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The Synthesis and Characterization of Photoluminescent Conjugated Frameworks Containing Silicon and Germanium

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The Synthesis and Characterization of Photoluminescent Conjugated Frameworks Containing Silicon and Germanium

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This is dedicated to my mother and all of my friends. Your love, support, and encouragement have motivated me throughout the years to continue my training as a chemist, as evidenced by this dissertation which serves as a milestone in a long and prosperous life of study.
Abstract

Siloles and 9-heterofluorenes (Si, Ge) are conjugated $\pi$-electron systems containing Group 14 atoms which demonstrate unique properties such as high electron affinity, mobility, and bathochromically shifted optical spectra relative to their all-carbon analogs. This is due to their low-lying lowest-unoccupied molecular orbital (LUMO) which is resultant of the $\sigma^*-\pi^*$ conjugation between the exocyclic groups at the Group 14 center and the butadiene unit of the ring. As a consequence, they have received considerable attention for their use as components for a wide variety of optical and electronic applications such as organic light emitting diodes (OLEDs), photovoltaic devices, field-effect transistors (FETs), and as chemical and biological sensors.

Siloles with conjugated organic moieties incorporated in the 2,5-substituents are of interest since modification of the substituents at these positions of the silole ring have the most dramatic effect on the optoelectronic properties of the silole. Platinum complexes containing polypyridine-based ligands have been reported to show unusually rich photophysical and polymorphism properties resulting from their ability to form Pt-Pt and/or $\pi-\pi$ interactions in solution and especially in the solid state resulting in a bathochromic shift in the emission with enhanced quantum yields. A series of platinum(II) complexes containing chelating polypyridine and phosphine ligands were coordinated to the 2,5 positions of a siloles by organic linker moieties in an attempt to form an array of photoluminescent platinum(II)-silole macrocycles.

Heterofluorenes demonstrate similar properties to siloles, only they are enhanced due to their fused-ring structure. Although their photoluminescent substituent effects remain unexplored relative to that of siloles. The synthesis and characterization of a series of
new highly fluorescent 2,7-alkynyl(aryl)-3,6-dimethoxy-9,9-diphenylsilafluorenes was investigated utilizing a modified multi-step synthetic pathway in which the final step utilizes palladium-catalyzed cross-coupling conditions to incorporate a variety of conjugated – alkynyl(aryl) groups at the 2,7-positions. Crystal structures were obtained for all successfully synthesized heterofluorenes herein.
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<table>
<thead>
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<th>Description</th>
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<tbody>
<tr>
<td>Abs</td>
<td>absorbance or absorption</td>
</tr>
<tr>
<td>acac</td>
<td>acetylacetone</td>
</tr>
<tr>
<td>ACQ</td>
<td>Aggregation-caused Quenching</td>
</tr>
<tr>
<td>AIE</td>
<td>Aggregation-induced Emission</td>
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<td>BHT</td>
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</tr>
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<td>butyl</td>
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<td>eV</td>
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<tr>
<td>Fl</td>
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<tr>
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<tr>
<td>HOMO</td>
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<tr>
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<tr>
<td>λ_{max}</td>
<td>wavelength of maximum absorption/emission</td>
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<tr>
<td>LUMO</td>
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NMR  Nuclear Magnetic Resonance
OLED  Organic Light Emitting Diode
OTf  trifluoromethanesulfonate, or triflate
PCT  Photoinduced Charge Transfer
Ph  Phenyl
Phen  1,10-phenanthroline
rt  room temperature
THF  tetrahydrofuran
TMEDA  N,N,N',N'-tetramethylethylenediamine
tpy  2,2';6',2''-terpyridine
UV-vis  UV-visible spectroscopy
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Chapter 1

1.1. Introduction

Over the past decade, there have been substantial advancements in display technologies as we have transitioned from cathode-ray tubes,\(^1\) to liquid-crystal displays,\(^2\) to organic light-emitting diodes (OLEDs)\(^3,4\) One of the most major impacts these advancements have had is the proliferation of mobile devices, which include smartphones, tablets, and laptops, of which there is a constant demand for improvement of this devices in terms of size, weight, durability, and battery longevity. However, there remains constant demand to further develop each component for even more sophisticated technologies. Often, there is substantial overlap in the potential applications of novel materials which could aid in overcoming these technological challenges. As a few examples, such materials could be developed to serve as OLEDs, organic field-effect transistors (OFETs), photovoltaics, molecular wires, and chemo- and biosensors.\(^5-13\) For these applications, \(\pi\)-conjugated materials could achieve these goals by being developed for each specific demand as their components are relatively abundant and generally inexpensive. This dissertation will discuss the approaches utilized in the synthetic development and elucidation of platinum, silicon, and germanium-based \(\pi\)-conjugated materials toward the aforementioned potential applications. Unsurprisingly, development of materials toward these applications can be complicated, as such, it is necessary to understand the fundamental concepts, properties and variables which must be considered when embarking on such an endeavor.

1.2. Photoluminescence

Photoluminescence is a general term which encompasses both fluorescence and phosphorescence. In both cases, energy (in this example, a photon) is absorbed, exciting
an electron within the molecule to a higher energy level on the order of $10^{15}$ s$^{-1}$, in which the electron maintains its singlet spin pairing ($S_0 \rightarrow S_1$). Upon relaxation from the nascent higher energy levels through the vibrational relaxation and internal conversion ($10^{-13}$-$10^{-11}$ s$^{-1}$) processes, either fluorescence occurs ($10^{-9}$-$10^{-7}$ s$^{-1}$) which is an allowed transition, as per selection rules, from singlet to ground state ($S_1 \rightarrow S_0$), or intersystem crossing. Fluorescence occurs through an allowed process in which the electron transitions back from the singlet to the ground state ($10^{-8}$-$10^{-3}$ s$^{-1}$) during which a photon is ejected from the molecule, otherwise known as emission (Equation 1-1).

$$S_0 + h\nu_{ex} \rightarrow S_1 \rightarrow S_0 + h\nu_{em}$$

Equation 1-1. Equation for fluorescent emission, where $S$ is a singlet. 0 and 1 represent ground and excited states, respectively.

$h =$ Planck’s constant, and $\nu =$ frequency of light. While excitation can occur to higher excited states, only the first is represented for simplicity.

Alternatively, the electron can undergo intersystem crossing ($10^{-3}$-$10^2$ s$^{-1}$) in which the spin state of the electron transitions from a singlet to triplet excited state ($S_1 \rightarrow T_1$) through strong spin-orbit coupling, which results in both states being neither purely singlet or triplet. In the excited triplet state, the spins of the two electrons are unpaired. As relaxation from a triplet excited state to a singlet ground state ($T_1 \rightarrow S_0$) is not an allowed process and relies on strong spin-orbit coupling to occur, it often provides a lower intensity (quantum yield or efficiency) when compared to singlet emission, and also occurs on a much slower timescale such that emission is noticeably delayed ($10^{-3}$-$10^2$ s$^{-1}$). An additional selection rule becomes relevant in the event a phosphorescent framework incorporates a transition metal atom. The Laporte rule $^{14}$ dictates that a molecule with a center of symmetry, transitions must involve a change in parity, or a flip
in the sign of all three spatial coordinates of an orbital, e.g., symmetric vs. antisymmetric. For example, a $g \rightarrow g$ or $u \rightarrow u$ transition would be forbidden (where $g = \text{gerade}$ (even) and $u = \text{odd}$ (ungerade)), but $g \rightarrow u$ and $u \rightarrow g$ would be allowed.\textsuperscript{14} The same applies for $p \rightarrow p$ and $d \rightarrow d$ transitions, which are forbidden, and the allowed $p \rightarrow d$ and $d \rightarrow p$ transitions, which are allowed.\textsuperscript{14} Overall, both processes can be summarized through the following equation:

$$S_0 + h\nu_{ex} \rightarrow S_1 \rightarrow T_1 \rightarrow S_0 + h\nu_{em}$$

**Equation 1-2.** Equation for phosphorescent emission, where $S$ is a singlet and $T$ is a triplet. $0$ and $1$ represent ground and excited states, respectively.

$h = \text{Planck's constant, and } \nu = \text{frequency of light. While excitation can occur to higher excited states, only the first is represented for simplicity.}$

Finally, there are a few general rules aside from the aforementioned selection parameters which must be considered when discussing photoluminescent molecules. The Kasha-Vavilov rule\textsuperscript{14} stipulates that the photoluminescent quantum yield is a term independent of that of the excitation wavelength. As such, it would be difficult to predict what the quantum yield of a novel molecule may be unless quantum yield measurements were available for molecular analogs. The mirror image rule\textsuperscript{14} states that the electronic absorption transitions are mirrored in the photoemission transitions. Finally, emission wavelengths tend to be lower energy than their excitation counterparts, otherwise known as a Stokes shift.\textsuperscript{14} A Jablonski diagram\textsuperscript{14} (Figure 1-1) below summarizes the aforementioned electronic transitions.
1.3. Factors Influencing Photoluminescence

Many factors have to be taken into account when considering a photoluminescent molecular framework. As described earlier, photoluminescence generally requires the presence of aromatic (π-conjugated) systems with optionally incorporated transition metals. This allows for kinetic competition between the fluorescence and phosphorescence processes, while substantially reducing the probability, or competitiveness, of radiationless processes. Accounting for these factors allows for tuning of the color (energy) of the luminescence, as well as its quantum yield. Quantum yield describes the efficiency of a molecule converting absorbed energy to photoemission, where a quantum yield of 0 (0%) describes no emission, and a quantum yield of 1.0 (100%) describes absolute efficiency. While molecules which provide low quantum yields of ca. 10% are quite visible, those of higher efficiency are more desirable for application purposes, especially when considering energy consumption. All organic
materials can absorb radiation since they possess vacant higher energy orbitals to which valence electrons can be excited. The wavelengths of energy absorbed and their subsequent fate are dependent upon the types of bonds within the molecule. Since the photoemission wavelength is usually lower energy than the excitation wavelength, molecules in which their greatest absorption lies in the ultraviolet region of the electromagnetic spectrum. Ultraviolet radiation can be further broken down into UV-A (400 – 315 nm), UV-B (315 – 280 nm), UV-C (280 – 200 nm) and UV-V (200 – 100 nm). At wavelengths shorter than 250 nm (UV-C and UV-V), the radiation has sufficient energy to predissociate, dissociate, or deactivate the electron in the excited state. Lower wavelengths of < 200 nm (UV-V) possess enough energy to rupture bonds. For these reasons, excitation wavelengths of 400 – 250 nm are most desired, and for strictly organic frameworks, the less energetic π-π* or n-π* transitions are observed. The lifetimes of these excited states are shorter, which means they have higher molar absorptivities. Finally, competition for a phosphorescent emission process is nullified as the required intersystem crossing is energetically out of reach during π-π* transitions as their inherent energy is lower than that required to unpair the excited π* electrons (Figure 1-2).

![Figure 1-2](image)

**Figure 1-2.** UV-Visible Absorption Electron Transitions. The two left-most transitions, \( n \rightarrow \pi^* \) and \( \pi \rightarrow \pi^* \) are the weakest, resulting in > 200 nm transitions.
As in the majority of cases, this means that luminophores (fluorescent compounds) are aromatic and excited by relatively low energy ultraviolet radiation. Some of the competing radiationless processes can be reduced by improving structural rigidity, which can be performed by removing or replacing substituents that would either freely rotate, flex, or bend. Incorporation of heteroatoms into the conjugated systems also allows for tuning of its photophysical and physical properties. Conjugation lowers the energy of the $\pi^*$ orbitals, reducing the anti-bonding character, and as a result of delocalization of the $\pi$-electrons the molecules show light-absorption in the 200-800 nm region.\textsuperscript{16}

Ultimately, this enables fluorescence in molecules which are otherwise non-emissive.

This results in the general principle that extending the conjugation of a system results in a bathochromic shift or redshift, or a shift of absorption and emission maxima to lower energy (longer) wavelengths as well as a marked increase in quantum efficiency. In this example, benzene exhibits an emission maximum around 288 nm, while naphthalene and anthracene demonstrate maxima around 325 and 375 nm, respectively, with respective quantum efficiencies at 0.033, 0.23, and 0.30.\textsuperscript{17,18}

As already stated, reducing radiationless pathways such as rotations, and increasing rigidity can significantly improve quantum efficiency. Extending the conjugation can be accomplished through coordination of additional aromatic units, or through incorporation of additional fused rings (Figure 1-3). In this example, biphenyl has an emission

\begin{center}
\includegraphics[width=\textwidth]{figure13.png}
\end{center}

\textbf{Figure 1-3.} Molecular structures of biphenyl (A), naphthalene (B), fluorene (C), and phenanthrene (D).
maximum at 325 and a quantum yield of 0.18.\textsuperscript{19} This value is marginally less than that of naphthalene, which could be considered a fused-ring analog to biphenyl.\textsuperscript{19} Naphthalene has a slight increase in quantum yield compared to that of biphenyl, likely due to the restriction in rotations which would provide a radiationless pathway. Fluorene is an example of a biphenyl system which has had its rotations restricted by locking them in place at their 2,2’-positions by a methylene bridge. This results in a bathochromic shift to 370 nm with a substantially improved quantum yield of 0.44.\textsuperscript{20} Phenanthrene can be considered a combination of both increasing the rigidity of a biphenyl unit while extending its conjugation compared to that of biphenyl. With respect to biphenyl, it would be expected that phenanthrene would be red-shifted with an increased quantum efficiency. While phenanthrene exhibits an absorption maximum that red-shifted to 365 nm compared to biphenyl, its quantum efficiency is actually lower at 0.125.\textsuperscript{19} This demonstrates that extending the π-conjugation of a system will not always increase the quantum efficiency, and that orientation of the fused rings can have a profound effect when anthracene is more than double that of phenanthrene.\textsuperscript{18,21}

The molecular environment must also be considered with respect to changes in temperature,\textsuperscript{22} oxygen,\textsuperscript{23} concentration,\textsuperscript{24} pH,\textsuperscript{25} and solvent polarity\textsuperscript{22} since all of these can have an influence on both the emission wavelength and quantum efficiency. Decreasing the temperature can decrease the rate of bending, flexing, rotating, and other molecular motions responsible for radiationless relaxation. Lowering the temperature can also have the added effect of increased solvent viscosity, resulting in a further decrease of molecular motions, as well as decreased frequency in intermolecular collisions which could further precipitate molecular motions responsible for radiationless relaxation.
Intermolecular collisions, especially with dioxygen could also result in external conversion or external quenching, which is the transfer of energy from an excited state molecule to either the solvent or a solute in solution,\textsuperscript{26} reducing emission by deactivating the excited state. While the mechanism by which dioxygen quenches photoluminescence has not been fully elucidated, a commonly accepted explanation is that paramagnetic dioxygen allows for intermolecular intersystem crossing from an excited state luminophore, ultimately relaxing non-radiatively.\textsuperscript{27} Since this involves the conversion between singlet and triplet states, dioxygen quenching has a significantly greater impact on phosphorescent luminophores (phosphors) than fluorescent luminophores (fluorophores), especially when considering the rates of each process. Aside from dioxygen, other solutes or impurities may also quench emission through a similarly believed mechanism as dioxygen, especially with heavier atoms such as mercury.\textsuperscript{28,29}

Luminophores which incorporate functional groups sensitive to changes in pH can also undergo a change in absorption maxima and quantum efficiency by altering the resonance forms of the luminophore. Similarly, the presence functional groups which can interact with the solute, or specific analytes, may also influence a change in emission wavelength and quantum efficiency.\textsuperscript{28} Concentration plays a role dependent upon the nature of the luminophore. At high concentrations, luminophores may undergo aggregation-caused quenching (ACQ) which results from intermolecular $\pi-\pi$ stacking interactions, or they may undergo aggregation-induced emission in which their quantum yield is actually enhanced at higher concentrations due to restrictions of molecular motions which result in radiationless relaxation. Alternatively, aggregation may result in enhanced emission, or more commonly called aggregation induced emission (AIE), in which the intermolecular
proximity reduces non-radiative processes which arise from molecular rotations and collisions. Concentration also plays a role when performing photoluminescence measurements as self-absorption can occur where the absorption and emission bands of a luminophore overlap. Solvent polarity can also directly impact solubility. By decreasing solubility, localized high concentrations, or aggregations of luminophores may be formed resulting in the same effects as described for high concentrations. Some of these concepts will be covered in greater detail in subsequent chapters as they become more relevant to each of the topics.

1.4. OLEDs

As stated in greater detail earlier, luminophores absorb energy in order to emit photons. While ultra-violet radiation was used as an excitation source as an example previously, luminescence can arise from a multitude of sources. Electroluminescence is when electrical current is applied to a luminophore resulting in emission and is the process by which the luminophores incorporated into OLEDs function. OLEDs are of particular interest as they are solid state thin-film light sources which boast the potential to produce thinner, more robust display technologies with high quantum yields and subsequently lower energy consumption. This affords the possibility of significantly improving current broadly-used technologies. The first, primitive OLED was developed by Tang et al., in which tris(8-hydroxyquinolinato)aluminum (Alq3) was utilized in fabrication of a green emissive device, and is still applied in OLEDs to this day. This has inspired great interest in improving the organic emissive layer sandwiched within an OLED assembly which continues to present, and will be the focus of this dissertation (Figure 1-4).
Figure 1-4. Simplified configuration of an OLED.

An OLED is composed of two electrodes, multiple organic layers which facilitate emission, and a substrate. The substrate is typically glass or plastic, each affording their own advantages and disadvantages. A glass substrate allows for greater bulk durability and lifetime of the materials, while a plastic substrate allows for greater flexibility with the added challenge of lower durability presently resulting in diminished quantum efficiency and color accuracy over time.\textsuperscript{35} The electrodes are comprised of an anode and a cathode which are related by their work functions. A work function is defined as the minimum energy needed to move an electron into a solid material from a vacuum, or vice-versa.\textsuperscript{38} A potential is applied to the device, injecting the electron via the cathode, which is a low work function material often made of calcium or magnesium, and alloyed with silver to improve stability. The electron then passes through the electron transport layer, which is a polymeric material which facilitates charge to the organic emissive layer while serving a dual-function as a prophylactic, mitigating the degradation which would result in direct contact with the cathode.\textsuperscript{39-41} The electron will then enter the lowest unoccupied molecular orbital (LUMO) of the organic emissive layer, facilitating the excitation and emission described earlier in this chapter, then exiting the material via the hole injection layer, which also serves the same dual-function as the electron transport layer, but for the anode. Finally, the electron will enter the highest occupied molecular
orbital (HOMO) of the anode, which is a high work function material often made of indium-tin oxide (ITO). The work functions of the anode and cathode must be compatible with that of the organic emissive layer limiting the scope of which can be utilized in the device. The HOMO-LUMO or band gap of the organic emissive layer, which is defined as the energy difference between the HOMO and LUMO, must be complementary to the work functions of the electrodes, such that charge transport is facilitated readily. In other words, the LUMO must be of comparable energy to that of the electron transport layer, and the HOMO to that of the hole injection layer.

To further complicate the selection process for the components which comprise the device, as the color of the fluorescence emission is dependent upon the HOMO-LUMO gap for each component of the organic emissive layer. Each luminophore has its own HOMO-LUMO gap and resulting emission color, which typically covers a range of the visible light spectrum, therefore, a number of luminophores must be selected such that their sum emissions cover the visible light spectrum as much as possible. However, there is often a mismatch where the emissions overlap in such a way that not all wavelengths within the spectrum are equally emitted, resulting in displays of varying subjective quality. Other factors must be considered outside the organic emissive layer, which can ultimately affect the lifetime performance of the emissive layer and overall device. The display brightness, or luminescence intensity, is governed by varied current which could influence the rate of degradation within the emissive layer. The International Commission on Illumination (CIE, for its French name, Commission Internationale de L’Eclairage) has defined standards based on the first defined quantitative links between colors defined physically by their wavelength, and how they are perceived.
physiologically in humans,\textsuperscript{46,47} resulting in the CIE 1931 RGB and XYZ color spaces, which are used for comparison with display technologies.

\subsection*{1.5. Materials}

As already established in lesser detail, the components within an OLED are tightly-packed thin-films consisting of small polymerized molecules, each of which possesses its own performance parameters which determine overall device performance. As these components are composed of $\pi$-conjugated organic materials, significant development efforts have been focused on their improvement. While their electronic and emissive properties must be considered, other issues must also be taken into account such as their quantum yield, lifetime, and air- and thermal stability. Ideally, charge transport must be optimized while maintaining or improving the above parameters, which would result in reduced energy consumption.\textsuperscript{45} All of these properties are resultant from the design of the core molecule, but can also be influenced by how it ultimately arranges within the solid state after polymerization and in film due to the resultant intermolecular distances and relative orientations. For example, planar $\pi$-conjugated materials can arrange in parallel arrangements in close proximity, allowing for intermolecular $\pi$-orbital interactions which result in a greater degree of delocalization of electrons. Delocalization in thin films can result in increased charge carrier mobilities but also quenching of quantum yield if the intermolecular distances are less than 4 Å.\textsuperscript{48,49} These interactions can be reduced by incorporating sterically demanding ligands into the framework which prevent alignment, resulting in offset arrangements, or force packing distances of greater than 4 Å. An alternative possibility would be to co-crystallize them with another system, such as an alkyl-based polymer, that would insulate them from intermolecular interactions.\textsuperscript{48,49} When forming thin films, a number of imperfections may be present, resulting in regions
which contain disorder or amorphous material which causes a localized breakdown in carrier mobility known as carrier build up and relies upon electrons transferring or hopping between molecules through less efficient means.⁴⁸,⁴⁹

As an electron traverses the materials of the device it will enter either a singlet or triplet state. In the case of an OLED, the organic emissive layer will be comprised of fluorophores which rely on relaxation from a singlet excited state \( (S_1 \rightarrow S_0) \), while electrons in a triplet excited state provide negligible luminescence, if any. An example can be made from looking at the possible spin states within the HOMO and LUMO. When an electron is excited, it is promoted out of the HOMO to a vacancy within the LUMO. In the first case (Scheme 1-1), the HOMO and LUMO both possess an electron with a spin of +1/2, or in other words, both spins are aligned and combine to a total spin number of 1. The same is true for the second case. The other possibility is that both spins are opposing, as shown in the third and fourth cases. As these are not pure quantum states (with respect to a singlet state where they would cancel out), they combine to form the third triplet state. Therefore, the triplet state has a multiplicity of three with the magnetic numbers of +1 (first case), -1 (second case), and 0 (combination of cases 3 and 4). Thus, the triplet and singlet states within an OLED form in the ratio of 3:1, meaning that roughly 75% of the electrons in an excited state within an OLED decay non-radiatively, limiting the overall device efficiency to approximately 25%.³⁶
As mentioned earlier, another concern is the lifetime of OLEDs, in which environmental and physical phenomena influence the rate of internal decomposition, which can result in reduced quantum yield and spectral broadening. This is a result of decomposition or oxidation within the organic emissive layers, or the conductive layers. This happens by the presence of air, which includes oxygen and/or water vapor, and is aided by the device facilitating charge transport and undergoing elevated temperatures due to normal inefficiencies. This emphasizes the importance of stability within novel emissive materials.

1.6. Group 14 Conjugated Materials

Of particular interest are heterocyclic materials which incorporate a Group 14 atom in place of carbon in existing organic materials, more specifically, materials which incorporate silicon or germanium. Metalloles are heterocycle analogs of cyclopentadiene such as silacyclopentadiene and germacyclopentadiene, which will be referred to as “silole” and “germole” respectively (Figure 1-5). Related dibenzosiloles and -germoles

![Figure 1-5. Generalized structures of a) cyclopentadiene, b) silole, c) germole, d) silafluorene, and e) germafluorene. The "R" substituents are enumerated as they are typically referred.](image)
are also known as silafluorenenes and germafluorenes and they possess the additional fused benzo-rings on the metallole core.\textsuperscript{20,24,37,51–53} While both are endowed with similar properties,\textsuperscript{54} only siloles are discussed at length in this dissertation due to their greater synthetic accessibility and subsequent selection for the research discussed in Chapter 2. These \( \pi \)-conjugated systems are of interest due to their low lying LUMO, which is a consequence of their \( \sigma^*-\pi^* \) conjugation between the exocyclic groups at the Group 14 center and the butadiene unit of the ring.\textsuperscript{55–57} This particular property results in a fluorophore capable of efficient charge transport and good quantum yield,\textsuperscript{58–63} especially when compared to that of (Alq\textsubscript{3}),\textsuperscript{28} and are described comprehensively in reviews by Corey.\textsuperscript{24,51} Furthermore, siloles rely on a photophysical property which contradicts aggregation-caused quenching (ACQ), referred to aggregation-induced emission (AIE).\textsuperscript{30} Since siloles lose much of their fluorescence intensity due to radiationless processes such as rotations, then restricting those rotations should (and does) improve quantum yield.\textsuperscript{24,64} As solubility of metalloles decreases,\textsuperscript{31} they begin to form aggregates in solution (Figure 1-6). These aggregates will begin to restrict rotations by preventing rotations of the peripheral phenyl rings through intermolecular collisions, and is further emphasized in the solid state by their propeller-like arrangement. Incorporation of sterically demanding substituents also prevents intermolecular \( \pi \)-orbital interactions, which would otherwise

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{Figure 1-6. Aggregation-induced emission (AIE) in solution, shown as a progression with decreasing solubility.}
\end{figure}
permit ACQ. These properties make siloles ideal for emissive solid-state applications, and have seen application as thin films in OLEDs, showing promise for potential consumer applications.

Also of interest are sila- and germafluorenes, which are heterocycle analogs to fluorene (Figure 1-7). These are somewhat structurally related to metalloles, in that they possess a 5-membered conjugated core which includes $\sigma^*-\pi^*$ conjugation between the exocyclic groups at the Group 14 center and the butadiene unit. The obvious difference is that there are fused rings at what would be the 2,3,4,5-substituents on metalloles. This affords the advantage of extended conjugation, and greater planarity in the core without peripheral rings that could otherwise permit radiationless relaxation evidence. The result of which is far reduced reliance upon AIE and subsequently greater quantum yield in solution. By incorporating sterically demanding substituents, ACQ can be eliminated in the solid state, realizing the possibility for OLED applications. Previous studies have indicated that altering the substituents in the 9-position in siloles have little photophysical effect. The 9-position is of interest for introduction of sterically demanding substituents, as their orientation would be locked perpendicular to the $\pi$-conjugated plane, potentially disallowing solid-state orientations and proximities which would permit ACQ.

**Figure 1-7.** Generalized structures of a) fluorene, b) silafluorene, and c) germafluorene. The "R" substituents are enumerated as they are typically referred.
1.7. Platinum Complexes

While the majority of luminophores discussed thus far have been fluorescent heavier Group 14 containing molecules, platinum(II) complexes have received attention recently due to their interesting excited-state triplet emission (phosphorescent) properties which arises from the following electronic states: ligand field (3^LF), 3^MLCT, and intraligand (3^ππ*). Like metalloles, platinum-based phosphors undergo AIE which is intensified in the solid state. Existing platinum(II) polypyridine molecules have seen application in thin film materials which undergo phosphorescence and emit light dependent upon modifications to the molecule which alter their electronics. To date, only one example of a combined platinum(II) polypyridine-silole material exists, which remains a largely unexplored class of materials. Fluorophores such as siloles could be coordinated to phosphors such as platinum(II) complexes to form novel materials of interest (Scheme 1-2). Using an ethynyl group as a linker is an attractive approach due to its structural rigidity and π-delocalization, which should allow charge transfer between the fluorophore and phosphor units. While these materials are less likely to see consumer level applications (such as OLEDs) due to their obvious difference in cost from the incorporation of platinum, platinum-based complexes have potential application for photocatalytic hydrogen production from water, biomarking, and molecular sensors.

**Scheme 1-2.** Generalized structures for platinum(II)-silole materials.
1.8. Research Objectives

Siloles represent a class of fluorophores which have undergone extensive investigation, development, and application. The photophysical properties of siloles can be modified by altering the 2,5-substituents, while the 1,1- and 3,4-substituents have marginal electronic influence. Meanwhile, known synthetic pathways to platinum(II) phosphors are facile and in good yields. Siloles, for example 1,1-dimethyl-2,3,4,5-tetraphenylsilole (TPS), are readily compatible with producing precursors necessary for formation of platinum(II)-silole complexes. As this project relies on a combination of known synthetic pathways with the final step utilizing a well-known high-yielding method, the research objective is mostly exploratory in investigating the potential properties resulting from platinum(II)-silole complexes, with the added ability to tune the photophysical properties of which can be altered by modifying the linker (ethylene) unit and ligand which forms the platinum(II) unit.

Silafuorenes and germafluorenes have demonstrated generally greater quantum yields in solution than that of siloles, which can be attributed to their fused-ring structure with reduced loss to radiationless molecular motions. However, the few methods that exist which afford sterically demanding ligands in the 9-position are either low yielding or difficult to reproduce. According to SciFinder, only six 2,7-disubstituted 9,9-diphenylsilafuorenes and two 9,9-diphenylgermafluorenes have been published based on a search performed using a generalized structure (Figure 1) indicating the substituted positions. After a synthetic method is established to access this new class of molecules, then palladium-catalyzed Sonagashira cross-coupling conditions can be employed to investigate a new class of 2,7-disubstituted silafuorenes and germafluorenes. The ultimate goal is to investigate the substituent effects on their
photophysical properties, as well as their stability and orientation in the solid state. The following three chapters describe the outcome of these efforts.
1.9. References

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(4) Corones, M. A (very) brief history of television displays. Reuters Blogs.
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Chapter 2
Luminescent Square-Planar
Platinum(II) Complexes Containing Silole Units

2.1. Introduction

Both platinum-based and silicon-based emissive materials have received attention recently due to their interesting photophysical properties. Both undergo excitation through absorption of light and subsequent conversion to charge, and then undergo emission either through phosphorescence and fluorescence to emit light dependent upon the formula and environment of the molecule. Square-planar d⁸ platinum(II) complexes are of interest due to their interesting excited-state triplet emission (phosphorescent) properties. Of those, platinum(II) complexes with multidentate polypyridine ligands such as 2,2'-bipyridine (bpy), 1,10-phenanthroline(phen), and 2,2':6',2"-terpyridine (tpy) are of interest due to their photophysical properties and polymorphism in both solution and the solid state.¹ As photoluminescent materials, both platinum(II) polypyridine complexes and silacyclopentadienes (siloles) have potential application for photocatalytic hydrogen production from water² and photoinduced charge separation,³ organic light-emitting diodes (OLEDs),⁴ molecular sensors and switches for pH, ions, and solvents.⁵,⁶ Polypyridine ligands provide an advantage in producing phosphorescence by inducing stability and rigidity through chelation and subsequently improving quantum efficiency. Square planar coordination geometry increases the probability of aggregation resulting in increased intermolecular Pt-Pt and π-π interactions which generally influence significant bathochromic shifts or redshifts in emission and decreased photoluminescence quantum yields.¹ This is due to the fact that phosphorescence arises from one of the following
electronic states: ligand field (3LF), 3MLCT, and intraligand (IL) 3π-π*, and intermolecular Pt-Pt interactions have shown a decrease of the metal-to-ligand charge-transfer (3MLCT) transition energy in binuclear compounds such as [Pt2(tpy)2(μ-pyrazolate)]3+. These weak Pt-Pt and π-π interactions can also lead to dimers or linear chain aggregates, altering their mechanical, solvent, and thermal sensitivity resulting in changes in emission color and intensity through a respective decrease in the 3MLCT or ligand-to-ligand charge-transfer (3LLCT) energy level, while reducing their solubility in solutions such as with ([Pt(tpy)(Cl)]+) to solid state Pt(II)-polypyridine stacking.

Phosphorescence in Pt(II)-polypyridine complexes can be tuned by modifying both the polypyridine and ancillary ligands, as evidenced by comparing the emissions which arise from IL 3π-π* excited states in complexes with strong-field ancillary ligands, such as [Pt(5,5′-Me2bpy)(CN)2]12 and [Pt(bpy)(en)]2+ (en = ethylenediamine), and those of complexes incorporating weak-field ancillary ligands such as [Pt(bpy)Cl2], which results in emissions originating from a 3LF excited state. The lowest excited state for Pt(II)-polypyridine complexes is the 3MLCT state, which arises from either low-lying π*-orbitals or strong electron-donating ancillary ligands. A strong ligand field results from π-back-donation to the pyridine ring which ensures a higher energy for nonemissive metal-centered (MC) d-d states, which would otherwise provide thermally accessible pathways for the radiationless relaxation of ligand-centered (LC)/MLCT excited states. The energy of the MLCT excited state can by tuned by modifying the ancillary ligand. For example, a redshift of the MLCT transitions of the complexes [Pt(tpy)(X)]+, X = Cl−, Br−, I− is observed as X is substituted from Cl− to the more π-basic (electron-donating) Br− and I−.
Acetylide- or ethylene-based functional groups are routinely used as linker or connector units due to their linear geometry, structural rigidity, extended π-delocalization and tunability.\(^{16}\) Acetylide-based ligands interact with metal centers through a \(\pi\)-\(d\pi\) overlap (Figure 2-1), and can serve as a building block for larger, more complicated systems.\(^{17}\) As earlier stated, the lowest energy absorption and emission bands for Pt(tpy) complexes originate from the MLCT and LLCT transitions: \(d\pi\text{(Pt)} \rightarrow \pi^*(tpy)\) and \(\pi(C≡C-C_6H_4-R) \rightarrow \pi^*(tpy)\). ([Pt(tpy)(Cl)]X) is found to be non-emissive in solution at room temperature due to the low-lying \(^3\)d-\(d\) excited state, unless emission is otherwise induced by adjusting solvent polarity thereby causing aggregation.\(^{19}\) In previous studies, the Cl- ligand was replaced with a strong \(\sigma\)-donor/\(\pi\)-acceptor alkynyl group such as \(C≡C-C_6H_4-R\) (R = H, Cl, NO\(_2\), CH\(_3\), OCH\(_3\), NH\(_2\), N(CH\(_3\))\(_2\), N(CH\(_2\)CH\(_2\)OCH\(_3\))\(_2\)).\(^{7,20}\) For this class of molecules, IL absorptions occur in the range of 286-350 nm, while an admixture of

![Figure 2-1](image_url)

**Figure 2-1.** Overlap between a filled \(d\pi\) orbital and an empty \(C≡C\) \(\pi^*\) orbital, resulting in \(\pi\) backbonding.

The M-\(C≡C\) bond is formed by the donation of a lone pair on the acetylide carbon to the empty \(d\alpha\) orbital (not shown) on the metal.\(^{18}\)
MLCT ($d_{π}(Pt) \rightarrow π^*(tpy)$) and LLCT ($π(C≡C-C_6H_4-R) \rightarrow π^*(tpy)$) absorptions occur between 432-546 nm. Emissions over a range of 560-665 nm are believed to be a mix of $3^1MLCT ([d_{π}(Pt) \rightarrow π^*(tpy)])$ and $3^1LLCT ([π(C≡CR) \rightarrow π^*(tpy)])$ transitions. The general trend observed is an increased redshifting as the arylalkynyl unit receives greater electron donation and increases in the order of: NO$_2$ < Cl < H < CH$_3$ < OCH$_3$ < NH$_2$ < N(CH$_3$)$_2$ < N(CH$_2$CH$_2$OCH$_3$)$_2$. To date, there is only one known reference in which a silole has been incorporated with a platinum complex (Scheme 2-1). In this example,

![Scheme 2-1. Synthetic scheme for a silole-based platinum(II) diyne (2-3).](image)

2,5-dibromo-1,1-dimethyl-3,4-diphenyilsilole was linked to a platinum complex that functioned as a non-emissive donor as a donor in a donor-acceptor system. The silole ($λ_{max} = 326$ nm) underwent a redshift when incorporated into a platinum(II) diyne material ($λ_{max} = 470$ nm). $^1P\{^1H\}$ NMR can also be a useful, one advantage that can be considered for complexes such as (2-3) which incorporate Pt-P coordination is that NMR-active phosphorus-31 isotopes are 100% abundant and are easily detected by $^{31}P\{^1H\}$ NMR. Furthermore, satellites emerge when coupled to platinum, which are directly proportionate to the abundance of NMR active platinum-195, 33.8%. These satellites are dependent upon their magnetic environment, and as a result, give rise to phosphorus-platinum coupling constants. Since phosphorous-platinum coupling constants tend to have a relative similarity within certain types of chemical environments, this could be used as a diagnostic tool in observing the occurrence of a reaction. In the case of (2-3),
$^{31}$P\textsuperscript{$\text{1H}$} NMR results indicated a chemical shift of $\delta$ 10.85 with a $^{1}J_{\text{Pt-P}}$ of 2643 Hz, which is typical for a trans-Pt-P complex.\textsuperscript{22} Little is known about the luminescent properties of platinum-silole systems given their novelty. The goal would be to further elucidate this process incorporating differing alkynyl linkers into luminescent square planar platinum(II)-silole. Tuning these moieties can be accomplished by varying the incorporated substituents which would extend their respective $\pi$-systems or conjugation, or improve their $\sigma$-donor/acceptor ability.

Siloles are silicon analogs of cyclopentadiene (cp) with solid state quantum yields as high as 97 ± 3\% (1,2-bis(1-methyl-2,3,4,5-tetraphenylsilole)ethane),\textsuperscript{23} and have served as emissive or electron-transport (ET) layers with external quantum efficiencies as high as 8\% (1-methyl-1,2,3,4,5-pentaphenylsilole),\textsuperscript{24} comparable to that of tris(8-hydroxyquinolinato)aluminum (Alq$_{3}$) which is known for its OLED applications.\textsuperscript{25} The HOMO and LUMO of the silole are about 0.4 eV and 1.2 eV lower, respectively, than that of cp.\textsuperscript{26} The greater difference in their LUMOs can be explained by the orbital interaction of the silole ring in which the low-lying LUMO of the silole arises from a mixture of the energetically comparable $\sigma^{*}$-orbital of the silylene and the $\pi^{*}$-orbital of the butadiene unit.\textsuperscript{26} This $\sigma^{*}$-$\pi^{*}$ conjugation occurs effectively as the orbitals are in phase and in a fixed perpendicular arrangement with respect to the plane of the silylene moiety.\textsuperscript{26} For the carbon analog, cp, $\sigma^{*}$-$\pi^{*}$ conjugation in the LUMO is negligible due to the much higher energy level of the corresponding exocyclic $\sigma^{*}$ orbital. The high electron-accepting property of the silole results from its available low-lying LUMO orbital and is further explained by comparison of the calculated HOMO and LUMO levels of its heterocyclic analogs.\textsuperscript{26}
The emissive properties of siloles can be tuned by modifying the donor/acceptor strengths and positions of ligands around the ring to varying degrees of success. For 3,4-substituents, investigation has been limited due to synthetic challenges and constraints. It is known that replacing hydrogen with phenyl substituents at these positions will result in blueshift in absorption and emission, however, this also significantly reduces quantum yields likely due to radiationless relaxation through torsional modes. Furthermore, while extending the HOMO and LUMO over a larger π-system commonly results in a redshifted absorption, minimal change occurs when substituting a larger π-system such as 9,9-dimethylfluoren-2-yl, suggesting inductive effects dominate over orbital delocalization. For 1,1-substituents, the effects are mostly inductive as well, yielding only small changes in the absorption maxima. The HOMO/LUMO orbitals at the of the silicon atom are mostly stabilized and destabilized by σ-electron-withdrawing and donating groups due to the aforementioned σ*-π* conjugation. Increasing the electronegativity of the 1,1-substituents generally leads to minor redshifts (305 to 318 nm) in absorption maxima in the order of H < alkyl < Ph < F in CHCl₃. Finally, for 2,5-substituents, the σ- and π-effects are much more significant due to the significant π-character of the carbon atoms at the 2,5-positions affecting the overall HOMO and LUMO of the silole core. Bulky aryl substituents which have a greater steric demand and associated strained dihedral angle will blueshift the emission. Aryl substituents which do not strain the dihedral angle will effectively extend the π system, resulting in a redshift in both absorption and emission. The absorption and emission of the silole can be significantly changed by modifying the meta- and para-positions of less sterically demanding aryl groups with weak/strong field ligands.
stated earlier, luminescent square planar platinum(II) complexes rely upon aggregation for their emissive properties by inducing Pt-Pt and π-π interactions.

The silole also exhibits aggregation-induced emission AIE for a different reason from that of the previously discussed platinum(II) complexes: restriction of intramolecular rotations (RIR). If the peripheral phenyl rings are permitted rotation then excited states will be effectively quenched, resulting in weak to no emission. In this case, more sterically demanding ligands at 3,4-positions can be advantageous when in less aggregated environments. Siloles generally show strong emission in the solid state.

2.2. Synthetic Overview

Initially, the ultimate goal of this project was the formation of a series of platinum(II)-silole complexes, which would then be verified and elucidated through multiple characterization techniques. The project was designed with expansion through variability in mind, where the target compounds could be altered by exchanging the platinum(II)-based ligands and the arylalkynyl linkers, as both could have impact on the net emissive and physical properties of the target complex (Figure 2-2). To achieve this goal, a number of synthetic methods would need to be employed in a parallel approach to obtain each unit pursuant to the target novel complexes. Entering this project, the

![Figure 2-2](image.png)

**Figure 2-2.** General target complexes in which the polypyridine ligands and linker units can be modified based on donor/acceptor ability. Left: A linear structure. Right: A macrocycle.
procedure for obtaining 2,5-disubstituted siloles had already been selected and established. The procedure, although at times challenging to reproduce, was selected due to the combined synthetic needs and feasibility in obtaining a silole incorporating the desired substituents.

Multiple literature procedures are available which utilize commercially available silanes (SiX₄), alkyltrihalosilanes (RSiX₃), and dialkylhalosilanes (R₂SiX₂), which must be distilled prior to use, for the synthesis of siloles. The methods included the salt metathesis (Curtis method) of 1,4-dilithio-1,4-diphenyl-1,3-butadiene and an appropriate R₂SiX₂ precursor, the formation of a zirconocene metallacycle from a (disubstituted)alkyne route, a one-pot titanium metallacycle (Yamaguchi) method, and the reductive cyclization (Tamao) method starting from a bis(phenyethyl)silane precursor. Modifying a silole at the 1,1- and 3,4- positions provides little electronic or π-influence on the optoelectronic properties. Further, the desired goal was to place 2,5-substituents which have alkynyl units that could subsequently coordinate to Pt(II)-polypyridine complexes. The Curtis method relied on the dimerization of diphenylacetylene with identical aryl substituents, limiting it to homo-substituted alkynes (Scheme 2-2a). The zirconocene method also relied on diarylacetylene precursors (Scheme 2-2b) which may be hetero-substituted, but larger scales were less desirable as the zirconocene reagent must be used in stoichiometric amounts. The Yamaguchi/Tamao method formed a metallacycle intermediate with the advantages of it being one-pot with a cheaper titanium catalyst (Scheme 2-2c). However, both approaches could
Overview of synthetic methods for siloles.

(a) The Curtis method which proceeds directly through salt metathesis. (b) Synthesis of the 1,4-diiodo-butadiene intermediate from a zirconocene metallacycle followed by silole formation through salt metathesis. (c) Synthesis of the 1,4-diiodo-butadiene intermediate from a titanium metallacycle followed by silole formation through salt metathesis.\(^{39}\) prove to be mechanistically problematic when dealing with 2,5-substituents such as \(p\)-phenylacetylene.

Reductive cyclization through the Tamao method was the most desirable route for the production of a silole with 2,5-arylalkynyl units due to an improved yield (>80%), and the Negishi-based carbon-carbon coupling mechanism for the formation of the final product, which was not sensitive to general alkyne ligands while providing versatility in modification of the 2,5-positions.

A general approach (Scheme 2-3) was followed by utilization of Wei’s protocol (Scheme 2-1).\(^{36-38}\) Tamao’s method was selected (Scheme 2-3),\(^{38}\) in which commercially available phenylacetylene was treated at -70 °C in THF using \(n\)-BuLi to undergo a lithium-halogen exchange with dimethyldichlorosilane to form bis(phenylethynyl)dimethylsilane in 85-93% yield.\(^{38}\) In the next step, lithium pellets
(with < 0.5% sodium) were reacted with naphthalene to produce lithium naphthalenide, which served as a radical source for the reductive cyclization of bis(phenylethynyl)dimethylsilane to produce the corresponding 2,5-dilithiosilole. At this point, ZnCl₂(TMEDA) was added to produce a less reactive 2,5-dizinc intermediate in preparation for Negishi coupling (Scheme 2-3a, top path to Scheme 2-3b). The 2,5-dibromosilole can be produced by addition of N-bromosuccinimide (NBS) for an alternate approach to Sonogashira coupling (Scheme 2-3a lower path). Formation of the product from bis(phenylethynyl)dimethylsilane, 2,5-dibromosilole, and 2,5-substituted silole after cross-coupling can be verified by a gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS), ¹H NMR, and 

\[ \text{Scheme 2-3. General approach to silole production.} \]

(a) The Tamao method for production of 2,5-dizinc and 2,5-dibromo siloles, both amenable to Sonogashira coupling. ³⁶–³⁸ (b) From the 2,5-dizinc intermediate, brominated alkyl and aryl substituents can be substituted to the 2,5-positions through cross-coupling. ³⁶–³⁸

¹³C{¹H} NMR spectroscopy. Bis(phenylethynyl)dimethylsilane and 2,5-aryl substituted siloles are stable toward decomposition indefinitely. Maintained at low temperature and shielded from light, 2,5-dibromosilole is stable for weeks but decomposes rapidly upon brief ambient light exposure. The 2,5-dizincsilole intermediate is not isolable. ³⁸

Recent literature has discussed the synthesis of 1,1-dimethyl-2,5-bis[4-
(trimethylsilyl-ethynyl)-phenyl]-3,4-diphenylsilole from commercially available 4-bromophenylacetylene beginning with the Tamao method\textsuperscript{36–38} and adapting methods from Tang.\textsuperscript{40,41} If necessary, the commercially available (4-bromophenylethynyl)trimethylsilane can be synthesized through the reaction of 1-bromo-4-iodobenzene with dichlorobis(triphenylphosphine)palladium(II), CuI, triethylamine, and trimethylsilylacetylene for 2 h under inert atmosphere.\textsuperscript{40} An alternative pathway to (4-bromophenylethynyl)trimethylsilane is through a Zn(OTf)\textsubscript{2}-catalyzed silylation of 1-bromo-4-ethynylbenzene and could be applied to other alkyne ligands (Scheme 2-4).\textsuperscript{42–44} 1,1-dimethyl-2,5-bis[linker]-3,4-diphenylsilole can be produced following established protocols.\textsuperscript{36,38,41}

\textbf{Scheme 2-4.} Silylation of alkynes (1 mmol) with 5 mol % of Zn(OTf)\textsubscript{2}, 1.5 equiv of TMS-OTf, and 1.5 equiv of Et\textsubscript{3}N in CH\textsubscript{2}Cl\textsubscript{2} (4 mL) at 23 °C for 12 h. Isolated yield after flash chromatography: \textsuperscript{a}10 mol % of Zn(OTf)\textsubscript{2}; \textsuperscript{b}15 mol % of Zn(OTf)\textsubscript{2}; Below: Commercially available linkers.
While the pathway for making the desired silole precursor had been selected, established, and planned, preliminary results had yet to be collected on developing the platinum(II)-polypyridine precursors, although it was expected such a process would be facile based on the perceived simplicity and resultant yield of well-known procedures.

A synthetic pathway was selected in order to access a bis-Pt(tpy)-silole complex. However, it was unknown as to whether a more direct approach would work (Scheme 2-5a), or if accessing an intermediate would be necessary to reach the final product (Scheme 2-5b). It was anticipated that 1-dimethyl-3,4-diphenyl-2,5-bis(4-((trimethylsilyl)ethynyl)phenyl)silole (2-6) might be able to coordinate directly to a platinum(II)-polypyridine complex directly in the presence of KF. While this was a well-known method for coordinating silylated alkynes to platinum(II) complexes, it had not yet been performed in the presence of a silole. The silole may undergo decomposition in the presence of KF. In the event that the silole decomposes due to the fluoride source,
an alternate path (Scheme 2-5b) was suggested. The only perceived drawback was the requirement of an additional synthetic step.

Once a general synthetic protocol for the target molecule (Figure 2-2) was established, a wider range of platinum(II)-polypyridine complexes were to be investigated including those in which polypyridine is either: bipyridine (bpy), phenanthroline (phen), or terpyridine (tpy). This would be further extended to analogs which had been modified with substituents in key positions which possessed one or more of the following properties: strong σ-donor, strong π-donor/acceptor, π-extension, and sterically demanding. It was expected that there may be additional challenges (and interest) in the cases of bpy and phen, which would leave two vacant Pt(d$_{x2-y2}$) orbitals with which to coordinate arylalkyl-siloles. Another point of variability was that of the linker used at the 2,5-positions of the silole e.g. 5-bromopenta-1,3-diyne, 1-bromo-4-ethynylbenzene, 4-bromo-4'-ethynyl-1,1'-biphenyl analogs which incorporated inductively withdrawing/donating substituents. Depending on the spectroscopic and electronic nature of the complex, modifying the linker could have minor to profound effects. Once a compound resembling those shown in Figure 2-2 was synthesized, it was expected that full characterization would be possible using a combination of the following techniques: $^1$H, $^{13}$C, $^{29}$Si, $^{195}$Pt nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared spectroscopy (FTIR), X-ray crystallography, elemental analysis (EA), ultraviolet-visible spectrophotometry (UV-Vis), fluorescence spectroscopy, and solid-state quantum yield measurements using an integrating sphere. Determination of oxidation and reduction potentials as well as theoretical calculations were options dependent upon collaboration.
Also of interest was a family of macrocycle complexes utilizing bidentate polypyridine ligands such as bpy and phen. While it was expected the absorption and emission data would be blueshifted with respect to their tpy analogs in the order of tpy > phen > bpy, it opens a coordination site on the metal center providing the possibility of a macrocycle (Figure 2-2) compound. This is a secondary consideration to platinum(II)-tpy complexes due to a suspected increased synthetic challenge. The potential for polymerization would potentially provide a significant synthetic challenge when pursuing a monomer unit. The same general platinum(II)-tpy to siloles approach would be applied when utilizing bidentate polypyridine complexes followed by application of the same array of characterization techniques.

2.3. Results and Discussion

2.3.1. Synthesis of symmetrical 2,5-disubstituted siloles

The synthesis of bis(diphenylethynyl)dimethylsilane (2-10) was accomplished by a lithium-halogen exchange (Equation 2-1).

$$\text{Ph} \quad \text{Si} \quad \text{Ph}$$

Equation 2-1. Synthesis of bis(phenylethynyl)dimethylsilane (2-10).

While dichlorodimethylsilane is commercially available, it was necessary to prepare the bis(phenylethynyl)dimethylsilane (2-10) precursor. Dichlorodimethylsilane was distilled over potassium carbonate prior to use in order to remove any acid produced from the hydrolysis of the dichlorosilane precursor, and could be used for at least a month without redistillation if maintained under inert atmosphere. The first step of the reaction was the
generation of lithium phenyacetylide at reduced temperature under inert atmosphere by addition of \(n\)-butyllithium. It was crucial \(n\)-butyllithium be added dropwise such that the temperature did not exceed -50 °C as the yield would be substantially reduced. The solution appeared milky yellow during the addition of \(n\)-butyllithium. Once the addition was complete, the reaction mixture temperature was elevated to 0 °C with an ice bath, and addition of dichlorodimethylsilane was performed such that the temperature did not exceed 10 °C in order to avoid a decreased yield. Lithium salt deposition occurred as the reaction mixture exceeded 15 °C and approached room temperature. Upon stirring at room temperature for at least 10 minutes, the crude reaction mixture was quenched with ammonium chloride and underwent an aqueous workup to obtain (2-10).

The procedures regarding the preparation of 2,5-disubstituted siloles were adapted from the originally developed one-pot procedure by Tamao\(^{36,46}\) and further refined by Pagenkopf \textit{et al.},\(^{38}\) who meticulously elucidated each facet of the reaction conditions. The reactions conditions were further investigated by coworkers.\(^{47}\) The structure of bis(phenylethynyl)dimethylsilane is important as Tamao’s procedure relies upon a unique \textit{endo-endo} intramolecular reductive cyclization stabilized by the terminal aryl groups to yield the intermediate dilit-hiosiliole (Equation 2-2). While this procedure (Equation 2-3)

\[ \begin{align*} \text{Equation 2-2. Mechanism for the intramolecular cyclization of bis(phenylethynyl)dimethylsilane.}^{36} \end{align*} \]
Equation 2-3. A generalized one-pot synthesis of 2,5-disubstituted silole.\textsuperscript{36,38,46}

is potentially very convenient due to it being one-pot, it can be difficult to reproduce due to the challenges that result from its reductive cyclization mechanism. To maximize yield, each detail within each step must be meticulously considered. In the first step, naphthalene and lithium pellets are placed in a flame-dried 4-neck round-bottom flask and maintained under inert atmosphere. Naphthalene is recrystallized from ethanol, and lithium pellets which have been stored under inert atmosphere must contain additional sodium content (0.5-1.0%) as stabilizers, otherwise the reaction may fail.\textsuperscript{38} The lithium pellets can be mashed under inert atmosphere prior to addition of solvent to expose additional surface area for greater solvation. The freshly-distilled solvent is added after naphthalene and lithium are added to the vessel due to it being potentially hygroscopic even under inert atmosphere. The reaction flask is then lowered into a sonic bath and the reaction mixture then undergoes sonication for at least 30 minutes or until fully dissolved. As sonication is applied, the lithium pellets will immediately release a deep dark green or black swirl, ultimately resulting in a deep dark green or black solution. The flask can be raised from the sonic bath and tilted for careful inspection to verify complete solvation of lithium. It was discovered that THF is required for this reaction to proceed, as attempts to perform this preparation with diethyl ether (Et\textsubscript{2}O) resulted in lithium not dissolving for at least an hour of sonication until the reaction mixture was adjusted to roughly 1% THF, at which point there was immediately partial solvation of the lithium suggesting the coordinative ability of the solvent plays a role. It should be emphasized that THF is dried as much as possible and freshly distilled prior to reaction.
Preparation of the bis(phenylethynyl)dimethylsilane solution in the addition funnel prior to sonication allows for the sonic bath to aid in dissolving the reagent. Prior to addition of the silane, the lithium naphthalenide solution should be carefully inspected for color change. The solution will transition from dark green, to brown, to red depending on its exposure to moisture. If the lithium naphthalenide solution is off-color, the silane in the addition funnel can be recovered if the reaction is terminated. Otherwise, it is imperative that the silane and lithium are fully dissolved and the concentration of both the silane and lithium naphthalenide solutions match that of Pagenkopf\textsuperscript{38} and Carroll\textsuperscript{47} in order to optimize yield. Addition occurred at room temperature dropwise (< 1 drop/sec) through an addition funnel to the rapidly stirring lithium naphthalenide solution. As with all other variables in this protocol, it is important that the rate of addition occurs slowly as to prevent localized high concentrations and substantial reduction of yield through formation of side products.\textsuperscript{38} It is thought that an addition rate that is too rapid might result in decreased conversion efficiency, yielding partially reduced products that did not complete their reductive cyclization.\textsuperscript{38}

Once the solution has stirred for the required time, the reaction mixture was cooled to 0 °C and ZnCl\textsubscript{2}(TMEDA) can be added as a solid. ZnCl\textsubscript{2}(TMEDA) serves the dual purpose of quenching the lithium naphthalenide reaction mixture as well as the formation of the transmetalation intermediate, 2,5-dizincsilole, for Negishi coupling. Preparation of ZnCl\textsubscript{2}(TMEDA) is also important, as previous preparations of ZnCl\textsubscript{2}(TMEDA) resulted in the formation of a gel-like reaction mixture.\textsuperscript{47} This phenomenon was inconsistent, however, and was further mitigated by subsequent dilution with additional THF.\textsuperscript{47} It was eventually observed that the ZnCl\textsubscript{2}(TMEDA) possessed a noticeable amine odor,
suggesting that excess TMEDA remained in the product following the preparation. \(^{48}\) Placing the \(\text{ZnCl}_2(\text{TMEDA})\) in an oven for at least 48 hours at 70 °C seemed to reduce the odor, suggesting that the excess TMEDA had been removed. \(^{49}\) Subsequent synthesis of 2,5-disubstituted siloles using the dried \(\text{ZnCl}_2(\text{TMEDA})\) did not result in a gel-like reaction mixture, even without subsequent dilution with THF. However, no difference in yield was noted between syntheses in which subsequent dilution occurred, and syntheses where it did not. Despite these findings, future experiments continued with dilution after addition of \(\text{ZnCl}_2(\text{TMEDA})\) to ensure that reaction mixture will stir consistently for the next 1.5 h once removed from the bath. \(^{47}\) It is suggested that the reaction mixture is not allowed to stir for more than 2 h as the (2-4) intermediate is sensitive to water, even in trace amounts, which is of particular concern within the confines of this protocol.

The final step is the addition of palladium(II) catalyst for Negishi cross-coupling simultaneously alongside side the desired aryl ligand. While \((\text{PPh}_3)_2\text{PdCl}_2\) was typically employed, it was found that \((\text{dppf})\text{PdCl}_2\) also provided good results, \(^{49}\) and can be employed for ligands which are more difficult to cross-couple. \(^{50}\) The reaction mixture generally remained dark green or black during this final step, but at times would adopt an almost imperceptibly browner tone. This did not seem to affect the final yield of the procedure, and proceeded overnight at reflux without incident.

**Characterization**

Bis(phenylethynyl)dimethylsilane was initially obtained as an oil and was recrystallized using boiling hexanes then yielding the product as white or off-white needle-like crystals. At times when recrystallization does not occur readily due to excess phenylacetylene, removal of some of the phenylacetylene from the oily mixture allows for successful
recrystallization. Decanting off the supernatant from each recrystallization attempt yielded additional crops. As purity was crucial for the following steps, recrystallization was performed until the identity and purity (>98%) of bis(phenylethynyl)dimethylsilane were determined by $^1$H and $^{13}$C\{$^1$H\} NMR, and GC, and melting point and comparison of the results to literature values.$^{36,38,46}$

2.3.1.1. 1,1-dimethyl-2,5-bis[4-(trimethylsilylethynyl)-phenyl]-3,4-diphenylsilole (2-6)

The synthesis of (2-6) was prepared by the Negishi cross-coupling of (2-4) and (2-5) according to (Equation 2-4).$^{38,49}$

\[ \text{Equation 2-4. Synthesis of 1,1-dimethyl-2,5-bis[4-(trimethylsilylethynyl)-phenyl]-3,4-diphenylsilole (2-6).}^{38,49} \]

The general procedure for the synthesis of 2,5-disubstituted siloles was followed with the addition of the desired 2,5-disubstituents being that of commercially available 4-bromo(phenylethynyl)trimethylsilane. The presence of the trimethylsilyl (TMS) group instead of a terminal alkynyl hydrogen was necessary as to prevent homocoupling to form R-C≡C-C≡C-R.$^{39}$

**Characterization**

Isolation of this compound was particularly challenging as one of the products of this protocol was a homocoupled product, in which (4-bromophenylethynyl)trimethylsilane (2-5) reacted at the 4-position of another (2-5) molecule forming 4,4'-bis(2-trimethylsilylethynyl)biphenyl (Figure 2-3). This homocoupling side reaction is common
Figure 2-3. Homocoupled product: 4,4'-bis((trimethylsilyl)ethynyl)-1,1'-biphenyl (2-11).

with Negishi coupling, and is a result of a second transmetalation between the diaryl metal intermediate and arylmetal halide (Scheme 2-6).

\[
\text{Ar}^-\text{Pd}^-\text{Ar} + \text{Ar}^-\text{Zn}^-\text{X} \rightarrow \text{Ar}^-\text{Pd}^-\text{Ar} + \text{Ar}^-\text{Zn}^-\text{X}
\]

\[
\text{Ar}^-\text{Pd}^-\text{Ar} \rightarrow \text{Ar}^-\text{Ar}^- + \text{Pd}(0)
\]

Scheme 2-6. Homocoupling side reaction in which \(\text{Ar}'^-\text{Ar}'\) is the product.

Unfortunately, the homocoupled product, \(\text{Ar}^-\text{Ar}'\) could not be ignored as an impurity as it contained the same functional groups as the desired silole, potentially interfering with coordination to platinum(II) compounds. As a result, a reduced overall yield (53\%) of the desired product occurred due to this side product formation. This is particularly undesirable considering the cost of platinum(II) complexes as well as the time invested into each parallel path towards the final step. The literature report regarding purification of this known silole involved use of silica gel chromatography with hexane as an eluent. Furthermore, no literature information was provided regarding the homocoupled product. However, when attempting to reproduce the literature procedure, no noticeable elution of the yellow band containing 1,1-dimethyl-2,5-bis[4-(trimethylsilyl)ethynyl]-phenyl]-3,4-diphenylsilole was observed even after several hundred milliliters of hexanes were added. By increasing the polarity (Et\(_2\)O:hexanes, 1:10), the yellow band eluted rapidly, resulting in a mixture of the target silole, homocoupled product, naphthalene, and partially reduced silanes, which were previously comprehensively elucidated by Carroll. Subsequent attempts were made by adjusting
the polarity by increments of 1% (Et₂O:hexanes, 1:100-10:100) as well as changing the identity of the solvents (EtOAc:hexanes, DCM:hexanes). Results varied but (2-6) and (2-11) consistently the same general retention time. Increasing the number of fractions collected resulted in a large array of fractions which all contained varying quantities of the homocoupled product. An alternate approach was attempted by rinsing the solid product which contained both the homocoupled product and the silole with cold pentane, with the intent to exploit a potential difference in solubility, however, each rinse resulted in a mixture of the silole and the homocoupled product. By GC analyses, the highest purity product isolated contained roughly 10% of the homocoupled product by relative integrated areas on the chromatogram. Eventually, column chromatography was attempted by applying a polarity gradient in which the mobile phase polarity was increased by increments of 1% until the band containing the silole eluted. Aliquots of 25 mL were then collected from the column and combined after screening by GC-MS. The residue from the combined fractions was recrystallized at least three times using hot pentane or until the remaining homocoupled product was less than 2% in composition.

An alternative consideration during this investigation was reducing the amount of (2-5), as it was added in 2.1 equivalents to bis(phenylethynyl)dimethylsilane. This reaction was performed with the assumption that bis(phenylethynyl)dimethylsilane would undergo full conversion to the 2,5-dizinc intermediate. The implication was that total consumption of the 2,5-dizinc intermediate occurred leaving excess (2-5), resulting in increased formation of the homocoupled product. This may be occurring in situ regardless of the presence of the 2,5-dizinc intermediate. Also, due to reasons previously outlined, there exists the possibility of a broad variance in conversion. The only way to know for certain
is to extract aliquots out of the solution and perform a titration,\textsuperscript{38} which may provide an estimate for what was generated \textit{in situ}. However, this may still not provide an accurate quantitation as the aliquot would only be representative of what was present in solution at the time of extraction.

2.3.1.1. 4-bromo-4’-[2-(trimethylsilyl)ethynyl]-1,1’-biphenyl (2-13)

The synthesis of (2-13) was prepared by the cross-coupling of (2-12) with 1-phenyl-2-trimethylsilylacetylene (Equation 2-5).\textsuperscript{52}

\begin{eqnarray*}
\begin{array}{c}
\text{Br} & \\
\text{2-12} & \\
\text{PdCl}_2(PPh_3)_2, CuI & \\
\text{24 h} & \\
\text{Br} & \\
\text{2-13} & \\
\end{array}
\end{eqnarray*}

\textbf{Equation 2-5. Synthesis of 4-bromo-4’-[2-(trimethylsilyl)ethynyl]-1,1’-biphenyl (2-13).}\textsuperscript{52}

4-bromo-4’-iodo-1,1’-biphenyl (2-12) as well as all other reagents utilized in its synthesis were commercially available. The reaction proceeded in good yield by Sonagashira cross-coupling using TEA as the solvent, after degassing with argon for 20 minutes by sparging.

\textbf{Characterization}

The product, (2-13), was obtained as a white solid after column chromatography. Purity was confirmed by GC and GC-MS as well as \textsuperscript{1}H and \textsuperscript{13}C{\textsuperscript{1}H} NMR spectroscopy.

2.3.1.2. 1,1-dimethyl-3,4-diphenyl-2,5-bis(4-bromo-4’-[2-(trimethylsilyl)ethynyl]-1,1’-biphenyl)silole (2-14)

The synthesis of (2-14) was prepared by the Negishi cross-coupling of (2-4) and (2-13) according to (Equation 2-6).
Equation 2-6. Synthesis of 1,1-dimethyl-3,4-diphenyl-2,5-bis(4-bromo-4’-[2-(trimethylsilyl)ethynyl]-1,1’-biphenyl)silole (2-14).

The general procedure for the synthesis of 2,5-disubstituted siloles was followed with the addition of the desired 2,5-disubstituents being that of 4-bromo-4’-[2-(trimethylsilyl)ethynyl]-1,1'-biphenyl, which had to be prepared separately (Equation 2-5).52

Characterization

The product, (2-14), was obtained as a yellow solid following the same purification and characterization protocol as that of (2-6).

2.3.1.3. Deprotection of 1,1-dimethyl-2,5-bis[4-(trimethylsilylethynyl)-phenyl]-3,4-diphenylsilole

The synthesis of (2-7) was accomplished by the deprotection of (2-6) (Equation 2-7).

Equation 2-7. Deprotection of 1,1-dimethyl-2,5-bis[4-(trimethylsilylethynyl)-phenyl]-3,4-diphenylsilole (2-6).41

Potassium carbonate was dissolved in a freshly distilled mixture of THF:MeOH (2:3, MeOH = methanol) and the trimethylsilylated silole. The following equilibrium takes place in situ, generating methoxy anions (Equation 2-8) capable of coordinating to the trimethylsilyl ligand, forming a pentavalent silicon intermediate (MeO)Me₃Si-C≡C-R.53

K₂CO₃ (s) + MeOH (l) ⇌ MeOK (aq) + KHCO₃ (s)

Equation 2-8. Equilibrium in THF:MeOH potassium carbonate solution.54
The pentavalent silane dissociates, cleaving Si-C in Si-C≡C-R in favor of formation of a Si-O bond, producing Me₃Si-OMe and H-C≡C-R, of which the proton in the latter originated from MeOH. The literature procedure utilized 1.25 equivalents of MeOH to one of the starting silole, although ratios as high as 4.0 have been employed with good yields (96%) suggesting that an excess, at least to 4.0 eq., does not have any appreciable adverse influence in the results. As a result, rather than performing silica gel chromatography on the silylated 2,5-disubstituted siloles, labor hours can be conserved by performing the procedure at 1.25 eq of MeOH and the resulting crude mixture used without purification for the subsequent step and reserving the chromatography step for the deprotected product. The idea is that any unreacted materials which would have otherwise previously been separated by column chromatography would be separated after the deprotection step, as the reaction conditions were mild enough that no side products should be produced. Once these were in hand, the platinum(II) precursors could be produced.

**Characterization**

There was no observable difference in solubility or retention time between the starting material and final product during column chromatography, as such, the product was isolated in an identical means to that of the starting material. Column chromatography was attempted by applying a polarity gradient in which the mobile phase polarity was increased by increments of 1% until the band containing the silole eluted. Aliquots of 25 mL were then collected from the column and combined after screening by GC-MS. The residue from the combined fractions was recrystallized at least three times
using hot pentane or until the remaining homocoupled product was less than 2% in composition. $^1$H and $^{13}$C{$^1$H} NMR spectroscopy are useful for tracking diagnostic shifts to confirm formation of products (Figure 2-4). As deprotection occurs, the shift related to the TMS group was no longer observed, while a new shift representing an alkynyl proton emerged, which became a useful diagnostic feature for confirming alkynyl coordination. For $^{13}$C{$^1$H} NMR spectroscopy, the alkynyl carbons for the starting silole become more shielded and shift upfield when deprotected, respectively, from $\delta$ 94.3 and 105.6 to 78.3 and 84.0 (Figure 2-5). The IR stretches for the starting silole and deprotected silole also change, respectively, $\nu$ (cm$^{-1}$): 2156 (C≡C) and 3291 (≡C-H), 2106 (C≡C).

![Figure 2-4. $^1$H NMR comparison of deprotection reaction between starting and product siloles.](image-url)
Figure 2-5. $^{13}$C-$^{1}$H NMR comparison of deprotection reaction between starting and product siloles.

If the starting material was not purified adequately prior to this step, then there would remain homocoupled product which would also be deprotected, and would serve as a source of side product resulting in diminished yield if utilized in reaction with platinum(II) complexes. Because of this, it is absolutely crucial that any homocoupled impurities be removed and represent less than 5% the product composition prior to proceeding to subsequent synthetic steps. As this was an intended precursor, absorption and emission spectra were recorded in DCM (Figures 2-6 and 2-7).
Figure 2-6. UV-Vis absorption spectrum of 2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole.

Figure 2-7. Fluorescence emission spectrum of 2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole.
2.3.1. Synthesis of platinum(II)-polypyridines

2.3.1.1. Dichloro(1,5-cyclooctadiene)platinum(II) (2-16)

The synthesis of dichloro(1,5-cyclooctadiene)platinum(II) (2-16) was performed according to Equation 2-9.

\[
\begin{align*}
K_2\text{PtCl}_4 & \xrightarrow{\text{AcOH, 40\%}} \text{Cl}_2\text{Pt} \quad \text{96\%} \\
2-16
\end{align*}
\]

**Equation 2-9.** Synthesis of dichloro(1,5-cyclooctadiene)platinum(II) (2-16).\(^{56}\)

Commercially available potassium tetrachloroplatinate(II) was dissolved in 40% glacial acetic acid. 1,5-Cyclooctadiene (COD) was then added and the solution was refluxed for 1 h, during the course of which the solution turned from deep red to pale yellow. The reaction mixture was then returned to room temperature and stirred overnight. The final product, (2-16), was washed and dried at 100 °C overnight or until the product no longer contained an odor of 1,5-cyclooctadiene.\(^{65}\) While platinum(II)-polypyridine complexes could be accessed through other more direct protocols not involving a PtCl₂(COD) intermediate they often provided lower yields and long reaction times (100 h), which was of obvious concern given the cost of potassium tetrachloroplatinate(II) and tpy.\(^{57-64}\)

Synthesis of the following platinum(II)-polypyridine complexes was nearly quantitative when utilizing (2-16) as a starting material, minimizing overall loss of potassium tetrachloroplatinate(II) throughout the total synthesis while providing a shorter overall reaction time.\(^{57-64}\)

**Characterization**

The product, (2-16), was isolated in nearly quantitative yield as an off-white solid. Characterization is relatively simple as the reaction is straight forward and solubility
differences in the product and reactions are easily exploited. Due to the simplicity of this protocol, confirmation can be performed by $^1$H NMR spectroscopy and melting point. While $^1$H NMR experiments are usually performed with 16 or 32 scans, the solubility of PtCl$_2$(COD) was low in chloroform-$d$, so an experiment was run for 128 scans to acquire good resolution. The free 1,5-cyclooctadiene ligand provides singlets around ca. $\delta$ 2.27, 2.71 and 5.61, while the product has shifts at $\delta$ 1.5 and 2.40.$^{66}$

2.3.1.2. Chloro(2,2′:6′,2″-terpyridine)platinum(II) chloride dihydrate (2-17)

Chloro(2,2′:6′,2″-terpyridine)platinum(II) chloride dihydrate or [PtCl(terpy)]Cl was synthesized by refluxing PtCl$_2$(COD) in water with commercially available 2,2′:6′,2″-terpyridine (tpy)$^{67,68}$ or could be otherwise prepared through a series of one-pot syntheses in poor (6-32%) yields which are amenable to scale-ups (Equation 2-10).$^{69}$ The reaction mixture was refluxed for 1 hour providing a nearly quantitative yield. The final product was washed and dried overnight at 100 °C.

$$\text{Equation 2-10. Synthesis of chloro(2,2′:6′,2″-terpyridine)platinum(II) chloride dihydrate (2-17).}^{67,68}$$

A library of tpy analogs were commercially available and could also be synthesized in 30-55% yields: 4′-Chloro-2,2′:6′,2″-terpyridine,$^{70}$ 4′-Phenyl-2,2′:6′,2″-terpyridine,$^{71,72}$ 4′-(4-Chlorophenyl)-2, 2′:6′,2″-terpyridine,$^{71,72}$ 4′-(4-Methylphenyl)-2,2′:6′,2″-terpyridine,$^{71,72}$ 6,6″-Dibromo-2,2′:6′,2″-terpyridine,$^{73}$ along with other commercially available polypyridines.$^{74}$
Characterization

Characterization of (2-17) was originally thought to be fairly straight-forward, however solubility was determined to be a significant challenge. Despite the solvent employed, $^1$H NMR experiments often required at minimum 256 scans to obtain any appreciable resolution, although $^1$H NMR results were eventually obtained and matched literature values (Figure 2-8). Furthermore, it was realized that literature values did not contain $^{13}$C{$^1$H} NMR data for (2-17). This was obviously due to the solubility issues which necessitated substantially greater duration $^1$H NMR experiments, which were possible due to the isotope abundance (99.98%), while $^{13}$C{$^1$H} were virtually out of reach even after 12 hour experiments due to the abundance of carbon-13, (1.1%). FAB-HRMS was also employed to confirm formation of (2-17).

![Figure 2-8. $^1$H NMR spectrum of the aromatic region of (2-17).](image)

2.3.1.1. Attempted syntheses of [Pt(tpy)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole)]Cl$_2$ (2-18)
The synthesis of the silole-linked bis(terpyridine)platinum complex (Equation 2-11) was attempted several times without success toward the formation of \([\text{Pt(tpy)}-(2,5\text{-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole})]\text{Cl}_2\).

**Equation 2-11.** Attempted synthesis of \([\text{Pt(tpy)}-(2,5\text{-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole})]\text{Cl}_2\) (2-18).

Initially, protocols utilizing tetrabutylammonium fluoride (TBAF) or potassium fluoride (Scheme 2-5a)\(^{16,45}\) were attempted in which the silole prior to deprotection were directly utilized, however it was difficult to characterize the resulting mixture, as multinuclear NMR did not elucidate positive results due to the previously aforementioned solubility challenges. Additionally, no visual changes in the reaction were noted during any attempt. Due to these results, it was believed the alternative pathway outlined in Scheme 2-5b should be attempted in lieu of that of Scheme 2-5a, leading to production of the deprotected silole. No differences were observed compared to previous experiments utilizing Scheme 2-5a. Repeated attempts did not indicate formation of product, and in some cases indicated a mixture of starting materials by \(^1\text{H}\) NMR spectroscopy. The only evidence indicating formation of product was the disappearance of the \(^1\text{H}\) NMR shift associated with the terminal alkynyl-H, however, \(^1\text{H}\) NMR spectroscopy was inconclusive even at 1024 scans, resolution required for reliable integration was not obtained. HRMS did not result in detection of any ions associated with the desired product due to instrumental limitations. Due to these reasons, further investigation into the synthesis of this complex were postponed in favor of investigation into related
materials with the hopes that any knowledge obtained may elucidate the challenges related to confirming material. It was also believed that switching to ligands which would result in a neutral species may improve solubility in organic solvents.

2.3.1.2. Synthesis of platinum(II)-bipyridine and -phenanthroline complexes

The synthesizes of (2,2′-Bipyridine)dichloroplatinum(II) (2-19), (4,4′-di-tert-butyl-2,2′-bipyridine)dichloroplatinum(II) (2-20), (1,10-phenanthroline)dichloroplatinum(II) (2-21), and (3,4,7,8-tetramethyl-1,10-phenanthroline)dichloroplatinum(II) (2-22) were achieved by the reaction of potassium tetrachloroplatinate(II) and the appropriate bipyridine or phenanthroline in the presence of hydrochloric acid under reflux (Equation 2-12).\textsuperscript{63,76,77}

\begin{equation}
\text{Equation 2-12. Synthesis of platinum(II)-bipyridine and -phenanthroline complexes.} \textsuperscript{63,76,77}
\end{equation}

Both, $\text{K}_2\text{PtCl}_4$ and the appropriate bipyridine or phenanthroline were dissolved in 0.35 M HCl and heated under reflux overnight. The ligand, tbbpy, was selected not only because of the potential electronic influence the $t$-butyl groups at the 4,4′-positions may have on the absorption and emission, but also due to the added steric demand perpendicular to the plane of the ligand, relative to that of bpy, which was thought to improve solubility for characterization. The phen and Me₄phen ligands were selected due to their fused ring
systems, which may result in an improved quantum yields compared to that of the bipyridine systems.

All products were collected as yellow precipitates by filtration and washed with small volumes of MeOH and Et₂O, then dried overnight at room temperature under vacuum. It should be noted that these reactions can also be performed with PtCl₂(COD)⁶⁷,⁶⁸ as the precursor, however, it proceeds in excellent yields directly from K₂PtCl₄ (94-97%).

**Characterization**

Formation of complexes (2-19), (2-20), (2-21), and (2-22) resulted in obvious changes in color from the red/orange starting material to a bright yellow product. ¹H NMR spectroscopy results required at minimum 128 scans to obtain any appreciable resolution, but confirmed formation of the desired product. As these were intended precursors, absorption spectra were recorded in DCM (Figures 2-9 through 2-12).

![UV-Vis absorption spectrum of PtCl₂(bpy) in DCM. λ_{abs} (nm) = 282, 324, and 402.](image)

**Figure 2-9.** UV-Vis absorption spectrum of PtCl₂(bpy) in DCM. λ_{abs} (nm) = 282, 324, and 402.
Figure 2-10. UV-Vis absorption spectrum of PtCl$_2$(tbbpy) in DCM. $\lambda_{\text{abs}}$ (nm) = 282, 323, and 396.

Figure 2-11. UV-Vis absorption spectrum of PtCl$_2$(phen) in DCM. $\lambda_{\text{abs}}$ (nm) = 258, 278, 335, and 401.

Figure 2-12. UV-Vis absorption spectrum of PtCl$_2$(Me$_4$phen) in DCM. $\lambda_{\text{abs}}$ (nm) = 257, 283, 340, and 388.
2.3.1. Synthesis of platinum(II)-phosphine complexes

The syntheses of the chelating phosphine platinum complex, [1,3-bis(diphenylphosphino)propane]dichloroplatinum(II) (2-23), [1,2-bis(diphenylphosphino)ethane]dichloroplatinum(II) (2-24), and [1,1’-bis(diphenylphosphino)ferrocene]dichloroplatinum(II) (2-25), are shown in Equation 2-13.78

![Synthesis reaction diagram](image)

**Equation 2-13.** Synthesis of platinum(II)-phosphine complexes.78

The synthesis involves the reaction of (2-16) and 1,3-bis(diphenylphosphino)propane), 1,2-bis(diphenylphosphino)ethane, or 1,1’-bis(diphenylphosphino)ferrocene as a DCM slurry. Over the course of at least an hour, the slurry dissolved into a solution. The reaction mixture was stirred at room temperature for 48 h. No other changes in solution consistency or color were noted. The subsequent workup was straightforward and the product was obtained in good yields (76-93%).

**Characterization**

Chelating platinum(II)-phosphine complexes can be easily characterized by $^{31}$P{$^1$H} NMR spectroscopy due to the emergence of resonances containing satellites from $^1J_{Pt-P}$ coupling constants compared to singlets for the free (symmetric) phosphine ligand. Once coordinated to platinum, the phosphine can couple to the platinum center giving rise to satellite peaks due to the coupling of phosphorous-31 (100% abundance) to that of
platinum-195 (33.8% abundance), also resulting in a substantial change in shielding. In this case, uncoordinated dppp exhibits a $^{31}P\{^1H\}$ shift in CDCl$_3$ at $\delta$ -16.6, but upon formation of (2-23) the phosphorus center is deshielded and the chemical shift is observed at -5.4 ppm with a $^1J_{Pt-P} = 3408$ Hz, both of which correspond to literature values.$^{22,79}$ Uncoordinated dppe exhibits a $^{31}P\{^1H\}$ NMR chemical shift in CDCl$_3$ at $\delta$ -12.1. Upon formation of (2-24) the signal appears downfield at 41.0 ppm with a $^1J_{Pt-P} = 3617$ Hz,$^{80}$ both of which correspond to literature values.$^{22,79}$ The complex, (2-25) was characterized by $^{31}P\{^1H\}$ NMR spectroscopy and exhibited a downfield chemical shift of 13.1 ppm with a $^1J_{Pt-P} = 3766$ Hz, compared to the uncoordinated dppf which had a chemical shift of $\delta$ -16.8 in CD$_2$Cl$_2$, both of which correspond to literature values.$^{22,81}$ As these were intended precursors, absorption spectra were recorded in DCM (Figures 2-13 through 2-15). For all platinum(II)-phosphine complexes, $\lambda_{max}$ (nm) = N/A.

![Absorption Spectrum](image)

**Figure 2-13.** UV-Vis absorption spectrum of PtCl$_2$(dppp) in DCM. $\lambda_{max}$ (nm) = N/A.
2.3.1. Synthesis of platinum(II)-silole complexes

2.3.1.1. Pt(bpy)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole) (2-26)

The reaction of PtCl$_2$(bpy) with 2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole was carried out in the presence of copper(I) iodide and diisopropylamine as shown in Equation 2-14. The tentative product assignment is a dinuclear complex containing the alkynyl groups at each side of the silole coordinated to two different platinum centers.
Equation 2-14. Synthesis of Pt(bpy)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole) (2-26).

PtCl₂(bpy) was dissolved in DCM with copper(I) iodide, and 2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole with diisopropylamine. The resulting yellow reaction mixture turned orange as it stirred overnight at room temperature.

Characterization

While a change in color indicates a chemical reaction occurred, the \(^1\)H NMR analysis of the crude product mixture also indicated the absence of a singlet at ca. \(\delta\) 3.03, which is the shift corresponding to the terminal C≡C-H hydrogen from 2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole, suggesting that coordination of the alkynyl unit to the Pt center has occurred. IR spectroscopy revealed that the vibrational frequency of the starting silole at 3291 cm\(^{-1}\) (≡C-H) was absent in the product, also suggesting that C≡C was had undergone coordination. Due to low solubility, the \(^{13}\)C\({^1}\)H NMR spectrum only revealed solvent signals, even when NMR experiments were performed overnight.

Attempts at electrospray ionization (ESI) or fast atom bombardment (FAB) mass spectrometry (ESI- and FAB-MS) did not result in ionization. However, UV-Vis and Fluorescence measurements indicated changes in absorption and emission with respect to the starting silole (Figures 2-16 and 2-17).
Figure 2-16. UV-Vis absorption spectrum of Pt(bpy)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole) in DCM. $\lambda_{\text{abs}}$ (nm) = 283, 405.

Figure 2-17. Fluorescence emission spectrum of Pt(bpy)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole) in DCM. $\lambda_{\text{em}}$ (nm) = 560.

2.3.1.1. Pt(tbbpy)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole) (2-27)

A similar reaction was carried out with the silole and PtCl$_2$(tbbpy) as shown in Equation 2-15. The tentative product assignment is a dinuclear complex containing the alkynyl groups at each side of the silole coordinated to two different platinum centers.
Equation 2-15. Synthesis of Pt(tbbpy)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole) (2-27).

PtCl₂(tbbpy) was dissolved in DCM with copper(I) iodide, and 2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole with diisopropylamine. The yellow reaction mixture turned orange as it stirred overnight at room temperature.

Characterization

The complex (2-27) showed the same spectroscopic characteristics as described above for (2-26). UV-Vis and fluorescence measurements indicated changes in absorption in and emission with respect to the starting silole (Figures 2-18 and 2-19).

Figure 2-18. UV-Vis absorption spectrum of Pt(tbbpy)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole) in DCM. λ<sub>abs</sub> (nm) = 281, 393.
Figure 2-19. Fluorescence emission spectrum of Pt(tbbpy)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole) in DCM. $\lambda_{em}$(nm) = 546.

2.3.1.1. Pt(phen)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole) (3-28)

The reaction of the silole with PtCl$_2$(phen) is shown in Equation 2-16. The tentative product assignment is the dinuclear complex containing the alkynyl groups at each side of the silole coordinated to two different platinum centers.

Equation 2-16. Synthesis of Pt(phen)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole) (2-28).

PtCl$_2$(phen) was dissolved in DCM with copper(I) iodide, and 2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole with diisopropylamine. The yellow reaction mixture turned orange as it stirred overnight at room temperature.

Characterization
The complex (2-28) showed the same spectroscopic characteristics as described above for (2-26) and (2-27). UV-Vis and fluorescence measurements indicated changes in absorption in and emission with respect to the starting silole (Figures 2-20 and 2-21).

**Figure 2-20.** UV-Vis absorption spectrum of Pt(phen)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole) in DCM. $\lambda_{\text{abs}}$ (nm) = 268, 397.

**Figure 2-21.** Fluorescence emission spectrum of Pt(phen)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole) in DCM. $\lambda_{\text{em}}$ (nm) = 546.

**2.3.1.1. Pt(Me$_4$phen)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole) (2-29)**

The reaction between 2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole and PtCl$_2$(Me$_4$phen) is shown in Equation 2-17. The tentative product assignment is a
dinuclear complex containing the alkynyl groups at each side of the silole coordinated to two different platinum centers.

Equation 2-17. Synthesis of Pt(Me$_4$phen)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole) (2-29).

PtCl$_2$(Me$_4$phen) was dissolved in DCM with copper(I) iodide, and 2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole with diisopropylamine. The yellow reaction mixture turned orange as it stirred overnight.

Characterization

The complex (2-28) showed the same spectroscopic characteristics as described above for (2-26), (2-27), and (2-28). UV-Vis and fluorescence measurements indicated changes in absorption in and emission with respect to the starting silole (Figures 2-22 and 2-23).

Figure 2-22. UV-Vis absorption spectrum of Pt(Me$_4$phen)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole) in DCM. $\lambda_{abs}$ (nm) = 258, 282, 397.
**2.3.1.1. Pt(dppp)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole) (2-30)**

The reaction of 2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole with several platinum-phosphine complexes were also performed. The reaction of the silole with PtCl$_2$(dppp) is shown in Equation 2-18. The tentative product assignment is a dinuclear complex containing the alkynyl groups at each side of the silole coordinated to two different platinum centers.

**Equation 2-18.** Synthesis of Pt(dppp)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole) (2-30).

PtCl$_2$(dppp) was dissolved in DCM with copper(I) iodide, and 2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole with diisopropylamine. The reaction mixture was then stirred overnight at room temperature.
Characterization

The $^1$H NMR spectrum of the crude product mixture also indicated the absence of the alkynyl proton for the silole at ca. $\delta$ 3.03, suggesting that the alkynyl group had undergone coordination to the platinum center. IR spectroscopy did not show the stretching frequency for the alkynyl proton in the starting silole, further suggesting coordination of the alkynyl group to platinum. As observed with the previous described reactions, the $^{13}$C{$^1$H} NMR spectrum only revealed solvent signals, even when NMR experiments were performed overnight. $^{31}$P{$^1$H} experiments were performed on both the starting materials and the end product for comparison. Results indicated that the $^1J_{Pt-P}$ of the starting material, PtCl$_2$(dppp) (3408 Hz),$^{22}$ had reduced to 2409 Hz, which is similar to that of other $cis$-Pt(phosphine)(C≡CR) complexes (Figure 2-24).$^{82}$ This suggested at minimum the successful formation of a $cis$-Pt(phosphine)(C≡CR) complex, although did not confirm whether this is part of a macrocycle. The concern that the product may contain multiple chemical environments around the platinum center was further emphasized by other less positive results (Figure 2-25), in which there was substantial broadening and splitting. The broadening could result from contributions of multiple chemical environments surrounding the platinum center, or as a result of reduced solubility from the large macrocyclic structure. However, the splitting further supports the multiple environments theory.
Figure 2-24. An overlay of the starting material, PtCl₂(dppp) with the product, Pt(dppp)-silole demonstrating a substantial change in coupling constant (3408 → 2409 Hz) in line with literature values.²²,²³

Figure 2-25. $^{31}$P$\{^1$H$\}$ spectrum of Pt(dppp)-silole showing an extreme example of peak broadening and splitting found in the analysis of repeated attempted syntheses. The coupling constant found from the approximated satellite centers did correspond to literature values of similar coordination environments.²⁴
Attempts at electrospray ionization (ESI) or fast atom bombardment (FAB) mass spectrometry (ESI- and FAB-MS) did not result in ionization. However, UV-Vis and fluorescence measurements indicated changes in absorption in and emission with respect to the starting silole (Figures 2-26 and 2-27).

**Figure 2-26.** UV-Vis absorption spectrum of Pt(dppp)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole) in DCM. $\lambda_{\text{abs}}$ (nm) = 332, 408.

**Figure 2-27.** Fluorescence emission spectrum of Pt(dppp)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole) in DCM. $\lambda_{\text{em}}$ (nm) = 524.
2.3.1.1. Pt(dppe)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole) (2-31)

Equation 2-19 shows the reaction between 2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole and PtCl₂(dppe). The tentative product assignment is a dinuclear complex containing the alkynyl groups at each side of the silole coordinated to two different platinum centers.

Equation 2-19. Synthesis of Pt(dppe)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole) (2-31).

PtCl₂(dppe) was dissolved in DCM with copper(I) iodide, and 2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole with diisopropylamine. The reaction mixture was then stirred overnight at room temperature.

Characterization

The complex (2-31) showed the same spectroscopic characteristics as described above for (2-30). $^{31}P\{^1H\}$ experiments were performed on both the starting materials and the end product for comparison. Results indicated that the $^1J_{Pt-P}$ of the starting material, PtCl₂(dppe) (3620 Hz), had reduced to 2283 Hz, which is similar to that of other cis-Pt(phosphine)(C≡CR) complexes (Figure 2-28). This suggested at minimum the successful formation of a cis-Pt(phosphine)(C≡CR) complex, although did not confirm whether this is part of a macrocycle. The concern that the product may contain multiple chemical environments around the platinum center was further emphasized by other less
positive results (Figure 2-29), in which there was substantial broadening and splitting. The broadening could result from contributions of multiple chemical environments surrounding the platinum center, or as a result of reduced solubility from the large macrocyclic structure. However, the splitting further supports the multiple environments theory.

![Figure 2-28](image)

**Figure 2-28.** An overlay of the starting material, PtCl$_2$(dppe) with the product, Pt(dppe)-silole demonstrating a substantial change in coupling constant (3620 → 2283 Hz) in line with literature values.$^{22,82}$

![Figure 2-29](image)

**Figure 2-29.** $^{31}$P{$^1$H} spectrum of Pt(dppe)-silole showing an extreme example of peak broadening and splitting found in the analysis of repeated attempted syntheses. The coupling constant found from the approximated satellite centers did correspond to literature values of similar coordination environments.$^{82}$
The $^{13}$C{$^1$H} NMR spectrum only revealed solvent signals, even with long NMR experiments. Attempts at electrospray ionization (ESI) or fast atom bombardment (FAB) mass spectrometry (ESI- and FAB-MS) were unsuccessful due to lack of ionization of the product. UV-Vis and fluorescence measurements did indicate changes in absorption and emission with respect to the starting silole (Figures 2-30 and 2-31).

**Figure 2-30.** UV-Vis absorption spectrum of Pt(dppe)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole) in DCM. $\lambda_{abs}$ (nm) = 375.

**Figure 2-31.** Fluorescence emission spectrum of Pt(dppe)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole) in DCM. $\lambda_{em}$ (nm) = 528.
2.3.1.1. Pt(dppf)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole) (2-32)

The reaction of 2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole was also performed with the platinum complex, PtCl₂(dppf) as shown in Equation 2-20.

![Reaction Scheme](image_url)

**Equation 2-20.** Synthesis of Pt(dppf)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole) (2-32).

PtCl₂(dppe) was dissolved in DCM with copper(I) iodide, and 2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole with diisopropylamine. The reaction mixture was then stirred overnight at room temperature.

**Characterization**

The complex (2-32) showed the same spectroscopic characteristics as described above for (2-30) and (2-31). ³¹P{¹H} experiments were performed on both the starting materials and the end product for comparison. Results indicated that the ¹J_Pt-P of the starting material, PtCl₂(dppf) (3766 Hz), had reduced to 2371 Hz, which is similar to that of other cis-Pt(phosphine)(C≡CR) complexes (Figure 2-32). This suggested at minimum the successful formation of a cis-Pt(phosphine)(C≡CR) complex, although did not confirm whether this is part of a macrocycle. The concern that the product may contain multiple chemical environments around the platinum center was further emphasized by other less positive results (Figure 2-33), in which there was substantial broadening and splitting. The broadening could result from contributions of multiple chemical environments.
surrounding the platinum center, or as a result of reduced solubility from the large macrocyclic structure. However, the splitting further supports the multiple environments theory.

**Figure 2-32.** An overlay of the starting material, PtCl2(dppp) with the product, Pt(dppp)-silole demonstrating a substantial change in coupling constant (3766 → 2371 Hz) in line with literature values.81,82

**Figure 2-33.** 31P{1H} spectrum of Pt(dppf)-silole showing an extreme example of peak broadening and splitting found in the analysis of repeated attempted syntheses. The coupling constant found from the approximated satellite centers did correspond to literature values of similar coordination environments.82

The 13C{1H} NMR spectrum only displayed solvent signals even during an overnight experiment. Electrospray ionization (ESI) and fast atom bombardment (FAB) mass
spectrometry (ESI- and FAB-MS) experiments were unsuccessful due to lack of ionization. However, UV-Vis and fluorescence measurements indicated changes in absorption in and emission with respect to the starting silole (Figures 2-34 and 2-35).

Figure 2-34. UV-Vis absorption spectrum of Pt(dppf)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole) in DCM. \( \lambda_{\text{abs}} \) (nm) = 402.

Figure 2-35. Fluorescence emission spectrum of Pt(dppf)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole) in DCM. \( \lambda_{\text{em}} \) (nm) = 529.

2.3.1. Discussion

The degrees of success for the attempted syntheses of the aforementioned platinum((II)-polypyridine and –phosphine silole complexes were difficult to ascertain.
Pt(polypyrindine)-siloles were challenging to characterize mostly due to ionization and solubility issues, making $^{13}\text{C}\{{}^1\text{H}\}$ NMR, ESI-MS, FAB-MS, and MALDI-TOF data unobtainable. $^1\text{H}$ NMR for all Pt(polypyrindine)-siloles showed the absence of a singlet at ca. $\delta$ 3.03, which is the shift corresponding to the terminal C≡C hydrogen from 2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole, suggesting that C≡C was had undergone coordination. IR revealed that the vibrational frequency of the starting silole at 3291 cm$^{-1}$ (≡C-H) was absent, also suggesting that C≡C coordination had occurred. This is further supported by a color change of yellow (starting materials) to orange. While the methods discussed herein included the use of copper(I) iodide, copper(I) was difficult to remove from the final product, especially since repeated attempts at column chromatography using silica or alumina resulted in irreversible adsorption to the substrate in the presence of acetone, methanol, ethanol, dichloromethane, tetrahydrofuran, diethyl ether, dimethyl sulfoxide, pentane, hexanes, benzene, toluene, and all other readily available lab solvents even while undergoing sonication. Recrystallization in multiple solvent conditions also resulted in no substantial difference in observations. Finally, rinsing with solvents in which the monomeric units may be soluble but the final product insoluble (e.g. pentane) resulted in no observable spectroscopic differences by NMR. This made methods which provided elemental analysis information ineffective. There were also no successful attempts at forming any crystals suitable for single crystal x-ray diffraction.

Due to these difficulties and the minor success from $^1\text{H}$ NMR with Pt(polypyrindine)-siloles, it was thought that PtCl$_2$(phosphine) complexes could be employed since for example, cis-PtX$_2$(phosphines) typically have a coupling constant of ca. 3300 Hz,$^{22}$ while
cis-Pt(phosphine)-acetylide complexes exhibit coupling constants of ca. 2400 Hz. An added advantage was that readily available phosphines, dppp, dppe, and dppf contained sterically demanding substituents which may improve solubility by mitigating π-π stacking and other weak intermolecular interactions which prevent solvation. Results indicated that the coupling procedures described herein resulted in a change in phosphorus coupling constants (Figures 2-24, 2-28, 2-32). For example, PtCl₂(dppp) was found to have a $J_{Pt-P}$ of 3408 Hz, but after formation of Pt(dppp)-silole the coupling constant changed to 2409 Hz, which are in line with expected literature values. The other produced complexes, Pt(dppe)- and Pt(dppf)-silole followed suit.

$^1$H NMR for all Pt(phosphine)-siloles also exhibited the absence of a singlet at ca. $\delta$ 3.03 (R-$\ce{C≡C-H}$) suggesting that $\ce{C≡C}$ was had undergone coordination, which IR results supported with the absence of a vibrational frequency at 3291 cm$^{-1}$ (≡C-$\ce{H}$). No color changes were noted, which may support a reaction did occur in the attempted syntheses of Pt(polypyridine)-siloles. During these studies, a sample of a crude reaction mixture of (2-32) dissolved in DMSO-$d_6$ was placed in an NMR tube in an oven at 60 °C overnight. The following day, no observable quantity of DMSO-$d_6$ had evaporated, however the reaction mixture turned from a yellow to a brown color. $^{31}$P{$^1$H} results revealed that the coupling constant had returned to 3378 Hz, from ca. 2298 Hz, suggesting that a decomposition of bis-acetylide reductive-elimination had occurred, potentially forming a macrocycle sans the Pt(dppe) unit. A literature search revealed a singular result in which the same proposed reaction was utilized in formation of a molecular wire. Experimental details were not comprehensive, and the only details provided for the Pt(dppp)-thiophene macrocycle were the same arguments previously used for similar structures in this
dissertation, absence of shifts and vibrational frequencies associated with R-C≡C-H, as well as a similar change in $^{31}\text{P}\{^1\text{H}\}$ coupling constant.\textsuperscript{84}

Details regarding the starting compound in such as elemental analysis and $^{13}\text{C}\{^1\text{H}\}$ NMR were also absent, while proof of the existence of both the precursor to this compound as well as the product were used to support its structure, although MALDI-TOF was successful.\textsuperscript{84} $^{31}\text{P}\{^1\text{H}\}$ NMR results of Pt(phosphine)-siloles often varied substantially in the amount of experimental scans required to obtain spectral results, as well as peak broadening with respect to the starting PtCl$_2$(phosphine) which would suggests the possibility of fluxional, polymeric, or closely-related. In many cases, it was observed that the central peak was split, and in others the resolution obtained was great enough to see hints of splitting within the satellites (Figure 2-36).

**Figure 2-36.** Stacked spectra of 1) Pt(dppf)-silole and 2) PtCl$_2$(dppf) demonstrating broadening of the related shift and satellites. Inset: An example of observed peak splitting in Pt(dppf)-silole.

Since it was believed the peak broadening may be due to fluxionality and/or multiple closely related species, experiments were performed at reduced temperature in an attempt to improve resolution between each species (Figure 2-37). The separation between the
two peaks increases as temperature decreases with the exception of the final experiment at -80 °C, which is likely due to decreasing solubility as it approaches its freezing point (CD₂Cl₂, -96 °C). As already mentioned, these NMR experiments were performed on a crude reaction mixture which contained Cu(I), as attempted separations resulted in unrecoverable product or no observable change. To investigate the role of copper(I) cations, experiments were performed in which copper(I) iodide was not added. Because the role of copper for interaction with the alkynyl π-electrons to labilize the terminal hydrogen for deprotonation by the amine, the more Lewis basic triethylamine was utilized in lieu of diisopropylamine to compensate for the absence of copper(I) iodide. Unfortunately, this modified protocol only provided positive results where PtCl₂(dppe) was used, and in the cases of PtCl₂(dppe) and PtCl₂(dppf) very little to no reaction was observed even after one week. This resulted in more narrow peaks than that of experiments performed in the presence of copper(I) iodide (Figure 2-38). This suggested
Figure 2-38. Attempted synthesis of Pt(dppp)-silole using triethylamine instead of diisopropylamine(CuI).

Reaction time was extended on the order of days, however the peaks were narrowed with respect to experiments utilizing copper(I) iodide.

that copper(I) may play a role in the peak broadening as well as resulting in an upfield shift of Pt(dppp)silole relative to products which lack copper(I).

Alternatively, experiments were performed in which copper(I) iodide was added in substantial excess (Figure 2-39). The result was a substantial increase in peak broadening with respect to that of standard reactions containing copper(I) iodide and the triethylamine reactions performed in the absence of copper(I) iodide. This suggests

Figure 2-39. Pt(dppp)-silole with a large excess of copper(I) iodide. Peak broadening was substantially increased with greater splitting in the central peak (inset), suggesting multiple closely related magnetic environments.
that copper(I) plays a role in the formation of multiple magnetic environments. Since copper(I) seemed to elute in small amounts through silica gel plugs, as well as through multiple recrystallization attempts and rinses utilizing a broad array of solvents, it suggested copper(I) was interacting with the formed macromolecule.\textsuperscript{85}

Regardless, preliminary luminescence data was collected in order to observe any photophysical changes in the bulk material. For the Pt(polypyridine)-siloles, a small change in absorption was observed with a substantial change in emission (Figures 2-40 and 2-41). The starting silole had absorption and emission maxima of 368 and 411 nm, respectively. While the emission maxima for Pt(polypyridine)-siloles were redshifted in the order of 511 (-Me\textsubscript{4}phen), 544 (-tbbpy), 550 (-phen), and 588 nm (-bpy) (Figure 2-41). The slight blueshifting of the complexes containing the Me\textsubscript{4}phen and tbbpy ligands with respect to that of phen and bpy is likely due to the inductively donating methyl and \textit{t}-butyl substituents.
Figure 2-40. UV-Vis absorption spectrum of Pt(poly(pyridine))-siloles. $\lambda_{\text{abs}}$ (nm): PtCl$_2$(bipy), 283, 405. PtCl$_2$(tbbpy), 281, 393. PtCl$_2$(phen), 268, 397. PtCl$_2$(Me$_4$phen), 258, 282, 397.

Figure 2-41. Fluorescence emission spectrum of Pt(poly(pyridine))-siloles. $\lambda_{\text{em}}$ (nm): PtCl$_2$(bipy), 560. PtCl$_2$(tbbpy), 546. PtCl$_2$(phen), 546. PtCl$_2$(Me$_4$phen), 513.

For Pt(phosphine)-siloles, there was a substantial change in absorption maxima for Pt(dppp)-silole. There was also a substantial change in emission maxima for all complexes observed, although the distribution was narrow (Figures 2-42 and 2-43). The difference in absorption maxima may be due to twisting of the propylene group, reducing
Figure 2-42. UV-Vis absorption spectrum of Pt(phosphine)-siloles. $\lambda_{\text{abs}}$ (nm): PtCl$_2$(dppp), 332, 408. PtCl$_2$(dppe), 375. PtCl$_2$(dpff), 402.

Figure 2-43. Fluorescence emission spectrum of Pt(phosphine)-siloles. $\lambda_{\text{em}}$ (nm): PtCl$_2$(dppp), 524. PtCl$_2$(dppe), 528. PtCl$_2$(dpff), 529.

the degree of overlap in the phosphine-platinum orbitals, resulting in more monomeric ligand-like behavior of the peripheral phosphine phenyls. The emission maxima were 523 nm for Pt(dppp)-silole and 526 nm for Pt(dppe)-silole and Pt(dpff)-silole, which is still redshifted from that of the starting silole (368 nm). This suggests that the Pt(phosphine)
units have a contribution to the overall structure, but the phosphine ligand is not contributing, at least with respect to the polypyridine ligands.

However, the overall structures have not been entirely characterized. While it is desirable to assume the Pt-silole macrocycle has been successfully synthesized, the characterization data does not exclusively indicate that result. The Pt(tpy)-silole project was never revisited, and the Pt(polypyridine) and Pt(phosphine) studies allowed for two coordination sites on both precursors, resulting in the potential formation of both the desired macrocycles as well as chain polymerized products (Figure 2-44).

![Figure 2-44](image)

**Figure 2-44.** Potentially formed bulk materials. A macrocycle (top) or a chain polymerized fragment (bottom).

While studies indicated that some form of coordination had occurred, they did not conclusively indicate whether the resultant material is macrocyclic or polymeric. The studies which eliminated copper did not conclusively indicate a homogenous environment, and the studies which did not exclude copper but were at reduced temperature indicated temperature dependence independent from that of the influence of copper(I). The final conclusion is that the presence or absence of copper(I), combined
with inconclusive temperature-dependent studies, indicate the potential minimum presence of polymeric materials, although macrocycle materials could still be present.

2.4. Summary and Future Work

A series of platinum(II)-polypyridine and platinum(II)-phosphine complexes were synthesized following literature procedures. In parallel, two siloles were obtained utilizing combined literature procedures. Formation of all compounds was verified by NMR, IR, and in some cases, GC/MS and MS. The synthesized literature compounds underwent reactions in an attempt to form a series of platinum(II)-silole complexes which incorporated either polypyridine or phosphine moieties. Although characterization was challenging due to molecular weight and solubility issues, NMR and IR results indicated that coordination of the platinum(II)-phosphine or platinum(II)-polypyridine complex and the alkyne from the silole compound had occurred. All platinum(II) precursors were not luminescent, while the silole precursors as well as the platinum(II)-silole products fluoresced upon irradiation at 365 nm from a handheld UV lamp in the solid state. It was uncertain as to whether the synthesized compounds were chains, macrocycles, or a mixture. This uncertainty was not elucidated due to characterization, resource, and time constraints. However, the process did reveal a potential pathway for synthesizing a series of macrocycles from precursors which possess terminal alkynyl functional groups.

Future work could include analysis by liquid chromatography/mass spectrometry (LC/MS), in which the mixture could be analyzed to determine the masses of and various products which may be present. Purification could also be possible by coupling the apparatus to a UV-Vis spectrophotometer, as the products were all redshifted with respect to the starting materials in their absorption. Another possibility would be to utilize linkers
which incorporate NMR active nuclei which would provide additional diagnostic resonances.

2.5. Experimental

General

Unless otherwise indicated, all synthetic protocols were performed under an inert atmosphere of argon with flame-dried glassware using standard Schlenk techniques. The solvents, dichloromethane, diethyl ether, ethyl acetate, hexanes, chloroform, tetrahydrofuran, and methanol were purchased from Fischer Chemical or Sigma-Aldrich, and were used as received unless noted below. For air- and moisture-sensitive reactions, tetrahydrofuran and diethyl ether were dried over activated 4 Å sieves over several hours and then freshly distilled from Na/9-fluorenone under argon prior to use. Chloroform-\(d\) and dichloromethane-\(d_2\) were purchased from Cambridge Isotope Labs and dried over activated molecular sieves prior to use. The compounds ethynyltrimethylsilane, 1,5-cyclooctadiene, \(n\)-butyllithium in hexanes (1.6 M), (4-bromophenylethynyl)trimethylsilane, 4-bromo-4′-iodo-1,1′-biphenyl, 2,2′:6′,2″-terpyridine, 2,2′-bipyridine, 4,4′-di-tert-butyl-2,2′-bipyridine, 1,10-phenanthroline, 3,4,7,8-tetramethyl-1,10-phenanthroline, 1,3-bis(diphenylphosphino)propane, and 1,2-bis(diphenylphosphino)ethane were purchased from Sigma-Aldrich and used as received. Phenylacetylene was purchased from GFS Chemicals and used as received. Potassium tetrachloroplatinate was purchased from Pressure Chemical Company and used as received. Copper(I) iodide was purchased from Fisher Laboratory and used as received. Triethylamine (Acros Organics), diisopropylamine (Acros Organics), and \(N,N,N′,N′\)-tetramethylenediamine (Sigma-Aldrich) were dried over potassium hydroxide, distilled, and stored over potassium hydroxide for moisture-sensitive reactions.
Dichlorodimethylsilane was purchased from Sigma-Aldrich, distilled over anhydrous potassium carbonate under argon, and stored under argon prior to use. Lithium metal (pellets, 0.5-1% sodium content) was purchased from Sigma-Aldrich and stored in an inert atmosphere drybox, where it was weighed into vials for individual reactions. Zinc(II) chloride for air/moisture-sensitive reactions was purchased from Sigma-Aldrich and was flame-dried under vacuum until completely melted, then introduced to the glovebox, where it was ground with a mortar and stored. For individual reactions the material was weighed in the glovebox into a suitable container. Naphthalene (Fisher) was recrystallized from ethanol. Silica gel (Premium Rf, 200-400 mesh, 60 Å porosity) was purchased from Sorbent Technologies, Inc. Dichloromethane for optical spectra experiments (spectrophotometric grade) was purchased from Sigma-Aldrich and used as received.

Many precursor compounds were synthesized from standard literature procedures, including 1,2-bis(diphenylphosphino)ethane,\textsuperscript{78} 1,3-Bis(diphenylphosphino)propane,\textsuperscript{78} 1,1’-bis(diphenylphosphino)ferrocene,\textsuperscript{86} dichlorobis(triphenylphosphine)palladium(II),\textsuperscript{87} bis(phenylethynyl)dimethylsilane,\textsuperscript{38} and ZnCl\textsubscript{2}(TMEDA).\textsuperscript{48}

NMR spectra were recorded on a Bruker ARX-500 MHz or Agilent-600 MHz instrument at ambient temperature unless otherwise noted. Spectroscopic data recorded at 500 MHz for \textsuperscript{1}H, 126 MHz for \textsuperscript{13}C, 202 MHz for \textsuperscript{31}P, and 99 MHz for \textsuperscript{29}Si. Spectroscopic data were collected on the Agilent-600 MHz instrument at 600 MHz for \textsuperscript{1}H, 151 MHz for \textsuperscript{13}C, 243 MHz for \textsuperscript{31}P, and 119 MHz for \textsuperscript{29}Si. Chloroform-\textit{d} or dichloromethane-\textit{d}_\textsubscript{2} were used as the NMR solvents unless otherwise indicated, and all \textsuperscript{1}H and \textsuperscript{13}C spectra were referenced to residual protic solvent (for Chloroform-\textit{d}: 7.26 ppm for \textsuperscript{1}H and 77.36 ppm
for $^{13}$C; for dichloromethane-$d_2$: 5.33 ppm for $^1$H and 54.24 ppm for $^{13}$C). $^{29}$Si{$^1$H} spectra were externally referenced to tetramethylsilane (0 ppm). $^{31}$P{$^1$H} NMR spectra were referenced to external phosphoric acid (0 ppm). Chemical shifts are reported in parts per million (ppm), with coupling constants recorded in Hertz (Hz). Gas chromatography experiments were performed using a Shimadzu GC-14A gas chromatograph; GC-MS analyses were performed on a Hewlett Packard Model 5988A GC-MS instrument. Melting points were determined on a Mel-Temp capillary melting point apparatus and are uncorrected. UV-visible spectroscopic data were collected on a Cary (Varian) 50 Bio UV-visible spectrometer. Fluorescence spectra were recorded on a Cary (Varian) Eclipse fluorescence spectrometer, and were measured using the $\lambda_{\text{max}}$ value for each compound as determined by the absorption spectra. Quartz cuvettes were used for optical spectra data collection. Dichloromethane for optical spectra experiments (spectrophotometric grade) was purchased from Sigma-Aldrich and used as received. Infrared spectroscopic data were collected on a Thermo Scientific Nicolet 6700 equipped with a Smart OMNI-Sampler Germanium ATR Sampling Accessory.

**Synthesis of 1,1-dimethyl-2,5-bis[4-(trimethylsilylethynyl)-phenyl]-3,4-diphenylsilole (2-6)$^{39}$**

![Chemical Structure](image)

Lithium (pellets, 0.5-1% sodium, 0.329 g, 47.3 mmol) and naphthalene (6.62 g, 51.6 mmol) were added to a 3-neck round-bottom flask (250 mL) containing THF (72 mL). To a 100 mL pressure-equilibrating addition funnel (100 mL),
bis(phenylethynyl)dimethylsilane (3.0 g, 11.52 mmol) was added and diluted with THF (48 mL). The apparatus was then placed in a sonic bath for 2 h or until the lithium was fully dissolved. The resulting lithium naphthalenide solution should remain dark green (almost black) throughout this process. If the solution became brown or red, it meant the solution had been exposed to too much moisture, and should be scrapped prior to addition of bis(phenylethynyl)dimethylsilane. Addition of the silane was performed dropwise at room temperature to the rapidly stirring lithium naphthalenide solution over a minimum of 15 minutes. Once addition was complete, the solution was stirred for 20 minutes and then lowered into an ice bath to reduce the internal temperature to 0 °C. ZnCl\(_2\)(TMEDA) (12.57 g, 49.8 mmol) was then added as a solid followed immediately by THF (70 mL). The reaction mixture was then removed from the ice bath and allowed to stir for 1.5 h. (4-bromophenylethynyl)trimethylsilane (6.08 g, 24.00 mmol) and Pd(PPh\(_3\))\(_2\)Cl\(_2\) (0.364 g, 0.518 mmol) were simultaneously added to the reaction mixture as solids. Upon addition, the reaction mixture remained dark green. The reaction mixture was then refluxed overnight. The reaction mixture was then quenched with HCl (20 mL, 1 M) and extracted with DCM. The combined organic layers were washed with brine and water then dried over anhydrous magnesium sulfate. After removal of the solvent by rotoevaporation, the residue was purified by silica gel column chromatography, using hexane as an eluent, with increasing polarity by addition of diethyl ether in 1% increments. 1,1-dimethyl-2,5-bis[4-(trimethylsilylethynyl)-phenyl]-3,4-diphenylsilole was isolated as a yellow solid, 4.69 g, 67% yield. IR, \(\nu\) (cm\(^{-1}\)): 2156 (C≡C). \(^{1}\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) \(^{1}\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.24 – 7.21 (m, \(J = 6.3, 2.0\) Hz, 4H), 7.04 – 6.96 (m, 6H), 6.86 – 6.81 (m, 4H), 6.78 – 6.74 (m, 4H), 0.44 (s, 6H), 0.22 (s, 18H). \(^{13}\)C\{\(^{1}\)H\} NMR (126 MHz,
CDCl₃): δ 154.7, 141.8, 140.4, 138.4, 131.8, 130.0, 128.8, 127.6, 126.6, 120.1, 105.5, 94.3, 0.1, -3.8. These data corresponded to that of previously published literature values.⁴⁰,⁴¹ Appendix I: 1-2.

**Synthesis of 4-bromo-4’-[2-(trimethylsilyl)ethynyl]-1,1’-biphenyl (2-13)⁵²**

![2-13](image)

To a degassed solution of 4-bromo-4’-iodo-1,1’-biphenyl (5, 13.93 mmol) TEA (48.5 ml, 348 mmol) was added ethynyltrimethylsilane (1.450 g, 14.76 mmol), Pd(PPh₃)₂Cl₂ (0.293 g, 0.418 mmol), and CuI (0.159 g, 0.836 mmol) were then added to the 3-neck round-bottom flask (100 mL). Addition of the ethynyltrimethylsilane resulted in an immediate color change to dark brown. The reaction was then stirred at room temperature overnight. After removal of the solvent by rotoevaporation, the solid residue was dissolved in CH₂Cl₂ and purified by silica gel column chromatography using hexane as the eluent and the product was obtained as a white solid, 0.478 g, 47% yield. ¹H NMR (500 MHz, CD₂Cl₂): δ 7.59 – 7.55 (m, 2H), 7.52 (s, 4H), 7.5 – 7.44 (m, 2H), 0.28 (s, 9H). ¹³C{¹H} NMR (126 MHz, CD₂Cl₂): δ 140.2, 139.5, 132.8, 132.4, 129.0, 127.1, 122.9, 122.3, 105.0, 95.6, 0.1. These data were in agreement with known literature values.⁶⁵,⁸⁸ Appendix I: 3-4.
Synthesis of 1,1-dimethyl-2,5-bis[4-(trimethylsilylethynyl)-phenyl]-3,4-diphenylsilole (2-14)

This procedure was reproduced following the protocol for 1,1-dimethyl-2,5-bis[4-(trimethylsilylethynyl)-phenyl]-3,4-diphenylsilole, only instead of (4-bromophenylethynyl)trimethylsilane, ((4'-bromo-[1,1'-biphenyl]-4-yl)ethynyl)trimethylsilane was added. Lithium (pellets, 0.5-1% sodium, 0.172 g, 24.81 mmol) and naphthalene (6.62 g, 51.6 mmol) were added to a 3-neck round-bottom flask (150 mL) containing THF (38 mL). To a pressure-equilibrating addition funnel (50 mL), bis(phenylethynyl)dimethylsilane (1.572 g, 6.04 mmol) was added and diluted with THF (25 mL). The apparatus was then placed in a sonic bath for 2 h or until the lithium was fully dissolved. The resulting lithium naphthalenide solution should remain dark green (almost black) throughout this process. If the solution became brown or red, it meant the solution had been exposed to too much moisture, and should be scrapped prior to addition of bis(phenylethynyl)dimethylsilane. Addition of the silane was performed dropwise at room temperature to the rapidly stirring lithium naphthalenide solution over a minimum of 15 minutes. Once addition was complete, the solution was stirred for 20 minutes and then lowered into an ice bath to reduce the internal temperature to 0 °C. ZnCl₂(TMEDA) (6.58 g, 26.1 mmol) was then added as a solid followed immediately by THF (45 mL). The reaction mixture was then removed from the ice bath and allowed to stir for 1.5 h. 4-bromo-4'-[2-(trimethylsilyl)ethynyl]-1,1'-biphenyl (4.14 g, 12.57 mmol)
and Pd(PPh$_3$)$_2$Cl$_2$ (0.191 g, 0.272 mmol) were simultaneously added to the reaction mixture as solids. Upon addition, the reaction mixture remained dark green. The reaction mixture was then refluxed overnight. The reaction mixture was then quenched with HCl (10 mL, 1 M) and extracted with DCM. The combined organic layers were washed with brine and water then dried over anhydrous magnesium sulfate. After removal of the solvent by rotoevaporation, the residue was purified by silica gel column chromatography, using hexane as an eluent, with increasing polarity by addition of diethyl ether in 1% increments. 1,1-dimethyl-2,5-bis[4-((trimethylsilyl)ethyl)phenyl]-3,4-diphenylsilole was isolated as a yellow solid. 2.52 g, 55% yield. IR, $\nu$ (cm$^{-1}$): 2156 (C≡C). $^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta$ 7.59 – 7.57 (m, 2H), 7.54 – 7.49 (m, 4H), 7.48 – 7.44 (m, 6H), 7.42 – 7.37 (m, 4H), 7.31 – 7.25 (m, 6H), 6.98 – 6.92 (m, 4H), 0.44 (s, 6H), 0.19 (s, 18H). $^{13}$C-$^1$H NMR (126 MHz, CD$_2$Cl$_2$): $\delta$ 154.9, 141.8, 141.1, 141.1, 140.6, 140.4, 139.9, 139.5, 137.4, 132.8, 132.8, 132.7, 132.7, 132.5, 132.2, 132.0, 131.2, 130.4, 130.0, 129.9, 129.7, 129.4, 129.3, 129.2, 128.9, 128.9, 128.7, 128.2, 128.0, 127.9, 127.7, 127.4, 127.3, 127.3, 127.2, 127.2, 127.1, 127.1, 127.1, 126.9, 126.8, 123.6, 123.0, 122.9, 122.3, 105.3, 95.6, 95.3, 90.7, 89.5, 0.1, -3.6. These values were comparable to that of previously published literature values for similar complexes.$^{40,41}$

Appendix I: 5-6.

**Synthesis of 2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole (2-7)$^{41}$**

![2-7](image)

1,1-dimethyl-3,4-diphenyl-2,5-bis(4-((trimethylsilyl)ethyl)phenyl)-1H-silole (6.0 g, 9.88 mmol) was dissolved in 250 mL THF:MeOH (2:3) in a 500 mL 3-neck round-bottom flask. Potassium carbonate was then added (1.71 g, 12.36 mmol) and the reaction
mixture was stirred at room temperature overnight. The solution was initially pale yellow, but turned dark orange after about an hour of stirring as the potassium carbonate dissolved. After stirring overnight, the solution had turned darker orange, or brown. The reaction mixture was then neutralized by 3 M HCl solution, and the solution immediately turned cloudy. The organic solvents were removed by rotoevaporation and the reaction mixture was extracted three times using DCM (50 mL). The resulting solid appeared yellow/brown, which was purified by silica gel column chromatography, using hexane as the eluent, with increasing polarity by addition of diethyl ether in 1% increments. 2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole was isolated as a yellow solid, 4.48 g, 98% yield. IR, $\nu$ (cm$^{-1}$): 3291 (≡C-H), 2106 (C≡C).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.25 – 7.21 (m, 4H), 7.04 – 6.97 (m, 6H), 6.88 – 6.84 (m, 4H), 6.79 – 6.75 (m, 4H), 3.03 (s, 2H), 0.46 (s, 6H).

$^{13}$C{$^1$H} NMR (126 MHz, CDCl$_3$): $\delta$ 154.8, 141.7, 140.7, 138.4, 132.0, 130.0, 128.9, 127.7, 127.0, 119.2, 84.0, 78.3, -3.8. Absorption and emission (10 μM, DCM): $\lambda_{\text{abs}}$ (nm) = 263, 369. $\lambda_{\text{em}}$ (nm) = 412. These data were in agreement with known literature values.$^{41}$ Appendix I: 7-8.

**Synthesis of dichloro(1,5-cyclooctadiene)platinum(II) (2-16)$^{56}$**

Potassium tetrachloroplatinate (5.0 g, 12.05 mmol) was dissolved in glacial acetic acid (200 mL, 40%) in a round-bottom flask (500 mL) equipped with a reflux condenser forming a burgundy solution. 1,5-Cyclooctadiene (4.91 mL, 40.0 mmol) were then added. The reaction mixture was refluxed while stirring rapidly for 1 h, during the course of which the reaction mixture became pale yellow. The reaction mixture was then allowed
to return to room temperature and stirred overnight. Off-white needle-like crystals were collected by vacuum filtration and washed with water, ethanol, and diethyl ether (25 mL each). This process should remove the unreacted starting materials. The final product was then placed under vacuum for 1 h at 100 °C then allowed to dry in an oven overnight. As the reaction was nearly quantitative, recrystallization was not necessary to remove any impurities. Dichloro(1,5-cyclooctadiene)platinum(II) was isolated in high yield, 4.33 g, 96% yield. Mp: 260 °C (lit. 250-280 °C). \(^{56}\) \(^{1}\)H NMR (500 MHz, CDCl\(_3\)): \(\delta 5.75 \text{–} 5.51 \text{ (m, 4H, } J_{H,Pt} = 67 \text{ Hz}), 2.82 \text{ –} 2.64 \text{ (m, 4H), 2.37 \text{ –} 2.19 \text{ (m, 4H). These were in agreement to known literature values.}^{56,66}\) Appendix I: 9.

**Synthesis of chloro(2,2′:6′,2″-terpyridine)platinum(II) chloride dehydrate (2-17)**

To a suspension of PtCl\(_2\)(COD) (0.500 g, 1.336 mmol) in water (50 mL), 2,2′:6′,2″-terpyridine (0.315 g, 1.350 mmol) was added. The reaction mixture was stirred overnight at 50°C for 1 h. After 15 min all of the solid dissolved and the mixture became a transparent red/orange solution. After cooling to room temperature, the product was collected by vacuum filtration, washed thoroughly with diethyl ether (25 mL), and dried by rotoevaporation providing a red/orange solid product, 0.564 g, 91% yield. \(^{1}\)H NMR (500 MHz, CDCl\(_3\)): \(\delta 8.75 \text{ –} 8.72 \text{ (m, 2H), 8.67 \text{ –} 8.64 \text{ (m, 2H), 8.48 (d, } J = 7.8 \text{ Hz, 2H), 7.99 (t, } J = 7.8 \text{ Hz, 1H), 7.92 \text{ –} 7.86 \text{ (m, 2H), 7.39 \text{ –} 7.35 \text{ (m, 2H). HRMS (EI): calcd. for C}_{15}\text{H}_{11}\text{ClN}_3\text{Pt: 463.02893; found 463.0281. Appendix I: 10.}^{89}\)

Appendix I: 10.
Attempted synthesis of [Pt(tpy)-(1,1-dimethyl-2,5-bis[4-(trimethylsilylethynyl)phenyl]-3,4-diphenylsilole)]Cl₂ (Method A) (2-18)\(^9\)

\[
\text{[PtCl(tpy)]Cl (0.082 g, 0.165 mmol), and 1,1-dimethyl-3,4-diphenyl-2,5-bis(4-((trimethylsilyl)ethynyl)phenyl)-1H-silole, CuI (0.01569 g, 0.082 mmol), and KF (0.00958 g, 0.165 mmol) were dissolved in DCM:MeOH (30 mL, 2:1) in a round-bottom flask (100 mL) equipped with a reflux condenser and refluxed for 24 h. The solution was initially red/orange but turned burgundy overnight. The product was collected by vacuum filtration.} \quad 1^1\text{H NMR (500 MHz, CDCl}_3\): } \delta 7.27 – 7.24 (m, \text{J} = 7.0, 5.2 \text{ Hz}), 7.05 – 6.99 (m), 6.89 – 6.85 (m), 6.80 – 6.76 (m), 3.04 (s), 2.18 (s), 1.48 (s), 0.50 – 0.43 (m), 0.22 (s), 0.11 – 0.04 (m).

Attempted synthesis of [Pt(tpy)-(1,1-dimethyl-2,5-bis[4-(trimethylsilylethynyl)phenyl]-3,4-diphenylsilole)]Cl₂ (Method B) (2-18)\(^9\)

\[
\text{[PtCl(tpy)]Cl (0.082 g, 0.165 mmol), and 1,1-dimethyl-3,4-diphenyl-2,5-bis(4-((trimethylsilyl)ethynyl)phenyl)-1H-silole, CuI (0.01569 g, 0.082 mmol), and TBAF (0.162 mL, 0.162 mmol) were dissolved in DCM:MeOH (25 mL, 3:2) in a round-bottom flask (50 mL) equipped with a reflux condenser and refluxed for 24 h. The solution was initially red/orange but turned burgundy overnight. The product was collected by vacuum filtration.}
\]
filtration. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 2.65 (s), 1.78 (s), 0.79 (t, \(J = 51.2\) Hz), 0.29 (s).

Appendix I: 12.

**Attempted synthesis of [Pt(tpy)-(1,1-dimethyl-2,5-bis[4-(trimethylsilylethynyl)-phenyl]-3,4-diphenylsilole)]Cl\(_2\) (Method C) (2-18)\(^{91,92}\)**

\[
\text{[PtCl(tpy)]Cl (0.010 g, 0.020 mmol), and 2,5-bis(4-ethynlphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole (4.63 mg, 10.01 \(\mu\)mol), and CuI (1.907 \(\mu\)g, 0.0100 \(\mu\)mol) were dissolved in DCM (10 mL) and diisopropylamine (2.5 mL, 10.01 \(\mu\)mol) in a round-bottom flask (25 mL). The solution was stirred overnight at room temperature. The solution was initially red/orange but turned burgundy overnight. The product was collected by vacuum filtration. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.23 – 6.67 (m), 5.11 (s), 3.47 (s), 2.45 – 1.85 (m), 1.77 – 0.62 (m), 0.42 (s), 0.30 – -0.16 (m). Appendix I: 13.}

**Synthesis of (2,2'-bipyridine)dichloroplatinum(II) (2-19)\(^{63,76,77}\)**

\[
\text{K}_2\text{PtCl}_4 (0.250 g, 0.602 mmol) and 2,2'-bipyridine (0.099 g, 0.632 mmol) were dissolved in HCl (16 mL, 0.35 M) in a round-bottom flask (50 mL) equipped with a reflux condenser and refluxed for 2 h. The resulting yellow precipitate was collected by vacuum filtration, washed with water, methanol, and diethyl ether, (25 mL each) and dried for 24 h at room temperature under vacuum. The yellow product was obtained in high yield, 0.247 g, 97%. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 9.49 (td, \(J = 5.8, 2.2\) Hz, 2H), 8.58 (d, \(J =\) }
8.0 Hz, 2H), 8.43 – 8.38 (m, 2H), 7.86 – 7.81 (m, 2H). Absorption (DCM): \( \lambda_{\text{abs}} (\text{nm}) = 282, 324, \) and 402. Appendix I: 14.

**Synthesis of (4,4'-di-tert-butyl-2,2'-bipyridine)dichloroplatinum(II) (2-20)**

\[
\text{K}_2\text{PtCl}_4 \text{ (0.250 g, 0.602 mmol)} \text{ and 4,4'-di-tert-butyl-2,2'-bipyridine (0.170 g, 0.632 mmol) were dissolved in HCl (16 mL, 0.35 M) in a round-bottom flask (50 mL) equipped with a reflux condenser and refluxed for 2 h. The yellow product was collected by vacuum filtration, washed with water, methanol, and diethyl ether (25 mL each) and dried for 24 h at room temperature under vacuum. The yield of the product obtained was, 0.312 g, 97\%.} 
\]

\[\text{^1H NMR (500 MHz, CDCl}_3\text{: } \delta 9.55 – 9.52 \text{ (m, 2H), 7.89 – 7.85 (m, 2H), 7.53 – 7.47 (m, 2H), 1.46 (s, 18H). Absorption (DCM): } \lambda_{\text{abs}} (\text{nm}) = 282, 323, \text{ and 396. Appendix I: 15.} \]

**Synthesis of (1,10-phenanthroline)dichloroplatinum(II) (2-21)**

\[
\text{K}_2\text{PtCl}_4 \text{ (0.250 g, 0.602 mmol) and 1,10-phenanthroline (0.109 g, 0.602 mmol) were dissolved in HCl (16 mL, 0.35 M) in a round-bottom flask (50 mL) equipped with a reflux condenser and refluxed for 2 h. The yellow product was collected by vacuum filtration, washed with water, methanol, and diethyl ether (25 mL each) and dried for 24 h at room temperature under vacuum. The product was obtained in high yield, 0.284 g.} 
\]
94%. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 9.71 – 9.69 (m, 1H), 9.06 – 9.03 (m, 2H), 8.31 – 8.28 (m, 2H), 8.20 – 8.16 (m, 2H). Absorption (DCM): $\lambda_{abs}$ (nm) = 258, 278, 335, and 401. Appendix I: 16.

**Synthesis of (3,4,7,8-tetramethyl-1,10-phenanthroline)dichloroplatinum(II) (2-22)$^{63,76,77}$**

![2-22](image)

K$_2$PtCl$_4$ (0.250 g, 0.602 mmol) and 3,4,7,8-tetramethyl-1,10-phenanthroline (0.149 g, 0.632 mmol) were dissolved in HCl (16 mL, 0.35 M) in a round-bottom flask (50 mL) equipped with a reflux condenser and refluxed for 2 h. The yellow product was collected by vacuum filtration, washed with water, methanol, and diethyl ether (10 mL each), and dried for 24 h at room temperature under vacuum. The product was isolate in high yield, 0.258 g, 96%. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 9.65 (d, $J = 4.2$ Hz, 2H), 8.28 (s, 2H), 2.96 (s, 6H), 2.73 (s, 6H). Absorption (DCM): $\lambda_{abs}$ (nm) = 257, 283, 340, and 388. Appendix I: 17.

**Synthesis of [1,3-bis(diphenylphosphino)propane]dichloroplatinum(II) (2-23)$^{78}$**

![2-23](image)

PtCl$_2$(COD) (0.500 g, 1.336 mmol) and 1,3-bis(diphenylphosphino)propane (0.606 g, 1.470 mmol) were dissolved in DCM (30 mL) in a round-bottom flask (50 mL) equipped with a reflux condenser and refluxed for 2 h. The reaction mixture was initially a slurry, but over the course of an hour the starting materials dissolved forming a clear solution.
The reaction mixture was stirred at room temperature for 48 h. The reaction mixture was then reduced to the saturation point by rotary evaporation, diethyl ether (50 mL) was added to the mixture to obtain a white solid. The white solid was then collected by filtration and rinsed additional diethyl ether (50 mL). The product was obtained as a white solid, 0.775 g, 85%. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.78 (d, $J = 7.2$ Hz), 7.43 (m), 1.97 (d, $J = 77.3$ Hz), 1.25 (s). $^{31}$P$^1$H NMR (202 MHz, CDCl$_3$): $\delta$ -5.4 (d, $^{1}J_{Pt-P}$ = 3408 Hz). These values corresponded to that of previously published literature. Absorption (DCM): $\lambda_{max}$ (nm) = N/A. Appendix I: 18-19.

**Synthesis of [1,2-bis(diphenylphosphino)ethane]dichloroplatinum(II) (2-24)**

[Diagram of 2-24]

PtCl$_2$(COD) (0.500 g, 1.336 mmol) and 1,2-bis(diphenylphosphino)ethane (0.586 g, 1.470 mmol) were dissolved in DCM (30 mL) in a round-bottom flask (50 mL) equipped with a reflux condenser and refluxed for 2 h. The reaction mixture was initially a slurry, but over the course of an hour the starting materials dissolved forming a clear solution. The reaction mixture was stirred at room temperature for 48 h. The reaction mixture was then reduced to the saturation point by rotary evaporation, diethyl ether (50 mL) was added to the mixture to obtain a white solid. The white solid was then collected by filtration and rinsed with additional diethyl ether. The product was obtained as a white solid, 0.826 g, 93%. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.92 – 7.83 (m), 7.58 – 7.44 (m), 2.40 – 2.30 (m). $^{31}$P$^1$H NMR (202 MHz, CDCl$_3$): $\delta$ 39.4 (d, $^{1}J_{Pt-P}$ = 3620 Hz). These
values corresponded to that of previously published literature.\textsuperscript{22,81} Absorption (DCM): 
\[ \lambda_{\text{max}} \text{ (nm)} = \text{N/A}. \]

Appendix I: 20-21.

**Synthesis of [1,1'-bis(diphenylphosphino)ferrocene]dichloroplatinum(II) (2-25)\textsuperscript{86}**

![Diagram of 2-25](image)

PtCl\(_2\)(COD) (0.500 g, 1.336 mmol) and 1,1'-bis(diphenylphosphino)ferrocene (0.586 g, 1.470 mmol) were dissolved in DCM (30 mL) in a round-bottom flask (50 mL) equipped with a reflux condenser and refluxed for 2 h. The reaction mixture was initially a slurry, but over the course of an hour the starting materials dissolved forming a dark orange solution. The reaction mixture was stirred at room temperature for 48 h. The reaction mixture was then reduced to the saturation point by rotary evaporation, diethyl ether (25 mL) was added to the mixture to obtain a yellow-orange solid. The product was then collected by filtration and rinsed with additional diethyl ether (25 mL) to obtain a yellow-orange solid, 0.833 g, 76% yield. \( ^1 \text{H NMR} \) (500 MHz, CDCl\(_3\)): \( \delta \) 7.88 (m), 7.47 (m), 7.38 (t, \( J = 6.8 \text{ Hz} \)), 4.37 (s), 4.20 (s) \( ^{31} \text{P}\{^1 \text{H}\} \) NMR (202 MHz, CDCl\(_3\)): \( \delta \) 13.2 (d, \( J_{\text{Pt-P}} = 3766 \text{ Hz} \)). These values corresponded to that of previously published literature.\textsuperscript{22,81,86} Absorption (DCM): \( \lambda_{\text{max}} \text{ (nm)} = \text{N/A}. \) Appendix I: 22-23.
Synthesis of Pt(bpy)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole) (2-26)

![Diagram of Pt(bpy)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole)](image)

PtCl₂(bpy) (20 mg, 0.047 mmol), 2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole (21.92 mg, 0.047 mmol), and copper(I) iodide (0.090 mg, 0.474 µmol) were dissolved in DCM (16 mL) in a scintillation vial (20 mL) and diisopropylamine (4 mL, 0.047 mmol) was then added. The yellow reaction mixture turned orange as it stirred overnight. The product was collected by rotary evaporation as a crude yellow solid. 0.065 g, 84% yield. IR, ν (cm⁻¹): 2108 (C≡C) ¹H NMR (500 MHz, CD₂Cl₂): δ 8.18 – 7.10 (m, 68H), 0.38 – 0.36 (m, 12H). Absorption and emission (DCM): λₚₐₛₑₚ (nm) = 283, 405. λₑₘᵦₑₜ (nm) = 560. Appendix I: 24.

Synthesis of Pt(tbbpy)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole) (2-27)

![Diagram of Pt(tbbpy)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole)](image)

PtCl₂(tbbpy) (20 mg, 0.037 mmol), 2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole (20 mg, 0.037 mmol), and copper(I) iodide (0.71 mg, 0.374 µmol) were dissolved in DCM (16 mL) in a scintillation vial (20 mL) and diisopropylamine (4 mL,
0.047 mmol) was then added. The yellow reaction mixture turned orange as it stirred overnight. The product was collected by rotary evaporation as a crude yellow solid. 0.08 g, 98%. IR, $\nu$ (cm$^{-1}$): 2103 (C≡C). $^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta$ 7.96 (d, $J = 2.2$ Hz), 7.54 – 7.49 (m), 7.28 – 7.26 (m), 7.18 – 7.14 (m), 6.99 – 6.90 (m), 6.80 – 6.76 (m), 6.71 – 6.67 (m), 1.46 – 1.29 (m), 0.38 (s). Absorption and emission (DCM): $\lambda_{\text{abs}}$ (nm) = 281, 393. $\lambda_{\text{em}}$ (nm) = 546. Appendix I: 25.

**Synthesis of Pt(phen)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole) (2-28)**

PtCl$_2$(phen) (20 mg, 0.045 mmol), 2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole (20.74 mg, 0.045 mmol), and copper(I) iodide (0.085 mg, 0.448 µmol) were dissolved in DCM (16 mL) in a scintillation vial (20 mL) and diisopropylamine (4 mL, 0.047 mmol) was then added. The yellow reaction mixture turned orange as it stirred overnight. The product was collected by rotary evaporation as a crude yellow solid. 0.071 g, 95%. IR, $\nu$ (cm$^{-1}$): 2105 (C≡C). $^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta$ 8.12 – 6.79 (m), 0.53 – 0.39 (m). Absorption and emission (DCM): $\lambda_{\text{abs}}$ (nm) = 268, 397. $\lambda_{\text{em}}$ (nm) = 546. Appendix I: 26.
Synthesis of Pt(Me₄phen)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole) (2-29)

PtCl₂(bpy) (20 mg, 0.040 mmol), 2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole (18.42 mg, 0.040 mmol), and copper(I) iodide (0.076 mg, 0.398 µmol) were dissolved in DCM (16 mL) in a scintillation vial (20 mL) and diisopropylamine (4 mL, 0.047 mmol) was then added. The yellow reaction mixture turned orange as it stirred overnight. The product was collected by rotary evaporation as a crude yellow solid. 0.069 g, 97%. IR, ν (cm⁻¹): 2103 (C≡C). ¹H NMR (500 MHz, CD₂Cl₂): δ 8.02 – 7.90 (m, 20H), 7.82 – 7.76 (m, 6H), 7.74 – 7.69 (m, 6H), 7.61 – 7.53 (m, 21H), 7.48 (ddtd, J = 6.9, 5.4, 4.3, 1.9 Hz, 14H), 7.43 – 7.31 (m, 9H), 7.30 – 7.22 (m, 45H), 7.11 – 7.02 (m, 54H), 6.94 – 6.89 (m, 43H), 6.87 – 6.81 (m, 39H), 2.63 (s, 12H), 2.54 (s, 12H), 0.40 (s, 12H).

Absorption and emission (DCM): λₚₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑᵉ (nm) = 258, 282, 397. λₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑᵉ (nm) = 513. Appendix I: 27.
Synthesis of Pt(dppp)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole) (2-30)

PtCl₂(dppp) (20 mg, 0.029 mmol), 2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole (13.64 mg, 0.029 mmol), and copper(I) iodide (0.056 mg, 0.295 µmol) were dissolved in DCM (16 mL) in a scintillation vial (20 mL) and diisopropylamine (4 mL, 0.047 mmol) was then. The reaction mixture was stirred overnight at room temperature. The product was collected by rotary evaporation as a crude yellow solid. 0.057g, 91%.

IR, ν (cm⁻¹): 2112 (C≡C). ¹H NMR (300 MHz, CDCl₃): δ 7.79 – 7.56 (m), 6.94 (m), 6.79 (t, J = 8.2 Hz), 6.67 (m), 6.51 (t, J = 7.7 Hz), 6.43 – 6.31 (m), 5.52 (s), 5.26 (d, J = 0.8 Hz), 3.56 (m), 2.74 (m, J = 7.2 Hz), 1.38 (t, J = 7.2 Hz), 1.13 (q, J = 7.5 Hz). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ -9.3 (s, ¹J_P,P = 2409 Hz). Absorption and emission (DCM): λₕₐₑₛ (nm) = 332, 408. λₑₘₜₐₖ (nm) = 524. Appendix I: 28-29.
Synthesis of Pt(dppe)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole)

(2-31)

PtCl$_2$(dppe) (20 mg, 0.030 mmol), 2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole (13.93 mg, 0.030 mmol), and copper(I) iodide (0.057 mg, 0.301 µmol) were dissolved in DCM (16 mL) in a scintillation vial (20 mL) and diisopropylamine (4 mL, 0.047 mmol) was then added. The reaction mixture was then stirred overnight at room temperature. The product was collected by rotary evaporation as a crude yellow solid. 0.061 g, 96% yield). IR, ν (cm$^{-1}$): 2105 (C≡C). $^1$H NMR (500 MHz, CDCl$_3$): δ 7.94 – 7.75 (m), 7.60 – 7.32 (m), 7.26 – 7.20 (m), 7.00 (m), 6.90 – 6.81 (m), 6.80 – 6.70 (m), 6.67 (d, $J = 8.1$ Hz), 4.36 (m), 3.80 – 3.65 (m), 3.32 (t, $J = 25.5$ Hz), 3.02 (d, $J = 8.1$ Hz), 2.48 (m), 2.32 – 2.21 (m), 2.16 (t, $J = 14.7$ Hz), 1.93 – 1.78 (m), 1.42 (t, $J = 18.5$ Hz), 1.30 – 1.16 (m), 0.86 (m), 0.51 – 0.33 (m). $^{31}$P{$^1$H} NMR (202 MHz, CDCl$_3$): δ 46.2 (s, $^1$J$_{PP}$ = 2283 Hz). Absorption and emission (DCM): $\lambda_{abs}$ (nm) = 375. $\lambda_{em}$ (nm) = 528. Appendix I: 30-31.
Synthesis of Pt(dppf)-(2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole)

PtCl₂(dppe) (20 mg, 0.024 mmol), 2,5-bis(4-ethynylphenyl)-1,1-dimethyl-3,4-diphenyl-1H-silole (11.28 mg, 0.024 mmol), and copper(I) iodide (0.046 mg, 0.244 µmol) were dissolved in DCM (16 mL) in a scintillation vial (20 mL) and diisopropylamine (4 mL, 0.047 mmol) was then added. The reaction mixture was stirred overnight at room temperature. The product was collected by rotary evaporation as a crude yellow solid. 0.055 g, 93%. IR, ν (cm⁻¹): 2112 (C≡C). H NMR (500 MHz, CD₂Cl₂) δ 7.88 (d, J = 76.5 Hz), 7.59 – 7.20 (m), 7.02 (d, J = 7.2 Hz), 6.91 – 6.67 (m), 6.64 – 6.39 (m), 4.42 – 4.10 (m), 3.32 (s), 1.40 (d, J = 5.5 Hz), 1.25 (m), 0.51 – 0.23 (m). P{¹H} (202 MHz, CDCl₃): δ 14.3 (s, Jₚₚ = 2371 Hz). Absorption and emission (DCM): λₐₛₚ (nm) = 402. λₑₜₘ (nm) = 529. Appendix I: 32-33.
2.6. References

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Chapter 3

2,7-Disubstituted Silafluorenes

3.1. Introduction

Conjugated π-electron systems containing silicon have received substantial attention for their use as components for a wide variety of optical and electronic applications such as organic light emitting diodes (OLEDs), photovoltaic devices, field-effect transistors (FETs), and as chemical and biological sensors. The unique optoelectronic properties found in these silicon systems arises from the σ*−π* conjugation between the σ* orbital of the two exocyclic groups at the silicon center and π* orbital of the butadiene unit of the ring resulting in a low energy LUMO level. Silafluorenes are related to siloles (discussed in greater detail in Chapter 2) in that they both possess the same silicon butadiene core (Figure 3-1).

![Diagram of a) cyclopentadiene, b) silole, c) fluorene, and d) silafluorene.](image)

**Figure 3-1.** Generalized structures of a) cyclopentadiene, b) silole, c) fluorene, and d) silafluorene. The "R" substituents are enumerated as they are typically referred.

Incorporation of conjugated organic moieties on the ring allows for further electronic tuning. Silafluorenes represent a relatively new class of photoluminescent molecules which demonstrate smaller band gaps, deep blue emission, high electron affinity, improved thermal stability, and greater quantum yields than that of their fluorene and carbazole analogs. Silafluorenes are analogs of 9,9-dialkylfluorenes, which have
been of interest due to their deep blue emission and their ability to be incorporated into polysilafluorenes.\textsuperscript{11,24,26,27,30–37}

While theoretical studies have been performed investigating silafluorenes,\textsuperscript{20,38} they have not focused on the core as previous studies of siloles have, although they can used to explain silafluorenes. In siloles, the HOMO and LUMO are about 0.4 eV and 1.2 eV lower, respectively, than that of cp.\textsuperscript{39} The greater difference in their LUMOs can be explained by the orbital interaction of the silole ring in which the low-lying LUMO of the silole arises from a mixture of the energetically comparable $\sigma^*$-orbital of the silylene and the $\pi^*$-orbital of the butadiene unit.\textsuperscript{39} This $\sigma^*$-$\pi^*$ conjugation occurs effectively as the orbitals are in phase and in a fixed perpendicular arrangement with respect to the plane of the silylene moiety.\textsuperscript{39} For the carbon analog, cp, $\sigma^*$-$\pi^*$ conjugation in the LUMO is negligible due to the much higher energy level of the corresponding exocyclic $\sigma^*$ orbital. The high electron-accepting property of the silole results from its available low-lying LUMO orbital and is further explained by comparison of the calculated HOMO and LUMO levels of its heterocyclic analogs.\textsuperscript{39}

Commercially available blue emitting polyfluorenes generally have a much shorter lifetime compared to that of red and green emitters. As a result, there has been increased interest in strong blue emitters with high quantum efficiency, lifetime, and color purity. Unfortunately, some polyfluorenes can undergo a decrease in emission and spectral broadening resulting in a low-energy green band over time.\textsuperscript{40–42}

The synthesis of silafluorenes has traditionally been through the reaction of an $o,o'$-dilithiobiphenyl with an appropriate dichlorosilane.\textsuperscript{7,8} Silafluorenes containing substituents at the 2,7- or 3,6-positions have be prepared by a similar reaction starting
from a tetrahalobiphenyl precursor followed by the subsequent incorporation of a variety of organic substituents through a cross-coupling reaction.\textsuperscript{7,8,30,32,36,43} More recently, a number of transition metal-mediated syntheses of silafluorenes have been developed.\textsuperscript{8}

2,7- and 3,6-Dihalogenated silafluorenes have also been widely used for the preparation of new silafluorene-based polymers.\textsuperscript{8} Recently, a relatively simple, inexpensive, and high-yielding route to a tetra-halogenated biphenyl system has been developed by Huang et. al.,\textsuperscript{44} and recently improved by Ozin et. al.\textsuperscript{45} In this method, commercially available o-dianisidine can be brominated to form 4,4′-dibromo-3,3′-dimethoxy-1,1′-biphenyl, which by utilizing the \textit{para}-directing methoxy substituents, can undergo iodination to form 2,2′-diiodo-4,4′-dibromodiphenyl. 2,7-Dibromo-3,6-dimethoxy-9,9-diphenylsilafluorene can then be synthesized through a lithium-halogen exchange with 2,2′-diiodo-4,4′-dibromodiphenyl which preferentially exchanges with the iodo substituents to form the 2,2′-dilithio-4,4′-dibromodiphenyl intermediate.\textsuperscript{44,45} However, in our experience, we found that this reaction was low yielding for the preparation of 2,7-dibromo-3,6-dimethoxy-9,9-diphenylsilafluorene. Using a modified method, the experimental time was significantly reduced and the yield of 2,7-dibromo-3,6-dimethoxy-9,9-diphenylsilafluorene increased. With this improved route, the final step involving the synthesis of new 2,7-disubstituted silafluorenes was achieved by a standard palladium-catalyzed Sonagashira cross-coupling of 2,7-dibromo-3,6-dimethoxy-9,9-diphenylsilafluorene with the desired -alkynyl(aryl) linkages containing different terminal aryl groups. The synthesis and characterization of the new silafluorenes are described in the following sections.
3.2. Synthetic Overview

Given the limited number of 2,7-disubstituted-3,6-dimethoxy-9,9-
diphenylsilafuorenes, only two literature procedures existed for accessing their precursor, both of which followed a nearly identical protocol (Scheme 3-1). In this procedure, commercially available o-dianisidine (3-1) undergoes a Sandmeyer reaction, converting an aromatic amino group to a diazonium salt followed by its substitution with a bromide catalyzed by copper(I) bromide, forming the product 4,4′-dibromo-3,3′-dimethoxy-1,1′-biphenyl (3-2). The nitrous acid is prepared in situ from sodium nitrite and hydrobromic acid. Based on the proposed mechanism of this procedure (Scheme 3-2), it is expected that this would be readily scalable with minor deviations such as

Scheme 3-1. Synthetic overview for obtaining 4,4′-dibromo-2,2′-diiodo-5,5′-dimethoxy-1,1′-biphenyl (3-3).
small excesses in stoichiometry or elevations in temperature relative to the literature procedure\textsuperscript{45} would still result in successful formation of (3-2) in excellent yield. While investigating the utility of this procedure, it was determined that the 5,5\textsuperscript{'}-methoxy substituents had minimal influence on the structure in terms of absorption and emission,\textsuperscript{20,38} and were necessary for the preparation of 4,4\textsuperscript{'}-dibromo-2,2\textsuperscript{'}-diiodo-5,5\textsuperscript{'}-dimethoxy-1,1\textsuperscript{'}-biphenyl (3-3) by directing the 2,2\textsuperscript{'}-iodination (Scheme 3-3).\textsuperscript{45}

Like the procedure for the synthesis of (3-2), it was expected the procedure for (3-3) would also be insensitive to deviations, also allowing for ease of scaling. Furthermore, it was anticipated the 5,5\textsuperscript{'}-methoxy substituents would not interfere with subsequent steps of the reaction.\textsuperscript{44,49} Due to suspected ease of the first two steps in the overall protocol as well as there being no apparent photophysical drawbacks due to the methoxy substituent, 2,7-dibromo-3,6-dimethoxy-9,9-diphenylsilafluorene (3-4) remained a desirable candidate and accessible by a lithium-halogen exchange (Scheme 3-4).\textsuperscript{44,49} It was expected that (3-4) could be obtained by precise control of the experimental parameters which were determined in order to preferentially perform a lithium exchange with the
2,2’-diiodo substituents rather than the 4,4’-dibromo substituents in good yield (68%).\textsuperscript{49}

Once (3-4) was obtained, a series of complexes could be synthesized utilizing Sonagashira cross-coupling to form carbon-carbon bonds at the 2,7-positions (Figure 3-2). As Sonagashira cross-coupling is a well-known protocol in the literature that has been successfully utilized previously to produce 2,7-alkynyl(aryl)-3,6-dimethoxy-9,9-diphenylsilafafluorene analogs (Figure 3-2),\textsuperscript{49,50} it was expected that this final step would proceed as expected. A number of commercially available arylalkynyl ligands suitable for Sonagashira cross-coupling were selected for the final step, and are depicted in Figure 3-3. The ligands which would ultimately comprise a series of 2,7-alkynyl(aryl)-3,6-dimethoxy-9,9-diphenylsilafafluorene analogs, which would differ from one another

\textbf{Figure 3-2.} Previously published 2,7-alkynyl(aryl)-3,6-dimethoxy-9,9-diphenylsilafafluorene analogs.\textsuperscript{49,50}

\textbf{Figure 3-3.} A generalized Sonagashira cross-coupling of (3-2) for formation of 2,7-alkynyl(aryl)-3,6-dimethoxy-9,9-diphenylsilafafluorene analogs.\textsuperscript{44,49}
in terms of absorption, emission, melting point, quantum yield, solid-state crystal packing and other physical properties, some of which could be predicted utilizing spectrochemical trends. For example, it was expected that (3-5) would be blueshifted with respect to (3-10) due to the extended π-conjugation within (3-10). The new compounds were fully characterized by $^1$H and $^{13}$C{$_^1$H} NMR spectroscopy, elemental analysis, melting point, x-ray crystallography, HR-MS (EI) (except 3-9), UV-Vis and fluorescence spectroscopy, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

3.3. Results and Discussion

3.3.1. Synthesis of 4,4′-dibromo-3,3′-dimethoxy-1,1′-biphenyl (3-2)

The synthesis of (3-2) was performed by the Sandmeyer reaction of commercially available (3-1) with HBr (40%) and NaNO$_2$, in acetonitrile (MeCN) (Equation 3-1).

$$\text{H}_2\text{N}\begin{array}{c} \text{MeO} \\
\end{array}\begin{array}{c} \text{3-1} \\
\end{array}\begin{array}{c} \text{OH} \\
\end{array}\begin{array}{c} \text{NH}_2 \\
\end{array}\text{HBr\,(aq), CH}_3\text{CN NaNO}_2, \text{CuBr} \\
\end{array}\text{Br}\begin{array}{c} \text{MeO} \\
\end{array}\begin{array}{c} \text{3-2} \\
\end{array}\begin{array}{c} \text{96\%} \\
\end{array}\begin{array}{c} \text{OMe} \\
\end{array}$$

Equation 3-1. Synthesis of 4,4′-dibromo-3,3′-dimethoxy-1,1′-biphenyl (3-2).

Following a previously published procedure,$^{45}$ (3-1) was dissolved in a 3-necked flask equipped with an addition funnel containing HBr and MeCN. The majority of (3-1) was dissolved in the MeCN as the reaction mixture was cooled to 0 °C. A chilled saturated sodium nitrate solution was then added dropwise to the reaction mixture such that the internal temperature did not exceed 10 °C. The reaction was subsequently stirred for 30 minutes maintaining the temperature below 10 °C. For addition of the CuBr solution (40% HBr), the literature procedure utilized a glass tube attachment which attached to the addition funnel stem and was submerged into the reaction mixture to prevent a CuBr side reaction with atmospheric O$_2$. As this was not available, the atmosphere within the
reaction flask was purged with argon, and maintained under argon atmosphere throughout the hour-long addition. After maintaining the reaction mixture at reflux (80 °C) for at least 1 hour, the reaction mixture was cooled to room temperature and stirred for an additional hour, during which an insoluble white precipitate appeared. During this process, small bubbles should be rapidly produced and evolved from the reaction mixture, indicating loss of N\textsubscript{2} from the Sandmeyer conditions. It should be noted that during aqueous workup, washing the DCM solution of (3-2) with 10 wt% NaOH results in rapid pressure buildup, requiring constant and consistent venting of the separatory funnel as to avoid harm or injury. After workup, the solution was dried with MgSO\textsubscript{4} and filtered, resulting in a crude light brown powder in excellent yield (96%) with ≥ 95% purity (GC), suitable for the next step.

**Characterization**

Isolation of this compound was fairly straightforward. Once the aqueous workup was completed, the resulting solid was light brown and pure enough to proceed to the next step. While flash chromatography could be performed to remove the discoloration and obtain a white product through recrystallization in DCM:ethanol (EtOH), there was no advantage in performing purification as the following step proceeded in excess. Furthermore, the impurity was not detectable by GC/GC-MS or \textsuperscript{1}H NMR. For \textsuperscript{1}H NMR, a singlet at ca. δ 3.79 resulted from the aryl-NH\textsubscript{2} ligand for (3-1), which was absent in the product (3-2) (Figure 3-4). \textsuperscript{13}C{\textsuperscript{1}H} NMR results indicated uniform deshielding by 2-9 ppm, which support the substitution of a –Br ligand in place of –NH\textsubscript{2}, although there were not obvious diagnostic differences.
3.3.2. Synthesis of 4,4'-dibromo-2,2'-diiodo-5,5'-dimethoxy-1,1'-biphenyl (3-3)\textsuperscript{45}

The starting material, (3-2), was reacted with KIO$_3$, and I$_2$ in an acetic acid solution and refluxed overnight (Equation 3-2).

\begin{equation}
\text{Br}_-\text{MeO}_-\text{3-2} \quad \text{KIO}_3, \text{I}_2, \text{AcOH, H}_2\text{SO}_4 \quad 80 \degree \text{C for 12 h} \quad \text{Br}_-\text{MeO}_-\text{3-3}
\end{equation}

\textbf{Equation 3-2.} Synthesis of 4,4'-dibromo-2,2'-diiodo-5,5'-dimethoxy-1,1'-biphenyl (3-3)\textsuperscript{45}

To a three-neck flask, (3-2), KIO$_3$, and I$_2$ were dissolved in glacial acetic acid, which was further acidified by H$_2$SO$_4$ (20%), then refluxed overnight. As the reaction proceeded, a large amount of precipitate formed. Once cooled to room temperature, H$_2$O was added to precipitate further product, which was subsequently collected by filtration. After workup, the product was obtained as a crude light brown powder in excellent yield (96%) with $\geq$ 95% purity (GC). Although utilizing this material as a light brown powder was not ideal.
Characterization

Recrystallization in DCM:EtOH resulted in products with progressively greater purity, however, the recrystallization process resulted in diminishing returns and never provided a fully white product. Flash chromatography was performed using 1:1 DCM:hexanes, removing the vast majority of the brown impurity. The desired product would elute as a clear fraction. The mild brown impurity occasionally remained, but could be further diminished in the isolated product by recrystallization in DCM:EtOH. Since the impurity was not detectable by GC/GC-MS or ¹H NMR, both characterization methods did not show an improved purity, even when the material was completely white. As stoichiometry was of the utmost importance in reaction to follow, there was concern that the brown impurity had an influence on the stoichiometry of the reaction when treated as a fully pure product. Because of this, flash chromatography and recrystallization was performed for this step repeatedly until the isolated product was white or off-white. The next step was viewed as a bottle-neck for throughput for the entire protocol, as high yields were initially difficult to obtain, and could still be drastically diminished if experimental parameters were not tightly constrained. For ¹H NMR, (3-2) exhibited a doublet at ca. δ 7.58 which is assigned to the proton adjacent to the Br substituent. In (3-2), the proton between the methoxy substituent and the five-membered ring is observed as a doublet at 7.04 ppm showing long-range coupling to the other set of ortho-protons. In (3-3) this resonance is deshielded to ca. δ 8.04 as a singlet. The deshielding also supports that an iodo substituent has been coordinated to the aromatic ring. Finally, while (3-2) possessed a doublet and multiplet in the aromatic region, (3-3) exhibits two singlet resonances, which integrate to two protons each, relative to that of
the methoxy substituent at δ 3.88, suggesting that each of the two protons that are related by symmetry, are also isolated from one another. $^{13}\text{C}^{1\text{H}}$ NMR indicated a substantial increase in shielding parameter for the iodo-substituted carbon (Figure 3-6). This diagnostic resonance is also useful the characterization of (3-4) as it will once again undergo a substantial change in shielding parameter once coordinated the dichlorodiphenylsilane moiety.

Figure 3-5. $^1\text{H}$ NMR of (3-3) showing absence of the double resonance from the internal proton in (3-3) from (3-2).
3.3.3. Synthesis of 2,7-dibromo-3,6-dimethoxy-9,9-diphenylsilafuorene (3-4)

To a four-necked flask equipped with an addition funnel, thermometer, and magnetic stirrer, (3-3) was dissolved in freshly distilled THF. A lithium-halogen exchange reaction was performed followed by subsequent addition of dichlorodiphenylsilane to form (3-4) (Equation 3-3).

\[ \text{Br} \text{-} \text{MeO} \text{-} \text{H} \text{-} \text{OMe} \rightarrow \text{Br} \text{-} \text{MeO} \text{-} \text{Br} \]

Equation 3-3. Synthesis of 2,7-dibromo-3,6-dimethoxy-9,9-diphenylsilafuorene (3-4).

Only two published literature procedures existed in order to access (3-4).\(^{44,49}\) The first report was in 2006 by Chen et al.,\(^{44}\) which varying yields for an array of (3-4) analogs in
which the 9,9-position was altered with combinations of alkyl and cycloalkyl substituents with various yields (Figure 3-7, left). The desired product, (3-4), was reported in 12% yield. The second report was in 2010 by Li et al., which discussed a similar protocol in which a 68% yield was obtained (Figure 3-7, right). Other synthetic variables were also considered, including the difference in overall experimental time, such as with the first published method, the reaction mixture was stirred for 30 minutes at -100 °C prior to addition of dichlorodiphenylsilane and stirring overnight at room temperature.

Meanwhile, the second literature required over eight hours of experimental time. In practical terms, it would require ca. 10 hours of work, during which temperature must be maintained for 2 h. Despite appearing less convenient, Li et al.’s protocol was selected for its reported yield.

**Figure 3-7.** An overview of both reported synthetic protocols for (3-4).
Using Li’s protocol,\textsuperscript{49} the starting material, (3-3), was dissolved in THF in a flame-dried 3-necked flask equipped with a magnetic stirrer, and subsequently chilled to -90 °C. While rapidly stirring, \textit{n}-BuLi was added dropwise via syringe, such that the temperature did not exceed -98 °C. Once the addition was complete, the reaction mixture was maintained between -100 °C and -98 °C for 2 h. After 2 h, dichlorodiphenylsilane was added dropwise via syringe, such that the temperature did not exceed -98 °C, after which the reaction flask was removed from the methanol bath and allowed to warm to room temperature. Upon reaching room temperature, the reaction mixture was equipped with a flame-dried reflux condenser and maintained under reflux for 6 h. After 6 h, the reaction mixture was cooled to room temperature and stirred overnight at room temperature.

Initial attempts at reproducing Li \textit{et al.}’s protocol resulted in convoluted \textit{^1}H NMR spectra indicating multiple indeterminate products. GC-MS was performed in an attempt to determine the overall composition, yielded a “forest” of peaks. This result was unexpected as it was assumed there were a much more limited range of possibilities which could occur within the given conditions. Furthermore, GC-MS did not indicate the formation of (3-4), even in trace amounts.

The first consideration was verifying the purity and/or dryness of all starting materials and equipment, including the solvent. Once verified, the Schlenk manifold was inspected for leaks, and additional focus was placed on ensuring the dryness of the reaction flask and environment. GC-MS continually indicated the same “forest” of results, with intermittent small quantities of product (< 5%) with a ca. 19 min retention time. In terms of throughput, it was not realistic to attempt to overcome this limitation through scaling, in an attempt to continue with the project and synthesize an array of 2,7-
alkynyl(aryl)-3,6-dimethoxy-9,9-diphenylsilafuorenes.

The second consideration was that the lithium-halogen exchange did not proceed as expected, either due to poor temperature control resulting loss in selectivity, localized high concentrations of \( n\text{-BuLi} \) during addition, or an overall excess of \( n\text{-BuLi} \). The result would be the loss of lithium-halogen exchange selectivity, or excess \( n\text{-BuLi} \) reaction, corresponding to at minimum partial reaction at the bromide positions. This would result in coordination of the silane moiety at undesired (3-3) positions, or lithiated positions which did not react with a silane moiety, which would become silanols or protonated, respectively during aqueous workup (Figure 3-8).

In an attempt to address these considerations, the stirring rate was increased to the fastest possible given the apparatus and conditions. Initial experiments were limited to a 15 mL 3-necked flask due to their scale. Since a glass alcohol thermometer was used to monitor temperature, adequate submersion within the reaction mixture was also required. These two practical variables limited the size of the magnetic stirrer which could be used, providing a limit to the overall rate of stirring. An additional challenge which became apparent was the probability of the reaction mixture freezing. While the methanol bath

![Figure 3-8](image-url)

**Figure 3-8.** Possible products from loss of lithium-halogen exchange selectivity (top) and the resultant products (bottom).
was chilled to ca. -90 °C (THF freezes at -108.4 °C), a layer along the inner wall of the reaction flask would freeze due to locally low short-lived temperatures from intermittent addition of liquid nitrogen (-196 °C). To further complicate matters, the methanol bath would occasionally freeze (-97.6 °C), causing the reaction flask to become mired and occasionally fracture within the bath. It was also difficult to view the reaction mixture within the flask, both due to atmospheric vapor condensation on the exterior of the flask as well as the depth at which it must be submerged. As a result, small portions of the reaction mixture would unknowingly remain in the solid state during addition of n-BuLi, and remain unobserved until removal from the bath after silane addition. The assumption was that the reaction mixture which remained in solution was exposed to an excess of n-BuLi, resulting in the possible formation of the aforementioned side products (Figure 3-8). Experiments were also performed in which the rate of the n-BuLi addition was decreased from 1 drop/2 sec to 1 drop/10 sec, with no noticeable improvement in yield of (3-4). Finally, experiments were performed with molar deficits of n-BuLi (1.9 equiv), as well as experiments in which temperature was decreased to -100 °C without any observed improvement. With continued effort, the experimental conditions were fine-tuned to attempt to reproduce the literature report, however with marginal improvement of results as indicated by GC-MS experiments. This included increasing the scale of the reaction to aid in the aforementioned issues of localized freezing, stirring rate and localized high concentration of n-BuLi. After exhaustive repeated attempts, the protocol was reproduced in what was perceived as flawless with respect to the literature, providing the best overall results, with an approximate yield of 15%. (Figure 3-9).
Figure 3-9. GC-MS of the highest yielding reaction mixture following the reported Li et al. protocol.49

The next step was to investigate the effect concentration may have as the protocol was performed at 0.1 M (with respect to (3-3)). As mentioned earlier, the stirring rate was considered as an influence on the reaction mixture freezing. By reducing the reaction concentration, the volume could be increased without increasing the scale of starting material (3-3) utilized, allowing for a larger magnetic stirrer to further agitate the reaction mixture, greater ease of temperature control, and overall reduction in potential for localized high n-BuLi concentrations during addition. The reaction mixture also developed into a slurry halfway through the addition of n-BuLi, increasing the chances of the reaction mixture freezing due to the increased viscosity, which was mitigated by decreasing the concentration. Initial studies at substantially reduced concentration (0.01 M) returned various unreacted starting materials (Figure 3-10), suggesting the protocol had a lower concentration limit. A subsequent study was performed at a mid-point concentration (0.05 M) which provided similar results to Figure 3-9 only with a reduced quantity of side products.
A desirable yield still remained inaccessible by the protocol, as such, other variables were investigated further in an attempt to elucidate competing mechanisms. While attempting to identify the “forest” of results (Figure 3-9), the associated fragmentation patterns were often inconclusive due to poor response, but unreacted starting material (3-3) as well as compounds which resulted from partial reaction with n-BuLi and subsequent aqueous workup were still apparent (Figure 3-10). Multiple peaks were associated with what appeared to be unreacted dichlorodiphenylsilane, which had subsequently reacted to produce silanols and subsequently undergone silanol condensation resulting in fragments of polydiphenylsiloxane (PDPS).\textsuperscript{51} It was thought that the previous unidentifiable peak at ca. 18 min (Figure 3-9) which seemed to be the major product, may possibly represent a competitive product of formation of (3-4). The parent ion \((m/z = 593)\) may be a product of silanol condensation (Figure 3-11a) or a fragment of a much larger product not detected by the method. These suggested structures seemed chemically

**Figure 3-10.** Partially reacted \(n\)-BuLi products which did not undergo reaction with dichlorodiphenylsilane.

**Figure 3-11.** Suggested products (a,b) represented by the GC-MS peak at ca. 18 min.
reasonable, further supported by the lack of $^{79}\text{Br}(50.54\%)$ and $^{81}\text{Br}(49.46\%)$ isotope peaks. Additional material may also be lost due to any of the molecules depicted in Figure 3-11 condensing into larger structures which may not elute from the column due to molecular weight or affinity, although no carryover was observed in subsequent solvent blank (DCM) runs. It may also be possible that potential side products exceed the detection limits of the coupled GC-MS instrument.

Since the major product that remained was one of the silanol products rather than the desired product (3-3), and all of the efforts had already been made to mitigate localized high concentrations of $n$-BuLi during addition, including slowing the rate of addition to 1 drop/10 sec. The next consideration was that the addition of dichlorodiphenylsilane was too rapid, resulting in localized high concentrations. Unfortunately, experiments in which the silane was added slowly (1 drop/10 sec) did not result in any appreciable improvement.

Nearly all experimental parameters had been investigated without resolution. The previously tabled protocol by Chen et al.,$^{44}$ (Figure 3-7, left) resumed consideration as their reported yield (12%) was comparable to what was being achieved using current methods despite having a much shorter protocol (30 min stir, no reflux). Preliminary results from performing Li et al.’s protocol with a 30 minute stirring period subsequent to complete lithiation without the 6 hour reflux indicated a yield comparable to what was being achieved using the Li et al.$^{49}$ protocol (Figure 3-7, right). At the same time, Dr. Christopher Spilling had suggested a process referred to as “scrambling” may also be occurring, in which the di-lithiated derivative of (3-3) reacts through an intermolecular lithiation step (Figure 3-12) at the halogenated positions of other molecules of (3-3). This
seemed reasonable as despite how precisely the reported parameters had been accounted for, there remained an inconsistent distribution of products related to lithiated materials at varying positions. Although the condensation product(s) (Figure 3-11) remained the major product in all cases. If “scrambling” were an influence, the thought was that scrambling was a matter of probability which increased as time passed during addition of $n$-BuLi. An experiment was performed utilizing a modified protocol by Chen et al. (Figure 7, left),\textsuperscript{44} in which the stirring time subsequent to addition of $n$-BuLi was reduced from 30 min to 15 min. The results were markedly improved with respect to all prior attempts of all variations of both protocols (Figure 3-13) with an approximate yield of 68%. This result led to additional experiments where the time was further reduced to

\[\text{Figure 3-12. Some potential “scrambling” products.}\]

\[\text{Figure 3-13. Synthetic results for a shortened Chen et al.\textsuperscript{44} protocol (15 min) resulting in improved yield of (3-4).}\]
determine if the yield could be improved more. Indeed, repeating the procedure, but removing the stir time between completion of \( \text{n-BuLi} \) addition and addition of silane further improved the yield. “Scrambling” was believed to become a consideration the moment the first drop of \( \text{n-BuLi} \) is added to the reaction mixture, which could also be further reduced by decreasing the time required for the addition of \( \text{n-BuLi} \). Lithiation was assumed to occur instantaneously, even at \(-100\, ^\circ\text{C}\), making temperature control the greatest challenge during the addition of \( \text{n-BuLi} \) as the process is not only exothermic, but the \( \text{n-BuLi} \) solution was at a much higher temperature than the reaction mixture.

During this investigation, each time an experiment was completed, the methanol bath was set aside to be reused the following day. At the time of being set aside, the methanol bath was around \(-90\, ^\circ\text{C}\). After the methanol bath had reached room temperature, it was stored for re-use in a subsequent experiment. Each subsequent day the methanol bath was used, it was observed to freeze less frequently upon reducing its temperature to \(-90\, ^\circ\text{C}\). This was likely due to water vapor condensing into the methanol bath. A test was performed in which a \( \text{H}_2\text{O}:\text{MeOH} \) \((1:4)\) bath was prepared, which did not freeze when reduced even below \(-100\, ^\circ\text{C}\), at which point it developed a gel-like consistency. This was particularly advantageous becomes the flask would no longer become mired, or stuck in the bath, eliminating the risk of fracture, and the reaction mixture was easier to monitor for localized freezing as visibility was improved. Finally, this allowed for greater consistency, as it was later discovered that the delay between addition of silane and when the flask was removed from the bath also has an effect on yield. This resulted in the development of the following protocol (Figure 3-14).
A flame-dried four-necked flask containing compound (3-3) was dissolved in freshly distilled THF (0.5 M). The solution was chilled using a MeOH/H₂O/liq. N₂ bath and was maintained at ≤ -95 °C by the addition of small amounts of liq. N₂ during the reaction. With rapid stirring, n-BuLi (1.6 M in hexanes) was added rapidly dropwise from the addition funnel in a nearly a constant stream over 2.5 min while not allowing the reaction mixture temperature to exceed -90 °C. The reaction was immediately quenched by the rapid addition of dichlorodiphenylsilane. The reaction mixture was then immediately removed from the methanol bath, at which point it warmed to room temperature and stirred overnight. See the Experimental Section 3.4 for further details.

While initial yields were comparable to the best reported literature yield (68%),⁴⁹ yields were improved by increasing the fractions collected during flash chromatography.
The standard GC-MS method utilized within the Wilking group resulted in GC-MS experiments which required 21 minutes until the peak related to (3-4) would elute. As no autosampler was available, manual injections were necessary, making a large amount of manually injected column fractions impractical. Additional time was required between each experiment for the GC oven temperature to decrease back to the initial temperature. A new method was developed in which the initial and final temperature were both 320 °C, eliminating the ramp and cool down times (Table 3-1). It should be noted while this method allowed for rapid screening of (3-4), it excluded all other potential impurities which would normally elute prior to 17 min utilizing the standard method. If flash chromatography was successful, those components should not be present, however, recrystallization was still performed followed by a GC-MS experiment utilizing the standard method to ensure the product was pure enough to proceed to the next step.

<table>
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<th>New Method</th>
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<tr>
<td><strong>Run Time (min)</strong></td>
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</table>

**Characterization**

The $^1$H NMR spectrum of (3-4) exhibited a series of complex resonances for the aromatic protons centered at $\delta$ 7.53 and 7.30 for the Si-Ph groups. The most diagnostic feature
indicating the formation of the heterocycle was the singlet at 7.79 which represented the isolated proton between the methoxy substituent and the five-membered ring (Figure 3-15). The singlet at 3.93 which for six protons was associated with the methoxy groups. These values corresponded to literature values.44,49

The $^{13}$C{$^{1}$H} NMR spectrum of (3-4) exhibited ten resonances for the aromatic carbons from $\delta$ 105.2-158.2. The resonance at $\delta$ 158.2 was associated with the ring carbons bearing the methoxy groups while the resonance at $\delta$ 149.0 was associated with the $\beta$-carbon of the central five-membered ring (Figure 3-16). The resonance for the methoxy substituents appeared at $\delta$ 56.4. These values corresponded to literature values.44,49

**Figure 3-15.** Comparison of the $^1$H NMR spectra of the starting material (3-3) and (3-4).
3.3.4. Synthesis of 2,7-alkynyl(aryl)-3,6-dimethoxy-9,9-diphenylsilafluorenes

3.3.4.1. 2,7-(1-ethynyl-3-fluorobenzene)-3,6-dimethoxy-9,9-diphenylsilafluorene (3-5)

The synthesis of (3-5) was performed by the reaction of (3-4) with Pd(PPh₃)₄, CuI, and 1-ethynyl-3-fluorobenzene in piperidine overnight at 80 °C (Equation 3-4).

Equation 3-4. Synthesis of 2,7-(1-ethynyl-3-fluorobenzene)-3,6-dimethoxy-9,9-diphenylsilafluorene (3-5).

The reactants, (3-4), Pd(PPh₃)₄, CuI, and 1-ethynyl-3-fluorobenzene were dissolved in piperidine under an argon atmosphere. The reaction flask was submerged in an oil bath.
and stirred overnight at 80 °C. After stirring for 1 h at 80 °C, the reaction mixture faintly fluoresced upon irradiation at 365 nm from a handheld UV lamp, indicating formation of the product. The reaction mixture was cooled to room temperature the following morning, at which point it appeared orange and gel-like. The product was purified by silica gel chromatography followed by recrystallization and obtained as a yellow solid in good yield (67%).

**Characterization**

The $^1$H NMR spectrum of (3-5) exhibited a series of complex resonances for the aromatic protons from $\delta$ 7.03-7.65. The most diagnostic feature indicating the formation of the heterocycle was the singlet at $\delta$ 7.88 which represented the isolated proton between the methoxy substituent and the five-membered ring. The singlet at $\delta$ 4.09 which integrated for six protons was associated with the methoxy groups. These values corresponded to literature values for similar structures (Figure 3-17).$^{49,50}$

The $^{13}$C{$^1$H} NMR spectrum of (3-5) exhibited 16 resonances, some with $^{19}$F coupling, for the aromatic carbons from $\delta$ 104.0-162.8. The alkynyl carbons exhibited resonances at $\delta$ 93.5 (d, $^4J_{C-F} = 3$ Hz) and 87.2. The resonance for the methoxy substituents appeared at $\delta$ 56.1. These values corresponded to literature values for similar structures (Figure 3-18).$^{49,50}$ UV-Vis and fluorescence spectroscopy measurements were also performed, and are discussed comparatively with other complexes in the summary to this chapter (Figures 3-19 and 3-20).
Figure 3-17. Comparison of the $^1$H NMR spectra of the starting material (3-4) and (3-5).

Figure 3-18. Comparison of the $^{13}$C{$^1$H} NMR spectra of the starting material (3-4) and (3-5).
Figure 3-19. Normalized UV/Vis spectrum of (3-5). $\lambda_{\text{abs}}$ (nm) (50 $\mu$M, DCM) = 285, 336, and 373.

Figure 3-20. Normalized fluorescence spectrum of (3-5) collected at the $\lambda_{\text{max}}$ absorption value. $\lambda_{\text{em}}$ (nm) (5 $\mu$M, DCM) = 403 and 426.
3.3.4.2. 2,7-(4-ethynyltoluene)-3,6-dimethoxy-9,9-diphenylsilafluorene (3-6)

The synthesis of (3-6) was performed by the reaction of (3-4) with Pd(PPh$_3$)$_4$, CuI, and 4-ethynyltoluene in piperidine overnight at 80 °C (Equation 3-5).

The reactants, (3-4), Pd(PPh$_3$)$_4$, CuI, and 4-ethynyltoluene dissolved in piperidine under an argon atmosphere. The reaction flask was submerged in an oil bath and stirred overnight at 80 °C. After stirring for 1 h at 80 °C, the reaction mixture faintly fluoresced upon irradiation at 365 nm from a handheld UV lamp, indicating formation of the product. The orange reaction mixture was cooled to room temperature the following morning. The product was purified by silica gel chromatography followed by recrystallization and obtained as a yellow solid in good yield (63%).

Characterization

The $^1$H NMR spectrum of (3-6) exhibited a series of complex resonances for the aromatic protons from $\delta$ 7.14-7.65. The most diagnostic feature indicating the formation of the heterocycle was the singlet at $\delta$ 7.88 which represented the isolated proton between the methoxy substituent and the five-membered ring. The singlet at $\delta$ 4.08 which integrated for six protons was associated with the methoxy groups. The singlet at $\delta$ 2.36 represented the methyl groups from 4-ethynyltoluene and integrated to six protons. These values corresponded to literature values for similar structures (Figure 3-21).$^{49,50}$
The $^{13}\text{C}[^1\text{H}]$ NMR spectrum of (3-6) exhibited 14 resonances for the aromatic carbons from $\delta$ 104.0-162.5. The alkynyl carbons exhibited resonances at $\delta$ 95.0 and 85.6. The resonance for the methoxy substituents appeared at $\delta$ 56.1, and the resonance for the methyl groups from 4-ethynyltoluene appeared at $\delta$ 21.6. Both integrated to six protons. These values corresponded to literature values for similar structures (Figure 3-22). 49, 50 UV-Vis and fluorescence spectroscopy measurements were also performed, and are discussed comparatively with other complexes in the summary to this chapter (Figures 3-23 and 3-24).
Figure 3-21. Comparison of the $^1$H NMR spectra of the starting material (3-4) and (3-6).

Figure 3-22. Comparison of the $^{13}$C$\{^1$H$\}$ NMR spectra of the starting material (3-4) and (3-6).
Figure 3-23. Normalized UV/Vis spectrum of (3-6). $\lambda_{\text{abs}}$ (nm) (50 μM, DCM) = 287, 336, and 373.

Figure 3-24. Normalized fluorescence spectrum of (3-6) collected at the $\lambda_{\text{max}}$ absorption value. $\lambda_{\text{em}}$ (nm) (5 μM, DCM) = 405 and 426.
3.3.4.3. 2,7-(4-tert-butylphenylacetylene)-3,6-dimethoxy-9,9-diphenylsilafluorene (3-7)

The synthesis of (3-7) was performed by the reaction of (3-4) with Pd(PPh$_3$)$_4$, CuI, and 4-tert-butylphenylacetylene in piperidine overnight at 80 °C (Equation 3-6).

![Equation 3-6. Synthesis of 2,7-(4-tert-butylphenylacetylene)-3,6-dimethoxy-9,9-diphenylsilafluorene (3-7).]

The reactants, (3-4), Pd(PPh$_3$)$_4$, CuI, and 4-tert-butylphenylacetylene dissolved in piperidine under an argon atmosphere. The reaction flask was submerged in an oil bath and stirred overnight at 80 °C. After stirring for 1 h at 80 °C, the reaction mixture faintly fluoresced upon irradiation at 365 nm from a handheld UV lamp, indicating formation of the product. The reaction mixture was cooled to room temperature the following morning, at which point an orange precipitate formed. The product was purified by silica gel chromatography followed by recrystallization and obtained as a yellow solid in good yield (79%).

**Characterization**

The $^1$H NMR spectrum of (3-7) exhibited a series of complex resonances for the aromatic protons from $\delta$ 7.37-7.65. The most diagnostic feature indicating the formation of the heterocycle was the singlet centered at $\delta$ 7.87 which represented the isolated proton between the methoxy substituent and the five-membered ring. The singlet at $\delta$ 4.07 which integrated for six protons was associated with the methoxy groups. The singlet at $\delta$ 1.32 represented the $t$-butyl groups from the (4-tert-butylphenyl)alkynyl group and integrated
to 18 protons. These values corresponded to literature values for similar structures (Figure 3-25).\textsuperscript{49,50}

The $^{13}$C\{$^1$H\} NMR spectrum of (3-7) exhibited 14 resonances for the aromatic carbons from $\delta$ 104.1-162.6. The alkynyl carbons exhibited resonances at $\delta$ 94.9 and 85.6. The resonance for the methoxy substituents appeared at $\delta$ 56.2, and the resonances for the $t$-butyl groups from (4-$t$ert-butylphenyl)alkynyl group appeared at 34.9 and 31.3. These values corresponded to literature values for similar structures (Figure 3-26).\textsuperscript{49,50} UV-Vis and fluorescence spectroscopy measurements were also performed, and are discussed comparatively with other complexes in the summary to this chapter (Figures 3-27 and 3-28).
Figure 3-25. Comparison of the $^1$H NMR spectra of the starting material (3-4) and (3-7).

Figure 3-26. Comparison of the $^{13}$C{$^1$H} NMR spectra of the starting material (3-4) and (3-7).
Figure 3-27. Normalized UV/Vis spectrum of (3-7). $\lambda_{\text{abs}}$ (nm) (50 μM, DCM) = 288, 340, and 375.

Figure 3-28. Normalized fluorescence spectrum of (3-7) collected at the $\lambda_{\text{max}}$ absorption value. $\lambda_{\text{em}}$ (nm) (5 μM, DCM) = 405 and 429.
3.3.4.4. 2,7-(1-ethynyl-4-phenoxybenzene)-3,6-dimethoxy-9,9-diphenylsilafluorene (3-8)

The synthesis of (3-8) was performed by the reaction of (3-4) with Pd(PPh$_3$)$_4$, CuI, and 1-ethynyl-4-phenoxybenzene in piperidine overnight at 80 °C (Equation 3-7).

![Equation 3-7. Synthesis of 2,7-(1-ethynyl-4-phenoxybenzene)-3,6-dimethoxy-9,9-diphenylsilafluorene (3-8).](image)

The reactants, (3-4), Pd(PPh$_3$)$_4$, CuI, and 1-ethynyl-4-phenoxybenzene dissolved in piperidine under an argon atmosphere. The reaction flask was submerged in an oil bath and stirred overnight at 80 °C. After stirring for 1 h at 80 °C, the reaction mixture faintly fluoresced upon irradiation at 365 nm from a handheld UV lamp, indicating formation of the product. The reaction mixture was cooled to room temperature the following morning, at which point it appeared orange and gel-like. The product was purified by silica gel chromatography followed by recrystallization and obtained as yellow needles in good yield (68%).

**Characterization**

The $^1$H NMR spectrum of (3-8) exhibited a series of complex resonances for the aromatic protons from δ 7.04-7.66. The most diagnostic feature indicating the formation of the heterocycle was the singlet at δ 7.87 which represented the isolated proton between the methoxy substituent and the five-membered ring. The singlet at δ 4.08 which integrated for six protons was associated with the methoxy groups. These values corresponded to literature values for similar structures (Figure 3-29).$^{49,50}$
The $^{13}$C-$^{1}$H NMR spectrum of (3-8) exhibited 18 resonances for the aromatic carbons from δ 104.0-162.6. The alkynyl carbons exhibited resonances at δ 94.3 and 85.6. The resonance for the methoxy substituents appeared at δ 56.1. These values corresponded to literature values for similar structures (Figure 3-30).$^{49,50}$ UV-Vis and fluorescence spectroscopy measurements were also performed, and are discussed comparatively with other complexes in the summary to this chapter (Figures 3-31 and 3-32).
Figure 3-29. Comparison of the $^1$H NMR spectra of the starting material (3-4) and (3-8).

Figure 3-30. Comparison of the $^{13}$C{$^1$H} NMR spectra of the starting material (3-4) and (3-8).
Figure 3-31. Normalized UV/Vis spectrum of (3-8). $\lambda_{\text{abs}}$ (nm) (50 $\mu$M, DCM) = 288, 340, and 377.

Figure 3-32. Normalized fluorescence spectrum of (3-8) collected at the $\lambda_{\text{max}}$ absorption value. $\lambda_{\text{em}}$ (nm) (5 $\mu$M, DCM) = 410 and 434.
3.3.4.5. 2,7-(4-ethylbiphenyl)-3,6-dimethoxy-9,9-diphenylsilafluorene (3-9)

The synthesis of (3-9) was performed by the reaction of (3-4) with Pd(PPh$_3)_4$, CuI, and 4-ethylbiphenyl in piperidine overnight at 80 °C (Equation 3-8).

The reactants, (3-4), Pd(PPh$_3)_4$, CuI, and 4-ethylbiphenyl were dissolved in piperidine under an argon atmosphere. The reaction flask was submerged in an oil bath and stirred overnight at 80 °C. After stirring for 1 h at 80 °C, the reaction mixture faintly fluoresced upon irradiation at 365 nm from a handheld UV lamp, indicating formation of the product. The reaction mixture was cooled to room temperature the following morning, at which point a yellow precipitate formed. The product was purified by silica gel chromatography followed by recrystallization and the product was obtained as a yellow solid in moderate yield (54%).

Characterization

The $^1$H NMR spectrum of (3-9) exhibited a series of complex resonances for the aromatic protons from $\delta$ 7.37-7.67. The most diagnostic feature indicating the formation of the heterocycle was the singlet at $\delta$ 7.91 which represented the isolated proton between the methoxy substituent and the five-membered ring. The singlet at $\delta$ 4.11 which integrated for six protons was associated with the methoxy groups. These values corresponded to literature values for similar structures (Figure 3-33).
The $^{13}$C\{\textsuperscript{1}H\} NMR spectrum of (3\textbf{-}9) exhibited 18 resonances for the aromatic carbons from $\delta$ 104.0-162.6. The alkynyl carbons exhibited resonances at $\delta$ 94.7 and 87.0. The resonance for the methoxy substituents appeared at $\delta$ 56.2. These values corresponded to literature values for similar structures (Figure 3\textsuperscript{-}34).\textsuperscript{49,50} UV-Vis and fluorescence spectroscopy measurements were also performed, and are discussed comparatively with other complexes in the summary to this chapter (Figures 3\textsuperscript{-}35 and 3\textsuperscript{-}36).
**Figure 3-33.** Comparison of the $^1$H NMR spectra of the starting material (3-4) and (3-9).

**Figure 3-34.** Comparison of the $^{13}$C{$^1$H} NMR spectra of the starting material (3-4) and (3-9).
Figure 3-35. Normalized UV/Vis spectrum of (3-9). $\lambda_{\text{abs}}$ (nm) (50 μM, DCM) = 292, 340, and 384.

Figure 3-36. Normalized fluorescence spectrum of (3-9) collected at the $\lambda_{\text{max}}$ absorption value. $\lambda_{\text{em}}$ (nm) (5 μM, DCM) = 417 and 440.
3.3.4.6. 2,7-(2-ethynyl-6-methoxynaphthalene)-3,6-dimethoxy-9,9-
diphenylsilafuorene (3-9)

The synthesis of (3-10) was performed by the reaction of (3-4) with Pd(PPh$_3$)$_4$, CuI, and 2-ethynyl-6-methoxynaphthalene in piperidine overnight at 80 °C (Equation 3-9).

![Reaction Scheme](image)

**Equation 3-9.** Synthesis of 2,7-(2-ethynyl-6-methoxynaphthalene)-3,6-dimethoxy-9,9-
diphenylsilafuorene (3-10).

The reactants, (3-4), Pd(PPh$_3$)$_4$, CuI, and 2-ethynyl-6-methoxynaphthalene dissolved in piperidine under an argon atmosphere. The reaction flask was submerged in an oil bath and stirred overnight at 80 °C. After stirring for 1 h at 80 °C, the reaction mixture faintly fluoresced upon irradiation at 365 nm from a handheld UV lamp, indicating formation of the product. The reaction mixture was cooled to room temperature the following morning, at which point a yellow precipitate formed. The product was purified by silica gel chromatography followed by recrystallization and obtained as a yellow solid in moderate yield (54%).

**Characterization**

The $^1$H NMR spectrum of (3-10) exhibited a series of complex resonances for the aromatic protons from $\delta$ 7.12-7.70. The most diagnostic feature indicating the formation of the heterocycle was the singlet at $\delta$ 7.93 which represented the isolated proton between the methoxy substituent and the five-membered ring. The singlets at $\delta$ 4.12 and 3.93 which integrated for six protons each were associated with the methoxy groups on the
silafluorene and 2-ethynyl-6-methoxynaphthalene respectively. These values corresponded to literature values for similar structures (Figure 3-37).\textsuperscript{49,50}

The $^{13}$C\{$^1$H\} NMR spectrum of (3-10) exhibited 18 resonances for the aromatic carbons from $\delta$ 104.0-162.6. The alkynyl carbons exhibited resonances at $\delta$ 95.4 and 86.0. The resonance for the methoxy substituents appeared at $\delta$ 56.2 and 55.5. These values corresponded to literature values for similar structures (Figure 3-38).\textsuperscript{49,50} UV-Vis and fluorescence spectroscopy measurements were also performed, and are discussed comparatively with other complexes in the summary to this chapter (Figures 3-39 and 3-40).
Figure 3-37. Comparison of the $^1$H NMR spectra of the starting material (3-4) and (3-10).

Figure 3-38. Comparison of the $^{13}$C$($$^1$H$)$ NMR spectra of the starting material (3-4) and (3-10).
Figure 3-39. Normalized UV/Vis spectrum of (3-10). $\lambda_{\text{abs}}$ (nm) (50 μM, DCM) = 280, 340, and 388.

Figure 3-40. Normalized fluorescence spectrum of (3-10) collected at the $\lambda_{\text{max}}$ absorption value. $\lambda_{\text{em}}$ (nm) (5 μM, DCM) = 420 and 445.
3.3.4.7. Attempted synthesis of 2,7-(4-ethynylaniline)-3,6-dimethoxy-9,9-
diphenylsilafluorene (3-11)

The synthesis of (3-11) was performed by the reaction of (3-4) with Pd(PPh₃)₄, CuI, and 4-ethynylaniline in piperidine overnight at 80 °C (Equation 3-10).

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{Br} & \quad \text{Br} \\
\text{MeO} & \quad \text{OMe} \\
\text{H₂N} & \quad \text{NH₂} \\
80 \degree C, 12 h &
\end{align*}
\]

**Equation 3-10.** Attempted synthesis of 2,7-(4-ethynylaniline)-3,6-dimethoxy-9,9-
diphenylsilafluorene (3-11).

The reactants, (3-4), Pd(PPh₃)₄, CuI, and 4-ethynylaniline dissolved in piperidine under an argon atmosphere. The reaction flask was submerged in an oil bath and stirred overnight at 80 °C. After stirring for 1 h at 80 °C, the reaction mixture faintly fluoresced upon irradiation at 365 nm from a handheld UV lamp, indicating formation of the product. The reaction mixture was cooled to room temperature the following morning, at which point a yellow precipitate formed.

**Characterization**

While a fluorescent yellow precipitate was formed, it was necessary to separate the remaining palladium(II) and copper(I) species from the reaction mixture. Silica gel chromatography provided this result in addition to separating and isolating the desired analytes. However, unlike all other silafluorenes discussed herein, (3-11) often eluted as a mixture of brown, orange, and yellow components. Brown components were never observed in (3-5) through (3-10). While (3-5) through (3-10) are highly soluble in DCM, these brown components exhibited significantly reduced solubility, but still remained fluorescent in solution. For reactions in which silica gel chromatography was performed,
the overall yield was substantially reduced with each iteration. Reduced solubility provided diminished $^1$H and no $^{13}$C{ $^1$H} NMR results. For $^1$H NMR, the singlets at δ 4.07 and 3.81 which integrated for six protons and four protons, respectively, were associated with the −OMe and −NH$_2$ on the silafluorene and 4-ethynylaniline. These values corresponded to literature values for similar structures (Figure 3-41).$^{49,50}$

![Figure 3-41. Comparison of the $^1$H NMR spectra of the starting material (3-4) and (3-11).](image)

Melting point measurement as well as DSC/TGA experiments did not reveal any observable phase transitions. Interestingly, (3-11) underwent a bathochromic shift in emission when dissolved in a coordinating solvent such as MeOH relative to its emission when dissolved in DCM, suggesting that the 4-ethynylaniline ligands undergo a substantial electronic change upon interaction with the environment. A potential solution for obtaining this compound would be to basify the silica gel column prior to use utilizing diisopropylamine or TEA.
3.3.5. X-Ray Crystal Structures

Crystals of sufficient quality for silafluorenes (3-5) through (3-10) were grown by slow evaporation from CHCl₃ (or CDCl₃) solutions as thin yellow crystals. Compound 3-5 refined with one molecule of chloroform per two molecules of 3-5. The structures were solved and refined to reasonable geometries and residual electron densities and are summarized in Table 3-2. A summary of the crystal data and intensity parameters for the crystal structures that were obtained are provided in Appendix II (1 through 12). The molecular structures of (3-5) through (3-10) are shown in Figures 3-42 through 3-47.

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</table>
Goodness-of-fit on $R^2$ | 1.033 | 1.009 | 1.015 | 0.995 | 1.019 | 1.048
---|---|---|---|---|---|---
respectively with selected bond distances and angles. All compounds exhibit similar structural parameters within the silafluorene core to that of previously published 2,7-disubstituted-3,6-dimethoxy-9-silafluorene analogs.\textsuperscript{45,49,50} For compounds (3-5), (3-6), and (3-10) all have a 2,7-substituent coplanar with their silafluorene cores, with torsion angles of 2.19° (C2-C3-C15-C16), 178.12° (C2-C3-C15-C16), and 113.79° (C2-C3-C15-C16), respectively, while the substituents opposite of those are twisted out of plane by 49.54° (C11-C10-C23-C28), 113.79° (C11-C10-C24-C29) and 4.99° (C11-C10-C28-C37), respectively. The related compound, 2,7-(ethynylphenyl)-3,6-dimethoxy-9,9-diphenylsilafluorene exhibited a molecular structure whereby one of the terminal phenyl groups is essentially coplanar with the silafluorene core with a torsion angle of 7.39°, whereas the other terminal phenyl group is almost perpendicular with a torsion angle of 89.24°.\textsuperscript{49} Both phenyl substituents on compound (3-7) are substantially twisted out of plane with torsion angles of 83.63° (C2-C3-C15-C16) and 134.61° (C11-C10-C27-C32), while both rings are coplanar in compound (3-8) at 1.31° (C2-C3-C15-C16) and 11.30° (C11-C10-C29-C34). For the biphenyl substituents in compound (3-9), the phenyl rings immediately bound to the silafluorene core have torsion angles of 168.89° (C11-C10-C29-C34) and 33.34° (C33-C32-C35-40), while the other phenyl rings are both twisted 32.68° (C2-C3-C15-C16) and 37.13° (C17-C18-C21-C22) with respect to the former rings.

Compounds (3-5) through (3-10) all crystallized in a parallel arrangement, but are offset partially due to the phenyl rings on silane moiety, which sterically block the majority of intermolecular overlap. Compound (3-9) crystallized with the closest
intermolecular distances of 7.025 Å, eliminating any possibility of π-stacking
interactions. Compounds (3-5) through (3-8) and (3-10) all possess intermolecular
aromatic ring distances of 4.080 - 4.184 Å, but are offset such that there is minimal
intermolecular orbital overlap between conjugated systems (Figures 3-48 through 3-53).

![Figure 3-42. Molecular structure of 3-5.](image)

Hydrogen atoms and solvent molecules have been removed for clarity. Thermal ellipsoids
are drawn at the 50% probability level. Selected bond distances (Å), bond angles (deg),
and torsion angles (deg) for 3-5: Si1-C1 = 1.865(2), Si1-C12 = 1.862(3), Si1-C37 =
1.861(3), Si1-C31 = 1.869(3), C1-C6 = 1.407(4), C6-C7 = 1.489(3), C7-C12 = 1.411(3),
C13-C14 = 1.195(4), C21-C22 = 1.197(4), C37-Si1-C31 = 111.56(12), C6-C1-Si1 =
109.70(17), C1-C6-C7 = 114.9(2), C12-C7-C6 = 114.3(2), C7-C12-Si1 = 109.95(18),
C12-Si1-C1 = 91.16(11), C2-C3-C15-C16 = 2.19, C11-C10-C23-C28 = 49.54.

![Figure 3-43. Molecular structure of 3-6.](image)

Hydrogen atoms and solvent molecules have been removed for clarity. Thermal ellipsoids
are drawn at the 50% probability level. Selected bond distances (Å), bond angles (deg),
and torsion angles (deg) for 3-6: Si1-C1 = 1.867(3), Si1-C12 = 1.869(3), Si1-C37 =
1.867(3), Si1-C31 = 1.867(3), C6-C7 = 1.477(4), C1-C6 = 1.416(4), C7-C12 = 1.413(4),
C13-C14 = 1.193(4), C22-C23 = 1.200(4), C37-Si1-C31 = 108.97(13), C6-C1-Si1 =

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109.1(2), C1-C6-C7 = 114.9(3), C12-C7-C6 = 115.5(3), C7-C12-Si1 = 108.7(2), C1-Si1-C12 = 91.70(13), C2-C3-C15-C16 = 178.12, C11-C10-C24-C29 = 152.81.

Figure 3-44. Molecular structure of 3-7. Hydrogen atoms and solvent molecules have been removed for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å), bond angles (deg), and torsion angles (deg) for 3-7: Si1-C1 = 1.916(7), Si1-C12 = 1.955(8), Si1-C37 = 1.791(8), Si1-C43 = 1.802(9), C1-C2 = 1.406(8), C2-C3 = 1.420(9), C3-C4 = 1.392(9), C4-C5 = 1.388(9), C5-C6 = 1.375(9), C6-C7 = 1.472(9), C1-C6 = 1.414(9), C7-C12 = 1.408(9), C13-C14 = 1.201(7), C25-C26 = 1.211(8), C37-Si1-C43 = 115.3(5), C6-C1-Si1 = 114.3(5), C1-C6-C7 = 113.0(7), C12-C7-C6 = 115.1(7), C7-C12-Si1 = 112.1(5), C1-Si1-C12 = 85.4(3), C2-C3-C15-C16 = 83.63, C11-C10-C27-C32 = 134.61.

Figure 3-45. Molecular structure of 3-8. Hydrogen atoms and solvent molecules have been removed for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å), bond angles (deg), and torsion angles (deg) for 3-8: Si1-C1 = 1.854(3), Si1-C12 = 1.860(3), Si1-C49 = 1.861(3), Si1-C43 = 1.863(3), C6-C7 = 1.493(4), C1-C6 = 1.405(4), C7-C12 = 1.413(4), C13-C14 = 1.194(4), C27-C28 = 1.198(4), C49-Si1-C43 = 108.78(15), C6-C1-Si1 = 108.9(2), C1-C6-C7 = 115.3(3), C12-C7-C6 = 114.3(3), C7-C12-Si1 = 108.9(2), C1-Si1-C12 = 92.13(15), C2-C3-C15-C16 = 1.31, C11-C10-C29-C34 = 11.3.
Figure 3-46. Molecular structure of 3-9.
Hydrogen atoms and solvent molecules have been removed for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å), bond angles (deg), and torsion angles (deg) for 3-9: Si1-C1 = 1.8667(17), Si1-C12 = 1.8700(17), Si1-C47 = 1.8631(18), Si1-C41 = 1.8660(18), C6-C7 = 1.494(2), C1-C6 = 1.407(2), C7-C12 = 1.414(2), C13-C14 = 1.191(2), C27-C28 = 1.195(2), C47-Si1-C41 = 110.12(8), C6-C1-Si1 = 109.48(12), C1-C6-C7 = 114.97(15), C12-C7-C6 = 114.58(14), C7-C12-Si1 = 109.31(12), C1-Si1-C12 = 91.48(7), C2-C3-C15-C16 = 32.68, C17-C18-C21-C22 = 37.13, C11-C10-C29-C34 = 168.89, C33-C32-C35-40 = 33.34.

Figure 3-47. Molecular structure of 3-10.
Hydrogen atoms and solvent molecules have been removed for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å), bond angles (deg), and torsion angles (deg) for 3-10: Si1-C1 = 1.8551(10), Si1-C12 = 1.8638(9), Si1-C47 = 1.8594(10), Si1-C41 = 1.8682(10), C6-C7 = 1.4848(12), C1-C6 = 1.4086(12), C7-C12 = 1.4151(13), C13-C14 = 1.2046(13), C26-C27 = 1.2063(13), C47-Si1-C41 = 108.82(4), C6-C1-Si1 = 110.45(6), C1-C6-C7 = 114.02(8), C12-C7-C6 = 114.94(8), C7-C12-Si1 = 109.43(6), C1-Si1-C12 = 91.10(4), C2-C3-C15-C16 = 113.79, C11-C10-C28-C37 = 4.99.
Figure 3-48. The packing arrangement of (3-5) illustrating separation of adjacent molecules.

Figure 3-49. The packing arrangement of (3-6) illustrating separation of adjacent molecules.
Figure 3-50. The packing arrangement of (3-7) illustrating separation of adjacent molecules.

Figure 3-51. The packing arrangement of (3-8) illustrating separation of adjacent molecules.
Figure 3-52. The packing arrangement of (3-9) illustrating separation of adjacent molecules.

Figure 3-53. The packing arrangement of (3-10) illustrating separation of adjacent molecules.
3.3.6. Absorption and Fluorescence Studies

All of the new silafluorenes were observed to have strong blue emission both in solution and the solid state, whose physical properties vary upon the alkynyl(aryl) linkages employed. All compounds exhibit similar absorption and emission spectra. The normalized UV-vis absorption and emission spectra of (3-5) through (3-10) are shown in Figures 3-54 and 3-55, and are labeled in the order of their absorptive and emissive energies ((3-5) > (3-6) > (3-7) > (3-8) > (3-9) > (3-10)). Details of their photophysical properties are summarized in Table 3-3. All of the electronic transitions of silafluorenes (3-5) through (3-10) arise from π-π* where the electron transitions are from the initial and excited states, which are HOMO/HOMO-1 and LUMO/LUMO+1, respectively, and are significantly delocalized over the entire bridged silafluorene network.20,29 The median absorption of 376 nm for (3-5) through (3-10) is in agreement with the theoretical absorption maxima around 371 nm for 2,7-disubstituted silafluorenes29 while the absorptions at ca. 340 and 288 nm are due to the silafluorene core.20 The related previously synthesized silafluorene analogs exhibit similar experimental absorption and emission values except for the terminal triphenylamine derivative which showed red-shifted absorption and emission properties.49 In general, strong π-donor and -acceptor substituents can exhibit considerably red-shifted absorption and emission maxima with respect to groups which are primarily inductive, while extending conjugation also results in red-shifts.43,52 Compounds (3-5) through (3-10) follow this general trend. The new compounds, (3-5) through (3-7) incorporate inductive groups to their alkynyl(aryl) substituents, while (3-8) through (3-10) incorporate π-accepting substituents which also extend the conjugation. The absorption and emission maxima are nearly identical for (3-
Figure 3-54. Overlay of all normalized UV-Vis spectra for (3-5)-(3-10). $\lambda_{\text{abs}}$ (nm) (50 $\mu$M, DCM): (3-5), 285, 336, 373. (3-6), 287, 340, 374. (3-7), 288, 340, 375. (3-8), 288, 340, 377. (3-9), 292, 340, 384. (3-10), 280, 340, 388.

Figure 3-55. Overlay of all normalized fluorescence spectra for (3-5)-(3-10). $\lambda_{\text{em}}$ (nm) (5 $\mu$M, DCM): (3-5), 403, 426. (3-6), 405, 426. (3-7), 405, 429. (3-8), 410, 434. (3-9), 417, 440. (3-10), 420, 445.

5) through (3-7), but within the subset, (3-5) incorporates an inductively electron-withdrawing substituent and possesses the highest energy absorptions and emissions with respect to (3-6) and (3-7), which possess progressively more inductively donating substituents. These inductive effects are in agreement with previously predicted and
observed trends.\textsuperscript{43,49,50,52–55} For (3-8) through (3-10), the trend in increasing red-shifted maxima follows that of effective extended conjugation. The phenoxy substituted alkynyl(aryl) compound ((3-8)) is slightly red-shifted ($\lambda_{\text{em}} = 410, 434$) to that of the previously published methoxy substituted -alkynyl(aryl) ($\lambda_{\text{em}} = 406, 428$).\textsuperscript{50} Compound (3-9) is red-shifted with respect to (3-8), likely due to its increased conjugation through absence of the oxygen atom.

The compound with the most red-shifted maxima of all previously discussed, (3-10), is red-shifted with respect to (3-9) likely due to the increased conjugation through a fused-ring system rather than the freely rotating rings in (3-9). Compounds (3-5) through (3-10) all exhibit very high quantum yields in the order of (3-6) > (3-8) > (3-7) > (3-10) > (3-9) > (3-5). These yields are also comparable to that of previous analogs, which exhibited quantum yields of 75-89\%, with the exception of the triphenylamine derivative, which had a quantum yield of 46\%.\textsuperscript{38} With quantum yield measurements, it is difficult to assign a trend due to the narrow distribution of values with the combined error introduced through the comparative method. The silafluorenes (3-5) through (3-10) show fluorescence in the solid-state but the emission values were not measured.

**Table 3-3.** UV-Visible and fluorescence spectra data for silafluorenes (3-5)-(3-10). All measurements performed in CH$_2$Cl$_2$.  \textsuperscript{a}1x10\(^{-5}\) M. \textsuperscript{b}1x10\(^{-6}\) M. \textsuperscript{c}Excited at 350 nm with anthracene as a standard. \textsuperscript{d}Melting points measured by DSC. \textsuperscript{e}Decomposition temperatures (5% weight loss) measured by TGA. The $\Phi_F$ is the average value of repeated measurements within ±5\% error.

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<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}$ \textsuperscript{a} \textsuperscript{absorbance (nm)}</th>
<th>log $\varepsilon$</th>
<th>$\lambda_{\text{max}}$ \textsuperscript{b} \textsuperscript{fluorescence (nm)}</th>
<th>$\Phi_F$ \textsuperscript{c}</th>
<th>$T_m$ \textsuperscript{d}/$T_d$ \textsuperscript{e} (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3-5)</td>
<td>285, 336, 373</td>
<td>4.80</td>
<td>403, 426</td>
<td>0.80</td>
<td>245/350</td>
</tr>
<tr>
<td>(3-6)</td>
<td>287, 340, 374</td>
<td>4.93</td>
<td>405, 426</td>
<td>0.89</td>
<td>251/363</td>
</tr>
</tbody>
</table>
The thermal properties for (3-5) through (3-10) were evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), and the results are listed in Table 3-3. DSC analyses of (3-5) through (3-10) showed relatively high melting points, while no glass transition temperatures were observed. The TGA results indicate all of the new compounds have good thermal stability. The decomposition temperatures ($T_d$) corresponding to 5% weight loss were measured as 350, 363, 403, 362, 450, and 448 °C for (3-5) through (3-10), respectively, which are much higher than their carbon analogs. The order of stability in terms of decomposition is in the order of (3-9) > (3-10) > (3-7) > (3-6) > (3-8) > (3-5). This is consistent with the earlier studies which indicate that thermal stability may be improved through incorporation of a heteroatom (such as silicon) or by increasing the molecular volume.\textsuperscript{22,57,58}

While (3-5) exhibits the highest energy absorption and emission maxima, it also has the lowest quantum yield. Compound (3-6) provides the greatest quantum yield while having nearly identical maxima to that of (3-5), with the added benefit of marginally greater thermal stability. The most thermally stable compound, (3-9), is substantially red-shifted to that of (3-5) with a similarly relatively low quantum yield.
3.4. Summary and Future Work

A series of 2,7-disubstituted-alkynyl(aryl)-3,6-dimethoxy-9,9-diphenylsilafluorenes with different -alkynyl(aryl) substituents were synthesized and characterized in good yields ranging from 54-79%. All of the new silafluorenes described herein exhibit a high energy emission maxima between 403-420 nm and high fluorescence quantum yields in the range of 0.80-0.89 with fluorescence in both the solution and solid states.

Further studies of this class of molecules with different -alkynyl(aryl) substituents are currently underway which further investigate the trends elucidated in this study. Future work could include alkynyl(aryl) substituents incorporating functional groups which are sensitive to pH, ions, allowing for potential applications as chemical sensors.

3.5. Experimental

General

Unless otherwise indicated, all synthetic protocols were performed under an inert atmosphere of argon with flame-dried glassware using standard Schlenk techniques. The solvents, acetonitrile, dichloromethane, hexanes, chloroform, tetrahydrofuran, pentane and methanol were purchased from Fischer Chemical or Sigma-Aldrich, and were used as received unless noted below. For air- and moisture-sensitive reactions, tetrahydrofuran was dried over activated 4 Å sieves over several hours and then freshly distilled from Na/9-fluorenone under argon prior to use. "O"-dianisidine was purchased from Alfa Aesar and used as received. The compounds, 1-ethynyl-3-fluorobenzene, 1-ethynyl-4-phenoxybenzene, 2-ethynyl-6-methoxynaphthalene, 4-ethynylbiphenyl, 4-ethynyltoluene, 4-"tert"-butylphenylacetylene, 4-ethynylaniline, KIO3, I2, and n-BuLi in hexanes (1.6 M) were all purchased from Sigma Aldrich and used without further purification. Dichlorodiphenylsilane was purchased from Sigma Aldrich and distilled from potassium.
carbonate under argon prior to use. Both 4,4ʹ-dibromo-3,3ʹ-dimethoxy-1,1ʹ-biphenyl and 4,4ʹ-dibromo-2,2ʹ-diodo-5,5ʹ-dimethoxy-1,1ʹ-biphenyl were synthesized according to a literature procedure. Silica gel (Premium Rf, 200-400 mesh, 60 Å porosity) was purchased from Sorbent Technologies, Inc. Dichloromethane for optical spectra experiments (spectrophotometric grade) was purchased from Sigma-Aldrich and used as received.

All NMR spectra were collected on an Agilent 600 MHz (1H recorded at 600 MHz, 13C at wrong numbers -151 MHz, and 29Si at 119 MHz) or on a Bruker Avance-300 MHz (1H recorded at 300 MHz, 13C at 75 MHz, and 19F at 282 MHz) at ambient temperature unless otherwise noted. Chloroform-d₁ was purchased from Cambridge Isotopes, Inc., and used as the solvent unless otherwise indicated, and all ¹H and ¹³C spectra were referenced to residual protic solvent (for Chloroform-d₁: 7.26 ppm for ¹H and 77.36 ppm for ¹³C).

29Si{¹H} spectra were externally referenced to tetramethylsilane (0 ppm). Chemical shifts are reported in parts per million (ppm) and coupling constants reported in Hertz (Hz).

Elemental analyses were performed by Robertson Microlit Labs, Inc., Ledgewood, NJ. A JEOL M Station-JMS 700 mass spectrometer was used to obtain high resolution mass spectra by fast atom bombardment (FAB) or (EI) conditions, using 3-nitrobenzyl alcohol (NBA) as a matrix and dichloromethane as a solvent. X-ray intensity data were measured using a Bruker Apex II diffractometer equipped with a CCD area detector. Melting point determinations were obtained on a Mel-Temp melting point apparatus and are uncorrected. UV-vis and fluorescence spectra were measured on a Cary 50 Bio UV-visible and Cary Eclipse Fluorescence spectrophotometer, respectively. Emission spectra were measured using the λ_max value for each compound as determined by the absorption
spectra. Chemical shifts are reported in parts per million (ppm), with coupling constants recorded in Hertz (Hz). Gas chromatography experiments were performed using a Shimadzu GC-14A gas chromatograph; GC-MS analyses were performed on a Hewlett Packard Model 5988A GC-MS instrument. Melting points were determined on a Mel-Temp capillary melting point apparatus and are uncorrected. UV-visible spectroscopic data were collected on a Cary (Varian) 50 Bio UV-visible spectrometer. Fluorescence spectra were recorded on a Cary (Varian) Eclipse fluorescence spectrometer. Quartz cuvettes were used for optical spectra data collection. Infrared spectroscopic data were collected on a Thermo Scientific Nicolet 6700 equipped with a Smart OMNI-Sampler Germanium ATR Sampling Accessory. Thermogravimetric Analyses (TGA) were performed on a TA Instruments Q500 and Differential Scanning Calorimetry measurements were performed on a TA Instruments Q2000.

**Synthesis of 4,4’-dibromo-3,3’-dimethoxy-1,1’-biphenyl (3-2)**

Following a previously published procedure, 4-o-Dianisidine (10 g, 40.9 mmol), 41 mL 40% HBr, 160 mL H2O, and 160 mL acetonitrile were combined in a three-necked round-bottom flask (1000 mL) equipped with a pressure-equilibrating addition funnel (250 mL), thermometer and magnetic stirrer under standard atmospheric conditions. The majority of the starting material dissolved in acetonitrile. The reaction was cooled to 0 °C in an ice bath, and sodium nitrite (7.2 g, 104.4 mmol) dissolved in a minimal amount of water was chilled and added dropwise to the reaction such that the temperature does not exceed 10 °C. Following addition, the reaction mixture was stirred at below 10 °C for 30 min. To
prevent a side reaction with O\textsubscript{2} in the following step, the reaction atmosphere was purged with argon. CuBr (13.0 g, 90.6 mmol) is dissolved in 160 mL of 40\% HBr and added to the addition funnel. The CuBr/HBr solution was added over the course of 1 h such that the temperature does not exceed 10 °C. The solution is then allowed to warm to room temperature and was subsequently heated to reflux (80 °C) for at least 1 h until an insoluble white solid becomes apparent. The solution was then cooled and extracted with 250-300 mL of dichloromethane, washed with 10 wt \% NaOH and brine, and dried with MgSO\textsubscript{4} before removing the solvent by rotoevaporation. The crude, light brown powder was sufficiently pure to proceed to the next step, yield: 14.62 g, 96\%. Mp: 141-142 °C (lit. 140-143 °C).\textsuperscript{45} \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 7.58 (d, 2H), 7.06 – 7.00 (m, 4H), 3.97 (s, 6H). \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (126 MHz, CDCl\textsubscript{3}) \(\delta\) 156.6, 141.7, 134.0, 121.0, 111.8, 111.2, 56.7. These data were consistent with the literature values.\textsuperscript{45} Appendix I: 34-35.

**Synthesis of 4,4’-dibromo-2,2’-diiodo-5,5’-dimethoxy-1,1’-biphenyl (3-3)\textsuperscript{45}**

Following a previously published procedure,\textsuperscript{45} 4,4’-dibromo-3,3’-dimethoxy-1,1’-biphenyl (13.0 g, 34.9 mmol), KIO\textsubscript{3} (3.3 g, 15.4 mmol), and I\textsubscript{2} (9.6 g, 38.0 mmol) were added to a large three-neck round-bottom flask (1000 mL) equipped with a reflux condenser, thermometer, and magnetic stirrer. The starting material was dissolved in a mixture of 260 mL acetic acid and 26 mL of 20 wt\% H\textsubscript{2}SO\textsubscript{4}. The solution was heated to 80 °C for 12 h. Large amounts of insoluble product precipitated as the reaction proceeded. Once cooled to room temperature, an additional 250 mL of H\textsubscript{2}O was added to precipitate further product. The precipitate was collected by filtration, dried by
rotoevaporation, and redissolved by a minimal amount of dichloromethane. The solution was extracted with 10 wt % NaOH (25 mL), washed with brine, and dried with MgSO₄ before removing the solvent by rotoevaporation. The crude product was then purified by a silica gel plug utilizing dichloromethane as an eluent, then recrystallized in dichloromethane and ethanol. The resulting white crystalline powder was then collected by filtration, yield: 20.9 g, 96%. Mp: 148-149 °C (lit. 147-150 °C).[^1H NMR] (500 MHz, CDCl₃) δ 8.04 (s, 2H), 6.73 (s, 2H), 3.88 (s, 6H).[^13C NMR] (126 MHz, CDCl₃) δ 156.2, 148.2, 142.2, 113.3, 112.5, 87.7, 56.5. These data were consistent with literature values.[^Appendix I: 36-37]  

**Synthesis of 2,7-dibromo-3,6-dimethoxy-9,9-diphenylsilafuorene (3-4)**

![Diagram of 3-4](image)

To a flame-dried four-necked round-bottom flask (250 mL) equipped with a pressure-equilibrating addition funnel (25 mL), thermometer, and magnetic stirrer under argon, 4,4’-dibromo-2,2’-diiodo-5,5’-dimethoxy-1,1’-biphenyl (5.0 g, 8 mmol) was dissolved in freshly distilled THF (160 mL). The solution was chilled to -95 °C in a methanol/N₂ bath. At 95 °C, there is risk of the methanol bath freezing and fracturing the four-necked flask. Addition of water (H₂O:MeOH, 1:4) mitigates this possibility, resulting in a bath with a gel- or slush-like consistency even at -100 °C. At this point, the reaction mixture was stirring as rapidly as possible, such that a deep whirlpool was formed. Meanwhile, the thermometer was submerged within the reaction mixture as much as possible without disturbing the magnetic stirrer. A small cryogenic storage dewar containing liquid nitrogen was also
nearby for quick and convenient addition of liquid nitrogen during addition of \( n \)-BuLi. A syringe was charged with dichlorodiphenylsilane (3.37 mL, 16.03 mmol) and was carefully left in the septum of the reaction flask, as the silane can freeze around –90 °C within the syringe tip during addition of silane, requiring removal of the syringe to allow the frozen silane to melt before continuing the addition. This could result in the introduction of error from multiple sources. A solution of \( n \)-BuLi in hexanes (1.6 M) was removed from the 5 °C refrigerator and quickly transferred to the addition funnel to minimize the time it was allowed to warm. Although the temperature of the \( n \)-BuLi is not crucial, and haste is not a necessary component in transferring it to the addition funnel for the overall reaction yield, it did reduce the rate at which temperature increased during addition. Just prior to addition of \( n \)-BuLi, liquid nitrogen was added to the methanol bath so that the temperature was slowly decreasing below -95 °C. As soon as the temperature decreases beyond -95 °C, addition of 10.3 mL \( n \)-BuLi (1.6 M in hexanes) was then added dropwise such that it is nearly a constant stream over 2.5 min to the rapidly stirring solution, while not allowing the reaction mixture temperature to exceed -90 °C in order to ensure selectivity for a lithium-iodine exchange. Liquid nitrogen was added to the bath during the addition to mitigate increasing temperature. If the temperature appeared as if it would exceed -90 °C, the addition was halted until the temperature began decreasing. The clear solution immediately turned yellow after the first drop of \( n \)-BuLi was added. Once roughly half of the \( n \)-BuLi reagent had been added to the reaction mixture, a yellow slurry developed, which gradually redissolved as the \( n \)-BuLi addition was completed. Immediately after the addition of \( n \)-BuLi was completed, the syringe containing dichlorodiphenylsilane was quickly transferred from the storage vessel septum to the
reaction flask septum. The syringe needle was inserted just enough that the silane could be rapidly injected in a quick, smooth motion, to reduce the chances of it freezing within the syringe tip. Once the silane addition was complete, the temperature of the reaction mixture increased sharply, but did not exceed -84 °C. A small amount of liquid nitrogen was utilized to stabilize the reaction mixture temperature. Once the temperature began decreasing, the pale yellow reaction mixture was removed from the bath around -85 °C or lower and stirred overnight. During this period, the reaction mixture slowly approached room temperature over the course of an hour. The reaction mixture was then quenched with saturated ammonium chloride solution and extracted with chloroform. The organic layer was then washed with brine, dried with magnesium sulfate, and filtered. The solvent was then removed by rotoevaporation. The product was then purified by chromatography (silica gel, dichloromethane/hexane 1/1) and recrystallized in dichloromethane:ethanol. The resulting white crystalline powder (3.36 g, 76%) was then collected by filtration and confirmed by comparison to literature values.\textsuperscript{44,49} \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): δ 7.79 (s, 2H), 7.56 – 7.50 (m, 4H), 7.38 – 7.23 (m, 8H), 3.93 (s, 6H). \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (75 MHz, CDCl\textsubscript{3}): δ 158.2, 149.0, 138.2, 135.5, 134.4, 131.8, 130.5, 129.6, 128.4, 105.2, 56.4.

Appendix I: 38-39.

2,7-(1-ethynyl-3-fluorobenzene)-3,6-dimethoxy-9,9-diphenylsilafluorene (3-5)

![2,7-(1-ethynyl-3-fluorobenzene)-3,6-dimethoxy-9,9-diphenylsilafluorene (3-5)](image)

To a 15 mL three-necked round-bottom flask equipped with a reflux condenser and magnetic stirrer under argon, 2,7-dibromo-3,6-dimethoxy-9,9-diphenylsilafluorene (0.250 g, 0.453 mmol), Pd(PPh\textsubscript{3})\textsubscript{4} (0.052 g, 0.045 mmol), and CuI (0.018 g, 0.092 mmol) were
added, followed by piperidine (5.2 mL, 52.5 mmol) and 1-ethynyl-3-fluorobenzene (0.155 mL, 1.34 mmol). The reaction mixture was stirred at 80 °C overnight. The following morning, the reaction mixture was concentrated, then subsequently purified by silica gel chromatography using dichloromethane:hexane as an eluent. The product was then recrystallized in dichloromethane:pentane, and rinsed with pentane, and dried by rotoevaporation. The product was isolated as a bright yellow powder, yield: 0.190 g, 67% yield. Mp: 251-252 °C. X-ray-quality crystals were obtained by slow evaporation of a dichloromethane solution of the product at room temperature. ¹H NMR (600 MHz, CDCl₃): δ 7.88 (s, 2H), 7.65 (d, 4H), 7.49 – 7.41 (m, 2H), 7.41 – 7.28 (m, 10H), 7.27 – 7.23 (m, 2H), 7.05 – 7.00 (m, 2H), 4.09 (s, 6H). ¹³C{¹H} NMR (151 MHz, CDCl₃): δ 162.8, 162.5 (d, J_C-F = 246 Hz), 150.3, 139.0, 135.6, 132.2, 130.4, 129.9 (d, J_C-F = 9 Hz), 128.5, 128.3, 127.6 (d, J_C-F = 3 Hz), 125.5 (d, J_C-F = 9 Hz), 118.45 (d, J_C-F = 15.1 Hz), 115.6 (d, J_C-F = 21 Hz), 112.5, 104.0, 93.5 (d, J_C-F = 3 Hz), 87.2, 56.1. ²⁹Si{¹H} NMR (119 MHz, CDCl₃): δ -17.6. ¹⁹F NMR (564 MHz, CDCl₃): δ -113.1 (m). Anal. Calcd for C₄₂H₂₈F₂O₂Si: C, 79.98; H, 4.47. Found: C, 80.01; H, 4.22. HRMS (EI): calcd. for C₄₂H₂₈F₂O₂Si: 631.19049; found 630.18268. Absorption (50 μM) and emission (5 μM) (DCM): λ_abs (nm) = 285, 336, and 373. λ_em (nm) = 403 and 426. log ε = 4.80. Φ_F = 0.80. T_m/T_d (°C) = 245/350. λ_ex = 350 nm with anthracene as a standard. Appendix I: 40-43; Appendix II: 1-2.
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2,7-(4-ethynyltoluene)-3,6-dimethoxy-9,9-diphenylsilafuorene (3-6)

To a 15 mL three-necked round-bottom flask equipped with a reflux condenser and magnetic stirrer under argon, 2,7-dibromo-3,6-dimethoxy-9,9-diphenylsilafuorene (0.250 g, 0.453 mmol), Pd(PPh₃)₄ (0.052 g, 0.045 mmol), and CuI (0.018 g, 0.092 mmol) were added, followed by piperidine (5.2 mL, 52.5 mmol) and 4-ethynyltoluene (0.170 mL, 1.34 mmol). The reaction mixture was stirred at 80 °C overnight. The following morning, the reaction mixture was concentrated, then subsequently purified by silica gel chromatography using dichloromethane:hexane as an eluent. The product was then recrystallized in dichloromethane:pentane, and rinsed with pentane, and dried by rotoevaporation. The product was isolated as a bright yellow powder, yield: 0.178 g, 63% yield. Mp: 246-247 °C. X-ray-quality crystals were obtained by slow evaporation of a dichloromethane solution of the product at room temperature. ¹H NMR (600 MHz, CDCl₃): δ 7.88 (s, 2H), 7.67 – 7.64 (m, 4H), 7.48 – 7.40 (m, 6H), 7.39 – 7.34 (m, 6H), 7.17 – 7.12 (m, 4H), 4.08 (s, 6H), 2.36 (s, 6H). ¹³C{¹H} NMR (151 MHz, CDCl₃): δ 162.5, 150.0, 138.9, 138.4, 135.6, 132.5, 131.6, 130.3, 129.1, 128.39, 128.31, 120.5, 113.0, 104.0, 95.0, 85.6, 56.1, 21.6. ²⁹Si{¹H} NMR (119 MHz, CDCl₃): δ -17.6. Anal. Calcd for C₄₄H₃₄O₂Si: C, 84.85; H, 5.50. Found: C, 84.60; H, 5.54. HRMS (EI): calcd. for C₄₄H₃₄O₂Si: 622.23279; found 622.234. Absorption (50 μM) and emission (5 μM) (DCM): λₘₐₓ (nm) = 287, 336, and 373. λₑₘ (nm) = 405 and 426. log ε = 4.93. Φₕ = 0.89. Tₘ/Tₕ (°C) = 251/363. λₑₙ = 350 nm with anthracene as a standard. Appendix I: 44-46; Appendix II: 3-4.
2,7-(4-tert-butylphenylacetylene)-3,6-dimethoxy-9,9-diphenylsilafuorene (3-7)

To a 15 mL three-necked round-bottom flask equipped with a reflux condenser and magnetic stirrer under argon, 2,7-dibromo-3,6-dimethoxy-9,9-diphenylsilafuorene (0.250 g, 0.453 mmol), Pd(PPh\(_3\))\(_4\) (0.052 g, 0.045 mmol), and CuI (0.018 g, 0.092 mmol) were added, followed by piperidine (5.2 mL, 52.5 mmol) and 4-tert-butylphenylacetylene (0.242 mL, 1.34 mmol). The reaction mixture was stirred at 80 °C overnight. The following morning, the reaction mixture was concentrated, then subsequently purified by silica gel chromatography using dichloromethane:hexane as an eluent. The product was then recrystallized in dichloromethane:pentane, and rinsed with pentane, and dried by rotoevaporation. The product was isolated as a bright yellow powder, yield: 0.253 g, 79% yield. Mp: 341-342 °C. X-ray-quality crystals were obtained by slow evaporation of a dichloromethane solution of the product at room temperature. \(^1\)H NMR (600 MHz, CDCl\(_3\)): δ 7.88 – 7.86 (m, 2H), 7.67 – 7.64 (m, 4H), 7.50 – 7.47 (m, 4H), 7.45 – 7.40 (m, 2H), 7.39 – 7.34 (m, 10H), 4.07 (s, 6H), 1.32 – 1.30 (m, 18H). \(^{13}\)C\(^{1}\)H NMR (151 MHz, CDCl\(_3\)): δ 162.6, 151.5, 150.0, 138.9, 135.6, 132.5, 131.4, 130.3, 128.4, 128.3, 125.4, 120.6, 113.2, 104.1, 94.9, 85.6, 56.2, 34.9, 31.3. \(^{29}\)Si\(^{1}\)H NMR (119 MHz, CDCl\(_3\)): δ -17.6. Anal. Calcd for C\(_{50}\)H\(_{46}\)O\(_2\)Si: C, 84.94; H, 6.56. Found: C, 84.69; H, 6.45. HRMS (EI): calcd. for C\(_{50}\)H\(_{46}\)O\(_2\)Si: 706.985; found 706.32666. Absorption (50 μM) and emission (5 μM) (DCM): \(\lambda_{\text{abs}}\) (nm) = 288, 340, and 375. \(\lambda_{\text{em}}\) (nm) = 405 and 429. \(\log \varepsilon = 4.90\). \(\Phi_F = 0.85\). \(T_m/T_d\) (°C) = 301/403. \(\lambda_{\text{ex}} = 350\) nm with anthracene as a standard.

Appendix I: 47-49.; Appendix II: 5-6.
2,7-(1-ethynyl-4-phenoxybenzene)-3,6-dimethoxy-9,9-diphenylsilafluorene (3-8)

To a 15 mL three-necked round-bottom flask equipped with a reflux condenser and magnetic stirrer under argon, 2,7-dibromo-3,6-dimethoxy-9,9-diphenylsilafluorene (0.250 g, 0.453 mmol), Pd(PPh₃)₄ (0.052 g, 0.045 mmol), and CuI (0.018 g, 0.092 mmol) were added, followed by piperidine (5.2 mL, 52.5 mmol) and 1-ethynyl-4-phenoxybenzene (0.242 mL, 1.34 mmol). The reaction mixture was stirred at 80 °C overnight. The following morning, the reaction mixture was concentrated, then subsequently purified by silica gel chromatography using dichloromethane:hexane as an eluent. The product was then recrystallized in dichloromethane:pentane, and rinsed with pentane, and dried by rotoevaporation. The product was isolated as bright yellow needle-like crystals, yield: 0.240 g, 68% yield. Mp: 227-229 °C. X-ray-quality crystals were obtained by slow evaporation of a dichloromethane solution of the product at room temperature. ¹H NMR (600 MHz, CDCl₃): δ 7.87 (s, 2H), 7.66 – 7.65 (m, 4H), 7.52 – 7.51 (m, 4H), 7.45 – 7.41 (m, 2H), 7.39 – 7.34 (m, 10H), 7.14 (t, J = 12 Hz, 2H), 7.04 (d, J = 12 Hz, 4H), 6.96 (d, J = 6 Hz, 4H), 4.08 (s, 6H). ¹³C{¹H} NMR (151 MHz, CDCl₃): δ 162.6, 157.6, 156.6, 150.0, 138.8, 135.6, 133.3, 132.4, 130.3, 130.0, 128.4, 128.3, 123.9, 119.5, 118.4, 118.2, 113.0, 104.0, 94.3, 85.6, 56.1. ²⁹Si{¹H} NMR (119 MHz, CDCl₃): δ -17.6. Anal. Calcd for C₅₄H₃₈O₄Si: C, 83.26; H, 4.92. Found: C, 82.97; H, 4.83. HRMS (EI): calcd. for C₅₄H₃₈O₄Si: 778.25397; found 778.252. Absorption (50 μM) and emission (5 μM) (DCM): λ(abs) (nm) = 288, 340, and 377. λ(em) (nm) = 410 and 434. log ε = 4.90. Φ_F = 0.87.
To a 15 mL three-necked round-bottom flask equipped with a reflux condenser and magnetic stirrer under argon, 2,7-dibromo-3,6-dimethoxy-9,9-diphenylsilafluorene (0.250 g, 0.453 mmol), Pd(PPh$_3$)$_4$ (0.052 g, 0.045 mmol), and CuI (0.018 g, 0.092 mmol) were added, followed by piperidine (5.2 mL, 52.5 mmol) and 4-ethynylbiphenyl (0.239 g, 1.34 mmol). The reaction mixture was stirred at 80 °C overnight. The following morning, the reaction mixture was concentrated, then subsequently purified by silica gel chromatography using dichloromethane:hexane as an eluent. The product was then recrystallized in dichloromethane:pentane, and rinsed with pentane, and dried by rotoevaporation. The product was received as a bright yellow powder, yield: 0.183 g, 54% yield. Mp: 326-328 °C. X-ray-quality crystals were obtained by slow evaporation of a dichloromethane solution of the product at room temperature. $^1$H NMR (600 MHz, CDCl$_3$): δ 7.91 (s, 2H), 7.69 – 7.66 (m, 4H), 7.64 – 7.57 (m, 12 H), 7.47 – 7.42 (m, 6H), 7.40 – 7.34 (m, 8H), 4.11 (s, 6H). $^{13}$C{$^1$H} NMR (151 MHz, CDCl$_3$): δ 162.6, 150.1, 140.9, 140.5, 138.9, 135.6, 132.4, 132.1, 130.4, 128.9, 128.4, 128.3, 127.7, 127.1, 127.0, 122.5, 112.9, 104.0, 94.7, 87.0, 56.2. $^{29}$Si{$^1$H} NMR (119 MHz, CDCl$_3$): δ -17.6. Anal. Calcd for C$_{54}$H$_{38}$O$_2$Si: C, 86.83; H, 5.13. Found: C, 86.73; H, 4.96. Absorption (50 μM) and emission (5 μM) (DCM): λ$_{abs}$ (nm) = 292, 340, and 384. λ$_{em}$ (nm) = 417 and 440. log
\( \varepsilon = 4.82 \). \( \Phi_F = 0.82 \). \( T_m/T_d \ (^{\circ}C) = 290/450 \). \( \lambda_{em} = 350 \text{ nm} \) with anthracene as a standard.

Appendix I: 53-55; Appendix II: 9-10.

2,7-(2-ethynyl-6-methoxynaphthalene)-3,6-dimethoxy-9,9-diphenylsilafluorene (3-10)

To a 15 mL three-necked round-bottom flask equipped with a reflux condenser and magnetic stirrer under argon, 2,7-dibromo-3,6-dimethoxy-9,9-diphenylsilafluorene (0.250 g, 0.453 mmol), Pd(PPh\(_3\))\(_4\) (0.052 g, 0.045 mmol), and CuI (0.018 g, 0.092 mmol) were added, followed by piperidine (5.2 mL, 52.5 mmol) and 2-ethynyl-6-methoxynaphthalene (0.244 g, 1.34 mmol). The reaction mixture was stirred at 80 \(^{\circ}C\) overnight. The following morning, the reaction mixture was concentrated, then subsequently purified by silica gel chromatography using dichloromethane:hexane as an eluent. The product was then recrystallized in dichloromethane:pentane, and rinsed with pentane, and dried by rotoevaporation. The product was isolated as a bright yellow powder, yield: 0.185 g, 54% yield. Mp: 294-295 \(^{\circ}C\). X-ray-quality crystals were obtained by slow evaporation of a dichloromethane solution of the product at room temperature. \(^1\)H NMR (600 MHz, CDCl\(_3\)): \( \delta \) 8.01 (s, 2H), 7.93 (s, 2H), 7.73–7.67 (m, 8H), 7.60–7.57 (m, 2H), 7.46–7.42 (m, 2H), 7.40–7.37 (m, 6H), 7.19–7.14 (m, 2H), 7.12–7.11 (m, 2H), 4.12 (s, 6H), 3.93 (s, 6H). \(^{13}\)C\({}^{\text{\textsuperscript{1}H}}\) NMR (151 MHz, CDCl\(_3\)): \( \delta \) 162.6, 158.4, 150.0, 138.9, 135.6, 134.2, 132.5, 131.4, 130.3, 129.5, 129.2, 128.6, 128.4, 128.3, 126.8, 119.4, 118.5, 113.1, 105.9, 104.0, 95.4, 86.0, 56.2, 55.5. \(^{29}\)Si\({}^{\text{\textsuperscript{1}H}}\) NMR (119 MHz, CDCl\(_3\)): \( \delta \) -17.6. Anal. Calcd for C\(_{52}\)H\(_{38}\)O\(_4\)Si: C, 82.73; H, 5.07. Found: C, 82.45; H, 4.97. HRMS (EI): calcd. for
C_{52}H_{38}O_{4}Si: 754.25397; found 752.252. Absorption (50 μM) and emission (5 μM) (DCM): $\lambda_{\text{abs}}$ (nm) = 280, 340, and 388. $\lambda_{\text{em}}$ (nm) = 420 and 445. log $\varepsilon$ = 4.95. $\Phi_F$ = 0.84. $T_m/T_d$ (°C) = 280/448. $\lambda_{\text{ex}}$ = 350 nm with anthracene as a standard. Appendix I: 56-58; Appendix II: 11-12.

**Attempted synthesis of 2,7-(4-ethynylaniline)-3,6-dimethoxy-9,9-diphenylsilafluorene (3-11)**

![Chemical Structure](image)

To a 15 mL three-necked round-bottom flask equipped with a reflux condenser and magnetic stirrer under argon, 2,7-dibromo-3,6-dimethoxy-9,9-diphenylsilafluorene (0.250 g, 0.453 mmol), Pd(PPh$_3$)$_4$ (0.052 g, 0.045 mmol), and CuI (0.018 g, 0.092 mmol) were added, followed by piperidine (5.2 mL, 52.5 mmol) and 4-ethynylaniline (0.157 g, 1.34 mmol). The reaction mixture was stirred at 80 °C overnight. The following morning, the reaction mixture was concentrated, then subsequently purified by silica gel chromatography using dichloromethane:hexane as an eluent. The product was then recrystallized in dichloromethane:pentane, and rinsed with pentane, and dried by rotoevaporation. The product was isolated a brown-yellow solid, although yield was not measured. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.84 (s, 2H), 7.69 – 7.57 (m), 7.43 – 7.30 (m), 6.63 (d, $J = 8.6$ Hz), 4.07 (s, 6H), 3.81 (s, 4H), 3.50 (s), 3.24 – 3.14 (m), 1.95 (s). Appendix I: 59.
3.6. References


Chapter 4

2,7-Disubstitued Germafluorenes

4.1. Introduction

Heavier Group 14 conjugated π-electron systems containing germanium centers and alkynyl linkages provide unique electronic and optical enhancements attributed to their σ*-π* conjugation between the σ* orbital of the two exocyclic groups at the germanium center and π* orbital of the butadiene unit of the ring resulting in a low energy LUMO level analogous to what is observed for the related silicon-containing analogs.\(^1\)\(^-\)\(^16\) This σ*-π* conjugation occurs effectively as the orbitals are in phase and in a fixed perpendicular arrangement with respect to the plane of the germylene moiety. Germafluorenes are related to silafluorenes (discussed in greater detail in Chapter 3) in that they both possess the same Group 14 butadiene core (Figure 4-1).

![Diagram of fluorene, silafluorene, and germafluorene](image)

**Figure 4-1.** Generalized structures of a) fluorene, b) silafluorene, and c) germafluorene. The "R" substituents are enumerated as they are typically referred.

Commercially available blue emitting polyfluorenes generally have a much shorter lifetime compared to that of red and green emitters, often undergoing a decrease in emission and spectral broadening resulting in a low-energy green band over time.\(^17\)\(^-\)\(^19\) As a result, there has been increased interest in strong blue emitters with high quantum efficiency, lifetime, and color purity. Germafluorenes are analogs of 9,9- silafluorenes,
which have been of interest due to their deep blue emission.\textsuperscript{2,20–30} The synthesis of germafluorenes have been less studied compared to silafluorenes.\textsuperscript{31–36}

Recently, a relatively simple, inexpensive, and high-yielding route to a tetra-halogenated biphenyl system has been developed by Huang et al.,\textsuperscript{37} and recently improved by Ozin et al.\textsuperscript{38} In this method, commercially available \textit{o}-dianisidine can be brominated to form 4,4′-dibromo-3,3′-dimethoxy-1,1′-biphenyl, which by utilizing the \textit{para}-directing methoxy substituents, can undergo iodination to form 2,2′-diiodo-4,4′-dibromodiphenyl. 2,7-Dibromo-3,6-dimethoxy-9,9-diphenylgermafluorene can then be synthesized through a lithium-halogen exchange with 4,4′-dibromo-2,2′-diiodo-5,5′-dimethoxy-1,1′-biphenyl which preferentially exchanges with the iodo substituents to form the 2,2′-dilithio-4,4′-dibromo-5,5′-biphenyl intermediate.\textsuperscript{37,39}

Using a modified method to access 2,7-dibromo-3,6-dimethoxy-9,9-diphenylgermafluorene, which provided a significantly reduced experimental time with substantially increased yield, the germanium analog was formed. The final step involving the synthesis of new 2,7-disubstituted germafluorenes was achieved by a standard palladium-catalyzed Sonagashira cross-coupling of 2,7-dibromo-3,6-dimethoxy-9,9-diphenylgermafluorene with the desired -alkynyl(aryl) linkages containing different terminal aryl groups. The synthesis and characterization of the new germafluorenes are described in the following sections.

4.2. Synthetic Overview

Given the limited number of 2,7-disubstituted 9,9-diphenylsilafluorenes, only two literature procedures existed for accessing their precursor, both of which followed a nearly identical protocol (Scheme 4-1).\textsuperscript{38} In this procedure, commercially available \textit{o}-dianisidine
(4-1) undergoes a Sandmeyer reaction, converting an aromatic amino group to a diazonium salt followed by its substitution with a bromide catalyzed by copper(I) bromide, whereby the amino groups are exchanged for bromides, forming the product 4,4'-dibromo-3,3'-dimethoxy-1,1'-biphenyl (4-2). The nitrous acid was prepared in situ from sodium nitrite and hydrobromic acid based on the proposed mechanism of this procedure (Scheme 3-2). It was expected that this reaction would be readily scalable with minor deviations such as small excesses in stoichiometry or elevations in temperature relative to the literature procedure and would still result in successful formation of (4-2) in excellent yield. While investigating the utility of this procedure, it was determined that the 5,5'-methoxy substituents had minimal influence on the structure in terms of absorption and emission, and were necessary for the preparation of 4,4'-dibromo-2,2'-diiodo-5,5'-dimethoxy-1,1'-biphenyl (4-3) by directing the 2,2'-iodination (Scheme 4-2). Like the procedure for the synthesis of (4-2), it was expected the...
procedure for (4-3) would also be insensitive to deviations, also allowing for ease of scaling. Furthermore, it was anticipated that the 5,5’-methoxy substituents would not interfere subsequent steps of the reaction.\cite{37,39} Due to suspected ease of the first two steps in the overall protocol as well as there being no apparent photophysical drawbacks due to the methoxy substituent, 2,7-dibromo-3,6-dimethoxy-9,9-diphenylgermafluorene (4-4) remained a desirable candidate which was accessible by a lithium-halogen exchange (Scheme 4-3).\cite{37,39} It was expected that (4-4) could be obtained by precise control of the experimental parameters which were determined in order to preferentially perform a lithium-halogen exchange with the 2,2’-diiodo substituents rather than the 4,4’-dibromo substituents in good yield (68%).\cite{39} Once (4-4) was obtained, a series of complexes could be synthesized utilizing Sonagashira cross-coupling to form carbon-carbon bonds at the 2,7-positions. As Sonagashira cross-coupling is a well-known protocol in the literature that has been successfully utilized previously to produce 2,7-alkynyl(aryl)-3,6-dimethoxy-9,9-diphenylsilafluorene analogs (Figure 4-2),\cite{39,45} it was expected that this final step would proceed as expected. A number of commercially available arylalkynyl ligands suitable for Sonagashira cross-coupling were selected for the final step, and are depicted in Figure 4-3. The ligands which would ultimately comprise a series of 2,7-
alkynyl(aryl)-3,6-dimethoxy-9,9-diphenylsilafluorene analogs, which would differ from one another in terms of absorption, emission, melting point, quantum yield, solid state crystal packing and other physical properties, some of which could be predicted utilizing spectrochemical trends. For example, it was expected that (4-6) would be blueshifted with respect to (4-10) due to the extended π-conjugation within (4-10). The new compounds were fully characterized by $^1$H and $^{13}$C($^1$H) NMR spectroscopy, elemental analysis, melting point, HR-MS (EI) (except 4-9), UV-Vis and fluorescence spectroscopy, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Compounds 4-7, 4-9, and 4-10 were structurally characterized by X-ray crystallography.
4.3. Results and Discussion

4.3.1. Synthesis of 4,4′-dibromo-3,3′-dimethoxy-1,1′-biphenyl (4-2)\textsuperscript{38}

The synthesis of (4-2) was performed by the Sandmeyer reaction of commercially available (4-1) with HBr (40%) and sodium nitrite, in acetonitrile (Equation 4-1).

\[
\begin{align*}
\text{H}_2\text{N} & \quad \begin{array}{c}
\text{MeO} \\
\text{4-1} \\
\text{OMe} \\
\end{array} \quad \begin{array}{c}
\text{NH}_2 \\
\text{MeO} \\
\text{OMe} \\
\end{array} & \quad \xrightarrow{\text{HBr (aq), CH}_3\text{CN}} \quad \begin{array}{c}
\text{Br} \\
\text{MeO} \\
\text{OMe} \\
\end{array} \\
\text{NaNO}_2, \text{CuBr} & \quad 80 \degree \text{C}, 1 \text{ h} & \quad \text{Br} \\
& & \text{MeO} \\
\end{align*}
\]

\textbf{Equation 4-1.} Synthesis of 4,4′-dibromo-3,3′-dimethoxy-1,1′-biphenyl (4-2)\textsuperscript{38}

Following a previously published procedure,\textsuperscript{38} (4-1) was dissolved in a 3-necked flask equipped with an addition funnel containing HBr, and MeCN. The majority of (4-1) was dissolved in the MeCN as the reaction mixture was cooled to 0 °C. Chilled saturated sodium nitrate solution was then added dropwise to the reaction mixture such that the internal temperature did not exceed 10 °C. The reaction was subsequently stirred for 30 minutes maintaining the temperature below 10 °C. For addition of the CuBr solution (40% HBr), the literature procedure utilized a glass tube attachment which attached to the addition funnel stem and was submerged into the reaction mixture to prevent CuBr side reaction with atmospheric O\textsubscript{2}. As this was not available, the atmosphere within the reaction flask was purged with argon, and maintained under argon atmosphere throughout the hour-long addition. After maintaining the reaction mixture at reflux (80 °C) for at least 1 hour, the reaction mixture was cooled to room temperature and stirred for an additional hour, during which an insoluble white precipitate appeared. During this process, small bubbles should be rapidly produced and evolved from the reaction mixture, indicating loss of N\textsubscript{2} from Sandmeyer conditions. It should be noted that during aqueous workup, washing the DCM solution of (4-2) with 10 wt% NaOH results in rapid
pressure buildup, requiring constant and consistent venting of the separatory funnel as to avoid harm or injury. After workup, the solution is dried with MgSO$_4$ and filtered, resulting in a crude light brown powder in excellent yield (96%) with ≥ 95% purity (GC), suitable for the next step.

Characterization

Isolation of this compound was fairly straight forward. Once aqueous workup was completed, the resulting solid was light brown and pure enough to proceed to the next step. While, flash chromatography could be performed to remove the discoloration and obtain a white product through recrystallization in DCM:ethanol (EtOH), there was no advantage in performing purification as the following step proceeded in excess. Furthermore, the impurity was not detectable by GC/GC-MS or $^1$H NMR. For $^1$H NMR, a singlet at ca. δ 3.79 resulted from the (4-1) aryl-NH$_2$ ligand, which was absent in the product (4-2) (Figure 4-4). $^{13}$C{$^1$H} NMR results indicated uniform deshielding by 2-9 ppm, which support the substitution of a –Br ligand in place of –NH$_2$, although there were not obvious diagnostic differences.

Figure 4-4. $^1$H NMR of (4-2) showing absence of –NH$_2$ proton peak from (4-1).
4.3.2. Synthesis of 4,4’-dibromo-2,2’-diiodo-5,5’-dimethoxy-1,1’-biphenyl (4-3)\textsuperscript{38}

The starting material, (4-2), was reacted with KIO\(_3\), and I\(_2\) in an acetic acid solution and refluxed overnight (Equation 4-2).

\textbf{Equation 4-2.} Synthesis of 4,4’-dibromo-2,2’-diiodo-5,5’-dimethoxy-1,1’-biphenyl (4-3).\textsuperscript{38}

To a three-neck flask, (4-2), KIO\(_3\), and I\(_2\) were dissolved in glacial acetic acid, which was further acidified by H\(_2\)SO\(_4\) (20%), then refluxed overnight. As the reaction proceeded, a large amount of precipitate formed. Once cooled to room temperature, H\(_2\)O. After workup, the product was obtained as a crude light brown powder in excellent yield (96%) with ≥ 95% purity (GC). Although utilizing this material as a light brown powder was not ideal.

**Characterization**

Recrystallization in DCM:EtOH resulted in products with progressively greater purity, however, the recrystallization process resulted in diminishing returns and never provided a fully white product. Flash chromatography was performed using 1:1 DCM:hexanes, removing the vast majority of the brown impurity. The desired product would elute as a clear fraction. The brown impurity occasionally remained, but could be further diminished in the isolated product by recrystallization in DCM:EtOH. Since the impurity was not detectable by GC/GC-MS or \(^1\)H NMR, both characterization methods did not show an improved purity, even when the material was completely white. As stoichiometry was of the utmost importance in reaction to follow, there was concern that
the brown impurity had an influence on the stoichiometry of the reaction when treated as a fully pure product. Because of this, flash chromatography and recrystallization was performed for this step repeatedly until the isolated product was white or off-white. The next step was viewed as a bottle-neck for throughput for the entire protocol, as high yields were initially difficult to obtain, and could still be drastically diminished if experimental parameters were not tightly constrained. The $^1$H NMR spectrum (Figure 4-5) for (4-2), the proton between the methoxy substituent and the five-membered ring is observed as a doublet at ca. 7.58 ppm showing long-range coupling to the other set of ortho-protons. In (4-3) this resonance is deshielded to ca. δ 8.0 as a singlet. The deshielding also supports than an iodo substituent has been coordinated to the aromatic ring. Finally, while (4-2) possessed a doublet and multiplet in the aromatic region, (4-3) exhibits two singlet resonances, which integrate to two protons each, relative to that of the methoxy substituent at ca δ 4.0, suggesting that each of the two protons that are related by symmetry and are also isolated from one another. $^{13}$C{$^1$H} NMR indicated a substantial increase in shielding parameter for the iodo-substituted carbon (Figure 4-6). This diagnostic resonance is also useful for the characterization of (4-4) as it will once again undergo a substantial change in shielding parameter once reacted with the dichlorodiphenylgermane moiety.
Figure 4-5. $^1$H NMR of (4-3) showing absence of the double resonance from the internal proton in (4-3) from (4-2).

Figure 4-6. $^{13}$C{ $^1$H} NMR of (4-3) showing the substantial increased shielding resultant from iodo coordination.

4.3.3. Synthesis of 2,7-dibromo-3,6-dimethoxy-9,9-diphenyldiphenyldifluorone (4-4)\textsuperscript{37,39}
The 1,1,-diphenyl-2,7-dibromo-3,6-dimethoxy-silafluorene (4-4) was prepared according to the procedure shown in Equation 4-3, in a reaction with conditions analogous to those described for the related silicon analog (Equation 4-3). A lithium-halogen exchange reaction was involved in the initial step followed by subsequent addition of dichlorodiphenylgermane to form (4-4) (Equation 4-3).

**Equation 4-3.** Synthesis of 2,7-dibromo-3,6-dimethoxy-9,9-diphenylgermafluorene (4-4).\(^{37,39}\)

The precursor, dichlorodiphenylgermane is significantly more expensive than dichlorodiphenylsilane. Due to this, the following procedure is performed exactly as that of the synthesis of 2,7-dibromo-3,6-dimethoxy-9,9-diphenylsilafuorene (3-4), except instead of adding 2 equiv. of silane, 1.1 equiv of germane is added. The synthetic challenges and considerations of this procedure are described in comprehensive detail in Chapter 3, Section 3.3.3. It is important that the reaction procedure and conditions are followed carefully for this reaction to be successful (see Experimental Section 4.4 for experimental details).

A four-necked flask containing compound (4-3) was dissolved in freshly distilled THF (see Experimental). The solution was chilled to -95 °C, at which point addition of n-BuLi occurred. The reaction was immediately quenched by rapid addition of dichlorodiphenylgermane. The reaction mixture was immediately removed from the methanol bath, at which point it warmed to room temperature and stirred overnight. The product (4-4) was purified by column chromatography and isolated in 67% yield.
Characterization

The $^1$H NMR spectrum (Figure 4-7) of (4-4) exhibited a series of complex resonances for the aromatic protons from $\delta$ 7.41-7.59. The most diagnostic feature indicating the formation of the heterocycle was the singlet at 7.88 which represented the isolated proton between the methoxy substituent and the five-membered ring. The singlet at 4.01 which integrated for six protons was associated with the methoxy groups. These values were similar to that of the silicon analog discussed in Chapter 3 as well as its literature values.$^{37,39}$

The $^{13}$C{$^1$H} NMR spectrum (Figure 4-8) of (4-4) exhibited ten resonances for the aromatic carbons from $\delta$ 105.8-157.7. The resonance at $\delta$ 157.7 was associated with the ring carbons bearing the methoxy groups while the resonance at $\delta$ 105.8 was associated with the $\alpha$-C-Br carbon of the central five-membered ring. The resonance for the methoxy substituents appeared at $\delta$ 56.4. These values were similar to that of the silicon analog discussed in Chapter 3 as well as its literature values.$^{37,39}$
Figure 4-7. Comparison of the $^1$H NMR spectra of the starting material (4-3) and (4-4).

Figure 4-8. Comparison of the $^{13}$C{$^1$H} NMR spectra of the starting material (4-3) and (4-4).

4.3.4. Synthesis of 2,7-alkynyl(aryl)-3,6-dimethoxy-9,9-diphenylgermafluorenes
4.3.4.1. 2,7-(1-ethynyl-3-fluorobenzene)-3,6-dimethoxy-9,9-diphenylgermafluorene (4-5)

The synthesis of (4-5) was performed by the reaction of (4-4) with Pd(PPh3)4, CuI, and 1-ethynyl-3-fluorobenzene in piperidine overnight at 80 °C (Equation 4-4).

**Equation 4-4.** Synthesis of 2,7-(1-ethynyl-3-fluorobenzene)-3,6-dimethoxy-9,9-diphenylgermafluorene (4-5).

The reactants, (4-4), Pd(PPh3)4, CuI, and 1-ethynyl-3-fluorobenzene were dissolved in piperidine under an argon atmosphere. The reaction flask was submerged in an oil bath and stirred overnight at 80 °C. After stirring for 1 h at 80 °C, the reaction mixture faintly fluoresced upon irradiation at 365 nm from a handheld UV lamp, indicating formation of product. The reaction mixture was cooled to room temperature the following morning, at which point it appeared orange and gel-like. The product was purified by silica gel chromatography followed by recrystallization and (4-5) was obtained as a yellow solid in good yield (67%).

**Characterization**

The 1H NMR spectrum (Figure 4-9) of (4-5) exhibited a series of complex resonances for the aromatic protons from δ 7.03-7.59. The most diagnostic feature indicating the formation of the heterocycle was the singlet at δ 7.85 which represented the isolated proton between the methoxy substituent and the five-membered ring. The singlet at δ 4.09 which integrated for six protons was associated with the methoxy groups. These values corresponded to literature values for similar structures.39,45
The $^{13}$C-$^{1}$H NMR spectrum (Figure 4-10) of (4-5) exhibited 16 resonances, some with $^{19}$F coupling, for the aromatic carbons from δ 104.7-162.5. The alkynyl carbons exhibited resonances at δ 93.7 (d, $J_{C:F} = 3.4$ Hz) and 87.2. The resonance for the methoxy substituents appeared at δ 56.2. These values corresponded to literature values for similar structures.$^{39,45}$

UV-Vis and fluorescence spectroscopy measurements were also performed, and are discussed comparatively with other complexes in the summary to this chapter (Figures 4-11 and 4-12).
Figure 4-9. Comparison of the $^1$H NMR spectra of the starting material (4-4) and (4-5).

Figure 4-10. Comparison of the $^{13}$C{$^1$H} NMR spectra of the starting material (4-4) and (4-5).
Figure 4-11. Normalized UV/Vis spectrum of (4-5). $\lambda_{\text{abs}}$ (nm) (50 $\mu$M, DCM) = 278, 331, and 371.

Figure 4-12. Normalized fluorescence spectrum of (4-5) collected at the $\lambda_{\text{max}}$ absorption value. $\lambda_{\text{em}}$ (nm) (5 $\mu$M, DCM) = 401 and 424.
4.3.4.2. 2,7-(4-ethynyltoluene)-3,6-dimethoxy-9,9-diphenylgermafluorene (4-6)

The synthesis of (4-6) was performed by the reaction of (4-4) with Pd(PPh$_3$)$_4$, CuI, and 4-ethynyltoluene in piperidine overnight at 80 °C (Equation 4-5).

![Equation 4-5. Synthesis of 2,7-(4-ethynyltoluene)-3,6-dimethoxy-9,9-diphenylgermafluorene (4-6).](image)

The reactants, (4-4), Pd(PPh$_3$)$_4$, CuI, and 4-ethynyltoluene were dissolved in piperidine under an argon atmosphere. The reaction flask was submerged in an oil bath and stirred overnight at 80 °C. After stirring for 1 h at 80 °C, the reaction mixture faintly fluoresced upon irradiation at 365 nm from a handheld UV lamp, indicating formation of product. The orange reaction mixture was cooled to room temperature the following morning. The product was purified by silica gel chromatography followed by recrystallization and (4-6) was obtained as a yellow solid in good yield (63%).

Characterization

The $^1$H NMR spectrum (Figure 4-13) of (4-6) exhibited a series of complex resonances for the aromatic protons from $\delta$ 7.15-7.60. The most diagnostic feature indicating the formation of the heterocycle was the singlet at $\delta$ 7.86 which represented the isolated proton between the methoxy substituent and the five-membered ring. The singlet at $\delta$ 4.09 which integrated for six protons was associated with the methoxy groups. The singlet at $\delta$ 2.37 represented the methyl groups of the 4-tolylethynyl ligand and integrated to six protons. These values corresponded to literature values for similar structures.$^{39,45}$
The $^{13}$C{\textsuperscript{1}H} NMR spectrum (Figure 4-14) of (4-6) exhibited 13 resonances for the aromatic carbons from $\delta$ 104.7-162.1. The alkynyl carbons exhibited resonances at $\delta$ 95.2 and 85.6. The resonance for the methoxy substituents appeared at $\delta$ 56.2, and the resonance for the methyl groups from 4-ethynyltoluene appeared at 21.7. These values corresponded to literature values for similar structures.$^{39,45}$ UV-Vis and fluorescence spectroscopy measurements were also performed, and are discussed comparatively with other complexes in the summary to this chapter (Figures 4-15 and 4-16).
Figure 4-13. Comparison of the $^1$H NMR spectra of the starting material (4-4) and (4-6).

Figure 4-14. Comparison of the $^{13}$C($^1$H) NMR spectra of the starting material (4-4) and (4-6).
Figure 4-15. Normalized UV/Vis spectrum of (4-6). $\lambda_{\text{abs}}$ (nm) (50 $\mu$M, DCM) = 274, 332, and 375.

Figure 4-16. Normalized fluorescence spectrum of (4-6) collected at the $\lambda_{\text{max}}$ absorption value. $\lambda_{\text{em}}$ (nm) (5 $\mu$M, DCM) = 404 and 427.
4.3.4.3. 2,7-(4-tert-butylphenylacetylene)-3,6-dimethoxy-9,9-diphenylgermafluorene (4-7)

The synthesis of (4-7) was performed by the reaction of (4-4) with Pd(PPh₃)₄, CuI, and 4-tert-butylphenylacetylene in piperidine overnight at 80 °C (Equation 4-6).

\[ \text{Equation 4-6. Synthesis of 2,7-(4-tert-butylphenylacetylene)-3,6-dimethoxy-9,9-diphenylgermafluorene (4-7).} \]

The reactants, (4-4), Pd(PPh₃)₄, CuI, and 4-tert-butylphenylacetylene were dissolved in piperidine under an argon atmosphere. The reaction flask was submerged in an oil bath and stirred overnight at 80 °C. After stirring for 1 h at 80 °C, the reaction mixture faintly fluoresced upon irradiation at 365 nm from a handheld UV lamp, indicating formation of product. The reaction mixture was cooled to room temperature the following morning, at which point an orange precipitate formed. The product was purified by silica gel chromatography followed by recrystallization and obtained as a yellow solid in good yield (79%).

**Characterization**

The ¹H NMR spectrum (Figure 4-17) of (4-7) exhibited a series of resonances for the aromatic protons from δ 7.41-7.59. The most diagnostic feature indicating the formation of the heterocycle was the singlet at δ 7.88 which represented the isolated proton between the methoxy substituent and the five-membered ring. The singlet at δ 4.01 which integrated for six protons was associated with the methoxy groups. The singlet at δ 2.17
represented the \( t \)-butyl groups from the 4-\( tert \)-butylphenylalkynyl ligand and integrated to 18 protons. These values corresponded to literature values for similar structures.\textsuperscript{39,45}

The \( ^{13}\text{C} \{^1\text{H} \} \) NMR spectrum (Fig. 4-18) of (4-7) exhibited 13 resonances for the aromatic carbons from \( \delta \) 104.8-162.2. The alkynyl carbons exhibited resonances at \( \delta \) 95.2 and 85.6. The resonance for the methoxy substituents appeared at \( \delta \) 56.3, and the resonances for the \( t \)-butyl groups for the 4-\( tert \)-butylphenylalkynyl ligand appeared at 34.9 and 31.3. These values corresponded to literature values for similar structures.\textsuperscript{39,45} UV-Vis and fluorescence spectroscopy measurements were also performed, and are discussed comparatively with other complexes in the summary to this chapter (Figures 4-19 and 4-20).
Figure 4-17. Comparison of the $^1\text{H}$ NMR spectra of the starting material (4-4) and (4-7).

Figure 4-18. Comparison of the $^{13}\text{C}[^1\text{H}]$ NMR spectra of the starting material (4-4) and (4-7).
Figure 4-19. Normalized UV/Vis spectrum of (4-7). $\lambda_{\text{abs}}$ (nm) (50 $\mu$M, DCM) = 274, 332, and 374.

Figure 4-20. Normalized fluorescence spectrum of (4-7) collected at the $\lambda_{\text{max}}$ absorption value. $\lambda_{\text{em}}$ (nm) (5 $\mu$M, DCM) = 404 and 428.
4.3.4.4. 2,7-(1-ethynyl-4-phenoxybenzene)-3,6-dimethoxy-9,9-diphenylgermafluorene (4-8)

The synthesis of (4-8) was performed by the reaction of (4-4) with Pd(PPh$_3$)$_4$, CuI, and 1-ethynyl-4-phenoxybenzene in piperidine overnight at 80 °C (Equation 4-7).

![Equation 4-7. Synthesis of 2,7-(1-ethynyl-4-phenoxybenzene)-3,6-dimethoxy-9,9-diphenylgermafluorene (4-8).]

The reactants, (4-4), Pd(PPh$_3$)$_4$, CuI, and 1-ethynyl-4-phenoxybenzene were dissolved in piperidine under an argon atmosphere. The reaction flask was submerged in an oil bath and stirred overnight at 80 °C. After stirring for 1 h at 80 °C, the reaction mixture faintly fluoresced upon irradiation at 365 nm from a handheld UV lamp, indicating formation of product. The reaction mixture was cooled to room temperature the following morning, at which point it appeared orange and gel-like. The product was purified by silica gel chromatography followed by recrystallization and obtained as yellow needles in good yield (68%).

Characterization

The $^1$H NMR spectrum (Figure 4-21) of (4-8) exhibited a series of multiplet resonances for the aromatic protons from $\delta$ 6.96-7.59. The most diagnostic feature indicating the formation of the heterocycle was the singlet at $\delta$ 7.85 which represented the isolated proton between the methoxy substituent and the five-membered ring. The singlet at $\delta$ 4.08 which integrated for six protons was associated with the methoxy groups. These values corresponded to literature values for similar structures.$^{39,45}$
The $^{13}\text{C}^\text{'H}'$ NMR spectrum (Fig. 4-22) of (4-8) exhibited 18 resonances for the aromatic carbons from $\delta$ 104.7-162.1. The alkynyl carbons exhibited resonances at $\delta$ 94.6 and 85.7. The resonance for the methoxy substituents appeared at $\delta$ 56.2, which integrated to six protons. These values corresponded to literature values for similar structures.$^{39,45}$ UV-Vis and fluorescence spectroscopy measurements were also performed, and are discussed comparatively with other complexes in the summary to this chapter (Figures 4-23 and 4-24).
Figure 4-21. Comparison of the $^1$H NMR spectra of the starting material (4-4) and (4-8).

Figure 4-22. Comparison of the $^{13}$C$[^1]$H NMR spectra of the starting material (4-4) and (4-8).
Figure 4-23. Normalized UV/Vis spectrum of (4-8). $\lambda_{\text{abs}}$ (nm) (50 $\mu$M, DCM) = 274, 333, and 377.

Figure 4-24. Normalized fluorescence spectrum of (4-8) collected at the $\lambda_{\text{max}}$ absorption value. $\lambda_{\text{em}}$ (nm) (5 $\mu$M, DCM) = 409 and 433.
4.3.4.5. 2,7-(4-ethynylbiphenyl)-3,6-dimethoxy-9,9-diphenylgermafluorene (4-9)

The synthesis of (4-9) was performed by the reaction of (4-4) with Pd(PPh₃)₄, CuI, and 4-ethynylbiphenyl in piperidine overnight at 80 °C (Equation 4-8).

\[
\text{Equation 4-8. Synthesis of 2,7-(4-ethynylbiphenyl)-3,6-dimethoxy-9,9-diphenylgermafluorene (4-9).}
\]

The reactants, (4-4), Pd(PPh₃)₄, CuI, and 4-ethynylbiphenyl were dissolved in piperidine under an argon atmosphere. The reaction flask was submerged in an oil bath and stirred overnight at 80 °C. After stirring for 1 h at 80 °C, the reaction mixture faintly fluoresced upon irradiation at 365 nm from a handheld UV lamp, indicating formation of product. The reaction mixture was cooled to room temperature the following morning, at which point a yellow precipitate formed. The product was purified by silica gel chromatography followed by recrystallization and obtained as a yellow solid in moderate yield (54%).

Characterization

The \(^1\)H NMR spectrum (Figure 4-25) of (4-9) exhibited a series of multiplet resonances for the aromatic protons from δ 7.37-7.67. The most diagnostic feature indicating the formation of the heterocycle was the singlet at δ 7.91 which represented the isolated proton between the methoxy substituent and the five-membered ring. The singlet at δ 4.11 which integrated for six protons was associated with the methoxy groups. These values corresponded to literature values for similar structures.\(^{39,45}\)

The \(^{13}\)C\(^{\text{(1H)}}\) NMR spectrum (Fig. 4-26) of (4-9) exhibited 17 resonances for the aromatic carbons from δ 101.1-162.2. The alkynyl carbons exhibited resonances at δ 95.0 and
87.1. The resonance for the methoxy substituents appeared at δ 56.3, which integrated to six protons. These values corresponded to literature values for similar structures.\textsuperscript{39,45} UV-Vis and fluorescence spectroscopy measurements were also performed, and are discussed comparatively with other complexes in the summary to this chapter (Figures 4-27 and 4-28).
Figure 4-25. Comparison of the ¹H NMR spectra of the starting material (4-4) and (4-9).

Figure 4-26. Comparison of the ¹³C{¹H} NMR spectra of the starting material (4-4) and (4-9).
Figure 4-27. Normalized UV/Vis spectrum of (4-9). $\lambda_{\text{abs}}$ (nm) (50 $\mu$M, DCM) = 286, 334, and 384.

Figure 4-28. Normalized fluorescence spectrum of (4-9) collected at the $\lambda_{\text{max}}$ absorption value. $\lambda_{\text{em}}$ (nm) (5 $\mu$M, DCM) = 417 and 440.
4.3.4.6. 2,7-(2-ethynyl-6-methoxynaphthalene)-3,6-dimethoxy-9,9-
diphenylgermafluorene (4-10)

The synthesis of (4-10) was performed by the reaction of (4-4) with Pd(PPh₃)₄, CuI, and 2-ethynyl-6-methoxynaphthalene in piperidine overnight at 80 °C (Equation 4-9).

Equation 4-9. Synthesis of 2,7-(2-ethynyl-6-methoxynaphthalene)-3,6-dimethoxy-9,9-
diphenylgermafluorene (4-10).

The reactants, (4-4), Pd(PPh₃)₄, CuI, and 2-ethynyl-6-methoxynaphthalene were dissolved in piperidine under an argon atmosphere. The reaction flask was submerged in an oil bath and stirred overnight at 80 °C. After stirring for 1 h at 80 °C, the reaction mixture faintly fluoresced upon irradiation at 365 nm from a handheld UV lamp, indicating formation of product. The reaction mixture was cooled to room temperature the following morning, at which point a yellow precipitate formed. The product was purified by silica gel chromatography followed by recrystallization and obtained as a yellow solid in moderate yield (54%).

Characterization

The ¹H NMR spectrum (Figure 4-29) of (4-10) exhibited a series of complex resonances for the aromatic protons from δ 7.11-8.00. The most diagnostic feature indicating the formation of the heterocycle was the singlet at δ 7.90 which represented the isolated proton between the methoxy substituent and the five-membered ring. The singlets at δ 4.11 and 3.93 which integrated for six protons each were associated with the methoxy
groups on the germafluorene and 2-ethynyl-6-methoxynaphthalene, respectively. These values corresponded to literature values for similar structures.\textsuperscript{39,45}

The $^{13}$C\{$^1$H\} NMR spectrum (Figure 4-30) of (4-10) exhibited 19 resonances for the aromatic carbons from $\delta$ 104.8-162.2. The alkynyl carbons exhibited resonances at $\delta$ 95.6 and 86.1. The resonance for the methoxy substituents appeared at $\delta$ 56.3 and 55.5, which integrated to six protons each. These values corresponded to literature values for similar structures.\textsuperscript{39,45} UV-Vis and fluorescence spectroscopy measurements were also performed, and are discussed comparatively with other complexes in the summary to this chapter (Figures 4-31 and 4-32).
Figure 4-29. Comparison of the $^1$H NMR spectra of the starting material (4-4) and (4-10).

Figure 4-30. Comparison of the $^{13}$C($^1$H) NMR spectra of the starting material (4-4) and (4-10).
Figure 4-31. Normalized UV/Vis spectrum of (4-10). \( \lambda_{\text{abs}} \) (nm) (50 \( \mu \text{M}, \text{DCM} \)) = 278, 336, and 388.

Figure 4-32. Normalized fluorescence spectrum of (4-10) collected at the \( \lambda_{\text{max}} \) absorption value. \( \lambda_{\text{em}} \) (nm) (5 \( \mu \text{M}, \text{DCM} \)) = 418 and 443.
4.3.5. X-Ray Crystal Structures

Crystals of sufficient quality for germafluorenes (4-7), (4-9), and (4-10) were grown by slow evaporation from chloroform or dichloromethane (see the Experimental Section) as thin yellow needles which shimmered blue under ambient lighting conditions. The structures were solved and refined to reasonable geometries and residual electron densities by Dr. Nigam P. Rath, the departmental crystallographer at UM-St. Louis, and are summarized in Table 4-1. A summary of the crystal data and intensity parameters for the crystal structures that were obtained are provided in Appendix II (13 through 18).

<table>
<thead>
<tr>
<th>Table 4-1. Crystallographic and Data Collection Parameters for (4-7), (4-9), and (4-10).</th>
<th>4-7</th>
<th>4-9</th>
<th>4-10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
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<td>C₅₄H₃₈O₂Ge</td>
<td>C₅₂H₃₈O₄Ge</td>
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<td>P 1</td>
<td>P2₁/c</td>
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<td>12.3334(8)</td>
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<td>c, Å</td>
<td>19.8723(10)</td>
<td>13.7595(9)</td>
<td>11.1484(13)</td>
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<td>114.807(3)</td>
<td>90</td>
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<td>90</td>
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<td>1961.0(2)</td>
<td>2111.7(3)</td>
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The molecular structures of (4-7), (4-9), and (4-10) are shown in Figures 4-33, 4-34, and 4-35, respectively. All compounds exhibit similar structural parameters within the germafluorene core to that of silafluorenes (3-5) through (3-10) as well as previously published silafluorene analogs. For silafluorenes (3-5) through (3-10), the average Si-C distance in the five-member core of the silafluorene analogs is 1.8753 Å, while the average Ge-C distance for germafluorenes (4-5) through (4-10) is 1.9346 Å. For silafluorenes (3-5) through (3-10), the average α-β carbon distance is 1.4110 Å, while the average α-β carbon distance for germafluorenes (4-5) through (4-10) is 1.3985 Å. For silafluorenes (3-5) through (3-10), the average β-β carbon distances is 1.4850 Å, while the average β-β carbon distance for germafluorenes (4-5) through (4-10) is 1.4903 Å. The decreased electronegativity of germanium results in an average elongated M-C distance in germafluorenes (4-5) through (4-10) with respect to silafluorenes (3-5) through (3-10), also affecting the average α-β carbon distance. Meanwhile, the β-β carbon distance for all heterofluorenes discussed remains relatively unchanged. The average C-Si-C angle for silafluorenes (3-5) through (3-10) is 90.495°, while the average C-Ge-C angle for germafluorenes (4-5) through (4-10) is 109.2867°. The average Si-α-β carbon angle for silafluorenes (3-5) through (3-10) is 110.0267°, while the average Ge-α-β carbon angle

<table>
<thead>
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<th>$Z$</th>
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</thead>
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<tr>
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<td>1.014</td>
<td>0.983</td>
</tr>
</tbody>
</table>
for germafluorenes (4-5) through (4-10) is 99.455°. The average α-β-β carbon angle for silafluorenes (3-5) through (3-10) is 114.6508°, while the average α-β-β carbon angle for germafluorenes (4-5) through (4-10) is 115.83°. These differences in angles are resultant from the differences in M-C distances in both ranges of heterofluorenes. These parameters are consistent with that of similar published germafluorenes. Compound (4-10) has the 2,7-substituents coplanar with its germafluorene core, with a torsion angles of 61.87° and 172.26°. Both m-fluorophenyl substituents on compound (4-7) are substantially twisted out of plane with torsion angles of 9.87° (C25-C24-C28-C33) and 112.72° (C6-C5-C9-C14). For the biphenyl substituents in compound (4-9), the phenyl rings immediately bound to the germafluorene core have torsion angles of 32.43° (C2-C3-C15-C16) and 37.52° (C17-C18-C21-C22), while their respective phenyl rings are both twisted 169.42° (C11-C10-C29-C34) and 32.86° (C33-C32-C35-40) with respect to the former rings. For compound (4-10), the 6-methoxynaphthalene substituents are both twisted 61.87° (C2-C3-C15-C16) and 172.26° (C11-C10-C28-C37) with respect to the germafluorene core. Compounds (4-7), (4-9), and (4-10) all crystallized in a parallel arrangement, but are offset partially due to the phenyl rings on the germanium moiety, which sterically block the majority of intermolecular overlap.

Compounds (4-9) and (4-10) crystallized with intermolecular distances between adjacent molecules of 7.045 and 9.068 Å, eliminating any possibility of π-stacking interactions. Compound (4-7) possesses intermolecular aromatic ring distances of 4.000 Å, but are offset such that there is minimal intermolecular orbital overlap between conjugated systems (Figures 4-36 through 4-38).
Figure 4-33. Molecular structure of (4-7). Hydrogen atoms and solvent molecules have been removed for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å), bond angles (deg), and torsion angles (deg) for (4-7): Ge1-C1 = 1.935(2), Ge1-C20 = 1.937(2), Ge1-C39 = 1.930(2), Ge1-C45 = 1.932(2), C1-C2 = 1.407(3), C2-C3 = 1.395(3), C3-C4 = 1.381(3), C4-C5 = 1.405(3), C5-C6 = 1.400(3), C2-C21 = 1.490(3), C20-C21 = 1.407(3), C21-C22 = 1.392(3), C22-C23 = 1.381(3), C23-C24 = 1.411(3), C24-C25 = 1.392(3), C1-C6 = 1.388(3), C20-C25 = 1.386(3), O1-C4 = 1.369(2), O1-C19 = 1.421(3), O2-C23 = 1.357(2), O2-C38 = 1.424(3), C5-C7 = 1.438(3), C7-C8 = 1.194(3), C24-C26 = 1.430(3), C26-C27 = 1.196(3), C39-Ge1-C45 = 108.91(9), C2-C1-Ge1 = 109.43(14), C1-C2-C21 = 116.14(18), C20-C21-C2 = 115.57(18), C21-C20-Ge1 = 109.67(14), C1-Ge1-C20 = 89.16(8), C4-O1-C19 = 117.39(17), C23-O2-C38 = 117.59(16), C6-C5-C9-C14 = 112.72, C25-C24-C28-C3 = 39.87.
Figure 4-34. Molecular structure of (4-9).
Hydrogen atoms and solvent molecules have been removed for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å), bond angles (deg), and torsion angles (deg) for (4-9): Ge1-C1 = 1.9376(13), Ge1-C12 = 1.9399(13), Ge1-C47 = 1.9255(14), Ge1-C41 = 1.9385(14), C1-C2 = 1.3857(18), C2-C3 = 1.3977(19), C3-C4 = 1.4064(19), C4-C5 = 1.3858(18), C5-C6 = 1.3945(18), C6-C7 = 1.4838(18), C7-C8 = 1.3954(19), C8-C9 = 1.3857(18), C9-C10 = 1.4103(19), C10-C11 = 1.3929(19), C11-C12 = 1.3894(18), C1-C6 = 1.4022(19), C7-C12 = 1.4045(18), O1-C4 = 1.3570(16), O1-C53 = 1.4263(17), O2-C9 = 1.3591(16), O2-C54 = 1.4234(17), C3-C13 = 1.4283(18), C13-C14 = 1.2017(19), C10-C27 = 1.4287(18), C27-C28 = 1.1979(19), C47-Ge1-C41 = 114.70(6), C6-C1-Ge1 = 109.13(9), C1-C6-C7 = 116.31(11), C12-C7-C6 = 116.06(12), C7-C12-Ge1 = 109.10(9), C1-Ge1-C12 = 89.20(6), C4-O1-C53 = 117.09(11), C9-O2-C54 = 117.87(11), C2-C3-C15-C16 = 32.43, C17-C18-C21-C22 = 37.52, C11-C10-C29-C34 = 169.42, C33-C32-C35-40 = 32.86.
Figure 4-35. Molecular structure of (4-10).
Hydrogen atoms and solvent molecules have been removed for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å), bond angles (deg), and torsion angles (deg) for (4-10): Ge1-C1 = 1.939(8), Ge1-C12 = 1.919(9), Ge1-C39 = 1.959(9), Ge1-C45 = 1.908(9), C1-C2 = 1.382(11), C2-C3 = 1.374(11), C3-C4 = 1.428(12), C4-C5 = 1.373(11), C5-C6 = 1.386(11), C6-C7 = 1.497(11), C7-C8 = 1.400(11), C8-C9 = 1.409(11), C9-C10 = 1.373(12), C10-C11 = 1.384(11), C11-C12 = 1.379(11), C1-C6 = 1.412(11), C7-C12 = 1.398(11), O1-C4 = 1.354(10), O1-C51 = 1.450(10), O3-C9 = 1.352(10), O3-C52 = 1.440(10), C3-C13 = 1.426(12), C13-C14 = 1.185(11), C10-C26 = 1.444(12), C26-C27 = 1.185(11), C45-Ge1-C39 = 116.3(4), C6-C1-Ge1 = 109.3(6), C1-C6-C7 = 115.5(8), C12-C7-C6 = 115.4(8), C7-C12-Ge1 = 110.5(6), C1-Ge1-C12 = 89.1(4), C4-O1-C51 = 117.4(7), C9-O3-C52 = 117.1(7), C2-C3-C15-C16 = 61.87, C11-C10-C28-C37 = 172.26.

Figure 4-36. The packing arrangement of (4-7) illustrating separation of adjacent molecules.
**Figure 4-37.** The packing arrangement of (4-9) illustrating separation of adjacent molecules.

**Figure 4-38.** The packing arrangement of (4-10) illustrating separation of adjacent molecules.
4.3.6. Absorption and Fluorescence Studies

All of the new germafluorenes were observed to have strong blue emission both in solution and the solid-state and whose physical properties vary upon the alkynyl(aryl) linkages employed. All compounds exhibit similar absorption and emission spectra. The normalized UV-vis absorption and emission spectra of (4-5) through (4-10) are shown in Figures 4-39 and 4-40, and are labeled in the order of their absorptive and emissive energies: ((4-5) > (4-6) > (4-7) > (4-8) > (4-9) > (4-10)). Details of their photophysical properties are summarized in Table 4-2. All of the electronic transitions of germafluorenes (4-5) through (4-10) arise from π-π* transitions where the electron transitions are from the HOMO/HOMO-1 and LUMO/LUMO+1, which are significantly delocalized over the entire bridged germafluorene network. The median absorption of 376 nm for (4-5) through (4-10) is similar to that of the silafluorene analogs (3-5) through (3-10), 371 nm. These are also in agreement for the theoretical absorption spectra for similar germafluorenes, which arise from the heterofluorene core. The related previously synthesized silafluorene analogs exhibit similar experimental absorption and emission values except for the terminal triphenylamine derivative which showed red-shifted absorption and emission properties. In general, strong π-donor and π-acceptor substituents can exhibit considerably red-shifted absorption and emission maxima with respect to groups which are primarily inductive, while extending conjugation also results in red-shifts. Compounds (4-5) through (4-10) follow this general trend. The new compounds, (4-5) through (4-7) incorporate inductive substituents at their -alkynyl(aryl) substituents, while (4-8) through (4-10) incorporate π-accepting substituents which also extend the conjugation. The absorption and emission maxima are nearly identical for
Figure 4-39. Overlay of all normalized UV-Vis spectra for (4-5)-(4-10). $\lambda_{\text{abs}}$ (nm) (50 μM, DCM): (4-5), 278, 331, 371. (4-6), 274, 332, 375. (4-7), 274, 332, 374. (4-8), 274, 333, 377. (4-9), 286, 334, 384. (4-10), 278, 336, 388.

Figure 4-40. Overlay of all normalized fluorescence spectra for (4-5)-(4-10). $\lambda_{\text{em}}$ (nm) (5 μM, DCM): (4-5), 401, 424. (4-6), 404, 427. (4-7), 404, 428. (4-8), 409, 433. (4-9), 417, 440. (4-10), 418, 443.

(4-5) through (4-7), but within the subset, (4-5) incorporates an inductively electron-withdrawing substituent and possesses the highest energy absorptions and emissions with respect to (4-6) and (4-7). The latter two compounds possess progressively more
inductively donating substituents (Me and 1'Bu). These inductive effects are in agreement with previously predicted and observed trends.\textsuperscript{39,45,49–53} For (4-8) through (4-10), the trend in increasing red-shifted maxima follows that of effective extended conjugation.

The phenoxy substituted alkynyl(aryl) compound (4-8) is slightly red-shifted ($\lambda_{\text{em}} = 410, 434$) to that of the previously published methoxy substituted -alkynyl(aryl) ($\lambda_{\text{em}} = 406, 428$).\textsuperscript{45} Compound (4-9) is red-shifted with respect to (4-8), likely due to its increased conjugation through absence of the oxygen atom.

The compound with the most red-shifted maxima of all previously discussed, (4-10), is red-shifted with respect to (4-9) likely due to the increased conjugation through a fusing-ring system rather than the freely rotating rings in (4-9). Compounds (4-5) through (4-10) all exhibit very high quantum yields in solution in the order of (4-6) > (4-7) > (4-10) > (4-8) > (4-5) > (4-9). With quantum yield measurements, it is difficult to assign a trend due to the narrow distribution of values with the combined error introduced through the comparative method. The new germafluorenes show emission in the solid-state but the emission values were not measured.

Table 4-2. UV-Visible and fluorescence spectra data for germafluorenes (4-5)-(4-10). All measurements performed in CH$_2$Cl$_2$. $^a$1x10$^{-5}$ M. $^b$1x10$^{-6}$ M. $^c$Excitation at 350 nm with anthracene as a standard. $^d$Melting points measured by DSC. $^e$Decomposition temperatures (5% weight loss) measured by TGA. The $\Phi_F$ is the average value of repeated measurements within ±5% error.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}^a$ absorbance (nm)</th>
<th>$\log \varepsilon$</th>
<th>$\lambda_{\text{max}}^b$ fluorescence (nm)</th>
<th>$\Phi_F^c$</th>
<th>$T_m^d/T_d^e$ (°C)</th>
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</thead>
<tbody>
<tr>
<td>(4-5)</td>
<td>278, 331, 371</td>
<td>4.25</td>
<td>401, 424</td>
<td>0.65</td>
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<tr>
<td>(4-6)</td>
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<td>4.54</td>
<td>404, 427</td>
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<td>255/395</td>
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<tr>
<td>(4-7)</td>
<td>274, 332, 374</td>
<td>4.59</td>
<td>404, 428</td>
<td>0.77</td>
<td>350/401</td>
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</table>
The thermal properties for (4-5) through (4-10) were evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), and the results are listed in Table 4-2. DSC analyses of (4-5) through (4-10) showed relatively high melting points, while no glass transition temperatures were observed. The TGA results indicate all of the new compounds have good thermal stability. The decomposition temperatures ($T_d$) corresponding to 5% weight loss were measured as 345, 395, 401, 370, 401, 445 °C for (4-5) through (4-10), respectively, which are much higher than their carbon analogs.$^{54}$ The order of stability in terms of decomposition is in the order of (4-10) > (4-9) > (4-7) > (4-5) > (4-6) > (4-8). This is consistent with the earlier studies which indicate that thermal stability may be improved through incorporation of a heteroatom (such as silicon) or by increasing the molecular volume.$^{55-57}$

While (4-5) exhibits the highest energy absorption and emission maxima, it also has the lowest quantum yield. Compound (4-6) provides the greatest quantum yield while having nearly identical maxima to that of (4-5), with the added benefit of marginally greater thermal stability. The most thermally stable compound, (4-7), is slightly redshifted to that of (4-5) with the second highest quantum yield.

### 4.4. Summary and Future Work

A series of different -alkynyl(aryl) substituents were incorporated into 2,7-disubstituted-alkynyl(aryl)-3,6-dimethoxy-9,9-diphenylgermafluorenes. The resultant
compounds were isolated in good yields ranging from 50-80%, characterized, and exhibit a high energy emission maxima between 401-418 nm with high fluorescence quantum yields in the range of 0.80-0.89 with fluorescence in both the solution and solid states.

Future work could include alkynyl(aryl) substituents incorporating functional groups which are sensitive to pH, ions, allowing for potential applications as chemical sensors. Meanwhile, further studies of this class of molecules with different -alkynyl(aryl) substituents are currently underway which further investigate the trends elucidated in this study.

4.5. Experimental

General

Unless otherwise indicated, all synthetic protocols were performed under an inert atmosphere of argon with flame-dried glassware using standard Schlenk techniques. The solvents, acetonitrile, dichloromethane, hexanes, chloroform, tetrahydrofuran, pentane and methanol were purchased from Fischer Chemical or Sigma-Aldrich, and were used as received unless noted below. For air- and moisture-sensitive reactions, tetrahydrofuran was dried over CaH₂ over several days then freshly distilled from Na/9-fluorenone under argon prior to use. O-dianisidine was purchased from Alfa Aesar and used as received. The compounds, 1-ethynyl-3-fluorobenzene, 1-ethynyl-4-phenoxybenzene, 2-ethynyl-6-methoxynaphthalene, 4-ethynylbiphenyl, 4-ethynyltoluene, 4-tert-butylphenylacetylene, KIO₃, I₂, and n-butyllithium in hexanes (1.6 M) were all purchased from Sigma Aldrich and used without further purification. Dichlorodiphenylgermane was purchased from Gelest Inc. and used as received. Both 4,4’-dibromo-3,3’-dimethoxy-1,1’-biphenyl and 4,4’-dibromo-2,2’-diiodo-5,5’-dimethoxy-1,1’-biphenyl were synthesized according to a literature procedure.³⁸ Silica gel (Premium Rf, 200-400 mesh, 60 Å porosity) was
purchased from Sorbent Technologies, Inc. DCM for optical spectra experiments (spectrophotometric grade) was purchased from Sigma-Aldrich and used as received. All NMR spectra were collected on an Agilent 600 MHz (\(^1\)H recorded at 600 MHz and \(^{13}\)C at 151 MHz or on a Bruker Avance-300 MHz (\(^1\)H recorded at 300 MHz, \(^{13}\)C at 75 MHz, and \(^{19}\)F at 282 MHz) at ambient temperature unless otherwise noted. Chloroform-d\(_1\) was purchased from Cambridge Isotopes, Inc., and used as the solvent unless otherwise indicated, and all \(^1\)H and \(^{13}\)C spectra were referenced to residual protic solvent (for Chloroform-d\(_1\): 7.26 ppm for \(^1\)H and 77.36 ppm for \(^{13}\)C). Chemical shifts are reported in parts per million (ppm), with coupling constants recorded in Hertz (Hz).

Elemental analyses were performed by Robertson Microlit Labs, Inc., Ledgewood, NJ. A JEOL M Station-JMS 700 mass spectrometer was used to obtain high resolution mass spectra by fast atom bombardment (FAB) or (EI) conditions, using 3-nitrobenzyl alcohol (NBA) as a matrix and dichloromethane as a solvent. X-ray intensity data were measured using a Bruker Apex II diffractometer equipped with a CCD area detector. Melting point determinations were obtained on a Mel-Temp melting point apparatus and are uncorrected. UV-vis and fluorescence spectra were measured on a Cary 50 Bio UV-visible and Cary Eclipse Fluorescence spectrophotometer, respectively. Emission spectra were measured using the \(\lambda_{\text{max}}\) value for each compound as determined by the absorption spectra. Gas chromatography experiments were performed using a Shimadzu GC-14A gas chromatograph; GC-MS analyses were performed on a Hewlett Packard Model 5988A GC-MS instrument. Melting points were determined on a Mel-Temp capillary melting point apparatus and are uncorrected. UV-visible spectroscopic data were collected on a Cary (Varian) 50 Bio UV-visible spectrometer. Fluorescence spectra were
recorded on a Cary (Varian) Eclipse fluorescence spectrometer. Quartz cuvettes were used for optical spectra data collection. Infrared spectroscopic data were collected on a Thermo Scientific Nicolet 6700 equipped with a Smart OMNI-Sampler Germanium ATR Sampling Accessory. Thermogravimetric Analyses (TGA) were performed on a TA Instruments Q500 and Differential Scanning Calorimetry measurements were performed on a TA Instruments Q2000.

**Synthesis of 4,4′-dibromo-3,3′-dimethoxy-1,1′-biphenyl (4-2)**

Following a previously published procedure, o-Dianisidine (10 g, 40.9 mmol), 41 mL 40% HBr, 160 mL H₂O, and 160 mL acetonitrile were combined in a three-necked flask (1000 mL) equipped with a pressure-equilibrating addition funnel (250 mL), thermometer and magnetic stirrer under standard atmospheric conditions. The majority of the starting material dissolved in acetonitrile. The reaction was cooled to 0 °C in an ice bath, and sodium nitrite (7.2 g, 104.4 mmol) dissolved in a minimal amount of water was chilled and added dropwise to the reaction such that the temperature does not exceed 10 °C. Following the addition, the reaction mixture was stirred at below 10 °C for 30 min. To prevent a side reaction with O₂ in the following step, the reaction atmosphere was purged with argon. CuBr (13.0 g, 90.6 mmol) was dissolved in 160 mL of 40% HBr and added to the addition funnel. The CuBr/HBr solution was added over the course of 1 h such that the temperature does not exceed 10 °C. The solution was then allowed to warm to room temperature and was subsequently heated to reflux (80 °C) for at least 1 h until an insoluble white solid becomes apparent. The solution was then cooled and extracted with
250-300 mL of dichloromethane, washed with 10 wt % NaOH and brine, and dried with MgSO₄ before removing the solvent by roteovaporation. The crude, light brown powder was sufficiently pure to proceed to the next step, yield: 14.62 g, 96%. Mp: 141-142 °C (lit. 140-143 °C).³⁸ ¹H NMR (500 MHz, CDCl₃): δ 7.58 (d, 2H), 7.06 – 7.00 (m, 4H), 3.97 (s, 6H). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 156.6, 141.7, 134.0, 121.0, 111.8, 111.2, 56.7. These data were consistent with the literature values.³⁸ Appendix I: 34-35.

**Synthesis of 4,4’-dibromo-2,2’-diiodo-5,5’-dimethoxy-1,1’-biphenyl (4-3)**³⁸

Following a previously published procedure,³⁸ 4,4’-dibromo-3,3’-dimethoxy-1,1’-biphenyl (13.0 g, 34.9 mmol), KIO₃ (3.3 g, 15.4 mmol), and I₂ (9.6 g, 38.0 mmol) were added to a large three-neck flask (1000 mL) equipped with a reflux condenser, thermometer, and magnetic stirrer. The starting material was dissolved in a mixture of 260 mL acetic acid and 26 mL of 20 wt% H₂SO₄. The solution was heated to 80 °C for 12 h. Large amounts of insoluble product precipitated as the reaction proceeded. Once cooled to room temperature, an additional 250 mL of H₂O was added to precipitate further product. The precipitate was collected by filtration, dried by rotoevaporation, and redissolved by a minimal amount of dichloromethane. The solution was extracted with 10 wt % NaOH (50 mL), washed with brine, and dried with MgSO₄ before removing the solvent by rotoevaporation. The crude product was then purified by a silica gel plug utilizing dichloromethane as an eluent, then recrystallized in dichloromethane and ethanol. The resulting white crystalline powder was then collected by filtration, yield: 20.9 g, 96%. Mp: 148-149 °C (lit. 147-150 °C).³⁸ ¹H NMR (500 MHz, CDCl₃): δ 8.04 (s,
2H), 6.73 (s, 2H), 3.88 (s, 6H). $^{13}$C$\{^{1}$H$\}$ NMR (126 MHz, CDCl$_3$): δ 156.2, 148.2, 142.2, 113.3, 112.5, 87.7, 56.5. These data were consistent with literature values. Appendix I: 36-37.

**Synthesis of 2,7-dibromo-3,6-dimethoxy-9,9-diphenylgermafluorene (4-4)**

![Diagram of 4-4](image)

To a flame-dried four-necked round-bottom flask (250 mL) equipped with a pressure-equilibrating addition funnel (25 mL), thermometer, and magnetic stirrer under argon, 4,4'-dibromo-2,2'-diiodo-5,5'-dimethoxy-1,1'-biphenyl (5.0 g, 8 mmol) was dissolved in freshly distilled THF (160 mL). The solution was chilled to -95 °C in a methanol/N$_2$ bath. At 95 °C, there is risk of the methanol bath freezing and fracturing the four-necked flask. Addition of water (H$_2$O:MeOH, 1:4) mitigates this possibility, resulting in a bath with a gel- or slush-like consistency even at -100 °C. At this point, the reaction mixture was stirring as rapidly as possible, such that a deep whirlpool was formed. Meanwhile, the thermometer was submerged within the reaction mixture as much as possible without disturbing the magnetic stirrer. A small cryogenic storage dewar containing liquid nitrogen was also nearby for quick and convenient addition of liquid nitrogen during addition of n-BuLi. A syringe was charged with dichlorodiphenylgermane (2.18 mL, 8.82 mmol) and was carefully left in the septum of the reaction flask, as the germane can freeze around – 90 °C within the syringe tip during addition of germane, requiring removal of the syringe to allow the frozen germane to melt before continuing addition. This could result in the introduction of error from multiple sources. A solution of n-BuLi
in hexanes was quickly transferred from the refrigerator to the addition funnel to minimize the time it was allowed to warm. Although the temperature of the n-BuLi is not crucial, and haste is not a necessary component in transferring it to the addition funnel for the overall reaction yield, it did reduce the rate at which temperature increased during addition. Just prior to addition of n-BuLi, liquid nitrogen was added to the methanol bath so that the temperature was slowly decreasing below -95 °C. As soon as the temperature decreases beyond -95 °C, addition of 10.3 mL n-BuLi (1.6 M in hexanes) was then added dropwise such that it is nearly a constant stream over 2.5 min to the rapidly stirring solution, while not allowing the reaction mixture temperature to exceed -90 °C in order to ensure selectivity for a lithium-iodine exchange. Liquid nitrogen was added to the bath during the addition to mitigate increasing temperature. If the temperature appeared as if it would exceed -90 °C, the addition was halted until the temperature began decreasing. The clear solution immediately turned yellow after the first drop of n-BuLi was added. Once roughly half of the n-BuLi reagent had been added to the reaction mixture, a yellow slurry developed, which gradually redissolved as the n-BuLi addition was completed. Immediately after the addition of n-BuLi was completed, the syringe containing dichlorodiphenylgermane was quickly transferred from the storage vessel septum to the reaction flask septum. The syringe needle was inserted just enough that the germane could be rapidly injected in a quick, smooth motion, to reduce the chances of it freezing within the syringe tip. Once the germane addition was complete, the temperature of the reaction mixture increased sharply, but did not exceed -84 °C. A small amount of liquid nitrogen was utilized to stabilize the reaction mixture temperature. Once the temperature began decreasing, the pale yellow reaction mixture was removed from the bath around -
85 °C or lower and stirred overnight. During this period, the reaction mixture slowly approached room temperature over the course of an hour. The reaction mixture was then quenched with saturated ammonium chloride solution and extracted with chloroform. The organic layer was then washed with brine, dried with magnesium sulfate, and filtered. The solvent was then removed by rotocell. The product was then purified by chromatography (silica gel, dichloromethane/hexane 1/1) and recrystallized in dichloromethane:ethanol. The resulting white crystalline powder (3.21 g, 67%) was then collected by filtration and confirmed by comparison to literature values.\(^{37,39}\)

\(^{1}\)H NMR (300 MHz, CDCl\(_3\)): δ 7.88 (s, 2H), 7.59 (d, J = 1.8 Hz, 2H), 7.57 (d, J = 2.4 Hz, 2H), 7.41 (dd, J = 4.6, 3.1 Hz, 8H), 4.01 (s, 6H).

\(^{13}\)C\(^{1}\)H NMR (75 MHz, CDCl\(_3\)): δ 157.7, 147.3, 137.8, 134.6, 134.1, 131.3, 129.9, 128.70, 112.8, 105.8, 56.4. Appendix I: 60-61.

**2,7-(1-ethynyl-3-fluorobenzene)-3,6-dimethoxy-9,9-diphenylgermafluorene (4-5)**

![Structure of 4-5](image)

To a 15 mL three-necked flask equipped with a reflux condenser and magnetic stirrer under argon, 2,7-dibromo-3,6-dimethoxy-9,9-diphenylgermafluorene (0.250 g, 0.419 mmol), Pd(PPh\(_3\))\(_4\) (0.048 g, 0.042 mmol), and CuI (0.016 g, 0.085 mmol) were added, followed by piperidine (4.81 mL, 48.6 mmol) and 1-ethynyl-3-fluorobenzene (0.149 mL, 1.240 mmol). The reaction mixture was stirred at 80 °C overnight. The following morning, the reaction mixture was concentrated, then subsequently purified by silica gel chromatography using dichloromethane:hexane as an eluent. The product was then recrystallized in dichloromethane:pentane, and rinsed with pentane, and dried by rotoevaporation. The product was isolated as a bright yellow powder. 0.202 g, 71% yield.
Mp: 234-235 °C. X-ray-quality crystals were obtained by slow evaporation of a dichloromethane solution of the product at room temperature. ¹H NMR (600 MHz, CDCl₃): δ 7.85 (s, 2H), 7.59 (d, J = 6.6 Hz, 4H), 7.44 – 7.35 (m, 8H), 7.30 (d, J = 19.5, 13.6, 6.7 Hz, 4H), 7.25 (d, J = 11.5 Hz, 4H), 7.03 (t, J = 7.8 Hz, 2H), 4.09 (s, 2H).

¹³C{¹H} NMR (151 MHz, CDCl₃): δ 162.5 (d, ¹J_C-F = 246.3 Hz), 162.3, 148.7, 138.6, 134.8, 134.6, 130.4, 130.0, 130.0 (d, ¹J_C-F = 8.7 Hz), 128.7, 127.6 (d, ¹J_C-F = 3.0 Hz), 125.5 (d, ¹J_C-F = 9.5 Hz), 118.5 (d, ¹J_C-F = 22.7 Hz), 115.6 (d, ²J_C-F = 21.2 Hz), 112.7, 104.7, 93.7 (d, J = 3.4 Hz), 87.2, 56.2. ¹⁹F NMR (564 MHz, CDCl₃): δ -113.16 (dd, J = 15.0, 7.5 Hz).


Absorption (50 μM) and emission (5 μM) (DCM): λₚₛₑₛ (nm) = 278, 331, and 371. λₑₘₑₜ (nm) = 401 and 424. log ε = 4.25. Φₜ = 0.65. Tₘ/Tₑ (°C) = 301/345. λₑₓₜ = 350 nm with anthracene as a standard. Appendix I: 62-64.

2,7-(4-ethyltoluene)-3,6-dimethoxy-9,9-diphenylgermafluorene (4-6)

To a 15 mL three-necked flask equipped with a reflux condenser and magnetic stirrer under argon, 2,7-dibromo-3,6-dimethoxy-9,9-diphenylgermafluorene (0.250 g, 0.419 mmol), Pd(PPh₃)₄ (0.048 g, 0.042 mmol), and CuI (0.016 g, 0.085 mmol) were added, followed by piperidine (4.81 mL, 48.6 mmol) and 4-ethyltoluene (0.144 mL, 1.240 mmol). The reaction mixture was stirred at 80 °C overnight. The following morning, the reaction mixture was concentrated, then subsequently purified by silica gel chromatography using dichloromethane:hexane as an eluent. The product was then
recrystallized in dichloromethane:pentane, and rinsed with pentane, and dried by rotoevaporation. The product was isolated as a bright yellow powder. 0.221 g, 79% yield, Mp: 265-266 °C. X-ray-quality crystals were obtained by slow evaporation of a dichloromethane solution of the product at room temperature. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.86 (d, J = 3.5 Hz, 2H), 7.63 – 7.57 (m, 4H), 7.49 – 7.43 (m, 4H), 7.43 – 7.35 (m, 8H), 7.15 (d, J = 7.6 Hz, 4H), 4.09 (s, 6H), 2.37 (s, 6H). $^{13}$C{$^1$H} NMR (151 MHz, CDCl$_3$): $\delta$ 162.1, 148.3, 138.5, 138.4, 134.8, 131.7, 130.3, 129.8, 129.2, 128.7, 120.5, 113.3, 104.7, 95.2, 85.6, 56.2, 21.7. Anal. Calcd for C$_{44}$H$_{34}$O$_2$Ge: C, 79.19; H, 5.14. Found: C, 78.86; H, 5.23. HRMS (EI): calcd. for C$_{44}$H$_{34}$O$_2$Ge: 667.38; Found, 668.177. Absorption (50 μM) and emission (5 μM) (DCM): $\lambda_{abs}$ (nm) = 274, 332, and 375. $\lambda_{em}$ (nm) = 404 and 427. log $\varepsilon$ = 4.54. $\Phi_f$ = 0.83. $T_m/T_d$ (°C) = 255/395. $\lambda_{ex}$ = 350 nm with anthracene as a standard.  


2,7-(4-tert-butylphenylacetylene)-3,6-dimethoxy-9,9-diphenylgermafluorene (4-7)

To a 15 mL three-necked flask equipped with a reflux condenser and magnetic stirrer under argon, 2,7-dibromo-3,6-dimethoxy-9,9-diphenylgermafluorene (0.250 g, 0.419 mmol), Pd(PPh$_3$)$_4$ (0.048 g, 0.042 mmol), and CuI (0.016 g, 0.085 mmol) were added, followed by piperidine (4.81 mL, 48.6 mmol) and 4-tert-butylphenylacetylene (0.196 mL, 1.240 mmol). The reaction mixture was stirred at 80 °C overnight. The following morning, the reaction mixture was concentrated, then subsequently purified by silica gel chromatography using dichloromethane:hexane as an eluent. The product was then recrystallized in dichloromethane:pentane, and rinsed with pentane, and dried by
rotoevaporation. The product was received as a bright yellow powder. 0.156 g, 50% yield. Mp: 324-325 °C. X-ray-quality crystals were obtained by slow evaporation of a dichloromethane solution of the product at room temperature. $^1$H NMR (600 MHz, CDCl$_3$): 7.88 (s, 2H), 7.59 (d, $J = 1.8$ Hz, 2H), 7.57 (d, $J = 2.4$ Hz, 2H), 7.41 (m, 8H), 4.01 (s, 6H), 2.17 (s, 18H). $^{13}$C{$^1$H} NMR (151 MHz, CDCl$_3$): δ 162.2, 151.5, 148.3, 138.5, 134.8, 131.5, 130.3, 129.8, 128.7, 125.4, 120.6, 113.4, 104.8, 95.2, 85.6, 56.3, 34.9, 31.3. Anal. Calcd for C$_{50}$H$_{46}$O$_2$Ge: C, 79.91; H, 6.17. Found: C, 79.75; H, 6.04. HRMS (EI): calcd. for C$_{50}$H$_{46}$O$_2$Ge: 751.539; Found, 752.2709. Absorption (50 μM) and emission (5 μM) (DCM): $\lambda_{abs}$ (nm) = 274, 332, and 374. $\lambda_{em}$ (nm) = 404 and 428. $\log \varepsilon = 4.59$. $\Phi_f$ = 0.77. $T_m/T_d$ (°C) = 350/401. $\lambda_{ex}$ = 350 nm with anthracene as a standard.

Appendix I: 67-68; Appendix II: 13-14.

2,7-(1-ethynyl-4-phenoxybenzene)-3,6-dimethoxy-9,9-diphenylgermafluorene (4-8)

To a 15 mL three-necked flask equipped with a reflux condenser and magnetic stirrer under argon, 2,7-dibromo-3,6-dimethoxy-9,9-diphenylgermafluorene (0.250 g, 0.419 mmol), Pd(PPh$_3$)$_4$ (0.048 g, 0.042 mmol), and CuI (0.016 g, 0.085 mmol) were added, followed by piperidine (4.81 mL, 48.6 mmol) and 1-ethynyl-4-phenoxybenzene (0.241 mL, 1.240 mmol). The reaction mixture was stirred at 80 °C overnight. The following morning, the reaction mixture was concentrated, then subsequently purified by silica gel chromatography using dichloromethane:hexane as an eluent. The product was then recrystallized in dichloromethane:pentane, and rinsed with pentane, and dried by rotoevaporation. The product was received as bright yellow needle-like crystals. 0.276 g,
80% yield. Mp: 218-219 °C. X-ray-quality crystals were obtained by slow evaporation of a dichloromethane solution of the product at room temperature. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.85 (s, 2H), 7.59 (d, $J = 6.6$ Hz, 4H), 7.52 (d, $J = 8.6$ Hz, 4H), 7.43 – 7.33 (m, 12H), 7.14 (t, $J = 7.4$ Hz, 2H), 7.06 – 7.02 (m, 4H), 6.96 (d, $J = 8.6$ Hz, 4H), 4.08 (s, 6H). $^{13}$C($^1$H) NMR (151 MHz, CDCl$_3$): $\delta$ 162.1, 157.6, 156.6, 148.4, 138.5, 134.8, 134.7, 133.4, 130.3, 130.0, 129.8, 128.7, 124.0, 119.6, 118.5, 118.2, 113.2, 104.7, 94.6, 85.7, 56.2. Anal. Calcd for C$_{54}$H$_{38}$O$_4$Ge: C, 78.76; H, 4.65. Found: C, 78.57; H, 4.58. HRMS (EI): calcd. for C$_{54}$H$_{38}$O$_4$Ge: 823.517. Found, 824.198. Absorption (50 μM) and emission (5 μM) (DCM): $\lambda_{abs}$ (nm) = 274, 333, and 377. $\lambda_{em}$ (nm) = 409 and 433. $\log \varepsilon$ = 4.58. $\Phi_f$ = 0.68. $T_m/T_d$ (°C) = 201/370. $\lambda_{ex}$ = 350 nm with anthracene as a standard. Appendix I: 69-70.

2,7-(4-ethynylbiphenyl)-3,6-dimethoxy-9,9-diphenylgermafluorene (4-9)

To a 15 mL three-necked flask equipped with a reflux condenser and magnetic stirrer under argon, 2,7-dibromo-3,6-dimethoxy-9,9-diphenylgermafluorene (0.250 g, 0.419 mmol), Pd(PPh$_3$)$_4$ (0.048 g, 0.042 mmol), and CuI (0.016 g, 0.085 mmol) were added, followed by piperidine (4.81 mL, 48.6 mmol) and 4-ethynylbiphenyl (0.221 g, 1.240 mmol). The reaction mixture was stirred at 80 °C overnight. The following morning, the reaction mixture was concentrated, then subsequently purified by silica gel chromatography using dichloromethane:hexane as an eluent. The product was then recrystallized in dichloromethane:pentane, and rinsed with pentane, and dried by rotoevaporation. The product was received as a bright yellow powder. 0.221 g, 62%
yield. Mp: 328-329 °C. X-ray-quality crystals were obtained by slow evaporation of a dichloromethane solution of the product at room temperature. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.91 (s, 2H), 7.67 (d, 4H), 7.65 – 7.57 (m, 12H), 7.49 – 7.41 (m, 6H), 7.41 – 7.34 (m, 8H), 4.11 (s, 6H). $^{13}$C{$^1$H} NMR (151 MHz, CDCl$_3$): $\delta$ 162.2, 148.52, 141.0, 140.6, 138.60, 134.8, 132.2, 129.9, 129.0, 129.8, 127.8, 127.2, 127.1, 126.5, 122.6, 104.8, 101.1, 95.0, 87.1, 56.3. Anal. Calcd for C$_{54}$H$_{38}$O$_2$Ge: C, 81.94; H, 4.84. Found: C, 81.54; H, 4.81. Absorption (50 μM) and emission (5 μM) (DCM): $\lambda_{abs}$ (nm) = 286, 334, and 384. $\lambda_{em}$ (nm) = 417 and 440. $\log \varepsilon$ = 4.55. $\Phi_f$ = 0.64. $T_m/T_d$ (°C) = 297/401. $\lambda_{ex}$ = 350 nm with anthracene as a standard. Appendix I: 71-72; Appendix II: 15-16.

2,7-(2-ethynyl-6-methoxynaphthalene)-3,6-dimethoxy-9,9-diphenylgermafluorene (4-10)

To a 15 mL three-necked flask equipped with a reflux condenser and magnetic stirrer under argon, 2,7-dibromo-3,6-dimethoxy-9,9-diphenylgermafluorene (0.250 g, 0.419 mmol), Pd($\text{PPh}_3$)$_4$ (0.048 g, 0.042 mmol), and CuI (0.016 g, 0.085 mmol) were added, followed by piperidine (4.81 mL, 48.6 mmol) and 2-ethynyl-6-methoxynaphthalene (0.226 g, 1.240 mmol). The reaction mixture was stirred at 80 °C overnight. The following morning, the reaction mixture was concentrated, then subsequently purified by silica gel chromatography using dichloromethane:hexane as an eluent. The product was then recrystallized in dichloromethane:pentane, and rinsed with pentane, and dried by rotoevaporation. The product was received as a bright yellow powder. 0.202 g, 60% yield. Mp: 295-296 °C. X-ray-quality crystals were obtained by slow evaporation of a
dichloromethane solution of the product at room temperature. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 8.00 (s, 2H), 7.90 (s, 2H), 7.73 – 7.66 (m, 4H), 7.61 (d, $J = 6.7$ Hz, 4H), 7.57 (d, $J = 8.4$ Hz, 2H), 7.43 (s, 2H), 7.42 – 7.36 (m, 6H), 7.15 (dd, $J = 8.9$, 2.3 Hz, 2H), 7.11 (s, 2H), 4.11 (s, 6H), 3.93 (s, 6H). $^{13}$C{$^1$H} NMR (151 MHz, CDCl$_3$): $\delta$ 162.2, 158.4, 148.4, 138.6, 134.8, 134.2, 131.4, 130.4, 129.8, 129.5, 129.3, 128.7, 128.7, 126.9, 119.5, 118.6, 113.3, 106.0, 104.8, 95.6, 86.1, 56.3, 55.5. Anal. Calcd for C$_{52}$H$_{38}$O$_4$Ge: C, 78.1; H, 4.79. Found: C, 77.88; H, 4.79. HRMS (EI): calcd. for C$_{52}$H$_{38}$O$_4$Ge: 799.496; Found, 800. $\lambda_{\text{abs}}$ (nm) = 278, 336, and 388. Absorption (50 μM) and emission (5 μM) (DCM): $\lambda_{\text{em}}$ (nm) = 418 and 443. $\log \varepsilon = 4.51$. $\Phi_f = 0.75$. $T_m/T_d$ (°C) = 298/445. $\lambda_{\text{ex}}$ = 350 nm with anthracene as a standard. Appendix I: 73-74. ; Appendix II: 17-18.
4.6. References


Appendix I

NMR Spectroscopic Data

Appendix I-1. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 1,1-dimethyl-2,5-bis[4-(trimethylsilyl)ethynyl]-phenyl]-3,4-diphenylsilole (2-6). ......................... 264

Appendix I-2. $^{13}$C{$^1$H} NMR (126 MHz, CDCl$_3$) spectrum of 1,1-dimethyl-2,5-bis[4-(trimethylsilyl)ethynyl]-phenyl]-3,4-diphenylsilole (2-6). ......................... 265

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- **A (m)** 7.84
- **B (m)** 7.47
- **C (m)** 7.22
- **D (ddd)** 7.00
- **E (m)** 6.85
- **F (m)** 6.76
- **G (d)** 6.67
- **H (dt)** 4.36
- **I (m)** 3.73
- **J (t)** 3.32
- **K (d)** 3.02
- **L (dd)** 2.48
- **M (m)** 1.85
- **N (t)** 1.42
- **O (m)** 1.27
- **P (t)** 0.87
- **Q (m)** 0.84
- **R (dd)** 0.84
- **S (m)** 0.40

f1 (ppm)

- 8.5
- 8.0
- 7.5
- 7.0
- 6.5
- 6.0
- 5.5
- 5.0
- 4.5
- 4.0
- 3.5
- 3.0
- 2.5
- 2.0
- 1.5
- 1.0
- 0.5
- 0.0
- 0
- 20
- 40
- 60
- 80
- 100
- 120
- 140
- 160
- 180
- 200
- 220
- 240
- 260
- 280
- 300
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X-Ray Crystallography

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Empirical formula  \( \text{C}_{85}\text{H}_{57}\text{Cl}_{3}\text{F}_{4}\text{O}_{4}\text{Si}_{2} \)  
Formula weight  1380.83  
Temperature  100(2) K  
Wavelength  0.71073 Å  
Crystal system  Triclinic  
Space group  \( P \overline{1} \)  
Unit cell dimensions  
\( a = 10.8704(9) \ \text{Å} \)  
\( \alpha = 83.471(5)^\circ \)  
\( b = 11.9328(10) \ \text{Å} \)  
\( \beta = 71.515(5)^\circ \)  
\( c = 15.0473(13) \ \text{Å} \)  
\( \gamma = 68.378(5)^\circ \)  
Volume  1720.9(3) \( \text{Å}^3 \)  
Z  1  
Density (calculated)  1.332 Mg/m\(^3\)  
Absorption coefficient  0.233 mm\(^{-1}\)  
\( F(000) \)  714  
Crystal size  0.289 x 0.151 x 0.125 mm\(^3\)  
Theta range for data collection  1.836 to 26.880\(^\circ\)  
Index ranges  
\(-13 \leq h \leq 13, \ -15 \leq k \leq 15, \ -18 \leq l \leq 18 \)  
Reflections collected  29081  
Independent reflections  7185 [\( R(\text{int}) = 0.0384 \)]  
Completeness to theta = 25.242\(^\circ\)  100.0 \%  
Absorption correction  Semi-empirical from equivalents  
Max. and min. transmission  0.8620 and 0.7724  
Refinement method  Full-matrix least-squares on \( F^2 \)  
Data / restraints / parameters  7185 / 80 / 489  
Goodness-of-fit on \( F^2 \)  1.033  
Final R indices [\( I > 2 \sigma(I) \)]  \( R1 = 0.0633, \ wR2 = 0.1571 \)  
R indices (all data)  \( R1 = 0.0818, \ wR2 = 0.1720 \)  
Extinction coefficient  n/a  
Largest diff. peak and hole  1.493 and -1.503 e.Å\(^{-3}\)  

**Appendix II-2.** Crystal parameters for 2,7-(1-ethynyl-3-fluorobenzene)-3,6-dimethoxy-9,9-diphenylsilafluorene (\textbf{3-5}).
Appendix II-3. 2,7-(4-ethyltoluene)-3,6-dimethoxy-9,9-diphenylsilafluorene (3-6).
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<td>Crystal system</td>
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<td>c = 23.0436(11) Å</td>
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<td>$\alpha$ = 90°</td>
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<td></td>
<td>$\beta$ = 102.887(3)$\degree$</td>
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<td>Z</td>
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<td>Density (calculated)</td>
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<td>Absorption coefficient</td>
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<td>F(000)</td>
<td>1312</td>
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<td>Crystal size</td>
<td>0.266 x 0.149 x 0.075 mm$^3$</td>
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<td>Theta range for data collection</td>
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<td>Independent reflections</td>
<td>6253 [R(int) = 0.1153]</td>
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<td>Completeness to theta = 25.242$\degree$</td>
<td>100.0 %</td>
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<td>Absorption correction</td>
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<td>Max. and min. transmission</td>
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<td>Refinement method</td>
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<td>Extinction coefficient</td>
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<td>Largest diff. peak and hole</td>
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**Appendix II-4.** Crystal parameters for 2,7-(4-ethynyltoluene)-3,6-dimethoxy-9,9-diphenylsilafluorene (3-6).
Appendix II-5. 2,7-(4-tert-butylphenylacetylene)-3,6-dimethoxy-9,9-diphenylsilafuorene (3-7).
Empirical formula  
C$_{50}$H$_{46}$O$_2$Si

Formula weight  
706.96

Temperature  
100(2) K

Wavelength  
0.71073 Å

Crystal system  
Triclinic

Space group  
P $\overline{1}$

Unit cell dimensions  
a = 8.6693(4) Å  
$\alpha$ = 82.507(2)$^\circ$.

b = 12.6841(6) Å  
$\beta$ = 83.597(2)$^\circ$.

c = 18.8639(8) Å  
$\gamma$ = 78.312(2)$^\circ$.

Volume  
2006.21(16) Å$^3$

Z  
2

Density (calculated)  
1.170 Mg/m$^3$

Absorption coefficient  
0.098 mm$^{-1}$

F(000)  
752

Crystal size  
0.558 x 0.326 x 0.225 mm$^3$

Theta range for data collection  
1.093 to 31.093$^\circ$.

Index ranges  
-12$\leq$ h $\leq$ 12,  
-18$\leq$ k $\leq$ 18,  
-27$\leq$ l $\leq$ 27

Reflections collected  
41602

Independent reflections  
12596 [R(int) = 0.0317]

Completeness to theta = 25.242$^\circ$  
99.3 %

Absorption correction  
Semi-empirical from equivalents

Max. and min. transmission  
0.8622 and 0.8048

Refinement method  
Full-matrix least-squares on F$^2$

Data / restraints / parameters  
12596 / 135 / 951

Goodness-of-fit on F$^2$  
1.015

Final R indices [I>2sigma(I)]  
R1 = 0.0538, wR2 = 0.1338

R indices (all data)  
R1 = 0.0863, wR2 = 0.1584

Extinction coefficient  
n/a

Largest diff. peak and hole  
0.419 and -0.535 e.Å$^{-3}$

**Appendix II-6.** Crystal parameters for 2,7-(4-tert-butylphenylacetylene)-3,6-dimethoxy-9,9-diphenylsilafuorene (3-7).
Appendix II-7. 2,7-(1-ethynyl-4-phenoxybenzene)-3,6-dimethoxy-9,9-diphenylsilafuorene (3-8).
Empirical formula  
Formula weight  
Temperature  
Wavelength  
Crystal system  
Space group  
Unit cell dimensions  
Volume  
Z  
Density (calculated)  
Absorption coefficient  
F(000)  
Crystal size  
Theta range for data collection  
Index ranges  
Reflections collected  
Independent reflections  
Completeness to theta = 25.000°  
Absorption correction  
Max. and min. transmission  
Refinement method  
Data / restraints / parameters  
Goodness-of-fit on F²  
Final R indices [I>2sigma(I)]  
R indices (all data)  
Extinction coefficient  
Largest diff. peak and hole  

**Appendix II-8.** Crystal parameters for 2,7-(1-ethynyl-4-phenoxybenzene)-3,6-dimethoxy-9,9-diphenylsilafuorene (3-8).
Appendix II-9. 2,7-(4-ethylbiphenyl)-3,6-dimethoxy-9,9-diphenylsilafluorene (3-9).
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<td>Density (calculated)</td>
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</tr>
</tbody>
</table>

**Appendix II-10.** Crystal parameters for 2,7-(4-ethynylbiphenyl)-3,6-dimethoxy-9,9-diphenylsilafuorene (3-9).
Appendix II-11. 2,7-(2-ethynyl-6-methoxynaphthalene)-3,6-dimethoxy-9,9-diphenylsilafluorene (3-10).
Empirical formula \( \text{C}_{52}\text{H}_{38}\text{O}_{4}\text{Si} \)
Formula weight 754.91
Temperature 100(2) K
Wavelength 0.71073 Å
Crystal system Triclinic
Space group \( P \overline{1} \)
Unit cell dimensions
\[
\begin{align*}
a &= 9.3163(7) \text{ Å} & \alpha &= 80.503(4)^\circ. \\
b &= 12.8339(10) \text{ Å} & \beta &= 84.054(4)^\circ. \\
c &= 19.0752(14) \text{ Å} & \gamma &= 70.047(4)^\circ. \\
\end{align*}
\]
Volume 2111.7(3) Å\(^3\)
Z 2
Density (calculated) 1.187 Mg/m\(^3\)
Absorption coefficient 0.101 mm\(^{-1}\)
\(F(000)\) 792
Crystal size 0.368 x 0.321 x 0.267 mm\(^3\)
Theta range for data collection 1.705 to 36.401°.
Index ranges \(-15 \leq h \leq 15, -21 \leq k \leq 20, -31 \leq l \leq 31\)
Reflections collected 80649
Independent reflections 20085 \([R(\text{int}) = 0.0377]\)
Completeness to theta = 25.242° 99.9 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.8625 and 0.8130
Refinement method Full-matrix least-squares on \(F^2\)
Data / restraints / parameters 20085 / 2 / 556
Goodness-of-fit on \(F^2\) 1.048
Final R indices \([I > 2\sigma(I)]\)
\(R1 = 0.0501, wR2 = 0.1383\)
R indices (all data) \(R1 = 0.0718, wR2 = 0.1541\)
Extinction coefficient n/a
Largest diff. peak and hole 0.645 and -0.444 e.Å\(^{-3}\)

Appendix II-12. 2,7-(2-ethynyl-6-methoxynaphthalene)-3,6-dimethoxy-9,9-diphenylsilafluorene (3-10).
Appendix II-13. 2,7-(4-tert-butylphenylacetylene)-3,6-dimethoxy-9,9-diphenylgermafluorene (4-7).
Empirical formula \( \text{C}_{50}\text{H}_{46}\text{GeO}_{2} \)
Formula weight 
751.46
Temperature 100(2) K
Wavelength 0.71073 Å
Crystal system Triclinic
Space group \( \text{P}\bar{\text{1}} \)
Unit cell dimensions:
\[ a = 12.7045(7) \text{ Å} \quad \alpha = 112.268(3)^\circ. \]
\[ b = 17.4941(9) \text{ Å} \quad \beta = 91.962(3)^\circ. \]
\[ c = 19.8723(10) \text{ Å} \quad \gamma = 99.094(3)^\circ. \]
Volume 4014.4(4) Å³
Z 4
Density (calculated) 1.243 Mg/m³
Absorption coefficient 0.802 mm⁻¹
\( F(000) \) 1576
Crystal size 0.335 x 0.228 x 0.177 mm³
Theta range for data collection 1.329 to 27.605°.
Index ranges \(-16 \leq h \leq 16, \ -22 \leq k \leq 22, \ -25 \leq l \leq 25\)
Reflections collected 69793
Independent reflections 18202 [R(int) = 0.0442]
Completeness to theta = 25.242° 99.1 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.8621 and 0.7764
Refinement method Full-matrix least-squares on \( F^2 \)
Data / restraints / parameters 18202 / 0 / 990
Goodness-of-fit on \( F^2 \) 1.016
Final R indices [I>2sigma(I)] \( \text{R1} = 0.0403, \ w\text{R2} = 0.0841 \)
R indices (all data) \( \text{R1} = 0.0730, \ w\text{R2} = 0.0958 \)
Extinction coefficient n/a
Largest diff. peak and hole 0.631 and -0.391 e.Å⁻³

**Appendix II-14.** Crystal parameters for 2,7-(4-tert-butylphenylacetylene)-3,6-dimethoxy-9,9-diphenylgermafluorene (4-7).
Appendix II-15. 2,7-(4-ethynylbiphenyl)-3,6-dimethoxy-9,9-diphenylgermafluorene (4-9).
Empirical formula: C_{54}H_{38}GeO_{2}
Formula weight: 791.43
Temperature: 100(2) K
Wavelength: 0.71073 Å
Crystal system: Triclinic
Space group: P \bar{1}
Unit cell dimensions:

\[ a = 12.3334(8) \text{ Å} \quad \alpha = 114.807(3)^\circ. \]
\[ b = 13.1508(9) \text{ Å} \quad \beta = 102.785(3)^\circ. \]
\[ c = 13.7595(9) \text{ Å} \quad \gamma = 90.815(4)^\circ. \]
Volume: 1961.0(2) Å\(^3\)
Z: 2
Density (calculated): 1.340 Mg/m\(^3\)
Absorption coefficient: 0.825 mm\(^{-1}\)
F(000): 820
Crystal size: 0.363 x 0.221 x 0.149 mm\(^3\)
Theta range for data collection: 1.684 to 31.637°.
Index ranges:

\[-18 \leq h \leq 18, \quad -19 \leq k \leq 19, \quad -20 \leq l \leq 19\]
Reflections collected: 62224
Independent reflections: 12984 [R(int) = 0.0404]
Completeness to theta = 25.242°: 99.9 %
Absorption correction: Semi-empirical from equivalents
Max. and min. transmission: 0.8623 and 0.7954
Refinement method: Full-matrix least-squares on F\(^2\)
Data / restraints / parameters: 12984 / 0 / 516
Goodness-of-fit on F\(^2\): 1.014
Final R indices [I>2sigma(I)]:

\[ R1 = 0.0365, \quad wR2 = 0.0825 \]
R indices (all data):

\[ R1 = 0.0513, \quad wR2 = 0.0891 \]
Extinction coefficient: n/a
Largest diff. peak and hole: 0.599 and -0.280 e.Å\(^{-3}\)

**Appendix II-16.** Crystal parameters for 2,7-(4-ethynylbiphenyl)-3,6-dimethoxy-9,9-diphenylgermafluorene (4-9).
Appendix II-17. 2,7-(2-ethynyl-6-methoxynaphthalene)-3,6-dimethoxy-9,9-diphenylgermafluorene (4-10).
Empirical formula C_{52}H_{38}GeO_{4}
Formula weight 799.41
Temperature 100(2) K
Wavelength 0.71073 Å
Crystal system Monoclinic
Space group P2_1/c
Unit cell dimensions

a = 17.1271(19) Å \( \alpha = 90^\circ \).
b = 21.292(2) Å \( \beta = 107.175(8)^\circ \).
c = 11.1484(13) Å \( \gamma = 90^\circ \).

Volume 3884.2(8) Å^3
Z 4
Density (calculated) 1.367 Mg/m^3
Absorption coefficient 0.837 mm^{-1}
F(000) 1656
Crystal size 0.426 x 0.098 x 0.047 mm^3
Theta range for data collection 1.570 to 24.998°.
Index ranges

-20 \leq h \leq 20, -25 \leq k \leq 25, -12 \leq l \leq 13

Reflections collected 29512
Independent reflections 6825 [R(int) = 0.2833]
Completeness to theta = 25.000° 99.7 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.8620 and 0.5362
Refinement method Full-matrix least-squares on F^2
Data / restraints / parameters 6825 / 477 / 518
Goodness-of-fit on F^2 0.983
Final R indices [I>2sigma(I)]

R1 = 0.0859, wR2 = 0.1404
R indices (all data)

R1 = 0.2707, wR2 = 0.2066
Extinction coefficient n/a
Largest diff. peak and hole 0.568 and -0.497 e.Å^{-3}

Appendix II-18. Crystal parameters for 2,7-(2-ethynyl-6-methoxynaphthalene)-3,6-dimethoxy-9,9- diphenylgermafluorene (4-10).