FILM STABILIZATION AND PHOTOPHYSICS OF UNCONVENTIONAL CONJUGATED POLYMERS

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FILM STABILIZATION AND PHOTOPHYSICS OF UNCONVENTIONAL CONJUGATED POLYMERS

A Dissertation Presented

By

KARA MARTIN

Submitted to the Graduate School of the University of Massachusetts Amherst in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

SEPTEMBER 2018

Polymer Science and Engineering
FILM STABILIZATION AND PHOTOPHYSICS OF UNCONVENTIONAL
CONJUGATED POLYMERS

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By

KARA MARTIN

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ABSTRACT

FILM STABILIZATION AND PHOTOPHYSICS OF UNCONVENTIONAL CONJUGATED POLYMERS

SEPTEMBER 2018

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Directed by: Professor Kenneth R. Carter

Conjugated polymers offer a unique opportunity to develop high performing, flexible, lightweight, and large area electronic devices. With advances in conjugated polymer understanding and synthesis, the use of polymers as active layer materials in electronic applications, rather than just substrate materials, has become more promising. However, defects in morphological stability, as well as imperfect electronic understanding, are still present, limiting the use of these materials in commercializable electronics. Fundamental understanding of structure-property relationships can allow for facile synthetic solutions to major drawbacks of conjugated polymer integration in standard device architectures. Chapter 1 presents background research on the history of conjugated polymer development and the electronic device architectures these materials are typically incorporated in.

Chapter 2 presents the use of thiol-ene chemistry to stabilize poly(3-alkylthiophene) films through a grafting-to procedure. This offers a simple way to produce highly oriented, insoluble, semi-conducting films through facile synthetic tuning of the polymers end-groups and side chains. In Chapter 3, the photophysics of carborane containing poly(dihexylfluorene) polymers is discussed. These unique class of materials
experience drastic solvatochromism making them highly coveted for simple sensing applications. Through extensive spectroscopic investigations, a complete understanding of the excited-state dynamics is presented. Chapter 4 extends on Chapter 3 by demonstrating a straightforward method to synthesize carborane containing poly(dihexylfluorene)s with emissive properties that change with fluorene conjugation length, allowing for emission color tuning of the polymer solid and solution states. Lastly, Chapter 5 presents the synthesis of novel poly(bisthienyl carborane) and poly(bisthienyl carborane-alt-thiophene) is presented. This is the first example of a soluble conjugated polymer implementing a strong donor aromatic group and a strong acceptor carborane junction in the repeat unit. The fascinating excited-state characteristics are determined through femtosecond and nanosecond spectroscopy, showing the polymer can promote triplet formation on the carborane unit, making it useful for triplet sensitization applications.

The work presented in this thesis shows that straightforward synthetic techniques can be used to highly affect the properties of common conjugated polymers, making them more robust or beneficial for electronic applications. Side-chain and backbone engineering is a necessary technique for furthering the development of useful and applicable “plastic” electronics.
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CHAPTER 1

USING CHEMISTRY TO ALTER AND TUNE THE STRUCTURE AND ELECTRONIC PROPERTIES OF CONJUGATED POLYMERS

1.1 Introduction to Conjugated Polymers

The promise of lightweight, economical, transparent, and flexible electronics that have comparable charge transport properties to heavier, rigid, non-recyclable solid-state inorganic devices motivates research into conjugated polymers. While polymeric materials have found their way into substrate applications for device structures, the realization of a full organic electronic device requires high performing conducting or semi-conducting “plastics”. The onset of conjugated or conducting polymer research began in the 1970s with the discovery and synthesis of cis and trans poly(acetylene), from exposure of acetylene to a Ziegler catalyst to form metallic looking films\textsuperscript{1-5}. Chemically doping, introducing charge carriers to the conjugated pi-system, significantly increases conductivities of this already conductive material to be comparable to metallic conductivities ($10^5$ S/cm)\textsuperscript{6}. The mode of charge propagation in conjugated polymers comes from delocalization of electrons throughout the aromatic backbone of the material\textsuperscript{7-9}. Aromatic systems include alternating saturated and unsaturated carbon bonds, which leads to overlapping p-orbitals over the σ bonds, lowering the energy of the system and allowing π electron delocalization through those overlapping p-orbitals (Figure 1.1)\textsuperscript{10}. Delocalization facilitates lower energy charge injection, excitation, or doping. At the time, doped poly(acetylene) was the leading conductive polymer with regards to conductivity measurements, with doped poly(thiophene) and doped poly(pyrrole) showing lower
conductivities (<200 S/cm), with these values decreasing with decreasing temperatures. Over the course of 10 years, conductivities were improved with a greater understanding of charge transport failure mechanisms, such as morphological inconsistencies in the polymeric film, and the interaction of the charged polymer with light, synthetic diversity in the polymeric repeat structure as well as doping mechanisms, and conductivity dependence on environmental factors like temperature$^7,11-12$.

Figure 1.1: Schematic showing delocalization of $\pi$ electrons along the backbone of hexa-1,3,5-triene (top) and energy band schematic showing $\pi$ and $\pi^*$ bands for ethylene, 1,3-dibutadiene, oligo(acetylene), and poly(acetylene) (bottom). With conjugation, discrete $\pi$ bands increase and become closer, making continuous low energy bands.
In 1985, the synthesis of the first fully solubilizable poly(thiophene) derivative was carried out by adding a hexyl side chain to the 3-position on the thiophene ring to produce poly(3-hexylthiophene) (P3HT)\textsuperscript{13-16}. Side-chain engineering offered a new way to produce conjugated polymers with higher molecular weights, corresponding to longer conjugation lengths, as well as materials with side-chain induced self-assembling long-range crystallinity allowing for the formation of well-ordered, higher conducting films\textsuperscript{17}. Additionally, side-chains included in the conjugated polymer structure allowed for the synthesis of materials that could be readily solubilized in a variety of solvents, and in some cases even water\textsuperscript{18-21}. Solution processability is a considerable advantage over the canonical conducting polymers, which are insoluble at high molecular weights and typically synthesized through electropolymerization onto a metallic substrate. While oligomeric versions of these materials can be solution polymerized, this synthesis usually results in high percentages of insoluble material, which limits the potential use of such materials in wide-scale commercial electronics applications. Solubilizing polymer through side-chain engineering, enables the polymerization of higher molecular weight materials, greater repeat unit diversity, and materials with fewer backbone defects, increasing the conjugation length of the polymer and therefore improving electronic properties. The ability to produce solution processable, highly variable, materials into uniform films that include long-range crystalline structures is the hallmark of conjugated polymers, and the most significant argument for their employment in electronic device architectures over inorganic materials, which have intrinsically higher conductivities\textsuperscript{21-23}.
Following the synthetic integration of distinctive side chains into aromatic molecules for soluble conjugated polymer synthesis, began the synthesis of unique aromatic building blocks for the generation of novel conjugated polymers. Diverse aromatic repeat units have allowed for a library of conjugated materials with various characteristics to be developed, making them useful in a wide variety of device applications, including organic/polymeric light emitting diodes, field effect transistors, photovoltaic cells, and sensors. Some fundamental building blocks typically used in conjugated polymer design include fluorene, thiophene, phenyl, benzothiadiazole, and rylene diimide based aromatic monomers (Figure 1.2). The electronic and structural properties of each of these building blocks have significant impacts on the characteristics distinctive to the final synthesized, conjugated polymer. For example, the choice of building block can profoundly affect the band gap, mode of charge propagation, thin film crystal structure, light absorption, and excited-state properties of the synthesized, conjugated polymer. The aromatic repeat unit can also affect how a conjugated polymer conducts charge, whether that be holes (p-type) or electrons (n-type). Tuning the conjugated polymer repeat unit structure can allow for the refinement of specific characteristics which can aid in the development of higher performing organic electronics. While particular attributes of a specific repeat unit design may be advantageous for some electronic architectures, they can also be detrimental to others. For instance, polymerization of this monomer to poly(9,9-dihexylfluorene) yields a material that experiences low degrees of crystallinity in the thin film, without extensive treatment to produce the crystalline beta-phase, and is typically entirely amorphous due to the high degree of rotation between the aromatic bonds. Rotational freedom allows for the
material to be highly emissive in the solid-state making it coveted for light emitting diode applications, something more crystalline conjugated polymers, like poly(3-hexylthiophene), are not capable of due to intermolecular quenching\textsuperscript{29-30}. However, this material does not propagate holes well because of the amorphous nature and therefore has very low hole mobilities in field effect transistor structures. Synthetically tuning conjugated polymer backbones and side chains can offer a handle on solubility, charge propagation, and desired application. It is necessary to understand the fundamentals on how synthetic tuning affects material properties to synthesize polymers with characteristics in line with the device applications.

Figure 1.2: Examples of typical aromatic backbone repeat units used to design conjugated polymers for specific device architectures (a). Examples of synthetically altering end-caps or side-chains to produce conjugated polymers with different properties (b). Adapted from Progress in Polymer Science 38 (2013) 1832–1908
1.2 Electronic Device Structures

The degree of variability found in the backbone or side chains of modern conjugated polymers allows for the integration of these materials into a wide assortment of electronic device architectures. Typically, conjugated polymers are used as active layers, conducting charge through a device structure between electrodes, but can also be useful in interlayer materials. Interlayer materials help with charge injection or collection from active layers and electrodes by aligning the energy levels between both interfaces, and also aiding in more uniform contact between electrodes and active layers\textsuperscript{31-32}. The conventional device structures that employ conjugated polymers as both active layer or interface materials are light emitting diodes (LED), photovoltaic cells (PV), and field effect transistors (FET) (Figure 1.3). Each system requires different polymer properties to be effective, and tuning the backbone and sidechains helps amplify those properties. While these three device structures are described in more detail below and are the relevant applications of the polymers synthesized in this thesis, conjugated polymers are not limited to these three device architectures, and use in a wide variety of applications like electrochromic and sensing devices is standard\textsuperscript{22,33}.

PVs utilize conjugated polymers in the active layer of the device and as interlayer materials. The most common example of organic PVs includes PEDOT:PSS, a standard, commercial conducting polymer dispersed in water, as the hole transport layer and P3HT as the donor material. Accepting materials consist of PCBM (phenyl-C\textsubscript{61}-butyric acid methyl ester) or other functionalized fullerenes. The active layer includes a mixture of both PCBM and P3HT to form a bulk heterojunction. With exposure of the bulk heterojunction sandwiched between two electrodes to the visible light spectrum, P3HT is
excited to its lowest unoccupied molecular orbital (LUMO) or singlet excited state, forming an exciton, which is a bound electron in the LUMO and hole, or absence of the electron, in the highest occupied molecular orbital (HOMO). The excited electron transfers to the acceptor unit, PCBM, known as the dissociation of the exciton, and holes and electrons propagate to the respective electrodes producing current from the cell. The driving force of the electron transfer is the lower energy LUMO of the acceptor unit compared to the donor unit\textsuperscript{34}. The diffusion length of an exciton is \textasciitilde 10 nm, meaning a bulk heterojunction must be well mixed enough that the exciton can make it from the P3HT domain to the PCBM domain. Additionally, the domains must be long enough to make contact with the electrodes. If the domains are significantly phase separated, the exciton will recombine, before being transferred to the acceptor moiety, lowering the efficiency of the PV. For a successful PV, both donor and acceptor moieties need to form bicontinuous interpenetrating nanoscale networks, in addition to possessing a broad absorption over the visible spectrum, have high hole mobilities, and corresponding energy levels\textsuperscript{35-41}. Polymers that are advantageous for solar cell applications form crystalline domains and have low band gaps within the bulk heterojunction to allow for high hole transport through the domain to the electrode\textsuperscript{23,42}. Bulk heterojunction films are usually annealed to initiate the formation of a desired morphology that contains a small degree of crystalline domain formation while maintaining even mixing of both moieties. Over annealing, will phase segregate both domains to the point that there are limited interfaces for exciton dissociation. The basic organic PVs usually consist of a vertical stack of ITO anode, hole transport layer, bulk heterojunction and calcium cathode. Often other interlayers are used to tune the energy levels further for more efficient charge transport.
Organic light emitting diodes are similar in structure to PVs, in that they also consist of a vertically stacked ITO anode, hole transport layers, active layer, hole blocking layers and Ca cathode system. Electrodes inject electrons and holes into the active layer, where they recombine to produce light. Depending on the band gap of the material, the active layer will emit a specific color, with coveted emission colors being, green, red, blue, and white. Polymeric films that emit high quantum yields of light are typically amorphous, as high crystallinity can generate intermolecular emission quenching, lowering the quantum yield. Additionally, oxidation to the active layer, intermolecular phenomenon like excimer formation, and crystallization of the active layer over time can contribute to defects that alter the desired emission color and quantum efficiency. Conjugated polymers with considerable radiative decay from the excited state are also useful for chemical sensing applications in that they can either undergo interesting excited state processes that allow for a change in emission color upon exposure to an analyte, or the analyte might react with the polymer backbone to change the conjugation length and therefore the emission color. Thus, variations of radiative conjugated polymers can find uses in both sensing and LED applications.

Conjugated polymers also can find applications in field effect transistors, which may be the simplest device structure of the described three, consisting of a gate, dielectric, active layer, and source/drain electrodes. The most basic field effect transistor utilized a silicon gate, and silicon dioxide dielectric, as well as gold source and drain electrodes. Applying a voltage across the gate polarizes the dielectric, which injects charges into the active layer material. The charges flow through the channel between the source and drain to produce a current. Typically, conjugated polymers find their way into the active layer of
FET structures and materials that have high hole or electron mobilities are usually highly crystalline\textsuperscript{54-56}. Defects in the crystalline structure can cause charge traps and limit the device activity. Conducting polymers like PEDOT:PSS can also be used as gate or electrode structures because they are highly conductive\textsuperscript{57}. Additionally, depending on the FET architecture, specific microstructures are more beneficial for higher mobilities. For example, P3HT in the edge-on orientation has higher charge mobilities than in the end-on or face-on orientations, because this microstructure promotes charge propagation down the length of the backbone between the source and drain electrodes\textsuperscript{58}.

LED, PV, and FET device structures emerged as inorganic based electronics, and while highly effective, consist of rigid, cumbersome, and costly metallic or metal oxide components. Conjugated polymers, which are chemically variable, economic, and easily processable, open up the possibility of producing these device structures on flexible, large area substrates. However, polymeric materials still suffer from defects, which include short activity lifespans when exposed to environmental or processing conditions, which can diminish the efficiency of all three described devices. Such defects can consist of morphological disorder, film delamination, or oxidation of the polymeric material over time in the active layer film. The instability of conjugated polymeric films to repeated charging, exposure to air, heat, water, as well as solvents and solvent vapors are the most significant drawbacks to their commercialization in electronics.
1.3 Modes of Structural Support of Conjugated Polymer Films

Chemically cross-linking or grafting conjugated polymers in active layer film structures presents a possible solution to extending the lifetime of active layer films when exposed to common environmental or processing stressors. Both techniques for film
stabilization require some chemical functionalization, whether that be of the polymer, the substrate, or both.

Cross-linking has found use as a way to stabilize the morphologies of bulk heterojunctions in PVs as well as the active emissive layers in LEDs\textsuperscript{48, 59-62}. There are numerous methods to produce a cross-linked bulk heterojunction that can include solely cross-linking the donor, the acceptor, binding the donor and acceptor together, or dispersing the donor and accepting materials within a non-conjugated cross-linked matrix\textsuperscript{63-68}. Many of the chemistries used to carry out cross-linking are thermally or light initiated to keep by-products from the active layer. These can include thermally initiated styrenic and diene groups, as well as UV active bromide and azide groups. Chemical moieties used in cross-linking are incorporated as end-caps or within the side chains of the polymers used in the bulk heterojunction. Upon exposure to a specific wavelength or heat, the film is cross-linked, freezing the desired morphology in place. For example, azide functionalized P3HT was thermally cross-linked to PCBM and bulk heterojunctions of the cross-linked film showed no detrimental phase segregation after 15 hrs of annealing, while non-crosslinked films were significantly phase separated\textsuperscript{66}. The balance with cross-linking is the reaction needs to happen at an optimum annealing time, and therefore light initiated cross-linking is ideal in that the film can be annealed to the desired morphology which can be frozen in place by exposure to a specific wavelength, while thermally initiated cross-linking poses the risk of over annealing the film.

Thiol-ene chemistry is a very fast, high yielding, UV light initiated reaction that has found considerable use in cross-linking of LED active layers\textsuperscript{59-61}. For instance, cross-linking vinyl functionalized copolymer of fluorene and fluorenone repeat units with vinyls
incorporated in the side chains with bulky thiol cross-linkers showed a quenching of the undesired green emission associated with oxidized fluorene to fluorenone, as the cross-linker helped break up aggregation in the film. Additionally, tuning the amount and size of cross-linker to functionalized polymer allowed for tuning the intensity of green light from the fluorenone emission as well as blue light from the fluorene emission, allowing for a white emitter to be produced from one polymer. Cross-linking layers of different emissive conjugated polymers through thiol-ene chemistry allowed for each layer to emit individually, which promoted an additive effect of the observed emission color. Blending the same polymers in the active layer film, resulted in one emissive polymer out emitting compared to the other, and therefore the emission color observed was representative of only one component of the blend. Thiol-ene chemistry has not found much use in bulk heterojunction cross-linking, because thiol moieties will preferentially react with PCBM or other fullerene derivatives. It has been useful in cross-linking interlayers, which allow for better interface connectivity and act as a hydrophobic barrier, protecting the active layer from humidity.

Grafting as a mode of film stabilization has typically found more implementation in stabilizing FET active layers than in other device structures, as a way to graft highly oriented dielectrics that seed active layer microstructures. However, grafting is not limited to FET structures and interlayer applications, and active layers of PV devices also benefit from grafting. Grafting presents itself in three possible methods: grafting-from, grafting-through, and grafting-to. In grafting-from, catalysts are anchored on the surface of a substrate, and this functionalized substrate is exposed to polymerization reaction conditions to enable the formation of polymer brushes grown off the substrate surface. The
films formed through grafting-from have a dense brush like morphology and can have thicknesses comparable to spun coat films. Grafting-through is less researched and involves exposing a functionalized substrate to a polymerization which enables the polymer to either grow off or graft to the functionalized substrate. Finally, grafting-to is the simplest method of grafting and entails functionalizing a synthesized polymer with reactive groups that correspond to a functionalized substrate. Introducing the polymer to the substrate can occur in the melt or solution phase, where a chemical reaction proceeds to chemically bind the polymer to the surface. Grafting facilitates the generation of insoluble films, and these grafted films can endure exposure to solvent baths or solvent vapors without delamination or damage to the film. Additionally, grafting can allow for control over the film orientation, as well as precision over the density and position of a polymer on the surface. There is a significant degree of chemistries utilized for all three methods, including metal catalyzed carbon-carbon bond forming reactions, silanization, esterification, and click chemistries, with many of these methods being similar to those described for cross-linking.
A beautiful example of highly ordered, thick conjugated polymer films is reported by Youm et al. In this report, poly(thiophene) was grafting from a surface that was functionalized with a nickel catalyst through Kumada catalyst transfer polymerization. Films were as thick as 100 nm, and through grazing incidence wide-angle scattering, grafted films were shown to be highly ordered with an orientation unique to the graft and unseen in other more established film formation methods\textsuperscript{72}. Moreover, careful placement of the initiator molecule allowed for patterning of the dense poly(thiophene) brushes and the poly(thiophene)s were regioregular, unlike poly(thiophene) films produced through electropolymerization, observed through absorption spectroscopy. This simple method for dense, oriented, insoluble conjugated brushes is not limited to poly(thiophene)s and can be
utilized for a variety of different monomers. Grafting-from using Kumada chemistry has been applied to generate dense \(\sim 10\) nm thick poly(3-methylthiophene) hole transport layers for PV applications. The grafted hole transport layers had comparable performance to the archetypal PEDOT:PSS hole transport layer in P3HT:PCBM based PVs. The advantage of utilizing the poly(3-methylthiophene) hole transport layer is that it is not hydroscopic like PEDOT:PSS. PEDOT:PSS retains small quantities of water and \(O_2\) which contribute to failure in the bulk heterojunction over time. Grafted poly(3-methylthiophene), which is also characterized by insolubility, showed repeated reusability, where finished bulk heterojunctions could be removed by solubilizing those films in good solvents for P3HT/PCBM blends, leaving the interlayer and ITO substrate free for reuse\(^73\).

The major drawback to grafting-from procedures is the length of time needed to produce thick, dense films, which can range anywhere from 6 hrs to 48 hrs. Additionally, it can be challenging to avoid common film defects like loops forming when propagating chain ends terminate the brush polymerization. Loops can also form close to the surface, and consist of only a few monomer units, making the film patchy. Grafting-to is a more straightforward method to produce insoluble polymer brushes\(^74-80\). In many cases, polymers are end-capped with silane groups, and grafting can be as simple as exposing the silane-containing polymers to a \(SiO_2\) substrate to produce well-defined grafts. This method has shown useful for forming dielectrics, with a good example being the grafting of dimethylchlorosilane end-capped poly(styrene) to \(SiO_2\). Lower molecular weight poly(styrene) had higher grafting densities due to the smaller radius of gyration of the polymer, allowing it to diffuse to the surface more efficiently to chemically bind to the surface, while higher molecular weight poly(styrene) has much lower grafting densities.
The grafting density of the dielectric profoundly impacted the crystal structure order of the active layer, and subsequently how well the active layer conducted a charge. Higher grafting densities promoted crystallization of the active layers, while lower grafting densities produced less ordered films. Additionally, grafting dielectrics to the gate/substrate allows for reduced current leakage and pinhole defects due to the covalent attachment of the dielectric brush to the surface. Furthermore, grafting-to can also be used to formulate insoluble active layers for FETs based on a silicon gate/substrate and gold electrode architecture. Utilizing azide-alkyne chemistry, -yne functionalized P3HT is grafted to azide functionalized SiO\textsubscript{2}, and high grafting densities are achieved, allowing for charge transport through the film upon voltage turn on.

Grafting-to is often used to functionalize nanoparticles with polymeric materials to form composite dispersions. For example, using azide-alkyne click chemistry, P3HT was grafted to graphene oxide (GO) dispersions to form a P3HT-GO composite suspended in THF. The photophysical properties of the composite were markedly different from neat P3HT, as well as the P3HT-GO blend. The blend showed P3HT pancaked against the GO sheets due to pi-pi interactions, while the grafts showed brushes of P3HT from the GO surface, due to the covalent attachment of the P3HT end group to the sheet. Additionally, the photoluminescence spectra of the graft showed decreased emission intensity which was thought to be quenching due to an electron transfer from the excited P3HT to the graphene oxide sheet. Upon further investigation of the decay lifetimes associated with the graft, it was observed that the graft was forming a non-radiative ground state complex between the P3HT and the GO, rather than undergoing an excited state photoelectron transfer that would lead to emission quenching. Functionalized P3HT has also been grafted to a wide
variety of metal oxide nanoparticles and metal surfaces utilizing carboxylic acid end capped P3HT that chemisorbs to the metal oxide surface by the promotion of an ionic species consisting of the carboxylate anion and the cationic metal oxide. In this way, grafting-to can aid in the quick formation of covalently bound nanoparticle composites with interesting photophysical properties. The junction formed between the two grafted moieties can help aid in effective exciton dissociation, making this system advantageous for solar cell applications. Additionally, forming this junction between a donor and acceptor system can also facilitate other photophysical processes, including excimer formation, charge transfer states, and ground state phenomena. Grafting a polymer onto a surface can aid in promoting material properties that span use in a variety of applications.

1.4 Fundamentals of Excited State Properties

Synthetically tuning conjugated polymer backbones, side chains, and end-groups allows for the design of materials that can have hallmark application performances, by designing an electronic structure specific to the device application in question, as well as adding side-chain or end group functionalities to aid in stabilizing the active layer film of that conjugated material. Understanding the fundamentals of conjugated polymer systems helps successfully design polymeric backbones for specific device applications. All organic electronic devices operate by generating charge carriers in the aromatic backbone of the polymeric/small molecular active layer. Charge carriers can form when the polymer is excited from the ground state or from the HOMO to the excited LUMO, to create the hole/electron exciton pair. Such excited-state processes can be shown through Jablonski diagrams, which illustrate excitation from the ground state to a higher singlet excited state, which is followed by fast internal conversion to the lowest singlet state
From this state, a lot of processes can take place, with the most common being radiative or non-radiative decay from the singlet state to the ground state \(^8^6\). Promotion to the singlet state or a charged state happens when the material absorbs light or becomes electrically charged upon exposure to a voltage. In a simple P3HT FET example, applying a voltage to the gate charges the dielectric which in turn promotes hole formation in the P3HT backbone, which propagates along the backbone of the polymer. A less efficient method of hole transport occurs by charge hopping between the aromatic units of neighboring polymer chains. As a negative bias is applied across the electrodes, the free “excited” electrons do not move throughout the active layers. Electrodes are chosen to have work functions close to the HOMO of the active layer to collect the holes as they propagate through the active layer.

![Jablonski diagram](image)

**Figure 1.5:** Jablonski diagram showing many pathways of decay upon excitation to singlet states reproduced from *Chemical Society Reviews* 2013, 42 (12), 5323-5351.

Including different moieties into an active layer or into a repeat unit structure of a conjugated polymer adds to the complexity of excited state processes upon exposure to an excitation wavelength or applied voltage. As described above, this is the foundation of PV operations, in that upon excitation of a donor unit to the exciton species, the excited
electron is donated to the accepting group to promote charge propagation to respective electrodes. The aromatic properties of the repeat unit determine how well the material donates or excepts an electron. Donors are typically electron rich, and common donor building blocks include thiophene and benzene rings. Thiophenes usually are better donors due to greater degrees of delocalized electrons compared to benzenes and are considered strong donors. They also have lower oxidation potentials, corresponding to higher HOMO levels than accepting moieties. Synthetically altering the monomer can promote planarization of the polymer or oligomeric system, which can enhance charge carrier characteristics and crystallization properties, and change the bang gap and HOMO/LUMO levels. On the other hand, electron accepting units are electron poor and contain electron withdrawing functionalities like carbonyl groups to help facilitate electron acceptance and have lower lying HOMOs and LUMOs.\(^{87}\)

Outside of photoelectron transfer processes that govern PV applications or propagating charges in FETs, conjugated polymers with unique repeat unit structures can experience other more complicated photophysical processes that aid in distinctive optical characteristics making them useful for chemical or biosensing, LED applications, or chemical synthesis. For example, in the excited state, pKa’s decrease. Excited conjugated materials containing ionizable groups can experience an alteration in the emission wavelength as more hydrogen scavengers are introduced to the system. The conjugated system becomes more ionic, and the conjugation structure changes.\(^{88-90}\) This tunable change in fluorescence can allow for sensing of the microenvironment of biological systems. Even changing the conjugated length of a conjugated polymer will alter the emission properties. If an analyte chemically reacts with a polymeric system, the
conjugation length will be shortened, and blue shift the absorption and emission maxima. Additionally, aromatic systems with pi-pi systems that are in close proximity, due to a non-linear polymer structure or aggregated systems can form excimers or excited-state dimers. Upon excitation, an excited molecule coordinates with a non-excited molecule to create an ionic state, which can be radiative or non-radiative. Excimer states are lower energy than the local excited state (LES) of the aromatic material or the singlet excited state, and therefore, when radiative, show a red-shifted emission compared to the LES. Designing systems that allow for aggregation properties upon exposure to an analyte and hence excimer formation can guarantee a simple sensing system based on a change in fluorescence. Additionally, as described for PV applications, donor-acceptor junctions can profoundly alter the excited state properties of a conjugated polymer. In addition to aiding in exciton dissociation, charge transfer states promoted between donor-acceptor moieties can produce highly fluorescent states, or states with no fluorescence at all, deviating from the singlet fluorescence of both the donor or acceptor. When fluorescent, the emission properties of charge-transfer states are characterized by solvatochromism, in the emission is red-shifted when exposed to polar analytes. Lastly, molecules that access vibrational or rotational non-radiative mechanisms of decay in dilute solutions can experience aggregated induced emission (AIE) or AIE enhancement. This is facilitated by freezing the molecules in place so that the only mechanism of decay from the excited state is through a radiative process. Conjugated polymers and oligomers can be synthetically designed to better access these excited state pathways based on choice of repeat unit or side chains.
1.5 Carboranes

Carborane (C2B10H12) is a unique electron deficient, icosahedral boron containing molecule. The hallmark properties of this compound are that it experiences high thermal and electrochemical stability. Integration into the backbone of polymeric materials shows enhanced thermal stability. This made it coveted for conjugated polymer applications, and these materials are typically unstable at high temperatures. Integration of p- or m-carborane into conjugated polymer backbone structures improves thermal and electrochemical stability without altering the optoelectronic properties of the system. P- and m-carborane lower the conjugation length of the polymer as the aromatic units do not overlap with the boron atoms in the carborane molecule. Alternatively, o-carborane integrated into a conjugated polymer structure shows overlap of the aromatic HOMO and LUMO with the C-C bond in the carborane, showing conjugation through the carborane molecule. This highly influences the emission properties of aromatic systems with carborane integrated into the backbone. Many systems have been investigated and typically consist of weak donor units like fluorene, carbazole, and triphenylamine based aromatic units with the strong donor carborane. Its long been understood that these systems experience the strong solvatochromism characteristic of an intramolecular charge transfer state, but real experimental proof of this state has long eluded scientists. Additionally, because these systems are non-linear polymers, due to the sharp bond angle between the carborane and the aromatic unit, they also experience other photophysical phenomena light aggregated induced emission or excimer formation, and often emission from the singlet aromatic state is observed. Understanding the dynamics of these systems can help design efficient chemical sensing applications, as well as allow for emission color...
tuning, by balancing the effects of different radiative processes in the polymeric system to produce materials with coveted emission colors, like white, for LED applications.

1.6 Outline of Dissertation

Chapter 1 introduces conjugated polymers, their use in different device architectures, and how synthetically tuning the structure, be in the aromatic backbone or the side chains and end groups, can aid in designing unconventional materials with coveted properties for electronic applications. The dissertation work focuses on the synthetic altering of well-defined conjugated polymers to produce materials that can be integrated into stable, insoluble, well oriented, semi-conducting films, or create materials with fascinating excited-state properties for sensing applications. Understanding the history of conjugated polymers, as well as the current research, helps for the design in novel higher performing materials.

Chapter 2 focuses on vinyl functionalizing side-chains and end-groups of poly(3-alkylthiophene)s for use in thiol-ene grafting-to applications. By functionalizing silicon dioxide wafers with thiol moieties, it is possible to graft vinyl-functionalized poly(thiophene)s to the surface and produce insoluble films. The films are formed quickly and have high grafting densities. Additionally, they maintain a characteristic microstructure of poly(thiophene) making them useful for active layer and interlayer applications.

Chapter 3 describes the synthesis, steady-state, and time-resolved characterization of carborane containing poly(dihexylfluorene) as well as an alternating copolymer of the bis(fluorenyl) carborane monomer and dihexylfluorene. Both polymers display similar
optoelectronic properties, and experience extreme solvatochromism. The solvatochromism is due to the formation of an intermolecular charge transfer state in the excited state of both system. The state is formed upon excitation of the fluorene singlet state which donates energy to form the charge transfer state across the fluorene-carborane bridge. This state then decays radiatively or non-radiatively depending on the environment of the polymer. This information details the first spectroscopic evidence of the interplay between the fluorene singlet state and the intramolecular charge transfer state. Understanding the photophysics of these unique materials allows for smarter design of LED and sensing devices.

Chapter 4 shows the random copolymerization of the dibromo-(bisfluorenyl)carborane with 2,7-dibromo-9,9-dihexylfluorene, with increasing conjugation length of the aromatic fluorene block as well as the spectroscopic characterization of the four copolymer as related to the homopolymer. Changing the fluorene conjugated length allows for overall emission properties to change based on the balancing of fluorene local excited state character and intermolecular charge transfer state character. This enables the production of films of different emission colors, as well as improves the quantum yield as compared to the homopolymer. It is even possible to produce a white emitting film. This simple synthetic procedure allows for tunable emission properties from single carborane containing poly(fluorene)s.

Chapter 5 introduces the novel synthesis of soluble carborane containing poly(thiophene)s. These distinctive materials are polar in nature and dissolve in polar solvents like DMSO and DMF, deviating from typical thiophene or carborane containing polymers which are hydrophobic. The polar polymer can be excited by visible and UV
light to form an excited geminate pair over the thiophene-carborane bridge that decays over several picoseconds. The decay of the geminate pair catalyzes the back electron transfer of energy to produce a triplet state on the thiophene moiety. The copolymer poly(bisthienyl carborane-alt-thiophene) sees a triplet energy transfer from the oligothiophene triplet to form a triplet on the carborane moiety. Additionally, as these materials are non-linear, intermolecular and intramolecular aggregates can be formed which show broad emission properties. This is an exciting study on the photophysics of a previously undescribed system.

1.7 References


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CHAPTER 2
SURFACE GRAFTING OF FUNCTIONALIZED POLY(THIOPHENE)s USING THIOL-ENE CLICK CHEMISTRY FOR THIN FILM STABILIZATION

2.1 Introduction

Conjugated polymer films experience many forms of disruption when exposed to common processing or environmental stressors, like delamination, morphological disorder, and undesirable solubility. This can be limiting when incorporating conjugated polymer films into unique device architectures built upon multiple films because the solvents or solvent vapors present during processing procedures can damage underlying conjugated polymer films, limiting the device function. Additionally, conjugated polymer films have short lifespans, with time and heat upending the morphologies and crystal structures necessary for competitive charge transport through the polymer film.

Grafting conjugated polymers to substrate surfaces presents a unique solution to the above-mentioned thin film instability issues. Grafted polymers are chemically bound to a surface, which enables the films to be solvent resistant and tolerate exposure to solvent vapors without significant swelling. Polymers can be grafted to a surface by functionalizing the polymer and the substrate with complimentary chemical moieties, and introducing the polymer to the substrate by either solution or melt processes, and this method is termed “grafting-to”.

The ultimate thickness of these grafted films, as measured by ellipsometry or AFM, is dictated by either reaction time or how well the modified polymers diffuse to the surface, where they chemically react with the surface functionalities. The dynamics that determine whether the grafted thickness is reaction mediated or diffusion mediated is dependent on the molecular weight of the grafting polymer, with higher molecular weights typically
associated with diffusion limited grafting. Additionally, annealing time and reaction
temperature can heavily effect grafting thickness, with many grafting-to reactions
happening in the melt phase\(^6-8\). Grafting density, a measurement of the polymer molecular
weight as related to the thickness of the grafted film, is an important parameter for
characterizing the effectiveness of a grafting reaction, and higher grafting densities are
important for grafted films to be beneficial when incorporated into electronic device
structures\(^9\). Therefore, tuning the reaction conditions to produce thicker grafted films, will
also improve the grafting densities of the insoluble films. Grafting-to can enable the
simplistic formation of insoluble polymer films over fast reaction times, while other
methods of grafting, like grafting-from and grafting-through are more complex and time
consuming. Additionally, control over brush length and density is more controllable
through grafting-to mechanisms as the polymer is synthesized prior to grafting\(^2,10-12\).

Many different reaction chemistries have been used to create insoluble conjugated
copolymer films or brushes through grafting-to procedures, including azide-alkyne click
chemistry, sulfur-gold interfaces, condensation chemistries, silane chemistries, and carbon-
carbon bond forming reactions like Heck coupling\(^13-17\). In addition to insolubility, grafting
can aid in producing or enhancing desired structure/property relationships of grafted
copolymer films or brushes that can improve overall electronic device function. For example,
grafting of functionalized poly(3-hexyl thiophene)s (P3HT) to nanoparticles like TiO\(_2\),
ZnO, or graphene showed higher solar cell efficiencies when compared to non-grafted
analogs, indicating more efficient exciton dissociation at the grafted interface than in the
blended film\(^9,18\). Thiol functionalized P3HT grafted to gold surfaces formed monolayer
films that aided in templating thin film microstructures spin-coated directly on top of the
grafted monolayers. This enhanced hole mobility properties by an order of magnitude compared to the non-grafted analogs\textsuperscript{13}.

Click chemistry is particularly advantageous for grafting-to applications because it often does not yield by-products that may be inimical to charge transport through an active layer, can be achieved under mild conditions, is nearly quantitative, and has fast reaction times. The most commonly employed click chemistry used for grafting-to applications is the azide-alkyne cyclo-addition reaction. Conjugated polymer films grafted through azide-alkyne click chemistry have been shown to be solvent impervious, and have charge carrier mobilities comparable to non-grafted, ultra-thin devices. Furthermore, the azide-alkyne grafting-to reaction was shown to be time dependent with thicker films and higher grafting densities formed after longer exposure of the polymer and substrate to the reaction conditions\textsuperscript{19}.

Thiol-ene chemistry has also been used for grafting purposes, and has been mainly employed to photo-polymerize non-conjugated di-functionalized monomers from a functionalized surface for patterning applications, or to anchor bio-compatible materials to substrates and nanoparticles\textsuperscript{8,20-23}.

Within the realm of conjugated polymer electronics, thiol-ene click chemistry has primarily been used to stabilize conjugated networks through cross-linking, which has aided in the stabilization of active layers for organic light emitting diodes and photovoltaic cells\textsuperscript{24-26}. For example, using thiol-ene chemistry to cross-link hole transport layer (HTL) vinyl functionalized 4,4',4''-tris(N-carbazolyl)triphenylamine showed improved charge injection and higher PCEs compared to non-cross-linked materials. It is theorized that cross-linking aided in improving morphological characteristics that allowed for better
interfacial contact. Additionally, the thiol-ene cross-linked HTL improved the photo and oxidative stability of the device which could be due to its hydrophobic nature, allowing for protection of the active layer to common stressors.

While thiol-ene chemistry has proven effective in cross-linking conjugated polymer active layers, only a few reports detail the use of thiol-ene chemistry for grafting-to applications of semi-conducting polymers to underlying surfaces. In one report, vinyl functionalized poly(dialkyl fluorene)s were grafted to thiol modified silicon substrates using thiol-ene click chemistry. These grafted films maintained the same optoelectronic properties as the analogous spin-coated films, even after rinsing the film with good solvents for the linear polymers. Additionally, it is possible to use this technique to directly pattern surfaces with conjugated polymer 2D structures.

In this study, we extend the application of thiol-ene click grafting to two distinctly functionalized poly(3-alkyl thiophenes). The synthesis of telechelic end-capped regioregular poly(3-hexyl thiophene) and the synthesis of regioregular poly[(3-hexylthiophene)-ran-(3-undecenylthiophene)] (functionalized P3HT) were carried out through Ni mediated McCullough polymerization and characterized through MALDI-TOF and $^1$H NMR. Silicon dioxide (SiO$_2$) wafers were functionalized with thiol moieties through the vapor silanation reaction of 3-mercaptopropyltriethoxysilane and the success of the reaction was characterized by contact angle measurements. From here, functionalized P3HT was spun coat onto the surface of the thiol modified SiO$_2$ and exposed to 150°C to bring the polymer above its glass transition temperature and 254 nm UV light to initiate the thiol-ene reaction. After a period of time the substrate was exposed to a good solvent for the polymer, CHCl$_3$, to remove any unreacted, interpenetrated polymer and
characterized through contact angle. The insoluble film was characterized through x-ray photoelectron spectroscopy (XPS) to determine the chemistry of insoluble film formation. Finally, the grafting density and solid-state structure of grafted films, before and after rinsing, for both functionalized poly(thiophenes), were analyzed and compared to the morphology of the spin-coated films. It was found that thiol-ene chemistry offers an effective and fast method for grafting highly dense insoluble polymer films that maintain the characteristic microstructure of P3HT.

2.2 Experimental Section

2.2.1 Materials

All materials were purchased from Sigma Aldrich or VWR and used without further purification. Tetrahydrofuran (THF) was dried over sodium/benzophenone and distilled before using. Silicon substrates (P-doped, 0.01–0.018 ohm·cm, 200 nm thermally grown SiO$_2$) were purchased from University Wafers. Gold for metal evaporation was purchased from Kurt Lesker.

2.2.2 Instrumentation

All nuclear magnetic resonance (NMR) spectra were acquired on a Bruker 500 (500 MHz) spectrometer and internally referenced via residual solvent signal (CHCl$_3$: $^1$H 7.26 ppm). MALDI-TOF was performed on a MicroFlex LRF MALDI-TOF from Bruker Daltonics (Billerica, MA). Mass spectral data were obtained at the University of Massachusetts Mass Spectrometry Center. Dithranol (40 mg/ml in THF) was used as a matrix for both polymers (10 mg/ml in THF). Dithranol solution was mixed with poly(thiophene) solution at a 1:1 ratio and spotted on a target. XPS was performed on a Quantum 2000 Scanning ESCA Microprobe from Physical Electronics. Deconvolutions
of Cs1 peaks were made on MultiPak software using a Guassian Lorentzian mixed function ratio with a Shirley background. FWHM for the integrations ranged between 1.5 and 2. Film thicknesses were measured by a Dektak 150 profilometer or a DI 3000 AFM four in the Scanning Probe Microscopy Facility at University of Massachusetts Amherst.

2.2.3 Synthesis of 3-undecenylthiophene

The procedure for this Kumada coupling is based off of reference 31. A clean multi-neck round bottom flask, fitted with rubber septa, a condenser, and an oval shaped stir bar, was dried by alternating pulling vacuum and purging with N₂ three times while being heated with a heat gun. While the apparatus was drying, 3-bromothiophene (0.95 eq.), Ni(dppp)Cl₂ (0.0042 eq.), and 11-bromo-1-undecene (1 eq.) were being purged with N₂ in separate vials. 1.2 equivalents of magnesium turnings were added to the dried round bottom and the drying procedure was repeated until the magnesium was very shiny and staticky. After the round bottom cooled, a crystal of iodine was added. Then vacuum was pulled on the apparatus for 10 minutes. The apparatus was flushed with N₂ and 15 equivalents of ethyl ether or 2-methyltetrahydrofuran were added, resulting in a dark red solution. (Tetrahydrofuran is not a suitable solvent for this reaction.) The 11-bromo-1-undecene was removed from its vial by a dry syringe and added drop-wise over the course of 45 minutes to the main apparatus at room temperature. As the Grignard forms, the solution consecutively turns orange, yellow, pale yellow, white, then clear and begins to bubble and heat up. This is followed by a slow darkening of the solution to grey. A dark grey solution is a good indicator that the Grignard has formed. After the 11-bromo-1-undecene is added in full, the reaction is heated to 29° C for 4 hours. 3-bromothiophene was transferred from its vial with a dry syringe and added drop-wise to the solution over
30 minutes at 29° C. Then while the reaction flask was under positive N₂ pressure, the septum was removed and Ni(dppp)Cl₂ was added in bulk to the solution. The solution turns red-ish. The reaction was heated to reflux overnight. After 12 hours, the reaction is a red/black color. If the reaction is run in ethyl ether, it’s easy for the solvent to evaporate off during the reflux, which may lead to a greyish sludge after 12 hours. The round bottom is placed in an ice bath and 12M HCl (1:1 ratio of total reaction moles to HCl) is added to the solution. The solution is extracted three times with ether, followed by three washes with water. The organic phase is dried over MgSO₄, filtered, and condensed through rotary evaporation. Thin layer chromatography shows two spots before purification, the top most spot is the product, while the bottom spot is bisthiophene. The product is purified on a silica column with hexanes. The final product is a clear oil. The best yield achieved was 52%.

\(^1\)H NMR (CDCl₃, 500MHz) Reference 7.26 ppm: 7.23 (m, 1H), 6.93 (d, 1H), 6.91 (m, 1H), 5.83 (m, 1H), 4.96 (m, 2H), 2.63 (t, 2H), 2.03 (m, 2H), 1.60 (m, 4H), 1.29 (m, 14H)

2.2.4 Synthesis of 2-bromo-3-undecenylthiophene

This procedure for the lithium halogen exchange is based off of reference 31. A multi neck round bottom flask was dried in the same way as reported for the 3-undecenylthiophene synthesis. The round bottom was placed in a dry ice/acetone bath at -78° C. 15 eq. of dry tetrahydrofuran (THF) were added to the round bottom by a dry syringe. 1.06 eq. of t-butyl lithium were added to the cold round bottom drop-wise using a very dry syringe and the solution turned yellow. Before addition of t-butyl lithium the syringe was attached to a N₂ line and purged with N₂ for 15 minutes. 1 eq. of N₂ purged 3-undecenylthiophene was added drop-wise to the solution over the course of 15 minutes.
The reaction was run at -78° C for 1 hour. The solution was a light orange/yellow color. 2.1 eq. of carbon tetrabromide were dissolved in a minimum amount of THF and purged with N\textsubscript{2}. This was added by a dry syringe to the reaction vessel drop-wise over the course of 15 minutes at -78° C. The solution turned orange. The solution was reacted for 1 hour at room temperature. The solution was quenched with ice, worked up, and purified in the same manner as 3-undecenylthiophene. If the solution turns black, it has failed due to the introduction of oxygen. The yields ranged between 40-60%.

\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 500MHz) Reference 7.26 ppm: 6.88 (d, 1H), 6.79 (d,1H), 5.81 (m, 1H), 4.97 (m, 2H), 2.54 (t, 2H), 2.04 (m, 2H), 1.61 (m, 4H), 1.26 (m, 14H)

2.2.5 Synthesis of poly(3-hexylthiophene-ran-3-undecenylthiophene)

This procedure for the McCullough method is based off of reference 31. In a dry scintillation vial, 1.66 eq. of 2-bromo-3-hexylthiophene and 1 eq. of 2-bromo-3-undecenylthiophene were added and purged with N\textsubscript{2}. The total amount of moles for this mixture was set as 1 eq. for the following polymerization. In a multi neck round bottom flask, that was dried as previously reported, 11 eq. of dry THF were added. The reaction vessel was cooled to -78°C. 1 eq. of diisopropylamine (DIPA) was added to the cold reaction vessel. The solution was light yellow. The DIPA was never purged before addition to the reaction vessel, but it wouldn’t hurt to do that. Following the DIPA, 1 eq. of n-butyl lithium was added with a dry syringe. The reaction was stirred for 1 hour at -78° C. Then the thiophene mixture (1 eq.) was added to the reaction vessel drop-wise over the course of 30 minutes and stirred for 1 hour at -78° C. The solution turned dark yellow. 1.3 eq. of dried zinc chloride dissolved in a minimal amount of dry THF was added drop-wise to the reaction vessel over the course of 15 minutes and reacted at -78° C for 1 hour.
The solution turned bright orange. The reaction vessel was warmed to room temperature and 0.009 eq. of Ni(dppp)Cl$_2$ was added to the reaction vessel. The solution turned red. As the reaction ran, the solution turned dark red, almost looking black. The reaction was run for 14 hours at room temperature while covered in aluminum foil, and then precipitated into cooled methanol. The product was filtered and purified by Soxhlet extraction using methanol, hexanes, and chloroform. Each solvent was run for 8 hours, while heating at 100° C. The final product appears to be golden/purple flakes in the solid state. When dissolved, the polymer fluoresces bright yellow.

$^1$H NMR (CDCl$_3$, 500MHz) Reference 7.26 ppm: 6.98 (s, 1H), 5.79 (m, 1H), 4.93 (dd, 2H), 2.80 (t, 2H), 2.01 (m, 0.22), 1.69 (m, 2H), 1.34 (m, 8H), 0.89 (t, 3H)

2.2.6 Synthesis of vinyl mono-capped P3HT

The synthesis for the vinyl capped P3HT is the same as the synthesis for poly(3-hexylthiophene-ran-3-undecenylthiophene) with the substitution of 2-bromo-3-hexylthiophene as the sole monomer and has similar color changes. After Ni(dppp)Cl$_2$ was added to the reaction vessel, the reaction proceeded for 5 minutes before being placed in an ice bath for 10 minutes. The amount of vinyl magnesium chloride that was added was calculated from a 30:1 ratio to the moles of nickel catalyst. Vinyl magnesium chloride was added quickly to the reaction vessel by syringe, and then the entire solution was immediately poured into cooled methanol. The polymer was purified in the same way as poly(3-hexylthiophene-ran-3-undecenylthiophene). MALDI-TOF indicates that the polymer is terminated with bromide and vinyl groups.

$^1$H NMR (CDCl$_3$, 500MHz) Reference 7.26 ppm: 6.97 (s, 1H), 5.49 (d, 1H), 5.12 (d, 2H), 2.81 (t, 2H), 1.69 (m, 2H), 1.44 (m, 2H), 1.33 (d, 4H), 0.90 (t, 3H)
2.2.7 Synthesis of telechelic vinyl di-capped P3HT

The mono-capped P3HT (1 eq.) was dried and placed in a scintillation vial with a septum and a small stir bar. It was moved into a glovebox where Pd(PPh$_3$)$_4$ (0.04 eq.) was added to the scintillation vial. The vial was capped, moved back to the hood and put under a nitrogen line. Dry toluene (6 eq.) was added to the scintillation vial. N$_2$ purged tributyl(vinyl)stannane (60 eq.) was added to the solution and the reaction was heated to 100° C and reacted for 24 hours. Since the equivalents of the catalyst and the stannane group are in excess in order to cap the bromine end group of the polymer, they are malleable. The solution was precipitated into methanol and purified in the same way as poly(3-hexylthiophene-ran-3-undecenyli thiophene). MALDI-TOF indicates the polymer is terminated by vinyl groups.

$^1$H NMR (CDCl$_3$, 500MHz) Reference 7.26 ppm: 6.98 (s, 1H), 6.44 (q, 1H), 6.14 (dd, 1H), 5.66 (dd, 1H), 2.81 (t, 2H), 1.71 (m, 2H), 1.43 (m, 2H), 1.34 (d, 4H), 0.91 (t, 3H)

2.2.8 Organic Field Effect Transistor Fabrication

Si/SiO$_2$ (200 nm) substrates were cleaned by sonication for 10 minutes in a series of solvents, which included acetone, ethanol, and isopropyl alcohol (IPA). IPA is the cleanest solvent and therefore should always be used last. The substrates were dried with a stream of N$_2$ and placed in piranha acid for four hours. The substrates were individually placed in scintillation vials containing DI water to rinse off remaining piranha acid. To do this, DI water was flushed into the scintillation vials repeatedly and poured out. The substrates were dried by a stream of N$_2$ and those being used for grafted films were modified with MPTS. The substrates were moved to the glove box. 5 mg samples of functionalized poly(thiophene) were made and moved to the glove box. Solutions of 5
mg/ml of functionalized poly(thiophene) was made with dry, glove box quality chlorobenzene. These solutions stirred at 55°C overnight, covered in aluminum foil. The solutions were spun onto the substrates through a 0.45 µm PTFE syringe filter at 1000 rpm for 60 seconds. The substrates were annealed and then grafted as described above. Then the substrates were exposed to chloroform and then dried for 5 minutes at 150°C. Au source drain were thermally evaporated through a shadow mask (W/L= 16) at 5x10^{-6} Torr. The devices were measured in ambient environment outside the glove box.

2.3 Results and Discussion

2.3.1 Synthesis of Alkene Functionalized Poly(thiophene)s

Alkene functionalized poly(thiophene)s were synthesized to test the efficacy of thiol-ene click chemistry as a covalent binder between the polymer and a thiol modified silicon dioxide wafer. Poly(3-pentenylthiophene) (P3PNT), a polymer containing terminal alkene moieties on the side chains, was synthesized by polymerizing 2-bromo-5-chlorozinc-3-pentenylthiophene with a nickel catalyst using the McCullough method$^{30-31}$. The polymerization resulted in a polymer that fluoresced a bluish white color when exposed to UV light, in stark contrast to the bright yellow/orange fluorescence characteristic of low dispersity and high molecular weight poly(thiophene)s. The MALDI-TOF spectrum of P3PNT revealed that the polymer consisted of highly dispersed molecular weights. Mechanistically, it has been hypothesized that the active Ni(0) can coordinate with the pendant alkenes present in the monomer and oligomeric or polymeric products. This alkene coordination competes with the polymer forming reaction by breaking its complex with the thiophene ring, which limits the effectiveness of the polymerization$^{32}$. 
Although this polymer was not used for subsequent studies in electronic devices, it was used in thiol-ene click surface reactions (vide infra).

To circumnavigate the polymerization complication, a random copolymer of 3-undecenylthiophene and 3-hexylthiophene (pP3HT), with a molar ratio of 2:3, was synthesized by the McCullough method (Figure 2.1). It was anticipated that the long undecene chain would be less likely to interact with the Ni(0) catalyst, but after allowing the solution to react for 14 hours, 3-undecenylthiophene was only incorporated at 14% (determined by $^1$H NMR). $M_n$ was determined to be about 5460 g/mol via MALDI-TOF, while $D$ was 1.02.

**Figure 2.1: Synthesis of poly(3-pentenylthiophene) (top) and poly[(3-hexylthiophene)-ran-(3-undecenylthiophene)] (bottom).**
To study the reactivity of chain-end –ene functionalized polymers, vinyl end-capped P3HT (xP3HT) was synthesized using the McCullough method from 2-bromo-5-chloro-3-hexylthiophene. The reactions were set up and allowed to proceed at room temperature for 5 minutes and then cooled to 0°C and allowed to react for 10 additional minutes. The growing polymer chains were terminated by adding an excess of vinyl-Grignard reagent. Cooling the reaction before introducing the Grignard reagent was critical to reduce the presence of hydrogenated end groups, formed by magnesium-halogen exchange\textsuperscript{33}. The vinyl mono-capped P3HT was characterized by \textsuperscript{1}H NMR and MALDI-TOF to confirm the success of the vinyl-Grignard capping. Attempts to substitute the bromide end group of the vinyl mono-capped P3HT were first made using Kumada coupling. The mono functionalized polymer and Ni(dppp)Cl\textsubscript{2} were cooled to 0°C and vinyl-MgCl solution was added drop-wise. The MALDI-TOF analysis showed that the resulting polymer was terminated by hydrogen rather than the desired vinyl group. The vinyl substitution was successfully accomplished using Stille coupling to make a telechelic vinyl polymer by reacting the mono-capped P3HT with tributyl(vinyl)stannane in toluene.
at 100°C for 24 hours, using a catalytic amount of Pd[PPh₃]₄. The product was characterized by ¹H NMR and MALDI-TOF. The Mₙ of the telechelic polymer was found to be 4575 g/mol with a D ~ 1.01.

Figure 2.3: MALDTI-TOF of telechelic vinyl end capped poly(3-hexyl thiophene). The end cap molecular weight is 54 g/mol and the repeat unit molecular weight is 166 g/mol.
2.3.2 Thiol-Ene Surface Grafting of Polythiophenes

Heavily doped p-type silicon substrates, with a 200 nm thermally grown silicon dioxide layer, were sequentially sonicated in acetone, ethanol, and isopropanol to remove contaminants, followed by immersion in a piranha cleaning solution (a mixture of 3:1 sulfuric acid to hydrogen peroxide) for four hours and rinsing with water. This process produced a hydrophilic surface with a non-discernable water contact angle (WCA) less than 5°. The cleaned silicon wafers were then functionalized with (3-mercaptopropyl)triethoxysilane (MPTS), through vapor phase deposition and concurrent condensation of the MPTS with the native SiO$_2$ surface. This was accomplished by placing the silicon wafers in a petri dish overnight at 100° C next to a shallow glass dish containing 0.1 ml of MPTS on a hot plate. Successful silanation of the surface was probed by measuring the change in WCA. The WCA of the treated surfaces varied between 73° to 87°. The higher contact angles of the MPTS monolayer may be due to less oriented
monolayers. The thiol modified wafers were transferred to a glovebox, where 5 mg/ml solutions of functionalized poly(thiophene) in chlorobenzene were spin-coated at 1000 rpm for 60 seconds with a 10 second ramp. The spin-coated resulting films had WCAs greater than 90°. The wafers were annealed at 150°C for 5 minutes and then exposed to 254 nm UV light inside the glovebox for a predetermined amount of time to graft the functionalized poly(thiophene)s to the surface. The grafted samples were introduced to chloroform using one of three procedures (vide infra), to remove any unreacted polymer. They were reheated to 150°C for 5 minutes to remove any residual solvent (Figure 2.5).

**Figure 2.5: Grafting schematic of vinyl functionalized poly(thiophene)s to thiol modified silicon dioxide wafers.**

Using the procedure described above, P3PNT was grafted in air to a MPTS monolayer, resulting in a film with a WCA of 101°. After immersion soaking in chloroform for 8 hours, the film was dried to reveal an essentially unchanged WCA of 103° showing that an insoluble film was produced as a result of the grafting procedure. XPS is done on the samples to understand the chemical nature of the grafted surfaces. Using a 75° take off angle, it was possible to probe the upper 4-5 nm of the film’s surface. XPS of this
surface is shown in Figure S10 and the C1s peak includes a shoulder which could be deconvoluted into four peaks. The principle integration at 284.71 eV represents 70% of bonds to carbon. An adjacent integration, at 285.94 eV, represents 15% of the bonds to carbon, and is indicative of hydroxyl groups bonded to the alpha carbon of the thiophene ring. This position is easily oxidized upon exposure to radical oxygen species. The smallest integrations at 287.25 eV and 288.93 eV compromise 16% of bonds to carbon and represent carbonyl and carboxyl groups, respectively, signifying further oxidation of P3PNT\textsuperscript{35}.

A series of control experiments were performed to confirm that a thiol-ene click reaction was the most effective method for the formation of insoluble thin films. These experiments used non-functionalized P3HT and P3PNT to show that both the vinyl groups in P3PNT, and the MPTS coated substrate were required for grafting. The UV-initiated grafting reactions were performed in air in order to partially oxidize the P3PNT, as described above. The XPS of oxidized poly(thiophene)s have a distinctive C1s peak, with the largest integration at 284.75 eV due to the methylene carbons and aromatic bonds between carbon. Three smaller integrated curves protrude like a shoulder from the 284.75 eV peak, which represent various degrees of poly(thiophene) oxidation. This characteristic peak can be used as a label to determine if P3PNT is present on the wafer, which would indicate that thiol-ene click grafting was successful (Figure 2.6)\textsuperscript{35-37}.  

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Figure 2.6: XPS of oxidized P3PNT on thiol modified silicon dioxide showing C1s peak characteristic of oxidized polythiophene.

The first control experiment involved spin-coating P3PNT onto a clean SiO$_2$ substrate and exposing it to 254 nm UV light at 150°C for 1 minute. The WCA of the spin-coated film was 93°. The film was immersion soaked in chloroform for 8 hours. After drying, the contact angle decreased noticeably to 63°. The C1s peak for this sample did not possess the oxidation shoulder characteristic of oxidized poly(thiophene)s. The small amount of carbon content detected is likely due to residual organic compound contamination either from the chloroform treatment or adsorbed air during handling (Figure 2.7). This experiment showed that there was not any residual P3PNT on the silicon wafer after the chloroform immersion soak, suggesting that UV exposure and heat are insufficient to induce radical cross-linking or fixing of the polymer to the SiO$_2$ surface on this time scale.
In the second control experiment, poly(3-hexylthiophene) was spin-coated onto a MPTS modified substrate and received the same UV-grafting procedure as described in the first control experiment. The WCA of the resulting film was 98°. The film was then immersion soaked in chloroform for 8 hours. After drying, the WCA was observed to decrease to 86°, which is within the range associated with a non-substituted MPTS monolayer. The C1s peak is symmetric and can be deconvoluted into two integrals, one at 284.75 eV and one at 286.10 eV, with the 284.75 eV peak dominating. This spectrum is comparable to reported spectra of MPTS monolayers, representing methylene carbons (284.75 eV), as well as oxygen bonds to carbon from ethoxy groups in the film (286.10 eV) (Figure 2.8)\textsuperscript{34,38}. This control experiment indicated that the MPTS monolayer remained on the wafer, but immersion soaking in chloroform removed all of the poly(3-hexylthiophene).
Figure 2.8: XPS of control 2 where un-functionalized P3HT is “grafted” to thiol modified silicon dioxide. C1s peak characteristic of MPTS monolayer.

From the controls, it seems evident that both the thiol and vinyl moieties are necessary for insoluble polythiophenes film formation. The XPS and WCA measurements support the claim that thiol-ene click chemistry is the mechanism of insoluble film formation for these conditions, and no other chemistry, namely vinyl cross-linking, is responsible for anchoring P3PNT to the substrate surface. In Figure 2.9, a bar graph depicts the elemental composition of each sample for the grafted P3PNT film, the first control, the second control, and the rinsed grafted P3PNT film.
2.3.3 Morphology/Microstructure

Both xP3HT and pP3HT were grafted to MPTS monolayers in a N₂ glovebox for 10 minutes using the previously described procedure. After grafting, some samples were rinsed with chloroform, which entails dropping 0.3 mL of chloroform on the surface of the grafted film and then immediately spinning it off at 2000 rpm for 60 seconds, in the glovebox at room temperature. This was done to remove polymer that did not covalently graft to the surface. XPS was performed on the non-oxidized spin-coated, grafted, and grafted and rinsed samples of xP3HT and pP3HT to gain an understanding of the elemental composition of these samples (Figures 2.10 and 2.11). Between the two polymer samples the XPS spectra were analogous. Although, there was major differences in elemental composition between the spin-coated, grafted, and grafted and rinsed films. In the spin-coated film for xP3HT, oxygen made up 50% of the sample, while carbon, sulfur, and silicon made up 43%, 0%, and 7%, respectively. In the grafted film of xP3HT, the oxygen
content was much lower, at 11%, while the sulfur content increased to 2% incorporation. The grafted and rinsed film of xP3HT displayed an even further decrease in oxygen to 4% composition, accompanied by an increase in sulfur to 7% composition. Similarly, in the spin-coated film of pP3HT, oxygen made up 25% of the sample, while carbon, sulfur, and silicon made up 65%, 0%, and 10%, respectively. The grafted film of pP3HT exhibited a similar decrease in oxygen content as the grafted film of xP3HT, to 10%, and a rise in sulfur content to 2% incorporation. The grafted and rinsed film of pP3HT showed a significant decrease in oxygen to 3%, and an increase in sulfur to 6% inclusion. The decrease in the O1s peak upon exposure of the samples to the grafting procedure is most likely due to annealing the sample at 150°C, while the spin-coated sample was not annealed. Interestingly, the S2p peak shows an increase in intensity as the sample goes through the grafting procedure, with the grafted and rinsed sample having the highest composition of sulfur. While this is most likely due to the decrease in the O1s peak, allowing the weak S2p peak to be detected, as the elemental compositions determined through XPS are all relative to each other, it prompted interest in the microstructure of the grafted film. XPS images the top of the films, and a significant change in the film surface may indicate a microstructural change.
Figure 2.10: XPS of non-oxidized xP3HT showing the O1s, C1s, and S2p spectra for the spin-coated, grafted, and grafted and rinsed films.

Figure 2.11: XPS of non-oxidized pP3HT showing the O1s, C1s, S2p spectra for the spin-coated, grafted, and grafted and rinsed films.
To investigate the microstructure of these films, grazing-incidence wide angle X-ray scattering (GIWAXS) experiments were performed on the spin-coated, grafted, and rinsed samples of xP3HT and pP3HT (Figure 2.12). The angle was changed to probe the microstructure throughout the film, and the microstructure was observed to be constant from the interface of the substrate and the graft to the surface of the film. The GIWAXS from the as spun samples show similar orientation for both polymers. The (100) reflection, along with higher-order reflections, is centered at \( q = 0.34 \, \text{Å}^{-1} \) (\( d = 18.5 \, \text{Å} \)) along the \( q_z \)-axis. The (010) reflection is present at \( q = 1.70 \, \text{Å}^{-1} \) (\( d = 3.70 \, \text{Å} \)) along the \( q_{xy} \)-axis. These reflection positions are characteristic of an edge-on orientation with the lamella layer structure oriented normal to the film and the \( \pi-\pi \) interchain stacking in the plane of the film.

After exposure to UV-light and heat to induce grafting, no morphological differences could be resolved from the scattering. This indicates that the grafting procedure does not affect the microstructure of the poly(thiophene) films. After the films were rinsed, a clear rearrangement could be seen in the structure of the films. The pP3HT samples showed a change in preferred orientation with the (100) reflection present in the plane. Higher-order reflections were absent in this sample, indicating that the film is less ordered after rinsing. xP3HT shows a similar change in orientation, but a more ordered system, as the (100)-axis is oriented in the plane and the (010) reflection is present normal to the film. This film also shows a dual texture with the (100)-axis also present normal to the film, but the main reflection positions are representative of a face-on orientation.
Figure 2.12: Grazing incidence wide angle X-ray scattering (GIWAXS) where, (top) 2D image maps of spin-coated, grafted, and grafted and rinsed pP3HT films; and (bottom): 2D image maps of spin-coated, grafted, and grafted and rinsed xP3HT films.

Obata et al. used simulations to show that in the bulk P3HT film, edge-on orientation is energetically favorable for P3HT due to the gain in interaction energy between the P3HT molecules, and that this is observed for P3HT films on both hydrophilic and hydrophobic self-assembled monolayers. This could explain why the spin-coated and grafted samples for both functionalized poly(thiophenes) are almost identical. Seeing that grafting is diffusion limited, the orientation of the polymer at the interface may be different from the bulk. The face-on orientation can be favorable when there is a gain in the intermolecular interaction energy between P3HT molecules and the self-assembled monolayer. Additionally, face-on alignment is most likely to occur on hydrophilic self-assembled monolayers, like MPTS. This orientation in the bulk can occur when P3HT molecules act as seeds for face-on crystallization during specific processing conditions. As
functionalized poly(thiophenes) at the MPTS surface begin to graft, the interactions between the polymer and the MPTS surface may prevail over the polymer-polymer interactions, causing a shift from edge-on to face-on.

Film Thicknesses and Grafting Density

Both xP3HT and pP3HT were grafted to MPTS surfaces with certain procedural variations. The grafting times were varied between 1, 5, and 10 minutes. Additionally, the grafted films were exposed to chloroform using three different methods to remove residual unreacted polymer. The first method was rinsing, as described above, and the film was only exposed to chloroform for a few seconds. The second method, immersion soaking, required placing the grafted film and 10 mL of chloroform into a scintillation vial, and then setting the vial on a vortex mixer for 24 hours. The last method, puddle and rinse, involved dropping 0.3 mL of chloroform onto a grafted film, full wetting the surface, resting on the spin-coater chuck. After 30 seconds of the chloroform swelling the grafted film, the spin-coater ramped to 1000 rpm over a period of 5 seconds, and then spun consistently for 60 seconds, to remove the unreacted polymer that dissolved in the chloroform droplet. These three methods vary the time that the graft was exposed to chloroform. The WCAs of the grafted films were measured after chloroform exposure for each of the grafting times. AFM and profilometry were used to determine the thicknesses of the films. In Figure 2.13 the thicknesses of the grafted and exposed films are plotted against grafting times for each solvent exposure method. For both pP3HT and xP3HT, rinsing was the least effective method for removing unreacted, interpenetrated polymer, while puddle and rinse was the most effective method. Previous reports describe the calculation of grafting density for both silane monolayers and the polymer grafts. The MPTS monolayer thickness was
around 0.4 nm (Figure S11), corresponding to a grafting density of 1 molecule/nm$^2$. Consequently, it should not be possible for the grafted polymer films to have a grafting density higher than the MPTS density. Grafting densities greater than 1 chain/nm$^2$ are suggestive of residual interpenetrated polymer, or the beginning of vinyl cross-linking. As the puddle and rinse method removed the interpenetrated polymer most efficiently for both xP3HT and pP3HT, it seems that the high grafting densities for xP3HT for the 10 minute graft times could be a result of secondary vinyl cross-linking reactions. This is likely due to the well-known diradical formation between two styrenic end groups upon exposure to heat. The diradical has an extremely short lifetime, allowing it to quickly ring close. This is one of the possible reactions from the Flory mechanism of styrene thermally initiated auto-polymerization. Aliphatic alkenes do not undergo this reaction and are not apt to undergo these kinds of thermally initiated reactions as readily as styrenic materials. For example, a previous report on the thermal cross-linking of poly(3-(5-hexenyl)thiophene), describes needing 2 hrs of 150$^\circ$C heating to create a cross-linked network of this polymer$^{39}$. The high grafting densities from the rinse method are most likely due to interpenetrated polymer.
Figure 2.13: (top) Thicknesses of grafted films after different solvent exposure methods, the calculated grafting densities and WCAs for pP3HT. The thickness of the spin-coated film was 56±1 nm. (bottom) Thicknesses of grafted films after different solvent exposure methods, the calculated grafting densities, and WCAs for xP3HT. The thickness of the spin-coated film was 57±2 nm.
2.3.4 Electronic Properties

Organic field effect transistors (oFETs) were fabricated with a bottom gate, top contact architecture using both grafted pP3HT and xP3HT films as the active layer, and the native SiO\textsubscript{2} as the dielectric. Active layers were grafted for 1, 5, and 10 minutes, followed by puddle and rinse with chloroform. The hole mobilities were calculated using the slope of $\sqrt{I_{DS}}$ versus $V_{GS}$ line, in the saturation regime (Figures 2.14). The channel length of the electrodes was 100 µm, while the width was 2000 µm. The dielectric capacitance of SiO\textsubscript{2} is $1.7 \times 10^{-8}$ F/cm$^2$. The devices turned on under negative gate

![Figure 2.14: Transfer characteristics of grafted and rinsed xP3HT (red) and pP3HT (black).](image-url)
voltages, demonstrating hole transport through the grafted and swelled film. The transfer
curves generated for xP3HT and pP3HT based devices are shown in Figure 6. The linear
hole mobilities were calculated to be on the order of $10^{-6}$ cm$^2$V$^{-1}$s$^{-1}$ for both pP3HT and
xP3HT grafted and swelled active layers, for each grafting time. The low mobility for
these films could be a result of many factors, including the face-on orientation, the thinness
of the films, and high contact resistance. Previous reports indicate that face-on orientation
leads to hole mobilities 100x lower than edge-on P3HT films. Charge transport in the
direction of the pi-pi stacking is more effective in the architecture of typical oFETs when
the film has edge-on orientation. It has also been shown that in monolayers of P3HT, oFET
mobilities are typically on the order of $10^{-5}$-$10^{-4}$ cm$^2$V$^{-1}$s$^{-1}$, even for monolayers exhibiting
edge-on orientation. In this report, it is explained that ultra-thin films may be strained due
to their contact with two interfaces (air, substrate) causing them to lose the crystalline order
that a bulk film might possess. It is also possible that interfacial defects between the
monolayer and the substrate can hinder charge transport entirely, where in a bulk film, the
upper layers of polymer would help assist charge transport across such defects.

2.4 Conclusions

This study showed thiol-ene click chemistry effectively grafts functionalized
poly(thiophene)s to MPTS modified SiO$_2$ surfaces. Grafting times between 5-10 minutes
were enough to achieve high grafting densities for both end and pendant functionalized
poly(thiophene)s. Puddle and rinsing the grafted films with chloroform was the most
effective method for removing interpenetrated, non-grafted polymer. The success of the
grafting experiments was reliably tested by contact angle and x-ray photoelectron
spectroscopy (XPS). Two controls were used to validate that the fabricated films were a
result of alkene functionalized poly(thiophenes) grafting to the substrates by thiol-ene click chemistry, as opposed to the alkene functionalities radically cross-linking to create impervious networks. Unexpectedly, the grafting procedure did not affect the microstructure of the film, maintaining an edge-on orientation from the as spun film to the grafted film. The grafts that were rinsed in chloroform showed a significant change in microstructure to a face-on orientation, with the xP3HT graft being more ordered than the pP3HT graft, showing that the 2-point grafting system maintained a higher degree of orientation to the multi-point grafting system. Even after swelling with chloroform, these films were electrically active, demonstrating hole transport in field-effect transistor device structures. The mobilities were low for poly(thiophene) derivatives, but in line with ultra-thin films, which may experience interfacial strain and defects to a greater degree than bulk films do.

2.5 Future Outlook

Thiol-ene click surface grafting offers a simplistic and rapid method to fabricate well oriented, solvent resistant, electroactive, ultra-thin films. The film thicknesses can range from a couple nanometers to around 10-15 nanometers depending on the timeframe that the substrate is exposed to the grafting procedure. The insoluble grafted films have thicknesses that are in line with hole or electron transport layers. Additionally, as graftingchemically binds the polymer to the substrate surface, there is good connectivity at the interface between the electroactive film and the substrate and grafting ensures that there are no defects at the interface between the polymeric graft and the substrate. This can allow for the quick production of stable interlayers which can offer enhanced charge injection in organic light emitting diode or photovoltaic cell device architectures. Interlayer
engineering is important in such device applications, as adhesion problems and imbalanced work functions between the active layer and the electrode can greatly diminish the functionality and efficiency of such devices\textsuperscript{41}. Additionally, using 2-point grafting over multipoint grating can allow for highly structured insoluble thin films. Therefore, these thin grafts can act as a seeding layer for a subsequent active layer to guide desired microstructures. Face-on orientations are important for P3HT/fullerene based organic photovoltaic cells as it allows for more effective charge hoping between the vertically stacked electrodes. Additionally, vinyl end capping conjugated oligomers or polymers is a simple procedure that can extend across a variety of different polymerization methods and is not limited to vinyl grignard quenching of the McCullough method. The grafting-to of vinyl functionalized poly(thiophene)s to thiol modified silicon wafers is a model system, and this information should be transferable to other vinyl and thiol modified networks. Thiol-ene chemistry can offer an efficient method to formulate insoluble charge transport layers that can also act as a seeding agent to guide the crystal structure of an active layer.

2.6 References


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CHAPTER 3

EXCITED STATE CHARACTERIZATION OF CARBORANE-CONTAINING POLY(DIHEXYL FLUORENE)S

3.1 Introduction

Materials with variable emission properties, like solvatochromism, are coveted for sensor applications, as they can enable environmental or biological analyte detection without the use of expensive analytical instrumentation.1-5 Fluorescent conjugated organic macromolecules are an attractive class of materials for use in sensors as they can be easily synthesized and processed, and many show amplified sensing ability due to their electronic features, – as compared to small molecules.6-9 The wide variety of conjugated building blocks available allow for the controlled design of materials that can be tailored to sense specific environmental conditions. In particular, it is possible to produce materials that exhibit multiple emissive pathways such as excimer formation, excited state proton transfer, aggregated induced emission (AIE), or internal charge transfer (ICT), all of which can be affected by changes in the materials surroundings.10-14 Understanding the basis of such emissive pathways can illuminate how a material’s fluorescence properties may change in response to environmental variations, leading to the customized design of materials with excellent detection abilities.15-16

The icosahedral boron cluster, ortho-Carborane (C\(_2\)B\(_{10}\)H\(_{12}\)), displays unique electronic, steric, and chemical properties, including high hydrophobicity, high thermal and chemical stabilities, and three dimensionally delocalized electrons.17-22 Carboranes have been combined with conjugated systems in an attempt to provide thermal stability to semi-conducting polymers.17, 20, 23-25 Incorporating carborane into conjugated backbones also drastically influences the emission properties of these systems, which are influenced by the
dihedral angle between the carbon-carbon bond in carborane and the pi-conjugated unit.

For this reason, carborane has been widely studied in many conjugated monomer and polymer systems with aromatic building blocks including p-phenylene-ethynylene, naphthalene, carbazole, and triphenylamine, to name a few. These studies have shown that introducing carborane into a conjugated system can cause the system to experience excimer emissions, AIE, crystallization induced emission, ICT, and twisted ICT, in addition to the local emission of the conjugated building block. By altering the environment around the molecule or polymer, the intensity of these emissions can be tuned, causing a variety of fluorescent colors to be observed from the same material.

ICT states are of particular interest, because they are highly variable in response to environmental changes, making molecules or polymers that exhibit ICT states favorable for sensor applications. Such states are formed between electron donors and acceptors, and can be exceptionally fluorescent. Since carborane is a strong electron acceptor, ICT states can be readily formed between an aromatic electron donor molecule bonded to carborane, though in some cases ICT states are entirely independent of the aromatic excited states.

ICT states exhibit major emission peak changes with polarity changes, which usually involve a linearly increasing Stokes shift with increasing polarity. ICT states can also be affected by AIE, increasing in intensity with increasing concentration. Materials that exhibit ICT states can be used to detect trace amounts of analyte, a function important in the fields of chemistry, biology, and environmental science. There are many detailed reports of small molecules and polymers that experience ICT states used to detect pH changes, sugar molecules, and metal ions.
In the work described here, two carborane containing poly(dihexylfluorene)s were synthesized by standard cross-coupling techniques, and their fluorescent properties were studied. PFCy was synthesized by Yamamoto polymerization of a brominated bis(fluorenyl) carborane monomer, and PFCs was synthesized by polymerizing the brominated bis(fluorenyl) carborane monomer with 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester through Suzuki coupling. Both polymers were characterized with gel permeation chromatography (GPC) and $^1$H NMR. The polymers were functionalized with styrenic end groups to be used in thiol-ene click grafting experiments. UV-visible absorption spectroscopy (UV/VIS), photoluminescence spectroscopy (PL), time resolved photoluminescence spectroscopy (trPL), spectroelectrochemistry, and transient absorption spectroscopy (TA) were used to characterize the excited-state properties and to identify the nature of the excited states that dominate the fluorescent properties of both polymers. Taken together these experiments reveal that the carborane group in the backbone of the poly(dihexyl fluorene)s allows the excited fluorene to donate an electron to the carborane site, thereby generating an ICT state. Consequently, a radical cation is formed on the fluorene and a radical anion is formed on the carborane. The steady-state emission properties of the polymers are dependent on emissions from both the fluorene local excited state (LES) and the ICT state. Therefore, PFCs and PFCy have different emission properties because PFCs has more local excited state character than PFCy. Thin films and solutions of these polymers are exceptionally solvatochromic, and are able to sense analytes that have distinct polarities due to the effect polarity has on the ICT state. Along with this, the ICT state of PFCs undergoes an aggregated induced emission enhancement (AIEE) to a degree in the thin film state. In the
aggregated state, the ICT state can only decay radiatively. This is a useful property for thin-film sensors, as changes to the ICT state are greatly enhanced and easy to observe by the naked eye. An in-depth understanding of the photophysical properties of these polymers is important to further their use in sensing applications. The knowledge gained from this study will allow for further manipulation of the assembly of these emitting building blocks to design polymers for higher sensitivity detection.

3.2 Experimental Section

3.2.1 General Materials and Methods

All reagents were used as received and purchased from Sigma Aldrich.

3.2.2 Spectroelectrochemical Analysis

Spectroelectrochemical measurements were performed in an inert glove box environment using a USB2000+ Ocean Optics Spectrometer and a CH Instruments 660D Electrochemical Analyzer. Polymer films were coated onto ITO (indium-doped tin oxide) and were used as working electrodes. A platinum wire counter electrode and a silver wire quasi-reference electrode were used to complete the electrochemical cell. Tetrabutylammonium hexafluorophosphate (tTBAPF6, 100mM) in acetonitrile was used as the supporting electrolyte. Potentials were applied from 0V to 1.8V in increments of 0.2V to produce the radical cation, and potentials were applied from 0V to -1.2V in increments of 0.2V to produce the radical anion. These values were chosen because both polymers oxidize and reduce in these regions. The radical anion and cation of both PCFy and PCFs showed distinct, clearly observable absorption features.
3.2.3 Time-Resolved Photoluminescence Spectroscopy (trPL)

Time-resolved PL was performed on an ISS Chronos BH time-resolved fluorescence spectrometer. Solutions with concentrations of 0.1 mg/ml and 1 mg/ml in toluene, CHCl$_3$, and DMF were all analyzed. A 400-nm longpass filter was used to ensure that only the polymer emission was collected for the sample and not light from the 370-nm excitation nano-LED. The instrument response function was recorded using a dilute solution of coffee creamer in water. The fluorescent lifetimes of each sample were fit to exponential decays deconvolved from the instrument response.

3.2.4 Transient Absorption Measurements (TA)

TA measurements were carried out using 370 nm excitation for both polymers and the isolated dimers, and 315 nm excitation for the fluorene monomer. TA samples were comprised of ~0.002 mg/ml solutions of the respective species. The steady-state absorption spectra were recorded before and after TA to ensure that the polymers were not degraded during the experiment. A detailed description of the TA setup is described elsewhere.

3.2.5 PFCy Synthesis

The monomer, 1,2-bis(7-bromo-9,9-dihexyl-fluorenyl)-carborane (1 eq.), bipyridine (2.5 eq) and Ni(COD)$_2$ (2.5 eq) were all added to a round bottom flask, equipped with a stir bar and sealed with a rubber septum in a glovebox to maintain an inert environment. After being taken out of the glovebox, dry toluene (0.275M) was added to the round bottom, followed by 1,5 COD (2.5 eq). The round bottom was place in a hot bath at 80°C for 24 hours. To endcap the polymer, 0.125 eq of 4-bromostyrene end-capper can be added before addition of toluene and 1,5 COD and polymerized as usual. The
solution was dried with nitrogen to concentrate it and then poured into slightly acidic methanol (0.1M). The polymer recovered was a greyish solid33-34.

3.2.6 PFCs Synthesis

1,2-bis(7-bromo-9,9-dihexyl-fluorenyl)-carborane (1 eq) and 9,9-dihexylfluorene-2,7-diboronic acid bis (1,3-propanediol) ester (1 eq) were added to a round bottom flask with a stir bar and a rubber septa. In a glovebox, Pd(PPh3) (0.05 eq) was added to the flask, followed by the addition of dry toluene. The reaction was run with a 0.5M concentration of 4:1 toluene to water. A 2M potassium carbonate in water solution was made and degassed for an hour before being added to the reaction flask. Finally, a few drops of Aliquot 336 were added to the reaction flask as the phase transfer agent and the reaction was refluxed at 80°C for 12 hours. To end cap the reaction excess 4-bromostyrene and (4-vinylphenyl)boronic acid are added to the reaction sequentially. The dark reaction mixture was concentrated under nitrogen flow and then precipitated into slightly acidic methanol to reveal a light yellow solid35.

1H NMR (CDCl3, 500MHz) Reference 7.26 ppm: 8-7 (br, 30H), 6.8 (m, 1), 5.7 (d, 1H), 5.3 (d, 1H), 3.5-2.1 (br, 10H), 2-1.5 (br, 12H), 1.44 (m, 2H), 1.5-0.4 (br,?H)

3.3 Results and Discussion

3.3.1 Synthesis

![Figure 3.1: Repeat unit structures for PFCs and PFCy with Mₙ values. R is equal to C₆H₁₃.](image)
The brominated bis(fluorenyl) carborane monomer was synthesized using a procedure from an aforementioned report.\textsuperscript{34} PFCy was then polymerized from the brominated bis(fluorenyl) carborane monomer using Yamamoto coupling chemistry in the presence of 10 wt. % of 4-bromostyrene as an end cap functionality. PFCs was polymerized via Suzuki coupling of the brominated bis(fluorenyl) carborane monomer with 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester, which was quenched with excess 4-bromostyrene.\textsuperscript{35} Polymers were characterized with $^1$H NMR and GPC giving a $M_n$ of 4149 Da for PFCy and an $M_n$ of 3667 Da for PFCs (Figure 2). The low molecular weight of these materials is due to the kinked nature of the carborane monomer\textsuperscript{34} The repeat unit structures for both polymers, PFCy and PFCs, are shown in Figure 3.1.

![Figure 3.2: GPC trace of PFCy (red) and PFCs (blue). Peak at 1690 s is an artifact of the instrument.](image-url)
3.3.2 Steady-State Properties

Figure 3.3: Absorption spectra of PFCy (left) and PFCs (right) in toluene, CHCl₃, and DMF. PFCy shows a maximum absorbance at 340 nm in toluene and CHCl₃, and at 343 nm in DMF. All spectra have a shoulder at 315 nm. PFCs shows maximum absorbances at 358 nm and 317 nm in toluene and CHCl₃, and at 362 nm and 317 nm in DMF. The bathochromic shift in the DMF spectra could be due to aggregation, as the polymer has lower solubility in this solvent.
Figure 3.4: PFCy and PFCs PL spectra in toluene (a), chloroform (b), and DMF (c) at concentrations of 10, 5, 2.5, 1.25, 0.625, 0.3, 0.12, and 0.07 mg/ml. The deep red curve represents the 10 mg/ml solution and the purple curve represents 0.07 mg/ml solution. The curves in between these anchors range from 5-0.12 mg/ml in the order of the rainbow. The PL maxima are marked with translucent bands representative of the approximate color observed at each wavelength, allowing for easy observation of the polarity dependence of the redder (ICT) emission band.

The absorption and PL spectra were measured for both PFCy and PFCs in toluene, chloroform, and dimethylformamide (DMF) at varying concentrations. The absorption spectra are relatively unchanged between the three solvents, and follow typical Beer-Lambert behavior (Figure 3.3).

The PL spectra reveal drastic spectral shifts across all three solvents for both PFCy and PFCs. In general, the emission intensities increase and the emission peaks experience
hypsochromic shifts in solutions with decreasing concentration, due to less intermolecular quenching effects.

The emission spectra of PFCy in toluene show a broad peak that experiences a hypsochromic shift from 575 nm to 545 nm with decreasing concentration (Figure 3.4, translucent green band). An additional small shoulder at ~438 nm is observed in the spectra (translucent blue band). In chloroform, a similar hypsochromic shift is observed for the major emission band from 610 nm to 585 nm with decreasing concentration. Further, this main band is noticeably red shifted compared to the spectra in toluene (Figure 3.4, translucent yellow band). A blue-shift in the peak at ~450 nm is observed in CHCl₃ that shifts from 460 nm to 440 nm with decreasing polymer concentration. Unfortunately, PFCy has low solubility in DMF and the peak intensities are significantly reduced compared to the other two solvents. In DMF, the redder emission peak that dominated the emission spectra in toluene and chloroform (at 650 nm, translucent orange band) is dramatically quenched, and the dominating emission peak becomes the blue peak, which shifts from 470 nm to 440 nm with decreasing concentration.

The PFCs solutions show similar features to the PFCy solutions for all three solvents. In toluene, two major emission bands are apparent. The largest band is positioned at 440 nm and experiences a hypsochromic shift to 425 nm with decreasing concentration (Figure 3.4, translucent blue band). The band at 560 nm (translucent green-yellow band) does not show major shifts with changes in concentration. In a similar fashion to toluene, the chloroform samples have a 440 nm emission band that shifts to 425 nm with dilution, and is substantially more intense than the emission band at 620 nm (translucent orange
band). In DMF, the emission spectrum is comprised of only one major emission band that blue shifts from 455 nm to 425 nm as the concentration decreases.

The emission spectra observed for both PFCs and PFCy are similar in nature. The overall fluorescence intensities increase with decreasing concentration, and the emission peaks experience hypsochromic shifts for the bluer emission band in the PFCs solutions and hypsochromic shifts for both emission bands in the PFCy solutions with decreasing concentration. These spectral trends can be attributed to diminished effects of intermolecular quenching and aggregation in the dilute solutions.

A notable solvent dependence arises for the emission of both PFCs and PFCy. The redder emission band experiences a bathochromic shift as the solvent is varied from toluene to chloroform to DMF for both PFCs and PFCy, indicating a strong polarity dependence. The redder emission peak also diminishes in emission intensity as the solvent polarity increases. These two results suggest that the redder emission band represents emission from an ICT state. ICT states are polar in nature as they consist of anions and cations tethered together over a molecular bridge. In more polar environments ICT states are stabilized and usually red shift as the polarity of the environment increases. Further, it has been reported that the quantum yield of ICT states diminishes with increasingly polar environments. The reduction in emission intensity occurs because the electron in the more stabilized ICT state returns to the ground state through non-radiative pathways, rather than via emission of a photon.

The ICT band (~540 nm) is the most intense emission for PFCs in the solid state, as only a shoulder appears for the bluer LES band at ~425 nm (Figure 3.5). When aggregated, the ICT state emission intensity is often enhanced as the state is restricted and
mainly decays through radiative pathways, rather than non-radiative rotational or vibrational pathways. In Table 3.1 the quantum yield efficiencies are listed for both polymers in the three studied solvents, as well as in the aggregated state. The aggregated state was formed by dispersing a THF solution of the polymer in a 1:99 volume ratio with water. PFCy shows no emission enhancement in the aggregated state, while PFCs has a slightly higher quantum yield in the aggregated state than in the toluene solution. The solid-state emission of the PFCs ICT state does have a significantly higher emission intensity than the solution state in toluene, and the LES emission is entirely quenched in the solid-state. This indicates the ICT state in PFCs experiences some degree of aggregated induced emission enhancement (AIEE).

<table>
<thead>
<tr>
<th></th>
<th>PFCy</th>
<th>PFCs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LES</td>
<td>ICT</td>
</tr>
<tr>
<td>Toluene</td>
<td>x</td>
<td>0.4</td>
</tr>
<tr>
<td>CHCl3</td>
<td>x</td>
<td>0.1</td>
</tr>
<tr>
<td>DMF</td>
<td>0.01</td>
<td>x</td>
</tr>
<tr>
<td>Aggregated</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

Table 3.1: Quantum yields of PFCy and PFCs in toluene, CHCl3, DMF, and in the aggregated state with an error of ± 1.2% for the LES and ICT states. PFCy shows a low LES QY in DMF and no measurable QY in any other solution or the aggregated state. PFCy has an appreciable QY in toluene that drops off in CHCl3, and is not measurable for DMF or the aggregated state. PFCs on the other hand has measurable QYs for the LES in all three solutions, but not the aggregated state, and measurable QYs for the ICT in toluene and the aggregated state.
Figure 3.5: Solid-state emissions of PFCs and PFCy films spun-coat onto glass slides. PFCy shows emission characteristics similar to the toluene solution of that polymer, while PFCs shows prominent ICT character.

The bluer band is assigned to originate from the LES of the conjugated dihexyl fluorene unit between each carborane. The increased intensity of the ~440 nm peak, compared to the ICT emission, from PFCy to PFCs is attributed to the increased number of emitting conjugated fluorene dimer segments in the PFCs polymer repeat unit. The shape of the bluer peak for the PFCs solution spectra, which has a slight shoulder around 445 nm, suggests the emission of a fluorene dimer (Figure 3.6).
Figure 3.6: Absorption spectra of fluorene dimer at different concentrations (left), photoluminescence spectra of fluorene dimer at different concentrations (right), and lifetimes of 0.1 mg/ml samples in chloroform (inlet table) from trPL. Lifetime data shows a mono-exponential fit of ~700 ps for the radiative decay from the conjugated fluorene LES.

The solvent polarity dependence of the ICT emission was further investigated using the Mataga-Lippert relationship. PL spectra were recorded of both polymers in a series of solvents including: toluene, chloroform (CHCl₃), ethyl acetate, tetrahydrofuran (THF), dichloromethane (DCM), and acetone. The Mataga-Lippert equation (1) is used to relate the Stoke’s Shift of the redder peak to the polarity of the solvent.

$$\bar{\nu}_a - \bar{\nu}_f = \frac{2(\mu_e - \mu_g)^2}{\hbar c a^3} \Delta f (1)$$

In this equation, $\bar{\nu}_a$ is the peak absorption in wavenumbers and $\bar{\nu}_f$ is the peak fluorescence in wavenumbers. The term $\mu_e - \mu_g$ represents the difference between the excited state and ground state dipole moments. $\Delta f$ is the solvent polarity parameter, which relates the dielectric constant to the refractive index of a given solvent, and ‘a’ is the Onsager radius of the chromophore. $\hbar$ and $c$ are Planck’s constant and the speed of light, respectively. If the Onsager radius is known for a given material, it is possible to calculate the change in excited-state dipole from the slope of the line generated by (1). A linear relationship can be indicative of an ICT state, which would be more polar in nature than the ground state due to the redistribution of charges from the standard Frank Condon excited state.²⁶,²⁹ For
both PFCy and PFCs, the Mataga-Lippert relation shows a linear correlation between the Stokes Shift of the polymer solutions and the polarity of the solvent the polymer is dissolved in, further evidence of the ICT state (Figure 3.7).

**Figure 3.7:** PL spec. of PFCy in 6 different solvents (top). Mataga-Lippert plot of the Stoke’s Shift of the redder emission band, or the ICT emission band, against the solvent polarity parameter (bottom). For each solvent, the peak emission is listed beneath. The equation of the trend line and the $R^2$ value are listed at the bottom right corner of the Mataga-Lippert plot.

### 3.3.3 Time Resolved Photoluminescence Measurements

Time resolved photoluminescence (trPL) was used to measure excited state lifetimes of both PFCy and PFCs. Additionally, the fluorene dimer was examined in order to isolate a radiative lifetime for the fluorene LES. trPL emission data were collected in
two ways: (1) emission from the entire spectrum was collected in one kinetic trace or (2) a
monochromater was used to select specific emission wavelengths for the emission decay
acquisition. The emission decays collected using technique (1) produced excellent signal
to noise, low background counts and good reproducibility. However, emission from both
PL peaks were present in the decay profile and lead to bi-exponential decay behavior. The
emission decays collected using technique (2) required longer acquisition times because
only a small fraction of the emission spectrum was being collected. The background counts
were increased due to the longer collection times, and the signal to noise was not as good
as that of technique 1. Both techniques contributed valuable information in deciphering the
nature of the excited states and their lifetimes and are presented below.

Technique (1): For PFCy and PFCs, two relevant lifetimes (\(\tau_1\) and \(\tau_2\)) were extracted
by fitting bi-exponential functions to the emission decay. The first lifetime, \(\tau_1\), ranges from
0.4–0.8 ns and the second lifetime, \(\tau_2\), ranges from 1–2 ns across all concentrations and
solvents used in these studies (Table 3.2 for PFCy and Table 3.3 for PFCs). The PFCy
DMF 1 mg/ml sample could not be detected by trPL due to its low emission. Across all
samples, the fraction of \(\tau_2\) increases with decreasing concentration. Along with this,
lifetimes tend to be faster in DMF than in toluene or CHCl₃ for both polymers, and lifetimes
are faster in the 0.1 mg/ml solutions than in the 1 mg/ml solutions.

Technique (2): Single-wavelength lifetimes were extracted at fixed emission
wavelengths determined from emission peak maxima of the polymers in toluene, CHCl₃,
and DMF, in order to determine which emission band was associated with the lifetimes
obtained from Technique 1 (Table 3.4 for PFCy and Table 3.5 for PFCs). 0.1 mg/ml
solutions were used owing to their higher emission intensities. For PFCy, at emission
wavelengths of 435 nm for toluene and 440 nm for chloroform, one lifetime of ~0.5 ns was fit with a high intensity fraction (~90%). For the PFCy DMF sample, two relevant lifetimes were fit at an emission wavelength of 440 nm: 0.36 ns (66%) and 0.89 ns (33%). At 545 nm and 585 nm for the PFCy toluene and chloroform samples, two relevant lifetimes were used to fit the decay: ~0.7 ns and 2 ns (Table 3.4). For PFCs, a similar trend is observed, with high intensity fractions (~99%) observed for the ~0.5 ns lifetime associated with the 425 nm emission band, and a biexponential decay associated with 560 nm emission band for the toluene sample (Table 3.5). For PFCs, the redder ICT emission bands in CHCl₃ and DMF were not detectable due to low emission intensity. The biexponential nature of the redder emission bands for both polymers could be due to the detector picking up the tail end emission from the bluer emission band.

The \( \tau_1 \) values extracted from the ~400 nm single-wavelength experiments can be compared to the lifetime of the fluorene dimer, which was fit to a mono-exponential decay with a lifetime of ~0.7 ns (Figure 7 (inset table)). Therefore, it is possible to assign \( \tau_1 \) to the radiative decay of fluorene dimers within the polymer backbones. Assigning \( \tau_2 \) to the ICT state is consistent with the spectral trends observed for PFCy, namely that the emission intensity for the redder peak increases in the steady-state emission spectra as the concentration decreases from 1 mg/ml to 0.1 mg/ml in the toluene and chloroform solutions. Likewise, the fraction of \( \tau_2 \) contribution in the trPL decreases as the concentration increases, indicating that these two observations are linked. The low \( \tau_2 \) intensity fraction of the DMF solutions, mirror to the very low intensity seen for the redder peak in the steady-state emission spectra.
Table 3.2: Broad spectrum trPL (technique 1) lifetimes determined for PFCy in a series of solvents. Times determined from bi-exponential decays, fractions, and chi squared are listed.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\tau_1$ (ns)</th>
<th>$f$</th>
<th>$\tau_2$ (ns)</th>
<th>$f$</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1 mg/ml</td>
<td>0.54</td>
<td>55.8%</td>
<td>1.84</td>
<td>44.3%</td>
<td>1.28</td>
</tr>
<tr>
<td>1 mg/ml</td>
<td>0.83</td>
<td>66%</td>
<td>2.38</td>
<td>28.2%</td>
<td>1.19</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1 mg/ml</td>
<td>0.43</td>
<td>55.5%</td>
<td>1.09</td>
<td>30.1%</td>
<td>1.17</td>
</tr>
<tr>
<td>1 mg/ml</td>
<td>0.74</td>
<td>74.4%</td>
<td>2.41</td>
<td>20.3%</td>
<td>1.10</td>
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<tr>
<td>DMF</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1 mg/ml</td>
<td>0.48</td>
<td>84.9%</td>
<td>1.12</td>
<td>15.1%</td>
<td>1.19</td>
</tr>
</tbody>
</table>

Table 3.3: Broad spectrum trPL (technique 1) lifetimes determined for PFCs in a series of solvents. Times determined from bi-exponential decays, fractions, and chi squared are listed.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\tau_1$ (ns)</th>
<th>$f$</th>
<th>$\tau_2$ (ns)</th>
<th>$f$</th>
<th>$\chi^2$</th>
</tr>
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<tbody>
<tr>
<td>Toluene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1 mg/ml</td>
<td>0.48</td>
<td>60.9%</td>
<td>1.21</td>
<td>39.1%</td>
<td>1.28</td>
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<tr>
<td>1 mg/ml</td>
<td>0.73</td>
<td>82%</td>
<td>1.66</td>
<td>16.5%</td>
<td>1.02</td>
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<tr>
<td>CHCl$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1 mg/ml</td>
<td>0.46</td>
<td>66.5%</td>
<td>0.93</td>
<td>32.7%</td>
<td>1.12</td>
</tr>
<tr>
<td>1 mg/ml</td>
<td>0.66</td>
<td>94.1%</td>
<td>2.15</td>
<td>3.39%</td>
<td>1.13</td>
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<td>DMF</td>
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<td></td>
</tr>
<tr>
<td>0.1 mg/ml</td>
<td>0.39</td>
<td>48.9%</td>
<td>0.81</td>
<td>45.9%</td>
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<td>1 mg/ml</td>
<td>0.58</td>
<td>81.2%</td>
<td>1.2</td>
<td>15.9%</td>
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</table>
Table 3.4: Single-wavelength trPL (technique 2) lifetimes determined for PFCy in a series of solvents at emission peak maxima relevant to each system. All samples had a concentration of 0.1 mg/ml. Times determined from bi-exponential decays, fractions, and chi squared are listed. \( \tau_1 \) is the radiative lifetime from the fluorene LES, \( \tau_2 \) is the radiative lifetime of the ICT state.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \tau_1 ) (ns)</th>
<th>f</th>
<th>( \tau_2 ) (ns)</th>
<th>f</th>
<th>( \chi^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
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</tr>
<tr>
<td>435 nm</td>
<td>0.46</td>
<td>92%</td>
<td>1.72</td>
<td>8%</td>
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<td>545 nm</td>
<td>0.75</td>
<td>67%</td>
<td>2.20</td>
<td>33%</td>
<td>1.08</td>
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<td>CHCl_3</td>
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<tr>
<td>440 nm</td>
<td>0.49</td>
<td>90.6%</td>
<td>1.6</td>
<td>9.4%</td>
<td>1.07</td>
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<tr>
<td>585 nm</td>
<td>0.67</td>
<td>72.3%</td>
<td>2.52</td>
<td>27.6%</td>
<td>1.14</td>
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<td>DMF</td>
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<td></td>
</tr>
<tr>
<td>440 nm</td>
<td>0.36</td>
<td>66.6%</td>
<td>0.89</td>
<td>33.4%</td>
<td>1.12</td>
</tr>
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</table>

Table 3.5: Single-wavelength trPL (technique 2) lifetimes determined for PFCs in a series of solvents at emission peak maxima relevant to each system. All samples had a concentration of 0.1 mg/ml. Times determined from bi-exponential decays, fractions, and chi squared are listed. \( \tau_1 \) is the radiative lifetime from the fluorene LES, \( \tau_2 \) is the radiative lifetime of the ICT state.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \tau_1 ) (ns)</th>
<th>f</th>
<th>( \tau_2 ) (ns)</th>
<th>f</th>
<th>( \chi^2 )</th>
</tr>
</thead>
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<td>Toluene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>425 nm</td>
<td>0.46</td>
<td>99%</td>
<td>6.54</td>
<td>1%</td>
<td>1.19</td>
</tr>
<tr>
<td>CHCl_3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>425 nm</td>
<td>0.55</td>
<td>98%</td>
<td>12.7</td>
<td>2%</td>
<td>1.32</td>
</tr>
<tr>
<td>DMF</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>425 nm</td>
<td>0.57</td>
<td>99%</td>
<td>2.99</td>
<td>1%</td>
<td>1.26</td>
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<tr>
<td>Toluene</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>560 nm</td>
<td>0.69</td>
<td>50%</td>
<td>1.39</td>
<td>50%</td>
<td>1.13</td>
</tr>
</tbody>
</table>
3.3.4 Spectroelectrochemistry

Figure 3.8: Spectroelectrochemical absorption profiles of the radical cation (small blue dash) and the radical anion (long red dash) for PFCy (top) and PFCs (bottom). For both polymers, the summation of the radical anion and cation to give the presumed ICT absorption is shown in purple. Above the spectra is a cartoon representation of the blue radical cation on fluorene and the red radical anion on carborane creating the purple ICT state.

Through spectroelectrochemistry, it is possible to visualize the absorption spectra of reduced and oxidized chemical species. Consequently, identifying an ICT absorption profile through this technique is viable, as the ICT excited state would represent a convolution of a radical cation and radical anion tethered over a molecular bridge. Thin film spectroelectrochemistry was carried out for both PFCy and PFCs in order to establish the absorption profiles of both polymer ICT states. Solution state spectroelectrochemistry
was thwarted because no appropriate solvent and electrolyte combination fell within the oxidation window for either polymer. Oxidizing PFCy from 0V to 1.8V, shows the growth a broad peak with maxima at 480 nm and 525 nm (Figure 8, small blue dash). This oxidative spectroelectrochemistry band strongly resembles the radical cation absorption spectrum of the oxidized fluorene dimer, which demonstrates that the oxidized PFCy species is a fluorene radical cation. Reducing PFCy from 0V to -1.2V, shows a spectrum with a broad peak at 470 nm, and is likely a radical anion localized on the carborane moiety (Figure 8, long red dash). The summation of the radical cation and radical anion absorption curves show what the ICT excited state absorption should resemble for PFCy (Figure 8, purple line). PFCs was similarly oxidized and reduced to give broader radical anion and radical cation absorption profiles. The summation of the radical anion and radical cation absorption curves for PFCs give a presumed ICT for this polymer (Figure 3.8).
3.3.5 Transient Absorption Spectroscopy

Figure 3.9: Transient absorption spectra of PFCy in toluene, chloroform, and DMF (left). The transient absorption spectra are taken at a range of times from 0 to 3 ns. The LES excited state grows in at 650 nm before forming the broad ICT state at 495 nm to 550 nm. As the polarity of the solvent increases from toluene to DMF, the ICT forms faster. Transient absorption spectra of PFCs in toluene, chloroform, and DMF (right). The LES excited state grows in at 700 nm before forming the broad ICT state at 500 nm to 600 nm. Trends seen in these spectra are nearly identical to trends seen in the PFCy samples, though red-shifted.
Figure 3.10: Transient absorption profiles of the fluorene monomer (left) and dimer (right) at different time delays. Single-wavelength lifetimes taken at 550 nm for fluorene show a bi-exponential fit with lifetimes of $860 \pm 60$ ps and $86 \pm 9$ ps. For the dimer, single-wavelength lifetimes of $860 \pm 3$ ps and $100 \pm 7$ ps were extracted at 630 nm. With conjugation from the monomer to the dimer, the main absorption band of the excited state red shifts. From literature and data not shown in this paper, we know that with further conjugation the fluorene LES broadens and further red shifts from the dimer.

Figure 3.11: Global Analysis spectra for PFCy (left) and PFCs (right) in toluene, CHCl$_3$, and DMF. The Global Analysis details the lifetimes (tables) of the electron
transfer ($\tau_{BT}$) from the LES (magenta curve) and the radiative decay ($\tau_{CT}$) of the ICT state (lime green curve) for all three samples. The infinite curve represents the residual spectrum remaining at the end of our time delay (black curve). The ICT forms much faster in DMF than toluene. The valley included in the LES curve is indicative of electron transfer from LES to form the ICT state. The PFCs sample in DMF does not show the electron transfer, as it is faster than the instrument detection. In addition to the ICT decay, it shows the radiative decay from the LES.

### Toluene

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<th>Time (nm)</th>
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<th>Time (ps)</th>
<th>f</th>
<th>Time (ps)</th>
<th>f</th>
</tr>
</thead>
<tbody>
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<td>650</td>
<td>698.2 ± 70.4</td>
<td>+0.57</td>
<td>4.9 ± 0.6</td>
<td>+0.43</td>
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</tr>
<tr>
<td>620</td>
<td>959.4 ± 174.5</td>
<td>+0.57</td>
<td>5.39 ± 1.4</td>
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<tr>
<td>540</td>
<td>1078.7 ± 78.7</td>
<td>+0.87</td>
<td>142.4 ± 97.9</td>
<td>+0.1</td>
<td>7.10 ± 2.2</td>
<td>-0.04</td>
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<tr>
<td>500</td>
<td>1316.7 ± 134.1</td>
<td>+0.87</td>
<td>107.7 ± 25.8</td>
<td>+0.08</td>
<td>7.75 ± 2.5</td>
<td>-0.05</td>
</tr>
</tbody>
</table>

### CHCl$_3$

<table>
<thead>
<tr>
<th>Time (nm)</th>
<th>Time (ps)</th>
<th>f</th>
<th>Time (ps)</th>
<th>f</th>
<th>Time (ps)</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td>650</td>
<td>2.9 ± 0.9</td>
<td>+1</td>
<td>303.1 ± 6</td>
<td>+0.20</td>
<td>0.9 ± 0.003</td>
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<tr>
<td>620</td>
<td>738.8 ± 33.1</td>
<td>+0.4</td>
<td>180.5 ± 25.7</td>
<td>+0.08</td>
<td>3.4 ± 1.6</td>
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<td>540</td>
<td>890.6 ± 78.7</td>
<td>+0.72</td>
<td>202.6 ± 69.5</td>
<td>+0.16</td>
<td>2.4 ± 0.5</td>
<td>-0.20</td>
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<tr>
<td>500</td>
<td>962.8 ± 134.1</td>
<td>+0.65</td>
<td>28.4 ± 6.3</td>
<td>+0.13</td>
<td>0.9 ± 0.003</td>
<td>-0.61</td>
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</tbody>
</table>

### DMF

<table>
<thead>
<tr>
<th>Time (nm)</th>
<th>Time (ps)</th>
<th>f</th>
<th>Time (ps)</th>
<th>f</th>
<th>Time (ps)</th>
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</tr>
</thead>
<tbody>
<tr>
<td>620</td>
<td>396.3 ± 43.3</td>
<td>+0.26</td>
<td>28.4 ± 6.3</td>
<td>+0.13</td>
<td>0.9 ± 0.003</td>
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<tr>
<td>570</td>
<td>524.7 ± 46.9</td>
<td>+0.19</td>
<td>62.9 ± 16.2</td>
<td>+0.19</td>
<td>1.0 ± 0.001</td>
<td>-0.61</td>
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</tbody>
</table>

Figure 3.12: Tabulated single-wavelength lifetimes taken at pertinent peak transient absorption bands of PFCy in toluene, chloroform, and DMF. The pink boxes represent electron transfer lifetimes, the blue boxes represent LES radiative decay, the green boxes represent ICT radiative decay, and the grey boxes represent ICT non-radiative decay. The signs in front of the fraction values represent whether the amplitude of the fit was negative or positive. Negative amplitudes depict energy transfer, while positive amplitudes depict decay.
### Figure 3.13: Tabulated single-wavelength lifetimes taken at pertinent peak transient absorption bands of PFCs in toluene, chloroform, and DMF.

The pink boxes represent electron transfer lifetimes, the blue boxes represent LES radiative decay, the green boxes represent ICT radiative decay, and the grey boxes represent ICT non-radiative decay. The signs in front of the fraction values represent whether the amplitude of the fit was negative or positive. Negative amplitudes depict energy transfer, while positive amplitudes depict decay.

Femtosecond transient absorption spectroscopy (fs-TA) was used to determine the nature and lifetimes of the excited states of both PFCy and PFCs (Figure 9). The experiments were run in toluene, chloroform, and DMF and produced similar excited-state absorption bands across all three solvents. As a comparison, fs-TA was completed on both...
the fluorene monomer and dimer to identify the spectral contribution of the LES excited state within the polymer spectra (Figure 3.10).

For PFCy in toluene, an initial excited state is formed with a peak > 650 nm. During the first few picoseconds, this excited state evolves into a second state with a peak at ~495-500 nm and a shoulder ~620-650 nm. The species at ~495-500 nm persists for several nanoseconds. In comparison, the excited state of the fluorene monomer shows a sharp absorption at 550 nm, while the excited state of the dimer had a sharp absorption at 630 nm (Figure 3.10), showing that the fluorene LES excited state absorption red shifts with increasing conjugation. These results and the fact that the fluorene within PFCy experiences additional conjugation, lead to assignment of the 650 nm peak seen in the PFCy excited-state spectra to the fluorene LES (Figure 3.9, magenta line). The absorption band at ~495-500 nm is likely the ICT state as it resembles the combination of the fluorene radical cation and carborane radical anion absorptions determined from spectroelectrochemistry (Figure 3.9, lime green line). The similarity of these spectra indicates that PFCy efficiently accesses an internal charge transfer state bridged across the fluorene-carborane.

Global analysis, a technique used to determine relevant spectral contributions for individual lifetimes extracted from the entire dataset, identified two pertinent spectra that contribute to the excited state evolution of the polymer\textsuperscript{36}. For PFCy in toluene, the first spectrum evolves with a lifetime of ~12.9 ps (Figure 3.11) that shows the decay of the LES at > 650nm concomitant with a growth of the peak between 495-500nm. This spectrum confirms that the LES feeds the ICT state via photo-induced charge transfer. After formation of the ICT state, represented by the green spectrum in Figure 3.11, it decays with
a lifetime on the order of 1.1 ns. In corroborated with trPL, it is possible to identify the lifetime of 1.1 ns as the radiative decay of the ICT state.

fs-TA was completed for PFCy in chloroform and DMF (Figures 3.9). While the overall spectra look fairly similar to the toluene spectra, the global analysis (Figure 3.11) shows more rapid electron transfer from the LES to form the ICT, as well as a faster decay of the ICT state. In chloroform, the LES band at 650 nm has a lifetime of 3.7 ps and the ICT state decays with a lifetime of 670.7 ps. In DMF, the trend continues, with the excited state electron transfer (~2.1 ps) being so fast that the absorption of the LES is difficult to collect as it runs into the instrument response of our TA experimental setup. The ICT state also decays very fast, at ~265.3 ps. This trend is also observed in the trPL data.

PFCs was also studied in toluene, chloroform, and DMF (Figure 3.9 and 3.11). The absorption bands follow the trends observed for PFCy bands for all three solvents, however the LES (~700 nm) and ICT (~540 nm) bands are modestly red-shifted. The global analysis of PFCs in toluene reflects both ICT formation (~32.4 ps) and radiative decay (1.3 ns) in a similar fashion to the PFCy. In chloroform, the ICT formation (~4.9 ps) and radiative decay (747.9 ps) are again faster than in toluene.

In DMF, PFCs displays a very fast electron transfer from the LES to the ICT (~1 ps), and the ICT undergoes a much faster recombination. While the electron transfer can be observed in the TA spectra, the global analysis for this sample does not capture the event, as the process reaches the detection limit of the instrument. The global analysis shows that along with ICT formation and decay (~17.7 ps), the LES independently radiatively decays (~684.4 ps). This observation is confirmed by the pL spectra for this sample which only show LES emission. It may be possible to visualize this radiative decay from the LES
because radiative decay from ICT minimally contributes to the possible decay mechanisms of the excited electrons in this particular sample. In all of the other samples, radiative decay from the ICT is a main contributor.

The trends determined from these data sets, show that photo-induced electron transfer from the fluorene LES to form the ICT state becomes faster in more polar solvents. The ICT, ionic in nature, is more stabilized in polar solvents, as opposed to toluene, and is therefore easier to form. The ICT radiatively decays after formation, and this decay is faster in the more polar solvents, due to the reduced band gap of this stabilized excited state.

The global analysis results were further verified by single-wavelength fittings at peak absorption wavelengths in the overall TA spectra (Figure 3.12 and 3.13). In addition to radiative lifetimes (from trPL) and the electron transfer lifetime (from global analysis), there is a third lifetime associated with non-radiative decay from the ICT state, discovered through the single-wavelength fittings.

For the PFCy toluene sample, the radiative lifetime extracted from the single-wavelength fitting of the ICT state at 500 nm and 540 nm (~1000-1300 ps), makes up 87% of decay intensity. The non-radiative lifetime (~100 ps) makes up ~8% of the decay and the electron transfer lifetime makes up ~5% of the decay. The electron transfer lifetime has a negative amplitude which represents the transfer of energy from the LES to form the ICT. Alternatively, the non-radiative and radiative lifetimes have positive amplitudes that represent decay. The single-wavelength fittings at 650 nm and 620 nm show radiative decay (~700 ps) and electron transfer (5 ps), both with positive amplitudes indicating they
are decay pathways of the LES state. LES radiative decay makes up 57% and electron transfer make up 43% of the decay profile for the LES.

For the PFCy chloroform sample, the radiative lifetime extracted from the single-wavelength fitting of the ICT state at 500 nm (~900 ps), makes up 65% of decay intensity. The non-radiative lifetime (~200 ps) makes up ~16% of the decay and the electron transfer lifetime makes up ~20% of the decay. The single-wavelength fittings at 650 nm only show electron transfer. At 620 nm radiative decay (~700 ps) is 40% of the decay pathways from the LES and electron transfer (5 ps) is 60%.

In DMF, the radiative decay of the ICT (~400 ps) comprised of 19% of the decay profile, while non-radiative decay (~60 ps) made up 19%, and electron transfer (~1 ps) made up 60% of the tri-exponential decay. Decay of the LES was primarily through electron transfer.

For PFCs, similar trends were observed. In toluene, only lifetimes associated with electron transfer, LES radiative decay, and ICT radiative decay were determined through single-wavelength fitting. In chloroform, at 500 nm, a tri-exponential decay could be fit to all three lifetimes associated with ICT radiative and non-radiative decay, and electron transfer. In DMF, all wavelengths sampled were tri-exponential.

The non-radiative lifetime has minimal contributions to ICT decay in the PFCy toluene sample, and no contributions to the PFCs toluene sample. The non-radiative lifetime increases in fraction for both PFCy and PFCs chloroform samples and the PFCy DMF sample, and it dominates in the PFCs DMF sample (Figure 3.14). The ICT state shows little to no emission in the chloroform and DMF spectra for both polymers (Figure 3.4). In toluene, the ICT state may be rigid due to its instability as an ionic state in a non-
polar solvent, and therefore unable to decay by rotational or vibrational means. This can be likened to AIE, which forces molecules to emit radiatively when vibrational or rotational paths are inhibited by aggregation. While the polymer itself is not aggregated in toluene, this could be understood as an intramolecular restriction. In chloroform and DMF, the ICT state is stabilized by the polar environment and able to find non-radiative pathways to decay, lessening the radiative emission from the ICT state.

Figure 3.14: Fraction of decay lifetimes under ICT state for PFCy (a) and PFCs (b) as well as excited-state manifold schematic (right). Green bars represent radiative decay from the ICT state, grey bars represent non-radiative decay from the ICT state, and magenta bars represent ICT formation after donation of an electron from the fluorene unit to the carborane unit.

3.4 Conclusions

Carborane containing poly(dihexyl fluorenes) were synthesized by standard cross-coupling techniques to produce polymers with interesting solvatochromic properties. Through a series of comprehensive steady state, lifetime, and transient spectroscopies, the
nature of the excited states and dynamics of both polymers were determined. When the LES of the conjugated fluorene section of the polymer is excited by UV light, photo-induced electron transfer to a neighboring carborane cage occurs, generating a radical anion on the carborane and a radical cation on the fluorene unit, and thus represents an ICT state. The rate of the electron transfer can be tuned by the polarity of the environment the polymer experiences. Once the ICT is formed, it can either decay radiatively or non-radiatively and tends to exhibit more non-radiative decay in the more polar environments. This could be due to its stability in this state, allowing it to find rotational or vibrational pathways to decay. This data explains the interesting solvatochromism displayed in the PL spectra of these and other carborane-containing conjugated polymers. Understanding the excited states that dominate the useful emissive properties of these polymers, and how these excited states are altered by their environments, will allow for the design of polymers that have tunable emissive properties, enabling desired emissive colors for OLED applications, or polymers with higher detection limits for polar analytes.

3.5 References


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intramolecular charge transfer and aggregation-induced emission of BODIPY derivatives.

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CHAPTER 4
SYNTHETIC EMISSION TUNING OF CARBORANE CONTAINING POLY(DIHEXYL FLUORENE)S

4.1 Introduction

Ortho-carborane (C2B10H12), an icosahedral boron cluster, possesses unique electronic, steric, and chemical properties, including high hydrophobicity, high thermal and chemical stabilities, and strong electron accepting characteristics. Integration of carborane into molecular and polymeric aromatic backbones has been shown to drastically influence the emission properties of these systems. In many cases, this is due to the formation of an intramolecular charge transfer (ICT) state between the pi-conjugated moiety and the carborane molecule. The ICT state is typically characterized as an additional emission band in the photoluminescence (PL) spectra to the local excited state (LES) emission from the pi-conjugated moiety, that experiences solvatochromic behavior and/or aggregated induced emission (AIE), AIE enhancement (AIEE), crystallization-induced emission enhancement (CIEE), and the ICT state can also be influenced by twisting between the plane of the aromatic excited state and the C1-C2 bond of the carborane molecule (twisting-induced charge transfer (TICT)). Furthermore, the ICT state is typically comprised of charged species making it polar in nature.

Interest in inclusion of carborane into a wide variety of aromatic structures has been unwavering over the past 30 years because these easily synthesized molecules and polymers have many applications owing to the interesting and unique photophysical properties experienced by these materials in both the solution and solid state. AIE, AIEE, or CIEE experiencing materials are appreciably useful in optoelectronic devices, as they have highly intense solid-state emission properties. Along with this, the typical
solvatochromic nature of these materials are advantageous in chemical and biological sensing applications as the emission properties in both the solid-state and solution-state are highly responsive to environmental changes, like polarity, pH, or ionic materials\textsuperscript{17-20}. Finally, aromatic functionalized carborane containing materials can be utilized as photosensitizers for solar cell applications as they commonly are comprised of tethered electron donors and electron acceptors, are easy to synthesize, and can have low energy absorption wavelengths\textsuperscript{14}.

The synthesis and extensive characterization of carborane containing poly(dihexylfluorene)s has been previously reported showing that these polymers experience solvatochromism and some degree of AIEE due to the formation of an ICT state in the excited state manifold of the polymer between the fluorene unit and the carborane molecule\textsuperscript{21-23}. The solvatochromism is visible in both the solution and solid-state, and when films of these polymers are introduced to solvent vapors an emission color change is evident, making this polymer an interesting material for chemical sensing\textsuperscript{24}. The homopolymer of bis(fluorenyl) carborane, synthesized through Yamamoto coupling, has proven a practical model system in understanding the photophysical phenomena that govern the excited state properties of this system\textsuperscript{21}. Introducing an extra fluorene monomer into the repeat unit through alternating copolymerization of dibromo-bis(dihexylfluorenyl)carborane with 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester through Suzuki coupling increases the LES emission intensity relative to the ICT state emission intensity. This is a result of a higher conjugation of fluorene units in the polymer backbone, allowing for a greater quantity of radiative decay from the LES as compared to the homopolymer. The solid-state and solution-state emission properties
of the alternating copolymer are visibly different from the homopolymer after this synthetic change and can be characterized by a color change due to the increased LES emission, as well as an overall increase in the aggregated quantum yield. The ability to synthetically tune the solution and solid-state emission properties of this class of polymers by extending the conjugation length of the fluorene by one monomer can allow for the fabrication of materials with easy analyte detection by eye, as well as materials with coveted solid-state emission colors, like white emitters.

The random copolymerization of differing equivalents of 2,7-dibromo-9,9-dihexylfluorene and dibromo-bis(9,9-dihexylfluorenyl) carborane is reported. This is done in order to synthesize four random copolymers with increasing degrees and conjugation lengths of conjugated dihexylfluorene in the polymeric backbone to compare to the photophysical properties of the bis(9,9-dihexylfluorenyl) carborane homopolymer. In addition to changing the PL properties by increasing the degree of LES radiative emission, increasing feed ratios of dihexylfluorene also produced polymers with higher molecular weights due to the more linear nature of the polymer chain. Steady-state, photoluminescence, and time-resolved characterization methods are used to understand how extending the extent and length of the conjugated dihexylfluorene in the polymeric backbone effects the excited-state and photophysical properties of these polymers. Polymers with higher extents of conjugated fluorene in the backbone had more intense fluorene LES emissions, as compared to the ICT emission, and more intense fluorene LES absorptions determined through transient absorption (TA). This allowed for the fabrication of materials with higher quantum yields in the aggregated state as compared to the homopolymer, as well as the ability to alter the emission color through balancing the
radiative decays of both the LES to the ICT states. This simple procedure for tuning the solution and solid-state properties of carborane containing poly(9,9-dihexylfluorene)s can allow for a class of carborane-containing polymers with minimal amounts of carborane incorporation, which can increase the molecular weight of the polymers and thus the processing ability, but still maintain the interesting properties of that carborane moiety.

4.2 Experimental Section

4.2.1 General Materials and Methods

All reagents were used as received and purchased from Sigma Aldrich.

4.2.2 Characterization

$^1$H NMR of the polymers was acquired using a Bruker 500 MHz Ascend fitted with a cryo-probe in deuterated chloroform. Gel permeation chromatography of the polymers was performed using an Agilent 1260 series system with a refractive index detector, a 5 μm guard column, two 5 μm analytical Mixed-C columns, and a 5 μm analytical Mixed-D column connected in series and incubated at 40 °C with THF as the eluent at a flow rate of 1.0 mL/min. The polymers were compared to poly(styrene) standards. UV/Vis spectroscopy was done on a Shimadzo 3600.

4.2.3 Time-Resolved Photoluminescence Spectroscopy (trPL)

Time-resolved PL was performed on an ISS Chronos BH time-resolved fluorescence spectrometer. Solutions with concentrations of 0.1 mg/ml in toluene and CHCl3, were all analyzed. The instrument response function was recorded using a dilute solution of coffee creamer in water. The fluorescent lifetimes of each sample were fit to exponential decays deconvolved from the instrument response. A 280 nm LED was used
as the excitation source. Light from this source is apparent in the decay profiles and is characterized by a lifetime greater than 2 ns.

4.2.4 Transient Absorption Measurements (TA)

TA measurements were carried out using 370 nm excitation for all polymers and the isolated dimers, and 315 nm excitation for the fluorene monomer. TA samples were comprised of ~0.002 mg/ml solutions of the respective species. The steady-state absorption spectra were recorded before and after TA to ensure that the polymers were not degraded during the experiment. A detailed description of the TA setup is described elsewhere\textsuperscript{25}.

4.2.5 \textit{y}, 50/50, 35/65, 20/80, 5/95 Synthesis

The monomer, 1,2-bis(7-bromo-9,9-dihexyl-fluorenyl)-carborane (1 eq., 0.5 eq., 0.35 eq., 0.2 eq., 0.05 eq. for \textit{y}, 50/50, 35/65, 20/80, and 5/95, respectively), bypyridine (2.5 eq), Ni(COD)\textsubscript{2} (2.5 eq), and 2,7-dibromo-9,9-dihexylfluorene (0 eq., 0.5 eq., 0.65 eq., 0.8 eq., 0.95 eq. for \textit{y}, 50/50, 35/65, 20/80, and 5,95, respectively) were all added to a round bottom flask, equipped with a stir bar and sealed with a rubber septum in a glovebox to maintain an inert environment. After being taken out of the glovebox, dry toluene (0.275M) was added to the round bottom, followed by 1,5 COD (2.5 eq). The round bottom was place in a hot bath at 80°C for 24 hours. To endcap the polymer, 0.125 eq of 4-bromostyrene end-capper can be added before addition of toluene and 1,5 COD and polymerized as usual. The solution was dried with nitrogen to concentrate it and then poured into slightly acidic methanol (0.1M). The polymers recovered were greyish solids.
4.3 Results and Discussion

4.3.1 Synthesis

Figure 4.1: Synthetic schematic of carborane containing copolymers.

<table>
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<th>m eq:</th>
<th>n eq:</th>
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<th>2.05 ppm</th>
<th>m:n</th>
<th>M_n (kDa)</th>
<th>PDI</th>
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<td>-</td>
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<td>-</td>
<td>0:1</td>
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</tr>
</tbody>
</table>

Table 4.1: Equivalents of all five polymers, integrations of alpha aliphatic $^1$H NMR peaks for carborane (1.83 ppm) and fluorene (2.05 ppm) blocks, ratios determined through $^1$H NMR, $M_n$ in kDa, and PDI for all five polymers. Ratios from $^1$H NMR are determined by comparing the carborane integration which integrates to 8 hydrogens for the repeat unit, to the integrations for the fluorene integration. For the fluorene unit, the alpha aliphatic hydrogens integrate to 4.

The brominated bis(fluorenyl) carborane monomer (1,2-bis(7-bromo-9,9-dihexyl-9H-fluoren-2-yl)-closo-dicarbodecaborane) was synthesized using a procedure from an
aforementioned report. Four polymers were then randomly co-polymerized from the brominated bis(fluorenyl) carborane monomer and 2,7dibromo-9,9-dihexyl-9H-fluorene using Yamamoto coupling chemistry with varying equivalents of carborane monomer and 2,7dibromo-9,9-dihexyl-9H-fluorene. These ratios consisted of 0.5 equivalents of carborane monomer to 0.5 equivalents of 2,7dibromo-9,9-dihexyl-9H-fluorene (50/50), 0.35 equivalents of carborane monomer to 0.65 equivalents of 2,7dibromo-9,9-dihexyl-9H-fluorene (35/65), 0.2 equivalents of carborane monomer to 0.8 equivalents of 2,7dibromo-9,9-dihexyl-9H-fluorene (20/80), and 0.05 equivalents of carborane monomer to 0.95 equivalents of 2,7dibromo-9,9-dihexyl-9H-fluorene (5/95). Additionally, a homopolymer (100/0) of the bis(fluorenyl) carborane monomer was synthesized through Yamamoto polymerization. Polymers were characterized with ¹H NMR and GPC giving number average molecular weights of 5549 Da, 4843 Da, 6812 Da, 6394 Da, and 8521 Da for 100/0, 50/50, 35/65, 20/80, 5/95, respectively. Molecular weights and 2,7-dibromo-9,9-dihexyl-9H-fluorene equivalents of all five polymers are listed in Table 4.1. The low molecular weight of these materials is due to the kinked nature of the carborane monomer, but with increasing fluorene presence in the polymer backbone, the molecular weights increase. GPC trace is shown in Figure 4.2.
Figure 4.2: GPC trace of homopolymer (red) and copolymers, 50/50 (yellow), 35/65 (green), 20/80 (blue), 5/95 (purple) showing the more linear structure of the 20/80 and 5/95 copolymer with higher fluorene conjugation length.

The $^1$H NMR for the homopolymer (100/0) shows the broad B-H stretches characteristic of carborane around 3.4 ppm and 2.6 ppm and sharp, vibronic peaks from 7.5-7.4 ppm representative of the aromatic hydrogens. Additionally, a broad peak at 1.8 ppm represents aliphatic hydrogens on the alpha carbons of the hexyl side-chains. The 50/50 polymer has an almost identical $^1$H NMR spectra to the homopolymer, with the addition of a small peak around 2 ppm, identifying aliphatic hydrogens on the alpha carbons of the hexyl side-chains of the oligomeric conjugated fluorene blocks in the
polymer backbone. Integrating the 1.8 ppm and 2 ppm peaks show a ratio of 0.75:1 fluorene repeat units to carborane monomer repeat units. The B-H stretch for 35/65 is no longer broad but shows sharper peaks at 3.5 ppm and 2.7 ppm, and the aromatic hydrogen peaks show a more gradual structure ranging from 7.8 ppm to 7.3 ppm, with distinct peaks at 7.8 ppm, 7.7 ppm, 7.55 ppm, and 7.3 ppm. The 7.8 ppm and 7.7 ppm correspond to the aromatic hydrogens on the conjugated fluorene in the polymer backbone. Integrating the 1.8 ppm and 2.0 ppm peaks show a ratio of 2:1 fluorene repeat units to carborane monomer repeat units. The 20/80 spectrum shows a negligible B-H stretch, and an increase in the 2.0 ppm band as well as an increase in the 7.8 and 7.7 ppm aromatic bands. Integrating the 2.0 ppm peak and the 1.8 ppm peak shows a ratio of 4:1 fluorene repeat units to carborane repeat units. The 5/95 spectrum also shows negligible B-H stretches, and only one alpha aliphatic H band at 2.0 ppm, as well as two sharper aromatic bands at 7.8 ppm and 7.7 ppm.

The distinction between the carborane monomer block and the conjugated fluorene block seen in the $^1$H NMR spectra give rise to the possibility that the polymer structures are more block like, and the carborane units are not randomly dispersed along the polymer backbone. This could be due to the fact that the carborane monomer is more electron accepting and the Ni catalyst preferentially binds to that monomer before the 2,7-dibromo-9,9-dihexylfluorene, polymerizing the carborane monomer before polymerizing the fluorene monomer. The repeat unit structures for all five polymers are shown in Figure 4.1. The $^1$H NMR comparisons are shown in Figure 4.3.
4.3 Steady-State Properties

All five polymers were characterized through absorption spectra in toluene, chloroform (CHCl₃), and dimethylformamide (DMF), with absorption maxima listed in Table 4.2 and corresponding spectra shown in Figure 4.4. The absorption maximum of each polymer is nominally the same across all three solvents, with slight variations in the absorption maxima due to fluctuating solubility of the polymers between the three solvents. The absorption maxima are dependent on the increasing conjugation length of the oligomeric fluorene block, with red-shifting maxima corresponding to polymers with higher degrees of fluorene conjugation, while solvent environment does not affect the ground state electronic properties of the carborane containing polymers.
Figure 4.4: Absorption spectra of 100/0 (red), 50/50 (yellow), 35/65 (green), 20/80 (blue), and 5/95 (purple) in toluene, chloroform, and DMF, with absorption maxima listed above each spectrum. The red shift in absorption corresponds to increasing molecular weight.

Photoluminescence spectra were determined for each of the five polymers in both toluene and CHCl3 at 0.1 mg/ml concentrations (Figure 4.5). The 100/0 and 50/50 polymer dissolved in toluene have singular PL maxima at 545 nm and 540 nm, respectively, corresponding to the internal charge transfer state (ICT). The 5 nm hypsochromic shift in emission maxima from 100/0 to 50/50 is due to the slightly lower molecular weight of 50/50 compared to 100/0.

<table>
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<th>Abs. (\lambda) (nm)</th>
<th>Em. (\lambda) Toluene (nm)</th>
<th>Em. (\lambda) CHCl3 (nm)</th>
<th>ICT (\phi)</th>
<th>LES (\phi)</th>
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Table 4.2: Absorption and emission maxima in toluene (\(^i\)), chloroform (\(^c\)), and DMF (\(^d\)), with quantum yields in toluene corresponding to emission maxima for the ICT state and LES, as well as in the aggregated state with \(\pm 2.2\%\) error. Quantum yields were calculated relative to a coumarin 153 standard in ethanol below absorbances of 0.1 a.u.
Figure 4.5: PL spectra of the five polymers in toluene and chloroform (left), and the solid-state PL spectra of the five polymers either spin-coated or drop-cast. Above the spectra are pictures of the solution state polymers in the two solvents, as well as the five polymers drop-cast onto glass slides. In the drop-cast picture, the films are resting on vials of acetone and the color change shows the solvatochromic response of the film to the polar vapor. It is possible to see the solid-state emission intensity increase from the 100/0 to 5/95 polymer. Polymers with fluorene blocks have clearer distinctions between sensing and non-sensing emissions. 5/95 also is a white emitter due to the balance of emissions from the LES and the AIEE experiencing ICT state.
Figure 4.6: PL of the aggregated polymers in 99:1 water to THF with 50/50 (yellow), 35/65 (green), 20/80 (blue), 5/95 (purple).

Three distinct pL emission bands at 410 nm, 430 nm, and 555 nm are observed for 35/65, 20/80, and 5/95 polymers in toluene. The vibrational peaks consistent with the 410 nm and 430 nm bands appearing in the 35/65, 20/80, and 5/95 polymers correspond to the local excited state (LES) of conjugated dihexylfluorene. The vibronic nature of this band denotes a high degree of dihexylfluorene conjugation within the backbones of these three polymers. This demonstrates that the random copolymers consist of blocks of conjugated dihexylfluorene and conjugated bis(fluorenlyl) carborane covalently stitched together, as opposed to the monomers being more evenly distributed along the polymer chain, which is consistent with the $^1$H NMR analysis. Along with this, the intensity of the LES emission band increases in intensity from 35/65 to 20/80 and 5/95, corresponding to a higher concentration of conjugated dihexylfluorene in the latter two polymers. There is also a 5
nm bathochromic shift from 430 nm to 435 nm from the 35/65 and 20/80 polymers to the 5/95 polymers, which is due to higher conjugation of dihexylfluorene segments in the 5/95 polymer, particularly. The broad band at 555 nm for 35/65, 20/80, and 5/95 is consistent with radiative emission from the ICT state, and is red-shifted 10 nm from the 100/0 polymer band and 15 nm for the 50/50 polymer band. The red-shift in the ICT state may be due to the higher molecular weight of the 35/65, 20/80, and 5/95 polymers compared to the 50/50 and 100/0 polymers.

In CHCl3, the trends are nominally the same, though radiative emission from the conjugated dihexylfluorene LES is apparent in all five polymers, due to the dampened ICT radiative emission intensity in polar environments. The ICT state red shifts 20 nm from 100/0 to 35/65, and is nearly non-radiative in 5/95. Macroscopically, all five polymers dissolved in toluene and chloroform, represent all of the colors of the rainbow. The presumed block like structure of these random copolymers allows for discrete radiative properties specific to the LES and ICT states to be enhanced by long range conjugation. Consequently, the overall emission properties of the dissolved polymers are determined by the blending of radiative LES and ICT blocks. Increasing the quantity and degree of conjugated LES relative to conjugated ICT enhances the “blue” emissions characteristic to oligomeric or polymeric dihexylfluorene, while increased quantities or degree of conjugated ICT enhances the “red” emissions characteristic of that state.

Photoluminescence spectroscopy was also completed on films of the five polymers on glass slides. To determine film processing effect on the emission properties, 1 mg/ml concentrations in toluene were spin-coated at 1000 rpm for 60 s or drop-casted onto clean glass slides. Both film formation methods produce comparable emission spectra for all
five polymers, with drop casting having higher emission intensities due to the thicker films generated through this method. 100/0 and 50/50 polymers have solid-state emission spectra influenced entirely by conjugated ICT states with peak maxima at 530 nm for both processing methods. 35/65 and 20/80 polymers have similar solid-state spectra with ICT state peak maxima at 545 nm, with additional quenched LES vibrations at 415 nm and 440 nm. Only 5/95 has substantial LES emissions at 420 nm and 440 nm, along with an ICT emission band at 550 nm.

Additionally, PL was completed on aggregated samples of the copolymers (Figure 4.6). The copolymers, dissolved in THF were dispersed in water with a volume ratio of 99:1 water to THF. The PL spectra look almost identical to the drop cast spectra. In the solid-state and aggregated PL spectra, 35/65, 20/80, and 5/95 all have more ICT character than LES character, deviating from the solution state PL spectra. This could be due to some degree of aggregated induced emission enhancement, preventing rotational and vibrational decay mechanisms around the C-C bond of carborane, promoting radiative decay. However, emission from the fluorene oligomers in the backbone of the polymers may also be quenched by intermolecular forces, therefore making the ICT emission seemingly more emissive. Quantum yield measurements suggest that the material in the aggregated or solid-state is less emissive than the solution state, which indicates that aggregated induced emission enhancement may not be the mechanism behind the change in emission spectra from solution-state to the solid-state and aggregated state (Table 4.2). However, the very variable emission spectra of the aggregates and solid-state samples could be due to the highly irregular structure of the materials due to the non-linearity of the polymer chain. It has been shown that films and crystals of other carborane containing
aromatic systems can have highly variable emission intensities upon heating, scratching, and grinding which will either increase emission or quench the emission\textsuperscript{27}. This could explain why 35/65 is more emissive in the spin-coated sample than in the aggregated or drop cast samples relative to 50/50 and 20/80.

### 4.3.3 Time Resolved Photoluminescence Measurements

<table>
<thead>
<tr>
<th>Toluene</th>
<th>$\tau_{\text{LES}}$ (ns)</th>
<th>$f_{\text{LES}}$</th>
<th>$\tau_{\text{CT}}$ (ns)</th>
<th>$f_{\text{CT}}$</th>
<th>$\tau_{\text{LED}}$ (ns)</th>
<th>$f_{\text{LED}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0</td>
<td>0.54 ± 0.04</td>
<td>16%</td>
<td>1.6 ± 0.02</td>
<td>66%</td>
<td>4.12 ± 0.09</td>
<td>18%</td>
</tr>
<tr>
<td>50/50</td>
<td>0.48 ± 0.2</td>
<td>20%</td>
<td>1.48 ± 0.24</td>
<td>56%</td>
<td>3.16 ± 0.32</td>
<td>24%</td>
</tr>
<tr>
<td>35/65</td>
<td>0.41 ± 0.03</td>
<td>15%</td>
<td>1.76 ± 0.04</td>
<td>75%</td>
<td>4.46 ± 0.11</td>
<td>10%</td>
</tr>
<tr>
<td>20/80</td>
<td>0.38 ± 0.02</td>
<td>38%</td>
<td>1.49 ± 0.1</td>
<td>51%</td>
<td>3.81 ± 0.4</td>
<td>11%</td>
</tr>
<tr>
<td>5/95</td>
<td>0.44 ± 0.01</td>
<td>74%</td>
<td>1.61 ± 0.11</td>
<td>21%</td>
<td>5.25 ± 0.21</td>
<td>5%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CHCl\textsubscript{3}</th>
<th>$\tau_{\text{LES}}$ (ns)</th>
<th>$f_{\text{LES}}$</th>
<th>$\tau_{\text{CT}}$ (ns)</th>
<th>$f_{\text{CT}}$</th>
<th>$\tau_{\text{LED}}$ (ns)</th>
<th>$f_{\text{LED}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0</td>
<td>0.55 ± 0.01</td>
<td>20%</td>
<td>1.45</td>
<td>59%</td>
<td>3.41 ± 0.02</td>
<td>21%</td>
</tr>
<tr>
<td>50/50</td>
<td></td>
<td></td>
<td>0.86 ± 0.01</td>
<td>61%</td>
<td>2.66 ± 0.03</td>
<td>39%</td>
</tr>
<tr>
<td>35/65</td>
<td>0.25 ± 0.01</td>
<td>26%</td>
<td>1.25 ± 0.02</td>
<td>62%</td>
<td>3.33 ± 0.09</td>
<td>12%</td>
</tr>
<tr>
<td>20/80</td>
<td>0.27 ± 0.01</td>
<td>37%</td>
<td>0.99 ± 0.01</td>
<td>50%</td>
<td>2.48 ± 0.04</td>
<td>12%</td>
</tr>
<tr>
<td>5/95</td>
<td>0.37 ± 0.004</td>
<td>81%</td>
<td>1.31 ± 0.01</td>
<td>19%</td>
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<td></td>
</tr>
</tbody>
</table>

**Table 4.3:** Radiative lifetimes determined through time-resolved photoluminescence in toluene or chloroform at concentrations of 0.1 mg/ml.

Time resolved photoluminescence (trPL) was used to measure radiative decay lifetimes of all five polymers in toluene and chloroform for 0.1 mg/ml concentrations and lifetimes are listed in Table 4.3. trPL emission from the entire spectrum was collected in one kinetic trace with excellent signal to noise, low background counts and good reproducibility. Emission from both the LES and ICT states are present in the decay profile and lead to bi-exponential decay behavior. Additionally, light from the 280 nm excitation LED was not filtered through a bandpass and is present in the decay profiles with lifetimes greater than 2 ns. The lifetime of radiative decay from the LES ($\tau_{\text{LES}}$) ranges from 0.25-
0.55 ns across all toluene and chloroform solutions. The lifetime of radiative decay from
the ICT ($\tau_{\text{ICT}}$) ranges from 0.86-1.76 ns across all solutions.

The 100/0, 50/50, and 35/65 samples in toluene have similar lifetime profiles, with
low fractions of lifetime associated with LES emission and higher fractions of ICT state
radiative emission lifetime. The 20/80 sample shows an increase in LES lifetime fraction
and a slight decrease in the ICT state lifetime fraction. The 5/95 sample shows a further
increase in LES lifetime fraction. These results reflect the pL emission spectra for all five
samples in toluene. The 100/0, 50/50, and 35/65 emission spectra are dominated with ICT
state emission, while the 20/80 sample has a mix of both LES and ICT state emission, and
the 5/95 sample has mainly LES emission. The chloroform samples for all five polymers
show a similar trend as the toluene samples, with the radiative decay from the ICT state
being the dominating lifetime for the y, 50/50, and 35/65 polymers and radiative decay
from the LES being the dominating lifetime in the 5/95 sample.
4.3.4 Transient Absorption Spectroscopy

Figure 4.7: TA spectra of 50/50, 35/65, 20/80, and 5/95 in toluene. The transient absorption spectra are taken at a range of times from 0 to 3 ns. The evolution of the ICT excited-state absorption band ~500 nm is apparent in 50/50, 35/65, and 20/80. The LES state ranging from 640 nm to 770 nm with conjugation, increases in intensity from 50/50 to 5/95 and is the dominating profile in the 5/95 spectra.
<table>
<thead>
<tr>
<th></th>
<th>(\tau_{ET} ) (ps)</th>
<th>(\tau_{CT} ) (ns)</th>
<th>(\tau_{LES1} ) (ps)</th>
<th>(\tau_{LES2} ) (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>50/50</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>495 nm</td>
<td>11.81 ± 2.91</td>
<td>1.72 ± 0.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>640 nm</td>
<td>9.29 ± 3.38</td>
<td>0.99 ± 0.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>35/65</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>505 nm</td>
<td>7.33 ± 0.58</td>
<td>1.65 ± 0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>660 nm</td>
<td>5.86 ± 0.28</td>
<td>746.40 ± 59.73</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>20/80</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>505 nm</td>
<td>9.22 ± 0.85</td>
<td>1.55 ± 0.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>660 nm</td>
<td>8.37 ± 1.07</td>
<td>872.9 ± 65.04</td>
<td>82.8 ± 5.94</td>
<td></td>
</tr>
<tr>
<td><strong>5/95</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>520 nm</td>
<td>23.11 ± 8.31</td>
<td>1.23 ± 0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>770 nm</td>
<td>7.12 ± 0.32</td>
<td>526.5 ± 141.37</td>
<td>101.22 ± 36.75</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.4: Single-wavelength lifetimes determined from the transient absorption spectra at pertinent wavelengths associated with the ICT state and LES absorption profiles for 50/50, 35/65, 20/80, 5/95.

Femtosecond transient absorption spectroscopy (fs-TA) was used to determine the nature and lifetimes of the excited states of 50/50, 35/65, 20/80, and 5/95 in toluene (Figure 4.7). As a comparison, fs-TA was completed on both the fluorene monomer and dimer to identify the spectral contribution of the LES excited state within the polymer spectra.

For 50/50 in toluene, an initial excited state is formed with a peak ~ 640 nm. During the first few picoseconds, this excited state evolves into a second state with a peak at ~495-500 nm and a shoulder ~540 nm. The species at ~495-500 nm persists for several nanoseconds. From previous research, the 640 nm peak can be assigned to the absorption of the conjugated fluorene LES, and the ~495 nm peak can be assigned to the absorption of the ICT state\textsuperscript{28-29}. This trend is similar for 35/65, with the initial LES forming over a few picoseconds with a broader peak ~660 nm and evolving into the ICT excited state ~505 nm.
nm, which also decays over the course of several nanoseconds. 20/80 maintains a similar spectral shape and nature to both 35/65 and 50/50, with the initial LES forming over a few picoseconds with a broader peak ~720 nm and evolving into the longer-lived ICT excited state ~510 nm. The TA spectra for 5/95 no longer shows the characteristic energy transfer and ICT state absorption profile typically seen with the carborane containing poly(fluorene)s. The initial excited state is formed around 770 nm and persists for nearly 100 picoseconds before evolving into a low intensity peak ~520 nm. Simulated emission ~ 430 nm is also present within this spectrum and mirrors the excited state decay profile. The 770 nm peak can be assigned to the highly conjugated poly(dihexylfluorene) LES. The 520 nm peak may be a minute concentration of ICT state absorption present in the backbone of the 5/95 polymer. With increasing fluorene conjugation from 50/50 to 5/95, it is clear to see the LES absorption red-shift and broaden from 640 nm to 770 nm.
systems in toluene.

Table 4.5: Lifetimes associated with global analysis spectra for the copolymeric systems in toluene.

<table>
<thead>
<tr>
<th></th>
<th>$\tau_{ET}$ (ps)</th>
<th>$\tau_{CT}$ (ns)</th>
<th>$\tau_{LES}$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50/50</td>
<td>4.79 ± 3.5</td>
<td>1.68 ± 0.35</td>
<td></td>
</tr>
<tr>
<td>35/65</td>
<td>8.04 ± 5.9</td>
<td>1.10 ± 0.41</td>
<td></td>
</tr>
<tr>
<td>20/80</td>
<td>2.0 ± 1.7</td>
<td>1.3 ± 0.92</td>
<td>104.4 ± 100</td>
</tr>
<tr>
<td>5/95</td>
<td>9.6 ± 4.5</td>
<td>0.99 ± 0.79</td>
<td>182.6 ± 73</td>
</tr>
</tbody>
</table>

Figure 4.8: Global analysis spectra for 50/50, 35/65, 20/80, 5/95. The blue curves correspond to the ICT radiative decay, the red curves correspond to the electron transfer from the LES to form the ICT, and the green curves correspond to radiative decay from the LES.
Global analysis, a technique used to determine relevant spectral contributions for individual lifetimes extracted from the entire dataset\textsuperscript{25}. Global analysis identified two pertinent spectra that contribute to the excited state evolution of the 50/50 and 35/65 polymers and three pertinent spectra for the 20/80 and 5/95 polymers (Figure 4.8). For the 50/50 polymer the LES spectrum evolves with a lifetime of \(~5\) ps and shows the decay of the LES is concomitant with the growth of the ICT absorption band \(~495\) nm, represented by a valley in the LES spectrum directly beneath the ICT growth. The ICT band decays over the course of \(~1.7\) ns. From trPL and previous works, this lifetime is associated with radiative decay of the ICT state. For the 35/65 polymer, the global analysis reflects both ICT formation \((\sim8\) ps) and radiative decay from the ICT state \((1.1\) ns). The LES and ICT spectra for the 35/65 polymer are broader and more red-shifted from the 50/50 spectra. The spectra confirm that the LES feeds the ICT state via photo-induced charge transfer and this process is ephemeral, lasting a few picoseconds.

The 20/80 polymer has two spectra associated with the LES that evolve over 2ps and 100 ps. The fast 2 ps LES spectrum could be representative of charge transfer from the LES to form the ICT state, and the longer lived LES spectrum is most likely radiative decay from the conjugated poly(dihexylfluorene)s blocks in the polymer backbone that are unaffected by carborane. Additionally, simulated emission is present in the global analysis spectra for the LES \((<500\) nm). The ICT state is represented by a \(~520\) nm band that decays over \(~1.3\) ns. There is no clear association between the LES and ICT state in the 20/80 global analysis. The ICT state absorption band is also significantly quenched relative to the LES band, due to the lower concentration of these states in the polymer backbone. The
5/95 polymer also shows 2 spectra associated with the LES that evolve over 10 ps and 183 ps in addition to simulated emission. The ICT state decays over the course of 0.99 ns. The spectra are similar to those for the 20/80 polymer, but are more defined and the LES spectra are more red-shifted. There is also no clear association between the LES and ICT state due to the minimal carborane content in the polymer backbone. The single wavelength analysis of the TA spectra at the pertinent wavelengths associated with the LES and the ICT state show similar lifetimes to those acquired through global analysis.

The transient absorption and global analysis spectra show that the 50/50 polymer maintains similar spectral shapes to that of the homopolymer. Introducing a 0.5 equivalent feed ratio of dihexylfluorene to the random copolymerization doesn’t extend the conjugated fluorene block significantly, which is evident from the TA. This is also apparent through the single-wavelength lifetime analysis and global analysis, showing lifetimes characteristic of electron transfer and ICT radiative decay. The 35/65 polymer has more LES excited state absorption but the single-wavelength analysis and global analysis show lifetimes still consistent with electron transfer and charge transfer radiative decay and does not show significant LES radiative decay. The 20/80 polymer has intensified LES excited state absorption and both the single-wavelength lifetime analysis and global analysis show LES radiative decay in addition to electron transfer and ICT state radiative decay. This shows that a 0.8 equivalent feed ratio of dihexylfluorene to the random copolymerization begins to extend the conjugated fluorene block enough to contribute individual photophysical properties of the conjugated fluorene LES to the overall spectra. The 5/95 polymer shows almost entirely LES photophysical properties in both the spectral shape of the TA curves, and the lifetimes associated with it. The TA
shows concisely how changing the feed ratios in the random co polymerizations effect the excited state properties of the synthesized polymers.

4.4 Conclusions

Four random carborane containing co-polymers were synthesized through Yamamoto polymerization with different equivalents of (1,2-bis(7-bromo-9,9-dihexyl-9H-fluoren-2-yl)-closo-dicarbodecaborane) and 2,7-dibromo-9,9-dihexylfluorene and the photophysical properties were compared to a homopolymer of (1,2-bis(7-bromo-9,9-dihexyl-9H-fluoren-2-yl)-closo-dicarbodecaborane). Increasing the reaction equivalents of 2,7-dibromo-9,9-dihexyl fluorene from 0.5 to 0.95 extended the degree of fluorene conjugation in the co-polymer backbone, which increased the molecular weight of the polymer and produced a polymer with a more linear structure, deviating from the kinked nature of the homopolymer. Additionally, the polymers with extended fluorene conjugation have red-shifted ground-state absorption profiles, and more LES emission characteristics than ICT emission characteristics in solution-state PL. Transient absorption and time-resolved photoluminescence spectroscopies show the formation of the ICT excited-state absorption band for 50/50, 35/65, and 20/80 samples with nearly negligible ICT excited-state characteristics in 5/95. Following this trend, LES excited state absorptions steadily increase in intensity and character from 50/50 to 5/95. While 5/95 and 20/80 have mainly LES excited-state and PL emission properties, in the solid-state, the small amount of ICT character is magnified. This allows for the production of materials with interesting film emission colors that can be tuned by balancing the emission intensities of both the LES and ICT bands.
4.5 References


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CHAPTER 5
SYNTHESIS AND PHOTOPHYSICAL CHARACTERIZATION OF DONOR-ACCEPTER JUNCTION POLY((BISTHIENYL) CARBORANE)

5.1 Introduction

Ortho-Carborane (C$_2$B$_{10}$H$_{12}$), the icosahedral boron cluster, is characterized by unique electronic, steric, and chemical properties including hydrophobicity, rigidity, and high thermal and chemical stabilities, as well as stability to hydrolysis$^{1-5}$. Such distinctive properties make o-carborane useful in a variety of applications, including cancer therapy, catalysis, gas separation, heat resistant materials and electronics$^{1, 6-17}$. O-carborane can be easily functionalized with reactive groups, oligomers, and polymers through both carbon and boron sites, making them easy to integrate into a variety of material structures$^{4, 18-21}$. Originally, ortho-, meta-, and para-carboranes were combined with conjugated systems as a way to provide thermal and electrochemical stability to semi-conducting polymers$^{3, 11, 22-25}$. It was found that integration of o-carborane into conjugated or aromatic backbones drastically influences the emission properties of these systems. Aromatic-carborane systems bound through the adjacent carbon-carbon bonds in o-carborane exhibit the formation of an intramolecular charge transfer (ICT) state upon donation of an excited electron from the aromatic unit to the carborane unit. Owing to the fact that o-carborane is held together through delocalized 3-center-2-electron bonding making the molecule electron deficient and therefore a good electron acceptor. These excited-state dynamics are unique to o-carborane systems and are not seen in m- or p-carborane systems$^{12, 20, 26-30}$. The ICT state is influenced by the dihedral angle between the carborane C-C bond and the pi-conjugated unit bound to it, and high degrees of twisting that angle can increase the quantum yield of the radiative decay of the ICT state$^{31}$. 

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For this reason, carborane has been widely studied in many conjugated monomer and polymer systems with aromatic building blocks including p-phenylene-ethynylene, naphthalene, carbazole, and triphenylamine, to name a few.\textsuperscript{18-20, 25, 27-28, 32-37} These systems have unique emission properties that include excimer emissions, aggregated induced emission (AIE), crystallization induced emission, intramolecular charge transfer (ICT), and twisted ICT, in addition to the local emission of the conjugated building block. Soluble aromatic-carborane junctions typically consist of weak aromatic donors, like fluorene or carbazole, that participate in a one electron transfer to the carborane unit to form an intramolecular charge transfer state in the excited state of the system. While phenyl based molecules work as donor systems due to the delocalized pi electrons in the benzene ring, they are not considered strong donors because of their high degree of aromaticity. On the other hand, thiophene based molecules have higher degrees of delocalization due to inclusion of a heteroatom in the aromatic ring\textsuperscript{38}. The synthesis and study of strong donor-carborane junctions have been carried out for thiophene based materials electropolymerized onto ITO electrodes to form an insoluble film, with o-carborane in the main poly(thiophene) chain. These films are conductive and have higher thermal and electrochemical resistances as compared to electropolymerized poly(thiophene). Additionally, the bisthienyl carborane monomer has a lower oxidation potential than that of thiophene, allowing for the monomer to be electropolymerized at lower oxidation potentials that will not disrupt the synthesized polymer, therefore overcoming the “poly(thiophene) paradox”\textsuperscript{24, 39-42}. It has also been found that m-carborane bound into the main chain of electropolymerized poly(thiophene) can produce durable electrochromic films\textsuperscript{43}. However, outside research done by the
Vicente group, there are not many reports of strong donor-carborane containing polymers. Additionally, there are no reports of soluble thiophene based carborane containing polymers or even soluble strong-donor based carborane containing polymers. The ability to synthesize soluble strong-donor based carborane containing polymers would aid in the photophysical study of these systems and allow for a comparison of such excited state dynamics to those already determined for weak donor based carborane containing systems. Strong donor based carborane containing polymers also offer a unique opportunity for triplet sensitization\textsuperscript{44}. Donor acceptor junctions are commonly used to guide triplet formation, particularly when the acceptor is a known triplet spin converter like fullerene. Donor molecules consist of aromatic systems capable of absorbing in the UV/Vis, allowing for low energy population of the acceptor singlet state through electron transfer from the excited donor. Once the acceptor singlet state is populated, intersystem crossing can occur to produce the triplet state. Triplet state access is useful for a variety of applications including photodynamic therapies, triplet-triplet annihilation upconversion, and photocatalytic reactions, but detailed research on how to synthesize effective, reproducible triplet sensitizers is infrequent. Triplet formation is well understood for heavy atom systems that include halogens or metal containing aromatic complexes. However aromatic systems sans-heavy atoms, are less studied for triplet sensitization, and an understanding of how to synthetically produce triplet forming molecules or polymers is less concrete. Carborane as a spin converter has not been studied to our knowledge, but detailed computational studies have shown that it can access the triplet state, and in ionic states, has small triplet-singlet energy gaps\textsuperscript{45-47}. Additionally, transient absorption has been used to visualize the absorption of a triplet state on the carba-closo-dodecaborate(−) anion,
(CB11H12-) after excitation with a 308 nm pulse, persisting for ~30 microseconds\textsuperscript{48}. Typically, carborane is used as a substituent to enable triplet formation on an aromatic or metal complex. When incorporated into iridium complexes or other metal complexes known for phosphorescence, it has been shown that carborane can increase the phosphorescence efficiency of the molecules through HOMO/LUMO tuning through the electron-withdrawing effects\textsuperscript{49-52}. Additionally, by forcing the carborane/Ir complexes into hindered structures, it is possible to further improve the phosphorescence by restricting rotation around the carborane C-C bond\textsuperscript{53}. As a bulky substituent, carborane also inhibits triplet-triplet annihilation in the solid-state. However, these systems are highly complex, and slight synthetic variations of the carborane moiety can improve or disrupt effective triplet formation and subsequent phosphorescence. Ultimately, in these studies, triplet states are not formed on the carborane, like typical donor-acceptor triplet sensitizers.

In this study, the novel synthesis of poly((bisthienyl) carborane) (homopolymer) and poly((bisthienyl)carborane-co-thiophene) (copolymer) are carried out through standard Yamamoto and Stille couplings, respectively, and characterized through DMF GPC, \textsuperscript{1}H NMR, and ATR-FTIR. These polymers show fairly high molecular weights for carborane containing conjugated polymers, and are also incredible polar, solvating in DMSO and DMF. Steady state and time resolved spectroscopies are used to determined excited state processes unique to these systems and compared to the steady-state and time-resolved profiles of a bithiophene control. These thiophene-carborane polymers prove to have complicated excited state dynamics due to their polarized states and aggregated geometry. It is shown that triplet states are accessed in both polymers, with a triplet forming on the oligothiophene of the homopolymer, and two triplet states forming on the oligothiophene
and carborane moieties of the copolymer, with the thiophene triplet state forming first, followed by an energy transfer to the carborane triplet state. This information sheds light on the exited state dynamics of soluble strong donor-carborane junctions in conjugated polymer systems, and also gives evidence for use of carborane as a spin-coupling moiety for triplet sensitization applications.

5.2 Experimental Section

5.2.1 Materials

All reagents were used as received and purchased from Sigma Aldrich.

5.2.2 Instrumentation

Molecular weights were calculated from GPC traces using a DMF GPC with 0.1M LiCl.

5.2.3 Spectroelectrochemistry

Spectroelectrochemical measurements were performed in an inert glove box environment using a USB2000+ Ocean Optics Spectrometer and a CH Instruments 660D Electrochemical Analyzer. Dilute polymer solutions (2 mg/ml) were made in DMSO. A platinum wire counter electrode and a silver wire quasi-reference and working electrode were used to complete the electrochemical cell. Tetrabutylammonium perchlorate (TBAP, 100mM) in DMSO was used as the supporting electrolyte. Potentials were applied from 0V to 1.8V in increments of 0.2V to produce the radical cation, and potentials were applied from 0V to -1.2V in increments of 0.2V to produce the radical anion. These values were chosen because both polymers oxidize and reduce in these regions.
5.2.4 Time-Resolved Photoluminescence Spectroscopy (trPL)

Time-resolved PL was performed on an ISS Chronos BH time-resolved fluorescence spectrometer. Solutions with concentrations of 0.1 mg/ml and 1 mg/ml in DMSO were all analyzed. A 400-nm longpass filter was used to ensure that only the polymer emission was collected for the sample and not light from the 370-nm excitation nano-LED. The instrument response function was recorded using a dilute solution of coffee creamer in water. The fluorescent lifetimes of each sample were fit to exponential decays deconvolved from the instrument response.

5.2.5 Transient Absorption Measurements (TA)

TA measurements were carried out using 370 nm excitation for both polymers, and 315 nm excitation for bithiophene and the bis(thienyl) carborane monomer. TA samples were comprised of ~0.002 mg/ml solutions of the respective species in degassed DMSO. The steady-state absorption spectra were recorded before and after TA to ensure that the polymers were not degraded during the experiment. A detailed description of the TA setup is described elsewhere\textsuperscript{35}.

5.2.6 Synthesis of bisthienyl acetylene

2-iodo thiophene (1 eq) was added to a dry round bottom flask with a stir bar, sealed with a septum and placed into an Ag glovebox. CuI (0.1 eq) and Pd(PPh\textsubscript{3})Cl\textsubscript{2} (0.06 eq) were added to the round bottom, sealed with septum, and removed from the glovebox. From here dry benzene (0.33M) was added to the flask under nitrogen. Then, 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (6 eq) is added to the flask, turning the reaction
mixture red. Trimethyl acetylene (0.5eq) purged with N\textsubscript{2}, was then added to the flask turning the reaction mixture a bright yellow. Finally, N\textsubscript{2} purged water (0.4 eq) is added to the flask, and the reaction mixture cascades through a series of colors, turning chartreuse, to orange, to dark red, until it is finally dark purple with a precipitate forming. It is left for 24 hrs and worked up with ether and dilute acid solution and brine. DBU is the best base to form the double coupling, using a weaker base like triethyl amine will only allow for one coupling, producing 2-trimethylsilane acetylene-thiophene. This is reproduced from reference 40.

\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 500MHz) Reference 7.26 ppm: 7.29 (dd, 2H), 7.24 (dd, 2H), 7.01 (dd, 2H)

5.2.7 Synthesis of 2,5-dibromo(bisthiényl) acetylene

Bisthiényl acetylene (1eq) is added to a round bottom with a stir bare and capped with a septum. The round bottom is degassed with N\textsubscript{2} through successive vacuum and purging events. Dry 0.1M THF is added to the reaction vessel and cooled to -40°. N-butyl lithium (2.2 eq) is added to the reaction vessel and left to react for 30 min. The reaction medium turns orange, and then yellow with a precipitate. Finally, Br\textsubscript{2} (2.2 eq) is added to the reaction flask, which turns red/orange and left for 30 minutes. This is simply worked up with ether and brine.

\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 500MHz) Reference 7.26 ppm: 7.21 (d, 2H), 7.11 (d, 2H)
5.2.8 Synthesis of 2,5-dibromo(bisthiényl) carborane

2,5-dibromo(bisthiényl) acetylene (1 eq) was dissolved in 0.2M toluene and degassed. In a separate reaction vessel, decaborane (1.5 eq) and dimethylsulfide (3.75 eq) were dissolved in 0.7M toluene under N₂. It is imperative to keep this solution as dry as possible, and if possible, add the decaborane in a glovebox. The decaborane solution is heated to 40°C for 2 hrs and then heated to 60°C for 3 hrs (clear solution). The thiophene solution is then added to the decaborane solution and heated to 80°C for 48 hrs, turning yellow over time with an orange precipitate. The toluene is dried off, preferably blown off by N₂ in the hood because the dimethylsulfide smells in a rotary evaporator. Methanol is added to the reaction vessel to kill the excess carborane formed, resulting in a bubbling solution. Once the bubbles dissipate, the methanol is blown off. The reaction mixture is dissolved in DCM and dispersed in silica, in order to run a dry packed hexanes column. While the product dissolves in hexanes, the byproducts create a sludge that inhibits dilution of all of the product in hexanes, so it is easier to dissolve everything in DCM and then dry pack the column and purify it all that way. The purified monomer will come out last on the TLC and have a yellow/white fluorescence under 365 nm UV light. Reproduced from reference 40.

¹H NMR (CDCl₃, 500MHz) Reference 7.26 ppm: 7.21 (d, 2H), 6.83 (d, 2H), 3.5-1.5 (10 H, br)
5.2.9 Yamamoto polymerization of 2,5-dibromo(bisthienyl) carborane

The monomer, 2,5-dibromo(bisthienyl) acetylene (1 eq.), bipyridine (2.5 eq) and Ni(COD)$_2$ (2.5 eq) were all added to a round bottom flask, equipped with a stir bar and sealed with a rubber septum in a glovebox to maintain an inert environment. After being taken out of the glovebox, dry toluene/DMF (0.275M) was added to the round bottom with the ratio of 1:2 toluene:DMF, followed by 1,5 COD (2.5 eq). The round bottom was placed in a hot bath at 80°C for 24 hours. The solution was dried with nitrogen to concentrate it and then poured into slightly acidic THF/Toluene (0.1M). It can then be reprecipitated into acid methanol, but the methanol must be cooled overnight to retrieve the pure polymer. The polymer recovered was a dark shiny solid. The polymer is highly polar and mainly dissolves in DMSO and DMF. 64% yield. $M_n$: 9700 g/mol with a PDI: 1.7

$^1$H NMR (DMSO, 500MHz) Reference 7.50 ppm: 6.53 (s), -2.00 (br)

5.2.10 Stille polymerization of 2,5-dibromo(bisthienyl) carborane

The monomer, 2,5-dibromo(bisthienyl) acetylene (1 eq.), 2,5-distannyl-thiophene (1 eq) and Pd(PPh$_3$)$_4$ (0.05 eq) were all added to a round bottom flask, equipped with a stir bar and sealed with a rubber septum in a glovebox to maintain an inert environment. After being taken out of the glovebox, dry toluene/DMF (1:2) (0.3M) was added to the round bottom. The round bottom was placed in a hot bath at 80°C for 24 hours. The solution was dried with nitrogen to concentrate it and then poured into slightly acidic THF/Toluene (0.1M). It can then be reprecipitated into acid methanol, but the methanol must be cooled overnight to retrieve the pure polymer. The polymer recovered was a dark shiny solid.
The polymer is highly polar and mainly dissolves in DMSO and DMF. 83% yield. 13000 g/mol with a PDI: 1.5

$^1$H NMR (DMSO, 500MHz) Reference 7.50 ppm: 8.02 (s), 7.63 (s), 7.62 (s), -2 (br)

5.3 Results and Discussion

5.3.1 Synthesis

The synthesis of the homopolymer and copolymer were simply carried out through Yamamoto and Stille condensation polymerizations, respectively. The monomer 2,5-dibromo-(bisthienyl) carborane was synthesized through straightforward procedures previously described. Initially, it was expected that polymers produced with the bisthienyl carborane repeat unit would be highly hydrophobic, and solubilizing side chains would be necessary for further analysis and characterization of the system. Integration of side chains into the carborane monomer proved difficult as they prevented carborane insertion into the acetylene moiety. Polymerizing the 2,5-dibromo-(bisthienyl)carborane with 3,4-dihexylthiophene through direct arylation (DA) polymerization presented itself as a possible method for producing the side chain containing thiophene-carborane polymer. This was carried out using a standard procedure.$^{54}$ The produced material was difficult to work up, as it became clear the polymer did not dissolve in the characteristic solvents for poly(3-alkylthiophene)s, such as toluene, chloroform, or hexanes, but rather dissolved in polar solvents like methanol and DMF. This indicated that the thiophene-carborane junction was polarized and was outcompeting solubilizing effects of the non-polar hexyl side chains. DA is a complicated procedure and it became difficult to purify the polymer from the ionic reaction conditions necessary for DA. Therefore, it was deduced that side chains were not necessary to polymerize a soluble carborane containing poly(thiophene),
and polymerizations were possible through standard cross-couplings of easily synthesized monomers. $^1$H NMR in DMSO shows a single aromatic peak for the HP ~6.53 ppm corresponding to the thiophene ring hydrogens in the repeat unit. Additionally, there is a weak broad peak ~ -2 ppm, which could indicate the presence of the nido-carborane anion (Figure 5.1). A similar spectrum is shown for the CP, with the addition of the weak -2 ppm broad peak (Figure 5.2). Observing this peak is evidence that the polymer has already formed a cationic/anionic tethered pair, or geminate pair in the ground-state of the polymer. It is also possible that the polymer is highly polarized due to the strong donor-strong acceptor junction, and the carborane is influenced by a negative dipole, which upshifts the H atoms on the molecule. Additionally, ATR-FTIR was used to further confirm the structures (Figure 5.3 and 5.4).

![Figure 5.1: $^1$H NMR of HP](image-url)
Figure 5.2: $^1$H NMR of CP. Spectra is difficult to dissolve due to micro aggregations in the solutions.

Figure 5.3: ATR-FTIR of HP
Figure 5.4: ATR-FTIR of CP.

5.3.2 Steady-State properties

UV/Vis and photoluminescence spectroscopy was carried out on both homopolymer (HP) and copolymer (CP) as well as the (bithienyl) carborane monomer and bithiophene as controls. Bithiophene shows a sharp pi-pi absorption at 340 nm in chloroform, with subsequent radiative decay from the singlet state at 370 nm (Figure 5.5). (Bithienyl) carborane experiences a broader absorption, with a maxima ~350 nm as well as a blue shifted absorption outside the detection of the spectral window. Radiative decay of the excited state ~415 nm is low intensity (Figure 5.6).
Figure 5.5: UV/Vis of bithiophene (left) and PL of bithiophene (right).

HP shows a strong pi-pi absorption at 350 nm with a broad shoulder extending from 400 nm to 600 nm. Additionally, there is a sharp absorption around 270 nm, similar to that observed for the monomeric species. This sharp absorption band could be due to aggregation associated with the kinked nature of the polymer structure. The emission properties of HP are highly variable and depend on concentration. At 5 mg/ml, the emission is completely quenched. Upon dilution to 1 mg/ml, a broad emission with a maximum at 560 nm is evident. Diluting to 0.1 mg/ml produces an emission spectra comprised of two bands, with maxima at 430 nm and 540 nm. Further dilution to 0.01 mg/ml changes the emission spectra even more with the band at 425 nm conserved and the
band at 540 nm significantly quenched (Figure 5.7).

**Figure 5.7: UV/Vis of HP in DMSO for four concentrations (left) and PL of HP in DMSO for four different concentrations (right).**

The absorption and emission spectra of the CP are nominally the same as HP. CP has a strong pi-pi absorption ~400 nm, red-shifted from HP, with a broad shoulder from 450 nm to 600 nm. CP shows moderate solvation in THF and IPA, in addition to dissolving in DMF and DMSO. Therefore, absorption spectra were taken in all four solvents. It is noted that in IPA and THF, the 450-600 nm shoulder is less pronounced, and in DMSO and DMF the shoulder is more defined. This shoulder, which is apparent in both HP and CP, is evidence of a ground state charge transfer complex forming between the thiophene and carborane. This may be enabled by the strong donor abilities of the thiophene molecule coupled with the strong accepting abilities of the carborane, as this shoulder is not evident in weak donor fluorene based carborane containing polymers. In less polar solvents, the ground state charge-transfer complex is less supported and may not be forming. Additionally, a film of CP on glass shows an absorption spectra almost identical to the concentrated 5 mg/ml solution in DMSO. As the polymer is non-linear and contains a
bulky moiety in the backbone, it may be forming an amorphous film, and therefore absorption in both film and solution states are comparable. The emission spectra show the same concentration effect as observed in the HP, though the spectra are nominally quenched. In concentrated solutions, the spectra are almost undetectable though more red-shifted than in dilute solutions. At 0.1 mg/ml the emission is broad and seemingly comprised of two bands ~480 nm and ~550 nm. Further dilution to 0.01 mg/ml shows quenching of both bands, with a slightly more intense 480 nm band (Figure 5.8).

![Figure 5.8: UV/Vis of CP for multiple concentrations and in the solid state (left) and PL of CP for multiple concentrations. Inlet table shows radiative lifetimes of CP in DMSO with 400 nm LP.](image)

### 5.3.3 Time-Resolved Photoluminescence

Photoluminescence shows two emission bands that are either quenched or emissive depending on concentration for both polymers. Time-resolved photoluminescence (TrPL) was used to identify the radiative lifetimes of the decay pathways associated with the two emission bands, by collecting emission from the entire spectrum in one kinetic trace. This was done for two concentrations, 1 mg/ml and 0.01 mg/ml. A 400 nm long pass filter was
used to filter out emission from the 370 nm excitation light. Additionally, other long passes and band passes were used to try to distinguish lifetimes for particular emission bands.

For the 1 mg/ml HP solutions, two relevant lifetimes ($\tau_1$ and $\tau_2$) were extracted by fitting bi-exponential functions to the emission decay. The first lifetime, $\tau_1$, is ~0.6 ns and the second lifetime, $\tau_2$, ranges from 1-2 ns, with $\tau_1$ contributing a larger fraction of decay to the exponential. Adding a 495 nm long pass to filter out the 430 nm emission band, shows a similar bi-exponential decay with lifetimes comparable to the full spectrum decay. Even with the 495 nm long pass, the bi-exponential nature of the redder emission band could be due to the tail end emission from the bluer emission band still being present past 495 nm. It is noted that the fraction of the longer lifetime, $\tau_2$, is larger upon use of the 495 nm long pass, indicating that the redder emission band associated with the concentrated solutions has a longer lifetime.

For the 0.1 mg/ml HP solution, both a 400 nm and 495 nm long pass was used in addition to a 425 nm band pass, in order to filter out the bluer emission band. Similarly, two lifetimes were extracted by fitting the bi-exponential functions to the emission decay. $\tau_1$ is ~0.9 ns and the second lifetime, $\tau_2$, ranges from 2-3 ns, with $\tau_1$ making up a large fraction of the decay pathways (~90%). This further indicates that the blue emission band is associated with the shorter lifetime, and the redder band is associated with the longer lifetime. As a comparison, radiative decay from bithiophene fits a mono-exponential function with a lifetime ~0.06 ns. The bithiophene lifetime is significantly smaller than the lifetimes associated with the radiative character of HP. Comparison of the HP to bithiophene emission characteristic demonstrates that the concentration dependent radiative emission associated with HP is not emission from the singlet state of the
oligothiophene component of the polymer backbone. As it is concentration dependent, it is likely that this emission is associated with different aggregated states of thiophene. In the concentrated solutions, the longer lifetime is dominating, and this may be associated with H aggregates formed by close polymer chain interaction. H aggregates are associated with cofacial stacking of the aromatic units, and the kinked nature of the polymer structure may facilitate this stacking in concentrated solutions. This would support the ~280 nm absorption band associated with both CP and HP polymers. In similar systems with H aggregates, this sharp absorption band is typically present. In the dilute solutions, intramolecular forces take over, with emission from the weakly coupled thiophene rings forced together by the angle of the carborane C-C bond (Figure 5.8). As there is no sharp transition between intra- and intermolecular forces, the bands are broad and still present in all concentrations, though more quenched or emissive depending on the dilution.

<table>
<thead>
<tr>
<th>1 mg/ml</th>
<th>( \tau_1 ) (ns)</th>
<th>( f_1 )</th>
<th>( \tau_2 ) (ns)</th>
<th>( f_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>400 nm LP</td>
<td>0.6 ± 0.02</td>
<td>70%</td>
<td>1.5 ± 0.05</td>
<td>30%</td>
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<tr>
<td>495 nm LP</td>
<td>0.52 ± 0.02</td>
<td>59%</td>
<td>1.3 ± 0.02</td>
<td>41%</td>
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</table>

<table>
<thead>
<tr>
<th>0.01 mg/ml</th>
<th>( \tau_1 ) (ns)</th>
<th>( f_1 )</th>
<th>( \tau_2 ) (ns)</th>
<th>( f_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>400 nm LP</td>
<td>0.9 ± 0.02</td>
<td>92%</td>
<td>3.6 ± 0.8</td>
<td>7%</td>
</tr>
<tr>
<td>495 nm LP</td>
<td>0.9 ± 0.04</td>
<td>92%</td>
<td>2.9 ± 0.5</td>
<td>8%</td>
</tr>
<tr>
<td>425 nm BP</td>
<td>0.6 ± 0.08</td>
<td>80%</td>
<td>2.1 ± 0.2</td>
<td>20%</td>
</tr>
</tbody>
</table>

Figure 5.9: Radiative lifetimes from TrPL for HP at 1 mg/ml and 0.01 mg/ml, using different long passes and band passes to isolate sections of the emission spectrum. At high concentrations (~1 mg/ml) intermolecular H aggregate emissions are a large part of the decay profile, while low concentrations see weak intramolecular aggregate emissions dominating the decay profile.
TrPl was also used to identify the decay lifetimes associated with radiation from the CP. As the CP shows less distinction between aggregated emission states and dilute emission states, and the emission is very broad across all dilutions, TrPl was only measured using a 400 nm long pass to remove excitation light, and no additional long passes or band passes were used to isolate specific emission bands. At 0.1 mg/ml concentrations, two lifetimes were extracted by fitting the bi-exponential functions to the emission decay. $\tau_1$ is $\sim$0.7 ns and the second lifetime, $\tau_2$, ranges from $\sim$3 ns, with $\tau_1$ making up a large fraction of the decay pathways ($\sim$90%). CP shows more intramolecular aggregation character and less intermolecular aggregation. This could be due to the extension of the repeat unit with the extra thiophene monomer disturbing cofacial packing of the chains, and making more disordered solutions.

5.3.4 Spectroelectrochemistry

![Figure 5.10: Spectroelectrochemistry of HP held at 1.1 V showing the formation of a geminate pair bound through the backbone of the polymer (left) and the oxidation of HP from 0 to 2V (right)](image)

Spectroelectrochemistry was utilized to identify absorption of the charged species for both polymers dissolved in DMSO with tetrabutylammonium perchlorate as the counter
electrolyte. The spectra determined through this method can be used to compare to transient absorption. If charged species are a dominating excited state they can be identified through spectroelectrochemistry. HP was oxidized from 0-2V and showed two oxidation peaks present at ~ 0.45V and ~1.2V. Absorption of the charged species is not apparent after applying a potential of 0.5V, but a broad absorption with a maximum ~500 nm grows in upon oxidizing the HP with 1.1V (Figure 5.10). Reducing HP from 0- -2V showed one broad reduction peak ~ -0.6V. No absorption spectra were observed for reducing the polymer, but this could be due to the fact that the absorption of the reduced species was outside the window of detection in this experiment, which started around 470 nm. The CP was also oxidized from 0-2V and showed a similar oxidation spectrum with two oxidation peaks around ~0.45V and ~1.5V. Regardless, the spectrum was less defined than the HP spectrum, and no absorption was noted for oxidation of CP at either of the peaks.

5.3.5 Transient Absorption

Both femtosecond (fs) and nanosecond (ns) transient absorption (TA) was used to determine the excited states of the thiophene-carborane polymeric system. The experiments were run in degassed DMSO at low concentrations. As a comparison fs-TA was done on the bithiophene monomer.

For the bithiophene monomer in chloroform, an initial excited state is formed ~490 nm persists for ~40 ps before decaying. A longer-lived species was noted ~410 nm but was not investigated. Bithiophene is excited to the singlet state which decays radiatively. The lifetime associated with excited state decay, ~40 ps, is comparable to the radiative decay lifetime, ~60 ps, determined through TrPl (Figure 5.11)
Figure 5.11: TA spectra of bithiophene in CHCl$_3$ over a 5 ns time frame showing singlet absorption. Inset table shows lifetimes determined through single-wavelength analysis at 490 nm.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>τ (ps)</th>
<th>f (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>505</td>
<td>4.77 ± 1.75</td>
<td>75.45%</td>
</tr>
<tr>
<td>550</td>
<td>92.03 ± 37.94</td>
<td>24.55%</td>
</tr>
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</table>

Figure 5.12: TA spectra (left) and global analysis (right) of HP in DMSO over a 5 ns time frame with single wavelength analysis at 505 nm (inset table). A large broad absorption is formed at 550 nm and quickly cools to 505 nm decaying over several picoseconds. The shape of the absorption band is comparable to the spectroelectrochemistry of the oxidized polymer.

HP in DMSO is initially excited by a 370 nm pump into a broad excited state with a maximum ~550 nm which experiences vibrational cooling over ~1 ps to a blue-shifted maximum ~505 nm that decays over several picoseconds. This broad absorption band is
similar in shape to the absorption band formed through oxidation of HP during spectroelectrochemistry, indicating the excited-state consists of a cationic thiophene species (Figure 5.12). Comparing the HP TA to the bisthiophene TA signifies that singlet thiophene character is not present in the HP. All of the spectroscopy done up to this point, suggests that the polymeric ground-state is a polarized charge-transfer complex, and can be excited into to form a cation on the thiophene and subsequently an anion on the carborane species. The geminate pair is bridged by the covalent bond between the thiophene and carborane, and can non-radiatively recombine over ~100 ps. Interestingly, after complete decay of the initial excited state, residual absorption bands red-shifted from 600 nm were noted, and therefore ns-TA was utilized to resolve longer-lived species. ns-TA showed a vibronic state with maxima at 620 nm and 575 nm that decayed over ~ 0.4 us (Figure 5.13). The shape of the triplet state is identical to past reports of oligothiophene T$_1$ states, indicating that recombination of the geminate pair promotes triplet formation on the thiophene oligomers in the repeat unit through back electron transfer$^{57}$. This is interesting, because it demonstrates delayed oligothiophene triplet formation without direct excitation into the singlet state of oligothiophene. This phenomenon can be compared to delayed triplet formation through excited hybrid charge transfer exciton (HCTE) states formed at inorganic/organic interfaces, commonly employed in PV applications. Upon cooling of the HCTE state, electrons can be converted to triplet states in the organic material which then decay characteristically. The charge-transfer exciton has a weak binding energy and therefore spin flip to form triplet states is susceptible in these systems.
Figure 5.13: ns-TA of HP showing oligomeric thiophene triplet formation upon decay of initial charge transfer state. The triplet state non-radiatively relaxes over 0.4 microseconds.

The CP shows similar excited state evolution and decay processes, with a broad excited state ~645 nm persisting for ~40 ps. This can be identified as the bound hole/electron pair on the thiophene-carborane bridge, which is red-shifted from the HP due to conjugation. This excited state is accompanied by simulated emission ~500 nm which remains for ~0.4 ns. This lifetime is associated with radiative decay from the intramolecular thiophene aggregates, determined through PL and TrPL. It should be noted that the growth of the geminate pair begins before simulated emission, and the two photophysical events do not happen simultaneously. This could indicate that forming the geminate pair enables intramolecular coupling between the cationic thiophene and the neutral thiophene not involved in the bridge. Finally, upon recombination, the long-lived triplet state on the thiophene oligomer is formed (~640 nm and 706 nm) persisting for ~10 us. Interestingly, a triplet energy transfer (TET) occurs, and the thiophene triplet state populates the carborane triplet state ~540 nm which persists for 64 us. It is unclear why TET occurs in the CP and not the HP. It is possible the geometry of the CP, which may be
less rigid, allows for the carborane triplet to be lower energy than the thiophene triplet, enabling the TET.

![Figure 5.14: TA spectra (left) and global analysis (right) of CP in DMSO over a 5 ns time frame with single wavelength analysis at 500 nm and 645 nm (inset table). A large broad absorption is formed at 645 nm associated with absorption of the geminate pair and after a few picoseconds simulated emission at 500 nm appears. Decay of the geminate pair is concomitant with absorption of the oligothiophene triplet state.](image)

<table>
<thead>
<tr>
<th></th>
<th>(\tau) (ps)</th>
<th>(f) (%)</th>
<th></th>
<th>(\tau) (ps)</th>
<th>(f) (%)</th>
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<tr>
<td>645 nm</td>
<td>2.33 ± 0.48</td>
<td>36.40%</td>
<td>500 nm</td>
<td>3.67 ± 1.37</td>
<td>12.11%</td>
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<tr>
<td></td>
<td>168.93 ± 5.91</td>
<td>36.84%</td>
<td></td>
<td>389.63 ± 40.99</td>
<td>62.56%</td>
</tr>
<tr>
<td></td>
<td>29.62 ± 6.2</td>
<td>26.76%</td>
<td></td>
<td>46.66 ± 11.03</td>
<td>25.32%</td>
</tr>
</tbody>
</table>

Figure 5.14: TA spectra (left) and global analysis (right) of CP in DMSO over a 5 ns time frame with single wavelength analysis at 500 nm and 645 nm (inset table). A large broad absorption is formed at 645 nm associated with absorption of the geminate pair and after a few picoseconds simulated emission at 500 nm appears. Decay of the geminate pair is concomitant with absorption of the oligothiophene triplet state.
Figure 5.15: ns-TA of CP showing oligomeric thiophene triplet formation upon decay of initial geminate pair. The triplet state non-radiatively relaxes over 10 microseconds before transferring energy to form a triplet state on the carborane moiety which decays over 65 microseconds.

5.4 Conclusions

Previously undescribed, soluble, carborane containing (polythiophene)s were synthesized through standard cross-coupling methods. Utilizing steady-state and time-resolved spectroscopies allowed for the detailed understanding of the excited state processes unique to these systems. Through UV/Vis spectroscopy, it is clear that the ground state of both polymers possesses charge-transfer character, making both polymers highly polar and soluble in polar solvents like DMSO and DMF. As the polymers are non-linear they experience emissive aggregates that are red-shifted or blue-shifted depending on solution dilution, with concentrated solutions having longer lived emissive intermolecular aggregates, and dilute solutions having shorter-lived emissive intramolecular aggregates. Transient absorption and spectroelectrochemistry show excitation into the ground state charge transfer complex to produce a geminate hole/electron pair bound covalently through the thiophene-carborane bridge. This pair
dissipates over several picoseconds promoting back electron transfer to form a triplet state on the thiophene oligomeric species in the polymer backbone, which decays over several microseconds. In the CP, a similar process is observed, but upon population of the thiophene triplet state, TET occurs to allow population of the carborane triplet state, previously unobserved in conjugated networks. Additionally, excitation into the geminate state also promotes radiative intramolecular aggregation in the CP. The strong donor-carborane junction enables a multitude of fascinating photophysics to occur, making this simple system a useful material in triplet sensitizer applications.

5.5 Future Outlook

This study presents the facile synthesis of a true donor acceptor junction between an aromatic unit and a carborane moiety. Carborane containing poly(thiophene) is polar in nature due to a dipole formed between the thiophene and carborane bridge. It is not clear whether the ground state is of the thiophene-carborane junction is a true geminate state with a cationic thiophene and an anionic nido-carborane, or if the state is simple very polar. Further analysis of the ground state of the polymer is necessary to determine the nature of the ground state. The geminate pair of a cationic thiophene species and anionic carborane species is formed upon excitation and decays non-radiatively over a several picoseconds. Decay of the geminate pair is concomitant with absorption of the oligothiophene triplet state, indicating back electron transfer from the charge transfer state to the triplet. In the copolymer, the oligothiophene triplet state populates the carborane triplet state which is substantially long lived through triplet energy transfer. This is a significant discovery showing that the carborane triplet state can be realized through excitation within a donor-acceptor copolymer. It is necessary to further understand the
geometry through DFT calculations of the CP repeat unit versus the HP repeat unit to determine how the triplet energy transfer occurs in the CP. Incorporating this polymer into a system in which triplet sensitization can be tested is the next step in utilizing this system, to determine its effectiveness as a triplet sensitizer. A system that includes a phosphorescent molecule that absorbs under 350 nm could gain energy from the visible light absorbing CP. Additionally, polymerizing the monomer 2,5-dibromo-(bisthienyl)carborane with a more aromatic/planar molecule can red-shift the absorption of the polymer. If the strong donor/acceptor junction is maintained, this can allow for an easy tool in visible light absorbing triplet sensitizer.

5.6 References


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