Crosslinkable Light Emitting Conjugate and Metallocene Polymers: Synthesis, Properties and Application

By

Jeffrey J. McDowell

A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy

Department of Chemistry
University of Toronto

© Copyright by Jeffrey J. McDowell 2013
Abstract: Numerous semiconductive organic materials are actively being pursued for application in sensing and electronics. Chapter one introduces conjugated polymers (CPs) and their many useful properties, including electroluminescence, which has helped foster growing demand for these materials in low-power organic light emitting diodes (OLED) for solid state lighting and additionally polychromatic displays. In the second chapter of this dissertation, we develop the concept of digrignard scavengers for use in nickel catalyst transfer polymerization of diarylmagnesate monomers into conjugate polymers within a unique mixed THF/1,4-Dioxane solvent system. Our initial findings include a polymerization method which permits the formation of an electronics grade copolymer with molecular weights in excess of $M_n = 50$ kg/mol within 15 minutes using a scalable, room temperature method. In chapter three, we discuss the synthesis and characterization of Polysilafluorenes (PSFs), which are an important class of light-emitting conjugate polymers noted for their characteristic brilliant solid state blue luminescence, high quantum efficiency, excellent solubility and improved thermal stability. In chapter four, we present a protocol for photopatterning derivatives of poly(3,6-dimethoxy-9,9-dialkylsilafuorenes) with resolutions exceeding 10 μm. The resultant crosslinked material possess characteristic blue photoluminescence with solid state quantum yields > 80%. In chapter five, we present a protocol for 3-D photopatterning derivatives of poly(3,6-dimethoxy-
9,9-dialkylsilafluorenes) with resolutions exceeding 200 nm using two photon direct laser writing techniques. In chapter six, we present a unique deep blue emitting copolymer, poly(3,6-dimethoxy-9.9′-dihexylsilafluorene-co-3.6-dimethoxy-2′,3′,6′,7′-tetrahexyloxy-9,9-spiro-9-silabifluorene) (PHSSF-co-PDHSF), which exhibits brilliant solid state blue luminescence, high quantum efficiency, excellent solubility and thermal stability. In chapter seven, we explore crosslinked conductive metalloocene polymer networks that mediate chemical, electronic and mechanical signals.
Acknowledgments

This work is dedicated to my loving wife Lisa and my parents for their support and encouragement over the years. I would also like to thank my supervisor Geoffrey Ozin and my numerous collaborators without whom this work may never have been completed.
# TABLE OF CONTENTS

Chapter 1 - Introduction

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0- Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.1- Introduction to Conjugate Polymers (CPs)</td>
<td>1</td>
</tr>
<tr>
<td>and Origin of Their Semiconducting Properties</td>
<td></td>
</tr>
<tr>
<td>1.1.1- Structural Characteristics of CPs</td>
<td>2</td>
</tr>
<tr>
<td>1.1.2- Small Molecule Components</td>
<td>5</td>
</tr>
<tr>
<td>1.2- Material Classes of Organic Semiconductors</td>
<td>6</td>
</tr>
<tr>
<td>1.2.1- Hole Injection Layer (HIL) Materials</td>
<td>6</td>
</tr>
<tr>
<td>1.2.1.1- Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)</td>
<td>7</td>
</tr>
<tr>
<td>(PEDOT:PSS)</td>
<td></td>
</tr>
<tr>
<td>1.2.1.2- Poly(thiophene-3-[2-(2-methoxyethoxy)ethoxy]-2,5-diyl)</td>
<td>8</td>
</tr>
<tr>
<td>(PlexcoreTM)</td>
<td></td>
</tr>
<tr>
<td>1.2.2- Hole Transport Layer (HTL) Materials</td>
<td>8</td>
</tr>
<tr>
<td>1.2.2.1- Polymer HTL Poly-TPD and PVK</td>
<td>9</td>
</tr>
<tr>
<td>1.2.2.2- Small molecule HTL α-NPD and TPD</td>
<td>10</td>
</tr>
<tr>
<td>1.2.2.3- Crosslinkable HTLs</td>
<td>10</td>
</tr>
<tr>
<td>1.2.3- Electron Transport Layer (ETL) Materials</td>
<td>13</td>
</tr>
<tr>
<td>1.3- Introduction to Organic Electronics</td>
<td>14</td>
</tr>
<tr>
<td>1.3.1- Organic Light Emitting Diodes (OLEDs)</td>
<td>17</td>
</tr>
<tr>
<td>1.3.1.1- Charge Transport In Amorphous Materials</td>
<td>17</td>
</tr>
<tr>
<td>1.3.1.2- Doping of Organic Semiconductors</td>
<td>20</td>
</tr>
<tr>
<td>1.3.1.3- Charge Carrier Injection</td>
<td>21</td>
</tr>
<tr>
<td>1.3.1.4- The Working Principles of OLEDs</td>
<td>23</td>
</tr>
<tr>
<td>1.3.1.5 Strategies for Improving Light Outcoupling Efficiency</td>
<td>24</td>
</tr>
<tr>
<td>1.4- Fabrication of Organic Light Emitting Diodes (OLEDs)</td>
<td>26</td>
</tr>
<tr>
<td>1.4.1- Deposition Methods</td>
<td>27</td>
</tr>
<tr>
<td>1.4.1.1 Thermal Evaporation</td>
<td>28</td>
</tr>
</tbody>
</table>
Chapter 4 - Synthesis and Application of Photolithographically Patternable Deep Blue Emitting Poly(3,6-dimethoxy-9,9-dialkylsilafluorene)s

4.0 Introduction

4.1 Results and Discussion

4.1.1 Photolithography Methods

4.1.2 Forster Energy Transfer in Patterned Films

4.1.3 Electroluminescent Device with Crosslinked Emissive Layer

4.1.4 DFB Laser with Crosslinked Emissive Layer

4.2 Conclusion

4.3 Experimental

4.3.1 Prilezhaev Epoxidation of Polymers PHCySF (4) and PHNSF (5)

4.3.2 Photopatterning of Polymer Films

4.3.3 Electroluminescent Device Fabrication

4.4 References

Supporting Information 3

Chapter 5 - 3-D Ultra High Resolution Two-Photon Laser Writing of Blue Light-Emitting Conjugate Polymers
Chapter 6 - Synthesis of Poly(Spirobisilafluorenes) and Their Improved Stability in Blue Emitting Polymer LEDs over Non-Spiro Analogs

6.0 Introduction

6.1 Results and Discussion

6.2 Conclusion

6.3 Experimental

6.3.1 HSSF Monomer Synthesis

6.3.2 Polymer Synthesis

6.3.3 Electroluminescent Device Fabrication

6.4 References

Supporting Information 4

Chapter 7 - Electroactuation of Alkoxyisilane-Functionalized Polyferroacenylsilane Microfibers

7.0 Introduction

7.1 Results and Discussion

7.2 Conclusion

7.3 Experimental Section

7.3.1 Electrospinning and Construction of Electrochemical Cell
7.3.2 SEIBIMM Mechanical Measurements and FT-IR-----------------------------293

7.4 References-----------------------------------------------------------------------------------------------295

Supporting Information 5-----------------------------------------------------------------------------------------------296

Chapter 8 – Conclusion-----------------------------------------------------------------------------------------------297

Statement of Contributions----------------------------------------------------------------------------------------------- 303

List of Publications, Presentations and Poster Contributions------305
Chapter 1

1.0 Introduction

For their “discovery and development of conductive polymers,” Alan Heeger, Alan MacDiarmid and Hideki Shirakawa shared the 2000 Noble Prize in Chemistry.[1] Indeed, since their initial 1977 report on the synthesis and characterization of a highly conductive poly(acetylenes), semiconducting conjugated polymers (CPs) have become the subject of major investigation worldwide.[2][3] Thousands of research groups are actively developing organic materials for application in sensing[4] and electronics[5], Figure 1. CP properties such as electroluminescence have fostered growing demand for the use of these materials in low-power organic light emitting diodes (OLED) for solid state lighting and additionally polychromatic displays.[6] The ability to tune absorption and physical properties of CPs by functional group modification (or production of copolymers) has lead to their use in organic photovoltaics (OPVs)[7]. Several classes of CPs, including poly(thiophenes), have sufficiently high carrier motilities to be channel materials in organic thin film transistors (OTFTs)[8]. The greatest appeal of semiconductive polymers is the ability to process these materials from solution using low energy roll-to-roll techniques which can potentially lower the overhead production cost of device manufacturing.[9]

1.1 Introduction to Conjugate Polymers (CPs) and Origin of Their Semiconductive Properties

The following sections briefly summarize key topics relevant to amorphous organic semiconductors including the mechanisms of charge transport, the origin of photoluminescence and electroluminescence and how these phenomenon are related to the atomic structure of the material.
1.1.1 Structural Characteristics of CPs

Of the four valence orbitals belonging to each carbon in a conjugated polymer chain, two of the 2p atomic orbitals and the 2s atomic orbital behave as hybridized sp$^2$ orbitals. This leaves a single electron occupying an unhybridized 2p$_z$ orbital per backbone carbon atom. Symmetry allowed overlap of p$_z$ π orbitals is therefore contiguous along the length of an ideally planar polymer chain, Figure 2.$^{[14]}$ This extended π system is orthogonal to coplanar σ bonded sp$^2$ hybrid orbitals. As with benzene, the p$_z$ electrons become delocalized above and below the plane of polymer backbone. As the name implies, electrons in the π system are not fixed to certain atoms but are free to move along the backbone of the carbon chain. Directing this charge flow with a voltage bias is the underlying operating principle behind the use of conductive polymers as semiconductors. For conjugated polymers, like the several popular classes illustrated in Figure 3, the sum of numerous π orbitals along the polymer chain results in an energy band of π
molecular orbital energies. The presence of an energy gap between the HOMO and LUMO energy levels results in the semiconductive nature of the material.\[15\]

CPs with a singular type of repeat unit (as with any polymer) are referred to as a homopolymers. Both poly(9,9-dioctylfluorene) (PFO) and poly(3-hexylthiophene) (P3HT) are common conjugated homopolymers. Polymers composed of multiple repeat unit types are known as copolymers and can be subdivided into statistical, alternating, and block copolymers. One notable green emitting statistical copolymer sold commercially for OLEDs and solid state lasers is poly(9,9-dioctylfluroene-co-benzothiadizaole) (F8BT)\[16\], Figure 4, however, there are numerous examples of copolymers made from two or more different monomers and the variability is limited only by the compatibility of monomers to the different types of polymerization reactions used to produce CPs. According to numerous reports in the literature, the use of thiophenes and structurally analogous monomers in nickel catalyzed, Grignard metathesis (GRIM) polymerization afforded well defined block copolymers with narrow polydispersity.

**Figure 2**: a) Prototypical poly(acetylene) chain showing several unhybridized $p_z$ orbitals and their overlap to form a continuous $\pi$ system. b) The linear combination of valence $p_z$ orbitals along an extended conjugated backbone results in contiguous bands of bonding and
(Cont’d From Figure 2)…antibonding states separated by an energy gap. The bottom “valence” band is fully occupied while the “conduction” band is empty.

Figure 3: Several examples of popular semiconductor families including poly(phenylalkynes) (PPP)[18], poly(phenylene vinylenes) (PPV) such as MEH-PPV[19], poly(thiophenes) (PT)[20], poly(anilines) (PANI)[21], poly(phenylalkynes) (PPP)[22] and poly(fluorenes) (PF)[23].

Figure 4: Common examples of semiconducting statistical copolymer poly(9,9-dioctylfluorene-co-benzothiadizaole) (F8BT)[16], an alternating copolymer poly[[9,9-dioctyl-2,7-divinylene fluorenylene)-alt-co-(9,10-anthracene)] (PVFA)[24] and block copolymers poly(3-hexylthiophene)-b-poly(9,9-dioctylfluorene) (P3HT-b-PFO)[17a] and poly(3-hexylthiophene)-b-poly(diketopyrrolopyrrole-terthiophene) (P3HT-b-DPP)[17b].
1.1.2 Small Molecule Components

Certain low molecule weight compounds can be useful charge transport materials as well as emitters, often be used in conjunction with polymer hosts in OLEDs. In many cases, small molecules are thermally evaporated under high vacuum to create layers vital to improving OLED efficiency. Some examples include hole transport materials such as TPD or IPD\textsuperscript{[25]}, structures are shown in Figure 5. Photoluminescent emitters, including dyes such as coumarins, anthracene, porphyrins, and DCM, frequently require a host matrix to prevent intermolecular quenching.\textsuperscript{[26]} Matrices can be polymer based (such as PVK) or a co-evaporated small molecule like Alq\textsubscript{3}.\textsuperscript{[27]}

\textbf{Figure 5:} Examples of several small molecules encountered in organic electronics including transport materials, phosphorescent and fluorescent emitters.
1.2 Material Classes of Organic Semiconductors

Organic compounds used in electronics vary considerably with respect to structure and properties, however, they are frequently categorized as being polymers or small molecules. The distinction is slightly more than a formality because different classes are usually associated with specific processing methods. Polymer based devices are considered by most to be useful in conjunction with solution processing methods while small molecules are usually deposited using thermal evaporation techniques under high vacuum (unless used in a mixture with polymer/dendrimers which have superior film forming properties). Within these two classes, several distinctions can be made with regards to material properties and the function each material fulfills in devices such as OLEDs and OPVs. The following sections briefly cover examples of hole injection materials (HIL), hole transport materials (HTM), and electron transport materials (ETM).

1.2.1 Hole Injection Layer (HIL) Materials

Hole injection refers to the process of transferring a positive charge (hole) from an electrode into a semiconducting layer within a device. A hole injection layer exist between the anode and a neighboring semiconducting layer and reduces the energy barrier associated with transferring a positive charge across the interface. Reducing of energetic barriers at interfaces enables not only lower operating voltage of the OLEDs, but also helps modulate hole carrier density to the level required for charge balance within the device, improving the lifetime of the device.\[28\] Many hole injection materials are polymers with extended \( \pi \) conjugation along the chain length. Many commercial materials are oxidatively doped to varying extents (either chemically or electrochemically) and available with conductivities ranging over several orders of
magnitude. This is a type of p-doping because removal of electrons from the valence band of the polymer generates positive vacancies (holes). Depending on the charge carrier density, thin films can exist in a semiconducting state all the way to a metallic state.[29]

1.2.1.1 Poly(3,4-ethylenedioxythiophene)-Poly(styrenesulfonate) (PEDOT:PSS)

PEDOT:PSS is one of the most commonly used commercial HIL materials because of its good electrical conductivity, environmental stability in its doped form, and sufficient thin film optical transparency.[30] PEDOT:PSS is easy to process into thin films from solution by spin casting, slot dye casting and other roll-to-roll techniques. It is often shipped as a water dispersion consisting of oxidized PEDOT stabilized with the polyanion poly(styrene sulfonate). Several grades of conductive PEDOT-PSS blends are commercially available.[31] Lower conductivity grades are often used as the HIL in OLEDs and OPVs on top of ITO electrodes. Recent reports have shown high conductivity PEDOT:PSS can be used successfully as an ITO replacement over large areas with high transparency and work functions of ~5.1 eV.[32] Despite the success of the PEDOT-PSS blends, it has been shown that the presence of the strongly acidic and hygroscopic PSS can sometimes degrade device lifetime (by leaching indium from ITO) and performance and several alternatives have been proposed (see the following section).[33].

Figure 6: Popular hole injection layer (HIL) polymers a) PEDOT:PSS and b) Plexcore™. Both are derived from poly(thiophenes) and are sold commercially as oxidized dispersions.
1.2.1.2 Sulfonated Poly(thiophene-3-[2-(2-methoxyethoxy)ethoxy]-2,5-diyl) (Plexcore™)

Plexcore™ is a high work function sulfonated polythiophene derivative and, like PEDOT:PSS, it is sold as an aqueous dispersion for spin coating conductive thin films for application as a hole injection layer in OLED applications.\textsuperscript{[34]} It has also been used successfully as a hole transport layer (HTL) in organic photovoltaic devices. The advantage of sulfonated polythiophenes over more common PEDOT:PSS is both the lower acidity and reduced hygroscopicity of thin films.\textsuperscript{[35]} Plexcore™ is sold commercially as 2 wt\% dispersions in a mixed solvent of either 1,2-propanediol/isopropanol/water or ethylene glycol monobutyl ether/water. Depending on the dispersion solvent and film drying/annealing conditions, resistivity of dry films can range from 25–3000 Ω·cm (similar to PEDOT:PSS) and have work functions between 5.1-5.2 eV.

1.2.2 Hole Transport Layer (HTL) Materials

Many OLEDs are fabricated with multiple layers deposited before and after the emissive layer for the purpose of reducing charge injection energy barriers (see section 1.3.14). It follows that materials deposited following the HIL are designed to serve as hole transport layers (HTL) which have HOMO energies that are intermediate to the HIL and the emissive layer. There are numerous HTL materials reported in the literature and many are sold commercially.\textsuperscript{[36]} They range from small molecule triphenylamine and carbazole derivatives (deposited through evaporation) to high molecular weight polymers which are spin cast from solution. The following section will briefly discuss some commonly encountered materials.
1.2.2.1 Polymer HTL: Poly-TPD and PVK

PVK is not a conjugate polymer, but has a saturated backbone formed (usually) through cationic or free radical polymerization of the vinyl group of 9-vinylcarbazole, see Figure 7.\[^{[37]}\] PVK is sold commercially as an off-white solid which dissolves readily in many organic solvents and has molecular weights ranging from 20 kDa to >100 kDa. The HOMO/LUMO energy of the polymer is reported to be 5.6 eV and 2.0 eV respectively. Charge transport in PVK has been studied extensively.\[^{[38]}\] The carrier mobility is strongly field dependent and relatively low, ranging from $10^{-8}$-10^{-5}$ cm^{2}/Vs depending on the temperature and electric field. As with many amorphous organic solids, charge transport occurs due to charge exchange between neighboring hopping sites, which, in the case of PVK, constitutes the pendant carbazole groups.

Poly(N,N′-bis(4-butylphenyl)-N,N′-bis(phenyl)benzidine or poly-TPD is a hole transport polymer which consists of triphenylamine repeat unit and is sold commercially as yellow-green fibrous solid with molecular weights in the range of 10-70 kDa. Poly-TPD is reasonably soluble in solvents such as dichlorobenzene. Poly-TPD has a slightly lower band gap than PVK with its HOMO/LUMO energy levels at 5.1 eV and 2.3 eV respectively.\[^{[39]}\] Hole mobilities are reported to be higher than PVK at $10^{-4}$-10^{-3}$ cm^{2}/Vs. Given the lower LUMO energy of poly-TPD – 2.3 eV is higher than the LUMO of many emitting materials – it serves as a poor electron blocking layer which helps to confine recombination with the emitting layer.

Figure 7: Structures of polymeric HTL materials PVK and Poly-TPD
1.2.2.2 Small molecule HTL: α-NPD and TPD

There are numerous small molecule hole transport materials available commercially and they are deposited as thin layers normally in conjunction with thermal evaporators. Two popular small molecule HTL materials, known as TPD \(^{[40]}\) and α-NPD \(^{[41]}\), are structurally similar to the polymers discussed in the previous section. Indeed, Poly-TPD is simply the polymer of TPD (with a butyl group instead of a methyl group). α-NPD is another benzidine based compound with naphthyl substituents being substituted for methylbenzene groups in TPD. While the structural modification of α-NPD may seem slight, it is reported to increase the T\(_g\) of the material beyond that of TPD (95°C versus 65°C respectively) and OLEDs using α-NPD as a HTL perform better with respect to operational lifetime\(^{[42]}\). This is believed to be due to the effects of resistive heating occurring within the layers of an operating OLED, which may cause the temperature to approach the T\(_g\) of one or more components and induce deleterious phase changes or migration between layers.

Evaporated HTL typically exhibit higher hole mobilities than spin cast polymer analogues. The hole mobility of TPD is independent of electric field up to \(~10^5\) V/cm and is particularly high even in amorphous TPD films or in polymer films doped with large weight percentages of TPD. Carrier mobilities of TPD can have been reported to exceed \(\mu_h = 10^{-3}\) cm\(^2\)/Vs\(^{[43]}\). Comparatively, α-NPD has slightly lower mobilities at \(\mu_h = 5\times10^{-4} \text{ to } 1\times10^{-3}\) cm\(^2\)/Vs. The HOMO/LUMO energies of α-NPD are 5.4 eV and 2.5 eV respectively, which is approximately the same as TPD \(^{[44]}\).

1.2.2.3 Crosslinkable HTLs

It is now becoming increasingly popular to use crosslinkable compounds for organic electronics\(^{[45]}\). For conventional HTL materials (as above) to serve their purpose in multilayer
OLEDs, they must have an appropriate solubility orthogonal to subsequent solvents used in the spin casting of additional layers. If not, bottom layers will redissolve and fail to generate well defined interfaces in the device. By photo or thermally crosslinking hole transporting materials, the solubility issue becomes moot as a network of covalent linkages throughout the HTL make it insoluble in every solvent. Additionally, crosslinking prevents the same thermally induced phase changes and interlayer migrations discussed in the previous section by locking compounds within a network.

Crosslinked HTLs are an increasingly important resource being adopted by more research groups as they turn their attention to phosphorescent dopants to harvest both singlet and triplet excitons in an effort to achieve higher efficiencies in PLED devices. In these devices, singlet and triplet excitons formed in the host have a high probability of transferring to the dopants via the Forster and Dexter energy transfer. Charge trapping and energy transfer to phosphorescent emitters result in devices which operate at very high efficiencies. One of the challenges associated with fabricating devices with host/dopant emissive layers stems from the restriction placed on the energy levels of the host. For dopants to operate as efficient charge traps, its HOMO/LUMO singlet and triplet states must fall within the bounds of the host. Wide band gap hosts are necessary for higher energy green and blue emitter electrophosphorescent PLEDs. HOMO energy level of large gap hosts (usually greater than -5.8 eV) make the process of efficiently injecting holes from ITO (~4.8 eV work function) to the emissive layer difficult if only one HTL is used and large injection barriers remain. To achieve more manageable energy barriers, a stepped profile can be created using multiple HTL materials. It is straightforward to evaporate several HTLs in succession, but solution processing requires orthogonal solvent methods to be developed, a tedious task which needs reoptimization for any changes in device architecture and materials.
Several solutions have been developed which consist of a wide gap polymer host made to be thermally crosslinkable. One example, Figure 8, developed by Jen et al., is a hole injecting/transporting polystyrene derivative (PS-TPD-PFCB) that possesses pendent TPD as side chains for hole transporting and phenyl trifluorovinyl ether (TFV) as crosslinking moieties. Bilayer fluorescent OLEDs using this polymer as the HTL have shown higher quantum efficiency and brightness with dopants compatible with TPD’s 5.4 eV HOMO energy. For hosts with even lower lying energy levels necessary for deep blue dopants, a true HTL energy gradient has been demonstrated using tandem layers of PEDOT:PSS/PS-TPD-PFCB and a recently reported TCTA derivative with 5.7 eV HOMO level called TCTA-TTFV. While not a polymer, TCTA-TTFV can be spun cast on top of a previously crosslinked layer of PS-TPD-PFCB. TCTA-TTFV is a thermally crosslinkable 4,4’,4”-tris(N-carbazolyl)triphenylamine derivative that bears either TFV or vinylbenzyl ether cross linking groups, Figure 8. TCTA-TTFV provides a low barrier pathway for injecting holes into blue-emitting electrophosphorescent devices.

QUPD is a photocrosslinkable hole transport material developed by Meerholtz et al. It is a TPD derivative with two acid sensitive oxetane groups which can undergo a cationic ring-open polymerization (ROP) which crosslinks the material. QUPD is spin-cast together with an iodonium photoinitiator. To initiate crosslinking, films are irradiated with UV light (λ= 366 nm, exposure = 5 s) and soft baked for 60 s at ~ 120°C. Films of 50 - 150 nm thickness can be made in this way which have excellent optical transparency (>90% above 415 nm), hole mobilities on the order of 10^-4-10^-3 cm^2/Vs and superior thermal stability with T_g = 250°C.
1.2.3 Electron Transport Layer (ETL) Materials

The material landscape is more sparsely populated with well performing ETL compounds, which are often chemically sensitive to their environments and hence more challenging to process. Electron mobilities are typically low ($\sim 10^{-6} \text{ cm}^2/\text{Vs}$) in most amorphous organics. 4,7-diphenyl-1,10-phenanthroline (a.k.a bathophenanthroline or BPhen) is among the more popular ETL materials used and it is deposited using thermal evaporation. Thin films are reported to have relatively high electron mobilities of $5 \times 10^{-4} \text{ cm}^2/\text{Vs}$, which is approximately two orders of magnitude higher than another popular ETL, tris(8-hydroxyquinolinato)aluminium (Alq3). BPhen’s large energy gap and a low HOMO energy level (HOMO/LUMO energies are 6.4 eV and 3.0 eV respectively) which makes it an ideal hole/exciton blocking material deposited on top of the emissive layer. That is, BPhen purposefully induces a large energy barrier to holes which might otherwise transverse the EML/cathode interface and effectively localizes holes and excitons in the EML. BPhen is often co-deposited with lithium and in the process becomes n-doped, improving the electron transport properties of the material and its role in creating ohmic contacts to any electrode without the need stringent consideration of work function alignment.
1.3 Introduction to Organic Electronics

The growing interest for organic electronic devices stems from their enticing low cost and simplified fabrication as well as the relative ease with which electronic properties can be tailored by alterations in chemical structure. Given the abundance of polymers and small molecules which have emissions spanning the visible spectrum, they are a convenient resource from which to construct next generation display technologies, Figure 10. Indeed, Samsung, LG, Sony, Panasonic and other technology market leaders have already begun replacing less efficient LCD technologies with small molecule emitter based AMOLEDs in the billion dollar smartphone and tablet market. These companies have also invested considerable capital in the development of organic based solid state lighting. Panasonic, LG and OSRAM have pilot product already on the market or slated for commercial retail within the next few years.\[54\] White organic light emitting diodes (or WOLEDs) are projected to be strong market competitors against compact fluorescent lights as low energy lighting alternatives to incandescent bulbs. WOLEDs are not only more power efficient, but can be made flexible and modular to allow for the broadest domestic and commercial application. While currently less prolific, there have also been numerous examples of small area, polymer based displays used as prototype car radio displays, MP3 players and
other simple infomatic displays targeted to defence applications by companies such as OSRAM and Cambridge Display Technologies (CDT).\textsuperscript{[55]}

**Figure 10:** The increasing integration of organic electronics into modern technology.

In addition to OLEDs, organic solid state lasers (OSSL) are another field in which interest in light emitting conjugate polymer continues to grow rapidly, Figure 11. Given many CP have broad PL emission, they make excellent gain medium in tunable wavelength lasers which are superior to many inorganic laser diodes. As pumping thresholds decrease with the production of higher efficiency gain materials and improved resonator designs, OSSL have the potential to become cheap and compact visible laser light sources for disposable, point-of-care medical diagnostics. This revolution has partly been enabled by the proliferation of compact and affordable blue-violet emitting inorganic laser diodes and LEDs.\textsuperscript{[56]} For example, indium gallium nitride based laser diodes have already proven to be a versatile and low-cost successor of immobile and power consuming gas lasers or frequency multiplied solid-state lasers currently being used as pump sources for conjugated polymer lasers.\textsuperscript{[57]} Portable instruments employing
laser-based analysis techniques and sensors (e.g. explosives detection) are now possible to construct and use in the field by front line workers such as customs officials and medical professionals in field hospitals in developing countries and war zones. There are, however, several factors which limit the present day development of LED pumped OSSL devices. Limited gain efficiency in some (but not all) conjugate polymers, low efficiencies of resonators accessible through present fabricated methods, as well as solubility and morphological constraints of the polymer themselves are all factors contributing to OSSL thresholds.

Of course, the holy grail of OSSL field is the development of electronically pumped lasers. Numerous challenges associated with this task have thus far prevented a functioning device.[58] For an electrically pumped OSSL, it has been found that loss mechanisms which increase a laser threshold include not only light absorption by the waveguide itself, but also include a significant absorption from the metal contacts required to drive current through the devices. Consequently, devices must be driven at higher currents to compensate for absorption which leads to rapid breakdown of the organic layer. Unfortunately, even without the previously mentioned losses, exitons generated from injected charge carriers also have an inherent absorption which cannot be eliminated by fine tuning device layer thicknesses to better confine light propagation to the gain medium.

In the advent electrically pumped OSSL become a reality, organic lasers are positioned to replace inorganic diode lasers in many common technologies already in use today. Blue laser diodes are key components in HD DVD and Blue-ray disk readers and many red and infrared laser diodes are used for signal transmission in telecommunications.[59] Because OSSL can be processed from solution, they may become a practical solution to mass production of future optical computing circuits.
Figure 11: Organic solid state lasers and their continued development in future optoelectronics. Future applications may include a) disk reading devices such as Blue Ray™ or b) a laser source for photonic integrated circuits composed of various transformative optical (TO) components. A group of TO-based photonic components can be integrated within conventional optical and optoelectronic devices, including waveguides and photodetectors, on a common planar substrate. These TO building blocks create complex photonic devices and systems, which can provide a wide range of functionalities with applications in optical communications, information processing and sensing.

1.3.1 Organic Light Emitting Diodes (OLEDs)

The preceding sections aim to review aspects of an OLED’s internal processes and fabrication. Given the rapid expansion of this field, however, it is impossible to cover all aspects of OLED design. Topics such as improved light out coupling from OLEDs to improve device irradiance by including nanoparticle scattering layers, roughening electrode surfaces, or incorporating more elaborate high refractive index grids will also be discussed.

1.3.1.1 Charge Transport In Amorphous Materials

As discussed in previous sections, low electrical conductance and charge carrier mobilities exemplify organic compounds used as components in electronic devices. However, different compounds can be allocated to fulfill different electronic roles because the transport of one charge carrier type (e.i. holes or electrons) is usually better than the other depending on the
material. Electrons are believed to be more susceptible to traps within the material, and hence their transport is more impeded. Though regioregular poly(3-hexylthiophene) (RR-P3HT) have recently been reported to have electron and hole mobilities in the same order of magnitude, as determined through time-of-flight mobility measurements.\[60\]

Conjugated polymers usually behave as p-type materials and have hole mobilities ranging from $10^{-7}–10^{-3}$ cm$^2$/Vs. In cases where polymers exhibit ambipolar transport properties, electron mobility is usually several orders of magnitude less than that of holes. In comparison to single crystalline inorganic solids, however, both carriers have low mobilities due to the inherent disorder in amorphous materials. With a lack of crystallinity in conductive polymer thin films, energy states are more localized compared to those found in single crystalline inorganic semiconductors. The mechanism by which charge is transported through glassy solids is theoretically described by the Miller-Abrahams model.\[61\] This model approximates charge transport and injection to hopping events occurring between spatially isolated states in the solid or the metallic electrode conduction band. According to the equation 1.0:

$$V = V_0 \exp (-2R\varphi) \left\{ \begin{array}{ll} \exp \left( \frac{E_2-E_1}{k_B T} \right) ; & E_2 > E_1 \\ 1 ; & E_2 < E_1 \end{array} \right. \quad (1.0)$$

The rate of charge hopping $V$ from an occupied site to an unoccupied site is related to the energy difference ($E_2-E_1$) between these states and the distance, $R$, separating these sites. $\varphi^{-1}$ is the decay length of the electronic wavefunction, $k_B$ is the Boltzmann constant, $T$ is the temperature of the solid, and $V_0$ is the frequency of hopping attempts, which has been shown empirically to be on the order of $10^{-12}$ s$^{-1}$ for many organic semiconductors.

As would be expected for a disordered solid, not all localized states are at the same energy. Shallow or deep traps states for polarons can result from defects including branched
chains, large torsion angles of neighboring rings, chain breaks, or conjugation defects etc. On this energy level landscape, charges have the smallest barrier to hopping when the energy difference between initial and final states is minimal. Charge carriers which occupy deeper energy states are impeded in the absence of sufficient thermal energy to promote it to more shallow states. If a state is so low in energy that an electron cannot escape (and hence does not contribute to the conduction of current through the material) it is referred to as a trap state. In general, the lower the energy state occupied by a carrier, the lower its mobility at a given temperature.

The charge carrier density in organic semiconductors is dependent on intrinsic factors such as the energy gap of the material and the Boltzmann distribution due to thermal excitation of carriers into higher energy states (hence low band gap organic semiconductors are usually more conductive). Extrinsic factors including defects (e.g. oxidation or reduction, see doping) can also increase the number of charge carriers present as well as the number of injected charge carriers.

It is trivial to illustrate that organic compounds are far more intrinsically insulating than electrically conducting. If certain liberties are taken in approximating the electronic structure of organic semiconductors to that of inorganic semiconductors\cite{62}, the intrinsic number of charge carriers can be estimated using the eqn 1.1:

\[
n_{\text{int}} = N_B e^{\Delta E/2kT}
\]

(1.1)

Where \( n_{\text{int}} \) is the intrinsic carrier concentration (i.e. the number of electrons in the conduction band and holes in the valence band) per unit volume in a semiconductor free of impurities or defects. \( N_B \) is the number of effectively available states per unit volume (it is on the order \( 10^{19} \) cm\(^{-3} \) in semiconductors like silicon and germanium).\cite{62} \( \Delta E \) is the energy gap between the
valence and conduction bands. \( k_B \) is the Boltzmann constant and \( T \) is the absolute temperature in Kelvin.

Once \( n_{\text{int}} \) is established, the conductivity of the material can also be roughly estimated by multiplying \( n_{\text{int}} \) by the elementary charge \( e \) and the estimated mobility \( \mu \). Empirically it is known the \( \mu \) is on the order of \( 10^{-4±6} \) cm\(^2\)/Vs for most organics\(^6\text{[63]}\) and this estimates intrinsic conductivity to be on the order of \( 10^{-25} \) S/m and essentially inconsequential. As elucidated above, charge carriers must be added to organic semiconductors due to the intrinsically low charge carrier densities in these materials. This is normally achieved through injection at an electrode, photogeneration, or doping. The latter topic has been mentioned briefly in the section on PEDOT:PSS and will now be covered further.

### 1.3.1.2 Doping of Organic Semiconductors

In much the same way doping of inorganic semiconductors involves the addition of elements which contribute to vacancies in the valence band (p-doping) or filling of states in the valence band (n-doping), the doping of organic semiconductors usually proceeds with the addition of chemical oxidants or reductants to semiconductor solutions which lead to the removal of the HOMO (p-doping) or injecting an electron into the LUMO (n-doping). Common dopants include oxidants such as AsF\(_5\), iodine, bromine, FeCl\(_3\) in addition to various strongly reducing metals like lithium or aluminium.\(^6\text{[64]}\) Somewhat large organic compounds such as tetracyanoquinodimethane (TCNQ) or Tris(4-bromophenyl)ammoniumyl hexachloroantimonate (TBA-SbCl\(_6\)) are used as more stable additives.\(^6\text{[65]}\) It is often reported that small dopants actively diffuse within device layers and result in reduced thermal stability. Frequently, this leads to EL quenching once dopants begin to migrate into the active layer. Larger dopant compounds are
less prone to migration and allow fabrication of well defined junctions (e.g. p-n or n-i-p junctions) which have proven successful in improving OLED performance and stability.

![Chemical Structures](image1)

**Figure 12:** a) Oxidative (p-type) doping of MEH-PPV films with controlled amounts of F4-TCNQ. b) Current density versus voltage characteristics of MEH-PPV films with various dopant:host molar ratios. At low bias voltages, the current density increases by 1–3 orders of magnitude with increasing doping concentrations.\(^{[65]}\)

### 1.3.1.3 Charge Carrier Injection

The injection of charge carriers into low mobility materials such as organic semiconductors is problematic because an accumulation of charge usually occurs at the organic/inorganic electrode interface. The result is a partially screening of the applied electric field and redistribution of the electric field within the device. The current-voltage (I-V) characteristics observed under these conditions is described as space-charge limited current (SCLC) behavior.\(^{[66]}\) I-V curves predicted by this model are nonlinear, typically quadratic. SCLC type injection is reported to be the principle mechanism operating in devices where strong injection is achieved from both electrodes.

Trap-Free SCLC is another injection condition observed when local increases in quasi-Fermi level result in charge immobilization in the deep HOMO/LUMO states of disordered glass
Organic solids. The Trap-Free SCLC model predicts I-V characteristics which follow an exponent power law \( I = V^t \) with \( 7 < t < 9 \).\(^{[67]}\) Lastly, in cases where large energy barriers exist at electrode/organic interfaces (with zero-field contact barriers being greater than \(0.25–0.30\) eV), current flow through the device is limited by injection and the phenomenon is known as injection limited current (ILC).\(^{[68]}\) ILC is an undesirable current regime for a device to operate in because only small current densities are possible, hence care has to be taken in the device design in order to ensure good injection properties. This usually requires the fabrication of an energy level gradient using multilayered designs with several different transport materials as discussed in the next section.

**Figure 13:** Illustrations of I-V characteristics for devices operating under Ohmic, SCLC and Trap-Free SCLC conditions. a) Experimental setup for measuring injection of carriers into organic solids. b) Experimental data acquired for a PPV derivative which clearly shows carrier injection to progress through all three regimes. c) Illustration of SCLC conditions when the density of injected charge is higher than available acceptor states leading to a space-charge build-up at the electrode. Note that due to band bending at the semiconductor/metal interface, it is favorable for holes (in the case of the anode) to flow back towards the electrode following injection.\(^{[66]}\)\(^{[67]}\)
1.3.1.4 The Working Principles of OLEDs

OLEDs are created as multilayer structures consisting of an emission layer (EML) sandwiched between hole transport layers (HTL) and electron-transport layers (ETL). Figure 14 is used to illustrate the events leading to light emission from a typical three layer OLED.[69]

![Diagram of OLED structure](image)

**Figure 14:** Internal processes resulting in exciton formation and photon emission within an OLED.[69]

I) Initially, both electrons and holes are injected into a device from the cathode and anode respectively. The Fowler-Nordheim model can be used to describe carrier injection from an electrode into an organic semiconductor as a tunnelling event which occurs across an energetic barrier formed by the mismatch between the work function of the electrode and the HOMO/LUMO level of the organic material. A complete description, however, requires consideration of both carrier backflow into the electrodes due to the low carrier mobility of the material and thermionic emission.
II) Positive and negative charges are directed in opposite directions through the organic layers by the applied voltage. Charge carriers are transported by hopping processes from localized state to localized state as described by the Miller-Abrahams model.

III) If two opposite charges encounter each other, a bimolecular Langevin-type recombination of electrons and holes occurs to form a coulombically bound exciton. Without the presence of phosphorescent emitters, roughly 25% of recombination events result in emissive singlet states due to spin-statistics and the higher multiplicity of triplets.

IV) The fate of a singlet exciton is to recombine and emit a photon. Before doing so however, excitons can undergo intramolecular transitions and propagate diffusively whilst gradually relaxing energetically within the density of states.

1.3.1.5 Strategies for Improving Light Outcoupling Efficiency

It has been well documented that light originating from electron-hole recombination within the active OLED propagates via various modes within the microcavity formed by the various layers and electrodes, Figure 15. Some light escapes from the substrates surface via external modes (as desired), however a large percentage of light remains confined within the substrate and ITO/organic-waveguided modes due to total internal reflection (refer to section 1.9.5.2 for definition of external quantum efficiency, EQE). In fact, it is estimated that as much as 80% of total generated light is trapped within waveguided modes of the substrate or emitted out from the edges of an OLED.\textsuperscript{170} Having only 20% of total generated light actually emanate from the device surface is clearly not optimal for a technology vying to dominate the flat panel display market.
With poor light extraction being the dominant factor limiting the external quantum efficiency of devices, more and more improved outcoupling methods are being developed to get higher efficiencies. Several strategies in the literature currently are based on light refraction and scattering to reduce internal reflection at layer interfaces. These include using textured (i.e. roughened) substrates, using micro-lenses on the backside of substrate surface, integrating a monolayer of silica microspheres as a scattering medium, and using high refractive index substrates.\cite{71} Other approaches have included integrating a low refractive index layer based on silica-aerogel into an OLED between the ITO transparent electrode and the glass substrate.\cite{72} Several authors have reported improved outcoupling as high as 50% by including a two-dimensional photonic crystal or using nanoporous and nanopatterned films\cite{73}. Liu et al. have reported using holographic patterning techniques to generate structured substrates.\cite{74}

Saxena et al. have used methods developed for making anti-reflective (AR) coating as a means of extracting more light. They demonstrated a roughly two-fold enhancement in luminance over conventional OLED by incorporating a single layer of MgF$_2$ with thickness of $\lambda/4$ on the backside of glass substrate of a conventional OLED.\cite{75} A similar index-matching layer has also been used for top emitting OLED by Hung et al.\cite{76}

Forrest et al. have shown enhancement of light outcoupling into substrate modes by a grid of low-refractive-index material embedded into the organic layer of an organic light-emitting device.\cite{77} The low-index grid (LIG) redirects modes normally trapped within the high-index organic and indium tin oxide layers (waveguiding modes) into the substrate. Simulations by the authors show that up to 50% more light can be extracted from the high-index region using an ultralow-index $n=1.03$ grid than a conventional device, and provided efficient substrate-to-air outcoupling, the external quantum efficiencies of LIG OLEDs can reach ~50%.
1.4 Fabrication of Organic Light Emitting Diodes (OLEDs)

Organic semiconductor materials are commonly classified into two categories: conjugated polymers and small molecules. Small molecule materials are low molecular weight organic solids that are typically deposited by thermal evaporation in vacuum, whereas polymers are usually spin-coated from solution. The big advantage of thermal evaporation is the ease of coating consecutive layers, hence allowing the simple fabrication of multilayer devices in which the thickness of each layer can be precisely controlled. In contrast, with solution processing, one must take into account the compatibility of each layer with the solvents used for coating the subsequent layers, or utilize photocrosslinkable materials to render the layers insoluble. The following sections will discuss some of the principle tools used in the creation of OLEDs as well as methods used to protect devices from ambient moisture and oxygen after their creation.
1.4.1 Deposition Methods

As organic semiconductors become increasingly integrated into electronics, new manufacturing processes are being devised for large area coating of thin films. The high demand for AMOLED displays has warranted the design and construction of increasingly higher throughput evaporation systems. Samsung has recently launched a Gen 6.5 AMOLED fabrication facility for processing 1.5 x 1.8 m substrates.\cite{78} The push for all-solution processing, however, continues. Emerging industries based on thin film photovoltaics are heavily reliant on the reduced overhead cost of solution processing to manufacture CdTe or CIGS PVs below market value.\cite{79} Industry scaled roll-to-roll machinery created for the PV industry is also applicable for other thin film technologies such as OTFTs, OLEDs and OSSLs. The following section discusses two common laboratory scale processing technologies.\cite{80}

![Industrial Evaporation and RTR solution processing.](image)

*Figure 16:* Industrial Evaporation and RTR solution processing\cite{80} including dye slot casting on flexible substrates (a-b) as well as industrial scale evaporation assemblies for multiplayer deposition of organics and metals (typical substrate sizes are ~ 1m² in current Gen facilities).
1.4.1.1 Thermal Evaporation

Organic small molecules and metal contact are usually deposited using thermal evaporation. Typically, deposition takes place in a high vacuum chamber ($10^{-6}$ mbar) with deposition rates on the order of a few Å/s. Several manufactures produce evaporation systems and offer tools with multiple organic and metal evaporation sources. Modern systems are computer controlled and are capable of performing multiple automated deposition steps and finely controlled co-depositions of several materials. Frequently, evaporation systems are contained within a glovebox to allow for oxygen-free device handling.\cite{81}

1.4.1.2 Solution processing

Commercial spin coaters are now widely available and the process has become a simple and popular process for forming thin films on rotating substrates.\cite{82} Substrate size can range from a few centimeters to several inches, but the process is usually limited to making lab scale devices. In the spin coating process, an excess amount of solution containing the layer material is dispensed onto the substrate. The substrate is then accelerated up to its final desired rotation speed (between 1000-5000 rpm) and the liquid is spread evenly by centrifugal force. Rotation lasts usually a minimum of 30-50 s so there has been sufficient time for excess liquid to spin off the edges of the substrate and the desired film thickness is achieved. Volatile solvents are usually fully evaporated by the time a routine has completed. Typical solvents are toluene, chloroform, dichlorobenzene, THF etc.

1.4.2 Encapsulation

Encapsulation is the final step performed in the OLED fabrication process to ensure a long device lifetime. Operating under ambient conditions, unencapsulated devices have vastly
smaller lifetimes than devices which are guarded from humidity and oxygen. The most likely contributor to environmental degradation of unencapsulated OLEDs is the exposure of the organic–cathode interface to atmospheric oxygen and water. Several studies have clearly linked delamination of metal cathodes as well as chemical changes within organic layers to oxidation.[83] Most laboratory scale OLED work is based on rigid glass substrates. Glass functions as an excellent oxygen and moisture barrier and the degradation of devices removed from glovebox systems is prevented from sealing the OLEDs under inert atmosphere (e.g., in a nitrogen or argon glove box with < 1ppm water and oxygen), using glass or metal lids sealed with epoxy resin.[84] In some reports, desiccants such as CaO or BaO are included in the packaging to react with any residual water incorporated in the package or diffusing through the epoxy seal. Thin film encapsulation techniques which are more suitable for flexible OLED substrate have been demonstrated by Wong et al.[85] Their method includes repeated depositions of alternation layers of CF₅ and Si₃N₄.
1.5 Organic Solid State Lasers (OSSLs)

The word laser is an acronym and stands for light amplification by stimulated emission of radiation. In general, a laser consists of an amplifying material (the gain medium) placed within a resonator (cavity) that provides positive feedback. Several different forms of resonators can be used to introduce feedback in organic semiconductor lasers as depicted in Figure 18. \[86\]

There exist numerous types of organic semiconductors relevant to lasing which include small molecules, conjugated dendrimers, conjugated polymers, and spiro-linked compounds which can be thermally or photolithographically crosslinked. These materials can be
incorporated into OSSL resonators through simple spin coating of solutions (of conjugated polymers for example) or via thermal evaporation if the gain medium’s volatility is sufficiently high. Lasing has been demonstrated for wavelengths over the complete visible range, the near UV, and also for the near-infrared. Of these reports, there are numerous examples of OSSLs based on solution processed polymer lasers. Given the limited number of ways materials can be processed, some resonators designs are more practical than others. Due to the ease with which DFB resonators can be constructed with most materials, it has become a popular approach in creating OSSLs and will discussed further in a latter section.

![Resonator designs](image)

**Figure 18** Examples of various resonator designs to introduce feedback in a laser. a) Planar microcavity. b) Fabry-Perot dye laser cavity. c) microring resonator formed by coating an optical fiber. d) spherical microcavity. e) distributed feedback laser (DFB). f) 2D DFB. The black arrows indicated the direction of propagating amplified emission. (adapted from [86])

### 1.5.1 Working Principles of Organic Solid State Lasers

The following section discusses theoretical and practical aspects of lasers. This includes the photophysical origins of light amplification, a detailed description of a popular laser design used in this thesis work and a few case examples of blue emitting organic laser materials.

### 1.5.1.1 Irradiation Processes in Organic Materials
The myriad of energy transitions occurring within optically excited organic compounds is a necessary topic of discussion prior to covering the complex subject of OSSLs. The textbook description of organic photophysical processes is usually represented visually with a Jablonski diagram discussed below, Figure 20, but a basic understanding of optical transitions begins with the Born-Oppenheimer approximation. A molecule at any given time is not only in a specific electronic state, but also a vibration and rotational state. Furthermore, the energy difference between vibrational states is considerably smaller than electronic states. It follows that when light is absorbed by a compound, an electron is promoted from one set of electronic, vibrational and rotational states to another set of higher energy states. Figure 19 illustrates several optical transitions involving the ground and first excited state of a compound resulting from light being absorbed at slightly different energies, the occurrence of which leads to broadened absorption peaks in practice. These vibronic energy curves (a representation of both electronic and vibrational potential energy) plot the energy of a compound’s vibronic states as a function of interatomic spacing.

The Born-Oppenheimer model states that electron transitions occur at rates which are essentially instantaneous with respect to the speed of more massive vibrating nuclei.\(^{[88]}\) The duration of a photon’s absorption or emission process is on the order of femtoseconds (\(10^{-15}\) s). This approximation greatly simplifies the process of calculating a compound’s potential curve, a process which amounts to a set of calculations for a given compound’s electronic states solved at different atomic configuration coordinates.

Another fundamental insight into optical transitions and an extension to the Born-Oppenheimer model, is the Franck-Condon principle, which explains the variable intensities of vibronic transitions (i.e. the shape absorption and emission spectra (often mirror images of each other and the energy gap which separates them)).\(^{[89]}\) The theory states that the intensity of a
transition (i.e. the probability of its occurrence) from the lowest vibrational level of the ground electronic state to a higher vibronic state is dependent on the overlap of vibrational wavefunction of the respective states, the determination of which is simplified by treating the atomic coordinates as static.\[^{[89]}\] Stated another way, electronic transitions between two vibronic states is favored when there is minimal atomic rearrangement involved. Hence an electronic transition between the lowest vibrational states is not necessarily the most probable (i.e. intense). This is the reason why estimates of a materials band gap using its absorption spectrum is more accurate when using the energy of the absorption onset as oppose to the absorption maximum.

Figure 19: a) Potential energy curves depicting the ground state and first excited state of a compound. Wavefunctions for each vibration state within an electronic state are also depicted. The Frank-Condon Principle states that transitions are most probable between vibronic states with highest vibrational wavefunction overlap (i.e. least atomic rearrangement). This results in absorption and PL spectra which are often mirror and broadened due to transitions of different intensity.

Referring again to the Jablonski diagram, Figure 20, the fate of an electronic returning to the ground states will now be outlined. After absorbing a photon, an electron in the ground state ($S_0$) is promoted into a singlet excited state ($S_1$). The molecule then rapidly relaxes (within
picoseconds, $10^{12}$ s) to the lowest vibrational level of the first excited electronic state according to the Kasha principle in a process referred to as internal conversion [90]. From this point, it may decay to the ground state either radiatively (in the form of fluorescence) or non-radiatively with the formation of heat. In the fluorescent pathway, vibrational relaxation prior to emission means that fluorescent photons have less energy than the initial excitation photon and a fluorescence spectrum is red shifted from an absorption spectrum with the energy gap separating them known as the Stokes shift. Because the intensity (i.e. probability) of a fluorescence transition is also dependent on the same vibrational wavefunction overlap effecting absorption, absorption and fluorescence spectra are usually mirror images of each other. Fluorescence lifetime (the time an electron spends in the excited state before decaying) is typically on the order of $\sim 1$ ns [91].

The excitation of an electron into an excited state cannot occur with a change in spin, that is, a singlet to triplet spin transition is forbidden by the rules of spin conservation. More accurately, such transitions are highly improbable (e.g. inefficient), but can occur in phosphorescent systems. As with fluorescence, a phosphorescent compound absorbs a photon of the correct energy to excite an electron from the ground state to an excited singlet state. As before, the excited electron loses energy by internal conversion and reaches the lowest vibrational level of the excited electronic state. Instead of decaying to the ground state, some molecules in the first excited singlet state convert to an excited triplet state (T) by a transition known as intersystem crossing. The lowest energy triplet state ($T_1$) is lower than singlet states and despite being a forbidden transition, intersystem crossing can be an energy neutral process when singlet electrons cross over to an equal energy vibronic triplet state and cascade down to the lowest $T_1$ state. From $T_1$, the molecule can decay to the ground electronic level either by emitting a photon or in a non-radiative manner. Given the process of intersystem crossing is forbidden, phosphorescent lifetimes (μs-s) are considerable longer than fluorescence lifetimes.
Figure 20. Jablonski diagram showing transitions between excited states and the ground state. Radiative processes are shown with straight lines, non-radiative processes are shown with wavy lines. IC = Internal conversion, ISC = Intersystem crossing, $h\nu_f$ = fluorescence, $h\nu_p$ = phosphorescence

1.5.1.2 Stimulated Emission

A precondition for lasing is the presence of stimulated emission. Conjugated polymers and dyes typically show strong stimulated emission for the transition from the lowest singlet state $S_{1,v} = 0$ to vibronic sublevels of the ground state $S_{0,v} = j$. The intensity of photons traveling through an amplifying medium is described using the exponential relation (1.3):

$$I = I_0 \exp[(g(\lambda) - \alpha)L]$$  \hspace{1cm} (1.3)

where $I_0$ is the initial intensity, $g$ is the wavelength dependent gain coefficient, $\alpha$ the loss coefficient and $L$ is the distance travelled in the gain medium. Light intensity within a cavity is predicted to grow exponentially with increasing gain and propagation distance, but this occurs under low intensity conditions due to saturation effects on gain with increasing field intensity. Of course, in real lasers, several kinds of light loss mechanisms exist which reduce the efficiency of the amplification process. Loss mechanisms include scattering, mirror losses, and optical
absorptions by polarons or triplet excitons. For lasing to occur, the gain per round trip must be greater than the respective losses.\textsuperscript{[92]}

In the first stage of the four stage laser model (Figure 21), a ground state electron is pumped into a short lived ($\sim 10^{-12}$ s) excited vibronic state. This state rapidly decays (non-radiatively) to the lasing excited state which has a larger lifetime and results in a rapidly increasing population of excited electrons in single molecules or localized emission centers along polymer chains. When population inversion is achieved (i.e. the population of excited state electrons exceeds the ground state), stimulated emission becomes the dominant deactivation pathway and laser oscillation begins.\textsuperscript{[93]}

Analogous to the photophysical transitions occurring in organic dye lasers, non-radiative transitions can also occur which deplete the laser state and repopulate the ground state. The transition corresponds to an internal conversion between two vibrational levels, the $S_0$ ground state and vibronic levels within the first excited state $S_1$. Borrowing from the theoretical descriptions established for dye lasers, stimulated emission and hence gain in polymer semiconductors are related to the volume density of excited states, $n_{S1}$ by the relation (1.4):

$$g(\lambda) = \sigma_{SE}(\lambda)n_{S1} \quad (1.4)$$

Several organic materials have a large cross-section for stimulated emission. $\sigma_{SE}$ on the order of $10^{-16}$ cm\(^2\) and can be used to fabricate solid-state lasers with low threshold excitation densities.\textsuperscript{[94]}
Figure 21: Illustration of the transitions occurring within the a) four stage laser model, where transitions (1) and (3) are optical absorption and emission and transitions (2) and (4) are non-radiative relaxations. b) A more accurate depiction of vibronic energy states in an organic semiconductor.

1.5.1.3 Amplified Spontaneous Emission (ASE)

Line narrowing (or gain narrowing) of conjugated polymer emission spectra was first observed in films of MEH-PPV containing strongly scattering TiO₂ nanoparticles.[95] The phenomenon was quickly discovered to extend to numerous other conjugated polymers thin films (without nanoparticle additives) and eventually determined to be amplified spontaneous emission. ASE is observed under conditions where the organic emitter (i.e. conjugate polymer) is cast as a thin film on a substrate with a lower refractive index to form a slab-type waveguide. The data one obtains from measuring ASE in materials provides information on the net gain and loss properties of a particular waveguide structure. Stimulated emission of photons leading to a significant increase in light output is initiated by the first spontaneously emitted photons arbitrarily propagating in the pumped region of the gain medium wherein a population inversion has occurred. Theoretically, the number of spontaneously emitted photons is amplified
exponentially as they propagate through the waveguide assuming optical gain is sufficiently high enough to overcome light losses.\[96\]

With a gradual increase in pumping energy, a conversion between the materials PL spectrum and ASE spectrum is observed, Figure 22. Changes in the emission spectrum occur because photons with energies that coincide with the spectral position of maximum gain experience the largest amplification. This manifests itself as an apparent narrowing of the PL spectrum as ASE becomes the dominant deactivation pathway. The threshold for ASE typically occurs at excitation densities of $10^{17}-10^{18}$ cm$^{-3}$, corresponding to excitation energy densities of 1-10 $\mu$J/cm$^2$ for pulsed optical excitation. These values are relatively low compared to most inorganic gain medium due to the higher stimulated emission cross-section of organic molecules. Typical ASE line widths range from 5 to 10 nm.\[97\]

![Figure 22: Example of spectral narrowing due to ASE. a) ASE occurring in thin films of Spiro-SPO.\[98a\] Note spectral narrowing increases as pump intensity increases. b) ASE occurring in thin films of PFO. The PL spectrum is dominated by the higher wavelength $\beta$-phase emission.\[98b\]](image)
1.6 Laser Resonators

In general, a laser consists of a gain medium placed within a resonator that provides positive feedback. The Fabry-Pérot cavity represents the simplest type of laser design and consists of the gain medium sandwiched between two parallel mirrors.\[99\] Thanks to the convenient solution processing of many organic gain materials, numerous resonators with diverse designs have been reported to give feedback in organic semiconductor lasers. Figure 18 illustrates a number of optically pumped lasers designs ranging from basic waveguides to more sophisticated structures employing distributed feedback geometries,\[100\] microcavities,\[101\] microrings\[102\] and photonic crystals.\[103\]

Lasing from an organic semiconductor material was first achieved using microcavity resonators, which are easy to fabricate and have an emission profile perpendicular to the plane of the substrate. Microcavity lasers also bear the closest semblance to OLEDs, and hence one of the more promising designs for realizing electrical pumped OSSLs. Despite having several advantages, microcavity lasers are prone to high light losses and roundtrip gain is low, resulting in relatively high threshold values. This can be circumvented (to some degree) if highly reflective dielectric mirrors are used on both sides of the cavity.\[104\]

With inorganic semiconductor lasers, the simplest means of fabricating a resonator is to cleave the layer to yield a flat, well defined facet capable of acting as a partially reflective mirror. Organic films do not cleave to produce useful facets, however, and various other methods have been devised so circumvent this problem. The most notable feedback system used in conjunction with organic films is based on Bragg scattering due to periodic modulation of the refractive index within the waveguide and the concept is central to the very popular distributed feedback laser (DFB) design.\[100\] Organic lasers also exist based on whispering-gallery-modes which occur due
to total internal reflection of light propagating within microring, microtoroid, microdroplet and microdisk resonators.

1.6.1 DFB Lasers

Kogelnik and Shank developed the idea of feedback due to a periodic structuring of a laser’s gain region in 1971, and hence initiated the development of distributed feedback lasers (DFBs).\(^{105}\) Feedback in DFBs is not the result of parallel reflective mirrors, but Bragg scattering due to periodic modulation of the refractive index within the gain layer. As mentioned, DFBs are a popular design within the field of OSSL development because it enables low laser thresholds and the possibility of tuning laser wavelength, Figure 23.\(^{106}\) In the literature, there are countless examples of DFB variants including two-dimensional DFB and photonic crystal (PC) lasers. This subclass of laser has proven successful due of its low thresholds, possibility of large-area single mode operation and their circular (diffraction-limited) output beam. Furthermore, the exact geometry of the output laser beam can be altered based on the periodicity or structure of the PC unit cell. The following section discusses some the fundamental optical principles underpinning DFBs.

**Figure 23:** Examples of DFB laser applications including a) Lab-on-Chip designs which incorporate optically pumped lasers and waveguides into microfluidic chips. b) Illustrates the
process of integrating lasers into the microfluidic chip fabrication process by using hot embossing of gratings (1) and DUV etching of PMMA based channels (2) followed by thermally bonding a lid. c) Microscope image of a chip laser photoexciting cyanine-3 labeled streptavidin bound biotinylated phospholipids.[106a] e) Illustration of an electronically switched, variable-wavelength polymer DFB laser. Under high voltage (~1-3 kV) the elastomer grating material undergoes an expansion whilst being held within a rigid holder. The resultant strain causes a periodic buckling pattern to develop which is suitable for feedback at the polymer emission wavelength.[106b]

1.6.1.1 The Working Principles of a 1D DFB Structure

As previously mentioned, in distributed feedback resonators, feedback is provided by Bragg scattering from periodic structures. Simplified models can be used to explain the working principles underlying distributed feedback structures.[107] If the modulation of refractive index, n, in a DFB structure is taken to be sinusoidal, it can be described mathematically using equation (1.5):

\[ n(z) = n + \Delta n \cos(2\beta_0 z) \]  

(1.5)

Where z indicates the direction of propagation, \( \beta_0 = \pi/\Lambda \), \( \Lambda \) is the modulation period, and \( \Delta n \) indicates the overall change in refractive index. \( \Delta n \) is dependent on respective refractive indices of the substrate and the waveguide material (silicon and SiO\(_2\) for examples), the modulation depth and modal intensity profile, I(x). Analogously, the gain coefficient, g, of a hypothetical material can be described using equation (1.6):

\[ g(z) = g + \Delta g \cos(2\beta_0 z) \]  

(1.6)

Where \( \Delta g \) denotes the overall change in the gain coefficient and is dependent on the modal intensity profile, I(x), and the local gain coefficient of the emitting material.
In the optically pumped thin film described equations (1.5) and (1.6), the corrugated surface results in scattering of guided waves in the slab (i.e. film). Back-scattered waves can couple to guided modes which travel in opposing directions and constructive interference between the different partial waves is achieved if the Bragg condition is fulfilled according to equation (1.7):

\[ m\lambda = 2n_{\text{eff}}\Lambda \]  

(1.7)

Note that \( n_{\text{eff}} \) is the effective refractive index of the waveguide structure, \( \Lambda \) the optical grating period and \( m \) the order of reflection. \( \lambda \) is the characteristic wavelength at which the coupling process between the two counterpropagating waves is strongest when the spatial modulation is such that the partial reflections of the incident waves from each successive modulation all interfere constructively. Figure 24 serves to visually illustrate the various processes occurring with a 1D DFB laser. Note that in first order DFB lasers based on optical 1D gratings, the emission occurs from the edges. Surface emission, perpendicular to the substrate plane, can be collected from second order interference.

Figure 24: Light propagation and reflection in a) First-Order and b) Second-Order 1D DFB lasers.
1.7 Emitter Materials Suitable for Lasing

Friend et al. have reported that the most suitable materials for lasing are those which emit in the blue part of the spectrum. Under these conditions, losses from excited-state absorption and Förster annihilation are lowest. While lasers with emissions in the red wavelength region rather than blue initially seem like they should be more efficient because they avoid reabsorption of light by the ground state, laser thresholds are not as low as expected. This is due to the longer wavelength absorptions by charge carriers and excitons, which introduce significant losses. Consequently, the rate of exciton quenching through the Förster mechanism is increased at larger laser wavelengths.

Given one of the goals of this thesis has been to develop blue emitting polymers suitable as laser materials, it seems appropriate to select several key blue emitters which dominate much of the OSSL literature today to illustrate several of the characteristics which require consideration when creating new CP gain material.

1.7.1 BN-PFO

Among the promising blue-emitting organic laser materials is a statistical copolymer consisting of a major 2,7-(9,9-dioctylfluorene) volume fraction and a minor fraction of 6,6´-(2,2´-octyloxy-1,1´-binaphthyl) spacer groups. The copolymer is known in the literature as BN-PFO. By incorporating BN spacer groups into the polyfluorene backbone, formation of microcrystalline domains is largely prevented. These domains are formed readily in spin cast films of PFO homopolymer, the microcrystallites are referred to as β-phase PFO. For an optimally formulated BN-PFO copolymer (~10-14% BN monomer), the β-phase is nonexistent and lasers constructed from this material have significantly improved thresholds. Figure 25
illustrates the reduced crystallinity of BN-PFO films deposited from spin casting toluene solutions by showing the noticeable differences in normalized absorption and photoluminescence of the copolymer with respect to analogously prepared PFO films. BN-PFO has an absorption peak at 382 nm and its PL spectrum features two vibronic peaks at 428 nm and 449 nm. Also note that the absorption and PL spectra overlap only slightly, minimizing light losses due to re-absorption of emitted photons. Gain measurements at the peak ASE wavelength indicate that BN-PFO is a promising gain material for short-wavelength organic lasers. A net gain of 60 cm$^{-1}$ was measured at an excitation energy of 253 nJ/pulse, while waveguide losses as low as $\alpha = 3$ cm$^{-1}$ were found in BN-PFO slab waveguides with a thickness of 210 nm.

1.7.2 F8DP

F8DP is another promising blue emitting copolymer consisting of 2,7-(9,9-dioctylfluorene) with 9,9-di(4-methoxy)phenylfluorene conjugated repeat units which is reported to have favourable gain properties and low laser thresholds.$^{[110]}$ As with BN-PFO, slab waveguides and DFB lasers can be prepared from spin casting solutions of the copolymer onto quartz substrates or optical gratings respectively. As with many polyfluorene derivatives, toluene serves as the optimal solvent which yields the best quality films. Polymer concentrations usually range from 10-20 mg/mL and spin rates of ~1000 rpm are appropriate for obtaining film thickness high enough for laser applications, Figure 25 shows the normalized absorption, PL and ASE spectra of F8DP slab waveguides on polished quartz substrates. The absorption band of F8DP has a single peak at 390 nm with an extinction coefficient of $3 \times 10^5$ cm$^{-1}$. The photoluminescence spectrum shows a structured emission that exhibits vibronic peaks at 425 nm, 450 nm, and 480 nm. In addition to the 0-0 transition dominating the spectrum, there is a slight blue shifting of F8DP’s vibronic peaks (by ~15 nm) relative to those of PFO. These spectral
differences can again be rationalized by morphological differences between F8DP and PFO, irregardless of F8DP film thickness or the solvent used for processing.

The singlet excited state lifetime of F8DP is $\tau = 352$ ps and its stimulated emission cross section is $\sigma_{SE} = 6.6 \times 10^{-16}$ cm$^2$. Combined with the material’s relatively high refractive index ($\eta = 1.94$), F8DP has proved to be a useful waveguide material which is capable of high optical confinement and large optical gain. Furthermore, F8DP is reported to have excellent charge carrier mobilities on the order of $10^{-3}$-$10^{-2}$ cm$^2$/Vs. Reports of materials such as these bolster confidence that electrically pumped OSSL may one day be a reality.

![Figure 25: Structure and absorption/PL spectra of blue emitting gain materials a) BN-PFO and b) F8DP.](image)

1.8 Absolute Quantum Yield

The determination of photoluminescence quantum yield (QY), that is, the number of photons emitted per absorbed photon for a luminescent material, is a topic of significant interest to researchers working on luminescent materials such as conjugated polymers, semiconductor
The ability to probe the efficiency of luminescence from a particular material is an invaluable tool when choosing luminescent materials for use in technologies such as biological imaging, dye lasers, and displays. Of particular interest, especially for thin film and powder samples which often display significant emission anisotropy is the determination of absolute quantum yield (AQY) using an integrating sphere as this allows the determination of the emission quantum yield of any sample using a single, simple set of measurements. There are two protocols which are commonly employed to make AQY measurements in this fashion – one requiring two separate measurements\textsuperscript{116}, and the other requiring three\textsuperscript{117}

In all cases when making quantum yield measurements we are interested in measuring the number of photons (or rather, as we work with ratios, in measuring some quantity directly proportional to said number, knowing that the constants of proportionality will cancel) contained within a specific peak. As a typical spectrometer measures a quantity proportional to the incident power, it is necessary to multiply the measured intensity at a given wavelength by that wavelength in order to arrive at a value proportional to the number of photons (for example, a properly calibrated spectrometer should measure the same signal if exposed to 1 mW/s of light at either 300 nm or 600 nm, but it will take twice as many 600 nm photons as 300 nm photons to deliver that power).

In the two measurement method (2MM), one records a spectrum with the excitation beam incident inside the empty sphere which acts as a ‘baseline’ and another with the sample within the sphere. In each case the spectrum is multiplied at each value by the wavelength as described above and then the peaks are integrated to yield values proportional to the number of photons in the excitation peak, $L$, and photoluminescence peak, $P$. If we use the subscript $a$ for the empty
sphere measurement, and the subscript \( b \) for the measurement with the sample then the expected areas of each peak in terms of the initial excitation \( L_a \) are approximately:

\[
L_a = L_a \\
L_b = f(1 - A)L_a + (1 - f)(1 - \mu)L_a \\
P_a = 0 \\
P_b = \eta fAL_a + \eta(1 - f)\mu L_a
\]

Where:

\( f \) is the fraction of photons in the incident beam which directly hit the sample.

\( A \) is the fraction of these photons which are absorbed by the sample.

\( \mu \) is the fraction of photons which do not directly hit the sample but which are eventually absorbed by it after one or more scattering events.

\( \eta \) is the photoluminescence quantum yield. We can then examine the meaning of the terms in the expressions for \( L_b \) and \( P_b \):

In \( L_b \), the first term, \( f(1-A)L_a \), represents photons which hit the sample on their initial pass into the sphere, but which are not absorbed by it (they may be scattered, reflected, or transmitted). The second term, \( (1-f)(1-\mu)L_a \), represents photons which do not initially hit the sample, and are not absorbed by it at a later time (note the assumption throughout that the only change to the potential photon loss mechanisms is the introduction of the sample, it is assumed
that a photon which is not absorbed by the sample has the same probability of ultimately being detected in both measurements).

In $P_b$, the first term represents photons which are emitted after an excitation photon has hit the sample and been absorbed by it on its initial entry into the sphere, before any scattering events. The second term accounts for photons emitted due to absorption of a photon that initially did not hit the sample but was absorbed at a later time. Note the implicit assumption that $\eta$ is identical in both of these processes, which essentially amounts to assuming that $\eta$ is independent of the irradiance, which is a strong assumption for single-photon processes but less accurate for multi-photon processes such as second harmonic generation and excited state absorption whose efficiencies are likely to be highly dependent on the intensity of light incident on the sample.

The simplicity of this method comes at the cost of neglecting a contribution to the quantum yield: photons which initially hit the sample, are not absorbed at that time (they are reflected, scattered, or transmitted) but are absorbed at a later time; and also of simplifying the expression for $L_b$ by omitting a factor $(1-\mu)$ in the term $f(1-A)La$ which should read $f(1-A)(1-\mu)La$ to account for the possibility of photons which are initially reflected/scattered/transmitted by the same being absorbed at a later time. These two simplifications essentially amount to assuming that the photons which are directly incident on the sample have their ultimate fate – detection, absorption, or loss by other means – determined by their first interaction with the sample.

Combining all of these areas, multiplying out, and cancelling, we find that the absolute quantum yield is given by:

$$\eta = \frac{P_b}{(La - L_b)} \quad (1.12)$$
Note in this case, the result is independent of the value of $f$. This may provide an experimental simplification, particularly if a spatially broad excitation source (such as an LED) or very small sample is used.

In contrast, the three measurement method (3MM) takes account of all possible contributions to the emission and excitation peaks, but we find that in this method it is – in principle at least, although we shall show later that in practice the requirement is not as strict as it might seem – necessary that we are able to conduct a measurement with $f=1$, that is, with all photons being directly incident upon the sample before scattering. In reality, this is likely not possible as many samples are likely to be contained, for example in a cuvette, which will naturally reflect some fraction of the incident light, and cause $f$ to be reduced. We present the derivation with a general $f$ parameter and then show that it reduces to an easily manageable form in the case $f=1$.

In the 3MM, the measurements ($a$, $b$, and $c$, respectively) made are:

- The excitation source incident inside the empty sphere
- The sample inside the sphere, but not directly in the path of the excitation beam.
- The sample inside the sphere and directly in the beam path.

(Note that measurement $a$ along with either $b$ or $c$ would be sufficient for the 2MM)

In each case the expected areas under the peaks are (where the meanings of the symbols are the same as defined in the 2MM section):

\[ L_a = L_a \]  
(1.13)

\[ L_b = (1 - \mu)L_a \]  
(1.14)

\[ L_c = [f(1-A)(1-\mu) + (1-f)(1-\mu)]L_a = [f(1-A) + (1-f)]L_b \]  
(1.15)
\[ P_a = 0 \quad (1.16) \]

\[ P_b = \eta \mu L_a \quad (1.17) \]

\[ P_c = [fA + (1 - f)\mu + f(1 - A)\mu] \eta L_a = fA\eta L_a + [(1 - f) + f(1 - A)]P_b \quad (1.18) \]

Note that we assume that the second experiment can be controlled such that \( f = 0 \), if this is not the case then we must use terms \( f_b \) and \( f_c \) to denote the different fractions of photons which are directly incident on the sample. It should, however, be straightforward to ensure that essentially no light is directly incident on the sample in the second experiment so this case is not discussed here but is, in theory at least, a simple extension; the difficulty arises when trying to ensure that every photon is directly incident on the sample in the third experiment.

Again, we can consider the meaning of all terms in these equations. The single term in \( L_b \), \((1 - \mu)L_a \) accounts for photons which are not initially incident on the sample (recall that none are in this experiment) and are not subsequently absorbed by the sample. In \( L_c \), the term \( f(1 - A)(1 - \mu)L_a \) represents photons which are initially incident on the sample, and are not absorbed by it upon incidence or at a later time (the possibility of absorption at a later time was neglected in the 2MM as explained above), and the term \((1 - f)(1 - \mu)L_a \) accounts for photons which are not initially incident on the sample and are not absorbed at a later time. In \( P_b \), \( \eta \mu L_a \) represents emission due to absorption of photons which are initially scattered by the walls of the sphere and are later absorbed. In \( P_c \), the term \( fA\eta L_a \) accounts for emission due to photons which are initially incident on the sample and absorbed by it at that time; \((1 - f)\mu \eta L_a \) is emission due to photons which are not initially incident on the sample, but which are absorbed by it at a later time; and \( f(1 - A)\mu \eta L_a \) accounts for emission due to photons which are initially incident on the sample, not absorbed but it at that time, but are absorbed at a later time (this contribution is neglected in the 2MM).

Combining all of these terms we find that the AQY is given by:
\[ \eta = \frac{P_c - [f(1 - A) + (1 - f)]P_b}{fAL_a} \]

Where the absorption co-efficient, \( A \) is given by:

\[ A = 1 - \frac{L_c - (1 - f)L_b}{fL_b} \]

In the special case, \( f=1 \), as was used in the original derivation by de Mello & Friend\(^7\), these equations reduce to:

\[ \eta = \frac{P_c - (1 - A)P_b}{AL_a} \]

And:

\[ A = 1 - \frac{L_c}{L_b} \]

Although this method is in principle more accurate, it suffers from the problem that it is necessary to know the value of \( f \), which, especially given the non-uniform distribution of light beams, is likely to be extremely difficult to measure or calculate with high accuracy in a typical lab. Using a laser or other focused light source to bring the excitation beam to a single spot on the sample and also avoids any direct excitation in the second experiment is likely to provide a reasonable approximation to the ideal \( f=1 \) case, although to achieve highly accuracy, losses due to, for instance, reflection from a cuvette, should be accounted for.
Figure 26: Diagramatic representations of the a) 3MM and b) 2MM AQY procedures.
1.9 Characterization of OLEDs

In order for an organic light-emitting device to be accepted in the market place as viable substitutes to conventional fluorescent and incandescent lighting or backlit LCD displays, OLEDs must provide a minimum light output at optimal efficiency. There are several (if not excessive amounts) of metrics used for the characterization of OLEDs. Measured parameters can be subdivided into radiometric and photometric values. As discussed below, radiometric measurements are an unbiased physical account of the number of photons emitting from or incident upon a surface, but photometric values are weighted to the sensitivity of the human eye and hence are more relevant for quantifying the perceived “brightness” of a light source. In general, OLEDs are sufficiently described if details of its emission colour, light output power and its electron-to-photon conversion efficiency are provided. To the confusion of many readers, many terms sound similar and are used interchangeably, including terms such as intensity and brightness, irradiance and illuminance, radianc e, luminous flux and radiant power. The following sections serve to clarify some the rhetoric encountered in the literature and provide a basic understanding of how light sources are measured and compared.

1.9.1 Lambertian Light Sources

A Lambertian surface is one which provides a uniform radiance (or luminance) in any direction (i.e. solid angle) a detector can be positioned to measure. Many diffuse (unfocused) light sources we encounter, including incandescent light bulbs and fluorescent lights have approximately Lambertian radianc e profiles. For example, at the same viewing distance, a table lamp appears equally bright regardless of the viewing angle. Many reports on the light emitting properties of OLEDs assume a Lambertian profile, however, this assumption is often inappropriate given these devices construction.[118]
Multilayered OLEDs comprising several organic and inorganic layers with varying refractive indices constructed on conductive glass substrates forms a rather complex optical microcavity which alter the emission properties with viewing angle. To accurately measure the total photon output of an OLED requires one to compensate for the non-uniform emission profile when measuring irradiance at a detector for a given solid angle or significant overestimates of efficiency can occur.

1.9.2 Measurement Geometry and Solid Angle

It is intuitive to imagine that a point source projects light with equal intensity into a spherical volume of space surrounding it. An important parameter known as solid angle, $\Omega$, is used as a geometric reference to normalize radiance measurements taken at arbitrary distances from the source.$^{[119]}$ A solid angle can be pictured, as illustrated in Figure 27, as a conical section of a sphere of arbitrary radius $r$. The equation relating solid angle, $\Omega$, to the radius of the sphere, $r$, and the area of the subtending spherical cap, $A$, is as follows:

$$\Omega = \frac{A}{r^2} \quad (1.0)$$

Solid angle can also be expressed according to eqn (1.1) where $\alpha$ is defined the apex angle of the cone drawn in Figure 27.

$$\Omega = 2\pi[1-\cos(\alpha/2)] \quad (1.1)$$

Most radiometric measurements do not require an accurate calculation of the spherical surface area to convert between units. Flat area estimates can be substituted for spherical area when the solid angle is less than 0.03 steradians, resulting in an error of less than one percent. This approximation is beneficial when the subtenting area is a photodetector of a known area.
Figure 27: a) Lambertian emission profile and b) definition of solid angle

1.9.3 Definitions of Common Optics Terminology

Radiant Power vs. Luminous Flux: Radiant power (sometimes called radiant flux) is a measure of radiometric power emanating from a light source. Radiant power is simply expressed in watts and is a measure of the rate of total energy flow for all photons, in joules per second.[120] Since photon energy is inversely proportional to wavelength, monochromatic lights sources emitting ultraviolet photons are more powerful than visible or infrared. Luminous flux is a measure of the power of visible light as perceived by the human eye and has units of lumens (lm).[130] Luminous flux is reported for a “standard” light-adapted eye, referred to as photopic flux, or for a “standard” dark-adapted state called scotopic flux. The normalization curves used in the conversion of radiant power to luminous flux are shown in Figure 28, note the eye’s sensitivity is highest for yellow-green wavelengths.
Irradiance vs. Illuminance: Irradiance is a measure of radiometric flux per unit area, or flux density incident on a surface on known area. Irradiance is typically expressed in W/cm² or W/m². Illuminance is a measure of photometric flux per unit area, or visible flux density. Illuminance is typically expressed in lux (or lm/m²).

Another unit often encountered in the literature pertaining to light measurements is the candela (cd). The candela is the SI base unit of luminous intensity, or the power emitted from a light source in a particular direction. It is photometric value which is normalized to the eye’s sensitivity. A light source measured as 1 cd isotropically emits 1 lm per steradian (so cd = lm/sr). As mentioned earlier, steradians are the unit of solid angle. Figure 29 serves to illustrate the relation between candela, lumens and steradians.
Figure 29: Relation of irradiance to measurement geometry from a 1 cd point source.

A solid angle equal to one steradian is measured for a conical section of light emanating from a point source and projecting onto an area of $r^2$ a distance $r$ away. Hence a light source with a luminous intensity of 1 cd will radiate light with an intensity of 1 lm/sr and the same light incident on 1 m$^2$ surface on meter away will have an illuminance of 1 lm/m$^2$ or 1 lux.

The Inverse Square Law: The inverse square law is a practically useful relationship which states that the irradiance from a point source on a surface a distance, $d$, away decreases with the inverse of the square of that distance.\[^{119}\] Hence, if a photodiode measures an irradiance of 36 W/m$^2$ at a distance of 1 meter from the source, the same diode will measure a value of 4 W/m$^2$ a distance of 3 meters away. Expressed as an equation:

$$E_1d_1^2 = E_2d_2^2$$ (1.2)

Where $E_1$ = Irradiance at Point 1 ($d_1$)

$E_2$ = Irradiance at Point 2 ($d_2$)

1.9.4 Conversion Between Units

In the absence of an integrating sphere, for example, it is sometimes necessary to interconvert between photometric or radiometric values in cases such as determining the radiant
power of a light source using irradiance measurements collected from a photodiode some distance \( d \) away. Simple conversion, however, comes at the risk of introducing error through assumptions such as a having an isotropic (Lambertian) source, which, as we know, is not strictly true of devices such as LEDs which can only emit into one hemisphere due to the mirroring effects of metal contacts.

Consider the example of a light source with an initial irradiance measurement of 60 mW/cm\(^2\) is measured at a photodiode (1 cm\(^2\) active area) 5 cm from the source. It is possible to determine the radiant power of the source by first calculating the radiant intensity (mW/sr) by using the inverse square law to determine the irradiance 1 cm away from the source:

\[
E_2 = \left(\frac{d_1}{d_2}\right)^2 E_1 \tag{1.3}
\]

\[
E_2 = 1500 \text{ mW/cm}^2 \tag{1.4}
\]

Since this value of irradiance is for an area of 1 cm\(^2\) measured a distance of 1 cm from the source:

\[
E_2 = 1500 \text{ W/cm}^2 = 1500 \text{ mW/sr} \tag{1.5}
\]

To find the radiant power emitted in all directions, the solid angle must be calculated. Since we assumed the source was a point source with emission occurring equally in all directions, the solid angle is that of a sphere or:

\[
A_{\text{sphere}} = 2\pi r^2 \tag{1.6}
\]

\[
\Omega = \frac{A}{r^2} = 2\pi r^2/r^2 = 2\pi \text{ (For Sphere)} \tag{1.7}
\]

Radiant Power = \( E_2(\Omega) = 9.4 \text{ W} \) \tag{1.8}
Note that if the source was an OLED, emission would only occur into one hemisphere and a value of $\alpha = 180$ would be substituted into eqn (1.1) and the radiant power would be halved.

1.9.5 Device Efficiency

The efficiency of OLEDs is characterized by quantum efficiency, power efficiency and luminous efficiency. Furthermore, the quantum efficiency of a device can also be differentiated into internal and external quantum efficiencies. The following section serves to introduce these metrics and establish their relationship with the processes occurring within a functioning OLED.

1.9.5.1 Internal Quantum Efficiency (IQE)

IQE is defined as the total number of photons generated inside a device per electron/hole pair injected, and is often denoted by $\eta_{\text{int}}$.\textsuperscript{[130]} Mathematically, the internal quantum of both electroluminescent and electrophosphorescent devices is described by:

$$\eta_{\text{int}} = \gamma \eta_s \Phi_f$$  \hspace{1cm} (1.9)

where:

$\gamma$ = is the charge balance factor (i.e. the fraction of injected charges that produce excitons)

$\eta_s$ = the singlet exciton efficiency (i.e. fraction of singlet excitons generated from injected charge carriers)

$\Phi_f$ = the PL quantum efficiency of the material

It is generally believed that for most organic materials during the operation of an electroluminescent device, spin statistics dictates at roughly 25% of electrons are injected into singlets states while 75% are injected into triplet states. Because triplet to single transitions are spin forbidden, fluorescence from relaxation of triplet states is normally very inefficient and
contributes negligibly to the EL of a device. Theoretically, this places an upper limit on the internal efficiency of OLEDs of roughly 25%.

The introduction of phosphorescent emitters has been mentioned previously and is known to increase device performance by harvesting triplet carriers and providing a high efficiency phosphorescent decay pathway.\[^{131}\] In such cases, both singlet and triplet states of the fluorescent host are transferred to the triplet state of a phosphorescent guest molecule. Harvesting of both singlet and triplet states allows IQE in triplet-emitting devices to approach 100% efficiency.

Several factors, however, prohibit ideal performance. Notably, it is well documented that deleterious effects of exciton–exciton quenching and polaron–exciton quenching decrease IQE. Additionally, excitons which initially form may also dissociate in many materials.\[^{132}\]

### 1.9.5.2 External Quantum Efficiency (EQE)

In many respects, EQE is a more practically (and easy to measure) gauge of device efficient and is defined as the total number of photons emitted from a device in the forward view direction per electron–hole pair, and is often denoted $\eta_{\text{ext}}$.\[^{133}\] External quantum efficiency is related to IQE by the simple equation:

$$\eta_{\text{ext}} = R_e \eta_{\text{int}}$$  \hspace{1cm} (2.0)

Where

$R_e = \text{the photon outcoupling efficiency (i.e. the ratio of photons generated within the active layer to the number of photons actually emitted from the device in the forward viewing direction).}$  

A more practical expression of $\eta_{\text{ext}}$ is simply the ratio of #Photons/#Electrons, which—when one considers the simplest means of acquiring data to complete the calculation—is best written according to eqn (2.1):
\[
\eta_{\text{ext}} = \frac{q \int \lambda P_{\text{OLED}} d\lambda}{hcI_{\text{OLED}}} 
\]

Where

\( P_{\text{OLED}} \) = the spectral power distribution of the OLED electroluminescence in W

\( I_{\text{OLED}} \) = the device operating current in amperes

\( c \) = speed of light

\( h \) = planck’s constant

\( q \) = the elementary charge

\( f \) = the fraction of light emitted from the device coupled to the detector. Using large aperture light collecting optics or an integrating sphere results in \( f \approx 1 \)

Several sources of error are possible when measuring OLED efficiency. Error can originate from an improperly calibrated detector as well as inefficient light collecting optics. Prior to measuring the power output of OLEDs, the power meter, whether a photodiode or CCD camera, must be properly calibrated against a standard light source so as to account for the responsivity of the detector as a function of wavelength.

The simplest method of maximizing light coupling from the device into a detector is using a detector large enough to completely cover the emissive area (i.e. under-filling a detector). This can be done in two ways. The most costly but effective method requires that a device operated within an integrating sphere be coupled to a CCD fiber spectrometer. To measure the external quantum efficiency of the device, efforts must be taken to mask edge-emitting light as well as any other light not emanating from the active, forward facing area of the OLED. The integrating sphere can account for all photons emitted from the device surface regardless of deviations from Lambertian emission.

Using a sphere to capture all light (including edge-emission) is the most accurate means of estimating the internal quantum efficiency of an OLED because it accounts for all light
leaving the device (either surface emission or waveguided light leaving the device in arbitrary directions). None-the-less, an accurate determination of $n_{\text{int}}$ still requires corrections accounting for internal processes such as light absorption by electrodes, surface plasmons, free carrier and exciton absorptions. Because every material has different optoelectronic properties, is difficult to make confident estimates of correction factors and reports of $n_{\text{int}}$ are all prone to uncertainty.

Without the use of an integrating sphere, a large area detector (such as a Si photodiode) may be used so long as the detector area is significantly larger than the emitting device area. To capture the most forward emitting light, the detector is placed in direct contact with the device and the power output can be used to calculate EQE only. Figure 30 illustrates the measurement geometry of both methods.

![Figure 30: Measurement geometry for EQE determination using a) an under-filled photodiode or b) an integrating sphere.](image)

### 1.9.5.3 Power Efficiency

The luminous efficiency or power efficiency is the lumen output per input electrical power of the device. It is measured candela per ampere (cd/A) and is often denoted $\eta_\text{L}$. In many ways, luminous efficiency is equivalent to $\eta_\text{ext}$ with exception that $\eta_\text{L}$ weights all photons incident at the detector according to the photopic response of the eye whereas $\eta_\text{ext}$ counts all
photons equally. Hence OLEDs which emit the majority of photons in a region insensitive to the eye (e.g. red and blue regions of the spectrum) would have a lower $\eta_L$ than $\eta_{ext}$ because a large portion of photons are not counted in the calculation of the former.[134]

Luminous efficiency is usually trivial to measure if one uses a commercial luminance meter to measure the luminous intensity of a fixed diameter spot on the OLED at a known solid angle in cd normalized to the device area (usually cd/m$^2$). $\eta_L$ is related to device luminance ($L$, cd/m$^2$), device area ($A$, m$^2$) and OLED current (in amperes) in the following equation:

$$\eta_L = \frac{AL}{IOLED}$$  \hspace{1cm} (2.1)

A note of caution should be made, however, with regards to error introduced by using luminance meters. While they offer a convenient route to measuring and calculating luminance, devices use a calibrated Si photodiode and explicitly assume that the emission profile of an OLED is Lambertian and the detector is located orthogonal to the surface of the light source. As previously stated, however, assuming Lambertian emission is occurring from OLEDs is unfounded given the waveguiding modes introduced by the microcavity.

Luminous efficiency is closely related to another efficiency metric known as luminosity or (perhaps somewhat confusingly) luminous power efficiency, $\eta_P$. $\eta_P$ has units of lm/W and is a measure of the amount of luminous flux (lm) emitted in the forward viewing direction with respect to the electrical power required to drive the OLED. Mathematically:

$$\eta_P = \frac{LF}{IOLEDV}$$  \hspace{1cm} (2.2)

$\eta_P$ can also be calculated from integrating the product of the spectral power distribution of an OLED by photopic response curve and dividing by the operating current according to the eqn (2.3):
\[ \eta_P = \frac{\Phi_0 \int g(\lambda)P_{OLED}(\lambda) d\lambda}{f I_{OLED} V} \] 

(2.3)

where

\( \Phi_0 \) = radiometric to photometric conversion factor of 683 lm/W

\( g(\lambda) \) = photopic response curve of the human eye

\( P_{OLED} \) = spectral power distribution of the OLED

\( I_{OLED} \) = device current

\( V \) = Operating voltage of the device

\( f \) = light coupling/collection factor \( \sim 1 \) if underfilling a detector or using an integrating sphere

Power efficiency is a popular metric for the solid state lighting industry and a benchmark value of 120 lm/W is often cited as the barrier to entry before OLED (particularly an white emitting OLED or WOLED) can begin to compete with the fluorescent lighting market (of course this is also contingent on stability and colour temperature (CCT) and colour rendering index (CRI) which will be discussed below).

1.9.6 Standardized OLED Emission Colour

Of course, one of the most important qualities of an OLED, regardless of application, is the colour of its emission. For the purposes of creating displays, maximizing qualities such as colour gamut are often discussed as motivation of developing new emitters. Colour gamut is the range of colours which a display pixel can reproduce and it is dependent on the combined emission of at least three RGB subpixels whose spectrum constitutes the primary colours of a display’s gamut. Gamuts are usually represented as a colour map using the CIE 1931 chromaticity format (discussed below).\[135\]

For WOLEDs and solid state lighting, light sources are usually characterized not only with respects to its emission coordinates on a CIE colour map, but also its correlated colour
temperature (CCT) and colour rendering index (CRI). The latter two metrics help quantify how well a white light source renders colours of objects it illuminates. Ideally, white light source’s emission should evenly span the visible spectrum to function as acceptable light sources in homes and offices.\cite{135}

**Figure 31:** CIE-1931 Chromaticity Diagram. (Note central arc indicates Planckian locus)

### 1.9.6.1 Commission International d’Eclairage (C-I-E) Chromaticity Diagram

The color of a light source is typically characterized in terms of CIE colorimetry system. Any colour can be expressed by the chromaticity coordinates $x$ and $y$ on the CIE chromaticity diagram shown in Figure 31, the boundaries of which plots monochromatic light or spectrum loci.\cite{135} All colours in the visible spectrum fall on or within the borders of the diagram.
The Planckian locus (a.k.a black body locus) is highly relevant to the light community and is often depicted on CIE colour diagrams because it is the path that an incandescent black body takes at various temperatures in a particular colour space. The Planckian locus is the basis of CCT and is essentially a reference by which the whiteness of a light source is judged. The CCT value of a light source is therefore the colour temperature of an Planckian radiator which best approximates it. The colours of most traditional light sources fall in the region between 2850 and 6500 K. For general illumination a light source should have CIE-1931 chromaticity coordinates (x,y) close to equal energy white (EEW) at (0.33, 0.33). For high gamut displays in RGB colour space, subpixels should have CIE coordinates as close to the borders as possible in the vicinity of monochromatic red, blue and green light.

The calculation of CIE chromaticity coordinates for a given device emission is relatively straight forward and involves the multiplication of the spectral power distribution of the device EL by the three CIE colour-matching functions (Figure 32).\cite{136} Integrating the resulting curve across all wavelengths gives the tristimulus values X, Y and Z according to:

\[
X = \int P_{EL} \bar{x} \, d\lambda \\
Y = \int P_{EL} \bar{y} \, d\lambda \\
Z = \int P_{EL} \bar{z} \, d\lambda
\]

Where

\(P_{EL}\) = the spectral power distribution of the device EL
\(\bar{x}, \bar{y}, \bar{z}\) = the CIE colour-matching functions

From the values X, Y and Z, the chromaticity coordinates x and y can be calculated using:

\[
x = \frac{x}{X+Y+Z} \tag{2.4}
\]
\[ y = \frac{Y}{X+Y+Z} \]  \hspace{1cm} (2.5)

**Figure 32:** Colour-matching functions used for the calculation of the tristimulus values.

### 1.9.6.2 Colour Rendering Index (CRI)

For a given light source, the CRI attempts to quantify how different a set of test colors appears when illuminated by the source compared to when the same test colors are illuminated by the standard illuminant with the same correlated color temperature.\[135\] It is measured in 0-100 scales and the highest possible CRI value is 100, and this occurs when there is no difference in color rendering between the light source and the standard illuminant, such as an incandescent lamp. Achieving illumination-quality white light generally requires a CRI value of 80 or greater.

It is believed that by 2015 WOLED efficiency will exceed 100 lm/W and have sufficient lifetimes and brightness to begin replacing indoor and outdoor light. Murano et al. have demonstrated white pin-OLEDs based on phosphorescent and fluorescent emitters with very high
power efficiency (>20 lm/W at 1000 cd/m²). They reported the CRI properties of their device to be as high as 85 and 95. Universal Display Corporation (UDC) has announced a prototype white OLED lighting panel with a high power efficiency >30 lm/W which is based on UDC’s proprietary phosphorescent OLED technology. The UDC light panel achieved a colour temperature of 4000 K and CRI of ~80, which is comparable to the colour temperature and power efficiency of a cool fluorescent lamp.

### 1.10 Introduction to Polysilafluorenes (PSFs)

Polysilafluorenes (PSFs) are an emerging class of polymer which is structurally analogous to polyfluorenes (PFs) and have comparably high luminescence quantum yields and solubility. As noted for the PSF repeat unit in Figure 33, the apical C9 atom in flourene is substituted for Si. There are several advantages to this substitution which has gained PSFs popularity as a stable blue emitting polymer superior to polyfluorenes. Despite being the dominant commercially supplied blue emitting polymer, PFs have gained notoriety for low OLED performance lifetime and unstable emission characteristics. This usually manifests itself as a broad and featureless higher wavelength green emission band in the luminescence spectrum which surpasses the desired 430 nm centered blue emission band. Over the past decade, there have been numerous investigations into the origin PF degradation and declining PL and EL efficiency and it is generally agreed to be the results of exciplex formation as well as the development of keto defects due to oxidation of the polymer chain. Consequently, several countermeasures have been proposed and synthesized.

To address the issue of exciplexs, which are a problem more inherent to the spacing of polymer chains, monomers with bulky sidechains installed on the C9 atom have been prepared and are designed to increase interchain separation. Exciplexs (a.k.a excimers), recall, are
shorted lived “excited complexes” which form by dimerization of two electronically excited species in close proximity. Because keto defects result from oxidation (normally due to ambient oxygen), their avoidance places strict conditions on material processing during fabrication of devices (i.e. low temperature processing under inert atmosphere, usually in a dedicated glovebox.).

Structural modifications which serve to limit oxiditative susceptibility inspired the creation of PSF and other heterofluorene based polymers. Because oxidation usually occurs on the C9 atom, it is rational to expect reduced risk of keto defects with the installation of heteroatoms with reduced vulnerability to oxidation. Several elements have proven viable substitutes.\[142\] Silicon, however, has dominated due to more accessible synthesis methods, large existing commercial supply of silane starting materials, superior polymer properties (i.e. high solubility and PL). Other group 4 elements, namely Ge, have also been explored, albeit to lesser extent than Si. Similarly, there are several notable group 3 phosphorus and nitrogen substituted fluorenes which have been successfully polymerized, but these classes of material have been limited primarily by reduced solubility and lower AQY.

In addition to the brilliant solid state blue luminescence of many polysilafluorenes, these polymers are also reported to have superior electron conductivity to PFs. The higher electron affinity and conductivity, which is particularly promising for OLEDs, originates from $\sigma^*-\pi^*$ conjugation between the $\sigma^*$ antibonding orbital of the exocyclic Si-C bond and the $\pi^*$ antibonding orbital of the butadiene fragment.\[143\] The remainder of this introductory section will concentrate on the many optoelectronic properties of PSFs and provide a brief overview of how these materials are beginning to proliferate into the field of organic electronics.
Figure 33: a) Structure of polysilafluorene and other heteroatomic analogues. b) $\sigma^* - \pi^*$ conjugation between the $\sigma^*$ antibonding orbital of the exocyclic Si-C bond and the $\pi^*$ antibonding orbital of the butadiene fragment.

1.10.1 Optoelectronic Properties of PSFs

Seminal work by Holmes et al. provided some of the earliest analysis of PSF photophysical properties.$^{[144]}$ Additionally, they were the first to report a complete synthetic route for producing pure 9,9-dihexyl-2,7-silafluorene monomers and its polymerization via Pd catalyzed Suzuki coupling (refer to section 1.9.6 for review of PSF synthesis methods)$^{[144]}$. In comparison to poly(9,9-diocetylfluorene) (PFO), poly(9,9-dihexylsilafluorene) (PSFH) show many similarities with respect to bandgap energy ($E_g$) and characteristics of its PL emission band. Similar to the well documented fine structure observed in the PL spectra of PFO thin films (with a principle 428 nm emission band originating from the PFO glassy phase and two vibronic sidebands centered at 445 nm and 475 nm), a solid state PSFH luminescence spectrum consists of a primary peak at 425 nm and two vibronic sidebands at 449 nm and 482 nm. The AQY of PSFH films is reported to be 62%, slightly higher than 60% reported for PFO. Figure 34 presents the absorption and emission spectra for PSFH. The absorption maximum $\lambda_{abs} = 390$ nm is nearly identical to that of PFO. If one takes the energy of a photon with frequency equal to the
absorption onset as the energy gap between the ground vibronic state and the first excited state, we can estimate the bandgap of PSFH (as well as PFO) to be approximately 2.93 eV.

Significant differences become apparent, however, between PSFH and PFO when thermal stability is tested. PSFH prepared by Holmes et al., with Mn = 109 kg/mol (PDI = 3.9), demonstrated impressive thermal stability with decomposition occurring at temperatures as high as 442°C. PSFH is also reported to have a relatively high glass transition temperature T_g = 149°C Holmes demonstrated the PL spectral stability of PSFH versus PFO by subjecting samples of the respective polymers to a high temperature annealing in air. Figure 35 clearly demonstrates that the PL of PSFH remains relatively unchanged over a period of 16h at a temperature of 250°C. PFO, however, develops a broad green band centered at 535 nm.

![Figure 34: Absorption spectra (a) and PL spectra (b) of PSFH homopolymers and PSFH-co-PFH copolymer thin films and solutions.][144]
Figure 35: Thermal/oxidative stability of PSFH (b) versus PFH (b) at elevated temperatures under ambient atmosphere.\textsuperscript{[144]}

Figure 36: Optoelectronic effects on increasing silafluorene volume fraction in poly(9,9-dimethyl-3,6-dimethoxysilafluorene-co-9,9-diocetylfluorene) copolymers.
1.10.2 Devices and Applications of PSFs

In the fabrication of optimal organic electronic devices such as OLEDs, OPVs and OTFTs, basic material properties such as HOMO/LUMO energy levels must be known. For chemists, the most convenient route to obtain approximate energy level values is by cyclic voltammetry (CV) Holmes et al. have used CV to determine the HOMO/LUMO levels of PSFH (5.8 and 2.2 eV respectively) and found them to be shifted slightly lower than values reported for PFO.[144]

Returning to the PDMSF-co-PFO polymers produced by Huang et al., the position of the energy levels in their series of copolymers was dependent on the volume fraction of silafluorene.[145] Increasing the fraction of silafluorene units in the polymer appears to increase the HOMO level slightly whilst simultaneously lowering the LUMO. In a series of copolymers where the volume fraction of PDMSF is increased from 10% to 50%, the LUMO level drops from -2.16 eV to -2.20 eV and the HOMO level increases from -5.83 eV to -5.79 eV. This trend is paralleled by a slight decrease in the measured Eg from 3.67 eV to 3.60 eV.

Triplet energy levels of PSFs have been reported by researchers interested in using these materials as hosts for triplet emitter complexes in OLEDs. It is important for triplet levels of the host to be relatively high energy compared to the dopant to avoid quenching of the emitter excited state by the polymer. For PSFH (polymerized through the C3 and C6 positions), triplet levels where as high as 2.55 eV (about 0.45 eV higher than PFO).[146] The value was determined from a phosphorescence spectrum taken of a polymer film cooled to 77 K excited with a 320 nm source. As the next section will demonstrate, high triplet energy levels mean PSFs have be used successfully as hosts for several small molecule green and blue emitters. PSFs are therefore
attractive OLED materials because they can be used in devices emitting all three primary colours required for high gamut displays.

### 1.10.3 PSF Based Light Emitting Diodes

As mentioned in Section 2.0, OLEDs fabricated with a PFO emission layer suffer from spectral instability caused by defects leading to higher wavelength green emissions. These defects occur faster in working OLEDs as the current driven through the device generates heat. PSFs, which have higher thermal stability compared to PFO, have been used in OLEDs which operate more efficiently with superior colour purity. Cao et al. have synthesized a novel series of copolymers (PSiFF) based on 3,6-silafluorene and 2,7-fluorene via the Suzuki polycondensation. The impact of including a 3,6-silafluorene comonomer was evident due to changes in the thermal, photophysical, electroluminescence and electrochemical properties of the copolymer.\[147\] Increased 3,6-silafluorene content in a polyfluorene chain led to almost complete suppression of unwanted low energy emission bands and significantly improved the efficiency and color purity of copolymer-based devices. Furthermore, electroluminescence spectra becomes increasingly blue-shifted for higher bandgap, 3,6-silafluorene rich copolymers. The device based on PSiFF90 with the configuration of ITO/PEDOT : PSS/PVK/polymer/Ba/Al showed a quantum efficiency of 3.34% and a luminous efficiency of 2.02 cd/A at a brightness of 326 cd/m² with CIE 1931 chromaticity coordinates of (0.16, 0.07). The results indicate poly(3,6-silafluorene-co-2,7-fluorene) is a promising and efficient blue-emitting polymer with excellent color purity.

Cao et al. have also produced another series of novel blue-emitting copolymers based on 3,6-silafluorene and 2,7-silafluorene using Suzuki polycondensation.\[148\] The devices fabricated from these copolymers exhibit an external quantum efficiency of 1.95%, a luminous efficiency of
1.69 cd A\(^{-1}\) and a maximal brightness of 6000 cd/m\(^2\). Devices are configured with the layers: ITO/PEDOT:PSS/PVK/polymer/Ba/Al. By incorporating 3,6-silafluorene units into the poly(2,7-silafluorene) main chain, color purity and efficiencies of the resultant OLED devices are superior to homopolymer devices. As with the fluorene copolymers discussed earlier, it is reasonable to assume that the 3,6-silafluorene comonomer shortens chain conjugation, forming more isolated emission centers and improving EL colour purity.

Further examples of silafluorene based copolymers used in OLEDs include a series of red and green light-emitting polymers created by Suzuki polycondensation of comonomers 4,7-di(4-hexyl-2-thienyl)-2,1,3-benzothiadiazole (DHTBT) and 2,1,3-benzothiadiazole (BT), respectively, with 2,7-dihexysilafluorene.\(^{[149]}\) The optoelectronic and thermal properties of the polysilafluorene copolymers appear to outperform the corresponding polyfluorene based polymers under conditions where comonomer volume fraction is roughly the same (~10% BT or DHTBT). Devices with the configuration of ITO/PEDOT:PSS/PVK/polymer/Ba/Al showed a maximum external quantum efficiency (EQE) of 2.89% and current efficiency of 2.0 cd A\(^{-1}\) for red emitting PSiF-DHTBT10 and a maximum EQE of 3.81% and current efficiency of 10.6 cd A\(^{-1}\) for green emitting PSiF-BT10.

Triplet emitting devices have been made using polymers of 3,6-silafluorene as high energy hosts. With triplet levels ~0.4 eV higher than PFO, poly(9,9-dioctyl-3,6-dibenzosilole) have a sufficiently high triplet energy (2.55 eV) to function as a host for several common electrophosphorescent emitters. Holmes et al. reported a green triplet emitting device fabricated using a 8wt% blend of polymer with fac-tris[2-(2-pyridyl-κN)-5-methylphenyl]iridium(III) [a.k.a. Ir(m-ppy)\(_3\)].\(^{[150]}\) The dopant/host layer was spincast from a 10 mg/ml toluene solution onto a PEDOT:PSS hole injection layer. Using LiF/Al as a cathode, the device produced a stable green emission centered at 540 nm. At a driving voltage of 4 V, efficient Forster energy transfer
from the singlet $\pi^*$ state of the host to the MLCT band of the guest occurs. Electrophosphorescence is achieved by fast intersystem crossing to the corresponding emissive triplet state of Ir(m-ppy)$_3$.

A highly efficient blue polymer phosphorescent organic light-emitting diode containing bis (2,4-difluorophenyl-2-pyridine)(2-(4H-1, 2, 4-triazol-3-yl)pyridine)Iridium(III) [a.k.a. Ir(PPF)$_2$(PZ)] in a poly(9,9-dihexyl-3, 6-silafluorene) host was reported by Cao et al.[50] Despite almost complete quenching of the iridium complexe’s PL by the host polymer, organic light-emitting diodes emit high-intensity blue light centered at 462 nm. The maximal external quantum and luminance efficiencies were, respectively, 4.8% photons/electrons and 7.2 cd/A at 644 cd/m$^2$. Device data and structures of the diode systems described in this section are summarized in Figure 37.
Figure 37: PSF OLEDs: their construction and device properties. a) Copolymers based on 3,6-silafluorene and 2,7-fluorene monomers have strong blue emission at 415 nm (left). Increasing silafluorene content suppresses higher wavelength PL and improves thermal stability (center). Device turn-on voltage is ~6V and maximum EQE = 3.34%. b) Copolymers based on 3,6-silafluorene and 2,7-silafluorene have strong blue PL and EL emission centered at 420 nm. OLEDs emit strongly in the blue and the emission band is narrowest for 2,7-silafluorene rich copolymer with 10% 3,6-silafluorene content (center). A maximum EQE = 1.95% and maximum brightness of 6000 cd m$^2$ is obtained for P36-27SF90 devices (right). c) 2,7-silafluorene copolymers containing BT or DHTBT units have green and red PL respectively (right). EL emission bands are nearly identical to PL and OLEDs with select composition of comonomers can produce all three primary colours (center). EQE of 2.89% and current efficiency of 2.0 cd A$^{-1}$ are obtained for red emitting PSiF-DHTBT10 and a maximum EQE of 3.81% and current efficiency of 10.6 cd A$^{-1}$ is obtained for green emitting PSiF-BT10 (left).
Triplet emitting devices have been made using polymers of 3,6-silafluorene as high energy hosts. a) Green triplet emitting devices were fabricated using a 8wt% blend of polymer with Ir(m-ppy)$_3$. OLEDs where driven at 4 V to yield a bright green EL emission peak at 520 nm (spectrum on the right). b) Blue polymer phosphorescent organic light-emitting diodes have been fabricated from an Ir(PPF)$_2$(PZ) emitter and a poly(9,9-dihexyl-3, 6-silafluorene) host system. The OLED emits a blue light centered at 462 nm with a maximum EQE and luminance efficiency of 4.8% and 7.2 cd/A respectively.

1.10.4 PSF Based Photovoltaics

Conventional organic photovoltaics consist of organic donor and acceptor components mixed in a bulk heterojunction. The most common electron transport material is [6,6]-phenyl-C61 butyric acid methyl ester (PCBM). There have been numerous hole transport polymers reported in the literature to date and these include at least one unique silafluorene copolymer, Figure 39.

Leclerc et al. first reported bulk heterojunction solar cell devices are fabricated from a soluble conjugated copolymer based on 2,7-silafluorene and 4,7-dithien-2-yl-2,1,3-
benzothiadiazole (DBT) units (PBSDTBT).[152] Using this material as the donor and [6,6]-phenyl-C61 butyric acid methyl ester (PCBM) as the acceptor, their cells had power conversion efficiencies of 1.6% under AM1.5 illumination with a modest fill factor of 55%. Moreover, the relatively large bandgap (1.9 eV) of this polymer yields cells with desirably large $V_{oc} = 0.97$ V.

Cao et al. have also reported high-performance polymer heterojunction solar cells fabricated from the same PSF-DBT copolymer/[PCBM] donor/acceptor mixture.[153] They report a considerably higher PCE of 5.4% with an open-circuit voltage of 0.90 V under AM1.5 irradiation. The difference in PCE with respect to Leclerc’s reports may be due to the higher molecular weights copolymers used by Cao or device fabrication protocols which may differ between the two groups. A short-circuit current of 9.5 mA cm$^{-2}$ and fill factor of 50.7% was also achieved. The authors surmise that the high $V_{oc}$ from PSF-DBT based solar cells originated from the copolymers lower HOMO level and the higher $J_{sc}$ is due to its broader absorption spectrum and higher hole mobility ($10^{-3}$ cm$^2$/Vs). These preliminary studies suggest that PSF derivatives are a promising class of electron donor materials for high performance bulk heterojunction polymer solar cells.

**Figure 39**: a) Both Leclerc and Cao have reported bulk heterojunction OPVs based on mixtures of PSF-DBT with PCBM. HOMO and LUMO energy of PSF-DBT is reported to be 5.70 and 3.81 eV meaning electron donation to PCBM is possible and cells are reasonably efficient under AM 1.5 illumination. b) PSF-DBT is a promising class of electron donor materials for OPVs because of its broader absorption spectrum and higher hole mobility ($10^{-3}$ cm$^2$/Vs). c) Cao has reported
PCE has higher as 5.4% with a $V_{oc} = 0.9$ V. The I-V characteristics of cells produced by Cao et al. is shown. FF = 50% and $J_{sc}$ is relatively high at 9.5 mA/cm$^2$.

1.10.5 PSF Based Organic Transistors

Marks et al. have reported the synthesis and full characterization of dithienosilole and silafluorene based homopolymers: poly(4,4-dihexyldithienosilole) (TS6) and poly(9,9-dioctylsilafluorene) (BS8), and their mono- and bithiophene copolymers.[154] The authors studied the impact of introducing silole derivatives into the main chain of polythiophenes. They reported that their copolymers were used in the preparation of air-stable organic thin-film transistors fabricated under ambient conditions having hole mobilities as large as 0.08 cm$^2$/Vs, low turn-on voltages, and current on/off ratios $> 10^6$. Unencapsulated OTFTs fabricated under ambient conditions were proven to be air-stable for extended periods of time, unlike prior regioregular poly(3-hexylthiophene) (P3HT)-based devices. DFT calculations showed that silicon substitution

---

**Figure 40:** Transfer characteristics (center) of OTFT devices fabricated with polymers 7 (a) and 10 (b) as a function of storage time in the air (The devices are noticeably resistant to oxidative effects over time and Drain-Source currents remain relatively stable over months. The on-off
cycling (left) of devices under ambient conditions at different gate voltages show remarkable stability for both polymers (switch rate = 0.03Hz).

stabilizes both the HOMO and LUMO levels of the dithienosilole and silafluorene cores, rendering the copolymers less susceptible to O₂ doping. The high degrees of π-delocalization in the silole-based polymers, implicit from theoretical and optical characterization data, is posited to be the underlying reason for ionization potentials and electron affinities to be elevated with respect to carbon counterparts.

1.10.6 Review of PSFs Synthesis Methods

Despite being a relatively new class of polymer, there are several unique synthetic pathways to polysilafluorene derivatives within the literature. A 2005 report by Holmes et al. have provided, arguably, the most popular method of producing 9,9-dialkylsilafluorene monomers. They have also demonstrated that Suzuki polycondensation is a viable route to produce high molecular weight polymer with modest PDI. As illustrated in Figure 41, their synthesis begins with the Ullman coupling of 1,4-dibromo-2-nitrobenzene using an equivalence of copper to form 4,4′-dibromo-2,2′-dinitrophenyl. The nitro groups were converted to iodide through a diazonium intermediate formed in a Sandmeyer type reaction. While the product can be obtained in high purity following work-up, the low yield for this reaction is presumably a consequence of intramolecular cyclization of the first formed iodo substituent onto the neighboring 2-position by the decomposition of the second diazonium substituent to give a dibenzoiodonium iodide salt. At cryogenic temperatures (~-100°C), selective lithiation of both iodide groups is achieved and a ring closing reaction with dichlorodialkylsilane produces the 2,7-dibromo-9,9-dialkylsilafluorene monomer. To perform a Suzuki crosscoupling polymerization, a fraction of the dibromo monomer is converted to a diboronic ester comonomer
following a second lithiation reaction. Polymer was obtained following the addition of both comonomers in equal portions in a mixed phase reaction. A catalytic amount of Pd(acac)$_2$:P(Ph)$_3$ (1:4) was added to initiate the polycondensation, which proceeds over two days at 80°C. Molecular weight reported by Holmes where high (Mn > 100 kg/mol) with broad dispersity (PDI ~ 3.9). Suzuki coupling has also been used to make copolymers of 2,7-dibenzosilole unit with thiophene and dithienyl-benzothiadiazole with application in thin-film transistors and polymer solar cells respectively.[154]

**Figure 41:** Holmes et al. synthesis of 2,7-dibromo-9,9-dialkysilafluorene monomer and its Suzuki polymerization. The monomer synthesis procedure can be described summarily as: (a)
Cu, DMF, 125 °C, Yield = 88%; (b) Sn, HCl, EtOH, 110 °C (bath temp.), Yield = 72%; (c) nitrosylsulfuric acid, concentrated H₂SO₄, 0 °C, then aq. KI, -10 to 50 °C, Yield = 30%; (d) t-BuLi (4 equiv), THF, -90 to -78 °C, then (C₆H₁₃)₂SiCl₂, 25 °C, Yield = 52%; (e) t-BuLi, diethyl ether, -78 °C, then 2-isopropoxy-4,4’,5,5’-tetramethyl-1,3,2-dioxaboralane, 25 °C, Yield = 86%. The polymerization procedure proceeds under the following conditions: (a) Pd(OAc)₂, tricyclohexylphosphine, NEt₄OH, toluene, 90°C, then PhB(OH)₂, then PhBr. Yield (7) = 93%, (9) = 94%.

A higher yielding alternate synthesis of silafluorene monomers was reported in 2008 by Huang et al.[156] This method was not complicated by a low-yielding iodination step, however, the product was a modified 2,7-dibromo-3,6-dimethoxy-9,9-dialkylsilafluorene with methoxy groups. The synthetic pathway to 2,7-dibromo-3,6-dimethoxy-9,9-dialkylsilafluorene is outlined in Figure 42. o-Dianisidine is a commercially available starting material and be easily converted to (X) by the reaction of an intermediate bis(diazonium) salt (formed in situ by the oxidation of (16) by NaNO₂) with CuBr. Iodination of (17) is directed at carbons C6 and C6’ by the electron donating methoxy groups at C3 and C3’. Yields of both reactions are high, averaging 85% for the Sandmeyer bromination deamination and 80% for the iodination. Following the complete lithiation of both iodide groups in (18) at low temperature, a wide range of commercially available dichlorosilanes of the form RR’SiCl₂ (such as di(n-hexyl)dichlorosilane used to make (1)) will react via a duel chloride substitution at silicon resulting in a closed five member silole ring. The reaction is maintained at -100°C throughout the lithiation step to ensure selectivity for iodide while both bromide groups remain unreacted.

Until the work featured in this thesis, there have been no examples of this monomer being converted to poly(3,6-dimethoxy-9,9-silafluorene) homopolymer. Potential reasons for this may be the low yield of diboronic ester synthesis which can be attributed to the effects of electron donating methoxy groups on the lithiation prior to the addition of the boronic ester.
Figure 42: Huang et al. of 2,7-dibromo-3,6-dimethoxy-9,9-dialkylsilafluorene monomers and its copolymerization with dioctylfluorene via Suzuki coupling. The monomer synthesis procedure can be described summarily as: (a) NaNO₂, CuBr, HBr (40%), 0°C; (b) I₂, KIO₃, H₂SO₄, AcOH, 90 °C; (c) 2 equiv. n-BuLi, 2 equiv. dichlorodimethylsilane, THF, −100 °C. %. The polymerization procedure proceeds under the following conditions: (d) Pd(PPh₃)₄ (2 mol%), toluene/2M K₂CO₃, 90°C.

3,6-dibromo-9,9-dialkylsilafluorenes have been prepared using diazonium intermediates and halide substitutions. Homopolymers of this monomer type have been reportedly produced using Suzuki and Yamamoto type reactions. Additionally, several copolymers with monomer ranging from comonomers 4,7-di(4-hexyl-2-thienyl)-2,1,3-benzothiadiazole (DHTBT) and 2,1,3-benzothiadiazole (BT) have been produced and used in application ranging from OPVS to OLEDs.
There have also been reports of radically different synthetic strategies with yield silafluorenes with asymmetric substitutions. An iridium catalyzed [2+2+2] cycloaddition reaction using dialkyne substituted silanes can produce a range of variably substituted monomers.\[159\] There have been several examples of using silafluorene monomers in the production of highly planar ladder-type polymers. This class of polymer has become an important fixture in organic devices because its rigid structure improves charge carrier mobilities important for many applications including OTFTs.

1.10.7 References


   b) OSRAM: http://ledlight.osram-os.com/ (Last Accessed 13/06/13)

   c) LG: http://ledlighting.lginnotek.com/support/newsNoticeView.jsp?no=841

   (Last Accessed 13/06/13)


PEDOT:PSS Supplier: Cleviouse - http://www.heraeus-clevios.com


[34] Plexcore Suppliers: (Sigma-Aldrich Plexcore® Organic Conductive Inks)


b) OSRAM: http://ledlight.osram-os.com/ (Last Accessed 13/06/13)

c) LG: http://ledlighting.lginnotek.com/support/newsNoticeView.jsp?no=841 (Last Accessed 13/06/13)

[55] Cambridge Display Technology: http://www.cdtltd.co.uk/ (Last Accessed 13/06/13)


[79] Solution Processing of CdTe or CIGS - Industrial Producers:

First Solar (CdTe) - http://www.firstsolar.com

Solar Frontier (CIGS) -http://www.solar-frontier.com (Last Accessed 13/06/13)


(Last Accessed 13/06/13)


[88] P.W. Atkins, R.S. Friedman, Molecular Quantum Mechanics, Oxford University Press, Oxford, 2004


2.0 Introduction

The seminal work done by Takakazu Yamamoto et al. beginning in the early 1970’s contributed greatly to the modern field of organonickel chemistry and provided many synthetic tools for aryl coupling. Many iconic polymers, including poly(thiophenes) and poly(phenylenes), were initially produced by his group using nickel catalyzed coupling of aryl halides to Grignards or Ullman-Type coupling of aryl halides using stoichiometric amounts of zero valent nickel.[1][2] Over four decades later, nickel catalyzed cross-coupling of haloaryl magnesium compounds has never been more popular as a potentially cost effective method of synthesizing all-conjugated semiconducting polymers for organic electronics. This is due in part to the convenience by which monomer stock can be prepared from widely available, and relatively inexpensive precursors. Common L NiCl₂ initiators (where L = Ph₂P(CH₂)ₙPPh₂ n = 2 - 3) are simple to synthesize, a fraction of the cost of Pd based aryl coupling catalysts, and environmentally stable to air and moisture.[3]

Thiophenes have had resounding success as substrates for this new generation of nickel catalyzed polymerizations.[4] Yet there are some complications arising from the premature termination of chain growth observed when applying these methods to other monomers, including 2,7-dibromo-9,9-dialkylfluorenes, due to the formation of digrignard by-products inevitably formed during the Grignard metathesis process.[5] There has been recent progress in
the controlled polymerization of PFO at low temperatures\textsuperscript{[10]} following Grignard metathesis of mixed halide 2-bromo-7-iodo-9,9-dialkylfluorenes. This protocol affords digrignard-free product at high conversion, but at the cost of additional synthetic and purification steps. We have chosen to focus on the development of conjugate polymer polymerization (and copolymeration) limited to room temperature operation given its advantage in cost, convenience and scalability. Nickel catalyzed transfer polymerization (CTP) of fluorenes are of particular interest because they are the building blocks of many polymers used in light emitting diode and organic laser applications.\textsuperscript{[6][7]} In this chapter we demonstrate the use of dihalide additives which act as digrignard scavengers and reduce chain termination in nickel catalyzed polymerization of fluorene-based diarylmagnesate monomers. Such monomers are generated via Grignard metathesis with iPr\textsubscript{2}Mg-LiCl in a mixed THF/1,4-Dioxane solvent system. Because digrignard scavengers are themselves converted into haloaryl magnesium compounds which can insert into a propagating polymer chain, the method we describe can be used to produce copolymer with low volume fractions of a different repeat unit. For example, using the scavenger 6,6’-dibromo-2,2’-dihexyloxybipthalene (BN), we were able to incorporation up to \textasciitilde5-10\% of 2,2’-dihexyloxybipthalene units into a poly(9,9-dioctylfluorene), discussed below. Our method may be particularly beneficial in cases where monomers are expensive or difficult to synthesize and it is desirable to convert them completely to Grignard so as to maximize polymer yield.

Our aforementioned reaction system was used to make electronics grade poly(9,9-dioctylfluorene) (PFO) (4), with molecular weights in excess of $M_n = 50$ kg/mol within 15 minutes (Scheme 1) using the common nickel diphos initiator, dppeNiCl\textsubscript{2} (where dppe = 1,2-bis(diphenylphosphino)ethane). Additionally, the copolymer poly(9,9-dioctylfluorene-co-4,4’-dihexyloxybipthalene)(BN-PFO) (5) was also produced with similar molecular weight in the
same time period. Polymer (5) is a technologically relevant copolymer reported to be amongst the lowest threshold organic lasing mediums available.⁹

![Scheme 1](image)

**Scheme 1:** (a) Grignard metathesis in THF/1,4-Dioxane resulting in the formation of diarylmagnesate (FO₂Mg) (2). (b) Dibromoaryls (FO)(1) and (BN)(3) function as crucial digrignard scavengers, denoted MA. The ratio of MA to (2) dictates polymer chain length (when mol% catalyst is kept constant with respect to Grignard monomer)

**Table 1.** Summary of Polymer Products, Properties and Reaction Conditions.

<table>
<thead>
<tr>
<th>#</th>
<th>Grignard Metathesis(min)</th>
<th>Scavenger/Monomer Ratio [MA]/[FO₂Mg]</th>
<th>2[FO₂Mg]/Ni Cat. Loading</th>
<th>Rxn Time (m)[a]</th>
<th>Mn[b] kDa</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>140</td>
<td>1</td>
<td>120</td>
<td>15</td>
<td>55</td>
<td>1.6</td>
</tr>
<tr>
<td>5</td>
<td>140</td>
<td>1</td>
<td>120</td>
<td>15</td>
<td>52</td>
<td>1.8</td>
</tr>
</tbody>
</table>

[a] Defined as the interval between 0 to >95% Grignard monomer conversion [b] Mₐ was measured following 5M HCl quench and dying. (GPC data is provided in supporting information)
Both the synthesis of organomagnesate monomers and the polymerization proceed rapidly at room temperature. The latter point represents a notable improvement over previous cryogenic methods.\[10] It should also be noted that without cold temperatures, the number averaged molecular weight of polyfluorenes synthesized via Grignard metathesis (GRIM) polymerization have not been reported to exceed 15 kg/mol.\[2\], likely due to significant amounts of digrignard formed during metathesis.

2.1 Results and Discussion

Specifying the exact structure of a Grignard reagent is difficult. Numerous species coexist in the complex Schlenk equilibrium. Dialkyl or diarylmagnesium compounds comprise a large percentage of the total magnesium compounds in addition to significant amounts of larger metallorganic clusters. The addition 1,4-dioxane, however, is well known to shift the schlenk equilibrium to the side of dialkyl or diarylmagnesium, Figure 1a, by precipitating a MgX$_2$-Dioxane adduct.\[11a\] Following the expansive work of Knochel et al,\[11\] it is known that under the above stated conditions, and in the presence of an equimolar amount of LiCl, the composition of the Grignard solution is predominantly R$_2$Mg-LiCl, where R = alky, aryl. Furthermore, our study confirmed that using dialkylmagnesate compounds, such as iPr$_2$Mg-LiCl (Figure 1b), improves metathesis rates significantly over a wide range of tested substrates compared to a THF control reaction using iPrMgCl-LiCl.\[12\] Figure 2a suggests the partial “ate” character of the magnesium complex expedites exchange, reducing the time needed for quantitative metathesis. In the case of 2,7-dibromo-9,9-dioctylfluorene (1), quantitative exchange is reduced from 12 h to just over 2 h, Figure 2a. As seen in figure 2, however, higher conversion of (1) occurs with a simultaneous increase in digrignard concentration, totaling roughly 5%-10% of the total Grignard species once conversion is complete. Scheme 2a illustrates both the established
catalytic cycle for nickel catalyst transfer polymerization and the stage at which chain
termination occurs due to digrignard coordination to nickel (preventing subsequent oxidative
addition following reductive elimination).

The role of the digrignard scavenger is to be present in sufficient concentration to
completely react with digrignard species, as per the reaction in Figure 1c, and have no impact on
the polymerization kinetics. He have found that the digrignard (6) (produced by adding two
equivalence of iPr₂Mg-LiCl to 2,7-dibromo-9,9-dioctylfluorene) is itself an effective reagents for
Grignard metathesis with potential scavengers like BN (3). Figure 2b plots the consumption of
(6) by BN over a period of 10 min when the reagent molar ratio is [BN]/[(6)] = 2. It is clear that
almost complete conversion is achieved with an excess of scavenger within this short period of
time, despite the sterically and electronically deactivating effects of the ortho alkoxy groups of
BN. [12]
Figure 1: a) Schlenk equilibrium existing between various “iPrMgCl” species. (I) In the presence of LiCl, the activated “iPrMgCl-LiCl” magnesate is formed. (II) Addition of 1,4-dioxane shifts the equilibrium largely to the highly reactive (iPr)2Mg-LiCl organomagnesate. b) Anionic Grignard metathesis occurs between (iPr)2Mg-LiCl organomagnesate and aryl dibromides (where Ar = 9,9-dioctylfluorene). BrArBr can undergo a single Mg/Br exchange to form the desired monomer, or, in the presence of excessive amounts of (iPr)2Mg-LiCl, a second exchange is possible and the undesired digrignard by-product is formed. c) Digrignard, inevitably formed during the complete conversion of BrArBr to diarylmagnesate monomer, is scavenged from the reaction solution by the addition a secondary BrAr’Br.  

2.1.1 Polymerization

Molecular weight analysis of polymer product strongly suggests premature chain termination is contributing to reduced chain length. Initially, we noted polymer chain length was
dependent on the fraction of unmetathesized starting material present in the reaction prior to initiating polymerization in cases where the monomer to nickel ratio, $2[\text{FO}_2\text{Mg}]/\text{Ni}$, is kept constant. Additionally, at higher degrees of Grignard conversion (>70%) we observed a significant broadening of the GPC peaks and a reduced linear dependent of the molecular weight on the ratio $2[\text{FO}_2\text{Mg}]/[\text{Ni}]$.

**Figure 2:** Plot of stoichiometric Grignard metathesis as a function of time. (a) Shows the rate of 100% conversion of FO to FO$_2$Mg. (b) Shows the rate of digrignard consumption by a stoichiometric excess of BN scavenger (3) by secondary Grignard metathesis (observed with $^1$H-NMR) in THF/Dioxane. The reagent ratio was $[\text{BN}]/[(3)] = 2$.  

---

Polymerization of Diarylmagnesate Monomers

McDowell, J.
Figure 3: a) Plot of degree of polymerization, $x_n$, against the molar fraction of $M_A/[\text{FO}_2\text{Mg}]$ for polymers (4) and (5) with monomer to nickel ratios of $2[\text{FO}_2\text{Mg}]/\text{Ni} = 150$. b) Plot of PFO (4) $M_n$ as a function of catalyst loading (when $10 < 2[\text{FO}_2\text{Mg}]/\text{Ni} < 120$) and $[\text{FO}]/[\text{FO}_2\text{Mg}] = 1$. Plot of PFO (4) $M_n$ as a function of scavenger to monomer ratio ($0 < [\text{FO}]/[\text{FO}_2\text{Mg}] < 1$) at constant catalyst loading of $2[\text{FO}_2\text{Mg}]/\text{Ni} = 120$.

For reactions where all FO (1) has been metathesized to FO$_2$Mg (2), adding one equivalent of scavenger M$_A$ (either FO (1) or BN (3)) and waiting 10-15 min before initiating polymerization results in higher $M_n$ then under condition without scavengers. Figure 3a plots $x_n$ of the two
polymers produced in our study as a function of the mole fraction of monomer M_A to the monomer at the time of initiation at constant catalyst loading of 2[FO_2Mg]/Ni = 120; refer to Scheme 1 and Table 1 for notation. GPCs for each plot point can be found in the supporting information (S3.1-2). \( x_n \) is found to be highest when \( M_A/[FO_2Mg] \) approaches unity, after which a plateau is reached. Figure 3b plots the \( M_n \) of polymer aliquots taken after 15 m of polymerization following near complete consumption of Grignard (as determined by \(^1\)H NMR). Two trends are demonstrated in this graph, the first being the linear dependence of \( M_n \) on the 2[FO_2Mg]/Ni ratio under conditions where one equivalence of scavenger is present and the second is the dependence of \( M_n \) on the scavenger to monomer ratio [FO]/[FO_2Mg] at constant catalyst loading of 2[FO_2Mg]/Ni = 120. PDI of polymers is modest and range from 1.5-2.2. The apparent increase in PDI at higher nickel loadings may be the result of disproportion between two nickel complexes as concentration increases, evidence for which appears in \(^{31}\)P NMR taken of a completed reaction solution (discussed below).

Figure 4a plots \( x_n \) as a function of time. The linear trend is consistent over a varied concentration range, while catalyst loading of 2[FO_2Mg]/Ni =100, which is consistent with prior reports of Kumada catalyst transfer polymerization (KCTP).
Figure 4: a) A plot of PFO (4) \( x_n \) versus time shows a linear rate of chain growth within a time period of 5 min. Halving the reaction concentration decreases the slope by approximately half. In the absence of equimolar amounts of digrignard scavenger (1), the growth rate is significantly less (triangles) due to significant chain termination. b) Decrease in \( x_n \) with the addition of 1-bromobenzene.

As one might expect, the addition of a monofunctional aryl halide, such as 1-bromobenzene (PhBr), would also act as a digrignard scavenger with the added function of becoming the end cap of a terminated chain. Figure 4b shows the effect on the molecular weight of PFO (4) when
scavenger FO (1) is exchanged incrementally for PhBr whilst the total concentration of both scavengers, \([\text{PhBr} + \text{FO}]\), remains equal to that of \(\text{FO}_2\text{Mg-LiCl}\) (2). As the amount of PhBr increases, we observe a rapid decline in molecular weight which clearly demonstrates that terminated, phenyl-capped chains are being formed.

Using higher catalyst loadings to obtain a clear signal, intermediate nickel complexes formed during and after polymerization were detected using \(^{31}\text{P}\) NMR, figure 5. A room temperature \(^{31}\text{P}\) NMR spectrum taken of a completed 9,9-dioctylfluorene polymerization ([FO]/[FO\(_2\)Mg] = 1, 2[FO\(_2\)Mg]/Ni = 8) shows the presence of three new nickel complexes. One complex has been identified as dppeNiBr(Ar\(_n\)Br) (where Ar =9,9-dioctylfluorene and \(n > 1\)). As previously reported, the two inequivalent phosphorous give rise to a set of doublets at 59.4 ppm and 40.5 ppm with \(^3\text{J}_{\text{P-Ni-P}} = 18\) Hz. The presence of a second set of doublets at 59.2 ppm and 40.1 ppm occurs due to the closely related chloride species, dppeNiCl(Ar\(_n\)Br), formed by rapid halide exchange with chloride in solution.

Most interestingly, the formation of dppeNiBr\(_2\) was discovered in relatively large amounts with respect to the other nickel species. At -10°C, the sharp \(^{31}\text{P}\) resonance peak belonging to the square planar dppeNiBr\(_2\) complex becomes readily apparent at 68 ppm. The identity of the peak was confirmed with a previous report by Sadler et al.\(^{[13]}\). We believe dppeNiBr\(_2\) may a product of disproportionation formed when the rate of this side reaction increases at higher catalyst loadings, Scheme 2b.\(^{[7][8]}\) dppeNiBr\(_2\) may also be forming if unreacted initiator dppeNiCl\(_2\) undergoes a complete halide exchange with the excess amounts of MgBr\(_2\) formed during the reaction.
Scheme 2: a). Catalytic cycle of nickel catalyst transfer polymerization with diarylmagnesate monomers proceeding through three stages: I) Transmetallation with a diarylmagnesate monomer (where Ar = 9,9-dioctylfluorene). II) Reductive elimination to form an associated complex. III) Oxidative addition to the propagating chain end. If a digrignard impurity coordinates to nickel, oxidative addition is not possible and chain growth terminates. IV) Given the presence of 1,4-Dioxane as a co-solvent, the MgBr₂ by-product is precipitated as the insoluble dioxane adduct. b) With high nickel loadings, disproportionation between nickel complexes to form a coupled chain and dppeNiBr₂ may be occurring, resulting in the 68 ppm signal in $^{31}$P NMR.
2.1.2 Analysis of Copolymer

As previously mentioned, using the scavenger 6,6'-dibromo-2,2'-dihexyloxy-1,1'-binapthalene, we were able to incorporate ~5-10% of 2,2'-dihexyloxybinapthalene units into a poly(9,9-dioctylfluorene), to form the statistical copolymer BN-PFO (5). Figure 6 shows a typical $^1$H-NMR obtained for a purified sample of polymer (5) which shows characteristic aromatic peaks of both 9,9-dioctylfluorene and 2,2'-dihexyloxy-1,1'-binaphthalene in the region of 8.2-6.8 ppm. Integration of the aromatic protons of the respective repeat units allows us to estimate a ratio of 8:1 with the highest fraction belonging to 9,9'-dioctylfluorene. Another analytically useful peak is found at 4.0 ppm and belongs to the methylene protons of the oxygen bound carbon found in each of the hexyloxy groups on the 2,2'-dihexyloxy-1,1'-binapthalene
Figure 6: $^1$H-NMR of polymers (5) following a 30 min polymerization. The reaction was quenched by the addition of 5 M HCl and unreacted monomer was removed by precipitating polymers in excess MeOH and fractioning in THF/Hexane. ($\blacksquare$) indicate hexyloxy methylene protons and ($\bullet$) indicate octyl side chain methylene protons.

repeat unit. An analogous multiplet can be seen at 2.3 ppm and corresponds to methylene protons on each octyl chain of the 9,9'-dioctylfluorene unit, specifically those located on the carbon adjacent to the apical C9 carbon. Both peaks integrates to give the expected 8:1 ratio of (1) and (3) repeat units respectively.

It has previously been reported that polymers with a high concentration of binaphthyl units are able to form stable amorphous glasses and show minimal formation of microcrystalline $\beta$-phase, which can significantly decrease the PL efficiency. In Figure 7, a film of PFO (4) spin cast from a toluene solution clearly shows prominent PL features where the dominant emission at $\lambda = 440$ nm (indicated by arrow) results from efficient energy transfer from the glassy PFO phase to the $\beta$-phase. Conversely, polymer (5), which has a binaphthyl content in the vicinity of ~10% (by NMR), shows an almost pure glass phase emission at $\lambda = 428$ nm with a noticeable absence
in high wavelength emission peaks. These results are consistent with prior reports with the difference being polymer (5) is produced in under 30 m, whilst previous of BN-PFO required days of reflux and stoichiometric amounts of Ni\textsuperscript{0}(PPh\textsubscript{3})\textsubscript{4}.

### 2.2 Conclusion

This chapter reveals that at high conversion of aryl dibromide starting materials to diarylmagnesate monomers for nickel catalyst transfer polymerization, the inevitable formation of a “digrignard” by-product leads to premature termination of growing chains shortly after initiation. Termination occurs due to the fact that digrignard impurities cannot undergo oxidation addition at the end of the propagating chain. Coordinatively unsaturated zero valent nickel quickly deactivates in a reaction yielding dppe\textsubscript{2}Ni\textsuperscript{0}. However, we report that such side reactions should not necessarily be viewed as a hindrance to achieving polymers with useful
properties when using additives dubbed digrignard scavengers. By adding aryl dibromides which undergo a secondary Grignard metathesis reaction to scavenge chain terminating digrignards, the potential for achieving high molecular weights is restored. As previously mentioned, we consider our method to be particularly beneficial in cases where aryl dibromides are expensive or difficult to synthesize and it is desirable to convert them completely to Grignard so as to maximize their polymer yield. Additionally, because digrignard scavengers needn’t be the same aryl dibromide as that converted into to the primary Grignard monomer, using this method is a straightforward method of including small volume fractions of comonomers, such as the copolymer poly(9,9-dioctylfluorene-co-4,4’-dihexyloxybinaphthalene)(BN-PFO) (5) (with roughly 10% BN units). All our polymerizations were carried out at room temperature, which simplifies any future plans to transition this technology from lab to market. The choice of a mixed solvent system of THF and 1,4-dioxane decreased the Grignard metathesis reaction time by 17% and improved reactivity towards sterically hindered and electron rich ortho alkoxy substrates.

Utilizing the knowledge presented in this chapter, we believe new methods of generating co-polymers appropriate of LED and organic laser applications are possible. Furthmore, these initial results warrant further work on the subject of endcapping, specifically development of functional endgroups which will enable subsequent polymerization of non-conjugated polymers by methods such as RAFT or ATRP. This may result in interesting phase segregated triblock polymers with large volume fractions of a light emitting block for use as gain mediums in polymer lasers.
2.3 Experimental Section

All synthesis was performed under inert atmosphere using standard schlenk line or glovebox techniques unless otherwise stated. Chemicals were purchased from TCI America and Sigma Aldrich and used without need for further purification. Tetrahydrofuran and 1,4-Dioxane were distilled over sodium/benzophenone prior to use. Dichloromethane was dried by refluxing over CaH₂ for several hours. Variable temperature $^1$H, $^{13}$C, $^{31}$P NMR was performed on a 400 MHz Varian Mercury Spectrometer. Solution and thin film absorption and photoluminescence spectra were recorded using a Perkin-Elmer 900 UV-Vis Spectrometer and a Perkin-Elmer LS-50B Luminescence Spectrophotometer. Polymer quantum efficiencies were calculated through the use of an integrating sphere using a method described elsewhere using a focused 365 nm LED as the excitation source\cite{22}. Polymer molecular weights were measured with a Viscotek GPC calibrated with respect to polystyrene standards using THF as an eluent and column temperature of 35°C.

**Preparation of 6,6’-dibromo-2,2’-binaphthol:**

In a dry Schlenk flask (100 mL), 2.1 g (7.34 mmol) of 2,2’-binaphthol was dissolved in freshly distilled dichloromethane (40 mL). The solution was cooled to -75°C in an acetone/dry ice bath. 1 mL (19.6 mmol) of neat Br₂ was then added dropwise via syringe over a period of 20-30 min with stirring. The solution was allowed to warm to room temperature and stir for an additional 2.5 h. The reaction was quenched with 50 mL of a 10% NaHSO₃ solution. The organic layer was separated, washed with brine and dried with MgSO₄ prior to removing the solvent by rotovap. Pure product was recrystallized using a mixture of benzene and cyclohexane (~3:1). Product yield was 2.5 g or 78%. $^1$H-NMR (CD₂Cl₂, 400 MHz)(ppm): 8.13 (s, 2H), 7.78 (d, 2H), 7.59 (d, 2H), 7.36 (d, 2H), 7.03 (d, 2H). $^{13}$C-NMR (CD₂Cl₂, 400 MHz)(ppm): 129.33, 127.18,
Preparation of 6,6′-dibromo-2,2′-dihexyloxy-1,1′-binaphthalene (3):

Add 2.0 g (2.27 mmol) of 6,6′-dibromo-2,2′-binaphthol and 1.17 mL (8.35 mL) 1-bromohexane to 3.69 g of K₂CO₃ in 5 mL of DMF. Heat and stir the reaction to 90°C for 14 h. Once cooled, the reaction residue was filtered through a plug of alumina to remove undissolved solids. The collected liquid was dried in vacuo with heating to remove both DMF solvent and unreacted 1-bromohexanes (bp = 153°C and 154-158°C respectively). The dried solid was redissolved in dichloromethane (10 mL) and washed three times with 5 mL H₂O, dried over MgSO₄ and rotovapped to dryness. Pure, clear rhombic crystals of (3) could be grown by slow evaporation of a concentrated THF solution. Product yield was 1.1 g or 80%. ¹H-NMR (CD₂Cl₂, 400 MHz) (ppm): 8.03 (s, 2H), 7.87 (d, 2H), 7.45 (d, 2H), 7.27 (d, 2H), 6.97 (d, 2H), 3.97 (m, 4H), 1.42 (m, 4H), 1.05-0.97 (m, 12H), 0.77 (t, 6H). ¹³C-NMR (CD₂Cl₂, 400 MHz) (ppm): 131.73, 129.38, 128.98, 128.49, 127.64, 126.25, 118.90, 116.30, 115.41, 68.82, 30.59, 28.48, 24.62, 21.76, 12.92. EI-MS (M⁺) = 610.1106  (Calc. Mass = 610.1122)

Preparation of Diarylmagnesate (2):

The room temperature Grignard metathesis of 2,7-dibromo-9,9-dioctylfluorene (1) was performed in a N₂ filled glove within a 5 mL scintillation vial. A 0.5 M solution of (1) was prepared using THF as a solvent. Additionally, a Grignard solution of isopropyl magnesium chloride (1.3 M in THF) activated by 1.0 equivalence of LiCl was prepared and used following 1 h of stirring to allow for the complete dissolution of the salt. The Grignard solution could be stored and used for several days in the glovebox without appreciable change. In a typical experiment, 2.0 mL (0.5 mmol) of 0.5 M (1) solution is diluted with 1.2 mL 1,4-dioxane and
stirred rapidly. 710 µL of 1.3 M iPrMgCl·LiCl (0.92 mmol) was added by a single injection. The formation of insoluble white MgCl₂-Diox adduct is observed almost immediately. The solution is stirred continuously for 140 min to complete the in situ generation of diarylmagnesate (2). The white MgCl₂-Diox precipitate is allowed to settle, and the clear pale yellow solution is separated. The solution can be stored for several hours, but largely decomposes to oligomeric products after a period of 24 h.

**Preparation of Poly(9,9-dioctylfluorene-co-4,4’-dihexyloxybinaphthalene) (5):**

For maximum molecular weight, a monomer feed ratio (Mₐ/(2)) of unity must be achieved.[ii] To accomplish this 78.4 mg (0.128 mmol) of 6,6’-dibromo-2,2’-dihexyloxy-1,1’-binaphthalene (3) was added to 1.0 mL of the above prepared solution of (2), where [4] = 128 mM. Polymerization is initiated by adding (5 - 6 mg or approximately 3-4 mol%) dppeNiCl₂. The solution immediately becomes yellow-orange and is stirred continuously for 15-20 m. As the polymerization progresses, additional MgBr₂-Diox precipitate is formed and the solution becomes steadily more opaque and viscous. The vial is removed from the glovebox and polymerization quenched by adding several drops of 5.0 M HCl and adding it dropwise to a large excess of methanol such that product precipitates as a fibrous yellow solid. Polymer is collected by suction filtration. For removal of residual monomer and oligomer, the crude polymer was soxhlet extraction with ethanol for 4-5 h. The polymer solid is characterized by GPC and ¹H NMR (S2.4). Optical properties were studied by collecting solution and solid state absorption and fluorescence spectra in addition to absolute quantum yield (See Below).

Yield: 64% ¹H-NMR (CD₂Cl₂, 400 MHz) (ppm): 8.19 (1H), 8.058 (1H), 7.86 (4H), 7.73 (8H), 7.48 (2H), 7.28 (1H), 7.18 (1H), 7.08 (1H), 6.98 (1H), 4.00 (4H), 2.17 (8H), 1.15-0.82 (aliphatic multiplets, 82H)
Polymerization of Diarylmagnesate Monomers McDowell, J.

**Poly(9,9-dioctylfluorene) (4):** Yield: 68% \(^1^H\)-NMR (CD\(_2\)Cl\(_2\), 400 MHz) (ppm): 7.89-7.70 (aromatic multiplet, 6H), 2.14-0.82 (aliphatic multiplet, 34H)

### 2.4 References


[14] When M/(2)<1, Nidppe$_2$, becomes more prevalent in the 31P NMR. We believe Nidppe$_2$ is formed in a second order reaction between two dppeNi0Solv$_2^*$ complexes because no free dppe is observed in the NMR.
**Supporting Information 1**

**Digriignard Scavengers in the Nickel Transfer Polymerization of Diarylmagnesate Monomers**

Content:

Section 1: 1H/13C NMR of Monomers (1-6) and Polymer Products (6-8):

- S1.1.0 – Monomer (1) 1H-NMR
- S1.1.1 – Monomer (1) 13C-NMR
- S1.2.0 – Monomer (3) 1H-NMR
- S1.2.1 – Monomer (3) 13C-NMR
- S1.3 – PFO (4) 1H-NMR
- S1.4 – PFO-co-BN (5) 1H-NMR

Section 2: GPC Data Complimenting Figure 3

- S2.1 – PFO (4)
- S2.2 – PFO-co-BN (5)

Section 3: Electronic Spectra of Polymers and recorded quantum yields

- S.3.1: Electronic Spectra of Polymers and recorded quantum yields

Table 1: Electronic Properties and Absolute Quantum Yields of Spin Cast Films:
Section 1: $^1$H/$^{13}$C NMR of Premonomers (1) and Scavenger (3) and Polymer Products (4-5)
The reaction was quenched by the addition of 5 M HCl and unreacted monomer was removed by precipitating polymers in excess MeOH and fractioning in THF/Hexane. (■) indicate hexyloxy methylene protons and (○) indicate octyl side chain methylene protons.
Section 2: GPC Data Complimenting Figure 3

S2.1 – PFO (4) (0.5 mol% catalyst with respect to Grignard)

S2.2 – PFO-co-BN (5) (0.5 mol% catalyst with respect to Grignard)
Section 3: Electronic Spectra of Polymers and recorded quantum yields

S3.1: Electronic Spectra of Polymers and recorded quantum yields (See Table Below)

Table 1: Electronic Properties and Absolute Quantum Yields of Spin Cast Films:

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Lambda_{\text{abs max}}$ (nm)</th>
<th>$\Lambda_{\text{ex}}$ (nm)</th>
<th>$\Lambda_{\text{em}}$ (nm)</th>
<th>Quantum Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(4)</td>
<td>389</td>
<td>365</td>
<td>441 (466)</td>
<td>86</td>
</tr>
<tr>
<td>(5)</td>
<td>380</td>
<td>365</td>
<td>426 (451) (484)</td>
<td>86</td>
</tr>
<tr>
<td>PhBr Capped</td>
<td>381</td>
<td>365</td>
<td>433 (459)</td>
<td>81</td>
</tr>
</tbody>
</table>

Chapter 3

Pure Blue Emitting Poly(3,6-dimethoxy-9,9-dialkylsilfluorenes) Prepared Via Nickel Catalyzed Cross-Coupling of Organomagnesate Monomers

3.0 Introduction

Nickel catalyst transfer polymerization (CTP) is a potentially cost effective large scale synthetic route for many electroluminescent conjugated polymers. Ni catalysts are less expensive than Pd base catalysts and boronic ester synthesis and purification is replaced by a simple in situ Grignard metathesis step. However, high magnesium-halide exchanges rates are not universal to all potentially interesting monomers and research integral to discovering truly general polymerization routes includes studying reaction conditions which yield rapid and near complete exchange of traditionally inactive aryl halide substrates. Less than ideal exchange rates are frequently observed when aryl halides are sterically encumbered or have electron rich deactivating substituents. The reader is referred to an extensive kinetics study of Mg/halide exchange by Mayr et al.

In this publication, poly(3,6-dimethoxy-9,9-dihexylsilfluorene) (PDHSF) along with several derivatives, Figure 1d, were synthesized by polycondensation of diarylmagnesate monomers using a modified protocol established for nickel catalyst transfer polymerization of analogous 2,7-dibromo-9,9-dialkyfluorenes. In this publication, we use the common nickel initiator dppeNiCl₂ to initiate relatively controlled chain-growth polymerization. 2,7-dibromo-9,9-dialkyfluorenes (1-8) with methoxy substituents in the 3 and 6 positions ortho to...
Figure 1: a) Highly transparent spin cast film of (10) and its PL. b) Solid state PL of (15) produced via our scalable synthesis. c) Solution phase PL of (14) in Toluene. d) Partial Grignard metathesis in THF/1,4-Dioxane resulting in the formation of diarylmagnesate monomer, denoted “M”. Limiting conversion prohibits the formation of digrignard by-product which terminates chain growth. At the same 2[M]/[Ni] ratio, the degree of Grignard conversion can have considerable impact on polymer chain length. Monomers (1-7) are depicted and side chains range in structure from simple alkyl groups to more functional cycloalkenyl groups.
bromine, represent a challenging substrate for quantitative Mg/Br metathesis. Incomplete exchange and long reaction times represent some major obstacles preventing the synthesis of 3,6-dimethoxy substituted PSF homopolymers by nickel catalysis methods to date. Including 1,4-dioxane as a solvent was discovered to significantly increase the Mg/Br exchange rate by a factor of 5, reducing the time required to achieve stoichiometric conversion to 2 h. Also, relatively fast rates of polymerization were observed. Polymers reached their maximum molecular weights within 30 min and were characterized with GPC molecular weight analysis and MALDI-TOF end-group analysis. We have found that polymer chain length is dependent on the fraction of starting material converted during the Grignard metathesis step. High molecular weights, $M_n > 50$ kg/mol, are obtained when Grignard metathesis is restricted to a maximum of $F_{\text{conv}} = 66\%$ and a monomer-to-initiator ratio of $2[M]/[Ni] = 150$ is used. $F_{\text{conv}}$ is the Grignard metathesis conversion factor and is defined as $F_{\text{conv}} = 2[M]/[SM]_0 \times 100\%$, where $[M]$ is the diarylmagnesate monomer concentration and $[SM]_0$ is the initial aryl dibromide starting material concentration. The factor of two is required because two aryl moieties are associated with each magnesium center. Conversion limits can be reasonably explained by considering the formation of digrignard by-products (formed at high degrees of Grignard conversion) which cause the premature termination of polymer chains. To the best of our knowledge, no nickel diphosphine catalyzed polymerizations of 3,6-dimethoxy-9,9-dialkylsilfluorene homopolymers have been reported with $M_n > 50$.

By obtaining solution-processable electronics grade PSF derived from dimethoxy substituted monomers, which are relatively straightforward to prepare and higher yielding than related monomer synthesis producing 2,7-dibromo substituted silafluorenes, we hope to increase interest in this subclass of polymer as emitters given the many promising properties they possess. PSF was initially reported by Holmes et al, and its most notable properties were a deep blue
emission, high quantum efficiency, excellent solubility and improved thermal stability.\textsuperscript{[11-13]} Another appealing trait was the improved electron affinity resulting from $\sigma^*-\pi^*$ overlap similar to that observed for earlier reports of molecular and polymeric siloles.\textsuperscript{[14]}

Conjugated polymers such as poly(9,9-dialkylfluorenes) (PF) have shown the highest potential as blue light emitting polymers in many optoelectronic devices to date.\textsuperscript{[15,16]} However, significant limitations to the development of commercial polymer LEDs exist due to the lack of stable blue emitters, not excluding poly(9,9-dialkylfluorenes). It is well known that, over extended periods of device operation, PF stability suffers from decreasing intensity of blue emission and the concurrent appearance of a broad, low-energy green band.\textsuperscript{[17,18]}

Polysilafluorenes are considered a promising substitute for existing blue polymer emitters. Early light emitting devices utilizing PSF as emitters decayed over time with a decrease in emission intensity but showed no sign of spectral broadening.\textsuperscript{[19-21]} PSF also functioned as a host of various lower band gap emitters.\textsuperscript{[22]} Such qualities are important in the fabrication of polychromatic devices with sufficiently high lifetimes so as to merit commercial value.
Scheme 1: a) Synthesis of 2,7-dibromo-3,6-dimethoxy-9,9-dialkyl-silafluorenes (1-7) beginning with o-dianisidine. The initial Sandmeyer reaction exchanges the amino groups for bromide. Iodination proceeds at the C6 and C6’ position as directed by the methoxy groups. The final lithiation and chlorosilane substitution reaction is preformed at low temperature (MeOH/N₂ slush bath) to select for the iodide groups. The procedure is adapted from earlier work by Huang et al. [43] b) Synthesis of cycloalkene containing dichlorosilanes used in the production of monomers (6) and (7).

Figure 2: Crystal structures of silafluorene monomers (1) and (4). Both compounds consist of a planar silafluorene moiety (note the apical Si atom). Additionally, monomer (4) posses a vinyl side chain which remains intact throughout the synthesis outlined in Scheme 1.
3.1 Results and Discussion

The synthetic pathway to 2,7-dibromo-3,6-dimethoxy-9,9-dialkylsilafluorene has been adapted from earlier reports by Huang et al.\cite{43} and is outlined in Scheme 1. o-Dianisidine is a commercially available starting material and can be easily converted to (17) by the reaction of an intermediate bis(diazonium) salt (formed \textit{in situ} by the oxidation of (16) by NaNO₂) with CuBr. Iodination of (17) is directed at carbons C6 and C6’ by the electron donating methoxy groups at C3 and C3’. Yields of both reactions are high, averaging 85% for the Sandmeyer bromination deamination and 80% for the iodination. Previously reported synthesis have suffered from reduced yields (yields ~ 15-20 %) due to incomplete iodination.\cite{23}

Following the complete lithiation of both iodide groups in (18) at low temperature, a wide range of commercially available dichlorosilanes of the form RR’SiCl₂ (such as di(n-hexyl)dichlorosilane used to make (1)) will react via a duel chloride substitution at silicon resulting in a closed five member silole ring. The reaction is maintained at -100°C throughout the lithiation step to ensure selectivity for iodide while both bromide groups remain unreacted. Figure 1d summarises the various monomer created by altering the dichlorosilane reagent. For many applications, it is desirable to have polymers with functionalized alkyl sidechains which can undergo further reactions post polymerization. Therefore, we explored creating monomers containing unsaturated double bonds which serve the dual purpose of providing additional functionality whilst sterically separating neighbouring chains to ensure efficient luminescence. As illustrated in Scheme 1b, both unique dichlorosilanes (20) and (21) were produced as part of this work and used to create the cycloalkene monomers (6) and (7) (the detailed procedure is outlined in the Experimental Section). In the creation of (20) and (21), we exploited the regioselective hydrosilylation of the terminal double bond over the internal double bond, as has been reported previously.\cite{24} Our analysis confirms the desired terminal silane can be obtained in
80% yield. Contributing to the loss in yield is the formation of a minor by-product (~10% yield) which results from the hydrosilylation of the internal double bond. This is most apparent in the $^1$H NMR of (21) (Supporting Information) where the terminal double bond resonance peaks can be seen at 5.0 ppm. In both compounds, more prominent proton resonance peaks from the internal double bond are apparent in the $^1$H NMR. In the case of (21), a mixture of endo and exo isomers exists as a result of 5-vinyl-2-norbornene starting material also being a mixture of stereoisomers.

In silafluorenes (6) and (7), evidence that the double bond remained unreacted during synthesis was provided by not only $^1$H NMR, but EI-MS. A mass spectrum of (7) revealed peaks characteristic of a retro Diels-Alder rearrangement frequently observed in 2-norbornene derivatives (See Supporting Information). Additional evidence of the correct structure of monomers (1-7) was obtained by growing crystals of silafluorenes (1) and (4) by slow evaporation of THF solutions and obtaining a single crystal X-ray structure for each, Figure 2.

Both silafluorene units are clearly planar with a C-C bond distances within the biphenyl moiety ranging marginally from 1.37-1.49 Angstroms. The C-Si bond lengths are, however, predictably larger with two sides of the silole ring being 1.87 Å. Both bromine are found in the desired 2 and 7 positions indicating selective lithiation of iodine predominates.
**Scheme 2:** Anionic Schlenk Equilibrium existing between Grignard species formed during the metathesis between iPrMgCl-LiCl and aryl dibromide monomers as reported by Knochel et al.\(^\text{10}\) The circled area highlights the dominant organomagnesate species involved when the reaction takes place with 1,4-dioxane as a co-solvent. Note the insoluble MgCl\(_2\)-Dioxane adduct is an important component of this equilibrium.

In an effort to replicate Grignard metathesis conditions reported previously in the literature,\(^\text{27}\) both iPrMgCl and silafluorene (1-7) were combined in a 1:1 ratio in THF prior to polymerization. Following 12 h, however, only approximately \(F_{\text{conv}} = 50\%\) of starting materials occurred, leaving 50% of iPrMgCl unreacted.

Higher conversion was found to occur when a salt additive, LiCl, was added to iPrMgCl in ratios ranging from \([\text{LiCl}]/[\text{iPrMgCl}] = 0.25 – 1.0\). LiCl is believed to activate iPrMgCl by breaking apart larger clusters and forming a new \(\mu\)-Cl bridged lithium organomagnesate complex.\(^\text{10}\) When a 1:1 ratio of LiCl/iPrMgCl was used, \(F_{\text{conv}} = 75\%\) was observed in 12 h, Figure 3, leaving 25% of iPrMgCl-LiCl unreacted. The highest rate of conversion, however, was obtained by using a mixed solvent system consisting of 30% v/v of 1,4-dioxane in tetrahydrofuran. Within 2 h, 2,7-dibromo-3,6-dimethoxy-9,9-dialkylsilafuorenes, was converted
F_{conv} \sim 90\% to bis(7-bromo-3,6-dimethoxy-9,9-dialkyilsilafluorene)magnesates, Figure 3., with no discernible iPrMgCl-LiCl remaining in solution. A small amount of digrignard by-product, however, on the order of 5\% of the starting material was discovered. Even at low levels, this impurity is believed to cause premature chain termination and significantly reduce molecular weight.

Scheme 2 illustrates the possible “anionic Schlenk equilibrium” existing between Grignard species formed during the Mg/Br exchange reaction occurring in a mixed solvent system such as THF/Dioxane. Formation of the insoluble MgCl$_2$-Dioxane adduct is obvious from the precipitation of a fine white solid within a few seconds of adding iPrMgCl-LiCl. As suggested by Knochel et al., the dominant Grignard species is likely the dialkylmagnesiate, (22), at early stages of the reaction, and the diarylmagnesiate (23) once metathesis has completed.\[10\]
Figure 3: Grignard metathesis of the dibromide DHSF (1) (denoted as $S_M$) into its diarylmagnesate monomer (M) via Grignard metathesis under different solvent conditions using iPrMgCl-LiCl (1:1) and plotted as a function of time. Solid lines trace the near stochiometric conversion of reagents in the presence of 1,4-dioxane within a period of 2h. In the absence of 1,4-dioxane, conversion rates are considerably slower (dashed lines) and the conversion is incomplete after 12 h. Small amounts of digrignard by-product are formed at high degrees of conversion ($F_{\text{conv}} > 66\%$) in 1,4-dioxane.

$^{31}$P NMR was used to detect various reaction products derived from the dppeNiCl$_2$ initiator during the polymerization of DOSF (2) (Figure 4), under conditions where $F_{\text{conv}} = 66\%$ and $[\text{M}] = 88$ mM. Large catalyst loadings ($2[\text{M}]/[\text{Ni}] = 10$) were used so that a clear signal is obtained. Following polymerization, the phosphorous resonance of the initiator dppeNiCl$_2$ (spectrum B, Figure 4) has been replaced by a new set of peaks corresponding to the nickel complex dppeNi(ArBr)$_n$X (where Ar = 9,9-dihexylsilafluorene) centered at 59.4 ppm and 41.7 ppm with $^3J_{\text{PNiP}} = 18$ Hz (spectrum C, Figure 4). The respective peaks actually consist of two closely spaced set of doublets which occur due to the simultaneous presence of dppeNi(ArBr)$_n$Br
and dppeNi(ArBr)_6Cl resulting from the rapid exchange of halide at the nickel center. A broad singlet is also present at 68 ppm and corresponds to dppeNiBr₂ which may be forming *in situ* as a product of disproportionation when catalyst loadings are very high (as in the case of our NMR studies). Readers are referred to several recent articles which have indicated that disproportionation can become an active pathway in nickel transfer polymerization reactions.[28,29] To support this observation, we independently synthesised dppeNiBr₂ using existing literature methods and the reference spectrum A is also shown in Figure 4a.[30] dppeNiBr₂ may also be forming if unreacted initiator dppeNiCl₂ undergoes a complete halide exchange with the excess amounts of MgBr₂ formed during the reaction.

The principle deactivation pathway of polymerization appears to be through the formation of inactive dppe₂Ni⁰. dppe₂Ni⁰ was observable in ³¹P NMR as a weak singlet at 45.6 ppm in the majority of NMR scale polymerization we preformed. The mechanism through which dppe₂Ni⁰ is formed is interesting. No “free” dppe was ever detected during our studies, which suggests a transfer of dppe might occur through a Ni(0) dimer when the concentration of coordinatively unsaturated dppeNi⁰* becomes excessive. Such cases include polymerizations with a high frequency of chain termination following the coupling of a polymer chain and an impurity (like digrignard) which would prevent subsequent oxidative addition of the reduced Ni(0) center to the terminus of the propagating chain.
Figure 4: $^{31}$P NMR analysis of various nickel diphos species present after the polymerization of PDOSF (2). Spectrum C represents a typical polymerization. dppeNiCl$_2$ initiator loading was 2[M]/[Ni] = 10 and the polymerization was completed in THF/Dioxane (7:3) at room temperature. Spectrum B is a reference spectrum of dppeNiCl$_2$ dissolved in THF/Dioxane (7:3). Spectrum A is a reference spectrum of dppeNiBr$_2$ produced using literature methods.$^{[30]}$ The peak indicated by a dark circle belongs to the decomposition product dppe$_2$Ni$^0$.

The conversion of monomer and the increase in polymer chain length were respectively monitored by $^1$H NMR and GPC by taking aliquots at regular time intervals. Figure 5a plots the average degree of polymerization, $x_n$, of PDOSF (10) and PHNSF (15) as a function of Grignard conversion $F_{\text{conv}}$ when the catalyst loading is held constant at 2[M]/[Ni] = 150. One can easily discern that maximum $x_n$ is obtainable when $F_{\text{conv}} = 66\%$. At this conversion, digrignard concentration is too low to cause significant chain termination. Under these conditions, the inset of Figure 5a shows $x_n$ increases at a linear rate with time. Additionally, the rate of chain growth is very fast, exceeding $x_n = 100$ within 10 min. Figure 5b plots the molecular weight of polymers PDOSF (10) and PHNSF (15) as a function of catalyst loading when $F_{\text{conv}} = 66\%$. One can see that for both polymers, $M_n$ follows a linear trend which closely approximates the calculated values determined by the ratio of activated aryl dibromide to nickel initiator, 2[M]/[Ni].
obtain $M_n > 50$ kg/mol for both polymers (10) and (15). Figure 5b also shows that PDI is moderately low for both polymers (especially at higher molecular weights) and ranges between 1.5-2.0. The results summarized in Figure 5 apply broadly to all polysilafluorenes (9-15) produced in this study, with the exception of polymer PDMSF (11) and PMVSF (12) which can only be obtained with a maximum $M_n = 10-14$ kg/mol and much broader PDI. This is likely due to the limited solubility of these polymers given their short side chains. Table 1 summarizes the optimal parameters for obtaining maximizing molecular weight of polymers (9-15).
Figure 5: a) The average degree of polymerization, $x_n$, of PDOSF (10) and PHNSF (15) as a function of Grignard conversion $F_{\text{conv}}$ when the $2[M]/[Ni] = 150$. The inset graph plots $x_n$ versus time. A trend fitting straight line is overlaid to highlight the linear relation of chain growth to reaction time when $F_{\text{conv}} = 66\%$ and $2[M]/[Ni] = 150$. b) Plot of the molecular weight of polymers PDOSF (10) and PHNSF (15) as a function of catalyst loading when $F_{\text{conv}} = 66\%$. PDI for both polymers ranges between 1.5-2.0.
Table 1. Summary of Polymer Products, Properties and Reaction Conditions.

<table>
<thead>
<tr>
<th>#</th>
<th>M.Wt.</th>
<th>R.U.</th>
<th>Grignard Metathesis</th>
<th>F_{conv} (%)</th>
<th>2[M]/[Ni] Ratio</th>
<th>Rxn Time (m)</th>
<th>M_n (kg/mol)</th>
<th>x_n</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>408.25</td>
<td>2</td>
<td>66</td>
<td>150</td>
<td>30</td>
<td>48.9</td>
<td>120</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>464.75</td>
<td>2</td>
<td>66</td>
<td>150</td>
<td>30</td>
<td>55.6</td>
<td>120</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>268.38</td>
<td>2</td>
<td>66</td>
<td>150</td>
<td>30</td>
<td>10.1</td>
<td>38</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>280.39</td>
<td>2</td>
<td>66</td>
<td>150</td>
<td>30</td>
<td>14.0</td>
<td>50</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>362.54</td>
<td>2</td>
<td>66</td>
<td>150</td>
<td>30</td>
<td>47.5</td>
<td>131</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>432.67</td>
<td>2</td>
<td>66</td>
<td>150</td>
<td>30</td>
<td>52.6</td>
<td>122</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>444.68</td>
<td>2</td>
<td>66</td>
<td>150</td>
<td>30</td>
<td>57.7</td>
<td>129</td>
<td>1.8</td>
<td></td>
</tr>
</tbody>
</table>

3.1.1 MALDI-TOF End-Group Analysis

Oligomers of PDHSF (9) (M_n = 3.1 kg/mol by GPC) where prepared from partially methathesized solutions of DHSF (1) (where F_{conv} = 66%) with a large initial concentration of dppeNiCl_2 initiator (2[M]/[Ni] = 8). End group analysis of oligomers was performed by means of matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry. Using a matrix consisting of α-cyano-3-methoxycinnamic acid, several coupled silafluorenes ranging from trimers to hexamers were resolved (see Figure 6 for 3 ≤ n ≤ 6). For each value of n
Figure 6: MALDI-TOF mass spectrum of PDHSF (9) oligomers. Two distinct groups of peaks indicate polymers with differing termini are formed following quenching of the reaction solution. One population of polymer chains is capped with Br on both ends while the other has Br/H termini.

(separated by 408 m/z, which is the mass per repeat unit), groupings of two distinct polymer populations possessing unique sets of chain end-groups were observed. The mass of these two populations differ by 80 m/z, which correspond to a single bromine. We can infer from this spectrum that the majority of chains are capped with two terminal bromines while a smaller portion of chains have both bromine and hydrogen terminus. The presence of hydrogen originates from the quenching step where a proton from HCl displaces Nickel or magnesium end caps.

3.1.2 NMR Analysis of Polymer Products

PSF polymers (9-15) produced in this paper were characterized by NMR (see Supporting Information for the complete set of spectrum). Typical $^1$H NMR spectra of the monomer DHSF
(1) and resultant polymer PDHSF (9) is shown in Figure 7a and Figure 8a respectively. In the aromatic region of the monomer spectrum, two distinct singlets are present at 7.63 ppm and 7.24 ppm which correspond to the two sets of equivalent protons at C1/C4 and C5/C8 respectively. Another analytically useful singlet peak is present at 3.93 ppm and belongs to the six equivalent methoxy protons at C3 and C6. Looking at the polymer spectrum in Figure 8a, the methoxy peak is still readily apparent, albeit shifted upfield slightly to 3.91 ppm and broadened. Both aromatic proton peaks have also shifted to 7.48 ppm (H_A) and 7.41 ppm (H_B) and broadened.

Monomers (4-7) have all been synthesised with unsaturated vinyl, cyclohexenyl and norborenyl side chains (details of their characterization can be found in the Experimental section and Supporting Information). Figure 7b is an ¹H NMR spectrum of monomer (7) wherein the alkene resonance peaks of both exo and endo stereoisomers of the (norbor-5-en-1-yl)ethane side group have been resolved as a set of overlapping multiplets. The dominant exo peaks are found at 5.97 ppm and 5.72 ppm while the minor endo multiplet is seen at 5.91 ppm. Polymerization of (7) results in a polymer with a fully conjugated backbone while maintaining the functionality of an unsaturated double bond, Figure 8b. Integration of the ¹H NMR of (15) indicates that double bond remains unreacted following polymerization (the ratio of aromatic protons to those of the double bond remain 2:1 as expected).
**Figure 7:** $^1$H NMR of (a) Monomer (1) and (b) Monomer (7) (Note peak at ~5.2 ppm is the CD$_2$Cl$_2$ solvent peak)
Figure 8: $^1$H NMR of (a) PDHSF (9) and (b) PHNSF (15). Note the continued presence of alkenyl protons in polymer (15) in the region of 5.8 ppm. (Note peak at ~5.2 ppm is the CD$_2$Cl$_2$ solvent peak)

3.1.3 Electronic Properties

PSF polymers (9-15) were analysed using cyclic voltammetry in order to determine HOMO energy levels from the onset oxidation potential. A typical CV (See Supporting Info) for PDHSF (9) shows a discernible oxidative onset at 0.55 V versus Fc/Fc$^+$. Using a pseudo Ag/AgCl reference electrode and measuring the oxidation potential relative to an internal standard (Fc/Fc$^+$)
couple), we used the following equation to do determine our polymer HOMO energy levels relative to vacuum (in units of eV)\(^{[31]}\):

\[
E_{\text{HOMO}} = -(E_{\text{onset,ox vs. Fc}} + 5.1)(\text{eV})
\]  

(1.0)

PDHSF has an approximate HOMO energy of -5.65 eV inherent to the silafluorene repeat unit. Table 2 summarizes electronic and absorption data and estimates of HOMO and LUMO energies for all polymers. Not surprisingly, given the conjugated backbone for these polymers are identical, the electronic properties in Table 2 do not vary significantly. The HOMO/LUMO energy gap, \(E_g\), was determined by equating the onset of absorption to the lowest energy transition \(S_0 \rightarrow S_1\). For PDHSF, the average value obtained by this estimate was \(E_g = 3.03\) eV. Adding this value to -5.65 eV HOMO energy level places the LUMO energy at -2.62 eV. Compare these energy level values to the HOMO/LUMO energies reported for a common blue emitting polymer like poly(9,9-dioctylfluorene), PFO has a HOMO = -5.84 eV and LUMO = -2.89 eV. It is clear that previous reports of higher LUMO energies for polysilafluorenes are consistent with our values. Our PSF LUMO levels align best with low work function metals such as Ca, which could be used as cathodes in electroluminescent devices. The higher energy LUMO levels (consistent with prior reports) also suggest that PSF (9-15) may also have similar triplet levels to previously reported PSF homopolymers, making them potentially suitable as host for phosphorescent emitters.\(^{[32]}\)
**Table 2: Optoelectronic Properties of Poly(3,6-dimethoxy-9,9-dialkylsilafuorenes) (9-15)**

<table>
<thead>
<tr>
<th>Sample #</th>
<th>λ&lt;sub&gt;abs&lt;/sub&gt; (nm)</th>
<th>λ&lt;sub&gt;em&lt;/sub&gt; (nm)</th>
<th>Eg (eV)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>QY&lt;sup&gt;a&lt;/sup&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>362</td>
<td>408</td>
<td>3.03</td>
<td>-5.65</td>
<td>-2.62</td>
<td>88[82]</td>
</tr>
<tr>
<td>10</td>
<td>362</td>
<td>412</td>
<td>3.02</td>
<td>-5.70</td>
<td>-2.70</td>
<td>90[86]</td>
</tr>
<tr>
<td>11</td>
<td>360</td>
<td>415</td>
<td>3.04</td>
<td>-5.62</td>
<td>-2.58</td>
<td>86[71]</td>
</tr>
<tr>
<td>12</td>
<td>361</td>
<td>416</td>
<td>3.01</td>
<td>-5.69</td>
<td>-2.68</td>
<td>79[69]</td>
</tr>
<tr>
<td>13</td>
<td>362</td>
<td>410</td>
<td>3.02</td>
<td>-5.62</td>
<td>-2.59</td>
<td>86[75]</td>
</tr>
<tr>
<td>14</td>
<td>363</td>
<td>412</td>
<td>3.03</td>
<td>-5.61</td>
<td>-2.58</td>
<td>87[78]</td>
</tr>
<tr>
<td>15</td>
<td>362</td>
<td>410</td>
<td>3.03</td>
<td>-5.61</td>
<td>-2.58</td>
<td>87[79]</td>
</tr>
<tr>
<td>PFO</td>
<td>386</td>
<td>420</td>
<td>2.95</td>
<td>-5.84</td>
<td>-2.89</td>
<td>93[89]</td>
</tr>
</tbody>
</table>

<sup>a</sup> Brackets indicate QY values obtained for thin films.

### 3.1.4 Optical Properties

As stated earlier in the introduction, poly(3,6-dimethoxy-9,9-dialkyl-silafluorene) derivatives have high potential to surpass more popular blue emitters such as poly(9,9-dialkylfluorenes) due to several features advantageous to the development of optoelectronic devices. Such features include the narrow deep blue emission observed for both solution and thin films. In the latter case, the formation of microcrystalline phases leading to red shifted and broadened emissions (such as the well documented β-Phase formed in PFs) are not observed. The elimination of β-phase PFO has been the topic of considerable interest over the past decade as it is considered
deleterious to the materials application as a pure blue emitter in PLEDs and thin film organic lasers. As can be seen from Figure 9a, select polymers (9), (14) and (15) have nearly identical solution phase fluorescence spectra when excited at their absorption maximum, $\lambda_{\text{abs}} = 360$ nm (remaining polymers, omitted for clarity, show similar solution spectra and can be seen in Supporting Information). Additionally, Figure 9b shows that for PDHSF (9) both thin film and solution phase fluorescence are very similar. Unique spectroscopic features also include deep blue photoluminescence, $\lambda_{\text{em}} = 410$ nm, which is approximately 30 nm lower than PFO, the PL of which is included in Figure 9b for comparison. The deeper blue PL is consistent with an earlier report by Huang et al. concerning the emission characteristics of 3,6-dimethoxy-9,9-dihexylsilafluorene and 9,9-dihexylfluorene copolymers.$^{[37]}$ The authors showed that the higher the silafluorene fraction became, the more pronounced the reduction in film microcrystallinity and the more blue shifted the co-polymer emission became. The authors used Suzuki coupling to produce co-polymers, but could only achieve a maximum 50% volume fraction of silafluorene repeat units.

It is believed that due to sterics, the presence of the methoxy groups result in a slight torsion between repeat units. The resulting slight discontinuity in conjugation between neighbouring repeat units isolates emission centers resulting in the observed narrow emission bandwidths. The luminescence efficiency of each polymer, measured as an absolute quantum yield, was high ($> 80\%$ in many cases) for both toluene solutions and thin films (see Table 2). The values were calculated based on the method reported by Friend et al. using an integrating sphere, a fiber optic spectrometer and a focused $\lambda_{\text{ex}} = 365$nm LED excitation source.$^{[38,39]}$
**Figure 9:** a) Absorption and PL of select polymer solutions in toluene. Note the deep blue emission centered roughly at 410 nm for all polymers. Absorption is also consistently centered on 360 nm. b) Thin film spectra of PDHSF (9) plotted in addition to solution spectra of the same material to highlight the desirable amorphous solid state emission. A leading commercial blue emitter, PFO, was also prepared as a reference and is included in (b). Note that PFO, in addition to having a primary blue emission peak originating from its amorphous phase, has two lower energy emission peaks emanating from microcrystalline (β-phases) regions.\(^{[33-36]}\)
3.1.5 Thermal Properties

Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) were used to study polymer thermal stability and observe possible phase transitions occurring in films as function of temperature. Figure 10 shows that selected TGA for polymers (10) and (15). All polymers show relatively high thermal stability with a minimal percentage loss of their initial mass over the range of 25-300°C. As shown for (10) and (15), polymers decompose rapidly under nitrogen, however, after temperatures exceed 360°C. We attribute the 11.5% weight change observed for samples of PHNSF (15) beginning at 269°C to the elimination of cyclopentadiene (Cp) via a retro Diels-Alder rearrangement.[25,26] Cp contributes roughly 14% to the repeat units total mass.

PFO, being a popular blue emitting polymer, is a meaningful standard with which to compare the thermal stability of our polymers. The onset temperature of PFO decomposition is approximately the same as its PDOSF (10) silafluorene analog. At temperatures exceeding 600°C, both (10) and (15) have lost 50% of their initial mass whereas PFO has lost closer to 60%. Hence, despite the replacement of the apical carbon with silicon, poly(3,6-dimethoxy-9,9-dialkylsilafuorenes) have no greater tendency to thermally degrade.

Investigation of phase transitions using DSC yielded additional surprising results. PSFs (9-15) show no discernable $T_g$ nor $T_m$/$T_c$ transitions despite multiple attempts at heating and cooling within a temperature window known to induce phase transitions in PFO (e.g. between 50-250°C).[40] The relevant DSC data for each of our polymers (9-15) is provided in the Supporting Information. From these results we can conclude that solid polymer product is initially amorphous following purification and drying. Increasing temperatures up to 250°C does not induce a glass transition nor do any exo/endothermic peaks appear indicating crystallization or melting of crystalline phases. The sample proceeds to decompose at more elevated
temperatures. We interpret these results as further evidence of inherently disordered, dissociative chains unable to crystallize due to torsional strain induced by steric crowding of methoxy groups and neighboring aryl protons.

![Graph showing thermal analysis of PDHSF (10), PHNSF (15) and PFO under nitrogen with a temperature ramp rate of 10°C/min.]

**Figure 10**: Thermal analysis of PDHSF (10), PHNSF (15) and PFO under nitrogen with a temperature ramp rate of 10°C/min.

### 3.2 Conclusion

Among the most notable properties of the poly(3,6-dimethoxy-9,9-dialkylsilafluorenes) produced as part of this study, we consider the narrow blue/violet emission the most appealing with regards to the use of these materials in optoelectronic devices such as polymer LEDs. We attribute this phenomenon to the structure of the repeat unit, specifically the presence of methoxy substituents which causes a slight torsion between silafluorene moieties. The result is the absence of a microcrystalline phase (analogous to the β-phase found in PFO thin films) as well as solution-like solid phase luminescence without undesirable higher wavelength emissions.

Polymers (9-15) are all soluble in common organic solvents (CHCl$_2$, Toluene, THF etc.) and can be easily processed into highly transparent thin films. Due to the slightly blue shifted
absorption of poly(3,6-dimethoxy-9,9-dialkylsilafuorenes) ($\lambda_{\text{abs}} = 360$ nm) versus poly(9,9-dialkylfluorenes) ($\lambda_{\text{abs}} = 393$ nm), we find spin cast films of the former material are almost undetectable whereas versus poly(9,9-dialkylfluorenes) films have a characteristic yellow hue. While such colouration is not deleterious to the performance of PLEDs, the desire for higher optical transparency offered by poly(3,6-dimethoxy-9,9-dialkylsilafuorenes) may arise as the demand for transparent displays increases in the years to come. Future work will focus on utilizing PSFs as emitters in solution process light emitting devices. The amorphous nature of thin films of our polymers, reminiscent of low threshold binaphol co-polymers of PFO$^{[41,42]}$, also make them ideal candidates for organic lasers. The emission and electronic properties of these polymers make them promising hosts for higher wavelength emitting dopants. Although not explored in this report, the presence of side chains with synthetically useful functional groups such as unsaturated double bonds (especially in the case of norbornenyl containing PHNSF (15)) allows a plethora of reactions to be exploited for the purpose of chain functionalization. For example, crosslinking via the double bonds of polymers (4-7) may provide an advantageous route to constructing multilayered OLEDs for white light emitting devices without need for orthogonal solvent methods.$^{[41,42]}$ Additionally, photocrosslinking in combination with a photomask may be used to produce photopatterned areas of electroluminescent polymer on pre-patterned conductive substrates to ultimately produce a pixelated LED using roll-to-roll processing.

3.3 Experimental Section

All syntheses were performed under inert atmosphere using standard Schlenk line or glovebox techniques unless otherwise stated. Chemicals were purchased from TCI America and Sigma Aldrich and used without need for further purification. Tetrahydrofuran and 1,4-Dioxane were
distilled over sodium/benzophenone prior to use. Proton, carbon and silicon NMR were performed on a 400 MHz Bruker Avance III Spectrometer. Single crystal x-ray structures were obtained from a Bruker Kappa Apex II spectrometer on crystals grown via slow evaporation from a THF solution. Solution and thin film absorption and photoluminescence spectra were recorded using a Perkin-Elmer 900 UV-Vis Spectrometer and a Perkin-Elmer LS-50B Luminescence Spectrophotometer. Polymer absolute quantum efficiencies were calculated through the use of an integrating sphere using a focused 365 nm LED (Thor Labs) as the excitation source. Polymer molecular weights were measured with a Viscotek GPC calibrated with respect to polystyrene standards using THF as an eluent and column temperature of 35°C. Cyclic voltammetry was performed on polymer samples in a solution of 100mM tetrabutylammonium hexafluorophosphate in dichloromethane (distilled from CaH2 under N2 prior to measurement). Potentials were measured using a Solartron 1278 potentiostat using platinum working and counter electrodes in addition to a Ag/AgCl pseudo reference electrode. Measurements were calibrated using ferrocene as an internal standard. Thermogravimetric and calorimetric data was acquired using a TA Instruments SDT Q600 simultaneous TGA/DSC system operated under an inert N2 atmosphere. Protons and carbons are labeled according to the scheme present above each compound’s respective spectra in the supporting information.

### 3.3.1 Monomer Synthesis

4,4'-dibromo-3,3'-dimethoxy-1,1'-biphenyl (17):

The synthesis of (17) is adapted from the Sandmeyer reaction outlined by Huang et al.\textsuperscript{[43]} o-dianisidine is oxidized to its diazonium salt and reacted with a bromide source to eliminate N2 and generate the appropriate aryl dibromide. 10.0g (40 mmol) o-dianisidine is combined with 40 mL 40% HBr, 160 mL H2O and 160 mL acetonitrile in a large three necked flasked equipped
with a thermometer, dropping funnel and efficient stirring. The majority of the starting material is dissolved in acetonitrile. The reaction is cooled to 0°C in ice/salt bath and 7.2 g (104.4 mmol) sodium nitrite, dissolved in 14 mL water is chilled and added dropwise to the reaction such that the temperature does not rise above 10°C. Following addition, the reaction is stirred a reduced temperature for 30 min. Meanwhile, freshly prepared CuBr is obtained by precipitation of CuNO₃ and NaBr in water.[44] The white precipitate is collected by filtration and dry in a vacuum oven prior to use. 13.0 g (90.6 mmol) CuBr is dissolved in aqueous 160 mL 40% HBr and added to the thoroughly rinsed dropping funnel. Glass tubing is used to extend the stem of the dropping funnel below the surface of the solution to prevent side reaction with atmospheric O₂. CuBr/HBr is added slowly, maintaining a temperature less than 10°C, over the course of 1 hr. The solution is then allowed to warm to room temperature and is subsequently heated to reflux (80°C) for 1 hr until an insoluble white solid becomes apparent. The solution is then cooled and extracted with 250-300 mL chloroform, washed with 10 wt% NaOH and brine, and finally dried with MgSO₄ before removing solvent by rotoevaporation. The crude, light brown powder is sufficiently pure to proceed to the next step. Yield is 13 g or 90%. ¹H-NMR (CD₂Cl₂, 400 MHz) (ppm): 7.53 (H_B, d, 2H; ³J_B,C = 7.9 Hz), 6.96 (H_A, s, 2H), 6.95 (H_C, dd, 2H; ³J_C,B = 9.8 Hz, ⁴J_C,A = 1.8 Hz), 3.10 (-OCH₃, s, 6H) ¹³C-NMR (CD₂Cl₂, 400 MHz) (ppm): 156.19 (C₃), 141.35 (C₁), 133.56 (C₃), 120.59 (C₆), 111.38 (C₄), 110.87 (C₂), 56.35 (-OCH₃). EI-MS (M⁺) = 369.9204 m/z (calc: 369.9213). MP = 140-143°C

4,4'-dibromo-2,2'-diiodo-5,5'-dimethoxy-1,1'-biphenyl (18):

Selective iodination at the 2 and 2' is directed by para substituted methoxy groups. 13.0g (34.9 mmol) (17), 3.3 g (15.4 mmol) KIO₃ and 9.6 g (38.0 mmol) I₂ are added to a large three neck flask equipped with a reflux condenser. The starting material is dissolved in a mixture of 260
mL acetic acid and 26 mL 20 wt% H2SO4. The solution is heated to 80°C for 12 h. Large amounts of insoluble product precipitate as the reaction proceeds. Once cooled to room temperature, an additional 250 mL of H2O is added to precipitate further product. The precipitate is collected by filtration, dried briefly under vacuum and redissolved in the minimum amount of CHCl3 (~200 mL). The solution is extracted with 10wt% NaOH, washed with brine, and finally dried with MgSO4 before removing the solvent by rotoevaporation. The crude product is then purified by recrystallization from boiling 95% ethanol (~45 mL EtOH/g of crude product). The resulting brown needle like crystals are collected by filtration and rigorously dried in a vacuum oven prior to being used in the following step. The yield of purified product following the first recrystallization is 12.4 g or 56%. Yield can be improved to 84 % by concentrating the supernatant cooling to produce another crop of crystals. 1H-NMR (CD2Cl2, 400 MHz) (ppm): 7.98 (H B, s, 2H), 6.66 (H A, s, 2H), 3.81 (-OCH3, s, 6H). 13C-NMR (CD2Cl2, 400 MHz) (ppm): 156.14 (C5), 148.16 (C1), 142.08 (C3), 113.30 (C6), 112.45 (C4), 87.56 (C2), 56.49 (-OCH3).

EI-MS (M+) = 621.7137 m/z (calc:621.7141). MP = 147-150°C

2-(cyclohex-3-en-1-yl)ethyl(hexyl)dichlorosilane (20):

5.46 mL (31.0 mmol) of 4-vinyl-1-cyclohexene was combined with 3.8 mL (21 mmol) n-hexyl dichlorosilane in 20 mL dry toluene. 0.63 mL (0.3 mol%) of 0.1M H2PtCl6 in THF was added to initiate the reaction. The reaction was heated at 60°C for 6 h. The unconsumed starting materials are removed by collecting all distillate at a bath temperature of 150°C under argon. The final clear product was collected under vacuum at 175°C at 1 mTorr. The yield of product was 5.04 mL (5.1g, d = 1.01 g/mL) or 83%. 1H-NMR (CD2Cl2, 400 MHz) (ppm): 5.60-5.47 (H A+B, m, 2H), 1.90 (H E/E', m, 2H), 1.83 (H D, m, 1H), 1.16-0.8 (H F/F', H C/C', Hexyl, Ethylene, m, 21H). 13C-NMR (CD2Cl2, 400 MHz) (ppm): 127.27 (C1), 126.88 (C2), 38.83 (C4), 36.33 (C3),
33.05 (C12), 31.23 (C11), 30.68 (C5), 28.59 (C7), 25.58 (C8), 24.76 (C9), 22.90 (C13), 14.57 (C14), 12.75 (C10), 9.06 (C6). $^{29}$Si-NMR (CD$_2$Cl$_2$, 400 MHz) (ppm): 30.44.

2-(Bicyclohept-5-en-2-yl)ethyl(hexyl)dichlorosilane (21):

4.5 mL (31.5 mmol) of 5-vinyl-2-norbornene (mixture of endo/exo isomers) was combined with 3.8 mL (21.0 mmol) n-hexyldichlorosilane in a 100 mL schlenk flask and dissolved in 20 mL dry toluene. 0.63 mL of 0.1 M H$_2$PtCl$_6$ (0.3 mol% Pt with respect to silane) in THF was added to initiate hydrosilylation. The reaction was heated to 60°C under argon for 6 h. Once cooled, the reaction flask was added to a vacuum distillation apparatus. The unconsumed starting materials are removed by collecting all distillate transferred at a bath temperature of 150°C under argon. After replacing the collection flask, the system is placed under vacuum. After insuring a good seal and well insulated still head, the bath temperature was increased to 110°C and a clear product is collected at 109 mTorr. The yield of product was 5.33 mL (5.5 g, d = 1.03 g/mL) or 85%. $^1$H-NMR (CD$_2$Cl$_2$, 400 MHz) (ppm): 6.05 (H$_C'$, dd, 1H, exo; $^3$J$_{C',C}$ = 5.8 Hz, $^3$J$_{C',D'}$ = 3.1 Hz), 6.01 (H$_C'$, dd, 1H, endo; $^3$J$_{C',C}$ = 5.9 Hz, $^3$J$_{C',D'}$ = 3.1 Hz), 5.95 (H$_C$, dd, 1H, endo; $^3$J$_{C,C'}$ = 5.9 Hz, $^3$J$_{C,D'}$ = 3.1 Hz), 5.84 (H$_C$, dd, 1H, exo; $^3$J$_{C',C}$ = 5.8 Hz, $^3$J$_{C',D'}$ = 3.1 Hz), 2.72 (H$_D$, m, 1H, exo), 2.68 (H$_D'$, m, 1H, exo), 2.52 (H$_E$, m, 1H, endo), 2.46 (H$_E$+H$_F$, m, 2H, endo), 2.29 (H$_G$, m, 1H, endo), 1.93 (H$_E$, m, 1H, exo), 1.79 (H$_E$+H$_F$, m, 2H, exo), 1.40 (H$_G$, m, 1H, exo), 1.35-0.70 (Hexyl+Ethylene, m, 17H), 0.42 (H$_F$, ddd, 1H, exo; $^3$J$_{F,F'}$ = 11.4 Hz, $^3$J$_{F,G}$ = 4.3 Hz, $^3$J$_{F,D'}$ = 2.6 Hz). $^{13}$C-NMR (CD$_2$Cl$_2$, 400 MHz) (ppm): 142.50 (C1, endo), 137.72 (C2, exo), 136.81 (C2, endo), 132.22 (C1), 49.89 (C9), 45.78 (C5), 43.06 (C3), 41.78 (C7), 37.92 (C4), 36.08 (C6), 32.42 (C13), 29.11 (C12), 27.40 (C8), 22.83 (C10), 20.53 (C14), 19.75 (C15), 14.27 (C11). $^{29}$Si-NMR (CD$_2$Cl$_2$, 400 MHz) (ppm): 34.03.
2,7-dibromo-3,6-dimethoxy-9,9-dihexylsilafluorene, DHSF (1):

Selective lithiation of the iodide substituents in (18) is achieved at low temperature by use of -110°C MeOH/N₂ slush bath. 4.0 g (6.41 mmol) (18) is dissolved in 60 mL dry THF in a schlenk flask under Ar. The solution is cooled and 8.07 mL (12.9 mmol) n-BuLi (1.6M in hexanes) is added dropwise over 30 min. It should be noted that over the course of the lithiation, a yellow, insoluble monolithiated intermediate forms and an appropriately large stir bar is required to agitate the thick slurry. Continued addition of n-BuLi redissolves the intermediate and the clear solution is stirred for an addition 30 min at reduced temperature. 1.96 mL (1.89g, 7.1 mmol) of Di-n-hexyldichlorosilane is injected into the solution and the flask is allowed to warm to room temperature and stir for 10 h. The reaction is quenched by the addition of water and the product is extracted with ether. The organic phase is washed with brine and dried with MgSO₄ before solvent removal by rotoevaporation. The crude flaky crystals are purified by recrystallization in ~200 mL boiling 95% ethanol. Following cooling in an ice bath, the pure beige flaky crystals are filtered and dried rigorously in vacuo prior to use in polymerization. Yield of the first crystallization is usually 2.1 g or 57%. Yield increases to 84% with the collection of a second crop of crystals. It should be noted that all silafluorenes (1-7) were prepared according to the above procedure by substituting the di-n-hexyldichlorosilane for the appropriate RR’SiCl₂. Note all silanes were commercially available, with the exception of (20) and (21). ¹H-NMR (CD₂Cl₂, 400 MHz) (ppm): 7.63 (H₇, s, 2H), 7.24 (H₆, s, 2H), 3.93 (-OCH₃, s, 6H), 1.16-1.13 (hexyl, 26H). ¹³C-NMR (CD₂Cl₂, 400 MHz) (ppm): 157.86 (C₃), 148.77 (C₅), 137.63 (C₁), 131.49 (C₆), 111.93 (C₂), 105.23 (C₄), 56.45 (-OCH₃), 33.17 (9), 31.54 (C₁₀), 23.92 (C₈), 22.72 (C₁₁), 14.02 (C₇), 12.40 (C₁₂). EI-MS (M⁺) = 566.0861 m/z (calc: 566.0851). MP = 153-156°C.
2,7-dibromo-3,6-dimethoxy-9,9-dioctylsilafluorene, DOSF (2):

\(^1\)H-NMR (CD\(_2\)Cl\(_2\), 400 MHz) (ppm): 7.62 (H\(_B\), s, 2H), 7.23 (H\(_A\), s, 2H), 3.91 (-OCH\(_3\), s, 6H), 1.15-1.09 (Octyl, m, 34H). \(^{13}\)C-NMR (CD\(_2\)Cl\(_2\), 400 MHz) (ppm): 158.05 (C3), 149.05 (C5), 137.85 (C1), 131.70 (C6), 112.16 (C2), 105.38 (C4), 56.63 (-OCH\(_3\)), 33.62 (C9), 32.20 (C12), 29.51 (C10), 29.50 (C11), 24.23 (C8), 23.20 (C13), 14.33 (C7), 12.66 (C14). EI-MS (M\(^+\)) = 622.1486 m/z (calc: 622.1477). MP = 151-154°C.

2,7-dibromo-3,6-dimethoxy-9,9-dimethylsilafluorene, DMSF (3):

\(^1\)H-NMR (CD\(_2\)Cl\(_2\), 400 MHz) (ppm): 7.65 (H\(_B\), s, 2H), 7.23 (H\(_A\), s, 2H), 3.93 (-OCH\(_3\), s, 6H), 0.30 (-CH\(_3\), s, 6H). \(^{13}\)C-NMR (CD\(_2\)Cl\(_2\), 400 MHz) (ppm): 158.17 (C3), 148.44 (C5), 137.52 (C1), 132.88 (C6), 112.39 (C2), 105.27 (C4), 56.73 (-OCH\(_3\)), 3.14 (-CH\(_3\)). EI-MS (M\(^+\)) = 425.9296 m/z (calc: 425.9286). MP = 211-215°C.

2,7-dibromo-3,6-dimethoxy-9,9-methylvinylsilafluorene, MVSF (4):

\(^1\)H-NMR (CD\(_2\)Cl\(_2\), 400 MHz) (ppm): 7.64 (H\(_B\), s, 2H), 7.20 (H\(_A\), s, 2H), 3.93 (-OCH\(_3\), s, 6H), 6.15 (H\(_C\)+D, dd, 1H; \(^3\)J\(_C\)+D = 14.1 Hz, \(^3\)J\(_C\)+C = 1.2 Hz), 6.14 (H\(_C\), dd, 1H; \(^3\)J\(_C\)+D = 12.3 Hz, \(^3\)J\(_C\)+C = 1.2 Hz), 5.93 (H\(_D\), dd, 1H; \(^3\)J\(_D\)+C = 14.1 Hz, \(^3\)J\(_D\)+D = 12.3 Hz), 3.96 (-OCH\(_3\), s, 6H), 2.10 (-CH\(_3\), s, 3H). \(^{13}\)C-NMR (CD\(_2\)Cl\(_2\), 400 MHz) (ppm): 157.99 (C3), 148.33 (C5), 137.52 (C1), 135.91 (C8), 133.43 (C6), 130.79 (C7), 112.22 (C2), 104.93 (C4), 56.23 (-OCH\(_3\)), -5.75 (-CH\(_3\)). EI-MS (M\(^+\)) = 437.92883 m/z (calc: 437.9286). MP = 175-180°C.

2,7-dibromo-3,6-dimethoxy-9-methyl-9-[2-(cyclohex-3-en-1-yl)ethyl]silafluorene, MCySF (5):

\(^1\)H-NMR (CD\(_2\)Cl\(_2\), 400 MHz) (ppm): 7.71 (HB, s, 2H), 7.27 (HA, s, 2H), 5.63 (HC+D, m, 2H), 4.03 (-OCH\(_3\), s, 6H), 2.21-1.91 (H\(_G\)+G', m, 3H), 1.8-0.8 (Hexyl, H\(_E\)+E'+H'H', m, 17H) 0.38 (-CH\(_3\), s, 3H). \(^{13}\)C-NMR (CD\(_2\)Cl\(_2\), 400 MHz) (ppm): 157.75 (C3), 148.13 (C5), 137.19 (C1), 131.65 (C6), 155
127.13 (C7), 126.54 (C8), 112.11 (C2), 104.81 (C4), 56.39 (-OCH3), 36.56 (C10), 35.53 (C9), 31.45 (C13), 30.43 (C11), 12.93 (C14), 11.03 (C12), -5.01 (-CH3). EI-MS (M+) = 522.0056 m/z (calc: 522.00484). MP = 143-146°C.

2,7-dibromo-3,6-dimethoxy-9-hexyl-9-[2-(cyclohex-3-en-1-yl)ethyl]silafluorene, HCySF (6):

$^1$H-NMR (CD$_2$Cl$_2$, 400 MHz) (ppm): 7.63 (H$_B$, s, 2H), 7.24 (H$_A$, s, 2H), 5.53 (H$_{C+D}$, m, 2H), 3.93 (-OCH$_3$, s, 6H), 1.96 (H$_{G/G'}$, m, 2H), 1.86 (H$_F$, m, 2H), 1.81-0.71 (Hexyl, H$_{E/E'+H/H'}$, m, 17H).

$^{13}$C-NMR (CD$_2$Cl$_2$, 400 MHz) (ppm): 158.12 (C3), 149.03 (C5), 137.81 (C1), 131.88 (C6), 127.53 (C7), 126.88 (C8), 112.11 (C2), 105.52 (C4), 56.61 (-OCH$_3$), 38.28 (C10), 36.83 (C9), 33.40 (C18), 31.82 (C17), 30.77 (C11), 28.66 (C13), 25.76 (C14), 24.18 (15), 22.99 (C19), 14.16 (C20), 12.57 (C16), 9.81 (C15). EI-MS (M+) = 592.47795 m/z (calc: 592.47774). MP = 140-145°C.

2,7-dibromo-3,6-dimethoxy-9-hexyl-9-[2-(Bicyclohept-5-en-2-yl)ethyl]silafluorene, HNSF (7):

$^1$H-NMR (CD$_2$Cl$_2$, 400 MHz) (ppm): 7.62 (H$_B$, s, 2H), 7.23 (HA, s, 2H), 6.07 (H$_C'$, dd, 1H, exo; $^3$J$_{C',C} = 5.8$ Hz, $^3$J$_{C',D'} = 3.1$ Hz), 6.01 (H$_C'$, dd, 1H, endo; $^3$J$_{C',C} = 5.8$ Hz, $^3$J$_{C',D'} = 3.0$ Hz), 5.96 (H$_C$, dd, 1H, endo; $^3$J$_{C,C'} = 5.9$ Hz, $^3$J$_{C,D'} = 3.0$ Hz), 5.81 (H$_C$, dd, 1H, exo; $^3$J$_{C',C} = 5.9$ Hz, $^3$J$_{C',D'} = 3.0$ Hz), 4.02 (-OCH$_3$, s, 6H), 2.72 (H$_D$, m, 1H, exo), 2.68 (H$_{D'}$, m, 1H, exo), 2.52 (H$_E'$, m, 1H, endo), 2.46 (H$_{E+E'+F'}$, m, 2H, endo), 2.29 (H$_G$, m, 1H, endo), 1.89 (H$_{E'}$, m, 1H, exo), 1.77 (H$_{E/E'+F/F'}$, m, 2H, exo), 1.34 (H$_G$, m, 1H, exo), 1.35-0.70 (Hexyl+Ethylene, m, 17H), 0.41 (H$_F$, ddd, 1H, exo; $^3$J$_{F,F'} = 11.4$ Hz, $^3$J$_{F,G} = 4.3$ Hz, $^3$J$_{F,D'} = 2.6$ Hz). $^{13}$C-NMR (CD$_2$Cl$_2$, 400 MHz) (ppm): 158.11 (C3), 148.94 (C5), 137.79 (C1), 137.12 (C8), 131.61 (C7), 130.28 (C6) 112.07 (C2), 105.37 (C4), 56.60 (-OCH$_3$), 49.79 (C15), 45.19 (C11), 42.96 (C9), 42.57 (C13), 33.39
(C19), 32.58 (C18), 31.68 (C10), 28.93 (C14), 24.21 (C20), 22.90 (C11), 14.23 (C17), 12.54 (C12), 11.62 (C16). EI-MS (M+) = 602.08645 m/z (calc: 602.08513). MP = 149-153°C.

3.3.2 Polymer Synthesis

**Preparation of Diarylmagnesate of (1):**

The following protocol can be used for any dibromo monomer (1-7). The room temperature Grignard metathesis of 2,7-dibromo-9,9-di(n-hexyl)silafluorene (1) was performed in a N₂ filled glovebox within a 5 mL scintillation vial. A 0.5 M solution of (1) was prepared using THF as a solvent. Additionally, a Grignard solution of isopropyl magnesium chloride (1.3 M in THF) activated by 1.0 equivalence of LiCl was prepared and used following 1 h of stirring to allow for the complete dissolution of the salt. The Grignard solution could be stored and used for several days in the glovebox without appreciable change. In a typical experiment, 2.0 mL (1.0 mmol) of 0.5 M (1) solution is diluted with 1.2 mL 1,4-dioxane and stirred rapidly. 510 µL of 1.3 M iPrMgCl·LiCl (0.66 mmol) was added by a single injection. The formation of insoluble white MgCl₂-Diox adduct is observed almost immediately. The solution is stirred continuously for 2 h to complete the in situ generation of diarylmagnesate. The white MgCl₂-Diox precipitate is allowed to settle, and the clear pale yellow solution is separated. The solution can be stored for several hours, but largely decomposes to oligomeric products after a period or 24 h. ¹H NMR confirms the quantitative conversion of 66% of starting material to diarylmagnesate (and the absence of digrignard impurities). The single methoxy peak at 3.93 ppm in the starting material becomes two distinct peaks at 3.91 ppm and 3.80 ppm when a small aliquot of the reaction is quenched with MeOH. The integration of these peaks can be an accurate way of determining the completeness of the metathesis and hence the relative ratio of the monomer to starting material (and digrignard).
Preparation of Poly(3,6-dimethoxy-9,9-dihexylsilafluorene) (PDHSF) (9):
The following represents a typical protocol for polymerization. Any of the dibromo monomers (1-7) can be successfully substituted into the steps below. For maximum molecular weight, Grignard exchange is limited to 66% as per the procedure described above. 2.0 mL of the above prepared solution, where [M] = 88 mM was used. Polymerization is initiated by 1.5 mg or 0.8 mol% dppeNiCl₂ (such that 2[M]/[Ni] = 120. The solution immediately becomes yellow-orange and is stirred continuously for 20-30 m. As the polymerization progresses, additional MgBr₂-Diox precipitate is formed and the solution becomes steadily more opaque and viscous. The vial is removed from the glovebox and polymerization quenched by adding several drops of 5.0 M HCl and followed by adding the solution dropwise to a large excess of methanol such that product precipitates as a fiberous white solid. The polymer is collected by suction filtration. For removal of residual monomer and oligomer, the crude polymer was soxhlet extraction with ethanol for 4 - 5 h. The polymer solid is characterized by GPC, ¹H NMR. Optical properties where studied by collecting solution and solid state absorption and fluorescence spectra in addition to absolute quantum yield. The yield of purified polymer is 75%, Mₙ = 42.3 kg/mol (PDI = 1.6). ¹H-NMR (CD₂Cl₂, 400 MHz) (ppm): 7.47 (H_B, s, 2H), 7.42 (H_A, s, 2H), 3.91 (-OCH₃, s, 6H), 1.37-0.77 (Hexyl, 26H).

Poly(3,6-dimethoxy-9,9-dioctylsilafluorene) (PDOSF) (10):
¹H-NMR (CD₂Cl₂, 400 MHz) (ppm): 7.56 (H_B, s, 2H), 7.50 (H_A, s, 2H), 4.00 (-OCH₃, s, 6H), 1.53-0.86 (Octyl, m, 34H).

Poly(3,6-dimethoxy-9,9-dimethylsilafluorene) (PDMSF) (11):
¹H-NMR (CD₂Cl₂, 400 MHz) (ppm): ¹H-NMR (CD₂Cl₂, 400 MHz) (ppm): 7.24 (H_B, s, 2H), 7.21 (H_A, s, 2H), 3.92 (-OCH₃, s, 6H), 0.40 (-CH₃, s, 6H).
Poly(3,6-dimethoxy-9,9-methylvinylsilafluorene) (PMVSF) (12):
1H-NMR (CD2Cl2, 400 MHz) (ppm): 7.24 (H_B, s, 2H), 7.22 (H_A, s, 2H), 6.07-5.85 (H_C'/C+D, m, 3H), 3.94 (-OCH3, s, 6H), 0.60-0.00 (-CH3, s, 3H).

Poly(3,6-dimethoxy-9-methyl-9-[2-(cyclohex-3-en-1-yl)ethyl]-silafluorene) (PMCySF) (13):
1H-NMR (CD2Cl2, 400 MHz) (ppm): 7.57 (H_B, s, 2H), 7.46 (H_A, s, 2H), 5.64 (H_C+D, m, 2H), 3.97 (-OCH3, s, 6H), 2.00-0.45 (Cy + Ethylene, m, 11H), 0.11 (-CH3, s, 3H)

Poly(3,6-dimethoxy-9-hexyl-9-[2-(cyclohex-3-en-1-yl)ethyl]-silafluorene) (PHCySF) (14):
1H-NMR (CD2Cl2, 400 MHz) (ppm): 7.48 (H_B, s, 2H), 7.42 (H_A, s, 2H), 5.55 (H_C+D, m, 2H), 3.91 (-OCH3, s, 6H), 2.22-0.77 (Cy+Ethylene+Hexyl, m, 24H).

1H-NMR (CD2Cl2, 400 MHz) (ppm): 7.45 (H_B, s, 2H), 7.44 (H_A, s, 2H), 6.1-5.81 (H_C+C', m, 2H), 3.91 (-OCH3, s, 6H), 2.73 (H_D, s, 1H), 2.64 (H_D', s, 1H), 1.89-0.60 (Hexyl, NB, Ethylene, m, 20H), 0.41 (H_F/F', m, 2H).

3.4 References


Supporting Information 2

Pure Blue Emitting Poly(3,6-dimethoxy-9,9-dialkylsilafluorenes) Prepared Via Nickel Catalyzed Cross-Coupling of Diarylmagnesate Monomers

Contents:

Section 1: $^1$H/$^{13}$C NMR of Intermediate Compounds, Monomers (1-7) and Polymer (9-15)

S1.1.0 – 4,4'-dibromo-3,3'-dimethoxy-1,1'-biphenyl (17) $^1$H-NMR

S1.1.1 – 4,4'-dibromo-3,3'-dimethoxy-1,1'-biphenyl (17) $^{13}$C-NMR

S1.2.0 – 4,4'-dibromo-2,2'-diiodo-5,5'-dimethoxy-1,1'-biphenyl (18) $^1$H-NMR

S1.2.1 – 4,4'-dibromo-2,2'-diiodo-5,5'-dimethoxy-1,1'-biphenyl (18) $^{13}$C-NMR

S1.3.0 – 2-(cyclohex-3-en-1-yl)ethyl(hexyl)dichlorosilane (20) $^1$H-NMR

S1.3.1 – 2-(cyclohex-3-en-1-yl)ethyl(hexyl)dichlorosilane (20) $^{13}$C-NMR

S1.3.2 – 2-(cyclohex-3-en-1-yl)ethyl(hexyl)dichlorosilane (20) $^{29}$Si-NMR

S1.4.0 – 2-(Bicyclohept-5-en-2-yl)ethyl(hexyl)dichlorosilane (21) $^1$H-NMR

S1.4.1 – 2-(Bicyclohept-5-en-2-yl)ethyl(hexyl)dichlorosilane (21) $^{13}$C-NMR

S1.4.2 – 2-(Bicyclohept-5-en-2-yl)ethyl(hexyl)dichlorosilane (21) $^{29}$Si-NMR

S1.5.0 – 2,7-dibromo-3,6-dimethoxy-9,9-dihexylsilafluorene (1) $^1$H-NMR

S1.5.1 – 2,7-dibromo-3,6-dimethoxy-9,9-dihexylsilafluorene (1) $^{13}$C-NMR

S1.6.0 – 2,7-dibromo-3,6-dimethoxy-9,9-diophtalsilafluorene (2) $^1$H-NMR

S1.6.1 – 2,7-dibromo-3,6-dimethoxy-9,9-diophtalsilafluorene (2) $^{13}$C-NMR
S1.7.0 – 2,7-dibromo-3,6-dimethoxy-9,9-dimethylsilafluorene (3) $^1$H-NMR

S1.7.1 – 2,7-dibromo-3,6-dimethoxy-9,9-dimethylsilafluorene (3) $^{13}$C-NMR

S1.8.0 – 2,7-dibromo-3,6-dimethoxy-9,9-methylvinylsilafluorene (4) $^1$H-NMR

S1.8.1 – 2,7-dibromo-3,6-dimethoxy-9,9-methylvinylsilafluorene (4) $^{13}$C-NMR

S1.9.0 – 2,7-dibromo-3,6-dimethoxy-9-methyl-9-[2-(cyclohex-3-en-1-yl)ethyl]silafluorene (5) $^1$H-NMR

S1.9.1 – 2,7-dibromo-3,6-dimethoxy-9-methyl-9-[2-(cyclohex-3-en-1-yl)ethyl]silafluorene (5) $^{13}$C-NMR

S1.10.0 – 2,7-dibromo-3,6-dimethoxy-9-hexyl-9-[2-(cyclohex-3-en-1-yl)ethyl]silafluorene (6) $^1$H-NMR

S1.10.1 – 2,7-dibromo-3,6-dimethoxy-9-hexyl-9-[2-(cyclohex-3-en-1-yl)ethyl]silafluorene (6) $^{13}$C-NMR

S1.11.0 – 2,7-dibromo-3,6-dimethoxy-9-hexyl-9-[2-(Bicyclohept-5-en-2-yl)ethyl]silafluorene (7) $^1$H-NMR

S1.11.1 – 2,7-dibromo-3,6-dimethoxy-9-hexyl-9-[2-(Bicyclohept-5-en-2-yl)ethyl]silafluorene (7) $^{13}$C-NMR

S1.12.0 – Poly(3,6-dimethoxy-9,9-dihexylsilafluorene) (PDHSF) (9) $^1$H-NMR

S1.13.0 – Poly(3,6-dimethoxy-9,9-dioctylsilafluorene) (PDOSF) (10) $^1$H-NMR

S1.14.0 – Poly(3,6-dimethoxy-9,9-dimethylsilafluorene) (PDMSF) (11) $^1$H-NMR

S1.15.0 – Poly(3,6-dimethoxy-9,9-methylvinylsilafluorene) (PMVSF) (12) $^1$H-NMR

S1.16.0 – Poly(3,6-dimethoxy-9-methyl-9-[2-(cyclohex-3-en-1-yl)ethyl]silafluorene) (PMCySF) (13) $^1$H-NMR
S1.17.0 – Poly(3,6-dimethoxy-9-hexyl-9-[2-(cyclohex-3-en-1-yl)ethyl]-silafuorene) (PHCySF) (14) 1H-NMR

S1.18.0 – Poly(3,6-dimethoxy-9-hexyl-9-[2-(Bicyclohept-5-en-2-yl)ethyl]silafuorene) (PHNSF) (15) 1H-NMR

S1.19.0 – Partial Grignard Metathesis of Monomer (9) (66% Conversion, MeOH Quenched) 1H-NMR

S1.19.1 – Grignard Metathesis of Monomer (9) (90% Conversion, MeOH Quenched) 1H-NMR

Section 2: Optoelectronic Polymer Properties

S2.1—Complete Solution Phase Absorption and Photoluminescence Spectra (Normalized)

S2.2-- Complete Solid Phase Photoluminescence Spectra (Normalized)

S2.3—Complete Set of Cyclic Voltammograms for polymers (9-15)

S2.3.1— PDHSF (9) (Solutions in DCM with 120mM TBAPF 6)

S2.3.2— (PDOSF) (10) (Solutions in DCM with 120mM TBAPF 6)

S2.3.3— (PDMSF) (11) (Solutions in DCM with 120mM TBAPF 6)

S2.3.4— (PMVSF) (12) (Solutions in DCM with 120mM TBAPF 6)

S2.3.5— (PMCySF) (13) (Solutions in DCM with 120mM TBAPF 6)

S2.3.6— (PHCySF) (14) (Solutions in DCM with 120mM TBAPF 6)

S2.3.7— (PHNSF) (15) (Solutions in DCM with 120mM TBAPF 6)

S2.4— TGA/DSC curves

S2.4.1— TGA/DSC (PDOSF) (10)

S2.4.2— TGA/DSC (PDMSF) (11)
S2.4.3 — TGA/DSC (PMVSF) (12)

S2.4.4 — TGA/DSC (PMCySF) (13)

S2.4.5 — TGA/DSC (PHCySF) (14)

S2.4.6 — TGA/DSC (PHNSF) (15)

S2.4.7 — EI-MS of HNSF (7) showing retro Diels-Alder fracturing of the norbornenyl group
Pure Blue Emitting Poly(3,6-dimethoxy-9,9-dialkylsilafluorenes)  
McDowell, J.

S1.1.0 – 4,4'-dibromo-3,3'-dimethoxy-1,1'-biphenyl (17) $^1$H-NMR

$J_{R,C} = 7.96$ Hz

S1.1.1 – 4,4'-dibromo-3,3'-dimethoxy-1,1'-biphenyl (17) $^{13}$C-NMR

S1.1.1 – 4,4'-dibromo-3,3'-dimethoxy-1,1'-biphenyl (17) $^{13}$C-NMR
S1.2.0 – 4,4′-dibromo-2,2′-diiodo-5,5′-dimethoxy-1,1′-biphenyl (18) $^1$H-NMR

S1.2.1 – 4,4′-dibromo-2,2′-diiodo-5,5′-dimethoxy-1,1′-biphenyl (18) $^{13}$C-NMR
S1.3.0 – 2-(cyclohex-3-en-1-yl)ethyl(hexyl)dichlorosilane (20) $^1$H-NMR

S1.3.1 – 2-(cyclohex-3-en-1-yl)ethyl(hexyl)dichlorosilane (20) $^{13}$C-NMR
S1.3.2 – 2-(cyclohex-3-en-1-yl)ethyl(hexyl)dichlorosilane (20) $^{29}\text{Si}$-NMR

S1.4.0 – 2-(Bicyclohept-5-en-2-yl)ethyl(hexyl)dichlorosilane (21) $^1\text{H}$-NMR
S1.4.1 – 2-(Bicyclohept-5-en-2-yl)ethyl(hexyl)dichlorosilane (21) $^{13}$C-NMR

S1.4.2 – 2-(Bicyclohept-5-en-2-yl)ethyl(hexyl)dichlorosilane (21) $^{29}$Si-NMR
S1.5.0 – 2,7-dibromo-3,6-dimethoxy-9,9-dihexylsilafluorene (1) $^1$H-NMR

S1.5.1 – 2,7-dibromo-3,6-dimethoxy-9,9-dihexylsilafluorene (1) $^{13}$C-NMR
Pure Blue Emitting Poly(3,6-dimethoxy-9,9-dialkylsilafuorenes)  
McDowell, J.

S1.6.0 –2,7-dibromo-3,6-dimethoxy-9,9-dioctylsilafuorene (2) $^1$H-NMR

S1.6.1 –2,7-dibromo-3,6-dimethoxy-9,9-dioctylsilafuorene (2) $^{13}$C-NMR
S1.7.0 –2,7-dibromo-3,6-dimethoxy-9,9-dimethylsilafluorene (3) \(^1\)H-NMR

S1.7.1 –2,7-dibromo-3,6-dimethoxy-9,9-dimethylsilafluorene (3) \(^13\)C-NMR
S1.8.0 –2,7-dibromo-3,6-dimethoxy-9,9-methylvinylsilafuorene (4) $^1$H-NMR

S1.8.1 –2,7-dibromo-3,6-dimethoxy-9,9-methylvinylsilafuorene (4) $^{13}$C-NMR
S1.9.0 –2,7-dibromo-3,6-dimethoxy-9-methyl-9-[2-(cyclohex-3-en-1-yl)ethyl]silafluorene (5)

$^1$H-NMR

S1.9.1 –2,7-dibromo-3,6-dimethoxy-9-methyl-9-[2-(cyclohex-3-en-1-yl)ethyl]silafluorene (5)

$^{13}$C-NMR
S1.10.0 –2,7-dibromo-3,6-dimethoxy-9-hexyl-9-[2-(cyclohex-3-en-1-yl)ethyl]silafluorene (6)

$^1$H-NMR

S1.10.1 –2,7-dibromo-3,6-dimethoxy-9-hexyl-9-[2-(cyclohex-3-en-1-yl)ethyl]silafluorene (6)

$^{13}$C-NMR
S1.11.0 –2,7-dibromo-3,6-dimethoxy-9-hexyl-9-[2-(Bicyclohept-5-en-2-yl)ethyl]silafluorene (7)

$^1$H-NMR

S1.11.1 –7-dibromo-3,6-dimethoxy-9-hexyl-9-[2-(Bicyclohept-5-en-2-yl)ethyl]silafluorene (7)

$^{13}$C-NMR
S1.12.0 – Poly(3,6-dimethoxy-9,9-dihexylsilafluorene) (PDHSF) (9) $^1$H-NMR

S1.13.0 – Poly(3,6-dimethoxy-9,9-dioctylsilafluorene) (PDOSF) (10) $^1$H-NMR
S1.14.0 – Poly(3,6-dimethoxy-9,9-dimethylsilafluorene) (PDMSF) (11) $^1$H-NMR

S1.15.0 – Poly(3,6-dimethoxy-9,9-methylvinylsilafluorene) (PMVSF) (12) $^1$H-NMR
S1.16.0 – Poly(3,6-dimethoxy-9-methyl-9-[2-(cyclohex-3-en-1-yl)ethyl]silafluorene) (PMCySF)
(13) $^1$H NMR

S1.17.0 – Poly(3,6-dimethoxy-9-hexyl-9-[2-(cyclohex-3-en-1-yl)ethyl]-silafluorene) (PHCySF)
(14) $^1$H-NMR
S1.18.0 – Poly(3,6-dimethoxy-9-hexyl-9-[2-(Bicyclohept-5-en-2-yl)ethyl]silafluorene) (PHNSF) (15) $^1$H-NMR

S1.19.0 – Partial Grignard Metathesis of Monomer (9) (66% Conversion, MeOH Quenched) $^1$H-NMR
S1.19.1 – Grignard Metathesis of Monomer (9) (90% Conversion, MeOH Quenched) $^1$H-NMR. Note the presence of both ~5% Starting material and 5% Digignard by-product.
S2.1—Complete Solution Phase Absorption and Photoluminescence Spectra (Normalized)

S2.2-- Complete Solid Phase Photoluminescence Spectra (Normalized)
Pure Blue Emitting Poly(3,6-dimethoxy-9,9-dialkylsilafluorenes)  

S2.3.1 — PDHSF (9)  

S2.3.2 — PDOSF (10)  

S2.3.3 — PDMSF (11)  

S2.3.4 — PMVSF (12)  

S2.3.5 — PMCySF (13)  

S2.3.6 — PHCySF (14)
S2.3.7 — PHNSF (15)

S2.4.1 — TGA/DSC (PDOSF) (10)

S2.4.2 — TGA/DSC (PDMSF) (11)

S2.4.3 — TGA/DSC (PMVSF) (12)

S2.4.4 — TGA/DSC (PMCySF) (13)
S2.4.5—TGA/DSC (PHCySF) (14)  
S2.4.1—TGA/DSC (PHNSF) (15)
S2.4.7— EI-MS of HNSF (7) showing retro diels alder fracturing of the norbornenyl group
Chapter 4

Synthesis and Application of Photolithographically Patternable Deep Blue Emitting Poly(3,6-dimethoxy-9,9-dialkylsilafuorene)s

4.0 Introduction

The increasing prevalence of organic electronics in modern society warrants continued development of technologies which efficiently store, process and display information. Commercialization of emerging display technologies places special demand on material costs and processing.[1-4] Polymer based light emitting diodes are often considered low cost alternatives to their small molecule counterparts given the ease in which solutions can be made into thin films over relatively large areas without need for energy intensive high vacuum evaporation.[5-8] While the formation of contiguous thin films is paramount to the creation of emissive layers in simple organic light sources, other design consideration must be addressed in more advanced technologies. Polychromic displays require creation of addressable subpixels consisting of at least one of each primary colour (red, green, blue or RGB) and the resolution of the ensemble must be high enough to render an image amicable to the human eye (< 50 µm). In modern active-matrix light emitting diode (AMOLED) devices, this is done by sequential vacuum evaporation of RGB emitters (through shadow masks) onto an array of transparent conductive electrodes (e.i. indium doped tin oxide (ITO)) which are powered by a thin-film transistor (TFT) backplane.[9] One method of shifting the AMOLED fabrication paradigm from
Figure 1: Conventional microscope images (a-b) and confocal fluorescent microscope images (c-d) of patterned films of PHNSF-E50 (1) and PHCySF-E50 (2) respectively. The low magnification image a) demonstrates the high degree of fidelity of a patterned film to the original shadow mask. The blue highlighted area in a) is magnified in b) to better illustrate the hexagonally packed microdisk array. e) illustrates the structure of both photopatternable polymers developed in this study (note the presence of epoxide groups on each polymer’s sidechains). The source of catalytic protons is the photoacid generator DtBPI-PF₆, which initiate the crosslinking following momentary exposure to UV light.
vacuum to solution processing is through the invention of conjugated light emitting polymers which serve the dual purpose of patternability and electroluminescence.

In this paper, we attempt to address some of the challenges in designing polymers suitable for creating pixelated polymer-based displays whilst utilizing protocols which can easily integrate such materials into existing microfabrication methods. We show that poly(silafluorene) (PSF) derivatives synthesized as part of this work are promising candidates which can not only be patterned with resolution < 50 μm, but are produced using a simplified route involving fewer synthetic steps than the prior art (figure 1a-d). Epoxidized polymers poly(3,6-dimethoxy-9-hexyl-9-[2-(Bicyclohept-5-en-2-yl)ethyl]silafluorene)(PHNSF-E50) (1) and poly(3,6-dimethoxy-9-hexyl-9-[2-(cyclohex-3-en-1-yl)ethyl]-silafluorene)(PHCySF-E50)(2) (see figure 1e) possess narrow solid state photoluminescence in the deep blue, can host numerous higher wavelength emitters and can be processed into thin crosslinked films which electroluminesce under an applied voltage.

Our work is motivated by the seminal papers of Meerholz et al. who popularized the concept of photopatterning conjugated polymers. Unlike common negative photopatternable resists such as SU8 (which employ epoxide groups), Meerholtz et al. utilized oxetane side chains as their mode of crosslinking. Oxetane derivatives consist of a four member oxygen containing ring which possess less internal strain than its three member counterpart. Consequently, oxetanes are less reactive toward ring opening, a fact exploited by Meerholtz in their production of poly(spirobifluorene-co-fluorene) derivatives via Suzuki coupling. It is doubtful that inadvertent ring opening of epoxides could be prevented under the conditions required for Suzuki. The trade-off for using less reactive crosslinking groups is the potential for patterning to requiring longer exposure/baking time, higher bake temperatures or higher loading of photoacid generator (PAG). The risk of over developing may be higher if crosslink
density does not exceed a threshold amount. The later point imposes limitations on the expected resolution.\textsuperscript{[17,18]} Oxetanes, however, are proven to be an effective crosslinking moiety in high resolution photopatterning.\textsuperscript{[12-16]}

**Scheme 1:** Mechanism of cationic ring opening polymerization (ROP) of norbornenyl oxide sidechains on polymer (1).\textsuperscript{a}

\textsuperscript{a}Each R group represents a connection to a polymer backbone. Sufficient crosslinks result in an insoluble material. The photoinduced decomposition of a PAG supplies a catalytic amount of acid which initiates the ROP.

The polymers (1) and (2) produced in this paper possess epoxide side chains which serve the dual purpose of reducing baking and UV light exposure time while additionally exploiting alternative synthetic pathways for the installation of crosslinkable moieties. Our post-polymerization epoxidation facilitates the overall synthesis (reducing synthetic steps and reaction time) while simultaneously improving performance of the material. Scheme 1 illustrates the process by which our epoxide functionalized poly(silafluorene)s crosslink (via a ring-opening polymerization) in the presence of an acid catalyst.
Using the I-line (365 nm) of a Karl Suss MA6 mask aligner, a 1 s exposure of the photoacid generator (PAG) Bis(4-tert-butylphenyl)iodonium hexafluoro-phosphate (DtBPI-PF₆)(3) generates sufficient protons to catalyze epoxide ring opening and form a bridging network of covalent C-O bonds which renders the material insoluble in developing solvents such as toluene or THF. This process was aided by a relatively low temperature soft bake at 90°C. Following development, the smallest feature of our test pattern (10 µm) became visible (figure 1). Photoluminescence of crosslinked areas exhibit no significant spectral changes or decline in quantum efficiency.

4.1 Results and Discussion

We utilized an efficient nickel catalyzed polymerization based on diarylmagnesate monomers to create poly(silafluorene)s PHCySF (4) and PHNSF (5) (figure 2 and 3) in good yield with number average molecular weights exceeding 50 kg/mol (See Supporting Information).[19] The polymerization was complete in less than 30 min and polymer was collected by simple precipitation in methanol. Excess monomer and oligomers were removed by subsequent soxhlet extraction with ethanol over 5-6 h. Synthetically useful cycloalkenes, specifically cyclohexenyl (Cy) and norbornenyl (NB) moieties, are present in the sidechain of each repeat unit of polymers (4) and (5) respectively. In our previous publication, (4) and (5) were studied with regards to their solution and thin film absorption and photoluminescence properties.[19] Both polymers were found to have a large band gap, ~3 eV, and solution like optical properties in thin films indicative of its predominantly amorphous nature. We attribute the absence of microcrystalline phases to the methoxy groups located at the 3 and 6 positions on the repeat unit. For reasons of sterics, these groups are believed to impart a slight torsion to the backbone which prevents the occurrence of crystalline packing.[20] Referring to the absorption
and photoluminescence spectra of polymers (4) and (5) in figure 4c, the formation of microcrystalline phases leading to red shifted and broadened emissions (such as the well documented β-Phase formed in poly(9,9-dialkyfluorene)s) are not observed.\cite{21-24} Additionally, figure 4c shows absorption and photoluminescence is essentially unchanged for thin films of polymer starting materials (PHCySF and PHNSF) and their epoxidized and crosslinked (XL) counterparts (PHCySF-E50 and PHNSF-E50). The unchanged position and shape of absorption and emission bands suggests that neither the epoxidation nor the photocrosslinking procedure resulted in chemical alteration of the silafluorene emission center. Absolute quantum yields (AQY) of both crosslinked thin films also remains high at 86% and 83% for PHNSF-E50 and PHCySF-E50 respectively.

In the interest of improving on the prior art, we deviated from the more synthetically complex process of oxetane functionalization (which would not have been compatible with our polymerization method) in favour of post-polymerization modification of the side-chain double bonds. Specifically, we employed the relatively simple process of converting the cycloalkene moiety into cycloalkene oxides using m-chloroperoxybenzoic acid (m-CPBA), e.g. the Prilezhaev reaction.\cite{25,26} This was accomplished via dropwise addition of m-CPBA/chloroform solution into a toluene solution of polymer cooled to 0°C.
Figure 2: $^1$H NMR confirms that m-CPBA oxidizes the strained double bonds of the PHNSF norbornenyl side groups without side reactions. In the presence of 1 equiv. m-CPBA, alkenyl protons H$_C$/H$_C$ (centered at 6.0 ppm) are \sim80\% converted to norbornenyl oxide protons H$_E$/H$_E$ (centered at 2.7 ppm). Resonance peaks of neighboring norbornenyl protons H$_D$/H$_D$ in PHNSF (at 2.6 ppm) are also observed to shift upfield during the conversion (corresponding H$_F$/H$_F$ resonance peaks occur at 2.4 ppm) PHNSF (5) is a superior reagent for Prilezhaev epoxidation (versus. PHCySF (4)) given the more complete oxidation of the norbornenyl double bond.

When conducting the reaction on an NMR scale using deuterated chloroform and toluene, the progress of the reaction was readily apparent from changes in the $^1$H NMR as reaction time progressed (figures 2 and 3). The norbornenyl moiety of polymer (5) was observed to be more reactive to epoxidation due in part to its higher internal strain energy relative to the non-bridged
Epoxidation was found to be rapid and high yielding (80-90% conversion) in the case of polymer (5) with a reagent molar ratio of [m-CPBA]/[NB] = 1 (figure 2). Norbornenyl protons resonance peaks centered at 6.0 ppm are replaced with those of norbornenyl oxide at 2.7 ppm. Furthermore, examination of aromatic proton resonance peaks in the region of 7.6-7.2 ppm suggests that oxidation is regioselective for the cycoalkene and undesirable oxidation of the polymer backbone remains undetectable by NMR.

In addition to complete epoxidation of polymer (5), quantitative conversion of 50% and 25% of sidechains is also possible by altering the equivalence of m-CPBA added. This tunability allows greater control over material properties such as crosslink density which can ultimately affect the resolution limit of developed features. Additionally, unreacted norbornenyl groups provide a handle for secondary sidechain modification which may be useful in the installation of pendant emitters for tailoring electroluminescence.
Figure 3: $^1$H NMR taken during the Prilezhaev epoxidation of polymer (4) with m-CPBA. Note the maximum conversion of cyclohexenyl (Cy) side chains to their cyclohexenyl oxide (CyO) analogs was ~50% after 30 min (despite 1 eqv. of m-CPBA having been added). CyO peaks at 3.0 ppm become apparent after several minutes of reaction whilst Cy peaks at 5.6 ppm simultaneously decreases. Peak integration is given in parentheses next to the corresponding peak.

After the addition of m-CPBA to a solution of polymer (4) (with a reagent molar ratio of [m-CPBA]/[Cy] = 1), only approximately 50% for cyclohexenyl groups had oxidized to cyclohexenyl oxide after a period of 30 min. Looking at figure 3, NMR shows the disappearance of alkene proton resonance at 5.6 ppm and the emergence of characteristic cyclohexene oxide peaks at 3.0 ppm.

For the purposes of photolithography in this paper, we limited of the conversion of cycloalkene side groups of polymers (4) and (5) to 50%. Purification of converted polymers,
designated PHNSF-E50 (1) and PHCySF-E50 (2), is initiated by precipitating the product through the injection of hexanes into the reaction solution. The polymer is separated from the solvent, dried, and re-dissolved in the minimum amount of THF. Precipitation of polymer from THF into dry methanol a total of two times was sufficient to remove any traces of unreacted m-CPBA (and its reaction by-products). Toluene solutions (16 mg/mL) of polymers (1) and (2) were subsequently made and stored with refrigeration until use.

4.1.1 Photolithography Methods

The generalized steps for producing a patterned surface are illustrated in scheme 2. Optimum results with respect to highest AQY, minimal baking temperature, lowest PAG loading and highest resolution were obtained by using 16 mg/mL toluene solutions of polymers (1) and (2). Polymer solutions were mixed 1:1 (v/v) with a 0.5 mg/mL DtBPI-PF$_6$ (in toluene) prior to use. For PHNSF-E50 and PHCySF-E50, this represents a 4 mol% loading of photoacid generator (with respect to epoxide groups). Spin casting the mixed solution at 3000 rpm produces transparent, contiguous films with an average thickness of 80 nm, as determined by AFM (Veeco Dimension 3100). A short 1 s exposure to UV light through a shadow mask and a brief post bake step at 90°C was used to create light emitting structures with resolvable features of <10 µm, figure 4a,b.
Figure 4: a) Photograph of a transparent patterned film of PHNSF-E50 on glass. b) Photograph of the same patterned film fluorescing under 365 nm illumination (with underlying printed logo removed). c) Solid state absorption (abs) and photoluminescence (PL) of polymer films. Note there is nearly complete overlap of absorption and PL spectra for thin films of polymer starting materials (PHCySF and PHNSF) and their epoxidized and crosslinked (XL) counterparts (PHCySF-E50 and PHNSF-E50). The unchanged position and shape of absorption and emission bands suggests that neither the epoxidation nor the photocrosslinking procedure resulted in chemical alteration of the silafluorene repeat unit. Absolute quantum yields (AQY) of both crosslinked thin films was performed using an integrating sphere and measured to be 86% and 83% for PHNSF-E50 and PHCySF-E50 respectively.
Following UV exposure, the photoluminescence of irradiated areas was noticeably diminished. This was presumably due to quenching by radicals generated during the photodegradation of the PAG. Following the soft bake, however, PL was fully restored. The pattern was revealed by gentle agitation of the substrate in a developing solvent such as toluene or THF for roughly 30 s.

### Scheme 2: Procedural Diagram for making photopatterned films of polymers (1) and (2).

I. O₂ Plasma Treated Substrate → II. Spincoat (4) or (5) With 3-4%PAG

III. UV Light + Shadow Mask Exposure, 1s

V. Develop in Toluene 30s

IV. Soft Bake, 90°C, 30s

---

### 4.1.2 Förster Energy Transfer in Patterned Films

In an attempt to alter the PL emission of patterned substrates to include all three primary colours, dopants suitable for efficient Förster energy transfer were added to PSF resist solutions prior to spin casting. The use of dopants to change emission wavelength is well documented and has been exploited in OLEDs based on sublimed molecular materials.[33-36] To a lesser extent, this approach has also been used in conjugated-polymer systems.[37] Figure 5a shows that following photopatterning and development, efficient energy transfer was observed to occur.
between the crosslinked host polymer and the added ~1 wt% of coumarin 540A (C540A, $\lambda_{\text{em}} = 532$ nm) or tetraphenylporphrin (TPP, $\lambda_{\text{em}} = 635$ nm). The result, as imaged using confocal fluorescence microscopy, is RGB patterns which demonstrate efficient single-step Förster transfer from blue to red or green emitters. The use of TPP allows an exceptionally large shift using a single-step transfer to obtain a saturated red emission. This is due mainly to the existence of a strongly blue absorbing Soret band which couples to a narrow Q-band red emission peak.\cite{38} Figure 5c shows
Figure 5: a) Three confocal fluorescence microscope images of patterned substrates ranging in emission colour from blue (neat PHNSF-E50), green (1 wt% C540A) and red (1 wt% TPP). b) Normalized fluorescence spectra ($\lambda_{ex} = 365$ nm) taken of C540A doped patterned films. c) Normalized fluorescence spectra ($\lambda_{ex} = 365$ nm) taken of TPP doped patterned films. Note that in both spectra there is complete suppression of the polymer emission in host/dopant systems.
the photoluminescence spectra for crosslinked films of polymer PHNSF-E50 (1) neat and films
doped with 1 wt% of TPP. The CIE coordinates corresponding to this host/dye system are x =
0.5694 and y = 0.2972. It is clear that even at low concentrations, the spectrum is dominated by
the PL of TPP, which has a characteristic set of narrow peaks at 653 nm and 714 nm.
Furthermore there is no apparent emission emanating from (1). Referring to figure 4 and the PL
spectra of both polymers (1) and (2), the emission maximum for these materials is 410 nm. This
overlaps perfectly with the absorption of TPP (at 418 nm), hence efficient Förster energy transfer
was anticipated.\[39\]

Analogously, the significantly broader absorption of C540A centres on 423 nm and fully
overlaps with the emission of the host polymer and complete energy transfer to the dye is
observed even at low loadings. Figure 5b shows the PL of the C540A doped films of polymer
(1). Excitation at 365 nm results in green emission (\(\lambda = 530\) nm) with no observable blue
emission from the polymer. The CIE coordinates corresponding to this host/dye system are x =
0.1919 and y = 0.4108).

For each dopant/host system the Förster Radius (\(R_0\)) was calculated as an initial indicator
of ideal dye concentration. \(R_0\) is defined as the minimum distance separating donor and acceptor
compounds such that intermolecular energy transfer and donor fluorescence are equally probable
relaxation channels. Radii for both TPP and C540A were calculated using the following
equation:\[35\]

\[
(R_0)^6 = \frac{0.5291K^2}{N_A\pi^2T}
\]

(1.0)

Where \(K^2 = 0.66\) for randomly oriented dipoles, \(N_A\) is Avogadro’s number, \(n\) is the
refractive index of the material (\(n_{PSF} = 1.75\) as measured by ellipsometry) and \(T\) is known as the
overlap integral of the normalized PL of the host material and the spectral extinction coefficient plotted against wavelength in wavenumbers and is defined by eqn 1.1.[35]

\[ T = \int_0^{\infty} F_D(\nu) \epsilon_A(\nu) \nu^4 d\nu \]  

(1.1)

Where \( F_D \) is the normalized PL spectrum of the donor as a function of wavelength, \( \epsilon_A \) is the decadic extinction coefficient of the acceptor (in M\(^{-1}\)cm\(^{-1}\)) and \( \nu \) is wavelength in cm. Reference absorption spectra taken of TPP and C540A used in the calculation of \( T \) can be found in the Supporting Information. The values of \( R_0 \) calculated for TPP and C540A in polymers (1) or (2) are 9.4 nm and 7.4 nm respectively. These values are notably larger than previous estimates of \( R_0 \) for TPP in poly(9,9-dioctylfluorene) (PFO) films due to greater host/dopant spectral overlap. On the basis of theory, we would expect a minimum dye concentration of 0.025 wt% and 0.03 wt% of TPP and C540A respectively to induce 50% of excited state electrons to decay to the ground state via intermolecular energy transfer. This is well within the concentration regime wherein minimal phase segregation is observed. If we plot the absolute quantum yields (AQY) of both dye/host systems as a function of dye loading (expressed in wt%), we observe a trend in energy transfer efficacy which closely correlates with the calculated value of intermolecular dye spacings.

Figure 6a plots the AQY of different compositions of the TPP/PHNSF-E50 within the range of 0.025-1.5 wt% TPP. Beginning at 0.025 wt% TPP, the total quantum yield of the system (48.2 %) has contributions from both PHNSF-E50 and TPP of 43.3% and 4.9% respectively. Keeping in mind the 86% AQY for films of PHNSF-E50 is a factor of 8.6 higher than the 10% AQY of TPP doped films of PMMA, a dye concentration of 0.025 wt% corresponds to the approximate Förster Radius. Assuming each molecule of TPP occupies a
Figure 6: A plot of AQY as a function of a) TPP and b) C540A dye loading over the range of 0.025-3 wt% in thin films of PHNSF-E50. The top x-axis corresponds to the approximate intermolecular distance between dye molecules. Maximum energy transfer is observed for loadings of ~ 1 wt% where no emissions from the polymer host are observed. The dashed line indicates the calculated $R_0$ determined by eqn. 1.0 and 1.1 and experimentally determined values of $R_0$. Similar results were obtained for thin films of PHCySF-E50.
spherical volume of \((4/3)\pi l^3\), the intermolecular distance \(l\) is calculated to be 9.8 nm. This discrepancy with the theoretical value of 9.4 nm, as previously rationalized in the case of PFO, is due to the extended conjugation of the polymer backbone and hence the wavefunction of an excited state is not limited to a single repeat unit. This extends the range of dipole-dipole interaction and increases the Förster Radius.\[^{35}\]

Following the increase of TPP concentration to 1 wt%, the AQY has only a single contribution from TPP at a maximum value of 10%. This can only be the result of near quantitative transfer of energy from the excited state of PHNSF-E50 to TPP whilst irradiated with 365 nm light. Note that increasing TPP concentration results in the eventual decline of AQY. It is safe to posit that reduced TPP intermolecular distance increases the probably of self-quenching via non-radiative pathways.\[^{35}\]

The AQY of C540A is significantly higher (82% in 1.5 wt% PMMA) than TPP, yet the calculated overlap integral is still comparable and consequently, a similar Förster Radius and dye concentration is expected for complete energy transfer. Because the AQY of both PHNSF-E50 and C540A are similar, we can conclude from figure 6b that the concentration of C540A corresponding to the Förster Radius is 0.03 wt%. Increasing the concentration of C540A to 1.2 wt% completely suppresses any emission from PHNSF-E50 and the AQY approaches the expected value 80%. Analogous to TPP, an increase in C540A concentration above 2 wt% resulted in a noticeable decline in AQY.

The ability of PSF to act as host is potentially important for applications since it allows a single material to be used as a blue light emitter, as a host for green emission dyes, and as a host for a red emission dye. These results demonstrate a unique potential for PSF to assist in the simple construction of ultra high resolution multicolour displays. Of course, covalently bonding dyes to the backbone would eliminate the risk of leaching dopant during the development stage,
but thus far leach rates we observed are slow enough such that desired spectral shifts were obtained. That said, we have already had considerable success in an initial attempt to covalently bind dopant emitters through emerging “click” chemistry methods based on tetrazine derivatives.\textsuperscript{[40-43]} Unlike copper catalyzed azide/alkyne cycloadditions, tetrazines react rapidly with norbornene moieties at room temperature without need of metal catalyst. This work will appear in a future publication.

\textbf{Figure 7:} a) Illustration of LED architecture indicating respective energy levels of layers. b) Photograph of a device under 9V operation. c) Plot of electroluminescence spectra obtained from device operating at 9V. d) CIE colour map highlighting the position of the blue-violet OLED EL.
4.1.3 Electroluminescent Device With Crosslinked Emissive Layer

Energy levels of polymer (5) was previously determined by cyclic voltammetry (CV).[19] It was found that HOMO/LUMO energy levels (5.7 eV and 2.7 eV respectively) reside slightly lower than most reported for PFO and found suitable for OLED applications. We estimate the energy levels of the corresponding polymers (1) are the same (given no changes occur to the conjugated silafluorene backbone during epoxidation). Light emitting devices were constructed in a N₂ filled glovebox on O₂ plasma treated ITO on glass. We employed a simple trilayer design using PEDOT:PSS as the hole injection layer (~10 nm) as well as a thin hole transport layer consisting of poly[N,N’-bis(4-butylphenyl)-N,N’-bis(phenyl)-benzidine] (poly-TPD) (~20 nm). A contiguous 80 nm emissive layer consisting of PHNSF-E50 was deposited by spin casting from an 8 mg/mL polymer solution in toluene. The solution also contains roughly 4 mol% (with respect to epoxide) of the PAG DtBPI-PF₆ (see Photolithography Methods). To crosslink the emissive layer, the device was briefly flooded with 365 nm UV light from a collimated LED source (190 mW, Thor Labs) and baked at 90°C for 30s. Residual unreacted polymer (if any) and PAG residues were removed by washing the layers with toluene. Remaining wash solvent was eliminated by placing the device in the glovebox antechamber and evacuating for 30 min. The device was completed following the evaporation of a low work function metal under low pressure onto a known area defined by a shadow mask. A calcium cathode, which best matches the LUMO energy of 2.7 eV, was found to yield the best performing devices. Figure 7a illustrates the device architecture and energy levels of the respective layers. A photograph of an encapsulated functional device operating at 9V is shown in figure 7b alongside its respective electroluminescence spectra. The EL is similar to the crosslinked thin film PL spectrum of (1) and consists of a single peak centred at 410 nm. The full width at half maximum (FWHM) of the EL peak is 166 nm. Figure 7d shows the location of
the device’s blue-violet emission on the CIE colour map. Its CIE coordinates are $x = 0.2042$ and $y = 0.2319$.

Performance data obtained for our champion device is presented in figures 8 and 9. Beginning with the I-V-L curve in figure 8, we observe the turn on voltage to be roughly 5 V. The device was operated up to 10 V and reached a maximum current density of 60 mA/cm$^2$. The maximum luminance measured for the device was 1690 Cd/m$^2$ at 10 V operation. Compared to current state-of-the-art blue emitting polymer OLEDs,$^{[43]}$ which can achieve maximum luminescence of 10500 Cd/m$^2$, our device performs moderately but represents an improvement over more closely related OLEDs based on photocrosslinked emissive layers such as those reported by Carter et al. which can obtain a maximum luminance of 150 Cd/m$^2$.\textsuperscript{[11]} Our device brightness is also comparable to the blue emitting crosslinked OLED devices reported by Meerholtz et al.\textsuperscript{[15]} Figure 9 show the maximum irradiance of our device was 54 W/m$^2$ at a current density of 53 mA/cm$^2$. The maximum external quantum efficiency of the device is 3.2\% when operating at 33 mA/cm$^2$ and corresponds to a maximum power efficiency of 1.62 lm/W.
Figure 8: Crosslinked PHNSF-E50 device characteristics: Luminance (solid squares) and current density (solid triangles) vs. bias voltage. The luminance reaches its maximum at 1690 Cd/m². The onset voltage was ~ 5 V. The inset shows the device architecture ITO/PEDOT:PSS (10 nm)/ Poly-TPD (20 nm)/ XL-PHNSF-E50 (80 nm)/ Ca/Al (50 nm/200 nm).

Figure 9: Plot of EQE and Irradiance as a function of current density. Note the maximum efficiency achieved was 3.2 % at 33 mA/cm² (corresponding to a power efficiency of 1.62 lm/W).
4.1.4 DFB Laser With Crosslinked Emissive Layer

In addition to electroluminescent devices, we explored the performance of crosslinked films of PHNSF-E50 and PHCySF-E50 as gain medium in thin film distributed feedback (DFB) lasers. The strong absorption and broad emission of conjugated polymers are features which make these materials ideal candidates for solid state lasers in the visible spectral range. There are many resonator configurations pre-existing in the literature including microcavities, microdisk, microtoroidal, microcone lasers in addition to distributed feedback structures.\cite{44} DFBs have gained particular attention due to their relatively simple fabrication from polymer solutions and their propensity for low threshold operation in combination with a well defined output beam.

Prior to building an actual laser, we examined the photophysical properties of our materials through the use of pump-probe measurements (at a repetition rate of 1 kHz and pulse duration of \~200 fs).\cite{45} Figure 10 presents evidence of gain in PHCySF-E50 which has been crosslinked after being spin cast onto a glass substrate. The ordinate of figure 10 is the change in the optical density (OD) at the probe wavelength so a coherence peak (representing an increase in absorption of the probe pulse) is due to further excitation of the excited carriers (by the pump) when pump photons (388 nm) and probe photons (489 nm) reach the sample at exactly the same time. Pump-induced absorption, however, becomes negative after several picoseconds when carriers have relaxed to luminescent
Figure 10: Measurement of optical gain in crosslinked films of PHCySF-E50 determined by time resolved pump-probe (388/489 nm).

Figure 11: Plot of fluorescent lifetime of in crosslinked films of PHCySF-E50, non-crosslinked films of PHCySF-E50 and a dilute solution in toluene (pump at 360 nm, probe at 440 nm).
energy states. Incoming probe photons cause carriers to recombine due to stimulated emission (SE). SE counterbalances the absorption of the probe pulse and is perceived as a negative absorption (e.g. a negative change in optical density).

Figure 11 plots the fluorescence lifetimes ($\tau$) of the same PHCySF-E50 crosslinked film in addition to a non-crosslinked film and a solution of the polymer in toluene. The fluorescence decay in the films is on the order of a few hundred picoseconds, which is consistent with the decay time of the stimulated-emission signal. It is clear from figure 11 that fluorescence is significantly longer lived in solution where chain separation is significant and quenching is reduced.

The inset of figure 12 illustrates the structure of the polymer DFB laser produced in this study. Note that there is a periodic modulation in the refractive index which results in diffractive feedback along one axis in the waveguide plane. As such, lasers were constructed by spin casting a thin polymer layer ($\sim$100 nm) from solution on corrugated silica structures produced by reactive ion etching (RIE) of thermally grown SiO$_2$ on silicon wafers. The gratings had a modulation depth of 100 nm and a grating periodicity of 200 nm with a duty cycle of 0.5. The system was optically pumped with a Q-switched frequency-tripled neodymium-doped yttrium ortho-vanadate (Nd:YVO$_4$) laser (AOT Inc.) with a wavelength of 355 nm and pulse duration of 0.5 ns. To prevent the photooxidation of the organic material, the sample was characterized in a vacuum chamber ($< 5 \times 10^{-5}$ mbar). Using an automated precision stage, the sample chamber is able to move in both directions within the plane orthogonal to the pump beam. Upon excitation, light propagating in a waveguide mode of the organic film is scattered by the periodic corrugations.[46-49] A wave is formed from scattered light from each corrugation combining coherently and propagating in a new direction. For a given period of the corrugation, the wavelength of light that will be diffracted is that which satisfies the Bragg condition:
\[ m\lambda = 2n_{\text{eff}}\Lambda \]  

(1.2)

Here, \( \lambda \) is the wavelength of the light, \( \Lambda \) is the period of the structure, and \( m \) is an integer that represents the order of the diffraction. \( n_{\text{eff}} \) is the effective refractive index of the waveguide. Given \( \Lambda = 200 \) nm in our system, second-order feedback (\( m = 2 \)) was measured from the surface of the film perpendicular to the plane of the waveguide.

The reflected wavelength is expected to equal \( n_{\text{eff}}\Lambda \). While second-order structures can provide a surface-emitted output, it comes at the cost of higher oscillator thresholds given that the out-coupled laser power represents a loss mechanism. Figure 12 shows the laser output of crosslinked films of PHNSF-E50 (1) and PHCySF-E50 (2). Slightly higher wavelength of the polymer (2) laser is due to a difference in organic layer thickness which impacts the value of \( n_{\text{eff}} \).

![Figure 12: Plot of second order laser emissions from crosslinked films of PHNSF-E50 and PHCySF-E50 on corrugated silica substrates (\( \Lambda = 200 \) nm). (Inset illustrates the structure of the laser and the measurement geometry).](image-url)
4.2 Conclusion

We have demonstrated a unique method of preparing photopatternable blue emitting conjugated polymers which are functionalized with pendent epoxide side groups. Post-polymerization epoxidation of cyclohexenyl and norbornenyl was accomplished using a well known oxidant, m-CPBA, and a straightforward method that yields product within minutes. We noted that due to the increased ring strain of norbornenyl moieties, the extent of epoxidation was more easily controlled and conversion could be greater than 80%. Solutions of polymer suitable for spin casting into contiguous transparent films were made in toluene. Adding an iodonium based PAG allowed films to be patterned with resolution < 10 µm following UV light exposure through a shadow mask. We believe polymers (1) and (2) have qualities superlative to the existing art given the minimal synthesis time required for our nickel catalyzed polymerization and signal step epoxidation whilst matching the performance of polymers produced by the lengthier Suzuki coupling polymerizations and more synthetically complex oxetane functionalization.

In future work, we will illustrate that the cycloalkene moieties purposefully left unreacted during epoxidation, are excellent functionalities through which further sidechain modifications can be made, specifically the tethering of auxiliary chromophores for full spectrum emission tuning in pixelated substrates. This will enable us to expand on our existing demonstration of a 3% EQE crosslinked blue emitting OLED and generate a patterned substrate with separate RGB electroluminescence. An emerging “click” chemistry method utilizing 2 + 4 cycloaddition of tetrazine derivatives represents a potentially revolutionary means of tailoring conjugate polymer emission. The catalyst free reaction is rapid at room temperature and the covalently bound chromophores would be prevented from phase segregating in thin films.
Our observation of amplified spontaneous emission from crosslinked polymer films is the first demonstration of this important quality in photopatternable PSF. In future work, we will expand upon the concept of patterning crosslinkable gain medium into resonators. Specifically, we will demonstrate how advanced lithography technologies, such as two photon direct laser writing, can be used to print 3D waveguiding structures. Potential structures could include toroids which have extremely high Q factor (> $10^7$) and could potentially reduce lasing thresholds to the limits of electrical excitation.

### 4.3 Experimental

Chemicals and solvents were purchased from TCI America and Sigma Aldrich and used without need for further purification. NMR was performed on a 400 MHz Bruker Avance III Spectrometer. Thin film absorption and photoluminescence spectra were recorded using a Perkin-Elmer 900 UV-Vis Spectrometer and a Perkin-Elmer LS-50B Luminescence Spectrophotometer. Polymer quantum efficiencies were calculated through the use of an integrating sphere using a focused 365 nm LED (190 mW, Thor Labs) as the excitation source and an Ocean Optics Maya Pro CCD optical fiber spectrometer. High resolution patterning of polymer films was done using a Karl Suss M6 mask aligner in a clean room facility. Laser spectra were recorded using a fiber coupled CCD camera and excitation was provided by Q-switched frequency-tripled neodymium-doped yttrium orthovanadate (Nd:YVO$_4$) laser (AOT-YVO-20QSP, Advanced Optical Technology Ltd.) with a wavelength of 355 nm. Gratings used for thin film laser substrates were produced using e-beam lithography and RIE of a thermally grown oxide layer on Silicon wafers. In the measurement of stimulated emission (SE), a Clark 2210 laser system was used with a 1 kHz repetition rate at 775 nm. Thin films on glass were irradiated with a 1-3 μJ/pulse collimated 3 mm beam with pulse durations of 200 fs. Pump and
probe wavelengths were derived from the second harmonic of the Clark output (388 nm) and 489 nm (non-collinear optical parametric amplification: NOPA) respectively. Measurements of fluorescence lifetimes used a 360 nm pump and a 440 nm probe (sum frequency mixing of the fundamental and appropriate NOPA wavelength) with a 150 fs pulse duration at 0.46 µJ/pump pulse. I-V-L characteristics of fabricated OLEDs were measured using a Keithley 2400 SourceMeter and a calibrated integrating sphere coupled to a fiber spectrometer and a silicon photodiode detector.

4.3.1 Prilezhaev Epoxidation of Polymers PHCySF (4) and PHNSF (5)

The synthesis of 2,7-dibromo-3,6-dimethoxy-9-hexyl-9-[2-(cyclohex-3-en-1-yl)ethyl]silafluorene (HCySF) and 2,7-dibromo-3,6-dimethoxy-9-hexyl-9-[2-(bicyclohept-5-en-2-yl)ethyl]silafluorene (HNSF) monomers and the procedure for their polymerization to PHCySF (4) and PHNSF (5) has been published by our group previously. Details for synthesizing both monomer and polymer starting materials is provided in chapter 3 along with characteristic spectral data. The following procedure for the selective epoxidation of cyclohexenyl and norbornenyl moieties (via the Prilezhaev reaction) is applicable to both polymers (4) and (5).

Prilezhaev Epoxidation of PHNSF (5):

Beginning with PHNSF (50 kg/mol, PDI = 1.8, see Supporting Information for synthesis details), the selective epoxidation of 50% norbornenyl side groups is accomplished by dissolving 200 mg of polymer (0.46 mmol norbornenyl moieties) in 11 mL of toluene in a large screw top vial. The solution was cooled in an ice bath until the temperature fell below 5°C. In a separate vial, a solution of 72% m-chloroperoxybenzoic acid (m-CPBA) was prepared in DCM (53 mg/ml, 0.25 M). mCPBA solution was also cooled in an ice bath. For a 50% epoxidation, 720 µL of the
cooled m-CPBA solution was slowly added dropwise to a rapidly stirring polymer solution. The reaction was continuously stirred at low temperature for a period of 10-15 min before removing from the ice bath and precipitating the product via the addition of hexanes. The product was allowed to settle (or collected using a centrifuge) and the solvent was removed prior to drying the white solid in vacuo. To remove residue of m-CPBA, the product was precipitated twice from a concentrated THF solution into methanol before finally being dissolved in toluene to make a 32 mg/mL solution. The reaction yield is quantitative excluding losses from material transfer during purification. (PHNSF-E50) (1): $^1$H-NMR (CD$_2$Cl$_2$, 400 MHz) (ppm): 7.45 (s, 2H), 7.46 (s, 2H), 6.12-5.81 (m, 1H), 3.91 (s, 6H), 2.71 (d, 1H), 2.60-0.39 (m, 22H).

(PHCySF-E50) (2): $^1$H-NMR (CD$_2$Cl$_2$, 400 MHz) (ppm): 7.47 (s, 2H), 7.42 (s, 2H), 5.55 (s, 1H), 3.91 (s, 6H), 3.01 (s, 1H), 1.91-0.77 (m, 24H).

4.3.2 Photopatterning of Polymer Films

The 16 mg/mL toluene polymer solutions (prepared in the previous section) were mixed in equal parts with a 0.5 mg/mL toluene solution of Bis(4-tert-butylphenyl)iodonium hexafluorophosphate (DtBPI-PF$_6$). The resultant mixture was filtered through 0.22 µm PTFE syringe filters prior to use. Thin, contiguous films (80-100 nm) of polymers (1) and (2), were formed by spin casting at rates of 1000 rpm for 2 min. Without a soft bake, substrates were photopatterned using a chromium-on-quartz shadow mask with a printed test pattern and the 365 nm I-line of a low pressure mercury arc lamp used in a Karl Suss M4 mask aligner. A N$_2$ stream was used to blanket the substrate from air during the exposure to prevent photooxidation. Samples were removed from the maskaligner and soft baked at 90°C for 30 s under a nitrogen blanket. Once cooled, patterns were developed by submerging the substrates in toluene and
lightly agitating the container. Removal of non-crosslinked material normally occurs within 30 s. The films were dried with a N₂ gun and analyzed with respect to PL via confocal microscope. In cases where Förster dopants were used, the above procedure was followed with the addition of the correct amount of either C540A or TPP added to the polymer solution prior to spin casting.

4.3.3 Electroluminescent Device Fabrication

OLEDs were prepared using prepatterned ITO substrates (7 ohm/sqr, Visiontek Inc.) which were cleaned using O₂ plasma for a period of 5 min. PEDOT:PSS (AL4083) was diluted (1:1 v/v) with distilled water prior to spin casting at 3000 rpm for 2 min (acceleration was set to 1000 rpm/s). The substrates were transferred to a N₂ filled glovebox and dried by heating at 110°C for 30 min on a hotplate. All subsequent processing was done under N₂. Once cooled, a hole injection layer (HIL) was deposited by spin casting a 10 mg/mL chlorobenzene Poly-TPD (American Dye Source) solution at 2000 rpm for 2 min (acceleration = 1000 rpm/s). The HIL layer was dried by baking substrate at 150°C for 30 min. Once cooled, the emissive polymer layer (either (1) or (2)) was deposited by spincasting an 8 mg/mL toluene solution (containing ~4mol% DtBPI-PF₆) at 1000 rpm for 2 min (acceleration = 1000 rpm/s). Without soft bake, the substrate was placed under a 365 nm UV LED (190 mW, Thor Labs) and exposed for 5 s. Crosslinking was completed by a 90°C soft bake for 30 s. Residual amounts of non-crosslinked material and PAG residues were removed by submerging the substrate in toluene within a large screw-top vial. The substrate was placed in the glovebox antechamber dried under vacuum for a period of 30 min prior to depositing a Ca/Al cathode. The optimal calcium layer thickness was 50 nm (deposited at a rate of 0.8 Å/s). The aluminium layer thickness was 200 nm (deposited at a rate of 1 Å/s). I-V-L device characteristics were measured following the encapsulation of the OLEDs to protect them from degradation.
4.4 References


Supporting Information 3

Synthesis and Application of Photolithographically Patternable Deep Blue Emitting Poly(3,6-dimethoxy-9,9-dialkylsilafluorene)s

S1.0: Photograph of a 2.54 cm x 2.54 cm PHNSF-E50 patterned substrate being illuminated by 365 nm collimated LED.
S1.1: Decadic Extinction Coefficient of C540A in PMMA used in the calculation of T and Forster Radius.

S1.2: Decadic Extinction Coefficient of TPP in PMMA used in the calculation of T and Forster Radius.
Chapter 5

3-D Ultra High Resolution Two-Photon Laser Writing of Blue Light-Emitting Conjugate Polymers

5.0 Introduction

Among the most exciting and technological relevant advances in optical lithography to occur within the last decade has been the development of two-photon, direct laser writing (DLW).\textsuperscript{[1]} The wide applicability of this technique across various disciplines has already begun to broadly impact the future of optical sensor construction,\textsuperscript{[2]} medical diagnostics\textsuperscript{[3]} as well as optical waveguide\textsuperscript{[4]} and laser design.\textsuperscript{[5]} The increased availability of DLW systems has initiated a paradigmatic shift away from conventional 3-D fabrication methods reliant on sequential deposition of single layers. Organic photovoltaics (OPV),\textsuperscript{[6]} organic light emitting diodes (OLED)\textsuperscript{[7]} and organic thin film transistors (OTFT)\textsuperscript{[8]} are beginning to evolve beyond present multilayered designs and into the domain of true three dimensional electronics yielding increased transistor densities (through improved vertical designs) and improved light collection and outcoupling for OPVs and OLEDs (by creating light diffusing grids and microlens).

With the emerging potential of two-photon DLW, however, comes the need to develop photoresist materials with more advanced function (electrical conduction, light emission, optical gain etc.) than what is currently available from commercial suppliers. SU-8 is a widely accepted photoresist used in the 3-D fabrication of ornate structures and waveguides for optical circuits,\textsuperscript{[9]} but it cannot perform as the photopatterned channel material in a vertical OTFT or be written
Figure 3: Examples of various structures produced by two-photon DLW writing in photosensitive films of PHNSF-E50/DtBPI-PF₆. Fluorescent micrographs were taken using a 365 nm excitation source. a) A fluorescent microscope image of a representative 50 µm x 50 µm dose test pattern consisting of a 2D grid of bars with elliptical cross-section (bar width = 800 nm). b) An SEM image of the aforementioned test pattern. Note the clearly resolved bars and good adhesion to the substrate. An illustration of the structure’s cross-section is depicted in the top right corner. c-d) Are both representative fluorescence and SEM images of 500 µm x 500 µm grid. The structure is relatively defect free and emits a strong and homogeneous PL identical to that of non-patterned films. e-f) Images of a truly 3-D bilayer 500 µm x 500 µm logpile structure. In the SEM image, a second row of bars can be seen stacked on an underlying grid. g) DLW can also be used produce luminescent graphics and text.
into optical structures which serve as both gain medium and resonator cavity. We report herein a blue light-emitting polymer developed for the explicit purpose of photolithographic patterning and report a method which permits the highest resolution patterning of a conjugate polymer to date using a laser based method. Because our method relies on a two photon absorption mechanism occurring within a microscopic focal volume (i.e. a voxel), patterning is neither diffraction limited nor restricted to two dimensions. Additionally, fabricating features with sub-micron resolution is well within the capabilities of our material.

There are a number of notable photopatternable light emitting polymers in the literature to date. Meerholtz et al. have designed polymers with acid sensitive oxetane sidechains and have reached resolutions as low as 1μm using a combination of conventional UV lithography, photoacids and shadow masks.\cite{10} Additionally, the authors have used laser interference lithography (LIL) techniques to generate photopatterned gratings with periodicities on the order of 300-400 nm. While LIL is an auspicious method of patterning periodic features (such as gratings) with sub-micron resolution, it is generally limited with respect to the variety of designs readily accessible.\cite{11}

Laser-based thermal crosslinking methods, which must be distinguished from the method described in this communication, are reliant on the decomposition of thermally sensitive acid generating compounds (TAGs) in laser exposed region of a conjugate polymer film.\cite{12} The polymer does not absorb the laser irradiation but a dye compound sensitive to laser wavelengths (typically within the near infrared (NIR) region) is added additionally to the TAG. Laser light from an inorganic diode incident on a polymer film are absorbed by the dye, converting the photons into heat by internal conversion. Localized heating in the irradiated regions rises rapidly
Figure 4: Schematic of the major components in a two-photon DLW system. Many design variations are possible, but all systems require components such as an ultrafast laser capable of delivering stable light pulse of several hundred femtoseconds. In addition to the proper focusing optics and computer control, a precision 3-D piezoelectric stage is required move the sample in all three coordinate planes to allow a pattern to be traced by the focused laser beam.

Over a period of microseconds. At sufficiently high temperatures, increased acidity in the film induces chemical changes in polymer side groups (such as tetrahydropyranyl (THP) groups) altering the solubility of light exposed regions.\textsuperscript{[13]}

Holdcroft et al. have developed several conjugate polymer variations which have pendent THP groups.\textsuperscript{[14]} In recent work, the authors have used a NIR flatbed laser scanner to generate 2-D patterned substrates using light-emitting polymers. Their patterning process requires two active layers be formed via sequential spin casting of polymer solutions. The first layer consists of the light-emitting polymer with THP side groups and the IBPF TAG. The second layer contains the NIR absorbing dye in a poly(methacrylate) matrix. By selectively etching light exposed regions, patterns were resolvable up to 10 μm.
Additional laser patterning technique including high power ablation\cite{15} and laser photobleaching\cite{16} also have respective advantages and offer high degrees of design freedom. Like thermal laser patterning, however, resolution limits of such methods are not reported to exceed several microns whilst also being limited to two dimensions.

By using a NIR femtosecond pulse laser system as opposed to a continuous wave laser source, a two-photon absorption processes is exploited for photopattering spin coated or dropcast films of our novel light-emitting polymer, poly(3,6-dimethoxy-9-hexyl-9-[2-(bicyclohept-5-en-2-yl)-ethyl]silafluorene) (PHNSF-E50), which has 50% of its norbornenyl sidechains converted to crosslinkable epoxide groups. Combined with \(~4\) mol\% photoacid, PHNSF-E50 can be fabricated into arbitrary microstructures using two-photon DLW whilst maintaining its efficient blue fluorescence, Figure 1.

Figure 1 showcases many of the structures produced in this study. Log piles are very common structures which are ever-present in many facets of photonics.\cite{17} Using two-photon DLW methods, they are straightforward and fast to produce. Hence, single layer log piles test grids were written at the initial stages of our study using a range of parameters (laser power, scan rates etc) to determine optimal writing conditions. Eventually, by spin casting thicker PHNSF-E50 films (\(~5\) µm), true 3-D bilayer log piles were produced, Figure 1e-f. SEM analysis reveals that each bar comprising the structures of Figure 1 is elliptical in profile which is consistent with the geometry of the writing volume.

There are several pre-existing fabrication methods used to create 3-D nano/microstructures, many of which are well suited for large area coverage. 3-D lithography methods such as phase-mask lithography and holographic lithography, for example, are capable of producing periodic 3-D structures several tens of microns thick over several square centimeters, but incur the costs associated with retooling the setup for each new structure.\cite{18}
That is to say, for each new design a different mask must be produced which is specific to a parameter set derived from non-trivial calculations. This places such methods outside of the scope of many laboratories in addition to making the method time consuming and expensive. Direct laser writing techniques offers fewer technical restrictions in planning new structures, but at the cost of reduced fabrication speeds inherent to serial scribing processes using a single beam (the same comparison can be made between conventional 2-D lithography and e-beam techniques). There are several challenging aspects in the construction of 3-D laser writing systems, but fortunately the widespread adoption of 3-D writing has meant the successful commercialization of more affordable laser writing systems with user interfaces designed for a diverse range of professionals without an extensive background in optics.\[9\]

Figure 2 summarizes important optical and geometric parameters of our two-photon DLW system. Within a voxel, light at the fundamental wavelength of the laser (light to which the photoresist must necessarily be transparent) has exceeded a threshold intensity such that a two-photon absorption is induced in a photosensitized film of PHNSF-E50 and polymerization can occur (details of crosslinking reaction are discussed below). The size and shape of voxels are dependent on the iso-intensity surfaces of the microscope objective in addition to the multiphoton exposure threshold inherent to the photoresist.

### 5.1 Results and Discussion

With the substrate secured to a 3-D precision piezoelectric stage, the sample is scanned relative to the focused volume of the laser beam and a pre-programmed design is serially traced in a manner of minutes. Given sufficient time, a near unlimited number of structures ranging in
Figure 5: Scheme illustrating the Prilehaev epoxidation of PHNSF (1) to PHNSF-E50 (2) using 0.5 molar equivalence of m-CPBA with respect to norbornenyl side groups. When combined with 3-4 mol% DIBPI-PF6 (3) (with respect to epoxide), the photosensitive mixture will undergo ring-opening polymerization during a soft bake at 80°C following two-photon DLW. (Note R = repeat unit of neighbouring polymer).

complexity and size can be fabricated from straightforward CAD inputs. Most importantly, multiple passes of the writing volume over the same region is possible given the nature of photo-initiated cationic ring-opening polymerization occurring within light exposed regions of PHNSF-E50 films during two-photon DLW (Figure 3). Because minimal polymerization results from the
initial exposure, the difference in refractive indices of exposed and unexposed regions of the PHNSF-E50 is small and during future passes of the beam, light propagation is unaltered.

The practical limitation of two-photon DLW resolution is both chemical and optical. With regards to the chemical process initiated in a photoresist following exposure, a voxel can become as small as the photosensitivity of the material will allow. In this respect, two-photon DLW is not a diffraction limited lithography method. However, like all resists, sensitivity threshold is neither infinitesimal nor sharply defined. Optically, laser sources are not perfectly stable and this complicates the process of operating at a constant threshold value for two-photon absorption. Due in part to these reasons and localized inhomogeneities within photoresists films, the resolution limit using a commercially available negative-tone photoresist such as SU-8 is as low as 120 nm for illumination at a wavelength of 780 nm in state-of-the-art systems.[19]

Referring to Figure 4, one observes that resolutions as low as 170 nm have been achieved using PHNSF-E50. Unlike SU-8, however, PHNSF-E50 is a high performance polymer which has previously been used as an efficient blue emissive material for OLEDs as well as a deep blue emitting gain medium in solid state polymer lasers.[20] PHNSF-E50 is a poly(9,9-dialkylsilafuorene) (PSF) derivative, where PSF is a class of polymer structurally analogous to poly(9,9-dialkylfluorenes) but consists of a silafluorene repeat unit where the 9-carbon has been substituted with silicon. Silafluorenes are best known for the oxidative stability and deep blue emission.[21] We have previously reported that polymers derived from 3,6-dimethoxy-2,7-dibromo-9,9’-dialkylsilafuorenes have superior film forming properties in addition to solution like photophysical characteristics. This we posited was due to the presence of methoxy substituents which result in a small arbitrary torsion between neighbouring repeat units. The effect of which is twofold. Firstly, isolated emission centers are generated which
Figure 6: SEM image depicting results of two-photon DLW dose test used in the optimization of writing parameters. The smallest resolvable feature yielded in the test was an impressive 170 nm (see inset of image).

contribute to the pure blue emission. Secondly, the reduced planarity of the chain prevents efficient stacking of chain segments and suppresses the formation of microcrystalline phases. Referred to as the β-phase in poly(9,9-dialkylfluorenes) (PF), microcrystalline regions are undesired from an emitter standpoint because they contribute to higher wavelength eximer peaks which broaden the emission considerably. Additionally, while the effect is not readily apparent in spin cast thin films, thicker films of PF are largely opaque because the random orientations of microcryalline phases act as light scattering centers. The high transparency of PHNSF-E50, due to the apparent lack of light scattering microcrystallites, means thicker films (> 100 µm) are possible and two-photon DLW can proceed without scattering of the laser, which would make the process of achieving a well defined writing volume impossible.
Similar to many commercial negative-tone resists, the photoinitiated crosslinking of PHNSF-E50 is enabled by pendant epoxide groups which undergo an acid catalyzed ring-opening polymerization (ROP), Figure 3. Protons are generated within a voxel by two-photon absorption and subsequent decomposition of the photoacid Bis(4-tert-butylphenyl)iodonium hexafluorophosphate (DtBPI-PF$_6$, (3)). Once protons are generated, ROP within the exposed regions is completed during a soft bake step and the insoluble regions can be developed by dissolving the non-crosslinked material in an appropriate solvent (i.e. toluene).

PHNSF-E50 is produced by a two step protocol beginning with polymerization of the silafluorene monomer: 2,7-dibromo-3,6-dimethoxy-9-hexyl-9-[2-(bicyclohept-5-en-2-yl)ethyl]silafluorene to produce PHNSF (1). Details of the monomer synthesis and its subsequent polymerization have been published by our group.$^{[22]}$ PHNSF is further reacted with variable amounts of m-chloroperoxybenzoic acid (m-CPBA) in a Prilezhaev epoxidation reaction. The reaction proceeds smoothly over a period of 10-15 min submerged in an ice bath following the dropwise addition of an m-CPBA solution. We found epoxidation to be near quantitative, however, conversions of 50% norbornenyl side groups to norbornenyl oxide (designated PHNSF-E50) was sufficient for effective crosslinking resulting in rigid structures.

Figure 4, depicts the result of a dose test used to establish the writing conditions for one of two DLW systems used in this study. Using a titanium:sapphire femtosecond laser which was coupled into an inverted optical microscope equipped with a high NA objective, groups of test lines are produced whilst the stage is moved at different velocities. Each test group is subdivided into lines produced at different exposure intensities, which is controlled with a mechanical shutter. There are three distinct regions which result, which we refer to as over exposed, optimally exposed and insufficiently exposed. Overly exposed areas become crosslinked but show signs of obvious damage incurred from light intensities far exceeding the threshold of the
material. These areas exhibit low or non-existent photoluminescence and written features are very poorly resolved. Development of optimally exposed regions, however, show high photoluminescence yield (AQY: ~ 80-85%, $\lambda_{em} = 410$ nm; see PL spectra provided in Supporting Information) and well resolved features with high fidelity to the path traced by the writing volume.

Each bar in the dose test is constructed by joining individual voxels. Of course, the absolute dimensions of a voxel can be adjusted by altering the laser pulse power. Higher energy pulses result in larger features just as decreasing the energy per pulse results in arbitrarily smaller features. The smallest obtainable feature is limited by the photosensitivity of PHNSF-E50/DtBPI-PF$_6$ films. As shown in the inset of Figure 4, the smallest resolvable feature was ~ 170 nm. This is very close to the best performance of commercial materials used in combination with a 800 nm Ti:Al$_2$O$_3$ DLW system. Regions exposed to even lower laser pulse energies do not crosslink sufficiently, however, and are destroyed in the development process.

Similar results were obtained using a frequency doubled 1045 nm uJewel D400-RV femtosecond fiber laser (IMRA America) operating at a 100 kHz repetition rate. The laser pulse duration was 200 fs. The bilayer log pile structure shown in Figure 1e-f was written using 10 mm/s scan rate and a 0.9 NA objective lens.

5.2 Conclusion

While this photonic structure (and others produced in this study) are not functional, that is, the PC lattice parameters are too large to yield a bandgap in the wavelength region of the polymer emission, we believe they clearly demonstrate the potential of combining a photopatternable conjugate polymer photoresist (and proven gain medium) with two-photon DLW to generate 3-D structures. In a future manuscript, we will show that methods developed during this study are
sufficient to construct whispering gallery mode lasers comprised of microsphere, microtoroid or microdisk resonators fabricated from the PHNSF-E50 gain medium. Future work oriented towards reducing written feature sizes will utilize advanced lithography techniques derived from the combination of two-photon DLW and stimulated emission depletion (STED) microscopy. STED has already been used to fabricate submicron structures using a two laser configuration.\textsuperscript{[23]}

We believe creating high Q-factor resonators for a new generation of solid state organic lasers and fabricating OLEDs and OPVs with performance enhancing 3-D components represents several of the exciting opportunities made possible by 3-D lithography of conjugated polymers and composites.

5.3 Experimental

The synthesis of HNSF monomer and the procedure for its polymerization to PHNSF (1) and the synthetic protocol for selective epoxidation of norbornyl side groups to their respective epoxide has been published by our group previously.\textsuperscript{[20, 22]} Details for synthesizing both monomer and polymer starting materials is provided in chapters 3 and 4 along with characteristic spectral data. Prilezhaev Epoxidation of PHNSF (1) to the corresponding PHNSF-E50 is provided below. Chemicals and solvents were purchased from TCI America and Sigma Aldrich and used without need for further purification. NMR was performed on a 400 MHz Bruker Avance III Spectrometer. Solution and thin film absorption and photoluminescence spectra were recorded using a Perkin-Elmer 900 UV-Vis Spectrometer and a Perkin-Elmer LS-50B Luminescence Spectrophotometer and spectral data is provided in the supporting information. Florescence microscopy images where acquired using an Olympus AX70 microscope equipped with a fluorescence lamp, digital camera and associated image capture software. Electron microscopy was performed using a Hitachi TM-1000 tabletop SEM.
5.3.1 Prilezhaev Epoxidation of PHNSF (1)

Beginning with PHNSF (50 kg/mol, PDI = 1.8, see chapter 3), the selective epoxidation of 50% norbornenyl side groups is accomplished by dissolving 200 mg of polymer (0.46 mmol norbornenyl moieties) in 11 mL of toluene in a large screw top vial. The solution was cooled in an ice bath until the temperature fell below 5°C. In a separate vial, a solution of 72% m-chloroperoxybenzoic acid (m-CPBA) was prepared in DCM (53 mg/ml, 0.25 M). mCPBA solution was also cooled in an ice bath. For a 50% epoxidation, 720 µL of the cooled m-CPBA solution was slowly added dropwise to a rapidly stirring polymer solution. The reaction was continuously stirred at low temperature for a period of 10-15 min before removing from the ice bath and precipitating the product via the addition of hexanes. The product was allowed to settle (or collected using a centrifuge) and the solvent was removed prior to drying the white solid in vacuo. To remove residue of m-CPBA, the product was precipitated twice from a concentrated THF solution into methanol before finally being dissolved in toluene to make a 32 mg/mL solution. The reaction yield is quantitative excluding losses from material transfer during purification. (PHNSF-E50) (2): \(^1\)H-NMR (CD\(_2\)Cl\(_2\), 400 MHz) (ppm): 7.45 (s, 2H), 7.46 (s, 2H), 6.12-5.81 (m, 1H), 3.91 (s, 6H), 2.71 (d, 1H), 1.91-0.39 (m, 22H).

5.3.2 Film Preparation and Direct Laser Writing

The 32 mg/mL toluene polymer solutions (prepared in the previous section) were mixed in equal parts with a 1.0 mg/mL toluene solution of Bis(4-tert-butylphenyl)iodonium hexafluorophosphate (DtBPI-PF\(_6\)) (representing ~ 4 mol% PAG with respect to epoxide groups). The resultant mixture was filtered through 0.45 µm PTFE syringe filters prior to use. Thick, contiguous films (3-5 µm) of the PHNSF-E50/DtBPI-PF\(_6\) mixture were prepared by spin casting the solution onto a thin glass cover slip at a slow rate (500 rpm for 2 min). For inverted
microscope two-photon DLW configurations, even thicker (~800 µm) films could be made by simply drop casting PHNSF-E50/DtBPI-PF₆ solutions.

For writing log pile structures, a frequency doubled 1045 nm uJewel D400-RV femtosecond fiber laser (IMRA America) operating at a 100 kHz repetition rate was used. The laser pulse duration was 200 fs. Structures were written with optimal resolution using a 10 mm/s scan rate and a 0.9 NA objective lens. Following writing, samples were soft baked at 80°C for 5 min and then allowed to cool for 2 min. Structures were developed by submerging the substrate in toluene with mild agitation. Following 5 min, the samples were dried with a N₂ stream and characterized with fluorescent microscopy and scanning electron microscopy.

Additional structures such as the dose test lines in Figure 4 and the “U of T” text in Figure 1g were written using a femtosecond 800 nm Ti:Al₂O₃ laser with an optimal pulse energy of 1 mW and scan rates of 1 mm/s. Development of structures using this system was identical that described earlier.

5.4 References


Direct Laser Writing of 3-D Conjugated Polymer Waveguides

McDowell, J.


Chapter 6

Synthesis of Poly(Spirosilabifluorene) Copolymers and Their Improved Stability in Blue Emitting Polymer LEDs over Non-Spiro Analogs

6.0 Introduction

Integrating nonplanar “spiro” compounds[1-4] into organic electronics shows promise for improving properties which are important for the efficient operation of devices such as organic light-emitting diodes (OLEDs),[5-11] organic phototransistors (OPTs),[12,13] organic solid-state lasers (OSSLs),[14-17] as well as organic thin film transistors (OTFTs).[18] Such properties include morphological, thermal and chemical stability, superior isolation of emitting centers and hence enhanced photo/electroluminescent quantum efficiencies, better solubility and improved solution processability.[19-22] Compounds which are considered “spiro” consist of two orthogonally arranged subsections centered on a tetravalent atom. There are many examples of symmetric as well as asymmetric spiro compounds in the literature, many common examples are spirobifluorenes (SF) derivatives.[23-27] SFs are rigid 3D structures due to the lack of rotational freedom of orthogonal fluorene subunits, the molecular structure of spirobifluorenes effectively disrupts regular crystalline packing and results in films which have solution like photophysical properties.[28, 29] Consequently, SFs are an increasing important class of compound used in the design of new solid state chromophores with improved performance over simpler fluorene derivatives which show a higher tendency to crystallize and hence exhibit reduced PL efficiency.[30, 31] The appealing electronic and optical properties of other SF derivatives,
including spiro-MeOTAD, has prompted their use in solar energy conversion as a charge transport material in, for example, dye sensitized solar cells.\cite{32, 33}

The silicon analogs of SFs, spirosilabifluorenes (SSFs), have unique characteristics which distinguish them as subsets of the newly explored class of compounds called siloles.\cite{34-40} Siloles, as well as silafluorenes and spirosilabifluorenes, are becoming increasingly popular components in organic electronics due to their brilliant solid state blue luminescence and superior electron conductivity.\cite{41-44} The higher electron affinity and conductivity, which is particularly promising for OLEDs, originates from $\sigma^*\pi^*$ conjugation between the $\sigma^*$ antibonding orbital of the exocyclic Si-C bond and the $\pi^*$ antibonding orbital of the butadiene fragment.\cite{45}
Figure 7: a) Illustration of PLED architecture indicating respective energy levels of layers. b) Photograph of a PHSSF-co-PDHSF device under 9V operation. c) EL spectrum of device featured in a). d) CIE colour map with white circle indicating the position of PHSSF-co-PDHSF PLED emission. e) Scheme illustrating the synthesis of both segments A and B which are reacted with SiCl4 to form the final spiro-bisilafluorene monomer (10).
Evidence for this phenomenon is obtained by measuring atypical bathochromic shifts in silole absorption spectrum and comparing results to corresponding carbon analogues.\cite{46} Kafihi et al. have reported a series of asymmetrically aryl-substituted 9,9’-spiro-9-silabifluorene derivatives which were prepared via the cyclization of the 2,2’-dilithiobiphenyls with silicon tetrachloride.\cite{46} These materials form amorphous films which are both transparent and stable due to a relatively high glass transition temperatures (Tg = 203-228°C). Solid state films of their materials were reported to have an intense violet-blue emission (\(\lambda_{em} = 398-415\) nm) with high absolute photoluminescence quantum yields of 30-55%. For many siloles, high PL efficiency can be attributed to a phenomenon known as aggregation induced emission (AIE).\cite{47} AIE compounds have significant potential as gain medium in solid state organic lasers in addition to light-emitting materials in OLEDs. In the latter case, SSFs have already shown impressive performance with OLED electroluminescence external quantum efficiencies as high as \(\eta_{eff} = 4.8\%\) (at 10 mA/cm\(^2\)).\cite{48} Many low molecular weight siloles, however, crystallize readily, contributing to device degradation when these materials are incorporated in OLED structures.\cite{49}

In an attempt to prevent this issue, we have prepared a unique deep blue emitting copolymer, poly(3,6-dimethoxy-9,9’-dihexylsilafluorene-co-3,6-dimethoxy-2’,3’,6’,7’-tetrahexyloxy-9,9-spiro-9-silabifluorene) (PDHSF-co-PHSSF), with a spirosilabifluorene repeat unit (10), which we expected to exhibit high glass transition temperatures, improved solid-state PL quantum yields and have superior OLED performance. As we will later demonstrate, a large volume fraction of spirosilabifluorene leads to EL intensities of working OLEDs being measurably more stable with improved lifetimes over non-spiro poly(silafluorenes) devices.
6.1 Results and Discussion

Figure 1e illustrates the synthetic steps taken to create our spirosilabifluorene monomer. To the best of our knowledge, there has been no prior attempt to polymerize SSFs and hence no polymer LEDs have been constructed using PSSFs. The synthesis is two-part, each resulting in a segment (referred to as segment A and B) which combines in a final cyclization step involving tetrachlorosilane. Segment A possesses two bromide groups necessary for the polymerization, details of which will be discussed below. Its synthesis begins with commercially available o-dianisidine (1) starting material which is easily converted to (2) by the reaction of an intermediate bis(diazonium) salt with CuBr (the latter is produced in situ by the oxidation of (1) by NaNO₂). Iodination of (2) is directed at carbons C5 and C5’ by the electron donating methoxy groups at C3 and C3’. Yields of both reactions are high, averaging 85% for the Sandmeyer bromination deamination and 80% for the iodination.

Notable features of segment B include four hexyloxy groups installed to increase solubility of the monomer and resultant polymer. Segment B is also the product of several high yielding steps beginning with catechol (4). Both hydroxyl groups are converted to hexyloxy following reflux with 1-bromohexanes in DMF. Following purification, (5) undergoes a single iodination after being stirred in an aqueous solution (acidified with H₂SO₄) with a slight access of I₂ and H₂O₂ oxidant. 1-iodo-3,4-dihexyloxybenzene (6) was collected as a pure liquid, the last fraction of a vacuum distillation which efficiently separates it from non-iodonated starting materials. To obtain the biphenyl (7), a unique aryl coupling procedure was used involving the reaction of (6) with the hypervalent iodine complex phenyliodine bis(trifluoroacetate), PIFA, in the presence of a yield improving additive BF₃-Et₂O. The mechanism by which aryl coupling occurs has been the subject of numerous reviews.[51, 52] This exothermic reaction is performed whilst cooling with a dry ice/acetone bath to control the rate, which is high despite the low
Poly(Spirobisilafluorenes) and Their Improved Stability in Blue Emitting Polymer LEDs  McDowell, J.

Product is formed readily by the time the reaction warms to room temperature. Pure (7) is obtained by crystallization at low temperatures from hexanes. The product forms white, blocky crystals which readily dissolve in organic solvents. Lithiation is performed at low temperatures using an acetone/dry ice bath by dissolving (7) in THF and adding two equivalence of n-butyl lithium. The metathesis is quantitative within a few minutes.

The first of two cyclization reactions begins with a duel substitution reaction involving lithiated (7) and SiCl₄ to form two LiCl and the ring-closed dichlorosilafluorene (9). Because the rate of substitution is quiet high, the order of addition is crucial to avoiding large amounts of unwanted symmetric spirosilabifluorenes. While maintaining a low temperature for both solutions, the soluble dilithiated (7) is added to a separate solution of SiCl₄ in THF. The reaction is complete by the time the solution warms to room temperature. Solvent is removed in vacuo from the moisture sentitive (9) and the crude product residue is redissolved in dry hexanes and cooled to precipitate out less soluble by-products. Removal of hexanes yields the pure dichlorosilafluorene segment and concentrated THF solutions of this compound can be stored for long periods of time with refrigeration. ²⁹Si NMR of (9) shows a single peak at 5.8 ppm, confirming the purity of the intermediate (see supporting information).

To complete the second cyclization and generate the final spirosilabifluorene monomer, segment A is reacted with two equivalence of n-BuLi in an analogous manner to the reaction with (7). However, it is necessary to maintain the temperature of this reaction at -100°C (using a nitrogen/MeOH slush bath) throughout the lithiation step to ensure selectivity for iodide while both bromide groups remain unreacted. A concentrated solution of the dichlorosilafluorene (9) in THF equalling one equivalence with respect to (8), is added and the final product is purified by crystallization from hexanes. Figure 2 shows the ¹H NMR of 2.7-dibromo-3.6-dimethoxy-2’,3’,6’,7’-tetrahexyloxy-9,9-spiro-9-silabifluorene (10). Additionally, ²⁹Si NMR of this
compound consists of a single resonance peak at -8.6 ppm belonging to the pure product. Complete characterization of (10) can be found in the experimental section and supporting information.

**Figure 2**: a) $^1$H NMR of monomer (10) (purified by crystallization from hexanes) and assignment of peaks. b) $^1$H NMR of copolymer PHSSF-co-PDHSF as well as the spectra of each monomer (for comparison). Broad aromatic peaks between 7.4-7.6 ppm belong to DHSF repeat units (as
reported previously \cite{50}. Integration of this broad set of peaks with respect to the remaining collection of four HSSF peaks gives an estimate of 1:1 DHSF to HSSF repeat units.
Prior to polymerization, the dibromide HSSF premonomer (10) converted to its respective diarylmagnesates by Grignard metathesis. The highest rate of conversion was obtained when using a mixed solvent system consisting of 30% 1,4-dioxane in tetrahydrofuran. Within 2 h, >95% of HSSF was converted to bis(bromo-3,6-dimethoxy-2’,3’,6’,7’-tetrahexyloxy-9,9-spiro-9-silabifluorene)magnesate (12). In a separate reaction, 2,7-dibromo-3,6-dimethoxy-9,9-dihexylsilafluorene was converted to its respective diarylmagnesate (11) under identical conditions. In both reactions, formation of an insoluble MgCl₂-Dioxane adduct is obvious from the precipitation of a fine white solid within a few seconds of adding iPrMgCl-LiCl.
Figure 3: a) Scheme illustrating the conversion of (10) to (12) via Grignard metathesis in a mixed THF:1,4-dioxane (7:3) solvent and the subsequent copolymerization b) of (11) and (12) to yield PHSSF-co-PDHSF. c) Characteristic solid state absorption and PL spectra of PHSSF-co-PDHSF plotted with comparison to EL.
We utilized an efficient nickel catalyzed polymerization based on diarylmagnesate monomers to create copolymers of (11) and (12) with roughly half of the repeat units derived from (11). PHSSF-co-PDHSF (13) was produced in good yield with number average molecular weights exceeding 50 kg/mol with a PDI = 1.8. The polymerization was complete in less than 30 min and polymerization was quenched by adding HCl followed by precipitation in methanol. Excess monomer and oligomers were removed by subsequent soxhlet extraction with EtOH over a period of 5-6 h. Figure 3a-b illustrates the reaction conditions used in the polymerization. Figure 2b shows a representative $^1$H NMR of the purified polymer.

Initial thermal analysis of the copolymer using TGA/DSC indicates the material is stable under nitrogen up to a temperature of 350°C, figure 4. Morphologically, there were no obvious phase transitions occurring within the temperature region of 25-250°C over numerous cycles. PSFs are known for their thermal stability, and our initial findings seem to indicate that adding HSSF into the polymer backbone does nothing if not improve this quality.$^{[53-55]}$

---

**Figure 8**: TGA/DSC of PHSSF-co-PDHSF over the temperature range 25-200°C. No $T_g$ or $T_m$ phase changes occur over multiple cycles.
The HOMO energy of the PHSSF-co-PDHSF copolymer was determined using cyclic voltammetry and the bandgap was determined from the solid-state absorption onset (CV can be found in supporting information and absorption spectrum is shown figure 3c). It was found that HOMO/LUMO energy levels (5.7 eV and 2.7 eV respectively) are identical to those reported earlier by our group for similar polysilafluorene.[50]

Light emitting devices were constructed in a N₂ filled glovebox on O₂ plasma treated ITO on glass. We employed a simple trilayer design using PEDOT:PSS as the hole injection layer (~10 nm) as well as a thin hole transport layer consisting of poly-TPD (~ 20 nm). A 100 nm emissive layer consisting of PHSSF-co-PDHSF was deposited by spin casting from a 10 mg/mL polymer solution in toluene. A Ca cathode, which best matches the copolymer LUMO energy of 2.7 eV, was found to yield the best performing devices. Figure 1a illustrates the device architecture and energy levels of the respective layers. A photograph of a functioning device operating at 9V is shown in figure 1b. A respective electroluminescence spectrum is shown in figure 1c. The EL peak maximum is nearly identical to the thin film PL spectra at ~410 nm. However, the FWHM of the EL emission is noticeably larger than the solid-state PL, figure 3c. Figure 1d shows the location of the device’s blue-violet emission on the CIE colour map with coordinates of x = 0.246 and y = 0.237.

Performance data obtained from devices with PHSSF-co-PDHSF and PDHSF emissive layers is presented in figure 5. PDHSF OLEDs were created for the purpose of comparison and to establish the impact of spirosilabifluorene on performance. The OLEDs tested both have 0.25 cm² emissive areas. Referring to the I-V curve, we observe the turn on voltage to be roughly 5 V in both devices. This is not surprising given the energy levels of both emissive materials are essentially identical. Both devices were operated up to 10 V and each reached a maximum current density of ~ 65 mA/cm². For the PHSSF-co-PDHSF device, the maximum irradiance of
the device was 40 W/m² at a current density of 60 mA/cm². The maximum efficiency of the device, in terms of EQE, was 2.9 % when operating at 38 mA/cm². Likewise, the PDHSF device operated at a maximum irradiance of 38 W/m² at a current density of 45 mA/cm². The maximum efficiency of the device was 2.5 % when operating at 30 mA/cm².

**Figure 9**: a) I-V plots of both PHSSF-co-PDHSF and PDHSF devices. In both cases, device turn-on occurs at ~ 5 V. Light was collected using a calibrated integrating sphere coupled to a fibre spectrometer. b) Plot of EQE and Irradiance as a function of current density of both PHSSF-co-PDHSF and PDHSF devices. Note the maximum efficiency achieved was 2.9 % at 38 mA/cm² for PHSSF-co-PDHSF and 2.5 % at 30 mA/cm² for PDHSF.
Over extended device operation times, however, a significant difference in performance emerges. Figure 6 plots the averaged EL intensity for the different devices over a period of 10 h (the data set consists of six total devices, with three of each type). When operating with a current density of 6 mA/cm², both device types show a gradual decline in EL intensity. The slope of the PHSSF-co-PDHSF device, however, is noticeably less than the PDHSF device. We posit the reason for such a noticeable deviation is the spirosilabifluorene unit. The inclusion of this rigid 3D structure in the polymer backbone leads to reduced interaction between neighbouring chains, preventing the degenerative effects of crystallization and excimer formation resulting in an overall increase in electroluminescent yield over a longer time frame.

![Figure 6: Plot of the EL intensity for both PHSSF-co-PDHSF and PDHSF devices. Over the course of 10 h, the EL intensity of the PDHSF device drops 20% more than the PHSSF-co-PDHSF device.](image)

6.2 Conclusion

In future work, we intend to increase the number of copolymers produced by this method with the aim of producing stable blue, green and red emitters for light emitting technologies. It would also be of considerable interest to combine the promising performance of these copolymers with
the additional functionality of photocrosslinkable versions of PSF which our group has previously reported on.\textsuperscript{56} Ultimately the goal is to develop longer lasting emitters which can be photolithographically patterned to allow for solution processed full colour thin-film displays driven by TFT backplanes as well combining multiple long lifetime polymer emitters to produce solution processed WOLEDs.

6.3 Experimental

All syntheses were performed under inert atmosphere using standard schlenk line or glovebox techniques unless otherwise stated. Chemicals were purchased from TCI America and Sigma Aldrich and used without need for further purification. Tetrahydrofuran and 1,4-Dioxane were distilled over sodium/benzophenone prior to use. Proton, carbon and silicon NMR were performed on a 400 MHz Bruker Avance III Spectrometer. Solution and thin film absorption and photoluminescence spectra were recorded using a Perkin-Elmer 900 UV-Vis Spectrometer and a Perkin-Elmer LS-50B Luminescence Spectrophotometer. Polymer quantum efficiencies were calculated through the use of an integrating sphere using a focused 365 nm LED as the excitation source.\textsuperscript{57} Polymer molecular weights were measured with a Viscotek GPC calibrated with respect to polystyrene standards using THF as an eluent and column temperature of 35°C. Cyclic voltammetry was performed on polymer samples in a solution of 100mM tetrabutylammonium hexafluorophosphate in dichloromethane (distilled from CaH\textsubscript{2} under N\textsubscript{2} prior to measurement). Potentials were measured using a Solartron 1278 potentiostat using platinum working and counter electrodes in addition to a Ag/AgCl pseudo reference electrode. Measurements were calibrated using ferrocene as an internal standard. Thermogravimetric and calorimetric data was acquired using a TA Instruments SDT Q600 simultaneous TGA/DSC
system operated under an inert N₂ atmosphere. Poly(3,6-dimethoxy-9,9-dihexylsilafluorene) (PDHSF) was prepared using a previously published procedure.[50]

6.3.1 HSSF Monomer Synthesis

4,4'-dibromo-3,3'-dimethoxy-1,1'-biphenyl (2):

The synthesis of (2) is adapted from the Sandmeyer reaction outlined by Haung et al.[58] o-dianisidine is oxidized to its diazonium salt and reacted with a bromide source to eliminate N₂ and generate the appropriate aryl dibromide. 10.0g (40 mmol) o-dianisidine is combined with 40 mL 40% HBr, 160 mL H₂O and 160 mL acetonitrile in a large three necked flask equipped with a thermometer, dropping funnel and efficient stirring. The majority of the starting material is dissolved in acetonitrile. The reaction is cooled to 0°C an ice/salt bath, 7.2 g (104.4mmol) sodium nitrite (dissolved in 14 mL water) is chilled and added dropwise to the reaction such that the temperature does not rise above 10°C. Following addition, the reaction is stirred at reduced temperature for 30min. Meanwhile, freshly prepared CuBr is obtained by precipitation of CuNO₃ and NaBr in water.[59] The white precipitate is collected by filtration and dried in a vacuum oven prior to use. 13.0 g (90.6 mmol) CuBr is dissolved in 160 mL 40% HBr (aqueous) and added to the thoroughly rinsed dropping funnel. Glass tubing is used to extend the stem of the dropping funnel below the surface of the solution to prevent side reaction with atmospheric O₂. CuBr/HBr is added slowly, maintaining a temperature less than 10°C, over the course of 1hr. The solution is then allowed to warm to room temperature and is subsequently heated to reflux (80°C) for 1hr until an insoluble white solid becomes apparent. The solution is then cooled and extracted with 250-300 mL chloroform, washed with 10 wt% NaOH and brine, and finally dried with MgSO₄ before removing solvent by rotoevaporation. The crude, light brown powder is sufficiently pure to proceed to the next step. Yield is 13 g or 90%. ¹H-NMR (CD₂Cl₂, 400
Poly(Spirobisilafluorenes) and Their Improved Stability in Blue Emitting Polymer LEDs

McDowell, J.

13C-NMR (CD2Cl2, 400 MHz) (ppm): 156.19, 141.35, 133.56, 120.59, 111.38, 110.87, 56.35. EI-MS (M+) = 369.9204 m/z (calc: 369.9213)

4,4'-dibromo-2,2'-diiodo-5,5'-dimethoxy-1,1'-biphenyl (3):

Selective iodination at the 2 and 2’ is directed by para substituted methoxy groups. 13.0 g (34.9 mmol) (2), 3.3 g (15.4 mmol) KIO₃ and 9.6 g (38.0 mmol) I₂ are added to a large three neck flask equipped with a reflux condenser. The starting material is dissolved in a mixture of 260 mL acetic acid and 26 mL 20 wt% H₂SO₄. The solution is heated to 80°C for 12 h. Large amounts of insoluble product precipitate as the reaction proceeds. Once cooled to room temperature, an additional 250 mL of H₂O is added to precipitate further product. The precipitate is collected by filtration, dried briefly under vacuum and redissolved in the minimum amount of CHCl₃ (~200 mL). The solution is extracted with 10wt% NaOH, washed with brine, and finally dried with MgSO₄ before removing the solvent by rotoevaporation. The crude product is then purified by recrystallization from boiling 95% ethanol (~45 mL EtOH/g of crude product). The resulting brown needle like crystals are collected by filtration and rigorously dried in a vacuum oven prior to being used in the following step. The yield of purified product following the first recrystallization is 12.4 g or 56%. Yield can be improved to 84% by concentrating the supernatant cooling to produce another crop of crystals. 1H-NMR (CD2Cl2, 400 MHz) (ppm): 7.98 (s, 2H), 6.66 (s, 2H), 3.81 (s, 6H). 13C-NMR (CD2Cl2, 400 MHz) (ppm): 156.14, 148.16, 142.08, 113.30, 112.45, 87.56, 56.49. EI-MS (M+) = 621.7137 m/z (calc: 621.7141)

o-dihexyloxybenzene (5):

In a 250 mL flask, add 5.0 g (45.4 mmol) of catechol and 74 g of K₂CO₃. Stir the suspension rapidly following the addition of 100 mL DMF and 23.4 mL (167 mmol) 1-bromohexane. The
reaction is heated to 90°C and stirred for an additional 14 h. Once cooled, excess K₂CO₃ is removed via filtration and the supernatant is placed in a vacuum distillation apparatus thereby allowing DMF solvent and unreacted 1-bromohexane to be collected by heating under reduced pressure. The remaining residue in the still-pot is redissolved in DCM (~200 mL). The crude product is washed three times with aqueous 10 wt% NaOH, dried with MgSO₄ and the solvent was removed by rotovap. The product was sufficiently pure to use in the following step. Yield is 4.4 g or 69%.  

\[ \text{EI-MS (M+)} = 602.08645 \text{ m/z (calc: 602.08513)}. \]

\[ \text{EI-MS (M+)} = 278.2246 \text{ m/z (calc:278.2239)}. \]

1-iodo-3,4-dihexyloxybenzene (6):

3.6 g (12.93 mmol) of (5) produced in the previous step is added to a 250 mL flask. 130 mL of H₂O is added and a medium rate of stirring is initiated. 3.3 g (12.93 mmol) of finely ground I₂ is added to the flask. The reaction was heated to 50°C. 1.5g (~1.5 mL) of 30 wt% H₂O₂ is added with continued stirring followed by 2 mL of conc. H₂SO₄. The reaction was stirred vigorously for 12 h at 50°C. Once cooled to room temperature, the reaction solution was extracted (x3) with 20 mL chloroform. The separated organic phase was washed with aqueous 10 wt% NaOH, dried with MgSO₄ and the chloroform was removed by rotovap. The residue was placed in a short path micro vacuum distillation apparatus equipped with three receiving flasks. Three fractions are collected during the distillation. A low temperature fraction of residual solvent is collected first (if at all). A mid-temperature fraction (135°C at 60 mTorr) is usually collected in small volumes and consists largely of unreacted starting material (5). At a bath temperature of 200°C, the highest fraction of reddish-brown oil is pure (6). Yield is 4.1 g or 78%.
Poly(Spirobisilafluorenes) and Their Improved Stability in Blue Emitting Polymer LEDs
McDowell, J.

400 MHz) (ppm): 7.15 (d, 1H), 7.12 (s, 1H), 6.59 (d, 1H), 3.92 (t, 4H), 1.77-0.90 (m, 22H). $^{13}$C-NMR (CD$_2$Cl$_2$, 400 MHz) (ppm): 150.14, 149.31, 129.86, 122.54, 115.72, 82.60, 69.43, 31.64, 29.23, 25.68, 22.62, 14.10. EI-MS (M$^+$) = 404.1212 m/z (calc: 404.1235)

2,2'-diiodo-4,4',5,5'-tetrahexyloxy-1,1'-biphenyl (7):

7.0 g (17.3 mmol) of (6) is added into a 250 mL schlenk flask with 85 mL of freshly distilled DCM. The solution was cooled to -78°C using an acetone/dry-ice bath. Once chilled, 2.1 mL (17.3 mmol) of BF$_3$-Et$_2$O was added dropwise by syringe. In a separate 50 mL schlenk flask, 3.72 g (8.65 mmol) of phenyliodine bis(trifluoroacetate) (PIFA) was dissolved in a minimum amount of DCM (~30 mL). The PIFA solution was added dropwise to the solution of (6) over the course of 5 minutes. Allow the reaction to stir for 3 h and slowly warm to room temperature. The reaction was quenched with H$_2$O and the solution extracted with chloroform, dried with MgSO$_4$ and rotovapped to dryness. The solid product was crystallized from hexanes (~75 mL) after chilling to -20°C over night. The yield of the first crystallization was 4.6 g or 65%. A second batch of crystals yielded an additional 1.2 g bringing the total yield to 83%. $^1$H-NMR (CD$_2$Cl$_2$, 400 MHz) (ppm): 7.30 (s, 2H), 6.71 (s, 2H), 4.00 (t, 8H), 1.82-0.89 (m, 44H). $^{13}$C-NMR (CD$_2$Cl$_2$, 400 MHz) (ppm): 149.16, 141.49, 122.82, 115.50, 88.20, 69.32, 31.57, 29.17, 25.55, 22.66, 14.01. EI-MS (M$^+$) = 806.2256 m/z (calc: 806.2268)

2,3,6,7-tetrahexyloxy-9,9-dichlorosilafluorene (9):

6.0 g (7.4 mmol) of (7) was added to a 100 mL schlenk flask and dissolved in 70 mL of freshly distilled THF. The reaction was subsequently cooled to -78°C using an acetone/dry-ice bath and 9.23 mL (14.86 mmol) of 1.6 M n-BuLi is added dropwise over 10 min. Caution must be taken to ensure sufficient stirring is possible when a thick slurry forms after half the n-BuLi addition is complete and the concentration of the largely insoluble monolithiated intermediate is highest.
The reaction is stirred at reduced temperature for 30 min. In a separate 250 mL schlenk flask, 3.9 mL (33.88 mmol) of SiCl₄ is dissolved in 35 mL of dry THF and chilled to -78°C. The chilled lithiation solution is transferred rapidly via cannula into the SiCl₄ solution with rapid stirring. The react is allowed to warm to room temperature and stirred for 12 h. Solvent and residual SiCl₄ are removed in vacuo using a vacuum manifold. The residue is redissolved in pentanes and filtered through a plug of celite to remove insoluble salts. The solution is chilled at -20°C overnight and the supernatant removed from the insoluble by-products. Removing the pentanes yields the final product as a clear transparent oil in 71% yield or 3.4 g. ¹H-NMR (CD₂Cl₂, 400 MHz) (ppm): 7.28 (s, 2H), 7.21 (s, 2H), 3.81 (t, 4H), 3.59 (t, 4H), 1.66-0.89 (m, 44H). ¹³C-NMR (CD₂Cl₂, 400 MHz) (ppm): 144.61, 138.03, 120.33, 111.13, 86.86, 68.45, 31.51, 29.24, 25.64, 22.66, 14.29. ²⁹Si-NMR (CD₂Cl₂, 400 MHz) (ppm): 5.84.

2.7-dibromo-3.6-dimethoxy-2',3',6',7'-tetrahexyloxy-9,9-spiro-9-silabifluorene, HSSF, (10):

Selective lithiation of the iodide substituents in (3) is achieved at low temperature by use of -110°C MeOH/N₂ slush bath. 4.62 g (7.4 mmol) (3) is added to a 250 mL schlenk flask and dissolved in 70 mL dry THF under Ar. The solution is cooled to -110°C and 9.32 mL (14.9 mmol) n-BuLi (1.6M in hexanes) is added dropwise over 30min. It should be noted that over the course of the lithiation, a yellow, insoluble monolithiated intermediate forms and an appropriately large stir bar is required to agitate the thick slurry. Continued addition of n-BuLi redissolves the intermediate and the clear solution is stirred for an additional 30 min at reduced temperature. In a separate schlenk flask, dissolve 4.8 g (7.4 mmol) of (9) in a minimum amount of dry THF. Add this solution via syringe to the solution of lithiated (3) and allow the flask to warm to room temperature and stir for 12 h. The reaction is quenched by the addition of H₂O and the product is extracted with ether. The organic phase is washed with brine and dried with
MgSO₄ before solvent removal by rotoevaporation. Pure blocky white crystals of (10) are obtained by crystallizing the crude powder from pentanes overnight at -20°C. Yield is 3.6 g or 51% following crystallization. ¹H-NMR (CD₂Cl₂, 400 MHz) (ppm): 7.55 (s, 2H), 7.47 (s, 2H), 7.33 (s, 2H), 6.83 (s, 2H), 4.17 (t, 4H), 4.11 (s, 6H), 3.88 (t, 4H), 1.9-0.91 (m, 44H). ¹³C-NMR (CD₂Cl₂, 400 MHz) (ppm): 158.91, 152.81, 150.73, 149.43, 138.66, 127.12, 122.71, 118.82, 112.58, 107.13, 105.47, 69.75, 56.78, 31.87, 29.78, 26.16, 23.05, 14.21. ²⁹Si-NMR (CD₂Cl₂, 400 MHz) (ppm): -8.59. EI-MS (M⁺) = 948.3000 m/z (calc: 948.2995)

6.3.2 Polymer Synthesis

**Preparation of Diarylmagnesates (12), HSSF₂Mg, and (11), DHSF₂Mg:**

The following procedure is equally applicable to both HSSF and DHSF and is carried out in separate reaction flasks prior to polymerization. For example, the room temperature Grignard metathesis of 2,7-dibromo-3,6-dimethoxy-2’,3’,6’,7’-tetrahexyloxy-9,9-spiro-9-silabifluorene, HSSF (10), was performed in a N₂ filled glovebox within a 5 mL scintillation vial. A 0.5 M solution of (10) was prepared using THF as a solvent. Additionally, a Grignard solution of isopropyl magnesium chloride (1.3 M in THF) activated by 1.0 equivalence of LiCl was prepared and used following 1 h of stirring to allow for the complete dissolution of the salt. The Grignard solution could be stored and used for several days in the glovebox without appreciable change. In a typical experiment, 2.0 mL (1.0 mmol) of a 0.5 M solution of (10) is diluted with 1.2 mL 1,4-dioxane and stirred rapidly. 510 µL of 1.3 M iPrMgCl·LiCl (0.66 mmol) was added by a single injection. The formation of insoluble white MgCl₂-Diox adduct is observed almost immediately. The solution is stirred continuously for 2 h to complete the *in situ* generation of diarylmagnesate (12). The white MgCl₂-Diox precipitate is allowed to settle, and the clear pale
yellow solution is separated. The solution can be stored for several hours, but slowly decomposes over a period of 24 h.

**Poly(3,6-dimethoxy-9,9’-dihexylsilafuorene-co-3,6-dimethoxy-2’,3’,6’,7’-tetrahexyloxy-9,9-spiro-9-silabifluorene) (PDHSF-co-PHSSF) (13):**

A monomer feed ratio $r = [\text{HSSF}_2\text{Mg}] / [\text{DHSF}_2\text{Mg}]$ of unity was achieved in the copolymerization. To accomplish this, 1.0 mL of DHSF$_2$Mg (11) solution (prepared as above) was added to 1.0 mL of the above prepared solution of HSSF$_2$Mg (12), where [HSSF$_2$Mg] = 88 mM. Polymerization is initiated by adding 1 mg or approximately 1 mol% dppeNiCl$_2$. The solution immediately becomes yellow-orange and is stirred continuously for 15-20 m. As the polymerization progresses, additional MgBr$_2$-Diox precipitate is formed and the solution becomes steadily more opaque and viscous. The vial is removed from the glovebox and the polymerization quenched by adding several drops of 5.0 M HCl followed by adding the solution dropwise to a large excess of methanol such that product precipitates as a fibrous white solid. Polymer is collected by suction filtration. For removal of residual monomer and oligomers, the crude polymer was soxhlet extracted with ethanol for 4-5 h. The polymer solid is characterized by GPC and $^1$H-NMR. Optical properties where studied by collecting solution and solid state absorption and fluorescence spectra in addition to absolute quantum yield (See figure 3c). The yield of purified polymer is 76 %. $^1$H-NMR (CD$_2$Cl$_2$, 400 MHz) (ppm): 7.6-7.4 (m, 4H, DHSF repeat unit), 7.4-6.6 (m, 16H, HSSF repeat unit), 4.2-3.6 (m, 34H), 2.0-0.4 (m, 114H). GPC: 53 kg/mol., PDI = 1.8

**6.3.3 Electroluminescent Device Fabrication**

OLEDs were prepared using prepatterned ITO substrates (7 ohm/sqr, Visiontek Inc.) which were cleaned using O2 plasma for a period of 5 min. PEDOT:PSS (AL4083, Clevios) was diluted (1:1
v/v) with DI water prior to spin casting at 3000 rpm for 2 min (acceleration was set to 1000 rpm/s). The substrates were transferred to a N2 filled glovebox and dried by heating at 110°C for 30 min on a hotplate. All subsequent processing was done under N2. Once cooled, a hole injection layer (HIL) was deposited by spin casting a 10 mg/mL chlorobenzene Poly-TPD (American Dye Source) solution at 2000 rpm for 2 min (acceleration = 1000 rpm/s). The HIL layer was dried by baking the substrate at 150°C for 30 min. Once cooled, the emissive polymer layer (either (PHSSF-co-PDHSF) or (PDHSF)) was deposited by spincasting an 10 mg/mL toluene solution at 1000 rpm for 2 min (acceleration = 1000 rpm/s). The substrate was placed in the glovebox antechamber and dried under vacuum for a period of 30 min prior to depositing a Ca/Al cathode. The optimal Ca layer thickness was 50 nm (deposited at a rate of 0.8 Å/s). The Al layer thickness was 200 nm (deposited at a rate of 1 Å/s). I-V-L device characteristics were measured following the encapsulation of the OLEDs to protect them from degradation. Radiance of each pixel (as a function of applied bias) was measured using a Keithley 2400 SourceMeter and a calibrated integrating sphere coupled to a fiber spectrometer.

6.4 References


Supporting Information 4

Synthesis of Poly(Spirosilabifluorene) Copolymers and Their Improved Stability in Blue Emitting Polymer LEDs over Non-Spiro Analogs

Section 1: $^1$H/$^13$C NMR of Intermediate Compounds

S1.1.0 – 4,4’-dibromo-3,3’-dimethoxy-1,1’-biphenyl (2) $^1$H-NMR

S1.1.1 – 4,4’-dibromo-3,3’-dimethoxy-1,1’-biphenyl (2) $^{13}$C-NMR

S1.2.0 – 4,4’-dibromo-2,2’-diiodo-5,5’-dimethoxy-1,1’-biphenyl (3) $^1$H-NMR

S1.2.1 – 4,4’-dibromo-2,2’-diiodo-5,5’-dimethoxy-1,1’-biphenyl (3) $^{13}$C-NMR

S1.3.0 – o-dihexyloxybenzene (5) $^1$H-NMR

S1.3.1 – o-dihexyloxybenzene (5) $^{13}$C-NMR

S1.4.0 – 1-iodo-3,4-dihexyloxybenzene (6) $^1$H-NMR

S1.4.1 – 1-iodo-3,4-dihexyloxybenzene (6) $^{13}$C-NMR

S1.5.0 – 2,2’-diiodo-4,4’,5,5’-tetrahexyloxy-1,1’-biphenyl (7) $^1$H-NMR

S1.5.1 – 2,2’-diiodo-4,4’,5,5’-tetrahexyloxy-1,1’-biphenyl (7) $^{13}$C-NMR

S1.6.0 – 2,3,6,7-tetrahexyloxy-9,9-dichlorosilafluorene (9) $^1$H-NMR

S1.6.1 – 2,3,6,7-tetrahexyloxy-9,9-dichlorosilafluorene (9) $^{13}$C-NMR

S1.6.2 – 2,3,6,7-tetrahexyloxy-9,9-dichlorosilafluorene (9) $^{29}$Si-NMR
S1.7.0 – 2.7-dibromo-3.6-dimethoxy-2’,3’,6’,7’-tetrahexyloxy-9,9-spiro-9-silabifluorene (10)

$^1$H-NMR

S1.7.1 – 2.7-dibromo-3.6-dimethoxy-2’,3’,6’,7’-tetrahexyloxy-9,9-spiro-9-silabifluorene (10)

$^{13}$C-NMR

S1.7.2 – 2.7-dibromo-3.6-dimethoxy-2’,3’,6’,7’-tetrahexyloxy-9,9-spiro-9-silabifluorene (10)

$^{29}$Si-NMR

S1.8.0 – 2.7-dibromo-3.6-dimethoxy-9,9-dihexylsilabifluorene (11) $^1$H-NMR

S1.8.1 – 2.7-dibromo-3.6-dimethoxy-9,9-dihexylsilabifluorene (11) $^{13}$C-NMR

S1.8.2 – 2.7-dibromo-3.6-dimethoxy-9,9-dihexylsilabifluorene (11) $^{29}$Si-NMR

S1.9.0 – Poly(3,6-dimethoxy-9,9’-dihexylsilafluorene-co-3.6-dimethoxy-2’,3’,6’,7’-tetrahexyloxy-9,9-spiro-9-silabifluorene) (PDHSF-co-PHSSF) (13) $^1$H-NMR

Section2: GPC Data:

S2.1.0 – Poly(3,6-dimethoxy-9,9’-dihexylsilafluorene-co-3.6-dimethoxy-2’,3’,6’,7’-tetrahexyloxy-9,9-spiro-9-silabifluorene) (PDHSF-co-PHSSF) (13) - GPC (THF Eluent, 35°C Column Temp., PS Standards):

S2.2.0 – Poly(3,6-dimethoxy-9,9’-dihexylsilafluorene) (PDHSF) - GPC (THF Eluent, 35°C Column Temp., PS Standards): PC Data:

Section3: Electrochemistry

S3.1.0 – CV of Poly(3,6-dimethoxy-9,9’-dihexylsilafluorene-co-3.6-dimethoxy-2’,3’,6’,7’-tetrahexyloxy-9,9-spiro-9-silabifluorene) (PDHSF-co-PHSSF) (13)
Section 1: $^1$H/$^{13}$C NMR of Intermediate Compounds

S1.1.0 – 4,4′-dibromo-3,3′-dimethoxy-1,1′-biphenyl (2) $^1$H-NMR

S1.1.1 – 4,4′-dibromo-3,3′-dimethoxy-1,1′-biphenyl (2) $^{13}$C-NMR
S1.2.0 – 4,4'-dibromo-2,2'-diiodo-5,5'-dimethoxy-1,1'-biphenyl (3) \(^{1}\text{H}-\text{NMR}\)

S1.2.1 – 4,4'-dibromo-2,2'-diiodo-5,5'-dimethoxy-1,1'-biphenyl (3) \(^{13}\text{C}-\text{NMR}\)
S1.3.0 – o-dihexyloxybenzene (5) $^1$H-NMR

S1.3.1 – o-dihexyloxybenzene (5) $^{13}$C-NMR
S1.4.0 – 1-iodo-3,4-dihexyloxybenzene (6) $^1$H-NMR

S1.4.1 – 1-iodo-3,4-dihexyloxybenzene (6) $^{13}$C-NMR
S1.5.0 – 2,2’-diiodo-4,4’,5,5’-tetrahexyloxy-1,1’-biphenyl (7) $^1$H-NMR

S1.5.1 – 2,2’-diiodo-4,4’,5,5’-tetrahexyloxy-1,1’-biphenyl (7) $^{13}$C-NMR
S1.6.0 – 2,3,6,7-tetrahexyloxy-9,9-dichlorosilafluorene (9) $^1$H-NMR

S1.6.1 – 2,3,6,7-tetrahexyloxy-9,9-dichlorosilafluorene (9) $^{13}$C-NMR
S1.6.2 – 2,3,6,7-tetrahexyloxy-9,9-dichlorosilafluorene (9) $^{29}$Si-NMR

S1.7.0 – 2,7-dibromo-3,6-dimethoxy-2’,3’,6’,7’-tetrahexyloxy-9,9-spiro-9-silabifluorene (10) $^1$H-NMR
S1.7.1 – 2.7-dibromo-3.6-dimethoxy-2’,3’,6’,7’-tetrahexyloxy-9,9-spiro-9-silabifluorene (10)

$^{13}$C-NMR

S1.7.2 – 2.7-dibromo-3.6-dimethoxy-2’,3’,6’,7’-tetrahexyloxy-9,9-spiro-9-silabifluorene (10)

$^{29}$Si-NMR
S1.8.0 – 2.7-dibromo-3.6-dimethoxy-9,9-dihexylsilabifluorene (11) \(^{1}\text{H-NMR}\)

S1.8.1 – 2.7-dibromo-3.6-dimethoxy-9,9-dihexylsilabifluorene (11) \(^{13}\text{C-NMR}\)
S1.8.2 – 2.7-dibromo-3.6-dimethoxy-9,9-dihexylsilabifluorene (11) $^{29}$Si-NMR

S1.9.0 – Poly(3,6-dimethoxy-9.9’-dihexylsilabifluorene-co-3,6-dimethoxy-2’,3’,6’,7’-tetrahexyloxy-9,9-spiro-9-silabifluorene) (PDHSF-co-PHSSF) (13) $^1$H-NMR
Section 2: GPC Data:

S2.1.0 – Poly(3,6-dimethoxy-9,9′-dihexylsilfluorene-co-3,6-dimethoxy-2′,3′,6′,7′-tetrahexyloxy-9,9-spiro-9-silabifluorene) (PDHSF-co-PHSSF) (13)- GPC (THF Eluent, 35°C Column Temp., PS Standards):

S2.2.0 – Poly(3,6-dimethoxy-9,9′-dihexylsilfluorene) (PDHSF)- GPC (THF Eluent, 35°C Column Temp., PS Standards):
Section 3: Electrochemistry

S3.1.0 – CV of Poly(3,6-dimethoxy-9.9’-dihexylsilafluorene-co-3.6-dimethoxy-2’,3’,6’,7’-tetrahexyloxy-9,9-spiro-9-silabifluorene) (PDHSF-co-PHSSF) (13)
Chapter 7

Electroactuation of Alkoxy Silane-Functionalized Polyferrocenylsilane Microfibers

7.0 Introduction

Crosslinked polymer networks that mediate chemical, electronic, optical and mechanical signals are enticing materials from which to construct manipulators, switches and sensors. For use in robotics, these materials should ideally exhibit large property changes in response to small stimuli, generate mechanical stress and strain in fast response to electric signals and be easy to process.[1, 2]

We report herein the electroactuation of polymer microfibers made from an ethoxysilane derivative of redox active polymethyvinylferrocenylsilane (PMVFS) (3), Scheme 1.[3] Crosslinked fibers of average diameter 2.0±0.4 µm are fabricated by electrospinning high molecular weight polymer solutions of (3) (0.1 ≤ m ≤ 1.0) after initiating the acid catalyzed condensation of ethoxysilane.[4] In cases of low crosslink density, resultant fibers rapidly respond (< 100 ms) to electrical stimuli applied either via an electrode or by titration with redox active compounds. Videos taken by optical microscope demonstrate that large strains occur within 10 ms when fibers are oxidized electrochemically on an electrode surface submerged in a supporting electrolyte, see Figure 1 and supporting information.

For m = 0.1, we observe a regular buckling of the fiber due to a non-covalent interaction with the substrate as compressive stress along the fiber length reaches a critical limit (discussed
later). Lateral and longitudinal strain in the fiber increases towards a maximum of 60 ± 23% and 58 ± 2% respectively. Localization of the buckling into larger disordered looped segments occurs immediately after the initial deformation. Furthermore, we observe that by applying a reducing potential, much of the strain generated during oxidation is reversible. Cycling between an applied potential of +1.5 V to -2.0 V produces a reversible 20% longitudinal strain, Figure 1b. We attribute reduced strain after multiple cycles to decreasing contact with the electrode surface.

7.1 Results and Discussion

In the preparation of actuating fibers, high molecular weight PFMVS (2) \(^{[5]}\) \((M_n = 140 \pm 11.6 \text{ kg/mol}, \text{PDI} = 1.26 \pm 0.04)\) was synthesized by anionic ring-opening polymerization.\(^{[4]}\) PFMVS vinyl groups were further functionalized through the Pt-catalyzed hydrosilylation using HSi(OEt)\(_3\) to afford PFS (3).\(^{[6, 7]}\) Analysis by \(^1\text{H}-\text{NMR}\) of (3) demonstrated the controlled and near quantitative addition of HSi(OEt)\(_3\) to 10%, 25%, 50%, and 100% of the vinyl groups.

The time required for hydrolytic gelation of PFS (3) varied considerably with the loading of alkoxyisilane side groups and the amount of catalyst used. p-toluene sulfonic acid hydrate (PTSA·H\(_2\)O) was used as a catalyst and showed no tendency to oxidize the polymer during the curing process. The average curing time with a catalyst loading of 10 mol% is listed in Table 1.
PTSA hydrate also increased the conductivity of electrospinning solutions and improved the uniformity of electrospun fibers by minimizing the amount of bead defects.

Figure 1: a) Oxidized electrospun fibers rapidly expand under +1.5 V potential in LiOTf/γ-butyrolactone. b) Cathodic potential decreases roughly 20% of the initial strain within 1 min. (scale bar = 10 µm)

Electrospinning solutions were prepared by adding a 20 mM PTSA·H₂O/THF solution to a 90 mg/mL (~10 wt%) solution of (3) in THF and thoroughly mixing before loading a syringe and placing it into a syringe pump. For 1mL of m = 0.1 hydrosilylated polymer solution, the addition of 16 µL PTSA·H₂O solution allowed 30 minutes before gelation. During this time, a 5kV potential was applied between the syringe needle and a conductive ITO or gold substrate. Fibers
are produced and collected at an average distance of 10 cm from the needle. Before analysis, fibers were allowed to age for 12 h under ambient conditions so as to maximize the Si-O-Si crosslink density. ITO substrates with collected fibers deposited on them were incorporated into miniature electrochemical cells containing 0.125M lithium triflate (LiOTf) in γ-butyrolactone as electrolyte and were examined using an optical microscope as shown in supporting information.

FT-IR illustrates the effectiveness of PTSA as a gelator and the formation Si-O-Si linkages in a fiber mat. A representative spectrum is shown in Figure 6 for fibers consisting of m = 1 hydrosilylated PMVFS and the same polymer cured with 10 mol% of PTSA after 12 h. Peaks at υ 1110 cm\(^{-1}\), 1088 cm\(^{-1}\) and 961 cm\(^{-1}\) are characteristic Si-OEt absorptions. Following the catalyzed condensation and formation of Si-O-Si crosslinks, only a broad absorption peak at 1039 cm\(^{-1}\) indicative of Si-O-Si linkages can be detected.

Increased degrees of hydrosilylation afforded higher crosslink densities and allowed the mechanical properties of the fibers to be controlled.\(^{8}\) The elastic modulii of polymer thin films were measured by the strain-induced elastic buckling instability for mechanical measurement (SIEBIMM) technique and are summarized in Table 1.\(^{9}\) It should be noted that the value of 9.60 GPa for m = 1 is consistent with values obtained for silica thin films and reaffirms our conclusion that the majority of ethoxysilane groups have condensed in the aged films. While SEIBIMM can only be considered a crude approximation to the actual modulus of the same polymer in the form of fibers, a decrease in strain is observed for fibers with largest values of E. Referring to supporting information video, the oxidation of m = 1 fibers results in fracture and little deformation of fibers.

Our observation that sinusoidal buckling is dependent, at least in part, on the presence of an underlying substrate, was investigated by positioning fibers across micron gaps in an etched silicon wafer and oxidized them using an excess amount of tris(4-bromophenyl)ammoniumyl
hexachloroantimonate in the same solvent electrolyte system used in the electrochemical cells, Figure 2. in regions over a gap, fibers were observed to deform into large randomly oriented
Table 1. Gelation Time and Mechanical Properties of Crosslinked Dry Films Obtained from (90 mg/mL) Solution of PFS 3 Following Addition of 10 mol% PTSA·H₂O

<table>
<thead>
<tr>
<th>m, Fraction Hydrosilylation</th>
<th>Catalyst Loading (mol %)</th>
<th>Average Curing Time (min)</th>
<th>E, Elastic Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>10</td>
<td>33 ± 4</td>
<td>1.7 ± 0.67</td>
</tr>
<tr>
<td>0.25</td>
<td>10</td>
<td>15 ± 2</td>
<td>5 ± 2.57</td>
</tr>
<tr>
<td>0.50</td>
<td>10</td>
<td>4.0 ± 0.2</td>
<td>8 ± 1.89</td>
</tr>
<tr>
<td>1.00</td>
<td>10</td>
<td>2.00 ± 0.04</td>
<td>9.6 ± 0.85</td>
</tr>
</tbody>
</table>

loops whereas fiber segments positioned over silicon were found to buckle regularly in a lateral direction prior to localization of strain in an analogous way to Figure 1a. The sine waveform is indicative of compressive loading of slender columns described by classical mechanics. For the Euler type buckling to occur, we approximate each microfiber as a beam initially bound electrostatically and/or through hydrogen-bonding to a substrate and prevented from longitudinal displacement. Consequently, oxidation induces an axially compressive force as the fiber volume increases. When pressure exceeds the stability bifurcation point, the fiber buckles with the substrate acting as a continuous foundation. The sinusoidal lateral displacement
Figure 2: Fibers oxidized chemically on etched silicon grating demonstrate the substrate effect on buckling. Inset is a photograph of a railway sun kink. White arrows indicate a trench 15 µm wide which fiber span periodically. (scale bar = 20 µm)

of buckled beams on a foundation has been described by Timoshenko. Railway sun kinks generated by thermal expansion of steel rails supported on closely spaced ties are a macroscopic example of this phenomenon, Figure 2 (inset).

7.2 Conclusion

In summary, we have prepared electrospun electroactive microfibers from a gelable PFS derivative possessing crosslinkable alkoxy silane pendant groups. These materials display interesting strain-induced buckling behavior on electroactuation at low voltages (1.5 - 2.0 V). In contrast to reported methods of making polyaniline (PANI) and polypyrrole (PPy) fibers, there is no need to electrospin PFS as part of a blend with high molecular weight nonconductive polymers or to use nonconductive fibers as polymerization templates. While pH responsive
Electrospun polyacrylonitrile (PAN) fibers show considerable promise and exhibit longitudinal strains of 40% under basic conditions,\textsuperscript{[14]} PAN is not inherently redox active and such systems require large potentials to actuate electronically via the hydrolysis of water. Our future work will concentrate on creating stronger PFS yarns consisting of hundreds of electrospun fibers. Such structures could potentially rival existing bilayer actuators\textsuperscript{[15]} in strength but maintain rapid response times because of significantly larger surface area to volume ratios and smaller ion diffusion lengths.

7.3 Experimental Section

All manipulations were preformed under inert conditions in either a N\textsubscript{2} filled glovebox or using schlenk techniques. Methylvinylidichlorosilane, Pt(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Karstedt’s catalyst, 2.1-2.4 wt-% in xylenes), n-butyllithium (1.6M in hexanes) were obtained from commercial suppliers. Solvent and silanes were pre-dried and distilled via standard methods immediately prior to use. Dilithioferrocene was prepared according to a previously published methods. NMR spectra were acquired on a Varian Mercury 400 spectrometer using C\textsubscript{6}D\textsubscript{6} as a solvent. Gel Permeation Chromatography (GPC) results were measured relative to polystyrene standards in THF using a Viscotek GPCmax. IR data was collected on a Perkin-Elmer FT-IR after preparing polymer samples as KBr pellets. Young’s moduli were estimated by thin film wrinkling of cured polymer samples on PDMS as observed through an Olympus BX41 optical microscope. Section 7.3.2 illustrates the sample holder used for modulus measurements. PDMS was prepared from a Sylgard 184 Silicone Elastomer Kit using a 0.5:10 ratio of curing agent to prepolymer \textit{versus} the standard 1:10 ratio so that softer substrates could be obtained. Polymer fibres were generated through a home built electrospinning setup using a Stanford Research Systems P5350- 5000V variable power supply.
Electrochemical measurements and polymer fibre actuation were conducted in a miniature electrochemical cell connected to an Epsilon Potentiostat. The construction of the cell is described in section 7.3.1.

**Methylvinylsilaf[1]ferrocenophane (1):**
In the synthesis of 1, FeLi₂·2/3TMEDA (20 g, 70 mmol) was dissolved in 250mL dry ether in a 500mL schlenk flask. The solution was cooled to -78°C in acetone/dry ice bath and methylvinylidichlorosilane (9.89mL, 75.7 mmol) was added slowly via a syringe. The reaction was then allowed to warm to room temperature and left to stir overnight. Ether solvent was removed \textit{in vacuo} and redissolved in ~150mL of pentane. The resulting solution was then filtered through a ~100g of celite and the product was allowed to crystallize when cooled to -40°C in a glove box freezer. Crude product was recrystallized at least two more times. Collected supernatant can be concentrated and cooled to further harvest crystals. Resultant red crystalline flakes were thrice purified by sublimation under reduced pressure. Yield of the unpurified product: 74% ¹H-NMR (C₆D₆, 400MHz, ppm): δ0.44 (s, 3H); δ3.97 ( m, 2H); δ4.09 (m, 2H); δ4.39 (m, 4H); δ6.24 (m, 3H). ¹³C-NMR (C₆D₆, 400MHz, ppm): δ -4.25; δ31.74; δ75.51; δ75.93; δ77.72; δ77.76; δ134.65; δ134.89

**Polymethylvinylferrocenosilane (PFMVS) (2):**
Anionic ROP of monomer to make high molecular weight PFMVS was conducted in a N₂ filled glove box. 1.0 g (3.93 mmol) of 1 was weighed into a 20mL vial into which 12.7mL of dry THF was added. Once dissolved, 6.3µL n-BuLi (0.010 mmol, 1.6M in hexanes) was added by microsyringe. The reaction solution was stirred moderately for 45 minutes at which point the colour has changed noticeably from red to amber. At this point, the polymer solution was septum capped, removed from the box and immediately quenched with dry, degassed methanol. Polymer
is collected by precipitation in 250mL of methanol. The orange gum was collected and residual methanol was removed by heating at 60-70°C in a vacuum oven for 12hrs. GPC analysis for ten samples: \( M_n = 140 \pm 11.6 \) kg/mol, PDIs, 1.26\( \pm \)0.04. Samples were measured relative to polystyrene standards. \(^1\)H-NMR (C\(_6\)D\(_6\), 400MHz, ppm): \( \delta \)0.59 (s, 3H); \( \delta \)4.12 (m, 4H); \( \delta \)4.29 (m, 4H); \( \delta \)5.83 (dd, 1H); \( \delta \)6.05 (dd, 1H); \( \delta \)6.52 (m, 1H). \(^{13}\)C-NMR (C\(_6\)D\(_6\), 400MHz, ppm): \( \delta \)-3.17; \( \delta \)69.98; \( \delta \)71.77; \( \delta \)73.86; \( \delta \)132.64; \( \delta \)137.96

**Hydrosilylation of Olefin Functionalized PFS Using HSi(OEt)\(_3\) (3):**

PFMVS vinyl groups were further functionalized through the Pt catalyzed addition of silane. In a typical reaction to produced 10% hydrosilylated PFMVS, 500mg (1.97mmol) of (2) is dissolved in 14 mL of dry toluene. 35\( \mu \)L (0.20mmol) of HSi(OEt)\(_3\) is added \textit{via} a microsyringe. 74 \( \mu \)L of Pt(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Karstedt’s catalyst) ( \( \sim \)2wt% Pt in xylene) was added and the reaction was placed on a Ar schlenk line and heated to 60°C with stirring for 2 h on an oil bath. In preparation for electrospinning, toluene was removed \textit{in vacuo} to yield approximately 532mg of a soft orange gum which was then redissolved in 6mL of ACS grade THF to give a 90mg/mL electrospinning polymer solution. \(^1\)H-NMR of (3) showing near quantitative addition of HSi(OEt)\(_3\) to 10%, 25%, 50% and 100% of vinyl groups. Reaction completeness was estimated by calculating the ratio of integrated proton peaks at \( \delta \)0.34ppm and \( \delta \)0.44ppm which correspond to silyl methyl groups of the reacted and unreacted polymer repeat unit respectively. Table 2 summarizes the observed degree of hydrosilylation \textit{versus} the target modification.
Table 2: Estimate of Reaction Completeness by Integration of Silyl Methyl Peaks

<table>
<thead>
<tr>
<th>Desired Degree of Hydrosilylation (%)</th>
<th>Expected Ratio of Methyl Peaks</th>
<th>Observed Ratio of Methyl Peaks</th>
<th>Observed Degree of Hydrosilylation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>9</td>
<td>10.08</td>
<td>9.0</td>
</tr>
<tr>
<td>25</td>
<td>3</td>
<td>4.74</td>
<td>17.4</td>
</tr>
<tr>
<td>50</td>
<td>1</td>
<td>1.32</td>
<td>43.0</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>0.17</td>
<td>85.3</td>
</tr>
</tbody>
</table>

$^1$H-NMR of 3 ranging from 10% (bottom), 25%, 50% and 100% (top) (C$_6$D$_6$, 400MHz)

Figure 3: $^1$H-NMR (C$_6$D$_6$, 400MHz, ppm): $\delta$0.33 (s, br); $\delta$0.44 (s); $\delta$0.59 (m); $\delta$0.85 (m); $\delta$1.16 (t); $\delta$3.75 (q); $\delta$3.95 (m); $\delta$4.17 (m); $\delta$5.71 (dd); $\delta$6.02 (dd); $\delta$6.34 (m).
7.3.1 Electrospinning and Construction of Electrochemical Cell

In a typical electrospinning experiment, a solution of PTSA hydrate in THF is added to a polymer solution immediately before loading a 1 mL syringe with a 25½ gauge needle (with a filed down tip) and placing it into a syringe pump set to a delivery rate of 0.20 mL/h. For 1mL of a 90mg/mL 10% hydrosilylated polymer solution, the addition of 16µL of 20mM PTSA·H₂O allows 30 minutes before gelation. In this time, a 5kV voltage is applied between the needle and substrate and the fibers are produced and collected. Before analysis, fibers were allowed to age for 12 h at room temperature so as to maximize the Si-O-Si crosslink density. ITO substrates were incorporated into a miniature electrochemical cell containing 0.5M lithium triflate (LiOTf) in γ-butyrolactone electrolyte and examined using an optical microscope. The cell is comprised of two equal size pieces of conductive ITO glass. The pieces are separated by a hot melt spacer (Dupont) cut into a frame with a small opening through which electrolyte can be injected. The three pieces of the cell, Figure 4b, are clamped together and placed in an 80°C oven for 10min during which time the spacer melts and fuses the structure together. By placing a small drop of electrolyte near the cell opening and placing the system under vacuum, fluid is drawn into the cavity, Figure 4c. The small opening is then sealed with an epoxy resin and electrical contacts are made by attaching copper tape to overhanging edges made by placing the initial ITO pieces slightly askew. Silver epoxy is then applied around the tape ends to insure sufficient electrical contact is made. The cell is the mounted onto a microscope stage for observation.
7.3.2 SEIBIMM Mechanical Measurements and FT-IR

SEIBIMM requires small compression forces to be applied to small PDMS slabs coated with thin polymer films. To simplify this process and improve reproducibility of the experiment over many samples, the sample holder shown in Figure 5 was constructed. The device is adjusted by a micrometer which controls the magnitude of force applied in the x direction by a spring. The polymer coated PDMS slab is held in place by steel bars which lay overtop the sample and are screwed into place. Elongation of the PDMS substrate results in compression in the y direction and causes wrinkling of the thin film. The device is mounted on a microscopes stage for modulus measurements.

FT-IR samples of the 100% hydrosilylated PMVFS were prepared by electrospinning fiber mats and incorporating this material into KBr pellets, Figure 6. Cured polymer (10mol% PTSA) mats were soxhlet extracted with tetrahydofuran after aging for 12hrs under ambient conditions. This process removes uncondensed sol (0.5 wt%) and the FT-IR of the remaining material is consistent with Si-O-Si crosslink formation.
Figure 5: Photograph of SEiBIMM sample holder and observed wrinkling of polymer films with hydrosilylation fraction ranging from $10\% \leq m \leq 100\%$ (scale bar = 100 µm)

Figure 6: FT-IR of a representative spectrum is shown in supporting information for fibres consisting of $m = 1$ hydrosilylated PMVFS and the same polymer cured with 10 mol% of PTSA after 12 h. Peaks at 1110 cm$^{-1}$, 1088 cm$^{-1}$ and 961 cm$^{-1}$ are characteristic Si-OEt absorptions. Following the catalyzed condensation and formation of Si-O-Si crosslinks, only a broad absorption peak at 1039 cm$^{-1}$ indicative of Si-O-Si linkages can be detected. (Black Line = Uncrosslinked Film; Dotted Line = Crosslinked Film)
### 7.4 References


[6] Full synthetic and fabrication details are reported in the supporting information


Supporting Information 5

Electroactuation of Alkoxyisilane-Functionalized Polyferrocenylsilane Microfibers

S1.0 $^1$H-NMR of 1 (C$_6$D$_6$, 400MHz)

S1.1 $^1$H-NMR of 2 (C$_6$D$_6$, 400MHz)
Chapter 8

Conclusion

Our initial findings included a polymerization method which permits the formation of electronics grade poly(9,9-dioctylfluorene) with molecular weights in excess of \( M_n = 50 \text{ kg/mol} \) within 15 minutes using a scalable, room temperature method. In contrast, the number averaged molecular weights of polyfluorenes synthesized via room temperature Grignard metathesis (GRIM) polymerization are not reported to exceed 15 kg/mol. The copolymer poly(9,9-dioctylfluorene-co-4,4'-dihexyloxybinaphthalene) (BN-PFO) was also produced with similar molecular weight in the same time period. BN-PFO is a technologically relevant copolymer because it was reported to be amongst the lowest threshold organic lasing mediums available. Both the synthesis of diarylmagnesate monomers and the polymerization proceed rapidly at room temperature. The use of a mixed solvent system of THF and 1,4-dioxane decreased the Grignard metathesis reaction time by 17% (of the existing art) and improved reactivity towards sterically hindered and electron rich ortho alkoxy substrates. Utilizing the knowledge disclosed in this document, we believe new methods of generating co-polymers appropriate for OLED and organic laser applications may be possible.

We discovered polysilafluorenes (PSFs) are an important class of light-emitting conjugate polymers which have brilliant solid state blue luminescence, high quantum efficiency, excellent solubility and improved thermal stability. Additionally, these polymers have superior electron conductivity to polyfluorenes. The higher electron affinity and conductivity, which is particularly promising for OLEDs, originates from \( \sigma^*-\pi^* \) conjugation between the \( \sigma^* \) antibonding orbital of the exocyclic Si-C bond and the \( \pi^* \) antibonding orbital of the butadiene...
Concluding Remarks

We present the synthesis and thorough characterization of several new derivatives of 2,7-dibromo-3,6-dimethoxy-9,9-dialkylsilafluorene monomers and demonstrate an efficient and controlled chain growth room temperature polymerization. In addition to silafluorene monomers with simple alkyl side chains, we increased the functionality of several of our monomers by incorporating vinyl, cyclohexenyl and norbornenyl moieties into their side chains, which we believe is useful for post-polymerization modification. (i.e. adding pendant emitters to tune PL). To produce polymers, we used a nickel catalyzed polycondensation of diarylmagnesate type monomers in a mixed solvent system of THF and 1,4-Dioxane (7:3). Using 1,4-dioxane as a solvent was discovered to significantly increase the Mg/Br exchange rate by a factor of 5, reducing the time required for stoichiometric conversion of sterically hindered and electron rich 2,7-dibromo-3,6-dimethoxy-9,9-dialkylsilafluorene to 2 h. Also, relatively fast rates of polymerization were observed with greater than 90% Grignard conversion occurring within 30 min and $M_n > 50$ kg/mol (PDI ~ 1.7). The resultant polymers possessed characteristic blue photoluminescence with solid state quantum yields > 80%. Polymer films have excellent transparency (with a measured $E_g \sim 3.0$ eV) and thermal stability as demonstrated by TGA/DSC. Energy levels determined using CV were -5.62 eV and -2.62 eV for HOMO and LUMO respectively.

Future work will focus on utilizing polysilafluorenes as emitter in solution processed light emitting devices. The amorphous nature of thin films of our polymers, reminiscent of low threshold binaphol co-polymers of PFO, also make them ideal candidates for organic lasers. The emission and electronic properties of these polymers make them promising hosts for higher wavelength emitting dopants. Although not explored in this work, the presence of synthetically useful functional groups such as unsaturated double bonds (especially in the case of our
norbornene containing polymers) allows a plethora of reactions to be exploited for the purpose of chain functionalization.

In chapter four, we presented a protocol for photopatterning derivatives of poly(3,6-dimethoxy-9,9-dialkylsilafuorennes) with resolutions exceeding 10 μm. The procedure began by converting our unique PSFs materials (M_n = 50-55 kg/mol, PDI = 1.7), possessing cyclohexenyl and norbornenyl side chains, to their respective epoxides using the Prilezhaev reaction and m-chloroperoxybenzoic acid (mCPBA). Using the I-line (365 nm) of a Karl Suss MA6 mask aligner, a 1 s exposure of the PAG Bis(4-tert-butylphenyl)iodonium hexafluoro-phosphate (DtBPI-PF_6) generated sufficient protons to catalyze epoxide ring opening and form a bridging network of covalent C-O bonds which rendered the material insoluble in developing solvents such as toluene or THF. The resultant crosslinked material possessed characteristic blue photoluminescence with solid state quantum yields > 80%. Polymer films had excellent transparency (with a measured E_g ~ 3.0 eV). Energy levels determined using CV were -5.62 eV and -2.62 eV for HOMO and LUMO respectively. Additionally, several device applications were demonstrated which incorporated crosslinked films. These include examples of solid state lasing in the region of 420-450 nm using crosslinked films on second order corrugated silica substrates (Λ = 200 nm). OLEDs were also prepared with a crosslinked emitting layer as part of a trilayer device which we reported as having a maximum efficiency of 3.2% at 33 mA/cm^2 and a stable blue-violet emission with an EL maximum at 410 nm (FWHM = 166 nm).

Photopatternable PSF epoxides were also shown to be efficient hosts for Forster energy transfer and we provided several examples of patterned layers incorporating small molecule emitters which emit in both the red and green whilst blue emission of the host is effectively suppressed.

In future work, it would be interesting to demonstrate that cycloalkene moieties purposefully left unreacted during epoxidation are excellent functionalities through which further
sidechain modifications can be made, specifically the tethering of auxiliary chromophores for full spectrum emission tuning in pixelated substrates. This will enable us to expand on our existing demonstration of a 3% EQE crosslinked blue emitting OLED and generate a patterned substrate with separate RGB electroluminescence. An emerging “click” chemistry method utilizing 2 + 4 cycloaddition of tetrazine derivatives represents a potentially revolutionary means of tailoring conjugate polymer emission. The catalyst free reaction is rapid at room temperature and the covalently bound chromophores would be prevented from phase segregating in thin films.

Direct laser writing (DLW) was explored as a convenient and auspicious technique for creating microstructures of arbitrary shape and size. The wide applicability of DLW across various disciplines has already begun to broadly impact the future of optical sensor construction, medical diagnostics as well as optical waveguide and laser design. We presented a protocol for 3-D photopatterning derivatives of poly(3,6-dimethoxy-9,9-dialkylsilafluorenes) with resolutions exceeding 200 nm using DLW techniques. Simple 3-D structures including logpiles and graphical text were created by the absorption of a femtosecond pulse laser beam focused tightly into a microscopic writing volume within films of our unique photocrosslinkable light emitting polymer PHNSF-E50. We presented initial results summarizing optimal scan rates and laser powers for writing polymer structures with maximum resolution and negligible damage to the material. Our sharply resolved laser written structures (which can be any arbitrary design and dimension) possessed a characteristic blue photoluminescence with solid state quantum yields > 80% and were successfully imaged with fluorescence microscopy.

In a future work, it would interesting to use methods developed during this study to construct whispering gallery mode lasers comprised of microsphere, microtoroid or microdisk resonators fabricated from the PHNSF-E50 gain medium. Additionally, reducing written feature
sizes utilizing more advanced lithography techniques derived from the combination of DLW and stimulated emission depletion (STED) microscopy could become fruitful. STED has already been used to fabricate submicron structures using a two laser configuration. We believe creating high Q-factor resonators for a new generation of solid state organic lasers and fabricating OLEDs and OPVs with performance enhancing 3D component is one of the numerous directions this work can be expanded.

Our unique deep blue emitting copolymer, poly(3,6-dimethoxy-9.9’-dihexylsilafuorene-co-3,6-dimethoxy-2’,3’,6’,7’-tetrahexyloxy-9,9-spiro-9-silabifluorene) (PHSSF-co-PDHSF), exhibited a brilliant solid state blue luminescence, high quantum efficiency, excellent solubility and thermal stability. We found that using PHSSF-co-PDHSF copolymers with large volume fractions of spirosilabifluorene as the emissive layer in OLEDs correlates to more stable EL intensity and improved lifetimes over non-spiro poly(silafluorene) devices. The HSSF monomer was prepared via a two-part procedure, with each part resulting in one of two biphenyl segments which combines in a final cyclization step involving tetrachlorosilane. One segment possesses two bromide groups necessary for the polymerization. We utilized an efficient nickel catalyzed polymerization based on diarylmagnesate monomers to create PHSSF-co-PDHSF in good yield with number average molecular weights exceeding 50 kg/mol with a PDI = 1.8. The polymerization was complete in less than 30 min. For PHSSF-co-PDHSF OLED devices, the maximum irradiance of the device was 40 W/m² at a current density of 60 mA/cm². The maximum device external quantum efficiency was 2.9 % when operating at 38 mA/cm². To measure OLED stability, we monitored normalized EL intensity for both PHSSF-co-PDHSF and PDHSF devices. Over the course of 10 h, the EL intensity of the PDHSF device drops 20 % more than the PHSSF-co-PDHSF device when operating at 6 mA/cm².
In future work, we intend to increase the number of copolymers produced by this method with the aim of producing stable blue, green and red emitters for light emitting technologies. It would also be of considerable interest to combine the promising performance of these copolymers with the additional functionality of photocrosslinkable versions of PSF. Ultimately the goal is to develop longer lasting emitters which can be photolithographically patterned to allow for solution processed full colour thin-film displays driven by TFT backplanes as well combining multiple long lifetime polymer emitters to produce solution processed WOLEDs.

Finally, we synthesized and characterized a novel class of high molecular weight electroactive polyferrocenylsilane (PFS) that has been functionalized with pendant alkoxyisilane groups and which can be conveniently gelled by sulfonic acid catalyzed condensation of the crosslinkable alkoxyisilanes. PFS electroactive gel are capable of converting an electrical signal to mechanical stress and strain as a result of a change in dimension in response to electrochemical oxidation or reduction coupled with transport of charge balancing ions and solvent molecules. Electrospinning of polymer solutions in a syringe was possible using 5kV voltage applied between a needle and ITO substrate on to which fibers are collected. ITO substrates were incorporated into miniature electrochemical cells containing lithium triflate/$\gamma$-butyrolactone electrolyte and examined using optical microscopy. Applying 2.0V anodic potential to the ITO resulted in immediate oxidation of PFS fibers followed by strain induced buckling. Buckling occured in many cases as regular sinusoid perturbations along the fiber and was reversible. Application of cathodic 2.5V potential caused most of the distorted fibers to return to their initial form. Such inherent shape memory is potentially useful in creating microswitches, microactuators and micromanipulators.
Statement of Contributions

The following list summarizes the experimental contributions made by myself, Jeffrey McDowell, and other individuals with regards to the completion of doctoral work included in this thesis. Student collaborators grouped according to their PI and institution is as follows:

Uli Lemmer (PI): Florian Maier-Flaig, Carsten Eschenbaum
Light Technology Institute (LTI), Karlsruhe Institute of Technology (KIT)
Kaiserstraße 12, 76131 Karlsruhe, Germany

Andreas-Neil Unterreiner (PI): Thomas J. A. Wolf
Institute of Physical Chemistry (KIT)
Kaiserstraße 12, 76131 Karlsruhe, Germany

Peter R. Herman (PI): Moez Haque, Laden Abolghasemi
Department of Electrical and Computer Engineering, University of Toronto, 10 King’s College Road, Toronto, ON, M5S 3G4

Dwight S. Seferos (PI): Dong Gao
Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, ON, M5S 3H6

Summary of Work:

I) Chemical Synthesis and Material Characterization: Jeffrey McDowell

1) Synthesis of silafluorene, bisilafluorene and ferrocenophane monomers and their characterization by NMR, EI-MS, DSC/TGA and melting point.-JM

2) Synthesis of polysilafluorenes, polybisilafluorenes and polyferrocenylsilanes and their characterization by NMR, DSC/TGA, MALDI-TOF MS, CV, Absorption/PL, Absolute quantum yield (AQY).-JM

II) Film Optimization and OLED Device Fabrication and Characterization: Jeffrey McDowell

1) Spin-coating parameter optimations/conductive substrate preparation.-JM

2) OLED fabrication (until final metal contact evaporation)-JM

3) OLED metal contact evap was performed in Prof. Dwight Seferos’ group with initial training by Dong Gao.-JM/DG
4) Design, construction of I-V-L characterization system (including Labview control program) and subsequent testing of completed devices.-JM

III) 2D Conventional UV Lithography: Jeffrey McDowell

1) Cleanroom preparation/cleaning of substrates use and maintenance of mask aligner/wet bench and optimization of patterning protocol. -JM

2) Fluorescence/ Electron microscopy of patterned substrates and determination of AQY.-JM

IV) Laser and Transient Absorption Studies: Jeffrey McDowell, Florian Maier-Flaig, Thomas J. A. Wolf

1) Material/sample preparation and data analysis.-JM

2) Laser grating preparation and measurements of laser peaks.-FM-F

3) Pump/Probe measurements and data analysis.-FM-F/TW

V) Two-Photon Direct Laser Writing: Jeffrey McDowell, Moez Haque, Laden Abolghasemi, Florian Maier-Flaig, Carsten Eschenbaum

1) Material/sample preparation and data analysis.-JM

2) Material characterization – SEM and fluorescence microscopy-JM

3) Creation of laser writing systems and programming/control of system during writing.-MH/LA/FM-F/CE
List of Publications, Presentations and Poster Contributions

Publications Publications and Manuscripts

- **Titania Encapsulation of Flat Gold Nanoparticles-A Simple Route to Au@TiO$_2$ Core-Shell Nanosheets.**

- **Electroactuation of Alkoxysilane-Functionalized Polyferrocenylsilane Microfibers.**

- **Measurement of Absolute Photoluminescence Quantum Yields Using Integrating Spheres-Which Way to Go?**

- **Assembling Photoluminescent Silicon Nanocrystals into Periodic Mesoporous Organosilica**

- **Digignard Scavengers in the Nickel Transfer Polymerization of Diarylmagnesate Monomers**
  Jeffrey J. McDowell, Isabel Schick, Geoffrey Ozin, *Polymer*. (Submitted, Out To Review)

- **Pure Blue Emitting Poly(3,6-dimethoxy-9,9-dialkylsilfluorenes) Prepared Via Nickel Transfer Polymerization of Organomagnesate Monomers**

- **Synthesis and Application of Photolithographically Patternable Deep Blue Emitting Polysilafluorenes Poly(3,6-dimethoxy-9,9-dialkylsilfluorenes)**

- **Out of the Blue: Advancement in Ultra High Resolution Two-Photon Laser Writing of Blue Light-Emitting Conjugate Polymers**
  Jeffrey J. McDowell, Moez Haque, Laden Abolghasemi, Daniel Faulkner, Florian Maier-Flaig, Carsten Eschenbaum, Uli Lemmer, Peter R. Herman, Geoffrey Ozin, *Advanced Materials*, (Accepted With Revisions)

- **Synthesis of Poly(spirobisilafluorenes) and Their Improved Stability In Blue Emitting Polymer LEDs over Non-Spiro Analogs**
  Jeffrey J. McDowell, Dong Gao, Dwight S. Seferos, Geoffrey Ozin, *Journal of Materials Chemistry C*, (Submitted)
Oral Presentation and Posters

- Jeffrey J. McDowell, Nicole Zacharia, Ian Manners, Geoffrey Ozin, Actuating Electroactive Fibers From Alkoxy silane Functionalized Polyferrocenylsilanes, *MRS Fall Meeting 2009*, Boston, MA, USA

- Jeffrey J. McDowell, Geoffrey Ozin, Synthetic Investigation of Silafluorene Based Polymers Via Kumada-Type Coupling and Their Material Applications As Photopatternable Electroluminescent Resists for 2D and 3D Lithography, *CRC 10th Anniversary Event 2010*, Toronto, ON, Canada

- Jeffre J. McDowell, Nicole Zacharia, Ian Manners, Geoffrey Ozin, Polyferrocenylsilanes (PFS) Based Electroactive Fiber Bundles Produced By Electrospinning, *CIFAR 2010*, Whistler, BC, Canada

- Jeffrey J. McDowell, Moez Haque, Laden Abolghasemi, Florian Maier-Flaig, Carsten Eschenbaum, Tobias Bocksrocker, Jeffrey Castrucci, Peter R. Herman, Uli Lemmer, Geoffrey Ozin, 3D & 2D Photopatterning of Highly Luminescent Polysilafluorene Conjugated Polymers: Lasing, and Electroluminescent Devices, *MRS Spring Meeting 2012*, San Francisco, CA, USA