

**BORON CONTAINING VINYL AROMATIC POLYMERS:
SYNTHESIS, CHARACTERIZATION AND APPLICATIONS**

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ABSTRACT OF THE THESIS

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Novel luminescent polystyrene-based organoborane polymers were synthesized via facile silicon-boron exchange reactions with boron tribromide. The Lewis acidity as well as the photophysical properties of the polymers were then fine tuned by variation of the organic π -system. The key step is a selective boron-tin exchange that allows for controlled and selective replacement of one of the bromine substituents by the chromophoric system, followed by substitution of the second bromine by a sterically hindered aryl group. The polymers and model compounds were fully characterized by multinuclear NMR spectroscopy. Molecular weights were determined by GPC. DSC and TGA were used to determine their thermal properties. Both polymers and model systems are highly emissive and UV-visible and fluorescence spectroscopy were used to ascertain their photophysical characteristics. To probe the use of the polymers as potential anion sensors, they were subjected to complexation

with fluoride ($[\text{Bu}_4\text{N}]\text{F}$ in THF) and their complexation was studied by ^{11}B NMR as well as UV-vis and fluorescence spectroscopy.

To counter the oxidative degradation of the systems a new strategy was adapted in which we prepared stannylcarbazole precursors which would act as chromophores. To further enhance the stability of the boron center in these systems the mesityl group was replaced by the bulkier 1,3,5-triisopropylphenyl group. The models and polymers synthesized show superior stability as compared to the compounds synthesized earlier. The compounds are also highly emissive in the blue region.

Systems that contain electroactive ferrocenyl groups in the side-chain of polystyrene were also synthesized. Cyclic voltammetry studies confirm the electroactive nature of these polymers. A quasi-reversible boron redox couple and a ferrocene-centered redox process were observed.

Finally, a trimethylsilyl-functionalized vinyl bithiophene monomer was prepared. This monomer was polymerized by a variety of methods including standard free radical polymerization (BPO, AIBN), via nitroxide-mediated polymerization (NMP) and also by anionic polymerization. Moderate molecular weights in the range of 4000 – 9000 were obtained.

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List of Abbreviations

Ar	Aryl
<i>n</i> -Bu	<i>n</i> -butyl
^t Bu	tert-butyl
Bipy	Bipyridine
Cp	Cyclopentadienyl
CT	charge-transfer
CV	cyclic voltammetry
EL	Electroluminescent
DMF	dimethylformamide
Fc	Ferrocenediyl or ferrocenyl
GC	gas chromatography
GC-MS	gas chromatography-mass spectrometry
LEDs	Light emitting diodes
HOMO	highest occupied molecular orbital
LUMO	lowest unoccupied molecular orbital
Mes	2,4,6-trimethylphenyl

NMR	nuclear magnetic resonance
Py	pyridine
Rc	ruthenocenyl
THF	tetrahydrofuran
TEMPO	2,2,6,6-tetramethylpiperidyl
TMS	Trimethylsilyl
Tip	2,4,6-triisopropylphenyl
OLED	organic light emitting diode
NLO	non-linear optical
UV-vis	Ultraviolet-visible
GPC	gel-permeation chromatography
PDI	polydispersity index
MALDI-TOF	matrix-assisted laser desorption ionization time of flight

Chapter 1. Introduction

1.1 Conjugated Polymers

Conjugated oligomers and polymers are compounds that consist of a framework of alternating single and double bonds. The single bonds are referred to as σ -bonds and the double bonds contain a σ -bond and a π -bond. Although the chemical structures of these compounds are represented as alternate single and double bonds, the electrons of the π -bonds are delocalized over the whole molecule. This delocalization of the π -electrons can give rise to interesting optical^{1, 2}, photoelectric as well as magnetic properties.³ Hence, conjugated oligomers and polymers have been a subject of extensive research and have found applications in various fields ranging from their use in batteries, as photoactive materials for solar cells, in photo- and electro-active devices and even as sensors.¹

The genesis of the field can be traced back to the mid 1970's which marked the discovery of the first conducting polymer – polyacetylene – by Shirakawa and the subsequent 12 fold increase in conductivity, which could be achieved upon oxidative doping of polyacetylene as observed by Heeger and MacDiarmid. Polyacetylene is not considered to be the best candidate for electronic and electro-optical applications due to its instability. But due to its simplistic structure as well as electronics it has been extensively studied and has proven to be the launch pad for studies on other conducting polymers.^{4, 5}

Polymers that have aryl rings in the backbone are another type of polymers that are considered suitable for electronic and opto-electronic applications. Poly(para-phenylene)'s (**PPP**) and poly(para-phenylenevinylene)'s (**PPV**) are some of the most actively studied

polymers in this class because of the extensively delocalized π -electron structure. Synthetic difficulties and solubility issues with these type of polymers have been the limiting factor in their applications as electroactive polymers. Aliphatic and solubilizing groups on the aryl rings have been employed to circumvent solubility issues. The stability of these polymers is much higher than that of polyacetylenes and hence they have been commercially employed in opto-electronic devices.^{1, 5}

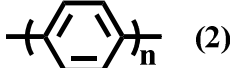
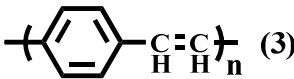
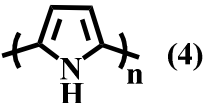
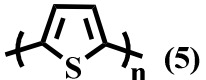
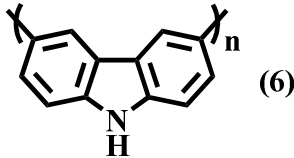
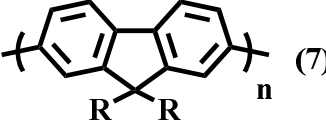
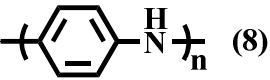
Polymer	Structure
Polyacetylene (PA)	 (1)
Poly(para-phenylene) (PPP)	 (2)
Poly(para-phenylenevinylene) (PPV)	 (3)
Polypyrrole (PP)	 (4)
Polythiophene (PT)	 (5)
Polycarbazole	 (6)
Polyfluorene (PF)	 (7) R = alkyl, aryl
Polyaniline (PA)	 (8)

Chart 1.1 Some Extensively Studied Conjugated Polymers.

Polyheterocycles like polythiophenes and polypyrroles make up the third type of conjugated polymers that are widely studied and employed for opto-electronic applications mainly due to their film forming capabilities. These polymers were also plagued with similar issues as the polyaryl polymers in terms of solubility but the ease of substitution on the 3-position of these heterocyclic compounds has been used to synthesize soluble materials. The easily oxidizable pyrrole moiety limits the chemical processability which also makes the polymer prone to oxidative degradation. Polythiophenes on the other hand show far superior stability, rich synthetic flexibility and chemical processability. Substituted polythiophenes have been widely studied due to their interesting electronic properties in both doped and undoped states.⁵

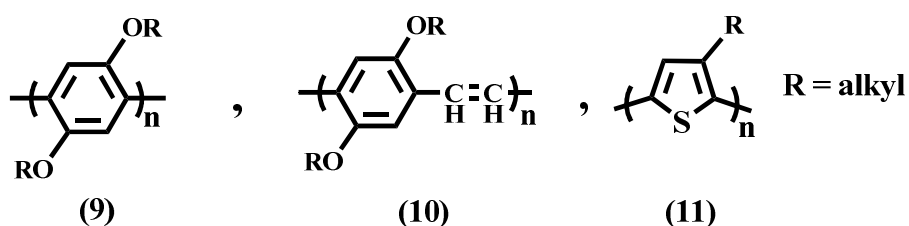


Chart 1.2 Substituted PPP, PPV and PT's.

Polyfluorenes and polycarbazoles are some of the other conjugated polymers that have been exploited as layers in Organic Light Emitting Device's (**OLED's**), as organic photovoltaic materials (**OPV**) and also for application in organic thin film transistors (**OTFT's**).

1.2 Applications of Conjugated Polymers

Due to the presence of highly delocalized π -electrons in their backbone, conjugated polymers find applications in a variety of fields. Some of these applications are briefly discussed in this section.

1.2.1 Conjugated Polymer in Photovoltaic Cells

A photovoltaic cell (**PV**) or a solar cell is a device which can convert solar energy into electrical energy via the photovoltaic effect. The need to develop renewable energy resources has motivated scientists to fabricate low-cost and efficient photovoltaic devices. Solar cells that we know are based on highly pure crystalline silicon, but the high cost of manufacturing has prevented their more widespread utility as a source of our electricity.⁶ Thin films of conjugated polymers present a potential alternative to crystalline silicon based devices. Conjugated polymers offer the following advantages: (a) ease and cost-effectiveness of synthesis; (b) thin films can be cast very easily on a variety of substrates using wet-processing techniques like spin-casting or even printing technologies; (c) organic semiconductor films are strong absorbers and high extinction coefficients (10^5 cm^{-1}) can be obtained, which make them excellent chromophores for optoelectronic applications; (d) the electronic band gap can be easily modified by chemical synthesis and (e) charge carrier mobilities comparable to amorphous silicon have been reported.⁶⁻⁹

Phthalocyanine (12), perylene (13), C_{60} -fullerene (14) derivatives are generally used for these applications and while their films must be deposited on a substrate by evaporation, polymers like poly(3-hexyl thiophene) (**P3HT**) (15), poly[2-methoxy-5-(2'-ethylhexoxy)-1,4-phenylenevinylene] (**MEH-PPV**) (16) and poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-p-phenylenevinylene] (**MDMO-PPV**) (17) can be cast by wet processing techniques.^{6, 7}

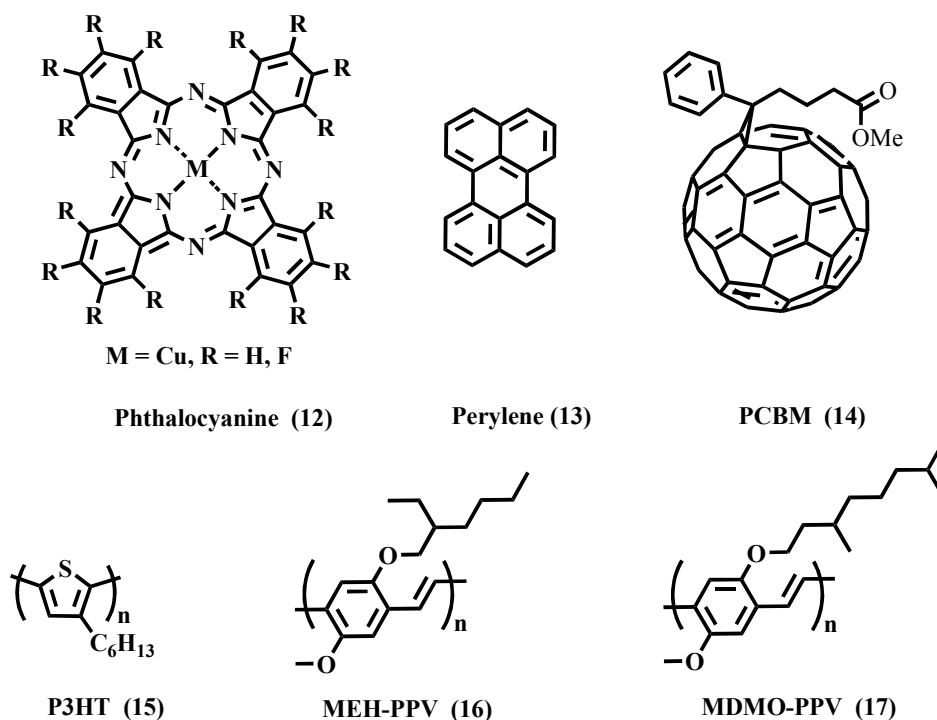


Chart 1.3 Some Commonly Used Organic Semiconductors for PV Applications.

One major limiting process in organic photovoltaic (**OPV**) devices is charge transport of the exciton to the donor-acceptor interface and recently Wong and co-workers were able to overcome this issue by incorporating an organometallic donor moiety into the polymer main-chain.^{10, 11} On similar lines Jen et al. synthesized a series of polymers that contain Pt metal in conjugation with an alkyne (18-19) which reportedly enhances intrachain charge transport of π -conjugated polymers. These polymers show high field-effect mobilities and high power conversion efficiencies.¹² Another possible solution for the short singlet exciton diffusion length may be the formation of triplet excitons, as they are expected to possess longer life times and diffusion lengths thereby increasing the efficiency of charge generation. Holdcroft et al. recently incorporated triplet forming Ir complexes into polyfluorene based polymer (20) which enhances solar cell conversion efficiencies.¹³

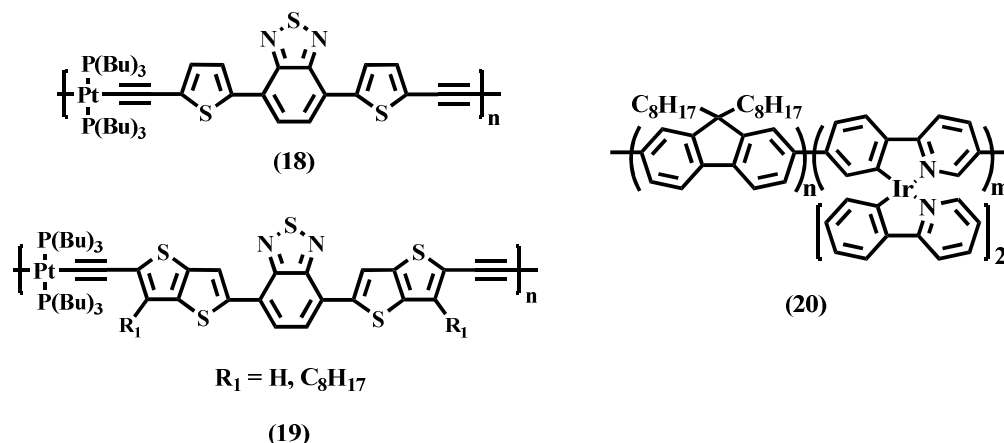


Chart 1.4 Enhanced Efficiency Polymers for PV Applications.

1.2.2 Conjugated Polymers as Emissive Layers in Organic Light Emitting Diodes (OLED's)

Since the discovery of electroluminescence (**EL**) from conjugated polymers by Holmes, Friend and co-workers, it has been a subject of great interest in the scientific community because of its potential applications in display technology.^{14, 15} Conventional light-emitting diodes are made of inorganic crystals like GaAs or GaN and though they are remarkable for many applications, they are not suitable for applications that involve large area displays and displays that require a flexible substrate.¹⁵ Conjugated polymers on the other hand can be advantageous in such cases since they can be easily patterned in large areas onto almost virtually any substrate via wet-processing techniques and they also possess the ability to emit in a range of colors that encompass the entire visible region by simple chemical modification methods.^{16, 17} A typical OLED device consists of the components shown in Figure 1.1. The most commonly used polymers in displays include the derivatives of poly(arylenevinylene)'s (**PAV**) and polyfluorenes (**PF**) where substituents on the side chain may determine the emission color, stability and solubility of the polymer.

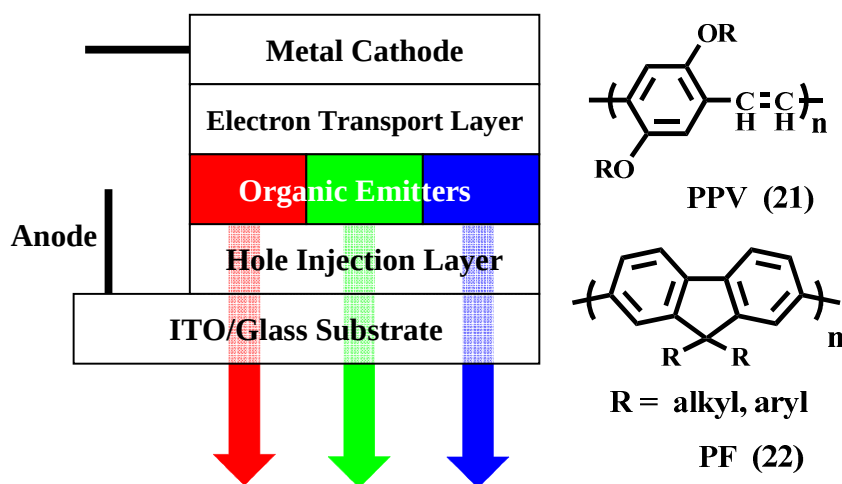


Figure 1.1 Structure of an OLED Device and Commonly Used Polymers as Emitters for OLED Applications.

Of the PAV family the most widely studied polymers are PPV derivatives. The parent compound PPV is insoluble and to counter the insolubility, derivatives like MEH-PPV (16), Chart 1.3, that contain alkyl, aryl, silyl or alkoxy chains are used. The derivatives with solubilizing groups show good solubility in common organic solvents and can be solution cast into thin films.¹⁵

The second most studied group of polymers for OLED applications are polyarylenes. A few examples are already shown in Chart 1.1 viz. PPP's (2), polycarbazoles (6) and PF's (7). One major advantage of polyarylenes is that the methods used for their synthesis generally produce polymers that are free of defects.¹⁵

1.2.3 Chemical Sensors based on Conjugated Polymers

Conjugated polymers have emerged as one of the most important classes of compounds for sensing applications as they readily convert chemical signals to an optical or an electrical event that can be measured. The most important characteristic that has the scientific community worldwide interested in the use of conjugated polymers as sensors is their ability

to produce signal amplification as a response to the interaction with an analyte. This concept of signal amplification by a conjugated polymer was first reported by Swager and co-workers in 1995 when they synthesized and used a PPE polymer (23) with cyclophane moieties incorporated into the backbone, which acted as a receptor for paraquat.^{18, 19}

Xi and coworkers synthesized crown ether functionalized PPV (24) for sensing of K^+ ions; since the crown ether was based on a benzo-18-crown-6 moiety, it did not show any selectivity for K^+ over Li^+ or Na^+ .²⁰ On similar lines Leclerc et al. synthesized a fluorescent probe for K^+ ion in the form of a polythiophene functionalized with 15-crown-5 as the receptor. This polymer showed selectivity for K^+ over Li^+ and Na^+ .²¹ In 2004, Liu et al. developed a PPE based sensor, functionalized with triethylene glycol monomethyl ether groups, which showed response to Li^+ and Na^+ but not to K^+ . By further tuning the sterics on the comonomer they were able to achieve selectivity for Li^+ over Na^+ .²² Recently Wang et al. synthesized thymine-functionalized polythiophene (25) for which they observed a red-shift in the absorption maximum with quenching of the fluorescence intensity in the presence of Hg^{2+} ; the process could be reversed by addition of Cl^- . This quenching was observed only for Hg^{2+} , while much less quenching was observed in the presence of Mg^{2+} , Ca^{2+} , Mn^{2+} , Co^{2+} and Ni^{2+} .²³ Other systems that employ copolymers of fluorene and 3-alkyl thiophenes (26) with 2,2'-bipyridine as sensors for transition metals and alkaline earth metals are also known.^{20, 24}

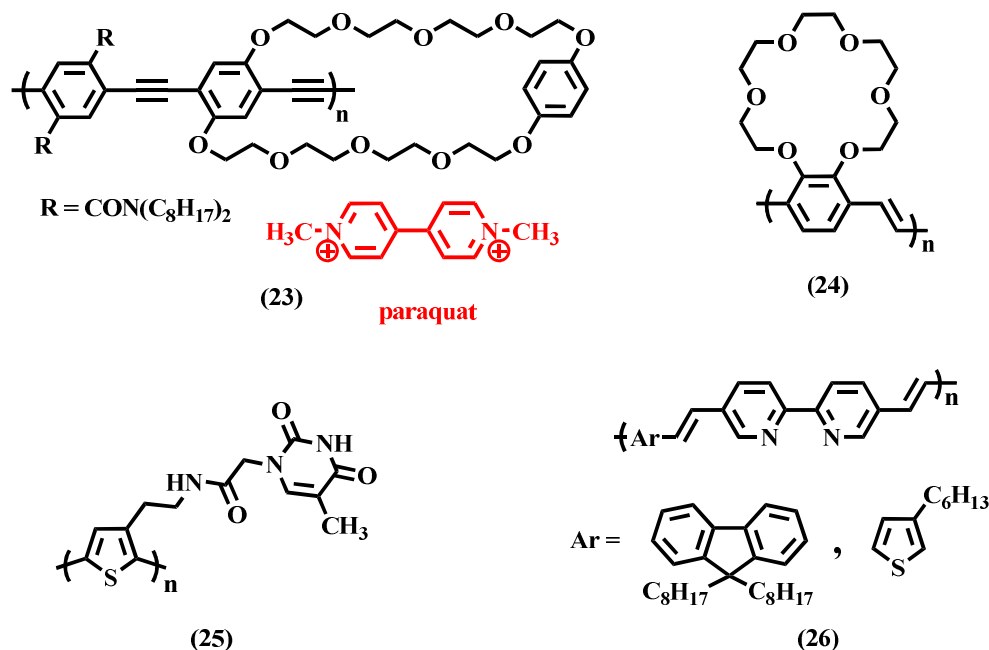


Chart 1.5 Examples of Conjugated Polymer Sensors.

Not only have conjugated polymers been used for detection of cations, they have also been employed as sensors for anions. For example, Fujiki et al. synthesized a σ -conjugated poly(silane) (27) for detection of fluoride. The polymer proved to be an efficient sensor for fluoride due to the affinity of the silicon center towards fluoride ions.²⁵ Recently Sun and co-workers reported a copolymer of poly(phenyleneethynylene) and dipyrrolylquinoxaline units (28) which showed a 34-fold signal amplification over its small molecule counterpart, but did not show selectivity for fluoride over phosphate.²⁶

Conjugated polymers have also been employed as sensors for explosives. In particular this work has been led by Swager at MIT who in 1998 used fluorescence quenching along with signal amplification of a PPE based polymer (29) to detect TNT, a primary explosive component in land mines.²⁷ Trogler and co-workers have reported the use of poly(siloles) for detection of nitroaromatics, specifically TNT. The tetraphenylsilole (30) showed 38% increase in sensitivity relative to an oligomeric compound.²⁸

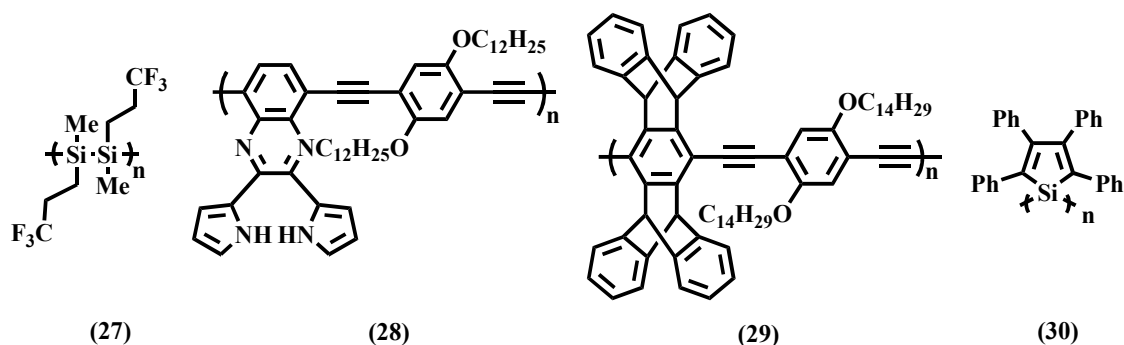


Chart 1.6 Examples of Polymer Sensors for Anions and for the Detection of Explosives.

1.3 Side-chain Functionalized Polymers

As opposed to their main-chain counterparts, side-chain functionalized polymers have received far less attention, particularly, non-conjugated polymers that bear side-chain functionalities. Recently there has been a surge in the study of such polymers due to certain advantages such as (i) polymers with controlled architecture can be obtained which leads to the possibility of the synthesis of block co-polymers, (ii) the facile variation of the degree of functionalization, and (iii) the possibility for attachment of more than one functionality to the polymers. Many of these polymers find applications in a variety of fields. For example, polymers that contain azobenzene chromophores show interesting nonlinear optical properties and owing to their photoactivity azo-polymers can be employed as photoswitches, in holographic data storage devices and also in photomechanical systems.²⁹ Poly(alkoxymethylmethacrylate)s (31), that contain a sudan type dye in the side-chain were studied for optical data storage applications.³⁰ Similarly Lu and coworkers have applied atom transfer radical polymerization (**ATRP**) to synthesize polyacrylates that bear substituted azobenzene (32) in the side chain for optoelectronic applications.^{31, 32} Also Asha and co-workers have reported the incorporation of fluorescent azobenzene dyes into the side-chain of

methyl methacrylate polymers which comprise of fluorophores like phenylphenol and naphthol moieties (33-34). These polymers show fluorescence at room temperature.³³

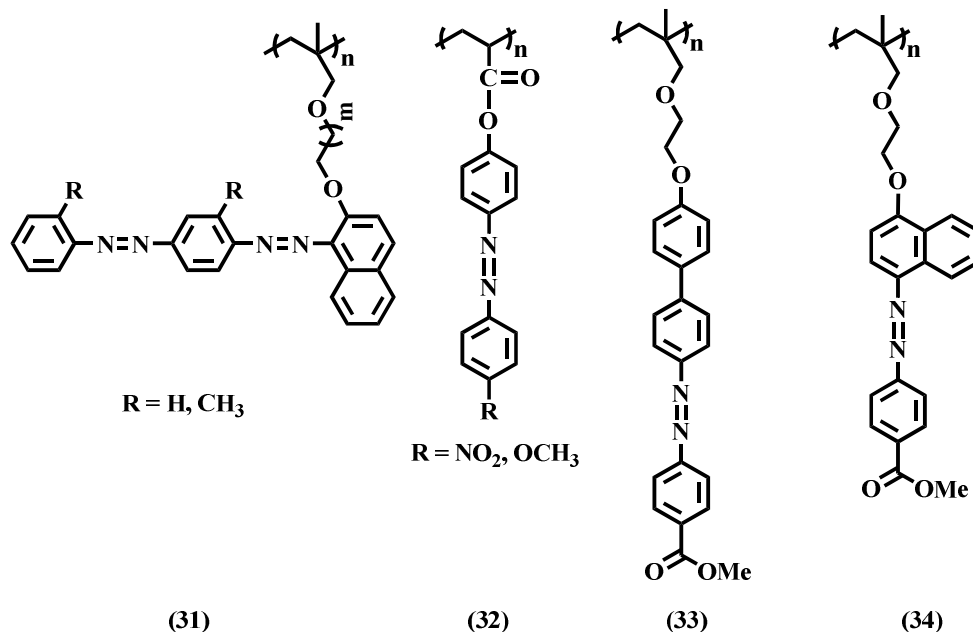


Chart 1.7 Examples of Azobenzene Containing Side-chain Polymers.

A graft copolymer that has a polythiophene back-bone with a quinoline side-chain (35) was prepared by Kallitsis et al. using a modified polythiophene as a macroinitiator for polymerization of vinylquinoline using ATRP.³⁴ The polymer showed interesting optical as well as electrochemical properties and was employed as a compatibilizing copolymer for a polymer blend for photovoltaic applications. Nuyken et al. have used free radical polymerization to synthesize a series of copolymers with styrene as the backbone, where one of the monomers is a styrene-functionalized hole conductor and the other is a styrene functionalized cross-linker (36). The hole-only devices made using these polymers showed higher onset values in comparison to their small molecule analogues.³⁵

So far very few examples of side-chain polymers for sensing of explosives are known. One example is the N-substituted-4-amino-1,8-naphthalimide substituted polystyrene (37)

reported by Pierre et al. The solution-cast polymer film shows quenching of the emission upon exposure to 2,4-dinitrotoluene (DNT) and hence can be used for sensing of explosive nitroaromatic compounds.³⁶

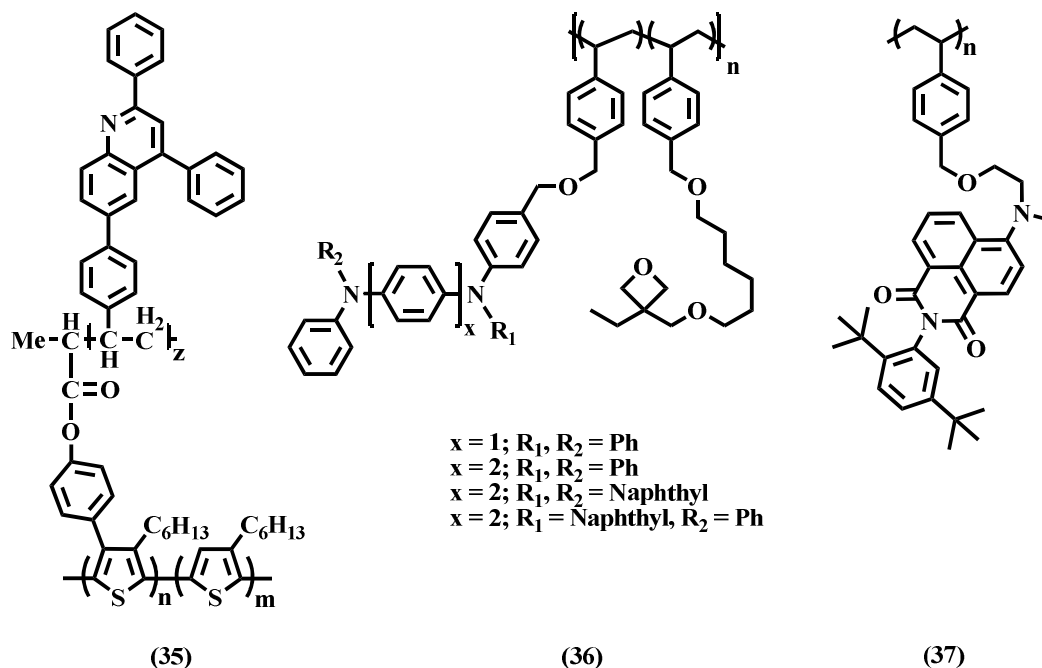


Chart 1.8 Examples of Side-chain Polymers for Photovoltaic Applications, as Hole Transport Materials and as Sensors for Explosives.

Combining the functionality of metal ions with organic polymers has been an extremely fertile area of research and most of the metal or metal complex containing polymers either incorporate the metals in the main-chain or at the terminus.³⁷ Relatively fewer systems exist that include metals in the side-chain of polymers. For example, Tew and co-workers have incorporated ruthenium-terpyridine complexes ($\text{Ru}(\text{terpy})_2$) into poly(acrylic acid) (38); these polymers can self assemble into ordered nanostructures and show lyotropic liquid crystalline properties.³⁷ Sleiman et al. have reported norbornene based homo and block copolymers that have Ru metal complexes as pendant groups via ring opening metathesis polymerization

(ROMP) (39); they show interesting optical as well as electrochemical properties.^{38, 39} On the other hand Weck and co-workers have prepared homo, diblock and random polymers based on norbornene and styrene that have metal complexes such as Ir, Ru and Pd (40-43) in the side chain and studied their use as highly phosphorescent materials for OLED applications.⁴⁰⁻

44

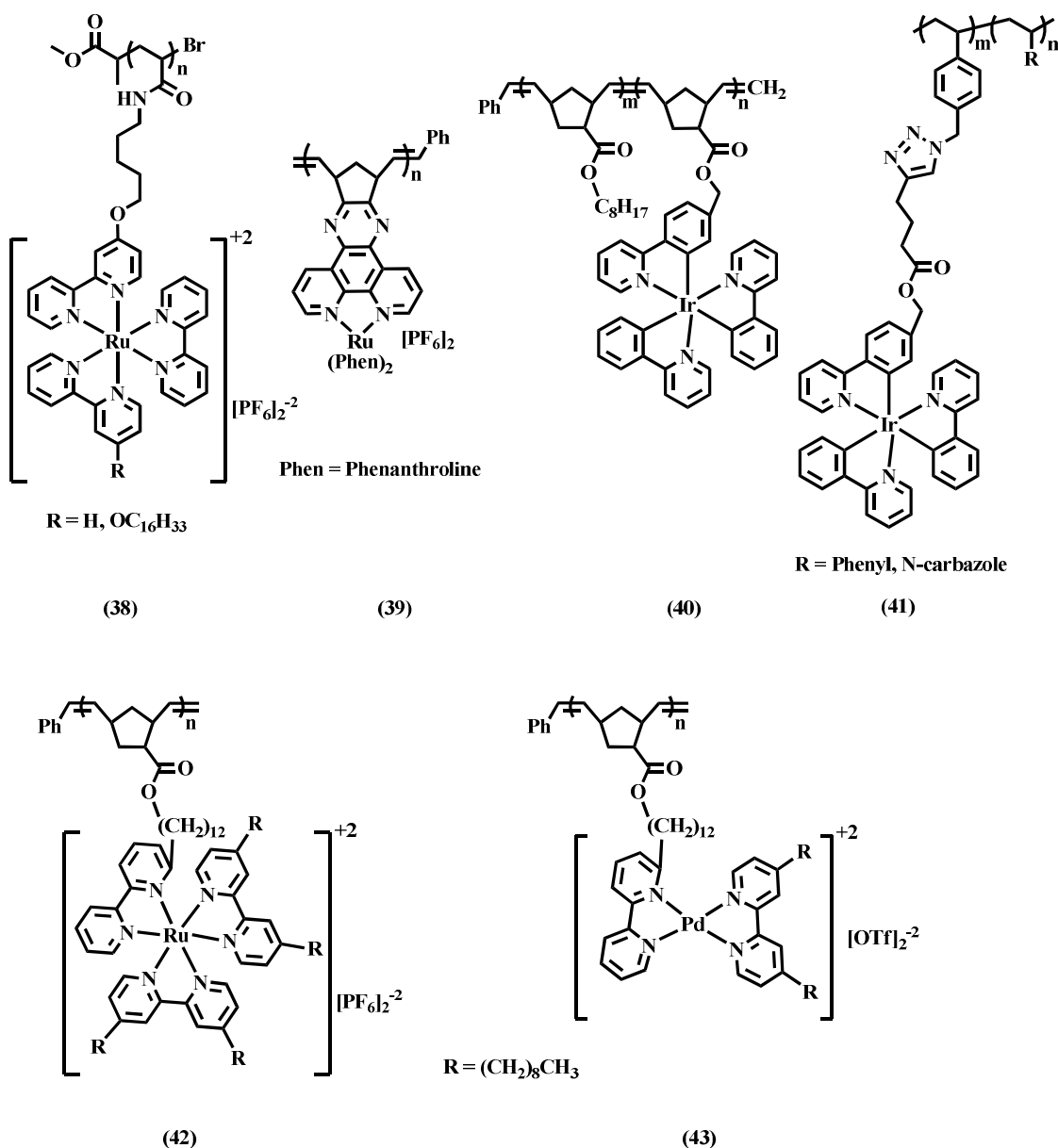


Chart 1.9 Examples of Side-chain Polymers Containing Ir, Ru and Pd Metal-complexes.

Polymers that have aluminum quinolate (Alq_3) moieties in the polymer side chain have also been realized. For example, Weck and co-workers were able to polymerize aluminum quinolate-functionalized norbornene monomers using ROMP, which yielded polymers with controlled molecular weights and low polydispersities (44).⁴⁵ The emission of these polymers was fine tuned by varying the ligands. A series that employed polystyrene instead of polynorbornene as the backbone was also developed by Weck et al. This system had styrene with functional handles dispersed in a random fashion throughout the polymer to which the Alq_3 moieties could be attached (45). Once again the optical properties could be easily tuned by changing the ligands on the quinoline moiety.⁴² The authors also reported the synthesis of copolymers of polycyclooctenes that bore Alq_3 functionalities and carbazole groups in the side-chain. They noted that the copolymers were able to retain the optical properties of their small molecule analogs and would be promising candidates as materials for OLED devices.⁴⁶

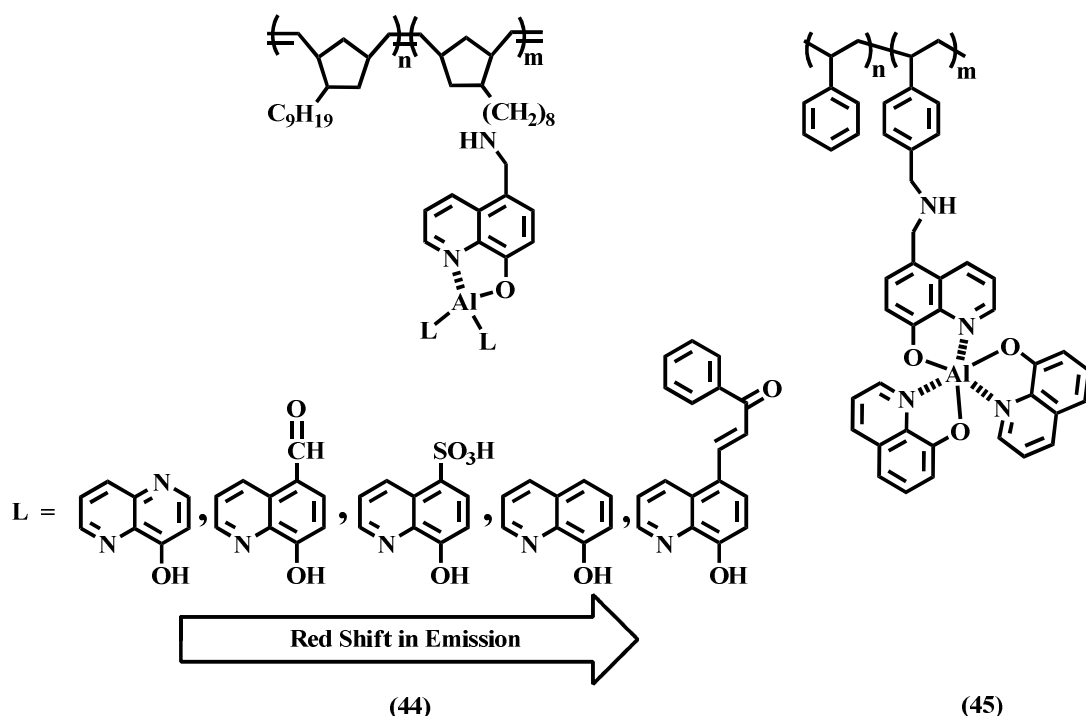


Chart 1.10 Examples of Side-chain Polymers Containing Aluminum Quinolate Moieties.

1.4 Organoboranes

Since the goal of my studies was to incorporate electron-deficient organoborane moieties into vinyl polymers, the chemistry and applications of organoboron containing small molecules will be briefly reviewed in this section.

The discovery of triethylborane by Frankland in 1859 marks the beginning of the chemistry of organoboron compounds. A breakthrough in the synthesis of organoboron compounds was the realization of hydroboration of alkenes by H. C. Brown in the mid 1950's. Organoboron compounds are primarily of interest because of their ability to act as Lewis acids which is due to the empty p-orbital on tri-coordinate boron. Boron can achieve its desired octet configuration either by overlapping with an organic π -system or by the formation of Lewis acid-Lewis base complexes (Figure 1.2).⁴⁷

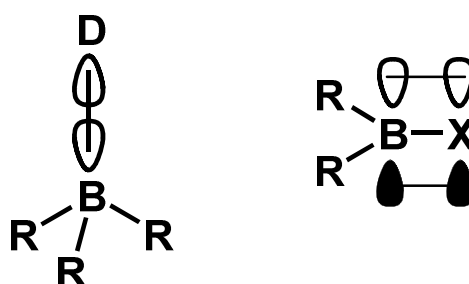


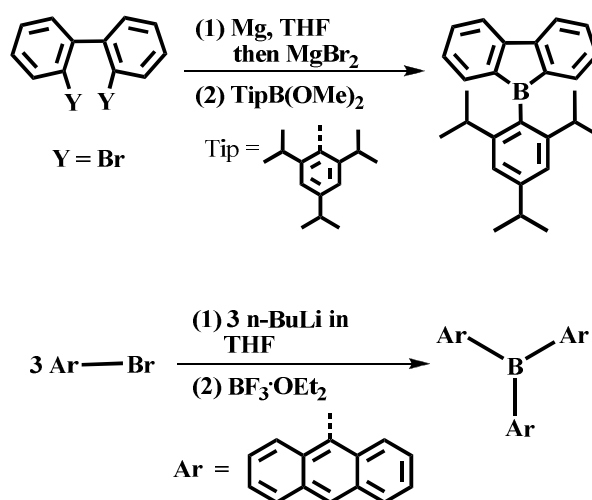
Figure 1.2 Schematic Illustration of Properties of Organoboron Compounds.

Organoboranes can be prepared by a variety of methods, the most important being transmetallation, boration of unsaturated compounds and C-H activation.⁴⁷

1.4.1 Synthesis of Organoboranes

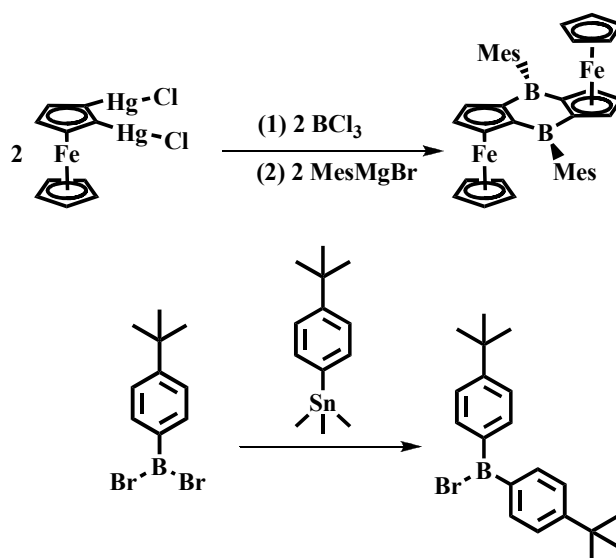
1.4.1.1 Transmetallation Using Organometallic Precursors

Transmetallation is one of the most important methods for the synthesis of organoboranes. Of the many organometallic reagents available for transfer of organic substituents to boron, organolithium and Grignard reagents are preferred (Scheme 1.1).^{48, 49}



Scheme 1.1 Examples of the Organometallic Reagents for Synthesis of Organoboron Compounds.

In certain cases organolithium and Grignard reagents tend to be too reactive, which may lead to side reactions. Hence organosilicon, organotin, organozinc, organocopper and organomercury compounds have also been employed in transmetallation reactions (Scheme 1.2).^{50, 51}



Scheme 1.2 Examples of the Organomercury and Organotin Reagents for Transmetalation to Boron.

1.4.1.2 Hydroboration Reactions

The discovery of hydroboration reactions by Brown was a breakthrough for the advancement of organoboron chemistry. This reaction is still one of the most important routes toward the synthesis of organoboranes. A library of hydroboration reagents is readily available for these reactions. Arylboranes (ArBH_2 and Ar_2BH) have been used as alternatives to alkylboranes to counter retrohydroboration reactions. Mesitylborane (46), triisopropylphenylborane (46) and dimesitylborane (47) as well as their polymer-supported versions are examples of stable hydroboration reagents available. Perfluorinated diarylborane (48) synthesized by Piers and co-workers using the commercially available trispentafluorophenylborane ($\text{B}(\text{C}_6\text{F}_5)_3$) shows remarkable activity as a hydroborating agent due to the electron-deficient nature of the boron and the formation of monomeric borane in solution (Chart 1.7).^{52, 53}

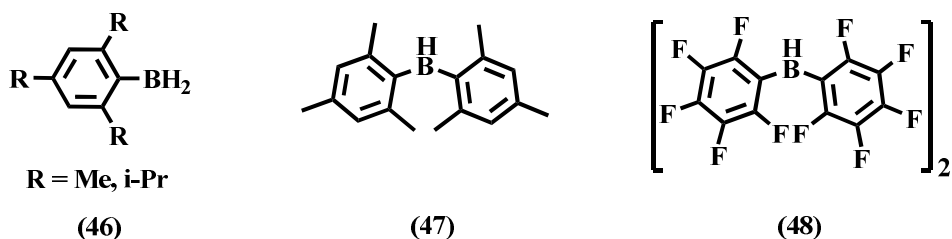


Chart 1.11 Examples of Arylboranes Used as Hydroboration Reagents.

1.4.2 Applications of Organoboranes

1.4.2.1 Organoboranes as Opto-electronic Materials

Tri-coordinate organoboron compounds are an important class of molecules as they can potentially be used as advanced materials. One of the most important characteristic of tri-coordinated boron compounds is the presence of an empty p-orbital on the boron which can overlap with an organic π -system. It is this p- π interaction that leads to interesting linear and non-linear optical properties as well as favorable electron transport abilities, which allow for the use of organoboranes as emission and electron conduction materials in OLED devices.^{47, 54, 55} The boron p-orbital is susceptible to nucleophilic attack and the latter can lead to either cleavage of the B-C bond or formation of a tetracoordinated boron species in which the extended conjugation is broken. As a general strategy sterically demanding groups like mesityl (2,4,6-trimethylphenyl) or triptyl (2,4,6-triisopropylphenyl) groups are used to provide stability to the boron center.⁵⁵

Many groups around the world have successfully synthesized such boron containing small molecules, one example being the synthesis of 3-boryl-2,2'-bithiophene (49) by Yamaguchi and co-workers. These bithiophene based π -electron materials show intense solid state emission which can be tuned by the use of either electron-withdrawing or electron-donating substituents and may be employed for optoelectronic applications.⁵⁶ Yamaguchi et al. also

synthesized phenylenevinylene (50) and phenyleneethynylene (51) based boron materials that show a solid state quantum efficiency of unity; the emission of the compounds can be fine tuned by using various substituents.⁵⁷ Wang at Queens University in Canada has synthesized a series of naphthylphenylamino functionalized organoboron compounds (52-53) that show intense blue emission and may be employed as hole transport or hole injection materials for electroluminescent (**EL**) devices.^{58, 59}

Shirota and co-workers have developed a series of π -electron compounds end-capped with boron moieties i.e. one, two or three thiophene units end-capped with dimesitylboryl groups (54). The compound with a bithienyl moiety (n=2) was found to have stronger electron-accepting ability than Alq₃, showed intense blue emission and could be used as a host matrix for emitters.⁶⁰ A similar molecule based on dithienothiophene (55) synthesized by Mazzeo and co-workers was found to emit bright white light from a single layer of spin-coated film.⁶¹ Shirota and his group have also synthesized a family of triarylboranes (56-58) that can be used as hole-blocking materials in combination with Alq₃ as the electron-transport material, allowing for blue and violet-blue emission.⁶²

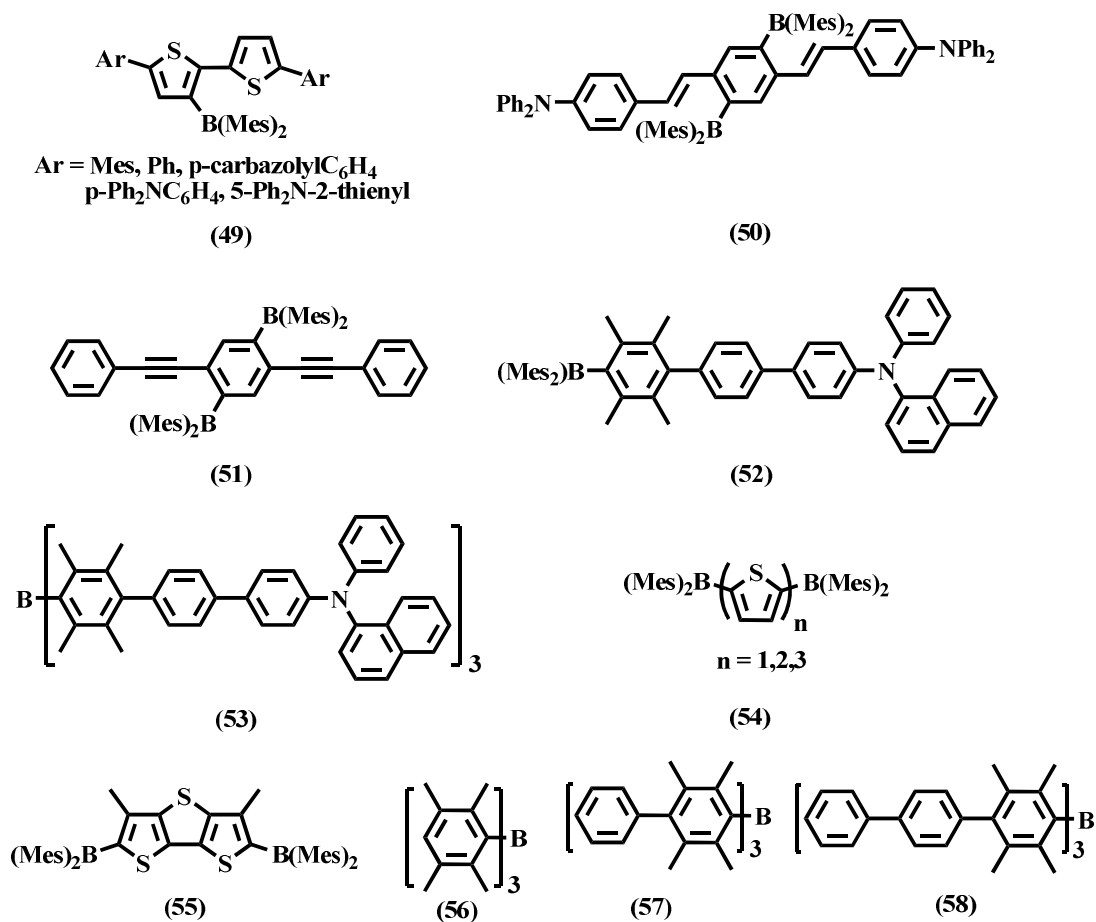


Chart 1.12 Examples of Boron Based Molecular Materials for Electroluminescent Devices.

Not only are tricoordinated organoboron molecules of interest as photo and electroluminescent materials, but a number of tetracoordinated organoboron molecules have also been reported. The boron quinolate compounds (59-60) are analogs of aluminum quinolato compounds. They are more stable compared to their Al counterparts and their emission properties can be fine tuned by varying the ligands.^{63, 64}

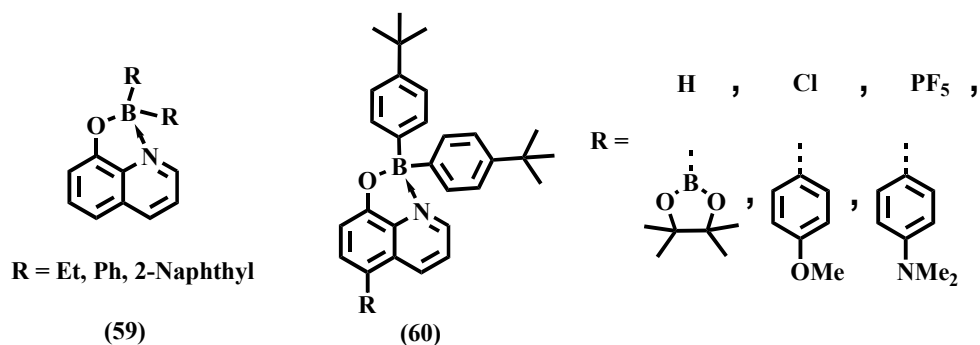


Chart 1.13 Examples of Tetracoordinated Organoboron Compounds for Electroluminescent Devices.

1.4.2.2 Organoboranes for Molecular Recognition

The ability of the empty boron p-orbital of triorganoboranes to form reversible donor-acceptor type complexes has been the basis of their use in sensing applications. Tricoordinate organoboron compounds have been exploited as effective probes for detection of anions; boronic acids and boronic esters have also been employed as efficient sugar sensors.⁶⁵ It is known that triarylboron compounds show significant affinity toward fluoride and cyanide. For instance, Fang and co-workers synthesized a series of phenylenevinylene type compounds (61-63) that act as “turn-off” sensors in the presence of fluoride ions, while no change in emission intensity or shifts in emission maxima are observed in the presence of other halides or even acetate, perchlorate, nitrite and nitrate ions.⁶⁶

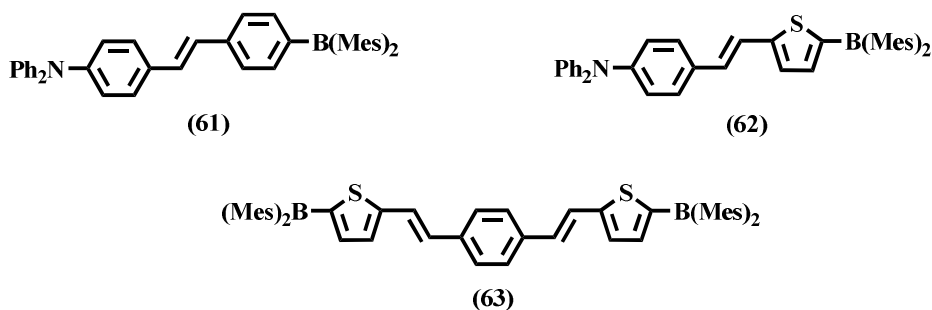


Chart 1.14 Triarylboron Compounds as Anion Sensors.

Wang et al. reported the synthesis of boron-indolyl complexes (64) which are capable of acting as blue emitters in OLED's and also can selectively bind fluoride, thereby leading to quenching of the indolyl-boron charge transfer emission.⁶⁷ They also synthesized a series of donor- π -acceptor compounds (65-69) to compare the origin of emission and also how their geometry affects binding. They inferred that there is a strong effect of the separation distance between donor and acceptor on the emission pathway and emission efficiency. Of the three classes the "U-shaped" (66-67) and "V-shaped" (68-69) molecules are promising candidates for sensing of fluoride.⁶⁸⁻⁷⁰

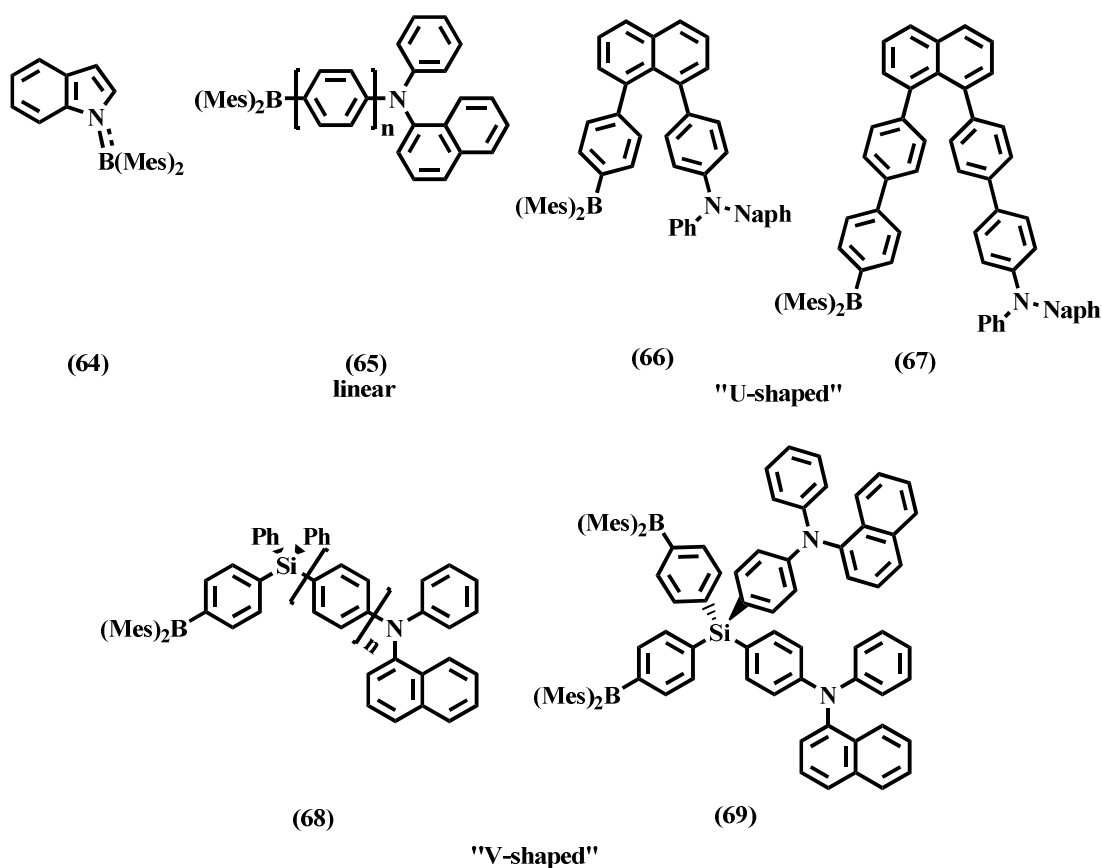


Chart 1.15 Donor- π -acceptor Molecules for Fluoride Binding.

A phosphorescent iridium-containing arylboron compound (70), which can be applied as a sensor that is selective for fluoride ions was developed by Li and co-workers. They observed

a pronounced red-shift in the emission spectra upon addition of the fluoride, the color of the solution changed from orange-red to yellow and the red emission was completely quenched upon complexation.⁷¹ Recently Gabbaï et al. also prepared a bidentate phosphorescent Lewis acid (71) for which they observed high selectivity for fluoride in partial aqueous medium and high binding constants due to the proximity of the two Lewis acids in the molecule.⁷² Wang et al. have also reported the synthesis of phosphorescent transition-metal complexes that have a triarylboron moiety and exhibit bright emission at room temperature. This emission is quenched in case of the Cu (72) and Pt (73) complexed materials in the presence of fluoride. The Cu-complex shows high quantum efficiency in the solid state and may be a promising candidate as a phosphorescent emitter in OLED devices.⁷³

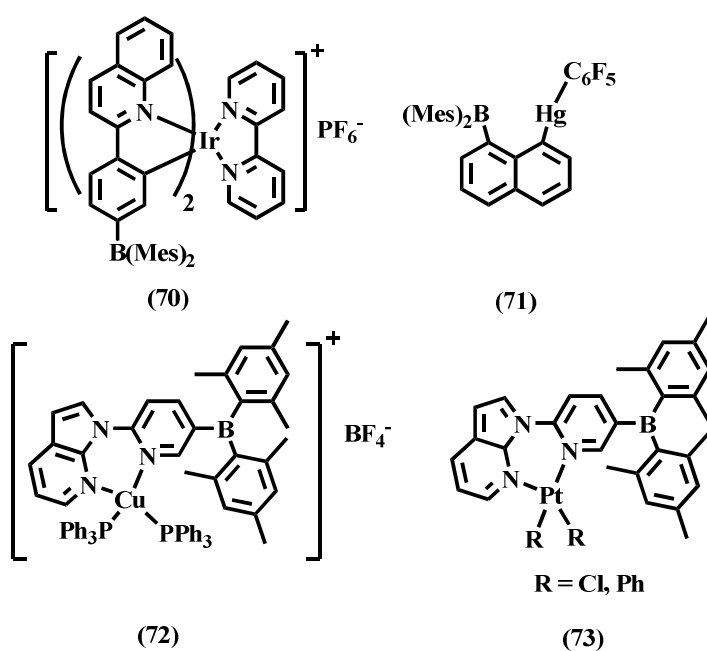


Chart 1.16 Examples of Phosphorescent Fluoride Sensors.

Wang and co-workers have also synthesized a molecule that features two dimesitylboron centers linked together by a 2,2'-bipyridyl (**2,2'-BIPY**) bridge which can effectively chelate

to metals ions, thus forming stable Cu(I) (74) and Pt(II) (75) complexes. These complexes were found to bind strongly to fluoride forming only a 1:1 adduct which did not further bind the second fluoride because of the decreased Lewis acidity of the boron center.⁶⁸

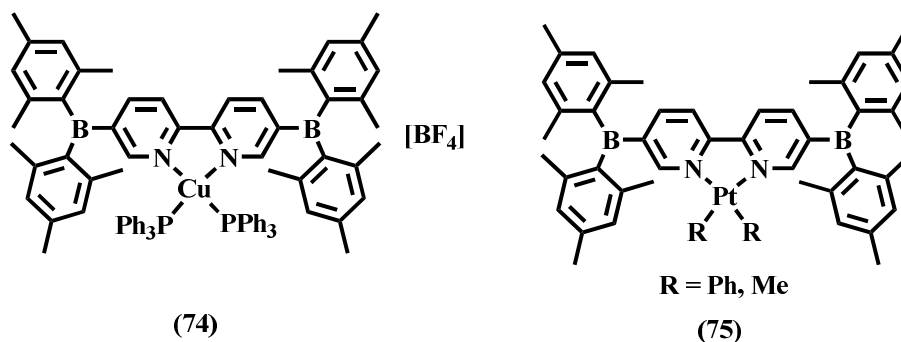


Chart 1.17 Examples of Organoboron Compounds containing Metal-complexes with 2,2'-Bipyridyl.

Gabbaï and co-workers reported several other fluoride sensors; one of them is based on a boradiazaindacene (**BODIPY**) cation (76) which in the presence of fluoride gets converted to a neutral BODIPY and exhibits “turn-on” characteristic.⁷⁴ Fluoride sensors that can be monitored via electrochemistry rather than fluorescence spectroscopy, for example a trinuclear Lewis acid (77) that can bind two fluoride ions and a phosphonium-borane (78) based fluoride chelator have been developed.^{75, 76}

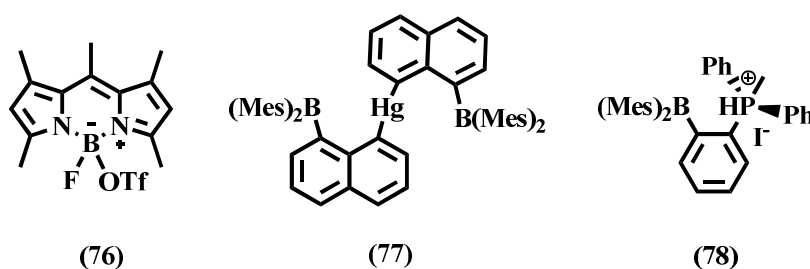


Chart 1.18 Some Sensors from Gabbaï and Co-workers.

It is interesting to note that molecules that contain a boron moiety, where boron itself does not partake in sensing of anions are also known. For example, Akkaya and co-workers

recently reported a BODIPY (79) containing molecule that can detect cyanide ions in solution at micromolar concentrations and changes in the absorption and emission can be monitored visually.⁷⁷ Maeda et al. have reported BF_2 complexes of dipyrrolylpropanedione (80-81) which behave as acyclic anion receptors and exhibit efficient anion binding behaviour.⁷⁸

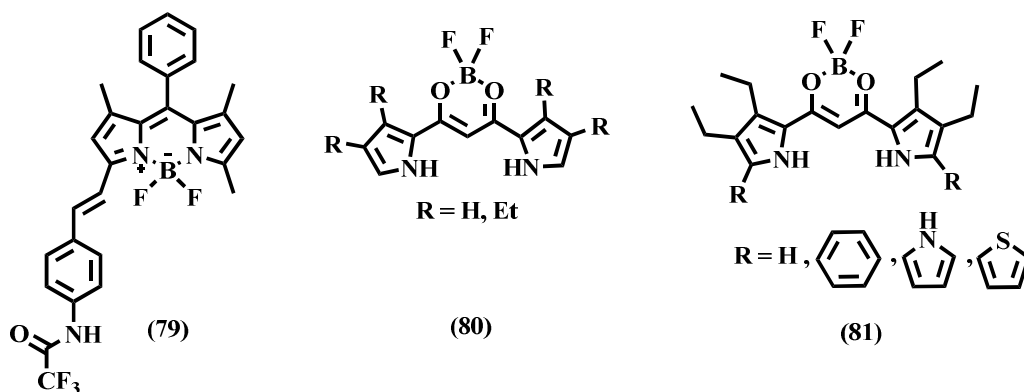


Chart 1.19 Examples of BODIPY and Other Complexes of BF_2 with Dipyrrolylpropanedione.

1.5 Organoboron Polymers

The first reports on the formation of boron polymers came in the early 1900's, when Alfred Stock discovered that boron and its hydrides could form compounds analogous to hydrocarbons, while working on boron hydride chemistry. Following his work, Burg and co-workers discovered that the adduct of diborane with phosphine yielded a trimer (82) which was stable at very high temperatures and also to reduction by sodium in liquid ammonia. They also found that if the same phosphinoborane unit was synthesized in the presence of a slight excess of base, it formed a ring opened compound (82p) with as many as 300 repeating units. Because of their high thermal stability and flame retarding properties, polymers that had alternate P and B atoms have been studied extensively since the 1950's. At the same time Heying and Schroeder synthesized a family of carbosiloxane rubbers under the trade name

DEXSIL (83-84) at Olin Laboratories in Connecticut. On similar lines carborane polymers with tin bridges (85) were also synthesized. During the same time Trofimenko and co-workers at DuPont were able to synthesize the first oligomeric boron bridged (1-pyrazolyl)borate systems (86).⁷⁹

Since the first reports of oligomeric and polymeric boron containing compounds, the polymer chemistry of boron has gained tremendous ground. Boron containing polymers now find applications in a variety of fields like their use as polymeric precursors for high performance materials, supramolecular nanomaterials, polymer supported catalysts for organic transformations, for drug delivery, as optical materials, sensors for nucleophiles etc. These developments have mainly been driven by three fundamental characteristics of boron; its electronic characteristic i.e. its ability to delocalize π -electrons because of the presence of the empty p-orbital, its nuclear characteristic i.e. its neutron capturing ability since it exists naturally in the form of two isotopes, one of which has a large cross-section for neutrons, and its characteristic to react with oxygen at high temperature to form B_2O_3 char or in the case of B-N containing compounds, the formation of boron-nitride ceramic materials.⁷⁹

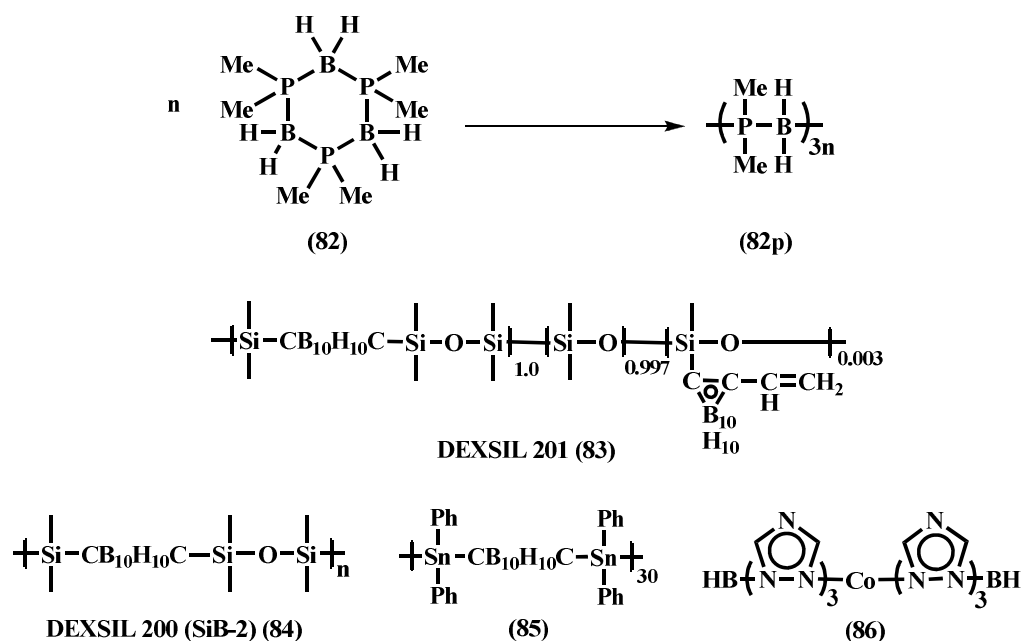
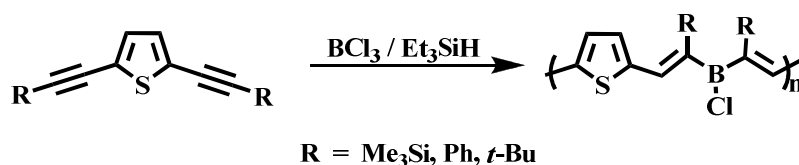


Chart 1.20 Early Examples of Boron-Containing Oligomers and Polymers.

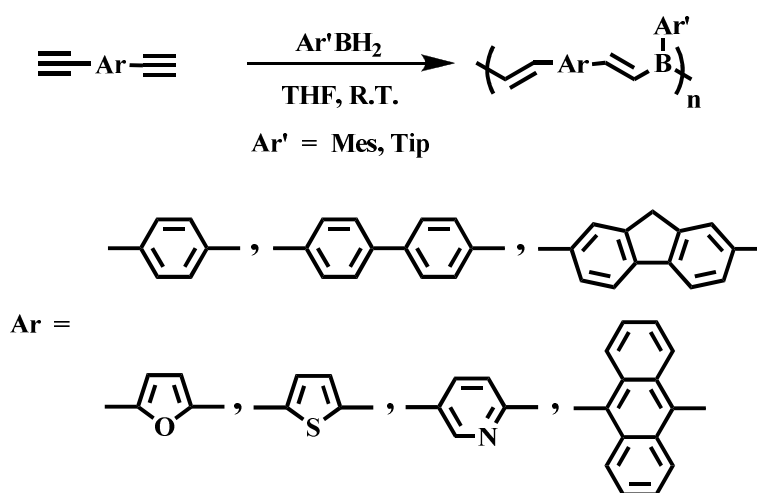
1.5.1 Main-chain Functionalized Organoboron Polymers

Organoboron containing polymers can be divided into three classes, the first one being main-chain functionalized organoboron polymers in which the boron atom is embedded into the main-chain of the polymer. Brown and co-workers reported the formation of organoboron polymers in 1945, but their physical characterization like yield, molecular weights etc. was not reported. Corriu et al. reported the synthesis of the first main-chain organoboron containing conjugated polymers via hydroboration polymerization (Scheme 1.3), but their characterization was hampered owing to their sensitivity to air and moisture.^{80, 81}



Scheme 1.3 First Examples of Boron-Containing Conjugated Polymers via Hydroboration Polymerization.

In the early 1990's Chujo and co-workers pioneered the hydroboration polymerization methodology and systematically studied the resulting polymers. Chujo et al. have been successful in synthesizing a number of polymers that bear a boron atom in the main-chain. The first stable polymer via hydroboration polymerization was obtained by reaction of mesitylborane with aromatic diynes. They reported molecular weights of ca. $M_n = 6500$. The polymers exhibited an intense emission upon irradiation with UV light and showed interesting electronic properties which indicated that the polymers were typical n-type conjugated polymers (Scheme 1.4).^{82, 83}



Scheme 1.4 Conjugated Boron-Containing Polymers.

Chujo and co-workers have synthesized a variety of other boron containing polymers, one example is a polymer that contains a ruthenium-phosphine complex along with boron centers

(87) which was realized by hydroboration polymerization of a tetrayne type monomer containing ruthenium-phosphine complex with mesitylborane. The polymer obtained showed intriguing photophysical properties i.e. the UV visible spectrum showed a peak at 514 nm in addition to the π - π^* transition at 359 nm, which can be attributed to the $d\pi$ - $p\pi$ transition owing to the presence of the ruthenium-phosphine complex. The authors also noted that the band due to the $d\pi$ - $p\pi$ transition was red-shifted by 141 nm compared to the ruthenium molecular compound which could be due to the push-pull effect between ruthenium and the organoboron unit and also due to the extension of π -conjugation.⁸⁴ Another similar example containing push-pull type systems was reported by Chujo et al. where metals like Pd and Pt were incorporated (88). Though they found no evidence of metal-to-ligand charge transfer (**MLCT**) bands in these cases, the polymers emitted intensely in the green region upon excitation at 390 nm.⁸⁵

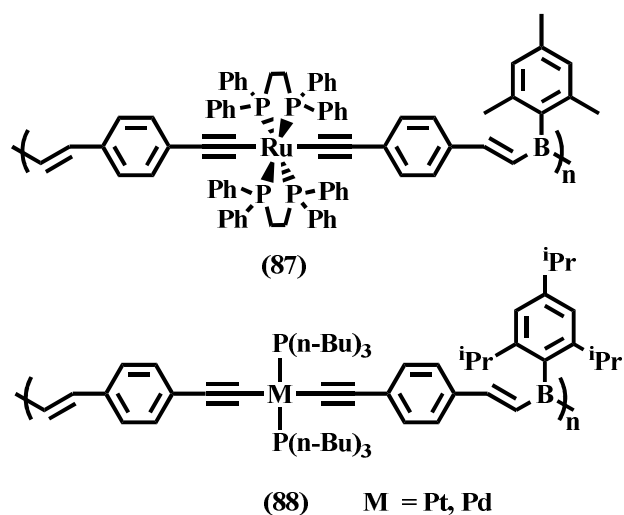


Chart 1.21 Metal Complex Containing Organoboron Polymers.

Other transition metal containing organoboron polymers are also known. For example, Wagner and co-workers have synthesized a variety of coordination polymers, by the reaction of bis-borylated ferrocene with 4,4'-bipyridine (**4,4'-BIPY**) (89) and its derivatives, which

show interesting charge transfer properties. They have also synthesized related polymers that have pyrazine linkers (90) instead of 4,4'-BIPY which are dark-green in color indicating charge-transfer interactions between the iron and pyrazine moieties.^{86, 87} The ring-opening polymerization (**ROP**) of boron bridged ferrocenophanes, a methodology developed by Manners and co-workers, has been utilized for the preparation of ferrocene containing organoboron polymers. Manners et al. also found that silyl-bridged ferrocenophanes could selectively ring open by reaction with boron halides, thus producing functionalized ferrocenylboranes that serve as precursors to boron-containing polymers (91).⁸⁸ More recently Jäkle and Wagner have reported the synthesis of a boron-halide containing polyferrocene obtained by the reaction of diborylated ferrocene with triethylsilane. This polymer was further modified by reaction with mesitylcopper yielding the stable derivative (92).⁸⁹⁻⁹¹

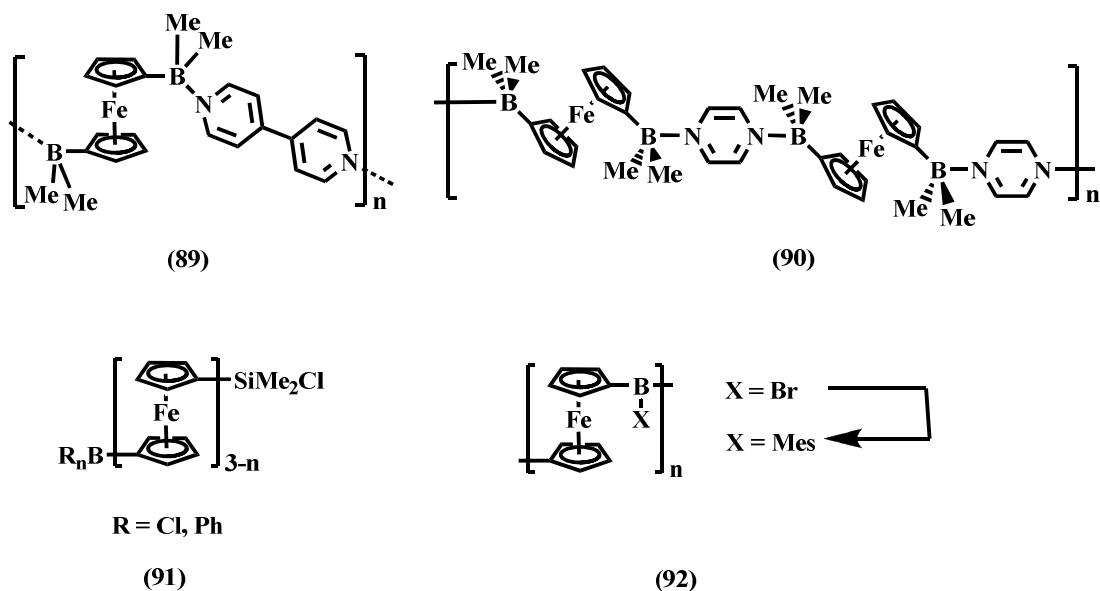


Chart 1.22 Ferrocene Containing Organoboron Polymers.

Other methodologies that have been gaining ground are the use of polycondensation and coupling chemistries for the synthesis of boron containing polymers. One of the first

examples of the use of organometallic polycondensation reactions for the synthesis of boron polymers reported by Chujo et al. dates back to 1998 where they coupled an aryldimethoxyborane with a di-Grignard reagent to afford poly(p-phenyleneborane)'s (**PPB**) (93).^{82, 92} Since then many examples of polymers synthesized via these methods have been reported. For example, Jäkle et al. have recently been able to incorporate boron into the main chain of polythiophenes (94) using a facile tin-boron exchange reaction which affords polymer in the range of $M_n = 6,500$ to 9,000. Interestingly, the emission wavelength can be fine tuned by changing the substituents on the boron center. The polymers were found to bind to pyridine and may find applications as sensors for nucleophiles.^{82, 93}

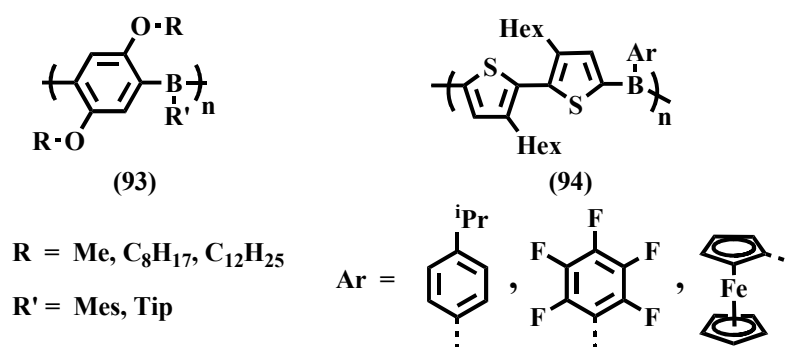
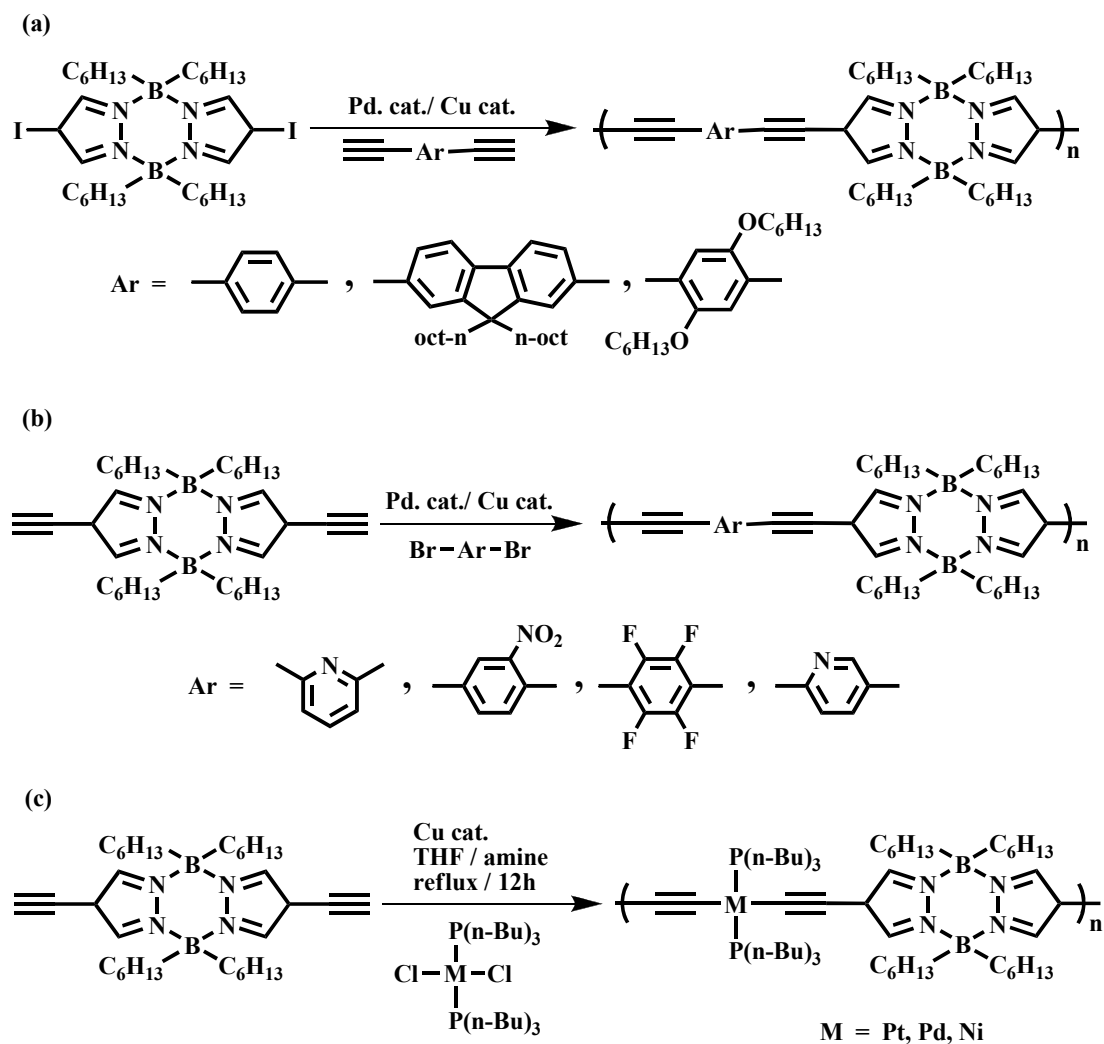


Chart 1.23 Examples of Organoboron Polymers Obtained via Polycondensation Routes.

Chujo et al. have also synthesized polymers that contain pyrazabole moieties in the main-chain using metal-catalyzed coupling reactions. Coupling between pyrazabole and diyne monomers (Scheme 1.5(a)) or coupling between diethynylpyrazabole and dibromoaryl compounds gave the corresponding polymers (Scheme 1.5(b)). No considerable red-shift in the UV-vis absorption was observed compared to the monomer units indicating no significant extension of conjugation via the pyrazabole moiety; however the polymers showed intense fluorescence upon excitation. In the case of the polymers that had an electron withdrawing group the fluorescence intensity shifted to shorter wavelengths, hence it was possible to tune

the emission by incorporating different groups into the polymer. Transition-metal containing pyrazabole polymers were also synthesized by dehydro-halogenation reactions, while MLCT absorption bands were observed only for Pt-containing polymers. No such bands were observed for polymers containing Pd or Ni as metals (Scheme 1.5(c)).^{82, 94-96}



Scheme 1.5 Pyrazabole Containing Polymers.

Most recently Chujo's group used coupling reactions to synthesize polymers that have organoboron quinolate moieties (95) in the backbone using a similar synthetic strategy shown

in Scheme 1.5(c). The polymers obtained showed intense blue-green emission with high quantum efficiencies.⁹⁷⁻¹⁰⁰

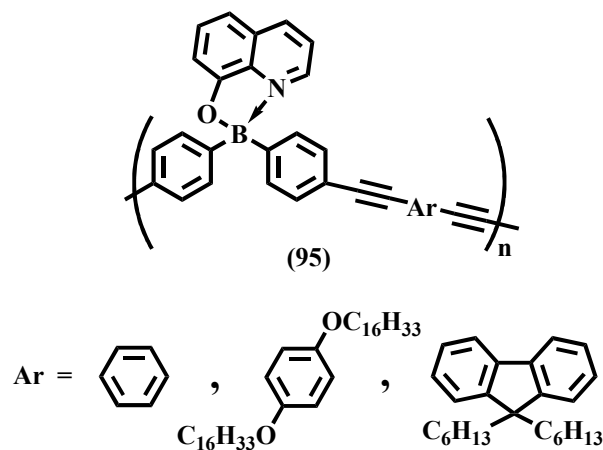


Chart 1.24 Organoboron Quinolato Polymers.

1.5.2 Side-chain Functionalized Conjugated Organoboron Polymers

Main-chain functionalized conjugated organoboron polymers have received a lot of attention, but comparatively few examples of side-chain functionalized conjugated organoboron polymers exist. Electrochemical synthesis of conjugated polymers that feature boronic acid or boronate moieties have been studied by Freund et al. and Fabre et al. Fabre and co-workers reported the synthesis of boronic acid and boronate ester functionalized polypyrrole (96), and its use as a fluoride sensor was studied electrochemically using cyclic voltammetry.^{101, 102} Freund and co-workers synthesized boronic acid functionalized polyaniline (**PABA**) and showed that the polymer could efficiently be used as a saccharide sensor (97).¹⁰³⁻¹⁰⁶ Recently, they also demonstrated that with controlled synthesis they could form conducting PABA nanoparticles, with an average size of 12-15 nm, without the use of surfactants as template. These nanoparticles were found to be extremely resistant to

degradation at extreme electrochemical potentials and hence may find applications as coatings or may be used for fabrication of nanoscale devices.¹⁰⁷

He and co-workers have developed a novel dopamine specific biosensor for the detection of dopamine in the diagnosis of Parkinson's disease. They used single-stranded DNA (**ss-DNA**) and single-walled carbon nanotubes (**SWNTs**) as templates for in-situ polymerization of self-doped PABA (98). They discovered that the ss-DNA and SWNTs acted as catalysts toward the polymerization of boronic acid functionalized aniline (**ABA**) and the polymerization occurred at higher rates. The quality and the stability of the polymer was greatly increased. The electrical performance of the SWNTs was greatly improved due to the presence of a thin film of PABA on the ss-DNA and SWNT. These nanocomposites showed much higher electrochemical stability through combined synergistic effects of their components.¹⁰⁸⁻¹¹²

Recently Jäkke et al. reported incorporation of electron deficient boron centers to the side chain of polythiophenes (99) and their photophysical and electrochemical properties.^{82, 113, 114} Related boron substituted poly(aryleneethynylene)s (**PAEs**) (100) have been recently reported by Yamaguchi et al.; they are soluble in common organic solvents and also show high emission intensities in solution as well as the solid state. Hence they may be used as building-blocks for emissive boron containing conjugated materials.^{82, 113, 115}

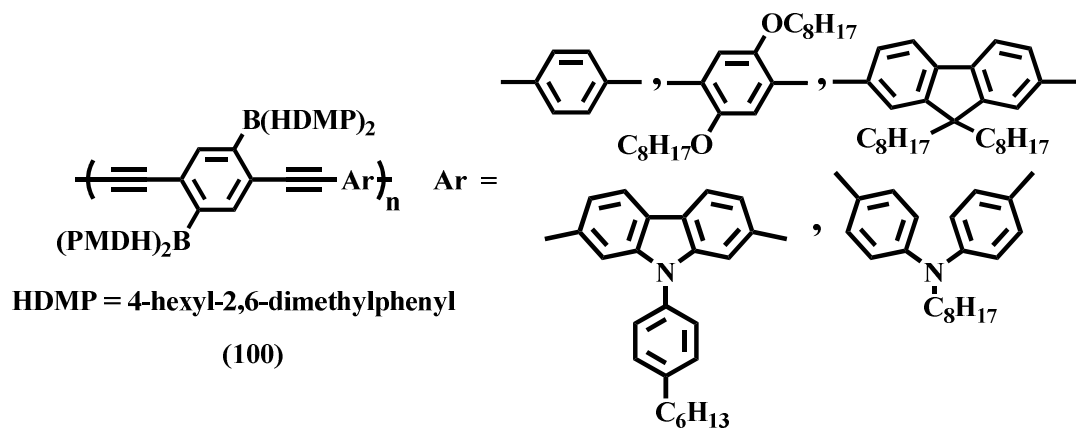
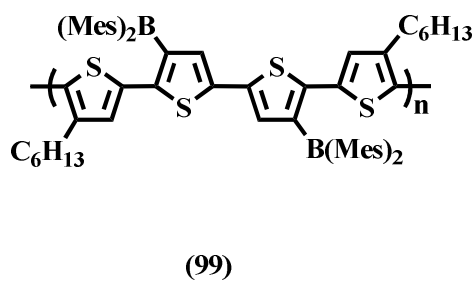
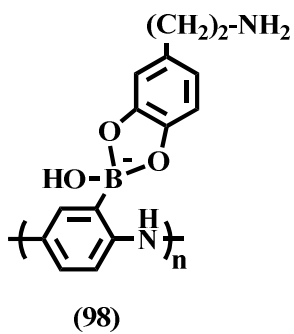
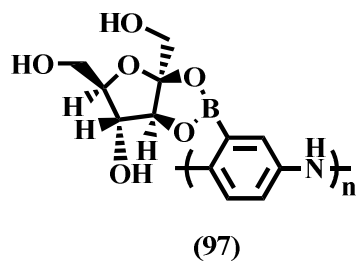
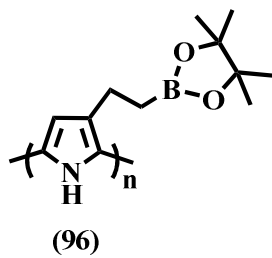


Chart 1.25 Side-chain Functionalized Conjugated Organoboron Polymers.

Chapter 2A. Polystyrene Based Luminescent Triaryl Boron Containing Polymers

2.1 Introduction to Side-chain Functionalized Boron Containing Polymers

Boron-containing polymers are an important class of materials in the field of inorganic and organometallic polymers. Of particular interest is the incorporation of organoboranes into the polymers because they can act as Lewis acids due to the empty p-orbital on the boron center. Boron containing polymers can be classified as main-chain and side-chain functionalized compounds. Polymeric compounds present certain advantages over small molecule analogues, such as the possibility of using solution processability (spin casting, roll printing, inkjet printing) for fabrication of devices and in case of sensor materials, the prospect of signal amplification.⁶⁵

While main-chain containing polymers have been extensively studied, comparatively few reports on side-chain functionalized organoboron polymers exist. Side-chain functionalization can offer various advantages like (i) the synthesis of soluble organoboron polymers with controlled architecture, high molecular weights, and varying degree of functionalization (ii) possibility of chain extension leading to the synthesis of copolymers with different functionalities and (iii) since the boron is attached as a pendant group, two different groups can be attached to the boron center thereby allowing polymers with varying degree of Lewis acidities to be obtained.⁶⁵

2.2 Synthesis of Side-chain Functionalized Boron Containing Polymers

Organoboron polymers can be synthesized either through the polymerization of boron-functionalized monomers or via post-polymer modification reactions. Both these methods have been used for the synthesis of boron containing polymers but polymerization of boron-functionalized monomer has received far more attention than post-polymer modification reactions. While polymerization of the functionalized monomer has been used widely, post-polymer modification reactions allow us to avoid issues, like compatibility of the monomer to polymerization techniques, which one may encounter with direct polymerization methods.⁶⁵

2.2.1 Synthesis from Organoboron Monomers

A variety of polymerization methods can be used to prepare side-chain functionalized organoborane polymers from organoboron monomers. Most widely used methods include standard free radical polymerization (101) and controlled free radical polymerization (102-103) due to their simplistic synthetic procedures and reasonable compatibility with B-C bonds.¹¹⁶⁻¹¹⁹ Ziegler-Natta polymerization on the other hand has been employed widely for highly reactive and strongly Lewis acidic monomers which tend to be not very well suited for other polymerization techniques (104-105).^{120, 121} Anionic polymerization can not be used for such monomers due to their incompatibility with initiators used. ROMP is another methodology that has been employed for the synthesis of boron containing polymers from boron containing monomers (106-107).^{122, 123}

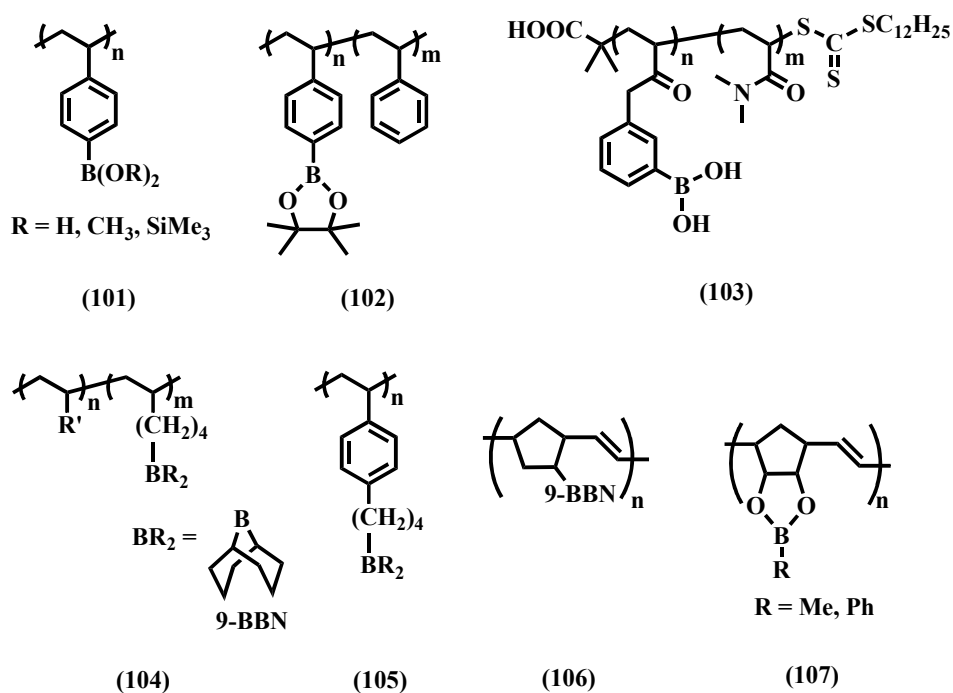


Chart 2.1 Examples of Boron Functionalized Polymers Synthesized from Boron-Containing Monomers via Free Radical, Controlled Free Radical, Ziegler-Natta and ROMP Techniques.

2.2.2 Synthesis via Post-polymer Modifications

Post-polymer modification is another route to the synthesis of organoboron containing side-chain polymers. This route is particularly interesting for the synthesis of polymers that cannot be obtained by polymerization of the functionalized monomers. Although this methodology may circumvent certain common issues of compatibility of organoboron monomers with given polymerization techniques, certain care must be taken that the functionalized or unfunctionalized monomer must be amenable to polymerization. The functional group on the polymer synthesized should selectively and quantitatively be replaced by boryl moieties. Organoboron polymers of this type can be synthesized from unfunctionalized polymers, polyolefins that contain olefinic groups in the backbone or side-chain and also from metalated polystyrenes.⁶⁵

2.3 Applications of Side-chain Functionalized Boron Containing Polymers

Examples of boron containing molecular materials as well as some conjugated polymeric systems and their properties and applications have been discussed in sections 1.4 and 1.5 respectively. In a broader sense these compounds (molecular materials and polymers) have found applications in linear and non-linear optics; as electron conduction layers and emission layers in OLED devices; and also as sensor materials. While few examples of side-chain functionalized organoboron polymers exist, even fewer examples of polyolefins that have photo or electroactive organoboron moieties in their side-chain can be found. Branger et al. synthesized polyurethanes that have triarylboron moieties in the side-chain and studied their applications as non-linear optical materials (108). The materials they synthesized had polyurethane as the backbone with azo-dyes as linkers, and dimesityl boryl groups as the electron accepting groups. The polymers showed high thermal and chemical stabilities and showed interesting electrochemical as well as non-linear optical properties.¹²⁴ Shirota and co-workers developed a new type of organoboron containing emitting vinyl polymer which showed high thermal stability, good film forming capability and also proved to be a good candidate as a green emissive material for high performance organic electroluminescent devices (109).^{125, 126}

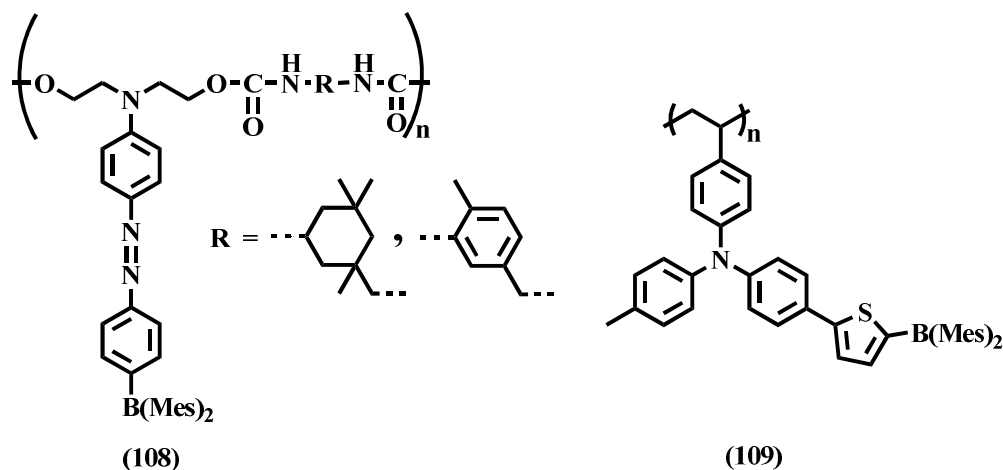


Chart 2.2 Examples of Photo/electroactive Organoboron Containing Polymers.

A few examples of tetra co-ordinated organoboron moieties covalently attached to the side-chain of polymers have also been reported. Jäkle and co-workers have reported the first examples of polymeric analogues of boron-quinolate complexes by the reaction of 8-hydroxy quinoline with thienyl substituted boron polymers (110). The polymers synthesized showed interesting photophysical properties and their emission could easily be fine-tuned by varying the quinolate ligand.^{127, 128} Another example of a similar boron-quinolate containing block co-polymer system (111) which showed green emission was later reported by Weck et al. The emission characteristics of both systems in solutions and films suggest that they may find applications as emissive layers in OLED devices.¹²⁸

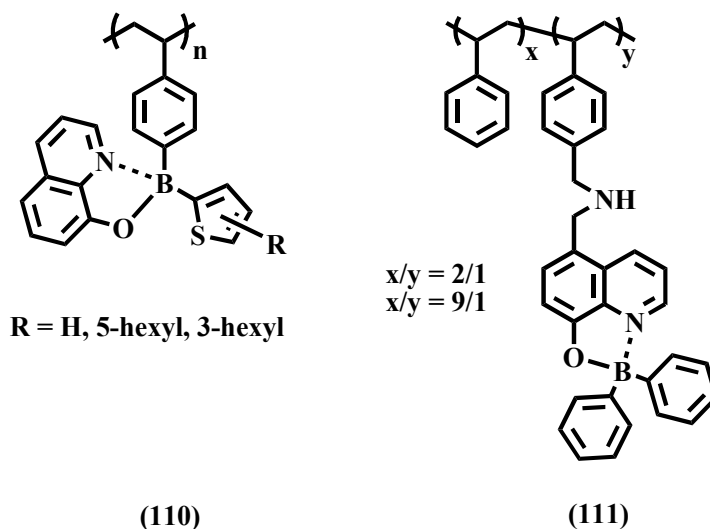
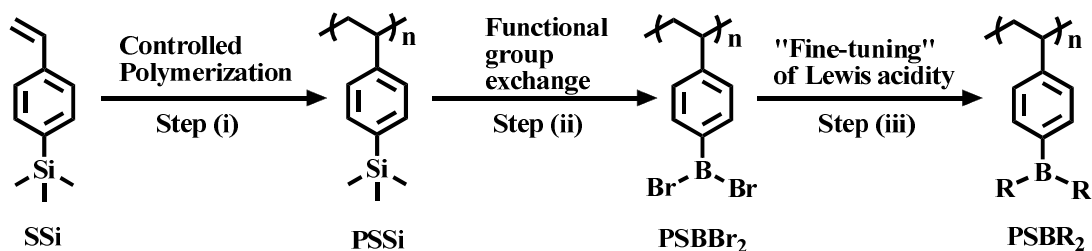


Chart 2.3 Examples of Boron-quinolate Containing Polymers for OLED Applications.

2.4 Side-chain Functionalized Organoboron Polymers via Si-B Exchange Reactions¹²⁹

Our group has developed a general strategy toward the synthesis of well-defined soluble organoboron polymers with controlled architecture, molecular weight and degree of functionalization.¹³⁰⁻¹³² Using this strategy we can selectively and quantitatively replace the substituents on the boron center and hence organoboron polymers with varying properties can be easily synthesized. This strategy involves the following steps (i) the quasi-living polymerization of the silylated functional monomer via atom-transfer radical polymerization (ATRP) to obtain the silyl functionalized polymer, (ii) exchange of the trimethylsilyl functional group with Lewis acidic boron centers and (iii) fine-tuning of the Lewis acidity of the boron center by substituent exchange reactions (Scheme 2.1).^{130, 131}

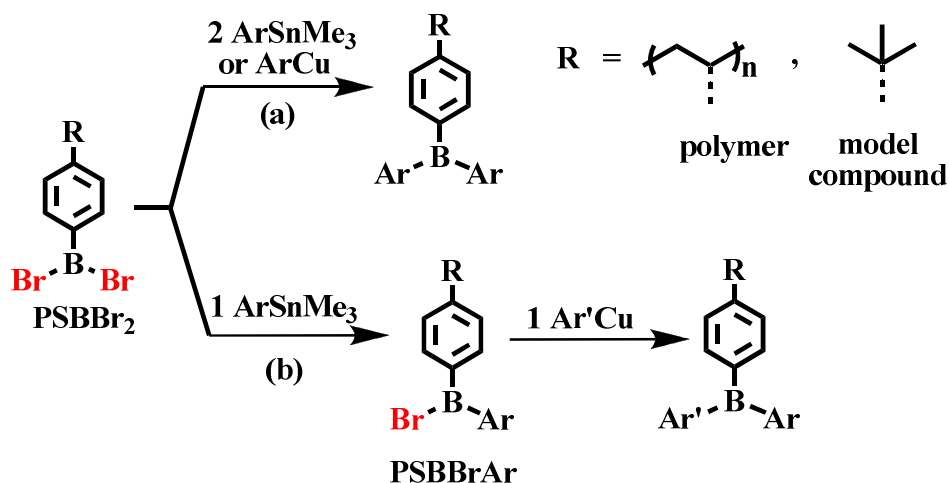


Scheme 2.1 Synthesis of Organoboron Containing Polymers.

2.5 Side-chain Functionalized Boron Containing Polymers with Bithiophene as the Chromophore¹³³

2.5.1 Synthesis

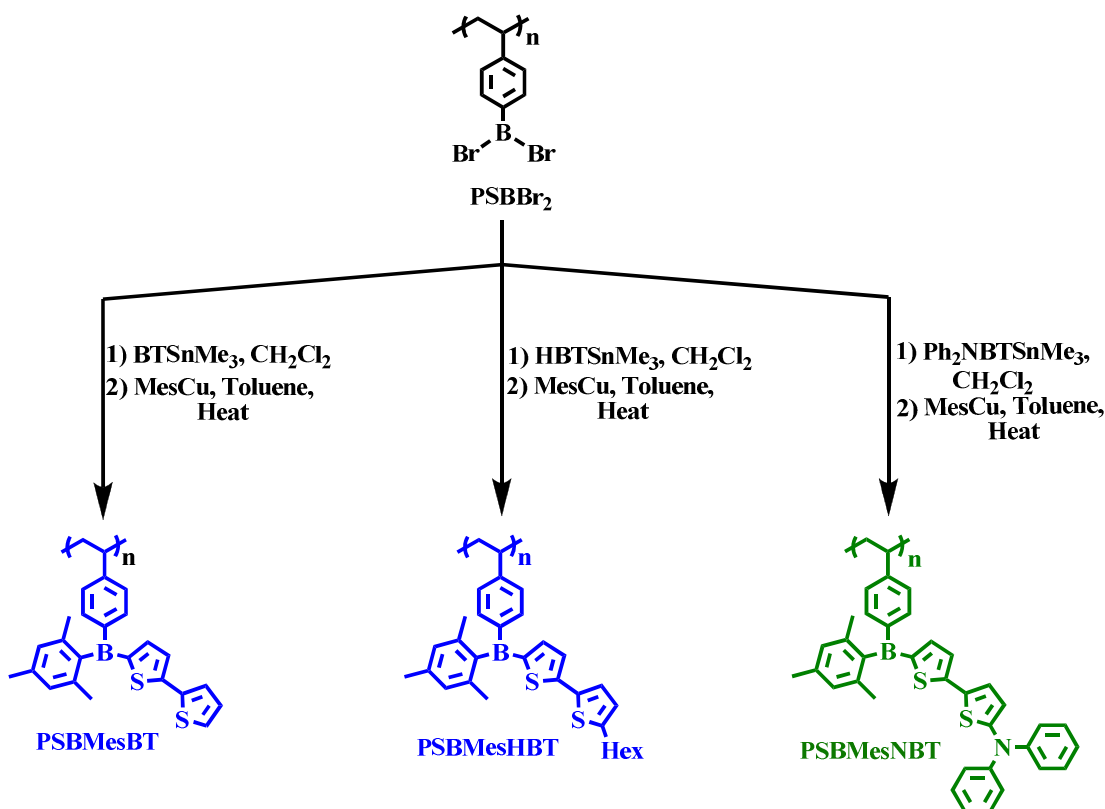
Using the synthetic strategy shown in Scheme 2.1, we have been able to successfully incorporate electron deficient boron centers that contain bithiophene and modified bithiophenes as the chromophores into the side-chain of polystyrene.¹³⁴



Scheme 2.2 Strategy for the Synthesis of Triarylborane Compounds.

The presence of boron in the side-chain of polymers allows for the attachment of two similar or two different aryl groups as opposed to only one exchange site in case of main-chain organoboron containing polymers.

From the literature it is known that in case of polymers that bear boron in the main-chain the presence of bulky groups like mesityl or 2,4,6-triisopropylphenyl is sufficient to sterically protect the boron center. Hence we developed a strategy for the synthesis of novel fluorescent triarylborane polymers PSBMesAr whose key design principle, is the use of one boron substituent for steric stabilization, while the second pendent group represents an extended organic π -system that can effectively overlap with the empty p orbital on boron. By taking advantage of the high selectivity of tin-boron exchange reactions, we were able to replace one of the bromine substituents of PSBBr₂ in a controlled manner to give the substituted polymer PSBBrAr (Scheme 2.2(b)). In a second step, the mesitylcopper toluene solvate [MesCu]₅·(C₇H₈) was used to attach bulky mesityl groups.¹³⁵ All polymers PSBMesAr were readily isolated by precipitation from toluene into hexanes and showed good solubility in common organic solvents such as toluene, THF, or CH₂Cl₂ (Scheme 2.3).



Scheme 2.3 Synthesis of Triarylborane Polymers PSBMesAr.

2.5.2 Characterization of Borylated Polystyrene with Bithiophene as the Chromophore

2.5.2.1 NMR Spectroscopy

The polymers PSBMesAr and their respective molecular model compounds MBMesAr were fully characterized by ^1H , ^{13}C , and ^{11}B NMR spectroscopy. The presence of a broad signal at about 47-50 ppm in the ^{11}B NMR spectra is typical of triarylborane compounds. However, in comparison to the model compounds, which represent one repeating unit of the polymer chain, a significant upfield shift of the ^{11}B NMR resonance of about 10-15 ppm was observed. The latter is tentatively attributed to additional shielding effects due to neighboring groups on the polymer chain. The ^1H NMR spectra showed broad overlapping signals that were not very informative. However, the ^{13}C NMR spectra correlate well with those of the

molecular models and thus further confirm the structure of the polymers with borane moieties containing mesityl and bithiophene substituents (Figure 2.1).

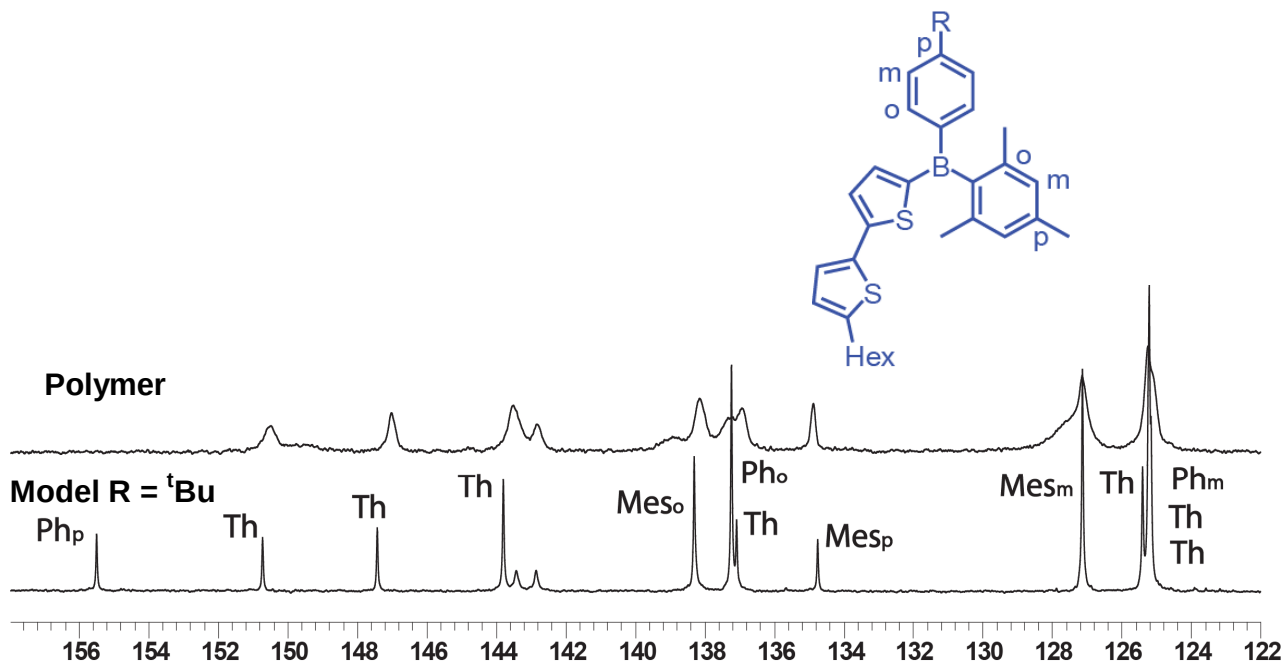


Figure 2.1 ^{13}C NMR Overlay of the Aromatic Region of MBMesHBT and PSBMesHBT.

2.5.2.2 Molecular Weight Determination

The molecular weight of the polymers was studied by GPC analysis in THF in the presence of 0.1 wt % $[\text{Bu}_4\text{N}]\text{Br}$. The molecular weights relative to polystyrene standards were found to be in the range expected on the basis of the MW of the poly(4-trimethylsilyl)styrene precursor. However, the bands are somewhat broadened (polydispersities (PDI) from 1.15 to 1.51), presumably due to a small degree of aggregate formation and interaction with the column material that also seems to impact the retention times (Table 2.1).

Table 2.1 Molecular Weight Data for the Polymers PSBMesBT, PSBMesHBT and PSBMesNBT Obtained from GPC.

Polymer	M_w	M_n	DP (M_n)	PDI
PSSi	28,860	26,000	147.45	1.11
PSBMesBT	40,174	26,550	66.64	1.51
PSBMesHBT	54,574	45,275	93.82	1.15
PSBMesNBT	60,412	46,016	81.36	1.31

2.5.2.3 Thermal Properties and Stability Toward Air and Moisture

The thermal characteristics of the polymers were examined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Polymers PSBMesBT, PSBMesHBT, and PSBMesNBT show glass transition temperatures (T_g) of 165, 139, and 165 °C, respectively, which are slightly higher than that of polystyrene, but in a similar range as that of the related triarylborane polymer poly(4-dithienylborylstyrene) (PSBTh₂, T_g = 148 °C).¹³¹ The TGA plots indicated that the mesityl-substituted polymers show high thermal stability with no significant decomposition up to ca. 250 °C. Above this temperature, multistep decomposition processes were observed. The residual weights at 800 °C were in the range of ca. 5-10% (Figure 2.2). The environmental stability of the polymers was considerably higher than for the related sterically unprotected polymers PSBAr₂ (Ar = hexylbithiophene). No substantial degradation was observed in the solid state over a period of 2 weeks, but additional sharp NMR signals corresponding to small molecule degradation products started to develop after ca. 2 weeks in solution. In comparison, polymers PSBAr₂ that lack the mesityl groups decompose within 24 h under similar conditions.¹³⁶

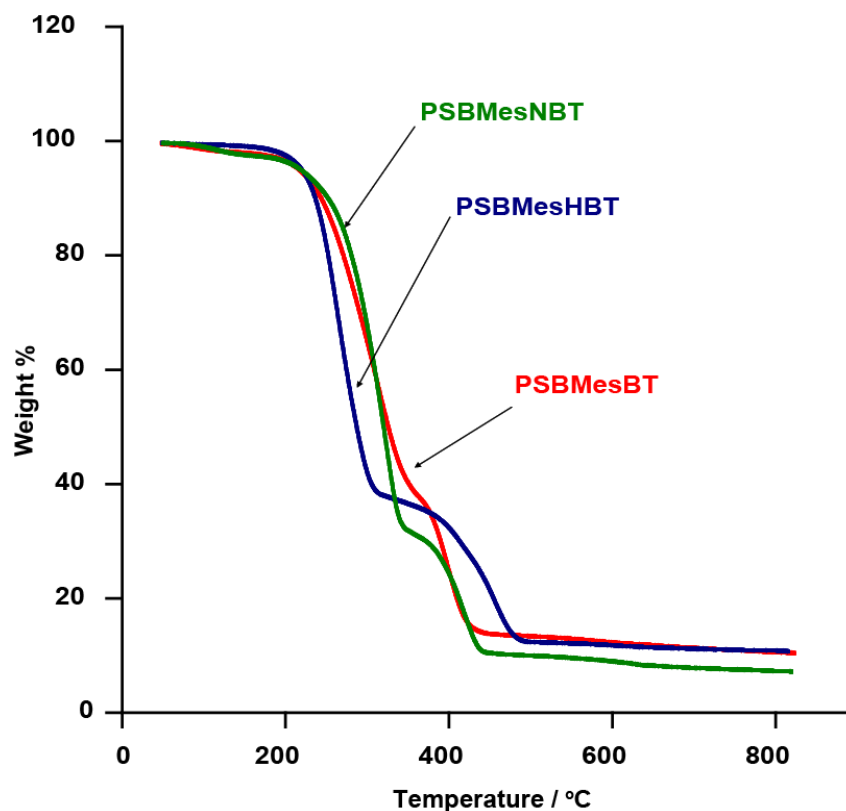
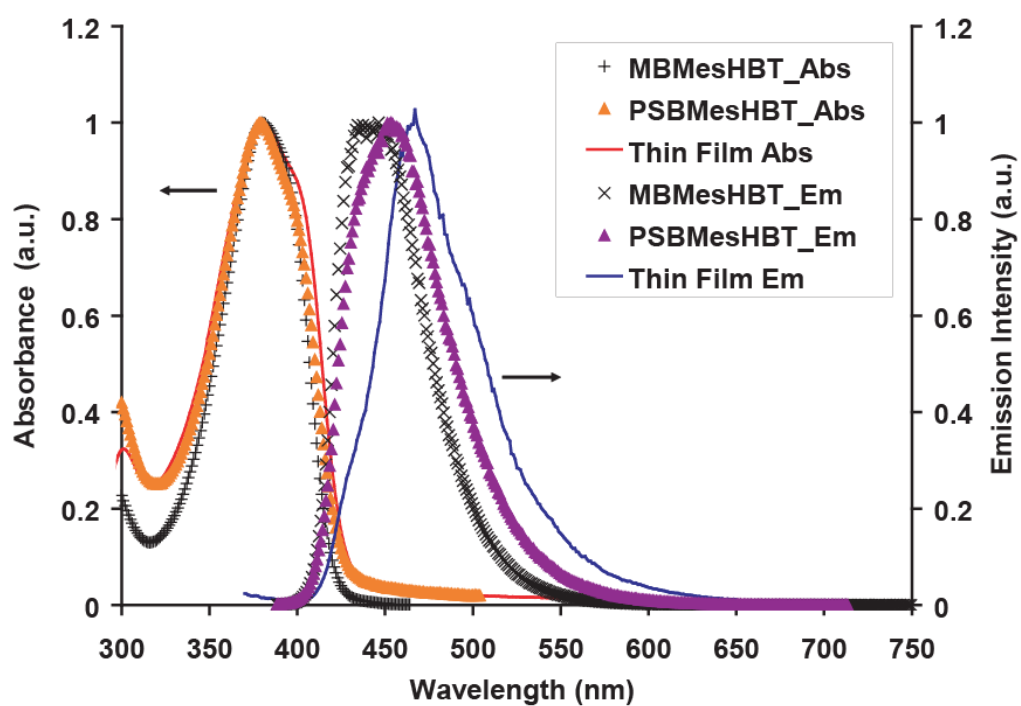


Figure 2.2 TGA Plots of the Triarylborane Polymers.

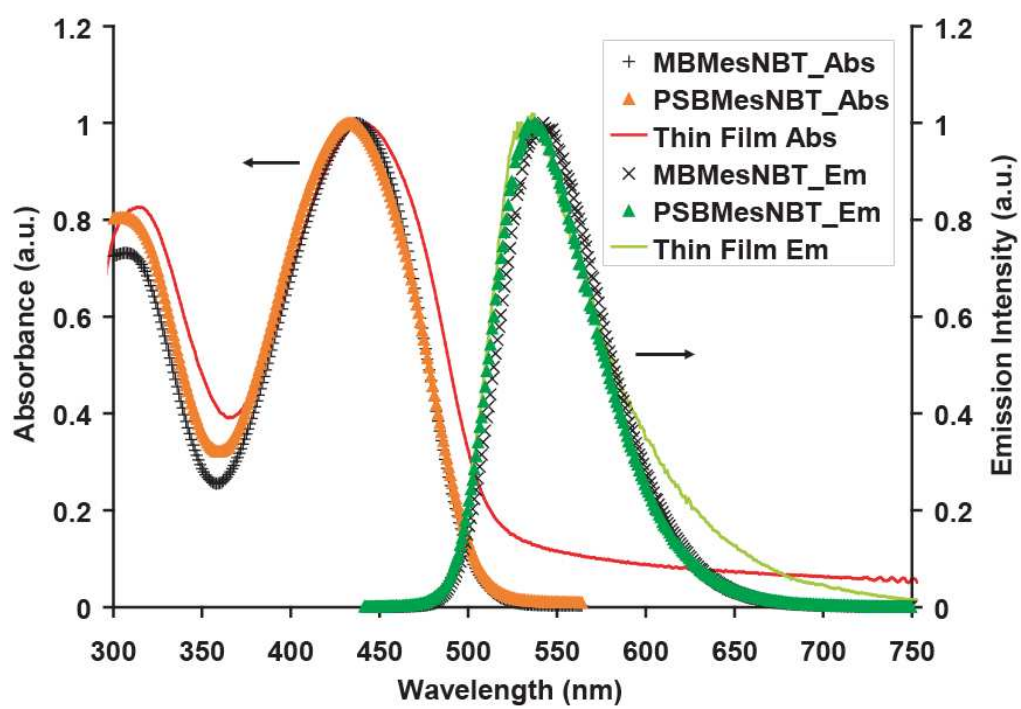
2.5.2.4 Photophysical Properties in Solution and Thin Films

All polymers PSBMesAr are strongly fluorescent in solution, and their thin films also show bright emission (Table 2.2, Figure 2.3). For instance, in CH_2Cl_2 solution, the polymers PSBMesBT and PSBMesHBT absorb at $\lambda_{\text{abs}} = 368$ and 380 nm, respectively, and emit bright blue light at $\lambda_{\text{em}} = 463$ and 455 nm. In contrast, the polymer PSBMesNBT has a yellow appearance due to an absorption at $\lambda_{\text{abs}} = 433$ nm and displays a yellow-green emission at $\lambda_{\text{em}} = 537$ nm, consistent with a bathochromic shift due to the donor- π -acceptor structure of the aminobithiophene substituents. The absorption data for the respective molecular model compounds are quite similar to those of the polymers, while the emission data differ significantly (Figure 2.3). This trend is most pronounced in the case of the unsubstituted

(b)



(c)



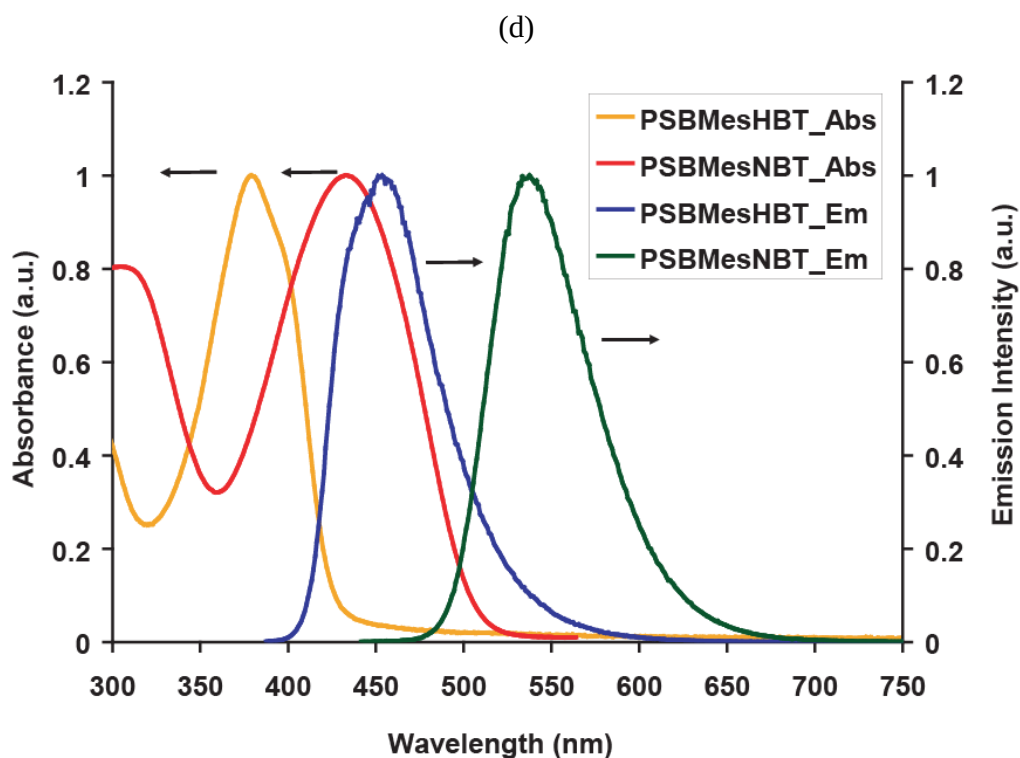


Figure 2.3 (a) Comparison of the Absorption and Emission Spectra of MBMesBT and PSBMesBT in CH_2Cl_2 Solution and as Thin Films Cast from Toluene. (b) Comparison of the Absorption and Emission Spectra of MBMesHBT and PSBMesHBT in CH_2Cl_2 Solution and as Thin Films Cast from Toluene. (c) Comparison of the Absorption and Emission Spectra of MBMesNBT and PSBMesNBT in CH_2Cl_2 Solution and as Thin Films Cast from Toluene. (d) Comparison of the Absorption and Emission Spectra of PSBMesHBT and PSBMesNBT.

Molecular mechanics calculations, which were performed by Dr. Venkatasubbaiah on a model trimer of PSBMesHBT indicate that conformations in which the bithiophene moieties are aligned with respect to each other are possible and energetically favorable (Figure 2.4).

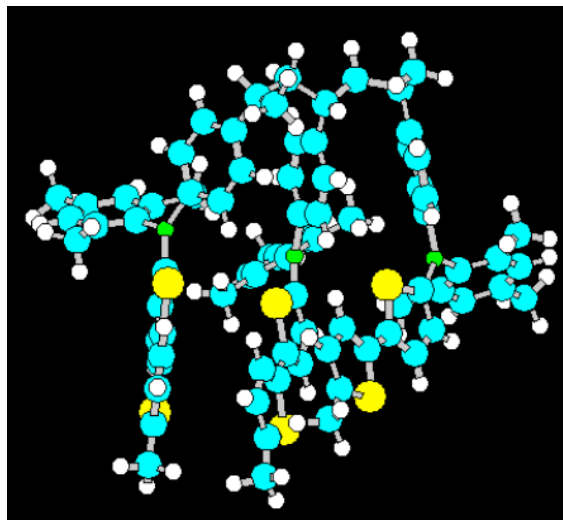
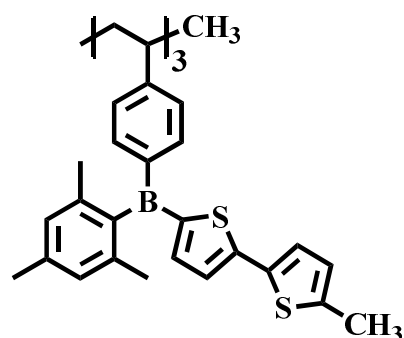


Figure 2.4 Molecular Mechanics Calculation for a Methyl Capped Trimer.

A further bathochromic shift was observed for thin films that were cast from toluene solution. Such an effect has also been reported for the luminescence of the respective vinylbithiophene polymers and been attributed to interpolymer aggregate formation.¹³⁷ The polymers PSBMesBT and PSBMesHBT show high quantum yields of 66% and 67% in CH₂Cl₂ solution, respectively, which are in a similar range to those of the molecular model compounds. However, a notably lower quantum yield of 35% was determined for PSBMesNBT in comparison to MBMesNBT (74%) (Table 2.2).

Table 2.2 Comparison of Photophysical Properties of Polymers and Model Compounds.

Polymer	PSBMesBT	PSBMesHBT	PSBMesNBT
λ_{abs} [nm] ($\lg \epsilon$) ^a	368 (4.5)	380 (4.3)	433 (4.5)
λ_{em} [nm] ^b	442, ^c 463	455	537
Φ_{F} ^d	0.66	0.67	0.35
λ_{abs} film [nm]	373	381	440
λ_{em} film [nm] ^b	468, 489 ^c	467	536
Model	MBMesBT	MBMesHBT	MBMesNBT
λ_{abs} [nm] ($\lg \epsilon$) ^a	367 (4.5)	381 (4.6)	436 (4.6)
λ_{em} [nm] ^b	425	437	540
Φ_{F} ^d	0.72	0.76	0.74

^a Data were acquired in CH₂Cl₂ solution (3.2 x 10⁻⁵ M of boron functional groups). ^b Excited at the absorption maxima. ^c Lower-intensity band or shoulder. ^d Anthracene used as a standard.

2.6 Applications of Borylated Polystyrenes as Anion Sensors

To explore their potential use in anion recognition, the polymers were first subjected to complexation with fluoride in THF solution. Fluoride binding upon addition of a 5-fold excess of Bu₄NF was evident from the ¹¹B NMR spectra, which display strongly upfield shifted signals at $\delta = 1.5$ to 4 ppm in ca. 20 mM solution in THF (for PSBMesAr, $\delta = \sim 50$ ppm and MBMesAr, $\delta = \sim 60$ ppm) (Table 2.3).

Table 2.3 Comparison of ^{11}B NMR Shifts of Models and Polymers Before and After Addition of Pyridine and Fluoride.

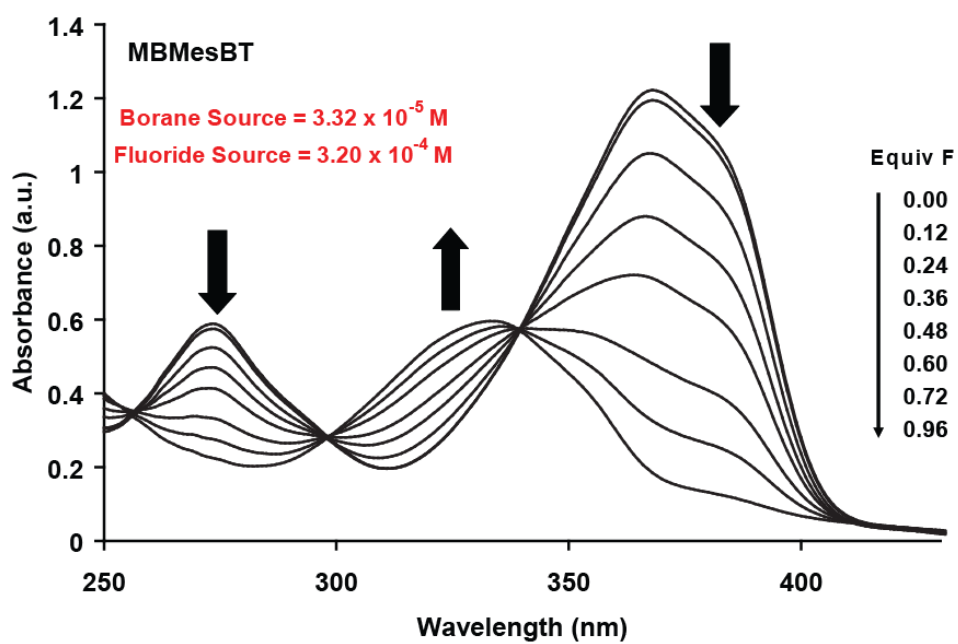
^{11}B NMR Shifts (ppm)	Free Lewis Acid ^a	Pyridine Addition ^b	Fluoride Addition ^c
MBMesBT	62	27.2	3.2
MBMesHBT	61	36.7	3.1
MBMesNBT	61	26.3	4.1
PSBMesBT	50	26.0	2.6
PSBMesHBT	50	35.3	1.7
PSBMesNBT	47	26.4	1.6

^a Data were acquired in CDCl_3 solution (2.0×10^{-6} M of boron functional groups). ^b 10 eq. Pyridine (2.0×10^{-5} M). ^c 5 eq. Tetrabutylammonium fluoride (TBAF) as the fluoride source (1.0×10^{-5} M).

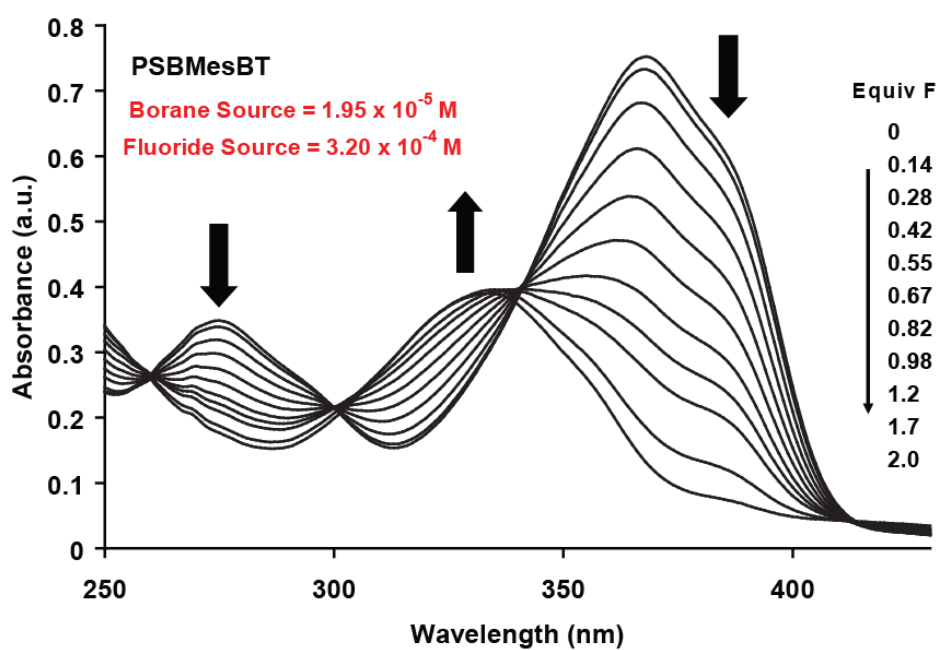
The complexation of the models MBMesBT, MBMesHBT, MBMesNBT and the polymers PSBMesBT, PSBMesHBT and PSBMesNBT with fluoride was further investigated by UV-vis and fluorescence spectroscopy in THF (Figure 2.5). Upon addition of aliquots of the fluoride source to a solution of MBMesBT, MBMesHBT, PSBMesBT and PSBMesHBT, a gradual decrease in intensity of the absorption band at ~ 380 nm was evident, and a new band at ~ 338 nm developed, which can be assigned to bithiophene groups with coordinated boron sites, $[\text{B}(\text{Mes})\text{ArF}]^-$ (Figure 2.5(a-d)). Similarly, fluoride addition to MBMesNBT and PSBMesNBT led to a new band at 362 nm that is blue-shifted by 70 nm relative to the absorption maximum of the uncomplexed compounds (Figure 2.5(e-f)). These shifts of the fluoride complexed polymers PSBMesBT, PSBMesHBT and the respective models MBMesBT and MBMesHBT, are similar in energy to those of 2-trimethylstannyl-2'-hexyl-5,5'-bithiophene ($\lambda_{\text{abs}} = 317$ nm, $\lambda_{\text{em}} = 379$ nm) and for PSBMesNBT and its corresponding

model MBMesNBT the shifts can be assigned to 2-trimethylstannyl-2'-diphenylamino-5,5'-bithiophene, ($\lambda_{\text{abs}} = 364 \text{ nm}$, $\lambda_{\text{em}} = 450 \text{ nm}$), respectively.

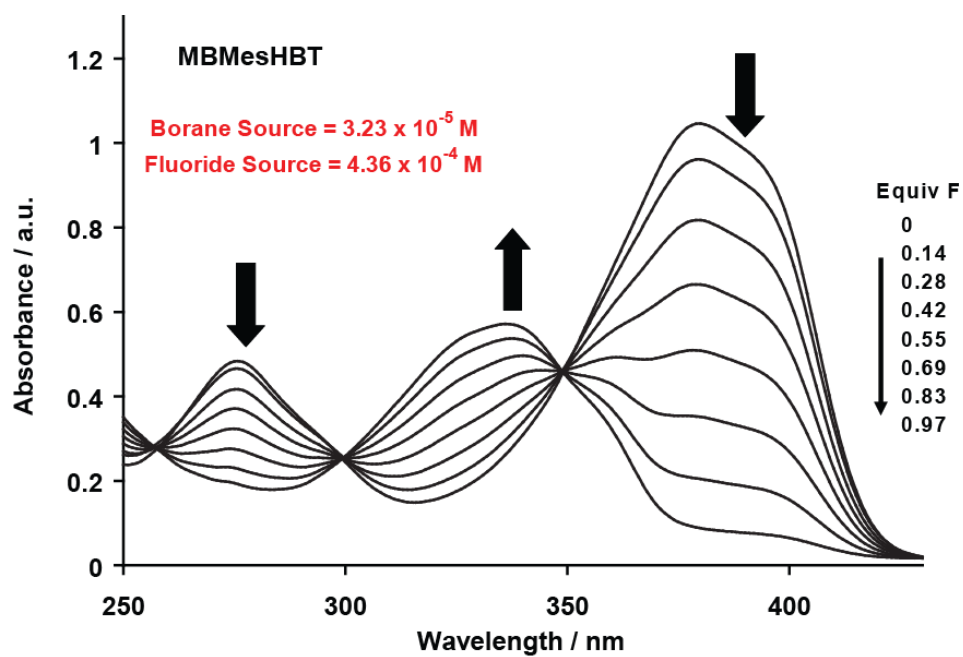
(a)



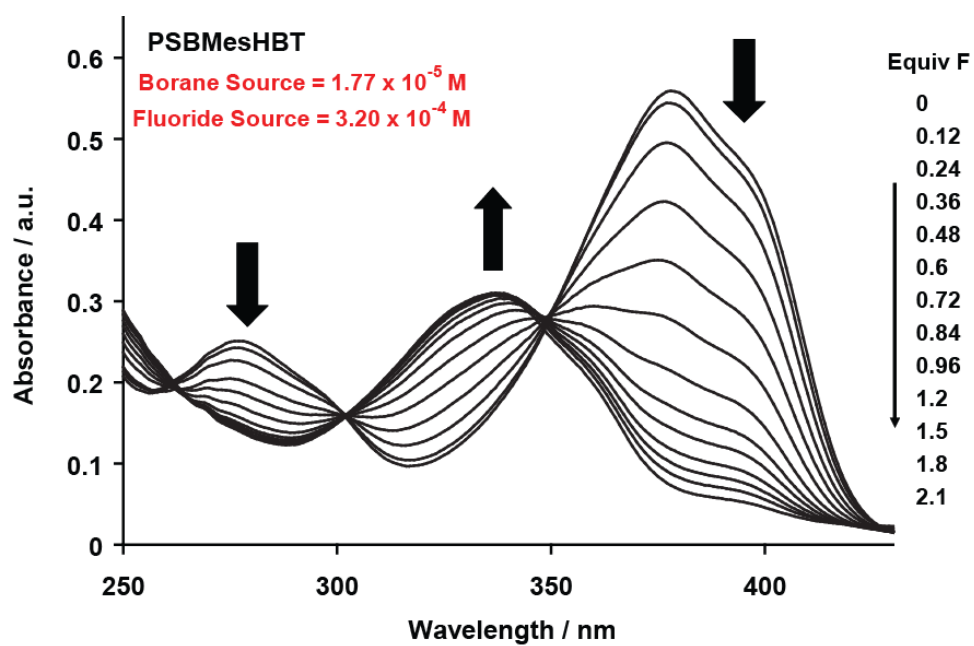
(b)



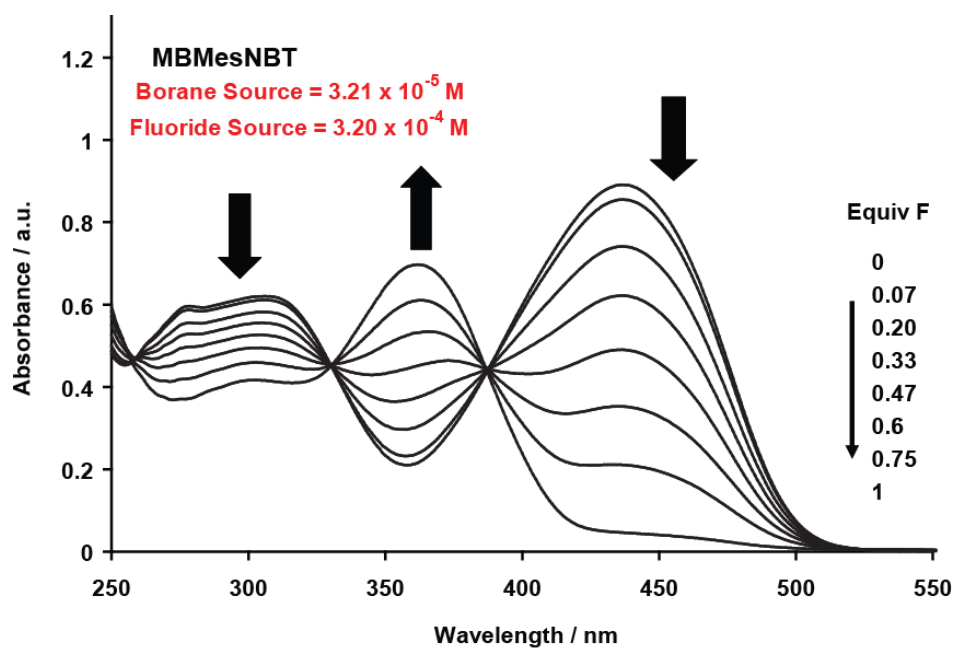
(c)



(d)



(e)



(f)

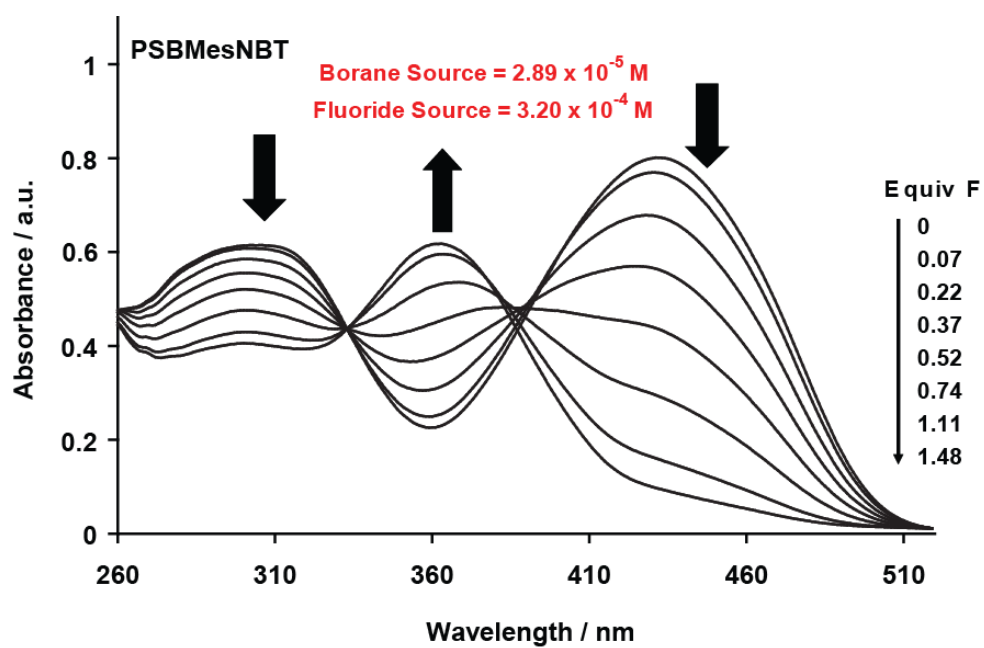


Figure 2.5 Absorption Spectra of Titration with Fluoride (a) MBMesBT; (b) PSBMesBT; (c) MBMesHBT; (d) PSBMesHBT; (e) MBMesNBT; (f) PSBMesNBT.

These results are consistent with TD-DFT calculations (Gaussian03)¹³⁸ that were performed by Dr. Venkatasubbaiah on the closely related molecular tricoordinate bithiopheneborane species PhBMesMeBT and PhBMesNBT and their respective fluoride complexes (Table 2.4, Figure 2.6). For both compounds, the calculations predict the distinct blue-shift of the absorption upon fluoride binding that is experimentally observed. This effect may be rationalized by inspection of the molecular orbitals involved in the transitions (Table 2.4).

Table 2.4 Calculated Electronic Transitions for PhBMesMeBT, PhBMesNBT, and Their Respective Fluoride Complexes from TD-DFT (B3LYP) Calculations.

Compound	Transitions	MO Contribution	Energy Gap eV (nm)	Oscillator Strength/f
PhBMesMeBT	$S_0 \rightarrow S_1$	HOMO-1 $\rightarrow$ LUMO	3.19 (388)	0.3452
		HOMO $\rightarrow$ LUMO		
	$S_0 \rightarrow S_2$	HOMO-1 $\rightarrow$ LUMO	3.27 (379)	0.4387
		HOMO $\rightarrow$ LUMO		
[PhBMesMeBT]F ⁻	$S_0 \rightarrow S_1$	HOMO $\rightarrow$ LUMO	3.53 (351)	0.6596
PhBMesNBT	$S_0 \rightarrow S_1$	HOMO $\rightarrow$ LUMO	2.65 (468)	1.2544
[PhBMesNBT]F ⁻	$S_0 \rightarrow S_1$	HOMO $\rightarrow$ LUMO	3.22 (386)	0.3125
		HOMO $\rightarrow$ LUMO+1		
	$S_0 \rightarrow S_2$	HOMO $\rightarrow$ LUMO	3.23 (384)	0.5713
		HOMO $\rightarrow$ LUMO+1		

The lowest energy absorption in the case of the tricoordinate species PhBMesMeBT corresponds to transitions from the HOMO and HOMO-1 orbitals to the LUMO orbital, while the absorption of PhBMesNBT can be assigned to a HOMO-LUMO excitation. For

both PhBMesMeBT and PhBMesNBT, the LUMO orbital shows significant overlap between the p orbital on boron and the bithiophene system, while the HOMO is primarily centered on the bithiophene moieties and shows only a minor contribution from boron (Figure 2.6). For PhBMesMeBT, the HOMO-1 is found on the mesityl group, indicating that the transition also involves a charge transfer from the mesityl to the bithiophene moiety. In the case of the aminobithiophene model, PhBMesNBT, the HOMO-LUMO transition entails charge transfer from the amino group to the borane center.

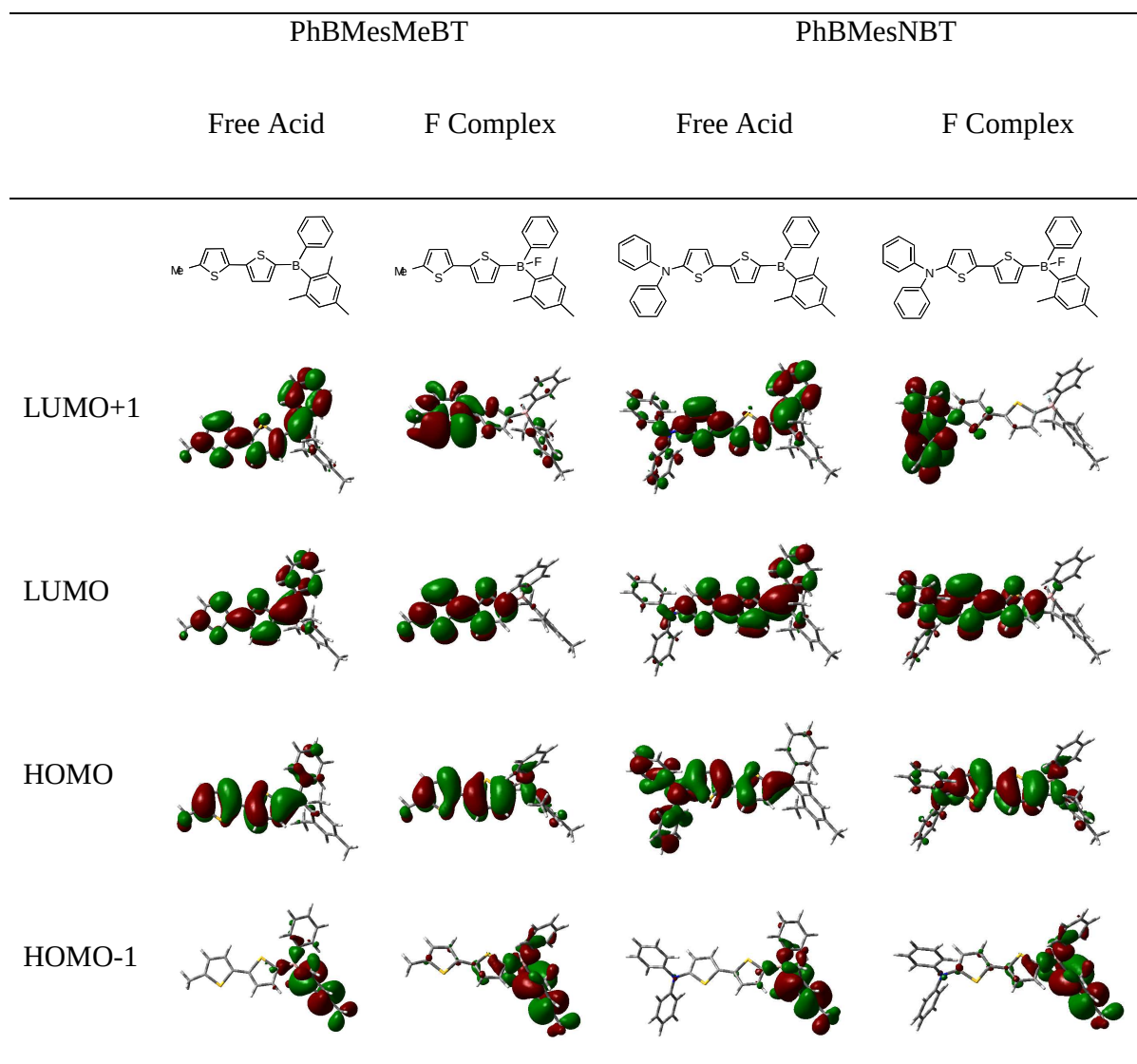


Figure 2.6 Molecular Orbital Diagram from TD-DFT Calculations of PhBMesMeBT and PhBMesNBT and Their Respective Fluoride Complexes.

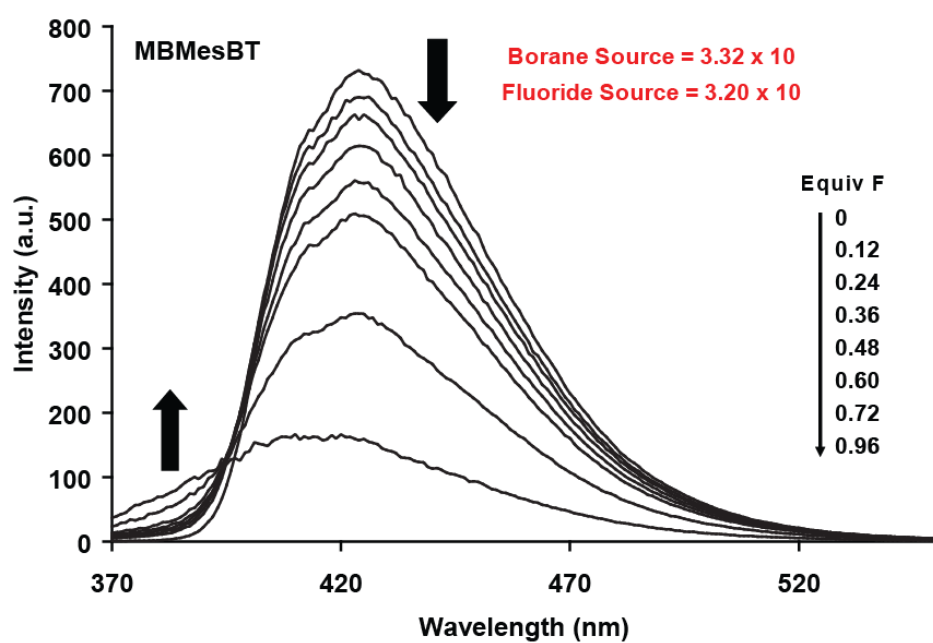
Upon fluoride complexation, the extended conjugation through the boron center is interrupted, and the boron p-orbital neither contributes to the HOMO nor the LUMO level of the borate complexes.^{48, 66, 139} While for the fluoride complex of PhBMesMeBT the lowest energy absorption corresponds to a bithiophene π - π^* transition, in the case of the fluoride

complex of PhBMesNBT, an additional charge-transfer contribution to the diphenylamino group (LUMO+1) is also present.

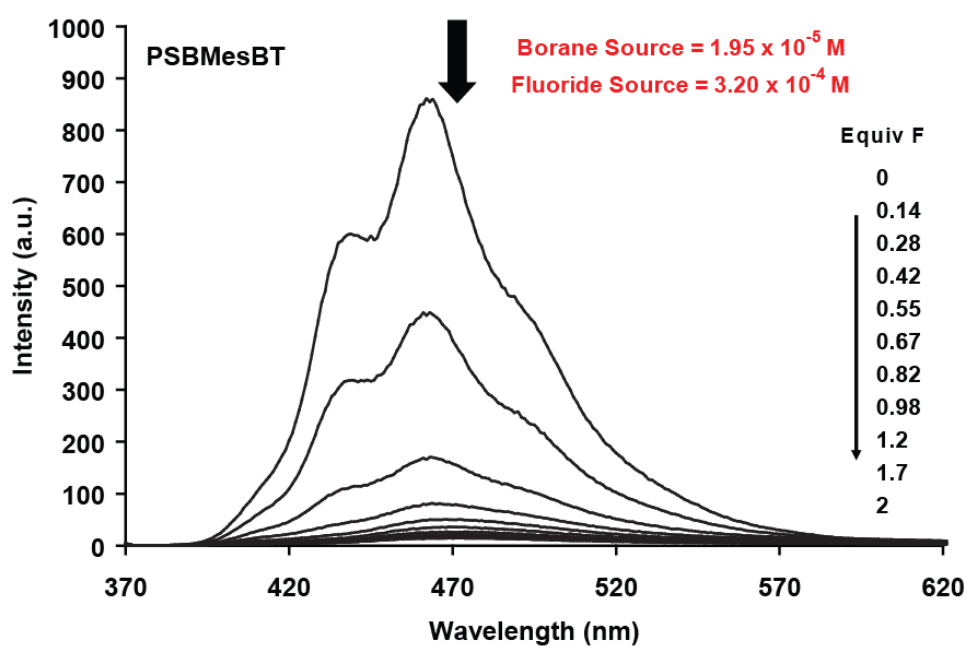
Further analysis of the fluoride titration data for PSBMesHBT assuming independent binding sites provided an estimate of the binding constant of $\lg K = 6.9$. The slightly lower binding constant in comparison to the model system MBMesHBT ($\lg K = 7.4$) most likely is due to neighboring group effects that are expected to play a significant role at the later stages of the titration (formation of a polyelectrolyte). Very similar binding constants were determined for PSBMesNBT ($\lg K = 6.9$) and the respective model compound MBMesNBT ($\lg K = 7.6$).

Upon fluoride addition, the emission intensity of PSBMesHBT at $\lambda = 461$ nm strongly decreased (Figure 2.6).¹⁴⁰⁻¹⁴² The luminescence quenching at low fluoride concentrations is considerably more effective for the polymer than for the molecular analog MBMesHBT, for which the changes in emission intensity correlate with the decrease in absorption intensity. Stern-Volmer analysis revealed an estimated 8-fold amplification effect for the polymeric material (Figure 2.8). In contrast, similar pronounced signal amplification was not observed for PSBMesNBT that contains diphenylamino groups attached to the bithiophene moieties.

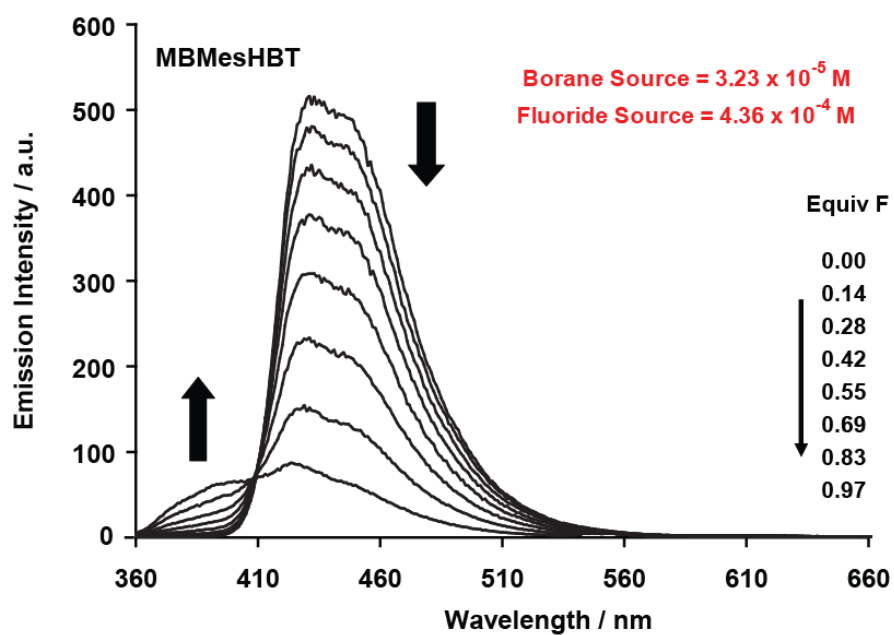
(a)



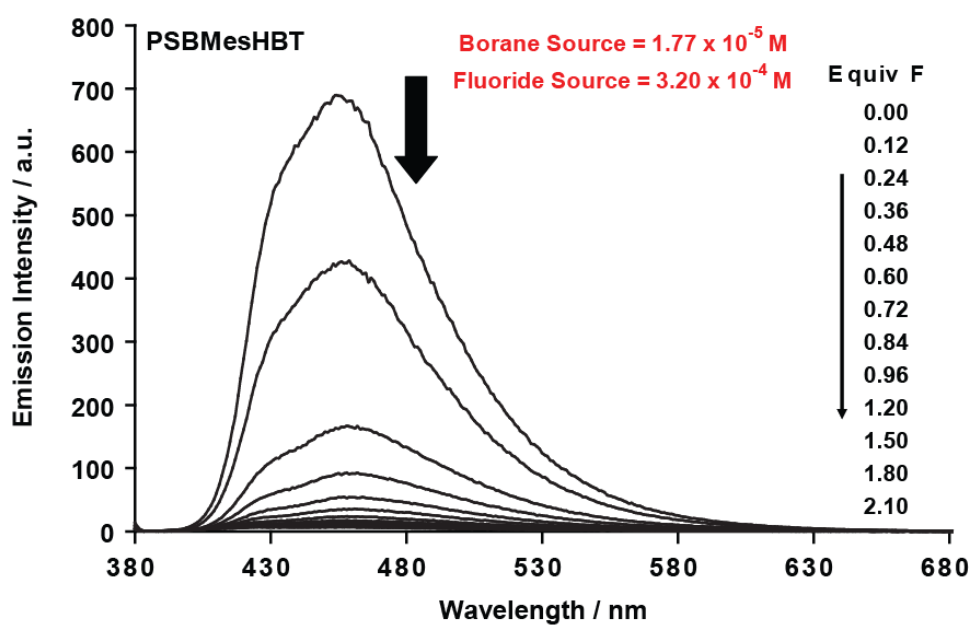
(b)



(c)



(d)



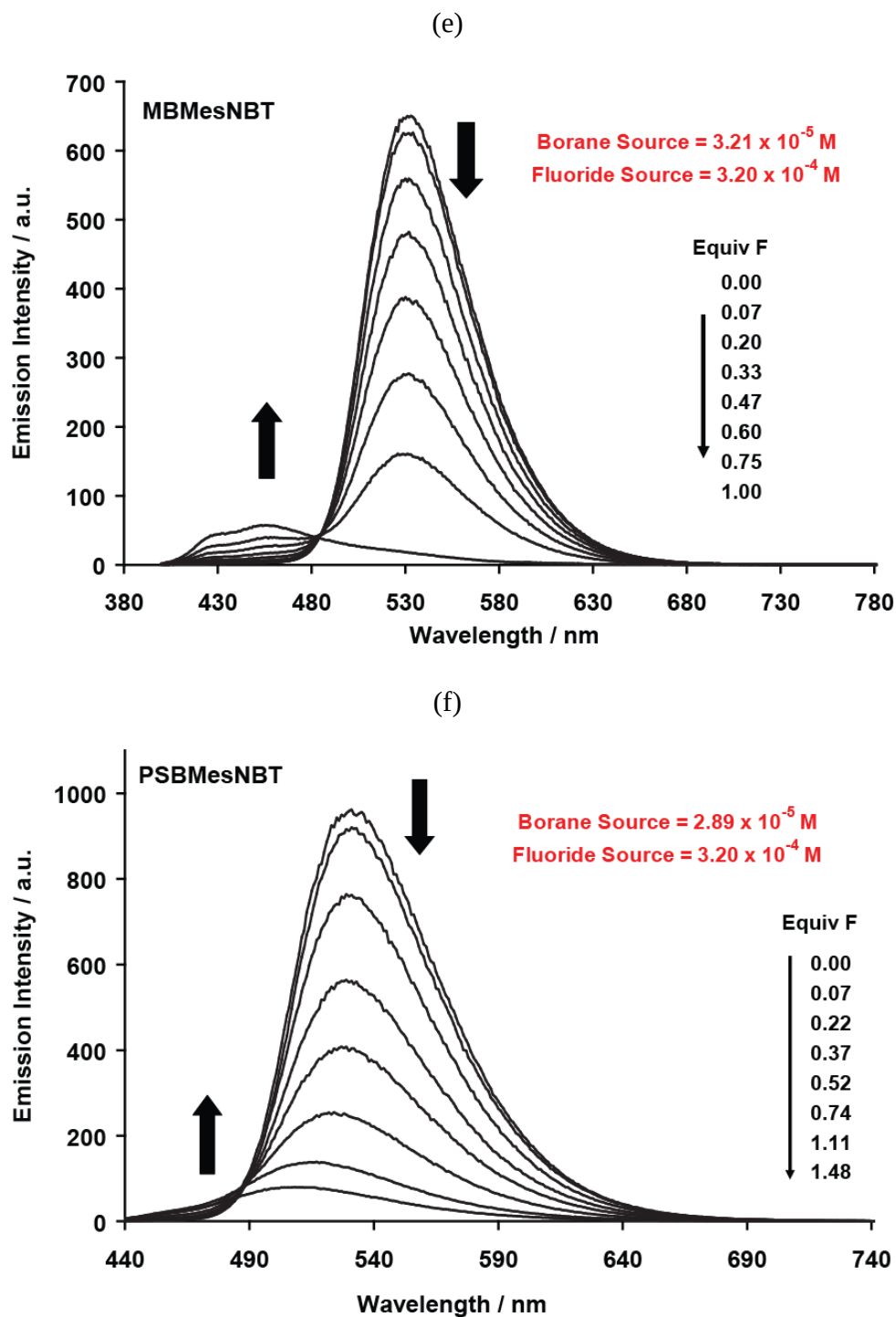


Figure 2.7 Fluorescence Spectra of Titration with Fluoride (a) MBMesBT ($\lambda_{\text{exc}} = 367$ nm); (b) PSBMesBT ($\lambda_{\text{exc}} = 368$ nm); (c) MBMesHBT ($\lambda_{\text{exc}} = 376$ nm); (d) PSBMesHBT ($\lambda_{\text{exc}} = 378$ nm); (e) MBMesNBT ($\lambda_{\text{exc}} = 306$ nm); (f) PSBMesNBT ($\lambda_{\text{exc}} = 432$ nm).

We tentatively attribute the different behavior of PSBMesHBT to efficient exciton migration along the polymer chain (and possibly also between polymer chains) with subsequent trapping at lower energy aggregate states that are weakly or non-emissive. In agreement with this interpretation is the lack of signal amplification for PSBMesNBT, which as discussed above does not show any spectroscopic evidence of aggregate formation in the excited state.

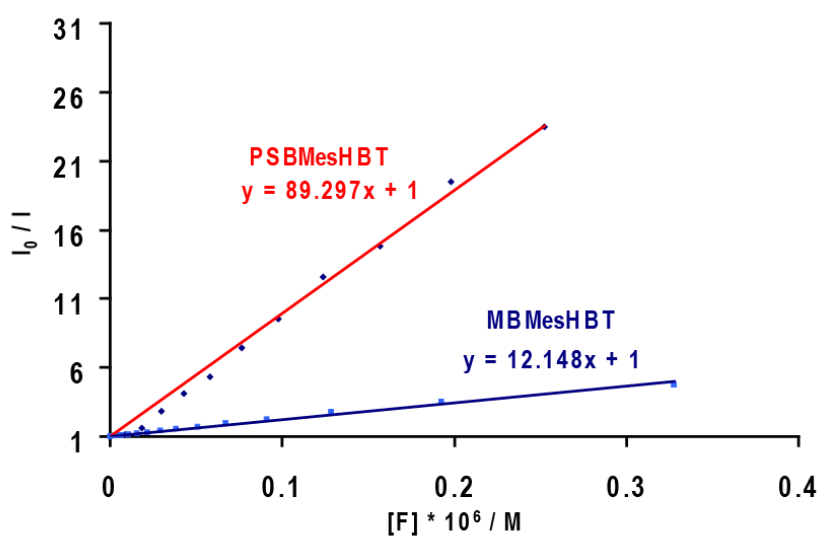


Figure 2.8 Stern-Volmer Analysis of MBMesHBT and PSBMesHBT.

To provide additional support we prepared a *random* copolymer that contains both hexylbithiophene and diphenylaminobithiophene substituents on boron (60:40). The absorption spectrum of this polymer reflects the presence of both chromophores with absorption maxima at $\lambda_{\text{abs}} = 384$ and 433 nm (shoulder).

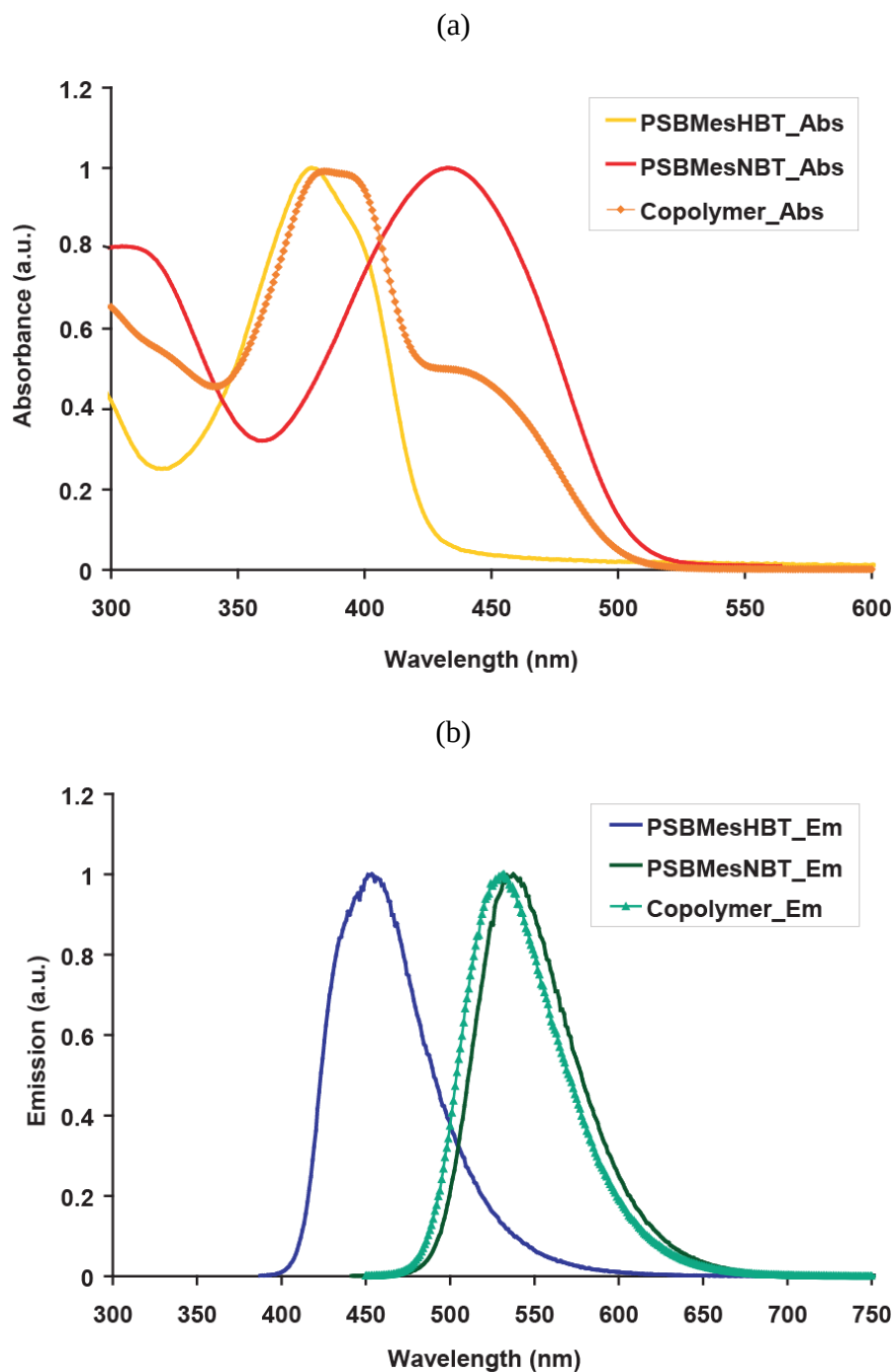
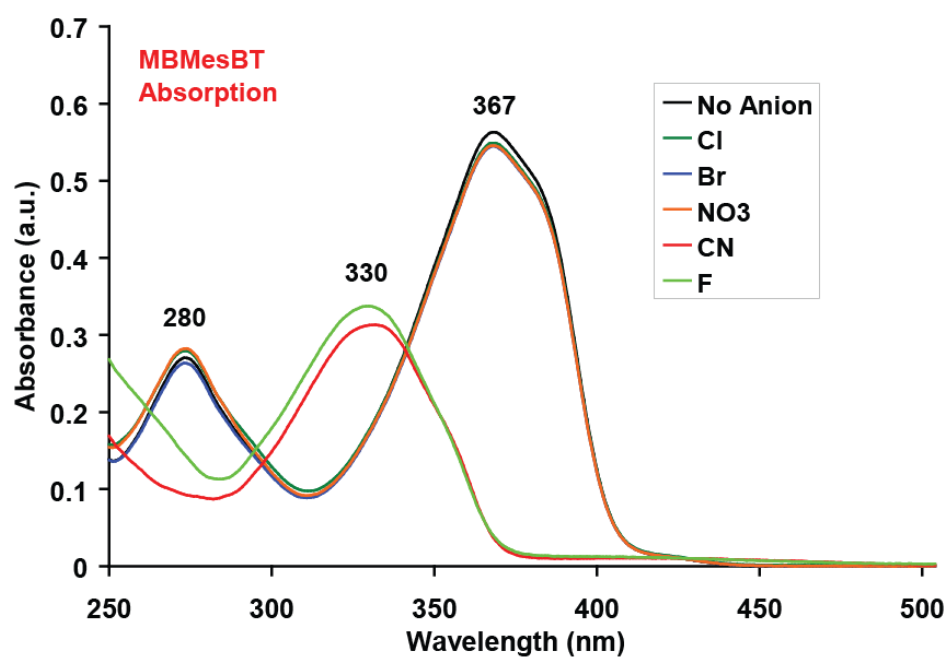


Figure 2.9 Comparison of (a) the Absorption Spectra of PSBMesHBT, PSBMesNBT, and the Respective *Random* Copolymer in CH_2Cl_2 Solution; (b) the Emission Spectra of PSBMesHBT, PSBMesNBT, and the Respective *Random* Copolymer in CH_2Cl_2 Solution (excitation at λ_{max}).

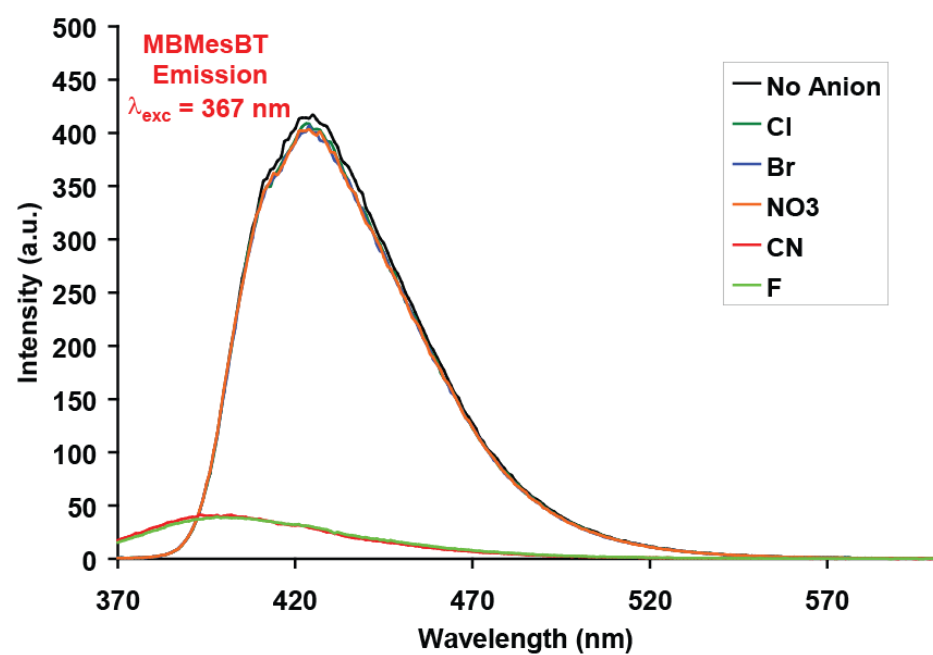
However, the fluorescence spectrum clearly shows emission from only the lower energy states of the boron-bound diphenylaminobithiophene moiety at $\lambda_{\text{em}} = 532$ nm. This suggests that exciton migration along the polymer chain indeed is a fast process that likely is responsible for the enhanced emission quenching of PSBMesHBT upon addition of small amounts of a fluoride source.¹⁴³

To determine the substrate selectivity of PSBMesHBT and PSBMesNBT, we performed a comparative study in which a solution of each polymer was treated under identical conditions with a 10-fold excess of fluoride, chloride, bromide, nitrate, and cyanide, respectively. The photophysical response was monitored by UV-visible absorption and emission spectroscopy. From examination of the absorption and emission data, it is evident that fluoride and cyanide bind strongly to the boron polymers, while the other anions showed no significant response (Figure 2.10).¹⁴⁴ Interestingly, when PSBMesHBT was excited at 330 nm, the decrease in emission intensity of the blue band at 461 nm upon nucleophile binding was accompanied by the development of a (weaker) new band at ca. 405 nm that reaches into the UV region, and can be attributed to emission from the bithiophene moieties with nucleophile-bound boron sites. This desirable feature of a "turn-on" sensor is clearly evident by visual observation for the green emissive PSBMesNBT, which upon fluoride addition shows a new blue emissive band at 457 nm with a shoulder at ca. 430 nm. These observations suggest that, while no signal amplification is found for PSBMesNBT, the polymer (and the respective model system) may serve as a wavelength-ratiometric probe for fluoride or cyanide.

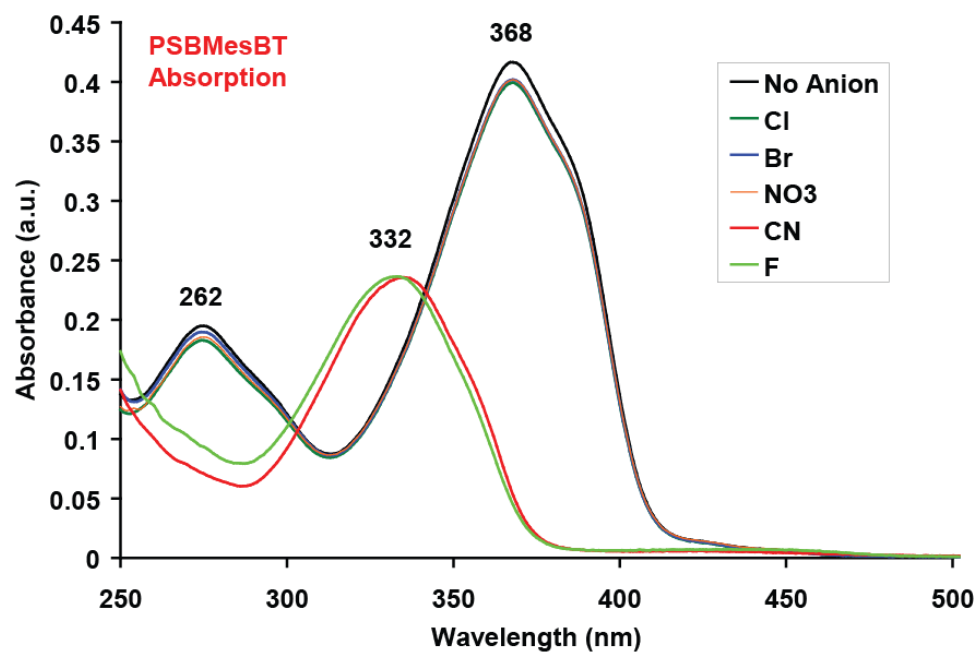
(a)



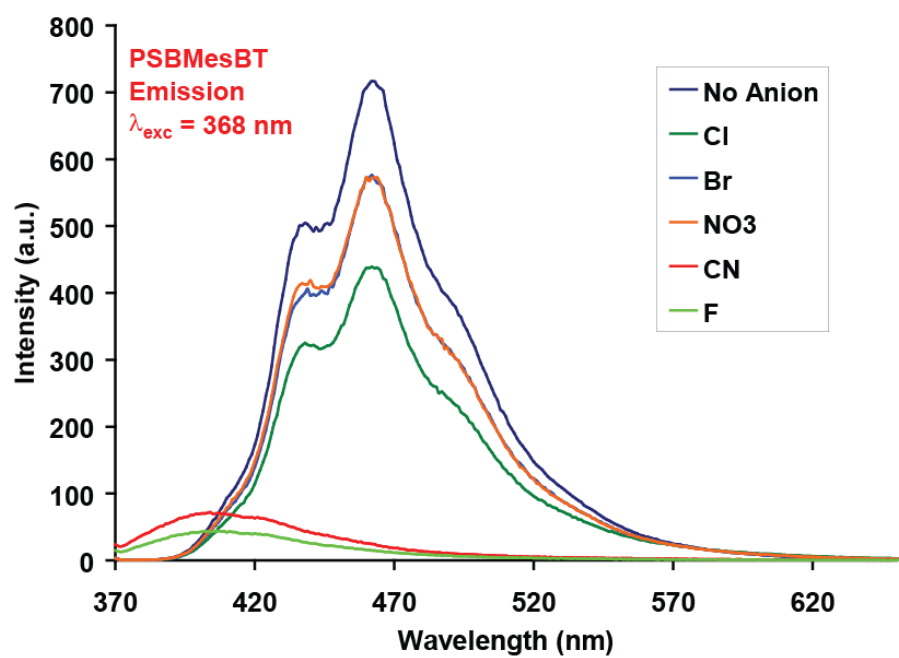
(b)



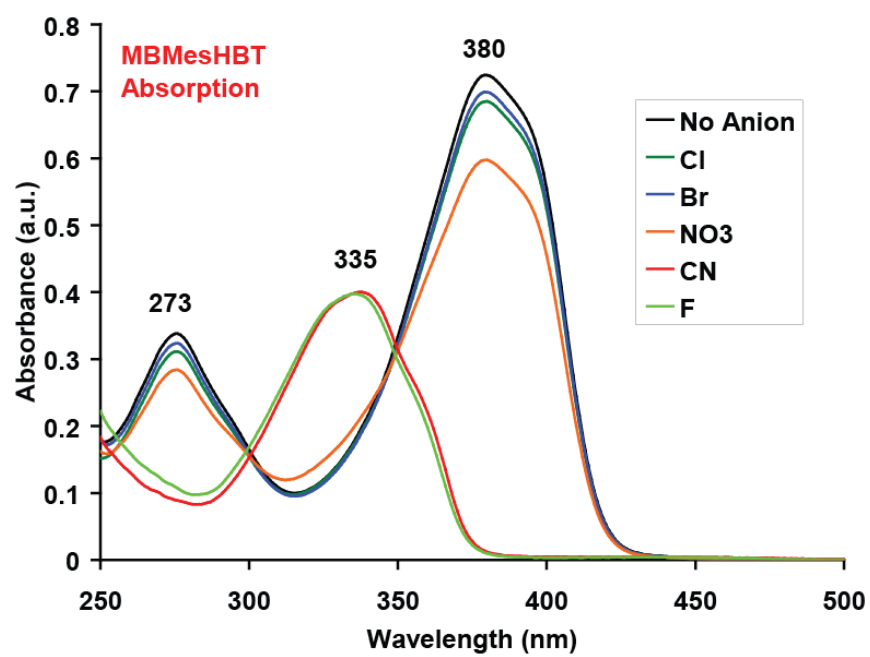
(c)



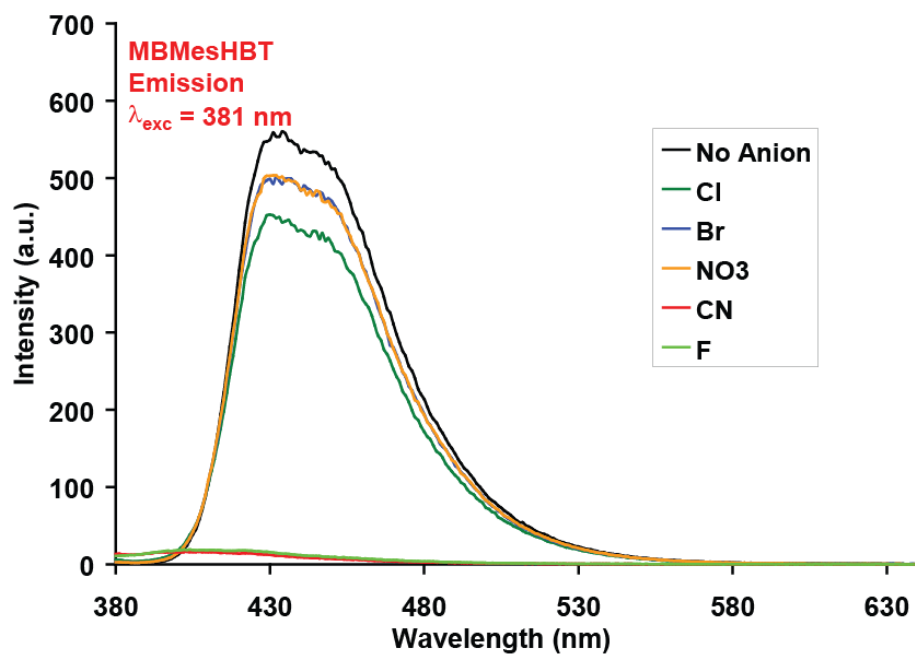
(d)



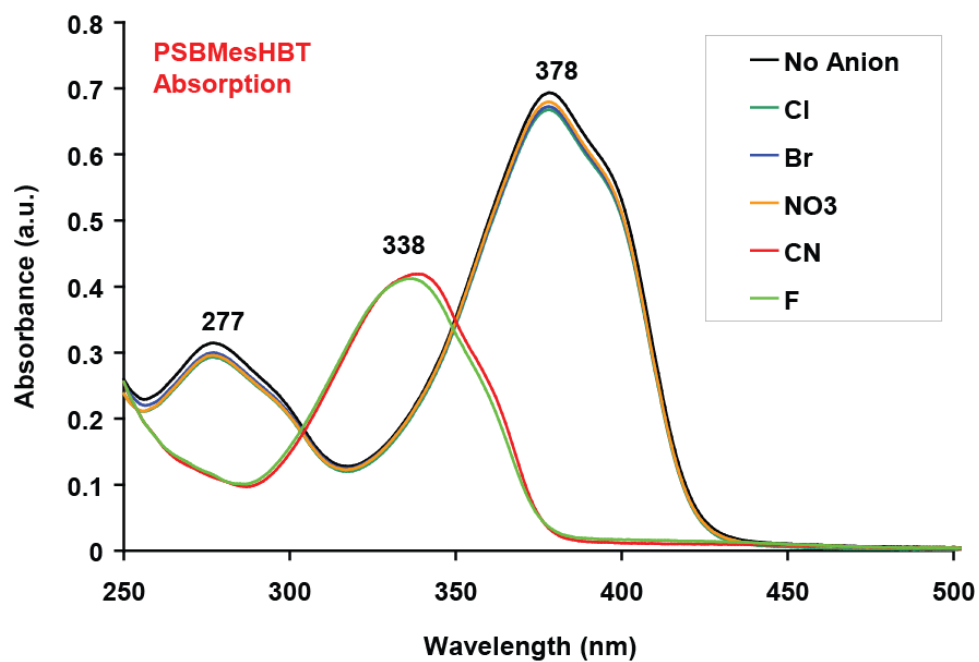
(e)



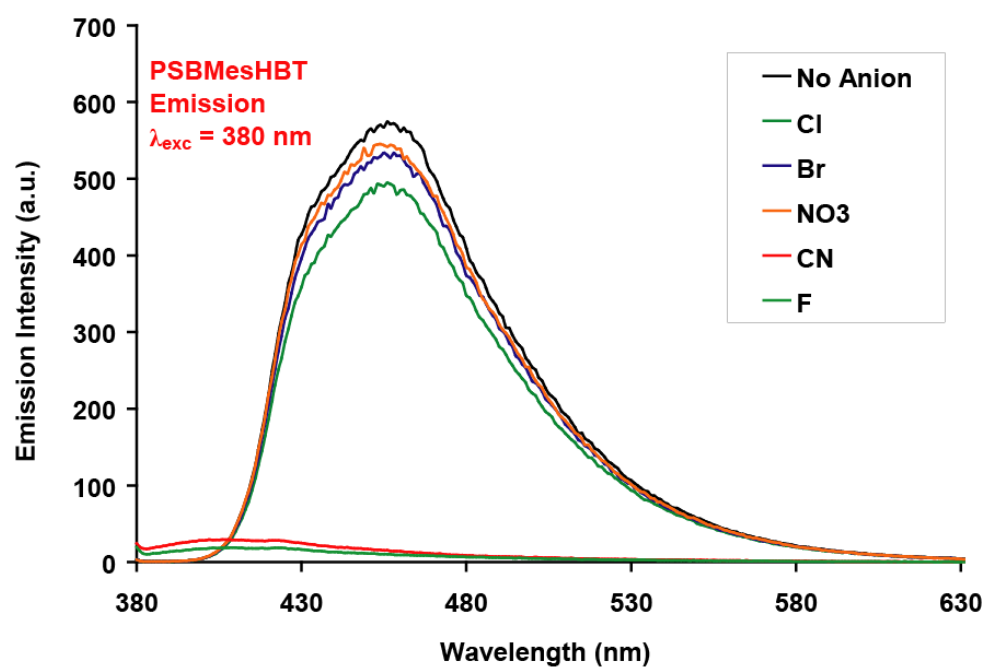
(f)



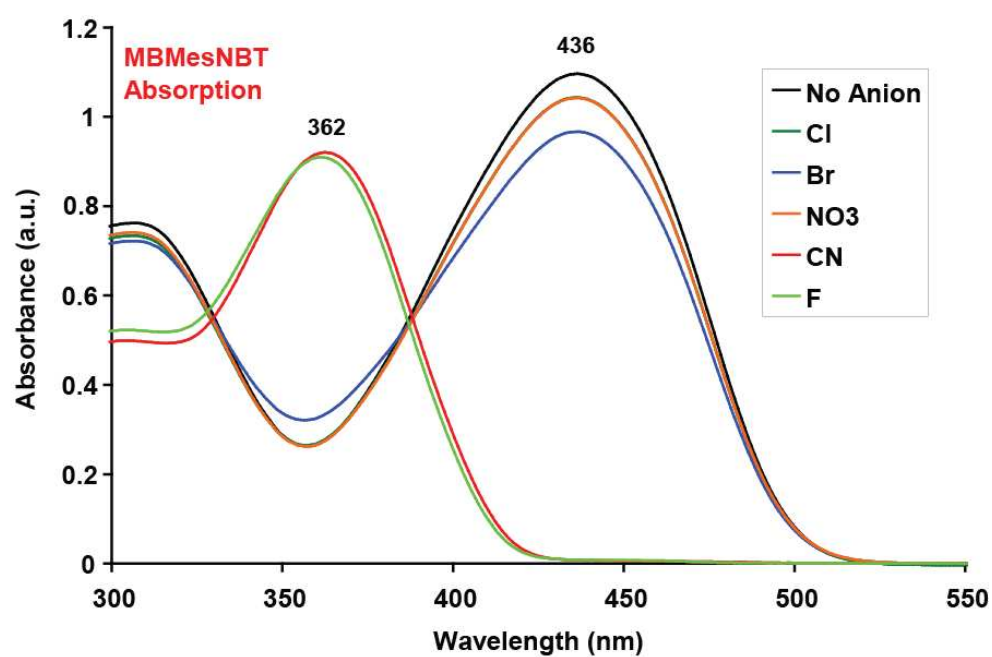
(g)



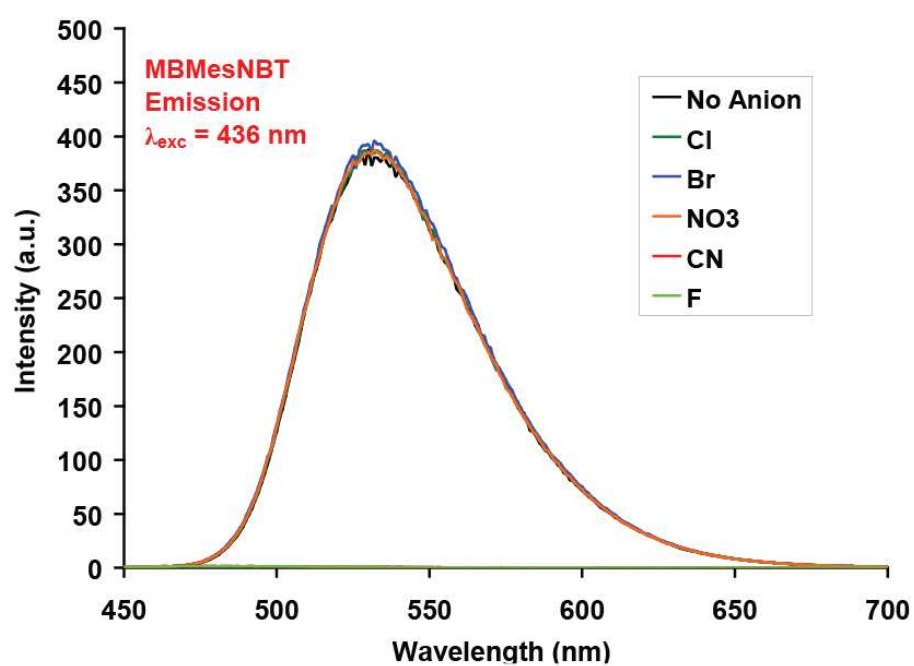
(h)



(i)



(j)



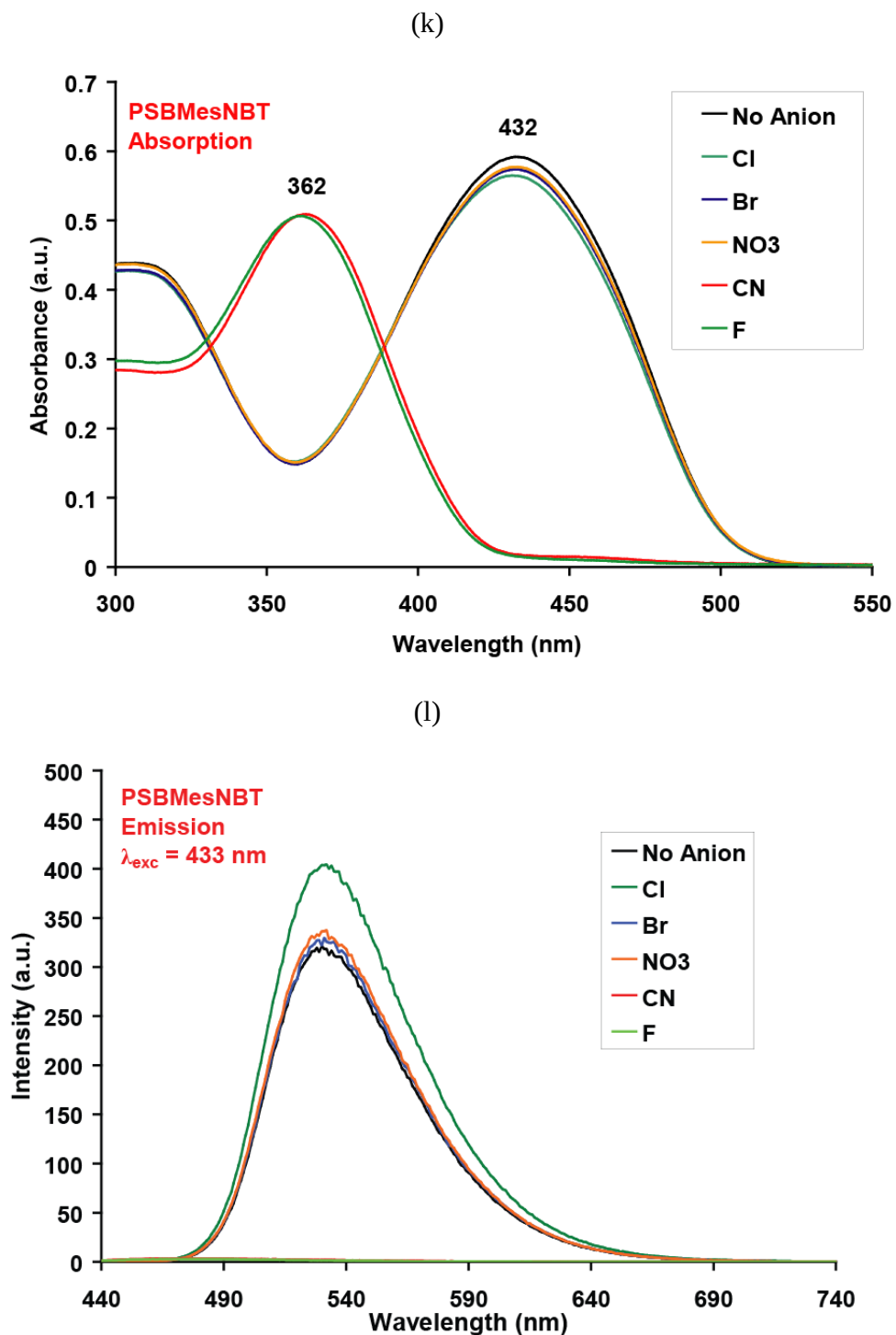


Figure 2.10 Comparison of Photophysical Properties of Model Systems and Polymers upon Titration with 10 Equiv Different Anions (Borane Source = $\sim 3.2 \times 10^{-5}$ M, Fluoride Source = $\sim 3.2 \times 10^{-4}$ M).

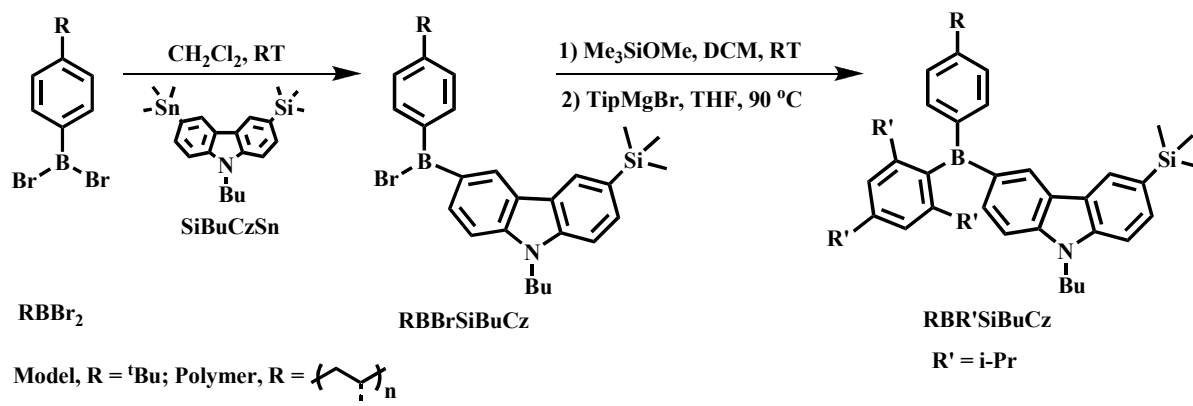
2.7 Triaryl Borane Compounds Bearing Carbazole Groups

Our interest in the synthesis of luminescent triarylboron containing polymers was to employ them for sensing of nucleophiles. As seen in section 2.5.2.3, the stability of the polymers that contain bithiophene or its derivatives as chromophores and mesityl group as the sterically demanding groups was limited to a few weeks. This limited stability was mainly due to the boron center which was not sterically very well protected, and also in part due to the presence of the bithiophene moieties which by themselves are sensitive, to air and moisture, to a certain extent. We decided to further probe the effect of attaching more stable chromophores like carbazoles and their derivatives. If a more sterically bulky group like the 2,4,6-triisopropylphenyl group would be attached to the boron center in addition to these chromophores, the compounds synthesized may show enhanced stability toward air and moisture.

2.7.1 Synthesis of Carbazole Containing Triarylborane Compounds

To realize our goal we synthesized trimethylstannyl functionalized carbazole precursor using literature known procedures. While the synthetic strategy to obtain the desired triaryl boron compounds remained the same as discussed in 2.5.1, the methodology to attach the sterically demanding group was slightly different. For example, the first bromine group on the BBr_2 compound was replaced using an organotin reagent and the second bromine was replaced by a methoxy group by reaction with methoxytrimethylsilane. The resulting RB(Ar)OMe compound was treated with (2,4,6-triisopropylphenyl)magnesium bromide to obtain the desired triarylborane compound. The polymer was purified by column chromatography to remove the magnesium salts followed by precipitation into ethanol, while

the model compound was purified by column chromatography followed by recrystallization from acetonitrile. Detailed syntheses are described in the experimental section.

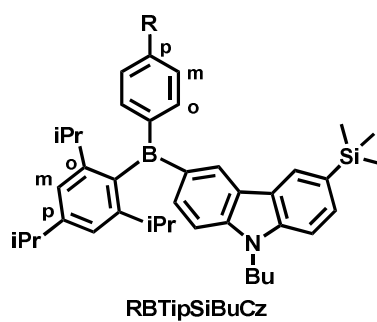


Scheme 2.4 Synthesis of Boron Compounds Containing Pendant Carbazole Moieties.

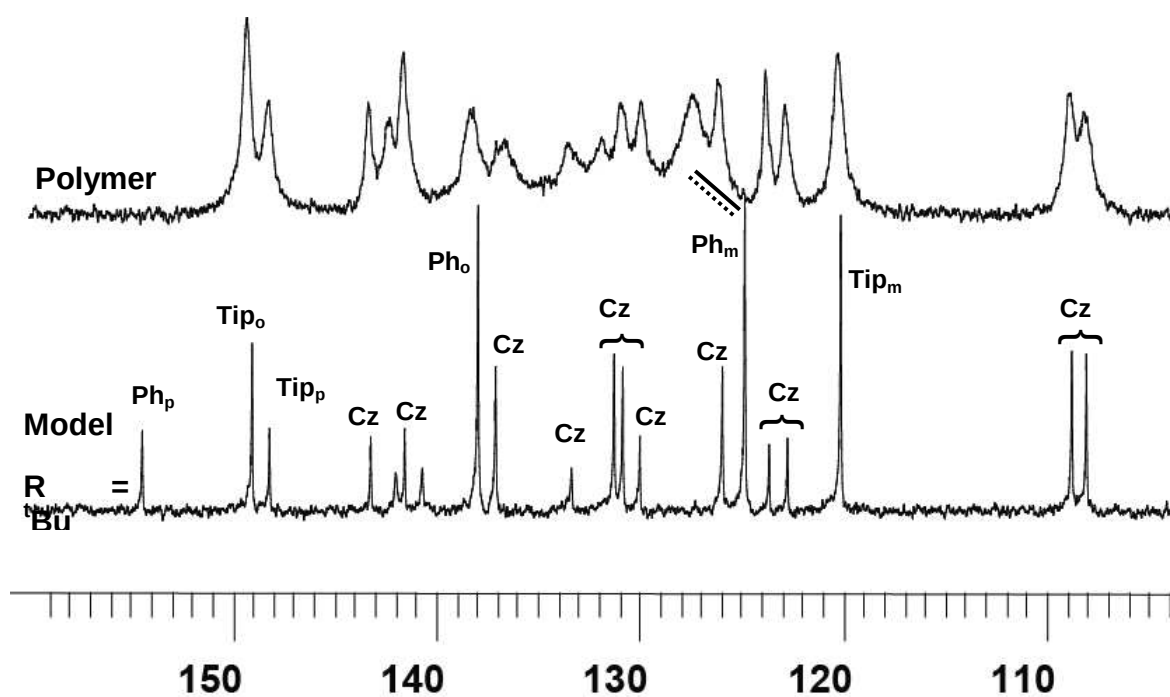
2.7.2 Characterization of Carbazole Containing Triarylborane Compounds

2.7.2.1 NMR Spectroscopy

Both, the polymer as well as model compound, were characterized by multinuclear NMR spectroscopy. The ^{11}B NMR characteristics are similar to those observed for the bithiophene containing compounds and, as expected for triarylboron containing compounds, a broad peak at 50 ppm for the polymer and a downfield shifted peak at 61 ppm for the respective model compound were observed. The peaks in the ^1H NMR spectrum for the polymer were broad and not very informative, but the integration of the protons in the aromatic and aliphatic regions were found to be close to the calculated number of protons for one repeat unit of the polymer. Also the ^{13}C NMR spectra of the model and polymer overlay perfectly, thus confirming that the polymer has both the N-butyltrimethylsilylcarbazole and 2,4,6-triisopropylphenyl moieties attached to it (Figure 2.11).



(a)



(b)

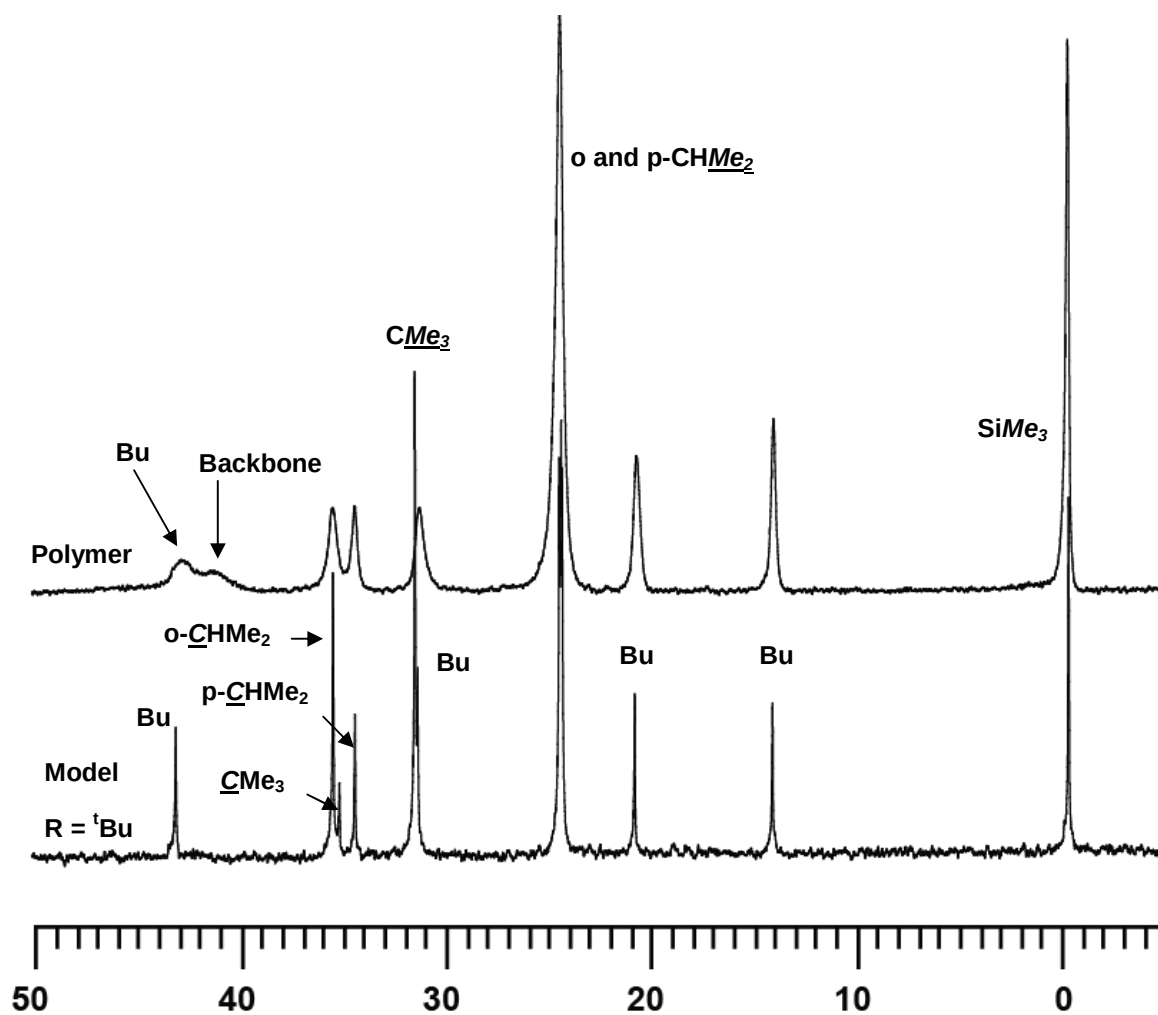


Figure 2.11 ^{13}C NMR Overlay of PSBTipSiBuCz and MBTipSiBuCz (a) Aromatic Region; (b) Aliphatic Region.

2.7.2.2 Molecular Weight Determination, Thermal Properties and Stability Toward Air and Moisture

The molecular weight studied by GPC analysis in THF relative to polystyrene standards was found in the range expected on the basis of the molecular weight of the silylated precursor ($M_w = 23800$, $DP_n = 119$, $PDI = 1.13$ (GPC-RI)), and the polydispersity was only slightly broadened (PSBTipSiBuCz, $M_w = 43976$, $M_n = 38296$, $DP_n = 63$, $PDI = 1.15$). A small high molecular weight shoulder ($\%_{Area} = 5.1$) is observed which corresponds to almost twice the weight of the main peak ($\%_{Area} = 94.9$) indicating that homo-coupling at the end groups may have occurred to a small extent. An alternative explanation may be incomplete substitution on the boron center during the attachment of the bulky Tip group which might lead to the formation of chemical crosslinks give rise to crosslinked high molecular weight polymers.

From DSC analysis it was evident that the polymer PSBTipSiBuCz shows a glass transition temperature of 187 °C, which is slightly higher than that observed for the bithiophene containing systems (165 °C). The higher glass transition temperature may be attributed to the rigidity of the carbazole moiety, in comparison to the bithiophene where the carbon-carbon bond connecting the two thiophene units are free to rotate which is not so in case of the carbazole, and in part also due to the presence of the bulky triisopropylphenyl group indicating an even lesser void volume (free space) within the polymer structure. Thermogravimetric analysis (TGA) data shows that the polymer PSBTipSiBuCz is thermally stable upto 256 °C, above which multistep decomposition of the polymer is observed. The residual weight at 800 °C was in the range of 7-9 % (Figure 2.12). The thermal stability and the residual ceramic weight of the carbazole containing polymer is comparable to the

bithiophene containing polymers PSBMesBT, PSBMesHBT and PSBMesNBT, thus indicating that the presence of the triisopropylphenyl group has little to no affect on the thermal stability of the polymer PSBTipSiBuCz.

The model compound MBTipSiBuCz and the polymer show excellent stability to oxygen and moisture in both solution as well as the solid state. In C_6D_6 and $CDCl_3$, the model compound is stable for a period of over 1 month and in the solid state it is stable toward both oxygen and moisture for over a period of 3 months. The polymer PSBTipSiBuCz on the other hand is stable in solution state for atleast 25 days and in the solid state for over a month. This indicates that the the presence of a more sterically demanding triisopropylphenyl group and a stable chromophore like the carbazole moiety enhances the stability of the compounds in comparison to the compounds that contain bithiophene as the chromophore and mesityl group as the sterically protecting group.

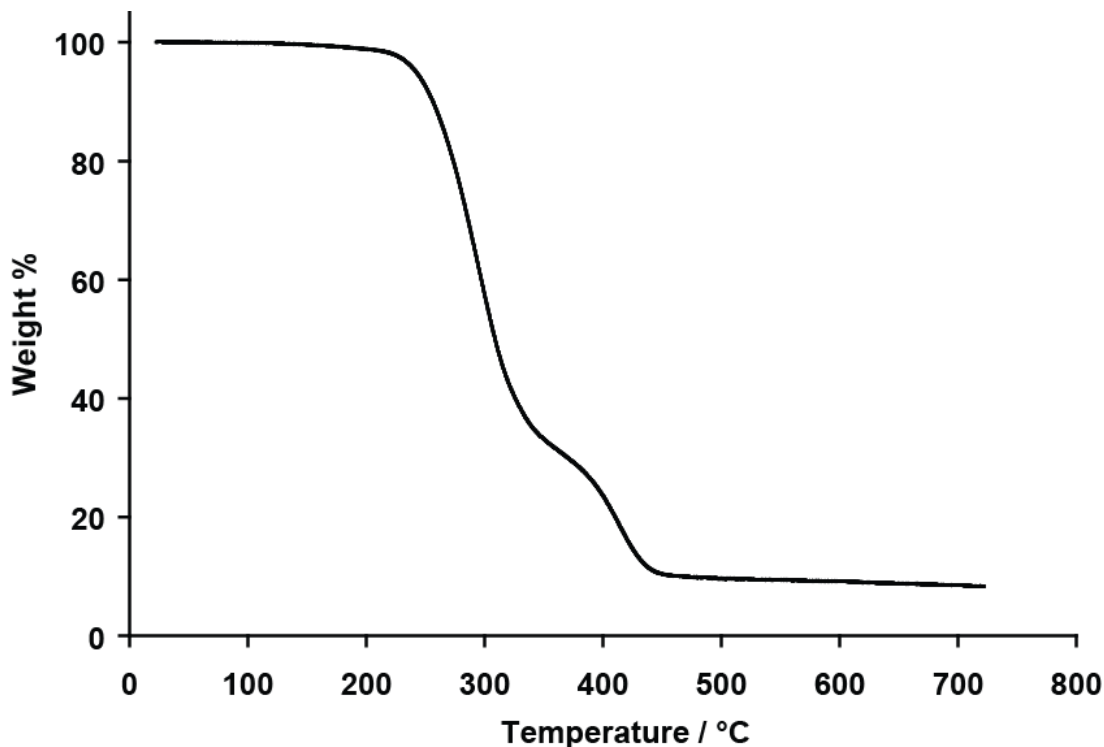


Figure 2.12 TGA Plot of the Polymer PSBTipSiBuCz.

2.7.2.3 Photophysical Properties

The absorption spectra of the polymer and the model compound in CH_2Cl_2 solution are quite similar and consist of multiple bands at 286 nm, 305 nm and 345 nm, respectively, while as a thin film the polymer absorption shows only a single band at 345 nm which can be attributed to the carbazole moiety. Both the polymer and the model compound emit bright blue light in solution as well as thin film upon excitation at the absorption maxima (Figure 2.13).

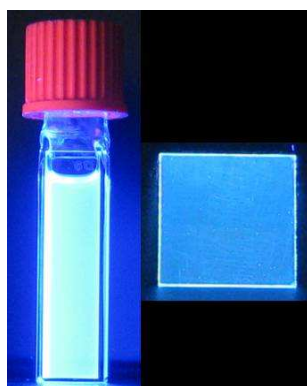


Figure 2.13 Blue Emission from CH_2Cl_2 Solution and Thin Film of PSBTipSiBuCz (excitation at $\lambda_{\text{max}} = 344 \text{ nm}$).

The fluorescence spectra for both the polymer and model compound consist of a single band, but the spectrum of the polymer PSBTipSiBuCz ($\lambda_{\text{em}} = 397 \text{ nm}$) is slightly blue shifted by $\sim 13 \text{ nm}$ in comparison to the model compound ($\lambda_{\text{em}} = 410 \text{ nm}$) and that of the polymer in the thin film is blue-shifted by $\sim 5 \text{ nm}$ ($\lambda_{\text{em}} = 392 \text{ nm}$) in comparison to the polymer in solution. The polymer and model compound show high quantum efficiencies of 68 and 72 %, respectively which are comparable to the bithiophene containing compounds which show quantum efficiencies of $\sim 75\%$ for the models and $\sim 66\%$ for the polymers. This suggests that the polymer, PSBTipSiBuCz, may be a potential candidate for OLED applications.

Table 2.5 Comparison of Photophysical Properties of MBTipSiBuCz and PSBTipSiBuCz in Solution and Thin Film.

Compound	MBTipSiBuCz	PSBTipSiBuCz	PSBTipSiBuCz Film ^d
λ_{abs} [nm] ($\lg \epsilon$) ^a	286 (27389), 304 (31432), 344 (32079)	285 (27765), 305 (27313), 345 (23645)	345
λ_{em} [nm] ^b	410	397	392
Φ_{F} ^c	72	68	---

^a Data were acquired in CH₂Cl₂ solution (3.6×10^{-5} M of boron functional groups). ^b Excited at the absorption maxima. ^c Anthracene used as a standard. ^d Thin film cast from toluene.

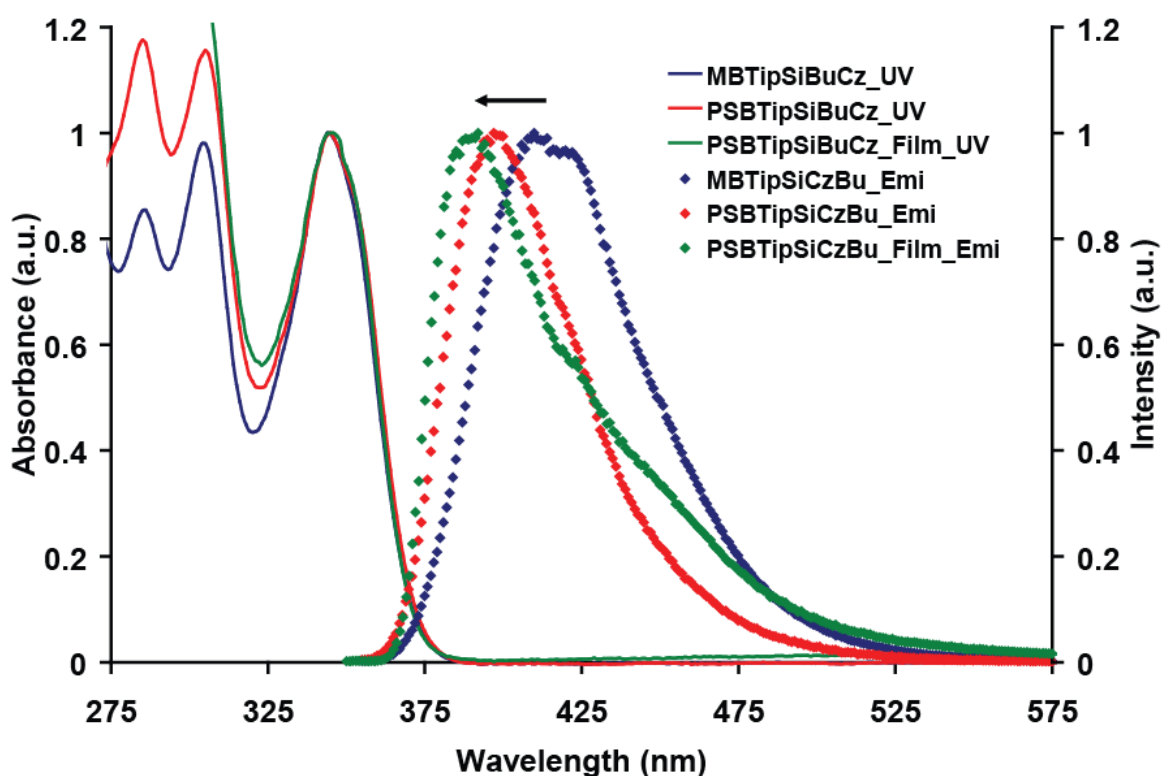


Figure 2.14 Comparison of the Absorption and Emission Spectra (excitation at $\lambda_{\text{max}} = 344$ nm) of MBTipSiBuCz and PSBTipSiBuCz in CH₂Cl₂ Solution and Thin Film.

Chapter 2B. Polystyrene Based Electroactive Triarylborane Polymers

2.8 Introduction to Polymers Bearing Redox Active Moieties

Transition metal containing polymers are an interesting class of materials in which the presence of the metal can lead to unusual electronic, magnetic, and optical properties. Broad attention has been given especially to ferrocene containing polymers, at least in part due to the opportunity to reversibly switch between the oxidation states of Fe(II) and Fe(III), combined with the exceptionally high stability of ferrocene under ambient conditions. The redox behavior of ferrocene-containing polymers has been widely studied, and a recent example that nicely illustrates this concept is that of block copolymers of polystyrene and poly(ferrocenylsilane) that reversibly form micellar structures upon oxidation of the iron centers.¹⁴⁵

To combine organometallic moieties with electron-deficient (tri-coordinate) organoboranes in one polymeric material is an attractive goal since overlap of the empty p-orbital on boron with an organic or organometallic π -system is known to lead to extended π conjugation and hence to dramatically alter the electronic and photophysical properties. The resulting materials are therefore expected to exhibit unique electronic characteristics. For instance, polymers in which ferrocene moieties alternate with Lewis acidic boron sites have been reported by Wagner et al. to display an exceptionally high degree of electronic communication between the ferrocene moieties as indicated by large redox couplings measured by cyclic voltammetry. Organometallic ruthenium complexes have been embedded

into conjugated organoboron polymers by Chujo *et al.*⁸⁴ These hybrid organometallic polymers show interesting photophysical properties as a result of the push-pull effect between the electron-rich ruthenium and electron-poor boron centers and the occurrence of both $d_{\pi}-p_{\pi}^*$ and $\pi-\pi^*$ electronic transitions. In addition, the observation of higher redox potentials for the polymer in comparison to the Ru building block suggests that the organoborane moieties withdraw electron density from the transition metal complex.

Examples of polymers that contain organoborane moieties attached as pendant groups are comparatively relatively rare; examples of which are shown in Section 2.3. Lequan *et al* described the attachment of triarylborane moieties to a polyurethane backbone through a diazo linker for applications as non-linear optical (NLO) materials.¹²⁴ Moreover, Shirota *et al* reported that polymerization of an organoborane-modified vinyltriphenylamine gives a polymeric material that acts as an efficient green emitter in a light emitting device (LED).¹²⁵

As seen in Section 2.4 we have successfully attached electron-deficient boron centers to the side chain of polystyrene using a polymer modification strategy that involves the efficient replacement of trimethylsilyl groups with BBr_3 .^{130, 146} Also in Section 2.5 we demonstrated that subsequent attachment of bithiophene moieties to the borylated polystyrene $PSBBr_2$ leads to strongly luminescent materials that can be used as chemosensors for the selective and highly efficient recognition of fluoride and cyanide.¹³⁴ Herein the discussion is on the preparation of polystyrene derivatives containing pendant electro-active ferrocenylborane moieties and the comparison of their properties with those of a metal-free dimesitylborane polymer.

2.8.1 Synthetic Strategy for Pendant Electroactive Polymers

The synthetic strategy is outlined in Scheme 2.5. Initial reaction of PSBr_2 with the mild organotin reagent, 2-trimethylstannylferrocene, in CH_2Cl_2 at RT gave the mono-substituted intermediate PSBrFc . This reaction was accompanied by an immediate color change to red, which is indicative of successful installment of the ferrocene moiety at the boron center. High selectivity for the desired mono-functionalization was confirmed for the model reaction of $^t\text{BuPhBBr}_2$ with FcSnMe_3 by ^1H NMR spectroscopy, which showed selective formation of $^t\text{BuPhFcBBr}$ and no evidence of the (t-butylphenyl)diferrocenylborane (Figure 2.15).

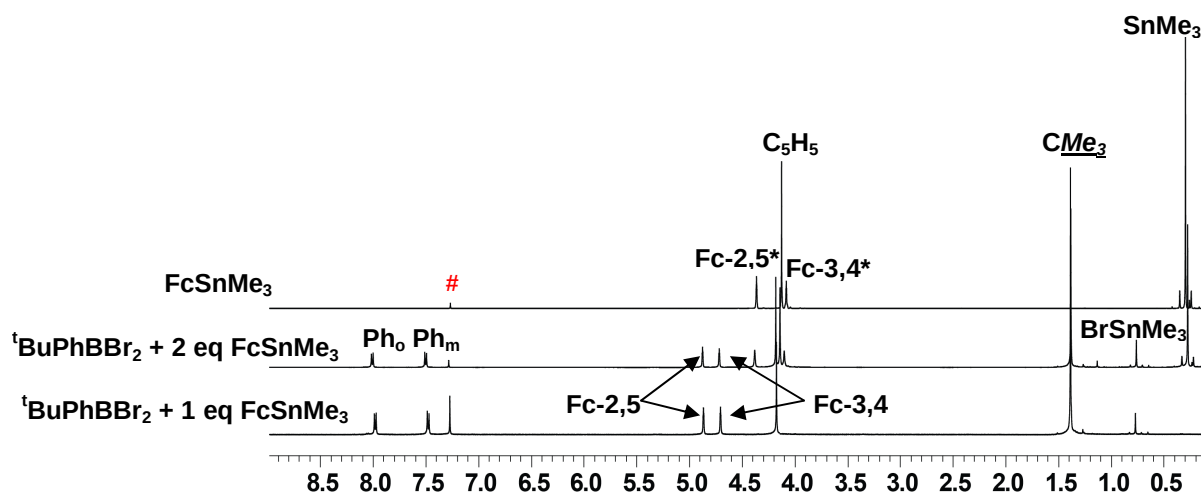
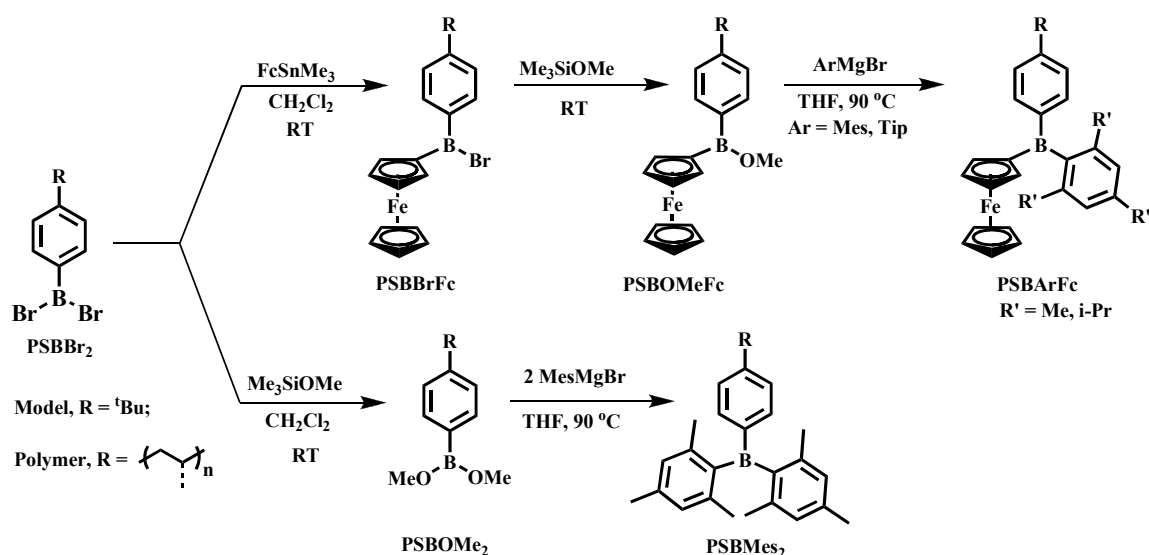


Figure 2.15 ^1H NMR Overlay of Ferrocenyltrimethyltin Precursor and Model Compound After Addition of 1eq and 2 eq of Ferrocenyltrimethyltin (Fc-2,5* and Fc3,4* = Signals from Ferrocenyltrimethyltin; # = CDCl_3).

The presence of a sterically demanding group like the 2,4,6-trimethylphenyl (mesityl, Mes) or 2,4,6-triisopropylphenyl (Tip) substituent is known to enhance the stability of the otherwise hydrolytically sensitive boron center.^{55, 147} Attachment of these bulky substituents was achieved by reaction with the respective Grignard reagents. The bromine substituents



Scheme 2.5 Synthesis of Boron Polymers Containing Pendant Electroactive Groups.

2.8.2 Characterization

2.8.2.1 Multinuclear NMR Spectroscopy

The polymers as well as model compounds were fully characterized by ^1H , ^{13}C and ^{11}B NMR spectroscopy (Table 2.6). The assignments of the proposed polymeric structures were confirmed by comparison with their respective model compounds. The presence of a broad ^{11}B NMR signal at ca. 50 - 60 ppm is typical of triarylborane polymers.^{114, 134} However, for all three polymers we observe an upfield shift of ca. 15 ppm relative to the molecular species (Figure 2.16). This may be the result of shielding effects due to neighboring aryl groups in the case of the polymers and is consistent with prior observations for polymers with bithiophene borane pendant groups.¹³⁴

Table 2.6 ^{11}B NMR Shifts (ppm) of Organoboron Polymers and Molecular Model Compounds.^[a]

Polymer	$\delta(^{11}\text{B}) / w_{1/2}$ (Hz)	Molecular Model	$\delta(^{11}\text{B}) / w_{1/2}$ (Hz)
PSBMesFc	57 / 1900	MBMesFc	70 / 1300
PSBTipFc	53 / 1800	MBTipFc	70 / 1750
PSBMes₂	57 / 2000	MBMes₂	73 / 1440

[a] Data were obtained at RT in CDCl_3 (ca. 8×10^{-3} M).

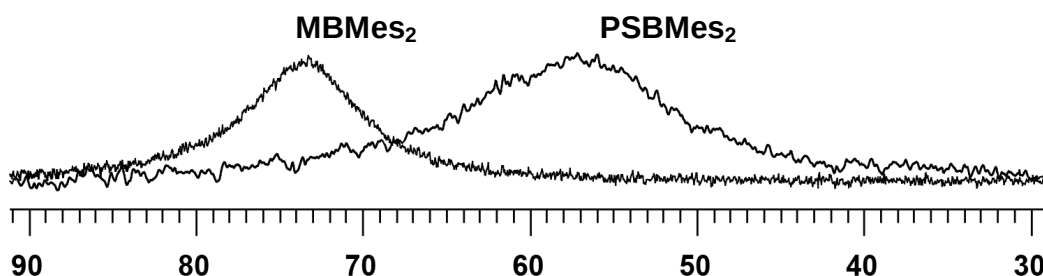


Figure 2.16 Comparison of the ^{11}B NMR Shifts of MBMes_2 and PSBMes_2 .

2.8.2.2 Molecular Weight Determination by Gel Permeation Chromatography

The polymers were further analyzed by gel permeation chromatography (GPC) in THF against PS standards. For all polymers a narrow band was found in the expected molecular weight range (PSBMesFc , $M_w = 27400$, $M_n = 23826$, $\text{DP}_n = 56$, $\text{PDI} = 1.15$; PSBTipFc , $M_w = 33700$, $M_n = 30360$, $\text{DP}_n = 60$, $\text{PDI} = 1.11$; PSBMes_2 , $M_w = 32223$, $M_n = 23826$, $\text{DP}_n = 68$, $\text{PDI} = 1.27$). A small high molecular weight shoulder was apparent in all three cases and a Gaussian fit suggested that the MW of this fraction is about double that of the main peak. This slight bimodality with still very narrow dispersities indicates that homo-coupling at the Br end groups may have occurred to a small extent (radical coupling). Such a process has, for example, been reported by Matyjaszewski to take place in the presence of Cu(I) species and has explicitly been exploited for the generation of telechelic polymers.¹⁴⁸ The high temperature employed during the installment of the bulky aryl groups likely favors the small extent of coupling ($< 15\%$) detected for the products.

2.8.2.3 Thermal Properties by Differential Scanning Calorimetry and Thermogravimetric Analysis

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed to examine the thermal characteristics and thermal stability. While for the polymers PSBMesFc and PSBMes₂ no glass transition temperature could be detected upto 250 °C, the polymer, PSBTipFc shows a relatively high glass transition temperatures (T_g) of 132 °C, compared to that of polystyrene ($T_g = 110\text{ °C}^{149}$), which may indicate that the polymer structure is more rigid due to the presence of the bulky tri-isopropylphenyl groups. Also possibly incomplete substitution on the boron center during the attachment of the bulky Mes or Tip groups may have lead to the formation of chemical crosslinks which give rise to crosslinked high molecular weight polymers. The TGA data demonstrate the high thermal stability of the polymers with no apparent decomposition upto ca. 275 °C for the polymers, PSBMesFc and PSBMes₂, while the polymer PSBTipFc is thermally stable upto 298 °C (Figure 2.17) which is higher in comparison to the bithiophene and carbazole (~250 °C) containing polymers, discussed in chapter 2A, indicating higher thermal stability of PSBTipFc and that the presence of the bulky triisopropylphenyl group enhances its thermal stability. Above this temperature multi-step decomposition processes were observed. The residual weights of the ferrocene polymers PSBMesFc and PSBTipFc at 800 °C were 22% and 15%, respectively, while the polymer with two mesityl groups, PSBMes₂, showed a slightly lower residual weight of 11%.

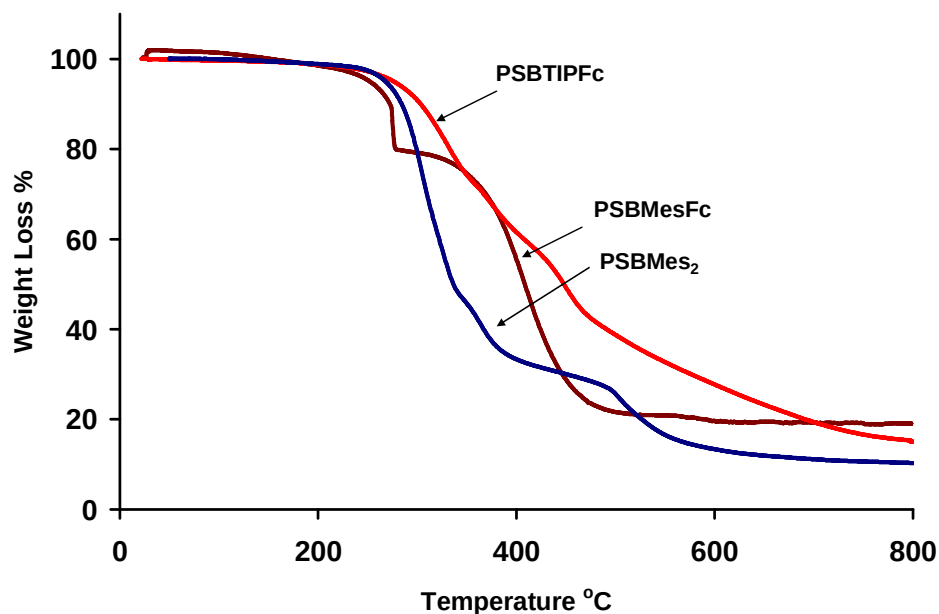


Figure 2.17 TGA Plots of the Polymers PSBMesFc, PSBTIPFc and PSBMes₂.

2.8.2.4 Comparison of Oxidative Stabilities of PSBMesFc, PSBTIPFc and PSBMes₂

To investigate their oxidative stability the polymers were exposed to air and moisture in wet CDCl₃ and C₆D₆. They were also kept under air as solids for a period of 1 month. Their degradation was monitored by ¹H NMR spectroscopy. In CDCl₃ as the solvent the polymer PSBMesFc was perfectly stable for upto 9 days and PSBTIPFc for ca. 21 days; in C₆D₆ PSBMesFc was found to be stable for 21 days, while PSBTIPFc was stable for about 1 month. No substantial degradation was observed for the polymers in the solid state for over 20 days for PSBMesFc and the polymer PSBTIPFc remained stable for over 1 month. As expected the polymer and model compound with two mesityl groups were stable for more than 6 months in solution as well as the solid state. This indicates that the stability of the boron center is dependent mainly on the steric effect of the substituents and that it increases

from the presence of one mesityl to one 2,4,6-triisopropylphenyl to two mesityl groups. A similar trend was observed for the model compounds MBMesFc, MBTipFc and MBMes₂.

2.8.2.5 Determination of the X-ray Structure of MBTipFc

The steric protection of the boron center by the isopropyl groups in ortho-position of the Tip substituent is evident from an X-ray structure determination that was performed on dark red single crystals of MBTipFc obtained from hexanes at $-20\text{ }^{\circ}\text{C}$. Two independent molecules are found in the unit cell; the geometric parameters of which are similar to one another and hence only one of them is displayed in Figure 2.18. The molecular structure of MBTipFc shows clearly that the isopropyl groups are positioned in close proximity to the empty p orbital on boron, thereby preventing attack of nucleophiles at the boron center. The boron atom is only slightly bent out of the Cp plane with $\text{Cp}(\text{centroid})\text{-C1-B1} = 177.60^{\circ}$ and 176.65° , respectively, for the two independent molecules. This is in contrast to the strong tilting of the electron deficient organoborane moiety toward the electron-rich Fe center typically observed for ferrocenylboranes,¹⁵⁰ and thus indicates that steric strain prevents more pronounced interaction with the Fe d orbitals. Steric effects are also reflected in the B-C bond lengths; the B-C bonds to the bulky Tip group of 1.587(3) and 1.583(3) Å are significantly longer than those to the t-butylphenyl group (1.562(3) and 1.566(3) Å). The B-C(Cp) bond lengths of 1.542(3) Å are comparatively shorter, but in a similar range as for other ferrocenylborane species (e.g. $\text{FcB}(\text{C}_6\text{F}_5)_2$, 1.501(4) Å;¹⁵¹ $\text{FcB}(\text{Mes})_2$, 1.546(7) Å).¹⁵²

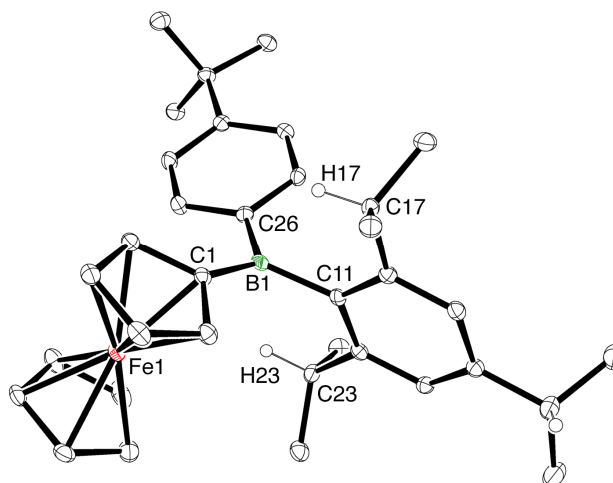
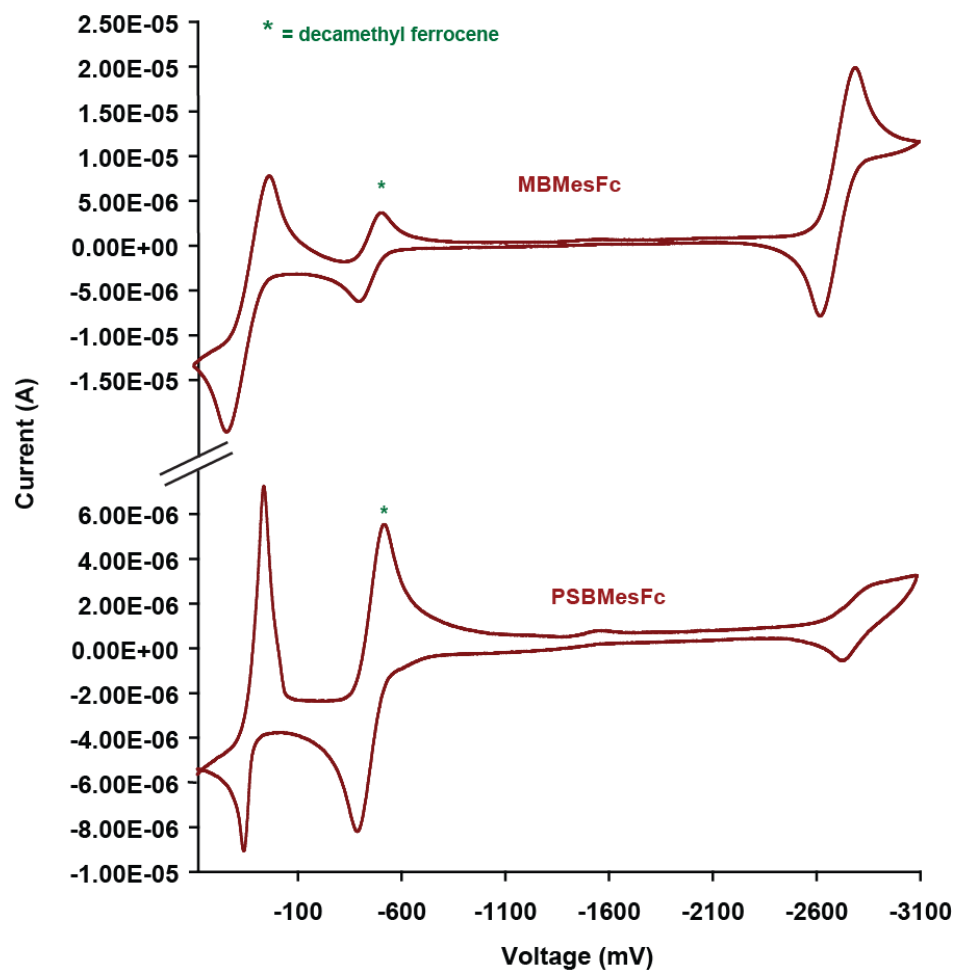


Figure 2.18 Molecular Structure of MBTipFc (ORTEP, 50% probability). All Hydrogens Except for Those on the CHMe₂ Groups are Omitted for Clarity. Selected Bond Lengths (Å): B1-C1 = 1.5416(3), B1-C11 = 1.5866(3), B1-C26 = 1.5620(3).

2.8.2.6 Examination of the Electronic Structure by UV-visible and Cyclic Voltammetry Studies

The electronic structure was examined by UV-visible spectroscopy in CH₂Cl₂. The dimesitylborane containing polymer and model compounds show bands at 323 nm and 309 nm, respectively. In case of the ferrocene containing polymer and model compounds, in addition to the band at ~ 367 nm, we observe a band at 485 nm which is characteristic of a d-d transition of the ferrocene moiety.^{153, 154}

(a)



(b)

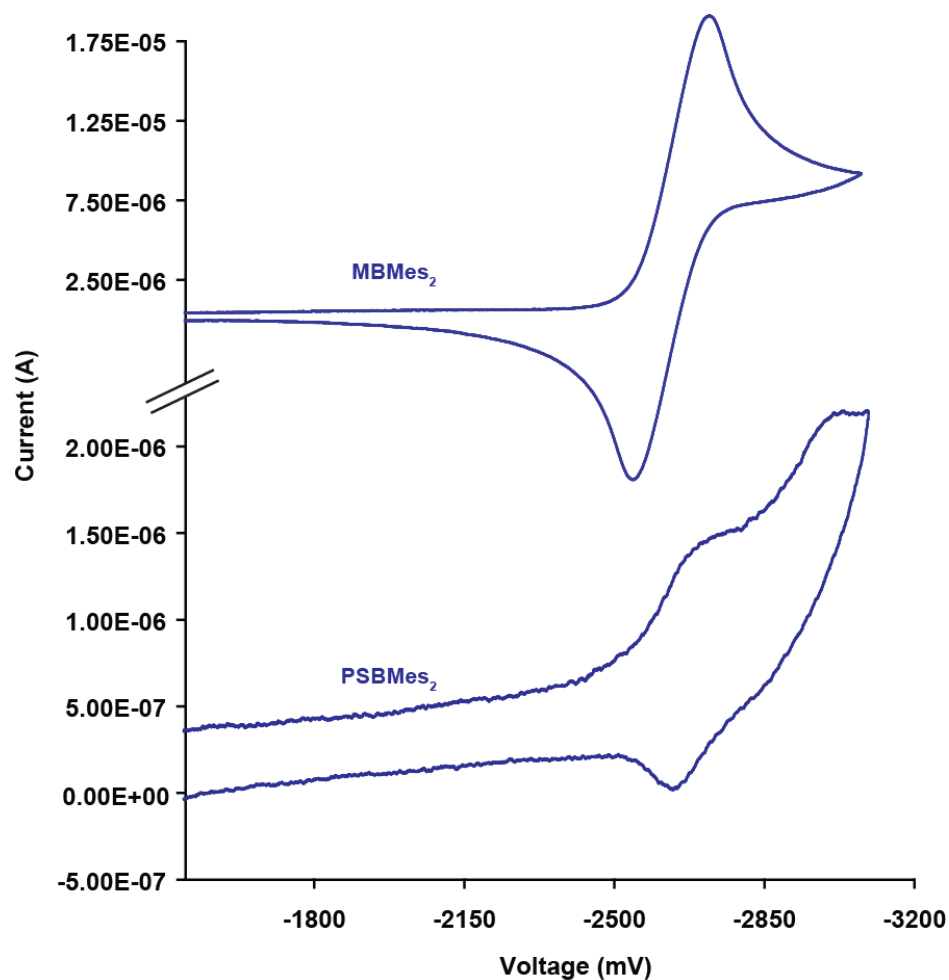


Figure 2.19 Cyclic Voltammograms of (a) MBMesFc and PSBMesFc (1.2×10^{-3} M); (b) MBMes₂ and PSBMes₂ (1.2×10^{-3} M) with 0.1M [Bu₄N]PF₆ in THF as the Supporting Electrolyte for Cathodic Scans (Scan Rate 100 mV/s).

Cyclic voltammetry studies were carried out in THF (cathodic scans) and CH₂Cl₂ (anodic scans) using [Bu₄N]PF₆ as the electrolyte (Figure 2.19). The polymers PSBMesFc and PSBTipFc exhibit a redox process at 131 mV and 129 mV, respectively, which originates from the ferrocene oxidation. The redox potentials are similar to those determined for the

respective molecular species MBMesFc ($E_{1/2} = 133$ mV) and MBTipFc ($E_{1/2} = 118$ mV). However, the shape of the redox waves for the polymers show signs of deposition of the oxidized polymeric material on the electrode. An additional redox process is observed in THF at $E_{1/2} = -2.83$ V for PSBMesFc and at $E_{1/2} = -2.81$ V for PSBTipFc, respectively, which is attributed to the reduction of the organoborane moieties. Again, similar redox potentials were recorded for the molecular model systems (MBMesFc, $E_{1/2} = -2.76$ V; MBTipFc, $E_{1/2} = -2.73$ V). For the polymer, PSBMes₂, a boron redox event at -2.72 V is observed which occur at a similar potential to the one observed for the corresponding model compound (MBMes₂, $E_{1/2} = -2.64$ V).

Table 2.7 Comparison of UV-visible and Cyclic Voltammetry Data.

	Absorption ^a		Boron Redox ^b		Ferrocene Redox ^c	
	$\lambda_{\max}$	Lg ϵ	$E_{1/2}$ (V)	ΔE_p (mV)	$E_{1/2}$ (V)	ΔE_p (mV)
PSBMesFc	294/368/484	4.3/3.4/3.1	-2.83	217	0.131	65
PSBTipFc	295/367/485	4.2/3.3/3.1	-2.81	51	0.129	76
MBMesFc	292/367/484	4.4/3.5/3.2	-2.76	257	0.133	117
MBTipFc	293/368/486	4.2/3.3/3.0	-2.73	150	0.118	133
PSBMes₂	261/323	4.5/4.2	-2.72	171	---	---
MBMes₂	267/309	4.1/4.1	-2.64	177	---	---

^a Data were acquired in CH₂Cl₂ at RT; ^b in THF / 0.1 M [Bu₄N]PF₆; ^c in CH₂Cl₂ / 0.1 M [Bu₄N]PF₆.

2.8.2.7 Applications as Chemosensors

Tricoordinate organoboranes are well-known to be able to form complexes with Lewis basic substrates, a property that has been widely exploited for chemosensor applications.

Notable in the case of ferrocenylboranes is the work by Aldridge and others on their use for the colorimetric and electrochemical detection of fluoride.¹⁵⁵ Binding studies performed on PSBMesFc and the respective model compound indicate that the boron centers do not significantly bind to pyridine as evident from a lack of a significant change in the ^{11}B NMR shift upon addition of a large excess of pyridine (>10 equiv). In contrast, $[\text{Bu}_4\text{N}]\text{F}$ binds to the boron centers easily as indicated by a significant upfield shift in the ^{11}B NMR to ca. 4 ppm (Figure 2.20). The selectivity for fluoride over pyridine is attributed to the steric bulk provided by the mesityl group. A similar result is obtained for PSBTipFc and the model MBTipFc.

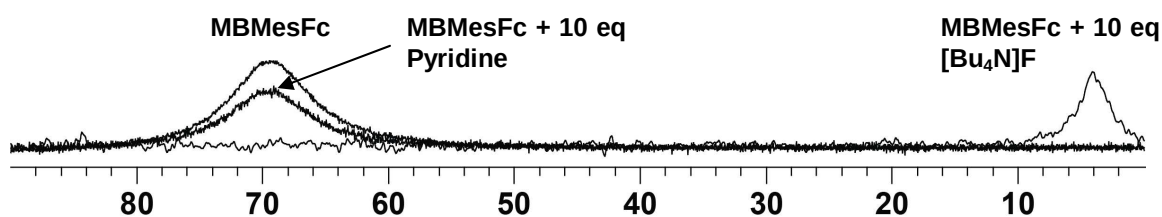
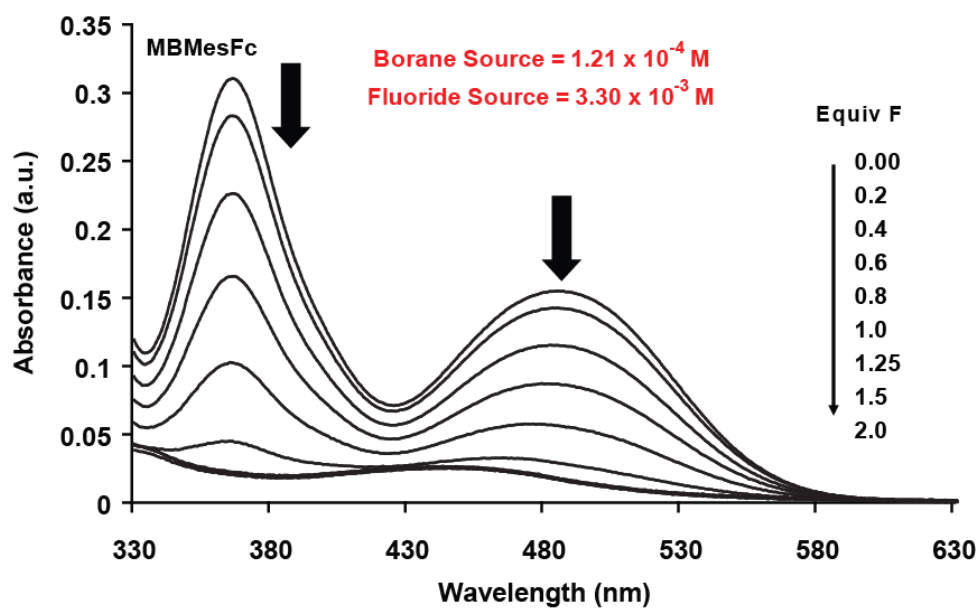


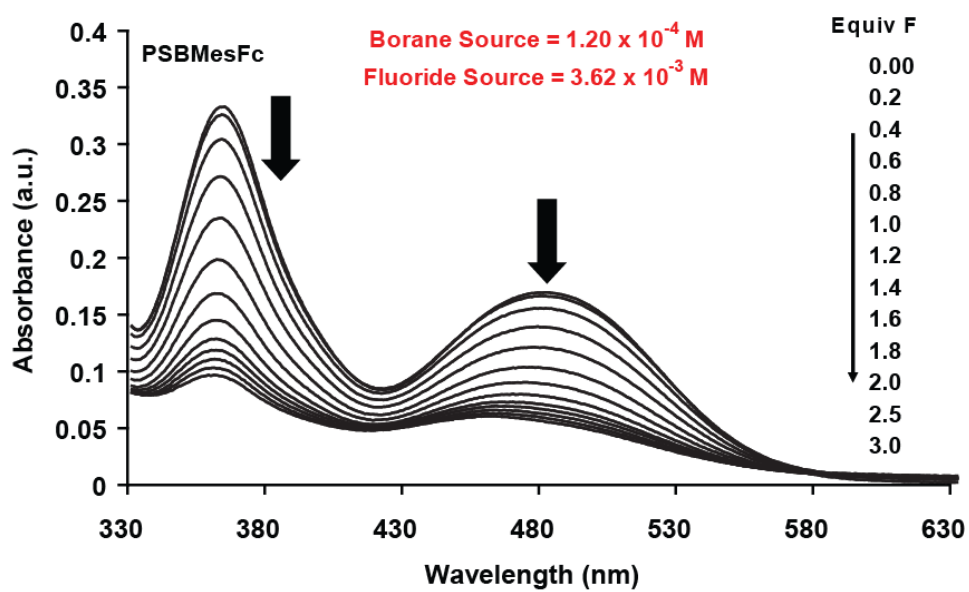
Figure 2.20 ^{11}B NMR Overlay of MBMesFc; MBMesFc After Addition of 10 eq Pyridine and MBMesFc After Addition of 10 eq $[\text{Bu}_4\text{N}]\text{F}$ as the Fluoride Source [Data Obtained at 5×10^{-3} M in CDCl_3 at RT].

UV-visible titrations were performed to determine the fluoride binding constants for the polymers (Figure 2.21). Noteworthy is that the binding constants determined for the polymers PSBMesFc ($2.9 \times 10^4 \text{ M}^{-1}$) and PSBTipFc ($2.7 \times 10^4 \text{ M}^{-1}$) are similar, but both are considerably smaller than for those of the model compounds, indicating a distinct polymer effect on the binding strength. Also from the binding constants determined for the model compounds, it can be inferred that binding of the fluoride to the model compound MBMesFc ($4.7 \times 10^6 \text{ M}^{-1}$) is much stronger than that for MBTipFc ($3.4 \times 10^6 \text{ M}^{-1}$).

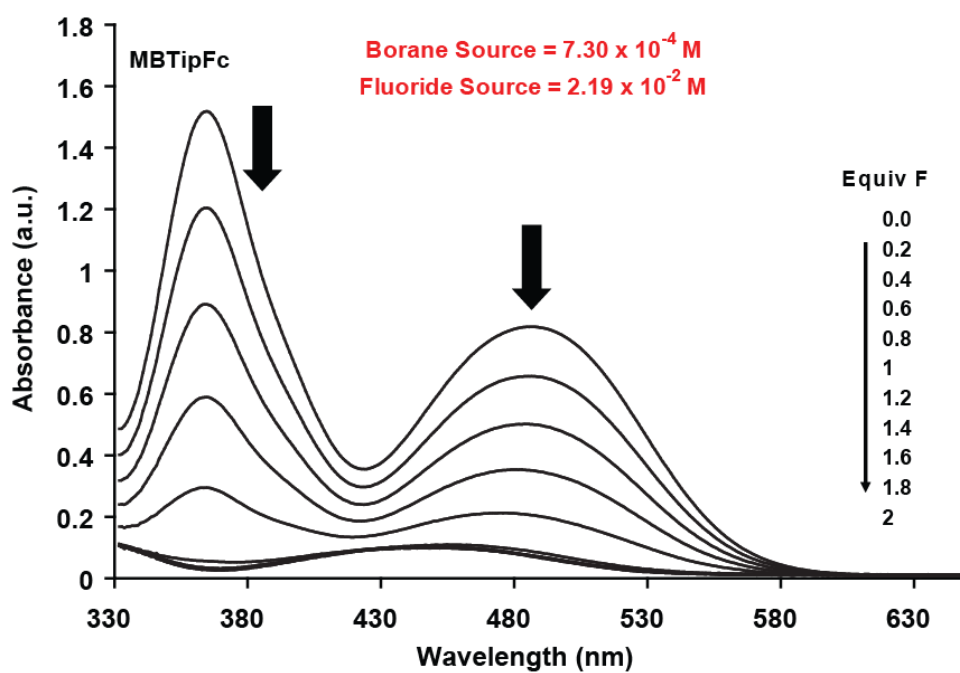
(a)



(b)



(c)



(d)

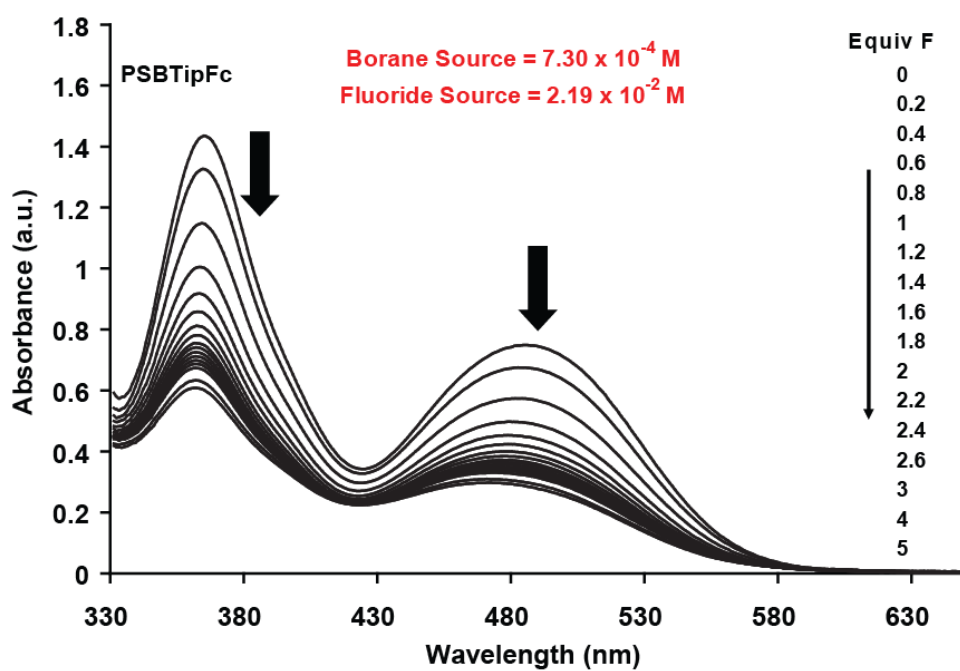


Figure 2.21 Spectral Titration of (a) MBMesFc; (b) PSBMesFc; (c) MBTipFc; and (d) PSBTipFc with Aliquots of $[\text{Bu}_4\text{N}]\text{F}$ in THF.

2.9 Conclusions

We have shown that organotin and organocopper reagents serve as convenient aryl-transfer reagents in the preparation of novel fluorescent triarylborane polymers and model systems. The photophysical characteristics, environmental stability, and the Lewis acidity of the boron centers can be fine-tuned through varying the substituents on the boron. Anion binding studies indicate that the presence of Lewis acidic boron moieties can be exploited for sensing of nucleophiles based on changes in the absorption and emission properties. Enhancement in the sensitivity for the polymer PSBMesHBT in comparison to its corresponding model MBMesHBT suggest that highly functionalized polyolefins may be an interesting alternative to conjugated polymers as efficient sensor materials. Though no enhancement in sensitivity is observed for the polymer PSBMesNBT, change in the emission from green to blue upon complexation shows that it may be employed as a wavelength ratiometric probe for fluoride and cyanide. The stability of the models and polymers can be enhanced by the attachment of more sterically demanding tri-isopropylphenyl groups in addition to more stable chromophores like substituted fluorenes and substituted carbazoles.

Also we have prepared three electroactive borylated polystyrene derivatives, two of which that bear an electron rich ferrocene moiety on boron with a mesityl or a triisopropylphenyl group for steric protection and one of which is a metal free boron containing polymer with two mesityl groups. According to cyclic voltammetry studies both ferrocene containing polymers undergo oxidation at a potential close to that of ferrocene itself, while reduction of the boron centers occurs at highly negative potentials of ca. -2.8 V relative to the ferrocene/ferrocenium couple and the polymer PSBMes₂ shows a similar boron reduction (-2.7 V) to the ferrocene containing polymers. The polymer with the bulkier triisopropylphenyl

group is relatively more stable than that with a mesityl group attached to boron, whereas fluoride complexation studies suggest that the polymers bind fluoride much more weakly than their corresponding model compounds and that the mesityl-substituted ferrocenylborane model binds fluoride much more strongly when compared to the triisopropylphenyl-substituted ferrocenylborane derivative. Further enhancement of the anion binding ability can be expected upon oxidation of the ferrocene sites in the polymer.¹⁵⁵

Chapter 3. Synthesis of a Vinyl Aromatic Monomer and its Polymerization

3.1 Conjugated Fluorene and Thiophene Polymers

Electrically-conducting polymers are of great interest for their applications as materials in electronic devices. For this purpose π -conjugated linear polymers like polyacetylene, poly(p-phenylenevinylene), polythiophenes, polyfluorenes, polycarbazoles, polyanilines etc. have been studied extensively, since high electrical conductivities can be achieved by doping these types of polymers (Chapter 1, Section 1.1 and 1.2). Particularly such materials find applications as emissive materials or charge transport materials in OLED devices, as linear and non-linear optical materials; and also electrochromic materials.

For example, Reynolds and Witker recently reported a series of electrochromic polymers consisting of carbazole, thiophene, bithiophene and also benzothiadiazole moieties which undergo changes in color upon oxidation depending on the electronic nature of the arylene unit paired with carbazole moiety (112).¹⁵⁶ These polymers may be of potential use as electrochromic materials. Also Ding and co-workers recently reported alternating and random fluorene-carbazole copolymers (113) which show blue emission in solution as well as films. Incorporation of the alternating polymer as a hole transport material into a device that employed Alq₃ as an electron conducting material led to good performance, which indicates that the polymers may be promising candidates as hole transporting materials for OLED devices.¹⁵⁷ Iraqi et al. have realized 2,7-linked carbazole polymers that show

solvatochromism i.e. they show blue (114) and blue-green emission (115) in toluene and the emission is red-shifted in polar solvents like CH_2Cl_2 and THF. Ionization potentials of ~ 5.0 eV indicate that the polymers may be of interest as hole conduction materials in electronic devices.¹⁵⁹ Cao and co-workers have synthesized and employed copolymers of fluorene and 4,7-di-2-thienyl-2,1,3-benzothiadiazole (**DBT**) as red emitters in OLED devices (116).¹⁶⁰

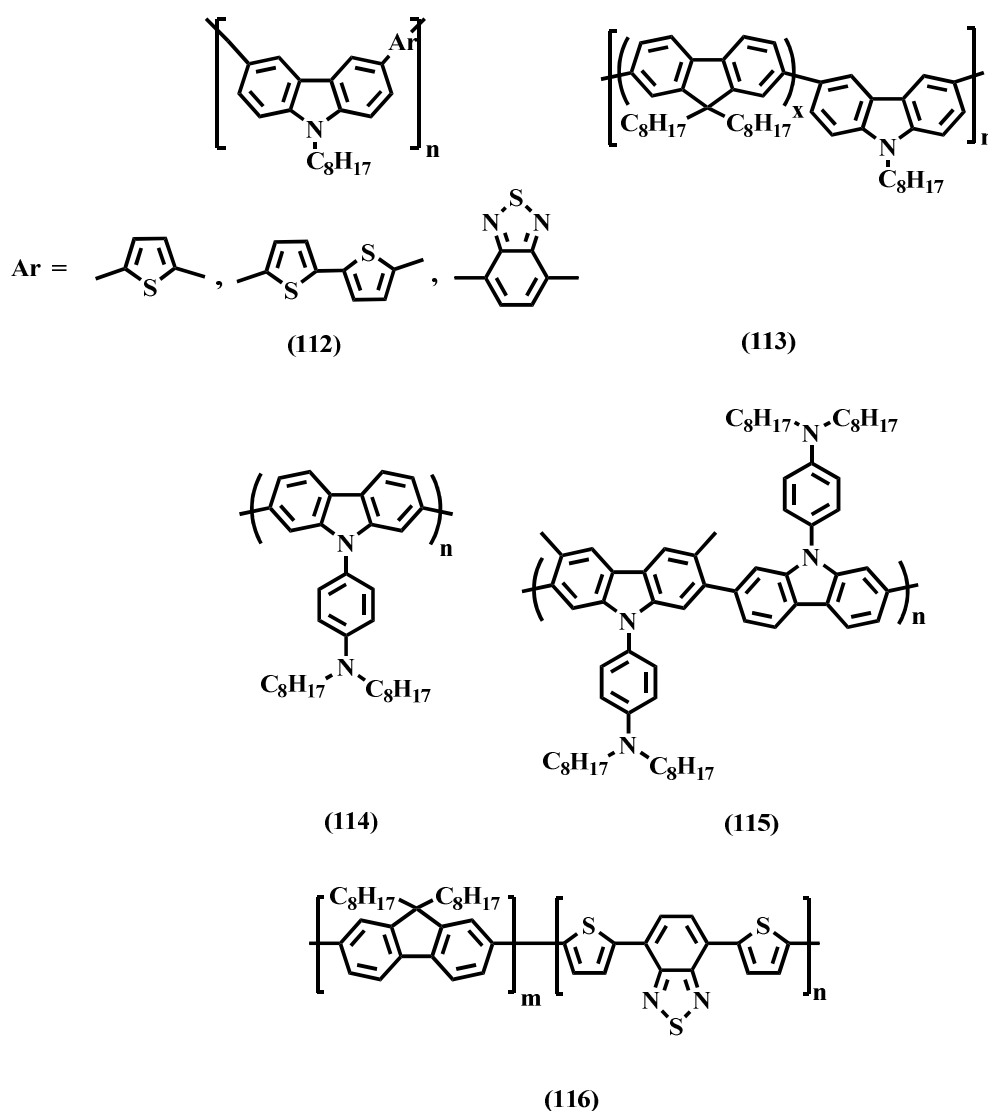


Chart 3.1 Examples of Main-chain Fluorene and Carbazole Based Conjugated Polymers.

Polythiophenes are another important class of conjugated polymers. In addition to the above mentioned applications, PT's and their derivatives have also been employed in field-effect transistors, solar cells, batteries and as luminescent sensors.

Recently Swager and co-workers reported a single-walled carbon nanotube/t-butylcalix[4]arene-substituted (SWCNT/calixerene) polythiophene (117) based resistance sensor which can sense minor structural differences in the analyte at a fast response rate. These SWCNT/polymer composites are promising candidates for selective chemical monitoring based on host-guest chemistry.¹⁶¹ Krebs et al. have very recently developed dithienylthienopyrazine polymers that contain thermocleavable ester functionalities for solar-cell applications (118). The solar-cell devices that incorporate the polymers with secondary and tertiary esters show good stability to oxygen during operation. The removal of water from these devices imparts stability to the device which exceeds hundreds of hours.¹⁶² Marder et al. have reported the development of all polymer solar-cells based on the blend of a perylene based polymer-acceptor (119) and a PT based polymer-donor (120). Both polymers show good solution processabilities. Short-circuit and power conversion efficiency (**PCE**) values obtained for the devices employing these polymers indicate that they may be promising donor-acceptor materials, respectively, for all polymer solar-cells.¹⁶³

Bolognesi et al. have developed devices that employ poly(3-pentylmethoxythiophene) (121) in combination with Alq₃. The devices show enhanced electroluminescence efficiencies in presence of the polyalkoxythiophene and also exhibit field-dependent tunable emission.¹⁶⁴ Andersson et al. have synthesized PT's with sterically demanding groups (122-123) in the side-chain. They were able to fine-tune the emission of the polymer films between blue and near-IR depending on the structure of the PT as well as by varying the side chain functionality.^{165, 166}

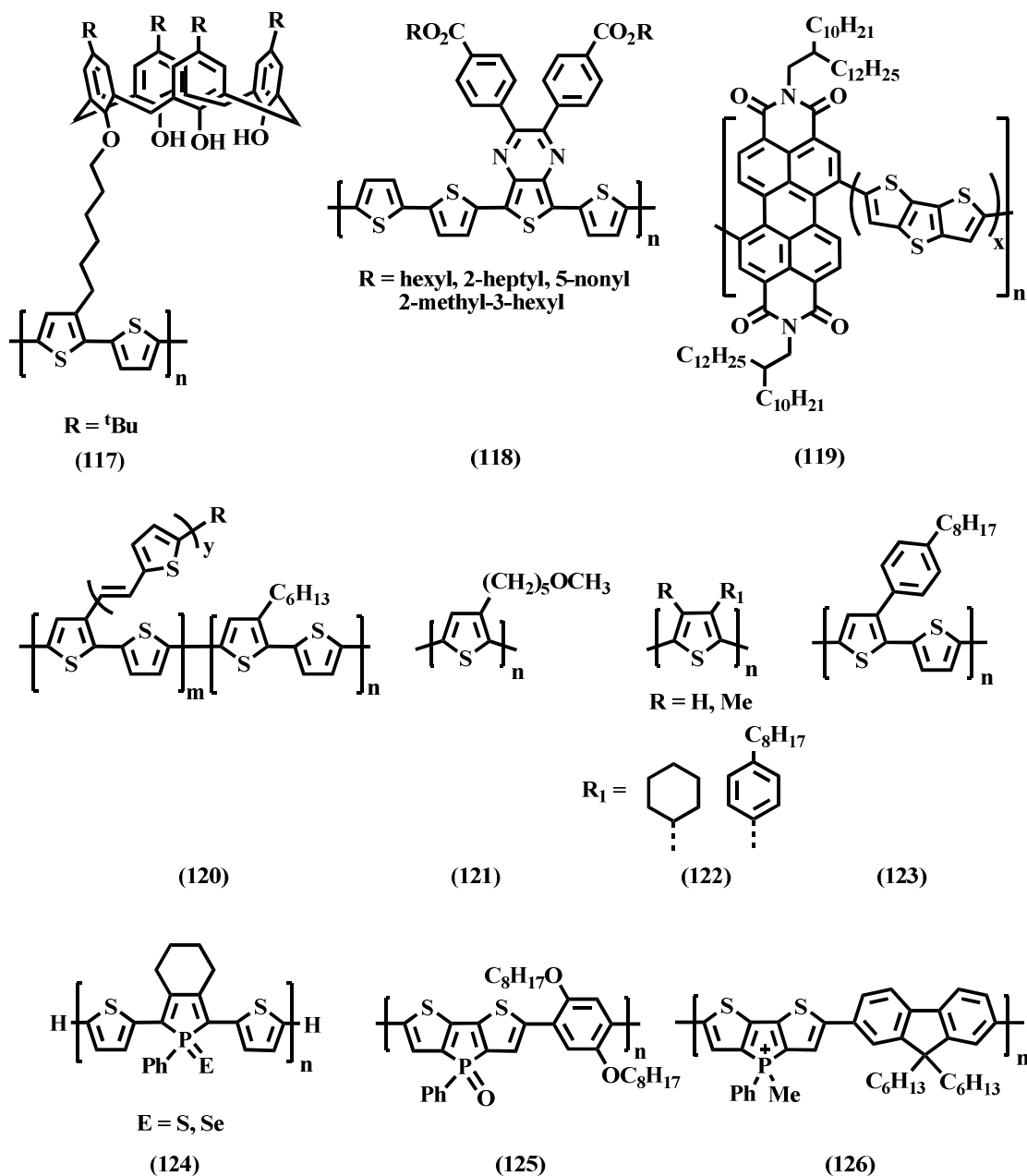


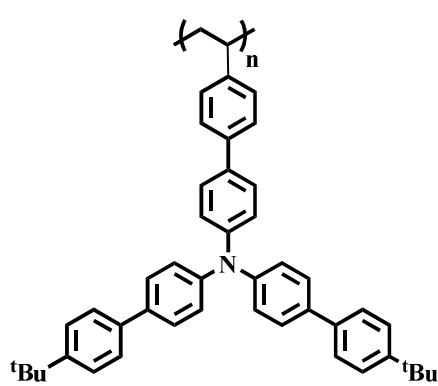
Chart 3.2 Examples of Main-chain Polymers of Thiophene and its Derivatives for Optoelectronic Applications.

Baumgartner and co-workers have synthesized a series of phosphole containing oligo- and polythiophene (124) based materials that may find applications as emissive materials in

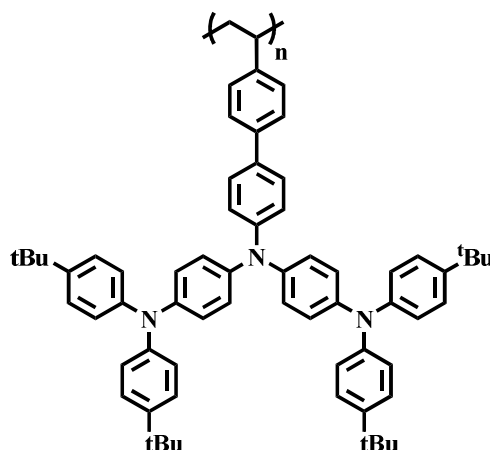
OLED devices. They have also developed polymers and co-polymers based on fused thienophospholes (125-126) that show interesting photophysical properties and may find applications as optoelectronic materials.¹⁶⁷

3.2 Non-conjugated Vinyl Polymers

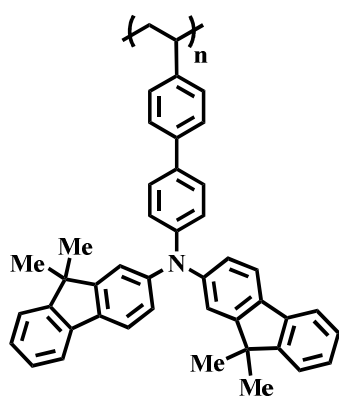
While conjugated polymers have been exploited as materials for electronics and optoelectronics, comparatively fewer reports exist on non-conjugated vinyl polymers bearing pendant π -conjugated groups, for such applications. The polymers that have a pendant organic π -system are expected to show characteristics like chemical stability, solubility in common organic solvents, solution processability, thin-film forming capabilities and also the possibility of incorporating a variety of pendant groups depending on the functionality desired. Such polymers have found applications as electrically conducting polymers; photoactive materials for photovoltaic devices, as photochemical resists, photo or electrochromic materials and also as materials for electroluminescent devices. A few examples of non-conjugated polymers that bear side-chain functionalities are shown in Chapter 1 (Section 1.3) and Chapter 2 (Section 2.3). In this section polymers that bear an extended π -electron system in the side chain will be discussed. For example Shirota and co-workers have successfully synthesized a series of vinyl polymers that bear arylamine functionalities in the side-chain (127-129). The polymers show high thermal stabilities, form uniform thin films from solutions and have been employed as hole-transport materials in OLED devices. They have also synthesized a benzothiadiazole containing polymer (130) that emits orange light with a quantum efficiency of 65%.¹⁶⁸



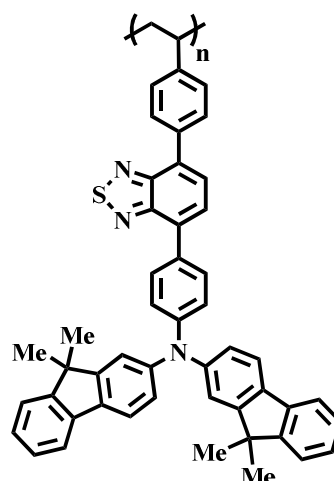
(127)



(128)



(129)



(130)

Chart 3.3 Examples of Vinyl Polymers Bearing Pendent Triarylamine Moieties as Hole-transport and Emitting Materials.

3.3 Non-conjugated Vinyl Polymers with Oligothiophene Pendant Groups

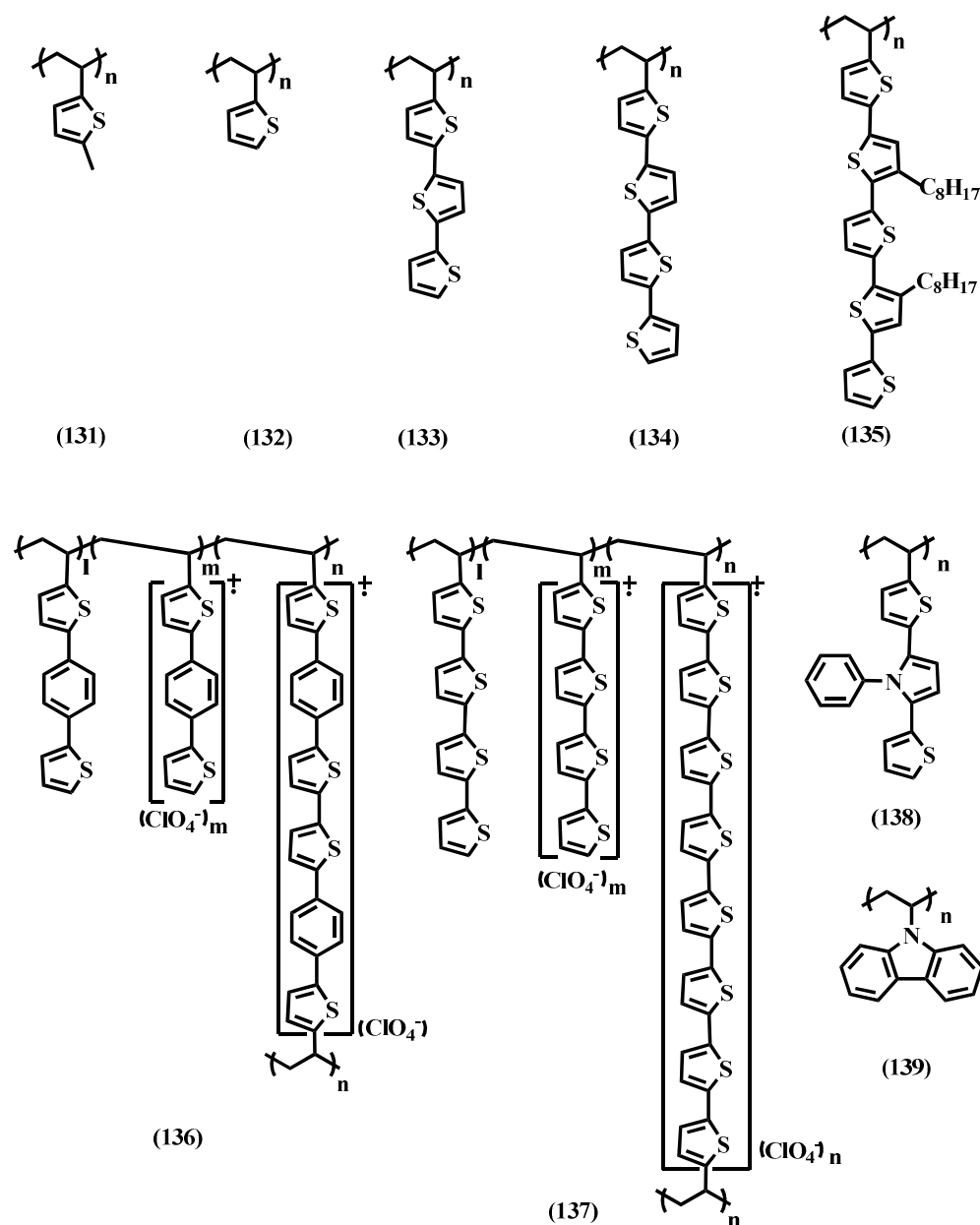
As seen in Section 3.1, polythiophenes constitute an important class of conjugated polymers. Oligomers of thiophene tend to form aggregates. It is known that the self-assembly of these compounds does not involve hydrogen-bonding type interactions, but rather many weak and directional interactions like van der Waals and π -stacking interactions, which

dictate the charge transport and emission properties of these types of compounds.¹⁶¹ To get a better handle on the properties of such compounds an alternative approach would be to attach the thiophene units through vinylic bonds. It can be expected that upon connection by a polyvinyl chain the through-space interaction of the thiophene units would be very different from when they are connected in series in the polymer chain. This could then give rise to new and interesting properties.

3.3.1 Synthesis and Applications of Vinyl Polymers Containing Pendant Thiophene Groups.

Polyvinylthiophene (131) was prepared by Trumbo in 1994 by free radical polymerization of the corresponding vinyl monomer and Fernandez et al. prepared polyvinylthiophene (132) by electrochemical polymerization.¹⁶⁹ Fernandez reported that electrochemical polymerization of vinylthiophene led to a considerable amount of cross-linking, which in part is due to the fact that the free α -position on the thiophene unit is very reactive and prone to oxidative coupling. Since then there has been considerable interest in the incorporation of thiophenes, bithiophenes and oligothiophenes into the side-chain of vinylic polymers as these polymers are expected to possess unique properties that are characteristic of both conjugated polymers and polyolefins. For example Shirota et al. have reported the synthesis of poly[2-[4-(2-thienyl)phenyl]-5-vinylthiophene] (136) by anodic polymerization of the vinyl group. The electrochemically-doped polymer showed a reversible color change from purple to colorless upon de-doping, indicating that the polymer may be an interesting material for electrochromic applications.¹⁶¹ They have also reported a series of poly(vinyloligothiophene)s (133-135, 137) that show electrical conductivity and can be obtained as deeply colored, smooth lustrous films. Their ability to reversibly change color upon de-doping and doping

may allow them to be used as electrochromic materials.¹⁷⁰ Ferraris et al. have reported various ratios of blends of poly(*N*-phenyl-2-(2'-thienyl)-5-(5'-vinyl-2''-thienyl)pyrrole) (138) with poly(*N*-vinylcarbazole) (139), which led to a variety of colors and could be of potential use for electrochromic materials.¹⁷¹



Recently Barbarella and co-workers have synthesized endcapped poly(α -vinyl- ω -alkyloligothiophene)'s (140-144) via free radical polymerization or oxidative polymerization to obtain polymers that show interesting photophysical properties. The fluorescence properties of the polymers can be tuned by changing the conjugation length of the pendants as well as their substituents. The polymers emit white light in thin films and hence may be potential candidates for OLED devices.¹⁷²

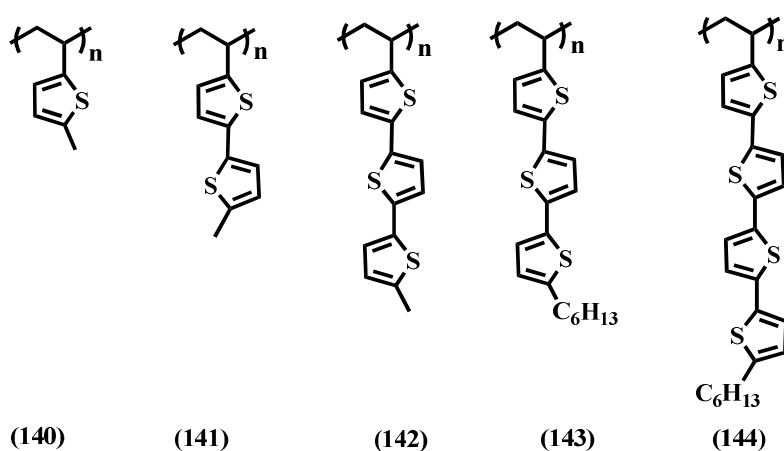


Chart 3.5 Examples of Vinyl Polymers Bearing Pendant Oligothiophenes for OLED Devices.

3.4 Synthesis of 5-Vinyl-5'-trimethylsilyl-2,2'-bithiophene Monomer.

Previously we have shown that polymerization of a silylated styrene monomer allows us to modify the polymer synthesized via post-polymerization modification techniques. Specifically, incorporation of Lewis acidic boron centers into the polystyrene side-chain followed by replacement of the bromines on the boron with a variety of aryl groups gives rise to interesting photophysical as well as electronic properties. Closer inspection of the molecular orbitals that involve charge transfer in the case of the styrene polymers PSBMesHBT and PSBMesNBT indicate a significant contribution from the phenyl ring of

the styrene backbone (See Chapter 2A, Section 2.6). Thus, attachment of an extended organic π -system to the backbone could give rise to some very interesting properties. Hence, we chose to synthesize a functionalized monomer with bithiophene as the extended π -system.

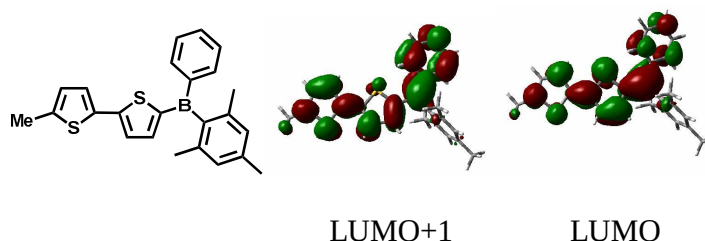
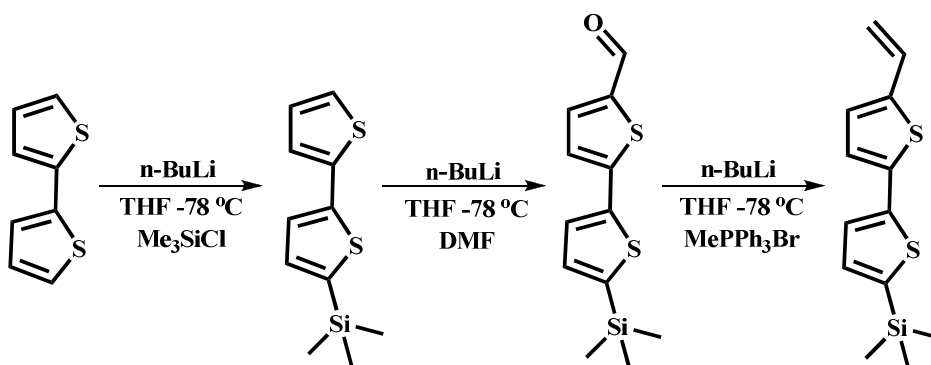


Figure 3.1. Orbital Plots for the Model System for PSBMesHBT.



Scheme 3.1 Synthesis of Vinylbithiophene Monomer.

The monomer was synthesized via multi step organic synthesis according to literature known procedure. The silylated bithiophene was subjected to subsequent Vilsmeier formylation^{169, 170} followed by Wittig olefination to obtain the desired monomer as a bright yellow low melting solid in 90% yield upon column chromatography using hexanes as the eluent (Scheme 3.1).

3.5 Polymerization of 5-Vinyl-5'-trimethylsilyl-2,2'-bithiophene.

In the past polymerization of vinylthiophene has been performed with the use of free radical initiators, electrochemical or oxidative polymerization, and in some cases by cationic polymerization. For example, Shirota and co-workers synthesized polymers (134) and (135)

by carrying out controlled-potential anodic oxidation at different potentials vs Ag/Ag^+ to obtain a smooth, dark colored film on the working electrode. Polymers (136) and (137) were also prepared in a similar fashion.¹⁷¹ The major disadvantage of using electrochemical polymerization is that there is no control over the molecular weight of the polymer obtained and in most cases the polymers tend to be insoluble in organic solvents, thus making their characterization by routine methods quite difficult.

On the other hand the polymer (138) was obtained by cationic polymerization of the corresponding monomer at low temperature using $\text{BF}_3\cdot\text{etherate}$ as the initiator in CH_2Cl_2 as the solvent. The polymer obtained was purified by repeated precipitation from THF into hexanes. Although its solubility in common organic solvents was good and a low PDI of 1.19 was obtained, the polymer showed a low molecular weight of $M_n = 2867 \text{ Da}$.^{173, 174}

The polymers (140) and (141) were obtained by free radical polymerization using benzoylperoxide (BPO) as the radical initiator.¹⁶³ The polymers (143) and (144) were synthesized by spontaneous oxidation in air at room temperature in the absence of any solvents. The polymer (142) was obtained by free radical polymerization using 2,2'-azobis(isobutyronitrile) (AIBN) as the initiator and degassed toluene as the solvent.¹⁶³ Polymer (144) was also synthesized via free radical polymerization using AIBN and toluene.¹⁶³ The characterization results for the polymers (140) – (144) are summarized in Table 3.1. The results indicate that the polymers obtained typically have low molecular weights with PDI's ranging from 1.2 to 2.2.

Table 3.1 Molecular Weight Data for Polymers 140-144 Obtained from GPC.

Polymer	Method of Polymerization	M_w	M_n	PDI
(140)	Free Radical ^a	4700	2800	1.7
(141)	Free Radical ^a	3800	1700	2.2
(142)	Spontaneous Oxidation	760	670	1.2
(143)	Free Radical ^b	5100	2800	1.8
(144)	Free Radical ^b	Insoluble, no data	Insoluble, no data	Insoluble, no data
(144)	Spontaneous Oxidation	1500	1000	1.5

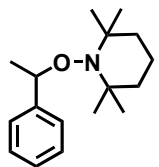
^a BPO used as the initiator; ^b AIBN as the initiator.

Since there were no polymerization methods in the literature that give polymers with high molecular weights and narrow polydispersities, a variety of methods were tried for the polymerization of the silylated bithiophene monomer to find a suitable method. The results are summarized in Table 3.2. The best results in terms of high molecular weights and narrow polydispersities were obtained in the case of nitroxide mediated polymerization (NMP) techniques when 2,2,6,6-tetramethylpiperidin-N-oxide (TEMPO) (Table 3.2, Entry 2a) or its phenyl capped derivative 2,2,6,6-tetramethyl-1-(1-phenylethoxy)piperidine (PhEtTEMPO) (Table 3.2, Entries 3b and 3c) were used as initiators. In case of the parent TEMPO, the reaction flask was charged with the monomer and initiator (no solvent was used, the reaction was carried out in bulk), then degassed several times using freeze-pump-thaw cycles (the solidified reaction mixture was allowed to come to room temperature, melted using a 35 °C water bath, between subsequent freeze-thaw cycles) before being immersed into an oil-bath which was pre-heated to 130 °C. The reaction was allowed to stir at that temperature for

24 h, before being immersed instantaneously into an ice-water bath. Upon immersion in the ice-water bath an increase in the viscosity of the reaction mixture was observed. The polymer was isolated by diluting the reaction with THF and precipitation into methanol. The polymer was further purified by subsequent reprecipitations from THF into methanol. When PhEtTEMPO was used as the initiator, toluene and anisole were employed as solvents. The solution remained homogenous throughout the reaction and no change in the viscosity of the mixture was observed. The reaction was stopped after 4 h by immersing the flask into an ice-water bath, at which point an increase in the viscosity of the reaction mixture was observed. Dilution with 0.5 mL of the solvent, followed by precipitation into methanol yielded the polymer in ~40% yield.

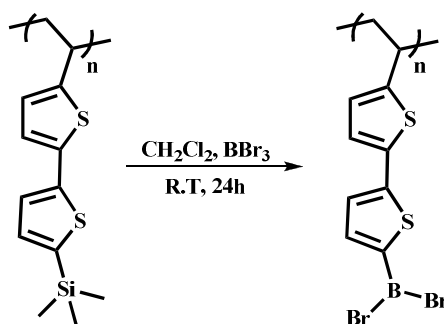
The molecular weights obtained by GPC can only be considered to be indicative of the actual weights if the hydrodynamic radius of the polymer is similar to that of the standards used (in this case polystyrene standards were used for GPC measurements). The weights obtained from GPC-RI in case of the silylated bithiophene polymer should be expected to be approximately half of the actual molecular weights. Results from GPC-LS ($M_n = 10290$; $M_w = 18660$) run on the silylated bithiophene polymer, synthesized via anionic polymerization, indicate that its molecular weight is indeed almost twice as much obtained from GPC-RI ($M_n = 4338$; $M_w = 8296$). Therefore, the polymers obtained actually have decent molecular weights and also narrow polydispersities compared to literature reports for similar polymers.

Table 3.2 Summary of Results for Polymerization of the Silylated Bithiophene Monomer.

	Polymerization	Reaction	Monomer : Initiator	M_n^*	M_w^*	PDI [*]	DP (M_n)	Yield (%)
	Method	Conditions						
1	ATRP ^a	Tol, 20h, 120 °C	100 (1:1) : 1	1345	3895	2.89	5.1	45
2a	NMP ^b	Bulk, 24h, 130 °C	50 : 1	8244	12614	1.53	31.2	64
2b		Bulk, 24h, 130 °C	100 : 1	6230	11314	1.81	23.6	62
3a	NMP ^c	Bulk, 4h, 120 °C	100 : 1	3360	7935	2.36	12.7	60
3b		Toluene, 4h, 120 °C	96 : 1	3432	4677	1.36	12.9	40
3c		Anisole, 4h, 120 °C	95 : 1	3631	4980	1.37	13.7	43
								
4a	Radical ^d	Bulk, 24h, 65 °C	100 : 1	2152	9168	4.26	8.1	54
4b	Radical ^e	Bulk, 16h, 90 °C	99 : 1	1261	5015	3.97	4.8	49
5	Anionic	THF, n-BuLi, -78 °C	13 : 1	4338	8296	1.91	16.4	57

^a Random co-polymerization with styrene; ^b TEMPO as the initiator; ^c PhEtTEMPO as the initiator; ^d AIBN as the initiator; ^e BPO as the initiator; * Data obtained from GPC-RI.

The trimethylsilylbithiophene polymer can now undergo post-polymerization modification by replacement of the trimethylsilyl functionalities with Lewis acidic boron centers via a reaction similar to the one used for silylated polystyrene. The silylbithiophene polymer obtained via anionic polymerization was subjected to reaction with BBr_3 at ambient temperature using CH_2Cl_2 as the solvent. An immediate color change from light yellow to green was observed upon addition of BBr_3 . The reaction mixture was allowed to stir for about 24 h and the dibromoboryl substituted polymer was characterized by ^1H and ^{11}B NMR spectroscopy.



Scheme 3.2 Borylation of Trimethylsilyl Functionalized Poly(vinylbithiophene).

A noticeable downfield shift in the ^1H NMR spectrum generally indicates the presence of an electron deficient group. The replacement of the trimethylsilyl functionality can easily be confirmed by ^1H NMR spectroscopy, where, we observe the disappearance of the slightly broad signal at 0.3 ppm (trimethylsilyl functional group) and the appearance of a sharp signal at 0.8 ppm (trimethylsilylbromide byproduct). Also the appearance of a broad peak at 50 ppm in the ^{11}B NMR confirms the presence of the boron moiety.

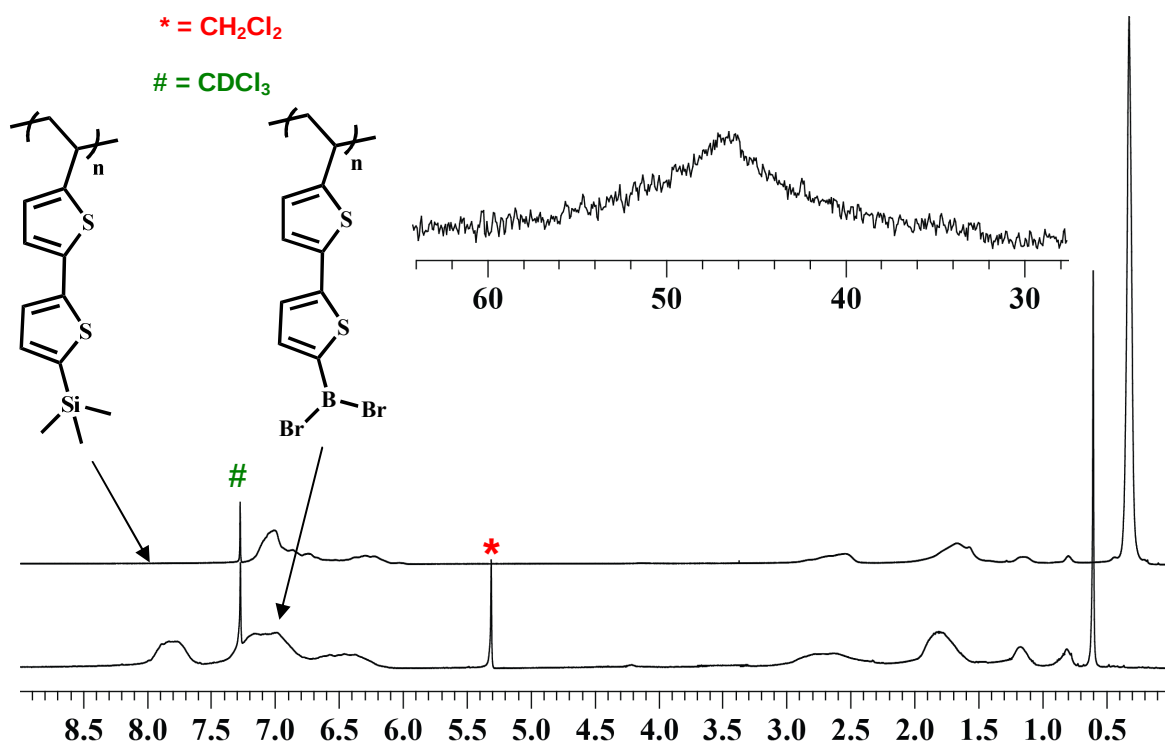


Figure 3.2 ^1H NMR Comparison of Silylated and Borylated Poly(vinylbithiophene) (Reaction Mixture). [Inset ^{11}B NMR of Borylated Poly(vinylbithiophene)].

3.6 Conclusion

We have synthesized a trimethylsilyl functionalized vinylbithiophene monomer which can be polymerized by a variety of polymerization techniques. From Table 3.2 (Entry 2a) it is apparent that of all the polymerization techniques, nitroxide mediated polymerization is the most suitable technique for the polymerization of this monomer. The results from GPC-RI indicate that the polymer shows moderate molecular weight and also narrow polydispersity. The silylbithiophene polymer can then undergo post-polymerization modification to replace the silyl functionality with Lewis acidic boron centers upon reaction with boron tribromide. We may then be able to replace the bromine centers with various aryl groups. Future work may involve further optimization of the polymerization of the monomer and also

transmetallation to boron centers. The resulting modified triarylborane polymers are expected to show interesting photophysical properties.

Experimental Section

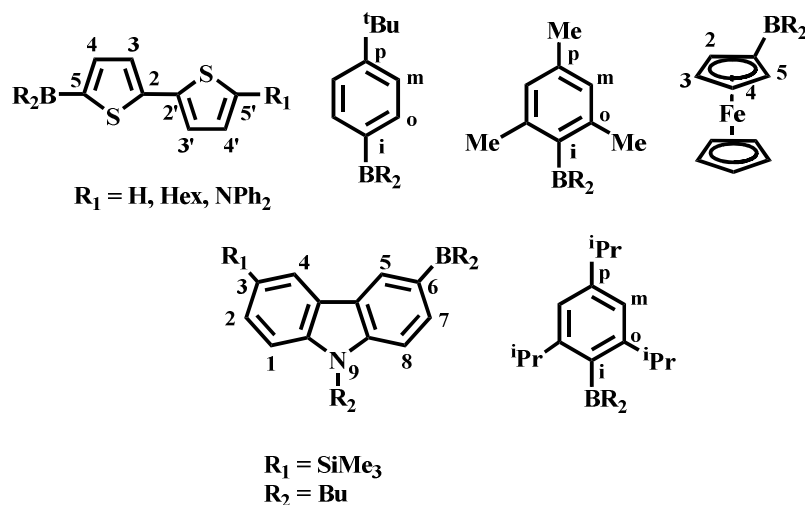
Materials and Methods

2-Bromothiophene, 1-bromohexane, 2-bromomesitylene, 1,3,5-triisopropylbenzene, fluorene, carbazole, *n*-BuLi (1.6M in hexanes), [Bu₄N]Cl, [Bu₄N]Br, and [Bu₄N]CN, Mg (turnings, 99.9%), Me₃SiCl (98%), BBr₃ (99.9%), CuBr (98%), 1-bromo-1-phenylethane (97%), anisole (99%), were purchased from Acros. The compounds Me₃SiOMe (98%) and *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA; 99%), BBr₃ (99+%), [Bu₄N]NO₃, and [Bu₄N]F (1M in THF) from Aldrich, and trimethyltin chloride (98%) from Strem Chemicals. BBr₃ was further purified by vacuum distillation. **Caution!** *BBr₃ is toxic and highly corrosive and should be handled appropriately with great care.* Fluorinated grease was used for ground glass joints in all reactions involving boron tribromide. The compounds 5-hexyl-2,2'-bithiophene, 2-trimethylstannylferrocene¹⁷⁵, mesitylmagnesium bromide¹⁷⁶, 2,4,6-triisopropylphenylmagnesium bromide^{135, 177}, mesitylcopper¹⁷⁸, 2,4,6-triisopropylphenylcopper¹⁷⁹, 3,6-dibromo-N-butylcarbazole¹⁸⁰ and 5'-(trimethylsilyl)-2,2'-bithiophene-5-carbaldehyde¹³¹ were synthesized according to literature procedures. 5-trimethylstannyl-2,2'-bithiophene and 5-hexyl-5'-trimethylstannyl-2,2'-bithiophene were obtained by adaptation of a literature procedure for the synthesis of 5-hexyl-5'-tributylstannyl-2,2'-bithiophene. Poly(4-trimethylsilylstyrene) (**PSSi**) of $M_n = 26,450$; $M_w = 29,200$; $PDI = 1.10$ and $M_n = 21,100$; $M_w = 23,800$; $PDI = 1.13$ (GPC-RI) were prepared as previously reported.^{130, 131} All reactions were carried out under inert atmosphere using Schlenk techniques or a glove box (Innovative Technologies). Ether solvents were distilled

from Na/benzophenone prior to use. Hydrocarbon and chlorinated solvents were purified using a solvent purification system (Innovative Technologies; alumina/copper columns for hydrocarbon solvents), and the chlorinated solvents were subsequently distilled from CaH₂ and degassed via several freeze-pump-thaw cycles.

Instrumentation.

All 499.893 MHz ¹H, 125.7 MHz ¹³C, 160.4 MHz ¹¹B NMR, 99.25 MHz ²⁹Si and 186.4 MHz ¹¹⁹Sn NMR spectra were recorded on a Varian INOVA spectrometer equipped with a boron-free 5 mm dual broadband gradient probe (Nalorac, Varian Inc., Martinez, CA). Solution ¹H and ¹³C NMR spectra were referenced internally to solvent signals. ¹¹B NMR spectra were referenced externally to BF₃ · Et₂O (δ = 0), ¹¹⁹Sn NMR spectra were referenced to SnMe₄ in C₆D₆ (δ = 0) and ²⁹Si NMR spectra were referenced to SiMe₄ in C₆D₆ (δ = 0). ¹¹B NMR spectra were acquired with boron-free quartz NMR tubes. All NMR spectra were recorded at ambient temperature unless noted otherwise. The abbreviations Th (2-thienyl), BT (2,2'-bithiophene), HBT (5-hexyl-2,2'- bithiophene), Ph (phenyl), Hex (*n*-hexyl), Cz (carbazolyl), Me (Methyl), Bu (Butyl), ^tBuPh (tert-butyl phenyl), Fc (ferrocenyl), Mes (mesityl / 2,4,6-triphenylmethyl) and Tip (2,4,6-triisopropylphenyl) are used for the peak assignments and the labeling scheme shown here was applied.



Solution UV-visible measurements were performed in CH_2Cl_2 using a Varian Cary 500 scan UV-Vis-NIR spectrophotometer with a 1 cm quartz cuvette. The fluorescence data were measured on a Varian Cary Eclipse Fluorescence spectrophotometer with the same solutions as those used in the UV-visible measurements. Anthracene was used as the standard for determination of the quantum yields (ϕ). The quantum yield of anthracene was adopted from the *Handbook of Photochemistry*¹⁸¹, and the concentration of anthracene in CH_2Cl_2 was 6.62×10^{-6} M. An SCS | G3P-8 Spin Coat System from Specialty Coating Systems Inc. was used to spin cast thin films from toluene on 1 cm x 1 cm glass slides from Fisher Scientific at 3000 rpm.

For the titration experiments sample solutions and $[\text{Bu}_4\text{N}]\text{F}$ solutions in THF were prepared using a microbalance (± 0.1 mg), microliter syringes, and volumetric glassware. The experiments were performed by successive addition of aliquots of a $[\text{Bu}_4\text{N}]\text{F}$ solution in THF. Binding constants were determined with the program HyperquadTM.

Gel permeation chromatography (GPC) analyses on polymers PSBMesBT, PSBMesHBT and PSBMesNBT were performed in THF with 0.1% $[\text{Bu}_4\text{N}]\text{Br}$ (1 mL/min) using a Waters

Breeze system equipped with a 717plus autosampler, a 1525 binary HPLC pump, a 2487 dual λ absorbance detector, and a 2414 refractive index detector. A series of styragel columns (Polymer Laboratories; 5 μm Mix-D, 5 μm Mix-C, and 10 μm Mix-B), which were kept in a column heater at 35 $^{\circ}\text{C}$, were used for separation. GPC analyses on all other polymers were performed in THF (1 mL/min) using a Waters Empower system equipped with a 717plus autosampler, a 1525 binary HPLC pump, a 2998 Photo Diode Detector, and a 2414 refractive index detector. A series of styragel columns (Polymer Laboratories; two 5 μm Mix-C columns in series), which were kept in a column heater at 35 $^{\circ}\text{C}$, were used for separation. The columns in all cases were calibrated with PS standards (Polymer Laboratories).

Differential scanning calorimetry (DSC) measurements were performed on a Perkin Elmer Differential Scanning Calorimeter Pyris 1 system with ca. 3-10 mg of polymer using the specified scan rate. Thermogravimetric analyses (TGA) were performed under N_2 atmosphere using a Perkin Elmer Pyris 1 system with ca. 5 mg of polymer at a heating rate of 20 $^{\circ}\text{C}/\text{min}$ from 50 $^{\circ}\text{C}$ to 800 $^{\circ}\text{C}$.

X-ray diffraction intensities were collected on a Bruker SMART APEX CCD diffractometer at $T = 100(2)$ K using $\text{CuK}\alpha$ (1.54178 $\text{\AA}$) radiations. Numerical absorption correction was applied, the structures were solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full matrix least squares procedures on F^2 . All non-hydrogen atoms were refined with anisotropic displacement coefficients. The H atoms were placed at calculated positions and were refined as riding atoms. All software and source scattering factors are contained in the SHELXTL program package.¹⁸²

GC-MS spectra were acquired on a Hewlett Packard HP 6890 Series GC system equipped with a series 5973 mass selective detector and a series 7683 injector. A temperature profile

with a heating rate of 20 °C/min from 50 °C to 300 °C was used. Mass spectral data in +FAB mode with NPOE (2-nitrophenyl octyl ether) as matrix were obtained at the Michigan State University Mass Spectrometry Facility, which is supported, in part, by a grant (DRR-00480) from the Biotechnology Research Technology Program, National Center for Research Resources, National Institutes of Health. Elemental analyses were obtained from Quantitative Technologies Inc. Whitehouse, NJ.

MALDI-TOF data were obtained at the Biological Mass Spectrometry Facility located at Piscataway, NJ on an ABI-MDS SCIEX 4800 MALDI-TOF-TOF instrument. Data was acquired in positive or negative mode as specified. Benzo[a]pyrene and dihydrobenzoic acid were used as the matrices as specified.

DFT calculations have been performed with the Gaussian03 program. Geometries and electronic properties are calculated by means of hybrid density functional B3LYP with the basis set of 6-31G(d). The input files and orbital representations were generated with Gaussview (scaling radii of 75%, isovalue of 0.02). Excitation data were calculated using TD-DFT (B3LYP).

Cyclic voltammetry was carried out on a CV-50W analyzer from BAS. The three-electrode system consisted of an Au disk as working electrode, a Pt wire as secondary electrode and a Ag wire as the reference electrode. The voltammograms were recorded with ca. 10^{-3} to 10^{-4} M solution in THF (reduction waves) or CH_2Cl_2 (oxidation waves) containing $[\text{Bu}_4\text{N}]\text{PF}_6$ (0.1 M) as the supporting electrolyte. The scans were referenced after the addition of a small amount of decamethylferrocene (reduction cycles and oxidation cycles) as internal standard. The potentials are reported relative to the ferrocene/ferrocenium couple (-548 mV in CH_2Cl_2 and -452 mV in THF).

Synthesis and Data for Chapter 2A (Bithiophene Pendant Groups)

A.) Organoboron Polymers

Synthesis of PSBMesBT: A solution of BBr_3 (0.60 g, 2.39 mmol) in CH_2Cl_2 (15 mL) was added dropwise to a solution of **PSSi** (0.35 g, ca. 1.98 mmol of Me_3Si groups) in CH_2Cl_2 (15 mL) and stirred for 14 h. A solution of 2-trimethylstannyl-5,5'-bithiophene (0.85 g, 2.58 mmol) in CH_2Cl_2 (15 mL) was added dropwise at ambient temperature. The reaction mixture turned light yellow and eventually yellow-greenish. The mixture was allowed to stir for 12 h at room temperature. All volatile components were then removed under high vacuum. The solid was taken up in toluene (30 mL), and a solution of $\text{MesCu}\cdot(\text{C}_7\text{H}_8)_{0.2}$ (0.53 g, 2.64 mmol) in toluene (15 mL) was added dropwise. Formation of a purple precipitate occurred. The reaction mixture was allowed to react for 1 h at ambient temperature and then refluxed for 24 h. Filtration through celite gave a pale yellow solution that shows blue luminescence. The solution was concentrated to ca. 3 mL and precipitated into hexanes (350 mL). The product was purified by repeated precipitation from toluene into hexanes. The precipitate was dried at 50 °C under high vacuum to obtain a fine light yellow powder (0.410 g, 37%).

PSBMesBT: ^{11}B NMR (160.386 MHz, CDCl_3): δ = 50 ppm ($w_{1/2}$ = 2900 Hz); ^1H NMR (499.893 MHz, CDCl_3): δ = 7.8-7.3 (br m, 4H, Ph_o and Th-H3,4), 7.1-6.9 (br m, 2H, Ph_m), 6.9-6.7 (br m, 1H, Th-H3'), 6.7-6.5 (br m, 4H, Th- H4',5' and Mes_m), 2.2 (br, 3H, p -Me), 1.8 (br, 6H, o -Me), the backbone protons are overlapping; ^{13}C NMR (125.69 MHz, CDCl_3): δ = 149.9, 143.9, 143.7, 142.6, 139.1, 138.8 (br), 138.5, 137.3, 136.9, 128.1, 127.2 (br), 125.9, 125.2 (aromatic C), 42-40 (polymer backbone), 22.7 (o -Me), 21.4 (p -Me); GPC-RI (THF vs. PS standards): M_n = 26,550, M_w = 40,174, PDI = 1.51; UV-Vis (CH_2Cl_2 , 3.2×10^{-5} M): λ_{max} = 262 nm (ϵ = 21,992), 368 nm (ϵ = 34,559); fluorescence (CH_2Cl_2 , 3.2×10^{-5} M): $\lambda_{\text{em,max}}$ =

442 (sh), 463 nm, $\Phi = 0.66$ ($\lambda_{\text{exc}} = 368$ nm); UV-Vis (thin film): $\lambda_{\text{max}} = 292$ nm, 373 nm; fluorescence (thin film): $\lambda_{\text{em,max}} = 468, 489$ (sh) nm ($\lambda_{\text{exc}} = 373$ nm); DSC (onset, 20 °C/min; second heating curve): $T_g = 165$ °C; TGA (20 °C/min; N₂): 51% weight loss between 248 °C and 339 °C; 15% weight loss between 381 °C and 417 °C; 9% residual mass at 800 °C; elemental analysis: calculated C 75.37, H 5.82; found C 75.50, H 6.07.

Synthesis of PSBMesHBT: A solution of BBr₃ (0.88 g, 3.51 mmol) in CH₂Cl₂ (15 mL) was added dropwise to **PSSi** (0.50 g, ca. 2.84 mmol of Me₃Si groups) in CH₂Cl₂ (15 mL) and stirred for 16 h. A solution of 5-trimethylstannyl-5'-hexyl-2,2'-bithiophene (1.70 g, 4.11 mmol) in CH₂Cl₂ (15 mL) was added dropwise at ambient temperature. The reaction mixture turned yellow and was allowed to stir for 12 h at room temperature. All volatile components were then removed under high vacuum. The yellow residue was taken up in toluene (30 mL), and MesCu•(C₇H₈)_{0.2} (0.79 g, 3.93 mmol) in toluene (15 mL) was added dropwise, leading to formation of a purple precipitate. The mixture was allowed to react for 3 h and then refluxed for 72 h. Filtration through celite gave a yellow solution, which was concentrated to ca. 3 mL and precipitated into cold hexanes (350 mL). The product was purified by repeated precipitation from toluene into hexanes and dried at 50 °C under high vacuum to give a fine yellow powder (0.84 g, 61%). ¹¹B NMR (160.386 MHz, CDCl₃): $\delta = 50$ ppm ($w_{1/2} = 2000$ Hz); ¹H NMR (499.893 MHz, CDCl₃): $\delta = 7.8$ -7.3 (br m, 4H, Ph_o and Th-H3,4), 7.1-6.9 (br m, 3H, Ph_m and Th-H3'), 6.7-6.1 (br m, 3H, Th-H4' and Mes_m), 2.7 (br m, 2H, Hex), 2.2 (br, 3H, *p*-Me), 1.8 (br, 6H, *o*-Me), 1.62 (br m, 2H, Hex), 1.3 (br m, 6H, Hex), 0.88 (br m, 3H, Hex), the backbone protons are overlapping; ¹³C NMR (125.69 MHz, CDCl₃): $\delta = 150.4, 147.0, 143.4, 142.8$ (br), 138.8 (br), 138.1, 137.0, 136.9, 134.8, 127.1, 125.2 (aromatic C), 42-40 (polymer backbone), 31.8, 31.7, 30.4, 29.0, 22.8, 14.3 (Hex), 22.8 (*o*-Me), 21.4 (*p*-

Me); GPC-RI (THF vs. PS standards): $M_n = 45,275$, $M_w = 54,574$, $PDI = 1.15$; UV-Vis (CH_2Cl_2 , 3.2×10^{-5} M): $\lambda_{\text{max}} = 275$ nm ($\epsilon = 18,220$), 380 nm ($\epsilon = 21,990$); fluorescence (CH_2Cl_2 , 3.2×10^{-5} M): $\lambda_{\text{em,max}} = 455$ nm, $\Phi = 0.67$ ($\lambda_{\text{exc}} = 380$ nm); UV-Vis (thin film): $\lambda_{\text{max}} = 301$ nm, 381 nm; fluorescence (thin film): $\lambda_{\text{em,max}} = 467$ nm ($\lambda_{\text{exc}} = 381$ nm); DSC (onset, 20 °C/min; second heating curve): $T_g = 139$ °C; TGA (20 °C/min; N_2): 39% weight loss between 242 °C and 358 °C and 19% between 417 and 456 °C; 12% residual mass at 800 °C; elemental analysis: calculated C 77.16, H 7.31; found C 75.92, H 7.08.

Synthesis of PSBMesNBT: A solution of BBr_3 (ca. 0.44 g, 1.76 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a solution of **PSSi** (0.255 g, ca. 1.45 mmol of Me_3Si groups) in CH_2Cl_2 (10 mL), and the mixture was stirred for 16 h. A solution of 5-trimethylstannyl-5'-diphenylamino-2,2'-bithiophene (0.93 g, 1.87 mmol) in CH_2Cl_2 (15 mL) was added dropwise at RT. The mixture turned dark red and was then allowed to stir for another 12 h. All volatile components were removed under high vacuum. The resulting dark red solid was taken up in toluene (20 mL), and a solution of $\text{MesCu} \cdot (\text{C}_7\text{H}_8)_{0.2}$ (0.39 g, 1.94 mmol) in toluene (10 mL) was added dropwise. Formation of a purple precipitate occurred. The reaction mixture was stirred for 1 h and then refluxed for 72 h. Filtration through celite gave an orange-red solution, which was concentrated to ca. 3 mL and precipitated into cold hexanes (350 mL). The product was purified by repeated precipitation from toluene into cold ether (350 mL). The solid was dried at 50 °C under high vacuum to obtain a fine yellow powder (0.49 g, 60%). For **PSBMesNBT**: ^{11}B NMR (160.386 MHz, CDCl_3): $\delta = 47$ ppm ($w_{1/2} = 2000$ Hz); ^1H NMR (499.893 MHz, CDCl_3): $\delta = 7.37, 7.16, 7.09, 6.97, 6.7\text{--}6.5, 6.5\text{--}6.3$ (aromatic H), 2.2 (br, 3H, *p*-Me), 1.8 (br, 6H, *o*-Me), the backbone protons are overlapping; ^{13}C NMR (125.69 MHz, CDCl_3): $\delta = 152.5, 150.2$ (br), 147.6, 143.3 (br), 142.7 (br), 138.1 (br), 136.9

(br), 129.5, 127.1 (br), 124.8 (br), 124.3 (br), 123.7, 123.3, 120.3 (aromatic C), 42-40 (polymer backbone), 22.8 (*o*-Me), 21.5 (*p*-Me); GPC-RI (THF vs. PS standards): M_n = 46,016, M_w = 60,412, PDI = 1.31; UV-Vis (CH_2Cl_2 , 3.2×10^{-5} M): λ_{max} = 301 nm (ϵ = 27,176), 433 nm (ϵ = 33,930); fluorescence (CH_2Cl_2 , 3.2×10^{-5} M): $\lambda_{\text{em,max}}$ = 537 nm, Φ = 0.35 (λ_{exc} = 433 nm); UV-Vis (thin film): λ_{max} = 440 nm; fluorescence (thin film): $\lambda_{\text{em,max}}$ = 536 nm (λ_{exc} = 440 nm); DSC (onset, 20 °C/min; second heating curve): T_g = 165 °C; TGA (20 °C/min; N_2): 60% weight loss between 275 °C and 337 °C; 13% weight loss between 397 °C and 436 °C; 8% residual mass at 800 °C; elemental analysis: calculated C 78.51, H 5.70, N 2.48; found C 76.91, H 5.66, N 2.10.

B.) Precursors and Model Compounds

Synthesis of 5-Trimethylstannyl-2,2'-bithiophene: A solution of $^n\text{BuLi}$ (113 mL, 1.6M in hexanes, 181 mmol) was added dropwise over a period of 90 min to a solution of 2,2'-bithiophene (25 g, 150 mmol) in THF (450 mL) at -78 °C. The mixture was stirred for 25 min and then allowed to slowly warm up to 0 °C. After cooling the reaction mixture back down to -78 °C, a solution of trimethyltin chloride (36.0 g, 181 mmol) in THF (100 mL) was added dropwise. The mixture was stirred at -78 °C for 3 h and then for an additional 12 h at ambient temperature. Quenching with aqueous NH_4Cl solution and extraction of the organic layer with ether gave a brown oily material upon evaporation of the solvents. Distillation at 105 °C under high vacuum (10^{-2} torr) gave the product as a colorless liquid (34.3 g, 69%). ^1H NMR (499.893 MHz, CDCl_3): δ = 7.36 (d, 3J = 3.5 Hz, 1H, Th-H3), 7.25 (m, 2H, Th-H3,3'), 7.17 (d, 3J = 3.5 Hz, 1H, Th-H4), 7.06 (d/pst, 3J = 23/29.5 Hz, 1H, Th-4'), 0.47 (s/d, $^3J(^{117/119}\text{Sn},\text{H})$ = 55.5/57.5 Hz, 9H, SnMe_3); ^{13}C NMR (125.69 MHz, CDCl_3): δ = 143.0 (Th), 137.7 (s/d, $^3J(^{117/119}\text{Sn},^{13}\text{C})$ = 5 Hz, Th), 137.4 (Th), 136.0 (s/d, $^4J(^{117/119}\text{Sn},^{13}\text{C})$ = 28 Hz, Th),

127.9, 125.2 (s/d, $^2J(^{117/119}\text{Sn}, ^{13}\text{C}) = 40 \text{ Hz}$), 124.2, 123.7 (Th), -8.0 (s/d, $^2J(^{117/119}\text{Sn}, ^{13}\text{C}) = 356/373 \text{ Hz}$, SnMe_3); ^{119}Sn NMR (186.413 MHz, CDCl_3): $\delta = -25.2 \text{ ppm}$; GC-MS ($t=12.7 \text{ min}$): m/z (%): 330 [M^+] (32), 315 [$\text{M}^+ - \text{CH}_3$] (100).

Synthesis of 5-Trimethylstannyl-5'-hexyl-2,2'-bithiophene: A solution of $^n\text{BuLi}$ (15.3 mL, 1.6M in hexanes, 24.5 mmol) was added dropwise over a period of 30 min to a solution of 2-hexyl-5,5'-bithiophene (5.10 g, 20.4 mmol) in THF (150 mL). The reaction mixture was stirred at 0°C for two hours and cooled down to -78°C . The solution was stirred for 12 h. All volatile components were removed under high vacuum, and the residue was taken up in toluene (15 mL). A solution of trimethyltin chloride (5.20 g, 26.1 mmol) in THF was then added slowly. The mixture was first stirred at -78°C for 3 h and then for an additional 12 h at ambient temperature. Quenching with aqueous NH_4Cl solution and extraction of the organic layer with ether gave a black oily material upon evaporation of the solvents. Distillation at 140°C under high vacuum (10^{-2} torr) gave the product as a colorless liquid (5.10 g, 60%). ^1H NMR (499.893 MHz, CDCl_3): $\delta = 7.21$ (d/dd, $^3J = 3.5 \text{ Hz}$, $^4J(^{117/119}\text{Sn}, \text{H}) = 5.0 \text{ Hz}$, 1H, Th-H3), 7.07 (d/dd, $^3J = 3.5 \text{ Hz}$, $^3J(^{117/119}\text{Sn}, \text{H}) = 23/29.5 \text{ Hz}$, 1H, Th-H4), 6.98 (d, $^3J = 3.5 \text{ Hz}$, 1H, Th-H3'), 6.68 (d, $^3J = 3.5 \text{ Hz}$, 1H, Th-H4'), 2.79 (t, $^3J = 7.0 \text{ Hz}$, 2H, Hex), 1.69 (m, 2H, Hex), 1.4-1.3 (m, 6H, Hex), 0.90 (t, 3H, Hex), 0.44 (s/d, $^3J(^{117/119}\text{Sn}, \text{H}) = 55.5/57.5 \text{ Hz}$, 9H, SnMe_3); ^{13}C NMR (125.69 MHz, CDCl_3): $\delta = 145.2$, 143.7, 136.5 (Th), 135.9 (s/d, $^4J(^{117/119}\text{Sn}, ^{13}\text{C}) = 27 \text{ Hz}$, Th-C3), 135.0 (Th), 124.8 (Th), 124.4 (s/d, $^3J(^{117/119}\text{Sn}, ^{13}\text{C}) = 40 \text{ Hz}$, Th-C4), 123.3 (Th), 31.8, 31.7, 30.3, 28.9, 22.8, 14.3 (Hex), -8.0 (s/d, $^1J(^{117/119}\text{Sn}, ^{13}\text{C}) = 356/373 \text{ Hz}$, SnMe_3); ^{119}Sn NMR (186.413 MHz, CDCl_3): $\delta = -25.6 \text{ ppm}$; GC-MS ($t=11.79 \text{ min}$): m/z (%): 414 [M^+] (40), 399 [$\text{M}^+ - \text{CH}_3$] (100).

Synthesis of 5-Trimethylstannyl-5'-diphenylamino-2,2'-bithiophene: A solution of $n\text{BuLi}$ (16.5 mL, 1.6M in hexanes, 26.4 mmol) was added at $-78\text{ }^{\circ}\text{C}$ over a period of 1 h to a solution of 5-diphenylamino-2,2'-bithiophene (7.30 g, 21.9 mmol) in THF (250 mL). The color gradually changed from yellow to green. The reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 20 min and slowly allowed to warm up to ambient temperature. After stirring for 3 h, the mixture was once again cooled to $-78\text{ }^{\circ}\text{C}$ and treated with a solution of Me_3SnCl (5.70 g, 28.6 mmol) in THF (100 mL). The reaction solution was allowed to warm to room temperature and stirred for 12 h. Standard aqueous workup provided a black oily material, which was crystallized from hot methanol to give a dark green solid (5.50 g, 50%). ^1H NMR (499.893 MHz, CDCl_3): δ = 7.28 (m, 4H, NPh_m), 7.19 (m, 4H, NPh_o), 7.17 (d, 3J = 4.0 Hz, 1H, Th-H4), 7.06 (d, 3J = 4.0 Hz, 1H, Th-H3), 7.05 (m, 2H, NPh_p), 6.96 (d, 3J = 4.0 Hz, 1H, Th-H3'), 6.61 (d, 3J = 4.0 Hz, 1H, Th-H4'), 0.38 (s/d, $^3J(^{117/119}\text{Sn}, \text{H})$ = 55.5/57.5 Hz, 9H, SnMe_3); ^{13}C NMR (125.69 MHz, CDCl_3): δ = 150.4 (Th), 147.9 (NPh_i), 143.6 (Th), 136.9 (Th), 135.9 (s/d, $^4J(^{117/119}\text{Sn}, ^{13}\text{C})$ = 28 Hz, Th-C4), 131.9 (Th-C8), 129.4 (NPh_m), 124.3 (s/d, $^3J(^{117/119}\text{Sn}, ^{13}\text{C})$ = 40.5 Hz, Th-C3), 123.3 (NPh_p), 122.8 (NPh_o), 122.2, 121.6 (Th), -8.0 (s/d, $^1J(^{117/119}\text{Sn}, ^{13}\text{C})$ = 356/373 Hz, SnMe_3); ^{119}Sn NMR (186.413 MHz, CDCl_3): δ = -25.6 ppm; GC-MS (t =23.86 min): m/z (%): 497 [M^+] (100), 482 [$\text{M}^+ - \text{CH}_3$] (7).

Synthesis of MBMesBT: A solution of 5-trimethylstannyl-2,2'-bithiophene (0.38 g, 1.15 mmol) in toluene (10 mL) was added dropwise to a colorless solution of $t\text{BuPhBBr}_2$ (0.35 g, 1.15 mmol) in toluene (10 mL). The resulting solution turned yellow upon complete addition. The reaction mixture was stirred for 12 h at ambient temperature. All volatile materials were removed under high vacuum and the resulting yellow solid was taken up in toluene (15 mL). A solution of $\text{MesCu}\cdot(\text{C}_7\text{H}_8)_{0.2}$ (0.24 g, 1.19 mmol) in toluene (5 mL) was added slowly,

which resulted in the formation of a purple precipitate. The reaction mixture was refluxed for 14 h and then stirred at room temperature for 2 h before being filtered through celite. The solvent was removed under high vacuum. Purification by repeated extraction with CH₃CN and crystallization from CH₃CN gave the product in the form of light yellow crystals (0.238 g, 55%). For **MBMesBT**: ¹¹B NMR (160.386 MHz, CDCl₃): δ = 62 ppm ($w_{1/2}$ = 1450 Hz); ¹H NMR (499.893 MHz, CDCl₃): δ = 7.87 (d, ³J = 8.5 Hz, 2H, Ph_o), 7.67 (d, ³J = 4.0 Hz, 1H, Th-H4), 7.48 (d, ³J = 8.5 Hz, 2H, Ph_m), 7.38 (d, ³J = 4.0 Hz, 1H, Th-H3), 7.34 (dd, ³J = 3.5 Hz, ⁴J = 1.5 Hz, 1H, Th-H3'), 7.30 (dd, ³J = 5.0 Hz, ⁴J = 1.0 Hz, 1H, Th-H5'), 7.05 (dd, ³J = 5.0 Hz, ³J = 4.0 Hz, 1H, Th-H4'), 6.88 (s, 2H, Mes_m), 2.37 (s, 3H, *p*-Me), 2.07 (s, 6H, *o*-Me), 1.37 (s, 9H, CMe₃); ¹³C NMR (125.69 MHz, CDCl₃): δ = 155.0 (Ph_p), 150.0 (Th), 143.6 (Th), 138.3 (Mes_o), 137.4 (Th), 137.3 (Ph_o), 137.2 (Mes_p), 128.3 (Th), 127.2 (Mes_m), 126.1 (Th), 126.0 (Th), 125.4 (Th), 125.3 (Ph_m), 35.2 (CMe₃), 31.4 (CMe₃), 22.9 (*o*-Me), 21.5 (*p*-Me); UV-Vis (CH₂Cl₂, 3.2 x 10⁻⁵ M): $\lambda_{\max}$ = 280 nm (ϵ = 19,960), 367 nm (ϵ = 34,560); fluorescence (CH₂Cl₂, 3.2 x 10⁻⁵ M): $\lambda_{\text{em,max}}$ = 425 nm, Φ = 0.72 (λ_{exc} = 367 nm); FAB-MS *m/z* (%): 428.2 [M⁺] (100), 413.1 [M⁺-CH₃] (6); elemental analysis: calculated C 75.69, H 6.82; found C 75.96, H 7.10.

Synthesis of MBMesHBT: A solution of 5-trimethylstannyl-5'-hexyl-2,2'-bithiophene (0.68 g, 1.65 mmol) in toluene (10 mL) was added dropwise to a colorless solution of ^tBuPhBBr₂ (0.500 g, 1.65 mmol) in toluene (10 mL). A solution of MesCu•(C₇H₈)_{0.2} (0.33 g, 1.64 mmol) in toluene (5 mL) was then added slowly, which resulted in the formation of a purple precipitate. The reaction mixture was refluxed for 12 h, stirred at room temperature for 2 h, and then filtered through celite. The solvent was removed from the resulting light yellow solution under high vacuum. Purification by repeated extraction with CH₃CN and

crystallization from CH₃CN gave the product in the form of yellow crystals (0.40 g, 48%). For **MBMesHBT**: ¹¹B NMR (160.386 MHz, CDCl₃): δ = 61 ppm ($w_{1/2}$ = 1900 Hz); ¹H NMR (499.893 MHz, CDCl₃): δ = 7.88 (d, ³J = 8.5 Hz, 2H, Ph_o), 7.66 (d, ³J = 3.5 Hz, 1H, Th-H4), 7.49 (d, ³J = 8.5 Hz, 2H, Ph_m), 7.31 (d, ³J = 3.0 Hz, 1H, Th-H3), 7.17 (d, ³J = 3.5 Hz, 1H, Th-H3'), 6.89 (s, 2H, Mes_m), 6.73 (d, ³J = 3.5 Hz, 1H, Th-H4'), 2.82 (t, ³J = 7.0 Hz, 2H, Hex), 2.39 (s, 3H, *p*-Me), 2.08 (s, 6H, *o*-Me) 1.71 (m, 2H, Hex), 1.4-1.3 (m, 6H, Hex), 1.39 (s, 9H, CMe₃), 0.92 (t, ³J = 7.0 Hz, 3H, Hex); ¹³C NMR (125.69 MHz, CDCl₃): δ = 155.5 (Ph_p), 150.7, 147.4, 143.8, 143.6 (Th), 143.4 (Mes_i), 138.3 (Mes_o), 137.3 (Ph_o), 137.1 (Mes_p), 134.8 (Th), 127.2 (Mes_m), 125.4, 125.3, 125.1 (Th), 125.2 (Ph_m), 35.2 (CMe₃), 31.8, 31.7 (Hex), 31.4 (CMe₃), 30.5, 28.9 (Hex), 22.9 (*o*-Me), 22.8 (Hex), 21.5 (*p*-Me), 14.3 (Hex); UV-Vis (CH₂Cl₂, 3.2 x 10⁻⁵ M): λ_{max} = 273 nm (ϵ = 18,780), 380 nm (ϵ = 41,150); fluorescence (CH₂Cl₂, 3.2 x 10⁻⁵ M): $\lambda_{\text{em,max}}$ = 437 nm, Φ = 0.76 (λ_{exc} = 380 nm); FAB-MS *m/z* (%): 512.3 [M⁺] (100), 469.3 [M⁺-CH₃] (11); elemental analysis: calculated C 77.32, H 8.06; found: C 77.28, H 8.09.

Synthesis of MBMesNBT: A solution of 5-trimethylstannyl-5'-diphenylamino-2,2'-bithiophene (0.51 g, 1.02 mmol) in toluene (5 mL) was added dropwise to a solution of ^tBuPhBBr₂ (0.300 g, 0.99 mmol) in toluene (5 mL). The color of the reaction mixture turned to orange-red with greenish-yellow fluorescence upon complete addition. After stirring for 12 h, all volatile components were removed under high vacuum. The resulting orange-red solid was taken up in toluene (10 mL), and a solution of MesCu•(C₇H₈)_{0.2} (0.21 g, 1.04 mmol) in toluene (5 mL) was added slowly, which resulted in the formation of a purple precipitate. The reaction mixture was refluxed for 12 h and then stirred at room temperature for 2 h. The mixture was filtered through celite and the solvent was removed under high vacuum.

Subsequent recrystallization from CH₃CN gave the product as a yellow powder (0.23 g, 39%). For **MBMesNBT**: ¹¹B NMR (160.386 MHz, CDCl₃): δ = 61 ppm ($w_{1/2}$ = 1600 Hz); ¹H NMR (499.893 MHz, CDCl₃): δ = 7.86 (d, ³J = 8.5 Hz, 2H, BPh_o), 7.63 (d, ³J = 3.5 Hz, 1H, Th-H4), 7.48 (d, ³J = 8.5 Hz, 2H, BPh_m), 7.30 (m, 4H, NPh_m), 7.23 (d, ³J = 4.0 Hz, 1H, Th-H3), 7.21 (m, 4H, NPh_o), 7.13 (d, ³J = 4.0 Hz, 1H, Th-H3'), 7.09 (m, 2H, NPh_p), 6.88 (s, 2H, Mes_m), 6.59 (d, ³J = 4.0 Hz, 1H, Th-H4'), 2.37 (s, 3H, *p*-Me), 2.07 (s, 6H, *o*-Me) 1.37 (s, 9H, CMe₃); ¹³C NMR (125.69 MHz, CDCl₃): δ = 155.5 (Ph_p), 152.8 (Th), 150.7 (Th), 147.7 (Nph_i), 143.8 (Th), 143.4 (Mes_i), 142.9 (Ph_i), 138.3 (Mes_o), 137.2 (Ph_o), 137.1 (Mes_p), 129.5 (NPh_m), 127.2 (Mes_m), 125.2 (Ph_m), 124.8 (Th), 124.3 (Th), 123.9 (NPh_p), 123.4 (NPh_o), 120.3 (Th), 35.2 (CMe₃), 31.4 (CMe₃), 22.8 (*o*-Me), 21.5 (*p*-Me); UV-Vis (CH₂Cl₂, 3.2 × 10⁻⁵ M): $\lambda_{\max}$ = 309 nm (ϵ = 26,700), 436 nm (ϵ = 38,960); fluorescence (CH₂Cl₂, 3.2 × 10⁻⁵ M): $\lambda_{\text{em,max}}$ = 540 nm, Φ = 0.74 (λ_{exc} = 436 nm); FAB-MS *m/z* (%): 595.2 [M⁺] (100); elemental analysis: calculated C 78.64, H 6.43, N 2.35; found C 78.00, H 6.54, N 2.46.

Synthesis and Data for Chapter 2A (Carbazole Pendant Groups)

A.) Organoboron Polymer

Synthesis of PSBTipSiBuCz: A solution of BBr₃ (0.41 g, 1.59 mmol) in CH₂Cl₂ (10 mL) was added dropwise to a solution of **PSSi** (0.25 g, ca. 1.44 mmol of Me₃Si groups) in CH₂Cl₂ (10 mL) and stirred for 20 h. A solution of 3-trimethylsilyl-9-butyl-6-(trimethylstannyl)-carbazole (0.93 g, 2.01 mmol) in CH₂Cl₂ (10 mL) was added dropwise and the reaction mixture turned light green. The mixture was allowed to stir for 20 h at RT, Me₃SiOMe (0.70 mL, 5.08 mmol) was added neat, and the solution was stirred for another 24 h. All volatile components were removed under high vacuum. The greenish solid residue was taken up in

THF (10 mL), a solution of TipMgBr (0.5 M in THF, 9.0 mL, 4.50 mmol) was added, and the mixture was allowed to react for 1 h at RT and then kept at reflux for 5 days. The polymer was passed through a short alumina column using toluene as the eluent to remove the magnesium salts. The solution was then concentrated to ca. 1.5 mL and precipitated into methanol (50 mL), followed by precipitation from toluene into ethanol (50 mL). The polymer was then dried, taken up in benzene and obtained as white powdery material upon freeze drying from benzene (0.37 g, 38.0 %). For **PSBTipSiBuCz**: ^{11}B NMR (160.386 MHz, CDCl_3): δ = 49 ppm ($w_{1/2}$ = 1200 Hz); ^1H NMR (499.893 MHz, CDCl_3): δ = 8.40 (br, 1H, Cz-5), 8.11 (br, 1H, Cz-4), 7.77 (br, 1H, Cz-7), 7.52 (br, 2H, Ph_o), 7.30-6.00 (v br, 7H, Ph_m , Tip_m, Cz-1,2,8), 4.3-3.4 (v br, 2H, Bu), 2.80 (v br, 1H, *p*-CHMe₂), 2.40 (v br, 2H, *o*-CHMe₂), 1.90-0.50 (m, br, 18H, *o*-CHMe₂, *p*-CHMe₂, Bu), 0.26 (s, br, 9H, SiMe₃); ^{13}C NMR (125.69 MHz, CDCl_3): δ = 149.0 (Tip_o), 147.9 (Tip_p), 143.0 (Cz), 142.0 (Ph_i /Tip_i), 141.3 (Cz), 137.9 (br, Ph_o), 136.4 (Cz), 133.3 (Cz_i), 131.6 (Cz), 129.7 (Cz), 129.6 (Cz), 127.1 (Ph_m), 125.9 (Cz), 123.6 (Cz), 122.6 (Cz), 120.0 (Tip_m), 108.6 (Cz), 107.9 (Cz), 42.7 (Bu-C1), 42-40 (polymer backbone), 35.4 (*o*-CHMe₂), 34.3 (*p*-CHMe₂), 31.2 (Bu-C2), 24.3 (*o*-CHMe₂, *p*-CHMe₂), 20.6 (Bu-C3), 13.9 (Bu-C4), -0.36 (Me₃Si); GPC-RI (THF vs. PS standards): M_n = 38300, M_w = 43980, PDI = 1.15, high molecular weight shoulder: M_n = 79490, M_w = 81610, PDI = 1.03 (%Area = 95:5); UV-Vis (CH_2Cl_2 , 3.5×10^{-5} M): λ_{max} = 285 (27770), 305 (27310), 345 (23650); fluorescence (CH_2Cl_2 , 3.5×10^{-5} M): $\lambda_{\text{em, max}}$ = 397 nm, Φ = 0.68 (λ_{exc} = 345 nm); DSC (onset, 40 °C/min; second heating curve): T_g = 187 °C; TGA (10 °C/min; N₂): 56 % weight loss between 256 °C and 320 °C; 14 % weight loss between 396 °C and 427 °C; 8% residual mass at 800 °C; elemental analysis: calculated C, 82.46; H, 8.90; N, 2.29; found C 80.43, H 8.61, N 2.32.

B.) Precursors and Model Compounds

Synthesis of $\text{Me}_3\text{SiBuCzSnMe}_3$: A solution of $n\text{BuLi}$ (1.6M in hexanes, 10.2 mL, 16.3 mmol) was added dropwise over a period of 90 min to a solution of 3-trimethylsilyl-6-bromo-9-butyl-carbazole (6.10 g, 16.3 mmol) in diethylether (350 mL) at -78°C . The mixture was stirred for 25 min and then allowed to slowly warm up to 0°C . After cooling the reaction mixture back down to -78°C , a solution of trimethyltin chloride (3.40 g, 17.10 mmol) in ether (20 mL) was added dropwise. The mixture was stirred at -78°C for 3 h and then for an additional 12 h at ambient temperature. Quenching with aqueous NH_4Cl solution and extraction of the organic layer with ether gave a yellowish-brown oily material upon evaporation of the solvents. Crystallization from hot methanol gave the pure product as a white crystalline material (5.69 g, 76 %). For $\text{Me}_3\text{SiBuCzSnMe}_3$: ^1H NMR (499.893 MHz, CDCl_3): δ = 8.29 (s, 1H, Cz-H4), 8.26 (s, 1H, Cz-H5), 7.59 (dd, 3J = 8.0 Hz, 1H, Cz-H7), 7.54 (dd, 3J = 8.5 Hz, 1H, Cz-H2), 7.43 (d, 3J = 8.0 Hz, 1H, Cz-H8), 7.29 (s, 1H, Cz-H1), 4.28 (t, 2H, 3J = 7.0 Hz, Bu-H1), 1.84 (m, 2H, Bu-H2), 1.39 (m, 2H, Bu-H3), 0.95 (t, 3H, 3J = 7.0 Hz, Bu-H1), 0.3 (s/d, $^3J(^{117/119}\text{Sn}, \text{H})$ = 52.5/54.5 Hz, 9H, SnMe_3); ^{13}C NMR (125.69 MHz, CDCl_3): 141.1, 141.0, 132.7 (s/d, $^3J(^{117/119}\text{Sn}, ^{13}\text{C})$ = 44 Hz), 130.7, 130.2, 129.1, 127.9 (s/d, $^2J(^{117/119}\text{Sn}, ^{13}\text{C})$ = 41 Hz), 125.7, 123.3, 122.7, 108.9 (s/d, $^2J(^{117/119}\text{Sn}, ^{13}\text{C})$ = 52 Hz), 108.5, 43.0, 31.4, 20.8, 14.1, -0.29 , -9.0 (s/d, $^1J(^{117/119}\text{Sn}, ^{13}\text{C})$ = 333/347 Hz, SnMe_3); ^{119}Sn NMR (186.413 MHz, CDCl_3): δ = -23.3 ppm; GC-MS (t =23.5 min): m/z (%): 459 [M^+] (20), 444 [$\text{M}^+ - \text{CH}_3$] (100).

Synthesis of MBTipSiBuCz : A solution of 3-trimethylsilyl-9-butyl-6-(trimethylstannyl)-carbazole (0.24 g, 0.52 mmol) in CH_2Cl_2 (5 mL) was cooled to ca. -10°C and added dropwise to a pre-cooled solution (-10°C) of $t\text{BuPhBBr}_2$ (0.15 g, 0.51 mmol) in CH_2Cl_2 (5

mL). The greenish solution was allowed to warm to RT and then stirred for 1 h. Me₃SiOMe (0.12 mL, 0.87 mmol) was added neat and the resulting faint green reaction mixture was stirred for another 1 h. All volatile components were removed under high vacuum. The residue was taken up in THF (10 mL) and a solution of TipMgBr (0.5 M in THF, 1.1 mL, 0.55 mmol) was added. The reaction mixture was stirred at RT for 30 min and then heated to 80 °C for 4 days. The solvent was removed under high vacuum to leave behind a green solid, which was extracted with hexanes. Purification by column chromatography using alumina as the stationary phase and hexanes as the eluent gave the pure product as a white powdery material (0.24 g, 73%). For **MBTipSiBuCz**: ¹¹B NMR (160.386 MHz, CDCl₃): δ = 61.8 ppm (*w*_{1/2} = 1900 Hz); ¹H NMR (499.893 MHz, CDCl₃): δ = 8.69 (s, 1H, Cz-5), 8.28 (s, 1H, Cz-4), 7.84 (d, ³J = 8.5 Hz, 1H, Cz-7), 7.79 (d, ³J = 8.0 Hz, 2H, Ph_o), 7.63 (d, ³J = 8.0 Hz, 1H, Cz-8), 7.51 (d, ³J = 8.0 Hz, 2H, Ph_m), 7.44 (d, ³J = 8.0 Hz, 1H, Cz-2), 7.40 (d, ³J = 8.0 Hz, 1H, Cz-1), 7.03 (s, 2H, Tip_m), 4.32 (t, ³J = 7.0 Hz, 2H, Bu), 2.98 (m, 1H, *p*-CHMe₂), 2.54 (m, 2H, *o*-CHMe₂), 1.89 (m, 2H, Bu), 1.44 (m, 2H, Bu), 1.40 (s, 9H, CMe₃), 1.35 (d, ³J = 7.0 Hz, 6H, *p*-CHMe₂), 0.97 (m, 12H, *o*-CHMe₂), 0.87 (m, 3H, Bu), 0.36 (s, 9H, SiMe₃); ¹³C NMR (125.69 MHz, CDCl₃): δ = 154.4 (Ph_p), 149.0 (Tip_o), 148.2 (Tip_p), 143.2 (Cz), 142.0 (Ph_i/Tip_i), 141.5 (Cz), 140.7 (Tip_i/Ph_i), 137.9 (Ph_o), 137.1 (Cz), 133.4 (Cz_i), 131.3 (Cz), 130.8 (Cz), 130.0 (Cz), 125.9 (Cz), 124.8 (Ph_m), 123.6 (Cz), 122.7 (Cz), 120.1 (Tip_m), 108.8 (Cz), 108.0 (Cz), 43.2 (Bu-C1), 35.5 (*o*-CHMe₂), 35.2 (CMe₃), 34.4 (*p*-CHMe₂), 31.5 (CMe₃), 31.4 (Bu-C2), 24.5, 24.4, 24.3 (*o*-CHMe₂, *p*-CHMe₂), 20.8 (Bu-C3), 14.1 (Bu-C4), -0.34 (Me₃Si); UV-Vis (CH₂Cl₂, 3.7 × 10⁻⁵ M): λ_{max} = 286 (27400), 304 (31430), 344 (32100); fluorescence (CH₂Cl₂, 3.7 × 10⁻⁵ M): λ_{em,max} = 409 nm, Φ = 0.72 (λ_{exc} = 344 nm); elemental analysis: calculated C, 82.34; H, 9.42; N, 2.18; found C 81.69, H 9.09, N 2.14;

High-resolution MALDI-TOF (positive mode, matrix: Dihydroxybenzoic acid): m/z = 641.4820 (calcd for $^{12}\text{C}_{44}^{1}\text{H}_{60}^{11}\text{B}^{14}\text{N}^{28}\text{Si}$ 641.4590).

Synthesis and Data for Chapter 2B (Ferrocene/Mesityl Pendant Groups)

A.) Organoboron Polymers

Synthesis of PS-B(Fc)Mes: A solution of BBr_3 (0.21 g, 0.84 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a solution of **PSSi** (0.123 g, ca. 0.69 mmol of Me_3Si groups) in CH_2Cl_2 (10 mL) and stirred for 20 h. A solution of FcSnMe_3 (0.448 g, 1.28 mmol) in CH_2Cl_2 (10 mL) was added dropwise and the reaction mixture turned dark red. The mixture was allowed to stir for 20 h at RT, Me_3SiOMe (0.25 mL, 1.81 mmol) was added neat, and the solution was stirred for another 24 h. All volatile components were removed under high vacuum. The orange-red solid residue was taken up in THF (10 mL), a solution of MesMgBr (0.5 M in THF, 2.8 mL, 1.4 mmol) was added, and the mixture was allowed to react for 1 h at RT and then kept at reflux for 5 days. The mixture was filtered and the filtrate was concentrated to ca. 4 mL and precipitated into ether (350 mL). The product was purified by repeated precipitation from THF into ether (350 mL) and filtering through a short alumina plug using dichloromethane as the solvent. The precipitate was dried at 50 °C under high vacuum to obtain a fine orange-red powder (0.195 g, 67%). **For PS-B(Fc)Mes:** ^{11}B NMR (160.386 MHz, CDCl_3): δ = 57 ppm ($w_{1/2}$ = 1900 Hz); ^1H NMR (499.893 MHz, CDCl_3): δ = 7.8-7.4 (br m, 2H, Ph_o), 6.9-6.4 (br m, 4H, Ph_m and Mes_m), 4.5, 4.3 (br m, 2 x 2H, Fc-H_{3,4} and Fc-H_{2,5}), 4.0 (br, 5H, C_5H_5), 2.3 (br, 3H, *p*-Me), 1.9 (br, 6H, *o*-Me), polymer backbone protons were not resolved; ^{13}C NMR (125.69 MHz, CDCl_3): δ = 149.0, 143.7, 140.3 (br), 138.2, 136.5, 127.3, 75.0 (Fc-C_{2,5}), 74.3 (Fc-C_{3,4}), 69.5 (C_5H_5), 42-40 (polymer backbone), 23.3 (*o*-Me), 21.5 (*p*-Me); GPC-RI (THF vs. PS standards): M_n = 23800, M_w = 27400, PDI =

1.15, high molecular weight shoulder: $M_n = 61216$, $M_w = 65212$, $PDI = 1.07$ (%Area = 83.4:16.6); UV-Vis (CH_2Cl_2 , 3.18×10^{-5} M): $\lambda_{\text{max}} = 294$ nm ($\epsilon = 22,997$), 368 nm ($\epsilon = 3,456$), 484 nm ($\epsilon = 1,885$); DSC (onset, 10 °C/min; second heating curve): T_g not observed; TGA (20 °C/min; N_2): 16% weight loss between 278 °C and 324 °C; 43% weight loss between 416 °C and 603 °C; 22% residual mass at 800 °C; elemental analysis: calculated C 77.55, H 6.51; found C 77.04, H 6.71.

Synthesis of PS-B(Fc)Tip: The polymer was prepared in analogy to the procedure for **PS-B(Fc)Mes** from BBr_3 (0.82 g, 3.27 mmol), **PS-Si** (0.50 g, ca. 2.84 mmol of Me_3Si groups), FcSnMe_3 (1.56 g, 4.49 mmol), Me_3SiOMe (1.4 mL, 9.94 mmol), and TipMgBr (0.5 M in THF, 20 mL, 3.52 mmol). Yield: 0.89 g, 62%. For **PS-B(Fc)Tip**: ^{11}B NMR (160.386 MHz, CDCl_3): $\delta = 56$ ppm ($w_{1/2} = 2800$ Hz); ^1H NMR (499.893 MHz, CDCl_3): $\delta = 8.0$ -7.4 (br m, 2H, Ph_o), 7.1-6.2 (br m, 4H, Ph_m and Mes_m), 4.6, 4.2 (br m, 2 x 2H, Fc-H3,4 and Fc-H2,5), 4.0 (br, 5H, C_5H_5), 2.9 (br, 1H, $p\text{-CHMe}_2$), 2.5 (br, 2H, $o\text{-CHMe}_2$), 1.54-1.49 (br m, 6H, $o\text{-CHMe}_2$), 1.49-1.20 (br m, 6H, $p\text{-CHMe}_2$), 1.20-0.50 (br m, 6H, $p\text{-CHMe}_2$), polymer backbone protons were not resolved; ^{13}C NMR (125.69 MHz, CDCl_3): $\delta = 148.9$, 147.9, 142.0 (br), 137.2, 126.8, 119.9, 76.0 (Fc-C2,5), 73.5 (Fc-C3,4), 69.5 (C_5H_5), 42-40 (polymer backbone), 35.0 ($p\text{-CHMe}_2$), 34.3 ($o\text{-CHMe}_2$), 24.5 ($o\text{-}$ and $p\text{-CHMe}_2$); GPC-RI (THF vs. PS standards): $M_n = 30400$, $M_w = 33700$, $PDI = 1.11$, high molecular weight shoulder: $M_n = 70851$, $M_w = 73707$, $PDI = 1.04$ (%Area = 90.9:9.1); UV-Vis (CH_2Cl_2 , 3.2×10^{-5} M): $\lambda_{\text{max}} = 295$ nm ($\epsilon = 15850$), 367 nm ($\epsilon = 1995$), 485 nm ($\epsilon = 1260$); DSC (onset, 10 °C/min; second heating curve): $T_g = 132$ °C ; TGA (20 °C/min; N_2): 18.85% weight loss between 294 °C and 360 °C; 4% weight loss between 431 °C and 459 °C; 15% residual mass at 800 °C; elemental analysis: calculated C 78.90, H 7.83; found C 77.38, H 7.42.

Synthesis of PS-BMes₂: A solution of BBr₃ (0.92 g, 3.67 mmol) in CH₂Cl₂ (10 mL) was added dropwise to a solution of **PSSi** (0.52 g, ca. 2.93 mmol of Me₃Si groups) in CH₂Cl₂ (10 mL) and the mixture was stirred for 24 h. Me₃SiOMe (1.21 mL, 8.80 mmol) was added and the reaction mixture was stirred for another 24 h. All volatile components were removed under high vacuum. A slightly yellow solid remained which was taken up in THF (10 mL) and a solution of MesMgBr (0.5 M in THF, 17.3 mL, 8.80 mmol) was added. The mixture was allowed to react for 1 h at RT and then refluxed for 1 week. The solution was concentrated to ca. 4 mL and precipitated into ether (350 mL). The product was purified by repeated precipitation from THF into ether (350 mL). The precipitate was dried at 50 °C under high vacuum to give a fine white powder (0.67 g, 65%). For **PS-BMes₂**: ¹¹B NMR (160.386 MHz, CDCl₃): δ = 57 ppm ($w_{1/2}$ = 2000 Hz); ¹H NMR (499.893 MHz, CDCl₃): δ = 7.3-7.0 (br m, 2H, Ph_o), 6.8-6.5 (s, 2H, Mes_m), 6.5-6.2 (br m, 2H, Ph_m), 2.2 (br, 3H, *p*-Me), 1.8 (br, 6H, *o*-Me), polymer backbone protons were not resolved; ¹³C NMR (125.69 MHz, CDCl₃): δ = 149.1, 143.6, 141.9, 140.8 (br), 138.4, 136.8 (br), 128.4, 127.3, 42-40 (polymer backbone), 23.6 (*o*-Me), 21.4 (*p*-Me); GPC-RI (THF vs. PS standards): M_n = 32223, M_w = 41003, PDI = 1.27, high molecular weight shoulder: M_n = 66304, M_w = 70155, PDI = 1.06 (%Area = 87.4:12.6); UV-Vis (CH₂Cl₂, 3.18 x 10⁻⁵ M): λ_{max} = 261 nm (ϵ = 17,526), 323 nm (ϵ = 31,723) ; DSC (onset, 20 °C/min; second heating curve): T_g not observed; TGA (20 °C/min; N₂): 61% weight loss between 283 °C and 387 °C; 13% weight loss between 490 °C and 579 °C; 11% residual mass at 800 °C.

B.) Model Compounds

Synthesis of MB(Fc)Mes: A solution of FcSnMe₃ (0.290 g, 0.83 mmol) in CH₂Cl₂ (5 mL) was cooled to ca. -10 °C and added dropwise to a pre-cooled solution (-10 °C) of ^tBuPhBBr₂

(0.253 g, 0.83 mmol) in CH_2Cl_2 (5 mL). The dark red colored reaction mixture was allowed to warm to RT and then stirred for 1 h. Me_3SiOMe (0.24 mL, 1.70 mmol) was added neat and the resulting orange-red solution was stirred for another 1 h. All volatile components were removed under high vacuum. The residue was taken up in THF (10 mL) and a solution of MesMgBr (0.5 M in THF, 1.70 mL, 0.85 mmol) was added. The reaction mixture was stirred at RT for 30 min and then heated to 60 °C for 3 days. The solvent was removed under high vacuum to leave behind a red solid, which was extracted with hexanes. Purification by column chromatography using alumina as the stationary phase and hexanes as the eluent gave the pure product as a red crystalline material (0.260 g, 70%). For **MB(Fc)Mes**: ^{11}B NMR (160.386 MHz, CDCl_3): δ = 69.7 ppm ($w_{1/2}$ = 1300 Hz); ^1H NMR (499.893 MHz, CDCl_3): δ = 7.89 (d, 3J = 8.5 Hz, 2H, Ph_o), 7.44 (d, 3J = 8.5 Hz, 2H, Ph_m), 6.86 (s, 2H, Mes_m), 4.69, 4.45 (2 x pst, $^{3/4}J$ = 1.5 Hz, 2 x 2H, Fc-H2,5 and Fc-H3,4), 4.26 (s, 5H, C_5H_5), 2.36 (s, 3H, $p\text{-Me}$), 2.12 (s, 6H, $o\text{-Me}$), 1.39 (s, 9H, CMe_3); ^{13}C NMR (125.69 MHz, CDCl_3): δ = 154.8 (Ph_p), 143.9, 139.6 (Ph_i and Mes_i), 138.5 (Mes_o), 136.8 (Ph_o), 136.7 (Mes_p), 127.2 (Mes_m), 125.0 (Ph_m), 77.8, 74.3 (Fc-C2-5), 75 (br, Fc-C1), 69.5 (C_5H_5), 35.2 (CMe_3), 31.4 (CMe_3), 23.2 ($o\text{-Me}$), 21.4 ($p\text{-Me}$); UV-Vis: (CH_2Cl_2 , 3.23×10^{-5} M): λ_{max} = 292 nm (ϵ = 27,680), 367 nm (ϵ = 3,830), 484 nm (ϵ = 1,980); GC-MS (t = 20.34 min): m/z (%): 448 [M^+] (100), 432 [$\text{M}^+ - \text{CH}_3$] (3.1); elemental analysis: calculated C 77.71, H 7.42; found C 77.68, H 7.46.

Synthesis of MB(Fc)Tip: The compound was prepared in analogy to the procedure for **MB(Fc)Mes** from FcSnMe_3 (0.499 g, 1.43 mmol), $^t\text{BuPhBBr}_2$ (0.425 g, 1.40 mmol), Me_3SiOMe (0.50 mL, 3.63 mmol), and TipMgBr (0.5 M in THF, 4.2 mL, 2.1 mmol). Yield: 0.485 g, 65%. For **MB(Fc)Tip**: ^{11}B NMR (160.386 MHz, CDCl_3): δ = 70 ppm ($w_{1/2}$ = 1750 Hz); ^1H NMR (499.893 MHz, CDCl_3): δ = 7.96 (d, 3J = 8.5 Hz, 2H, Ph_o), 7.45 (d, 3J = 8.5

Hz, 2H, Ph_m), 6.97 (s, 2H, Mes_m), 4.64, 4.47 (2 x pst, $^3J = 1.5$ Hz, 2 x 2H, Fc-H2,5 and Fc-H3,4), 4.26 (s, 5H, C₅H₅), 2.93 (m, 1H, *p*-CHMe₂), 2.67 (m, 2H, *o*-CHMe₂), 1.38 (s, 9H, CMe₃), 1.33 (d, $^3J = 7.0$ Hz, 6H, *o*-CHMe₂), 1.11 (d, $^3J = 7.0$ Hz, 6H, *p*-CHMe₂), 0.98 (d, $^3J = 7.0$ Hz, 6H, *p*-CHMe₂); ^{13}C NMR (125.69 MHz, CDCl₃): δ = 154.8 (Ph_p), 149.0 (Tip_o), 148.0 (Tip_p), 142.0, 140.3 (Ph_i and Tip_i), 137.3 (Ph_o), 124.7 (Ph_m), 119.9 (Tip_m), 77.8, 73.4 (Fc-C's), 73.5 (br, Fc-C1), 69.5 (C₅H₅), 35.2 (CMe₃), 34.4 (*o*-CH and CMe₃), 31.4 (*p*-CH), 24.7(*o*-CHMe₂), 24.4(*o*-CHMe₂); UV-Vis (CH₂Cl₂, 3.18×10^{-5} M): $\lambda_{\text{max}} = 293$ nm ($\epsilon = 15,876$), 368 nm ($\epsilon = 2,200$), 486 nm ($\epsilon = 1,114$); GC-MS ($t = 35.78$ min): m/z (%): 532 [M^+] (100); elemental analysis: calculated C 78.96, H 8.52; found C 78.77, H 8.54. High resolution MALDI-TOF (positive mode, matrix: Benzo[a]pyrene): $m/z = 532.3135$ (calcd for $^{12}\text{C}_{35}^{1}\text{H}_{45}^{11}\text{B}^{56}\text{Fe}$ 532.2965).

Synthesis of MBMes₂: Me₃SiOMe (0.20 mL, 1.45 mmol) was added dropwise to a precooled solution (−10 °C) of ^tBuPhBBr₂ (0.20 g, 0.66 mmol) in CH₂Cl₂ (5 mL). The reaction mixture was allowed to warm to RT and stirred for 1 h. All volatile components were removed under high vacuum. The solid was taken up in THF (10 mL), and a solution of MesMgBr (0.5 M in THF, 2.7 mL, 1.35 mmol) was added. The reaction mixture was stirred at room temperature for 30 min and then heated to 90 °C for 3 days. The solvent was removed under high vacuum to leave behind a colorless solid. The residue was extracted with hexanes. Purification by column chromatography using alumina as the stationary phase and hexanes as the solvent gave the pure product as a white crystalline material (0.161 g, 64%). For **MBMes₂**: ^{11}B NMR (160.386 MHz, CDCl₃): δ = 73.1 ppm ($w_{1/2} = 1440$ Hz); ^1H NMR (499.893 MHz, CDCl₃): δ = 7.47 (d, $^3J = 8.5$ Hz, 2H, Ph_o), 7.37 (d, $^3J = 8.5$ Hz, 2H, Ph_m), 6.82 (s, 4H, Mes_m), 2.33 (s, 6H, *p*-Me), 2.03 (s, 12H, *o*-Me), 1.35 (s, 9H, CMe₃); ^{13}C NMR

(125.69 MHz, CDCl₃): δ = 155.8 (Ph_p), 142.9, 142.1 (Ph_i and Mes_i), 138.5 (Mes_o), 136.8 (Ph_o), 136.7 (Mes_p), 127.2 (Mes_m), 125.0 (Ph_m), 35.2 (CMe₃), 31.4 (CMe₃), 23.6 (*o*-Me), 21.4 (*p*-Me); UV-Vis (CH₂Cl₂, 3.71 x 10⁻⁵ M): λ_{max} = 267 nm (ϵ = 12,038), 309 nm (ϵ = 13,765) ; GC-MS (*t*=30.78 min): *m/z* (%): 382 [M⁺] (1), 263 [M⁺-C₉H₁₁] (100). elemental analysis: calculated C 77.71, H 7.42; found C 77.68, H 7.46.

Table A.1 Crystal data and structure refinement for MBMes₂ and MBTipFc

Compound	MBMes ₂	MBTipFc
Empirical formula	C ₂₈ H ₃₅ B	C ₃₅ H ₄₅ BFe
<i>M_r</i>	382.37	532.37
<i>T</i> (K)	100(2)	100(2)
Wavelength (Å)	1.54178	1.54178
Crystal system	Triclinic	Monoclinic
Space group	P-1	P2(1)/n
Unit cell dimensions, <i>a</i> (Å)	11.8155(5)	19.4236(3)
<i>b</i> (Å)	12.0028(5)	10.7105(2)
<i>c</i> (Å)	17.5536(7)	28.4388(5)
α (°)	75.173(2)	90
β (°)	76.741(2)	95.1660(10)
γ (°)	83.430(2)	90
<i>V</i> (Å ³)	2338.28(17)	5892.27(18)
<i>Z</i>	4	8
ρ_{calc} (Mg/m ³)	1.086	1.200
μ (MoK α) (mm ⁻¹)	0.442	4.238

F(000)	832	2288
Crystal size (mm)	0.44 x 0.26 x 0.23	0.34 x 0.30 x 0.13
θ range (°)	3.82 to 66.52	2.88 to 67.27
Index ranges	-13 $\leq h \leq$ 13 -13 $\leq k \leq$ 14 -20 $\leq l \leq$ 20	-23 $\leq h \leq$ 22 -12 $\leq k \leq$ 12 -30 $\leq l \leq$ 33
Reflections collected	17101	45604
Independent reflections	7477 [R(int) = 0.0322]	10027 [R(int) = 0.0412]
Absorption correction	None	Numerical
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	7477 / 0 / 541	10027 / 0 / 685
Goodness-of-fit on F ²	1.042	1.024
Final R indices [I > 2 σ (I)]	R1 = 0.0554 wR2 = 0.1512	R1 = 0.0368 wR2 = 0.0905
R indices (all data)	R1 = 0.0641 wR2 = 0.1621	R1 = 0.0546 wR2 = 0.0987
Peak / hole (e.Å ⁻³)	0.293 and -0.260	0.302 and -0.287

Synthesis and Data for Chapter 3 (Vinylbithiophene Compounds)

A.) Functionalized Vinylbithiophene Monomer

Synthesis of VBTSi: To a colorless suspension of MeP(Ph)₃Br (16.8 g, 46.91 mmol) in THF at -50°C, a solution of nBuLi (1.6 M in hexanes, 29.3 mL, 46.9 mmol) was added dropwise. The resulting yellow solution was stirred for another 2 h, and a solution of 5-trimethylsilyl-5'-carbaldehyde-2,2'-bithiophene (10 g, 37 mmol) was added. The color changed from yellow to brown. The resulting brown reaction mixture was allowed to warm to room temperature and further stirred for another 12 h at ambient temperature. Quenching with aqueous NH₄Cl solution and extraction of the organic layer with ether gave a yellow oily material upon evaporation of the solvents. Upon purification by column chromatography using alumina gel as the stationary phase and hexanes as the eluent the pure product was obtained as a low melting bright yellow solid (9.51 g, 96%). For **VBTSi**: ¹H NMR (499.893 MHz, CDCl₃): δ = 7.22 (d, ³J = 3.5 Hz, 1H, Th-4), 7.14 (d, ³J = 3.5 Hz, 1H, Th-3'), 7.05 (d, ³J = 3.5 Hz, 1H, Th-3), 6.87 (d, ³J = 3.5 Hz, 1H, Th-4'), 6.77 (d, ³J = 3.5 Hz, 1H), 5.56 (d, ^{trans}J = 17.5 Hz, 1H), 5.16 (d, ^{cis}J = 10.5 Hz, 1H), 0.39 (s, 9H, SiMe₃); ¹³C NMR (125.69 MHz, CDCl₃): δ = 142.6 (Th), 142.1 (Th), 140.1 (Th), 136.4 (Th), 134.9 (Th), 130.0, 127.0 (Th), 125.2 (Th), 124.1 (Th), 113.4, 0.1 (SiMe₃); ²⁹Si NMR (99.33 MHz, CDCl₃): δ = -6.34 ppm; GC-MS (t=8.56 min): m/z (%): 264 [M⁺] (70), 249 [M⁺-CH₃] (100). High resolution MALDI-TOF (positive mode, matrix: Dihydroxybenzoic acid): m/z = 264.0556 (calcd for ¹²C₁₃¹H₁₆³²S₂²⁸Si 264.0457).

B.) Functionalized Vinylbithiophene Polymer

[Entries 1-5, Table 3.2]

1.) By ATRP (co-polymerization with styrene): In a glovebox, the vinylbithiophene monomer (0.74 g, 2.78 mmol), styrene (0.29 g, 2.79 mmol), 1-bromo-1-phenylethane (16.2 mg, 90 μ mol), copper(I) bromide (8.1 mg, 60 μ mol), and PMDETA (10.1 mg, 60 μ mol) were charged into a 25 mL Schlenk flask, and 1.02 g of toluene were added. The flask was then taken out of the glovebox, degassed by three freeze-pump-thaw cycles, and subsequently immersed in an oil bath preset at 110 °C. The solution viscosity increased slightly over the course of the reaction time, but no change in color was observed. After stirring for 5 h the flask was cooled to room temperature, and the reaction mixture was precipitated into excess methanol. The yellow precipitate was collected by filtration and redissolved in THF. The THF solution was then passed through a short column packed with ca. 5 g neutral alumina and concentrated to ca. 3 mL. The light yellow colored co-polymer was recovered by precipitation into methanol and dried under vacuum at 50 °C for 24 h (yield: 0.67 g, 45%).

2.) By NMP using TEMPO: (2a) The vinylbithiophene monomer (0.48 g, 1.83 mmol) and the initiator 2,2,6,6-tetramethylpiperidin-N-oxide (TEMPO) (5.7 mg, 36 μ mol) were charged to a 10 mL Schlenk flask and degassed three times before being immersed into an oil-bath preset at 130°C. The reaction was allowed to proceed at that temperature for 24 h before cooling it in an ice water bath, at which point an increase in the viscosity of the reaction mixture was observed. The cooled mixture was then diluted with 1.5 mL THF and precipitated into methanol. Reprecipitation was repeated two more times and the product was obtained as a light yellow powdery solid (0.31 g, 64%). **(2b)** The monomer (0.46 g, 1.73 mmol) and initiator (2.7 mg, 17 μ mol) were charged to a 10 mL Schlenk flask and the

polymerization was carried out in similar fashion to (2a). Repeated precipitation from THF into methanol yielded the polymer as a yellowish solid (0.29 g, 62%).

3.) By NMP using PhEtTEMPO: (3a) The vinylbithiophene monomer (0.5 g, 2.0 mmol) and the initiator 2,2,6,6-tetramethyl-1-(1-phenylethoxy)piperidine (PhEtTEMPO) (5.0 mg, 19 μ mol) were charged to a 10 mL Schlenk flask and degassed three times before being immersed into an oil-bath preset at 120°C. The solution remained homogenous throughout the reaction and no change in the viscosity of the mixture was observed. The reaction was stopped after 4 h by immersing the flask into an ice-water bath, at which point an increase in the viscosity of the reaction mixture was observed. The cooled mixture was then diluted with 1.5 mL of THF and precipitated into methanol. Reprecipitation from THF into methanol was repeated two more times and the product was obtained as a light yellow powdery solid (0.32 g, 60%). **(3b)** The monomer (0.55 g, 2.07 mmol), initiator (5.6 mg, 21 μ mol) and toluene (0.55 g) were charged to a 10 mL Schlenk flask and the polymerization was then carried out in a similar fashion to (3a). The change in viscosity was not as pronounced as in 3a, though the reaction mixture did seem slightly more viscous at the end of the reaction. Repeated precipitation from THF into methanol yielded the polymer as a yellowish solid (0.22 g, 40%). **(3c)** The monomer (0.63 g, 2.37 mmol), initiator (6.4 mg, 24 μ mol) and anisole (0.63 g) were charged to a 10 mL Schlenk flask and the polymerization was then carried out in similar fashion to (3a). Repeated precipitation from THF into methanol yielded the polymer as a yellowish solid (0.27 g, 43%).

4.) By Free Radical Polymerization: (4a) Using AIBN as the initiator: The vinylbithiophene monomer (0.51 g, 1.95 mmol) and the initiator azobisisobutyronitrile (AIBN) (3.2 mg, 19 μ mol) were charged to a 10 mL Schlenk flask and degassed thrice before

being immersed into an oil-bath preset at 65°C. The reaction was allowed to proceed at that temperature for 24 h before cooling it in an ice water bath. The cooled mixture was diluted with 2 mL of THF and precipitated into methanol. Reprecipitation from THF into methanol was repeated two more times and the product was obtained as light yellow powdery solid (0.28 g, 54%). **(4b)** Using BPO as the initiator: The monomer (0.46 g, 1.76 mmol), initiator benzoyl peroxide (BPO) (4.3 mg, 18 μ mol) and toluene (0.55 g) were charged to a 10 mL Schlenk flask, degassed thrice and immersed in an oil bath preset at 90°C and allowed to react for 16h. The reaction mixture was then cooled by immersing in an ice-water bath. The cooled mixture was diluted with 2 mL of THF and precipitated into methanol. Repeated precipitation from THF into methanol yielded the polymer as a yellowish solid (0.23 g, 49%).

5.) By Anionic Polymerization: The monomer (0.5 g, 1.9 mmol) and THF (0.5 mL) was charged to a 10 mL Schlenk flask and degassed several times via freeze-pump-thaw cycles. This solution was then cooled to -78°C using dry ice-acetone mixture. A solution of n-BuLi (1.6 M in hexanes, 0.152 mL, 0.24 mmol) was then added to this yellow solution via a syringe. Upon addition the color immediately changed to dark red indicating that the initiation had occurred. This mixture was reacted at that temperature for 24 h. For termination the reaction mixture was added to a large excess of methanol. The precipitate was filtered, washed with methanol and purified by repeated precipitation from THF into methanol (0.29 g, 57%).

For **PVBTSi**: ^1H NMR (499.893 MHz, CDCl_3): δ = 7.2 – 6.6 (m, 3H), 6.6 – 6.0 (m, 1H), 2.9–2.4 (br, m, 1H), 2.1–1.4 (br, 2H), 0.31 (s, 9H, SiMe_3); ^{13}C NMR (125.69 MHz, CDCl_3): δ = 148.6 (br, Th), 143.2 (Th), 138.8 (Th), 134.9 (Th), 125.0 (br, Th), 125.7 (Th), 123.5 (Th), 36.9 (polymer backbone), 0.20 (SiMe_3) ; ^{29}Si NMR (99.33 MHz, CDCl_3): δ = -6.59 ppm.

GPC-RI (THF vs. PS standards): $M_n = 4,338$; $M_w = 8,296$; $PDI = 1.91$; GPC-LS (THF vs. PS standards): $M_n = 10290$; $M_w = 18660$; $PDI = 1.83$; DSC (onset, 20 °C/min; second heating curve): $T_g = 91$ °C; TGA (10 °C/min; N₂): 71 % weight loss between 331 °C and 381 °C; 7 % weight loss between 509 °C and 591 °C; 22% residual mass at 800 °C.

5.) Borylation of the Trimethylsilyl Functionalized Bithiophene synthesized by Anionic Polymerization (PVBTBBr₂): A solution of BBr₃ (0.13 g, 0.53 mmol) in CH₂Cl₂ (10 mL) was added dropwise to a solution of **PVBTSi** (0.11 g, ca. 0.42 mmol of Me₃Si groups) in CH₂Cl₂ (10 mL) and the mixture was stirred for 24 h. about 1.5 mL of the reaction mixture was taken and its ¹H and ¹¹B NMR were recorded. For **PVBTBBr₂**: ¹¹B NMR (160.386 MHz, CDCl₃): $\delta = 49$ ppm ($w_{1/2} = 1900$ Hz); ¹H NMR (499.893 MHz, CDCl₃): $\delta = 7.8$ -7.5 (br, s, 1H), 7.2 – 6.6 (m, 2H), 6.6 – 6.0 (m, 1H), 2.9 – 2.4 (br, m, 1H), 2.1 – 1.4 (br, 2H).

References and Notes

1. McCullough, R. D.; Belot, J. A.; Rheingold, A. L.; Yap, G. P. A. *J. Am. Chem. Soc.* **1995**, 117, 9913.
2. Fang, M.-C.; Watanabe, A.; Matsuda, M. *J. Organomet. Chem.* **1995**, 489, 15.
3. Harrison, M. G.; Friend, R. H.; Optical Applications. In *Electronic Materials: The Oligomer Approach*, Müllen, K.; Wegner, G., Eds. WILEY-VCH Verlag GmbH: Weinheim, 1998.
4. Burroughes, J. H.; Friend, R. H., The Semiconductor Device Physics of Polyacetylene. In *Conjugated Polymers*, Bredas, J. L.; Silbey, R., Eds. Kluwer Academic Publishers: 1991.
5. Allcock, H. R.; Lampe, F. W.; Mark, J. E., *Contemporary Polymer Chemistry*. Third ed.; Pearson Education, Inc.: Upper Saddle River, NJ, 2003.
6. Gunes, S.; Neugebauer, H.; Sariciftci, N. S. *Chem. Rev.* **2007**, 107, (4), 1324-1338.
7. Coakley, K. M.; McGehee, M. D. *Chem. Mater.* **2004**, 16, (23), 4533-4542.
8. Alam, M. M.; Jenekhe, S. A. *Chem. Mater.* **2004**, 16, (23), 4647-4656.
9. Murphy, A. R.; Frechet, J. M. J. *Chem. Rev.* **2007**, 107, (4), 1066-1096.
10. Wong, W.-Y.; Wang, X.-Z.; He, Z.; Djurisic, A. B.; Yip, C.-T.; Cheung, K.-Y.; Wang, H.; Mak, C. S. K.; Chan, W.-K. *Nat. Mater.* **2007**, 6, (7), 521-527.

11. Wong, W. Y.; Wang, X. Z.; He, Z.; Chan, K. K.; Djurisic, A. B.; Cheung, K. Y.; Yip, C. T.; Ng, A. M. C.; Xi, Y. Y.; Mak, C. S. K.; Chan, W. K. *J. Am. Chem. Soc.* **2007**, 129, (46), 14372-14380.
12. Baek, N. S.; Hau, S. K.; Yip, H.-L.; Acton, O.; Chen, K.-S.; Jen, A. K. Y. *Chem. Mater.* **2008**, 20, (18), 5734-5736.
13. Schulz, G. L.; Holdcroft, S. *Chem. Mater.* **2008**, 20, (16), 5351-5355.
14. Zhang, Q.; Chen, J. S.; Cheng, Y. X.; Geng, Y. H.; Wang, L. X.; Ma, D. G.; Jing, X. B.; Wang, F. S. *Synth. Met.* **2005**, 152, (1-3), 229-232.
15. Schubert, E. F.; Gessmann, T.; Kim, J. K. Inorganic Semiconductors for Light-emitting Diodes; Grimsdale, A. C. The Synthesis of Electroluminescent Polymers. In *Organic Light-Emitting Devices: Synthesis, Properties and Applications*, Müllen, K.; Scherf, U., Eds. WILEY-VCH Verlag GmbH & Co: Weinheim, 2006.
16. Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature* **1992**, 357, (6378), 477-479.
17. Dodabalapur, A. *Sol. State Commun.* **1997**, 102, (2-3), 259-267.
18. Thomas, S. W.; Joly, G. D.; Swager, T. M. *Chem. Rev.* **2007**, 107, (4), 1339-1386.
19. Zhou, Q.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, 117, (26), 7017-7018.
20. Liu, H.; Wang, S.; Luo, Y.; Tang, W.; Yu, G.; Li, L.; Chen, C.; Liu, Y.; Xi, F. *J. Mater. Chem.* **2001**, 11, 3063.
21. Béra-Abérem, M.; Ho, H.-A.; Leclerc, M. *Tetrahedron* **2004**, 60, (49), 11169.

22. Chen, Z.; Xue, C.; Shi, W.; Luo, F. T.; Green, S.; Chen, J.; Liu, H. *Anal. Chem.* **2004**, 76, (21), 6513-6518.
23. Tang, Y. H., F.; Yu, M.; Feng, F.; An, L.; Sun, H.; Wang, S.; Li, Y.; Zhu, D. *Macromol. Rapid Commun.* **2006**, 27, (6), 389.
24. Ding, A.-L. P., J.; Yu, W.-L.; Lai, Y.-H.; Huang, W. *Thin Solid Films* **2002**, 417, (1-2), 198.
25. Saxena, A.; Fujiki, M.; Rai, R.; Kim, S.-Y.; Kwak, G. *Macromol. Rapid Commun.* **2004**, 25, (20), 1771-1775.
26. Wu, C.-Y.; Chen, M.-S.; Lin, C.-A.; Lin, S.-C.; Sun, S.-S. *Chem. Eur. J.* **2006**, 12, (8), 2263-2269.
27. Yang, J. S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, 120, (46), 11864-11873.
28. Content, S.; Trogler, W. C.; Sailor, M. J. *Chem. Eur. J.* **2000**, 6, (12), 2205-2213.
29. Ding, L.; Russell, T. P. *Macromolecules* **2007**, 40, (6), 2267-2270.
30. Manickasundaram, S.; Kannan, P.; Hassan, Q.; Palanisamy, P. *J. Mater. Sci.: Materials in Electronics* **2008**, 19, (11), 1045-1053.
31. Li, N.; Xu, Q.; Lu, J.; Xia, X.; Wang, L. *Macromol. Chem. Phys.* **2007**, 208, (4), 399-404.
32. Deng, L.; Furuta, P. T.; Garon, S.; Li, J.; Kavulak, D.; Thompson, M. E.; Frechet, J. M. J. *Chem. Mater.* **2006**, 18, (2), 386-395.
33. Smitha, P.; Asha, S. K. *J. Phys. Chem. B* **2007**, 111, (23), 6364-6373.

34. Economopoulos, S. P.; Chochos, C. L.; Gregoriou, V. G.; Kallitsis, J. K.; Barrau, S.; Hadziioannou, G. *Macromolecules* **2007**, 40, (4), 921-927.
35. Bacher, E.; Bayerl, M.; Rudati, P.; Reckefuss, N.; Muller, C. D.; Meerholz, K.; Nuyken, O. *Macromolecules* **2005**, 38, (5), 1640-1647.
36. Pierre, L. L. B.; Edouard, T. O.; Francoise, S.; Jean, P. M.; Isabelle, L.; Noella, L.; Robert, P.; Vesna, S.; Hugh, D.; Gareth, R.; Brigitte, L. In *Detection of nitroaromatic compounds based on photoluminescent side chain polymers*. John, C. C.; Arturas, Z.; Anthony, W. V.; James, G. G.; Francois, K., Eds. SPIE: 2005; p 59900S.
37. Aamer, K. A.; Tew, G. N. *Macromolecules* **2007**, 40, (8), 2737-2744.
38. Chen, B.; Sleiman, H. F. *Macromolecules* **2004**, 37, (16), 5866-5872.
39. Rezvani, A.; Bazzi, H. S.; Chen, B.; Rakotondradany, F.; Sleiman, H. F. *Inorg. Chem.* **2004**, 43, (16), 5112-5119.
40. Wang, X. Y.; Prabhu, R. N.; Schmehl, R. H.; Weck, M. *Macromolecules* **2006**, 39, (9), 3140-3146.
41. Carlise, J. R.; Wang, X. Y.; Weck, M. *Macromolecules* **2005**, 38, (22), 9000-9008.
42. Kimyonok, A.; Domercq, B.; Haldi, A.; Cho, J. Y.; Carlise, J. R.; Wang, X. Y.; Hayden, L. E.; Jones, S. C.; Barlow, S.; Marder, S. R.; Kippelen, B.; Weck, M. *Chem. Mater.* **2007**, 19, (23), 5602-5608.
43. Wang, X.-Y.; Kimyonok, A.; Weck, M. *Chem. Commun.* **2006**, (37), 3933-3935.
44. Carlise, J. R.; Weck, M. *J. Poly. Sci. A: Polym. Chem.* **2004**, 42, (12), 2973-2984.

45. Kimyonok, A.; Weck, M. *Macromol. Rapid Commun.* **2007**, 28, (2), 152-157.
46. Kimyonok, A.; Xiang-Yong, W.; Weck, M. *Polym. Rev.* **2006**, 46, (1), 47-77.
47. Jäkle, F., Boron: Organoboranes. In *Encyclopedia of Inorganic Chemistry*, 2nd ed.; King, R. B., Ed. Wiley: Chichester, 2005, 560-598.
48. Yamaguchi, S.; Akiyama, S.; Tamao, K. *J. Organomet. Chem.* **2002**, 652, (1-2), 3-9.
49. Yamaguchi, S.; Akiyama, S.; Tamao, K. *J. Am. Chem. Soc.* **2000**, 122, (26), 6335-6336.
50. Venkatasubbaiah, K.; Pakkirisamy, T.; Doshi, A.; Lalancette, R. A.; Jäkle, F. *Dalton Trans.* **2008**, 4507 - 4513.
51. Qin, Y.; Kiburu, I.; Shah, S.; Jakle, F. *Org. Lett.* **2006**, 8, (23), 5227-5230.
52. Jäkle, F., *Encyclopedia of Inorganic Chemistry*. 2nd ed.; Wiley-VCH: 2005.
53. Roesler, R.; Har, B. J. N.; Piers, W. E. *Organometallics* **2002**, 21, (21), 4300-4302.
54. Weber, L.; Werner, V.; Domke, I.; Stammmler, H.-G.; Neumann, B. *Dalton Trans.* **2006**, 3777 - 3784.
55. Entwistle, C. D.; Marder, T. B. *Chem. Mater.* **2004**, 16, (23), 4574-4585.
56. Wakamiya, A.; Mori, K.; Yamaguchi, S. *Angew. Chem. Int. Ed.* **2007**, 46, (23), 4273-4276.
57. Zhao, C. H.; Wakamiya, A.; Inukai, Y.; Yamaguchi, S. *J. Am. Chem. Soc.* **2006**, 128, (50), 15934-15935.

58. Jia, W. L.; Moran, M. J.; Yuan, Y.-Y.; Lu, Z. H.; Wang, S. *J. Mater. Chem.* **2005**, 15, 3326 - 3333.
59. Fenghong, L.; Wenli, J.; Suning, W.; Yiqun, Z.; Zheng-Hong, L. *J. Appl. Phys.* **2008**, 103, (3), 034509.
60. Shirota, Y.; Kageyama, H. *Chem. Rev.* **2007**, 107, (4), 953-1010.
61. Mazzeo, M.; Vitale, V.; Della Sala, F.; Anni, M.; Barbarella, G.; Favaretto, L.; Sotgiu, G.; Cingolani, R.; Gigli, G. *Adv. Mater.* **2005**, 17, (1), 34-39.
62. Kinoshita, M.; Kita, H.; Shirota, Y. *Adv. Func. Mater.* **2002**, 12, (11-12), 780-786.
63. Wu, Q.; Esteghamatian, M.; Hu, N. X.; Popovic, Z.; Enright, G.; Tao, Y.; D'Iorio, M.; Wang, S. *Chem. Mater.* **2000**, 12, (1), 79-83.
64. Qin, Y.; Kiburu, I.; Shah, S.; Jäkle, F. *Org. Lett.* **2006**, 8, (23), 5227-5230.
65. Jäkle, F. *J. Inorg. Organomet. Polym. Mater.* **2005**, 15, (3), 293-307.
66. Liu, Z. Q.; Shi, M.; Li, F. Y.; Fang, Q.; Chen, Z. H.; Yi, T.; Huang, C. H. *Org. Lett.* **2005**, 7, (24), 5481-5484.
67. Cui, Y.; Li, F.; Lu, Z.-H.; Wang, S. *Dalton Trans.* **2007**, 2634 - 2643.
68. Sun, Y.; Ross, N.; Zhao, S. B.; Huszarik, K.; Jia, W. L.; Wang, R. Y.; Macartney, D.; Wang, S. *J. Am. Chem. Soc.* **2007**, 129, (24), 7510-7511.
69. Liu, X. Y.; Bai, D. R.; Wang, S. *Angew. Chem. Int. Ed.* **2006**, 45, (33), 5475-5478.
70. Bai, D.-R.; Liu, X.-Y.; Wang, S. *Chem. Eur. J.* **2007**, 13, (20), 5713-5723.

71. Zhao, Q.; Li, F.; Liu, S.; Yu, M.; Liu, Z.; Yi, T.; Huang, C. *Inorg. Chem.* **2008**, 47, (20), 9256-9264.
72. Melaimi, M.; Gabbai, F. P. *J. Am. Chem. Soc.* **2005**, 127, (27), 9680-9681.
73. Zhao, S. B.; McCormick, T.; Wang, S. *Inorg. Chem.* **2007**, 46, (26), 10965-10967.
74. Hudnall, T. W.; Gabbai, F. P. *Chem. Commun.* **2008**, 4596 - 4597.
75. Dorsey, C. L.; Jewula, P.; Hudnall, T. W.; Hoefelmeyer, J. D.; Taylor, T. J.; Honesty, N. R.; Chiu, C.-W.; Schulte, M.; Gabbai, F. P. *Dalton Trans.* **2008**, 4442 - 4450.
76. Hudnall, T. W.; Kim, Y.-M.; Bebbington, M. W. P.; Bourissou, D.; Gabbai, F. P. *J. Am. Chem. Soc.* **2008**, 130, (33), 10890-10891.
77. Ekmekci, Z.; Yilmaz, M. D.; Akkaya, E. U. *Org. Lett.* **2008**, 10, (3), 461-464.
78. Maeda, H.; Fujii, Y.; Mihashi, Y. *Chem. Commun.* **2008**, 4285 - 4287.
79. Kolel-Veetil, M. K.; Keller, T. M. The State of the Art in Boron Polymer Chemistry. In *Macromolecules Containing Metal and Metal-Like Elements, Volume 8, Boron-Containing Polymers*. Abd-El-Aziz, A. S.; Carraher Jr., C. E.; Pittman Jr., C. U.; Sheats, J. E.; Zeldin, M., Eds. John Wiley & Sons: Hoboken, 2007.
80. Jäkle, F. *Coord. Chem. Rev.* **2006**, 250, (9-10), 1107-1121.
81. Corriu, R. J.-P.; Deforth, T.; Douglas, W. E.; Guerrero, G.; Deforth, T.; Siebert, W. S. *Chem. Commun.* **1998**, 963 - 964.
82. Matsumi, N.; Chujo, Y. *Polym. J.* **2008**, 40, (2), 77-89.

83. Matsumi, N.; Naka, K.; Chujo, Y. *J. Am. Chem. Soc.* **1998**, 120, (20), 5112-5113.
84. Matsumi, N.; Chujo, Y.; Lavastre, O.; Dixneuf, P. H. *Organometallics* **2001**, 20, (12), 2425-2427.
85. Matsumoto, F.; Matsumi, N.; Chujo, Y. *Polym. Bull.* **2001**, 46, (4), 257-262.
86. Fontani, M.; Peters, F.; Scherer, W.; Wachter, W.; Wagner, M.; Zanello, P. *Eur. J. Inorg. Chem.* **1998**, 1998, (10), 1453-1465.
87. Grosche, M.; Herdtweck, E.; Peters, F.; Wagner, M. *Organometallics* **1999**, 18, (22), 4669-4672.
88. Jäkle, F.; Berenbaum, A.; Lough, A. J.; Manners, I. *Chem. Eur. J.* **2000**, 6, (15), 2762-2771.
89. Heilmann, J. B.; Qin, Y.; Jäkle, F.; Lerner, H.-W.; Wagner, M. *Inorg. Chim. Acta* **2006**, 359, 4802–4806.
90. Heilmann, J. B.; Scheibitz, M.; Qin, Y.; Sundararaman, A.; Jäkle, F.; Kretz, T.; Bolte, M.; Lerner, H.-W.; Holthausen, M. C.; Wagner, M. *Angew. Chem. Int. Ed.* **2006**, 45, 920 –925.
91. Ma, K.; Scheibitz, M.; Scholz, S.; Wagner, M. *J. Organomet. Chem.* **2002**, 652, (1-2), 11-19.
92. Matsumi, N.; Naka, K.; Chujo, Y. *J. Am. Chem. Soc.* **1998**, 120, 10776-10777.
93. Sundararaman, A.; Victor, M.; Varughese, R.; Jäkle, F. *J. Am. Chem. Soc.* **2005**, 127, (40), 13748-13749.

94. Matsumoto, F.; Chujo, Y. *Macromolecules* **2003**, 36, (15), 5516-5519.
95. Matsumoto, F.; Chujo, Y. *Pure Appl. Chem.* **2006**, 78, (7), 1407-1411.
96. Matsumoto, F.; Nagata, Y.; Chujo, Y. *Polym. Bull.* **2005**, 53, (3), 155-160.
97. Nagata, Y.; Chujo, Y. *Macromolecules* **2007**, 40, (1), 6-8.
98. Nagata, Y.; Chujo, Y. *Macromolecules* **2008**, 41, (8), 2809-2813.
99. Nagata, Y.; Chujo, Y. *Macromolecules* **2008**, 41, (10), 3488-3492.
100. Nagata, Y.; Otaka, H.; Chujo, Y. *Macromolecules* **2008**, 41, (3), 737-740.
101. Nicolas, M.; Fabre, B.; Marchand, G.; Simonet, J. *Eur. J. Org. Chem.* **2000**, (9), 1703-1710.
102. Nicolas, M.; Fabre, B.; Simonet, J. *J. Electroanal. Chem.* **2001**, 509, (1), 73-79.
103. Deore, B. A.; Braun, M. D.; Freund, M. S. *Macromol. Chem. Phys.* **2006**, 207, (7), 660-664.
104. Shoji, E.; Freund, M. S. *Langmuir* **2001**, 17, (23), 7183-7185.
105. Shoji, E.; Freund, M. S. *J. Am. Chem. Soc.* **2001**, 123, (14), 3383-3384.
106. Shoji, E.; Freund, M. S. *J. Am. Chem. Soc.* **2002**, 124, (42), 12486-12493.
107. Deore, B. A.; Yu, I.; Woodmass, J.; Freund, M. S. *Macromol. Chem. Phys.* **2008**, 209, (11), 1094-1105.
108. Ali, S. R.; Ma, Y.; Parajuli, R. R.; Balogun, Y.; Lai, W. Y. C.; He, H. *Anal. Chem.* **2007**, 79, (6), 2583-2587.

109. Ma, Y.; Ali, S. R.; Wang, L.; Chiu, P. L.; Mendelsohn, R.; He, H. *J. Am. Chem. Soc.* **2006**, 128, (37), 12064-12065.
110. Ma, Y.; Ali, S. R.; Dodoo, A. S.; He, H. *J. Phys. Chem. B* **2006**, 110, (33), 16359-16365.
111. Ma, Y.; Chiu, P. L.; Serrano, A.; Ali, S. R.; Chen, A. M.; He, H. *J. Am. Chem. Soc.* **2008**, 130, (25), 7921-7928.
112. Ma, Y.; Cheung, W.; Wei, D.; Bogozi, A.; Chiu, P. L.; Wang, L.; Pontoriero, F.; Mendelsohn, R.; He, H. *ACS Nano* **2008**, 2, (6), 1197-1204.
113. Elbing, M.; Bazan, Guillermo C. *Angew. Chem. Int. Ed.* **2008**, 47, (5), 834-838.
114. Li, H.; Sundararaman, A.; Venkatasubbaiah, K.; Jäkle, F. *J. Am. Chem. Soc.* **2007**, 129, (18), 5792-5793.
115. Zhao, C. H.; Wakamiya, A.; Yamaguchi, S. *Macromolecules* **2007**, 40, (11), 3898-3900.
116. Lennarz, W. J.; Snyder, H. R. *J. Am. Chem. Soc.* **1960**, 82, (9), 2169-2171.
117. Letsinger, R. L.; Hamilton, S. B. *J. Am. Chem. Soc.* **1959**, 81, (12), 3009-3012.
118. Qin, Y.; Sukul, V.; Pagakos, D.; Cui, C.; Jäkle, F. *Macromolecules* **2005**, 38, (22), 8987-8990.
119. Roy, D.; Cambre, J. N.; Sumerlin, B. S. *Chem. Commun.* **2008**, (21), 2477-2479.
120. Ramakrishnan, S.; Berluche, E.; Chung, T. C. *Macromolecules* **1990**, 23, (2), 378-382.

121. Chung, T. C.; Janvikul, W. *J. Organomet. Chem.* **1999**, 581, (1-2), 176-187.
122. Ramakrishnan, S.; Chung, T. C. *Macromolecules* **1989**, 22, (7), 3181-3183.
123. Wolfe, P. S.; Wagener, K. B. *Macromol.* **1999**, 32, (24), 7961-7967.
124. Branger, C.; Lequan, M.; Lequan, R. M.; Large, M.; Kajzar, F. *Chem. Phys. Lett.* **1997**, 272, (3-4), 265-270.
125. Mutaguchi, D.; Okumoto, K.; Ohseido, Y.; Moriwaki, K.; Shirota, Y. *Org. Electronics* **2003**, 4, (2-3), 49-59.
126. Kageyama, H.; Mutaguchi, D.; Hashimoto, K.; Nagamatsu, D.; Tanaka, M.; Okumoto, K.; Ohseido, Y.; Shirota, Y. In *Hole-transporting and emitting pendant polymers for organic electroluminescent devices*. Zakya, H. K.; Franky, S., Eds. SPIE: 2006; p 63330G.
127. Qin, Y.; Pagba, C.; Piotrowiak, P.; Jäkle, F. *J. Am. Chem. Soc.* **2004**, 126, (22), 7015-7018.
128. Wang, X. Y.; Weck, M. *Macromolecules* **2005**, 38, (17), 7219-7224.
129. Taken in part from references 130-132.
130. Qin, Y.; Cheng, G.; Sundararaman, A.; Jäkle, F. *J. Am. Chem. Soc.* **2002**, 124, (43), 12672-12673.
131. Qin, Y.; Cheng, G.; Parab, K.; Achara, O.; Jäkle, F. *Macromolecules* **2004**, 37, 7123-7131.

132. Qin, Y.; Sukul, V.; Pagakos, D.; Cui, C.; Jäkle, F. *Macromolecules* **2005**, 38, (22), 8987-8990.
133. This chapter has been adapted from ref 134.
134. Parab, K.; Venkatasubbaiah, K.; Jäkle, F. *J. Am. Chem. Soc.* **2006**, 128, (39), 12879-12885.
135. Sundararaman, A.; Jäkle, F. *J. Organomet. Chem.* **2003**, 681, (1-2), 134-142.
136. Parab, K.; Yang, Q.; Haleem, S.; Jäkle, F. *Polym. Mater. Sci. Eng. Prepr.* **2005**, 93, 422-423.
137. Melucci, M.; Barbarella, G.; Zambianchi, M.; Benzi, M.; Biscarini, F.; Cavallini, M.; Bongini, A.; Fabbroni, S.; Mazzeo, M.; Anni, M.; Gigli, G. *Macromolecules* **2004**, 37, (15), 5692-5702.
138. DFT calculations were performed with the Gaussian03 program (Revision C. 02, Frisch, M. J.; et al.; Gaussian, Inc.: Wallingford CT, 2004). Geometries and electronic properties were calculated by means of the hybrid density functional B3LYP with the basis set of 6-31G(d). The input files and orbital representations were generated using Gaussview. Excitation data were calculated using TD-DFT (B3LYP) methods.
139. Yamaguchi, S.; Akiyama, S.; Tamao, K. *J. Am. Chem. Soc.* **2001**, 123, 11372-11375.
140. Geddes, C. D. *Meas. Sci. Technol.* **2001**, 12, (9), R53-R88.
141. Antonisse, M. M. G.; Reinhoudt, D. N. *Chem. Commun.* **1998**, 443 - 448.

142. Bianchi, A.; García-España, E. Thermodynamics of Anion Complexation. Bianchi, A. Bowman-James, K.; García-España, E., Eds., *Supramolecular Chemistry of Anions*. Wiley-VCH: New York, 1997.
143. Broadwater, S. J.; Hickey, M. K.; McQuade, D. T. *J. Am. Chem. Soc.* **2003**, 125, (37), 11154-11155.
144. Badugu, R.; Lakowicz, J. R.; Geddes, C. D. *Dyes and Pigments* **2005**, 64, (1), 49-55.
145. Rider, D. A.; Winnik, M. A.; Manners, I. *Chem. Commun.* **2007**, (43), 4483-4485.
146. Qin, Y.; Cheng, G.; Achara, O.; Parab, K.; Jäkle, F. *Macromolecules* **2004**, 37, (19), 7123-7131.
147. Entwistle, C. D.; Marder, T. B. *Angew. Chem. Int. Ed.* **2002**, 41, (16), 2927-2931.
148. Sarbu, T. L., K.-Y.; Spanswick, J.; Gil, R. R.; Siegwart, D. J.; Matyjaszewski, K. *Macromolecules* **2004**, 37, (26), 9694-9700.
149. Rieger, J. J. *Thermal Anal.* **1996**, 46, (3-4), 965-972
150. Scheibitz, M.; Bolte, M.; Bats, J. W.; Lerner, H.-W.; Nowik, I.; Herber, R. H.; Krapp, A.; Lein, M.; Holthausen, M.; Wagner, M. *Chem. Eur. J.* **2005**, 11, (2), 584-603.
151. Carpenter, B. E.; Piers, W. E.; Parvez, M.; Yap, G. P. A.; Rettig, S. J. *Can. J. Chem.* **2001**, 79, 857-867.
152. Broomsgrove, A. E. J.; Addy, D. A.; Bresner, C.; Fallis, I. A.; Thompson, A. L.; Aldridge, S. *Chem. Eur. J.* **2008**, 14, (25), 7525-7529.

153. Elsner, O.; Ruiz-Molina, D.; Ratera, I.; Vidal-Gancedo, J.; Rovira, C.; Veciana, J. *J. Organomet. Chem.* **2001**, 637-639, 251-257.
154. Donald, R. S.; Ralph, S. B. *J. Chem. Phys.* **1961**, 35, (2), 516-531.
155. Venkatasubbaiah, K.; Doshi, A.; Nowik, I.; Herber, Rolfe H.; Rheingold, Arnold L.; Jäkle, F. *Chem. Eur. J.* **2008**, 14, (2), 444-458.
156. Witker, D.; Reynolds, J. R. *Macromolecules* **2005**, 38, (18), 7636-7644.
157. Li, Y.; Ding, J.; Day, M.; Tao, Y.; Lu, J.; D'iorio, M.; *Chem. Mater.* 2004, 16, (11), 2165-2173.
158. Liu, B.; Bazan, G. C. *Chem. Mater.* **2004**, 16, (23), 4467-4476.
159. Iraqi, A.; Simmance, T. G.; Yi, H.; Stevenson, M.; Lidzey, D. G. *Chem. Mater.* **2006**, 18, (24), 5789-5797.
160. Hou, Q.; Xu, Y.; Yang, W.; Yuan, M.; Peng, J.; Cao, Y. *J. Mater. Chem.* **2002**, 12, 2887-2892.
161. Wang, F.; Yang, Y.; Swager, T. M. *Angew. Chem. Int. Ed.* **2008**, 47, (44), 8394-8396.
162. Petersen, M. H.; Gevorgyan, S. A.; Krebs, F. C. *Macromolecules* **2008**, 41 (23), 8986-8994.
163. Zhan'ao, T.; Erjun, Z.; Xiaowei, Z.; Xiang, W.; Yongfang, L.; Stephen, B.; Seth, R. *M. Appl. Phys. Lett.* **2008**, 93, (7), 073309.
164. Bolognesi, A.; Botta, C.; Cecchinato, L.; Fattori, V.; Cocchi, M. *Synth. Met.* **1999**, 106, (3), 183-186.

165. Inganäs, O.; Berggren, M.; Andersson, M. R.; Gustafsson, G.; Hjertberg, T.; Wennerström, O.; Dyreklev, P.; Granström, M. *Synth. Met.* **1995**, 71, (1-3), 2121-2124.
166. Andersson, M. R.; Berggren, M.; Gustafsson, G.; Hjertberg, T.; Inganäs, O.; Wennerström, O. *Synth. Met.* **1995**, 71, (1-3), 2183-2184.
167. Hobbs, M. G.; Baumgartner, T. *Eur. J. Inorg. Chem.* **2007**, 2007, (23), 3611-3628.
168. Imae, I.; Nawa, K.; Ohsedo, Y.; Noma, N.; Shirota, Y. *Macromolecules* **1997**, 30, (3), 380-386.
169. Trumbo, D. L. *Polym. Bull. (Berlin)* **1994**, 33, 75-82.
170. Imae, I.; Noma, N.; Shirota, Y. *Synth. Met.* **1997**, 85, (1-3), 1385-1386.
171. Meeker, D. L.; Mudigonda, D. S. K.; Osborn, J. M.; Loveday, D. C.; Ferraris, J. P. *Macromolecules* **1998**, 31, (9), 2943-2946.
172. Lukevics, E.; Barbarella, G.; Arsenyan, P.; Shestakova, I.; Belyakov, S.; Popelis, J.; Pudova, O. *J. Organomet. Chem.* **2001**, 636, (1-2), 26-30.
173. Lenze, N.; Neumann, B.; Salmon, A.; Stammel, A.; Stammel, H.-G.; Jutzi, P. *J. Organomet. Chem.* **2001**, 619, 74-87.
174. Rebiere, F.; Samuel, O.; Kagan, H. B. *Tetrahedron Lett.* **1990**, 31, 3121-3124.
175. Siedel, W.; Burger, I. *Anorg. Allg. Chem.* **1978**, 447, 199.
176. Scott, Natalie M.; Schareina, T.; Tok, O.; Kempe, R. *Eur. J. Inorg. Chem.* **2004**, (16), 3297-3304.

177. Miller, A. R.; Curtin, D. Y. *J. Am. Chem. Soc.* **1976**, 98, (7), 1860-1865.
178. Eriksson, H.; Hakansson, M. *Organometallics* **1997**, 16, (20), 4243-4244.
179. Nobel, D.; Koten, G. v.; Spek, A. L. *Angew. Chem.* **1989**, 101, (2), 211-213.
180. Wong, K.-T.; Chen, Y.-M.; Lin, Y.-T.; Su, H.-C.; Wu, C.-c. *Org. Lett.* **2005**, 7, (24), 5361-5364.
181. Murov, S. L.; Carmichael, I.; Hug, G. L., *Handbook of Photochemistry*. 2nd ed.; Marcel Dekker Inc.: New York, 1993.
182. Sheldrick, G. *SHELXTL (5.10)*; Bruker XRD, Madison, WI.

Appendix – List of Publications

1. “Synthesis and Characterization of Electroactive Triarylborane Polymers.” **Parab, K.**; Jäkle, F. *Manuscript in prep.*
2. “Luminescent Triarylborane-Functionalized Polystyrene: Synthesis, Photophysical Characterization, and Anion Binding Studies.” **Parab, K.**; Venkatasubbaiah, K.; Jäkle, F. *J. Am. Chem. Soc.* **2006**, *128*, 12879-12885.
3. “A New Route to Organoboron Polymers via Highly Selective Polymer Modification Reactions.” Qin, Y.; Cheng, G.; Achara, O.; **Parab, K.**; Jäkle, F. *Macromolecules* **2004**, *37*, 7123-7131.
4. “Lewis Acidic Organoboron Polymers.” Qin, Y.; Cheng, G.; **Parab, K.**; Sundararaman, A.; Jäkle, F. *Macromolecular Symposia* **2003**, *196*, 337-345.

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Educational Background

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Degree achieved: B.Sc. in Chemistry.

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2002 – Present Department of Chemistry, Rutgers University-Newark, Newark, NJ.
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Awards

- Principal C.T. Bhastana Award for achieving highest marks in Organic Chemistry, 1999.
- Graduate Research Poster Award at 38th Middle Atlantic Regional Meeting, 2006.