic semiconducting materials with a fiber-like morphology. Many of the existing methods suffer from the limitation of requiring very specific conditions and monomers. Employing the grafting-from method of bottlebrush synthesis, RAFT and SET-LRP polymerization techniques are used to produce long fiber-like nanowires from arbitrary semiconducting monomers. These cylindrical nanofibers can be applied to a diverse range of organic semiconductors, with potential applications in macroscale optoelectronic devices or as functional nanoscale objects.

Lay Summary

This thesis demonstrates new methods for synthesizing organic materials with applications in electronic devices. Organic materials have significant advantages over inorganic materials, which often contain expensive metals and are more difficult to use in the large-scale synthesis of electronic devices. Furthermore, organic materials tend to be less expensive. Due to these advantages, newer technologies tend to incorporate organic materials in devices, such as televisions made from organic light emitting diodes (OLEDs). In the interest of contributing to the shift from inorganic-based to organic-based devices, this thesis focuses primarily on the development of novel methods to more efficiently synthesize organic materials with applications in electronic devices.

Preface

The design for the research presented in Chapter 2 was done by me, Han Hao (Ph.D. student, Dr. Schafer's group), Dr. Zachary Hudson, and Dr. Laurel Schafer. The synthesis and characterization of compounds **1-7** were done by Han Hao and the synthesis and characterization of compound **8** were done by me. The DFT calculations of compound **8** were done by Dr. Hudson. The research in Chapter 2 has been published, with Han Hao completing the research related to the compounds that do not contain boron and me completing the research related to the triarylborane containing compound. The writing related to the research completed by Han Hao was done by Han Hao, Dr. Hudson and Dr. Schafer. The writing related to the research completed by me was done by Dr. Hudson and myself.

Hao, H.; Thompson, K. A.; Hudson, Z. M.; Schafer, L. L. Chem. Eur. J. 2018, 24, 5562–5568.

The design for the research presented in Chapter 3 was done by myself and Dr. Hudson. The monomers were synthesized by Christopher Tonge (Ph.D. student, Dr. Hudson's group) and Ethan Sauvé (Ph.D. student, Dr. Hudson's group). All other synthesis was completed by me. All characterization was done by me except for the AFM images, which were obtained by Ethan Sauvé. A manuscript based on this research is currently in progress, with writing contributions from Dr. Hudson and myself.

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List of Symbols and Abbreviations

AFM	Atomic force microscopy
ATRP	Atom transfer radical polymerization
BCP	Block copolymer
Ð	Dispersity
dn/dc	Refractive index increment
DP	Degree of polymerization
E _{1/2}	Half wave potential
EML	Emitting layer
ETL	Electron transport layer
GPC	Gel permeation chromatography
НОМО	Highest occupied molecular orbital
HTL	Hole transport layer
ICT	Intramolecular charge transfer
IQE	Internal quantum efficiency
J	Coupling constant
LRP	Living radical polymerization
LUMO	Lowest unoccupied molecular orbital
M _n	Number average molecular weight
MWD	Molecular weight distribution
NMR	Nuclear magnetic resonance spectroscopy
OLED	Organic light-emitting diode
ORTEP	Oak Ridge Thermal-Ellipsoid Plot Program

OTFT	Organic thin film transistors
PDI	Polydispersity index
RAFT	Reversible addition-fragmentation chain transfer
RDRP	Reversible deactivation radical polymerization
RI	Refractive index
ROMP	Ring-opening metathesis polymerization
SARA	Supplemental activation and reducing agent
SEC	Size exclusion chromatography
SET	Single-electron transfer
TADF	Thermally activated delayed fluorescence
UV-Vis	Ultraviolet-visible
δ	Chemical shift
8	Molar extinction coefficient
λ	Wavelength
$arPhi_F$	Fluorescence quantum yield

Acknowledgements

I would first like to thank my supervisor, Dr. Zachary Hudson, for his guidance and encouragement throughout my studies. I greatly valued his advice and his constant inspiration to improve my skills and my ability to think critically and independently as a scientist. Of note, I would very much like to thank him for his patience as I dealt with a chronic medical condition which affected my abilities when I first joined the lab. Due to his flexibility and understanding, I was able to complete my studies at an initially slower pace that allowed me to overcome my injury.

I would also like to thank my co-workers and research collaborators, whose knowledge and advice were invaluable and simplified many aspects of my research that would otherwise have been much more difficult. I would like to thank the exceptional chemistry staff and faculty at UBC who were always willing and able to provide assistance, as well as NSERC for their financial contributions.

Lastly, I would like to thank my family for their constant support throughout a challenging point in my life. Their encouragement helped provide me with the strength and confidence necessary to continue to pursue my education and overcome any adversities I encountered.

Chapter 1 : Introduction

1.1 Organic Semiconductors

Organic semiconductors receive considerable attention due to their applications in electronic and optoelectronic devices, such as solar cells, sensors, organic thin-film-transistors and light-emitting diodes (OLEDs). Interest in organic materials results from their intrinsic advantages over inorganic semiconductors. Organic materials are generally inexpensive, compatible with large area, low cost, and low temperature manufacturing techniques, and are compatible with highthroughput roll-to-roll processing. The flexible and lightweight nature of organic materials is also advantageous. Furthermore, organic materials can be produced on glass, plastic films, or metal foils. This contrasts with devices made from inorganic materials, which often require high-purity crystalline substrates.¹ Two major classes of organic semiconductors are small molecules and conjugated polymers. Small molecule semiconductors are appealing as they can be efficiently purified and can form ordered structures which allow for high charge carrier mobilities. Small molecules can also be used as model systems for fundamental studies of exciton and charge carrier dynamics.² Polymeric semiconductors, the other major class of organic semiconductors, have some distinct advantages over molecular semiconductors. Thin films of polymeric materials are generally very smooth and uniform, allowing for excellent control over a large range of the film structural and morphological characteristics. Solution rheological properties can be tuned efficiently for polymeric materials, allowing for more effective printing compared to small molecules. Furthermore, polymers are not susceptible to interlayer diffusion during thermal cycles in device fabrication and typically exhibit robust mechanical properties.³ As molecular and polymeric semiconducting materials both have distinct advantages, we will explore both classes in this thesis. Although organic semiconductors have many applications, we will focus largely on the applications of these materials in organic LEDs.

1.2 Luminescence

OLEDs operate based on luminescence, which is the emission of light from an electronically excited state of a species. There are two main forms of luminescence: fluorescence and phosphorescence. Fluorescence is when the emission arises from a singlet excited state (S) and phosphorescence is when the emission arises from a triplet excited state (T). The excited states are formed by promoting an electron from a ground state to a higher energy state. This often occurs by the absorption of light and can be considered as occurring from the highest occupied molecular orbital (HOMO) to a higher energy orbital, such as the lowest unoccupied molecular orbital (LUMO) (Figure 1.1).⁴



Figure 1.1 Simplified molecular orbital diagram, showing the promotion of an electron from the HOMO to the LUMO upon excitation with light energy (taken from Ref 4).

The terms singlet excited state and triplet excited state describe the nature of the excited state orbital relative to the ground state orbital. In a singlet excited state, the spin of the promoted electron is preserved, whereas in a triplet excited state, the promoted electron has flipped its spin state. In the excited state, there are many pathways by which a species can return to the ground state.⁵ These are commonly shown in a Jablonski diagram (Figure 1.2). Excited states can rapidly convert to lower energy states of the same multiplicity through the loss of heat energy (relaxation) in a process known as internal conversion. Excited states can also return to the ground state by emitting a photon (radiative decay). Singlet and triplet states can interconvert to lower energy states

in a process known as intersystem crossing. This process is slower than internal conversion but can be greatly accelerated in the presence of a heavy atom. Excited states can also return to the ground state through nonradiative decay by intermolecular energy transfer to other molecules through collisions, which is referred to as quenching.



Figure 1.2 Jablonski diagram summarizing the various states and photophysical processes observed in the singlet and triplet states (taken from Ref. 4).

1.3 Organic Light-Emitting Diodes (OLEDs)

The simplest structure of an organic light-emitting diode consists of organic layers stacked between an anode and a cathode (Figure 1.3). Electrons and holes are injected from the electrodes to the organic layers where recombination and light emission occurs. The emitting layer (EML), which is used for the light emission, consists of dopant and host materials which have high quantum efficiencies and high carrier mobilities. The EML is between the hole transport layer (HTL) and the electron transport layer (ETL), which bring carriers into the EML for recombination. When voltage is applied to the OLED, electrons supplied from cathode and holes supplied from the anode travel to the EML where they recombine, producing light.⁶ Hole transport layers are commonly made of p-type organic semiconductors and electron transport layers are often made of n-type organic semiconductors.^{7,8} The host material for an emissive layer can also be made of a p-type organic semiconductor. Electron-rich triarylamines have found widespread use as p-type materials in organic electronics. In contrast, n-type materials often contain electron-deficient heterocycles such as pyridines, triazines, oxadiazoles or benzimidazoles.



Figure 1.3 Illustration of a three-layer OLED stack (taken from Ref. 7).

The EML is the core of an OLED and devices can be categorized into four types based on the emitters. Upon electrical excitation, 25% singlets are formed and 75% triplets are formed. The triplets are at a lower energy than the singlets. In a fluorescent OLED, only the singlets decay radiatively through fluorescence. This process is fast, usually occurring within nanoseconds. Since the triplets cannot decay radiatively, the theoretical maximum internal quantum efficiency (IQE) of these devices is 25% (Figure 1.4a). A less common type of OLED, the triplet-triplet fluorescent OLED, involves two triplet excitons fusing to form one singlet exciton through a process known as triplet fusion (Figure 1.4b). As a result, relaxation occurs from the singlet state, improving the IQE to 62.5%. Phosphorescent OLEDs work by incorporating heavy metal atoms, such as iridium or platinum, into the emitters. The incorporation of heavy atom reduces the triplet lifetime from milliseconds or seconds to microseconds, allowing for efficient phosphorescent emission. The singlet exciton can undergo intersystem crossing to the triplet state for light emission, allowing for 100% IQE (Figure 1.4c). Thermally activated delayed fluorescent (TADF) OLEDs are the most recent type of OLED developed and are emerging as next-generation organic electroluminescent materials.⁹ By reducing the energy between the singlet and triplet state to less than 0.3 eV, triplets can jump back to the singlet state due to thermal energy in a process known as reverse intersystem crossing (RISC). Consequently, all emission is through fluorescence via a combination of prompt fluorescence (25%) and thermally activated delayed fluorescence (75%) (Figure 1.4d). TADF OLEDs are advantageous as they can achieve 100% IQE without incorporating a heavy atom in the organic material. This greatly reduces the material cost and allows for more flexibility in organic molecular design.



Figure 1.4 Illustration of the emission mechanisms of OLEDs: (a) fluorescence; (b) TTF; (c) phosphorescence; (d) TADF (taken from Ref. 6).

1.4 N-containing Conjugated Materials

1.4.1 Synthesis of nitrogen-containing π -conjugated materials

An element commonly found in organic semiconductors is nitrogen. Nitrogen-containing π -conjugated materials can be found in countless natural and synthetic materials, playing a key role in biochemical processes, optoelectronic devices, and modern pharmaceuticals.^{10–14} Many biologically and industrially important small molecules, macrocycles, and polymers are based on π -conjugated amines, and as such the potential uses for atom-economical syntheses of these compounds are vast. Due to their broad-ranging importance, many synthetic methods to produce π -conjugated amines are known, with condensation and cross-coupling reactions among the most common.^{15–18} While many of these reactions proceed with excellent yield and selectivity, the use of strong mineral acids, expensive metal catalysts, high temperatures, and stoichiometric reagents remain common features of these processes.

1.4.2 Hydroamination

A particularly interesting synthetic reaction involving nitrogen is hydroamination. In contrast to the reactions discussed previously, hydroamination reactions provide an atomeconomical catalytic route to amine-containing compounds, involving no additional reactants or by-products other than the hydroamination catalyst. These reactions can proceed under mild conditions when an appropriate catalyst is used, resulting in the addition of an N-H bond across an unsaturated C-C bond. There have been several studies which have employed atom-economic reactions in the preparation of conjugated materials, but activated substrates are required for these reactions to proceed.^{19,20} Using an efficient hydroamination catalyst with high regioselectivity, a broader scope of N-containing conjugated materials can be accessed. Schafer and coworkers previously reported a Ti-bis(amidat)bis(amido) catalyst, which can catalyze hydroamination between terminal alkynes and primary amines to produce anti-Markovnikov products selectively (Figure 1.5).²¹



Figure 1.5 Regioselective hydroamination catalyzed by a Ti-bis(amidate)bis(amido) complex (taken from Ref. 22).

In hydroamination reactions involving primary amines and alkynes, extended conjugation can stabilize the enamine product, reducing tautomerization to the imine form.²³ For example, in the reaction of *sec*-butylamine with *tert*-butylacetylene only the imine tautomer is observed, while the reaction of aniline with phenylacetylene results in an enamine:imine ratio of 82:18.²⁴ Since aryl groups have been shown to shift the equilibrium between enamine and imine tautomers to the more hydrolytically stable enamine product, enamine-based π -conjugated materials can be accessed exclusively if incorporated into an extended π system (Figure 1.6).²²



Isolable Conjugated Enamines

Figure 1.6 Catalytic synthesis of conjugated enamines via Ti-catalyzed hydroamination (taken from Ref. 22).1.4.3 Triarylboranes

A specific class of materials known as triarylboranes can be incorporated into π -conjugated materials possessing nitrogen. The interaction between the boron and the nitrogen in a conjugation system allows for interesting properties relevant to optoelectronic applications. Boron-based optoelectronic materials have gained widespread attention due to the π -accepting nature of the *p*-orbital on three-coordinate boron.^{25–28} Air- and moisture-stable triarylboranes can be prepared by introducing steric hindrance around the boron center, effectively protecting the empty *p*-orbital on boron and allowing it to act as a strong π -acceptor in organic π -systems. Such compounds can be excited with light when an appropriate electron donor such as an amine or phosphine is present (Figure 1.7). This generates a highly polarized and emissive excited state resulting from an intramolecular charge transfer (ICT) between the electron-accepting boron and the electron donor. These features allow triarylboranes to be used in a variety of fields such as nonlinear optics,^{29–31} anion sensing,^{32–34} hydrogen activation and storage,^{35,36} and as emitters and electron transport materials in organic light-emitting diodes.^{37–40}



Figure 1.7 π -accepting triarylborane and π -donating triarylamine in a conjugated π -system (taken from Ref. 34).

1.5 Conductive Fiber-like Nanowires

1.5.1 Cylindrical Micelles

Although molecular semiconducting materials are of great interest and have many useful applications, polymeric semiconducting materials are another major class with some distinct advantages over molecular materials. The focus of this thesis is on semiconducting polymeric materials with a fiber-like morphology. These nanowires can be synthesized by taking advantage of the inherent properties of certain classes of polymers. A particularly interesting example is based on the self-assembly of block copolymers (BCPs), which has been used to form a wide variety of cylindrical (fiber-like) micelles (Figure 1.8).^{41–43} These types of micelles have a cylindrical core and a surrounding corona, with physical properties distinct from traditional spherical micelles.



Figure 1.8 (A) Three dimensional cartoon of a fiber-like micelle; (B) TEM image of a synthetic fiber-like micelle (taken from Ref. 43).

Consequently, a tremendous amount of attention in a variety of research areas has been dedicated to the synthesis and investigation of cylindrical micelles. Cylindrical micelles have found uses such as templates for inorganic nanoparticles,^{44–46} building blocks for superstuctures,^{47–49} synthetic dendritic cells for immunotherapy,^{50,51} constituents of thermoresponsive gels for biomedical applications,^{52,53} and nanocarriers for cancer drug delivery.^{54–57} Furthermore, recent advances have described examples of fiber-like micelles with novel photophysical characteristics,^{58,59} their assembly into complex semiconducting structures,^{60–63} and their fabrication of hybrid nanowires composed of a *p*-type conjugated polymer and *n*-type inorganic quantum dots.^{64,65} Nevertheless, evaluation of cylindrical micelles for their potential as functional electroactive materials in devices remains underexplored.^{66,67} Specifically, uniform samples of low length dispersity have not been thoroughly investigated. Although fibers fabricated from solely π -conjugated homopolymers have been studied in detail,^{68–70} these nanostructures exhibit limited colloidal stability and accessing uniform samples of controlled length is often difficult. This represents a major challenge as limited morphological control hinders the optimization of these nanomaterials for many applications.

Recently, Manners and coworkers demonstrated a synthetic route to solution-processable, electroactive fiber-like micelles of controlled length from π -conjugated diblock copolymers via the self-assembly of thiophene-based BCPs.⁷¹ Using tunneling atomic force microscopy (AFM) measurements, it was demonstrated that the individual wires exhibit appreciable conductivity. Furthermore, these fibers were incorporated as the active layer in field-effect transistors. Although useful, this method is very narrow in scope, requiring specific crystallization-driven self-assembly conditions for ordered fiber-like wires to form. Other recent advances have also been made in the controlled synthesis of ordered semiconducting nanowires. The self-assembly of conjugated block copolymers at a liquid-air interface was used in the fabrication of well-ordered nanoarrays of conjugated polymers.⁶⁶ Controlled growth of polythiophene nanofibers has recently been

demonstrated by electropolymerization of the thiophene monomer, with formation occurring in hollow TiO₂ nanotube arrays.⁷² Semiconducting nanofibers were also recently prepared by light-induced crystallization-driven self-assembly.⁷³ Living self-assembly was possible, allowing for excellent length control and narrow size distribution. Although all these methods represent significant progress towards the controlled synthesis of semiconducting nanowires, they all suffer from the limitation of requiring very specific conditions and monomers to be successful.

1.5.2 Bottlebrush Polymers

A specific type of polymer which will be explored to circumvent these limitations is the bottlebrush polymer. Bottlebrush polymers are a type of branched or graft polymer in which polymeric side-chains are attached to a linear polymer backbone, and remain extended into a wire-like morphology in solution due to the steric demands of the side chains (Figure 1.9).⁷⁴ There are



Figure 1.9 Cartoon illustration of a bottlebrush polymer. The backbone polymer is shown is grey and the sidechains are shown in purple.

three main synthetic approaches to bottlebrush polymers, termed 'grafting-from', 'graftingthrough', and 'grafting-to' (Figure 1.10).⁷⁵ In the grafting-from approach the bottlebrush backbone is synthesized first. The side-chains are subsequently grown from the backbone, using the individual monomer units of the backbone as initiators for polymerization. This method is advantageous as bottlebrushes with very long backbones can be prepared. Additionally, block copolymer side-chains can be easily incorporated through sequential polymerization reactions, resulting in core-shell type bottlebrushes. A disadvantage of this method, however, is that protection and deprotection of functional groups is often required, which increases synthetic complexity. The grafting-through approach involves initially preparing reactive polymeric sidechains known as macromonomers. The macromonomers are then polymerized, forming a bottlebrush polymer. Some major advantages of this method include achieving 100% grafting density and its synthetic simplicity. Bottlebrush polymers can be prepared in just two steps using controlled polymerization for the synthesis of the macromonomer followed by polymerization of the macromonomer, avoiding protection-deprotection chemistry entirely. Some drawbacks include difficulty removing unreacted macromonomer from the final product and limitations in achieving large backbone degrees of polymerization (DPs). The grafting-to method involves preparation of the bottlebrush backbone and side-chains separately, followed by a coupling reaction to attach the side-chains to the backbone. This method has not been widely used as it typically produces bottlebrushes with low grafting densities due to the coupling reaction having to overcome steric interactions between side-chains. However, this method has the advantage of facilitating the independent characterization of the bottlebrush backbone and side-chains separately. Recent work by Matyjaszewski and coworkers has shown that ATRP-type polymerization techniques are wellsuited for the synthesis of bottlebrush polymers through the grafting-from approach.^{76,77} Structures with precisely controlled molecular weights and low polydispersities, with good functional group tolerance, were accessible.



Figure 1.10 Grafting from, grafting through, and grafting to methods of bottlebrush synthesis (taken from Ref. 75).1.5.3 Atom Transfer Radical Polymerization (ATRP)

Atom transfer radical polymerization (ATRP) is a type of reversible deactivation radical polymerization (RDRP). It involves a fast activation-deactivation process which maintains equilibrium between the active (propagating macroradical) and dormant (halide-terminated propagating macroradical) species.⁷⁸ The activator is usually Cu(I)X/L and the deactivator is Cu(II)X₂/L, where X is Cl or Br and L is an N-ligand. The activation step involves homolytic atom transfer of the halide from P_n -X to the copper (I) catalyst, generating the propagating macroinitiator and the copper (II) catalyst. In the deactivation step, the halide is transferred back from the copper (II) deactivator to the propagating macroinitiator (Figure 1.11). ATRP allows for the polymerization of a wide variety of monomers with different chemical functionalities.⁷⁷ It is more tolerant than ionic polymerization methods and can provide excellent control over molecular weight and polydispersity.



Figure 1.11 Mechanism of ATRP (taken from Ref. 78).

1.5.4 Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerization

Another major class of polymerization is reversible addition-fragmentation chain transfer (RAFT) polymerization. Like ATRP, the RAFT process is a reversible deactivation radical polymerization. It is one of the most versatile and powerful polymerization techniques for the synthesis of complex polymer architectures.^{79,80} Polymerizations can be performed in a large range of solvents, over a wide temperature range, without metals, and with high functional group tolerance. There exists a large range of available RAFT agents to cover most monomer classes that can undergo radical polymerization. RAFT involves a degenerative transfer system, in which there is no change in the overall number of radicals during the activation-deactivation process. The propagating species is in equilibrium with the dormant species via a degenerative chain transfer steps that form the basis of the RAFT mechanism are considered degenerate as they involve a reversible transfer of the functional chain end-group between the dormant chains and the propagating radicals. In contrast, the ATRP equilibrium is established through a mechanism of reversible termination of the propagating chain (Figure 1.12).



Figure 1.12 Reversible-deactivation radical polymerization by (a) reversible termination; (b) degenerative chain transfer (taken from Ref. 80).

The overall process can be viewed as an insertion of monomer units between the S-R bond of the RAFT agent to give a polymer (Figure 1.13). Since degenerative chain transfer does not



Figure 1.13 Overall outcome of the RAFT process (taken from Ref. 80).

create radicals, a source of radicals is required in RAFT polymerizations. This is typically an azo initiator such as 2,2'-azobisisobutyronitrile (AIBN). The first step of the mechanism is activation, where an initiator derived radical (I^{\bullet}) is formed (Figure 1.14). This radical propagates with the monomer to make a polymeric radical, which adds to the RAFT agent (1) and enters an equilibrium between active and dormant species. The intermediate (3) fragments to give the macro-RAFT agent (2) and the expelled RAFT agent-derived radical (R^{\bullet}), which reinitiates polymerization. In an effective RAFT process, the rate of the addition/fragmentation equilibrium is higher than the rate of propagation. This should result in less than one monomer unit added per activation cycle and

therefore all chains having a similar degree of polymerization.



Figure 1.14 Mechanism of RAFT Polymerization (taken from Ref. 79).

1.5.5 Cu(0) Reversible Deactivation Radical Polymerization (RDRP)

A particularly interesting type of atom transfer radical polymerization is Cu(0) Reversible Deactivation Radical Polymerization (RDRP), also known as Cu(0)-mediated living radical polymerization.⁸¹ Cu(0) RDRP is a very robust polymerization technique which allows access to rapid polymerization of acrylates, methacrylates, and acrylamides.^{82–84} Compared to other living radical polymerization (LRP) techniques, Cu(0) RDRP is one of the simplest and easiest to perform. It can be conducted at ambient temperature and does not require strict deoxygenating procedures. Other advantages include narrow molecular weight distributions (MWDs), high endgroup functionality even at quantitative conversions, and facile purification when heterogeneous catalysis using a copper wire as the Cu(0) source is employed.

There are two proposed models regarding the mechanism of Cu(0) RDRP, known as Single

Electron Transfer Living Radical Polymerization (SET-LRP) and Supplemental Activator and Reducing Agent Atom Transfer Radical Polymerization (SARA ATRP).^{85–87} SET-LRP also involves an equilibrium between an active propagating macroradical and a dormant halide terminated macroradical species; however, the initiation step is mediated by a single electron transfer (SET) from a Cu(0) electron donor to an electron accepting alkyl halide on the initiator. The Cu(I)X species that is generated is inactive in SET-LRP, unlike in ATRP, instantaneously disproportionating into highly active Cu(0) and Cu(II)X₂ in the presence of polar solvents and suitable N-containing ligands (Figure 1.15). The Cu(II)X₂ species in SET-LRP acts as the deactivator, as in ATRP.

SARA-ATRP involves the traditional Cu(I) activation and Cu(II) of deactivation reactions of ATRP, but includes Cu(0) as a supplemental activator of alkyl halides and a reducing agent for Cu(II) through comproportionation.⁸⁷ This is in contrast to SET-LRP, where Cu(0) is the primary activator and is generated via disproportionation rather than contributing to a comproportionation process. Unlike in SET-LRP, there is minimal disproportionation in SARA ATRP as Cu(I) primarily activates alkyl halides. Both models use the same components and involve the same reactions, but their contributions to the overall polymerization are vastly different (Figure 1.15).



Figure 1.15 Mechanisms of SARA ATRP and SET-LRP (taken from Ref. 87).

1.5.6 Polymerization of Organic Semiconductors by Cu(0) RDRP

Hudson and coworkers recently demonstrated the synthesis of a series of acrylic monomers based on both p-type and n-type organic semiconductor motifs commonly found in organic devices (Figure 1.16).^{88,89} The monomers were readily polymerized by Cu(0) RDRP at room temperature to high conversion with high yield and low polydispersities. The resultant polymers have photophysical and electrochemical properties which show promise for applications in optoelectronics.



Figure 1.16 Acrylic monomers based on (a) p-type organic semiconductor, and (b) n-type organic semiconductor motifs commonly used in organic devices.

In a subsequent publication, bottlebrush polymers were prepared by combining Cu(0) RDRP with ring-opening metathesis polymerization (ROMP).⁹⁰ Macromonomers were synthesized by direct growth of the previously developed monomers from a norbornene-functionalized initiator via Cu(0) RDRP. Macromonomers were then polymerized by ROMP, yielding bottlebrush polymers up to several hundred backbone degrees of polymerization in length (Figure 1.17). Atomic force microscopy images of bottlebrushes showed fiber-like morphologies up to several hundred nanometers in length. Diblock nanofibers could also be prepared, combining HTL, ETL and EML blocks. Furthermore, a triblock nanofiber with the structure of phosphorescent OLEDs on single macromolecules was demonstrated. These nanofibers can be made using arbitrary organic semiconductors without requiring crystallinity, selective solvation, or supramolecular techniques. This method provides a versatile synthetic route to semiconducting

nanofibers without the limitations imposed by the strict conditions often necessary for successful nanofiber synthesis.



Figure 1.17 Synthesis of norbornene-functionalized macromonomers from a series of organic semiconductors, and their reaction to form bottlebrush polymers by grafting-through ROMP (taken from Ref. 90).

Chapter 2 : Synthesis of *N*-containing Conjugated Materials by Hydroamination

2.1 Introduction

Ti-catalyzed hydroamination can be used for the facile and atom-efficient synthesis of a series of *N*-containing materials with extended π -conjugation. A variety of anilines and alkynes bearing electron-donating and electron-withdrawing substituents have been used to prepare these new conjugated molecules in good yields, with several showing strong π - π * absorption bands and high fluorescence quantum yields. To further demonstrate the versatility of hydroamination as a viable route for the efficient synthesis of a broad range of conjugated systems, a boron-containing diyne has been used. In this first example of using a boron-containing alkyne as a substrate for catalytic hydroamination, a new donor-acceptor material has been prepared which shows bright, solvent-dependent fluorescence characteristic of B-N based conjugated materials.

2.2 Experimental

2.2.1 General Experimental Information

All reagents were obtained from Sigma Aldrich, Alfa Aesar or TCI and used without further purification unless otherwise specified. Dry hexanes, ether, and tetrahydrofuran were obtained from an in-house solvent drying system in which the solvents are passed through dried alumina columns. Benzene was dried over molecular sieves. Solvents were degassed by three freeze-pumpthaw cycles. Reactions were performed under an N₂ atmosphere unless otherwise specified.

¹H and ¹³C NMR spectra were measured at room temperature on a Bruker AV III HD 400 MHz spectrometer. Chemical shifts (δ) reported are in parts per million (ppm) and referenced to the residual solvent peak. Coupling constants (J) are given in Hertz (Hz). Signal multiplicities are

denoted as: s, singlet; d, doublet; t, triplet; dd, doublet of doublets; m, multiplet; br, broad. UV-Vis spectra were collected on an Agilent Cary 60 UV/Vis Spectrophotometer. Fluorescence spectra were collected on an Edinburgh Instruments FS5 spectrofluorometer. Fluorescent quantum yields were measured following the IUPAC technique reports, using quinine sulfate in 0.5 M H_2SO_4 solution as the reference.^{91–95}

Geometry optimizations and single point calculations were performed with Gaussian 09^{96} at the B3LYP/6-311G+(d) level of theory.

2,5-diethoxy-1,4-diethynylbenzene and 2,5-difluoro-1,4-diethynylbenzene were prepared according to literature procedures.^{97,98} Mesityl copper and MesBCl₂ were prepared according to literature procedures.^{99,100}
2.2.2 Experimental Methods

Compound 8:



Synthesis of 8a:

5-bromo-2-iodo-m-xylene (6.94 g, 22.3 mmol) was placed in a 250 mL round-bottom flask and dissolved in 75 mL of dry diethyl ether. The solution was cooled to -78° C and 1.6 M n-BuLi in hexanes (14.7 mL, 23.4 mmol) was added dropwise over 10 minutes. The solution was stirred for 1 hour, after which a white precipitate formed. A solution of MesBCl₂ (11.2 mmol) in 75 mL of toluene was added dropwise via cannula, with the appearance of a bright orange colour. The solution was stirred for 16 hours and allowed to warm slowly to room temperature. The mixture was washed three times with water followed by brine. The organic layer was dried with MgSO₄ and filtered. The product was purified by flash chromatography using hexanes as the eluent to yield 2.45 g of **8a** as a white solid. Yield = 44%.

¹H NMR (400 MHz, CDCl₃) δ = 7.10 (s, 4H), 6.75 (s, 2H), 2.27 (s, 3H), 1.98 (s, 6H), 1.97 (s, 6H), 1.96 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ = 145.5 (br), 142.7, 142.4, 140.8, 140.3, 130.7, 129.1, 124.0, 23.1, 22.84, 22.80, 21.4 ppm. HRMS (EI) calc'd for C₂₅H₂₇BBr₂: 495.06089. Found: 495.06115.

Synthesis of 8b:

2.67 mL (18.8 mmol) of ethynyltrimethylsilane, 12 mL of NEt₃ and 100 mL of 2methyltetrahydrofuran were mixed and degassed via three freeze-pump-thaw cycles. The solution was added to a 250 mL three-necked flask with a stir bar and condenser containing a mixture of **8a** (2.34 g, 4.70 mmol), CuI (0.089 g, 0.470 mmol), and PdCl₂(PPh₃)₂ (0.330 g, 0.470 mmol), yielding a dark red suspension. The suspension was heated to reflux and stirred for three days, after which the solvents were removed under reduced pressure. The remaining solid was dissolved in CH₂Cl₂ then washed with water three times followed by brine. The organic layer was dried over MgSO₄ and filtered through celite. The product was purified by flash chromatography using hexanes as the eluent to yield 1.25 g of **8b** as a yellow solid. Yield = 50%.

¹H NMR (400 MHz, CDCl₃) δ = 7.06 (s, 4H), 6.74 (s, 2H), 2.27 (s, 3H), 1.97 (s, 6H), 1.94 (s, 6H), 1.93 (s, 6H), 0.24 (s, 18H); ¹³C NMR (101 MHz, CDCl₃) δ = 147.8 (br), 140.9, 140.7, 140.5, 140.2, 131.2, 129.0, 123.8, 105.6, 94.7, 23.0, 22.9, 22.7, 21.4, 0.1 ppm. HRMS (EI) calc'd for C₃₅H₄₅BSi₂: 531.31892. Found: 531.31910.

Synthesis of 8c:

Under an air atmosphere, **8b** (1.26 g, 2.37 mmol), 200 mL of 1:1 tetrahydrofuran:methanol, and 1.06g (18.9 mmol) of KOH in water (50 mL) were added to a 500 mL round-bottom flask with a stir bar. The solution was stirred for 16 hours and the solvent was removed under reduced pressure. The residue was partitioned in CH_2Cl_2 and water then extracted three times with CH_2Cl_2 . The combined organic layers were washed with water then brine, then dried over MgSO₄ and filtered. The product was purified by flash column chromatography using 1:9 CH_2Cl_2 :hexanes as the eluent to yield 0.77g of **8c** as a yellow solid. Yield = 84%.

¹H NMR (400 MHz, CD₂Cl₂) δ = 7.09 (s, 4H), 6.79 (s, 2H), 3.13 (s, 2H), 2.28 (s, 3H), 2.01 (s, 6H), 1.99 (s, 6H), 1.98 (s, 6H); ¹³C NMR (101 MHz, CD₂Cl₂) δ = 148.3 (br), 143.3 (br), 141.2, 141.1, 140.9, 140.7, 131.5, 129.3, 123.2, 84.3, 77.7, 23.1, 22.9, 22.8, 21.4 ppm. HRMS (EI) calc'd for C₂₉H₂₉B: 381.23986. Found: 38.23948.

Synthesis of 8:

8c (0.100g, 0.258 mmol) in a 20 mL vial equipped with a stir bar was dissolved in 5 mL of dry benzene. 47 μ L (0.515 mmol) of freshly distilled aniline and 128.7 μ L (12.9 μ mol) of a 0.1 M solution of Ti catalyst in benzene were added *via* microsyringe. The solution was heated to 40 °C and stirred for 16 hours, after which the solvent was removed under reduced pressure. The solid was triturated with a 1:5 mixture of benzene and hexanes then twice more with hexanes to yield 0.128 g of compound **8** as a yellow solid. Yield = 87%.

¹H NMR (400 MHz, CD₂Cl₂) δ = 7.35 (dd, *J* = 13.8, 11.8 Hz, 2H), 7.25 (dd, *J* = 8.6, 7.2 Hz, 4H), 6.89 – 6.84 (m, 10H), 6.76 (s, 2H), 6.16 (d, *J* = 11.8 Hz, 2H), 5.81 (d, *J* = 13.8 Hz, 2H), 2.27 (s, 3H), 2.02 (s, 6H), 2.01 (s, 6H), 1.98 (s, 6H); ¹³C NMR (101 MHz, CD₂Cl₂) δ = 144.8 (br), 143.0, 141.5, 140.8, 139.4, 139.3, 129.9, 128.8, 128.7, 128.0, 124.1, 120.2, 114.0, 105.8, 23.3, 23.1, 23.0, 21.3 ppm. HRMS (EI) calc'd for C₄₁H₄₃N₂B: 573.35556. Found: 573.35611.

2.3 Results and Discussion

Initial efforts by Ph.D. student Han Hao focused on investigating the known Ti precatalyst, shown in Figure 1.1, as a suitable regioselective catalyst for the preparation of *N*-conjugated molecules. To test this method, a reaction was carried out between 1,4-dialkynylbenzene and 4-(trimethylsilylalkynyl)aniline. Using 5 mol% Ti catalyst in hexanes at 40 °C, the product precipitates from solution over 16 h, and can be isolated in high yield (90%) with high purity by



Scheme 2.1 Synthesis of conjugated dienamine 1

simple suction filtration (Scheme 2.1). The ¹H NMR spectrum of **1** in DMSO-*d*₆ (Figure A1) shows three peaks at 8.93, 7.46, and 5.83 ppm which can be assigned to the N-<u>H</u>, the α - =C<u>H</u> and the β -=C<u>H</u> in an enamine group. The coupling constants between the two =C<u>H</u> are around 13.7 Hz and are consistent with a *trans*- C-C double bond. Furthermore, no peaks were observed above 9.5 ppm, indicating that no imine was present in solution phase. Single crystals of **1** could be obtained as thin yellow plates simply by carrying out this reaction at room temperature in toluene without stirring. X-ray diffraction analysis confirms that 1,4-di[4-[2-(trimethylsilyl)ethynyl]anilino]-Eethenylbenzene is formed regioselectively from this hydroamination reaction (Figure 2.1), with compound **1** having C_i symmetry in the solid state. The bond length and angle data for the C-N and C-C bonds in the enamine group are consistent with reported literature values for conjugated enamines.¹⁰¹ This first result showed that Ti catalyzed hydroamination can be used successfully to produce highly conjugated dienamines regio- and stereoselectively.



Figure 2.1 ORTEP representation of the solid state molecular structure of compound **1** structure in crystal. Drawn in 50% probability. Hydrogens are assigned from Q peaks. Selected Bond Lengths (Å) and Angles (°): C3-C4: 1.467(5); C4-C5: 1.340(5); C5-N1: 1.381(5); N1-C6: 1.404(5); C3-C4-C5: 124.7(3); C4-C5-N1: 125.2(4); C5-N1-C6: 125.4(3) (taken from Ref. 22).

In THF solution, compound **1** is a deep orange colour and displays strong fluorescence under UV irradiation (Figure 2.2). Compound **1** exhibits an absorption maximum (λ_{max}) at 400 nm with an absorption coefficient of 8.3 x 10⁴ cm⁻¹ mol⁻¹L, and an emission maximum (λ_{Em}) at 445 nm in THF. This compound exhibits a photoluminescence quantum yield up to 0.26 in THF at 1×10⁻⁶ mol⁻¹L, decreasing to 13% if the concentration is raised to 1×10⁻⁵ mol⁻¹L. We hypothesize that this phenomenon results from intermolecular π -stacking, resulting in aggregation, which quenches the



Figure 2.2 UV-Vis absorption (2×10-5 M) and emission spectrum (2×10-6 M, normalized) of compound **1** in THF solution (taken from Ref. 22).

fluorescence of this material.

Having demonstrated that this Ti catalyst could be used to produce a conjugated enamine, a variety of related compounds **2-7** were synthesized by Han Hao using the same conditions (Scheme 2.2). The absorption spectra of compounds **2-7** in THF are given in Figure A2, with absorption data summarized in Table A1.



Scheme 2.2 Scope of selected conjugated enamines with isolated yields.

To study the versatility of hydroamination in the synthesis of functional π -conjugated materials, a boron-containing dialkyne was synthesized to explore a novel route to access donor-acceptor π -conjugated enamines. The first step in the synthesis of this dialkyne involved a lithium-halogen exchange reaction of 5-bromo-2-iodo-*m*-xylene with *n*-butyllithium, followed by addition of dichloromesitylborane to yield a triarylborane containing two *para*-bromine atoms (Scheme

2.3). Dichloromesitylborane was synthesized by first reacting 2-bromomesitylene with magnesium, followed by reaction with copper(I) chloride. This provided mesitylcopper(I), which was subsequently reacted with boron trichloride to yield the target dichloromesitylborane. A Sonogashira reaction with ethynyltrimethylsilane followed by subsequent deprotection yielded the desired dialkyne. Finally, a hydroamination reaction using the Ti catalyst and two equivalents of aniline resulted in a highly fluorescent donor-acceptor material, **8**. Notably, this is the first example of catalytic hydroamination using a boron containing substrate.



Scheme 2.3 Synthesis of boron containing donor-acceptor conjugated dienamine 8.

The incorporation of a boron center into the conjugated dienamine results in a significant red-shift of both the absorption maximum (425 nm) and the emission maximum (534 nm) relative to dienamines **1-7** (Figure 2.3). Compound **8** displays strong solvatochromic donor-acceptor behavior, with an emission maximum of 440 nm in hexanes, shifting to 580 nm in acetonitrile (Figure 2.4).



Figure 2.3 UV-Vis absorption and emission spectrum (normalized) of compound **8** in THF solution (1×10⁻⁵ M) (taken from Ref. 22).



Figure 2.4 Solvatochromic behavior of 8 in various solvents at 10⁻⁵ M concentration (taken from Ref. 22).

A HOMO-LUMO gap of 3.17 eV was determined by DFT calculation, resulting from a HOMO to LUMO charge transfer to the empty *p*-orbital of the electron-withdrawing boron center (Figure 2.5). DFT indicates a pinwheel structure around the boron center to reduce steric interactions of the *ortho*-methyl groups. This is confirmed experimentally by the inequivalence of methyl protons in the ¹H NMR spectrum (Figure A3) and methyl group carbon atoms in the ¹³C NMR spectrum, which is consistent with hindered rotation in this congested system.



Figure 2.5 HOMO (left) and LUMO (right) diagrams of compound 8 (taken from Ref. 22).

2.4 Conclusions

In summary, Ti-catalyzed hydroamination has been shown to be an efficient method for the synthesis of conjugated enamines, giving high yields of a single product using only simple filtration purification procedures. These compounds were found to be strongly colored. Using this methodology, a donor-acceptor conjugated enamine was also prepared, displaying high photoluminescence quantum efficiency and strong solvatochromism. These methods represent a convenient route to new *N*-containing π -conjugated materials, which may provide access to new luminescent materials with applications in organic light-emitting diodes, fluorescent labeling dyes, and chemical sensors.

Chapter 3 : Synthesis of Fiber-like Nanowires from Semiconducting Monomers

3.1 Introduction

The grafting-through approach to bottlebrush synthesis has been demonstrated as an effective and versatile method in the synthesis of fiber-like nanowires from arbitrary semiconducting monomers. Nevertheless, it suffers from some drawbacks. The grafting-through method has limitations in achieving large backbone degrees of polymerization due to the steric bulk around the growing chain end at longer lengths. Additionally, a macromonomer must be prepared for each monomer of interest, increasing synthetic complexity when many monomers are of interest. The grafting-from approach, however can produce bottlebrush polymers with long backbones allowing for the formation of long wire-like fibers. Furthermore, a wide variety of bottlebrush polymers can be synthesized from a single macroinitiator. Herein we investigate the versatile synthesis of fiber-like nanostructures using the grafting-from approach, yielding semiconducting nanowires from arbitrary organic semiconductors. This novel method provides an advancement in synthetic methodology, allowing an alternative route to the versatile synthesis of ordered semiconducting nanowires from arbitrary organic semiconductors. To avoid the synthetic complexity often associated with the grafting-from method related to protection and deprotection steps, two orthogonal polymerization methods were used. First, RAFT polymerization was used to synthesize long macroinitiators of various lengths. Cu(0) RDRP was then used to synthesize bottlebrush polymers by growing semiconducting monomers directly from the backbone macroinitiator.

3.2 Experimental

3.2.1 General Experimental Information

All reactions and manipulations were carried out under a nitrogen atmosphere using standard Schlenk or glove box techniques unless otherwise stated. Dry 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 reagents were purchased from Sigma-Aldrich or Alfa Aesar and used as received unless otherwise stated. M1,⁸⁸ M2,⁸⁸ M3,⁸⁸ M4,⁸⁹ M5⁸⁹ and 2-(2-bromoisobutyryloxy)ethyl methacrylate¹⁰² (BiBEM) were prepared according to literature procedures. N-Methyl-2-pyrrolidone (NMP), N,Ndimethylacetamide (DMAc), p-xylene and anisole were distilled, then degassed and stored under N₂. Et₃N was dried by distillation on CaH₂ onto activated molecular sieves then degassed and stored under N₂. The ¹H NMR spectra were measured on a Bruker AV III HD 400 MHz spectrometer with CDCl₃ as solvent. Absorbance measurements were made on a Cary 60 spectrometer and fluorescence measurements were made on an Edinburgh Instruments FS5 spectrofluorometer. Absolute photoluminescence quantum yields were determined using an Edinburgh Instruments SC-30 Integrating Sphere Module; dichloromethane and toluene were used as the solvents and spectra were obtained at concentrations of 0.01 mg mL⁻¹.

Atomic force microscopy (AFM) images were obtained using an Asylum Instruments Cypher S AFM system in tapping mode at scan rates of 0.1 Hz. Samples were prepared by spincoating solutions of polymer onto freshly cleaved highly-oriented pyrolytic graphite (HOPG) at 2500 rpm for 30 s at concentrations of ~0.001 mg mL⁻¹. Samples were placed in a vacuum oven (60 °C) for at least 2 h before images were obtained using Mikromasch HQ:NSC14/No Al or HQ:NSC19/No Al probes, with typical resonance frequencies f and spring constants k of (f = 160 kHz, k = 5 N/m) and (f = 65 kHz, k = 0.5 N/m) respectively.

SEC experiments were conducted in chromatography-grade THF at concentrations of 0.5 - 2 mg mL⁻¹ using a Malvern OMNISEC GPC instrument equipped with a Viscotek TGuard column (CLM3008), and Viscotek T3000 (CLM3003) and T6000 (CLM3006) GPC columns packed with porous poly(styrene-*co*-divinylbenzene) particles regulated at a temperature of 35 °C. Signal response was measured using differential viscometer, differential refractive index, photodiode array and right- and low-angle light scattering detectors. Calibration of interdetector distances was performed using a polystyrene standard from Malvern Inc. Refractive index increments (dn/dc) were determined using 100% mass recovery methods from Malvern OMNISEC software version 10.2 with each polymer sample being run at least five times to ensure reproducibility of the calculated refractive index increment.

Cyclic voltammograms were recorded using a BASi Epsilon Eclipse potentiostat at room temperature using a standard three-electrode configuration (working electrode: 3 mm diameter glassy carbon; reference electrode: RE-5B Ag/AgCl electrode in saturated aqueous KCl (BASi Inc.), referenced externally to ferrocene/ferrocenium (0.543 V in 1,2-difluorobenzene);¹⁰³ counter electrode: Pt wire) in 0.2 M tetrabutylammonium hexafluorophosphate in 1,2-difluorobenzene. Experiments were run at a scan rate between 100 and 250 mV s⁻¹ in dry degassed electrolyte solution with ~1 mg mL⁻¹ of analyte.

3.2.2 Experimental Methods





Synthesis of PBiBEM₂₀₀

In a nitrogen atmosphere glovebox, to a 20 mL vial capped with a Teflon-lined lid and equipped with a magnetic stir bar was added BiBEM (5.00 g, 17.9 mmol, 1000 eq.) and 11.2 mL of *p*-xylene. The solution was degassed by three freeze-pump-thaw cycles outside the glovebox then returned into the box. 48 μ L of an azobisisobutyronitrile (AIBN) solution (*C* = 12.2 mg mL⁻¹; AIBN: 0.59 mg, 3.6 μ mol, 0.2 eq.) and 80 μ L of a 2-cyano-2-propyl benzodithioate (CPBDT) solution (*C* = 49.8 mg mL⁻¹; CPBDT: 3.97 mg, 17.9 μ mol, 1 eq.) were added. The reaction was heated to 60 °C. After 1 hour and 40 minutes, PBiBEM was isolated by precipitation into methanol, then dissolved in dichloromethane and precipitated into hexanes.

Yield = 743 mg; Conversion = 18 %; M_n = 55900 Da; PDI = 1.44



Synthesis of PBiBEM493

In a nitrogen atmosphere glovebox, to a 20 mL vial capped with a Teflon-lined lid and equipped with a magnetic stir bar was added BiBEM (5.02 g, 18.0 mmol, 2500 eq.) and 11.3 mL of *p*-xylene. The solution was degassed by three freeze-pump-thaw cycles outside the glovebox then returned into the box. 18 μ L of an AIBN solution (*C* = 13.3 mg mL⁻¹; AIBN: 0.24 mg, 1.4 μ mol, 0.2 eq.) and 34 μ L of a CPBDT solution (*C* = 46.7 mg mL⁻¹; CPBDT: 1.59 mg, 7.2 μ mol, 1 eq.) were added. The reaction was heated to 60 °C. After 1 hour and 30 minutes, PBiBEM was isolated by precipitation into methanol, then dissolved in dichloromethane and precipitated into hexanes.

Yield = 776 mg; Conversion = 18 %; $M_n = 138000 \text{ Da}$; PDI = 1.58



Synthesis of PBiBEM792

In a nitrogen atmosphere glovebox, to a 4 mL vial capped with a Teflon-lined lid and equipped with a magnetic stir bar was added BiBEM (0.69 g, 2.5 mmol, 1000 eq.) and 486 μ L of anisole. The solution was degassed by three freeze-pump-thaw cycles outside the glovebox then returned into the box. 10 μ L of an AIBN solution ($C = 12.7 \text{ mg mL}^{-1}$; AIBN: 0.12 mg, 0.75 μ mol, 0.3 eq.) and 55 μ L of a CPBDT solution ($C = 10 \text{ mg mL}^{-1}$; CPBDT: 0.55 mg, 2.5 μ mol, 1 eq.) were added. The reaction was heated to 60 °C. After 36 hours and 45 minutes, PBiBEM was isolated by two precipitations into methanol.

Yield = 452 mg; Conversion = 76 %; $M_n = 221000 \text{ Da}$; PDI = 1.34



Synthesis of PBiBEM493-g-poly(M1)17

In a nitrogen atmosphere glovebox, to a 4 mL vial capped with a Teflon-lined lid and equipped with a magnetic stir bar was added **M1** (202.1 mg, 0.57 mmol, 20 eq.), 200 μ L of a **PBIEM**₄₉₃ solution in DMAc (*C* = 40 mg mL⁻¹; PBIEM₄₉₃: 8.0 mg, 28 μ mol, 1 eq.), 109 μ L of a CuBr₂/Me₆TREN in DMAc solution (*C*_{Cu} = 3.75 mg mL⁻¹; CuBr₂: 0.4 mg, 2 μ mol, 0.065 eq.; Me₆TREN: 0.4 mg, 2 μ mol, 0.068 eq.), and 165 μ L of a 1,3,5-trimethoxybenzene in DMAc solution (*C* = 100 mg mL⁻¹; 1,3,5-trimethoxybenzene: 16.5 mg, 85 μ mol, 3 eq.). The total polymerization volume was kept to 1.01 mL of solvent. The mixture was stirred at room temperature for 10 minutes to allow all reagents to fully dissolve. A 1.4 cm piece of 18-gauge copper (0) wire was soaked in concentrated HCl for 15 minutes to remove surface impurities, then washed with water followed by acetone, dried *in vacuo* and taken into the glovebox. The wire was added to the mixture to initiate the polymerization. After 2 hours and 30 minutes, the polymerization was quenched by addition of water followed by filtration. The residue was purified by preparatory SEC in THF and fractions containing polymer were determined by SEC analysis. All fractions containing bottlebrush polymer were collected and dried *in vacuo* overnight.

Crude yield = 131 mg; Conversion = 85 %; $M_n = 1620 \text{ kDa}$; PDI = 1.34



Synthesis of PBiBEM493-g-poly(M2)17

In a nitrogen atmosphere glovebox, to a 4 mL vial capped with a Teflon-lined lid and equipped with a magnetic stir bar was added **M2** (190.0 mg, 0.43 mmol, 20 eq.), 150 µL of a **PBIEM**₄₉₃ solution in NMP (C = 40 mg mL⁻¹; PBIEM₄₉₃: 6.0 mg, 22 µmol, 1 eq.), 83 µL of a CuBr₂/Me₆TREN in NMP solution ($C_{Cu} = 3.75$ mg mL⁻¹; CuBr₂: 0.3 mg, 1 µmol, 0.065 eq.; Me₆TREN: 0.3 mg, 1 µmol, 0.068 eq.), and 126 µL of a 1,3,5-trimethoxybenzene in NMP solution (C = 100 mg mL⁻¹; 1,3,5-trimethoxybenzene: 12.6 mg, 65 µmol, 3 eq.). The total polymerization volume was kept to 0.95 mL of solvent. The mixture was stirred at room temperature for 10 minutes to allow all reagents to fully dissolve. A 1.1 cm piece of 18-gauge copper (0) wire was soaked in concentrated HCl for 15 minutes to remove surface impurities, then washed with water followed by acetone, dried *in vacuo* and taken into the glovebox. The wire was added to the mixture to initiate the polymerization. After 8 hours and 30 minutes, the polymerization was quenched by addition of water followed by filtration. The residue was purified by preparatory SEC in THF and fractions containing polymer were determined by SEC analysis. All fractions containing bottlebrush polymer were collected and dried *in vacuo* overnight.

Crude yield = 137 mg; Conversion = 85 %; $M_n = 2430$ kDa; PDI = 1.29



Synthesis of PBiBEM200-g-poly(M3)20

In a nitrogen atmosphere glovebox, to a 4 mL vial capped with a Teflon-lined lid and equipped with a magnetic stir bar was added **M3** (200.0 mg, 0.61 mmol, 20 eq.), 216 μ L of a **PBIEM**₂₀₀ solution in DMAc (*C* = 40 mg mL⁻¹; PBIEM₂₀₀: 8.6 mg, 30 μ mol, 1 eq.), 118 μ L of a CuBr₂/Me₆TREN in DMAc solution (*C*_{Cu} = 3.75 mg mL⁻¹; CuBr₂: 0.4 mg, 2 μ mol, 0.065 eq.; Me₆TREN: 0.5 mg, 2 μ mol, 0.068 eq.), and 179 μ L of a 1,3,5-trimethoxybenzene in DMAc solution (*C* = 100 mg mL⁻¹; 1,3,5-trimethoxybenzene: 17.8 mg, 91 μ mol, 3 eq.). The total polymerization volume was kept to 1.0 mL of solvent. The mixture was stirred at room temperature for 10 minutes to allow all reagents to fully dissolve. A 1.5 cm piece of 18-gauge copper (0) wire was soaked in concentrated HCl for 15 minutes to remove surface impurities, then washed with water followed by acetone, dried *in vacuo* and taken into the glovebox. The wire was added to the mixture to initiate the polymerization. After 4 hours and 30 minutes, the polymerization was quenched by addition of water followed by filtration. The polymer was dried *in vacuo* overnight. Yield = 168 mg; Conversion = 98 %; M_n = 1770 kDa; PDI = 1.58



Synthesis of PBiBEM493-g-poly(M3)18

In a nitrogen atmosphere glovebox, to a 4 mL vial capped with a Teflon-lined lid and equipped with a magnetic stir bar was added **M3** (204 mg, 0.62 mmol, 20 eq.), 221 µL of a **PBIEM**₄₉₃ solution in DMAc (C = 40 mg mL⁻¹; PBIEM₄₉₃: 8.8 mg, 31 µmol, 1 eq.), 121 µL of a CuBr₂/Me₆TREN in DMAc solution ($C_{Cu} = 3.75$ mg mL⁻¹; CuBr₂: 0.5 mg, 2 µmol, 0.065 eq.; Me₆TREN: 0.5 mg, 2 µmol, 0.068 eq.), and 183 µL of a 1,3,5-trimethoxybenzene in DMAc solution (C = 100 mg mL⁻¹; 1,3,5-trimethoxybenzene: 18.3 mg, 94 µmol, 3 eq.). The total polymerization volume was kept to 1.02 mL of solvent. The mixture was stirred at room temperature for 10 minutes to allow all reagents to fully dissolve. A 1.5 cm piece of 18-gauge copper (0) wire was soaked in concentrated HCl for 15 minutes to remove surface impurities, then washed with water followed by acetone, dried *in vacuo* and taken into the glovebox. The wire was added to the mixture to initiate the polymerization. After 4 hours, the polymerization was quenched by addition of water followed by filtration. The polymer was dried *in vacuo* overnight.

Yield = 159 mg; Conversion = 91 %; $M_n = 3430 \text{ kDa}$; PDI = 1.41



Synthesis of PBiBEM792-g-poly(M3)17

In a nitrogen atmosphere glovebox, to a 4 mL vial capped with a Teflon-lined lid and equipped with a magnetic stir bar was added **M3** (213 mg, 0.65 mmol, 20 eq.), 230 µL of a **PBIEM**₇₉₂ solution in DMAc (C = 40 mg mL⁻¹; PBIEM₇₉₂: 9.2 mg, 33 µmol, 1 eq.), 126 µL of a CuBr₂/Me₆TREN in DMAc solution ($C_{Cu} = 3.75$ mg mL⁻¹; CuBr₂: 0.5 mg, 2 µmol, 0.065 eq.; Me₆TREN: 0.5 mg, 2 µmol, 0.068 eq.), and 190 µL of a 1,3,5-trimethoxybenzene in DMAc solution (C = 100 mg mL⁻¹; 1,3,5-trimethoxybenzene: 19 mg, 98 µmol, 3 eq.). The total polymerization volume was kept to 1.06 mL of solvent. The mixture was stirred at room temperature for 10 minutes to allow all reagents to fully dissolve. A 1.6 cm piece of 18-gauge copper (0) wire was soaked in concentrated HCl for 15 minutes to remove surface impurities, then washed with water followed by acetone, dried *in vacuo* and taken into the glovebox. The wire was added to the mixture to initiate the polymerization. After 3 hours and 30 minutes, the polymerization was quenched by addition of water followed by filtration. The polymer was dried *in vacuo* overnight.

Yield = 167 mg; Conversion = 84 %; $M_n = 4360 \text{ kDa}$; PDI = 1.21



Synthesis of PBiBEM493-g-poly(M4)15

In a nitrogen atmosphere glovebox, to a 4 mL vial capped with a Teflon-lined lid and equipped with a magnetic stir bar was added **M4** (213 mg, 0.43 mmol, 20 eq.), 152 μ L of a **PBIEM**₄₉₃ solution in DMAc (*C* = 40 mg mL⁻¹; PBIEM₄₉₃: 6.1 mg, 21 μ mol, 1 eq.), 83 μ L of a CuBr₂/Me₆TREN in DMAc solution (*C*_{Cu} = 3.75 mg mL⁻¹; CuBr₂: 0.3 mg, 1 μ mol, 0.065 eq.; Me₆TREN: 0.3 mg, 1 μ mol, 0.068 eq.), and 125 μ L of a 1,3,5-trimethoxybenzene in DMAc solution (*C* = 100 mg mL⁻¹; 1,3,5-trimethoxybenzene: 12.5 mg, 64 μ mol, 3 eq.). The total polymerization volume was kept to 1.07 mL of solvent. The mixture was stirred at room temperature for 10 minutes to allow all reagents to fully dissolve. A 1.1 cm piece of 18-gauge copper (0) wire was soaked in concentrated HCl for 15 minutes to remove surface impurities, then washed with water followed by acetone, dried *in vacuo* and taken into the glovebox. The wire was added to the mixture to initiate the polymerization. After 38 hours, the polymerization was quenched by addition of water followed by filtration. The residue was purified by preparatory SEC in THF and fractions containing polymer were determined by SEC analysis. All fractions containing bottlebrush polymer were collected and dried *in vacuo* overnight.

Crude yield = 124 mg; Conversion = 73 %; M_n = 3960 kDa; PDI = 1.28 mg



Synthesis of PBiBEM493-g-poly(M5)19

In a nitrogen atmosphere glovebox, to a 4 mL vial capped with a Teflon-lined lid and equipped with a magnetic stir bar was added **M5** (201 mg, 0.56 mmol, 20 eq.), 194 μ L of a **PBIEM**₄₉₃ solution in DMAc (*C* = 40 mg mL⁻¹; PBIEM₄₉₃: 7.8 mg, 28 μ mol, 1 eq.), 108 μ L of a CuBr₂/Me₆TREN in DMAc solution (*C*_{Cu} = 3.75 mg mL⁻¹; CuBr₂: 0.4 mg, 2 μ mol, 0.065 eq.; Me₆TREN: 0.4 mg, 2 μ mol, 0.068 eq.), and 163 μ L of a 1,3,5-trimethoxybenzene in DMAc solution (*C* = 100 mg mL⁻¹; 1,3,5-trimethoxybenzene: 16.3 mg, 83 μ mol, 3 eq.). The total polymerization volume was kept to 1.01 mL of solvent. The mixture was stirred at room temperature for 10 minutes to allow all reagents to fully dissolve. A 1.4 cm piece of 18-gauge copper (0) wire was soaked in concentrated HCl for 15 minutes to remove surface impurities, then washed with water followed by acetone, dried *in vacuo* and taken into the glovebox. The wire was added to the mixture to initiate the polymerization. After 14 hours, the polymerization was quenched by addition of water followed by filtration. The residue was purified by preparatory SEC in THF and fractions containing polymer were determined by SEC analysis. All fractions containing bottlebrush polymer were collected and dried in vacuo overnight.

Crude yield = 169 mg; Conversion = 94 %; $M_n = 3840$ kDa; PDI = 1.44

3.3 Results and Discussion

Polyinitiator backbones were first prepared from BiBEM by reversible-addition chaintransfer (RAFT) polymerization, giving linear polymers with degrees of polymerization of 200, 493, and 792. The reaction is carried out using 2-cyano-2-propyl benzodithioate (CPBDT) as chain transfer agent in either *p*-xylene or anisole.^{102,104} The shorter two chains are most easily prepared at low conversion (< 20%) in *p*-xylene in under two hours, while PBiBEM₇₉₂ could be prepared at 76% conversion in anisole, though with a substantially longer reaction time (36 hours) (Scheme 3.1). This approach gives poly(α -bromoisobutyryl esters) with functionality orthogonal to the RAFT procedure, and suitable for grafting polymer chains by ATRP-type polymerizations.⁷⁷



Scheme 3.1 Synthesis of polyinitiators via RAFT polymerization and reaction to form bottlebrush polymers by grafting-from Cu(0)-RDRP using organic semiconductor-based monomers.

Concurrently, a series of acrylic monomers were prepared bearing organic semiconductors as benzylic functional groups. Monomers representative of hole-transport, electron-transport, and host materials commonly used in organic light-emitting diodes (OLEDs) or organic thin film transistors (OTFTs) were used, each of which can be prepared on a multigram scale.^{88,89} Carbazole-

based monomer **M3** was then grafted from each of the three polyinitiators to give bottlebrush polymers with side-chain lengths of 20, 18 and 17 units, respectively.

Bottlebrush polymers with $M_n = 1770$, 3430, and 4360 kDa were prepared with dispersities of 1.58, 1.41, and 1.21, dropping as longer chains were targeted. Interestingly, conversions up to 98% were observed for the Cu(0)-RDRP process despite the sterically demanding nature of the polymerization environment, and displayed first-order kinetics throughout the reaction. AFM height images of each of the PBiBEM-*g*-**M3** bottlebrushes demonstrates the clear progression to longer length fibers as the backbone length is increased, though short bottlebrushes < 50 nm in length can be observed in all cases (Figure 3.1). The bottlebrush side chain lengths were estimated by multiplying the percent conversion of monomer to polymer, determined by NMR spectroscopy, by the target side chain length. Side chain lengths in the grafting-from process can be quantified by calculating the initiation efficiency. This is typically done by cleaving the side-chains and comparing their molecular weights with those predicted if initiation were quantitative.¹⁰⁵ However, this cannot be done for our polymers as the side-chains cannot be selectively cleaved. As described in previous reports,¹⁰⁶ cleavage of the ester group linking the side-chains to the backbone would also result in side-chain degradation as the monomer units contain ester linkages.



Figure 3.1 GPC RI traces of macroinitiators (a) and bottlebrush polymers of M3 (c). Kinetic data for Cu(0)-RDRP polymerization of PBiBEM₄₉₃-g-poly(M3)₁₈ (b). Schematic illustrations and AFM height images of bottlebrush polymers based on 200 (d), 493 (e), and 792 (f) length polyinitiators on HOPG. Scale bars = 250 nm.

Bottlebrushes were then prepared by Cu(0)-RDRP of **M1-M5** using the PBiBEM₄₉₃ polyinitiator (Table 3.1). Monomer conversions ranging from 73% for the sterically bulky **M4** up to 94% for the smaller **M5** were obtained, giving bottlebrushes with $M_n = 1620-3840$ kDa and dispersities of 1.28-1.44. The reaction times needed to reach maximum conversion varied considerably from 3-5 hours for the p-type monomers **M1**, **M2** and **M3** compared to the n-type **M4** and **M5** (38 and 14 hours, respectively). It has been shown previously that reaction kinetics in Cu(0)-RDRP can be complicated by the presence of monomers bearing σ -donating nitrogen atoms capable of coordinating to Cu species in solution.⁸⁹

Entry	M_n	Đ	$\lambda_{max, abs}$	$\lambda_{max, em}$	$arPhi_F$	$E_{1/2}^{Ox}$ (V) ^d	$E_{1/2}^{Red}(\mathbf{V})^d$
	$(kDa)^a$		$(nm)^{b}$	$(nm)^c$			-
PBiBEM ₄₉₃ -	1620	1.34	303	457	0.14	0.42	/
<i>g</i> -poly(M1) ₁₇							
PBiBEM ₄₉₃ -	2430	1.29	304	465	0.28	0.47	/
<i>g</i> -poly(M2) ₁₇							
PBiBEM ₄₉₃ -	3430	1.41	293	347	0.22	0.57	/
<i>g</i> -poly(M3) ₁₈							
PBiBEM ₄₉₃ -	3960	1.28	292	411	< 0.01	/	-2.21
<i>g</i> -poly(M4) ₁₅							
PBiBEM ₄₉₃ -	3840	1.44	287	347	0.71	/	-2.72
<i>g</i> -poly(M5) ₁₉							

Table 3.1 Synthesis and properties of bottlebrush polymers

^{*a*} Determined by SEC in THF. ^{*b*} Measured in CH₂Cl₂ at 0.01 mg mL⁻¹. ^{*c*} Measured in toluene at 0.01 mg mL⁻¹. ^{*d*} Measured in 1,2-difluorobenzene relative to FeCp^{0/+}.

Interestingly, GPC refractive index traces of bottlebrush polymers isolated following the reaction consistently showed the presence of low molecular weight polymer for each material prepared in this way (Figure 3.2). These products had molecular weights in the range of 5600-10000 Da, closely approximating the expected molecular weights of the side chains grafted to the polyinitiator backbone in each case. Furthermore, the UV-visible spectrum of the low molecular weight polymer and the bottlebrush obtained by GPC photodiode array detection indicated that both were formed from the same organic semiconductor monomer.



Figure 3.2 (a) GPCs of PBiBEM₄₉₃-*g*-poly(**M2**)₁₇ before SEC (red) and after SEC (blue); (b) normalized absorbance spectra measured at retention times of 14 minutes (red) and 18 minutes (blue).

Moreover, repeated precipitation of the polyinitiator and preparatory size exclusion chromatography (SEC) did not reduce the proportion of low molecular weight byproduct in the reaction, ruling out the presence of BiBEM monomer impurities in the polymer sample. Autopolymerization of M1-M5 is also not observed in the absence of initiator over the reaction time scale. We believe these short chains to have cleaved from the main bottlebrush backbone as they become more sterically crowded as the grafting from polymerization of these relatively bulky monomers proceeds. The proportion of chains cleaved from the backbone also correlates reasonably well with the steric bulk of the monomer being used. Based on the relative integration of the high and low molecular weight refractive index peaks observed by GPC, the highest proportion of cleaved chains was observed for the bulky M2 (23%), while the lowest proportion (3.6%) was observed for M3, the smallest monomer of the series (Table 3.2). Similar behaviour has been previously observed for bottlebrush polymers where partial scission of lateral chains occurred.107 Spontaneous rupture of carbon-carbon covalent bonds in the macromolecular backbone has also been observed in brush-like macromolecules with long side chains.^{108,109} Fortunately, the short chains can be easily removed by passing the crude products over a reusable methacrylic size exclusion resin, affording pure bottlebrush nanofibers.

Entry	$M_n (Da)^a$	$M_n (Da)^b$	$\% \mathbf{RI}^{c}$
PBiBEM ₄₉₃ - <i>g</i> -poly(M1) ₁₇	3500	8900	17
PBiBEM ₄₉₃ - <i>g</i> -poly(M2) ₁₇	5300	9100	23
PBiBEM ₄₉₃ - <i>g</i> -poly(M3) ₁₈	4600	10000	3.6
PBiBEM ₄₉₃ - <i>g</i> -poly(M4) ₁₅	6800	8400	15
PBiBEM ₄₉₃ - <i>g</i> -poly(M5) ₁₉	4600	5600	19

Table 3.2 Properties of low molecular weight polymers observed by GPC

^{*a*} Determined by conventional calibration relative to polystyrene. ^{*b*} Determined by conventional calibration relative to linear polymers of the corresponding monomer. Molecular weights for these linear standards were determined by triple detection using the refractive index increment for each linear polymer.^{*c*} Percentage of sample composed of low molecular weight polymer based on integration of refractive index detector signals.

The photophysical properties of these fibers were then characterized by UV-visible and fluorescence spectroscopy as well as cyclic voltammetry (CV) (Figure 3.3). The emission spectra of PBiBEM₄₉₃-*g*-poly(**M1**)₁₇ and PBiBEM₄₉₃-*g*-poly(**M2**)₁₇ are dominated by broad exciplex emission in CH₂Cl₂, giving whitish-green emission with quantum yields (Φ) of 0.14 and 0.28, respectively, though some blue emission at 370 and 367 nm from the individual triarylamine chromophores can still be observed. The emission spectrum of PBiBEM₄₉₃-*g*-poly(**M3**)₁₈ contains both monomer and excimer emission in approximately equal proportion, and additionally was found to quickly plate the electrode with polymer during CV experiments. In contrast, PBiBEM₄₉₃*g*-poly(**M4**)₁₅ and PBiBEM₄₉₃-*g*-poly(**M5**)₁₉ show no excimer emission, with quantum yields of < 0.01 and 0.71, respectively.



Figure 3.3 Normalized absorbance spectra in toluene (solid) and photoluminescence spectra in CH₂Cl₂ (dashed) at 0.01 mg mL⁻¹, cyclic voltammetry and GPC RI traces of PBiBEM₄₉₃-*g*-poly(**M1**)₁₇ (a), PBiBEM₄₉₃-*g*-poly(**M2**)₁₇ (b), PBiBEM₄₉₃-*g*-poly(**M3**)₁₈ (c), PBiBEM₄₉₃-*g*-poly(**M4**)₁₅ (d), and PBiBEM₄₉₃-*g*-poly(**M5**)₁₉ (e).

3.4 Conclusions

Here we have demonstrated the use of a grafting-from strategy using RAFT polymerization and Cu(0)-RDRP for the preparation of nanofibers from both p- and n-type organic semiconductors. These methods employ brush growth from pre-synthesized linear polyinitiators, avoiding the difficulties in preparing long fibers encountered by a grafting-through approach. Cu(0)-RDRP was found to proceed with high conversion despite the steric congestion imposed by both the bulky monomers and the bottlebrush environment, reacting 74-98% conversion for all monomers examined. However, side chains were also found in the product mixture after the reaction, possibly due to cleavage from the main bottlebrush backbone due to steric factors. These methods provide a route to long cylindrical nanofibers which can be applied to a diverse range of organic semiconductors, with potential applications in macroscale optoelectronic devices or as functional nanoscale objects.

Chapter 4 : Conclusions

This thesis focused on the development of novel synthetic routes to both molecular and polymeric π -conjugated organic semiconducting materials with applications in electronic and optoelectronic devices.

We have demonstrated an atom-economical synthetic route to nitrogen-containing piconjugated materials based on Ti-catalyzed hydroamination which provides high yields using only simple filtration purification procedures. A variety of anilines and alkynes bearing electrondonating and electron-withdrawing substituents have been used to prepare these new conjugated molecules in good yields, with several showing strong π - π * absorption bands and high fluorescence quantum yields. Furthermore, the versatility of this method for the efficient synthesis of a broad range of conjugated systems has been demonstrated by using a boron-containing diyne. In this first example of using a boron-containing alkyne as a substrate for catalytic hydroamination, a new donor-acceptor material has been prepared which shows bright, solvent-dependent fluorescence characteristic of B-N based conjugated materials.

In addition, we have demonstrated the versatile synthesis of fiber-like nanostructures using the grafting-from approach to bottlebrush synthesis. Many of the current synthetic methods for preparing semiconducting nanowires suffer from the limitation of requiring very specific conditions and monomers to be successful. Long linear polyinitiators were synthesized by RAFT polymerization, followed by brush growth via Cu(0) RDRP. The use of the grafting-from strategy avoids the difficulties in preparing long fibers encountered by a grafting-through approach. Nanofibers from both p- and n-type organic semiconductors were synthesized and effective control over wire length was demonstrated. Cu(0)-RDRP was found to proceed with high conversion despite the steric congestion imposed by both the bulky monomers and the bottlebrush environment. These methods provide a route to long cylindrical nanofibers which can be applied to a diverse range of organic semiconductors, with potential applications in macroscale optoelectronic devices or as functional nanoscale objects.

Future investigations into the versatility of the demonstrated synthetic route to semiconducting nanowires should be conducted to explore whether this method is viable for more complicated bottlebrush architectures, such as bottlebrush copolymers. Block, random, and mixed bottlebrush copolymers could be synthesized and studied. A particularly intriguing possibility is the synthesis of core-shell bottlebrush copolymers. The synthesis of core-shell bottlebrush copolymers has literature precedent,⁷⁶ but their exploration using semiconducting monomers rather than simple commercial monomers is limited. For example, a core-shell bottlebrush copolymer with a core synthesized from a semiconducting monomer and a shell synthesized from a non-conductive monomer could provide a novel route to coaxial nanowires.

Semiconducting nanowires could also be synthesized using a different library of monomers. Side-chains could be synthesized using monomers with even more exciting properties such as electroluminescence, two-photon absorption, or thermally activated delayed fluorescence. This would provide an exciting and simple route to semiconducting nanowires having properties that are otherwise difficult to achieve due to the limited versatility of alternative synthetic methods.

Lastly, although these materials demonstrate properties that indicate their use in devices should be appropriate, it would be prudent to investigate these materials in a practical setting by incorporating them into devices and studying the performance. Furthermore, as linear polymers of the monomers presented in this thesis can be easily synthesized,^{88,89} a comparison of the performance of these monomers as linear polymers versus incorporated into a bottlebrush should be conducted to establish how the bottlebrush architecture affects the performance of semiconducting materials in devices.

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Appendix



Figure A1 Enamine and aromatic region of 400 MHz ¹H-NMR spectrum (ppm) of compound **1** in d_6 -DMSO at room temperature. Peaks at 8.9 (N*H*), 7.5 (C*H*) and 5.8 (C*H*) ppm are from enamine protons (taken from Ref. 22).



Figure A2 UV-Vis absorption $(2 \times 10^{-5} \text{ mol/L})$ and emission spectra $(2 \times 10^{-6} \text{ mol/L})$, normalized) of compounds 2-7 in THF solution (taken from Ref. 22).



~	Absorption Maxima	3	Emission Maxima	Fluorescence
Compound No.	(nm)	$(10^4 \text{cm}^{-1} \text{mol}^{-1} \text{L})$	(nm)	Quantum Yield
1	400	8.3	445	0.26
2	379	4.2	430	0.027
3	376	2.7	452	0.0088
4	360	3.3	440	0.045
5	399	5.0	448	0.075
6	379	4.8	457	0.0044
7	340	3.7	426	0.028

 Table A1 Absorption and emission data for compounds 1-7 (taken from Ref. 22).