Synthesis of New Light-Emitters via Zirconium-Mediated Coupling

by

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of

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Abstract

The work described within this thesis details explorations into the area of molecular luminogens, in particular using zirconium-mediated coupling to access novel classes of color tunable emitters based on germanium, tellurium, and butadienes.

Chapter 2 features new class of air-stable phosphors termed as spirocyclic germafluorene-germoles. This new library of color tunable luminogens was prepared using Suzuki-Miyaura, Stille, and zirconocene-mediated couplings. In addition, the synthesis and properties of homo- and co-polymers based on spirocyclic germafluorene-germole unit were explored and challenges associated with these materials are discussed herein.

Chapter 3 describes a new general Suzuki-Miyaura cross-coupling protocol for the synthesis of symmetrical diarylalkynes. They were further transformed into new tetraarylbutadienes, and their fluorescent properties and photo- and thermal stability were investigated. Attempts to prepare potentially blue luminescent tin-capped building block based on a cumyl-substituted tetraarylbutadiene for further Stille polymerization protocols is reported.

In Chapter 4 the synthesis and characterization of new symmetric tellurium heterocycles for both hole-transport and light-emitting applications is presented. This work builds upon the general alkyne synthesis route introduced in Chapter 3.

Preface

Portions of the work discussed in this thesis were completed in collaboration with other researchers within the Rivard group and Chemistry Department, as well as outside of the University of Alberta.

All X-ray crystallographic studies described in this thesis were performed by Dr. R. McDonald and Dr. M. J. Ferguson, including the mounting of crystals, set-up and operation of the diffractometer, refinement of the structures and preparation of all crystallographic data tables.

In chapter 2, lifetime, absolute quantum yield and aggregation-induced emission measurements were performed by Prof. G. He at Xi'an Jiaotong University (China). In chapters 3 and 4, these measurements were done by Mr. Y. Qi under his supervision.

In chapter 3, some microwave-assisted trials of precursor stability and screening of reaction conditions were performed with the assistance of Ms. A. Cottrell-Callback within WISEST (Women in Science, Engineering and Technology) Summer Research Program.

In chapter 4, computational analyses were performed by Dr. Mike Boone (Rivard group). In addition, photoelectron spectroscopy measurements were performed by Mr. H. Shimogawa under supervision of Prof. A. Wakamiya at Kyoto University (Japan). Electron and hole mobilities are currently being evaluated by Mr. N. Hohn under the supervision of Prof. P. Müller-Buschbaum at the Technical University of Munich (Germany).

I also would like to acknowledge the collaborators, whose work is not described in this thesis. I would like to thank Prof. R. H. Herber for Mössbauer Effect spectroscopy measurements (Hebrew University of Jerusalem, Israel) and Dr. Saeid Sadeh under supervision of Prof. J. Müller (University of Saskatchewan) for synthetic attempts towards ferrocenophanes.

According to the policy within our research group, each chapter of this thesis is essentially self-contained, and prepared in the form of a paper that is intended for publication in peer-reviewed journals.

A portion of this thesis has been published previously elsewhere, and these publications are listed below.

Chapter 2: Shynkaruk O., He G., McDonald R., Ferguson M. J., Rivard E., *Chem. Eur. J.* **2016**, *22*, 248-257.

Chapter 3: Shynkaruk O., Qi Y., Cottrell-Callbeck A., Torres Delgado W., McDonald R., Ferguson M. J., He G., Rivard E., *Organometallics*, **2016**, *35*, 2232-2241.

Publications, not highlighted in this thesis, are as follows:

(1) He G., Shynkaruk O., Lui M. W., Rivard E., *Chem. Rev.* **2014**, *114*, 7815-7880.

(2) Al-Rafia S. M. I., Shynkaruk O., McDonald S. M., Liew S. K., Ferguson M. J., McDonald R., Herber R. H., Rivard E., *Inorg. Chem.* **2013**, *52*, 5581-5589.

(3) He G., Kang L., Torres Delgado W., Shynkaruk O., Ferguson M. J., McDonald R., Rivard E., *J. Am. Chem. Soc.* **2013**, *135*, 5360-5363.

Dedicated to my grandfather Vitaliy Dubok and parents Marina Shynkaruk and Alexander Shynkaruk

"Never, never, never give up." – Winston Churchill

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Next, I must thank my dear family. They are always there for me despite being on the other side of the world, rooting for me and telling me not to give up. There are no words to express how blessed and grateful I am to have them.

None of what is described in this thesis would have been possible without an expertise of the wonderful staff at the University of Alberta. We are so lucky to work with them! I would like to express special gratitude to Dr. Wayne Moffat for accepting me in his Analytical and Instrumentation lab (family) and all his assistance with instruments, measurements and useful discussions. I would like to thank Dr. Bob McDonald and Dr. Michael Ferguson for all their help with X-ray crystallography; Jing Zheng for training me to do MALDI and all the immediate and continuous help with mass spectrometry; to Dr. Jason Cooke for giving me an opportunity to teach Advanced Inorganic Chemistry labs, making this experience enjoyable and guiding me to become a better teacher. In addition, I would like to thank Jennifer Jones, Dr. Randy Whittal, Ed Fu, Bernie Hippel, Ryan Lewis, Anita Weiler, Jason Dibbs, the wonderful staff of the NMR lab, electronic and machine shops.

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List of Symbols, Nomenclature or Abbreviations

{^{n}X}	Decoupled nucleus ^{n}X
2D	2-Dimensional
Å	Ångström
ACQ	Aggregation-Caused Quenching
AIE	Aggregation-Induced Emission
Ar	Aryl
avg.	Average
bipy	2,2'-bipyridine
br	Broad
Bp	Boiling point
BPin	Pinacolborane
°C	Degrees Celsius/centigrade
ca.	circa; approximately
Cl_2-py	2,6-dichloropyridine
COD	1,5-cyclooctadiene
Cp	Cyclopentadienyl ligand (η^5-C_5H_5)
Cp*	Tetramethylcyclopentadienyl ligand (η^5-C_5Me_5)
Cy	Cyclopentyl ligand
d	Doublet
dba	dibenzylideneacetone
dd	Doublet of Doublets

DFT	Density Functional Theory
DMAP	4-Dimethylaminopyridine
DMF	N,N-Dimethylformamide
dppe	Ethylenebis(diphenylphosphine)
dppf	1,1′-Ferrocenediyl-bis(diphenylphosphine)
DSC	Differential Scanning Calorimetry
dt	Doublet of Triplets
EL	Electroluminescence
EPR	Electron Paramagnetic Resonance
equiv.	Equivalent
Et	Ethyl (C_2H_5)
Et_2O	Diethyl ether
eV	Electron volt
Fl	Fluorene
FT-IR	Fourier Transform Infrared Spectroscopy
g	Gram
GRIM	Grignard Metathesis
GPC	Gel Permeation Chromatography
HOMO	Highest Occupied Molecular Orbital
Hz	Hertz
^{i}Bu	*iso*-butyl (Me_2CHCH_2)
^{i}Pr	*iso*-propyl (Me_2CH)
IR	Infrared

K	Kelvin
kcal	Kilocalorie
LUMO	Lowest Unoccupied Molecular Orbital
Me	Methyl (CH_3)
Mes	Mesityl
mg	Milligram
MHz	Megahertz
min	Minute
mL	Millilitre
mmol	Millimole
mol	Mole
Mp	Melting point
^{n}Bu	*n*-butyl (C_4H_9)
$^{n}J_{AB}$	n-bond AB coupling constant
M_n	Number average molecular weight
M_w	Weight average molecular weight
NBS	N-Bromosuccinimide
NMR	Nuclear Magnetic Resonance
LDA	Lithium diisopropylamide
LED	Light-Emitting Device
OLED	Organic Light-Emitting Device
PDAF	Poly(9,9'-dialkylfluorene)
PDI	Polydispersity Index

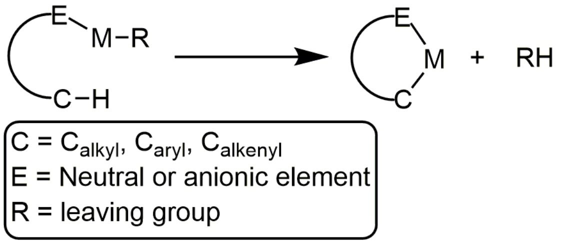
PF	Polyfluorene
Ph	Phenyl (C_6H_5)
PL	Photoluminescence
PLED	Polymer Light-Emitting Device
py	Pyridine
ppm	Parts per million
s	Singlet
^{s}Bu	*sec*-butyl
SGG	Spirocyclic Germafluorene-Germole
t	Triplet
TBAF	Tetrabutylammonium fluoride
^{t}Bu	*tert*-butyl (Me_3C)
td	Triplet of Doublets
T_d	Thermal decomposition
TGA	Thermogravimetric Analysis
THF	Tetrahydrofuran
TMEDA	*N*,*N*,*N′*,*N′*-Tetramethylethylenediamine
TPA	Triphenylamine
UV/Vis	Ultraviolet/Visible spectroscopy
vs.	Versus
XPhos	2-Dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl
δ	Partial charge or chemical shift in ppm
λ	Wavelength

λ_{ex}	Excitation wavelength
λ_{emis}	Emission wavelength
λ_{max}	Wavelength of maximum absorbance
η	Eta; the number of atoms through which a ligand coordinates
σ	Sigma
τ	Luminescence Lifetime
Φ	Luminescence Quantum Yield

Chapter One: Introduction

1.1. Brief overview of metallacycles

Metallacyclic compounds play a major role in the development of synthetic chemistry.[1] The most common synthetic route to metal-containing rings is cyclometallation (Equation 1.1),[2] where a M-C bond is formed during the cyclization process.[3,4] Selected examples of catalytically active metallacycles (**1-5**) are presented in Figure 1.1.



(1.1)

Heterocycles containing transition metals are known to activate olefins and acetylenes in catalytic processes (*e.g.*, complex **1**),[5] as well as for the electro- and photochemical reduction of water to hydrogen[6] (*e.g.*, complex **2**), cycloadditions,[7] and different functionalization reactions.[8] Moreover, five-membered heterocyclic compounds containing transition metals such as Pt, Pd, Rh, Ir, Ru, Os and Au, as well as N, P, O and S-coordinating atoms (*e.g.*, **3** and **4**) have been extensively explored as anticancer agents.[9] Cyclometallated platinum(II),[10] iridium(III)[11] and relatively unexplored gold(III) complexes (**5**)[12] have been explored in organic light-emitting devices as efficient phosphorescent luminophors with tunable color emission.

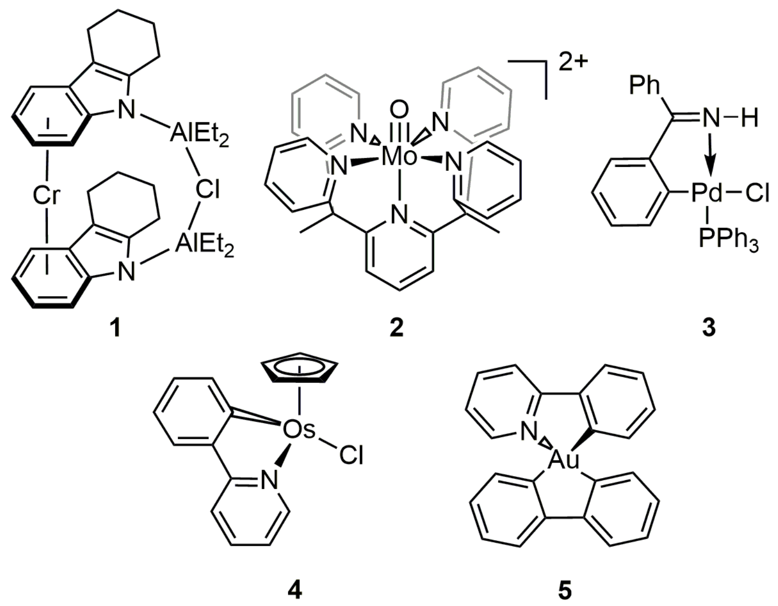


Figure 1.1. Selected examples of metallacycles.

Metallacycles have been thoroughly explored as building blocks in supramolecular chemistry,[13] where one of the main goals is to develop molecular architectures that have similar properties to natural systems.[14] Recent examples include chiral metallacycles that mimic natural enzymes,[14] metallacycles for fullerenes hosts[15] and supramolecular coordination complexes, obtained through coordination-driven self-assembly.[16] The latter also have been highlighted as an important strategy for synthesis of fluorescent metallacycles and metallocages for ion detection.[17]

Metallacycles have become a major area of investigation in organometallic chemistry, and are normally generated *in situ* during reductive coupling of two unsaturated organic substrates on a low valent transition metal center.[18] Zirconacycles are useful synthons[19] for the one-step preparation of carbocycles (important precursors in the synthesis of natural products and functional materials),[20] cyclic ketones,[21] pyridine and benzene derivatives,[1b] as well as polyacenes with electrical conductivity.[18b] Recent advances in the chemistry of group 4 metallacycles have been highlighted in multiple reviews by Tilley,[22] Tanabe[23], Takahashi,[24] and Rosenthal.[25]

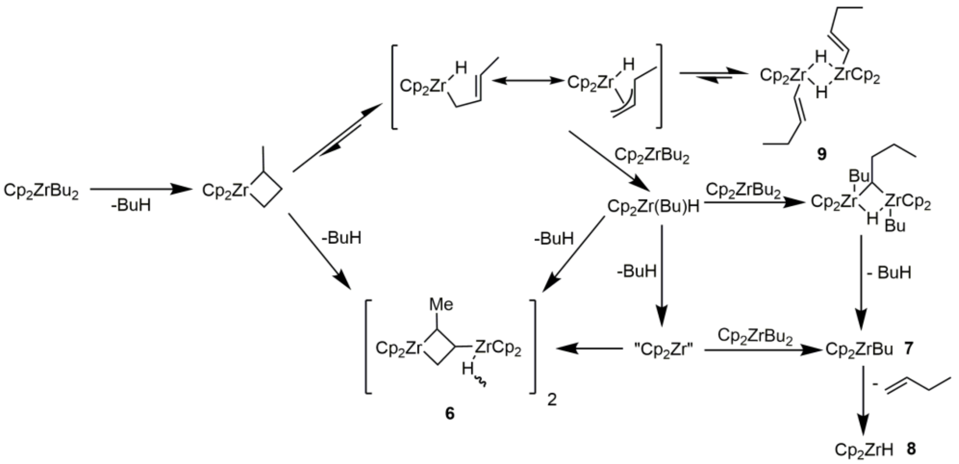
Another useful reaction of zirconacycles is Fagan-Nugent transformation,[26] affording main group element heterocycles with a wide range of applications from nitroaromatic explosives detection[27] to organic light-emitting devices.[28] Zirconacyclopentadienes, related heterocycles and their properties will be discussed in detail in the next section as these species play a central role in advancing the chemistry described in this Thesis.

1.2. Metallacycle transfer

1.2.1. Zirconacyclopentadienes

In the 1970s, Rausch and Floriani first reported the reductive coupling of the group 14 metallocenes $Cp_2M(CH_2)_2$ or $Cp_2M(CO)_2$ (M = Zr, Ti, Hf; Cp = η^5-C_5H_5) with alkynes to give symmetrically tetrasubstituted metallocyclopentadienes $Cp_2MC_4R_4$.[29,30] In 1961, the first tetraaryl-substituted zirconacyclopentadiene $Cp_2ZrC_4Ph_4$ was synthesized by Braye and Hübel from the condensation reaction between zirconocene dichloride (Cp_2ZrCl_2) and 1,4-dilithio-1,2,3,4-tetraphenylbutadiene; this latter reagent can be prepared from diphenylacetylene and finely divided lithium metal.[31]

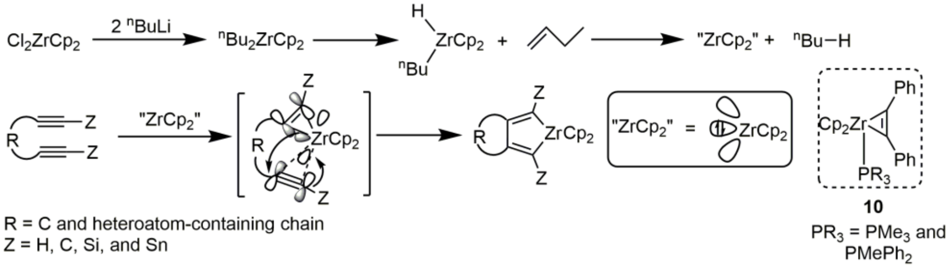
The field of zirconacyclopentadienes has grown immensely due to extensive development of various formally low-valent zirconium(II) precursors, many of which can be generated and used *in situ*. Examples of reactive sources of "$Cp_2Zr(II)$" include Cp_2ZrCl_2/Na,[32] Cp_2ZrCl_2/Mg,[30b] Cp_2ZrCl_2/Ln (Ln is an alloy of Ce, La, Nd, and Pr),[33] Cp_2ZrBu_2 (Negishi's reagent),[34] Cp_2ZrEt_2 (Takahashi's reagent),[35] and $Cp_2Zr(py)(Me_3SiCCSiMe_3)$ (Rosenthal's reagent).[36] Insights into the reaction of Cp_2ZrCl_2 with ^nBuLi to give the commonly used zirconacycle precursor Cp_2ZrBu_2 were provided by both the Negishi and Harrod groups. First, Negishi and co-workers reported the reversible displacement of Cp^- from a zirconium center during the reaction of excess ^nBuLi (3 equiv.) with Cp_2ZrCl_2, leading to the formation of a 1:1 mixture of $CpZrBu_3$ and LiCp.[37] Meanwhile, Harrod and co-workers studied decomposition of the reaction mixture of initially generated Cp_2ZrBu_2 (*i.e.*, "Cp_2Zr" source) at room temperature, where predominantly Zr(III) (**7** and **8**) and Zr (IV) (**6** and **9**) products were identified and characterized by EPR or multidimensional, multinuclear NMR spectroscopy (Scheme 1.1).[38]



Scheme 1.1. Products of thermal decomposition of dibutylzirconocene reaction mixture ("Cp_2Zr" source) at room temperature.
[Adapted with permission from Harrod and co-workers, *Organometallics*, **1997**, *16*, 1452-1464. Copyright 1997 American Chemical Society].

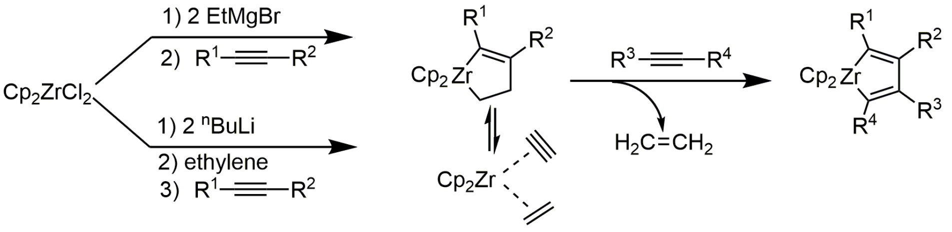
1.2.2. Synthesis of bicyclic zirconacycles

When linked diynes are reacted with $Cp_2Zr(II)$ sources, one can obtain bicyclic zirconacycles; a general mechanism for this reaction is presented in Scheme 1.2. Investigation of the mechanism was performed by Negishi[30c] and Takahashi,[39] using alkynes. In the reaction of "Cp_2Zr" with two equivalents of PhC≡CPh, zirconacyclopropene **10** (product of oxidative coupling) was trapped by stabilization with electron-donating phosphines PR_3 (PR_3 = PMe_3 and $PMePh_2$), and characterized by X-ray crystallography. Isolation of **10** supports the mechanism (Scheme 1.2), involving the initial generation of a zirconacyclopropene followed by its intramolecular carbometallation with the remaining free alkyne moiety of a diyne.[30c] In the proposed mechanism by Negishi and co-workers[30c] and later confirmed by DFT calculations from Tilley group,[40] the ratedetermining step in the reaction of Cp_2ZrCl_2 with ^nBuLi in the presence of diyne[34] is formation of "Cp_2Zr". "Cp_2Zr" is a 14-electron species with two valence-shell empty orbitals and at least one filled nonbonding orbital for π-complexation/carbometallation of diyne, leading to the formation of a zirconacycle.[30c, 34, 37b, 41]



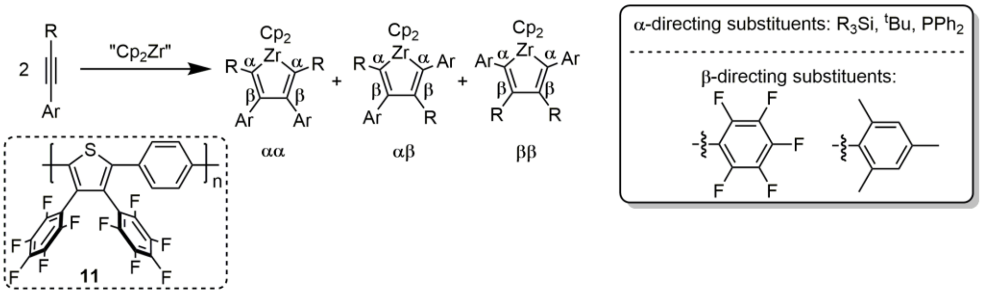
Scheme 1.2. Mechanism of formation of a zirconacycle. Structure of the isolated zirconacyclopropene **10**.
[Adapted with permission from Negishi and co-workers, *Tetrahedron Lett.* **1986**, *27*, 2829-2832 and *J. Am. Chem. Soc.* **1989,** *111*, 3336-3346. Copyright 1986 ScienceDirect and 1989 American Chemical Society].

Asymmetric zirconacycles can be obtained either by the step-wise addition of two different alkynes or by addition of two equivalents of an asymmetrically-substituted alkyne (R^1-C≡C-R^2). In the former case, Takahashi and co-workers[42] found that Cp_2ZrEt_2 or Cp_2ZrBu_2 in the presence of ethylene gas could be used to obtain unsymmetrical zirconacycles (Scheme 1.3). It is worth noting that when using Cp_2ZrEt_2 as a precursor (generated *in situ* from Cp_2ZrCl_2 and EtMgBr) small amounts (up to 10 %) of homocoupled alkynes (diynes) as well as low yields of cross-coupling products for silyl-substituted alkynes were reported,[35] while Cp_2ZrBu_2 in the presence of ethylene gas gave excellent selectivity and yields for β,β-isomer (Scheme 1.4).[30d]

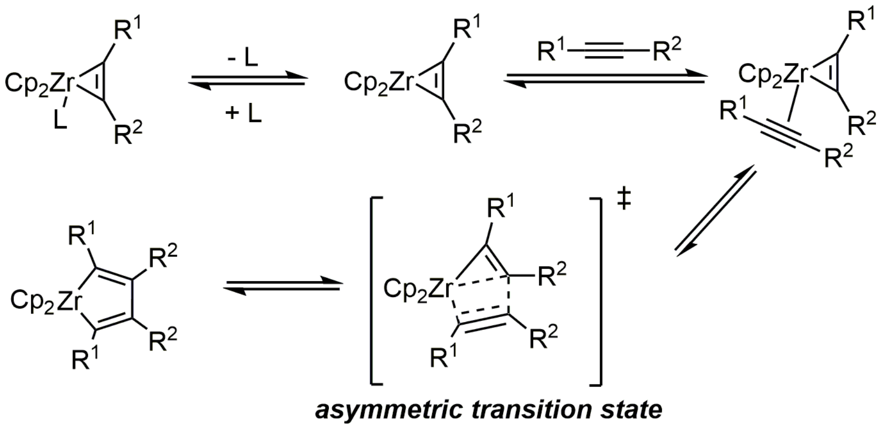


Scheme 1.3. Synthesis of asymmetrical zirconacycles using two different alkynes.
[Adapted with permission from Takahashi and co-workers, *Bull. Chem. Soc. Jpn.* **1999,** *72*, 2591-2602. Copyright 1999 The Chemical Society of Japan].

In the case of asymmetrical alkynes, substituents can adopt αα, αβ or ββ positions on a metallocyclopentadiene ring (Scheme 1.4), and Tilley's group investigated the regioselectivity of the reaction based on the steric and electronic nature of the substituents. Using Erker's findings about the reversibility of zirconacycle formation in the presence of $SiMe_3$/^{t}Bu-substituted alkynes,[43] Tilley and others reported that sterically demanding substituents (*e.g.*, R_3Si, ^{t}Bu,[44] PPh_2[45]) prefer to occupy α positions, while electron-withdrawing (*e.g.*, C_6F_5, mesityl) prefer β-positions, whereas mesityl groups (due to their steric bulk) also promote the reversibility of alkyne couplings.[22] Indeed, based on the step-wise mechanism (Scheme 1.5), both steric and electronic factors influence the structure of the transition state, and thus, the substitution pattern in the final product. For instance, based on multidimensional NMR spectroscopy studies and DFT calculations of the isomers, Tilley and co-workers rationalized that in the case of an electron-withdrawing C_6F_5 group, electronic factors (*i.e.*, charge distribution in the transition state) controls the orientation of at least one alkyne as they are coupled. During the formation of an asymmetric transition state, which has two unequally activated alkyne moieties, one strongly and one weakly bound alkyne is present at the zirconium center. This β,β-regioselective coupling reaction with C_6F_5-susbstituted alkyne was used to obtain electron-transporting conjugated polymers (*e.g.*, **11**).[40]

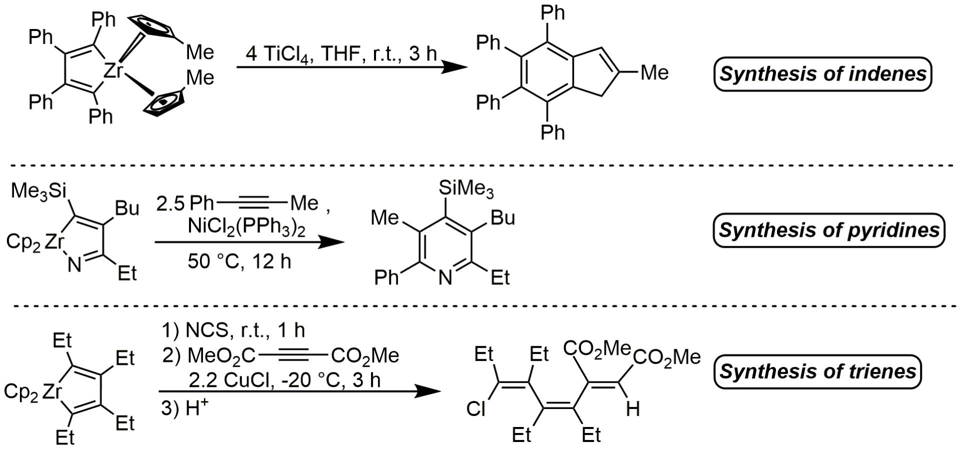


Scheme 1.4. Possible isomers of zirconacycles derived from coupling asymmetric alkynes. Structure of the conjugated polymer **11**. [Adapted with permission from Tilley and co-workers, *Acc. Chem. Res.* **2011**, *44*, 435-446. Copyright 2011 American Chemical Society].



Scheme 1.5. Step-wise mechanism of alkyne coupling to form asymmetric zirconacycles.
[Adapted with permission from Tilley and co-workers, *Acc. Chem. Res.* **2011**, *44*, 435-446. Copyright 2011 American Chemical Society.]

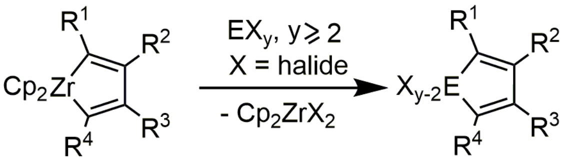
Zirconacycles are used in the synthesis of challenging organic compounds through reactions with different electrophiles to prepare benzene derivatives,[46] (hetero)acenes,[47] indenes,[48] fluorenes,[48] pyridines,[49] multi-substituted dienes,[50] enones,[51] and linear trienes.[52] Selected synthetic transformations are presented in Scheme 1.6. The transformation of greatest relevance to this Thesis is the reaction stated at the beginning of this Introduction, namely the preparation of inorganic element-containing five-membered metalloles via formal zirconium-element exchange.



Scheme 1.6. Selected synthesis of organic compounds using zirconacycles.

1.3. Metalloles: synthesis and challenges

Metalloles are derivatives of cyclopentadiene whereby a methylene unit is replaced by a main group element (E), such as S, Se, Te, N, P, As, Sb, Bi, Si, Ge, Sn, B, Al, Ga and others.[53] In 1988 William Nugent and Paul Fagan first reported the synthesis of main group five-membered heterocycles through the transfer of a butadiene fragment from zirconacyclopentadienes to main group elements, a process known as *metallacycle transfer* (Equation 1.2).[26] In general, these metallole syntheses are facile and versatile.[54] However due to low nucleophilicity of zirconacycles,[53] there are some reaction scope limitations, as evidenced by the very slow reaction of some p-block element halides with less polar E-X bonds. For example, $SiBr_4$ reacts with $Cp_2ZrC_4Me_4$ over two days at 150 °C to give only a 28 % yield of the resulting silole, $Br_2SiC_4Me_4$.[54]



(1.2)

Nugent and Fagan proposed various transition states for metallacycle transfer (Figure 1.2) based on the coordination number of the starting main group halide. Accordingly the authors emphasized that coordinative unsaturation and low steric bulk at the main group center facilitates metallacycle transfer. Also as one descends a group, the weaker nature of the E-X bonds coupled with the generally larger sizes of the main group elements leads to much faster reactivity.[54]

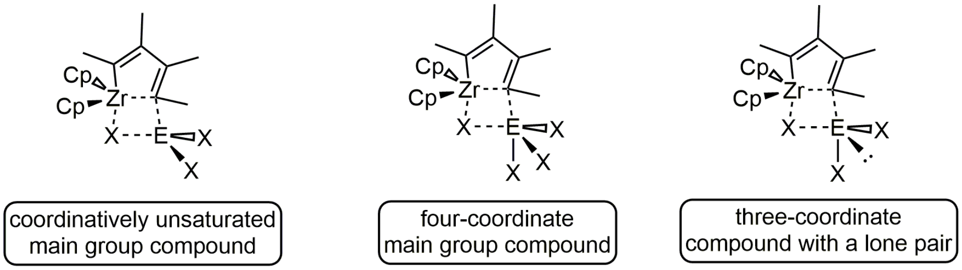
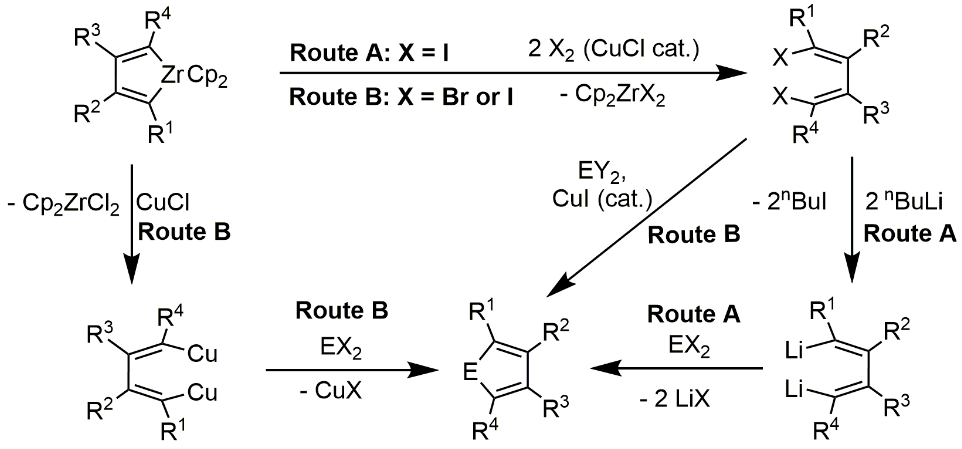


Figure 1.2. Proposed transition states during the first step of metallacycle transfer.
[Adapted with permission from Fagan and co-workers, *J. Am. Chem. Soc.* **1994,** *116*, 1880-1889. Copyright 1994 American Chemical Society.]

In order to expand the substrate scope and increase the effectiveness of metallacycle transfer, other strategies have been developed (Scheme 1.7) such as: a) transmetallation with 1,4-dilithio-1,3-butadienes[55] and b) copper-mediated transmetallation.[56] In general these alternate methods afford more reactive Li-C and Cu-C bonds in relation to the Zr-C bonds in zirconacyclopentadienes. Specifically protocols a/b outlined in Scheme 1.7 were used to gain access to boroles (routes A,[57] B[58]), alumoles (A),[59] siloles (A),[60] stannoles (B),[61] pyrroles (A,[62] B[63,64]), stiboles (A),[65] bismoles (A),[66] and thiophenes (B).[67]



Scheme 1.7. Alternative approaches for metallole formation. [Adapted with permission from Xi and co-workers, *Acc. Chem. Res.* **2015**, *48*, 935-946. Copyright 2015 American Chemical Society.]

Metalloles are of interest in understanding the fundamental reactivity profiles of inorganic heterocycles such as the Diels-Alder [4+2] cyclodimerization of boroles.[68] Metalloles are also frequently used as building blocks for optoelectronic materials[69] including in photovoltaic devices,[70] organic light-emitting diodes,[71] organic field effect transistors,[72] chemical sensors, and in bioimaging materials.[73] The main focus of this Thesis is synthesis and optoelectronic properties of new germoles and tellurophenes, and pertinent review articles discussing other group 14 and 16 element-containing heterocycles can be found in the literature.[53, 74]

1.4. Germoles: an overview

1.4.1. Synthesis

Germoles (or germacyclopentadienes) are π-building blocks with unique electronic and optical properties. One characteristic feature of these species is the presence of a low-lying LUMO due to σ*-π* conjugation in the ring, arising from effective mixing of the σ* orbitals of two exocyclic Ge-C bonds and the π* orbital of the butadiene moiety of the five-membered ring (Figure 1.3).[75] In comparison to the lighter silicon congeners (siloles), the energies of the Ge-R and Si-R σ* orbitals are similar, leading to comparable LUMO levels in each heterocycle. The germanium atom also stabilizes/lowers the HOMO level of the diene compared to the carbon analogues[75], thus possibly increasing the thermal stability of germoles.

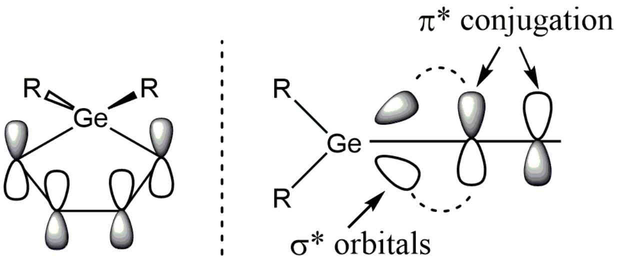
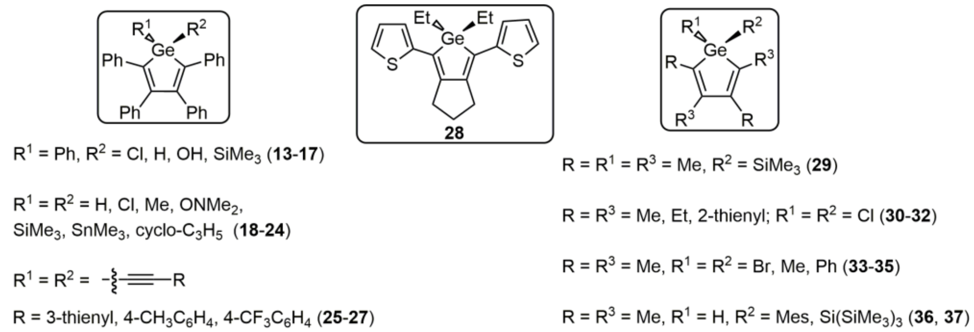


Figure 1.3. Left: π* orbital diagram of the butadiene moiety in a germole. **Right:** "Sideview" of interaction of Ge with two exocyclic ligands (*i.e.*, σ* orbital of exocyclic Si-C bonds) and the resulting σ*- π* orbital overlap.

The first germole derivative ($Ph_2GeC_4Ph_4$, **12**) was reported by Leavitt and co-workers in 1959 from the reaction of Ph_2GeCl_2 with 1,4-dilithiotetraphenylbutadiene.[76] In 1969 Curtis used a similar salt elimination reaction method to prepare a series of functionalized tetraphenylsubstituted germoles **13-17**[77] (Figure 1.4) and characterized these materials by elemental analysis. Since this important early work, interest in germacyclopentadienes has grown rapidly and a number of derivatives are now known (see Figures 1.4-1.6).[78]



R^1 = Ph, R^2 = Cl, H, OH, $SiMe_3$ (**13-17**)

R^1 = R^2 = H, Cl, Me, $ONMe_2$, $SiMe_3$, $SnMe_3$, cyclo-C_3H_5 (**18-24**)

R^1 = R^2 = –≡–R

R = 3-thienyl, 4-$CH_3C_6H_4$, 4-$CF_3C_6H_4$ (**25-27**)

R = R^1 = R^3 = Me, R^2 = $SiMe_3$ (**29**)

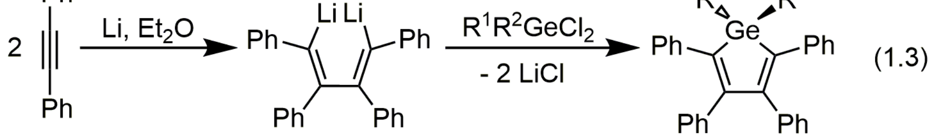
R = R^3 = Me, Et, 2-thienyl; R^1 = R^2 = Cl (**30-32**)

R = R^3 = Me, R^1 = R^2 = Br, Me, Ph (**33-35**)

R = R^3 = Me, R^1 = H, R^2 = Mes, $Si(SiMe_3)_3$ (**36**, **37**)

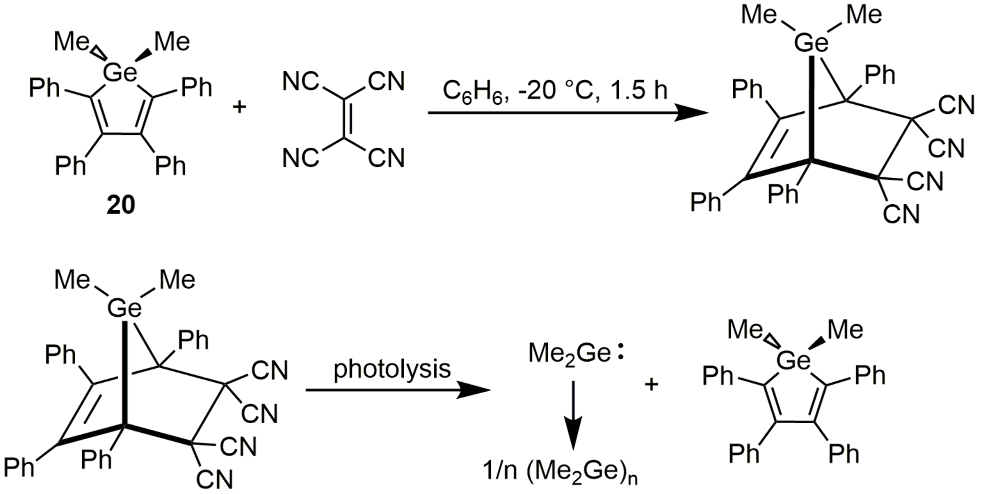
Figure 1.4. Representative examples of germoles.

Selected examples of germoles obtained by the initial dimerization of functionalized acetylenes in the presence of lithium metal (**13-27**) (Equation 1.3), followed by Fagan-Nugent transmetallation (**28-37**) are presented in Figure 1.4.



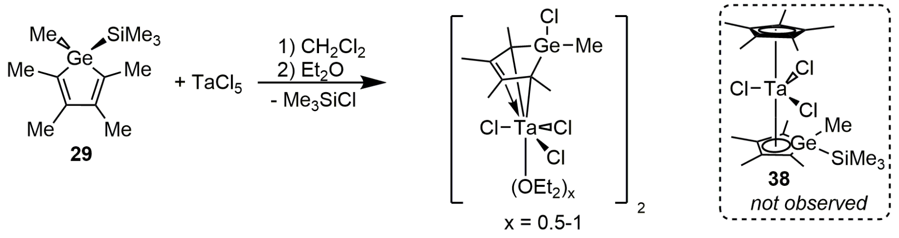
(1.3)

Electrochemical investigation of the germoles **19**, **20** and **22** showed at least two irreversible oxidation waves and a dependence of the oxidation potential on the nature of the germanium-bound substituents in the germacyclopentadiene ring. For example, compound **22**, bearing two electron-donating $SiMe_3$ groups, has an increased HOMO energy level and decreased oxidation potential when compared to **19** which has electron-withdrawing Cl groups at the germanium atom.[79] Density functional theory (DFT) was used to compute the electronic structures of **18** and **20** and showed that the HOMO and LUMO levels are mainly localized in the germole ring and on the two phenyl groups at the 2,5-positions.[80]



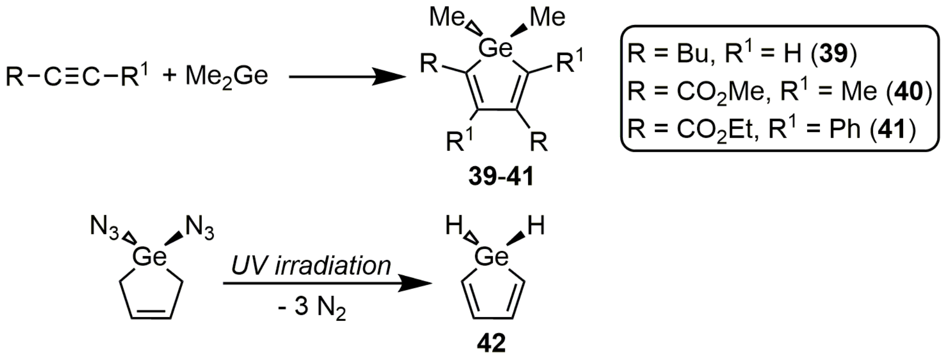
Scheme 1.8. Diels-Alder reaction of germole **20**.

Germoles **18**, **20** and **24** also take part in Diels-Alder cycloaddition reactions with different dienophiles (e.g., **20** with tetracyanoethylene, Scheme 1.8) to form 7-germanorbornadienes and 7-germanorbornenes, and the generated norbornenes were shown to be viable precursors for generation of reactive germylenes (R_2Ge:).[81] Tilley and co-workers reported a reaction between $(Me_3Si)(Me)GeC_4Me_4$ (**29**) and $TaCl_5$ to give an η^4-germole ligand instead of the target η^5-germolyl tantalum complex **38** (Equation 1.4).[78f]



(1.4)

Synthetic routes to germoles are not limited to the Fagan-Nugent metallacycle transfer reaction or to the coupling of 1,4-dilithiobutadienes with germanium halides. For example the asymmetrically-substituted germoles **39**-**41** were obtained from the reaction of the heavy carbene analogue dimethylgermylene, Me_2Ge, with the corresponding alkynes (Scheme 1.9).[82] In addition, the 1,1-dihydro-germole **42** was synthesized via UV irradiation of matrix isolated 1,1-diazido-1-germacyclopent-3-ene (Scheme 1.9)[83] while the tetrahydrogermoles ($R_2GeC_4H_4$; R = Me, Mes or ${}^nBu$; **43**-**45**) were obtained from the palladium-catalyzed coupling of cyclogermanes (*e.g.*, $(Mes_2Ge)_3$) with acetylenes (Figure 1.5).[84]



Scheme 1.9. Synthesis of germoles **39-42**.

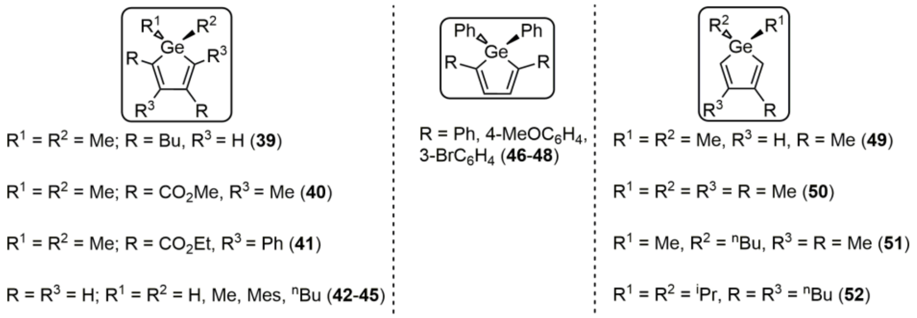
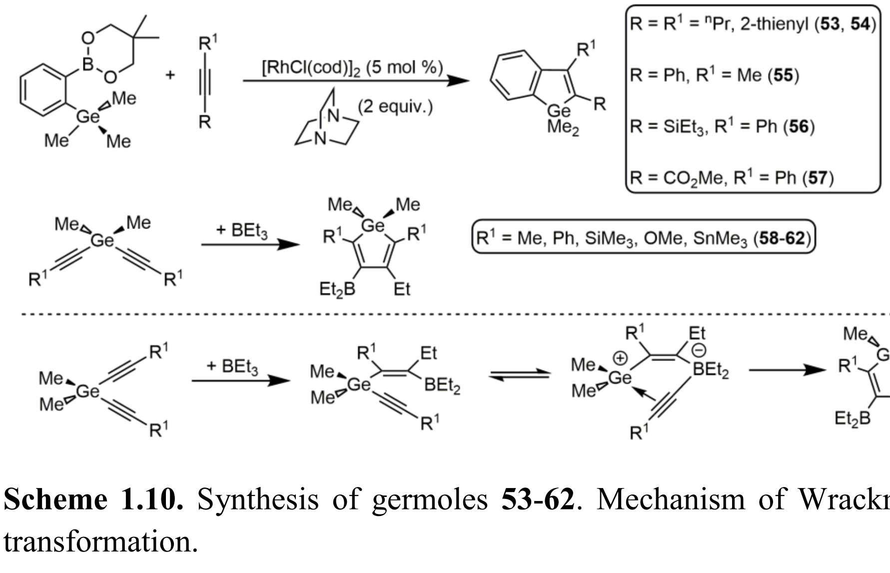


Figure 1.5. Selected examples of symmetric and asymmetric 2,5- and 3,4-substituted germoles.

Germoles functionalized exclusively at the 2- and 5-positions were obtained in good yield by Murakami and co-workers through the ruthenium-catalyzed (*i.e.*, [Cp*Ru(MeCN)$_3$]PF$_6$) trans-hydrogermylation of 1,3-diynes with dihydrogermanes (Ph$_2$GeH$_2$). The same strategy was successfully applied to synthesis of 2,2´-bigermoles.[85] Moreover, the area of 3,4-substituted germoles was extensively developed in the 1980s by Dubac and Manuel.[86] These germoles were obtained by the dehydration of 1-germacyclopent-4-en-3-ols on alumina (290-300 °C) or from the thermolysis of 1-germa-3-phenylcarbamoycyclopent-4-enes to give compounds **49**-**52** in good yield. The 3,4-substituted germoles obtained readily formed π-complexes with electron deficient metal carbonyls to give compounds of the general form (η^4-metallole)M(CO)$_3$ (M = Fe or Ru).[87]

Tobitsu and Chatani developed a modular synthesis of benzogermoles (*e.g.*, **53**-**57**) through the Rh(I)-catalyzed activation of C(sp^3)-Ge bonds in 2-germylphenylboronic esters in the presence of alkynes (Scheme 1.10).[88] Germoles with electron-deficient -BEt$_2$ substituents at the 3-position **59-63** (Scheme 1.10) were prepared by Wrackmeyer via the 1,1-organoboration of alkyn-1-ylmetal compounds Me$_2$Ge-C≡C-R^1 (R^1 = alkyl, aryl, silyl, or stannyl). The syntheses involved intermolecular and then intramolecular activation of the M-C bonds by electron-withdrawing triorganoborane BEt$_3$, followed by a selective new C-C bond formation via a 1,2-shift of an ethyl group from boron to carbon (Scheme 1.10).[78e, 89]



Scheme 1.10. Synthesis of germoles **53-62**. Mechanism of Wrackmeyer transformation.

1.4.2. Anionic germoles and the question of their aromaticity

The synthesis, structures, physical and chemical properties of mono- and dianions of germoles were extensively studied by Saito, West and Boudjouk.[90] Dianionic germoles are considered aromatic, while in contrast to the monoanionic siloles, there is no evidence of aromaticity within monoanionic germoles with the pyramidal geometries at the germanium atom (Figure 1.6).

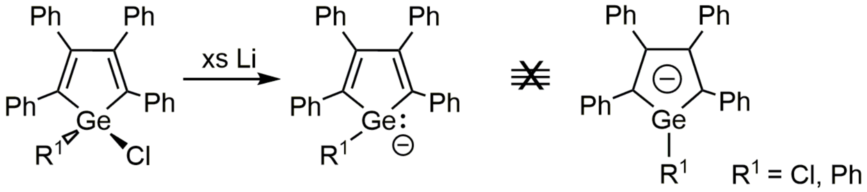


Figure 1.6. Synthesis of monoanionic germoles.

Reduction of 1,1-dichloro-derivatives **19** and **31** with excess lithium in THF gave the dianionic germoles $Li_2GeC_4R_4$ with η^5- and η^1/η^5-coordination modes of lithium and equal C-C distances within the germole ring (*i.e.*, delocalized π-system), as determined by X-ray crystallography.[91] The related dilithioplumbole $Li_2[PbC_4Ph_4]$ (**63**) was prepared by Saito and co-workers through the reduction of hexaphenylplumbole, and is the heaviest congener of the cyclopentadienyl dianion. This species was shown to have aromatic-type bonding in the PbC_4 ring by X-ray crystallography, NMR spectroscopy and theoretical calculations.[92] Moreover, Dysard and Tilley studied the coordination of the tetramethylgermole dianion $[GeC_4Me_4]^{2-}$, and demonstrated binding of this dianion to one metal (*e.g.*, Hf and Zr) in a η^5-fashion,[93] or to two metals (e.g., Hf/Rh and Hf/Ir) to yield bimetallic complexes with metals in σ,π-binding modes.[94] West and co-workers used $[GeC_4Ph_4]^{2-}$ in the reductive coupling of aldehydes to obtain 1,2-diols as the sole organic product.[95]

1.4.3. Molecular diaza-, dinaphto-, dithieno-, and diselenogermoles, and polymers of germoles, and their optoelectronic applications

The Heinicke group prepared various diazagermoles (**64**-**66**; Figure 1.7) which can be viewed as heavier homologues of diaminocarbenes.[96] Dinaphthoheteroles are of interest for their optoelectronic properties, thus Kurita and co-workers synthesized the first examples of optically active group 14 dinaphthogermoles (Figure 1.7). These species were prepared by a condensation reaction between 2,2'-dilithio-1,1'-binaphtyl and dichlorogermanes (Equation 1.5). Compounds **67** and **68** are fluxional on the NMR time scale at elevated temperatures (50-80 °C) and the estimated energy barrier for racemization in **68** is 80 ± 2 kJ mol^{-1}.[97]

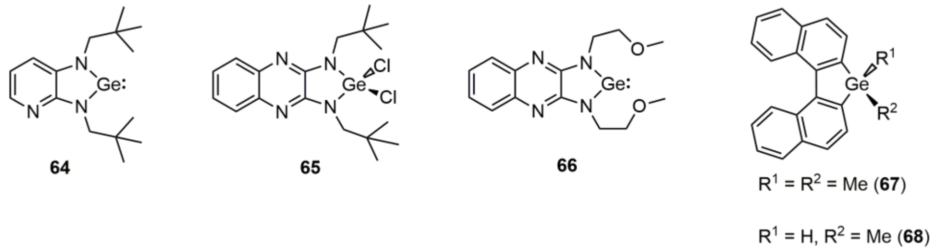
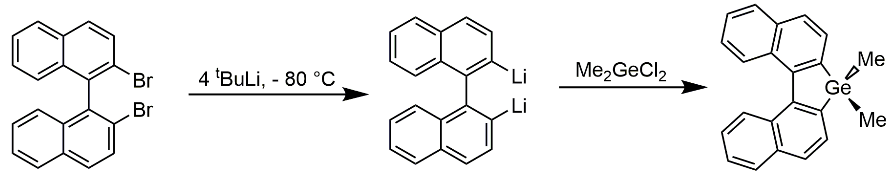


Figure 1.7. Selected examples of diaza- and dinaphthogermoles.



67

(1.5)

Element-bridged bithiophenes have been extensively used as building blocks in π-conjugated oligomers and polymers.[98] This planar and potentially conjugated unit shows novel properties when bridging inorganic elements are present. For example the incorporation of germanium has attracted great interest due to enhanced interchain interaction within the resulting dithienogermoles in the solid state, leading to useful carrier transporting properties. In addition, interaction of the π*-orbitals in bithiophene with the σ*-symmetric orbitals at germanium leads to significant lowering of the LUMO energy level and smaller HOMO-LUMO energy gaps.[99] For this reason, dithienogermoles (DTGs) (Figure 1.8) have been actively studied in organic photovoltaics by Ohshita,[100] Leclerc,[101] Reynolds,[102] Heeney,[103] and others.[104]

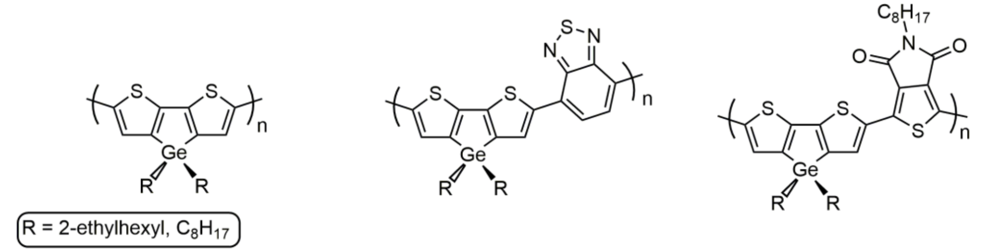
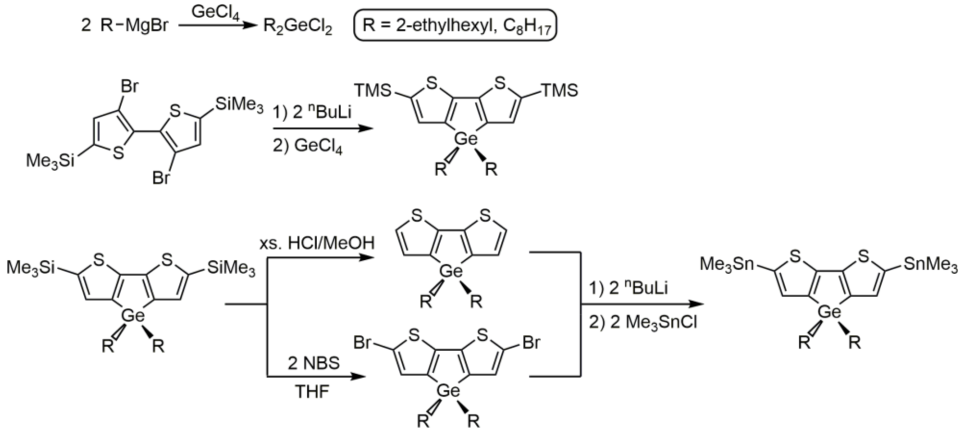
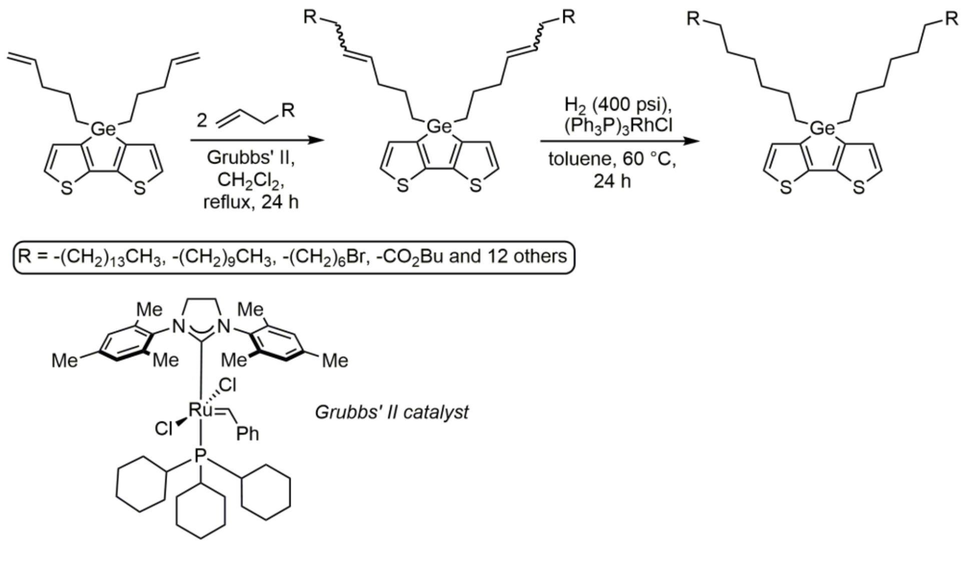


Figure 1.8. Common dithienogermole (DTG)-containing polymers in organic photovoltaics.

A general synthetic route to DTG units is presented in Scheme 1.11.[100a, 102a, 105] Compounds with this π-system exhibit higher stability to bases in comparison to their silicon analogues, thus facilitating purification by column chromatography.[105] The Reynolds group also developed a modular synthesis of an array of DTGs with variable alkyl chain lengths via olefin cross-metathesis followed by hydrogenation (Scheme 1.12); this procedure affords dithienogermoles with alkyl chain substituents not readily available using traditional methods.[106]



Scheme 1.11. Synthesis of functionalized dithienogermoles.



Scheme 1.12. Synthesis of DTG derivatives via olefin cross-metathesis.

Recently the Heeney group reported DTG-based bulk heterojunction solar cells with power conversion efficiencies (PCEs) as high as 7.2 % without the need for thermal annealing or processing additives.[107] Interestingly, in the same area of photovoltaics, donor-acceptor polymers based on dithienogermolocarbazole (*e.g.*, **69**; Figure 1.9) were made with recorded power conversion efficiencies of 4.05-4.50 %.[108] Furthermore, benzodiselenogermoles (**70**-**75**; Figure 1.9) were reported by Meunier and co-workers in 1991.[109] Heavier analogues of DTGs, diselenogermoles (DSGs), have also been explored as donor monomer units in low band gap conjugated polymers, leading to broader and more red-shifted absorption spectra in comparison to DTG analogues; polymer **76** was used a component in an inverted bulk heterojunction solar cell with a power conversion efficiency of 5.2%.[110]

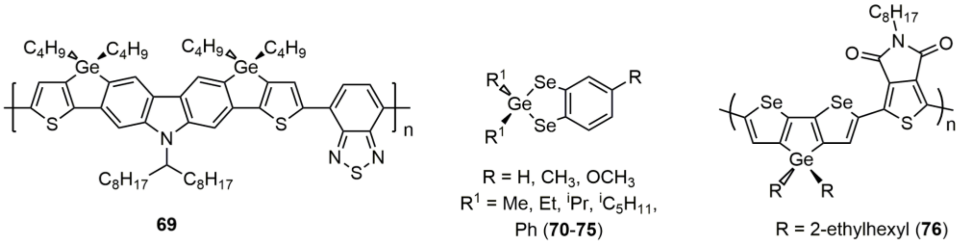


Figure 1.9. Selected examples of germole derivatives (**69**-**76**).

Germole heterocycles are also excellent candidates for electron transport materials due to their low-lying LUMO states. For instance, their lighter analogues, siloles, have similar LUMO energies as commonly used the nitrogen-containing electron transport materials (*e.g.*, 1,3,4-oxadiazole) in electroluminescent devices.[111]

Another fascinating application of group 14 heterocycles is the detection of nitroaromatic explosives by photoluminescent polygermoles (**77**-**79**; Figure 1.10).[27, 112] The blue-green fluorescent polymer **77** was obtained by the dehydrocoupling polycondensation of dihydrotetraphenylgermole **18** with either 0.2 mol % of $H_2PtCl_6{\cdot}xH_2O$ and an excess of cyclohexene or 1 mol % of Wilkinson's catalyst $RhCl(PPh_3)_3$;[113] Wurtz-type polycondensation of dihalogermoles can also yield polymers **77** and **78**.[112] Photoluminescence quenching within **77**-**79** may be monitored to detect nitrobenzene, 2,4-dinitrotoluene, 2,4,6-trinitrotoluene and picric acid.[27, 112] Wurtz-type coupling was used by Tomita *et al.*[114] to obtain a 1,1-dimethylgermole-containing polymer with a low lying LUMO of -3.95 eV, which is lower compared to the LUMO level of -2.59 eV in the thiophene-containing polymer **80**; as mentioned, a low-lying LUMO is preferred for an electron-transporting layer in organic semiconductors.[115]

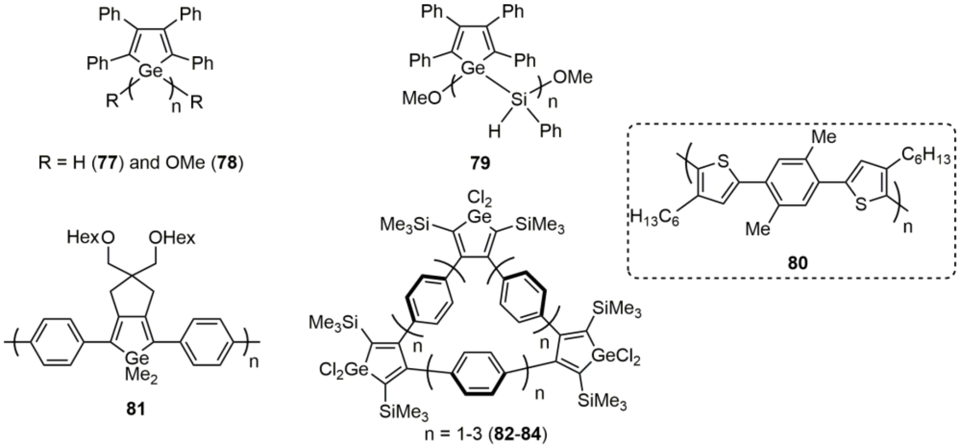
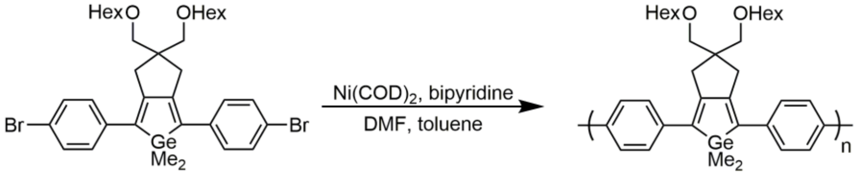


Figure 1.10. Selected examples of polymers and macrocycles containing germoles and structure of the thiophene polymer **80**.

The Tilley group reported the germole-incorporated conjugated polymer **81** via zerovalent nickel-mediated Yamamoto homocoupling of a dibromo-capped precursor (Equation 1.6). Polymer **81** displayed photoemission properties that were strongly dependent on chain length, where the sample with the highest molecular weight (M_n) of 20,000 strongly emitted green light with a quantum yield of 79 %.[116] The same group has also developed the synthesis of trigermole macrocycles **82**-**84** using the zirconocene "Cp_2Zr" coupling of alkynes, followed by subsequent Zr/Ge transmetallation; these compounds might be useful as supramolecular building blocks.[117] In addition, Tang and co-workers reported hyperbranched poly(phenylenegermolene)s, which had excellent thermal stabilities (> 350 °C) and cooling-enhanced blue light emission properties (due to restricted intramolecular motions of the phenyl peripheries at low temperatures).[118]



81

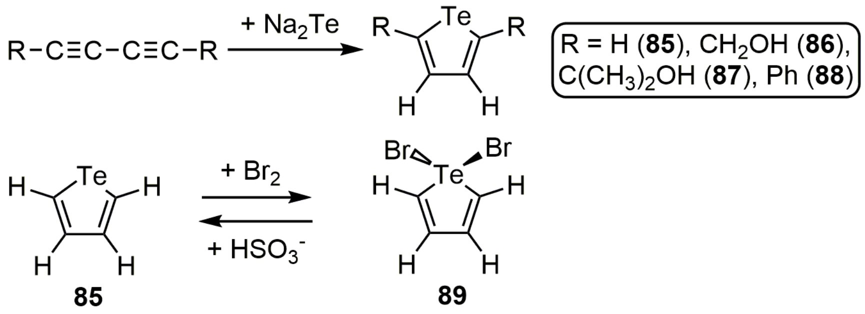
(1.6)

1.5. Tellurophenes: an overview

1.5.1. Synthesis of tellurium heterocycles

First reported attempt to prepare a tellurium heterocycle was in 1933,[119] however only in 1966 did Mack isolate examples of tellurophenes (**85**-**88**) via the reaction of functionalized 1,3-butadienes with Na_2Te (Scheme 1.13).[120] In addition, the dibromide derivative **89** was obtained upon treatment of **85** with elemental bromine; this species could be reconverted into tellurophene **85** by addition of HSO_3^- (Scheme 1.13).[120] Until very recently, Mack's tellurophene synthesis remained one of the most commonly used routes, although synthetic procedures have been improved over the years.[121] Recent developments include *in situ* synthesis of Na_2Te from $NaBH_4$ and elemental tellurium.[122] Another synthetic method, discovered by our group and highlighted in reviews by Rivard[74d] and Xi,[53] involves metallacycle transfer chemistry, *i.e.*, zirconacycle formation and subsequent Zr/Te transmetallation with THF-soluble

$TeCl_2$·bipy[123] (bipy = 2,2′-bipyridine) to obtain a range of tellurium heterocycles (**90-95**).



Scheme 1.13. Synthesis of tellurophenes **85-89** and reversible bromination of **85**.

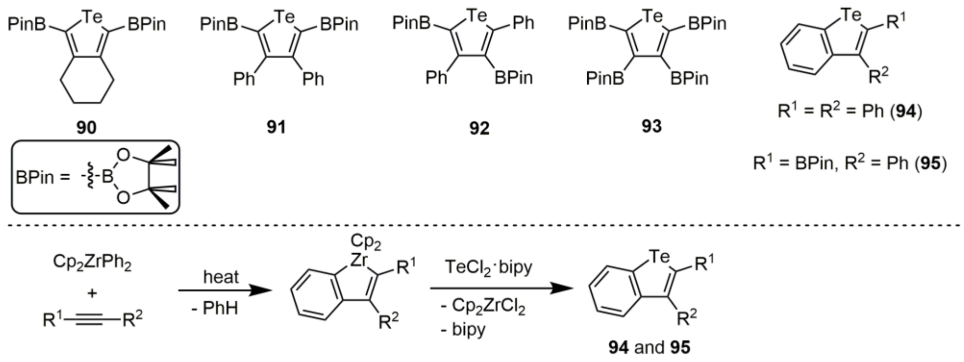


Figure 1.11. Selected examples of tellurophenes and benzotellurophenes prepared in the Rivard group.

Vargas showed [2+2] photosensitized cycloadditions of functionalized maleic anhydrides with tellurophenes.[124] In recent years McCormick, Carrera and Seferos studied the photochemistry of tellurophenes in detail, including the reversible oxidation of Te(II) heterocycles to Te(IV) halogenated derivatives;[125] the same group also prepared water-soluble tellurophenes for water splitting[126] and uncovered a detailed mechanism associated with the light-driven loss of halogens from dihalogenated tellurophenes (see Scheme 1.13).[127] Tellurium macrocycles,[128] specifically porphyrins with embedded tellurophene fragments,[129] have been shown to have anticancer activity, and this topic has been recently reviewed.[130] Tellurium-based monocationic compounds (*e.g.*, **96** after oxidation with 1 equivalent of $Cu(ClO_4)_2$) have been explored in charge delocalization phenomena of π-complexes[131] and as potential charge-conducting species (*e.g.*, **97**; Figure 1.12).[131,132] In 2012, the Tokitoh group was the first to isolate and study a tellurenyl (II) cation (**98**) by trapping with triphenylphosphane or butadienes (**99**; Figure 1.12).[133]

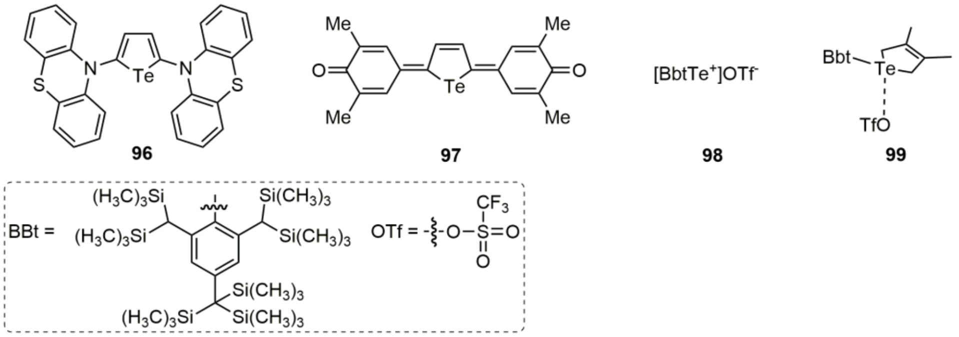
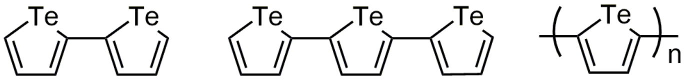


Figure 1.12. Structures of monocationic tellurophenes **96** and **97** as well as the tellurenyl (II) cation **98** and the butadiene-trapped **99**.

1.5.2. Polytellurophenes and their application in organic electronics

Tellurium-containing polymers have attracted attention from the materials community for the following reasons: (1) high polarizability and dielectric constants stemming from the presence of the heavy element, tellurium (Te); (2) narrow HOMO-LUMO gap (1.4-1.6 eV) in polytellurophenes leading to light absorption that extends to the near IR-region and more efficient solar light harvesting; (3) strong Te···Te intermolecular interactions leading to enhanced interchain electronic coupling and facilitation of charge transport;[74e] and (4) light-emission that is phosphorescent in nature, giving potential enhancement of LED efficiencies up to 100 % compared the maximum value of 25 % found in fluorescent emitters.[74d]

The first oligotellurophenes **100** and **101** were obtained as yellow/orange solids by the chemical oxidation of **85**.[134] The electrochemical polymerization of the parent tellurophene **85** as well the dimer and trimers **100** and **101** afforded the insoluble polytellurophene **102** as a black material with conductivities in the range of 10^{-5}-10^{-12} S cm^{-1}.[134,135]

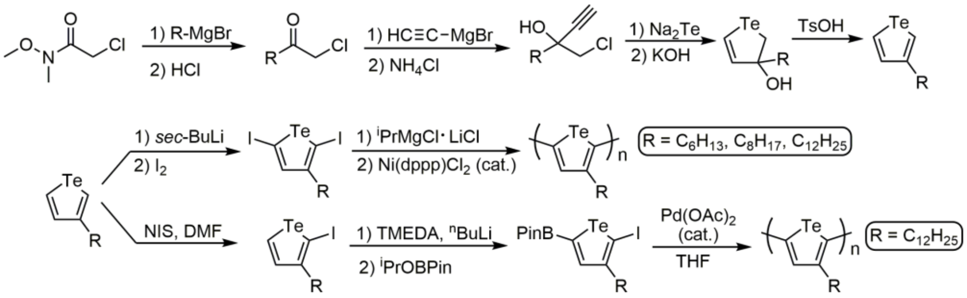


100 **101** **102**

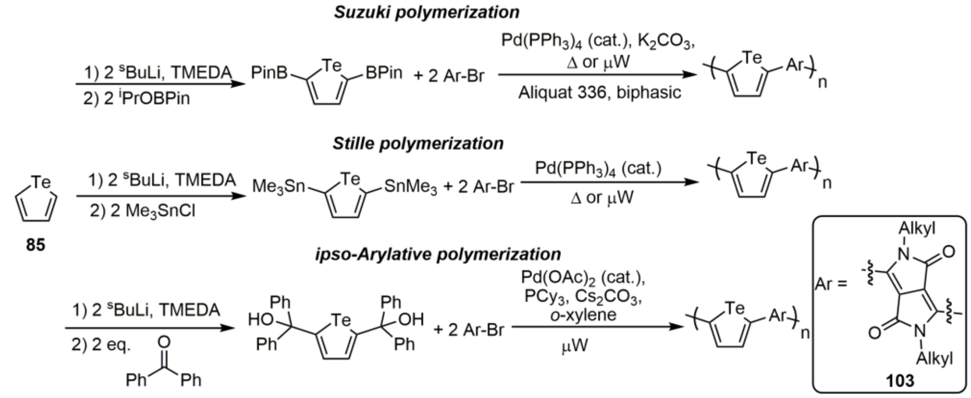
Figure 1.13. Parent oligo- and polytellurophenes.

During the past decade, improvements in synthetic protocols enabled the isolation of various soluble polytellurophenes including the landmark preparation of poly(3-alkyl)tellurophenes by Jahnke and Seferos at the University of Toronto (Scheme 1.14).[136] Other groups were also able to install reactive functional groups onto tellurium monomers[137]

(Scheme 1.15) allowing for the synthesis of a variety of copolymers using known cross-coupling methodologies.[138] The most recently class of tellurophene-copolymer are the donor-acceptor diketopyrrolopyrrole-tellurophene (DPP-Te) polymers (**103**) by Grubbs[139] and others.[140] These materials were tested in a range of optoelectronic devices, including within bulk heterojunctional solar cells, leading to a record power conversion efficiency of 4.4 % for a tellurium-containing donor layer.[139] It is important to note that preparation of pinacolborane-functionalized monomers by Rivard and coworkers (*via* metallaycle transfer chemistry; Figure 1.11)[138c] for Suzuki-Miyaura polymerization avoids the use of gaseous 1,3-butadiyne or Na_2Te, and overcomes the challenges related to competing oxidation chemistry at tellurium centers when preparing functionalized monomers.[74d]



Scheme 1.14. Synthesis of 3-alkyltellurophenes and their polymeric analogues.



Scheme 1.15. Functionalized tellurophene monomers and the diketopyrrolopyrrole-tellurophene DPP-Te polymer **103**.

In early 2015 Carrera and Seferos published an excellent review article about tellurium-containing homo- and copolymers and their role in high performance applications, such as in organic photovoltaics and field-effect transistors.[74e] Since then, the Seferos group has developed a method to achieve controlled living polymerization of alkyltellurophenes with number average molecular weights (M_n) of up to 25 kDa, [141] and studied them in high density polyethylene blends (*i.e.*, semiconductor:insulator blends) to understand their structure-property-function relationship and develop active layers for electronic devices.[142]

Recently tellurium heterocycles have emerged as a new class of light-emitting materials and the luminescence properties of these species will be discussed in Section 1.6.2.

1.6. The Aggregation-induced Emission (AIE) phenomenon

Aggregation-caused quenching (ACQ) is a phenomenon commonly observed in planar aromatic hydrocarbons (*e.g.*, perylene), wherby luminescence is often weakened or quenched at high concentrations or in the solid state.[143] In 2001 Prof. Ben Zhong Tang *et al.* discovered that 1,1-diphenyl-2,3,4,5-tetraphenylsilole can go from being essentially non-emissive in dilute solutions to a highly luminescent state in concentrated solutions or thin films due to the formation of aggregates.[144] This phenomenon was termed aggregation-induced emission (AIE). The origin of the AIE phenomenon lies in the restriction of intermolecular motion of ring-appended substituents which blocks non-radiative pathways and opens up the radiative channel (*i.e.*, luminescence). Since this initial key report, there have been thousands of articles dedicated to design and synthesis of new AIE systems, including recent reviews of the area published by Tang and co-workers.[145] This concept is not limited to inorganic heterocycles, but can also be seen in organic frameworks, such as the widely studied tetraarylethenes.[146] By overcoming ACQ real world applications of AIE-active luminogens (*i.e.*, light-emitters) are possible, such as their use in organic light-emitting diodes[147] and as fluorescence-based bioprobes.[148]

1.6.1. AIE effect in germoles

In early the 2000s, Tracey and Mullin actively studied heavier analogues of AIE-active siloles, such as 1,1-dimethyl- (**104**) and 1,1-diphenyl-2,3,4,5-tetraphenylgermoles (**105**).[149] They found greater photoluminescence efficiency of germoles in solution compared to the silicon analogues (up to two magnitudes greater).[149c] The efficiency of germole photoluminescence in the aggregated state was also 30 times greater than in their corresponding silole.[149b] Supported by TEM measurements, Tracey and Mullin showed that the initial formation of disordered aggregates occurred in mixed-solvent systems which then rearranged to yield ordered, and highly emissive, arrays of germole nanocrystals in *ca*. 35 mins.[149a] Recent findings in the area of AIE-active germoles have been recently reviewed in an excellent manner by Mullin and Tracey[150] as well as by Corey.[151]

1.6.2. AIE effect in tellurophenes – a new class of phosphorescent light-emitting units for optoelectronics

The incorporation of heavy atoms in molecular arrays is desirable due to their ability to promote light emission from triplet states, *i.e.* phosphorescence. Their large spin-orbit coupling facilitates cross-over between singlet (S) and triplet (T) excited states, termed *intersystem crossing*, thus leading to substantial population of excited triplet states T_n and enabling phosphorescence to occur. Phosphorescent luminogens potentially provide quantitative internal efficiencies of light-emitting devices (LED), when compared to fluorescent emitters (*i.e.*, their maximum internal efficiency is 25 % due to the statistical distribution of singlet states) if the emission is not quenched by: a) oxygen; b) molecular rotation in excited states leading to non-radiative pathway; and c) intermolecular self-quenching by triplet-triplet annihilation in the aggregated/solid state.[74d] In order to overcome these challenges phosphorescent emitters are generally encapsulated/suspended in host matrices, making LED manufacturing cumbersome and limiting the amount of luminogen that can be incorporated in a device. In addition, the most common phosphorescent emitters are based on the expensive elements Pt and Ir.[152]

There has been interest in replacing precious metals in phosphorescent species with the less expensive main group element, tellurium, but there are some added challenges. For example, tellurium compounds are known to form close Te···Te intermolecular interactions; these interactions facilitate charge transport but they can also enhance intermolecular self-quenching of luminescence. Consequently, most tellurophenes exhibit aggregation-caused quenching (ACQ) (discussed in Section 1.5). However, over the past decades, reports have emerged in the literature where authors describe luminescence from tellurium-based heterocycles. In 1989 Zander and Kirsch noted phosphorescence of the parent benzo- and dibenzotellurophenes **106** and **107** (Figure 1.14) in frozen ethanol at 77 K.[153] A few decades later Data *et al.* reported solid state photoluminescence (PL) at 690 nm (not indicated if under air or nitrogen) of an ethynylbenzene-bistellurophene polymer **108**, but its efficiency and nature were not investigated in detail. Other examples of organotellurium species with temperature-dependent PL are presented in Figure 1.13. For instance, compounds **109** and **110** were luminescent in frozen Me-THF at 77 K and predicted to be phosphorescent by density functional theory calculations,[125c] while the tellurapyrylium dye **111** exhibited a 5-fold increase in fluorescence intensity in an EtOH-MeOH glass at 77 K compared to room temperature.[154] In addition, the 1-telluro-1,3-butadiene derivative **112** exhibits blue fluorescence with a lifetime (τ) of 3.69 ns, and a moderate quantum yield (*Φ*) of 42 % in frozen Me-THF at 77 K.[155]

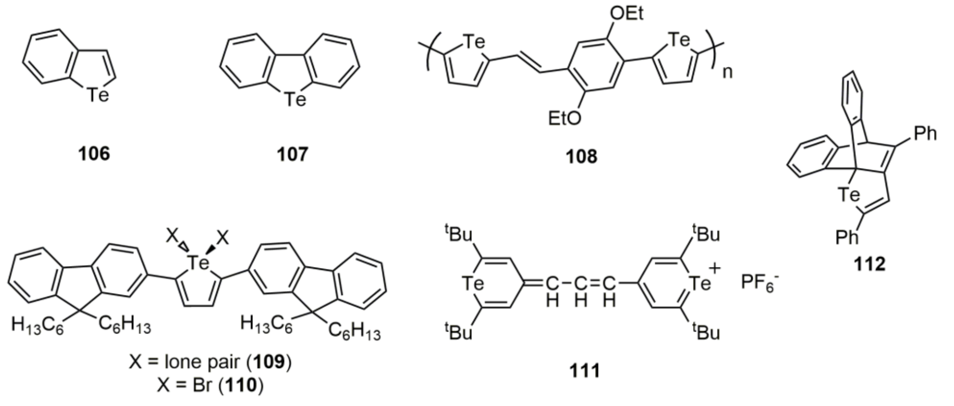


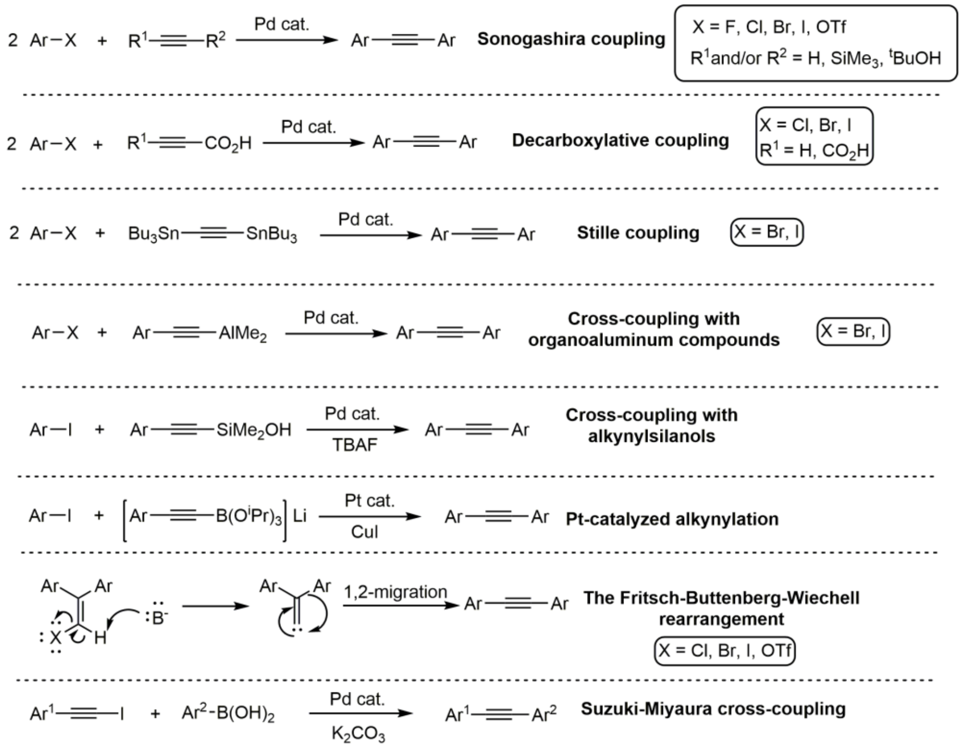
Figure 1.14. Selected luminescent organotellurium compounds.

In 2014 Dr. Gang He from our group discovered that the BPin-capped tellurophene **90** (Figure 1.11) afforded intense green phosphorescent emission in the film state (Φ = 12 % and τ = 166 μs) at room temperature in air.[156] Compound **90** was not emissive in dilute solutions, however exhibited enhancement of luminescence intensity in the aggregated/solid states, thus possessing AIE characteristics. This luminogen retained emission in matrices of poly(methylmethacrylate) (from 1 to 10 wt %). In addition, **90** could be used as an on/off reversible sensor for organic vapors. Additional investigations by modification of the substitutents on the tellurophene ring and computational methods showed that the emission in **90** occurs via singlet to triplet crossing in the excited state, and requires both a Te(II) center and a bulky BPin group to be present at the 2- or 5-positions of the heterocycle. In particular, the steric bulk of BPin substitutent prevents intermolecular interactions and self-quenching (e.g., triplet-triplet annihilation in the excited state) by keeping tellurium centers over 6 Å apart. Although benzotellurophenes have been thoroughly studied for decades,[157] a follow-up study by our group included phosphorescent examples of these species (**94** and **95**) as well as the first examples of color tunable phosphorescent regioisomers of tellurophenes (green **91** and orange **92** with Φ = 5 % in film state, Figure 1.11).[158] In 2015 Rivard published a review about phosphorescent BPin-capped tellurophenes.[74d]

1.7. Diarylalkynes: their synthesis and applications

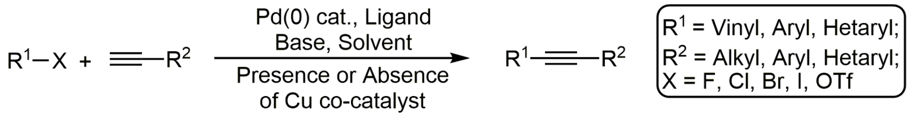
Diarylalkynes are important precursors for the synthesis of olefins,[159] ketones,[160] fused organic heterocycles[161] as well as functional inorganic heterocycles such as Te/B heterocycles,[162] π-conjugated systems,[163] vinyl cations,[164] clusters,[165] arylalkene polymers,[52b, 166] spirocycles,[167] and materials with a broad range of biological activities[168] (e.g., antitumor agents)[169] and nonlinear optical properties.[170] In addition, the use of diarylalkynes in the synthesis of main group luminophores is described in Section 1.8.

Various synthetic methods used to prepare diarylalkynes are summarized on the Scheme 1.16.

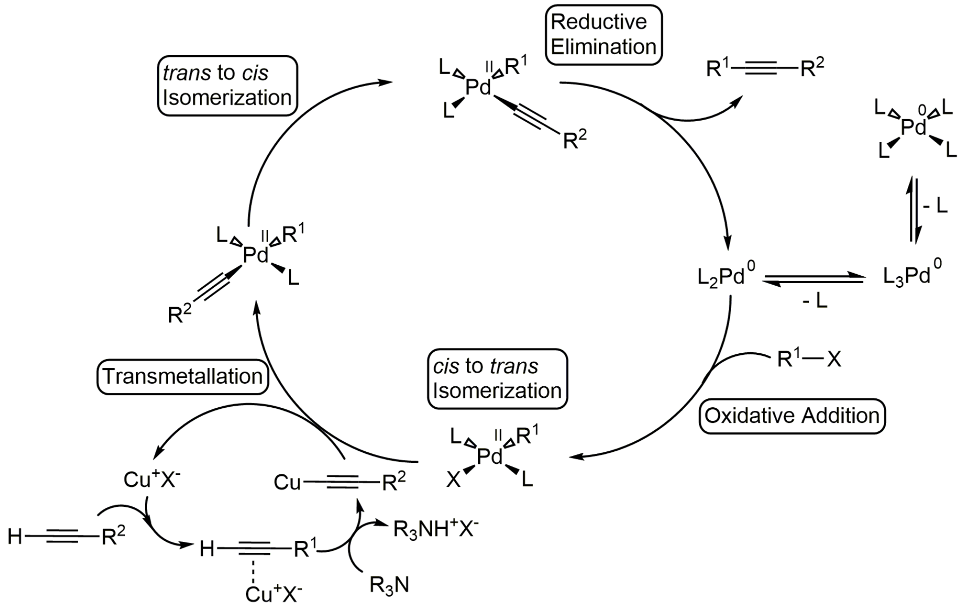


Scheme 1.16. Various syntheses of diarylalkynes.

Sonogashira coupling, the palladium-catalyzed coupling of alkenyl or aryl halides (or triflates) with terminal alkynes is, at this moment, the most common synthetic method used to prepare diarylalkynes (Equation 1.7). This reaction was first reported in 1985 by Sonogashira, Tohda and Hagihara where they noted that iodobenzene could react with acetylene gas at room temperature in the presence of $PdCl_2(PPh_3)_2$ catalyst, CuI in diethylamine, to give Ph-C≡C-Ph (tolan) in 6 hours in a 85 % yield. The proposed mechanism included the generation of an active Pd(0) catalyst, $Pd(PPh_3)_2$, through a reductive elimination of 1,4-diphenylbutadiyne from the Pd(II) intermediate $(Ph_3P)_2Pd(C{\equiv}CR)_2$. The role of CuI was to facilitate the deprotonation of acetylene by the amine via a Cu-acetylene π-complex. Subsequent oxidative addition of iodobenzene was followed by copper-catalyzed alkynylation and reductive elimination of the tolan regenerated active catalyst species (Scheme 1.17).[171] The availability of the catalyst and reagents, and the mildness of the reaction conditions and high yields of the alkynes made this reaction of great interest to the chemical community. Sonogashira coupling, in particular its mechanistic developments, reaction conditions and substrates scope have been extensively reviewed in the literature.[172] Recent advances in this field include metal nanoparticle-catalyzed,[173] ligand-, copper-, and transition metal-free couplings, as well as photo-induced and microwave-assisted protocols in green solvents (*e.g.*, water).[172c] A related *Sila-Sonogashira* method is known which involve the coupling of easier to handle alkylsilyl-protected acetylenes.[174]



(1.7)



Scheme 1.17. Mechanism of the copper co-catalyzed Sonogashira cross-coupling.
[Adapted with permission from Barbosa and co-workers, *RSC Adv.*, **2014**, *4*, 53442-53446. Copyright 2014 Royal Society of Chemistry].

The Sonogashira method possesses some drawbacks: 1) the cumbersome handling of gaseous acetylene leading to, 2) the use of protected acetylenes which limit aryl halide scope (*e.g.*, carbinol-based acetylenes require strong base KOH at the deprotection step and react with aryl iodide only),[175] 3) trimethysilylacetylene (H-C≡C-SiMe$_3$) and bis(trimethylsilyl)acetylene (Me$_3$Si-C≡C-SiMe$_3$) are also expensive precursors, which produce metal/organic waste at the deprotection step, and require copper co-catalyst in high loadings (e.g., 50 mol %),[176] 4) low product yield due to an alkyne homodimerization side reaction (to form bisalkynes R-C≡C-C≡C-R) requiring added purification steps, and 5) low overall yield of products at the end of time-consuming procedures, containing multiple steps including coupling-deprotection-coupling.

To avoid some of the abovementioned challenges with Sonogashira coupling, Lee and co-workers applied a new type of alkyne source, propiolic acid, in *decarboxylative coupling* to obtain a range of asymmetric diarylalkynes in moderate to good yields.[177] Related work in this field included one-pot protocols,[178] different alkynyl carboxylic[179] and α,β-ynoic acids as alkyne sources,[180] water as reaction media,[181] aryl, benzyl and vinyl halides and triflates[179a, 180] as well as commercially available aryl chlorides[182] as coupling partners.

The *Stille coupling* of bis(tributylstannyl)acetylene with aryl iodides affords good yields of symmetrical diarylalkynes.[183] The main disadvantages of this method are the need for expensive stannylated precursors and the highly toxic nature of the organometal byproducts (*e.g.* Me_3SnX and Bu_3SnX; X = halides).

The coupling of aryl halides with organoaluminium reagents is also possible, and in a recent report the use of alkynyldimethylaluminium reagents ($RC{\equiv}CAlMe_2$) as alkyne synthons to access a range of (a)symmetric diarylalkynes via Pd-catalyzed coupling with aromatic and heterocyclic electrophiles (*i.e.*, chloride, bromide, iodide and triflate). These $RC{\equiv}CAlMe_2$ reagents are obtained from terminal alkynes using inexpensive $AlMe_3$ through Et_3N-catalyzed metalation.[184] Other organoaluminium coupling partners include $Ar\text{-}Al^iBu_2$[185] and LiCl adducts of $Ar\text{-}AlMe_2$ (Ar = aryl).[186]

The coupling of sp^2-carbon centers with alkynylsilanols (e.g., $RC{\equiv}C\text{-}SiMe_2OH$), was reported by Chang and co-workers, and provides an alternative approach to sila-Sonogashira coupling with shorter reaction times and higher yields of substituted alkynes; however substrate scope is only limited to aryl iodides thus far.[187]

The Pt-catalyzed alkynylation of aryl halides can be used to synthesize a wide array of substituted alkynes. A drawback of this route is the use of expensive Pt catalysts and a substrate scope that is limited to aromatic and heterocyclic iodides without hydroxyl functionality.[188]

Transiently formed alkenylidenes $R_2C{=}C{:}$[189] (R = H, Ar) are also known to undergo 1,2-migration to yield alkynes.[190] In addition, the *Fritsch–Buttenberg–Wiechell rearrangement* of 1,1-diaryl-2-halo-alkenes produces the abovementioned alkylidene carbenes in the presence of strong base (e.g., NaOH), which then rearrange to provide a series of substituted diarylalkynes (Scheme 1.16). This method is extensively utilized in organic synthesis to obtain polyyne structures.[191]

Another important reaction used to prepare functionalized alkynes is *Suzuki-Miyaura* coupling. Liu, Sun and co-workers reacted arylboronic acids with thermally unstable 1-iodo-2-arylalkynes to afford unsymmetrical alkynes in good to excellent yields. Although this method includes two additional synthetic steps (overall) in comparison to Sonogashira coupling, it performs well in the presence of aldehyde functionalities.[192]

1.8. Organic light-emitting devices

Organic light-emitting devices (OLED) are solid state light-emitting devices based on organic semiconductors that exhibit electroluminescence. Electroluminescence (EL) is light generation created by electrical excitation.[143] EL from an organic compound was first demonstrated by Bernanose in 1953,[193] and the first light-emitting device based on an organic semiconductor was constructed with anthracene single crystals in 1965 but had a poor performance. In 1987 attention was brought back to OLEDs by Tang and VanSlyke who fabricated a two-layer green light-emitting device with tris-(8-hydroxyquinoline)aluminium (Alq_3) as the emissive and electron transport layer, and an aromatic diamine as a hole transport layer.[194] There are a large number of small molecule-based charge-transporting or emissive materials, created for OLEDs and some representative examples are included as Figure 1.15. Compared to liquid crystal displays, OLEDs require lower energy input, have a wider viewing angle and can be lighter in weight, thus making them highly attractive for applications in flat panel displays. The goals for

OLEDs are: 1) high internal quantum efficiency (radiative electron-hole recombinations); 2) low operation voltage; 3) high light-outcoupling efficiency (total light projected from the device into the air).[195]

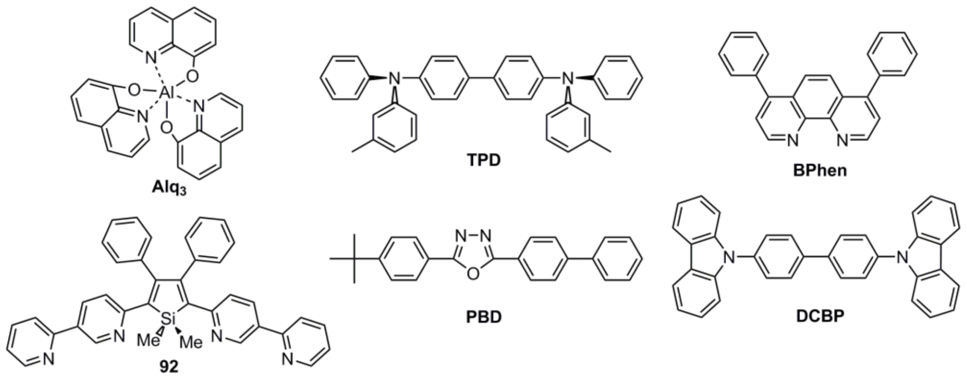


Figure 1.15. Structures of some molecular semiconductors that have been used in thin film EL devices. Alq_3 is used as electron transport and emissive layer, N,N'-bis(3-methylphenyl)-N,N'-diphenyl[1,1'-biphenyl]-4,4'-diamine (TPD) and 4,4′-bis(9-carbazolyl)-1,1′-biphenyl (DCBP) are used as a hole transport layer and 2-(4-biphenylyl)-5-(4-*tert*-butyl-phenyl)-1,3,4-oxadiazole (PBD), green alternative 4,7-diphenyl-1,10-phenanthroline (BPhen) along with silole **113** are used as an electron transport layer.

In the simplest version, an OLED consists of a single layer of electroluminescent compound and two electrodes (Figure 1.16). The anode (*e.g.*, indium tin oxide) is a hole-injecting electrode with high work function as well as is transparent to transmit light created during electroluminescence. The cathode (electron injecting electrode) is made of a thermally deposited metal with a low work function, *e.g.*, Ca, Mg or Al. When electrical current is applied to OLED, holes are injected into the HOMO level (or valence band) and electrons are injected into the LUMO level (or conduction band) of organic semiconductor. Under an electrical bias, charge carriers are driven out of the device through an external circuit, later recombining to form neutral bound excited states (*i.e.*, singlet or triplet excitons). In an LED, recombination of an electron and hole occurs via a radiative pathway, thus emitting light. Some requirements for an emissive layer are the ability to maintain a high quantum efficiency of light emission, and good injection and mobility of charge carriers.[196] To achieve these requirements multi-layered structure of light-emitting devices has been introduced in the early 1990s.[197] These multi-layered devices have a layer with good hole/electron affinity between emissive layer and an electrode to overcome the mismatch in energy between HOMO/LUMO and electrode work function, thus reducing charge injection barrier and improving charge injection and mobility.[198]

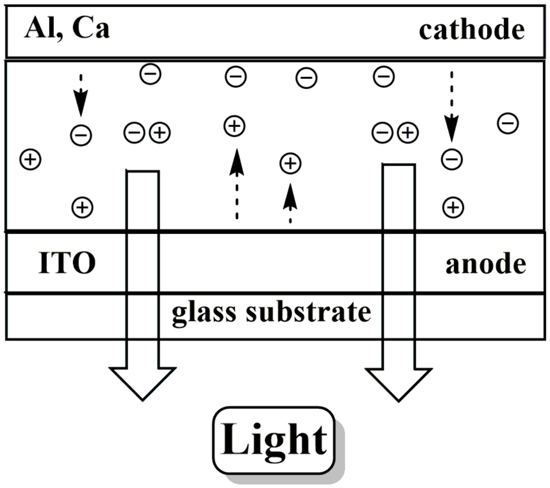


Figure 1.16. Structure of a single layer light-emitting device.
[Adapted with permission from Pron and Rannou, *Prog. Polym. Sci.* **2002**, *27*, 135-190. Copyright 2002 Elsevier].

Blue fluorescent emitters when combined with red and green emitters can lead to a white light-emitting device, which are themselves useful as components of full-color displays, as backlights for liquid crystal displays, and as alternatives to fluorescent bulbs and incandescent lamps. Other advantages of white OLEDs (WOLEDs) are large-area glare-free homogeneous emission and depending on the device architecture, the potential fabrication of LEDs on flexible substrates.[199] One challenge is that the maximum efficiency of blue-light-emitting devices is much lower than those reported for green or red[200] light-emitting devices (e.g., 12 %[201] for blue LEDs vs 29 %[202] for green LEDs) and thus limiting the overall efficiency of white OLEDs. In order to overcome this challenge, along with decreasing fabrication costs and simplifying the OLED structure, the design of improved blue emissive layers with enhanced stability and charge transport properties is an active field of study.[203]

Main criteria for blue emissive materials[198] include: 1) high luminescent quantum yield in the solid state; 2) high balanced electron and holes charge-transporting properties (especially important for single layer devices); 3) good film-forming properties (pinhole free) for spin-coating processing; 4) good thermal and chemical (oxidative) stability in order to prevent degradation during vapor deposition; 5) high color purity (chromaticity) as determined by suitable CIE (Commision Internationale d’Eclairage) coordinates; 6) environmental stability in order to avoid costly device encapsulation procedures; and 7) low cost fabrication of light-weight devices.

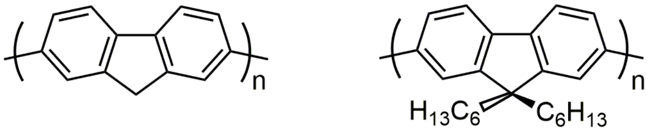
The main challenge for blue emitters is stability during device fabrication and operation. For example, polyfluorene (Figure 1.17), a commonly used emitter in blue EL devices, degrades quickly through either oxidation or via physical aggregation that reduces emission intensity.[204] Considerable efforts have been devoted to increasing the stability of molecular blue light-emitters and they will be discussed in the next section.

1.9. Molecular blue emitters

1.9.1. Polyfluorene and group 14 analogues

The *fluorene* unit is a cyclic cousin of rigid planar biphenyl, bridged by a carbon atom in position 9, with blue-violet fluorescent properties. Polyfluorenes (PFs) belong to the class of rigid-rod polymers linked at the 2- and 7-positions, where the methylene bridge (position 9) allows side chain modification and enhancement of polymer solubility and processability without dramatically changing the electronic structure of the backbone.

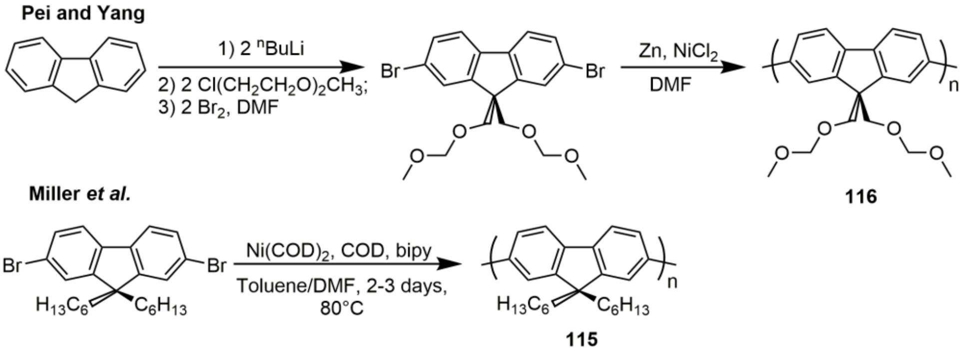
Parent polyfluorene first emerged from electrochemical community in 1985 where the anodic oxidation of fluorene[205] and electrochemical polymerization of various 9-substituted fluorenes was investigated (Figure 1.17).[206] The unsubstituted PF **114** was obtained as an electroactive insoluble film, whereas soluble poly(9,9'-dialkylfluorene) (*e.g.*, **115,** Φ = 83 %)[207] (PDAF) emerged as a novel class of materials for blue electroluminescent diodes.[208]



114 **115**

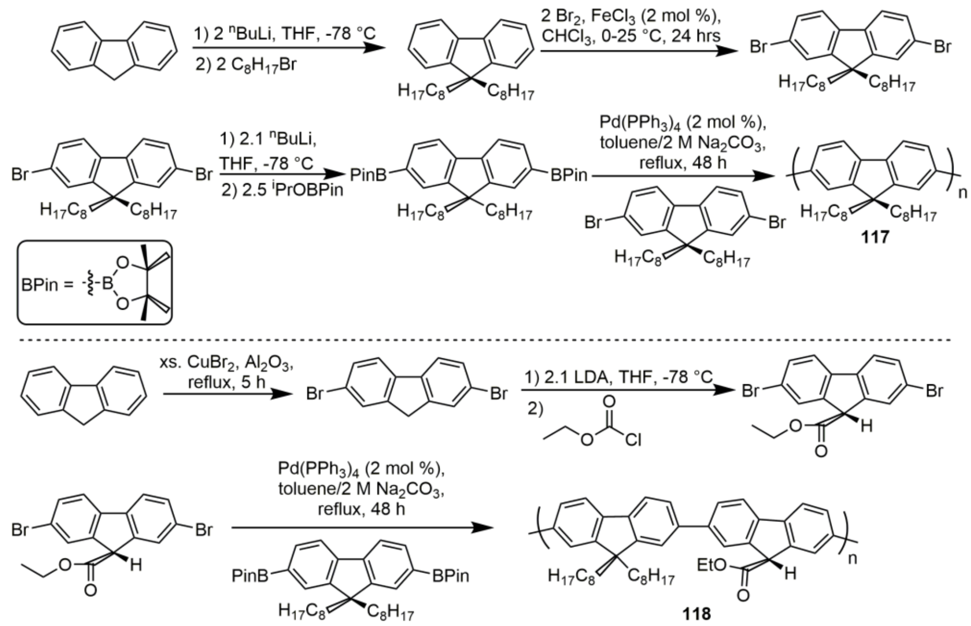
Figure 1.17. First reported polyfluorenes.

In the early 90s, the Yoshino group first obtained PDAF **115** as a low molecular weight (M_n up to 5000) polymer through electrochemical oxidation of dihexylfluorene using $FeCl_3$ in chloroform.[209] This synthesis also produced cross-linked structures as well as a large amount of metal residue, which negatively affected the performance of light-emitting devices.[210] In order to increase polymer molecular weight, hydrophilic 3,6-dioxaheptyl substituents were installed at the 9 position of nonpolar hydrophobic PDAFs to prolong polymer chain growth in polar solvents (*e.g.*, dimethyformamide). Thus, well-defined soluble high molecular weight PDAF **116** (M_n up to 94 000; Φ = 77 %) was first obtained by Pei and Yang from the nickel-catalyzed reductive polymerization of 2,7-dibromo-9,9-bis(3,6-dioxaheptyl)fluorene (Figure 1.18).[211] Another way to increase the molecular weight of PF bearing alkyl substituents and prevent early termination of chain growth and polymer precipitation is to use a solvent mixture consisting of polar and nonpolar solvents. This strategy was employed by Miller and co-workers to give **115** (M_n up to 18 000, ~54 fluorene units) from 2,7-dibromofluorene using $Ni(COD)_2$/COD/2,2'-bipyridyl (COD = cyclooctadiene) in a toluene-DMF solvent mixture (Scheme 1.18).[207, 212] Using the same reaction conditions, Scherf and co-workers obtained a range of very high molecular weight PFs (M_n up to 200 000, ~ 600 fluorene units) with various alkyl substituents (C_nH_{2n+1}, n = 4, 8, 10, 14 and others).[213]



Scheme 1.18. Yamamoto polycondensation of dihalofluorenes.

The Yamamoto polycondensation method shown in Scheme 1.18 produces regiospecific PDAFs from dihalofluorenes without side branched structures, although a large amount of metal impurities can be present due to high loadings of nickel and zinc metals.[214] Thus, Suzuki-Miyaura cross-coupling was used as an alternative way of polymerization using catalytic amount of $Pd(PPh_3)_4$ to produce **117** and **118** (Scheme 1.19).[215] Upon base doping with potassium *tert*-butoxide, the poly(fluorenylene) derivative **118** shows electrical conductivities of 10^{-6}-10^{-5} S cm^{-1} and thus could be potentially used as an electron-injecting material for light-emitting devices.[215,216]



Scheme 1.19. Synthesis of PFs via Suzuki-Miyaura cross-coupling.

The synthesis, physical and optoelectronic properties, as well as applications of PF homo- and copolymers[217] have been highlighted in several recent reviews.[214, 218] For instance, in addition to LED applications[219] (discussed below), PFs have been used as chemical sensors,[220] optically-pumped organic semiconductor lasers,[221] diagnostic tools for early detection of cancer-related biomarkers,[222] and as an active layer in organic photovoltaics.[223] Furthermore, polyfluorenes are a promising class of light-emitting materials. Introduction of different conjugated moieties to the PF backbone or at the methylene bridge allows efficient tuning of emissive properties. Interestingly, PFs are a class of conjugated polymers that possess high thermal stability (up to over 400 °C) and can emit a whole range of visible colors with high quantum yield. For instance, pure red, green, and blue light-emitting PFs can be used to produce efficient LEDs,[224] and are listed in Figure 1.18.

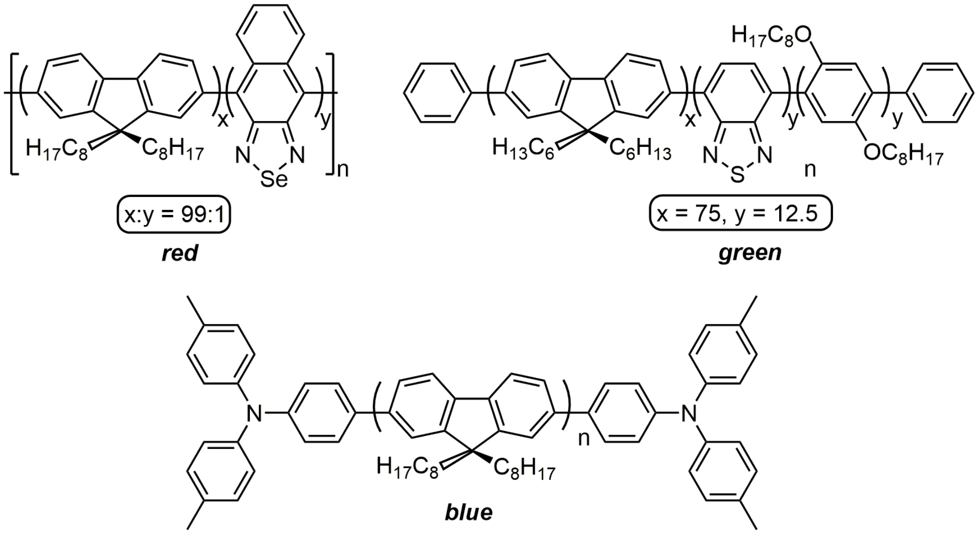
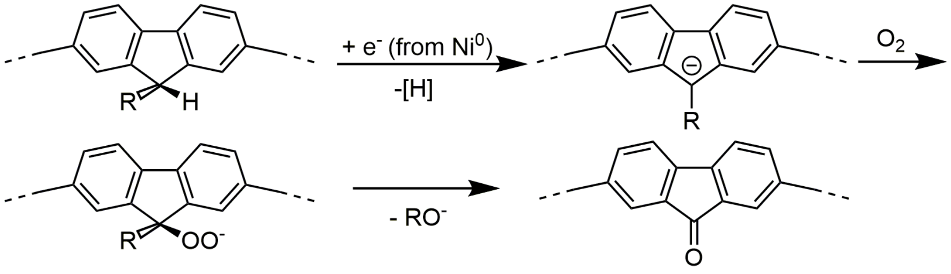


Figure 1.18. Red, green, and blue light-emitting PFs.

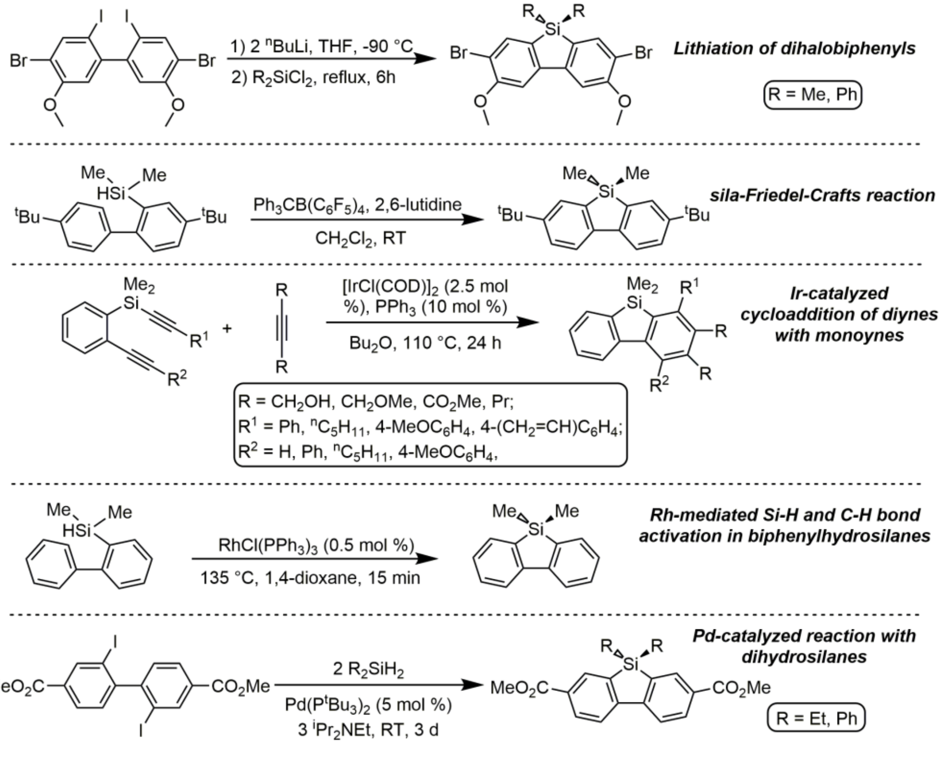
The biggest challenge related to color purity of PF is undesirable low-energy “green emission band”, which was debated to be a result of exciton trapping on the electron-deficient fluorenone defect sites (Scheme 1.20) or due to the formation of aggregates.[225] Accordingly, some approaches explored to increase color purity are: 1) purification of the monomer from monosubstituted 9-alkylfluorene derivatives (the latter species tend to oxidize and introduce fluorenone defect sites, Scheme 1.20),[226] 2) integration of a protecting layer between the PF and the cathode, 3) introducing hole-trapping sites (*e.g.*, triarylamine units) which would compete with exciton formation on ketone defects, 4) introducing bulky substituents to the PF backbone that decrease the exciton trapping on ketone defects and prevent aggregate formation.[214]



Scheme 1.20. Mechanism of formation of keto-defects arising from synthesis of 9-monoalkylated PF, proposed by Scherf and co-workers. Another pathway includes photo- or electro-oxidative degradation of 9,9'-dialkylated PF.
[Adapted with permission from Scherf *et al.*, *Adv. Mater.* **2002**, *14*, 374–378. Copyright 2002 Wiley-VCH].

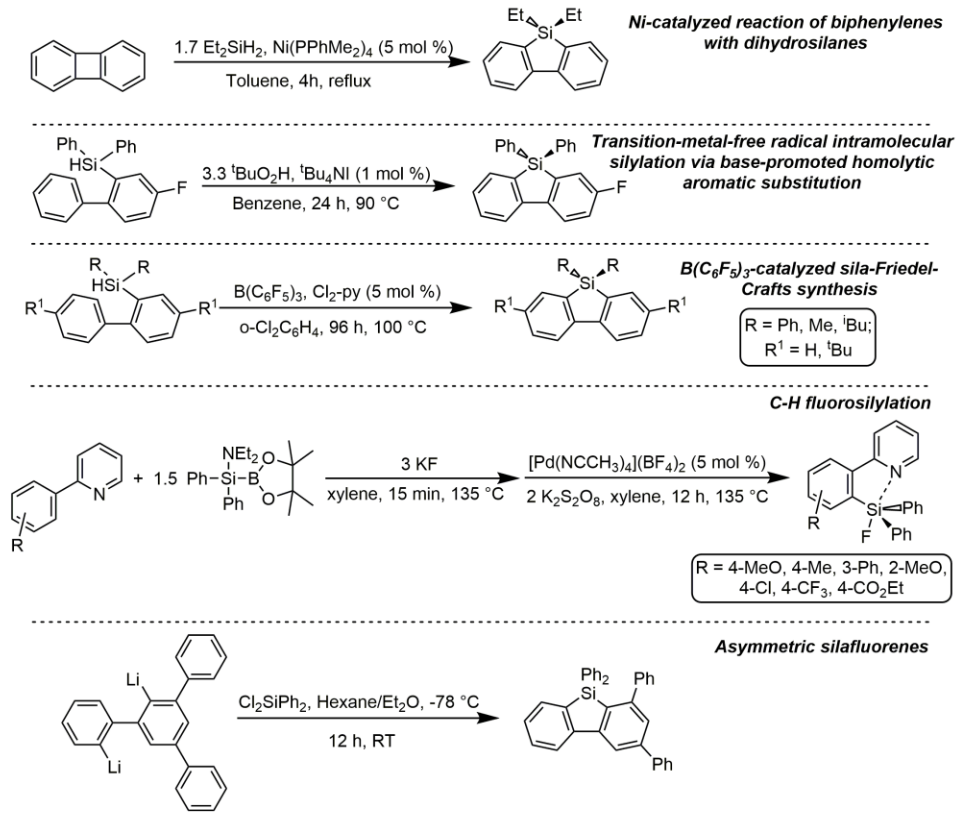
The replacement of carbon at the 9-position of a fluorene unit by other group 14 elements (*i.e.*, Si, Ge, Sn) was investigated by various research groups as a new approach to increase color stability of PFs. Key advances in this field are highlighted below.

A *Silafluorene, i.e.*, dibenzosilole analogue, was first obtained in 1955 by Gilman *et al.* via reaction of dilithiobiphenyl and Cl_2SiPh_2.[227] Interest in this field was rekindled in the early 2000s when it was found that polysilafluorenes could be used in blue emissive LEDs (M_n = 31 000, Φ = 60 %, no color degradation after 16 h at 250 °C in contrast to completely degraded PF)[228] as well as a material for bulk heterojunction solar cells with power conversion efficiencies approaching 1.6 %;[223c, 229] thin-film transistors were also fabricated based on silafluorene molecules with hole mobilities as high as 0.08 cm^2 V^{-1} s^{-1}.[230] The most common method to prepare silafluorenes is Gilman's initial method,[231] with the current focus on the use of substituted biphenyl precursors.[232] Other methods (Scheme 1.21) include sila-Friedel-Crafts reactions,[233] iridium-catalyzed [2+2+2] cycloaddition of alkynes and silicon-bridged diynes,[234] palladium-catalyzed intermolecular coupling of 2-(arylsilyl)aryl triflates,[232d] rhodium-mediated Si-H and Si-C bond activation in biphenylhydrosilanes,[235] palladium-catalyzed cross-coupling of 2,2'-diiodobiaryls with dihydrosilanes,[236] and ruthenium-catalyzed double trans-hydrosilylation of 1,3-diynes.[237]



Scheme 1.21. Common synthetic routes to silafluorenes.

The synthesis, properties, platinum cluster chemistry[238] and applications of silafluorenes and their derivatives have been very recently summarized by Corey[239] and Nacano.[240] Novel approaches to silafluorene derivatives developed since 2011 are nickel-catalyzed reactions of biphenylenes with Et_2SiH_2,[241] intramolecular silylation of biphenyl-2-hydrosilanes *via* silyl radicals,[242] base-promoted homolytic aromatic substitution,[243] $B(C_6F_5)_3$-catalyzed dehydrosilylation,[244] palladium-catalyzed C-H fluorosilylation (2-phenylpyridine-based equivalent of silafluorene),[245] double cyclization (difluorobenzosiloles),[246] synthesis of asymmetric silafluorenes,[247] and rhodium-mediated intramolecular C-H silylation by silacyclobutanes.[248] These new synthetic approaches are presented in Scheme 1.22. Interestingly, dianions of silafluorenes have also been isolated and studied by X-ray crystallography,[249] and these results have been summarized in the recent review by West.[90b]



Scheme 1.22. Novel approaches to the synthesis of silafluorenes.

Molecular and polymeric silafluorene derivatives (Figure 1.19) have been developed for the luminescence-based sensing of explosives,[250] photolithiographical patterning,[251] visible range emitters with high quantum yields,[252] rare deep blue fluorescent[253] and phosphorescent (when using iridium dopant) LEDs[254] with high operation stability, materials for electrochromic devices,[255] photosensitizer for light-driven hydrogen production,[256] polymer solar cells with good efficiencies (PCE = 4.05-6.05 %) and stabilities,[257] solid state UV-fluorophores (Φ = 35-54 %) with aggregation-enhanced emission properties,[258] and organic field effect transistors (mobility = 3×10^{-4} cm^2 V^{-1} s^{-1}).[259]

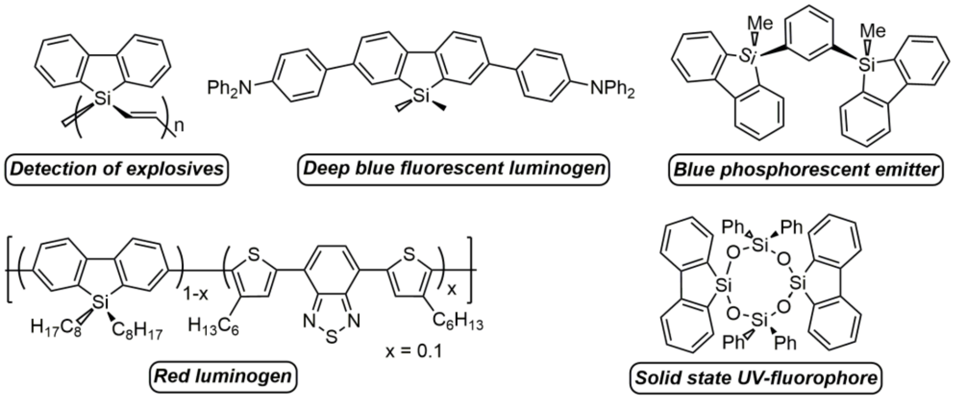
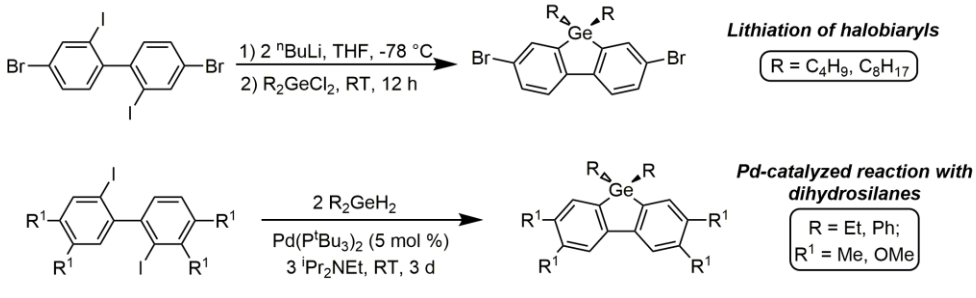


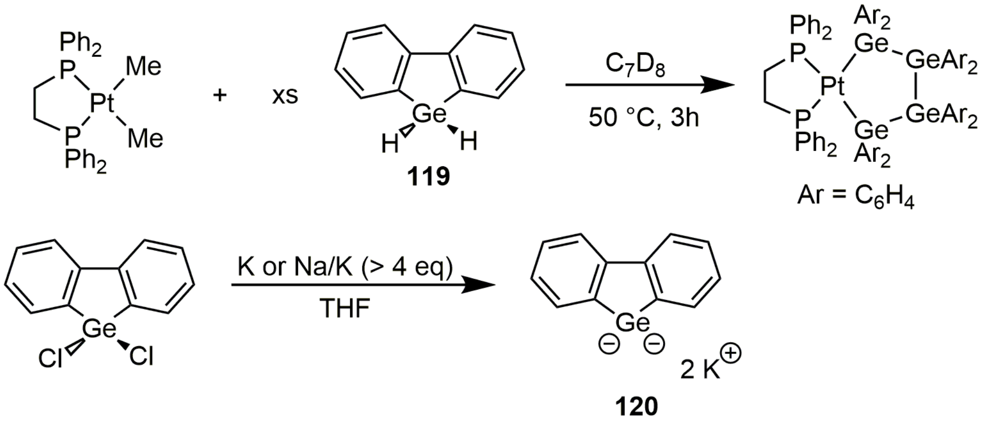
Figure 1.19. Selected examples of silafluorenes and their associated applications.

The corresponding *germafluorenes* have been significantly less explored in comparison to their silicon analogues. The first germafluorene was reported in 1994,[260] and since then only a handful of germafluorene derivatives can be found in the literature. The main synthetic routes to germafluorenes include condensation reaction of dilithiobiphenyls with dichlorogermanes,[232a, 261] and the palladium-catalyzed reaction of diiodobiaryls with dihydrogermanes (Scheme 1.23).[236]



Scheme 1.23. Synthesis of germafluorenes.

The Braddock-Wilking group investigated the reactivity of 9,9'-dihydrogermafluorene (**119**) with Pt(0) species $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ and identified a mixture of mono-, di- and trinuclear platinum-germanium products after activation of Ge-H bonds.[262] The authors also studied the thermolysis of **119** in the presence of (dppe)PtMe$_2$ (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) to obtain five-membered platinum-germanium metallacycles (dppe)Pt(GeR$_2$)$_4$ (R = C$_6$H$_4$) (Scheme 1.24).[263] Red crystals of the germafluorene dianion (**120**), in the form of potassium salt, were obtained by reduction of 9,9'-dichlorogermafluorene with sodium/potassium alloy in THF (Scheme 1.24) and characterized by X-ray crystallography.[264]



Scheme 1.24. Thermolysis of 9,9'-dihydrogermafluorene (**119**) in the presence of (dppe)PtMe$_2$ (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) and synthesis of germafluorene dianion **120**.

Density-functional theory revealed that germafluorenes are potentially good electron-transporting materials due to the presence of energetically low-lying LUMO states.[265] Moreover, replacement of the C-9 position in fluorenes with silicon or germanium tends to give to lower band gaps, enhance charge transport and promote closer intermolecular packing, leading to enhancement of solar cells efficiencies within bulk heterojunction devices.[69, 265] Compared to silicon, germanium has higher electronegativity (χ = 2.01 vs 1.90) (reducing the polarization of C-Ge bonds vs. C-Si linkages) and longer element-carbon bonds (1.96 vs 1.88 Å) which contribute to an increase in the overall stability and π-stacking interactions for germafluorenes.[69] Hence the germafluorene derivatives have been explored in organic photovoltaics[266] (overall device efficiencies (η) up to 2.8 %), as components of field-effect transistors (mobility = 0.04 cm^2 V^{-1} s^{-1}),[261] blue luminogens[252b] (Φ in solid state = 70 %) and as host materials for LEDs (Figure 1.20).[58, 267]

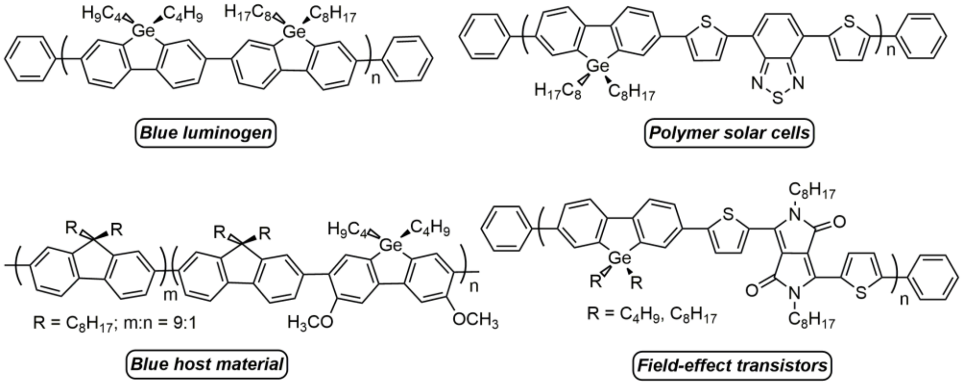
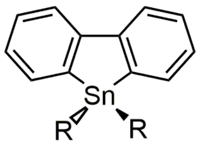
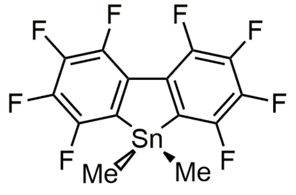


Figure 1.20. Selected examples of germafluorene co-polymers for optoelectronic applications.



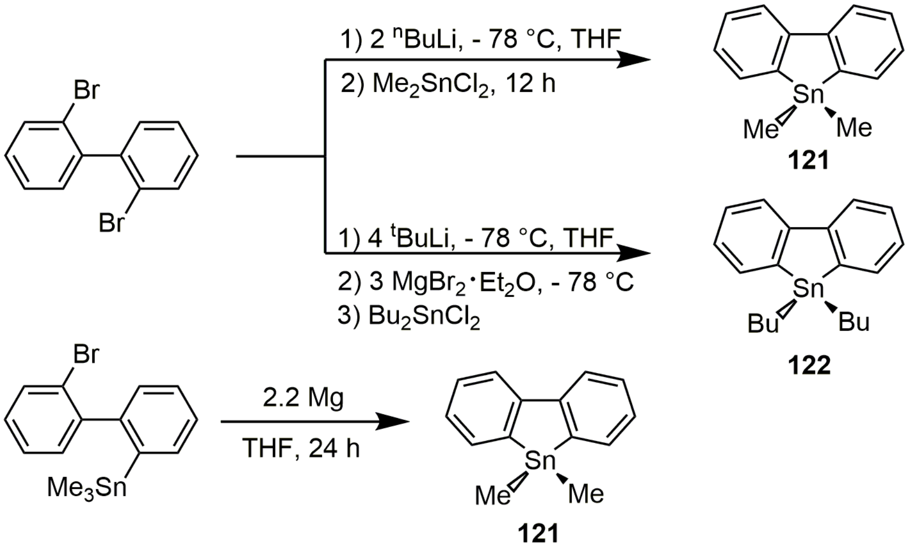
R = Me, Bu, Ph, 4-OMePh (**121-124**)



125

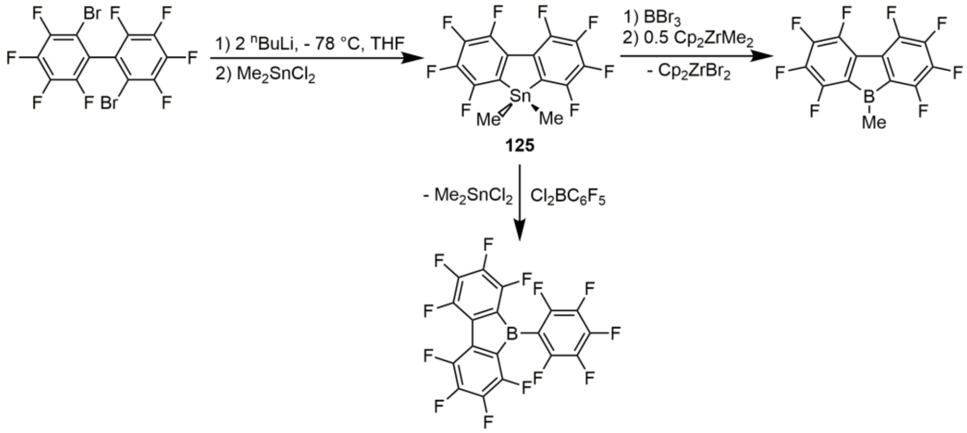
Figure 1.21. Stannafluorene derivatives reported in the literature.

Currently there are only a few reported examples of *stannafluorenes* in the literature (Figure 1.21).[268] Structural characterization of 9,9'-dibutyl-stannafluorene (**122**) by X-ray crystallography was reported in 1984 and revealed a similar planar heterofluorene structure as the abovementioned C, Si and Ge congeners.[268a] Stannafluorenes can be prepared through the reaction of lithiated biaryls with dihalostannanes (R_2SnX_2),[268b, 268c] as well as from the reduction of 2-bromo-2'-(trimethylstannyl)biphenyl with magnesium turnings (Scheme 1.25).[268d]



Scheme 1.25. Synthetic methods used to prepare stannafluorenes.

Stannafluorene dianions were obtained *via* reduction of **123** or **124** (Figure 1.21) with lithium or potassium, and their compositions were indirectly confirmed by trapping with electrophiles (such as MeI).[269] The dibutylstannafluorene **122** has been used in organic synthesis as a precursor for dibenzofulvenes,[268c, 270] functionalized triply annulated benzene derivatives,[268c, 271] and near IR absorbing tetracene diimides.[272] Equally important is the synthesis of 9-borafluorene Lewis acids by Piers and co-workers (Scheme 1.26) using the perfluorinated precursor **125** (Figure 1.21).[268b]

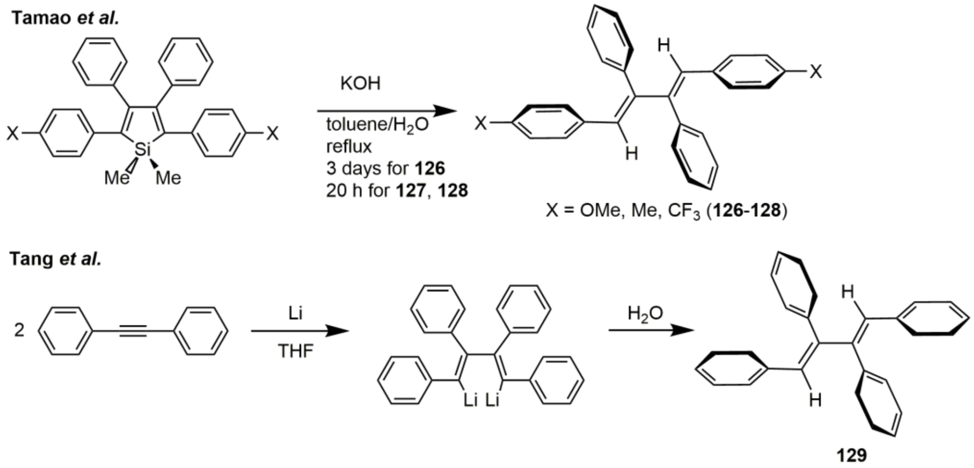


Scheme 1.26. Synthesis of 9-borafluorene Lewis acids using perfluorinated stannafluorene **125**.

1.9.2. Tetraarylbutadienes

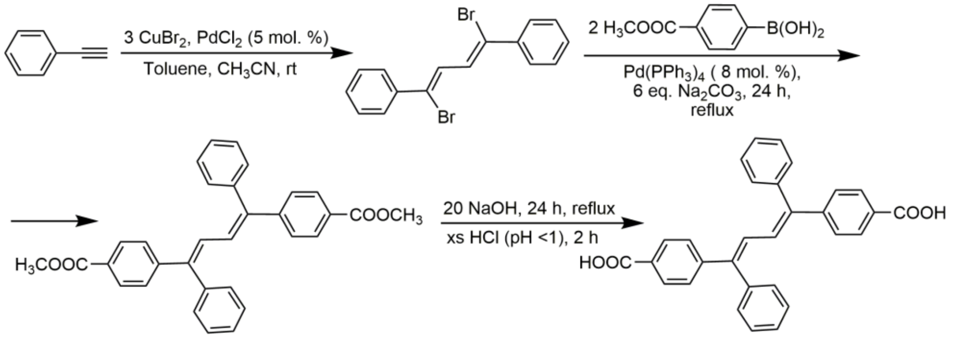
Extending π-conjugation within tetraarylethenes, an efficient class AIE luminophores,[273] by functional group modification leads to a new class of luminogen[274] with tunable emission properties.[275] Common synthetic approaches to aryl-substituted butadienes include transition metal-catalyzed isomerization,[276] palladium-catalyzed intermolecular coupling of aryl iodides, alkynes and alkenes,[277] cleavage of silole rings,[144b, 278] homocoupling of alkynes using Cp_2ZrCl_2 and mischmetall powder (an alloy of Ce, La, Nd, and Pr),[33] oxidation of diarylalkynes in superacid HSO_3F/PbO_2 mixtures.[279] In addition, butadienes are important precursors to substituted polycyclic organic hydrocarbons such as naphtalenes.[279]

Tetraarylbutadienes reported in the context of electroluminescent applications will now be discussed. In the early 2000s, Tamao and Tang reported the desilylation of siloles using either the strong base KOH or water to obtain substituted butadienes **126-129** (Scheme 1.27).[118b, 167] The structure of **126** was confirmed by X-ray crystallography and has a coplanar butadiene skeleton as well as higher degree of co-planarity with the 1,4-phenyl rings in relation to the precursor silole.[167] The authors noticed an absence of luminescence for **126-128** derivatives in the solution, however emission in the solid state (possibly via the aggregation-induced emission (AIE) effect) was not explored. In 2001, while studying blue luminescence of siloles, Tang and co-workers obtained the tetraphenyl butadiene **129** and examined its emission properties. However the authors did not find any emission for **129** in the film state, and hypothesized that the lack of visible light emission was due to structural rotation of butadiene moiety, leading to a nonplanar structure with ineffective π-conjugation. [118b]



Scheme 1.27. Synthesis of the tetraarylbutadienes **128-131**.

Interest in tetraarylbutadienes was revived in 2013 when Dong and co-workers first reported reversible hydrogen-bonding assisted piezochromic (*i.e.*, difference in emission color caused by mechanic stimuli) luminescence for the butadiene derivative **130**; this species was prepared as a white solid in three steps (Scheme 1.28) in an overall yield of 51 %. Compound **130** exhibits AIE (Φ_{THF} = 1.3 %) in THF-hexane mixtures (fraction of hexane, f_{hex}, = 90 % and Φ = 43 %), with a high solid state fluorescence quantum yield of 70 % and thermal stability up to 320 °C.[280] The photoluminescent color of **130** changed from blue to yellow-green upon grinding and when exposed to polar solvent (*e.g.*, THF, MeOH, EtOH) it eventually reverted back to the initial blue color of emission. The nature of this effect was investigated in depth by FT-IR, X-ray crystallography, powder X-ray diffraction and differential scanning calorimetry. The authors concluded that the unaltered solid has an ordered structure due to strong hydrogen bonding interactions between carboxylic acid groups in neighboring molecules, which are disrupted under high pressure.[280] Later Dong and co-workers reported a systematic study of the structural effects on the mechanochromic performance of substituted 1,3-butadienes **131**-**133** with donating (NPh_2) and/or electron withdrawing (CF_3, $COOCH_3$) groups (Scheme 1.29).[281] Among others, compound **132** exhibited blue fluorescence with the highest quantum yield in THF solution (35 %) and in the solid state (pristine powder, Φ = 83 %). Interestingly, derivative **133** with a donor-π-acceptor structure and large dipole moment had the most dramatic mechanochromic response, changing color from green to yellow during repeated fuming with solvent and grinding cycles.[281]



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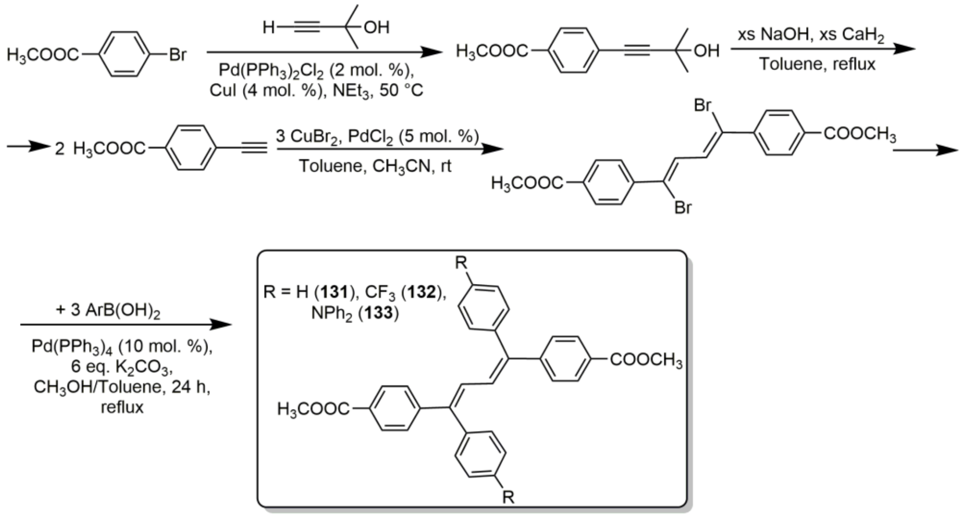
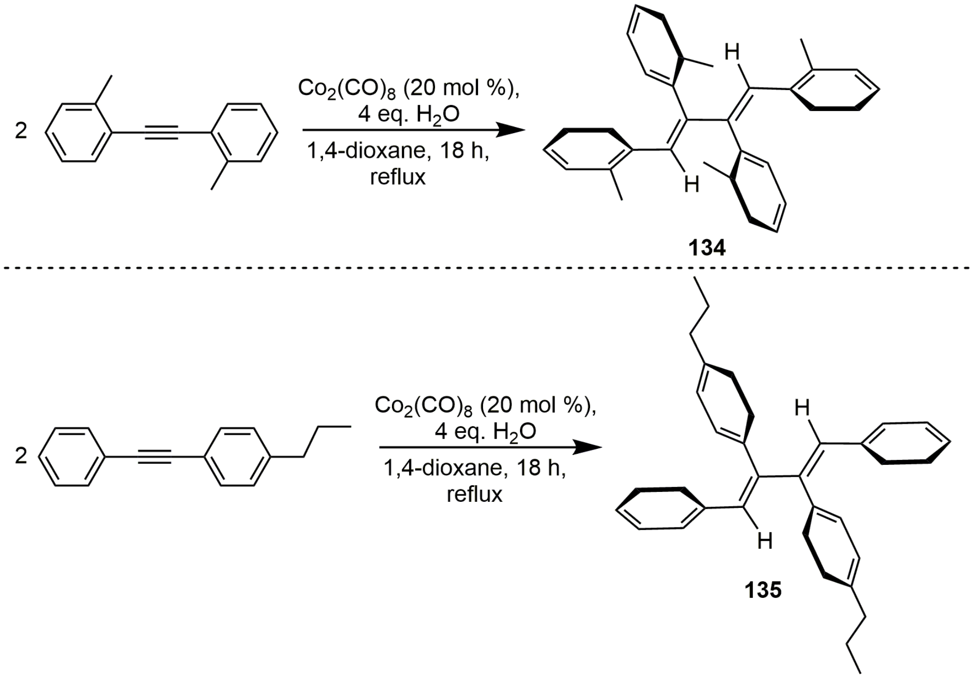
Scheme 1.28. Piezochromic tetraaryl-1,3-butadiene **130**.



Scheme 1.29. Mechanoluminescent butadienes **131-133** obtained by the Dong group.

In 2015 the Hsu group reported the reductive dimerization of internal diarylalkynes in the presence of substoichiometric amounts of $Co_2(CO)_8$ to yield regioselectively the tetraphenyl-1,3-butadienes **134** and **135** (Scheme 1.30). Both derivatives possess AIE properties in CH_3CN/H_2O mixtures, with blue light emission and high quantum yields of 83 % and 87 %, respectively when water fraction is 90 vol %.[274]



Scheme 1.30. Cobalt-mediated regioselective synthesis of aryl-substituted butadienes **134** and **135**.

1.10. The spiro-conjugation concept. Examples with spiro-annulated bifluorene and group 14 derivatives

The concept of spiroconjugation was first introduced in 1967 by Simmons and Fukunaga.[282] The authors described electronic delocalization in molecules containing two perpendicular π-systems joined by a common tetrahedral atom (Figure 1.22). Using this theory, they predicted absorption spectra of spirenes and polyene ketals. Recently, the concept of spiroconjugation has been comprehensively described in some review articles.[283]

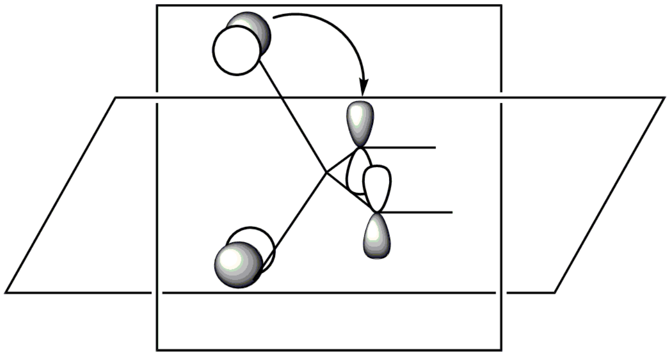
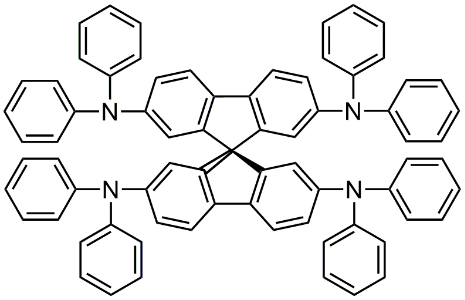


Figure 1.22. Through-space spiro-type interaction of p orbitals. [Adapted with permission from Bucknum and Castro, *J. Math. Chem.* **2004**, *36*, 381-408. Copyright 2004 Springer].

In recent years the spiroconjugation concept has attracted interest from the field of organic electronics.[284] The spirocyclic linkage allows the connection of two π-systems with different functions (*e.g.*, emission or charge transport) *via* a common sp^3-hybridized atom, thus opening a door to variety of multifunctional materials. In order to improve performance of organic optoelectronic devices, it is important to understand the morphology and microscopic organization of active materials.[284a] Amorphous materials with high glass transition temperature (T_g) are in particular demand due to absence of grain boundaries in their thin films, leading to spatial homogeneity of transport properties and diminishing of scattering effects compared to polycrystalline materials (*i.e.*, enhancement of device performance). Spiro-annulated compounds usually match the abovementioned criteria due to several reasons. First, they have increased molecular weight and cross-shaped rigid bulky structure, which effectively hinders crystallization and raises the glass transition temperature.[284b] For example, the T_g of 2,2',7,7'-tetrakis(diphenylamino)-9,9'-spirobifluorene (Spiro-TAD; **136**) is 133 °C, while the parent charge-transporting N,N,N',N'-tetraphenylbenzidine (TAD; **137**) has a glass transition temperature of 70 °C (Figure 1.23).[284a] Hence spiro-linked compounds have improved morphological stability compared to parent molecular species while retaining their electronic properties.



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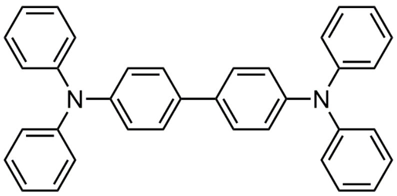


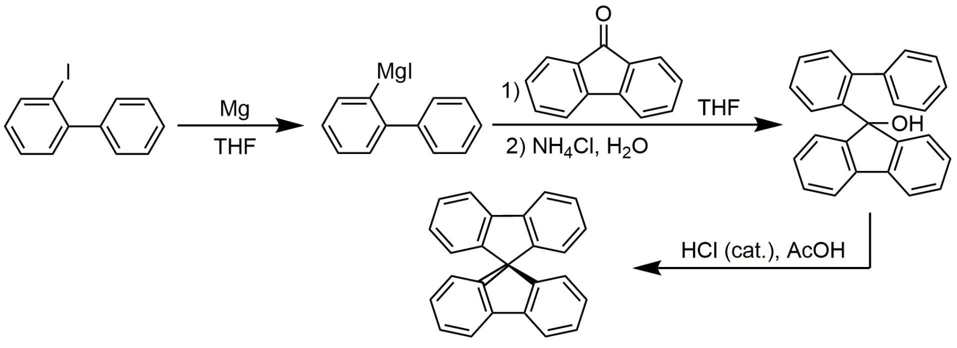
137

Figure 1.23. Structures of charge-transporting Spiro-TAD **136** and parent TAD **137** compounds.

A second major benefit of spiro-annulated compounds is suppressed intermolecular interactions arising from their bulky rigid structure due to perpendicular arrangement of two molecular moieties. This also results in increased solubility compared to parent molecules. Equally important is effective suppression of excimer formation in the solid state of spiroconjugated emitters, leading to their enhanced fluorescence efficiencies.[284c] Spirocyclic compounds have also been used as photo- and thermochromic compounds,[285] as active materials for photonics,[286] and as organic dyes based on intermolecular charge transfer.[287] The synthesis of functional spirocyclic compounds, their physical and electronic properties as well as applications in optoelectronic devices have been recently summarized.[284b, c]

There are many reported symmetric and asymmetric spiro compounds, while the most common examples are spirobifluorene derivatives. 9,9'-Spirobifluorenes have been investigated in solar cells, light-emitting devices, field-effect transistors, as well as a material for molecular recognition, optical data storage, and as precursors for chiral ligands and natural products.[288]

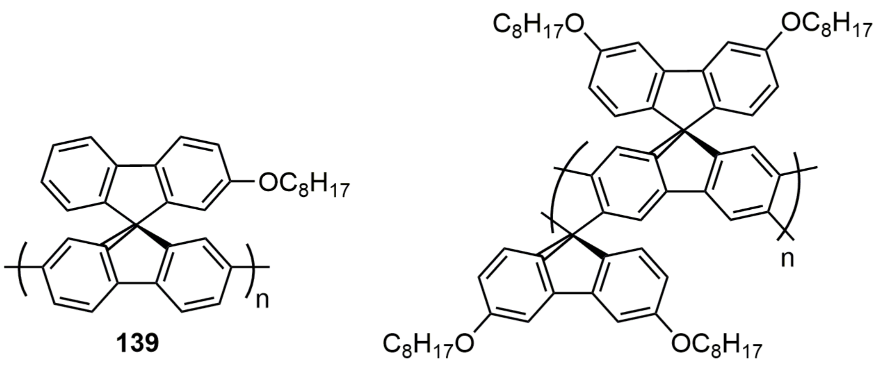
The most widely used synthetic route to spirobifluorenes was reported by Clarkson and Gomberg in 1930 (Scheme 1.31).[289] It involves reaction of a Grignard reagent with 9-fluorenone to yield 9-(biphenyl-2yl)-9-fluorenols. Finally, ring closure of the carbinol is catalyzed by hydrochloric acid to afford the desired spirofluorene. This procedure has been modified by various research groups (*e.g.*, expanded scope of biphenyls and metallating agents) and the overall yields range from 55 to 94 %.[284c, 290] Amongst other methods there are Friedel-Crafts reactions starting from 2,2'-diarylbenzophenones[291] and direct oxidative couplings.[288a, 292]



138

Scheme 1.31. Original synthesis of the 9,9'-spirobifluorene **138**.

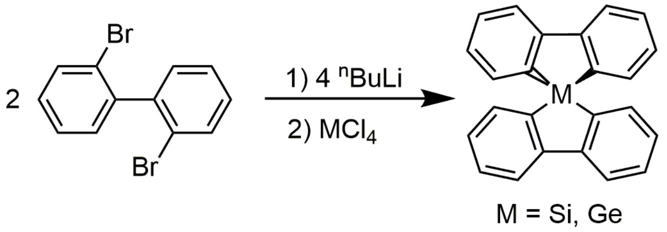
The main advantage of spirobifluorene is minimization of ketonic defects due to photo/thermal oxidation of the 9-position of the fluorene unit, thus producing blue emitters or phosphorescent host materials (when doped with iridium complexes)[293] with high thermal and color stability.[294] For example, polymer **139** (Figure 1.24) obtained *via* Suzuki-Miyaura polycondensation, exhibited a high quantum yield in solution of 91 % (quantum yield in solid state was not mentioned) as well as extremely good thermal (400 °C) and emission stability, staying purely blue after the film was annealed at 200 °C for three hours in air.[295] Another example includes polymer **140** with thermal stability up to 435 °C, and no observed defect-related green emission after annealing at 110 °C for 24 hours in air.[296] The synthesis and optoelectronic properties of spirobifluorene and its derivatives have been reviewed by Salbeck and co-workers[284b, c] as well as by Li and Bo.[294a]



139 **140**

Figure 1.24. Structures of the spirofluorene-based polymers **139** and **140**.

Incorporation of the heavier group 14 element, Si or Ge, into a spiro center of a bifluorene core gives a new class of compounds with photophysical properties that are similar to metalloles.[297] In common with the latter, spiroheterobifluorenes have σ(M-C)*-π* conjugation, therefore a small HOMO-LUMO energy gap, ensuring greater light absorption over the solar spectrum, as well as improved electron transport effects, compared to their carbon analogues.[298] At the same time, metalloles have a low glass transition temperature and are easy to crystallize, contributing to rapid degradation when incorporated in light-emitting devices.[299] In a similar fashion to heterofluorenes, the most common synthetic approach to spirocyclic analogues is the condensation of silicon/germanium tetrahalides with dilithiobiphenyl derivatives (Equation 1.8).[300] In the case of spirosilabifluorenes, asymmetric derivatives were obtained by Takai and co-workers *via* rhodium-catalyzed cyclization of bis(biphenyl)silanes.[301]



(1.8)

Spiro-linked silafluorenes (Figure 1.25) also have outstanding stability and emission characteristics.[297, 299] For example, the asymmetric derivative **141**, reported by Kafafi *et al.*, has a high glass transition temperature of 228 °C and easily forms a stable transparent amorphous film. It exhibits violet-blue luminescence in the solid state with high absolute quantum yield of 55 %. In 2015, the Ozin group showed that when incorporated into the blue LED, co-polymer **142** has 20 % higher emission stability over the corresponding silafluorene homopolymer.[297] Interestingly, the parent spirosilabifluorene **143** and its NO_2-substituted derivative **144** also performed well as highly selective fluoride sensors with detection limits as low as 5 μM (for **144**), which is close to residual concentration of fluoride in the drinking water.[302]

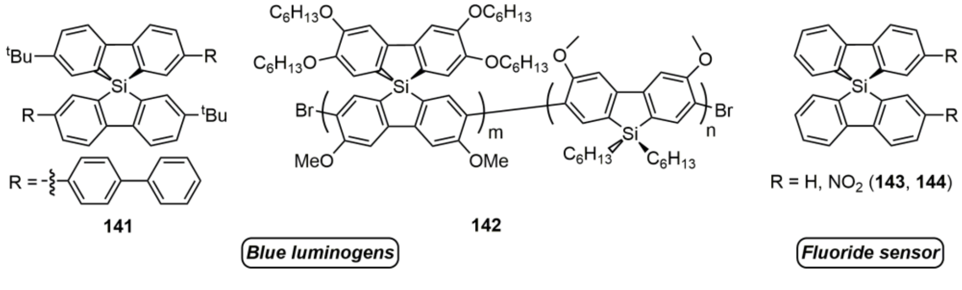


Figure 1.25. Spirosilabifluorenes used in LEDs and fluoride sensors.

Thus far, the main drawback associated with functionalized spiro(hetero)bifluorene compounds is their cumbersome multi-step synthetic procedures and the limited availability of suitable starting materials.[288a] Therefore in this Thesis development of a modular and facile synthesis of light-emitting spirocyclic germafluorene-based compounds will be discussed.

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Chapter 2: Modular Synthesis of Molecular and Polymeric Spirocyclic Germafluorene-Germoles: A New Family of Tunable Luminogens

2.1. Abstract

In this chapter the zirconium-mediated synthesis of a new class of air-stable luminogens, spirocyclic germafluorene-germoles (SGGs) is reported. These species contain ring-fused germafluorene and germole units that display color tunable fluorescence when peripheral aryl substituents are appended. Three distinct pathways are introduced for SGG modification: Stille, Suzuki-Miyaura and zirconocene-mediated couplings. Homopolymer and copolymers with alternating thiophene- or fluorene-thiophene repeat units were obtained using microwave-assisted Yamamoto or Stille pathways; these polymers exhibit blue luminescence and high thermal stability with no signs of degradation until *ca.* 370 °C. Thus, new libraries of molecular and polymeric spirocyclic germafluorene-germole light-emitters were prepared; they possess tunable luminescence, and desirable thermal- and photostabilities.

2.2. Introduction

Red, blue and green are the three main chromic components for achieving full color displays.[1] However obtaining long-term blue luminescence is very challenging due to the high propensity for material degradation during device operation. For example, the widely studied blue-emitting 9,9'-dialkylfluorenes[2a,b] and their polymers[2c,d] tend to form oxidized green emissive ketonic products over time. One strategy being explored to counteract undesired oxidation upon excitation is to construct heterofluorene emitters featuring intraring Si, Ge and Sn atoms, which leads to enhanced σ*-π* conjugation within the metallole fragment and a lowering of the LUMO state.[3] Initially reported by Holmes and co-workers,[4] the silicon analogues of poly(9,9'-dialkylfluorene)s (PDAFs), polysilafluorenes, show excellent optical and electronic properties, advantageous film forming properties, as well as improved thermal and spectral stability due to the presence of oxidatively robust Si-C linkages; furthermore, polysilafluorenes display enhanced electron affinity in relation to its organic counterparts due to σ*-π* conjugation within the silole fragment which lowers the energy of the LUMO state.[5] An added advantage of polysilafluorenes, such as poly(9,9'-dioctyl-3,6-silafluorene) is its high triplet energy of 2.55 eV, which enables this polymer to be used as the host for green electrophosphorescent emitters.[5d] Huang and coworkers investigated both silafluorenes and germafluorenes by computational methods and found that these heteroarenes are promising electron transport materials.[6] Later, the same group reported a random germafluorene-fluorene copolymer, and demonstrated its use as a host material in polymer light-emitting device.[7] In 2010, Leclerc and co-workers reported a series of germafluorene homo- and copolymers; they were able to construct field-effect transistors with hole mobilities of up to 0.04 $cm^2 (V\cdot s)^{-1}$ as well as bulk heterojunction solar cells with power conversion efficiencies as high as 2.8 %.[8]

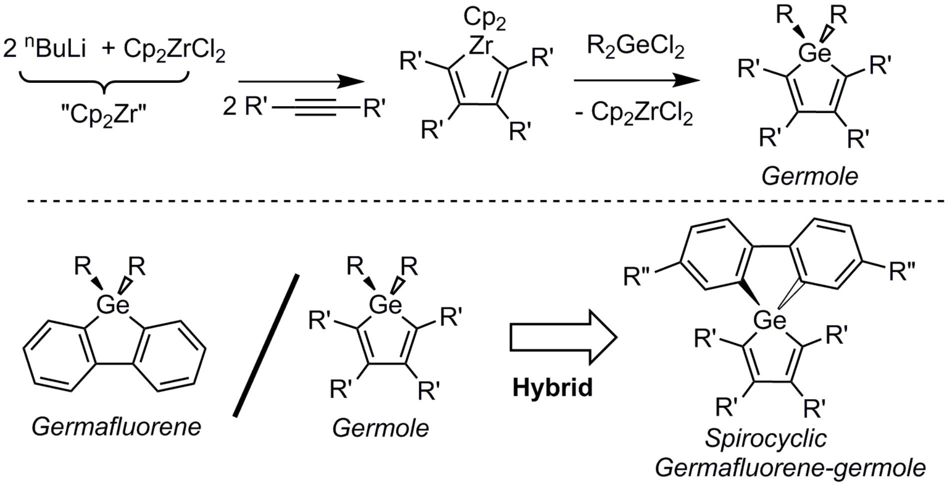
Another viable approach to increase the stability of emissive heterofluorenes[3e,9] is to orthogonally link two fluorene units within a spirocyclic arrangement; this process decreases quenching intermolecular interactions while concurrently improving the solubility and processability of the resulting materials.[10] However, the widespread implementation of spirocyclic compounds as light-emitting device components has been hampered by limited synthetic approaches.[11] Only this year, Ohshita and co-workers reported a series of oligomers and polymers containing alternating bithiophene and spiro-fused dipyridinogermole repeat units. Altering alkyl substituents on the thiophene main chain allowed tuning intramolecular photoinduced energy and electron transfer in these compounds, thus making them potential candidates for the photovoltaics.[12]

Five-membered metalloles $R_2EC_4R'_4$ (R and R′ = various substituents; E = Si to Pb) represent a prominent class of conjugated materials,[13] with useful properties such as efficient aggregation induced emission (AIE) and the colorimetric sensing of analytes reported.

Moreover, the peripheral R and R′ groups and inorganic intraring element (E) can be altered, leading to luminescence tailoring.[14]

Recently our group has explored the synthesis of structurally related phosphorescent tellurophenes via an efficient zirconium-mediated alkyne-coupling/atom substitution process.[15,16] A similar protocol has been used to access photoluminescent main group element-containing metalloles,[17] while Tilley and co-workers have also prepared a number of neutral and dianionic siloles and germoles, also with the assistance of Negishi's reagent "Cp_2Zr" (Cp = η^5-C_5H_5; Scheme 2.1).[18] In a promising recent development, the Staubitz group synthesized polystannoles with the help of Zr/Sn element substitution chemistry.[19]

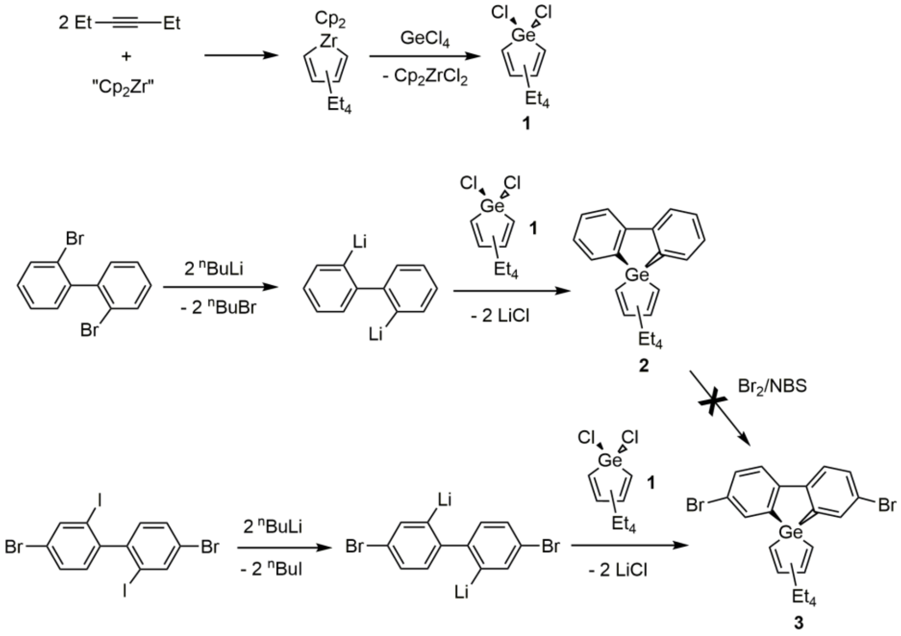
In order to create materials with enhanced processability, as found with spirofluorenes, while incorporating the tunable luminescence available to metallole units, the preparation of new hybrid materials was targeted, termed herein as spirocyclic germafluorene-germoles (SGGs; Scheme 2.1).[8,20] A potentially vast array of structurally distinct SGGs can be obtained from our highly modular synthetic approach, as well as on/off switching of the emission from each heterocyclic luminophore is possible via functional group control. This property should open the door to dual light emission, which has been recently used to achieve white photoluminescence from a single molecular entity.[21] In addition, blue light emission was observed for all polymeric spirogermafluorene analogues.



Scheme 2.1. Zirconocene-mediated synthesis of germoles and structure of the new spirocyclic germafluorene-germoles (SGGs) introduced in this chapter.

2.3. Results and discussion

This project began with the preparation of spirocyclic germafluorene-germoles (SGGs) containing tetraethylgermole GeC_4Et_4 as a core unit in order to impart solubility in common organic solvents (Scheme 2.2). The first analogue $FlGeC_4Et_4$ (**2**) (Fl = fluorenyl) was prepared by the condensation of readily available 2,2′-dilithiofluorene with the known dichlorogermole $Cl_2GeC_4Et_4$[18] (**1**). Compound **2** is air- and moisture-stable, yet non-emissive in solution and in the solid state. Attempts to directly install bromine substituents onto the germafluorene unit by treating **2** with *N*-bromosuccinamide (NBS) failed as undesired Ge-C bond scission transpired. As a result we needed to condense pre-brominated dilithiofluorene with **1** to yield the dibromo-functionalized germafluorene-germole **3** (Scheme 2.2). The structures of these SGGs were confirmed by single-crystal X-ray crystallography (Figures 2.1 and 2.2)[22] and as expected, perpendicular arrangements exist between the linked germole and germafluorene units (interplanar angles between each fused Ge heterocycle = 89.79(15)° and 84.82(6)°, for **2** and **3**, respectively). The central Ge-C bond distances in **2** and **3** fall within the narrow range of 1.932(4) to 1.955(4) Å, and are similar in value to the Ge-C distances found within known germafluorenes.[23]



Scheme 2.2. Synthesis of the alkylated SGGs **2** and **3**.

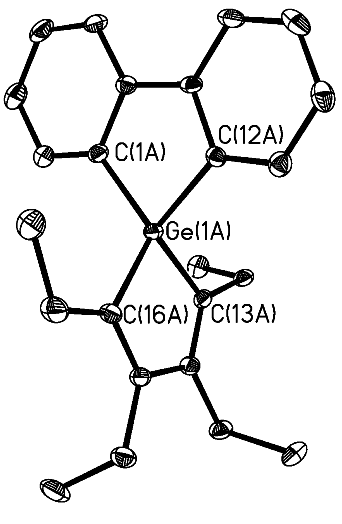


Figure 2.1. Thermal ellipsoid plot (30 % probability) of $FlGeC_4Et_4$ (**2**) (Fl = fluorenyl) with hydrogen atoms omitted for clarity. Only one molecule of the two in the asymmetric unit is shown. Selected bond lengths (Å) and angles (deg) with values due to the second molecule in the asymmetric unit listed in square brackets: Ge(1A)−C(1A) 1.955(4) [1.955(4)], Ge(1A)−C(12A) 1.949(4) [1.944(5)], Ge(1A)−C(13A) 1.936(4) [1.933(4)], Ge(1A)-C(16A) 1.932(4) [1.940(4)], C(1A)−Ge(1A)−C(12A) 89.19(19) [88.9(2)], C(13A)−Ge(1A)−C(16A) 90.84(19) [90.57(19)].

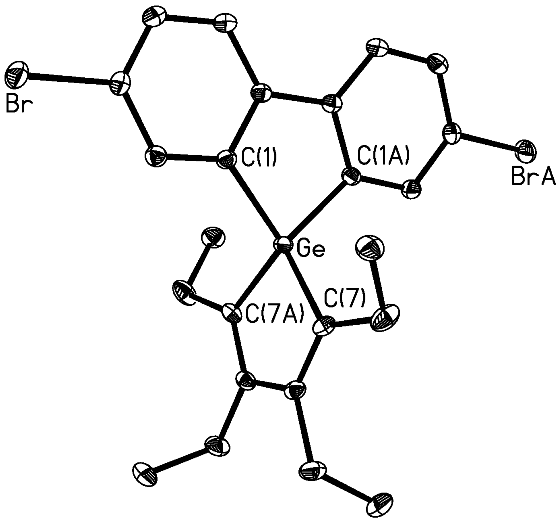
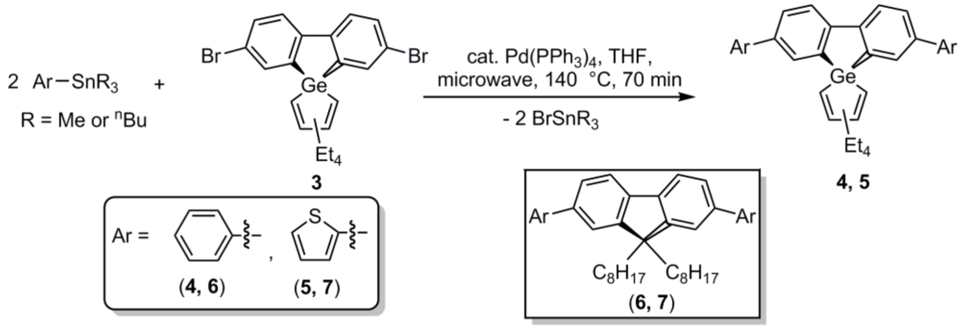


Figure 2.2. Thermal ellipsoid plot (30 % probability) of compound **3** with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge–C(1) 1.9494(14), Ge–C(7) 1.9359(14); C(1)–Ge–C(1A) 88.78(8), C(7A)–Ge–C(7) 90.77(9).

In order to verify if the dibrominated spirocyclic germafluorene-germole **3** could undergo Stille coupling with aromatic partners to yield emissive species with potentially extended π-conjugation, compound **3** was reacted with two equivalents of trimethylstannylbenzene[24] and 2-(trimethylstannyl)thiophene,[25] respectively, under microwave-assisted reaction conditions (Scheme 2.3). In each case $BrSnMe_3$ elimination transpired to yield the phenyl- and thiophene-capped SGGs **4** and **5** as colorless solids in unoptimized isolated yields of 30 and 15 % after recrystallization. Notably, the use of 2-(tributylstannyl)thiophene as a coupling partner with **3** afforded pure **5** in an elevated recrystallized yield of *ca.* 50 %.



Scheme 2.3. Preparation of the spirocyclic germafluorene-germoles **4** and **5** via Stille coupling.

While the thiophene-substituted spirocyclic germafluorene-germole **5** yielded crystals of suitable quality for X-ray analysis (Figure 2.3), the phenyl-capped derivative **4** consistently afforded poorly formed crystals upon recrystallization, so only atom connectivity could be determined. Of note, the thiophene groups in **5** are positionally disordered over two sites and exist in nearly co-planar arrangements with the proximal germafluorene unit (*e.g.*, S1(A)-C13(A)-C3(A)-C2(A) torsion angle = 6.3(10)°).

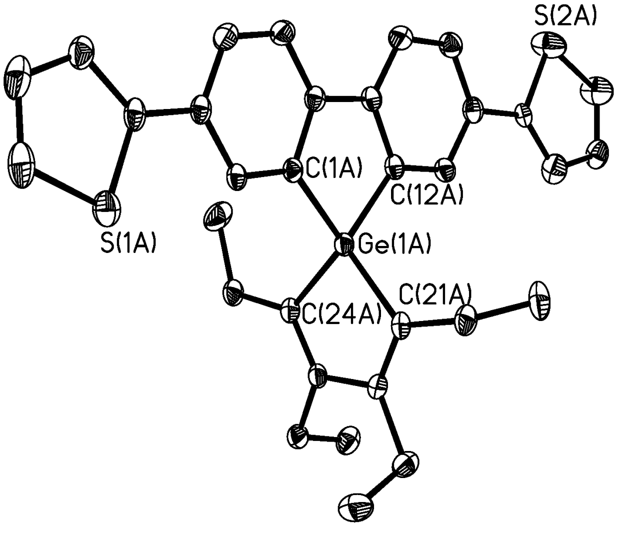


Figure 2.3. Thermal ellipsoid plot (30 % probability) of the thiophene-capped SGG **5** with hydrogen atoms omitted for clarity; only one molecule of the two in the asymmetric unit is shown. Selected bond lengths (Å) and angles (deg) with metrical parameters for the second molecule in the asymmetric unit listed in square brackets: Ge(1A)–C(1A) 1.945(2) [1.954(2)], Ge(1A)–C(24A) 1.937(2) [1.942(3)]; C(1A)–Ge(1A)–C(12A) 89.06(9) [89.36(10)], C(24A)–Ge(1A)–C(21A) 90.91(9) [90.92(11)].

Compounds **4** and **5** emit violet-blue light in THF solution when irradiated at 332 nm (**4**: λ_{emis} = 377 nm, Φ = 0.03) and 348 nm (**5**: λ_{emis} = 386 and 407 nm, Φ = 0.83; Figure 2.4), respectively.

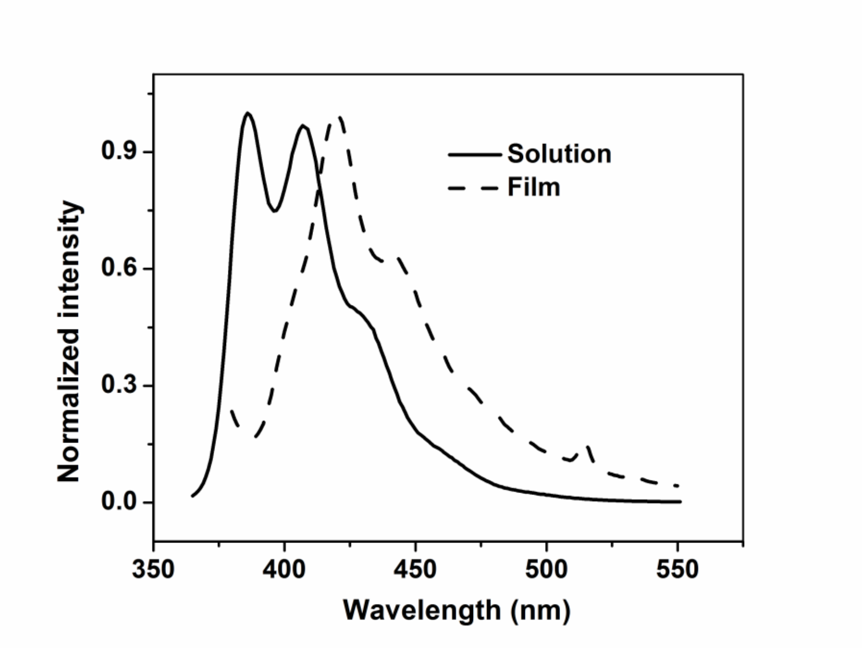


Figure 2.4. Normalized PL emission spectra of spirocyclic germafluorene-germole **5** in solution (THF) and film state.

This optical behavior mirrors that noted in the analogous phenyl- and thiophene-substituted dioctylfluorenes **6** and **7** prepared by Leclerc[26] (Scheme 2.3). However the phenyl-appended fluorene **6** has a significantly higher quantum yield of Φ = 0.64 in THF solution when compared to its germanium congener **4**. Due to the similarly high quantum yields of the thiophene-capped germafluorene **5** and dioctylfluorene **7** (Φ = 0.75),[26d] their optical, thermal and photostability properties were compared in more detail. Notably, compounds **5** and **7** absorb maximally at the wavelength (*ca.* 355 nm) in THF respectively (Figures 2.5 and 2.6), and both their fluorescence spectra have vibronic features, thus suggesting a high level of rigidity of the molecules in the first excited singlet state, leading to a narrow distribution of possible conformers.[26a] The fluorescence spectra of each species in the solid state is red-shifted by *ca.* 30 nm relative to in solution (Figures 2.4 and 2.7);[22] this effect can be explained by enhanced heterofluorene-thiophene coplanarity.

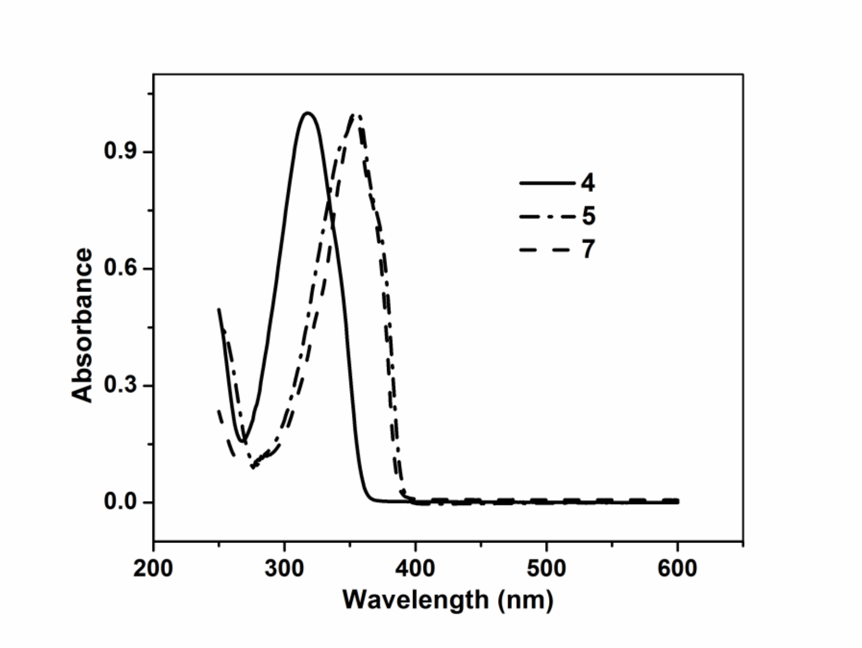


Figure 2.5. UV/Vis absorption spectra of the spirocyclic germafluorene-germoles **4** and **5** and fluorene **7** (normalized).

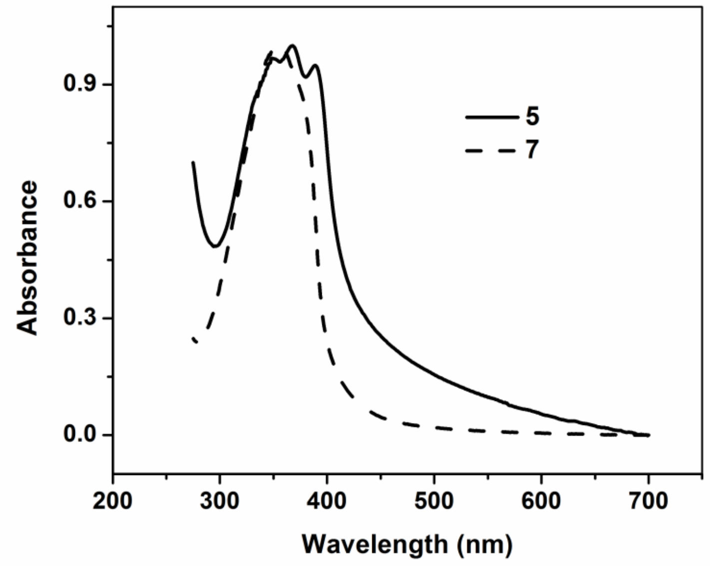


Figure 2.6. UV/Vis absorption spectra of compound **5** and fluorene **7** in the film state (normalized).

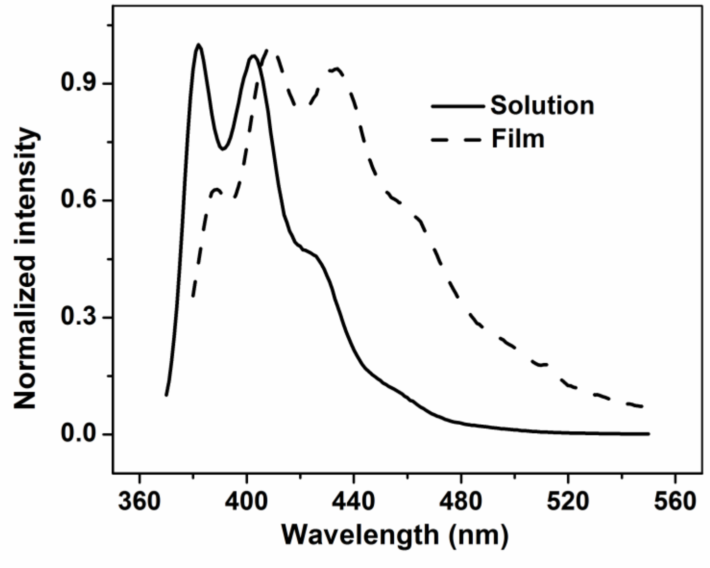


Figure 2.7. Normalized PL emission spectra of fluorene **7** in solution (THF) and film state.

Both compounds **5** and **7** exhibit fluorescence based on the lifetimes found: 0.94 ns and 1.05 ns, respectively. The close similarity of the absorption and emission profiles between compounds **5** and **7** (Figure 2.8) suggest that the π-manifolds within the bis(thienyl)biaryl portion of the germafluorene and fluorene residues are primarily involved in luminescence[26e] with little influence from the spirolinked Ge and C atoms, nor the germole unit in **7**.

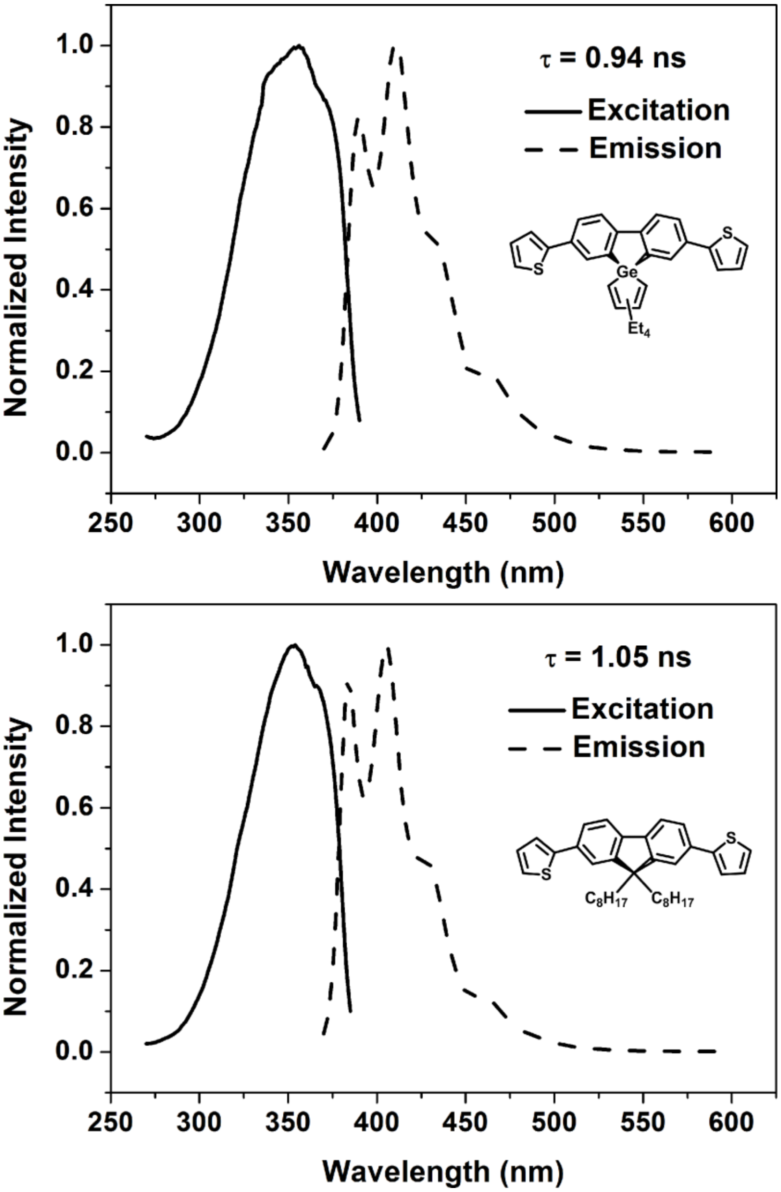


Figure 2.8. Emission and excitation spectra of **5** (top) and **7** (bottom) in THF.

To determine whether the incorporation of germanium within a spirocycle could increase the photostability for display applications, preliminary comparative irradiation experiments on thin films of **5** and **7** were performed under aerobic conditions (Figure 2.9). To the best of our knowledge, this is the first example of such a study for heterofluorenes and the resulting data would be of potential use in identifying candidates for the development of LEDs that work without substantial encapsulation.[27]

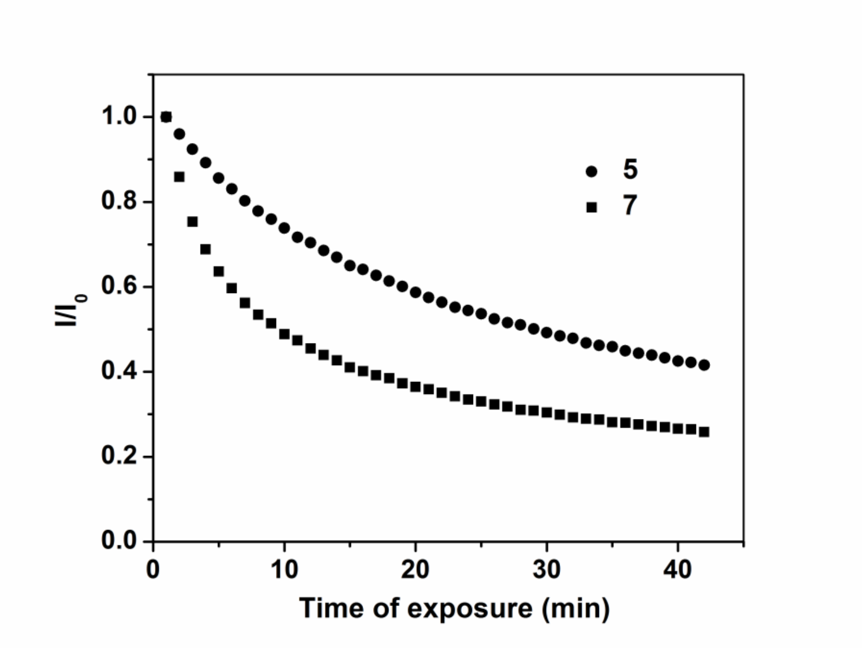


Figure 2.9. Time dependence of the fluorescence emission intensity of drop-cast thin films of **5** and **7** upon exposure to a 65 W xenon lamp in air.

Initially films of **5** and **7** were irradiated in air with a 450 W mercury lamp, however total sample decomposition (as verified by UV/Vis spectroscopy) and loss of emission was observed within five minutes. These data suggested that the light source was too strong to obtain the requisite comparative data; as a result, subsequent photostability trials were conducted with the 65 W xenon lamp found within our fluorimeter. We calculated the percent fluorescence intensity, and I/I_0

ratios, based on the photoluminescence intensity at the emission wavelength λ_{max}. From the data presented in Figure 2.9, the SGG **5** displays greater photostability in relation to the fluorene analogue **7** in the solid state: 42 % retention of emission intensity in **5** vs. 26 % retention in **7** after 40 minutes of exposure. We also compared the photostability of **5** and **7** in the film state to that in THF solvent (1.8×10^{-5} M concentrations; Figure 2.10). For these solution studies, using a 65 W xenon lamp as an irradiation source did not lead to any discernible photodegradation of either compounds **5** and **7**. However irradiating THF solutions with a 450 W mercury lamp for 10 min. the SGG **5** retained only 71 % of its initial emission intensity, while the fluorene **7** maintained 94 % of its initial photoluminescence. These initial photostability experiments reveal that although the reported spirogermafluorenes have similar emission abilities as known fluorenes, they can exhibit enhanced photostability in the solid state. Whether these differences are due to inherent chemical stabilities or changes in film morphologies in the solid state remains to be verified, and one needs to be cautious in drawing generalizations from this preliminary study. In the future a more comprehensive comparative photostability study (augmented by computational studies) using molecular spirocycles that differ only by C atom substitution with heavier group 14 elements should be done; fortunately the modular synthetic routes outlined in this chapter enables us to accomplish this task.

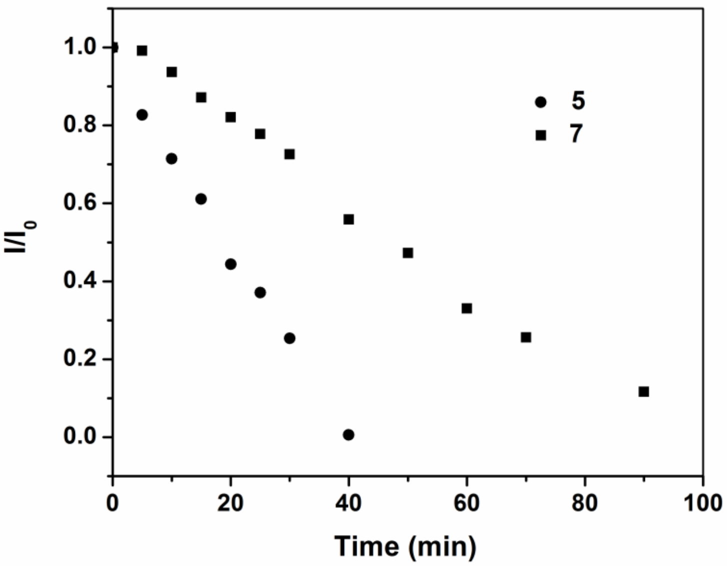


Figure 2.10. Time dependence of the emission intensity of spirocyclic germafluorene-germole **5** and fluorene **7** solution under 450 W mercury lamp (the distance of the lamp from the film was 8 cm).

In addition, the onset of thermal decomposition (5 % weight loss), T_d, of compounds **5** and **7** were evaluated under argon using thermal gravimetric analysis (Figure 2.11). Compound **5** showed a T_d at 319 °C, which is somewhat higher than the T_d of 290 °C obtained for the bis(thienyl)dioctylfluorene **7**. These early results are encouraging and point towards a high degree of thermal stability within a spirocyclic germafluroene-germole (SGG) molecular construct.[10]

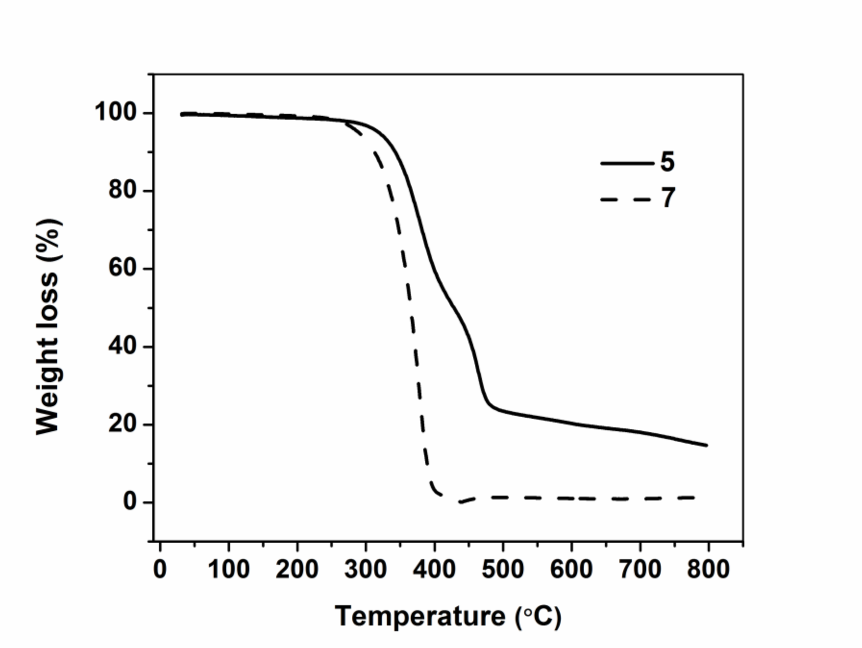
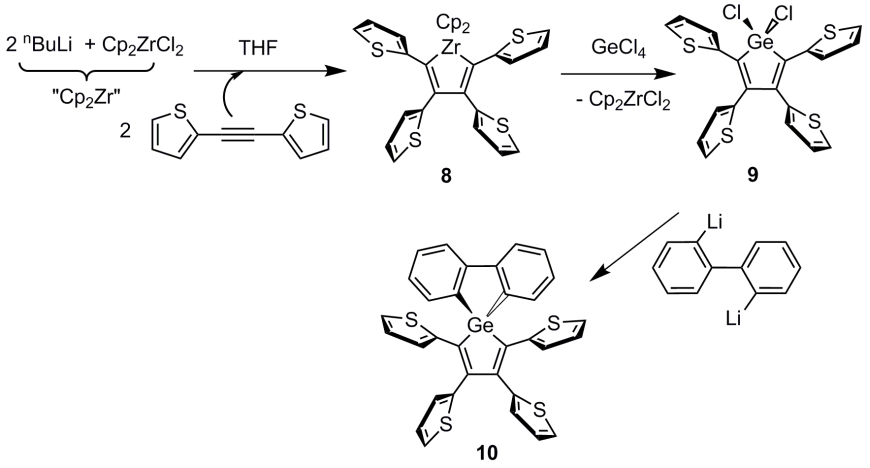


Figure 2.11. TGA thermograms of **5** and **7** measured under Ar (10 °C/min).

The similar nature of the emission profiles between the abovementioned spirocyclic germafluorene-germoles **4** and **5** and their related organic fluorene counterparts (**6** and **7**), point towards a non-emissive nature of the fused tetraethylgermole cores. A possible explanation is that inherently high degrees of free rotation are available to the ethyl group, which encourages non-radiative decay processes.[28] As a result, an analogous SGG, $FlGeC_4(2\text{-thienyl})_4$ (**10**) (Scheme 2.4) which contains thiophene-units about the germole core, was prepared. Motivation for this molecular design also comes from prior work on emissive metalloles containing aromatic side groups,[13e,29] and a desire to demonstrate an improved method of placing potentially light-harvesting thiophene groups about a metallole ring.[9a-c,30] It is expected that the disruption of intermolecular interactions and restrictive intramolecular motion within the flanking thiophene units could suppress non-radiative decay pathways, and enhance aggregation-induced emission,[9d,14b,17b] thus making the resulting SGGs efficient emitters in the solid state. As added background, Kafafi and co-workers constructed an efficient green light-emitting diode based on highly emissive ($\Phi = 0.87$) spirocyclic silafluorene-silole containing linked silafluorene and tetraphenylsilole units.[31]



Scheme 2.4. Preparation of the thiophene-substituted zirconocene (**8**), dihalogermole (**9**) and spirocyclic germafluorene-germole (**10**).

The synthetic route to FlGeC$_4$(2-thienyl)$_4$ (**10**) first involved alkyne coupling of two bis(2-thienyl)alkyne units to Cp$_2$Zr to yield the moisture-sensitive zirconacycle **8** as a red solid. In a subsequent step, compound **8** undergoes metallacycle transfer chemistry with GeCl$_4$ to yield the dichlorogermole **9** (Figure 2.12); this species was later converted into the target thiophene-decorated SGG **10** by treatment with 2,2′-dilithiobiphenyl (Scheme 2.4).

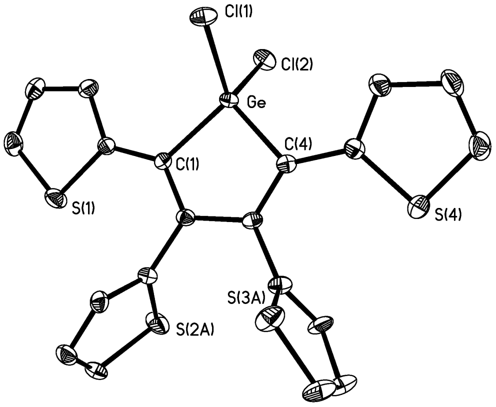


Figure 2.12. Thermal ellipsoid plot (30 % probability) of compound **9** with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge−C(1) 1.935(3), Ge−C(4) 1.932(3), Ge−Cl(1) 2.1362(8), Ge−Cl(2) 2.1279(7); Cl(1)−Ge−C(1) 115.27(19), C(12)−Ge−C(4) 113.37(9), Cl(1)−Ge−Cl(2) 104.33(4).

Compound **10** is an air- and moisture-stable yellow solid that is non-emissive in solution; however, unlike **2**, SGG **10** emits a bright yellow color in the solid state (λ_{emis} = 560 nm) due to restriction rotation of the peripherally located thiophene groups. SGG **10** forms emissive aggregated states in THF/water mixtures when the water content exceeds 70 vol. % (Figure 2.13). A luminescence lifetime of 3.22 ns was found for pure films of **10** drop-coated from THF (absolute quantum yield = 2.1 %), indicating that light emission is fluorescence. A blue-shift of the emission band (λ_{emis}) was seen at 70 vol. % water in THF by ca. 20 nm relative to aggregates in higher vol. % of water. A pronounced shift in λ_{emis} was not found during the aggregation-induced emission of our tellurophene phosphors,[16] however significant changes in λ_{emis} as a function of the degree of aggregation has been noted in related compounds based on silicon heterocycles, and has been attributed to conformational changes within the flexible side groups upon increasing aggregation.[14e]

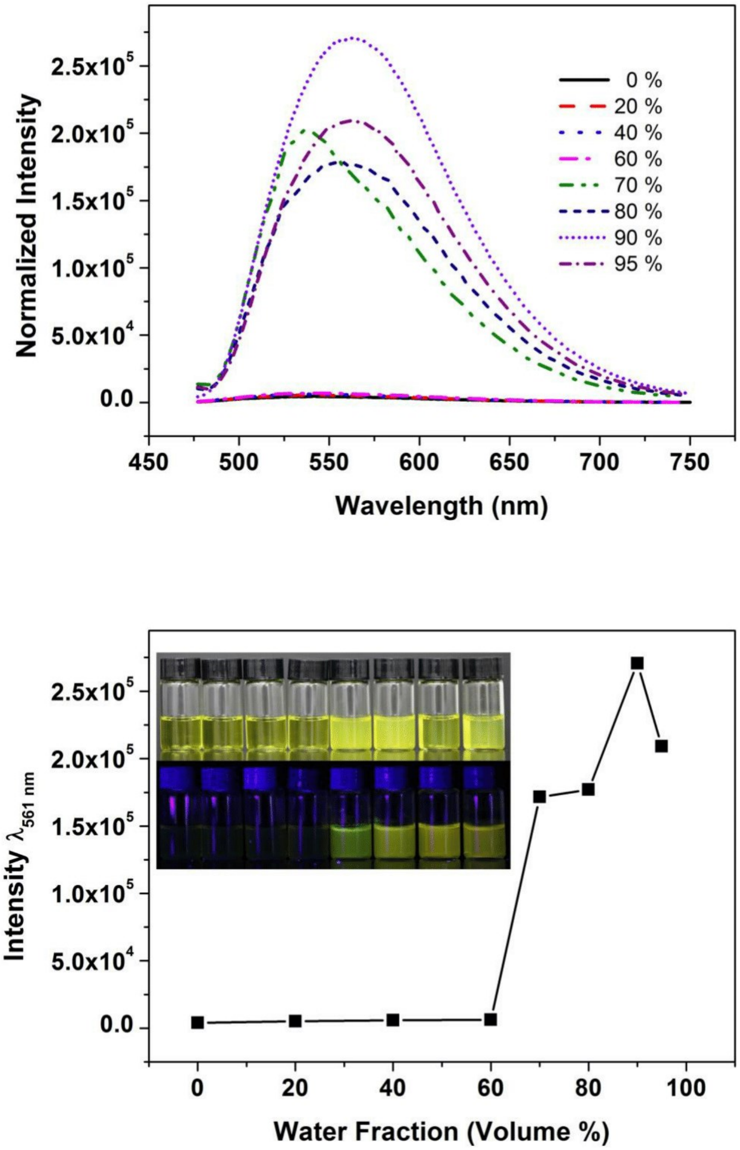


Figure 2.13. Top: Photoluminescence (PL) spectra of SGG **10** in different THF/water ratios; Bottom: emission intensity of SGG **10** as the THF/water ratio is altered. Inset: aggregates under UV light (λ_{ex} = 365 nm); [**10**] = 10^{-4} M.

Crystals of **10** of suitable quality for X-ray crystallographic analysis were obtained from CH_2Cl_2/hexanes, and revealed an expected perpendicular arrangement between the fused germafluorene and tetrathiophenyl-germole units (Figure 2.14). Interestingly, the thiophene substituents which are closest to the germafluorene array (2,5-positions about the germole) lie in nearly co-planar arrangements with respect to the germole GeC_4 ring, while the remaining thiophene groups are significantly canted (by 83.62(5)°); the Ge-C bond lengths are similar to what is observed within the abovementioned SGGs **2**, **3** and **5**.

Compound **10** absorbs at 434 nm in THF, which is red-shifted compared to the λ_{max} of 276 nm in the alkylated SGG, $FlGeC_4Et_4$ **2**, likely a direct result of the conjugated thienyl units present in **10**. In addition, compound **10** is thermally stable up to 238 °C (5 % weight loss) while the ethyl-substituted congener **2** shows degradation at 207 °C. Interestingly, compounds **10** should be amenable to further post-functionalization, such as the selective halogenation or lithiation of the peripheral thiophene groups, enabling the construction of extended structures and polymers containing **10** as a luminescent core.

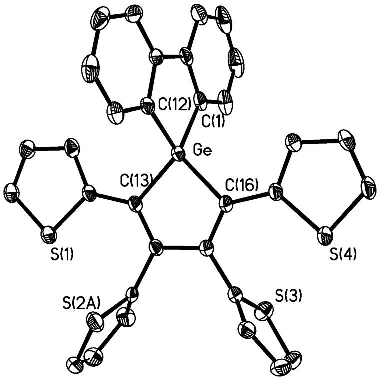
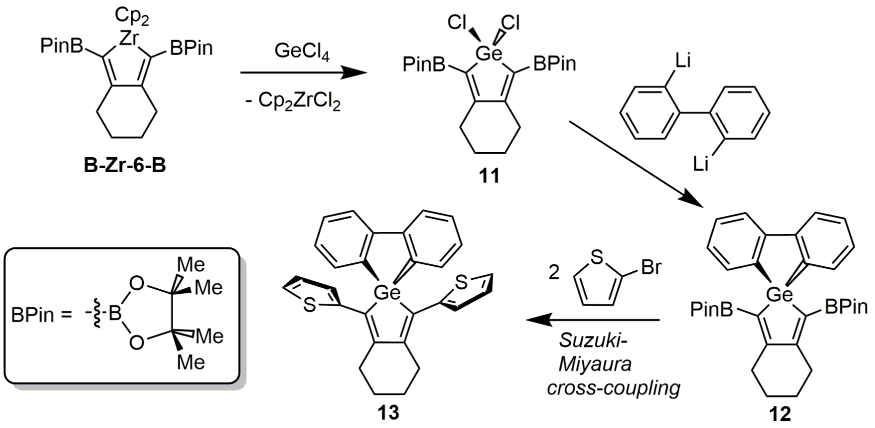


Figure 2.14. Thermal ellipsoid plot (30 % probability) of the SGG **10** with hydrogen atoms omitted for clarity. Only the major (70 %) orientation of the disordered thienyl group is shown. Selected bond lengths (Å) and angles (deg): Ge-C(1) 1.938(2), Ge-C(12) 1.928(2), Ge-C(13) 1.947(19), Ge-C(16) 1.943(2); C(12)-Ge-C(1) 89.99(9), C(13)-Ge-C(16) 90.26(9).

Given our prior experiences using Suzuki-Miyaura cross-coupling to yield metallole-based polymers[17a] (*i.e.,* polytellurophenes), we prepared a spirocyclic germafluorene-germole containing polymerizable pinacolborane (BPin) groups. Specifically the known pinacolborane-capped zirconacycle precursor **B-Zr-6-B**[16a, 16b] was combined with excess $GeCl_4$ to generate the requisite halogermole (**11**) as a yellow solid in a high yield of 85 % (Scheme 2.5). In a subsequent step, incorporation of a fluorene unit at Ge to give the SGG (**12**) was achieved by combining **11** with in situ generated 2,2'-dilithiobiphenyl.[32]



Scheme 2.5. Synthesis of the dihalogermole (**11**), pinacolborane-capped spirocyclic germafluorene (**12**) and Suzuki-Miyuara coupling involving **12** to obtain thiophene-capped spirogermafluorene (**13**).

The structures of compounds **11** and **12** were determined by single-crystal X-ray crystallography and are presented as Figures 2.15 and 2.16, respectively. As noted in previously reported pinacolboronate (BPin)-substituted tellurophenes,[16] the flanking BPin groups in **12** are arranged in a slightly twisted fashion in relation to the central metallole ring (by *ca.* 12.5 to 14.5°). However in contrast to the BPin-capped tellurophenes, which are phosphorescent in the solid state, compound **12** is non-emissive both in solution and in the condensed phase. In order to verify if the quenching of the luminescence was caused by the BPin groups, we explored the coupling of **12** with 2-bromothiophene to yield a SGG wherein the BPin groups are replaced by thienyl residues.

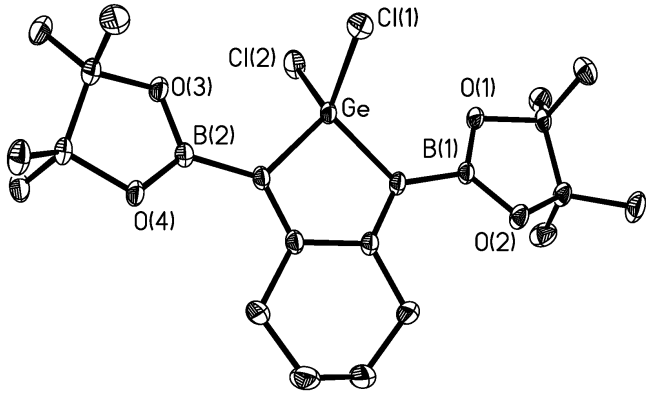


Figure 2.15. Thermal ellipsoid plot (30 % probability) of the dihalogermole (**11**) with hydrogen atoms and toluene solvate have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge−Cl(1) 2.1513(6), Ge−Cl(2) 2.1299(6), Ge−C1 1.9197(19), Ge−C8 1.9161(19), B(1)−O(1) 1.365(3), B(2)−O(3) 1.366(3), Cl(2)−Ge−Cl(1) 105.44(3), C(1)−Ge−C(8) 93.53(8), O(1)−B(1)−O(2) 113.74(17), O(3)−B(2)−O(4) 113.51(8).

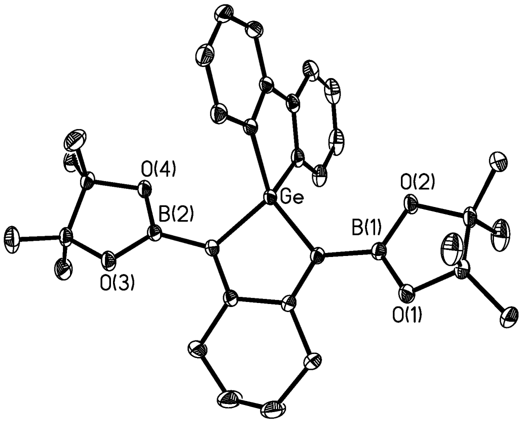


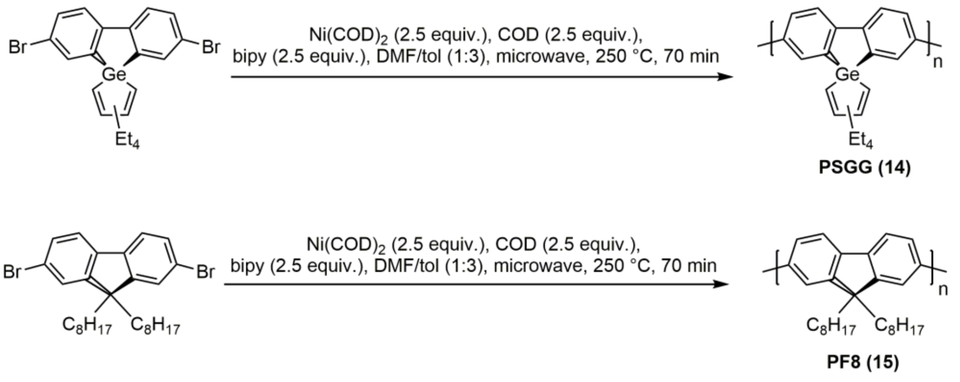
Figure 2.16. Thermal ellipsoid plot (30 % probability) of compound **12** with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg) with values due to a disordered BPin group in square brackets: Ge−C(1) 1.9488(14), Ge−C(8) 1.9345(14), Ge−C(32) 1.9469(15), Ge−C(21) 1.9391(15), B(1)−O(1A) 1.360(3) [1.392(5)], B(1)−O(2A) 1.365(3) [1.369(6)], B(2)−O(3) 1.3706(19); C(1)−Ge−C(8) 90.96(6), C(21)−Ge−C(32) 89.11(7), O(3)−B(2)−O(4) 112.33(14), O(1A)−B(1)−O(2A) 113.41(18) [109.9(3)].

Using unoptimized Suzuki-Miyaura cross-coupling conditions,[33] compound **13** was obtained in a 60 % crude yield. After rigorous purification procedures, pure **13** can be obtained as a yellow solid which absorbs at 423 nm in THF solution; this value is similar to the λ_{max} noted in the tetra-thienyl substituted SGG **10** (434 nm). Compound **13** exhibits green luminescence in solution with a relative quantum yield of 5.8 %; thus it appears in these SGGs the presence of flanking BPin group have a quenching effect (as in **12**). After optimization, the use of **12** as a co-monomer for future polymerization trials should be explored.

2.4. On the Road to Light-emitting Spirocyclic Germafluorene-Germole Polymers

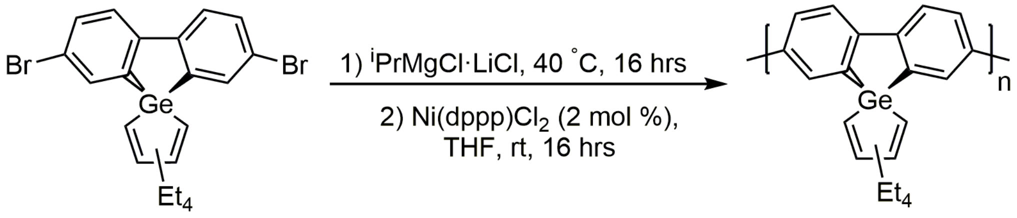
2.4.1. Synthesis and structural characterization of polymeric spirocyclic germafluorene-germoles

The Yamamoto coupling reaction is a dehalogenation polycondensation reaction of dihaloaromatic compounds X-Ar-X (X = halogen) promoted by Ni(0)-complexes and is a widely used synthetic pathway to light-emitting π-conjugated polymers.[34] Earlier Leclerc and co-workers used this reaction to obtain a homopolymer of 9,9′-dibutylgermafluorene albeit with limited solubility.[8] Using similar conditions and THF or DMF/toluene (1:1) solvent mixtures, the synthesis of the first SGG homopolymer (**14**) was attempted from **3**, however the reaction yielded only very low molecular weight species as determined by GPC, and no evidence for polymer formation was found by MALDI-MS. At the same time, microwave-assisted polymerization has been known to give high molecular weight polymers,[35] so the polymerization of 9,9-dioctylfluorene[36] was explored first as a model and afforded high molecular weight (M_n = 73,630 g mol^{-1} and M_w = 94,870 g mol^{-1}; confirmed by GPC) homopolymer PF8 (**15**) in a high yield of 92 % (Scheme 2.6). Under the same reactions conditions the SGG homopolymer **14** was produced from **3** as a yellow solid (M_n = 3,360 g mol^{-1} and M_w = 6,250 g mol^{-1}) in a moderate yield of 38 % (Scheme 2.6). However, even in the presence of the alkylated germole unit GeC_4Et_4, the short ethyl chains in **14** prevented the polymer from being fully soluble in common organic solvents, such as THF, CH_2Cl_2, acetone, DMF, ethyl acetate, DMSO, chloroform, toluene, and trichlorobenzene, which could also explain the lower yield and molecular weight compared to PF8 (**15**). It is worth noting, that during operation of the MALDI instrument very high laser power is required to obtain signal for polymer **14** (*i.e.*, it is not easily ionized, thus limiting detection of polymer chains with high molecular weight).



Scheme 2.6. Synthesis of the polyspirogermafluorene (**14**) and polyfluorene (**15**).

Another approach that could be used to obtain homopolymer **14** is Grignard metathesis (GRIM) polymerization, the Ni(II)-catalysed “quasi”-living chain-growth polymerization or dihaloarenes can afford high molecular weight polymers with narrow molecular weight distributions.[37] This reaction was first reported by McCullough[38] and Yokozawa[39] and was actively explored for poly(3-alkylthiophene)s[40] and polyphenylenes.[41] The Geng group also examined this reaction in the synthesis of PF8 (**15**).[37] When the GRIM polymerization of **3** (Scheme 2.7) was examined, the desired polymer **14** was obtained as a yellow powder with limited solubility in a 11 % yield (M_n = 2540 g mol^{-1} and M_w = 3610 g mol^{-1}; as determined GPC).



3 **PSGG (14)**

Scheme 2.7. Synthesis of the polyspirogermafluorene (**14**) via Grignard metathesis polymerization.

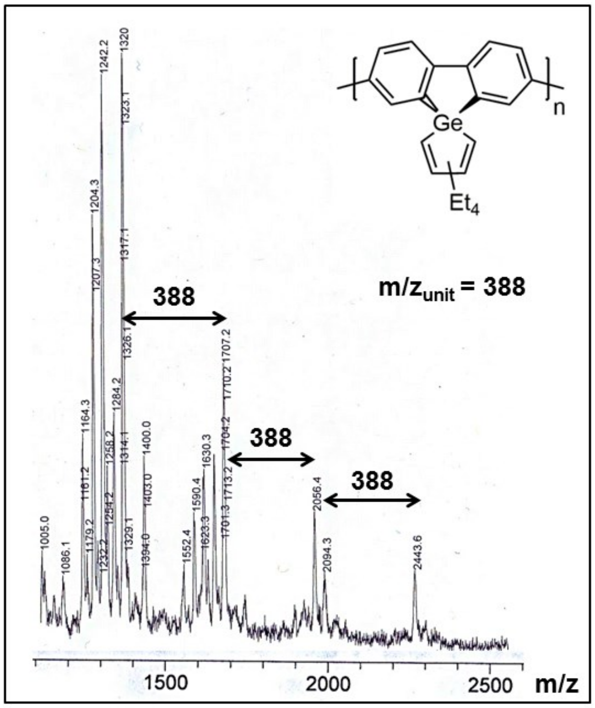
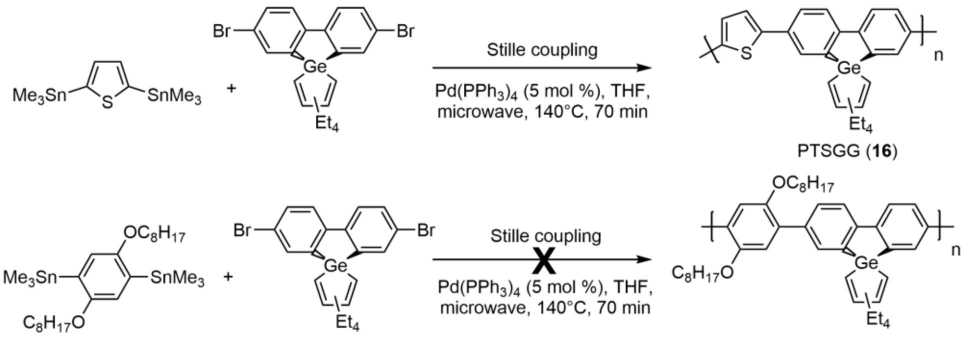


Figure 2.17. MALDI mass spectrum of the polyspirogermafluorene **14**.

Motivated by the blue luminescence noted in the thiophene-capped SGG (**5**) and its high quantum yield of 83 % (see Section 2.1.3), microwave-assisted Stille coupling route was employed to obtain the co-polymer PTSGG (**16**) from the coupling of **3** with 2,5-

bis(trimethylstannyl)thiophene.[42] Polymer **16** was obtained as a yellow powder in 13 % yield and this material also showed limited solubility in common organic solvents. Thus, in order to improve solution processability of the targeted polymer, the modified monomer 1,4-di(trimethyltin)-2,5-dioctyloxybenzene[43] was used under microwave-assisted Stille cross-coupling conditions (Scheme 2.8). Despite numerous attempts, starting materials were recovered after the reaction with no sign of reaction, as confirmed by multinuclear NMR spectroscopy. The outcome of the Stille cross-coupling is very sensitive to the steric hindrance of the substrates,[44] so future work should consist of employing lithium and copper(I) halides (*e.g.*, LiCl, CuI) as additives in order to promote the reaction.[45]



Scheme 2.8. Synthesis of the thiophene-SGG copolymer **16** and the attempted synthesis of an aryl-germafluorene copolymer.

2.4.2. Optical and thermal properties of polygermafluorenes and polyfluorene

During the past few decades, PF8 (**15**) has been a benchmark blue luminophore due to its highly efficient photo- and electroluminescence, good charge transport, easily tunable physical properties through chemical modifications, thermal stability and solubility in organic solvents.[34,46] Thus, it is of interest to compare the luminescence properties of our polymeric SGGs **14** and **16** to the polyfluorene **15**.

Table 2.1. Summarized physical and optical properties of polymers **14-16**.

Polym.	Yield, %	M_n, g mol^{-1}	M_w/M_n	UV-Vis (THF) λ_{max}, nm ($\varepsilon \times 10^{-4}$)*	TGA (°C)	Em. λ_{emis} (nm)	Quant. yield (Φ)
PSGG (**14**)	38	3360	1.86	382 (2.02)	370	420 (shoulder at 440)	0.67
PF8 (**15**)	92	73600	1.29	390 (0.777)	440	415 (shoulder at 439)	0.77
PTSGG (**16**)	11	1900	1.25	374 (1.79)	219	445	0.48

*per monomer repeat unit (mol^{-1} dm^3 cm^{-1})

In order to benchmark our studies, the optical and physical properties of PF8 (**15**) were measured and found to match those reported in the literature.[39-41] The optical properties of the polyspirocyclic germafluorene-germole **14** are remarkably similar to those of polyfluorene **15**. The absorption maximum in the UV-Vis spectrum of **14** and **15** are approximately the same (382 nm and 390 nm, respectively), while the thiophene-SGG copolymer **16** has a hypsochromic shift in absorbance to 374 nm potentially due to a slight decrease in π-conjugation (Figure 2.18).

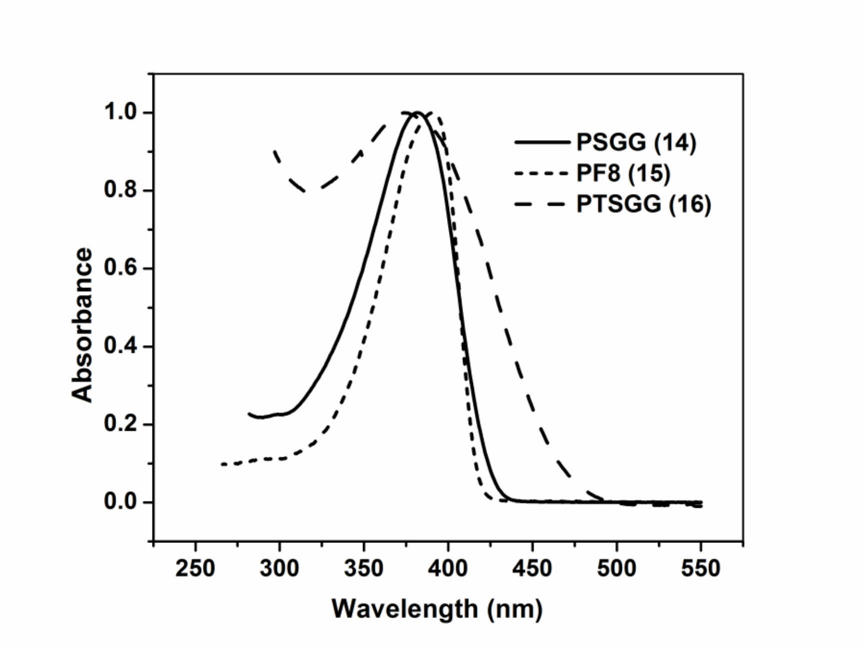


Figure 2.18. Normalized UV/Vis absorption spectra of compounds **14-16** in solution (THF).

Both polymers **14** and **15** have quite similar photoluminescence (PL) profiles with emission maxima in the blue region at *ca*. 420 nm due to having the same chromophore backbone (*i.e.*, fluorene) and well-resolved vibronic structure. In general, the presence of well-defined vibronic structures in the emission spectra indicates that the polymers have a rigid and well-defined backbone.[35-37] Copolymer **16** also emits in the blue region with an emission maximum at 445 nm (Figure 2.19).

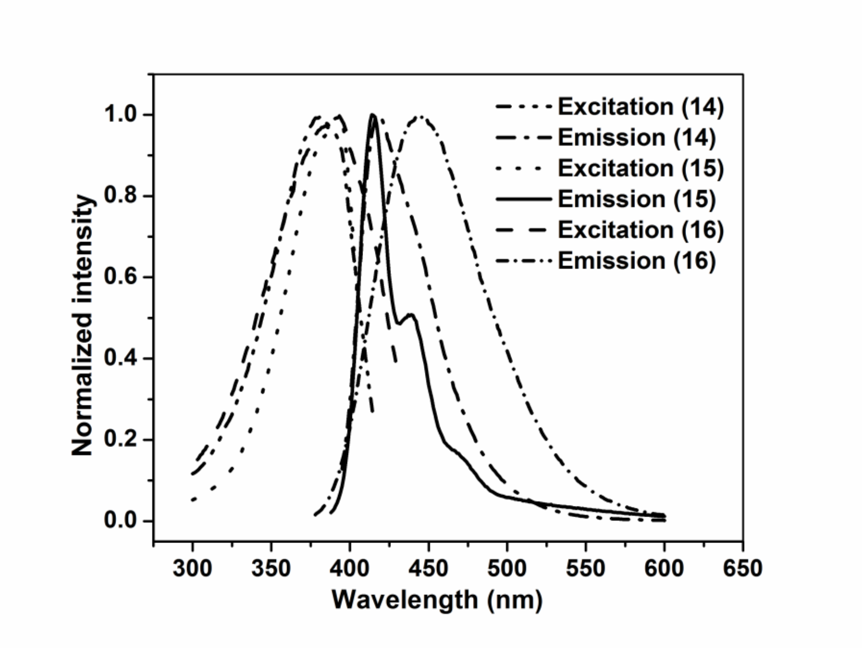


Figure 2.19. Normalized PL excitation and emission spectra of **14-16** in solution (THF).

While the SGG homopolymer **14** exhibits potentially useful blue emission, it showed a *ca.* 10 % lower fluorescence quantum yield than fluorene analogue **15** (67 % and 77 %, respectively). It is worth noting that copolymer **16** possesses a lower quantum yield of 48 %, while the analogous fluorene-thiophene copolymer has a quantum yield of 78 %, comparable to **14** and **15**.[38] To provide a reason for lower quantum yield of **16**, DFT calculations of the model systems would be required.[12]

Thermal stability is also an important parameter for display materials.[42] The polymeric SGG **14** shows a lower decomposition temperature (T_d) of 370 °C (5 % weight loss) than the polyfluorene **15** (T_d

= 440 °C); while copolymer **16** exhibits quite low thermal stability with a T_d of 219 °C possibly due to thermally labile thienyl groups (Figure 2.20).

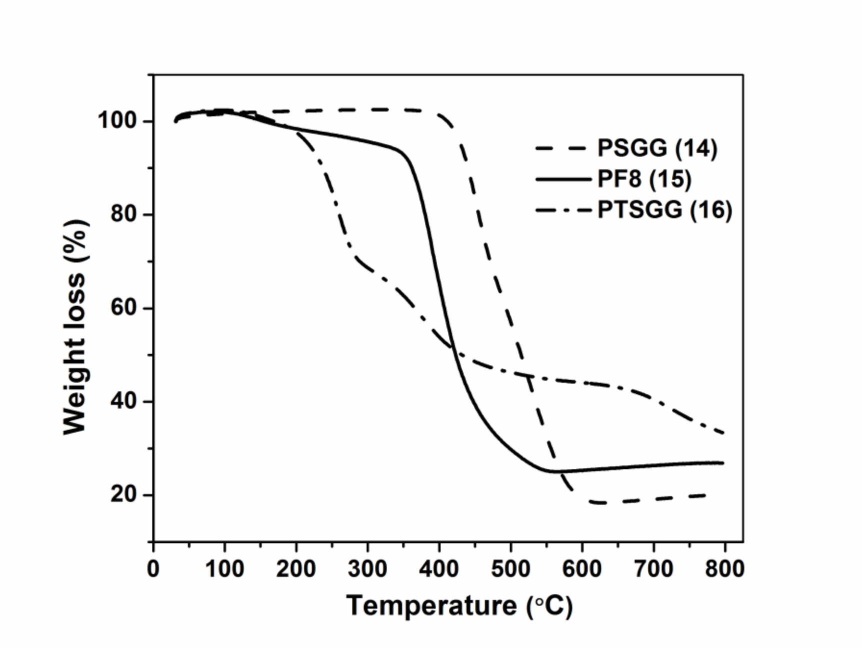


Figure 2.20. TGA thermograms of **14-16** measured under N_2 (scan rate = 10 °C/min).

2.5. Conclusions

In summary, a series of light-emitting and thermally stable molecular spirocyclic germafluorene-germoles (SGGs) were prepared with the help of metallacycle transfer chemistry and microwave-assisted Stille and Suzuki-Miyaura cross-coupling. By altering the nature of the peripheral substituents, photoluminescence from electronically separate germafluorene and germole units could be turned on or off, leading to blue, green and orange-yellow emission. Future work will involve the attempted preparation of "on/on" dual emission SGGs[21] with particular attention given towards obtaining white light emission within molecular or polymeric frameworks.

Lastly, blue-emitting homopolymers of spirocyclic germafluorene-germole and 9,9'-dioctylfluorene as well as a thiophene-SGG copolymer were prepared using microwave-assisted Yamamoto and Stille cross-coupling. The SGG homopolymer **14** had lower quantum yield and thermal stability that polyfluorene. It was discovered that presence of spirocyclic center did not provide enhanced solubility of the resulted polymers as expected, despite attempts to improve solubility via co-polymerization with a monomer bearing long alkoxy chains. Future work on improving the solubility of SGG polymers, for example, incorporation of different substituents (*e.g.*, cumyl) on the germole ring, is under way.

2.6. Experimental procedures

2.6.1. Materials and instrumentation

All reactions were performed using standard Schlenk and glovebox (MBraun) techniques under a nitrogen atmosphere. Solvents were all dried and degassed using a Grubbs-type solvent purification system[47] manufactured by Innovative Technology, Inc., and stored under an atmosphere of nitrogen prior to use. 1,7-Octadiyne and 2,2'-bipyridine were obtained from GFS Chemicals, germanium tetrachloride and zirconocene dichloride from Strem Chemicals Inc., 1,2-dibromobenzene from Alfa Aesar; all other chemicals were obtained from Aldrich. All commercially obtained chemicals were used as received. 2,2'-Dibromobiphenyl,[32a] $Cp_2ZrC_4Et_4$,[18] 4,4'-dibromo-2,2'-diiodobiphenyl,[48] trimethylstannylbenzene,[24] 2-trimethylstannylthiophene,[25] 2,5-bis(trimethylstannyl)thiophene,[42] 1,4-di(trimethyltin)-2,5-dioctyloxybenzene,[43] 2-tributylstannylthiophene,[49] 1,2-di(thiophen-2-yl)ethyne,[50] 2,5-dibromothiophene,[51] 9,9'-dioctyl-2,7-dibromofluorene,[52] and bis(cyclopentadienyl)zirconium(cyclohexane-1,2-diylidenebis{(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methanide}) (**B-Zr-6-B**),[16a] were prepared according to literature procedures. ^1H, $^{13}C\{^1H\}$ and $^{11}B\{^1H\}$ NMR spectra were recorded on a Varian DD2 MR-400 spectrometer and referenced externally to $SiMe_4$ (^1H, $^{13}C\{^1H\}$) and $F_3B{\bullet}OEt_2$ ($^{11}B\{^1H\}$). Elemental analyses were performed by the Analytical and Instrumentation Laboratory at the University of Alberta.

Mass spectra for small molecules were recorded using a MS-50G system (Kratos Analytical). Mass spectra for polymers were measured using an AB Sciex Voyager Elite MALDI system (AB Sciex, Foster City, CA, USA). Melting points were obtained in sealed glass capillaries under nitrogen using a MelTemp melting point apparatus and are uncorrected. UV/Vis measurements were performed using a Varian Cary 300 Scan spectrophotometer. The fluorescence measurements were conducted on a Photon Technology International (PTI) MP1 fluorescence system. All solution quantum yields were measured relative to quinine sulfate in 1 N H_2SO_4 assuming a quantum yield of 0.55.[53] Photoluminescence lifetimes were measured on a time-correlated single photon counting fluorescence spectrometer (Edinburgh Instruments FLS920) using an EPL-375 picosecond pulsed diode laser with vertical polarization (70.3 ps pulse width) as an excitation source; absolute quantum yields were measured with an integrating sphere system within the same fluorescence spectrometer. GPC was performed at 40 °C using THF as an eluent at a flow rate of 0.5 mL min^{-1}. GPC measurements were made using a GPC 270 Max instrument equipped with a Viscotek VE 2001 plus autosampler, three μ-Styragel columns, and a Viscotek VE 3580 refractive index (RI) detector. The columns were calibrated using polystyrene standards. Microwave reactions were performed using a Biotage Initiator Classic microwave reactor (Biotage, LLC, Charlotte, NC, USA). Photobleaching experiments on solutions were performed using an Ace-Hanovia 450 W mercury lamp (Ace Glass Inc., Vineland, NJ, USA). Photobleaching experiments on films were performed with a Photon Technology International (PTI) MP1 fluorescence system (xenon lamp, 65 W).

2.6.2. Synthetic procedures

2.6.2.1. Synthesis of 1,1-dichloro-2,3,4,5-tetraethyl-1H-germole (1)

This compound was synthesized according to a modification of a known procedure.[18] To a solution of $Cp_2ZrC_4Et_4$ (0.390 g, 1.0 mmol) in THF (10 mL) at room temperature was added $GeCl_4$ (138 µL, 1.2 mmol), and the mixture was stirred overnight to give a pale yellow solution. The volatiles were removed under vacuum and 10 mL of hexanes was used to extract the product. The extract was then filtered through a 1 cm plug of silica gel. The solvent was then removed from the filtrate to yield $Cl_2GeC_4Et_4$ (**1**) as a colorless oil that was used without further purification (0.265 g, 85 %). The corresponding ^1H and $^{13}C\{^1H\}$ NMR spectral data matched those reported previously by the Tilley group.[18]

2.6.2.2. Synthesis of 2,3,4,5-tetraethyl-spiro[germacyclopenta-2,4-diene-1,9'-[9H-9]germafluorene] (2)

A solution of 2,2'-dibromobiphenyl (0.177 g, 0.57 mmol) in 6 mL of Et_2O was cooled to -35 °C and ^nBuLi (454 µL, 2.5 M in hexanes, 1.1 mmol) was added dropwise. The reaction mixture immediately became yellow in color and was stirred for 3 hrs at room temperature. Afterwards this mixture, containing dilithiobiphenyl, was cooled down to -35 °C and a solution of **1** (0.175, 0.57 mmol) in 4 mL of diethyl ether was added, followed by stirring for 12 hrs at room temperature. A pale yellow solution formed over a white precipitate; this precipitate was allowed to settle and the yellow mother liquor was filtered through Celite. The solvent was removed from the filtrate under vacuum to yield crude **2** as a yellow oil which solidified upon standing (0.203 g, 92 %). The product was purified by column chromatography (silica gel, hexanes) and cooling of a saturated solution of **2** in hexanes to -30 °C resulted in the formation of colorless crystals of suitable quality for X-ray crystallography (0.135 g, 61 %). M.p. 80-82 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, $^3J_{HH} = 7.9$ Hz, 2H, Ar*H*), 7.55 (d, $^3J_{HH} = 7.2$ Hz, 2H, Ar*H*), 7.42 (td, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 1.3$ Hz, 2H, Ar*H*), 7.25 (td, $^3J_{HH} = 7.2$ Hz, $^4J_{HH} = 0.9$ Hz, 2H, Ar*H*), 2.41 (q, $^3J_{HH} = 7.6$ Hz, 4H, CH_2CH_3), 2.26 (q, $^3J_{HH} = 7.5$ Hz, 4H, CH_2CH_3), 1.11 (t, $^3J_{HH} = 7.5$ Hz, 6H, CH_2CH_3), 0.68 (t, $^3J_{HH} = 7.5$ Hz, 6H, CH_2CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 153.2, 146.9, 137.5, 135.8, 133.5, 129.5, 127.6, 121.6 (Fl-*C* and Ar-*C*), 23.5, 21.4 (CH_2CH_3), 15.9, 15.1 (CH_2CH_3); UV/Vis (THF): λ_{max} (ε) = 276 nm (1.42×10^4 mol^{-1}dm^{3}cm^{-1}); HR-MS (EI): m/z: 390.1405 $[M]^+$; $C_{24}H_{28}Ge$ calcd: 390.1403; elemental analysis calcd (%) for $C_{24}H_{28}Ge$: C, 74.08; H, 7.25; found: C, 73.61; H, 7.29.

2.6.2.3. Synthesis of 2',7'-dibromo-2,3,4,5-tetraethyl-spiro[germacyclopenta-2,4-diene-1,9'-[9H-9]germafluorene] (3)

A solution of 4,4'-dibromo-2,2'-diiodobiphenyl (1.967 g, 3.5 mmol) in diethyl ether (20 mL) was pre-cooled to -78 °C and 2.8 mL of ^{n}BuLi (2.5 M in hexanes, 7.0 mmol) was added dropwise over one hour, using addition funnel. The mixture was stirred for one more hour at -78 °C, and then a pre-cooled (-78 °C) solution of **1** (1.074 g, 3.5 mmol) in 15 mL of Et_2O was added. The mixture was then warmed to room temperature and stirred for 12 hrs. The mixture was diluted with 50 mL of diethyl ether and then washed with water (100 mL) and brine (100 mL), and the isolated organic fraction was dried over $MgSO_4$. The solvent was removed under vacuum to give crude **3** as a colorless solid (1.105 g, 58 %). Colorless crystals suitable for X-ray crystallography were obtained by slow cooling of a warm (*ca.* 40 °C) hexanes solution of **3** to 0 °C (0.770 g, 40 %). M.p. 192-194 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, $^3J_{HH}$ = 8.2 Hz, 2H, Ar*H*), 7.64 (d, $^3J_{HH}$ = 2.0 Hz, 2H, Ar*H*), 7.54 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 1.9 Hz, 2H, Ar*H*), 2.39 (q, $^3J_{HH}$ = 7.5 Hz, 4H, CH_2CH_3), 2.25 (q, $^3J_{HH}$ = 7.5 Hz, 4H, CH_2CH_3), 1.10 (t, $^3J_{HH}$ = 7.5 Hz, 6H, CH_2CH_3), 0.67 (t, $^3J_{HH}$ = 7.5 Hz, 6H, CH_2CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 154.1, 144.7, 140.2, 136.0, 134.8, 132.7, 123.2, 122.7 (Fl-*C* and Ar-*C*), 23.4, 21.6 (CH_2CH_3), 15.9, 15.0 (CH_2CH_3); UV/Vis (THF): λ_{max} (ε) = 288 nm (2.11×10^4 $mol^{-1}dm^3cm^{-1}$); HR-MS (EI): m/z: 545.9599 $[M]^+$;

$C_{24}H_{26}Br_2Ge$ calcd: 545.9613; elemental analysis calcd (%) for $C_{24}H_{26}Br_2Ge$: C, 52.71; H, 4.79; found: C, 52.53; H, 4.82.

2.6.2.4. Synthesis of 2',7'-diphenyl-2,3,4,5-tetraethyl-spiro[germacyclopenta-2,4-diene-1,9'-[9H-9]germafluorene] (4)

Compound **3** (0.162 g, 0.30 mmol), trimethylstannylbenzene (108 µL, 0.61 mmol), and $Pd(PPh_3)_4$ (0.017 g, 0.015 mmol) were dissolved in 3 mL of THF in a sealed 5 mL microwave vial. The solution was irradiated by microwave (70 min., 140 °C) and then the mixture was filtered. The volatiles removed from the filtrate and the residue purified by column chromatography (silica gel, hexanes:THF = 20:1) to yield **4** as a spectroscopically pure white solid (0.050 g, 31 %). This compound was recrystallized from a hexanes/diethyl ether mixture at -30 °C to yield colorless crystals of X-ray quality. M.p. 217-220 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Fl*H*), 7.84 (d, $^3J_{HH}$ = 1.7 Hz, 2H, Fl*H*), 7.72-7.67 (m, 6H, Fl*H* and Ph*H*), 7.46 (t, $^3J_{HH}$ = 7.6 Hz, 4H, Ph*H*), 7.36 (m, 2H, Ph*H*), 2.46 (q, $^3J_{HH}$ = 7.5 Hz, 4H, CH_2CH_3), 2.33 (q, $^3J_{HH}$ = 7.5 Hz, 4H, CH_2CH_3), 1.16 (t, $^3J_{HH}$ = 7.5 Hz, 6H, CH_2CH_3), 0.76 (t, $^3J_{HH}$ = 7.5 Hz, 6H, CH_2CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 153.5, 145.8, 141.2, 140.3, 138.5, 135.8, 132.1, 128.8, 128.6, 127.2, 127.1, 122.0 (Fl-*C* and Ph-*C*), 23.6, 21.5 (CH_2CH_3), 16.0, 15.2 (CH_2CH_3); UV/Vis (THF): λ_{max} (ε) = 318 nm (6.28×10^4 $mol^{-1}dm^3cm^{-1}$); Fluorescence emission (THF) (λ_{ex} = 332 nm): λ_{emis} = 377 nm, fluorescence quantum yield: Φ =

0.03, relative to quinine sulfate in 1.0 N H_2SO_4; HR-MS (EI): m/z: 542.2021 $[M]^+$; $C_{36}H_{36}Ge$ calcd: 542.2029; elemental analysis calcd (%) for $C_{36}H_{36}Ge$: C, 79.88; H, 6.70; found: C, 79.66; H, 6.82.

2.6.2.5. Synthesis of 2',7'-bis(2-thienyl)-2,3,4,5-tetraethyl-spiro[germacyclopenta-2,4-diene-1,9'-[9H-9]germafluorene] (5)

Compound **3** (0.162 g, 0.30 mmol), 2-trimethylstannylthiophene (104 µL, 0.59 mmol), and $Pd(PPh_3)_4$ (0.012 g, 0.011 mmol) were dissolved in 3 mL of THF in a sealed 5 mL microwave vial. The solution was irradiated by microwave (70 min., 140 °C), the volatiles were then removed under vacuum, and the remaining product was purified by column chromatography (silica gel, hexanes:THF = 20:1) to give **5** compound as a white solid (0.017 g, 14 %). This product was recrystallized from hot (40 °C) hexanes, by slow cooling to room temperature to afford X-ray quality crystals. M.p. 209-212 °C; TGA: T_{dec} = 319 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, $^3J_{HH}$ = 8.1 Hz, 2H, Fl*H*), 7.82 (d, $^4J_{HH}$ = 1.9 Hz, 2H, Fl*H*), 7.69 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.9 Hz, 2H, Fl*H*), 7.37 (dd, $^3J_{HH}$ = 3.6 Hz, $^4J_{HH}$ = 1.2 Hz, 2H, Thienyl*H*), 7.29 (dd, $^3J_{HH}$ = 5.1 Hz, $^4J_{HH}$ = 1.2 Hz, 2H, Thienyl*H*), 7.09 (dd, $^3J_{HH}$ = 5.1 Hz, $^4J_{HH}$ = 3.6 Hz, 2H, Thienyl*H*), 2.46 (q, $^3J_{HH}$ = 7.5 Hz, 4H, CH_2CH_3), 2.32 (q, $^3J_{HH}$ = 7.5 Hz, 4H, CH_2CH_3), 1.17 (t, $^3J_{HH}$ = 7.5 Hz, 6H, CH_2CH_3), 0.74 (t, $^3J_{HH}$ = 7.5 Hz, 6H, CH_2CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 153.6, 145.8, 144.6, 138.6, 135.7, 133.6, 130.7, 128.1, 127.4, 124.7, 123.1, 122.0

(Fl-*C*, thienyl-*C* and Ar-*C*), 23.6 (*C*H$_2$CH$_3$), 21.6 (*C*H$_2$CH$_3$), 15.9 (CH$_2$*C*H$_3$), 15.1 (CH$_2$*C*H$_3$); UV/Vis (THF): λ_{max} (ε) = 355 nm (4.92×10^4 mol^{-1}dm^{3}cm^{-1}); Fluorescence emission (THF) (λ_{ex} = 348 nm): λ_{emis} = 386 and 407 nm, fluorescence quantum yield: $\Phi = 0.83$, relative to quinine sulfate in 1.0 N H_2SO_4; Lifetime (1×10^{-5} M solution in THF): $\tau = 0.94$ ns; HR-MS (EI): m/z: 554.1161 $[M]^+$; $C_{32}H_{32}GeS_2$ calcd: 554.1157; elemental analysis calcd (%) for $C_{32}H_{32}GeS_2$: C, 69.46; H, 5.83; S, 11.59; found: C, 69.59; H, 5.71; S, 11.56.

2.6.2.6. Alternate preparation of 5 from 2-tributylstannylthiophene:

Compound **3** (0.102 g, 0.19 mmol), 2-tributylstannylthiophene (119 µL, 0.38 mmol), and Pd(PPh$_3$)$_4$ (0.011 g, 0.009 mmol) were dissolved in 3 mL of THF in a sealed 5 mL microwave vial. The solution was irradiated by microwave (70 min., 140 °C), the volatiles were then removed and the remaining product was purified by column chromatography (silica gel, hexanes:THF = 20:1) to give **5** compound as a white solid (0.053 g, 51 %).

2.6.2.7. Synthesis of 2,2'-(9,9-dioctyl-9*H*-fluorene-2,7-diyl) bisthiophene (7)

9,9'-Dioctyl-2,7-dibromofluorene (0.307 g, 0.56 mmol), 2-trimethylstannylthiophene (197 µL, 1.1 mmol), and Pd(PPh$_3$)$_4$ (0.032 g, 0.028 mmol) were dissolved in 5 mL of THF in a sealed 5 mL microwave vial. The solution was irradiated by microwave (70 min., 140 °C) and then the crude product was purified by column chromatography (silica gel, hexanes:THF = 20:1) yielding **7** as an oil (0.182 g, 59 %). ^{1}H and ^{13}C{^{1}H} NMR spectral data matched those reported previously by the Leclerc group.[26b,26d] TGA: T_{dec} = 290 °C. The physical data were identical to those previously reported.[26b,26d] HR-MS (EI): m/z: 554.3054; $C_{37}H_{46}S_2$ calcd: 554.3041; elemental analysis calcd (%) for $C_{37}H_{46}S_2$: C, 80.09; H, 8.36; S, 11.56; found: C, 79.58; H, 8.30; S, 11.03.

2.6.2.8. Synthesis of bis(cyclopentadienyl)zirconium-2,3,4,5-tetra(2-thienyl)methanide (8)

To a solution of Cp_2ZrCl_2 (0.610 g, 2.1 mmol) in THF (15 mL) at -78 °C was added dropwise a solution of ^{n}BuLi (1.63 mL, 2.5 M solution in hexanes, 4.1 mmol). After the reaction mixture was stirred at -78 °C for 1 h, a solution of 1,2-bis(thiophen-2-yl)ethyne (0.794 g, 4.2 mmol) in THF (15 mL) was added at -78 °C. The temperature was allowed to rise to room temperature, and the mixture was stirred for another 24 h. The solvent was removed under reduced pressure and the product was extracted with 25 mL of toluene, and the mixture was filtered through Celite. After the volatiles were removed from filtrate under reduced pressure to give **8** as a crude orange-red powder (1.080 g, 86 %) that was washed with cold hexanes (5 mL; -30 °C) to give a red solid (0.913 g, 73

%). M.p. 145-148 °C (decomp., turns brown); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (dd, $^3J_{HH}$ = 5.0 Hz, $^4J_{HH}$ = 1.0 Hz, 2H, Thienyl*H*), 7.04 (dd, $^3J_{HH}$ = 5.1 Hz, $^4J_{HH}$ = 1.0 Hz, 2H, Thienyl*H*), 6.79-6.76 (m, 4H, Thienyl*H*), 6.50 (dd, $^3J_{HH}$ = 3.3 Hz, $^4J_{HH}$ = 1.0 Hz, 2H, Thienyl*H*), 6.41 (s, 10 H, Cp*H*), 5.87 (dd, $^3J_{HH}$ = 3.6 Hz, $^4J_{HH}$ = 1.1 Hz, 2H, Thienyl*H*); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 185.7, 148.9, 142.6, 137.0, 127.8, 126.3, 126.0, 125.4, 125.0, 124.0 (Thienyl-*C*), 112.2 (Cp); UV/Vis (THF): λ_{max} (ε) = 422 nm (9.09×10^3 mol^{-1}dm^{3}cm^{-1}); HR-MS (MALDI): m/z: 599.9646; $C_{30}H_{22}S_4Zr$ calcd: 599.9662; elemental analysis calcd (%) for $C_{30}H_{22}S_4Zr$: C, 59.86; H, 3.68; S, 21.30; found: C, 59.32; H, 3.92; S, 19.26.

2.6.2.9. Synthesis of 1,1-dichloro-2,3,4,5-tetra(2-thienyl)-1H-germole (9)

To a dark red solution of **8** (0.349 g, 0.58 mmol) in 10 mL of THF at room temperature was added $GeCl_4$ (99 μL, 0.87 mmol) and the mixture was stirred overnight to give a lighter red solution. The solvent was removed under vacuum, and the product was extracted with 50 mL of hexanes in a Soxhlet apparatus. The solvent was removed from the extract to afford **9** as an orange solid (0.267 g, 88 %). X-ray quality orange crystals were obtained upon recrystallization from Et_2O/hexanes at room temperature (0.091 g, 30 %). M.p. 170-173 °C (decomp., turns into dark red oil); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (dd, $^3J_{HH}$ = 3.7 Hz, $^4J_{HH}$ =

1.1 Hz, 2H, Thienyl*H*), 7.4 (dd, ${}^3J_{HH}$ = 5.1 Hz, ${}^4J_{HH}$ = 1.2 Hz, 2H, Thienyl*H*), 7.23 (dd, ${}^3J_{HH}$ = 5.1 Hz, ${}^4J_{HH}$ = 1.2 Hz, 2H, Thienyl*H*), 7.00 (m, 4H, Thienyl*H*), 6.87 (dd, ${}^3J_{HH}$ = 3.5 Hz, ${}^4J_{HH}$ = 1.2 Hz, 2H, Thienyl*H*); ${}^{13}C\{{}^1H\}$ NMR (100 MHz, $CDCl_3$): δ 139.5, 138.0, 135.5, 131.5, 129.4, 129.2, 128.5, 128.1, 127.5, 126.8 (Thienyl-*C*); UV/Vis (THF): λ_{max} (ε) = 452 nm (1.51 × 10^4 $mol^{-1}dm^3cm^{-1}$); HR-MS (MALDI): m/z: 523.8396; $C_{20}H_{12}Cl_2GeS_4$ calcd: 523.8411; elemental analysis calcd (%) for $C_{20}H_{12}Cl_2GeS_4$: C, 45.84; H, 2.31; S, 24.47; found: C, 45.99; H, 2.80; S, 20.17. This compound routinely contains 5-10 % Cp_2ZrCl_2 and was used in this form for the next step.

2.6.2.10. Synthesis of 2,3,4,5-tetra(2-thienyl)-spiro[germacyclopenta-2,4-diene-1,9'-[9H-9]germafluorene] (10)

A solution of 2,2'-dibromobiphenyl (0.109 g, 0.35 mmol) in 4 mL of Et_2O was cooled to -35 °C and ${}^nBuLi$ (279 μL, 2.5 M solution in hexanes, 0.70 mmol) was added dropwise. The mixture immediately became yellow in color and was stirred for 3 hrs at room temperature. Afterwards this mixture (containing 2,2'-dilithiobiphenyl) was cooled down to -35 °C and a solution of **9** (0.183 g, 0.35 mmol) in 9 mL of Et_2O was added, followed by stirring for 12 hrs. A dark orange solution formed over a precipitate; this precipitate was allowed to settle and the mother liquor was filtered through silica gel. Volatiles were removed from mother filtrate and cold (-30 °C) 5 mL of acetone was added to yield a yellow precipitate (0.040 g, 19 %). The precipitate was then extracted with 10 mL of CH_2Cl_2 and after filtration and removal of the volatiles, 3 mL of cold (-30 °C) acetone was added to form yellow precipitate **10**. The acetone filtrate was decanted and precipitate **10** was dried under high vacuum (0.034 g, 16 %), giving 0.074 g of **10** and an overall yield of 35 %. Recrystallization of combined precipitates from a CH_2Cl_2/hexanes solution at room temperature resulted in the formation of yellow crystals of X-ray quality (0.025 g, 12 %). M.p. 221-223 °C (decomp., turns brown); TGA: $T_{dec} = 238$ °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, $^3J_{HH}$ = 7.7 Hz, 2H, Ar*H*), 7.82 (d, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 0.6 Hz, 2H, Ar*H*), 7.56 (m, 2H, Ar*H*), 7.39 (dd, $^3J_{HH}$ = 5.1 Hz, $^4J_{HH}$ = 1.1 Hz, 2H, Thienyl*H*), 7.35-7.32 (m, 2H, Ar*H*), 7.01 (dd, $^3J_{HH}$ = 5.1 Hz, $^4J_{HH}$ = 3.4 Hz, 2H, Thienyl*H*), 6.97 (dd, $^3J_{HH}$ = 5.0 Hz, $^4J_{HH}$ = 1.1 Hz, 2H, Thienyl*H*), 6.92 (dd, $^3J_{HH}$ = 3.5 Hz, $^4J_{HH}$ = 1.1 Hz, 2H, Thienyl*H)*, 6.56 (dd, $^3J_{HH}$ = 5.1 Hz, $^4J_{HH}$ = 3.9 Hz, 2H, Thienyl*H)*, 6.42 (dd, $^3J_{HH}$ = 3.7 Hz, $^4J_{HH}$ = 1.1 Hz, 2H, Thienyl*H)*; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 146.4, 143.5, 141.5, 138.4, 135.7, 134.4, 131.9, 130.9, 130.0, 128.8, 128.6, 127.5, 127.4, 127.3, 126.3, 122.3 (Ar-*C*, Thienyl-*C*); UV/Vis (THF): λ_{max} (ε) = 434 nm (2.59 × 10^4 $mol^{-1}dm^3cm^{-1}$); Lifetime (solid state): τ = 3.22 nm; quantum yield (solid state) = 2.08 %; HR-MS (MALDI): m/z: 605.9647; $C_{32}H_{20}GeS_4$ calcd: 605.9660; elemental analysis calcd (%) for $C_{32}H_{20}GeS_4$: C, 63.49; H, 3.33; S, 21.18; found: C, 60.07; H, 3.89; S, 20.18. Despite repeated attempts, combustion analyses gave consistently low values for and sulfur content. See Figures 2.21 and 2.22 for copies of the NMR spectra.

2.6.2.11. Synthesis of 2,2'-dichloro-(4,5,6,7-tetrahydro-2-benzogermophene-1,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (11)

To a solution of **B-Zr-6-B**[16a] (0.827 g, 1.4 mmol) in 25 mL of THF at room temperature was added $GeCl_4$ (253 μL, 2.2 mmol) and the mixture was stirred overnight to give a pale yellow solution. The solvent was removed under vacuum, and 15 mL of hexanes was used to extract the product. The extract was then filtered through a 1 cm plug of Celite. The solvent was removed from the filtrate to afford **11** as a yellow solid (0.610 g, 85 %). X-ray quality crystals were obtained upon recrystallization from hexanes at -35 °C (0.125 g, 16 %). M.p. 124-127 °C; ^1H NMR (400 MHz, C_6D_6): δ 2.85 (m, 4H, $C{=}CCH_2CH_2$), 1.24 (m, 4H, $C{=}CCH_2CH_2$), 1.07 (s, 24H, CH_3); $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ 166.7 (Ge-C=*C*), 83.6 (*C*(CH_3)$_2$), 30.8 ($C{=}CCH_2CH_2$), 24.8 (CH_3), 22.4 ($C{=}CCH_2CH_2$); $^{11}B\{^1H\}$ NMR (160 MHz, C_6D_6): δ 29.5 (br); UV/Vis (THF): λ_{max} (ε) = 327 nm (8.78×10^3 $mol^{-1}dm^3cm^{-1}$); HR-MS (EI): m/z: 502.1066; $C_{20}H_{32}B_2Cl_2GeO_4$ calcd: 502.1076; elemental analysis calcd (%) for $C_{20}H_{32}B_2Cl_2GeO_4$: C, 47.89; H, 6.43; found: C, 48.73; H, 5.90.

2.6.2.12. Synthesis of 4,5,6,7-tetrahydro-2-spiro[benzogermafluorene]-1,3-diyl-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (12)

A solution of 2,2'-dibromobiphenyl (0.175 g, 0.56 mmol) in 6 mL of Et_2O was cooled to -35 °C and $^{n}BuLi$ (449 µL, 2.5 M solution in hexanes, 1.1 mmol) was added dropwise. The mixture immediately became yellow in color and was stirred for 3 hrs at room temperature. Afterwards this mixture (containing 2,2'-dilithiobiphenyl) was cooled down to -35 °C and a solution of **11** (0.281 g, 0.56 mmol) in 4 mL of Et_2O was added, followed by stirring for 12 hrs. A pale yellow solution formed over a white precipitate; this precipitate was allowed to settle and the yellow mother liquor was filtered through Celite. The solvent was removed from the filtrate under vacuum to yield crude **12** as a yellow solid. The product was purified by column chromatography (silica gel, hexanes:THF = 10:1) and slow evaporation of a hexanes/THF solution of **12** at room temperature resulted in the formation of colorless crystals of X-ray quality (0.114 g, 35 %). M.p. 189-193 °C; ^{1}H NMR (400 MHz, C_6D_6): δ 7.76 (d, $^{3}J_{HH}$ = 7.6 Hz, 2H, Ar*H*), 7.62 (d, $^{3}J_{HH}$ = 7.2 Hz, 2H, Ar*H*), 7.18 (t, $^{3}J_{HH}$ = 7.6 Hz, 2H, Ar*H*), 7.05 (t, $^{3}J_{HH}$ = 7.6 Hz, 2H, Ar*H*), 3.24-3.21 (m, 4H, $C{=}CCH_2CH_2$), 1.60 (m, 4H, $C{=}CCH_2CH_2$), 0.82 (s, 24H, CH_3); $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): δ 169.9, 148.1, 137.0, 133.7, 129.6, 127.6, 121.9 (Fl-*C* and Ar-*C*), 82.6 ($C(CH_3)_2$), 32.7 ($C{=}CCH_2CH_2$), 24.6 (CH_3), 23.8 ($C{=}CCH_2CH_2$); $^{11}B\{^{1}H\}$ NMR (128 MHz, C_6D_6): δ 30.8 (br); UV/Vis (THF): λ_{max} (ε) = 312 nm (1.25×10^{4} $mol^{-1}dm^{3}cm^{-1}$); HR-

MS (EI): m/z: 584.2322; $C_{32}H_{40}B_2GeO_4$ calcd: 584.2324; elemental analysis calcd (%) for $C_{32}H_{40}B_2GeO_4$: C, 65.94; H, 6.92; found: C, 66.97; H, 7.10.

2.6.2.13. Synthesis of 4,5,6,7-tetrahydro-2-spiro[benzogermafluorene]-1,3-diyl-bis(2-thienyl) (13)

Compound **12** (0.200 g, 0.34 mmol), 2-bromothiophene (73 μL, 0.75 mmol), cesium fluoride (0.313 g, 2.06 mmol) and $Pd(PPh_3)_4$ (0.020 g, 0.017 mmol) were dissolved in 4 mL of acetonitrile in a sealed 5 mL microwave vial. The solution was irradiated by microwave (40 min., 140 °C), poured into 100 mL of water and extracted with 20 mL of chloroform. The organic layer was washed with 100 mL of water and 2 x 100 mL of brine. The aqueous fractions were combined and extracted with 10 mL of chloroform and washed with 100 mL of brine. Then all combined organic fractions were dried over $MgSO_4$. The solvent was removed in vacuo and the residue was purified was purified by column chromatography (silica gel, hexanes:CH_2Cl_2 = 5:1) and washed with pentane (10 mL) to give **13** as a yellow solid (0.010 g, 6 %). M.p. 130 °C (decomp., turns brown); TGA: T_{dec} = 214 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, $^3J_{HH}$ = 7.9 Hz, 2H, Ar*H*), 7.61 (d, $^3J_{HH}$ = 7.3 Hz, 2H, Ar*H*), 7.49 (td, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.1 Hz, 2H, Ar*H*), 7.25 (td, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 0.9 Hz, 7H, Ar*H*), 7.14 (dd, $^3J_{HH}$ = 5.1 Hz, $^4J_{HH}$ = 0.7 Hz, 2H, Thienyl*H*), 7.09 (dd, $^3J_{HH}$ = 5.1 Hz, $^4J_{HH}$ = 3.7 Hz, 2H, Thienyl*H*), 6.45 (dd, $^3J_{HH}$ = 3.4 Hz, $^4J_{HH}$ = 0.7 Hz, 2H, Thienyl*H*), 2.95-2.92 (m, 4H, C=CC*H*$_2$CH$_2$), 1.89 (m, 4H, C=CCH$_2$C*H*$_2$); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 148.7, 146.6, 142.3, 136.5, 134.1, 130.4, 128.3, 127.7, 127.1, 125.5, 125.4, 122.0 (Fl-*C*, thienyl-*C* and Ar-*C*), 30.9 (C=C*C*H$_2$CH$_2$), 23.2 (C=CCH$_2$*C*H$_2$); UV/Vis (THF): λ_{max} (ε) = 423 nm (1.13 × 10^4 mol^{-1}dm^{3}cm^{-1}); Fluorescence emission (THF) (λ_{ex} = 419 nm): λ_{emis} = 506 nm, fluorescence quantum yield: Φ = 0.058, relative to quinine sulfate in 1.0 N H_2SO_4; HR-MS (MALDI): m/z: 496.0369; $C_{28}H_{22}GeS_2$ calcd: 496.0375; elemental analysis calcd (%) for $C_{28}H_{22}GeS_2$: C, 67.91; H, 4.48; S, 12.95; found: C, 67.08; H, 4.89; S, 11.76. Despite repeated attempts, combustion analyses gave consistently low values for sulfur content (lower by ca. 1%). See Figures 2.23 and 2.24 for copies of the NMR spectra.

2.6.2.14. Synthesis of the spirocyclic germafluorene-germole homopolymer 14

Monomer **3** ($Br_2FlGeC_4Et_4$) (0.095 g, 0.18 mmol) was dissolved in 1.7 mL of toluene and combined with Ni(COD)$_2$ (0.120 g, 0.44 mmol), cyclooctadiene (54 μL, 0.44 mmol) and 2,2'-bipyridine (0.068 g, 0.44 mmol) in 1.8 mL of 1:1 toluene:DMF solution in a sealed 5 mL microwave vial. The mixture was irradiated by microwave (70 min., 250 °C) and cooled to room temperature. The reaction mixture was diluted with 20 mL of chloroform and washed with aqueous HCl (2.0 M, 10 mL). The organic layer was separated and washed again with 50 mL of aqueous HCl (2.0 M). The aqueous layers were combined and extracted with chloroform (50 mL). The combined organic layers were washed with saturated aqueous Na_4-EDTA (100 mL), water (100 mL) and then dried over $MgSO_4$. The solution was filtered through Celite, concentrated to 1 mL and polymer **14** was obtained as the yellow solid by precipitation into methanol (200 mL) with rapid stirring. The polymer was isolated by filtration, washed with 50 mL of methanol and then dried under vacuum (0.025 g, 38 %). Heating polymer **14** to reflux over 12 hours in common deuterated solvents could not dissolve enough material to obtain informative NMR spectra. $M_n = 3.36 \times 10^3$ g mol^{-1}, $M_w = 6.25 \times 10^3$ g mol^{-1}, PDI = 1.86 by GPC (relative to polystyrene standards). UV/Vis (in THF): λ_{max} = 382 nm, ε (per monomer repeat unit) = 2.02×10^4 mol^{-1}dm^{3}cm^{-1}. Fluorescence in THF (λ_{ex} = 379 nm): λ_{emis} = 420 nm and 440 nm (shoulder), fluorescence quantum yield: $\Phi = 0.67$, relative to quinine sulfate in 1.0 N H_2SO_4.

2.6.2.15. Synthesis of the 9,9'-dioctylfluorene homopolymer 15

The procedure was adapted from the literature.[36a] The monomer, 9,9'-dioctyl-2,7-dibromofluorene (0.105 g, 0.19 mmol), was dissolved in 1.7 mL of toluene and combined with $Ni(COD)_2$ (0.132 g, 0.48 mmol), cyclooctadiene (59 μL, 0.48 mmol) and 2,2'-bipyridine (0.076 g, 0.48 mmol) in 1.8 mL of 1:1 toluene:DMF solution in a sealed 5 mL microwave vial. The solution was irradiated by microwave (70 min., 250 °C) and then cooled to room temperature. The reaction mixture was diluted with 20 mL of chloroform and washed with aqueous HCl (2.0 M, 10 mL). The organic layer was separated and washed again with 50 mL of aqueous HCl (2.0 M, 10 mL). The resulting aqueous fractions were combined and extracted with chloroform (50 mL). The combined organic layers were then washed with saturated aqueous Na_4-EDTA (100 mL), water (100 mL) and then dried over $MgSO_4$. The solution was filtered through Celite, concentrated to 1 mL and **15** was precipitated into methanol (200 mL) with rapid stirring. The polymer was isolated by filtration, washed with 50 mL of methanol and then dried under vacuum (0.070 g, 94 %). The corresponding ^{1}H NMR spectral data matched those reported previously in the literature.[37] $M_n = 7.36 \times 10^4$ g mol^{-1}, $M_w = 9.49 \times 10^4$ g mol^{-1}, PDI = 1.29 by GPC (relative to polystyrene standards). UV/Vis (in THF): λ_{max} = 390 nm, ε (per monomer repeat unit) = 7.77×10^3 mol^{-1}dm^{3}cm^{-1}. Fluorescence in THF (λ_{ex} = 392 nm): λ_{emis} = 415 and 439 nm (shoulder), fluorescence quantum yield: $\Phi = 0.77$, relative to quinine sulfate in 1.0 N H_2SO_4.

2.6.2.16. Synthesis of the thiophene-SGG copolymer 16

Monomer **3** ($Br_2FlGeC_4Et_4$) (0.105 g, 0.19 mmol), 2,5-bis(trimethylstannyl)thiophene[42] (0.079 g, 0.19 mmol), $Pd(PPh_3)_4$ (0.011 g, 0.010 mmol) were dissolved in 2 mL of THF in a sealed 5 mL microwave vial. The solution was irradiated by microwave (70 min., 140 °C) and then filtered into the rapidly stirring 150 mL of methanol.

Polymer **16** was isolated by filtration, washed with methanol (50 mL) and then dried under vacuum (0.012, 13 %). Heating polymer **16** to reflux over 12 hours in common deuterated solvents could not dissolve enough material to obtain informative NMR spectra. $M_n = 1.90 \times 10^3$ g mol^{-1}, $M_w = 2.39 \times 10^3$ g mol^{-1}, PDI = 1.25 by GPC (relative to polystyrene standards). UV/Vis (in THF): λ_{max} = 374 nm, ε (per monomer repeat unit) = 1.79×10^4 mol^{-1}dm^{3}cm^{-1}. Fluorescence in THF (λ_{ex} = 358 nm): λ_{emis} = 445 nm, fluorescence quantum yield: Φ = 0.48, relative to quinine sulfate in 1.0 N H_2SO_4.

2.7. Crystallographic data

Table 2.2. Crystallographic data for compounds **2** and **3**.

	2	**3**
empirical formula	$C_{24}H_{28}Ge$	$C_{24}H_{26}Br_2Ge$
fw	389.05	546.86
cryst. dimens. (mm^3)	0.54 × 0.31 × 0.24	0.47 × 0.38 × 0.29
cryst. syst.	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)
unit cell dimensions		
a (Å)	9.464 (2)	13.0536 (9)
b (Å)	9.517 (2)	12.3124 (9)
c (Å)	25.290 (6)	13.7092 (10)
α (deg)	91.817 (3)	
β (deg)	90.409 (3)	96.0343 (8)
γ (deg)	115.529 (2)	
V (Å^3)	2053.7 (9)	2191.1 (3)
Z	4	4
ρ (g cm^{-3})	1.258	1.658
abs. coeff. (mm^{-1})	1.495	5.052
T (K)	173 (1)	173 (1)
2 Θ_{max} (deg)	56.94	56.75
total data	19172	9978
unique data (R_{int})	9903 (0.0229)	2687 (0.0147)
obs. data [$I > 2\sigma(I)$]	9182	2546
params.	452	123
R_1 [$I > 2\sigma(I)$]^a	0.0596	0.0210
wR_2 [all data]^a	0.1712	0.0556
Max/Min $\Delta\rho$ (e Å^{-3})	1.660/–0.970	0.287/–0.671

$^a R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table 2.3. Crystallographic data for compounds **5** and **9**.

	5	**9**
empirical formula	$C_{32}H_{32}GeS_2$	$C_{20}H_{12}Cl_2GeS_4$
fw	553.28	524.03
cryst. dimens. (mm^3)	0.14 × 0.13 × 0.06	0.37 × 0.10 × 0.02
cryst. syst.	triclinic	orthorhombic
space group	$P\bar{1}$ (No. 2)	$Pna2_1$ (No. 33)
unit cell dimensions		
a (Å)	13.9264 (8)	15.0191 (3)
b (Å)	15.4344 (10)	23.4380 (5)
c (Å)	15.8411 (11)	6.06693 (11)
α (deg)	61.160 (4)	
β (deg)	68.468 (4)	
γ (deg)	80.676 (3)	
V (Å^3)	2774.0 (3)	2135.67 (7)
Z	4	4
ρ (g cm^{-3})	1.325	1.630
abs. coeff. (mm^{-1})	3.032	7.933
T (K)	173 (1)	173 (1)
2 Θ_{max} (deg)	144.69	148.00
total data	19366	14870
unique data (R_{int})	10543 (0.0311)	4227 (0.0339)
obs. data [$I > 2\sigma(I)$]	8906	4180
params.	732	271
R_1 [$I > 2\sigma(I)$]^a	0.0382	0.0243
wR_2 [all data]^a	0.1082	0.0633
Max/Min $\Delta\rho$ (e Å^{-3})	0.542/–0.638	0.471/–0.856

$^a R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table 2.4. Crystallographic data for compounds **10**, **11** and **12**.

	10	**11·$C_6H_5CH_3$**	**12**
empirical formula	$C_{32}H_{20}GeS_4$	$C_{23.50}H_{36}B_2Cl_2GeO_4$	$C_{32}H_{40}B_2GeO_4$
fw	605.31	547.63	582.85
cryst. dimens. (mm^3)	0.31 × 0.10 × 0.04	0.56 × 0.40 × 0.30	0.43 × 0.20 × 0.19
cryst. syst.	monoclinic	triclinic	triclinic
space group	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
unit cell dimensions			
a (Å)	24.1517 (4)	9.4903 (7)	10.6516 (3)
b (Å)	21.4199 (4)	9.5303 (7)	11.2008 (3)
c (Å)	11.1333 (2)	15.7215 (12)	14.5895 (5)
α (deg)		76.8759 (9)	78.7523 (4)
β (deg)	109.9751 (7)	82.3002 (9)	88.5746 (4)
γ (deg)		86.8111 (9)	62.5303 (3)
V (Å^3)	5413.07 (17)	1371.84 (18)	1510.47 (8)
Z	8	2	2
ρ (g cm^{-3})	1.486	1.326	1.282
abs. coeff. (mm^{-1})	4.576	1.337	1.048
T (K)	173 (1)	173 (1)	173 (1)
$2\,\Theta_{max}$ (deg)	148.34	53.62	56.58
total data	104294	11521	13965
unique data (R_{int})	5492 (0.0509)	5834 (0.0216)	7236 (0.0095)
obs. data [$I > 2\sigma(I)$]	5000	4854	6814
params.	349	314	424
R_1 [$I > 2\sigma(I)$]^a	0.0313	0.0304	0.0298
wR_2 [all data]^a	0.0910	0.0782	0.0818
Max/Min $\Delta\rho$ (e Å^{-3})	0.568/–0.455	0.430/–0.286	1.024/–0.669

$^a R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

2.8. NMR spectral data

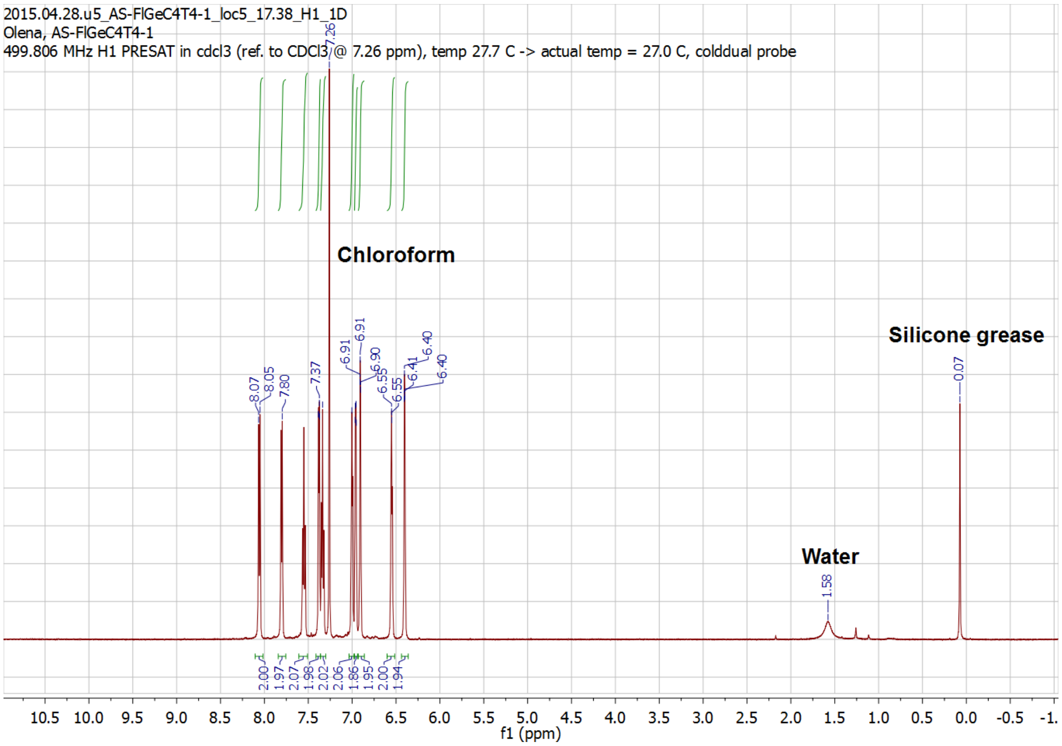


Figure 2.21.^{1}H NMR (in $CDCl_3$) spectrum of compound **10**.

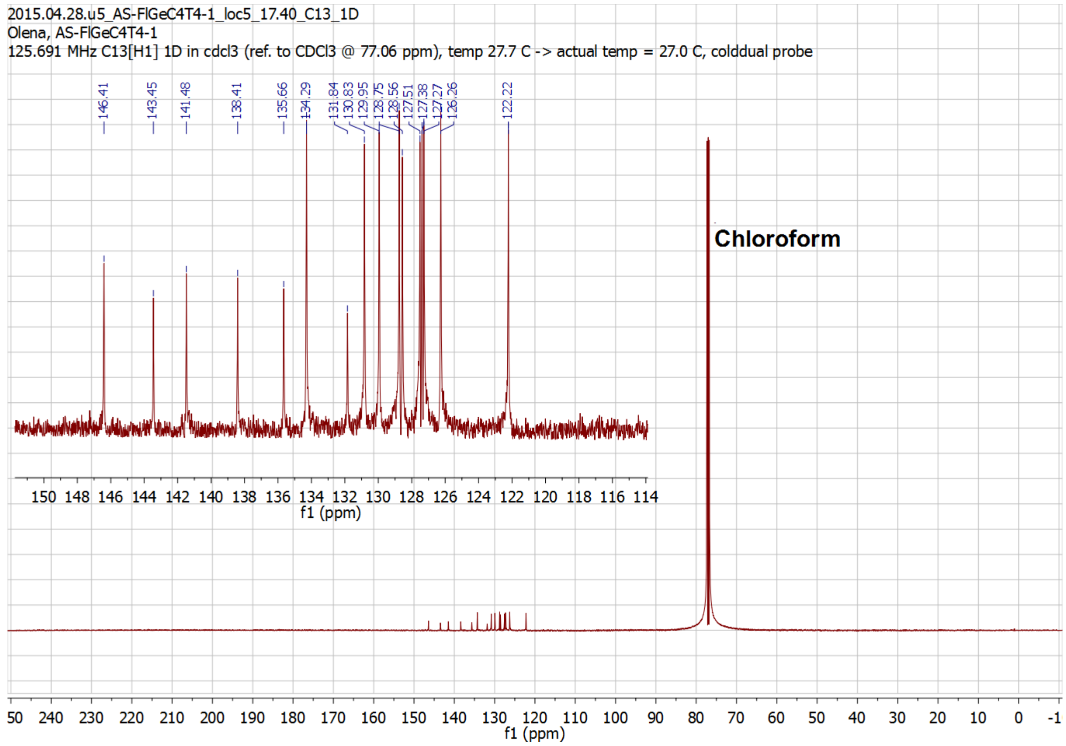


Figure 2.22. $^{13}C\{^{1}H\}$ NMR (in $CDCl_3$) spectrum of compound **10**.

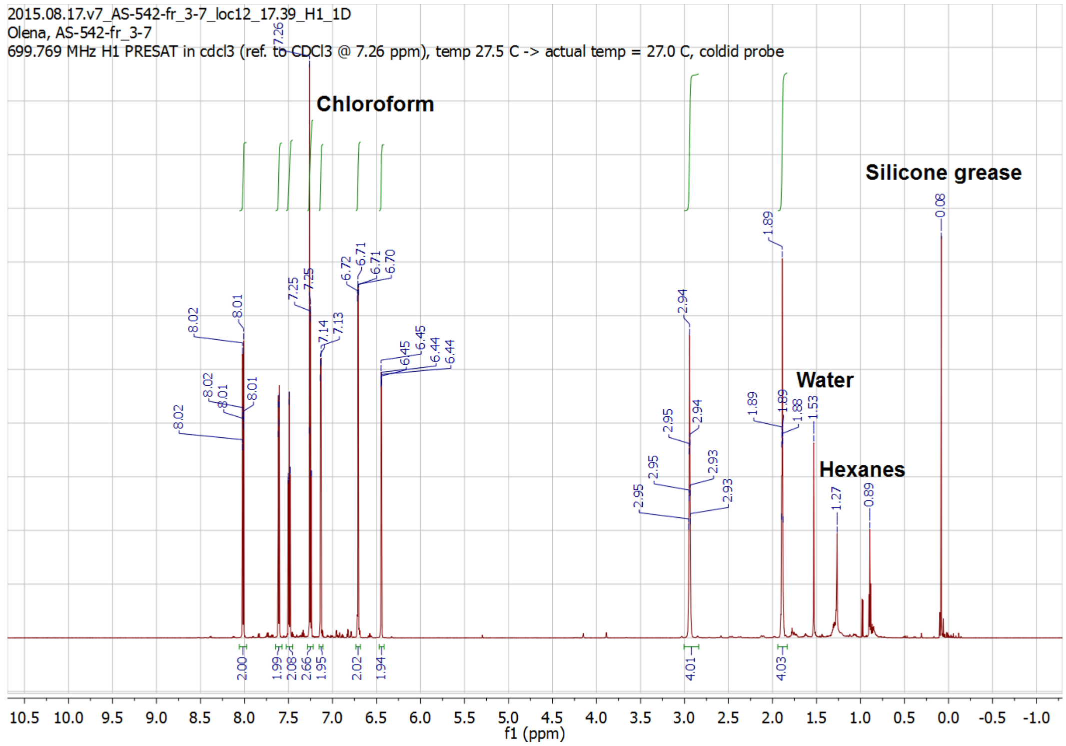


Figure 2.23. ^{1}H NMR (in CDCl$_3$) spectrum of compound **13**.

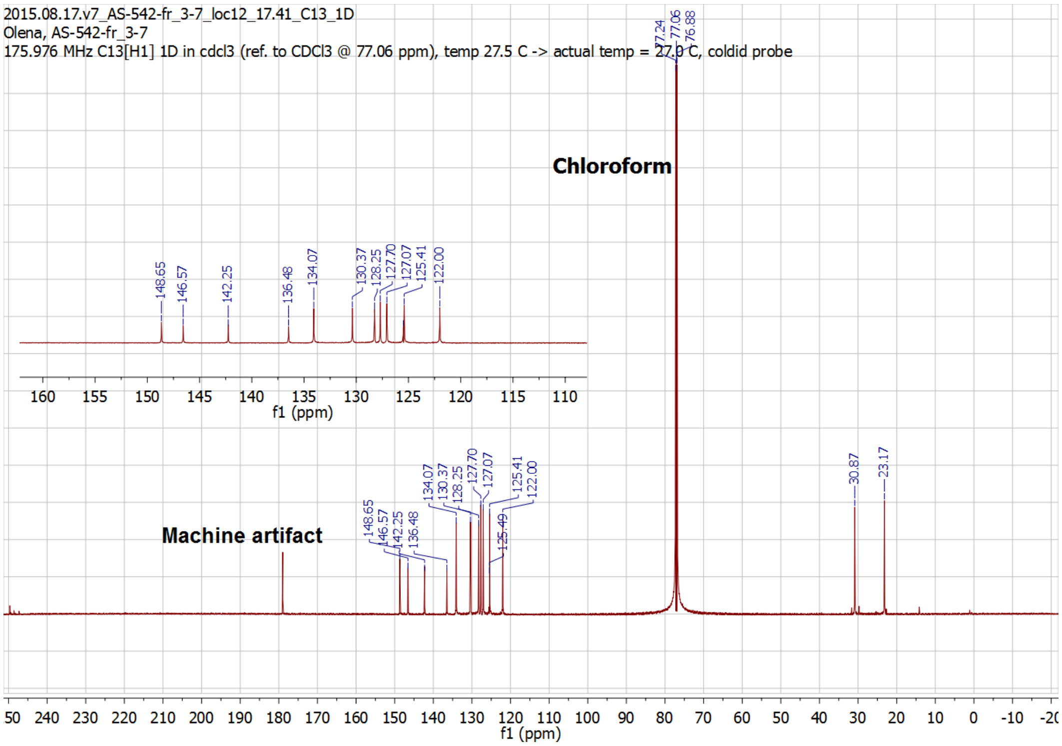


Figure 2.24. $^{13}C\{^{1}H\}$ (in $CDCl_3$) spectrum of compound **13**.

2.9. Ultraviolet–visible spectroscopy (UV/Vis) measurements

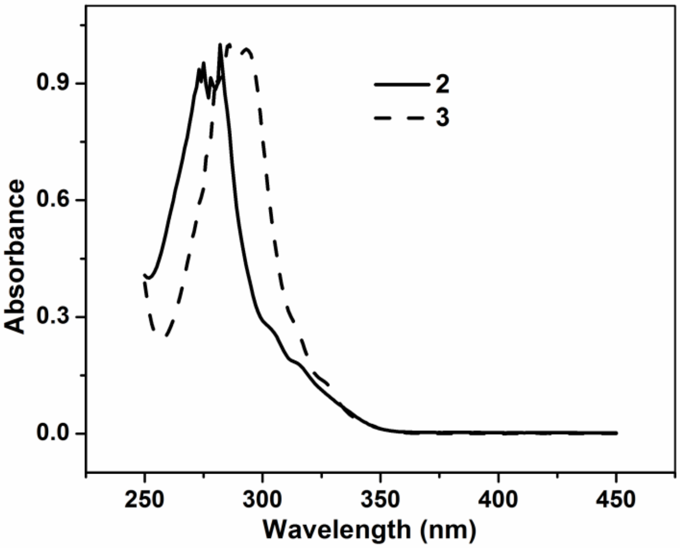


Figure 2.25. UV/Vis absorption spectra of compounds **2** and **3** (normalized).

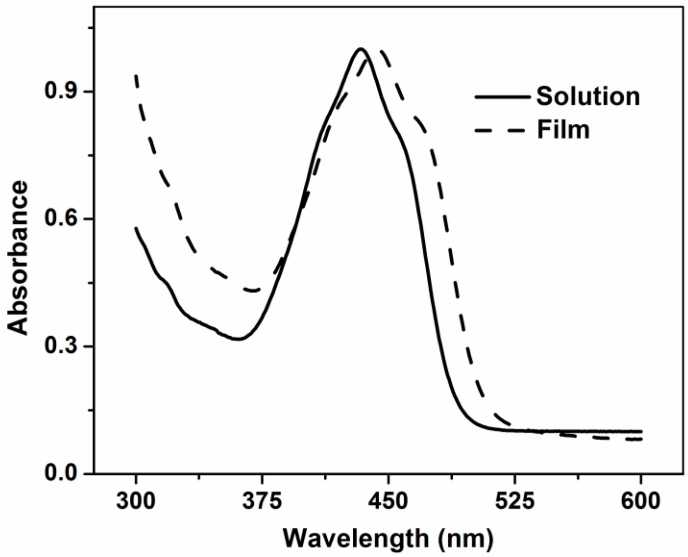


Figure 2.26. UV/Vis absorption spectra of compound **10** in solution (THF) and film state (normalized).

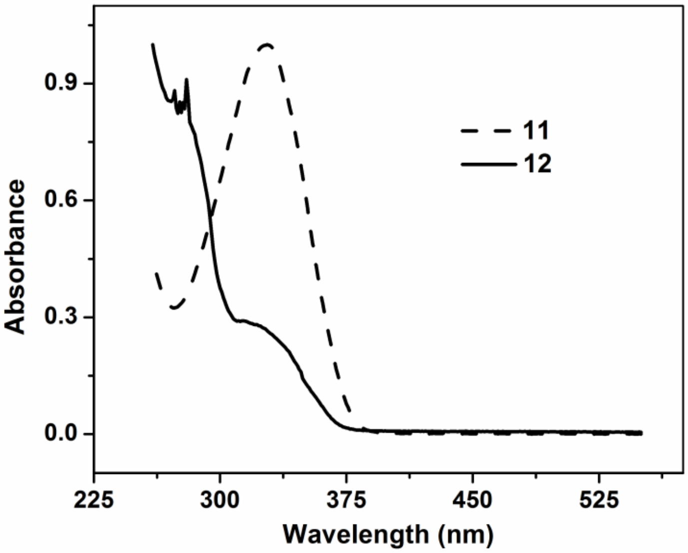


Figure 2.27. UV/Vis absorption spectra of germole **11** and the spirocyclic germafluorene-germole **12** (normalized).

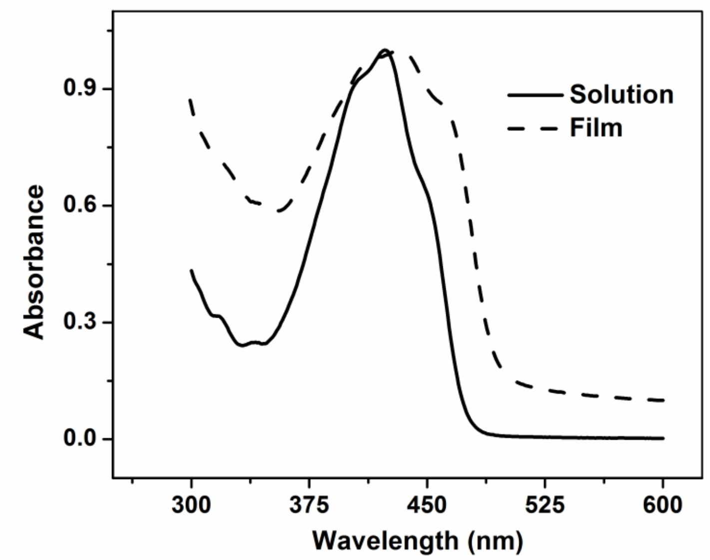


Figure 2.28. UV/Vis absorption spectra of compound **13** in solution (THF) and film state (normalized).

2.10. Photoluminescence spectra

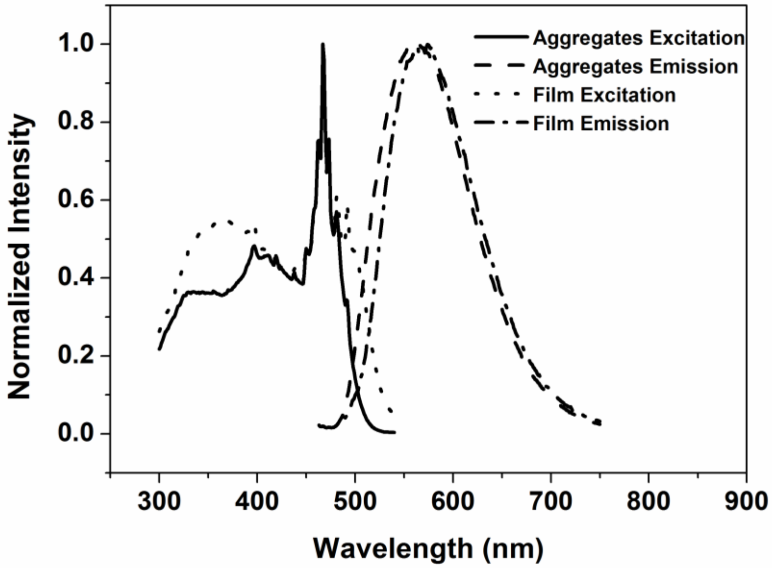


Figure 2.29. PL excitation and emission spectra of compound **10** in aggregated and film state.

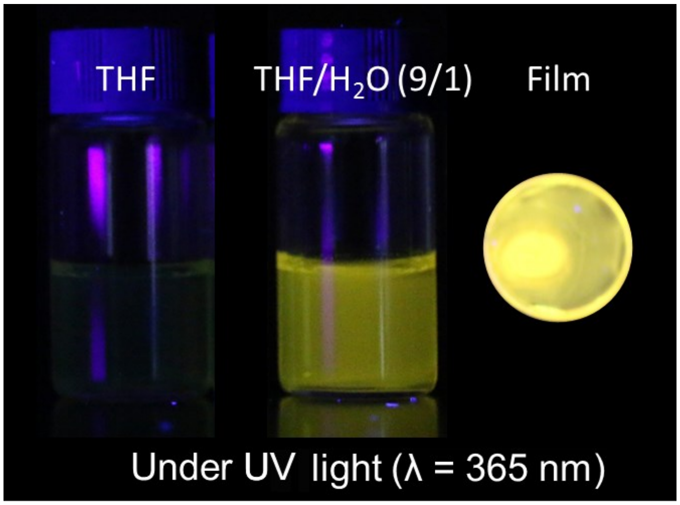


Figure 2.30. Images of SGG **10** in solution, aggregated and film state.

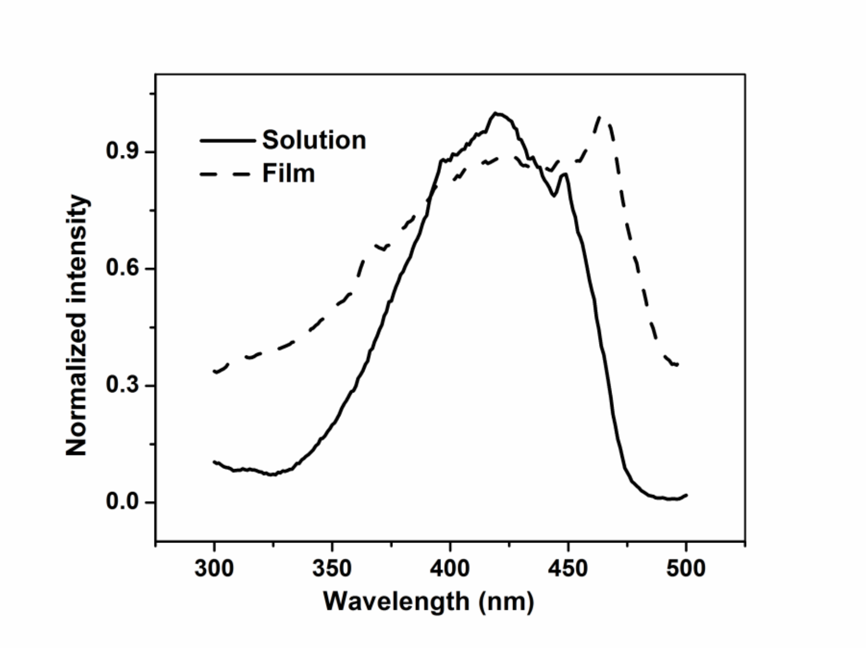


Figure 2.31. PL emission spectra of compound **13** in solution (THF) and film state.

2.11. References

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Chapter 3: Modular Synthesis of Diarylalkynes, their Efficient Conversion into Luminescent Tetraarylbutadienes and Use of the Latter for the Preparation of Polymer Building Blocks

3.1. Abstract

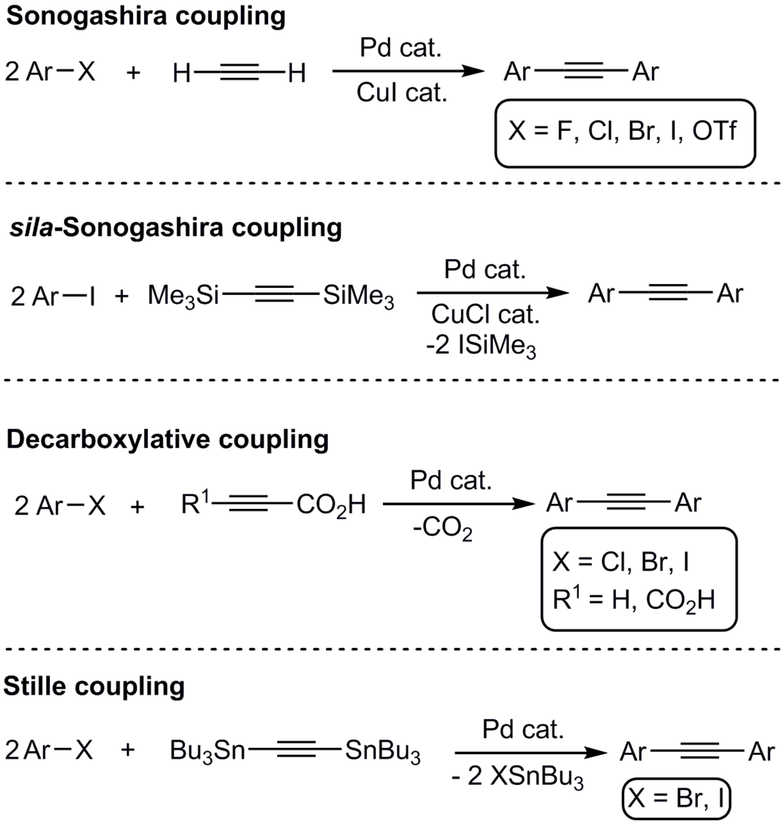
In this chapter, a series of electronically distinct symmetrical diarylalkynes were prepared via a general Suzuki-Miyaura cross-coupling protocol. These alkynes underwent zirconium-mediated coupling to yield zirconacycles that afford new tetraaryl-1,3-butadienes upon subsequent protonolysis; these butadienes display deep blue or green emission and represent promising building blocks for light-emitting devices. The presented synthetic pathway allows access to new libraries of molecular light-emitters with tunable luminescence and considerable thermal- and photostabilities. Initial attempts to synthesize the potentially luminescent polymer building block 1,4-bis(tributylstannyl)-1,2,3,4-tetra(4-isopropylbenzene)-1,3-butadiene are also described.

3.2. Introduction

Diarylalkynes are important precursors for the synthesis of olefins,[1,2] ketones,[3] fused organic heterocycles[4] as well as functional inorganic heterocycles such as luminescent benzofused-siloles,[5] Te/B heterocycles,[6] π-conjugated systems,[7] spirocycles,[8] vinyl cations,[9] arylalkene polymers,[10] and materials with a broad range of biological activities[11] (e.g., 5-azoindoles)[12] and nonlinear optical properties.[13]

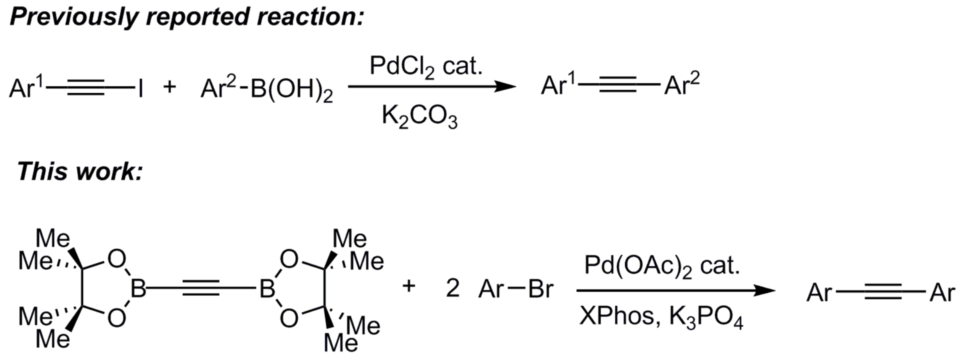
In general, the most common route to yield diarylalkynes is Sonogashira coupling: the palladium-catalyzed coupling aryl or alkenyl halides (or triflates) with terminal alkynes.[14] Recent developments in the Sonogashira methodology include nanoparticle-catalyzed, ligand-free, and/or metal-free coupling, as well as photocatalyzed and microwave-assisted reactions in water.[14c]

Despite the common use of Sonogashira coupling to form symmetric diarylalkynes, there are some drawbacks including limitations in aryl halide substrates scope when using protected acetylenes[15] and the multi-step nature of known protocols, leading to low overall yields. In order to overcome these limitations Lee[15,16] and others[17] focused attention on the development of decarboxylative alkyne coupling, where propiolic acid is used as an alkyne source (Scheme 3.1). Other methods of diarylalkyne synthesis (outlined in Scheme 3.1) include sila-Sonogashira coupling,[18] Stille coupling,[8c,19] the use of organoaluminum alkyne[20] or alkynylsilanol reagents,[21] the platinum-catalyzed alkynylation of aryl iodides,[22] and Suzuki-Miyaura cross-coupling.[23] In the latter method, Sun's group employed a successful multi-step synthesis using boronic acids and thermally unstable acetylene iodides as coupling partners to obtain unsymmetrical alkynes (Scheme 3.2).[23b]



Scheme 3.1. Selected examples of diarylalkyne synthesis.

Here the coupling of the easily prepared diborylethyne synthon, PinBC≡CBPin (**1**)[24] with various aryl bromides in a general palladium-catalyzed Suzuki-Miyaura cross-coupling reaction will be used to construct symmetric diarylalkynes (Scheme 3.2). Advantages of this methodology include a timesaving one-pot procedure (*i.e.,* reduction of work-up and purification steps compared to the Sonogashira method), and the use of commercially available aryl bromides as substrates. The resulting diarylalkynes can also be used to prepare tetraaryl-substituted 1,3-butadienes that exhibit color tunable luminescence and valuable solid state emission properties.[25,26] Accordingly the current study represents an efficient general synthetic methodology for accessing a wide library of luminogens. Furthermore, based on the latter, transformation into a monomer for Stille cross-coupling was explored in order to incorporate a luminescent unit into polymeric structures for polymer-based light-emitting device applications.



Scheme 3.2. Synthesis of diarylalkynes using Suzuki-Miyaura cross-coupling.

3.3. Results and discussion

3.3.1. Synthesis of diarylalkynes via Suzuki-Miyaura coupling

This project began with an evaluation of the stability of the diborylethyne reagent **1**[24] to base-induced pinacolboronate (BPin) cleavage (Table 3.1), termed protodeboronation, as this is a common side reaction during Suzuki-Miyaura cross-coupling.[27] In order to minimize reaction time, microwave irradiation was applied with compound **1** dissolved in either pre-dried THF or freshly distilled DMF (as these solvents readily absorb microwave irradiation). When DMF solutions of **1** were heated to 100 °C for 20 min, compound **1** was completely converted into the known hydroxide HOBPin[28] (as confirmed by multinuclear NMR spectroscopy), indicating the likely presence of residual water in the DMF. Upon careful examination of the protodeboronated product mixture, the known alkyne HC≡CBPin[29] could not be detected, suggesting that the alkyne unit was eliminated as acetylene. In contrast, a THF solution of PinBC≡CBPin (**1**) does not undergo decomposition, even after prolonged heating in the microwave reactor to 140 °C for 40 min; while under the same microwave conditions, **1** mixed in a 3:1 THF/H_2O mixture completely converted into HOBPin, indicating the key role of water in protodeboronation.

Table 3.1. Stability of compound **1** in THF or DMF under microwave irradiation (300 W).

Entry	Solvent*	Temperature (°C)	Time (min)	B-containing product of hydrolysis? (based on ^{1}H and ^{11}B NMR)
1	THF	70	40	no
2	DMF	70	40	no
3	THF	100	20	no
4	DMF	100	20	yes HO-BPin (100%)
5	THF	100	40	no
7	THF	140	40	no
8	THF/H_2O = 3:1	140	40	yes HO-BPin (100 %)

*THF was obtained from the Grubbs-type purification system and DMF was stirred overnight over CaH_2 (5% w/v), filtered and then freshly distilled from $CaSO_4$ and stored over molecular sieves.

Next the effect of added base on the stability of **1** was evaluated under microwave-assisted reaction conditions (Table 3.2). In each trial, compound **1** was dissolved in either THF or DMF (0.12 M solutions) and 6 equivalents of oven-dried K_3PO_4 was added. Upon the microwave heating of **1**/K_3PO_4 in THF at 70 °C for 40 min compound **1** completely decomposed into the bis-boryloxide PinBOBPin[30] and hydroxide HO-BPin; the same reaction carried out in DMF gave only HOBPin as a boron-containing product. In addition, heating **1**/K_3PO_4 to reflux in THF for 36 hrs led to partial decomposition of **1** (11 % according to ^{1}H and ^{11}B NMR spectroscopy) into PinBOBPin. One possible explanation for the formation of protodeboronation products with K_3PO_4 under seemingly non-aqueous conditions is the presence of residual water in the potassium phosphate, despite prior heating at 170 °C for 2 days. When **1** and CsF (2 equiv.) were heated in a microwave reactor to 70 °C for 40 min in THF, similarly rapid protodeboronation to yield HOBPin transpired. Not surprisingly, the use of aqueous potassium carbonate (6 eq.) as a base under the same microwave reaction conditions converted **1** into hydroxide HOBPin. These trials effectively show that protodeboronation is a reaction that will compete with C-C bond formation during Suzuki-Miyaura cross-coupling, leading to some reduction in yield of the target diarylalkyne (*vide infra*).

Table 3.2. Stability of compound **1** in the presence of base in THF or DMF under microwave irradiation (300 W).

Entry	Base&	Solvent*	Temperature (°C)	Time (min)	B-containing product? (based on ^{1}H and ^{11}B NMR)
1	K_3PO_4	THF	70	40	$O(BPin)_2$ (13 %) + HO-BPin (87 %)
2	CsF	THF	70	40	HO-BPin (100 %)
3	K_2CO_3	THF	70	40	HO-BPin (100 %)
4	K_3PO_4	DMF	70	40	HO-BPin (100 %)
5	K_3PO_4	THF	100	20	HO-BPin (100 %)
6	K_3PO_4	DMF	100	20	HO-BPin (100 %)
7	K_3PO_4	THF	100	40	HO-BPin (100 %)
8	K_3PO_4	DMF	100	40	HO-BPin (100 %)
9	K_3PO_4	THF	140	40	$O(BPin)_2$ (25 %) + HO-BPin (31 %) + **1** (44 %)
10	CsF	THF	140	40	$O(BPin)_2$ (17 %) + HO-BPin (83 %)
11	K_2CO_3	THF	140	40	HO-BPin (100 %)

&K_3PO_4 and CsF were dried in the oven (170 °C) for 48 hrs before use, 2.0 M aqueous solution of K_2CO_3 was freshly prepared and degassed prior to use; *THF was obtained from the Grubbs-type purification system and DMF was stirred overnight over CaH_2 (5% w/v), filtered and then freshly distilled from $CaSO_4$ and stored over molecular sieves.

4-Bromoisopropylbenzene was chosen as a substrate for cross-coupling optimization trials as the target diarylalkyne (4-^{i}PrC$_6$H$_4$)C≡C(C$_6$H$_4$^{i}Pr-4) (**2**) could only be previously prepared via challenging multi-step procedures.[31] The catalytic system $Pd_2(dba)_3$/XPhos (dba = dibenzylideneacetone)[32] was explored under different conditions, starting from microwave heating at 100 °C for 20 min and up to 140 °C for 40 min in different solvents (Table 3.3). The best isolated yield of **2** (Scheme 3.3) was 55 % and arose when a $Pd_2(dba)_3$−XPhos−K_3PO_4 pre-catalyst/ligand/base system was employed with microwave heating to 140 °C for 40 min in THF. The analogous reactions in DMF or toluene did not yield any product. In the case of DMF, the complete protodeboronation of **1** transpired, while in toluene, no reaction occurred as toluene is known to be a poor absorber of microwave radiation.[33] Interestingly, use of a THF/H_2O (3:1) solvent combination gave the desired product $(4\text{-}^{i}PrC_6H_4)C{\equiv}C(C_6H_4{}^{i}Pr\text{-}4)$ (**2**) in a 30 % isolated yield after purification by column chromatography, while on the other hand a DMF/H_2O (3:1) solvent medium did not lead to the formation of **2** with only protodeboronation transpiring. Overall the microwave-assisted trial reactions summarized in Table 3.3 helped identify a suitable solvent (THF) for future explorations.

Table 3.3. Optimization of reaction conditions to synthesize compound **2**.

Entry	**Cat., mol % of Pd**	**Ligand, mol %**	**Base$^{\&}$, eq.**	**Solv.***	**Temp. (°C)**	**Time (min)**	**Purif. yield, %**
1	$Pd_2(dba)_3$, 2	XPhos, 8	K_3PO_4, 6	THF	100	20	24
2	$Pd_2(dba)_3$, 2	XPhos, 8	K_3PO_4, 6	DMF	100	20	31
3	$Pd_2(dba)_3$, 2	XPhos, 8	K_3PO_4, 6	THF	100	40	35
4	**$Pd_2(dba)_3$, 2**	**XPhos, 8**	**K_3PO_4, 6**	**THF**	**140**	**40**	**55**
5	$Pd_2(dba)_3$, 2	XPhos, 8	K_3PO_4, 6	DMF	140	40	0
6	$Pd_2(dba)_3$, 2	XPhos, 8	K_3PO_4, 6	Toluene	140	40	0
7	$Pd_2(dba)_3$, 2	XPhos, 8	K_2CO_3 $_{(aq)}$, 6	THF	140	40	0
8	$Pd_2(dba)_3$, 2	$H^tBu_3PBF_4$, 8	K_2CO_3 $_{(aq)}$, 6	THF	140	40	0
9	$Pd_2(dba)_3$, 2	$H^tBu_3PBF_4$, 8	K_2CO_3 $_{(aq)}$, 6	DMF	140	40	0
10	$Pd_2(dba)_3$, 2	XPhos, 8	K_3PO_4, 6	THF:H_2O = 3:1	140	40	33
11	$Pd_2(dba)_3$, 2	XPhos, 8	K_3PO_4, 6	DMF:H_2O = 3:1	140	40	0

$^{\&}$$K_3PO_4$ and CsF were dried in the oven (170 °C) for 48 hrs before use, 2.0 M aqueous solution of K_2CO_3 was freshly prepared and degassed prior to use; *THF was obtained from the Grubbs-type purification system and DMF was stirred overnight over CaH_2 (5% w/v), filtered and then freshly distilled from $CaSO_4$ and stored over molecular sieves.

In order to effectively scale-up the reaction between 4-bromoisopropylbenzene and PinBC≡CBPin (**1**), conventional heating in refluxing THF for 36 hrs was applied with different catalyst/base combinations examined. Specifically Pd catalysts commonly used in

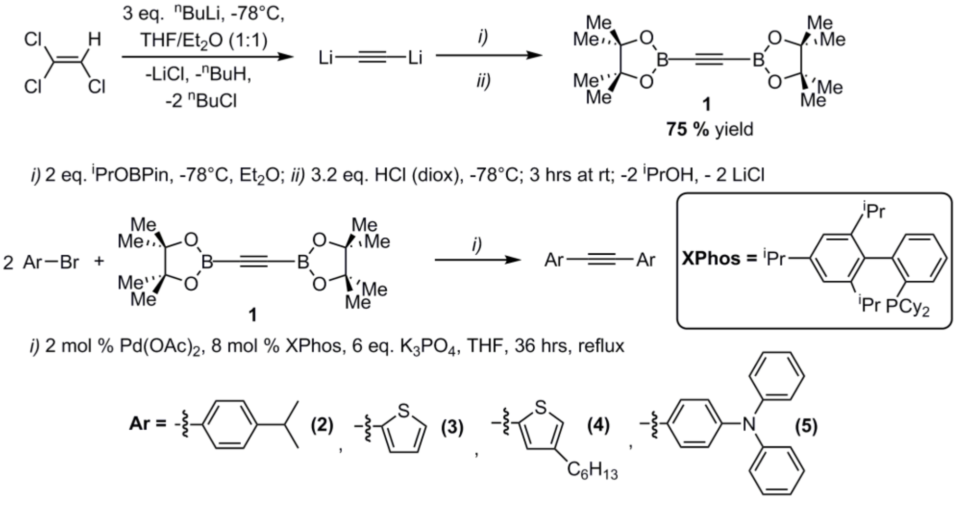
Suzuki-Miyaura cross-coupling were explored while using 6 equivalents of K_3PO_4 base in relation to **1**.[34a] The $Pd(OAc)_2$/XPhos (1:4 ratio; 2 mol. % of Pd) mixture afforded pure **2** in a 40 % isolated yield, which is comparable to the yield obtained with the $Pd_2(dba)_3$/XPhos combination mentioned above (35 % isolated yield of 2; 2 mol. % of Pd). However the use of 2 mol. % of $Pd(PPh_3)_4$ as a catalyst gave **2** in a much lower isolated yield of 20 % (Table 3.4). In addition, the $Pd(OAc)_2$/XPhos catalyst combination when mixed with two equiv. of CsF relative to **1** in THF, afforded the target alkyne **2** in a similar isolated yield of 40 %.[34b] In order to facilitate the handling of the reagents, the air-stable pre-catalyst $Pd(OAc)_2$ was chosen in future coupling reactions instead of the air-sensitive $Pd_2(dba)_3$. To investigate the effect of the $Pd(OAc)_2$/XPhos/K_3PO_4 mixture on the stability of **1**, a THF solution of **1** in the presence of $Pd(OAc)_2$/XPhos (1:4 ratio; 2 mol. % of Pd) and K_3PO_4 (6 eq.) was heated to reflux for 36 hrs leading to partial decomposition (*ca.* 40 %) of **1** into PinBOBPin; this represents a slight increase in protodeboronation when compared to heating **1** with 6 equiv. of K_3PO_4 in the absence of $Pd(OAc)_2$/XPhos (only 11 % decomposition occurred).

Table 3.4. Catalyst and base screening trials for the synthesis of **2** in refluxing THF.

Entry	**Catalyst, mol % of Pd**	**Ligand, mol %**	**Base$^{\&}$, eq**	**Solv.*, time refluxed (hrs)**	**Purified yield, %**
1	$Pd_2(dba)_3$, 2	XPhos, 8	K_3PO_4, 6	THF, 36	35
2	$Pd(OAc)_2$, 2	XPhos, 8	K_3PO_4, 6	THF, 36	40
3	$Pd(OAc)_2$, 2	XPhos, 8	CsF, 2	THF, 36	40
4	$Pd(PPh_3)_4$, 2	-	K_3PO_4, 6	THF, 36	20
5	$Pd(PPh_3)_4$, 2	-	CsF, 2	THF, 36	15
6	-	-	K_3PO_4, 6	THF, 18	9 % decomp. of **1** to $O(BPin)_2$
7	-	-	K_3PO_4, 6	THF, 36	11 % decomp. of **1** to $O(BPin)_2$
8 (no 4-bromoisopropyl benzene added)	$Pd(OAc)_2$, 2	XPhos, 8	K_3PO_4, 6	THF, 18	33 % decomp. of **1** to $O(BPin)_2$
9 (no 4-bromoisopropyl benzene added)	$Pd(OAc)_2$, 2	XPhos, 8	K_3PO_4, 6	THF, 36	40 % decomp. of **1** to $O(BPin)_2$

$^{\&}K_3PO_4$ and CsF were dried in the oven (170 °C) for 48 hrs before use; *THF was obtained from the Grubbs-type purification system.

To further investigate the developed synthetic procedure, the thiophene-substituted acetylenes **3** and **4** were prepared according to the conditions presented in Scheme 3.3 and in Table 3.5. After slight variations in the catalytic loadings and reaction times, it was found that a reaction mixture with a 1:4 ratio of the $Pd(OAc)_2$ pre-catalyst to the XPhos ligand in THF that is refluxed for 36 hrs gave repeatedly the best isolated yields of analytically pure bis(thienyl)alkynes **3** and **4** (40 and 51 % yield, respectively) after column chromatography. The symmetric alkyne **5** was also prepared, containing capping triphenylamine (TPA) groups due to the use of TPA units to achieve two-photon absorption and enhanced hole transport properties in optoelectronics.[35] The diarylalkynes **2**-**5** were obtained as very pure materials in *ca.* 30-50 % yield after column chromatography, however one can rapidly obtain alkynes **2**, **3** and **5** in > 90-95 % purity (according to ^1H NMR) by simply washing the crude alkynes **2**, **3** and **5** with Et_2O, leading to enhanced isolated yields: 73 % (**2**), 40 % (**3**) and 60 % (**5**).



Scheme 3.3. Synthesis of the symmetric diarylalkynes **2**-**5**.

Table 3.5. Optimization of reaction conditions when heating to reflux to synthesize **3**.

Entry	$Pd(OAc)_2$, mol %	XPhos, mol %	$K_3PO_4$$^{\&}$, eq.	Time, hrs	Purified yield, %
1	1	2	6	36	26
2	1	2	4.5	36	15
3	1	2	6	18	15
4	2	4	6	36	30
5	2	8	6	36	40

$^{\&}$$K_3PO_4$ was dried in the oven (170 °C) for 48 hrs before use and THF was obtained from the Grubbs-type purification system.

The structures of alkynes **2** and **5** were confirmed by single-crystal X-ray crystallography (Figures 3.1 and 3.2, respectively) and afforded expected metrical parameters; for example, the C≡C bond lengths in **2** and **5** are the same within experimental error [1.196(3) and 1.198(2) Å, respectively].

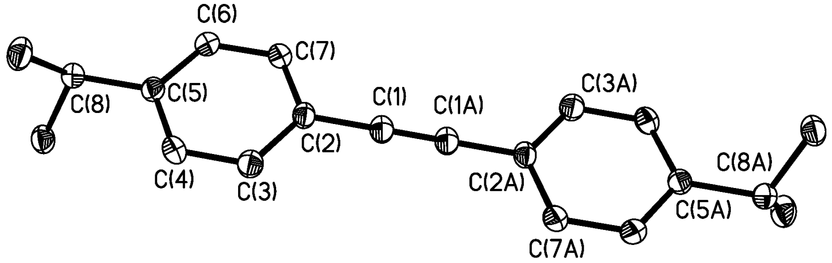


Figure 3.1. Thermal ellipsoid plot (30% probability) of compound **2** with hydrogen atoms omitted for clarity; a crystallographic inversion center (1/2, 0, 1/2) lies at the midpoint of the C(1)–C(1A) bond. Selected bond lengths (Å) and angles (deg): C(1)–C(1A) 1.196(3), C(1)–C(2) 1.435(17), C(2)–C(3) 1.394(2), C(3)–C(4) 1.391(19), C(5)–C(8) 1.522(17); C(1A)–C(1)–C(2) 178.75(19), C(1)–C(2)–C(3) 121.13(13), C(3)–C(2)–C(7) 118.64(12), C(4)–C(5)–C(8) 121.87(12), C(2)–C(3)–C(4) 120.02(13).

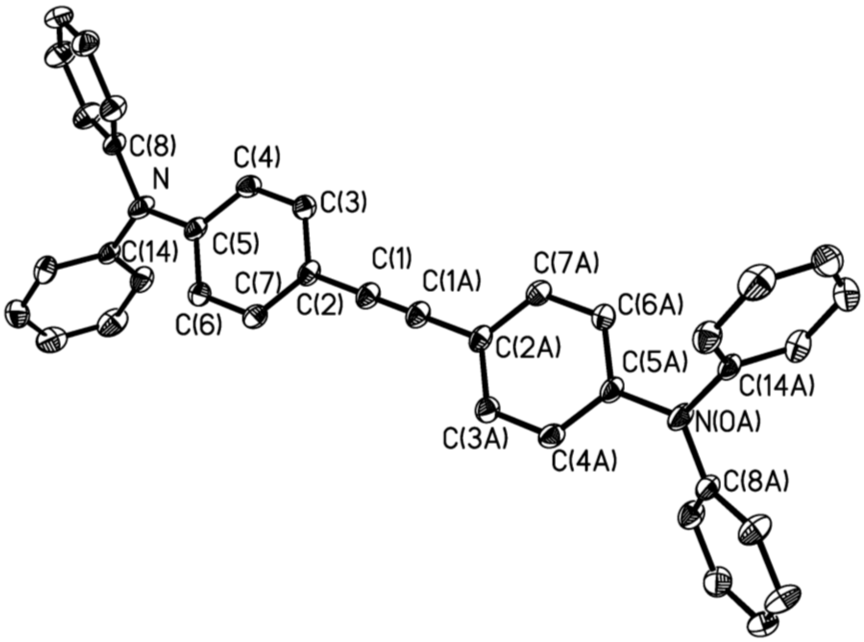


Figure 3.2. Thermal ellipsoid plot (30 % probability) of compound **5** with hydrogen atoms omitted for clarity; a crystallographic inversion center (1/2, 0, 1/2) lies at the midpoint of the C(1)–C(1A) bond. Selected bond lengths (Å) and angles (deg): C(1)–C(1A) 1.198(2), C(1)–C(2) 1.4336(15).

3.3.2. Tetraaryl-1,3-butadiene synthesis

The preparation of arylated 1,3-dienes has received limited attention in the literature,[26b,c] despite their novel reversible mechanochromic properties (i.e., changing emission color in response to external mechanical stimuli) and occasionally high fluorescence quantum yields in the solid state.[26a] Scheme 3.4 outlines the overall procedure used to prepare the symmetric tetraaryl-1,3-butadienes **7a**, **7b** and **8**. To begin, the cumyl-substituted zirconacycle $Cp_2ZrC_4(4\text{-}^iPrC_6H_4)_4$ **6a** and the previously reported tetrathiophene zirconacycle **6b** ($Cp_2ZrC_4T_4$; T = 2-thienyl)[32] were obtained by combining two equiv. of the alkynes **2** and **3** each with *in situ* generated "Cp_2Zr" (made from Cp_2ZrCl_2/2 ^{n}BuLi)[36a] in THF. The new zirconacycle **6a** was isolated as an air- and moisture-sensitive red solid in a high yield of 90 % and its structure was determined by single-crystal X-ray crystallography (Figure 3.3). The average Zr–C bond lengths in the five membered ZrC_4 ring in **6a** are 2.264(4) Å and in accordance with the reported Zr–C bond lengths in pinacolboronate-functionalized zirconacycles.[37] The cumyl groups adjacent to the Cp_2Zr unit are twisted from the five membered zirconacycle core by 55.80(6)° and 58.25(8)°, while the remaining cumyl-based rings are also canted by 55.80(8)° and 54.90(9)° to yield an overall propeller arrangement of the four cumyl groups in **6a**.

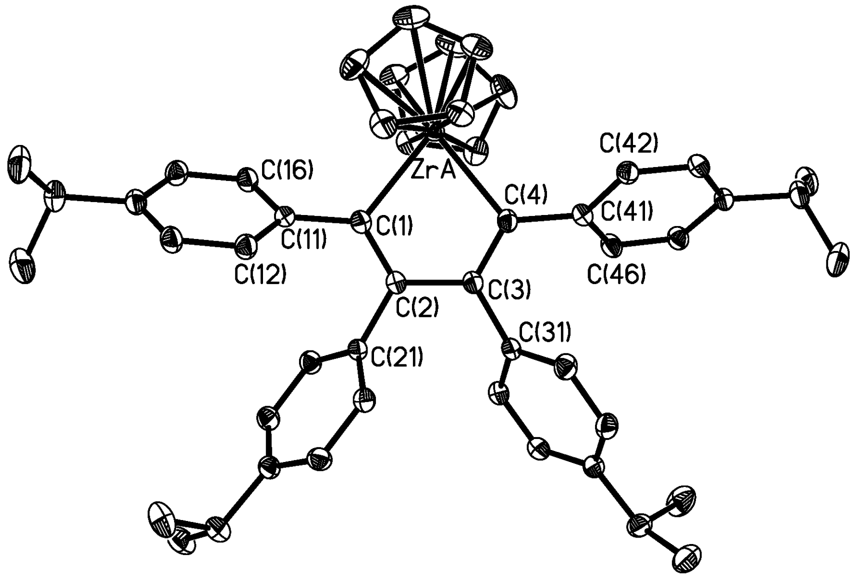
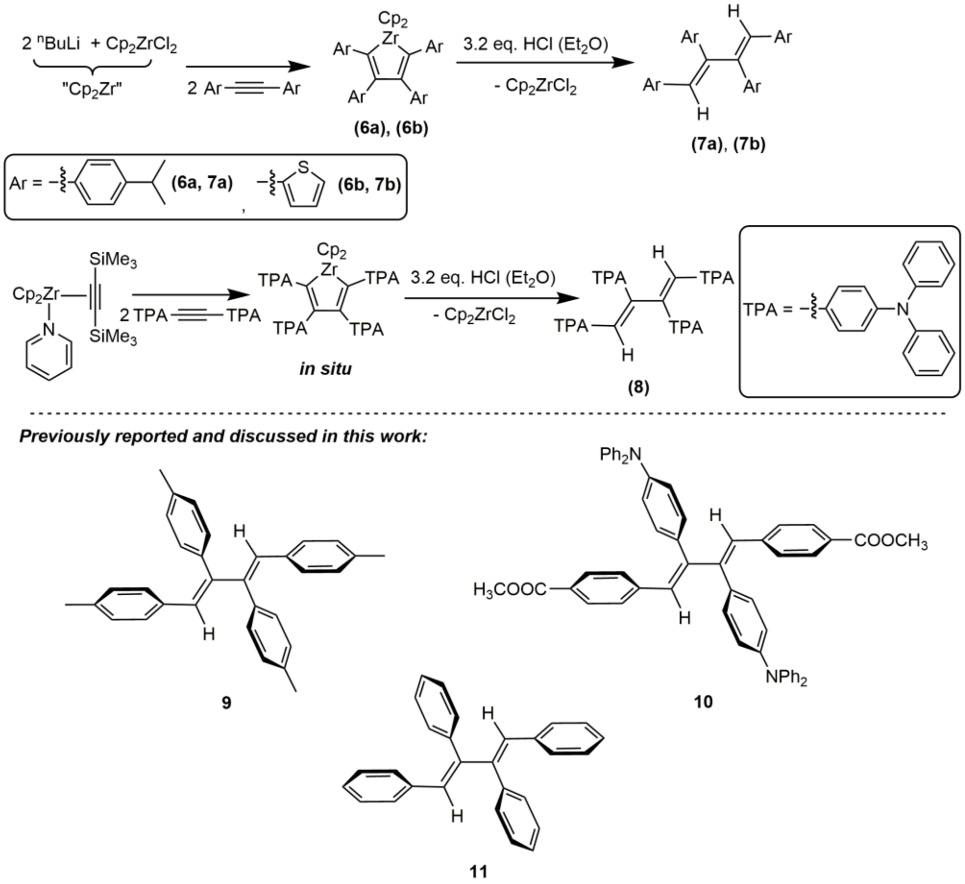


Figure 3.3. Thermal ellipsoid plot (30% probability) of compound **6a** with hydrogen atoms omitted for clarity; only one molecule of the two in the asymmetric unit is shown. Selected bond lengths (Å) and angles (deg) with metrical parameters for the second molecule in the asymmetric unit are listed in square brackets: Zr–C(1) 2.269(2) [2.259(3)], Zr–C(4) 2.267(3) [2.259(3)], C(1)–C(2) 1.363(4) [1.369(4)], C(2)–C(3) 1.489(3) [1.494(3)], C(3)–C(4) 1.366(3) [1.368(4)]; C(1)–Zr–C(4) 77.50(9) [78.27(9)].

Conversion of the zirconacycles **6a** and **6b** into the target 1,3-butadienes **7a** and **7b** with exclusive cis-trans-cis geometries of the appended aryl groups was readily accomplished by adding an excess of HCl in Et_2O (Scheme 3.4). The Cp_2ZrCl_2 by-product was effectively removed by filtration of a CH_2Cl_2:hexanes solution of the reaction products through a silica gel plug. Compound **7a** was obtained as a white solid (57 % yield) after further washing with hexanes, while compound **7b** was isolated as a yellow solid (40 % yield) after washing the crude material with cold (-35 °C) Et_2O. Both the cumyl-substituted butadiene **7a** and the thiophene-capped analogue **7b** yielded crystals of suitable quality for X-ray analysis and their respective structures are found as Figures 3.4 and 3.5. As in the previously characterized tetratolyl-1,3-butadiene **9** and tetraphenyl-1,3-butadiene **11** (Scheme 3.4),[26b,c] one of the four aryl rings in compound **7a** (containing C(41), Figure 3.4) is nearly coplanar with the butadiene core (dihedral angle of 4°), while the remaining rings are twisted from the diene unit by 34.9, 67 and 87.5°. Due to the significant twisting of the aryl groups and the presence of sterically encumbered isopropyl groups in **7a** there is a lack of substantial intermolecular π-π stacking; however significant intermolecular aryl---(H-C)Aryl contacts are present (as short as 2.46 Å). In the case of **7b**, the two terminally-positioned thienyl groups are only slightly twisted from the butadiene core by 8.8°, while the two remaining thienyl rings are arranged in a nearly perpendicular fashion.



Scheme 3.4. Synthetic route to the 1,3-butadienes **7a/b** and **8**, and structures of the known analogues **9-11**.

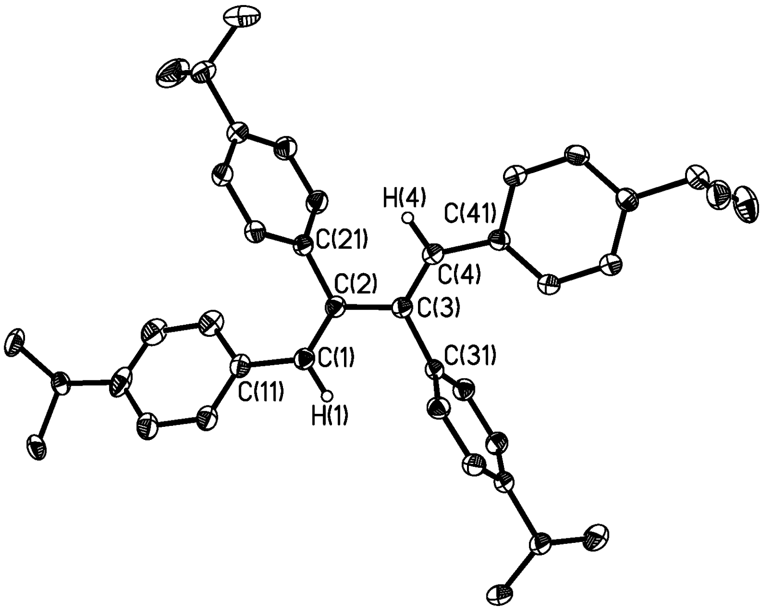


Figure 3.4. Thermal ellipsoid plot (30 % probability) of compound **7a** with selected hydrogen atoms omitted for clarity; remaining hydrogen atoms presented with arbitrarily small thermal parameters. Only the major orientation of the disordered isopropyl groups is shown. Selected bond lengths (Å) and angles (deg): C(1)–C(2) 1.347(3), C(2)–C(3) 1.477(3), C(3)–C(4) 1.347(3); C(2)–C(3)–C(4) 121.07(17), C(1)–C(2)–C(3) 121.70(17).

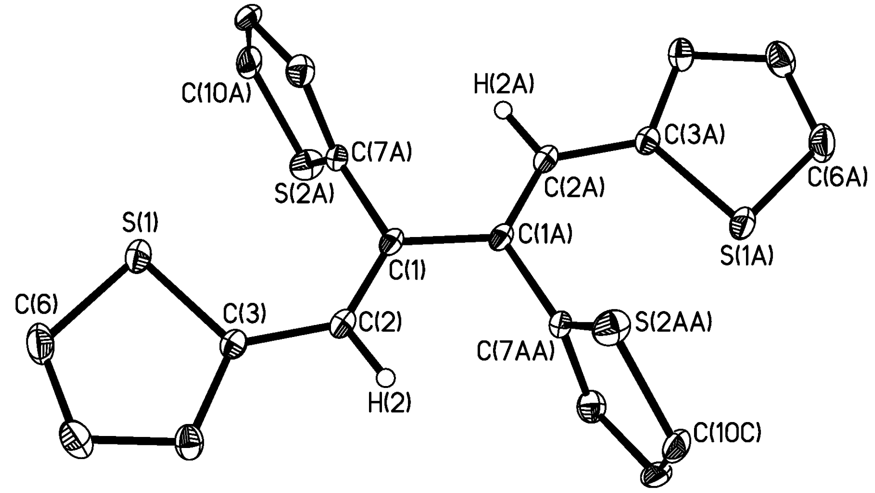


Figure 3.5. Thermal ellipsoid plot (30 % probability) of compound **7b** with selected hydrogen atoms omitted for clarity; remaining hydrogen atoms presented with arbitrarily small thermal parameters. Only the major orientation of the disordered thienyl groups is shown. A crystallographic inversion center (1/2, 0, 1/2) lies at the midpoint of the C(1)–C(1A) bond. Selected bond lengths (Å) and angles (deg): C(1)−C(1A) 1.477(2), C(1)−C(2) 1.351(2), C(2)−C(3) 1.4489(19); C(2)−C(1)−C(1A) 121.31(15), C(1)-C(1A)-C(2A) 121.31(15).

Although the triphenylamine (TPA)-functionalized butadiene **8** could be obtained using the zirconium source "Cp_2Zr" (generated from $Cp_2ZrCl_2/2\ {}^{n}BuLi$ *in situ*), it could also obtained via a slightly different one-pot procedure starting from the thermally stable and isolable Cp_2Zr source $Cp_2Zr(pyridine)(Me_3SiCCSiMe_3)$[36b] (Scheme 3.4). Specifically, $Cp_2Zr(pyridine)(Me_3SiCCSiMe_3)$ and two equivalents of (TPA)C≡C(TPA) **5** were combined in THF to yield a red solution containing the zirconacycle, $Cp_2ZrC_4(TPA)_4$, which was reacted in situ with an excess of HCl to give crude **8** as an orange solid. The resulting product contained Cp_2ZrCl_2 byproduct as well as unreacted **5**, thus additional purification by multiple washes with cold (-30 °C) Et_2O, followed by washing with acetone at room temperature were required to afford pure **8** as a bright yellow solid in a 26 % yield. Unfortunately, crystals of **8** of suitable quality for single-crystal X-ray crystallographic analysis could not be obtained.

3.3.3. Optical properties of the tetraaryl-1,3-butadienes 7a, 7b and 8

Tetraarylbutadienes are an emerging class of solid state emitters with high photoluminescence quantum yield, thus optical properties of **7a**, **7b** and **8** were studied in more detail. Compounds **7a** and **7b** undergo a drastic change from a nonemissive state in THF solution to highly emissive aggregated states in THF/H_2O mixtures when the water content exceeded 60% *v*/*v* and 80% *v*/*v*, respectively; this effect is termed aggregation-induced emission[25] and was previously observed for butadienes **9-11**.[26] The fluorescence emission spectra of **7a/b** in THF/H_2O are presented in Figures 3.6 and 3.7. In addition, compound **7a** emits a bright-blue color in the solid state (λ_{emis} = 426 nm and 463 nm) due to the restricted rotation of the peripheral cumyl groups (Figure 3.8). As a comparison, bright green photoluminescence (λ_{emis} = 506 nm) is noted in the solid state for **7b** with a spectral tail that extends to *ca.* 650 nm (Figure 3.9).

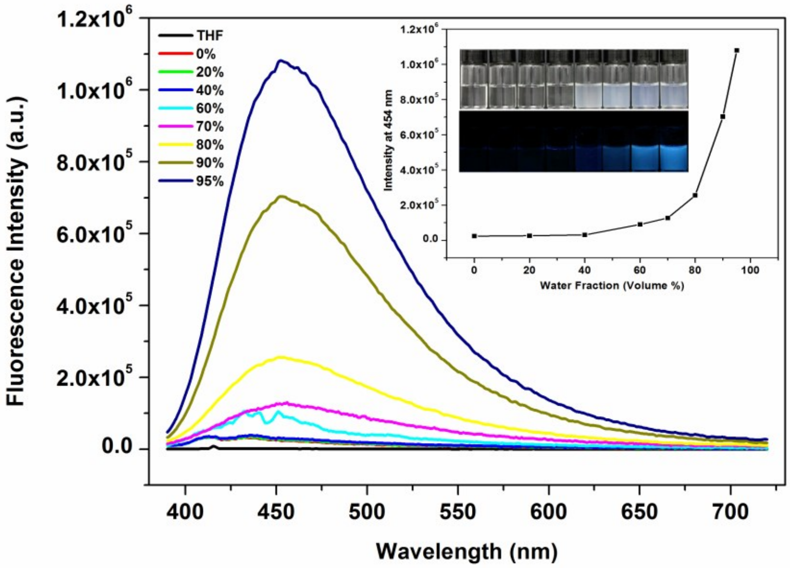


Figure 3.6. Photoluminescence (PL) spectra of **7a** in different THF/water ratios (listed as % water content). Inset: emission intensity of **7a** as the THF/water ratio is altered. Insert photo: aggregates under UV light (λ_{ex} = 365 nm); [**7a**] = 10^{-4} M.

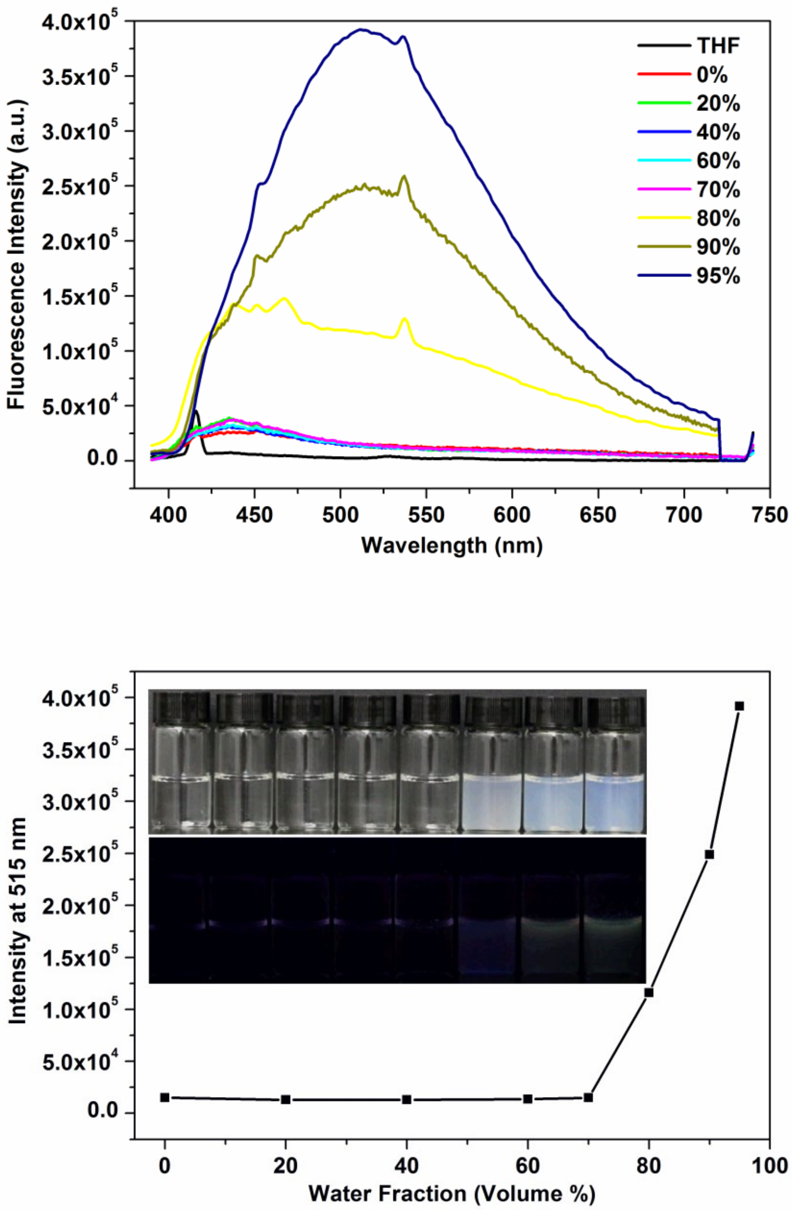


Figure 3.7. Top: Photoluminescence (PL) spectra of **7b** in different THF/water ratios. Bottom: emission intensity of **7b** as the THF/water ratio is altered. Inset: aggregates under UV light (λ_{ex} = 365 nm); [**7b**] = 10^{-4} M.

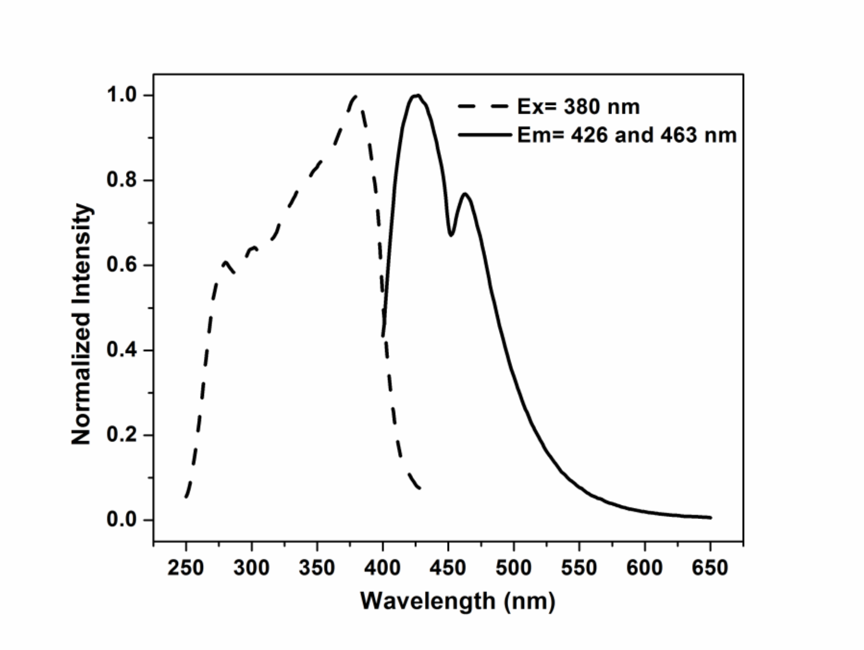


Figure 3.8. Normalized PL excitation and emission spectra of 1,3-butadiene **7a** in the film state.

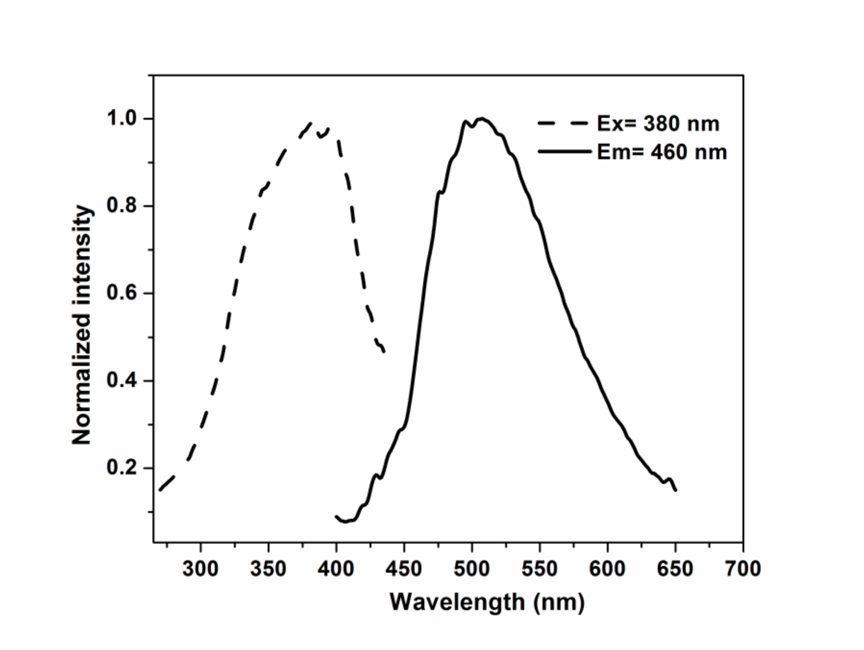


Figure 3.9. Normalized PL excitation and emission spectra of 1,3-butadiene **7b** in the film state.

Given the emissive nature of unsaturated compounds bearing triphenylamine (TPA) substituents, the luminescence of the alkyne **5** and its 1,3-butadiene derivative **8** was investigated. In agreement with previously reported emission data for **5** in $CHCl_3$,[35b] alkyne **5** displays blue emission in THF when irradiated at 267 and 322 nm (λ_{emis} = 413 nm, $\Phi_{absolute}$ = 79.7%; Figure 3.10), however this emission maxima is slightly blue-shifted when compared to in $CHCl_3$, where λ_{emis} = *ca.* 430 nm. The relative quantum yield of **5** and **8** (*vs.* quinine sulfate in 1.0 N H_2SO_4) is lower within predicted error[38] than their absolute quantum yield and is presented in the Section 3.6. The 1,3-butadiene analogue **8** shows a change of luminescence color upon aggregation, which one could conceivably take advantage of for sensing applications.[26c] When **8** is dissolved in THF, blue-green emission is observed (λ_{emis} = 472 nm, $\Phi_{absolute}$ = 34.6%, τ = 2.1 ns), however in the film state there is a substantial red-shift in λ_{emis} to 516 nm, corresponding to bright green emission (Figure 3.11). As a comparison, the relative quantum yield of the TPA-containing butadiene **10** (Scheme 3.4) in THF (Φ = 4.7%; λ_{emis} = 545 nm) is about 7-fold lower as in **8**, thus the added TPA units and overall steric bulk in **8** appear to hinder non-radiative decay pathways.[26a] Similarly to **5** and **10**,[26a] the UV/Vis spectrum of **8** shows absorption peaks at 305 and 380 nm in THF (Figure 3.12), however in line with the dramatic changes in emission data in the solid state, the longer wavelength absorption is red-shifted by *ca.* 30 nm to 410 nm, thus aggregation triggers enhanced conjugation within **8**.

The aggregation behavior of compound **8** is very different compared to the butadienes **7a/b** and **9-11** which do not show a change in photoluminescence color upon aggregation, but rather only an enhancement of emission intensity.[26] Under UV irradiation **8** undergoes a change from blue emission in pure THF (λ_{emis} = 472 nm) to green (λ_{emis} = 505 nm) when the water composition exceeds 60% *v/v* (Figure 3.13) in line with aggregation promoting restricted intramolecular motion and enhanced conjugation in **8**.

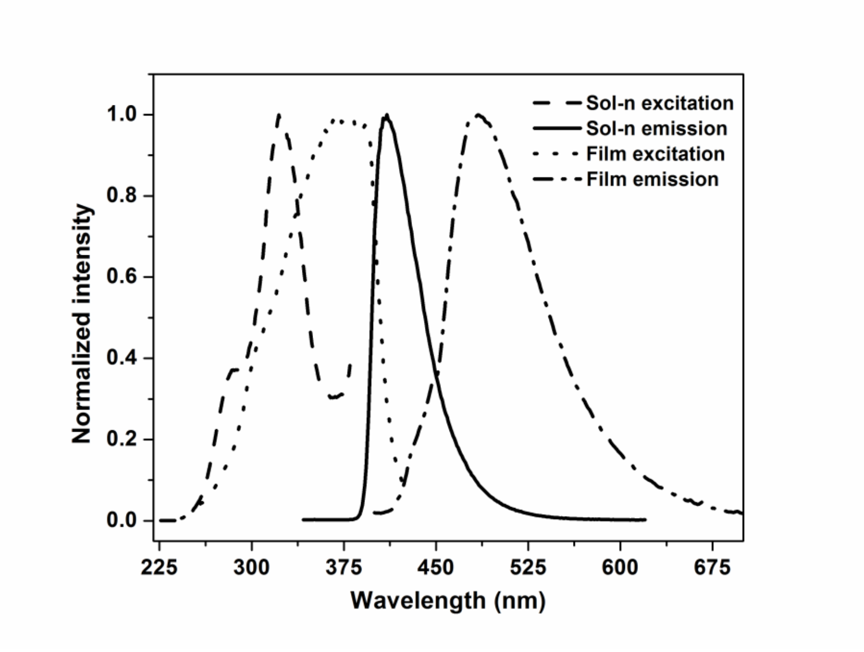


Figure 3.10. Normalized PL excitation and emission spectra of alkyne **5** in solution (THF) and film state.

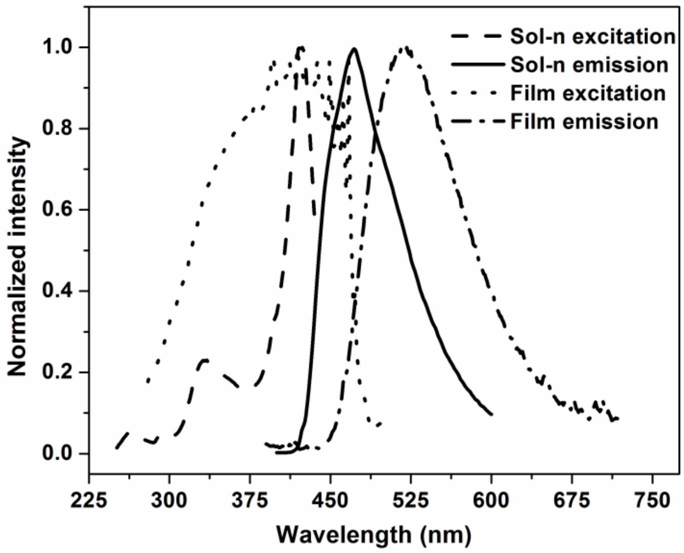


Figure 3.11. Normalized PL excitation and emission spectra of **8** with λ_{ex} = 423 nm in THF and λ_{ex} = 420 nm in the film state.

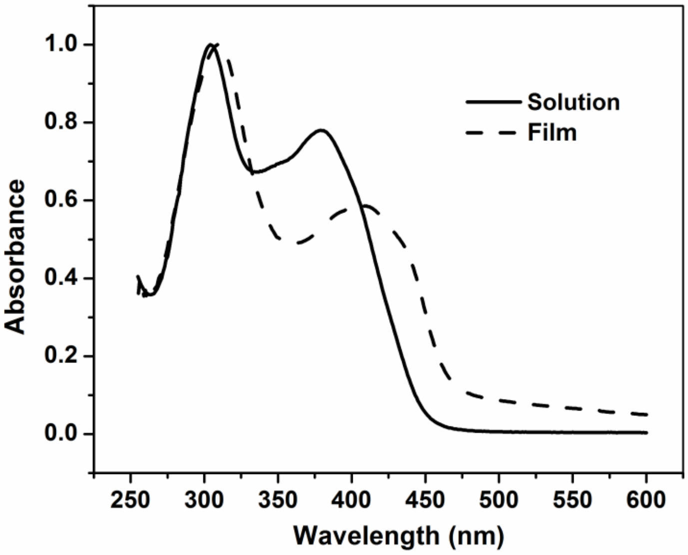


Figure 3.12. UV/Vis absorption spectra of compound **8** in solution (THF) and film state (normalized).

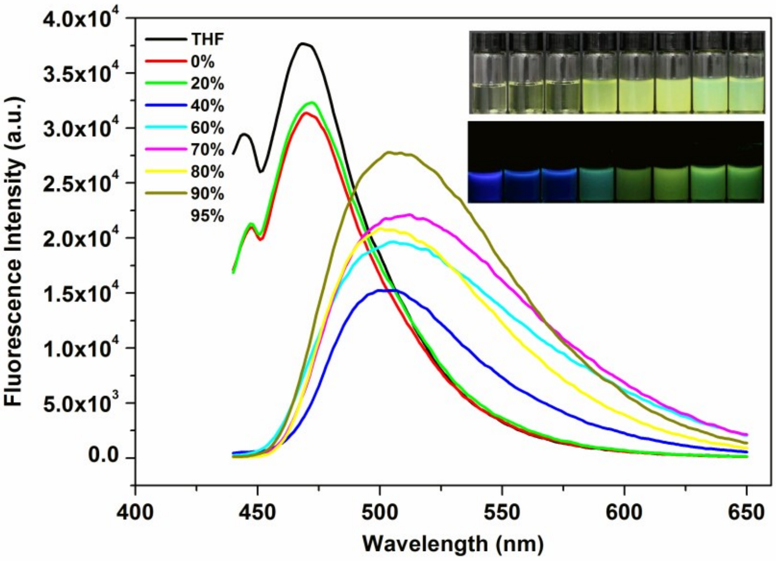


Figure 3.13. Photoluminescence (PL) spectra of **8** in different THF/water ratios (listed as % water content). Inset: aggregates under UV light (λ_{ex} = 365 nm); [**8**] = 10^{-4} M.

The solid state emission spectra for the butadienes **7a/b** and **8** were recorded from amorphous films (with amorphous character confirmed by X-ray powder diffraction; Figure 3.14). Compounds **5**, **7a**, **7b** and **8** all show fluorescence in the solid state according to the lifetimes found: 2.4, 1.0, 1.2, and 2.1 ns, respectively. The 1,3-butadiene analogue **7a** has the highest absolute quantum yield of 24.8% in the solid state, while the thiophene-capped analogue **7b** and alkyne **5** have similarly low quantum yields of 1.5% and 1.7%. Even though in solution the quantum yield of **8** was higher than **10** (Φ = 34.6% versus 4.7 %), in the solid state **8** has quantum yield of 10.7% while the previously reported TPA-substituted butadiene **10** has a solid state photoluminescence quantum yield of

40.1%.[26c, 39] Given the lack of X-ray data for **8**, it is difficult to provide a convincing reason for the reduced fluorescence efficiency of **8** in the solid state.

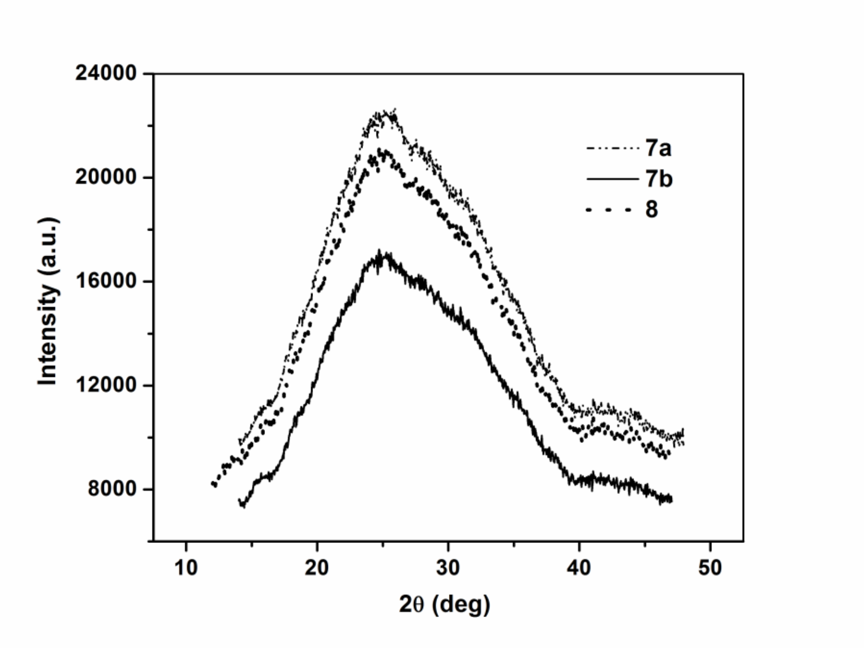


Figure 3.14. XRD patterns of films of the 1,3-butadienes used for photoluminescence measurements.

3.3.4. Photobleaching and thermal stability of functionalized tetraaryl-1,3-butadienes

To determine how the incorporation of cumyl, thienyl or triphenylamine groups within a butadiene framework affects the photostability, thin films of **7a/b** and **8** were irradiated under air. In each photostability trial, 30 μL of a 2.0×10^{-3} M THF solution of the butadiene was drop-casted onto a glass slide and each experiment was conducted in triplicate under aerobic conditions (see Figures 3.15 – 3.17). This is the first example of such a study for tetraaryl-substituted 1,3-butadienes and helps identify candidates for the development of LEDs that work without substantial encapsulation.[40] After drop-casting, the resulting films of **7a**, **7b** and **8** were irradiated in air with a 65 W xenon lamp found within our fluorimeter. The resulting I/I_0 ratios were derived from the recorded photoluminescence intensity at the emission wavelength, λ_{max}. The cumyl (4-isopropylbenzene)-substituted butadiene **7a** showed rapid degradation with 50 % retention of emission intensity ($I/I_o = 0.50$) after 23 minutes of exposure (Figure 3.15); the triphenylamine (TPA)-functionalized butadiene **8** retains half of the initial photoluminescence (PL) intensity after 16 minutes of exposure (Figure 3.17). Interestingly, the thiophene-appended butadiene **7b** shows considerably enhanced photostability[41] relative to **7a** and **8**, with a 50 % reduction in PL after 75 minutes of sustained exposure to the xenon lamp (Figure 3.16). A decrease of the emission intensity due to degradation of the butadienes was also verified by UV/Vis spectroscopy (see Section 3.6.6, Figures 3.54-3.56).

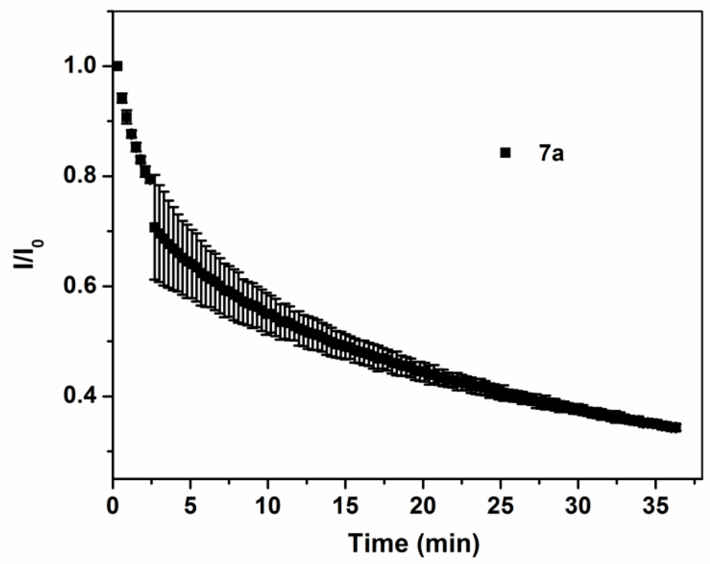


Figure 3.15. Time dependence of the fluorescence emission intensity of **7a** a drop-cast thin film (30 μL of 2 × 10^{-3} M THF solution) upon exposure to a 65 W xenon lamp in air. Film distance from lamp was 130 cm.

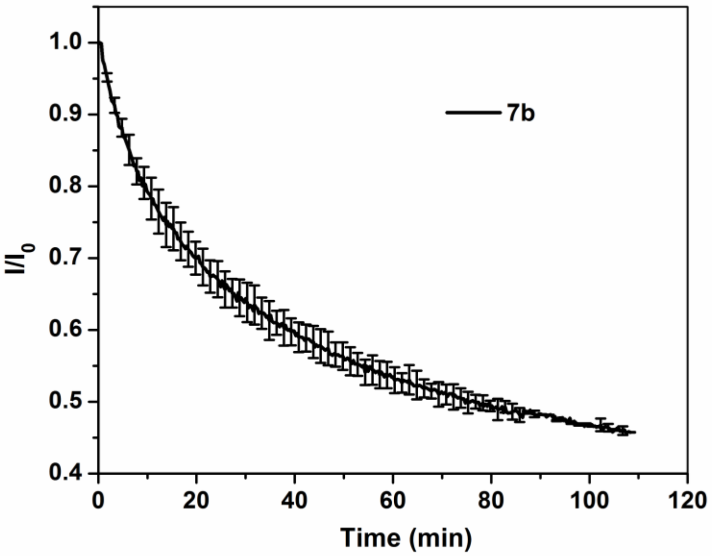


Figure 3.16. Time dependence of the fluorescence emission intensity of a drop-cast thin film of **7b** (from 30 μL of a 2.0 × 10^{-3} M THF solution) upon exposure to a 65 W xenon lamp in air. Film distance from lamp was 130 cm.

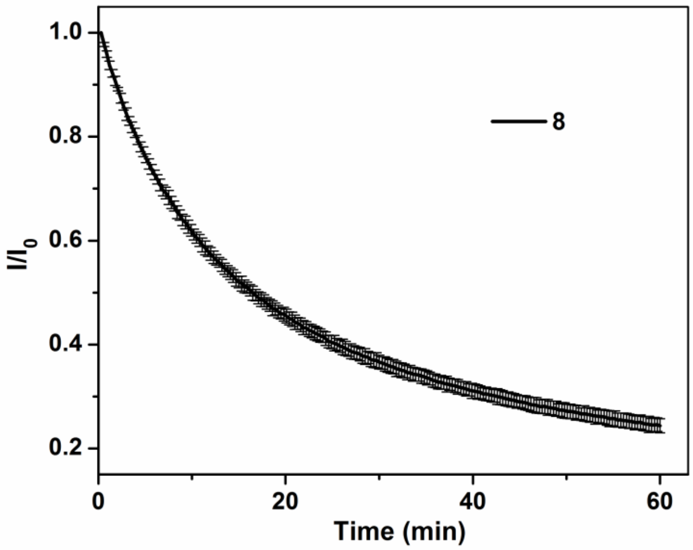


Figure 3.17. Time dependence of the fluorescence emission intensity of **8** a drop-cast thin film (30 μL of 2 × 10^{-3} M THF solution) upon exposure to a 65 W xenon lamp in air. Film distance from lamp was 130 cm.

Thermal stability is another important parameter to consider when selecting emitters for full color displays. The onset of thermal decomposition (5 % weight loss, T_d) of compounds **7a/b** and **8** were evaluated under nitrogen using thermal gravimetric analysis (Figure 3.18). The TPA-functionalized butadiene **8** has the highest thermal stability (T_d = 401 °C) in the series, followed by the cumyl-substituted butadiene **7a** (T_d = 267 °C) and thienyl analogue **7b** (T_d = 241 °C). This trend is mirrored by the precursor diarylalkynes **2-5** (Figure 3.19), albeit with lower thermal stabilities. The most thermally stable diarylalkyne is (TPA)C≡C(TPA) (**5**) with a T_d of 206 °C, followed by the cumyl-substituted alkyne **2** (T_d = 186 °C) and the thiophene-appended alkyne **3** (T_d = 118 °C). Surprised by the low apparent decomposition temperature of (2-thienyl)C≡C(2-thienyl) (**3**), we measured its melting point in a sealed capillary tube under nitrogen atmosphere and found that this compound melts at 97-100 °C without any decomposition; notable discoloration started at 175 °C and the melt became dark brown at 230 °C. Based on the DSC measurements under nitrogen atmosphere, the alkyne **3** melts at 97-100 °C (in agreement with melting point data) and decomposes at 179 °C, thus 118 °C is the temperature at which 5% weight loss occurred is most likely due to the evaporation of the alkyne. Compound **3** was also heated in refluxing toluene (*ca.* 110 °C) for 24 hrs with no sign of decomposition; such data is important as this alkyne is being increasingly used as a reagent in the chemical community, for instance in preparation of conducting and fluorescent polymers.[33]

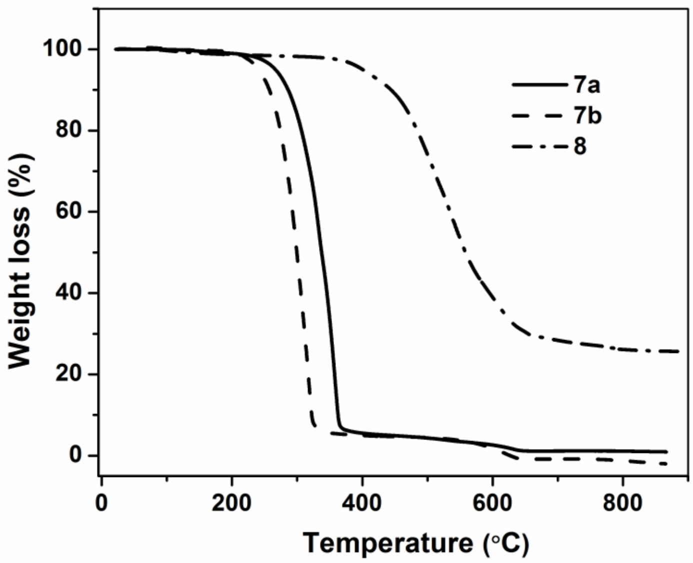


Figure 3.18. TGA thermograms of **7a**, **7b** and **8** measured under N_2 (scan rate = 10 °C/min).

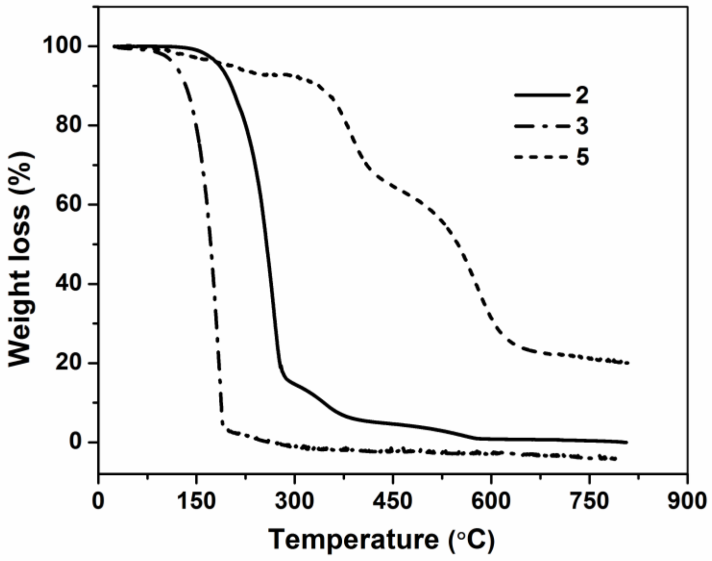


Figure 3.19. TGA thermograms of diarylalkynes **2-5** measured under N_2 (scan rate = 10 °C/min).

Compounds **7a/b** also yielded dramatic weight losses (up to 95%) when subjected to TGA under N_2 (Figure 3.18). During DSC analysis upon heating from ambient temperature to 600 °C, the onset of thermal decomposition/weight loss for **7a/b** and **8** was found at 230 °C, 271 °C, and 308 °C. The melting points of these species were extracted from DSC data and afforded values of 209 °C, 218 °C, and 274 °C, respectively (Figures 3.20 to 3.22), in agreement with those measured in sealed capillary tubes.

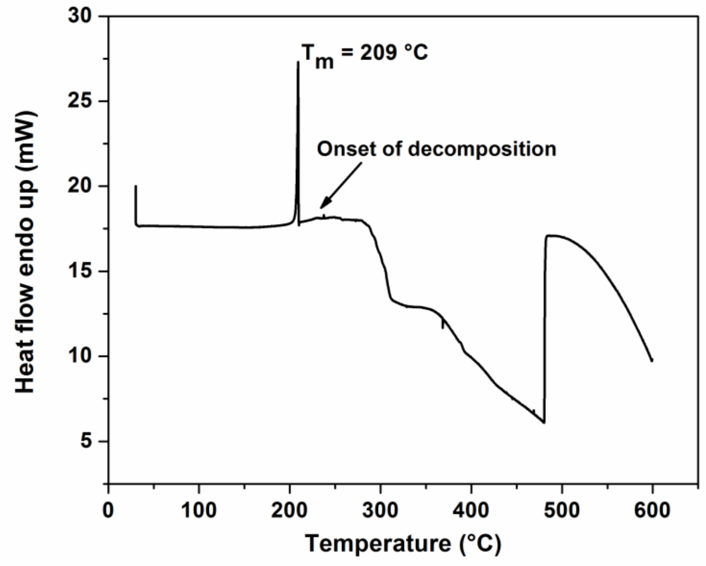


Figure 3.20. DSC trace of **7a** measured under N_2 (30-600 °C, scan rate = 10 °C/min).

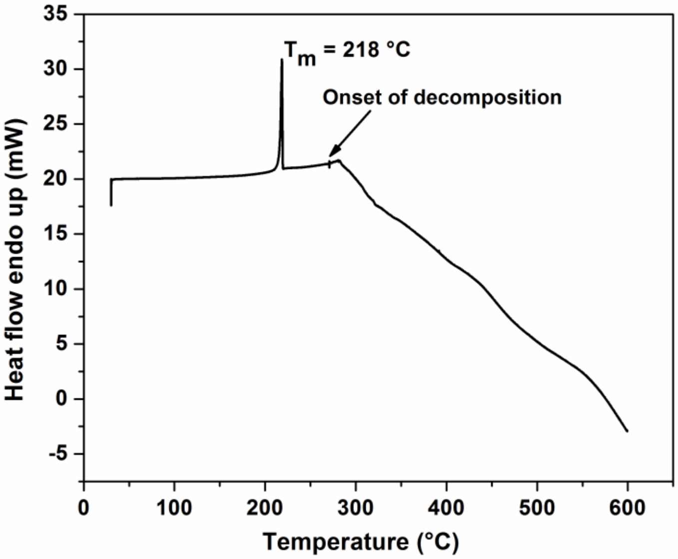


Figure 3.21. DSC trace of **7b** measured under N_2 (30-600 °C, scan rate = 10 °C/min).

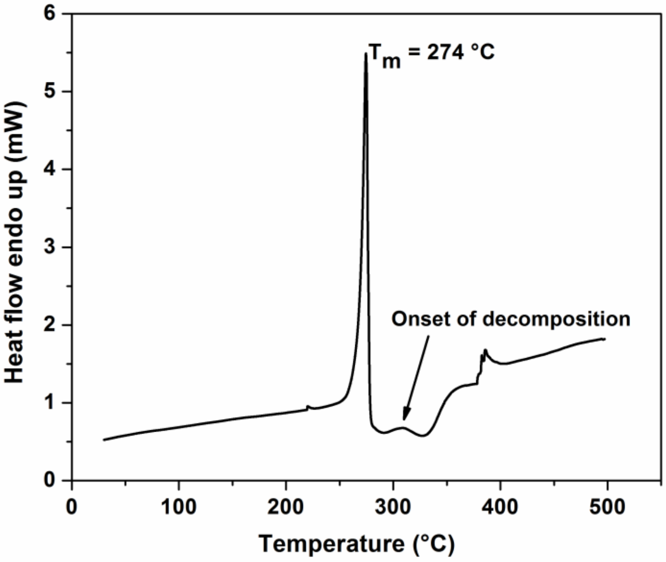


Figure 3.22. DSC trace of **8** measured under N_2 (30-500 °C, scan rate = 10 °C/min).

Compound **7a** also showed a crystallization temperature (T_c) of 130 °C which emerged upon cooling of the melt. To test possible decomposition, compounds **7a/b** and **8** where subjected to repeated heating and cooling cycles in the DSC to temperatures ca. 10 °C above noticeable melting events (Figures 3.23 to 3.25); the weight loss after these measurements was negligible (< 2 %), excluding the evaporation of butadienes **7a/b** and **8** during heating. It was found that the cumyl-capped butadiene **7a** has a stable melt, as noted by reoccurring melting/recrystallization after the first cycle. In contrast, recrystallization and melting were not observed after the first heating for compounds **7b** and **8**, thus confirming their decomposition upon melting. Thus the weight loss in **7a** noted during TGA could be due to evaporation (which is rapid above 230 °C), while in **7b** decomposition occurs upon melting.

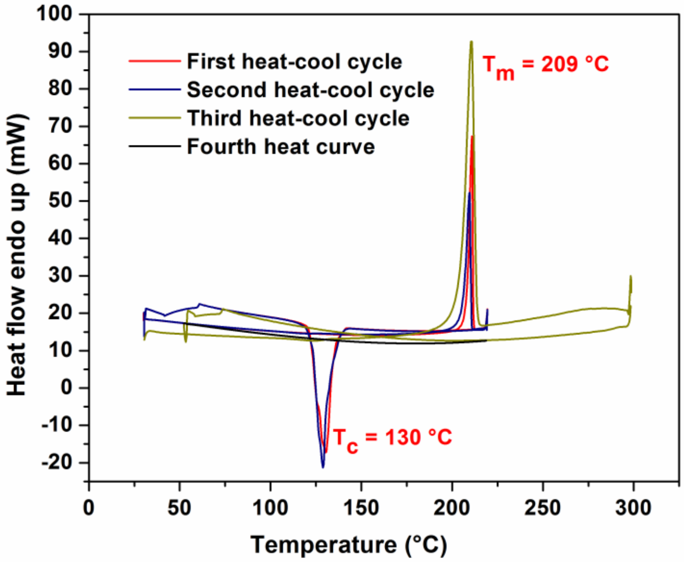


Figure 3.23. DSC cycles of **7a** measured under N_2 (first heating: 30-220 °C, scan rate = 10 °C/min; first cooling: 220-30 °C, scan rate = 30 °C/min; second heating: 30-220 °C, scan rate = 10 °C/min; second cooling: 220-30 °C, scan rate = 30 °C/min; third heating: 30-300 °C, scan rate = 10 °C/min; third cooling: 300-50 °C, scan rate = 30 °C/min; fourth heating: 50-220 °C, scan rate = 10 °C/min).

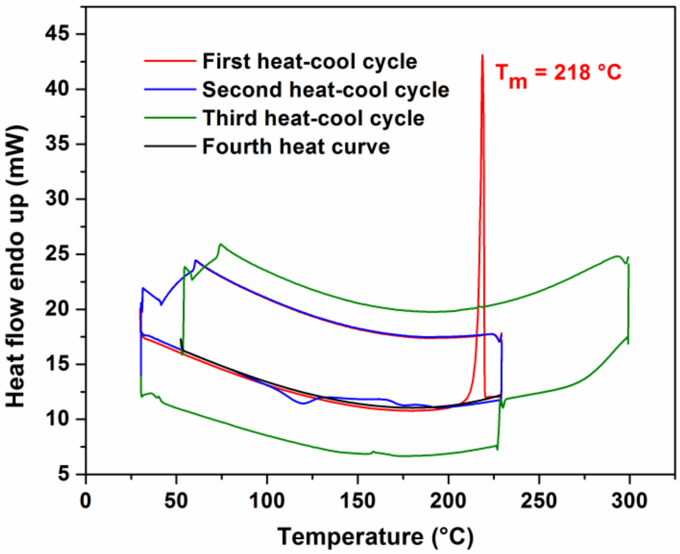


Figure 3.24. DSC cycles of **7b** measured under N_2 (first heating: 30-230 °C, scan rate = 10 °C/min; first cooling: 230-30 °C, scan rate = 30 °C/min; second heating: 30-230 °C, scan rate = 10 °C/min; second cooling: 230-30 °C, scan rate = 30 °C/min; third heating: 30-300 °C, scan rate = 10 °C/min; third cooling: 300-50 °C, scan rate = 30 °C/min; fourth heating: 50-230 °C, scan rate = 10 °C/min).

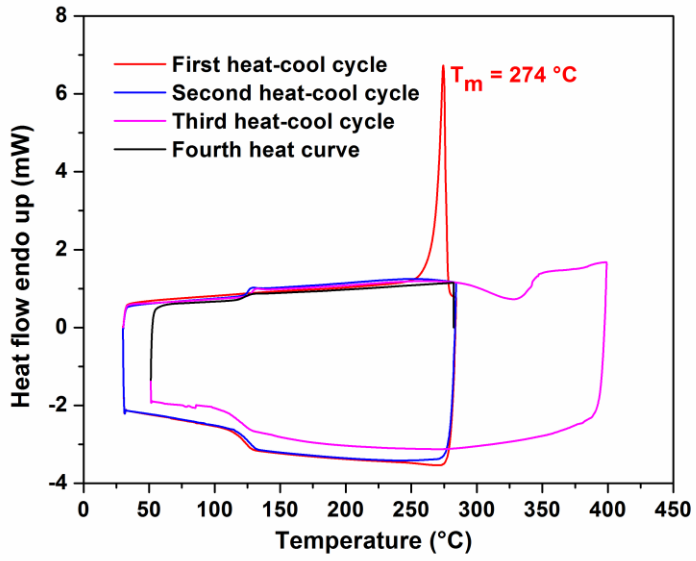


Figure 3.25. DSC cycles of **8** measured under N_2 (first heating: 30-285 °C, scan rate = 10 °C/min; first cooling: 285-30 °C, scan rate = 30 °C/min; second heating: 30-285 °C, scan rate = 10 °C/min; second cooling: 285-30 °C, scan rate = 30 °C/min; third heating: 30-400 °C, scan rate = 10 °C/min; third cooling: 400-50 °C, scan rate = 30 °C/min; fourth heating: 50-285 °C, scan rate = 10 °C/min).

3.4. Attempted synthesis of 1,4-bis(tributyllstannyl)-1,2,3,4-tetra(4-isopropylbenzene)-1,3-butadiene

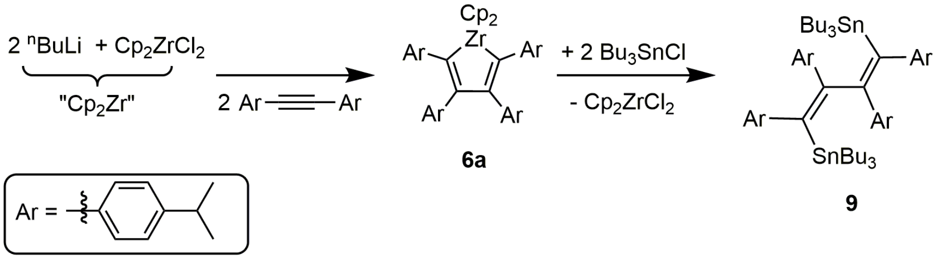
Polymer light-emitting diodes (PLEDs) are light-weight, easy to fabricate, and emissive at low power, making them promising candidates for use as main display components in our information society. However, in order to achieve tunable full color emission from PLEDs, some challenges associated with blue light-emitting polymers such as luminous efficiency, spectra and operating stability, need to be overcome.[42] Given the blue luminescent nature of some tetraarylbutadienes described already in this chapter, a subsequent goal was to incorporate these units into polymeric structures via known Stille coupling protocols. Accordingly the attempted synthesis of a suitable stannylated 1,3-butadiene monomer 1,4-bis(tributylstannyl)-1,2,3,4-tetra(4-isopropylbenzene)-1,3-butadiene was explored.

Stille cross-coupling is one of the most common routes in π-conjugated polymer synthesis[43] and specifically the distannylated olefin (E)-(R_3Sn)CH=CH(SnR_3), R = Me and Bu, has been widely used to make π-conjugated vinylene copolymers with interesting optoelectronic properties. For example, the most recent findings include co-polymers of heavier group 16 element heterocycles (e.g., selenophene and tellurophene)[44] as well as naphthodithiophene diimide.[45] However, distannylated 1,3-butadienes (R_3Sn)CH=CH-CH=CH(SnR_3) (R = Me and Bu) are not commonly studied due to their cumbersome syntheses, starting from either 2,4-hexadiyne[46] or 1,4-dichloro-1,3-butadiene.[47] An arylated distannyl butadiene can be synthesized via a Pd-catalyzed alkyne insertion chemistry involving terminal arylalkynes and Me_3Sn-SnMe_3.[48] As a result, Zn/Sn metathesis chemistry was thought to be explored as a way to gain access to stannylated butadienes.

Earlier in this chapter a modular synthesis of tetraaryl-substituted 1,3-butadienes was investigated and the cumyl-appended analogue (**7a**) which exhibits efficient blue luminescence in the solid state (i.e., absolute quantum yield is 24.8 %), while showing improved solubility in organic solvents compared to commonly used blue emitter 1,1,4,4-tetraphenyl-1,3-butadiene.[49] Thus, it was of interest to explore if transformation of **6a** into distannylated analogue of **7a** would be possible.

3.4.1. Results and discussion

The planned route to the distannylated butadiene monomer **9** started with the direct Zr/Sn metallacycle transfer reaction between the cumyl-substituted zirconacycle **6a** and two equivalents of Bu_3SnCl (Scheme 3.5). The choice of the appended butyl instead of methyl groups on tin was due to the 100-fold lower toxicity of the $^nBu_3Sn$-group. In addition, the trimethyltin derivatives have much lower boiling points, thus are more volatile when exposed to air.[50]



Scheme 3.5. Attempted synthesis of the monomer **9**.

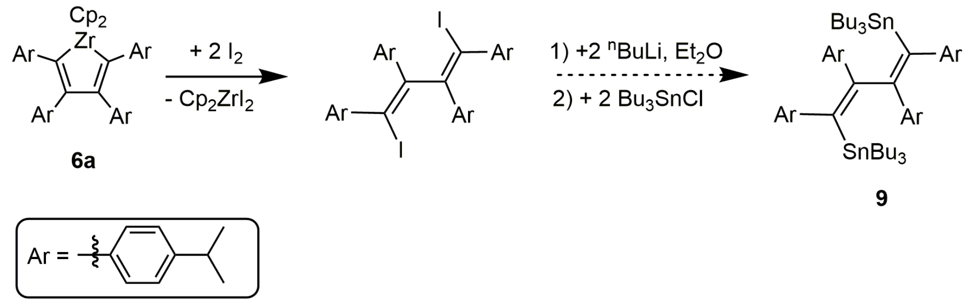
First, the most common solvent used in the zirconium-mediated transfer, *i.e.*, tetrahydrofuran, was tested. The reaction was monitored by multinuclear NMR spectroscopy, but no conversion to the product **9** was observed after 24 hours of stirring the zirconacycle **6a** with $ClSn^nBu_3$ at room temperature. Earlier it was noted by Fagan and Nugent that quantitative conversion of zirconacycles into stannoles takes a longer time compared to germoles (*i.e.*, 48 hours *versus* 2 min),[51] thus this reaction mixture (Scheme 3.5) was left stirring for another 48 hours, however complete decomposition of **6a** was found (four new *Cp* environments were detected by NMR spectroscopy) with no formation of the expected byproduct Cp_2ZrCl_2.

Previously, remarkable solvent effects have been reported for synthesis of siloles from zirconacycles using halosilanes reagents, with one documented case of reactivity occurring in chloroform and dichloromethane, but not in THF.[52] Thus the reaction was investigated between **6a** and $ClSn^nBu_3$ in different solvents, with aliquots being taken after 24 hours and 72 hours of stirring (Table 3.6). It was found that zirconacycle **6a** decomposes after 72 hours of stirring in THF (100 %) and halogenated solvents (*i.e.*, dichloromethane (100 %) and $CDCl_3$ (90 %)), as well as after 24 hours of stirring in acetonitrile (42 %) and heating in toluene at 85 °C (18 %). In all other cases only starting materials (and no Cp_2ZrCl_2) were observed by multinuclear (^1H and ^{13}C {^1H}) NMR spectroscopy with decomposition of **6a** occasionally noted.

Table 3.6. Metallacycle transfer between **6a** and two equiv. of $ClSn^nBu_3$ in various solvents.

Entry	**Solvent**	**Temperature (°C)**	**Time (hrs)**	**Product? (based on ^{1}H and ^{13}C{^{1}H} NMR)**
1	THF	22	24	starting materials
2	THF	22	72	**6a** decomp. (100 %)
3	Et_2O	22	24	starting materials
4	Et_2O	22	72	starting materials
5	Acetonitrile	22	24	**6a** decomp. (42 %)
6	Toluene	22	24	starting materials
7	Toluene	22	72	starting materials
8	Toluene	85	24	**6a** decomp. (18 %)
9	$CDCl_3$	22	24	**6a** decomp. (58 %)
10	$CDCl_3$	22	72	**6a** decomp. (90 %)
11	Dichloromethane	22	24	**6a** decomp. (37 %)
12	Dichloromethane	22	72	**6a** decomp. (100 %)

As a result of the abovementioned experiments, another approach to the monomer **9** was taken using a 1,4-diiodo-1,3-butadiene (Scheme 3.6) analogue as a reagent. In order to obtain this compound, procedure developed by Ashe and coworkers was applied; this synthetic protocol was also used to efficiently prepare $I_2C_4Et_4$ from $Cp_2ZrC_4Et_4$ and iodine in reproducibly excellent yields (> 80 %; Scheme 3.6).

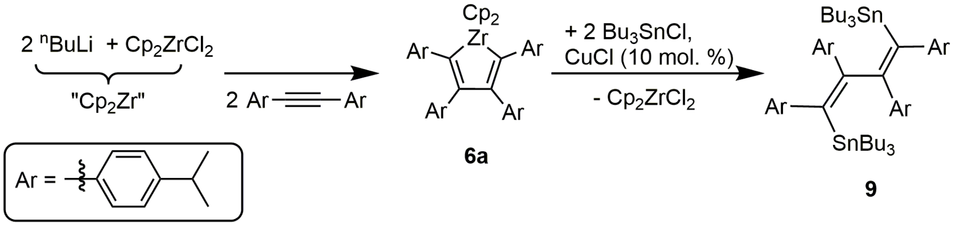


Scheme 3.6. Synthesis of the monomer **9** via 1,4-diiodo-1,3-butadiene.

The iodination of **6a** was tested three times, where slow addition of iodine (in THF) to this zirconacycle at -78 °C and -35 °C was performed under nitrogen atmosphere, followed by warming to room temperature for 3 hrs. In each case a complex mixture of products was obtained every time, although cleavage of cumyl groups of zirconacycle **6a** was not observed (based on the absence of cumyl iodide in the NMR spectra of the products).[53] When brominating agents, such as $CuBr_2$,[54] were combined with **6a**, large amounts of metallic precipitate formed as well as the decomposition of **6a**.

Lastly, I tried the transmetallation reaction between **6a** and $ClSn^nBu_3$ in the presence of catalytic amount (10 mol. %) of CuCl (Scheme 3.7); this method was developed by Takahashi and co-workers and allowed a very efficient transfer (in one hour) of zirconacycles into stannoles and spirostannoles in excellent yields (> 80 %).[55] When **6a** and two equiv. of $ClSn^nBu_3$ were combined with 10 mol. % of CuCl in THF, a complex mixture of products was generated with no sign of the expected Cp_2ZrCl_2 by-product, even after 48 hours of stirring. The Staubitz[56] and

Piers[57] groups used toluene as the solvent for this class of transformation, however use of toluene as a solvent yielded similarly complex reaction mixtures.



Scheme 3.7. Synthesis of the monomer **9** in the presence of catalytic amount of copper(I) chloride.

3.5. Conclusions

A general synthetic protocol to yield diarylalkynes and functionalized tetraaryl-1,3-butadienes *via* sequential Suzuki-Miyaura and zirconium-mediated alkyne coupling was developed. Altering the nature of the peripheral substituents appended to the butadiene unit leads to blue or green photoluminescence in the solid state. In addition, incorporation of these emissive units into polymeric structures for the fabrication of mechanically robust LEDs was attempted. The synthesis of the stannylated 1,3-butadiene $(^{n}Bu_3Sn)_2C_4Ar_4$ (Ar = cumyl) **9**, a possible monomer for later use in Stille coupling polymerization, was tested. Despite exploring Zr/Sn exchange in different solvents and temperatures, and in the presence of copper(I) chloride, no sign of the desired product was noted, possibly due to the sterically encumbered nature of the zirconacycle starting material **6a**. The future work will involve examining Zr/Sn transmetallation with less hindered zirconacycles as a possible entry to next generation blue PLEDs based on thermally stable butadiene units.

3.6. Experimental section

3.6.1. Materials and instrumentation

All reactions were performed using standard Schlenk and glovebox (MBraun) techniques under a nitrogen atmosphere. Solvents were all dried and degassed using a Grubbs-type solvent purification system[58] manufactured by Innovative Technology, Inc., and stored under an atmosphere of nitrogen prior to use. 4-Bromoisopropylbenzene was obtained from TCI America, palladium(II) diacetate and zirconocene dichloride from Strem Chemicals Inc., 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane from Oakwood Chemicals, pyridine from Caledon Laboratory Chemicals; all other chemicals were obtained from Aldrich. Commercially obtained chemicals were used as received except for pyridine (pyr), which was freshly distilled under nitrogen from potassium hydroxide.[59] Acetonitrile was dried over anhydrous potassium carbonate for 24 hours, then over boric anhydride, followed by distillation under nitrogen.[59] Bis(cyclopentadienyl)zirconium(2,3,4,5-tetra(2-thienyl)methanide) (**$Cp_2ZrC_4T_4$**),[32] $Cp_2Zr(pyr)(Me_3SiCCSiMe_3)$,[56] 2-bromo-3-hexylthiophene,[60] and 4-bromotriphenylamine[61] were prepared according to literature procedures. ^1H, $^{13}C^1$ and $^{11}B\{^1H\}$ NMR spectra were recorded on a Varian DD2 MR-400 spectrometer and referenced externally to $SiMe_4$ (^1H, $^{13}C\{^1H\}$) and $F_3B\bullet OEt_2$ ($^{11}B\{^1H\}$). Elemental analyses were performed by the Analytical and Instrumentation Laboratory at the University of Alberta. Mass spectrometry were recorded using a MS-50G system (Kratos Analytical). Melting points were obtained in sealed glass capillaries under nitrogen using a MelTemp melting point apparatus and are uncorrected. UV/Vis measurements were obtained using a Varian Cary 300 Scan spectrophotometer. The fluorescence measurements were conducted on a Photon Technology International (PTI) MP1 fluorescence system. All relative solution quantum yields were measured in comparison to quinine sulfate in 1.0 N H_2SO_4 as a standard, assuming a quantum yield of 0.55.[38a] Photoluminescence lifetimes were measured on a time-correlated single photon counting fluorescence spectrometer (Edinburgh Instruments FLS920) using an EPL-375 picosecond pulsed diode laser with vertical polarization (70.3 ps pulse width) as an excitation source; absolute quantum yields were measured with an integrating sphere system within the same fluorescence spectrometer. The X-ray powder diffraction patterns were collected on an Inel diffractometer equipped with a curved position-sensitive detector (CPS 120) and a Cu $K\alpha_1$ radiation source. Thermogravimetric analysis was performed under nitrogen atmosphere on Perkin Elmer Pyris 1 TGA. Differential scanning calorimetry measurements were conducted under nitrogen atmosphere on Perkin Elmer Pyris 1 DSC. Microwave reactions were performed using a Biotage Initiator Classic microwave reactor

(Biotage, LLC, Charlotte, NC, USA). Photobleaching experiments on films were performed with a Photon Technology International (PTI) MP1 fluorescence system (xenon lamp, 65 W).

3.6.2. Synthetic procedures

3.6.2.1. Synthesis of 1,2-bis(4',4',5',5'-tetramethyl[1',3',2']dioxaborolan-2'-yl)ethyne (1)

This compound was synthesized according to a modification of a known procedure.[24] To a 100 mL 1:1 mixture of THF and Et_2O at -78 °C was added a solution of ^{n}BuLi (2.5 M in hexanes, 75 mmol). Then 2.25 mL (25 mmol) of trichloroethylene in 25 mL of Et_2O was added dropwise over 15 min with stirring. After the addition was completed, the cooling bath was removed immediately and the resulting pale yellow mixture was stirred overnight to give white slurry. The mixture containing dilithioacetylide was then transferred via cannula to a pre-cooled (-78 °C) solution of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10 mL, 49 mmol) in Et_2O (100 mL), followed by stirring at -78 °C for four hours. Next the mixture was warmed up to the room temperature and stirred for four hours. The reaction mixture was then cooled down to -78 °C and 20 mL of HCl (4.0 M in dioxane, 80 mmol) was added and the flask followed by stirring for three hours at room temperature. The LiCl precipitate was allowed to settle and the supernatant was filtered through a pad of Celite. The volatiles were then removed from the filtrate under reduced pressure to give **1** as a brown semi-solid that was washed with cold pentane (2 × 10 mL; -30 °C) to give **1** as an air-stable light beige powder (5.195 g, 75 %). The corresponding ^{1}H and ^{13}C{^{1}H} NMR spectral data in C_6D_6 matched those reported previously by the Therien group.[24] ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 (s, 24H, C*H*$_3$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 84.7 (*C*(CH_3)$_2$), 24.6 (*C*H$_3$); ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$): δ 23.3 (br).

3.6.2.2. Stability trials for compound 1 in different solvents under microwave radiation (300 W)

Compound **1** (0.050 g, 0.18 mmol) was dissolved in 1.5 mL of solvent and heated in a microwave reactor under conditions presented in Table 3.1.

3.6.2.3. Stability of compound 1 in the presence of base in THF or DMF under microwave irradiation (300 W)

Compound **1** (0.050 g, 0.18 mmol) and either a solid K_3PO_4 (0.215 g, 1.08 mmol) or solid CsF (0.055 g, 0.36 mmol) or aqueous K_2CO_3 (0.54 mL, 2.0 M solution, 1.08 mmol) were dissolved in 1.5 mL of solvent and heated in a microwave reactor under the conditions presented in the Table 3.2.

3.6.2.4. Condition trials for synthesis of 1,2-bis(4-isopropylphenyl)ethyne (2) under microwave irradiation (300 W)

Compound **1** (0.100 g, 0.36 mmol), 4-bromoisopropylbenzene (109 μL, 0.72 mmol), $Pd_2(dba)_3$ (0.007 g, 0.0072 mmol), ligand (8 mol % relative to **1**) and either a solid K_3PO_4 (0.458 g, 2.16 mmol) or aqueous K_2CO_3 (1.1 mL, 2.0 M solution, 1.08 mmol) were dissolved in 3 mL of solvent and heated in a microwave reactor under the conditions presented in Table 3.3. Afterwards the reaction mixture was cooled to room temperature, poured into 50 mL of water and extracted with 10 mL of chloroform. The organic layer was washed with 40 mL of water and 2 × 40 mL of brine. The aqueous fractions were combined and extracted with 10 mL of chloroform and washed again with 2 × 40 mL of brine. Then the combined organic fractions were dried over $MgSO_4$. The solvent was removed in vacuo and the residue was purified by column chromatography (silica gel, ethyl acetate:hexanes = 1:20, $R_f = 0.74$) to give pure **2** in variable isolated yields (see Table 3.3).

3.6.2.5. Optimization of reaction conditions when heating to reflux to synthesize 2

Compound **1** (0.250 g, 0.899 mmol), 4-bromoisopropylbenzene (273 μL, 1.80 mmol), catalyst, 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (XPhos) (0.034 g, 0.072 mmol) and either solid

K_3PO_4 (1.146 g, 5.40 mmol) or CsF (0.273 g, 1.80 mmol) (Table 3.4) were dissolved in 10 mL of THF and heated to reflux for 36 hrs. Afterwards the reaction mixture was cooled to room temperature, poured into 50 mL of water and extracted with 10 mL of chloroform. The organic layer was washed with 40 mL of water and 2 × 40 mL of brine. The aqueous fractions were combined and extracted with 10 mL of chloroform and washed with 2 × 40 mL of brine. Then all combined organic fractions were dried over $MgSO_4$. The solvent was removed in vacuo and the residue was purified by column chromatography (silica gel, ethyl acetate:hexanes = 1:20, $R_f = 0.74$) to give pure **2** in various yields (see Table 3.4).

3.6.2.6. Synthesis of 1,2-bis(4-isopropylphenyl)ethyne (2)

Compound **1** (1.00 g, 3.60 mmol), 4-bromoisopropylbenzene (1.09 mL, 7.20 mmol), K_3PO_4 (4.58 g, 21.6 mmol), palladium(II) diacetate (0.016 g, 0.072 mmol), 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (XPhos) (0.137 g, 0.288 mmol) were mixed in a 100 mL flask under N_2. Degassed THF (20 mL) was then added and the mixture was stirred for 30 min at room temperature (for catalyst activation)[62] and the flask was then immersed in a pre-heated oil bath and the solvent was refluxed for 36 hrs. Afterwards the reaction mixture was cooled to room temperature, poured into 100 mL of water and extracted with 30 mL of chloroform. The organic layer was washed with 100 mL of water and 2 × 100 mL of brine. The aqueous fractions were combined and extracted with 20 mL of chloroform, and the organic layer washed with 2 × 100 mL of brine. Then all combined organic fractions were dried over $MgSO_4$. The solvent was removed *in vacuo* and the residue was purified by column chromatography (silica gel, ethyl acetate:hexanes = 1:20, R_f = 0.74) to give **2** as a light yellow solid (0.417 g, 44 %). X-ray quality colorless crystals were obtained upon recrystallization from ethyl acetate/hexanes at room temperature. In addition, the crude mixture can also be purified by washing with cold (-30 °C) diethyl ether (2 × 4 mL) to yield **2** as a pale brown solid (1.003 g of **1** gives 0.687 g of **2**, 73 % yield, ca. 95 % purity; see Figures 3.31 and 3.32). The corresponding ^{1}H NMR spectral data matched those reported previously in the literature.[31] TGA: T_{dec} = 186 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, $^3J_{HH}$ = 7.9 Hz, 4H, Ar*H*), 7.21 (d, $^3J_{HH}$ = 8.0 Hz, 4H, Ar*H*), 2.92 (sept, $^3J_{HH}$ = 6.9 Hz, 2H, C*H*$(CH_3)_2$), 1.26 (d, $^3J_{HH}$ = 6.9 Hz, 12H, C*H*$_3$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 149.1, 131.6, 126.5, 120.9 (Ar-*C*), 88.9 (-*C*≡*C*-), 34.1 (*C*H$(CH_3)_2$), 23.9 (*C*H$_3$); HR-MS (EI): m/z: 262.1721; $C_{20}H_{22}$ calcd: 262.1722; elemental analysis calcd (%) for $C_{20}H_{22}$: C, 91.55; H, 8.45; found: C, 90.73; H, 8.54.

3.6.2.7. Optimization of reaction conditions when heating to reflux to synthesize 1,2-bis(thiophen-2-yl)ethyne (3)

In a 100 mL flask, compound **1** (1.00 g, 3.60 mmol), 2-bromothiophene (731 μL, 7.56 mmol), K_3PO_4, palladium (II) diacetate, 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (XPhos) were mixed. Degassed THF (20 mL) was then added and then mixture was heated to reflux (Table 3.5). Afterwards the reaction mixture was cooled to room temperature, poured into 100 mL of water and extracted with 30 mL of chloroform. The organic layer was washed with 100 mL of water and 2 x 100 mL of brine. The aqueous fractions were combined and extracted with 20 mL of chloroform and washed with 2 × 100 mL of brine. Then all combined organic fractions were dried over $MgSO_4$. The solvent was removed in vacuo and the residue was purified by column chromatography (silica gel, hexanes, $R_f = 0.35$) to give pure **3** as a pale yellow solid; see below for the spectroscopic data of **3**.

3.6.2.8. Synthesis of 1,2-bis(thiophen-2-yl)ethyne (3)

In a 100 mL flask, compound **1** (1.00 g, 3.60 mmol), 2-bromothiophene (731 μL, 7.56 mmol), K_3PO_4 (4.58 g, 21.6 mmol), palladium (II) diacetate (0.016 g, 0.072 mmol), 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (XPhos) (0.137 g, 0.288 mmol) were mixed. Degassed THF (20 mL) was then added and the mixture was stirred for 30 min at room temperature (for catalyst activation)[62] and then the flask was inserted in a pre-heated oil bath and the solvent was refluxed for 36 hrs. Afterwards the reaction mixture was cooled to room temperature, poured into 100 mL of water and extracted with 30 mL of chloroform. The organic layer was washed with 100 mL of water and 2 × 100 mL of brine. The aqueous fractions were combined and extracted with 20 mL of chloroform, and the organic fractions were washed with 2 × 100 mL of brine. Then all combined organic fractions were dried over $MgSO_4$. The solvent was removed *in vacuo* and the residue was purified by column chromatography (silica gel, hexanes, $R_f = 0.35$) to give **3** as a pale yellow solid (0.275 g, 40 %). In addition, the crude residue can also be purified by washing with cold (-30 °C) diethylether (2 × 4 mL) to yield **3** as a dark brown solid (0.999 g of **1** gives 0.274 g of **3**, 40 % yield, ca. 95 % purity; Figures 3.35 and 3.36). The corresponding ^{1}H NMR and ^{13}C{^{1}H} spectral data matched those reported previously in the literature.[15, 63] DSC: T_{dec} = 179 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (dd, $^3J_{HH}$ = 5.1 Hz, $^4J_{HH}$ = 1.1 Hz, 2H, Thienyl*H*), 7.29 (dd, $^3J_{HH}$ = 3.7 Hz, $^4J_{HH}$ = 1.2 Hz, 2H, Thienyl*H*), 7.02 (dd, $^3J_{HH}$ = 5.1 Hz, $^4J_{HH}$ = 3.7 Hz, 2H, Thienyl*H*); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 132.1, 127.6, 127.2, 122.9 (Thienyl-*C*), 86.3 (-*C*≡*C*-); HR-MS (EI): m/z: 189.9915; $C_{10}H_6S_2$ calcd: 189.9911; elemental analysis calcd (%) for $C_{10}H_6S_2$: C, 63.12; H, 3.18; S, 33.70; found: C, 63.28; H, 3.13; S, 33.64.

3.6.2.9. Synthesis of bis(3-hexyl-2-thienyl)ethyne (4)

Compound **1** (1.013 g, 3.64 mmol), 2-bromo-3-hexylthiophene (1.892 g, 7.65 mmol), K_3PO_4 (4.642 g, 21.8 mmol), palladium(II) diacetate (0.016 g, 0.073 mmol), 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (XPhos) (0.139 g, 0.292 mmol) were mixed in a 100 mL flask under N_2. Degassed THF (20 mL) was then added and the mixture was stirred for 30 min at room temperature (for catalyst activation)[62] and then heated to reflux for 36 hrs. Afterwards the reaction mixture was cooled to room temperature, poured into 100 mL of water and extracted with 30 mL of chloroform. The organic layer was washed with 100 mL of water and 2 × 100 mL of brine. The aqueous fractions were combined and extracted with 20 mL of chloroform, and the $CHCl_3$ layer was washed with 2 × 100 mL of brine. Then all combined organic fractions were dried over $MgSO_4$. The solvent was removed *in vacuo* and the residue was purified by column chromatography (silica gel, petroleum ether, $R_f = 0.62$) to give **4** as a pale yellow oil (0.667 g, 51 %). The corresponding ^1H NMR and $^{13}C\{^1H\}$ spectral data matched those reported previously in the literature.[33,64] ^1H NMR (400 MHz, $CDCl_3$): δ 7.20 (d, $^3J_{HH} = 5.2$ Hz, 2H, Thienyl$H$), 6.91 (d, $^3J_{HH} = 5.2$ Hz, 2H, Thienyl$H$), 2.78 (t, $^3J_{HH} = 7.7$ Hz, 4H, Thienyl-CH_2), 1.66-1.72 (m, 4H, Thienyl-$CH_2(CH_2)_4$-CH_3), 1.33-1.42 (m, 12H, Thienyl-$CH_2(CH_2)_4$-CH_3), 0.92 (t, $^3J_{HH} = 7.1$ Hz, 6H, Thienyl-$(CH_2)_5$-CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 147.6, 128.3, 126.1, 118.4 (Thienyl-*C*), 88.0 (-*C*≡*C*-), 31.7, 30.4, 29.7, 29.1, 22.7 (Thienyl-(CH$_2$)$_5$-CH$_3$), 14.1 (Thienyl-(CH$_2$)$_5$-CH$_3$); HR-MS (EI): m/z: 358.1785; $C_{22}H_{30}S_2$ calcd: 358.1789; elemental analysis calcd (%) for $C_{22}H_{30}S_2$: C, 73.69; H, 8.43; S, 17.88; found: C, 73.92; H, 8.39; S, 17.48.

3.6.2.10. Synthesis of 1,2-bis(triphenylamine)-ethyne (5)

In a 100 mL flask, compound **1** (1.015 g, 3.65 mmol), 2-bromo-3-hexylthiophene (2.412 g, 7.44 mmol), K_3PO_4 (4.737 g, 22.3 mmol), palladium(II) diacetate (0.017 g, 0.074 mmol), 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (XPhos) (0.142 g, 0.298 mmol) were mixed. Degassed THF (20 mL) was then added and the mixture was stirred for 30 min at room temperature (for catalyst activation)^{62} and then heated to reflux for 36 hrs. Afterwards the reaction mixture was cooled to room temperature, poured into 100 mL of water and extracted with 30 mL of chloroform. The organic layer was washed with 100 mL of water and 2 × 100 mL of brine. The aqueous fractions were combined and extracted with 20 mL of chloroform, and the organic layer was washed with 2 × 100 mL of brine. Then all combined organic fractions were dried over $MgSO_4$. The solvent was removed in vacuo and the residue was purified by column chromatography (silica gel, hexanes:CH_2Cl_2 = 8:2, R_f = 0.38) to give **5** as a pale yellow solid (0.572 g, 31 %). Slow evaporation of a solution of **5** in 8:2 hexanes:CH_2Cl_2 at room temperature resulted in the formation of colorless crystals of X-ray quality (0.286 g, 15 %). The crude mixture can be also be purified by washing with with Et_2O (2 × 15 mL) to yield **5** as a light brown solid of ca. 90 % purity in 60 % yield (1.015 g of **1** gives 1.116 g of **5**; see Figure 3.41). TGA: T_{dec} = 206 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, $^3J_{HH}$ = 8.6 Hz, 4H, Ar*H*), 7.29-7.31 (m, 8H, Ar*H*), 7.07-7.14 (m, 12H, Ar*H*), 7.03 (d, $^3J_{HH}$ = 8.6 Hz, 4H, Ar*H*); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 147.7, 147.3, 132.4, 129.4, 124.9, 123.5, 122.6, 116.7 (Ar-*C*), 88.9 (-*C*≡*C*-); UV/Vis (THF): λ_{max} (ε) = 301 nm (4.02×10^4 mol^{-1} dm^3 cm^{-1}) and 369 nm (6.65×10^4 mol^{-1} dm^3 cm^{-1}); UV/Vis (film): λ_{max} = 312 and 367 nm; Fluorescence emission (THF) (λ_{ex} = 322 nm): λ_{emis} = 413 nm, fluorescence quantum yield: Φ = 48 %, relative to quinine sulfate in 1.0 N H_2SO_4; Absolute quantum yield (THF): Φ = 79.7 %; Lifetime (1×10^{-5} M solution in THF): τ = 1.4 ns; Fluorescence emission (film) (λ_{ex} = 383 nm): λ_{emis} = 484 nm; Lifetime (film): τ = 2.4 ns; Absolute quantum yield (film) = 1.7 %. The optical data matched those previously reported.[35b] HR-MS (EI): m/z: 512.2239; $C_{38}H_{28}N_2$ calcd: 512.2252; elemental analysis calcd (%) for $C_{38}H_{28}N_2$: C, 89.03; H, 5.51; N, 5.46; found: C, 88.27; H, 5.37; N, 5.43.

3.6.2.11. Synthesis of bis(cyclopentadienyl)zirconium-2,3,4,5-tetra(4-isopropylphenyl)methanide) (6a)

To a solution of Cp_2ZrCl_2 (0.183 g, 0.63 mmol) in THF (10 mL) at -78 °C was added dropwise a solution of ^nBuLi (0.49 mL, 2.5 M solution in hexanes, 1.2 mmol). After the reaction mixture was stirred at -78 °C for

1 h, a solution of **2** (0.328 g, 1.25 mmol) in THF (10 mL) was added at -78 °C. The temperature was allowed to rise to room temperature, and the mixture was stirred for another 24 hrs. The solvent was removed under reduced pressure and the product was extracted with 15 mL of toluene, and the resulting extract was filtered through Celite. The volatiles were then removed from filtrate under reduced pressure to give **6a** as a red powder (0.420 g, 90 %). This compound was recrystallized from hexanes at -35 °C to yield red crystals that were of suitable quality for X-ray crystallography. M.p. 119-124 °C (dec.); ^{1}H NMR (400 MHz, C_6D_6): δ 6.95 (two overlapping doublets, 8H, Ar*H*), 6.73 (d, $^{3}J_{HH}$ = 8.1 Hz, 4H, Ar*H*), 6.71 (d, $^{3}J_{HH}$ = 8.1 Hz, 4H, Ar*H*), 6.07 (s, 10H, Cp*H*), 2.66 (sept, $^{3}J_{HH}$ = 6.9 Hz, 2H, C*H*$(CH_3)_2$), 2.50 (sept, $^{3}J_{HH}$ = 6.9 Hz, 2H, C*H*$(CH_3)_2$), 1.11 (d, $^{3}J_{HH}$ = 6.9 Hz, 12H, C*H*$_3$), 0.99 (d, $^{3}J_{HH}$ = 6.9 Hz, 12H, C*H*$_3$); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 194.2, 146.3, 144.8, 143.3, 142.9, 139.6, 131.2, 127.8, 125.9, 125.0 (Ar-*C*), 112.1 (Cp), 33.81, 33.78 (*C*H$(CH_3)_2$), 24.2, 24.0 (*C*H$_3$); UV/Vis (THF): λ_{max} (ε) = 374 nm (6.78×10^{3} mol^{-1} dm^{3} cm^{-1}); HR-MS (MALDI): m/z: 744.3271; $C_{50}H_{54}Zr$ calcd: 744.3284; elemental analysis calcd (%) for $C_{50}H_{54}Zr$: C, 80.48; H, 7.29; found: C, 79.93; H, 7.50.

3.6.2.12. Synthesis of cis,cis-1,2,3,4-tetra(4-isopropylbenzene)-1,3-butadiene (7a)

To a solution of **6a** (0.421 g, 0.56 mmol) in 15 mL of Et_2O, was added a solution of HCl (0.9 mL, 2.0 M solution in Et_2O, 1.8 mmol). The red color of **6a** immediately disappeared to give yellow slurry. The mixture was stirred for 12 hrs at room temperature and then the solvent was removed under vacuum. The residue was dissolved in a 2:1 CH_2Cl_2:hexanes solvent mixture (5 mL) and filtered through a 1 cm plug of the silica gel. The solvent was removed from the filtrate and the resulting solid (0.220 g, 74 %) was washed with hexanes (2 × 5 mL) to yield **7a** as a white solid (0.168 g, 57 %). The product was crystallized from hexanes at -35 °C to give X-ray quality colorless crystals of **7a**. M.p. 198-201 °C; TGA: T_{dec} = 267 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, $^3J_{HH}$ = 8.1 Hz, 4H, Ar*H*), 7.24 (d, $^3J_{HH}$ = 8.1 Hz, 4H, Ar*H*), 6.89 (d, $^3J_{HH}$ = 8.1 Hz, 4H, Ar*H*), 6.66 (d, $^3J_{HH}$ = 8.1 Hz, 4H, Ar*H*), 6.24 (s, 2H, =C*H*-), 3.00 (sept, $^3J_{HH}$ = 6.9 Hz, 2H, C*H*(CH_3)$_2$), 2.76 (sept, $^3J_{HH}$ = 6.9 Hz, 2H, C*H*(CH_3)$_2$), 1.35 (d, $^3J_{HH}$ = 6.9 Hz, 12H, C*H*$_3$), 1.16 (d, $^3J_{HH}$ = 6.9 Hz, 12H, C*H*$_3$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 147.8, 147.2, 145.2, 137.6, 135.1, 131.2, 130.2, 129.5, 126.8, 125.9 (Ar-*C*), 34.0, 33.7 (*C*H(CH_3)$_2$), 24.2, 23.8 (*C*H$_3$); UV/Vis (THF): λ_{max} (ε) = 327 nm (3.06 × 10^4 mol^{-1} dm^3 cm^{-1}), 339 nm (3.49 × 10^4 mol^{-1} dm^3 cm^{-1}), and 356 nm (2.38 × 10^4 mol^{-1} dm^3 cm^{-1}); UV/Vis (film): λ_{max} = 331, 346 and 367 nm; Fluorescence emission (film) (λ_{ex} = 380 nm): λ_{emis} = 426 and 463 nm;

Lifetime (film): τ = 1.0 ns; Absolute quantum yield (film) = 24.8 %. HR-MS (EI): m/z: 526.3597; $C_{40}H_{46}$ calcd: 526.3600; elemental analysis calcd (%) for $C_{40}H_{46}$: C, 91.20; H, 8.80; found: C, 91.26; H, 9.01.

3.6.2.13. Synthesis of *cis*,*cis*-1,2,3,4-tetra(2-thienyl)-1,3-butadiene (7b)

To a solution of **6b**[32] (0.202 g, 0.34 mmol) in 10 mL of THF was added a solution of HCl (0.54 mL, 2.0 M solution in Et_2O, 1.09 mmol). The red color of **6b** immediately disappeared to give yellow slurry. The mixture was stirred for 12 hrs at room temperature and the solvent was removed under vacuum; the pale yellow residue was then dissolved in dichloromethane (5 mL) and filtered through a 1 cm plug of the silica gel with CH_2Cl_2:hexanes = 2:1 solvent mixture (30 mL). The solvent was removed from the filtrate and the product was washed with cold (-35 °C) Et_2O (5 mL) to yield **7b** as a bright yellow solid (0.051 g, 40 %). M.p. 198-200 °C; TGA: T_{dec} = 241 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (dd, $^3J_{HH}$ = 5.1 Hz, $^4J_{HH}$ = 1.1 Hz, 2H, Thienyl*H*), 7.25 (dd, $^3J_{HH}$ = 5.1 Hz, $^4J_{HH}$ = 3.4 Hz, 2H, Thienyl*H*), 7.13 (dd, $^3J_{HH}$ = 5.0 Hz, $^4J_{HH}$ = 1.1 Hz, 2H, Thienyl*H*), 7.05 (dd, $^3J_{HH}$ = 3.4 Hz, $^4J_{HH}$ = 1.1 Hz, 2H, Thienyl*H*), 6.85 (dd, 3JHH = 3.7 Hz, $^4J_{HH}$ = 1.3 Hz, 2H, Thienyl*H*), 6.80 (dd, $^3J_{HH}$ = 3.6 Hz, $^4J_{HH}$ = 0.7 Hz, 2H, Thienyl*H*), 6.73 (s, 2H, =C*H*-); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 140.9, 137.8, 134.3, 130.0, 129.3, 128.2, 128.1, 128.0, 127.8, 126.2; UV/Vis (THF): λ_{max} (ε) = 350, 367, and 387 nm (2.65×10^4, 3.61×10^4 and 2.81×10^4 mol^{-1} dm^3 cm^{-1}); UV/Vis (film): λ_{max} =

364, 384 and 410 nm; Fluorescence emission (film) (λ_{ex} = 383 nm): λ_{emis} = 506 nm; Lifetime (film): τ = 1.2 ns; Absolute quantum yield (film) = 1.5 %. HR-MS (EI): m/z: 381.9979; $C_{20}H_{14}S_4$ calcd: 381.9978; elemental analysis calcd (%) for $C_{20}H_{14}S_4$: C, 62.79; H, 3.69; S, 33.52; found: C, 62.76; H, 3.70; S, 32.98.

3.6.2.14. Synthesis of cis,cis-1,2,3,4-tetra(4-triphenylamine)-1,3-butadiene (8)

Compound **5** (0.316 g, 0.62 mmol) and $Cp_2Zr(pyr)(Me_3SiCCSiMe_3)^{44}$ (0.145 g, 0.31 mmol) were dissolved in 10 mL of THF, and the resulting mixture was allowed to stir for 12 hrs to give a dark red solution. A solution of HCl (0.6 mL, 2.0 M solution in Et_2O, 1.2 mmol) was added followed by stirring for 12 hrs at room temperature, resulting in an orange mixture. The solvent was removed under reduced pressure, and the residue was washed with cold Et_2O (2 × 5 mL, -35 °C) and then acetone (3 × 5 mL) to yield **8** as a bright yellow solid (0.083 g, 26 %). M.p. >250 °C; TGA: T_{dec} = 401 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-6.99 (m, 48H, Ar*H*), 6.81 (d, $^3J_{HH}$ = 8.8 Hz, 4H, Ar*H*), 6.72 (d, $^3J_{HH}$ = 8.8 Hz, 4H, Ar*H*), 6.32 (s, 2H, =C*H*-); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 147.8, 147.5, 146.9, 146.2, 144.1, 134.4, 131.7, 131.3, 130.5, 130.4, 129.3, 124.5, 124.4, 124.3, 123.0, 122.8, 122.5; UV/Vis (THF): λ_{max} (ε) = 305 and 380 nm (6.68 and 8.88 × 10^4 mol^{-1} dm^3 cm^{-1}); UV/Vis (film): λ_{max} = 310 and 410 nm; Fluorescence emission (THF) (λ_{ex} = 423 nm): λ_{emis} =

472 nm, fluorescence quantum yield: Φ = 13 %, relative to quinine sulfate in 1.0 N H_2SO_4; absolute quantum yield (THF): Φ = 34.6 %; Lifetime (1 × 10^{-5} M solution in THF): τ = 2.1 ns; Fluorescence emission (film) (λ_{ex} = 420 nm): λ_{emis} = 516 nm; Lifetime (film): τ = 2.0 ns; Absolute quantum yield (film) = 3.6 %. HR-MS (MALDI): m/z: 1026.4656; $C_{76}H_{58}N_4$ calcd: 1026.4661; elemental analysis calcd (%) for $C_{76}H_{58}N_4$: C, 88.86; H, 5.69; N, 5.45; found: C, 87.30; H, 5.69; N, 5.24. Despite repeated attempts, combustion analyses gave consistently low values for carbon content. See Figures 3.48 and 3.49 in the Section 3.6.4 for copies of the NMR spectra.

3.6.2.15. Attempted synthesis of the ($^nBu_3Sn)_2C_4Ar_4$ (Ar = cumyl) (9) in various solvents

To a solution of $Cp_2ZrC_4Ar_4$ (**6a**) (0.100 g, 0.134 mmol) in solvent (7 mL) (see Table 3.8) was added $^nBu_3SnCl$ (73 µL, 0.27 mmol), and the mixture was stirred over 24/72 hours to give a dark red solution. The volatiles were removed under vacuum and the residue was dissolved in $CDCl_3$ for NMR analysis.

3.6.2.16. Attempted synthesis of the $(Bu_3Sn)_2C_4Ar_4$ (Ar = cumyl) (9) in the presence of CuCl

To a solution of $Cp_2ZrC_4Ar_4$ (**6a**) (0.089 g, 0.12 mmol) in THF or toluene (5 mL) in the dark was added CuCl (0.002 g, 0.01 mmol), followed by stirred for 5 min. $^{n}Bu_3SnCl$ (65 μL, 0.24 mmol) was then added and the reaction mixture was stirred for 24 hours to give a dark red solution. The volatiles were removed under vacuum and the residue was dissolved in $CDCl_3$ for NMR analysis.

3.6.2.17. Attempted synthesis of the 1,4-diiodo-1,3-butadiene ($I_2C_4Ar_4$; Ar = cumyl)

To a cold (-78 °C) solution of $Cp_2ZrC_4Ar_4$ (**6a**) (0.202 g, 0.271 mmol) in THF (15 mL) was added dropwise a solution of iodine (0.137 g, 0.541 mmol) in 15 mL of THF over 30 min. The reaction mixture was then stirred for 30 min. at -78 °C, then the cold bath was removed and the flask was allowed to warm to the room temperature over the next three hours. Afterwards, the reaction mixture was extracted with 50 mL of dichloromethane and the organic layer was washed with aqueous $Na_2S_2O_3$ (2 × 50 mL), water (2 × 50 mL) and dried over $MgSO_4$. The volatiles were removed from the organic fraction *in vacuo* and the residue was dissolved in $CDCl_3$ for NMR analysis.

3.6.2.18. Reaction of $CuBr_2$ with zirconacycle 6a

To a dark red solution of $Cp_2ZrC_4Ar_4$ (**6a**) (0.102 g, 0.137 mmol) in THF (5 mL) was added solid $CuBr_2$ (0.186 g, 0.833 mmol) which led to the formation of a brown slurry after 5 min. The reaction mixture was allowed to stir for another 6 hrs to give a dark brown (black) solution and metallic precipitate. The volatiles were removed under vacuum and the residue was dissolved in $CDCl_3$ for NMR analysis.

3.7. Crystallographic data

Table 3.7. Crystallographic data for compounds **2** and **5**.

	2	**5**
empirical formula	$C_{20}H_{22}$	$C_{38}H_{28}N_2$
fw	262.37	512.62
cryst. dimens. (mm^3)	0.42 × 0.41 × 0.03	0.28 × 0.27 × 0.08
cryst. syst.	monoclinic	triclinic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
unit cell dimensions		
a (Å)	10.6089 (3)	5.61635 (9)
b (Å)	9.2470 (2)	11.25535 (19)
c (Å)	8.2942 (2)	11.73665 (18)
α (deg)		104.2892 (5)
β (deg)	103.0778 (12)	98.3322 (5)
γ (deg)		93.1680 (6)
V ($Å^3$)	792.56 (3)	708.16 (2)
Z	2	1
ρ (g cm^{-3})	1.099	1.202
abs. coeff. (mm^{-1})	0.457	0.534
T (K)	173 (1)	233 (1)
$2\Theta_{max}$ (deg)	145.42	147.63
total data	5299	4967
unique data (R_{int})	1577 (R_{int} = 0.0280)	2733 (R_{int} = 0.0311)
obs. data [$I > 2\sigma(I)$]	1420	2540
params.	91	182
R_1 [$I > 2\sigma(I)$]^a	0.0520	0.0515
wR_2 [all data]^a	0.1484	0.1453
Max/Min $\Delta\rho$ (e $Å^{-3}$)	0.388/–0.208	0.279/–0.221

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table 3.8. Crystallographic data for compounds **6a**, **7a** and **7b**.

	6a	**7a**	**7b**
empirical formula	$C_{50}H_{54}Zr$	$C_{40}H_{46}$	$C_{20}H_{14}S_4$
fw	746.15	526.77	382.55
cryst. dimens. (mm^3)	0.25 × 0.18 × 0.11	0.41 × 0.05 × 0.02	0.32 × 0.22 × 0.15
cryst. syst.	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
unit cell dimensions			
a (Å)	12.1953 (2)	11.4211 (2)	11.6007 (3)
b (Å)	17.8804 (3)	20.4302 (3)	6.55480 (10)
c (Å)	19.9108 (3)	14.2505 (2)	12.6109 (3)
α (deg)	99.7859 (7)		
β (deg)	100.4733 (8)	105.6028 (9)	110.6202 (5)
γ (deg)	102.8382 (7)		
V (Å^3)	4061.19 (11)	3202.61 (9)	897.50 (3)
Z	4	4	2
ρ (g cm^{-3})	1.220	1.093	1.416
abs. coeff. (mm^{-1})	2.446	0.453	4.833
T (K)	173 (1)	173 (1)	173 (1)
2 Θ_{max} (deg)	148.21	135.95	145.09
total data	15789	20490	5982
unique data (R_{int})	15789 (R_{int} = 0.0405)	5623 (R_{int} = 0.0646)	1776 (R_{int} = 0.0202)
obs. data [$I > 2\sigma(I)$]	14538	4172	1759
params.	917	446	143
R_1 [$I > 2\sigma(I)$]^a	0.0356	0.0584	0.0322
wR_2 [all data]^a	0.0987	0.1742	0.0951
Max/Min $\Delta\rho$ (e Å^{-3})	0.844/–0.499	0.357/–0.242	0.367/–0.400

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

3.8. NMR spectral data

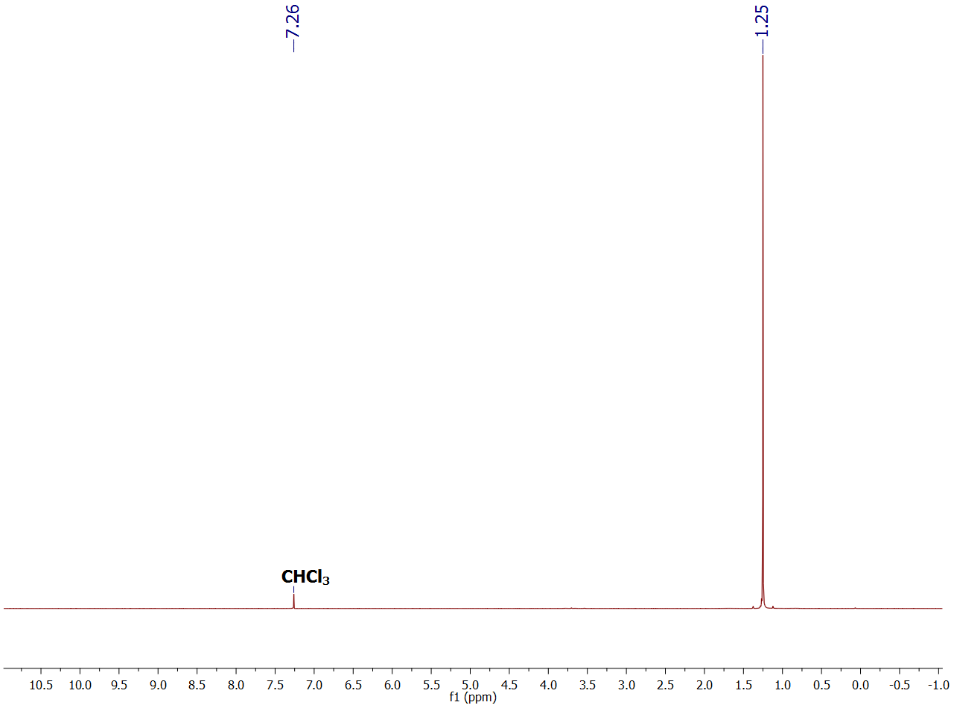


Figure 3.26. ^{1}H NMR (in CDCl$_3$) spectrum of compound **1**.

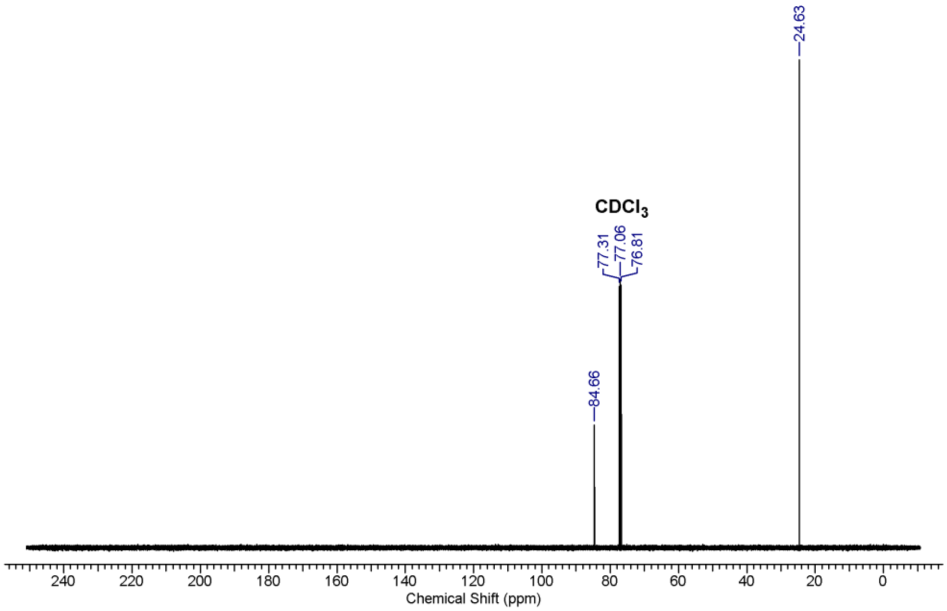


Figure 3.27. $^{13}C\{^1H\}$ NMR (in CDCl$_3$) spectrum of compound **1**.

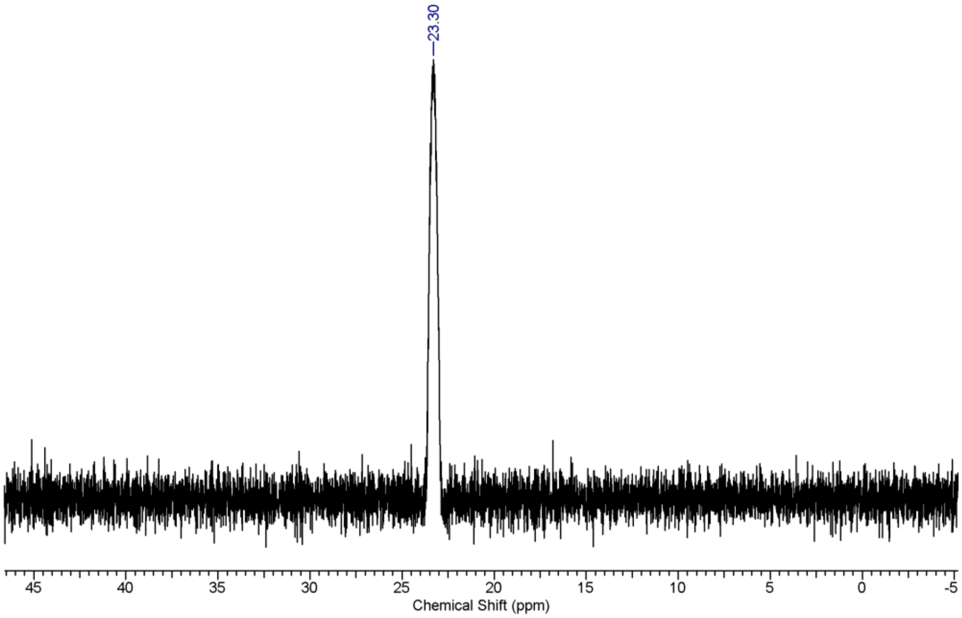


Figure 3.28. $^{11}B\{^1H\}$ NMR (in CDCl$_3$) spectrum of compound **1**.

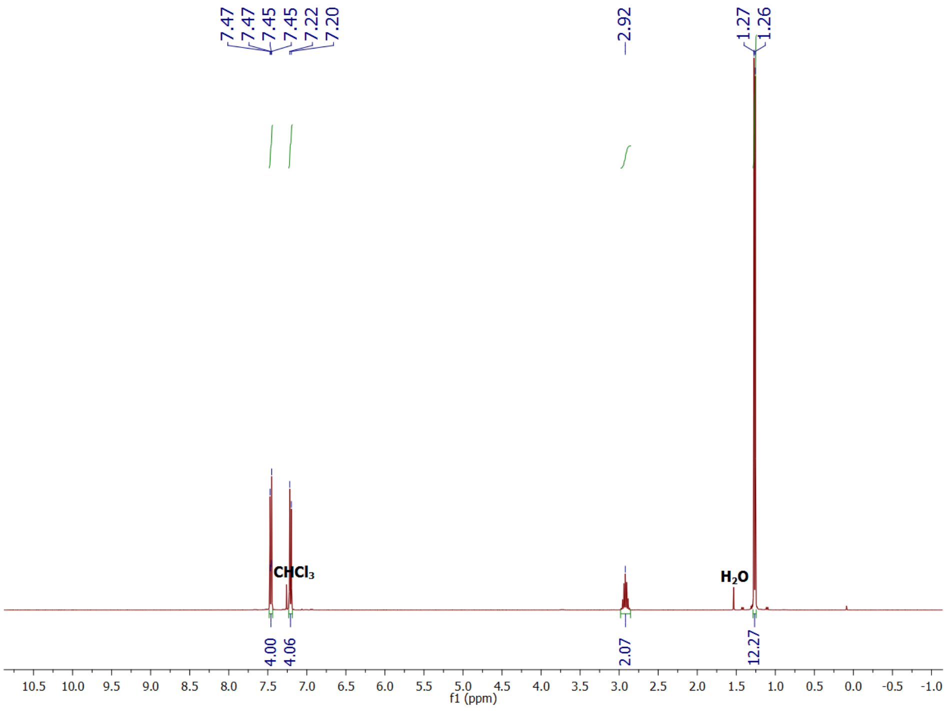


Figure 3.29. ^{1}H NMR (in CDCl$_3$) spectrum of 1,2-bis(4-isopropylphenyl)ethyne (**2**).

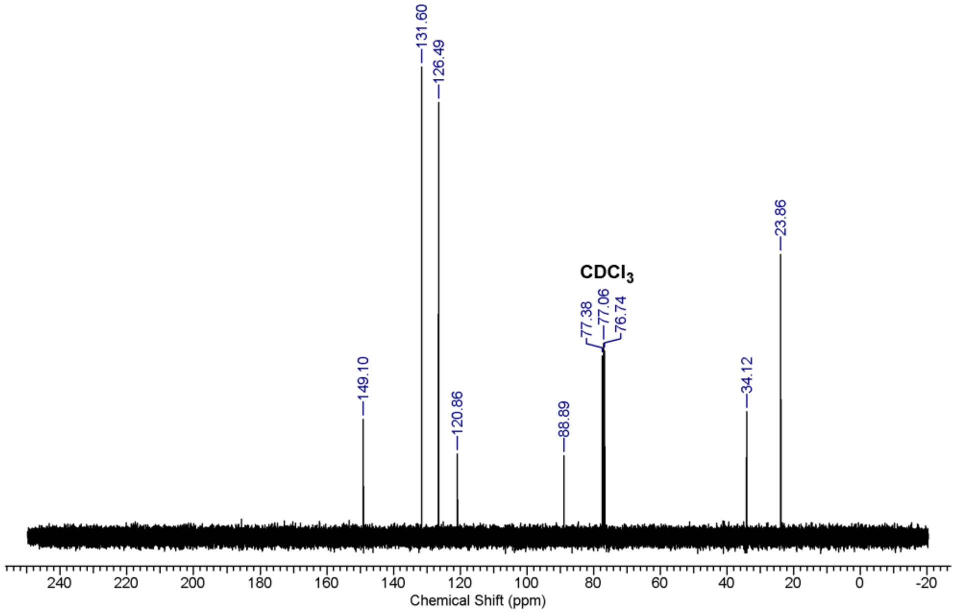


Figure 3.30. ^{13}C{^{1}H} NMR (in CDCl$_3$) spectrum of 1,2-bis(4-isopropylphenyl)ethyne (**2**).

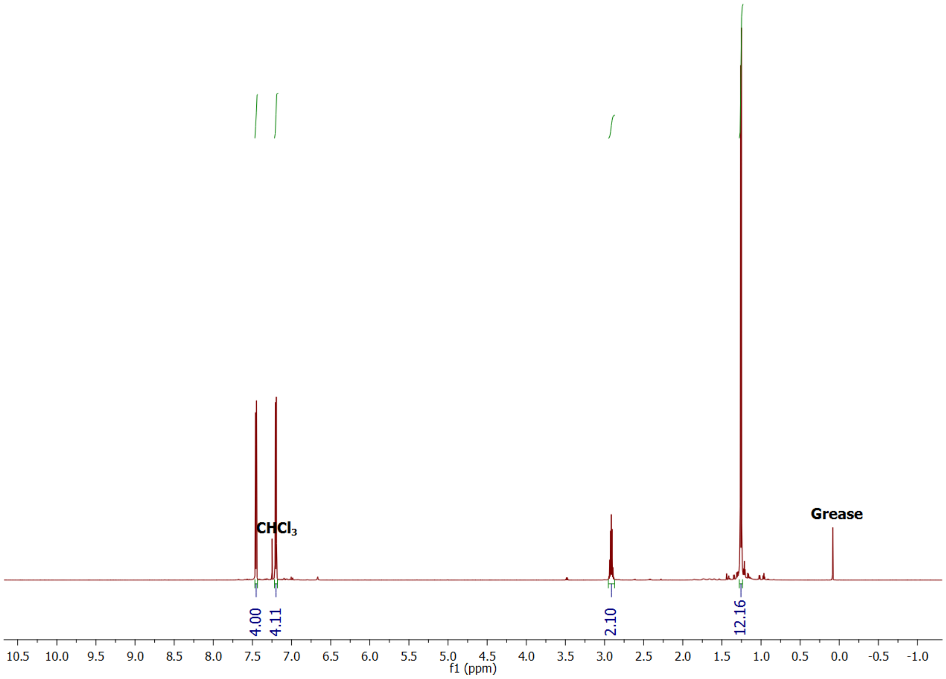


Figure 3.31. ^{1}H NMR (in $CDCl_3$) spectrum of crude **2** after alternative to column chromatography purification method: cold (-30 °C) diethyl ether wash (2 × 4 mL).

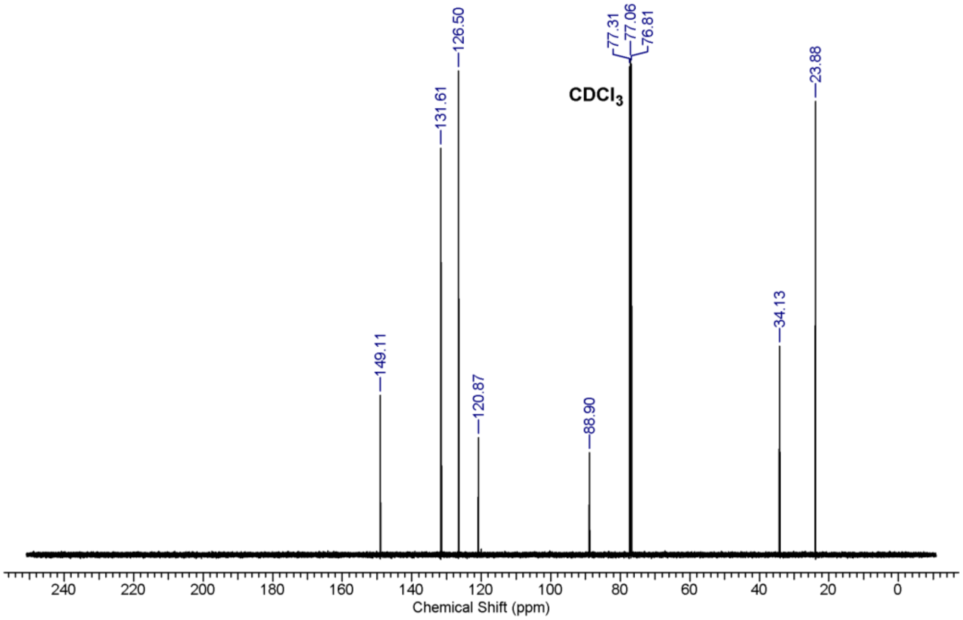


Figure 3.32. $^{13}C\{^{1}H\}$ NMR (in $CDCl_3$) spectrum of crude **2** after alternative to column chromatography purification method: cold (-30 °C) diethyl ether wash (2 × 4 mL).

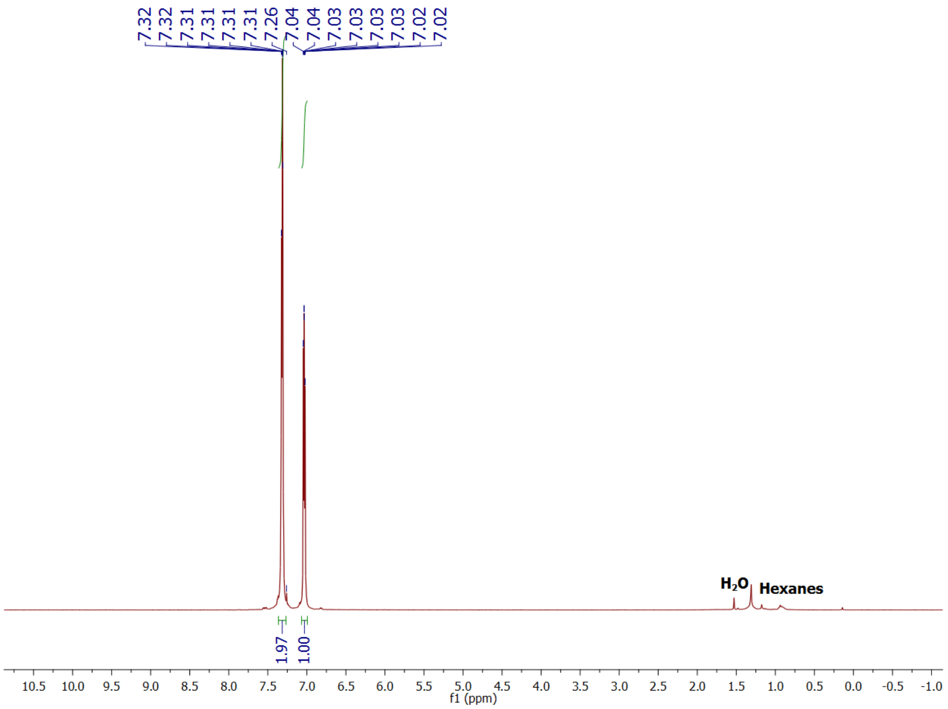


Figure 3.33. ^{1}H NMR (in CDCl$_3$) spectrum of 1,2-bis(thiophen-2-yl)ethyne (**3**).

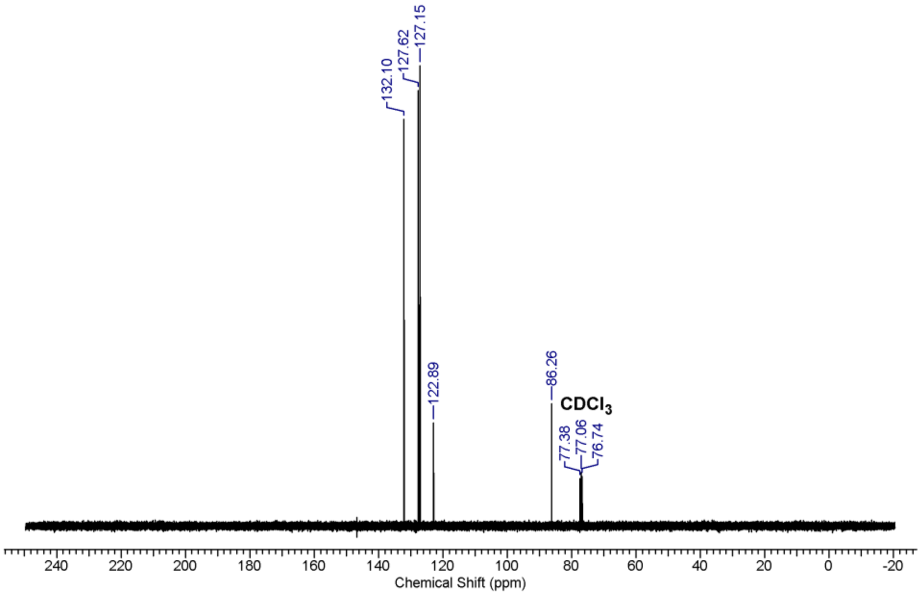


Figure 3.34. ^{13}C{^{1}H} NMR (in CDCl$_3$) spectrum of 1,2-bis(thiophen-2-yl)ethyne (**3**).

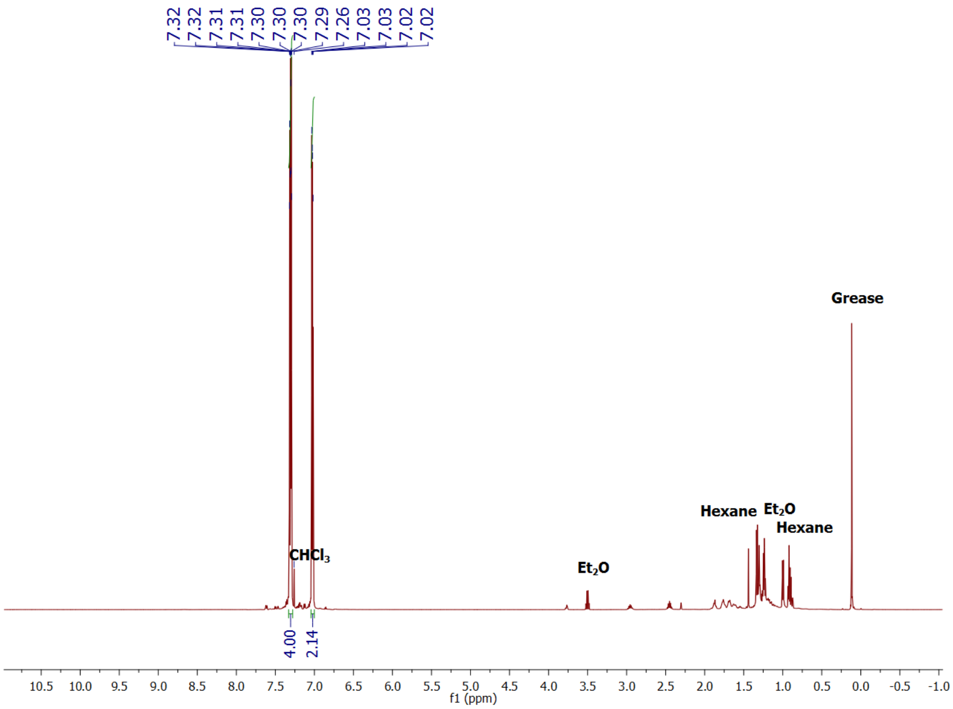


Figure 3.35. ^{1}H NMR (in $CDCl_3$) spectrum of crude **3** after alternative to column chromatography purification method: cold (-30 °C) diethyl ether wash (2 × 4 mL).

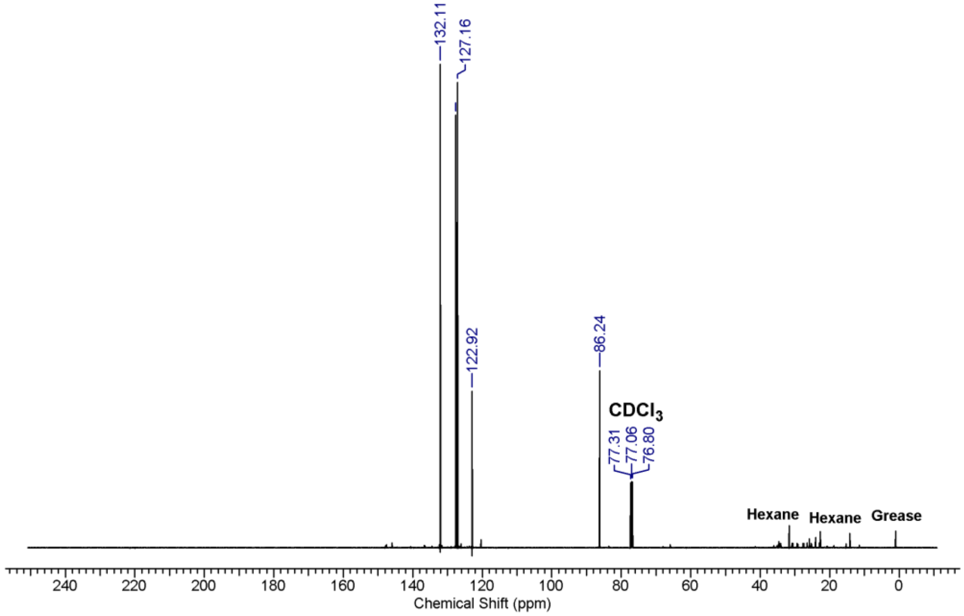


Figure 3.36. $^{13}C\{^1H\}$ NMR (in $CDCl_3$) spectrum of crude **3** after alternative to column chromatography purification method - cold (-30 °C) diethyl ether wash (2 × 4 mL).

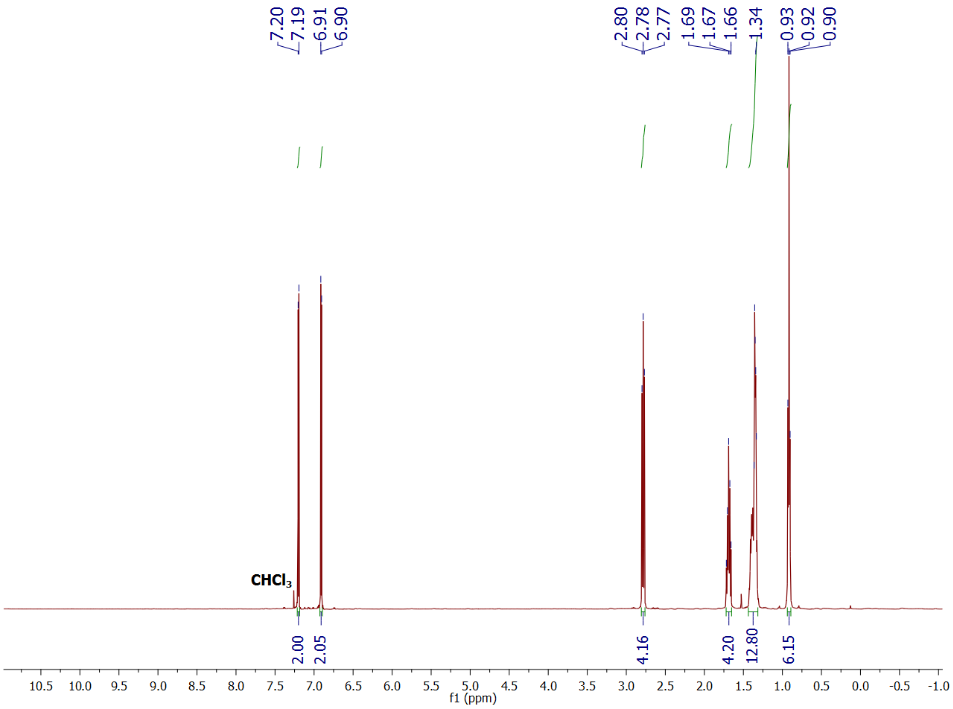


Figure 3.37. ^{1}H NMR (in CDCl$_3$) spectrum of bis(3-hexyl-2-thienyl)ethyne (**4**).

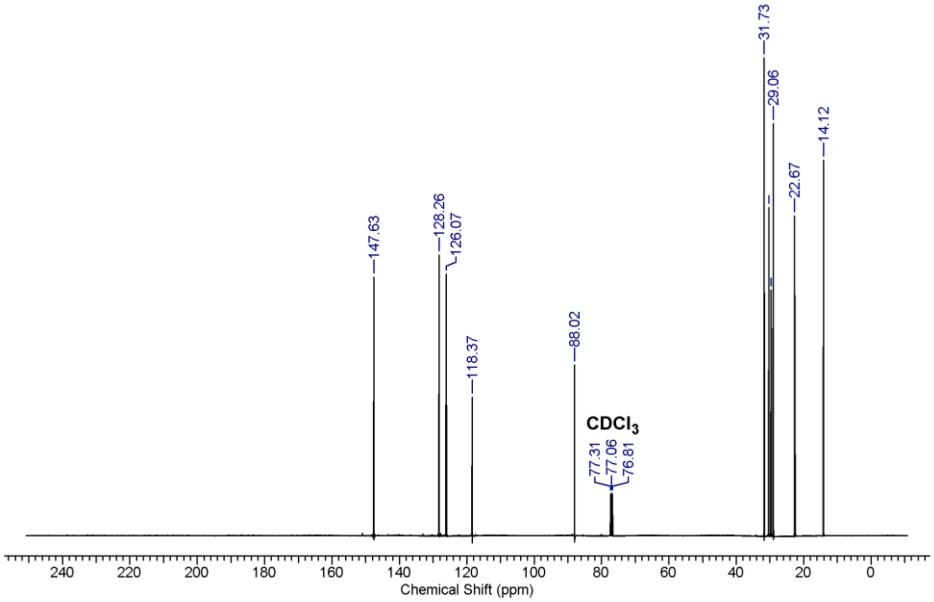


Figure 3.38. ^{13}C{^{1}H} NMR (in CDCl$_3$) spectrum of bis(3-hexyl-2-thienyl)ethyne (**4**).

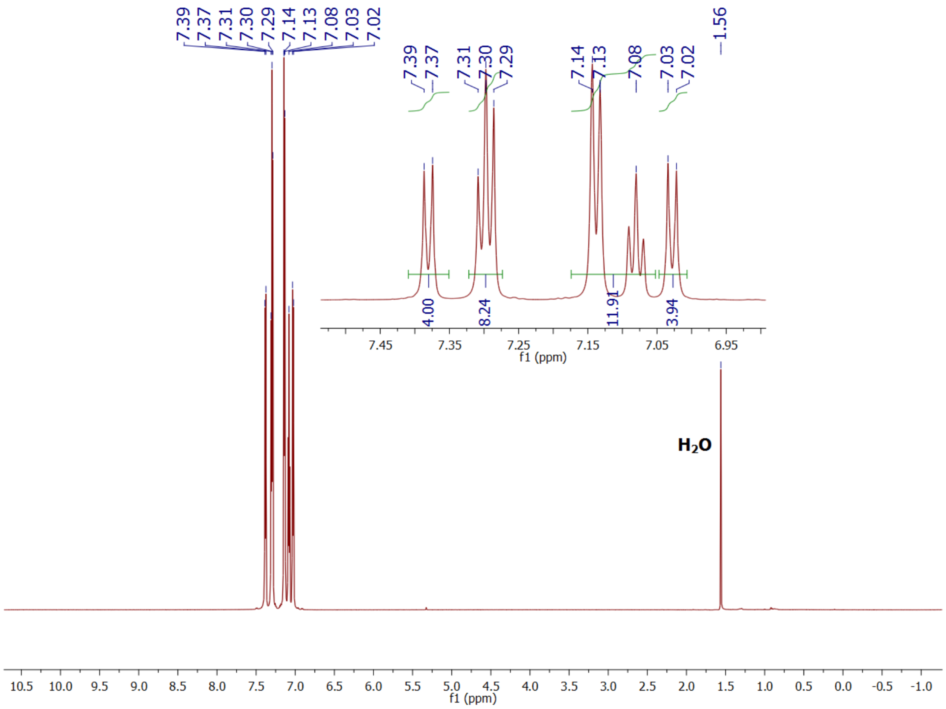


Figure 3.39. ^{1}H NMR (in $CDCl_3$) spectrum of 1,2-bis(triphenylamine)-ethyne (**5**).

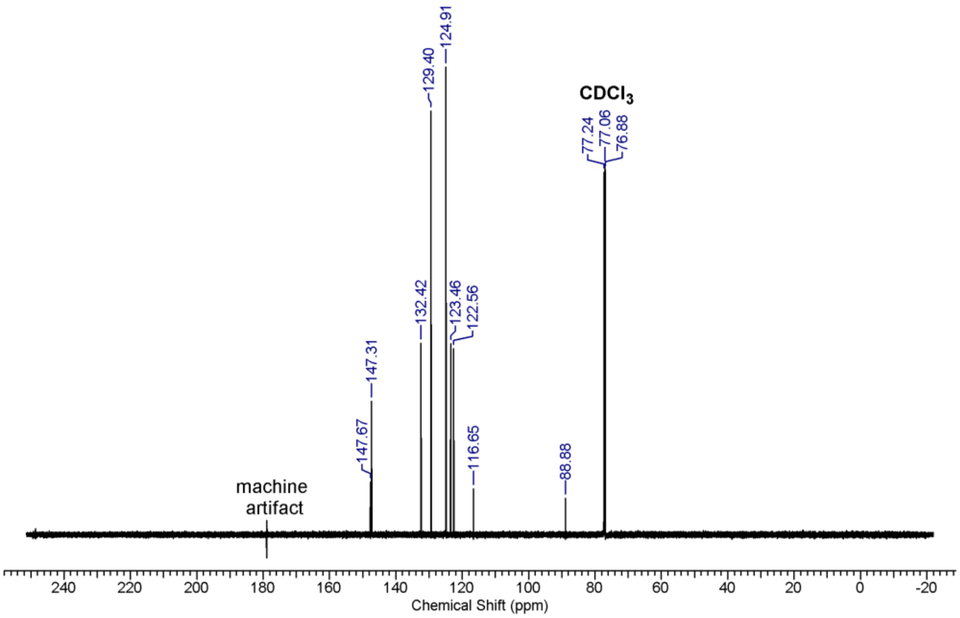


Figure 3.40. $^{13}C\{^1H\}$ NMR (in $CDCl_3$) spectrum of **5**.

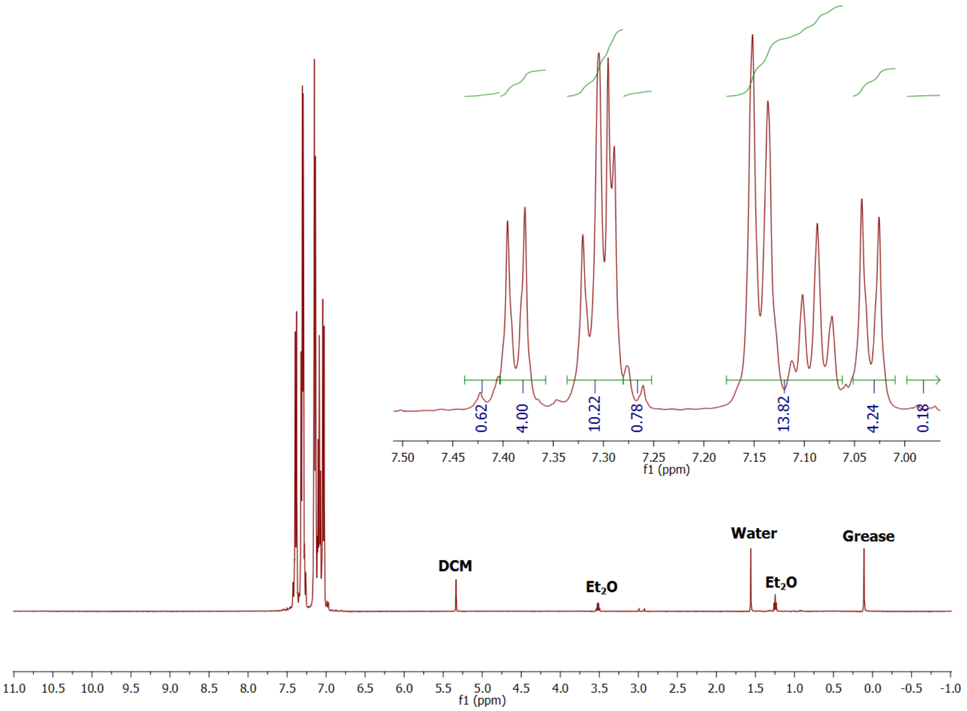


Figure 3.41. ^{1}H NMR (in $CDCl_3$) spectrum of crude compound **5** after diethyl ether wash.

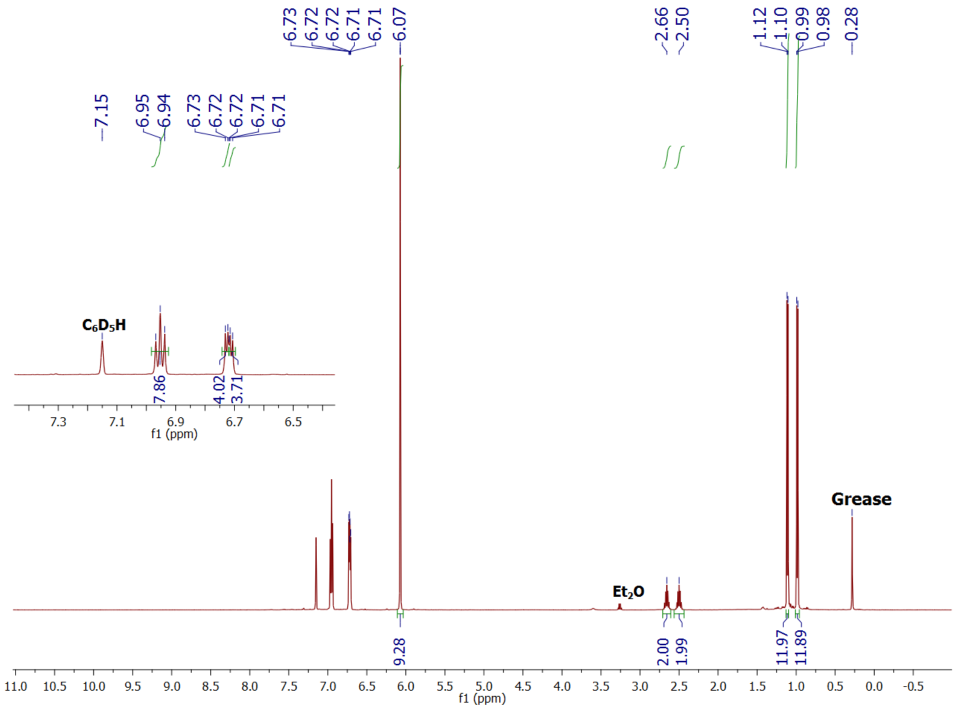


Figure 3.42. ^{1}H NMR (in C_6D_6) spectrum of bis(cyclopentadienyl)zirconium-2,3,4,5-tetra(4-isopropylphenyl)methanide (**6a**).

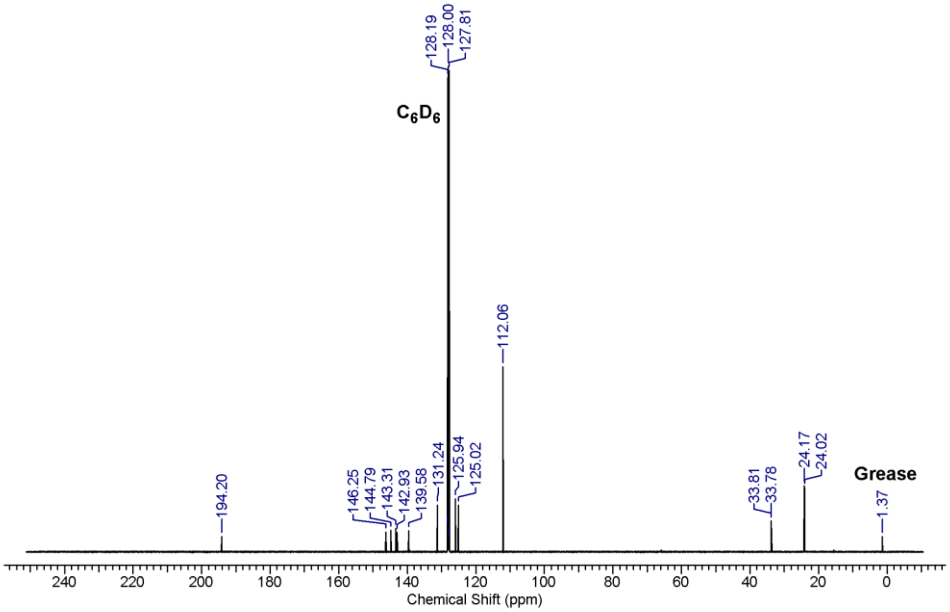


Figure 3.43. $^{13}C\{^{1}H\}$ NMR (in C_6D_6) spectrum of bis(cyclopentadienyl)zirconium-2,3,4,5-tetra(4-isopropylphenyl)methanide (**6a**).

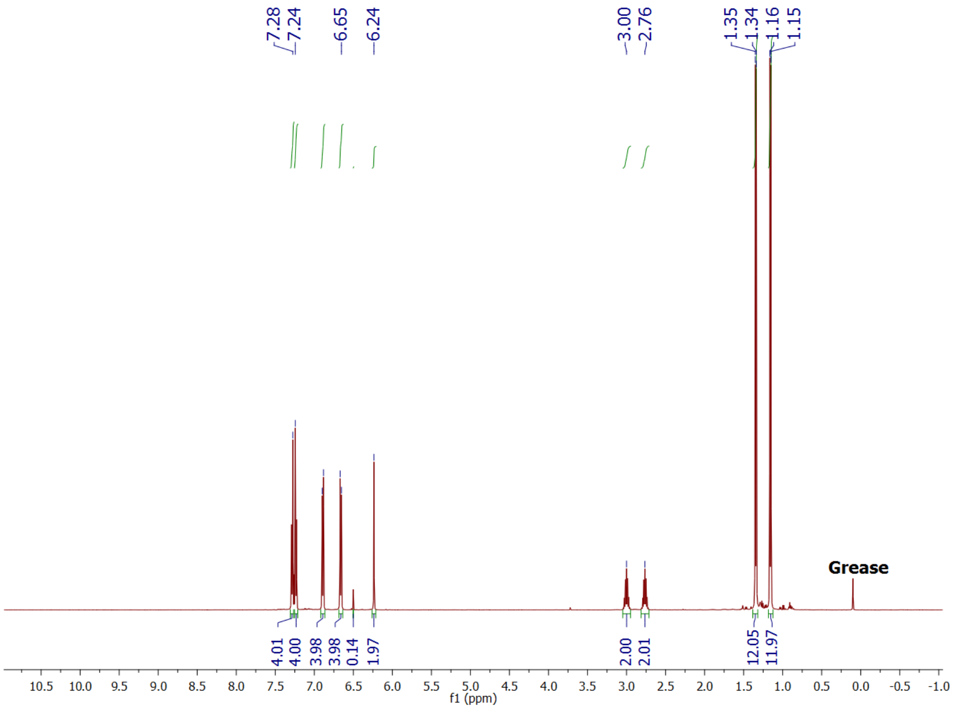


Figure 3.44. ^{1}H NMR (in $CDCl_3$) spectrum *cis*,*cis*-1,2,3,4-tetra(4-isopropylbenzene)-1,3-butadiene (**7a**).

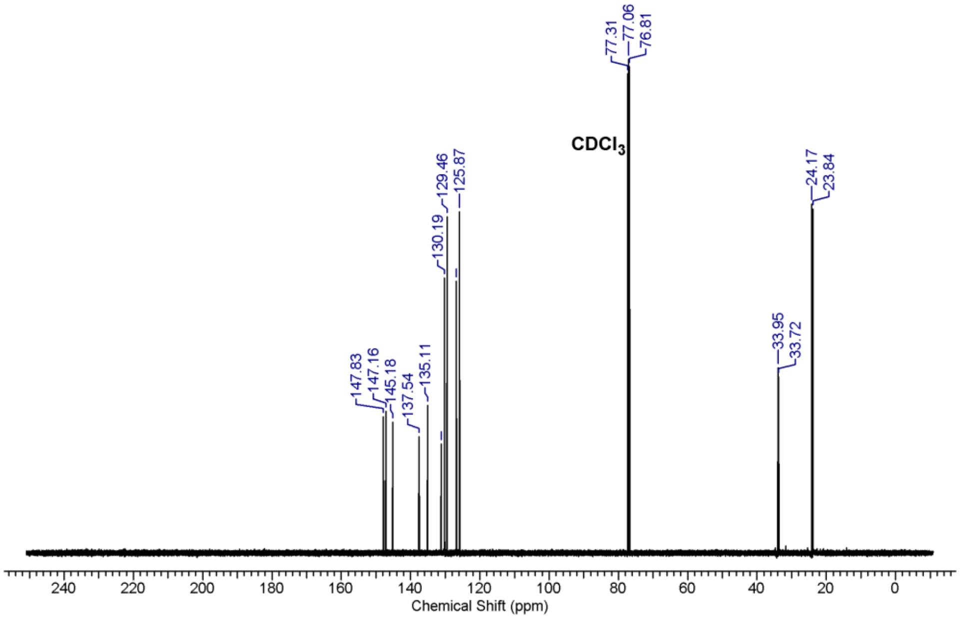


Figure 3.45. $^{13}C\{^{1}H\}$ NMR (in $CDCl_3$) spectrum of compound **7a**.

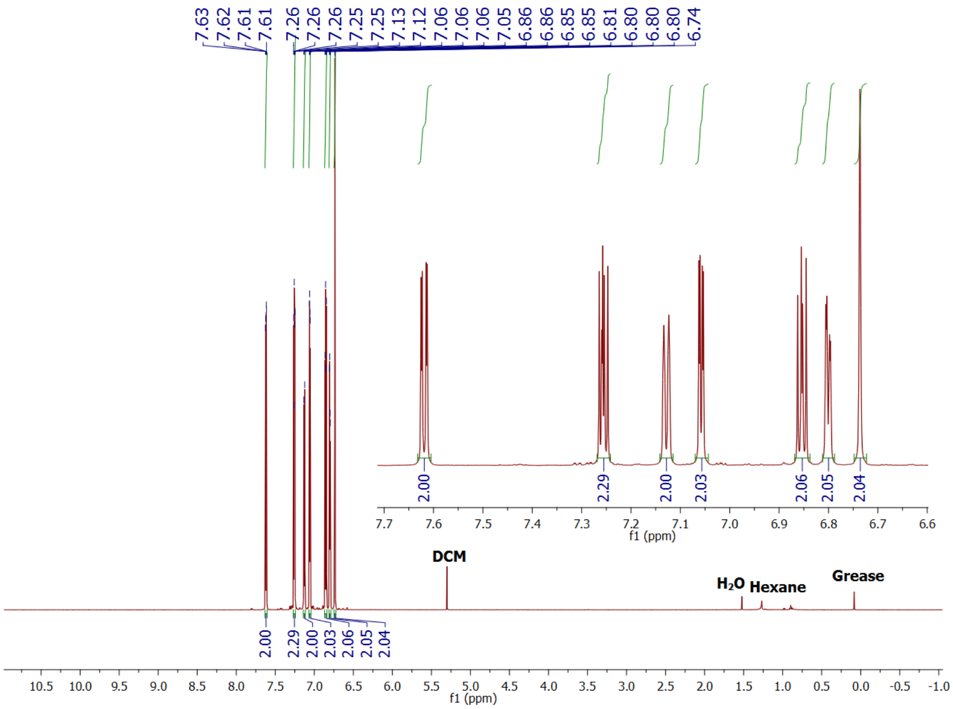


Figure 3.46. ^{1}H NMR (in $CDCl_3$) spectrum of *cis*,*cis*-1,2,3,4-tetra(2-thienyl)-1,3-butadiene (**7b**).

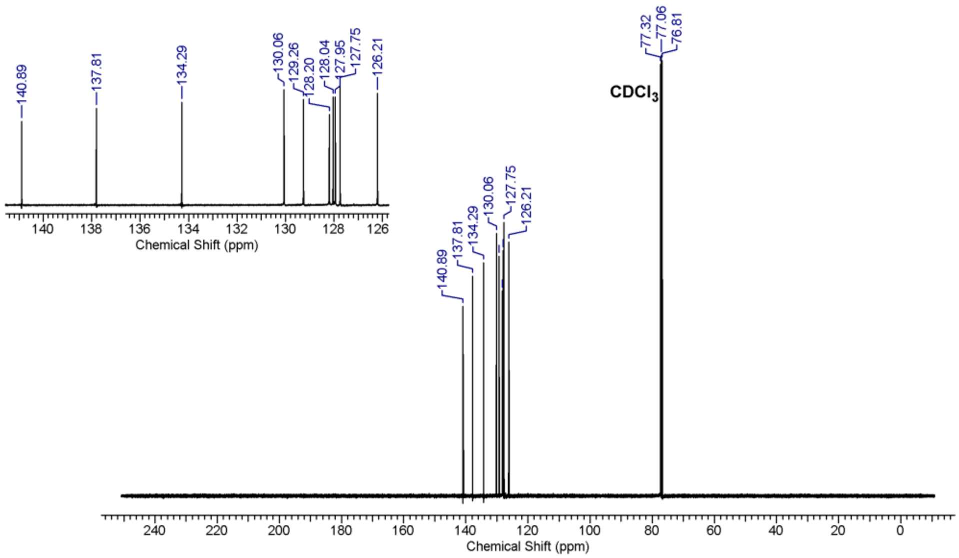


Figure 3.47. $^{13}C\{^{1}H\}$ NMR (in $CDCl_3$) spectrum of compound **7b**.

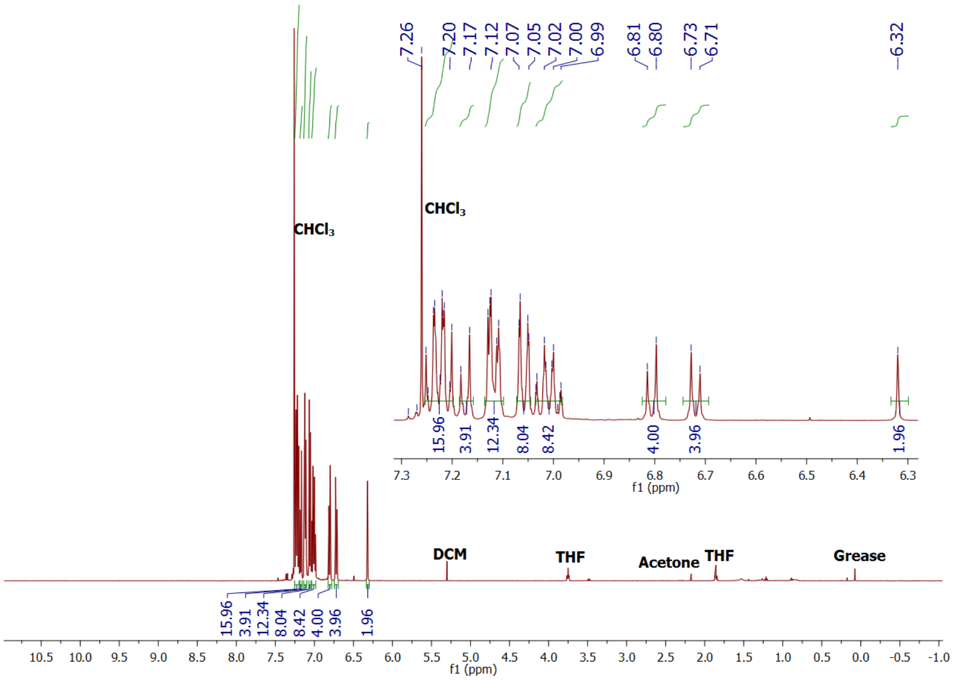


Figure 3.48. ^{1}H NMR (in $CDCl_3$) spectrum of *cis*,*cis*-1,2,3,4-tetra(4-triphenylamine)-1,3-butadiene (**8**).

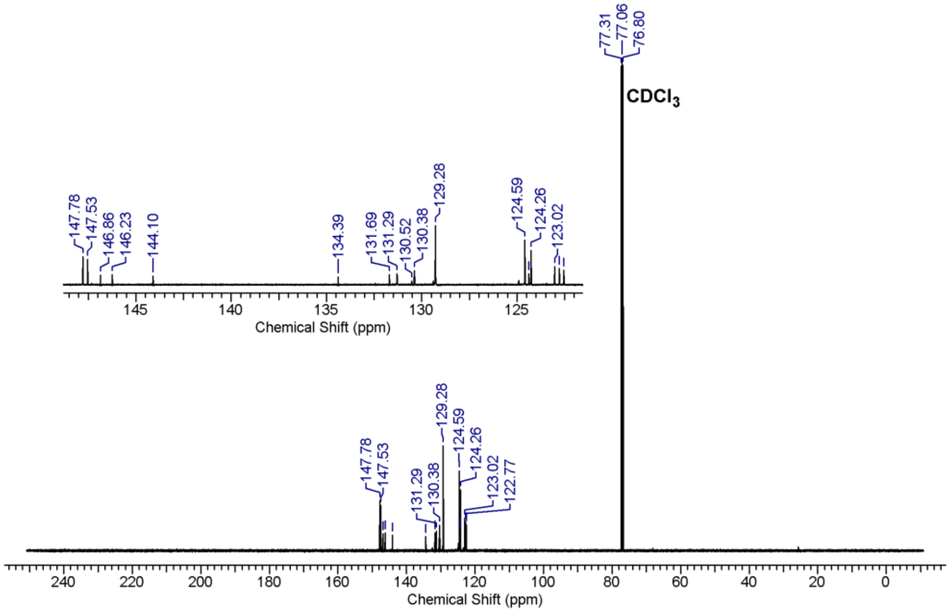


Figure 3.49. $^{13}C\{^1H\}$ NMR (in $CDCl_3$) spectrum of compound **8**.

3.9. Ultraviolet-visible spectroscopy (UV/Vis) measurements

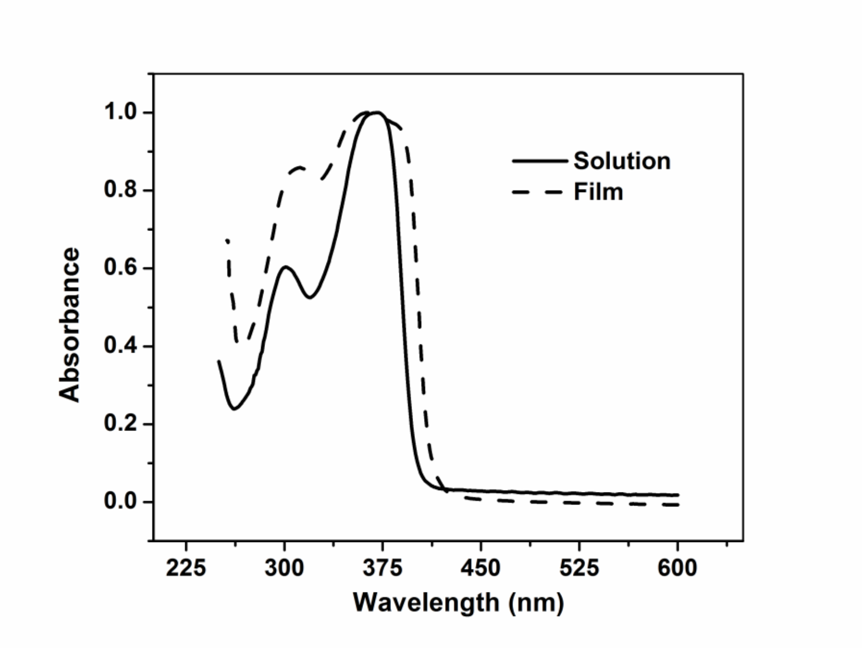


Figure 3.50. UV/Vis absorption spectra of compound **5** in solution (THF) and film state (normalized).

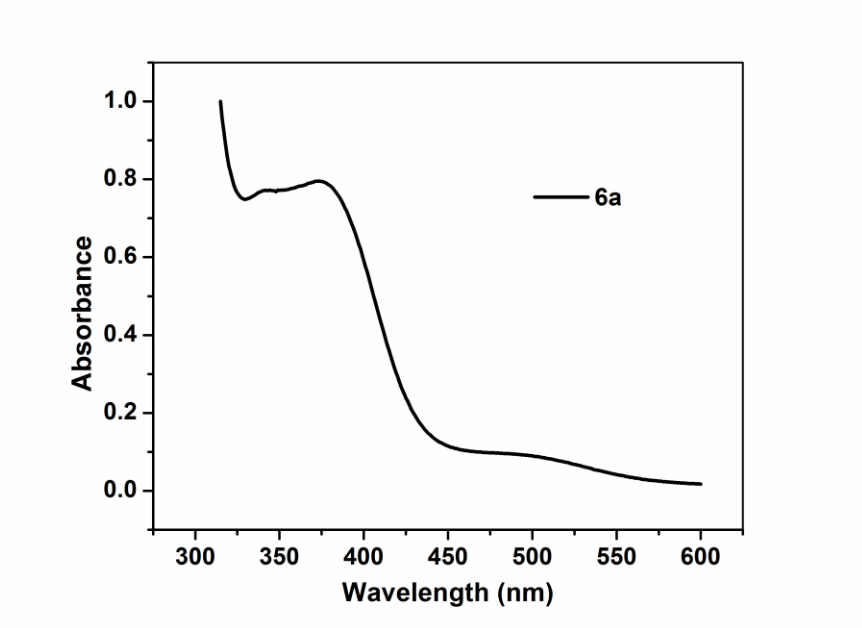


Figure 3.51. UV/Vis absorption spectrum of compound **6a**.

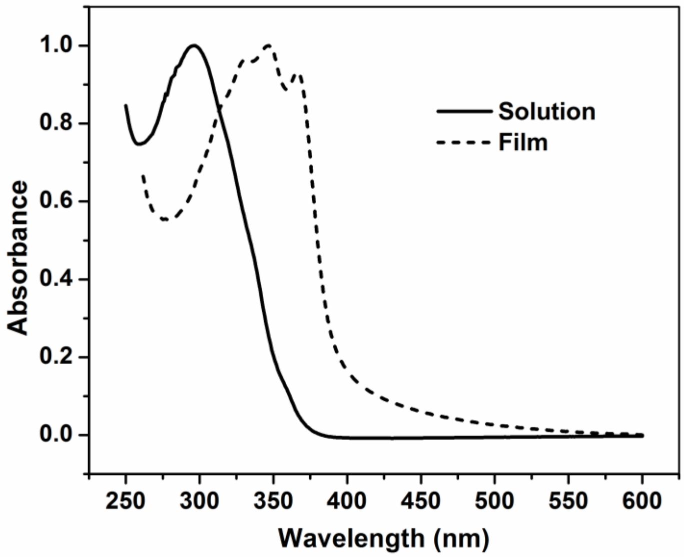


Figure 3.52. UV/Vis absorption spectra of compound **7a** in solution (THF) and film state (normalized).

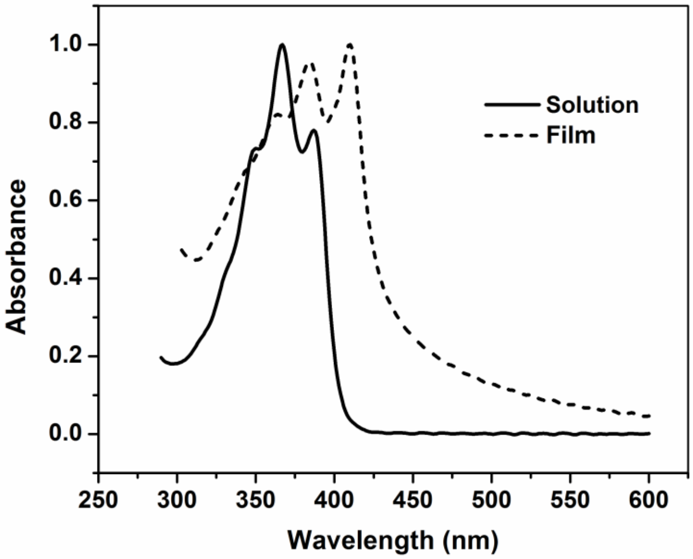


Figure 3.53. UV/Vis absorption spectra of compound **7b** in solution (THF) and film state (normalized).

3.10. Photostability studies

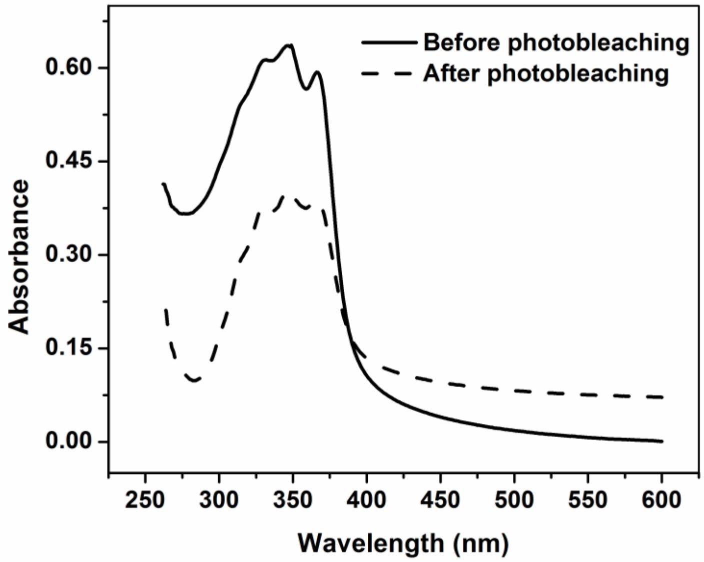


Figure 3.54. UV/Vis absorption spectra of the film of **7a** before and after photobleaching.

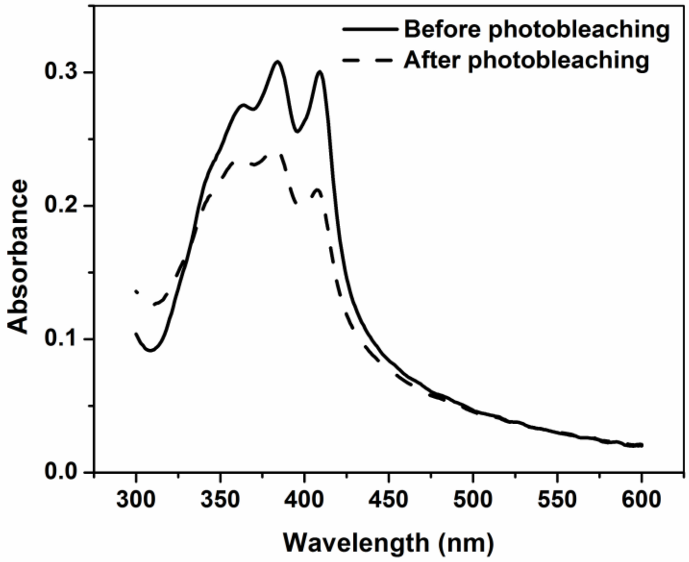


Figure 3.55. UV/Vis absorption spectra of the film of **7b** before and after photobleaching.

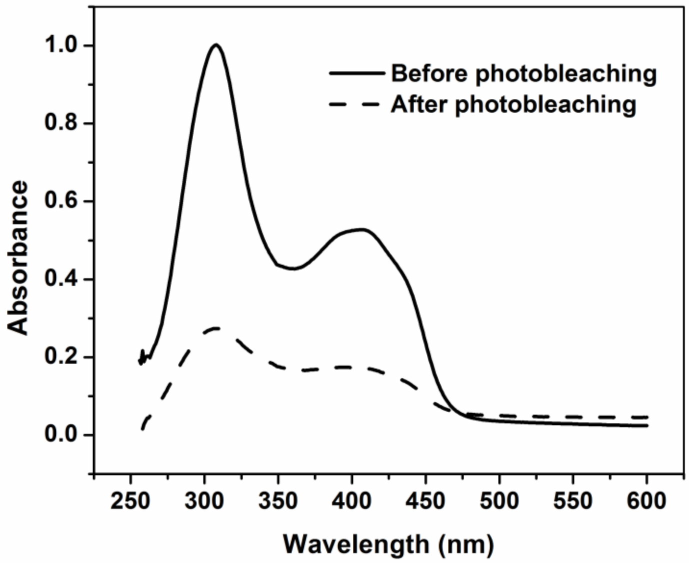


Figure 3.56. UV/Vis absorption spectra of the film of **8** before and after photobleaching.

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Chapter 4: Synthetic explorations of luminescent (a)symmetric tellurophenes

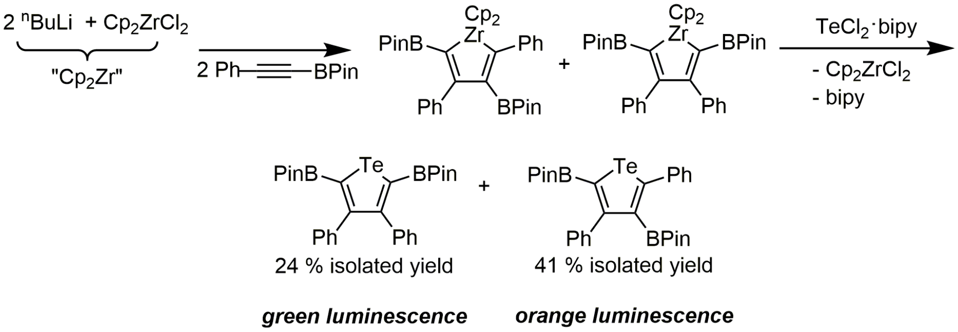
4.1. Abstract

In this chapter, a series of symmetrical tellurium heterocycles were prepared via zirconocene-mediated coupling. Despite possible excited state singlet-triplet crossing due to the heavy atom effect, triphenylamine (TPA)-bearing tellurophenes displayed green fluorescence in the solid state due to restriction of molecular motion of the sterically demanding amine substituents. In addition, some of the newly reported tellurophenes were investigated as possible hole transport layers in perovskite-based solar cells. The regioselective synthesis of phosphorescent asymmetric tellurophenes containing pinacolborane (BPin) group at the 2-positions was attempted, either via one-pot procedures or through the isolation of zirconacyclopropene intermediates. This synthetic strategy would allow access to new libraries of molecular luminescent light-emitters with considerable thermal stability.

4.2. Introduction

Sulfur-containing heterocycles, *i.e.*, thiophenes, are the most commonly used light-harvesting/charge-transporting materials, but their narrow light absorption range is a major limitation for optoelectronic applications such as in solar cells, or as photodetectors.[1] Substitution of a sulfur atom by heavier tellurium[2] creates a new class of materials with advantageous properties, such as decreased HOMO-LUMO energy gaps, high polarizability, high dielectric constants, and the ability to emit light from long-lived triplet excited states, *i.e.*, phosphorescence.[3] Narrow optical bandgaps increase solar light absorption, leading to potentially improved overall power conversion efficiencies of photovoltaic cells. On the other hand, phosphorescence, emission from triplet excited states, can lead to enhancement of LED internal emission quantum efficiencies beyond the theoretical maximum of 25 % for fluorophors to 100 %.[4] In addition, significant Te···Te intermolecular interactions cause enhanced interchain electronic coupling in the solid state, which potentially facilitates the mobility of charge carriers, a favorable property for organic photovoltaics and thin film transistors.[3]

In general, tellurophenes are non-emissive due to the "heavy-metal effect" whereby heavy elements encourage singlet-to-triplet crossing, leading to the formation of long-lived triplet excited states that are prone to self (triplet-triplet annihilation) or external (oxygen and/or solvent-mediated) quenching.[5] At the same time, luminescent behavior from tellurium heterocycles was originally noted in frozen solutions at 77 K, originating from the restriction of intramolecular rotations and the suppression of molecular aggregation and self-quenching.[5b, 6] Recently our group uncovered a new class of pinacolboronate (BPin)-capped tellurophenes which show efficient green phosphorescence in the solid state at room temperature and in the presence of water and oxygen.[7] Further studies revealed that Te(II) center and BPin group(s) placed at the 2- or 5-positions of a tellurophene ring are involved in the emission process. Asymmetric phosphorescent tellurophenes containing BPin and Ph groups were obtained as a mixture of isomers (Scheme 4.1), where each isomer had a different emission color (orange and green), thus enabling their manual separation under UV light.[8]



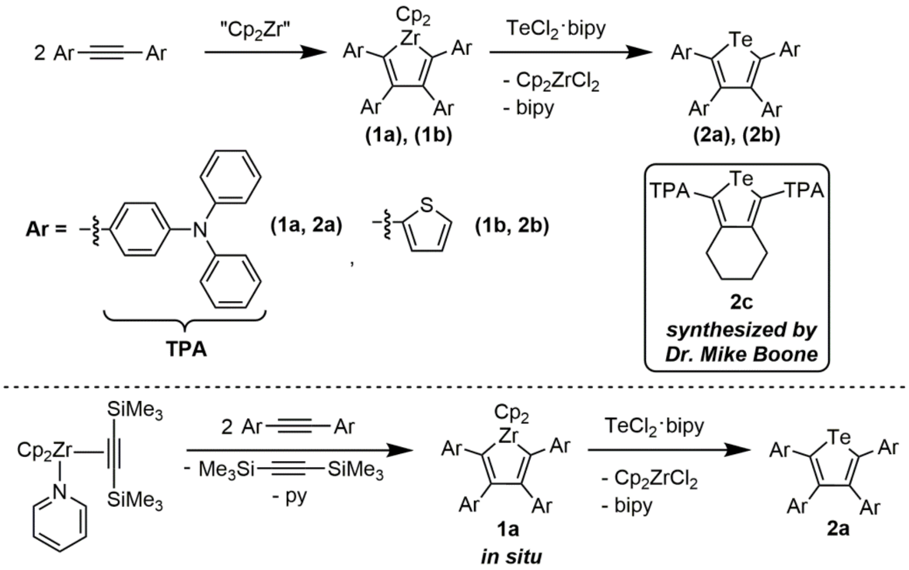
Scheme 4.1. Synthesis of asymmetric tellurophenes, reported in the Rivard group.

In this chapter new tellurium heterocycles with considerable thermal stability and potentially high carrier mobilities were synthesized *via* zirconium-mediated coupling. The development of a general regioselective synthetic protocol for generating phosphorescent asymmetrically-substituted tellurophenes (with BPin group at an adjacent position to tellurium) was attempted.

4.3. Results and discussion

4.3.1. Synthesis of the symmetrical tellurophenes 2a-c

Motivation for the molecular design of **2a-c** (Scheme 4.1) comes from prior work on emissive metalloles (*e.g.*, siloles),[9] and the enhanced two-photon absorption[10] and hole transport properties associated with triphenylamine (TPA)-based materials,[11] as well as the above mentioned properties one can obtain when heavy elements are present in heterole units.[12] Scheme 4.2 outlines the overall procedure used to prepare the symmetric tetrasubstituted tellurium heterocycles TeC_4(2-thienyl)$_4$ (**2a**) and $TeC_4(TPA)_4$ (**2b**; TPA = $-C_6H_4-N(C_6H_5)_2$). The disubstituted tellurophene **2c** was synthesized and characterized by Dr. Mike Boone, who graciously allowed this species to be included in this chapter for more insightful comparison of optoelectronic properties.



Scheme 4.2. Synthesis of symmetrical tellurium heteroles **2a-b**. Tellurophene **2c** was provided by Dr. Mike Boone.

To begin, the triphenylamine-substituted zirconacycle $Cp_2ZrC_4(TPA)_4$ (**1a**; TPA = $PhNPh_2$) and the previously reported tetrathiophene zirconacycle **1b** ($Cp_2ZrC_4T_4$; T = 2-thienyl)[9b] were obtained by combining two equiv. of the corresponding alkynes with *in situ* generated "Cp_2Zr" (made from Cp_2ZrCl_2/2 $^{n}BuLi$)[13] in THF. Formation of the zirconacycle **1a** was confirmed by multinuclear NMR spectroscopy and high-resolution mass spectrometry. Subsequent Zr/Te transmetallation chemistry between **1a**/**1b** and bipy•$TeCl_2$[14] yielded the target tellurophenes $TeC_4(TPA)_4$ (**2a**) and TeC_4T_4 (**2b**) as yellow solids in *ca.* 30 % yield after purification by column chromatography and further washing with hexanes. It is worth noting that tellurophene **2a** could also be obtained using a slightly different one-pot procedure. Specifically,

$Cp_2Zr(pyridine)(Me_3SiCCSiMe_3)$[15] and two equivalents of (TPA)C≡C(TPA) were combined in THF to yield a red solution containing the zirconacycle **1a**, which was reacted *in situ* with an excess of bipy•$TeCl_2$,[14] and after purification compound **2a** was obtained in a similar yield to the abovementioned procedure (when zirconacycle was isolated). Slow evaporation of CH_2Cl_2/Et_2O (**2a**) and THF/pentane (**2b**) solutions at room temperature yielded crystals of suitable quality for X-ray analysis and the respective structures of these tellurophenes are found as Figures 4.1 and 4.2. Unfortunately, despite repeated attempts, X-ray quality crystals of **2c** could not be obtained.

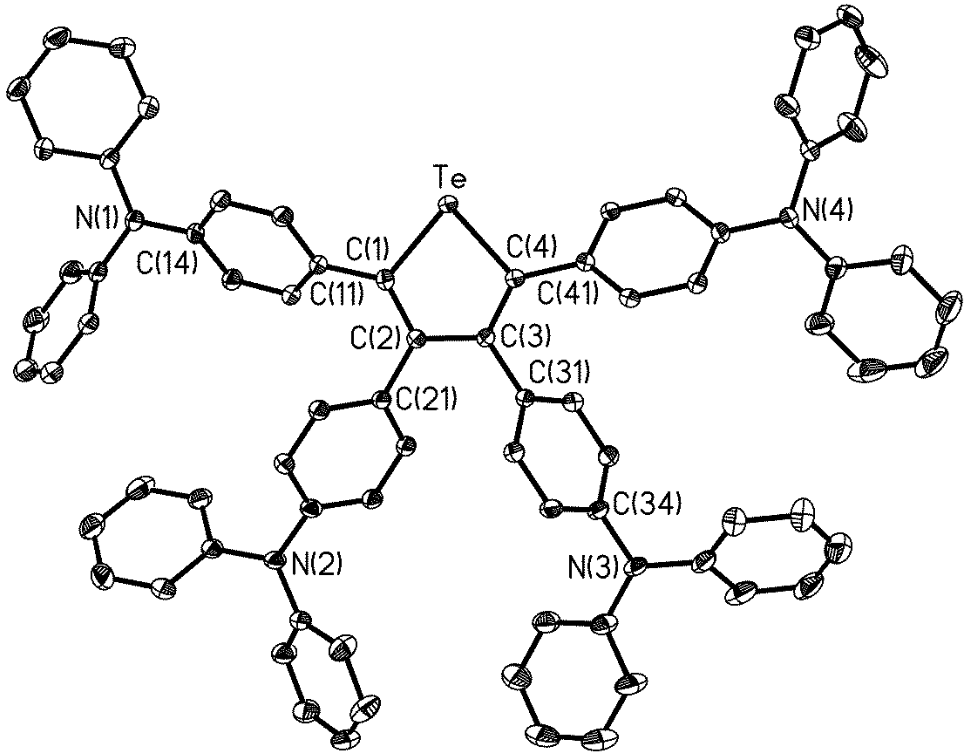


Figure 4.1. Thermal ellipsoid plot (30% probability) of compound **2a** with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Te–C(1) 2.055(2), Te–C(4) 2.066(2), C(2)–C(3) 1.462(3), N(1)–C(14) 1.423(3), N(3)–C(34) 1.434(3), C(1)–C(11) 1.485(3), C(3)–C(31) 1.493(3); C(1)–Te–C(4) 82.79(9), Te–C(1)–C(11) 118.63(16), Te–C(4)–C(41) 119.33(16), C(2)–C(3)–C(31) 121.43(19), C(3)–C(2)–C(21) 121.87(19).

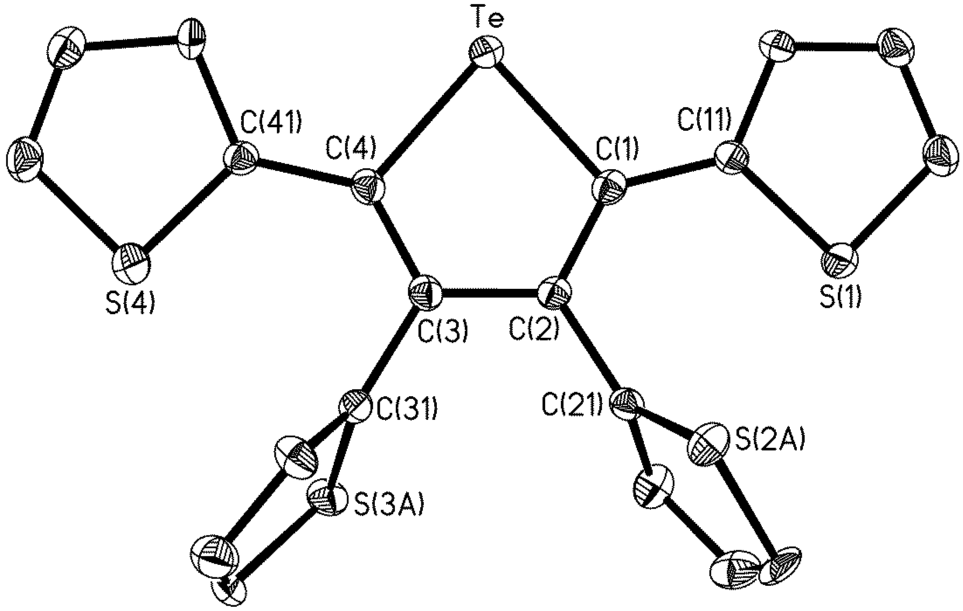


Figure 4.2. Thermal ellipsoid plot (30% probability) of compound **2b** with hydrogen atoms and chloroform solvate omitted for clarity. Selected bond lengths (Å) and angles (deg): Te–C(1) 2.071(5), Te–C(4) 2.087(5), C(2)–C(3) 1.443(8), C(2)–C(21) 1.493(7), C(4)–C(41) 1.447(8); C(1)–Te–C(4) 81.9(2), Te–C(1)–C(11) 117.3(4), Te–C(4)–C(41) 117.3(4), S(1)–C(11)–C(1) 123.7(4), S(4)–C(41)–C(4) 123.6(4).

In compound **2a**, the phenylene rings of TPA substituents that are appended to the TeC_4 core in the 2-, 3-, and 5-positions are canted by 41.20(8)°-44.54(7)°, while the remaining aryl group at the 4-position is twisted by 57.32(9)°. In contrast, in **2b** the thienyl substituents in 2,5-positions are almost co-planar with TeC_4 ring (*e.g.*, dihedral angle is 9.8(3)°), while the remaining thienyl groups are significantly canted by *ca.* 81°. The intraring Te-C bond lengths are similar to what is observed within earlier reported BPin-capped tellurophenes.[7-8, 16] The shortest intermolecular Te···Te distances in the solid state are 5.23 Å and 4.09 Å, for compounds **2a** and **2b**, respectively. In the case of **2a** the long Te---Te distance is indicative of a lack of significant interactions as the interatomic distance is greater than the sum of the van der Waals radii for two Te centers (4.12 Å);[17] this has been shown in the past to promote phosphorescence in the solid state by limiting triplet-triplet annihilation.[4]

4.3.2. Optical properties of the tellurophenes 2a-c

Because tellurophenes are an emerging class of solid state emitters,[4] the optical properties of the new tellurophenes **2a**-**c** were studied in more detail. The TPA-capped tellurophenes **2a** and **2c** show similar absorption in THF as triphenylamine itself (*i.e.*, λ_{max} = 300 nm).[18] Specifically, the tetraTPA-substituted tellurophene **2a** absorbs maximally at 302 nm, while the bis(TPA) tellurophene **2c** absorbs at λ_{max} = 307 nm; both of these species also have a shoulder at *ca.* 345 nm, which in the solid state becomes red-shifted by *ca*. 30 nm due to enhanced conjugation. Thus, the transition at 302 nm (**2a**) or 307 nm (**2c**) presumably corresponds to the triphenylamine unit, while the shoulder at 345 nm corresponds to π-π* transition in the tellurophene.

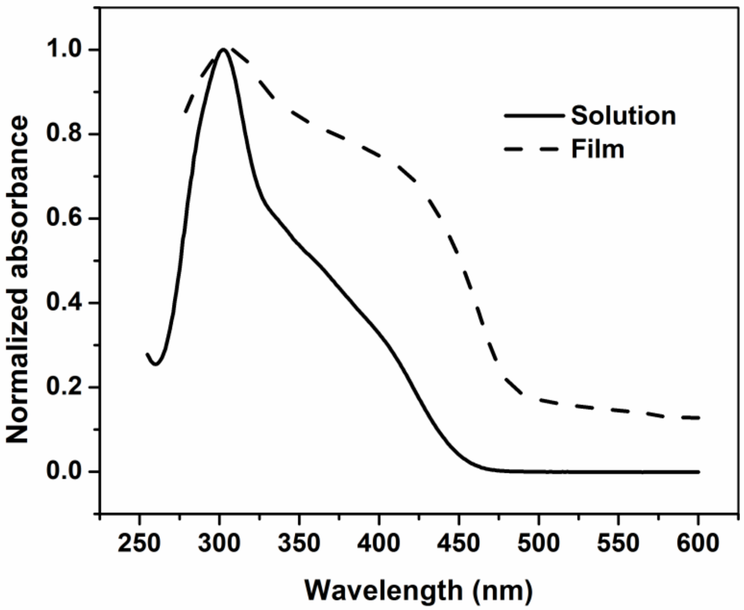


Figure 4.3. UV/Vis absorption spectra of compound **2a** in solution (THF) and film state.

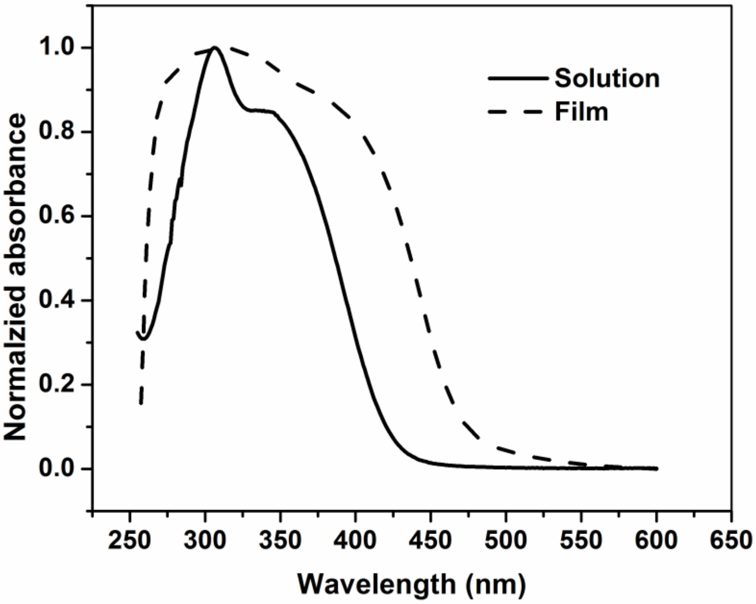


Figure 4.4. UV/Vis absorption spectra of compound **2c** in solution (THF) and film state.

Compound **2b** absorbs maximally at 394 nm with some discernable vibronic features. In the solid state an additional shoulder appears at 427 nm, presumably a result of extended conjugation. Moreover considerable tailing of the absorption to *ca*. 800 nm in films of **2b** was noted.[16, 19]

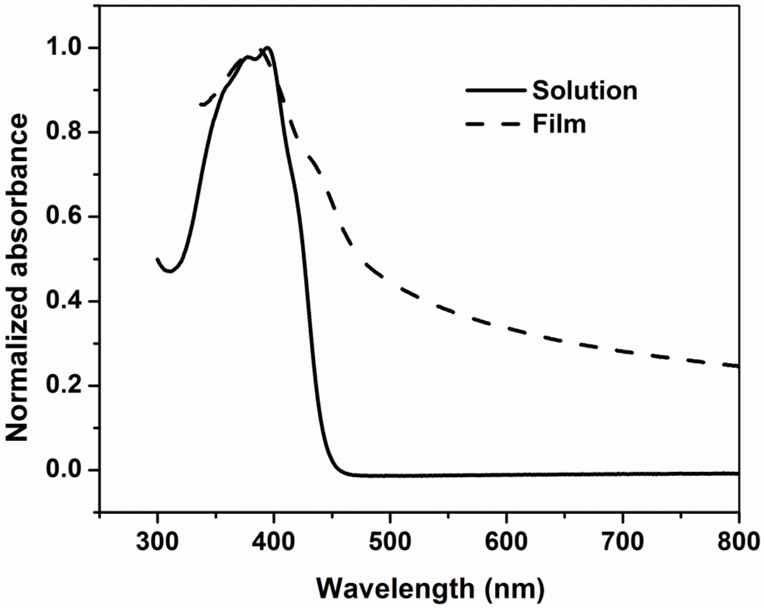


Figure 4.5. UV/Vis absorption spectra of compound **2b** in solution (THF) and film state.

The optical bandgaps were determined for **2a**-**2c** in THF solution (Figure 4.6) and they are 2.97 eV, 2.85 eV, and 3.06 eV, respectively. While the number of triphenylamine substituents did not significantly alter the optical bandgap (2.97 eV *vs* 3.06 eV), the thiophene-substituted **2b** has the smallest bandgap of 2.85 eV. Consistent with the red-shift of the absorption in the solid state, optical bandgaps for **2a-2c** decreased to 2.59 eV, 2.53 eV, and 2.72 eV, respectively (Figure 4.7).

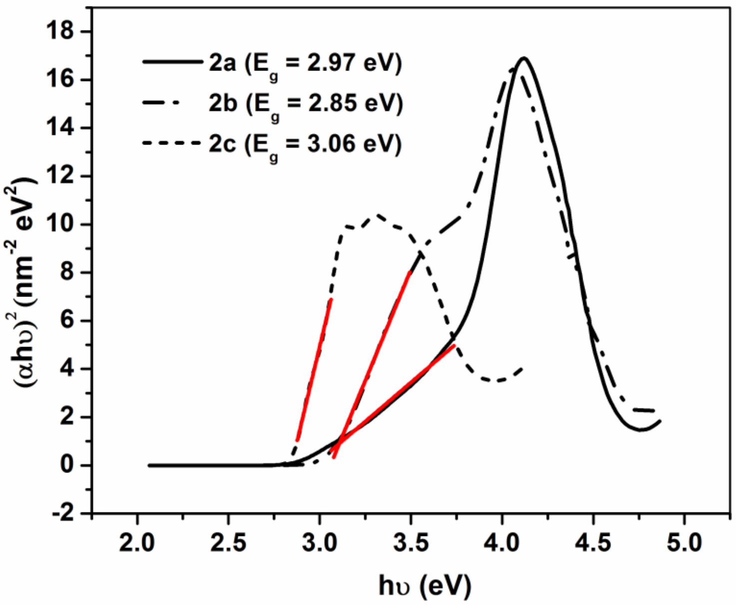


Figure 4.6. Optical bandgaps of tellurophenes **2a-2c** in solution (THF).

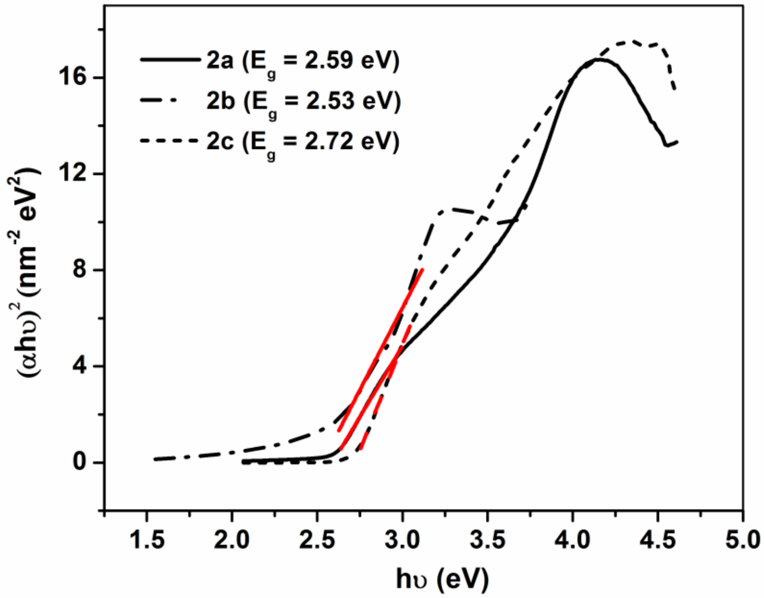


Figure 4.7. Optical bandgaps of tellurophenes **2a-2c** in film state.

In contrast to the non-emissive nature of **2b**, tellurophenes **2a** and **2c** show dramatic changes in emission character upon aggregation, which could be applied for sensing applications.[7] When **2a** and **2c** are dissolved in THF, blue-green emission is observed (λ_{em} = 472 and 484 nm, $\Phi_{absolute}$ = 11.8 % and 5.4 %, respectively), however in the film state there is a substantial red-shift in λ_{em} to 520 and 510 nm, corresponding to green colored emission (Figure 4.8 and 4.9). Tellurophenes **2a** and **2c** show fluorescence both in solution and in the solid state, according to the respective lifetimes: 1.8, 2.0 ns (**2a/c** in solution) and 1.8, 0.5 ns (**2a/c** in solid state). The tetrasubstituted analogue **2a** has a higher absolute quantum yield in both solution (11.8 % vs 5.4 %) and solid state (3.8 % vs 1.0 %), possibly due increased steric interaction between the four TPA groups, compared to **2c**, thus rotational non-radiative decay pathways are less efficient in **2a**.

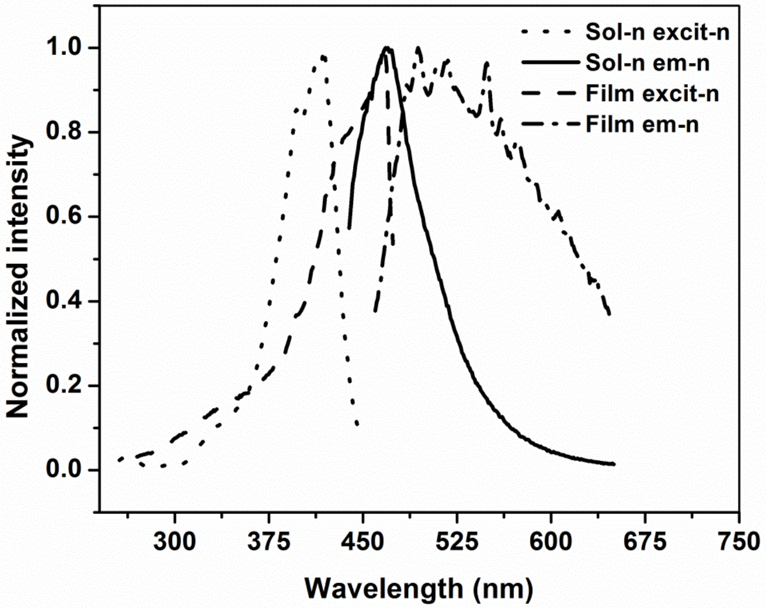


Figure 4.8. Normalized PL excitation and emission spectra of **2a** with λ_{ex} = 397 and 419 nm in THF, and λ_{ex} = 460 nm in the film state.

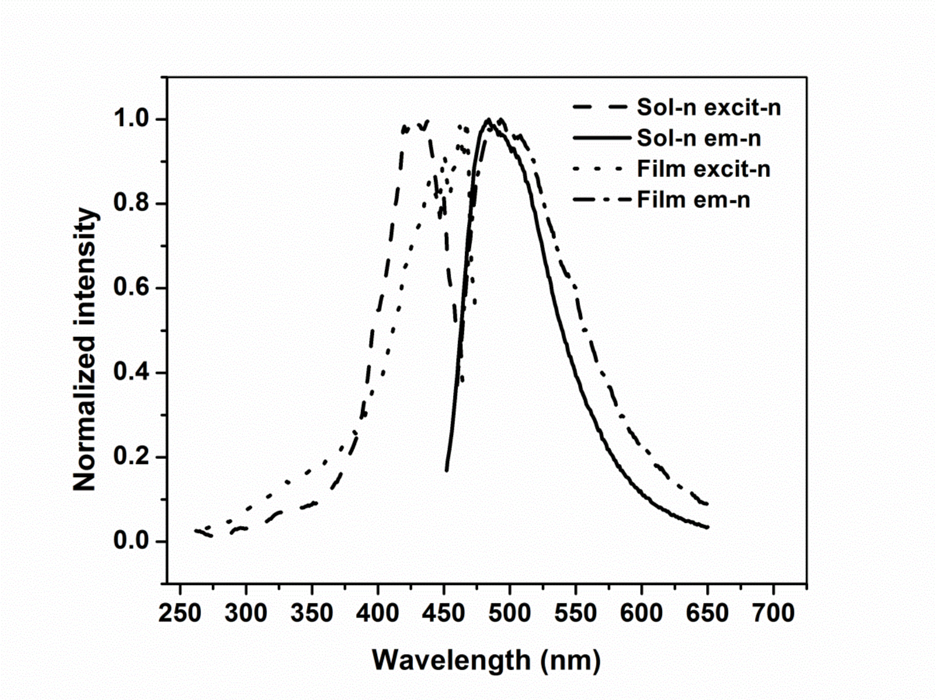


Figure 4.9. Normalized PL excitation and emission spectra of **2c** with λ_{ex} = 432 nm in THF and λ_{ex} = 440 nm in the film state.

To investigate the aggregation behavior of the tellurophenes **2a** and **2c**, miscible THF/H_2O mixtures were employed to adjust the solubility of tellurophenes and to eventually induce aggregation. The resulting emission spectra of **2a** and **2c** were recorded in various THF/H_2O mixtures, and the results are presented in Figures 4.10 and 4.11. Both derivatives have spectral tails that extend to *ca.* 650 nm. The tellurophenes **2a** and **2c** show aggregation-caused quenching[20] when the water fraction is over 60 %. Interestingly, **2a** shows color change from blue emission in pure THF (**2a**: λ_{em} = 472 nm) to green emission (**2a**: λ_{em} = *ca.* 505 nm) when the water composition exceeds 60 % (in aggregation state), albeit with much lower intensity.

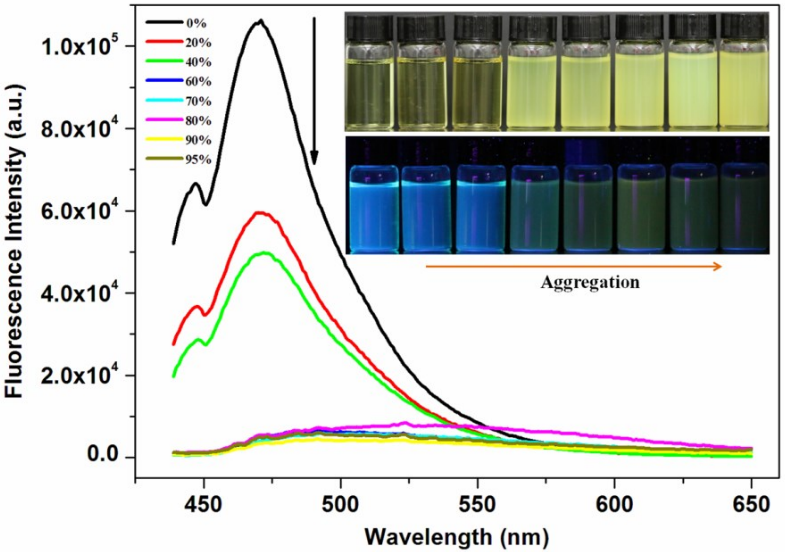


Figure 4.10. Photoluminescence (PL) spectra of **2a** in different THF/water ratios (listed as % water content). Inset: aggregates under UV light (λ_{ex} = 365 nm); [**2a**] = 10^{-4} M.

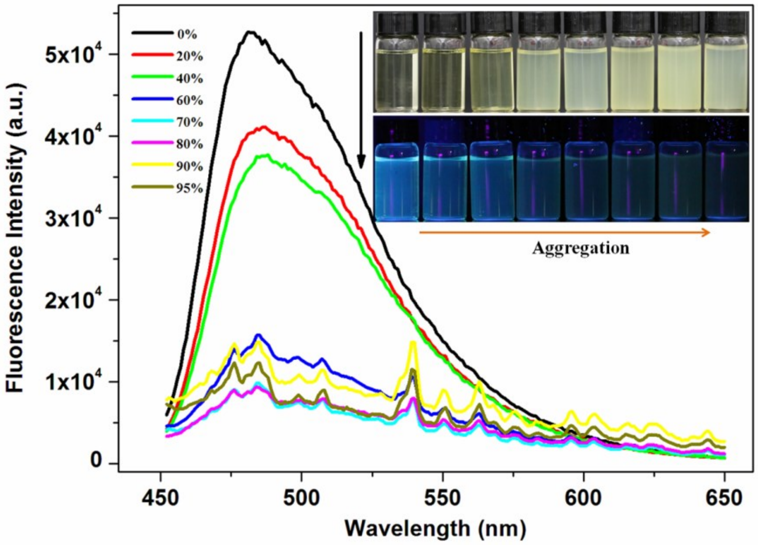


Figure 4.11. Photoluminescence (PL) spectra of **2c** in different THF/water ratios (listed as % water content). Inset: aggregates under UV light (λ_{ex} = 365 nm); [**2c**] = 10^{-4} M.

4.3.3. Thermal stability of functionalized tellurophenes

Thermal stability is a crucial parameter to consider when selecting functional materials for optoelectronic applications. The onsets of thermal decomposition (5 % weight loss, T_d) of compounds **2a**-**c** were evaluated under nitrogen using thermal gravimetric analysis (Figure 4.12). The tetrasubstituted tellurophene **2a** has the highest thermal stability (T_d = 457 °C), followed by the disubstituted **2c** (T_d = 299 °C). This trend could be explained by increase in the steric demand of heterocycles. The thiophene-capped tellurophene **2b** has the lowest decomposition temperature of 296 °C.

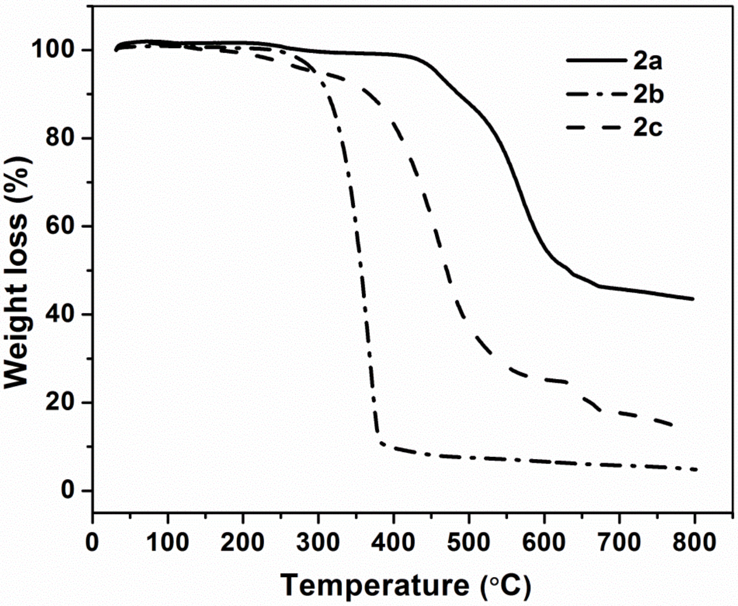


Figure 4.12. TGA thermograms of **2a-c** measured under N_2 (scan rate = 10 °C/min).

Surprised by dramatic weight loss of **2b** (up to 95 %), its thermal stability was further investigated by differential scanning calorimetry under nitrogen atmosphere. Upon heating from ambient temperature to 600 °C, the onset of thermal decomposition for **2b** was found at *ca.* 300 °C (in agreement with TGA data), while the melting point (T_m = 199 °C) was found to be in agreement with sealed capillary tube melting point data (Figure 4.13). The weight loss after the measurement was negligible (< 5 %), hence excluding the possibility that tellurophene **2b** evaporated during the study. Furthermore, to investigate the melt stability of **2b**, repeated heating-cooling DSC cycles (to temperatures *ca.* 20 °C above the melt) were performed under nitrogen atmosphere (Figure 4.14). Interestingly, it was found that tellurophene **2b** has a stable melt, as noted by reoccurring melting/recrystallization (T_c = 158 °C) after the first cycle.

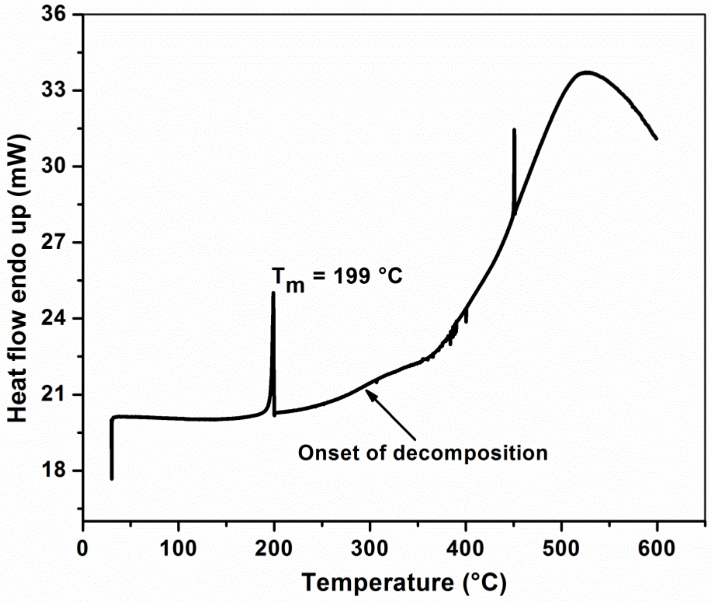


Figure 4.13. DSC trace of **2b** measured under N_2 (30-600 °C, scan rate = 10 °C/min).

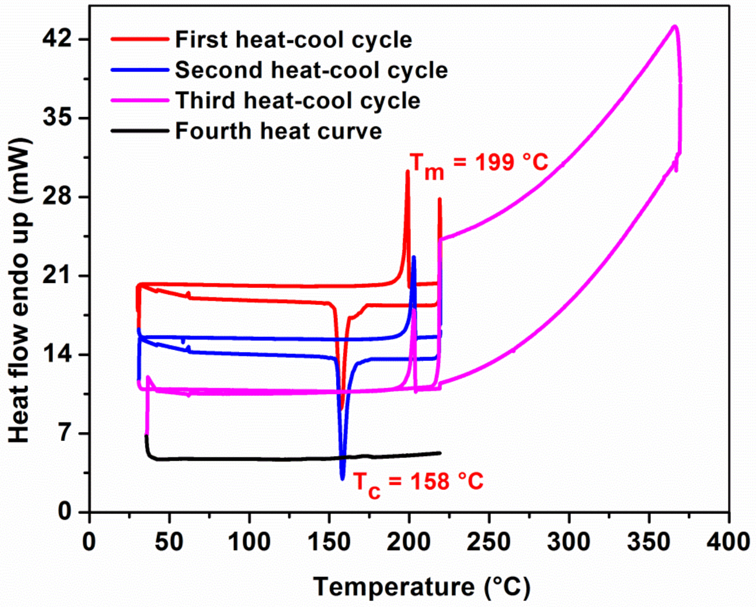


Figure 4.14. DSC cycles of **2b** measured under N_2 (first heating: 30-220 °C, scan rate = 10 °C/min; first cooling: 220-30 °C, scan rate = 30 °C/min; second heating: 30-220 °C, scan rate = 10 °C/min; second cooling: 220-30 °C, scan rate = 30 °C/min; third heating: 30-370 °C, scan rate = 10 °C/min; third cooling: 370-30 °C, scan rate = 30 °C/min; fourth heating: 30-220 °C, scan rate = 10 °C/min).

Tellurophenes **2a** and **2c** were also investigated by differential scanning calorimetry under nitrogen atmosphere. Upon heating tellurophene **2a** from ambient temperature to 600 °C, the onset of thermal decomposition was found at *ca.* 357 °C, while the crystallization (T_c) occurred at 178 °C and melting point (T_m) was found at 251 °C (Figure 4.15). Furthermore, to investigate the melt stability of **2a**, repeated heating-cooling DSC cycles (to temperatures *ca.* 15 °C above the melt) were performed under nitrogen atmosphere (Figure 4.16). Interestingly, it was found that tellurophene **2a** has a stable melt, as noted by reoccurring melting/recrystallization (T_c = 186 °C) after the first cycle. In contrast, crystallization at 178 °C was not observed after the first heating-cooling cycle.

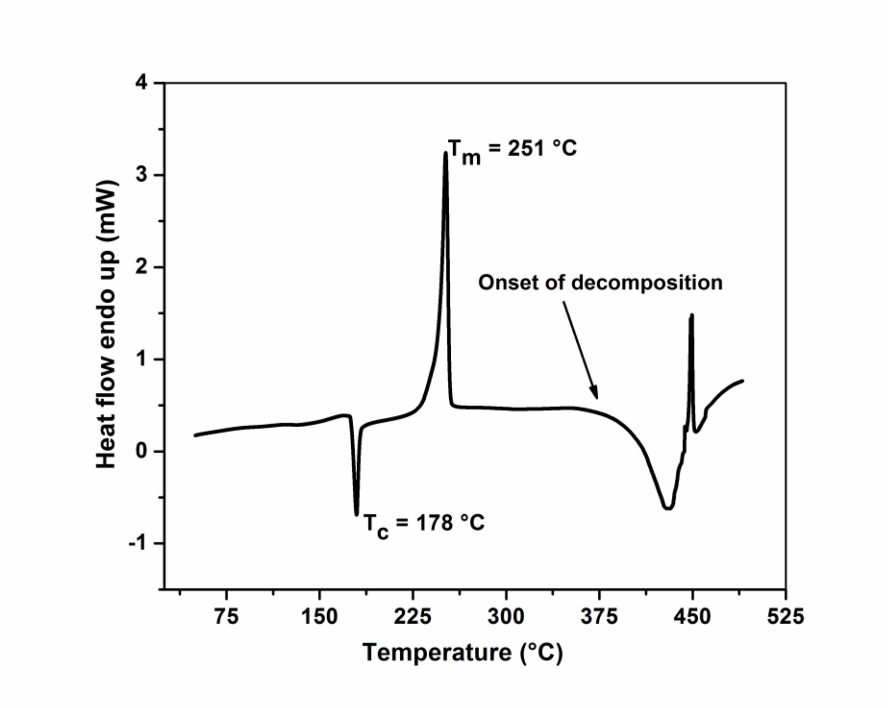


Figure 4.15. DSC trace of **2a** measured under N_2 (30-600 °C, scan rate = 10 °C/min).

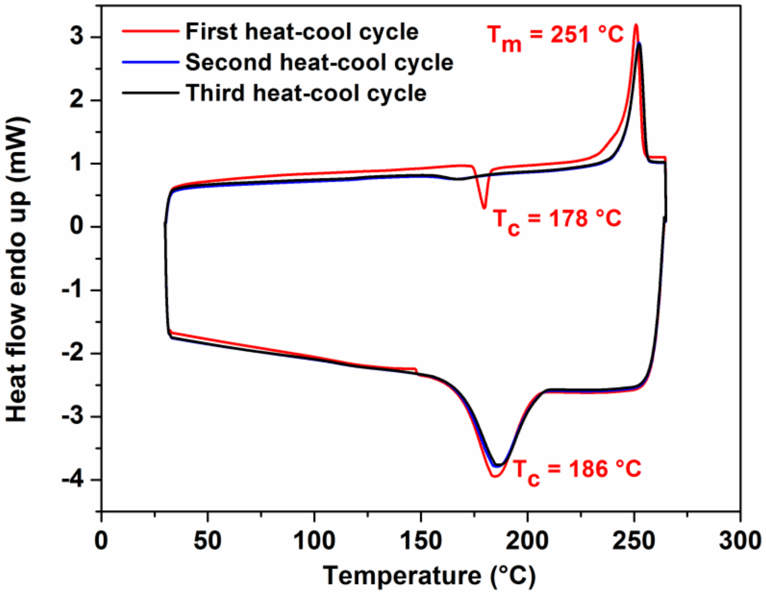


Figure 4.16. DSC cycles of **2a** measured under N_2 (first heating: 30-265 °C, scan rate = 10 °C/min; first cooling: 265-30 °C, scan rate = 30 °C/min; second heating: 30-265 °C, scan rate = 10 °C/min; second cooling: 265-30 °C, scan rate = 30 °C/min; third heating: 30-265 °C, scan rate = 10 °C/min; third cooling: 265-30 °C).

Upon heating tellurophene **2c** from ambient temperature to 600 °C, the onset of thermal decomposition was found at *ca.* 280 °C (in agreement with TGA data), however melting for **2c** was not observed (Figure 4.17).

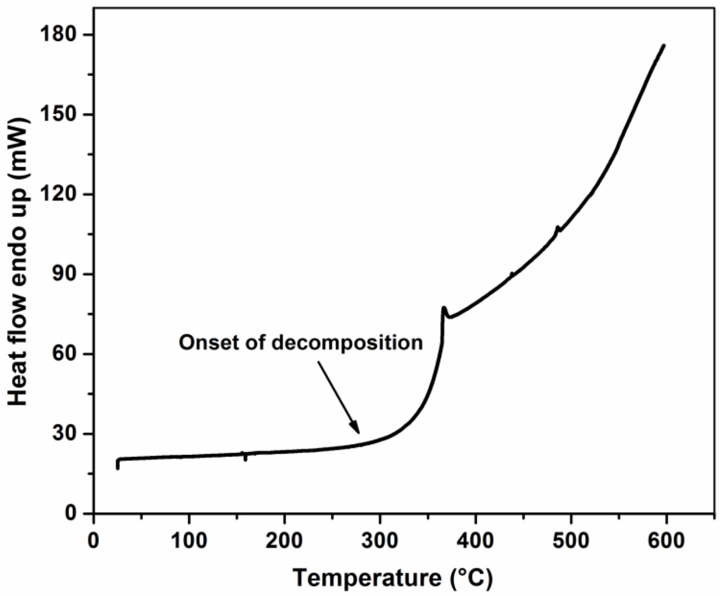


Figure 4.17. DSC trace of **2c** measured under N_2 (30-600 °C, scan rate = 10 °C/min).

4.3.4. Collaborative projects with tellurophenes 2a/c

Conjugated compounds bearing TPA substituents have been successfully used as hole transport layers in thin film transistors[21] and within solar cells.[22] Thus it would be beneficial to investigate the hole and electron mobility of tellurophenes **2a/c**. Samples were sent to the group of Prof. Peter Müller-Buschbaum at the Technical University of Munich (Germany) and the measurement of charge mobilities is currently under investigation.

At the same time, in collaboration with Dr. Mike Boone, the HOMO and LUMO energy levels of **2a/c** were probed by density functional theory calculations at B3LYP/6-31G(d) level of theory for all elements except tellurium, where B3LYP/LANL2DZ was used (Figure 4.18). In tellurophene **2a** the HOMO was found delocalized over the entire molecule, while in **2c** it was found to be located on the tellurium ring and attached TPA-substituents with little contribution from the alkyl –$(CH_2)_4$-linker. In both **2a/c** the LUMOs were located on the TeC_4 core and the adjacent phenyl rings.

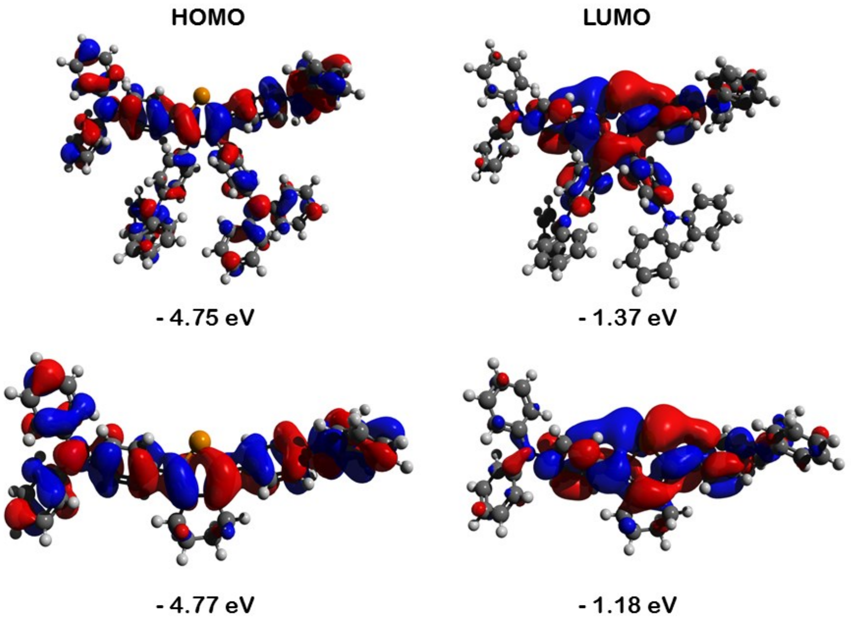


Figure 4.18. Calculated HOMO/LUMO plots for **2a** (top) and **2c** (bottom).

In collaboration with the Wakamiya group (Kyoto University, Japan), tellurophenes **2a/c** were sent to be tested as hole transport layers in perovskite solar cells. First, their HOMO energy levels were determined by photoelectron spectroscopy and found to be -5.58 eV (**2a**) and -5.59 eV

(**2c**), which is lower than HOMO level of the perovskite (-5.45 eV), indicating that hole extraction from the perovskite layer using these tellurophenes would be difficult. Thus new molecular systems (**3a/b**) were designed, which incorporated a thienyl spacer and electron-donating methoxy groups on the TPA units in order to increase the HOMO level (see Figure 4.19 and Scheme 4.2). Density functional theory calculations at the B3LYP/6-31G(d) level of theory (Figure 4.19) were performed by Mr. Shimogawa Hiroyuki in Kyoto and showed a delocalized HOMO level at -4.35 eV in **3b**, which based on their earlier work on hole-transporting two-dimensional π-systems of azulene,[23] would give an experimental value (*i.e.*, by photoelectron spectroscopy) in the range of -5.2 to -5.1 eV, suitable for application in perovskite solar cells.[24] Moreover the high LUMO level computed (-1.30 eV) is optimal for concurrent electron-blocking behavior in **3b**.

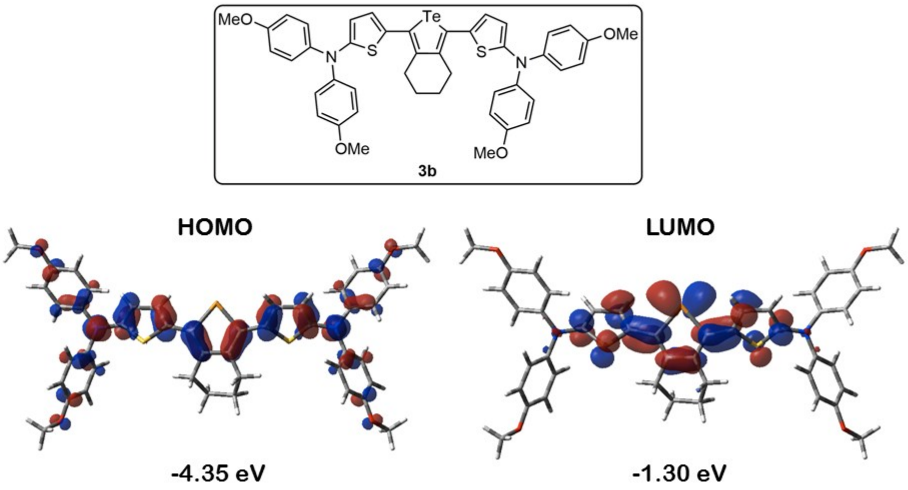
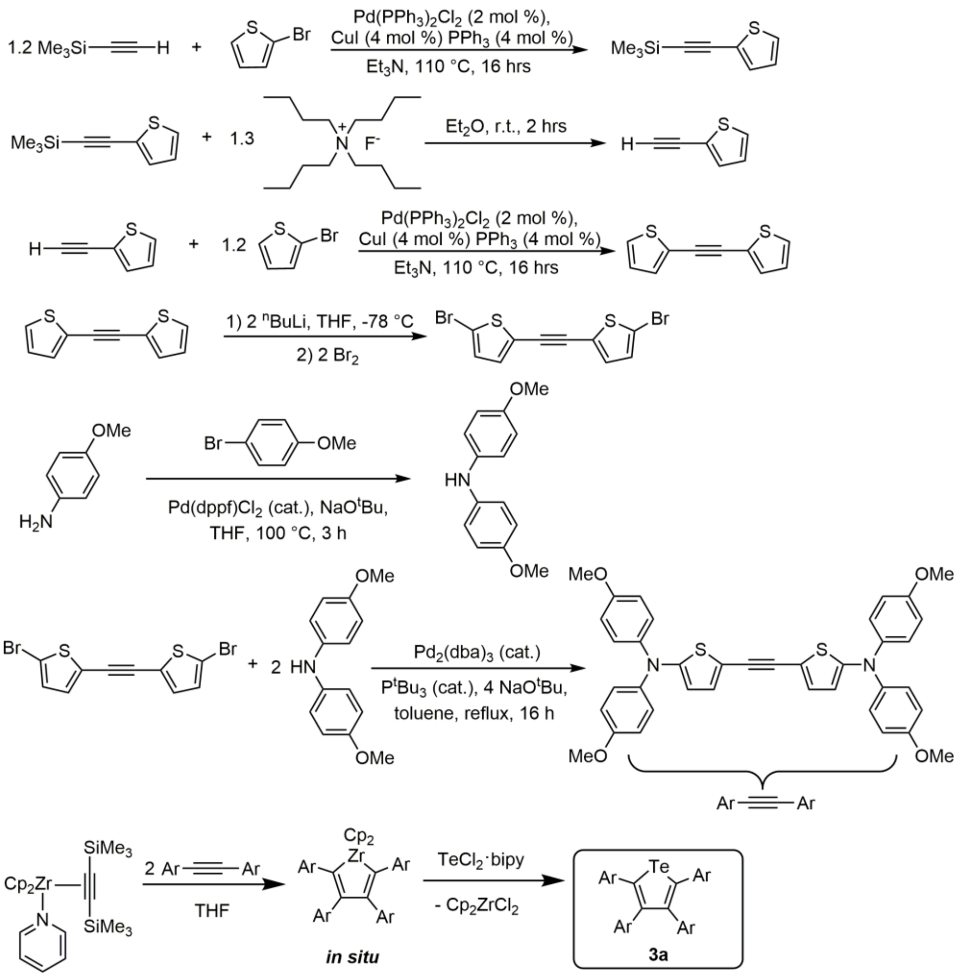


Figure 4.19. Calculated HOMO/LUMO plots of **3b**.

The synthetic route towards tellurophene **3a** is presented in Scheme 4.3, while tellurophene **3b** is currently being synthesized by Dr. Mike Boone.



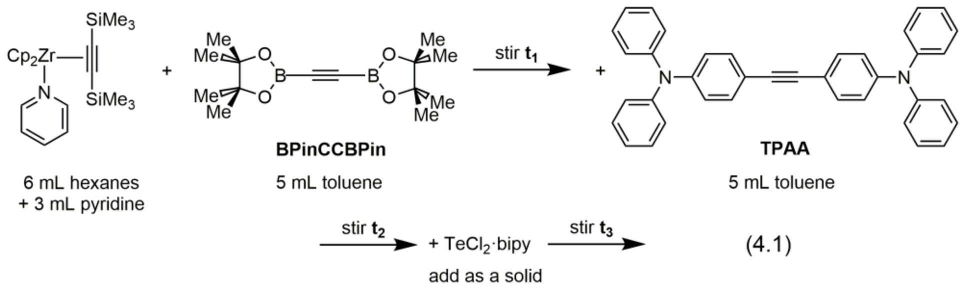
Scheme 4.3. Outline of planned synthesis for tellurophene **3a**.

The project began the multigram synthesis of pure 1,2-bis(thiophen-2-yl)ethyne *via* three-step Sonogashira coupling procedure (see also Chapter 3).[25] It was noticed that intermediate H-C≡C-T (T = thienyl) has a very short bench lifetime (~ 2 hours) and is sensitive to light, temperature and air. Attempts to install bromine substituents onto the thienyl units by treating (2-thienyl)-C≡C-(2-thienyl) with *N*-bromosuccinamide (NBS) failed and only starting materials were identified. As a result a lithiation/bromination procedure was adapted from the literature[26] and the target brominated alkyne was isolated as a yellow solid in 59 % yield after purification by column chromatography. The brominated precursor was further used to couple with bis(4-methoxyphenyl)amine[27] following reported Buchwald-Hartwig amination conditions for bromothiophene derivatives,[28] however at the end of the reaction only starting material were identified. Increasing catalytic loading (up to 4 % of $Pd_2(dba)_3$) did not lead to any particular improvement (starting materials were recovered). Future direction would involve the synthesis of iodinated 1,2-bis(thiophen-2-yl)ethyne and use of RuPhos-based catalyst/ligand system in Buchwald-Hartwig amination reaction to obtain the desired product.[29,30] Interestingly, the Grimsdale group studied the sulfur analogue of **3a** as a hole transport layer in the perovskite-based solar cell devices and obtained a high power conversion efficiency of 15.4 %.[31]

4.3.5. Synthesis of asymmetric tellurophenes

In 2014 Dr. Gang He discovered phosphorescence in a solid pinacolborane-capped tellurophene under ambient conditions at room temperature;[7] since then a variety of derivatives were obtained and studied in our laboratory, including asymmetrically substituted tellurophenes.[8] The latter species with PBin and Ph susbtituents were obtained as a mixture of isomers (2,5- and 2,4-$BPin_2$ regioisomers) that were manually separated under UV/Vis irradiation since these isomers each exhibited different green and orange emission colors. This procedure included synthesis of asymmetric BPin-containing alkynes[32] as well as a time-consuming purification protocol that could not be applied across a range of derivatives. Thus it would be beneficial to develop a general regioselective synthesis of asymmetric tellurophenes. These heterocycles constitute an emerging class of luminogen for LEDs, constructed without encapsulation of emissive active layers in host matrices.[4]

The study began with subsequent addition of BPin-C≡C-BPin and TPA-C≡C-TPA to $Cp_2Zr(pyridine)(Me_3SiCCSiMe_3)$[15] to trigger the selective formation of an asymmetrically substituted zirconacycle (Equation 4.1). After transmetallation with $TeCl_2$•bipy, only the symmetric derivative TeC_4BPin_4 and the starting TPA-capped alkyne, TPA-C≡C-TPA, were identified by multinuclear NMR spectroscopy (^1H, $^{13}C\{^1H\}$ and $^{11}B\{^1H\}$) and thin-layer chromatography (Equation 4.1); these compounds could be separated and isolated in pure form via column chromatography. Lower reaction temperatures (*i.e.*, -30 °C), longer reaction times (*i.e.*, 12 hours *vs.* 2 hours of stirring after TPA-C≡C-TPA addition) and switching the order of alkynes did not lead to any desired tellurophene. These trials are summarized in the Table 4.1.

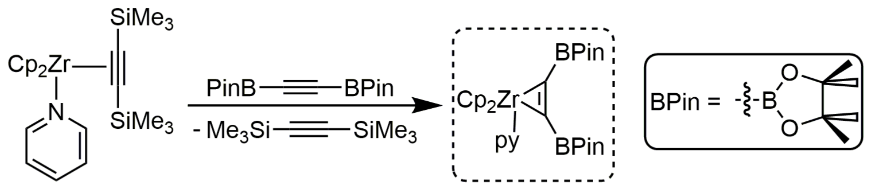


(4.1)

Table 4.1. Trials for synthesis of asymmetric tellurophene.

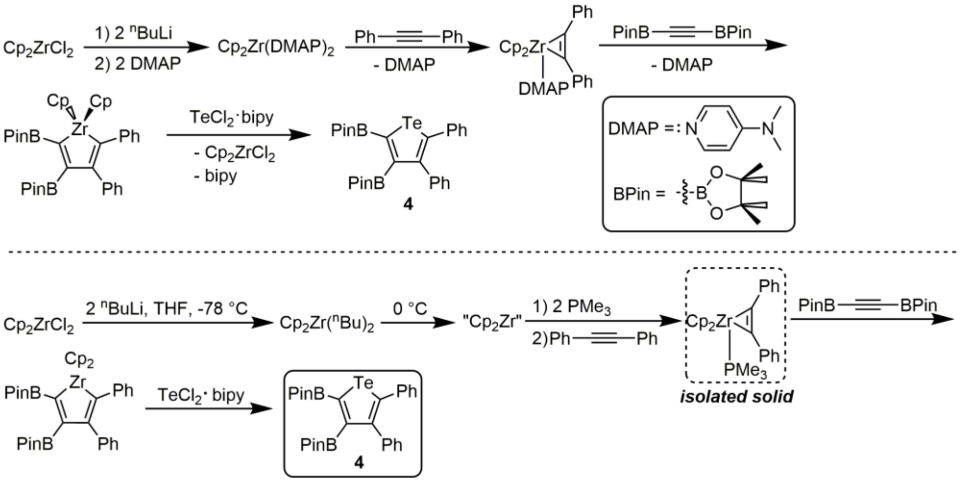
Entry	Order of alkynes	Temp. (°C)	t_1, hrs	t_2, hrs	t_3, hrs	Products (based on NMR and thin-layer chromat.)
1	BPinCCBPin TPAA	r.t.	0.5	2	16	TeC_4BPin_4, TPAA
2	BPinCCBPin TPAA	r.t.	0.5	16	16	TeC_4BPin_4, TPAA
3	BPinCCBPin TPAA	r.t.	0.5	16	2.5	TeC_4BPin_4, TPAA
4	BPinCCBPin TPAA	-30	0.25	1	16	TeC_4BPin_4, TPAA
5	TPAA BPinCCBPin	r.t	1	0.2	16	TPAA, BPinCCBPin

The next synthetic attempt included isolation of the BPin-capped zirconacyclopropene intermediate $Cp_2Zr(pyr)(PinBCCBPin)$, reported earlier by Rosenthal and co-workers (Equation 4.2).[33] However, their results could not be reproduced despite repeated attempts.



(4.2)

In 2000, the Gouygou group obtained asymmetric 2,3-Ph_2-phospholes *via* selective intramolecular cross-coupling of two different alkynes and *in situ* formation of asymmetric zirconacycle.[34] This reaction condition was applied towards the possible synthesis of the asymmetric tellurophene **4** (Scheme 4.4) where tolan (Ph-C≡C-Ph) and BPin-C≡C-BPin were used as alkyne sources. However, the reaction yielded only the starting alkynes as major products, which were identified by multinuclear NMR spectroscopy (^1H, $^{13}C\{^1H\}$ and $^{11}B\{^1H\}$) and thin layer chromatography.



Scheme 4.4. Attempted (top) and future (bottom) syntheses of the asymmetric tellurophene **4**.

Future work could include the isolation of a zirconacyclopropene intermediate through stabilization with phosphines (*e.g.*, PMe_3)[35] and testing its reactivity with BPin-C≡C-BPin to form an asymmetric zirconacycle in a regioselective manner (Scheme 4.4).

4.4. Conclusions

In summary, light-emitting and thermally stable symmetric tellurophenes were prepared with the help of metallacycle transfer chemistry. By altering the nature of peripheral substituents, photoluminescence could be turned on or off, occasionally leading to green emission in the aggregated state. Furthermore, increasing the number of the ring appended triphenylamine substituents leads to amplification of the fluorescence quantum yield. Future work will involve the attempted preparation of electron-rich tellurophenes for use as hole-transporting materials and the development of a regioselective synthesis of asymmetrically-substituted phosphorescent tellurophenes[35] in order to induce luminescence color tuning.

4.5. Experimental section

4.5.1. Materials and instrumentation

All reactions were performed using standard Schlenk and glovebox (MBraun) techniques under a nitrogen atmosphere. Solvents were all dried and degassed using a Grubbs-type solvent purification system[36] manufactured by Innovative Technology, Inc., and stored under an atmosphere of nitrogen prior to use. 2,2'-bipyridine was obtained from GFS Chemicals, zirconocene dichloride from Strem Chemicals Inc., pyridine from Caledon Laboratory Chemicals; all other chemicals were obtained from Aldrich. Commercially obtained chemicals were used as received except for pyridine, which was freshly distilled under nitrogen from potassium hydroxide.[37] Bis(cyclopentadienyl)zirconium-2,3,4,5-tetra(2-thienyl)methanide **$Cp_2ZrC_4T_4$**,[9b] bipy•$TeCl_2$,[14] $Cp_2Zr(pyr)(Me_3SiCCSiMe_3)$,[38] 1,2-bis(4',4',5',5'-tetramethyl[1',3',2']dioxaborolan-2'-yl)ethyne,[39] 2-(trimethylsilylethynyl)thiophene,[25c] 2-ethynylthiophene,[25a] and bis(4-methoxyphenyl)amine[27] were prepared according to literature procedures. ^{1}H, ^{13}C{^{1}H} and ^{11}B{^{1}H} NMR spectra were recorded on a Varian DD2 MR-400 spectrometer and referenced externally to $SiMe_4$ (^{1}H, ^{13}C{^{1}H}) and $F_3B{\bullet}OEt_2$ (^{11}B{^{1}H}). Elemental analyses were performed by the Analytical and Instrumentation Laboratory at the University of Alberta. Mass spectra for small molecules were collected using a MS-50G system (Kratos Analytical). Melting points were obtained in sealed glass capillaries using a MelTemp melting point apparatus and are uncorrected. UV/Vis measurements were performed using a Varian Cary 300 Scan spectrophotometer. Photoluminescence and lifetimes were measured on a time-correlated single photon counting fluorescence spectrometer (Edinburgh Instruments FLS920) using an EPL-375 picosecond pulsed diode laser with vertical polarization (70.3 ps pulse width) as an excitation source; absolute quantum yields were measured with an integrating sphere system within the same fluorescence spectrometer.

4.5.2. Synthetic procedures

4.5.2.1. Synthesis of 2,3,4,5-tetra{4-(diphenylamino)phenylene}tellurophene (2a)

$Cp_2Zr(pyr)(Me_3SiCCSiMe_3)$ (0.526 g, 1.12 mmol) and 1,2-bis(triphenylamine)-ethyne ($Ph_2N\text{-}C_6H_4\text{-}C\equiv C\text{-}C_6H_4\text{-}NPh_2$) (1.145 g, 2.23 mmol) were dissolved in 20 mL of THF, and the resulting mixture was allowed to stir for 12 hrs to give a dark red solution. Solid bipy•$TeCl_2$ (0.437 g, 1.23 mmol) was added directly to the vial and the resulting slurry was stirred for another 18 hrs. A dark green solution formed over a black precipitate; this precipitate was allowed to settle and the mother liquor was filtered through 1 cm plug of silica gel. The volatiles were removed from red colored filtrate and the crude product was purified by column chromatography (silica gel, CH_2Cl_2:hexanes = 1:2 as the eluent, $R_f = 0.38$) to yield **2a** as the orange-yellow powder which was further washed with room temperature hexanes (2 × 15 mL) to give **2a** as a bright yellow solid (0.322 g, 25 %). X-ray quality crystals of **2a** were obtained from slow evaporation of the CH_2Cl_2/Et_2O solution at the room temperature. M.p. 133-137 °C; TGA: T_{dec} = 457 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.23-7.27 (m, 8H, Ar*H*), 7.16-7.19 (m, 8H, Ar*H*), 7.08-7.10 (m, 8H, Ar*H*), 6.94-7.04 (m, 20H, Ar*H*), 6.79-6.87 (m, 12H, Ar*H*); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 148.6, 147.8, 147.6, 146.4, 145.8, 141.2, 135.8, 134.2, 132.0, 130.5, 129.3, 129.2, 124.7, 124.0, 123.2, 123.1, 122.54, 122.46; UV/Vis (THF): λ_{max} (ε) = 302 nm (7.31×10^5 $mol^{-1}dm^3cm^{-1}$), shoulder at

345 nm; UV/Vis (film): λ_{max} = 308 (shoulder at 375 nm); Fluorescence emission (THF) (λ_{ex} = 397 and 419 nm): λ_{em} = 472 nm, absolute fluorescence quantum yield: Φ = 11.8 %; Lifetime (1×10^{-5} M solution in THF): τ = 1.8 ns; Fluorescence emission (film) (λ_{ex} = 460 nm): λ_{em} = 520 nm; Lifetime (film): τ = 1.8 ns; Absolute quantum yield (film) = 3.8 %. HR-MS (EI): m/z: 1154.3533; $C_{76}H_{56}N_4Te$ calcd: 1154.3567; elemental analysis calcd (%) for $C_{76}H_{56}N_4Te$: C, 79.18; H, 4.90; N, 4.86; found: C, 78.65; H, 5.13; N, 4.70.

4.5.2.2. Synthesis of 2,3,4,5-tetra(2-thienyl)-tellurophene (2b)

$Cp_2ZrC_4(2\text{-thienyl})_4$[9b] (0.151 g, 0.25 mmol) and bipy•$TeCl_2$ (0.098 g, 0.28 mmol) were dissolved in 6 mL THF and the resulting mixture was allowed to stir at room temperature for 24 hrs. A dark green solution formed over a black precipitate; this precipitate was allowed to settle and the mother liquor was filtered through 1 cm plug of silica gel. The volatiles were removed from the filtrate and resulting crude product was purified by column chromatography (silica gel, THF:pentane = 1:2 as the eluent, R_f = 0.70) to yield **2b** as a green powder which was further washed with room temperature hexanes (2 × 5 mL) to give **2b** as a light yellow solid (0.037 g, 33 %). X-ray quality crystals of **2b** were obtained from slow evaporation of a THF/pentane solution at the room temperature. M.p. 196-197 °C; TGA: T_{dec} = 296 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (dd, $^3J_{HH}$ = 5.1 Hz, $^4J_{HH}$ = 1.1 Hz, 2H, Thienyl*H*), 7.14 (dd, $^3J_{HH}$ = 5.1 Hz,

$^4J_{HH}$ = 1.2 Hz, 2H, Thienyl*H*), 6.90-6.92 (two overlapping dd, $^3J_{HH}$ = 3.5 Hz, $^4J_{HH}$ = 1.2 Hz, 4H, Thienyl*H*), 6.86 (dd, $^3J_{HH}$ = 5.1 Hz, $^4J_{HH}$ = 3.7 Hz, 2H, Thienyl*H*), 6.82 (dd, $^3J_{HH}$ = 3.5 Hz, $^4J_{HH}$ = 1.2 Hz, 2H, Thienyl*H*); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 142.0, 140.7, 140.3, 134.9, 129.5, 127.7, 127.0, 126.9, 126.6 (Thienyl-*C*); UV/Vis (THF): λ_{max} (ε) = 394 nm (1.81×10^4 mol^{-1} dm^3 cm^{-1}); UV/Vis (film): λ_{max} = 386 and 427 (shoulder) nm; HR-MS (EI): m/z: 509.8871; $C_{20}H_{12}S_4Te$ calcd: 509.8884; elemental analysis calcd (%) for $C_{20}H_{12}S_4Te$: C, 47.27; H, 2.38; S, 25.24; found: C, 47.12; H, 2.51; S, 25.30.

4.5.2.3. Synthesis of 1,2-bis(thiophen-2-yl)ethyne

To a solution of 2-bromothiophene (0.43 mL, 4.41 mmol) in dry Et_3N (20 mL) were added $PdCl_2(PPh_3)_2$ (0.056 g, 0.080 mmol), PPh_3 (0.042 g, 0.160 mmol), CuI (0.031 g, 0.16 mmol), and 2-ethynylthiophene (0.433 g, 4.00 mmol). After stirring for 16 hours at 70 °C, the volatiles were removed *in vacuo* and the residue was dissolved in CH_2Cl_2 (50 mL) and filtered through 1 cm plug of silica gel. The solvent was removed from the filtrate and the crude product was purified by column chromatography (loaded as a 5 mL solution in CH_2Cl_2, silica gel, hexanes as eluent, R_f = 0.73) to yield 1,2-bis(thiophen-2-yl)ethyne as a white solid (0.433 g, 57 %). The corresponding ^1H and $^{13}C\{^1H\}$ NMR spectral data matched those reported previously in the literature.[40]

4.5.2.4. Synthesis of 1,2-bis(5-bromo-thiophen-2-yl)ethyne

A solution of 1,2-bis(thiophen-2-yl)ethyne (0.433 g, 2.28 mmol) in 20 ml of THF was cooled to -78 °C and ^{n}BuLi (2.0 mL, 2.5 M solution in hexanes, 5.0 mmol) was added dropwise. The reaction mixture turned into a light yellow slurry and the mixture was stirred for 45 min at -78 °C. Afterwards Br_2 (0.26 mL, 5.0 mmol) was added at -78 °C and the cold bath was removed immediately. The reaction mixture was stirred at room temperature for 4 hours, leading to the production of a brown solution. The resulting mixture was poured into 100 mL of saturated aqueous $Na_2S_2O_3$ and extracted with 50 mL of chloroform. The organic layer was washed again with saturated $Na_2S_2O_3$ (aq.) (100 mL), water (2 × 100 mL), brine (2 × 100 mL), and dried over $MgSO_4$. The solvent was removed *in vacuo* and the brown residue was purified by column chromatography (silica gel, compound loaded as a 3 mL solution in CH_2Cl_2, elution with petroleum ether:Et_2O = 99:1, $R_f = 0.71$) to give 1,2-bis(5-bromo-thiophen-2-yl)ethyne as a yellow solid (0.467 g, 59 %). The corresponding ^{1}H and $^{13}C\{^{1}H\}$ NMR spectral data matched those reported previously by the Tortech and Fichou.[26]

4.5.2.5. Attempted synthesis of 1,2-bis(5-(4-methoxyphenyl)amino-thiophen-2-yl)ethyne

A solution of $Pd_2(dba)_3$ (0.015 g, 0.016 mmol) and P^tBu_3 (0.010 g, 0.048 mmol) in 15 mL of toluene was stirred at room temperature for 30 min. To the resulting dark pink mixture was added 1,2-bis(5-bromo-thiophen-2-yl)ethyne (0.554 g, 1.59 mmol), bis(4-methoxyphenyl)amine (0.766 g, 3.34 mmol), and NaO^tBu (0.615 g, 6.37 mmol). The reaction flask was then immersed in a pre-heated oil bath (110 °C) and the solvent was refluxed for 16 hrs. Afterwards the reaction mixture was cooled to room temperature, extracted with 50 mL of dichloromethane and filtered through 2 cm plug of silica gel. The volatiles were removed from the filtrate *in vacuo*, and the dark brown residue was analyzed by thin-layer chromatography (CH_2Cl_2:hexanes = 3:1) and NMR spectroscopy (in $CDCl_3$) to reveal starting materials (alkyne and amine).

4.5.2.6. Attempted synthesis of 2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4,5-di(4-triphenylamine)tellurophene

To a solution of $Cp_2Zr(pyr)(Me_3SiCCSiMe_3)$ (0.273 g, 0.58 mmol) in 6 mL of hexanes and 3 mL of pyridine, was added a slurry of PinB-C≡C-BPin (0.145 g, 0.52 mmol, BPin = pinacolborane) in 5 mL of toluene, and the mixture was stirred for 30 min at room temperature. Afterwards, a solution of 1,2-bis(triphenylamine)-ethyne (0.297 g, 0.58 mmol) in toluene (5 mL) was added and the reaction mixture was stirred for 16 hours. Then solid bipy•$TeCl_2$ (0.226 g, 0.64 mmol) was added in one portion, and the reaction mixture was stirred for 16 hours. A dark red solution formed over a black precipitate; this precipitate was allowed to settle and the mother liquor was filtered through 1 cm plug of silica gel. The volatiles were removed from the filtrate and the crude residue was analyzed by NMR spectroscopy (in $CDCl_3$) and thin-layer chromatography (THF:hexanes = 2:1). The results are summarized in the Table 4.1.

4.5.2.7. Attempted synthesis of 2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4,5-diphenyltellurophene (4)

A solution of Cp_2ZrCl_2 (0.750 g, 2.57 mmol) in 25 mL of THF was cooled to -78 °C and ^{n}BuLi (2.0 mL, 2.5 M solution in hexanes, 5.0 mmol) was added dropwise. The yellow reaction mixture was allowed to stir for 15 min and 4-dimethylaminopyridine (0.611 g, 5.01 mmol) was added rapidly. The reaction mixture was warmed to room temperature over 75 min and stirred for a further 90 min. The resulting dark red solution was cooled to 0 °C, diphenylacetylene (0.457 g, 2.57 mmol) was added and the solution was stirred for 90 min. Afterwards of PinB-C≡C-BPin (0.713 g, 2.57 mmol) was added and the solution was warmed up to room temperature over 40 minutes and stirred for 2 hrs. The obtained dark orange mixture was cooled again to -78 °C and bipy•$TeCl_2$ (1.001 g, 2.83

mmol) was added rapidly, and the resulting mixture was allowed to stir at room temperature for 24 hrs. A brown solution formed over a black precipitate; this precipitate was allowed to settle and the mother liquor was filtered through 1 cm plug of silica gel. The volatiles were removed from the filtrate and the crude residue was analyzed by NMR spectroscopy (in $CDCl_3$) and thin layer chromatography (THF:hexanes = 2:1) to reveal unreacted diphenylacetylene and PinB-C≡C-BPin.

4.6. Crystallographic data

Table 4.2. Crystallographic data for compounds **2a/b**

	2a	**2b**
empirical formula	$C_{76}H_{56}N_4Te$	$C_{21}H_{13}Cl_3S_4Te$
fw	1152.84	627.50
cryst. dimens. (mm^3)	0.38 × 0.11 × 0.07	0.48 × 0.09 × 0.04
cryst. syst.	monoclinic	orthorhombic
space group	$P2_1/c$ (No. 14)	$Pna2_1$ (No. 33)
unit cell dimensions		
a (Å)	13.5430 (10)	19.7292 (12)
b (Å)	41.973 (3)	16.0519 (10)
c (Å)	10.4308 (7)	7.1294 (4)
α (deg)		
β (deg)	103.6079 (11)	
γ (deg)		
V (Å^3)	5762.8 (7)	2257.8 (2)
Z	4	4
ρ (g cm^{-3})	1.329	1.846
abs. coeff. (mm^{-1})	0.566	2.050
T (K)	173 (1)	173 (1)
2 Θ_{max} (deg)	55.11	56.44
total data	52176	20609
unique data (R_{int})	13298 (R_{int} = 0.0554)	5551 (R_{int} = 0.0445)
obs. data [$I > 2\sigma(I)$]	9312	4642
params.	730	292
R_1 [$I > 2\sigma(I)$]^a	0.0394	0.0337
wR_2 [all data]^a	0.1012	0.0873
Max/Min $\Delta\rho$ (e Å^{-3})	0.635/–0.522	1.285/–0.531

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

4.7. NMR spectral data

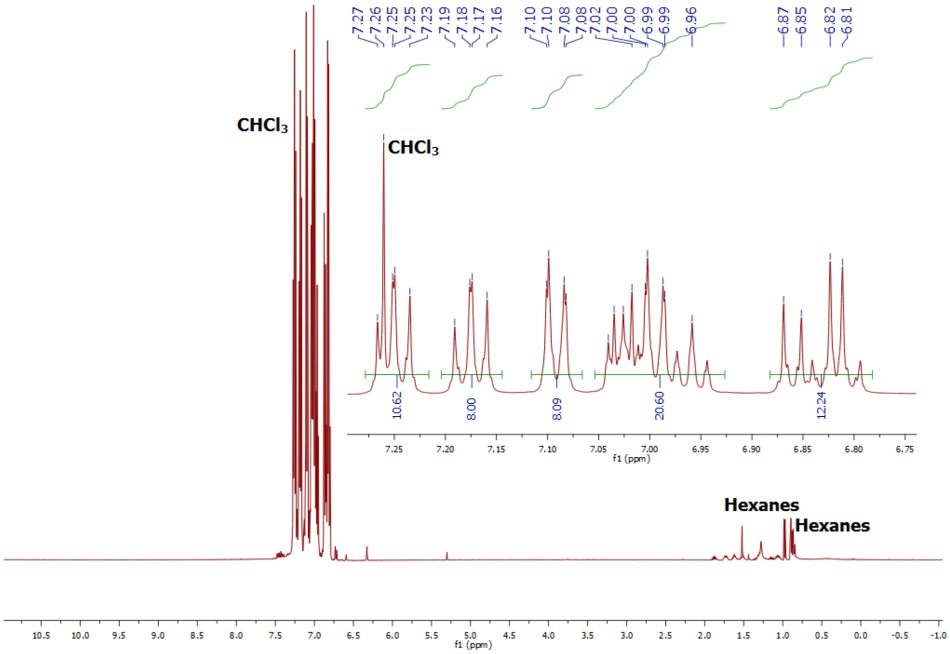


Figure 4.20. ^{1}H NMR (in $CDCl_3$) spectrum of compound **2a**.

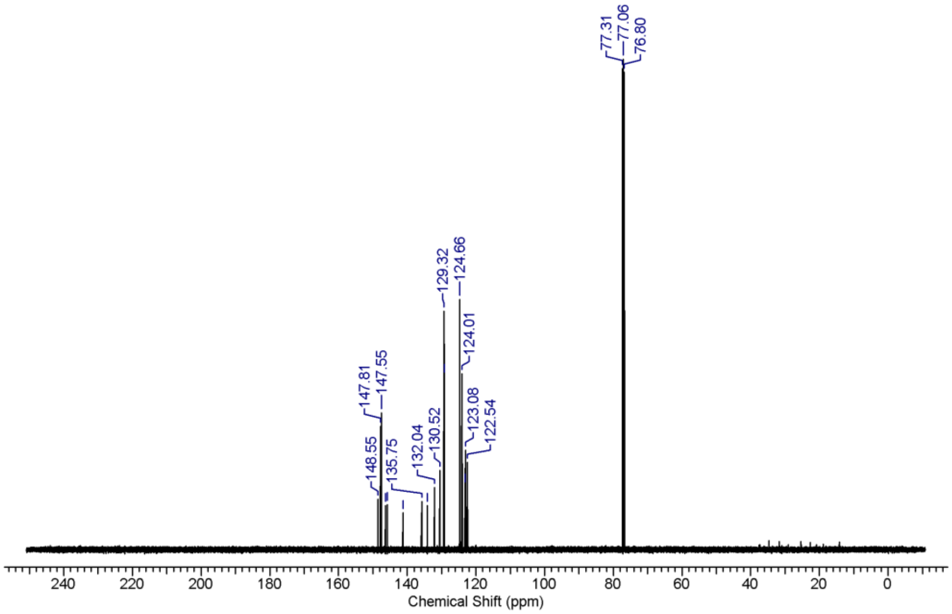


Figure 4.21. $^{13}C\{^1H\}$ NMR (in $CDCl_3$) spectrum of compound **2a**.

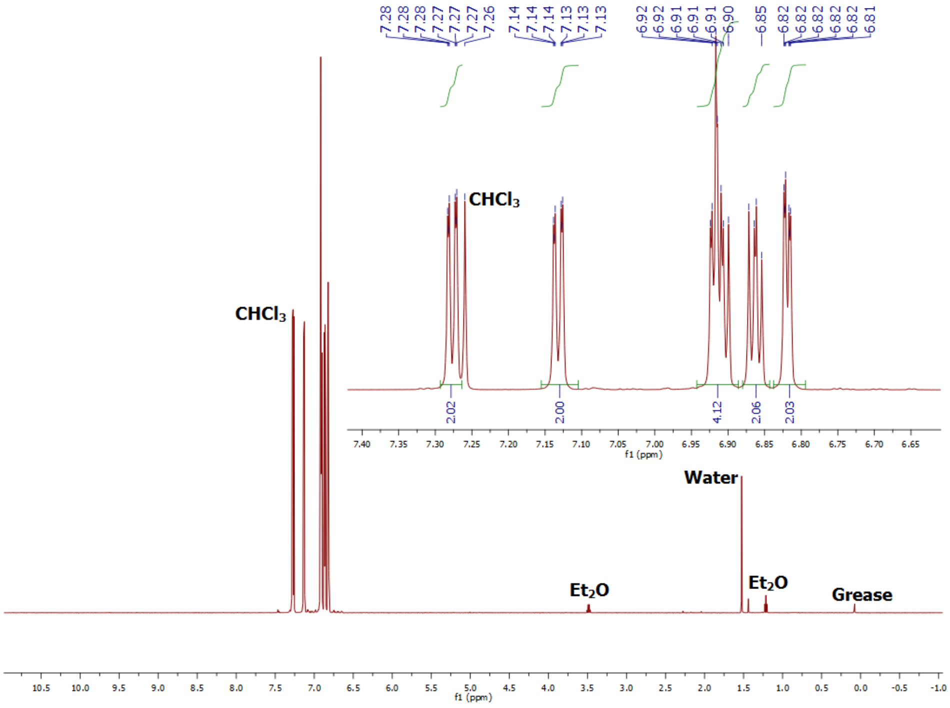


Figure 4.22. ^{1}H NMR (in $CDCl_3$) spectrum of compound **2b**.

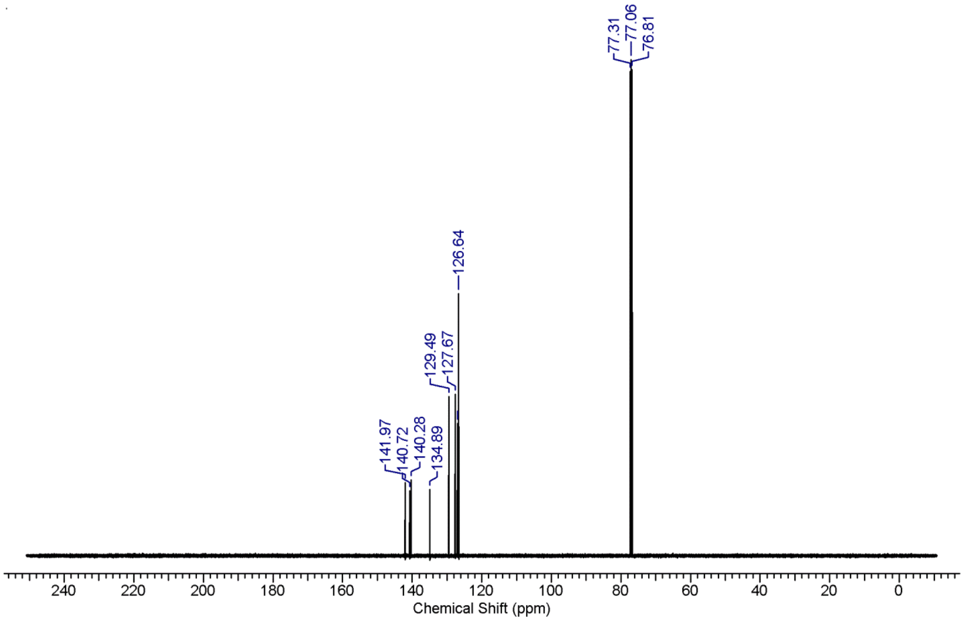


Figure 4.23. $^{13}C\{^{1}H\}$ NMR (in $CDCl_3$) spectrum of compound **2b**.

4.8. References

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Chapter 5: Summary and future work

5.1. Summary and future work

Chapter 2 described a modular synthesis of a new hybrid class of air-stable luminogen termed spirocyclic germafluorene-germoles (SGGs). SGGs contain germafluorene and germole rings appended in spirocyclic manner. At first zirconium-mediated coupling was used to obtain $Cl_2GeC_4Et_4$ which then participated in the condensation reaction with 2,2'-dilithiofluorene or its pre-brominated analogue to obtain $FlGeC_4Et_4$ (**1**) and $Br_2FlGeC_4Et_4$ (**2**) (Fl = fluorenyl; Figure 5.1). Because these analogues were not luminescent, in order to obtain emissive species with extended π-conjugation, Stille coupling with trimethylstannylbenzene and 2-(trimethylstannyl)thiophene was performed under microwave-assisted conditions.

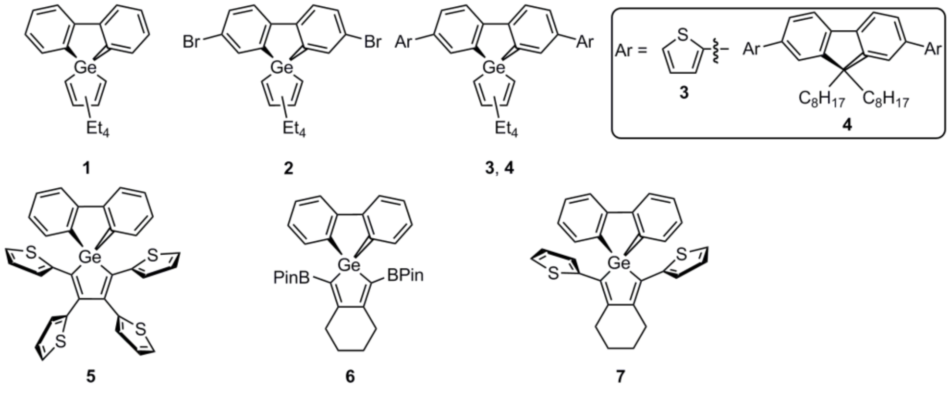
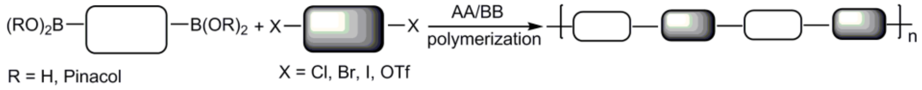


Figure 5.1. Structures of the spirocyclic germafluorene-germoles **1**-**7**.

The thienyl-substituted SGG **3** (Figure 5.1) exhibited blue photoluminescence with high quantum yield of 83 % in the solution; its dioctylfluorene analogue **4** was also prepared for further comparison of optical properties as well as photo- and thermal stability. Both compounds have similar absorption and emission profiles, leading to a conclusion that only the bis(thienyl)biaryl portion was primarily involved in the luminescence. However, the SGG analogue **3** exhibited greater thermal and photooxidative stability in the solid state, which is an important factor for application in light-emitting devices. Next FlGeC$_4$(2-thienyl)$_4$ (**5**) was obtained using our modular approach and it showed bright yellow emission in the solid state as well as aggregation-induced emission properties due to restriction rotation of the peripherally located thiophene groups. Moreover, the non-emissive SGG precursor (**6**), capped with pinacolborane (BPin) groups was synthesized. The BPin groups had a quenching effect on luminescence, however one analogue was used in Suzuki-Miyaura cross-coupling to obtain a green-emitting SGG **7**. Future work related to this BPin-capped co-monomer **6** includes optimization of its synthetic procedure. It was obtained only in 35 % yield after purification by column chromatography, followed by crystallization. Monomers for AA/BB-type polymerization (Equation 5.1) should have high degree of purity, otherwise there will be a dramatic reduction in the molecular weight of resulting polymers.[1]



(5.1)

Hence, scaling up the reaction to obtain at least 1 g of the pure monomer per synthesis should be probed. Next, monomers for future polymerization trials are presented on the Figure 5.2. Synthesis of the co-monomers could be found in the literature.[2] It would be of interest to investigate optical properties of the polymers (*e.g.*, quantum yield) as well as their thermal and photostability. Suzuki-Miyaura polymerization would give an access to a vast array of colour tunable luminescent polymers, which could be used as active layers in light-emitting devices, field-effect transistors and organic photovoltaics.

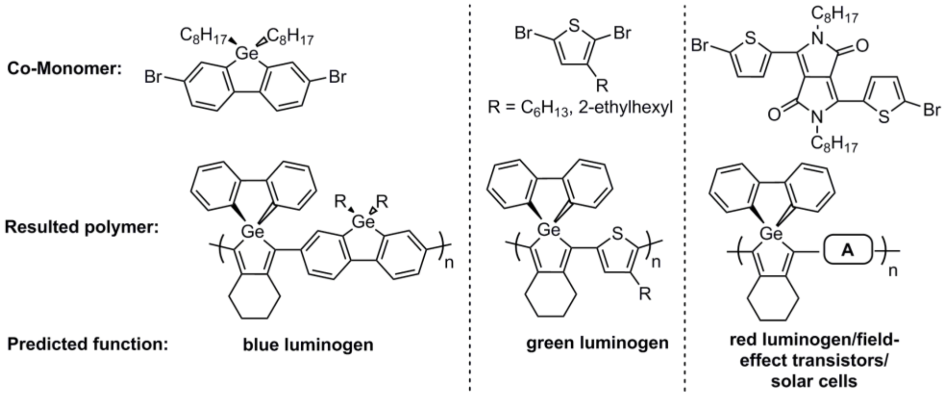
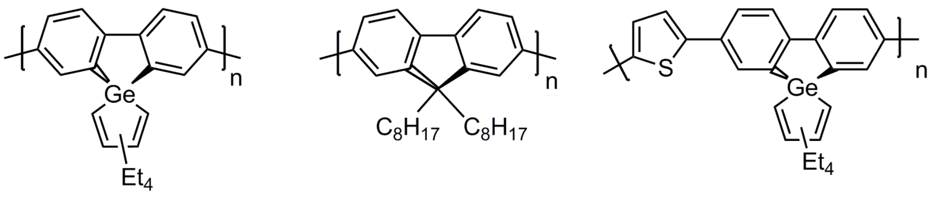


Figure 5.2. Possible co-monomers for future polymerization trials with BPin-capped SGG.

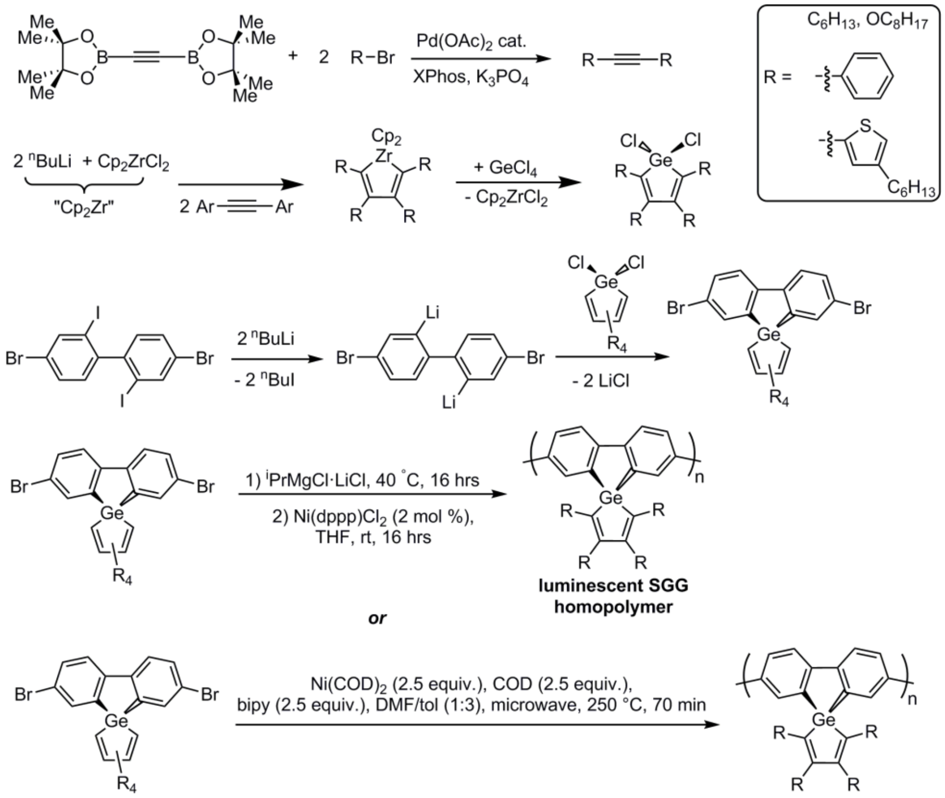
Blue emissive homopolymers of $FlGeC_4Et_4$ and 9,9'-dioctylfluorene were prepared using Grignard metathesis or microwave-assisted Yamamoto polymerization routes (Figure 5.3). The SGG homopolymer **8** had lower quantum yield and thermal stability than polyfluorene **9**. SGG co-polymer with thiophene (**10**) was obtained using microwave-assisted Stille polymerization.



8 **9** **10**

Figure 5.3. Structures of polymers **8-10**.

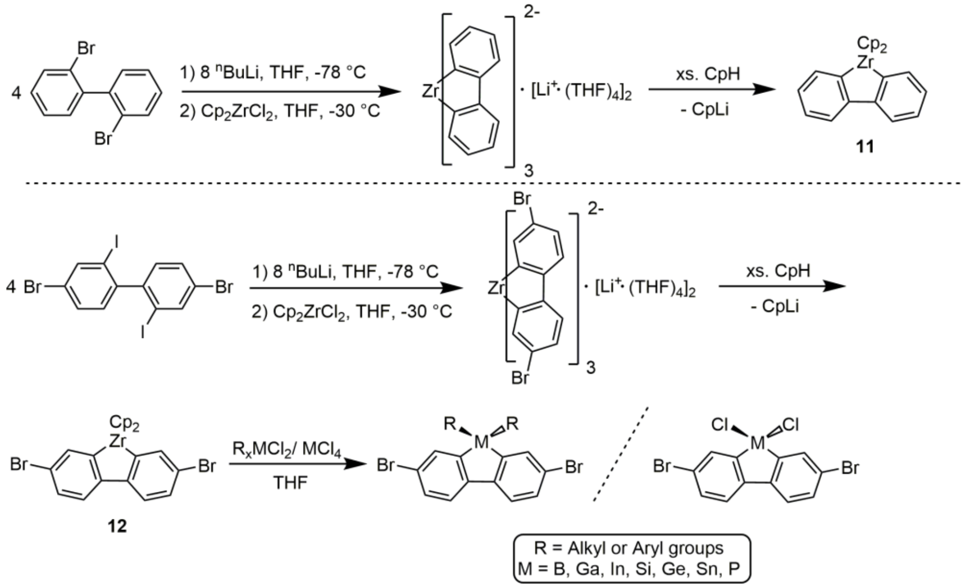
Unfortunately, it was found that spirocyclic center did not provide the expected increase in solubility in the resulting polymers, despite attempts to incorporate a monomer unit with long alkoxy chains. Future work would include improvement of the solubility and thermal stability of SGG homopolymers by structural modification of a germole ring. Fortunately, the modular synthetic routes outlined in Chapters 2 and 3 should allow this to be accomplished. Synthesis of SGG homopolymers, which could be obtained by Grignard metathesis or microwave-assisted Yamamoto polymerization are presented in Scheme 5.1. They would potentially have enhanced processability, thermal stability and color tunable emission.



Scheme 5.1. Synthetic route for the targeted light-emitting SGG homopolymers.

Another future direction could be improvement of the synthetic route to heterofluorenes. Currently most used synthetic method is lithiation of biphenyl derivatives with average yields of the products *ca.* 30 %,[3] thus it would be beneficial to obtain stable functionalized zirconacycle precursors, that could undergo one step metallacycle transfer to obtain any desired heterofluorenes. Parent zirconafluorene **11** (Scheme 5.2), indefinitely stable at 25 °C and in THF or Et_2O solutions, was reported in 86 % yield by Hilton and King.[4] The proposed synthesis of brominated zirconafluorene **12** is outlined on the Scheme 5.2. The metallacycle route is general, includes only one by-product of Cp_2ZrCl_2

that could be separated by precipitation in hexanes and does not require purification by column chromatography in contrast to the condensation route, reported by Wei group.[3] Notably, it could give an easy access to the class of dibenzotellurophenes (materials with nonlinear optical properties),[5] which is poorly explored due to the cumbersome nature of existing syntheses.[6]



Scheme 5.2. Preparation of zirconacycle precursors for the synthesis of heterofluorenes.

In conclusion, in this chapter it was found that by altering the nature of the peripheral substituents, photoluminescence from electronically separate germafluorene and germole units could be turned on or off, leading to blue, green and orange-yellow emission. In 2015 the Chi group discovered that a single organic molecule (Figure 5.4), showed "on/on" dual white light emission by combining blue- and yellow-light-emitting units.[7] Hence, future studies of SGGs would involve preparation of molecular or polymeric SGGs with "on/on" dual (preferably white) light emission.

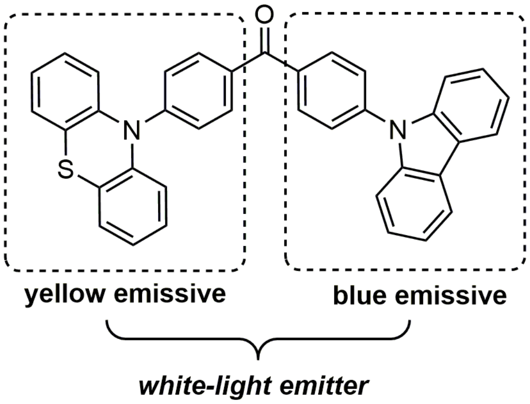
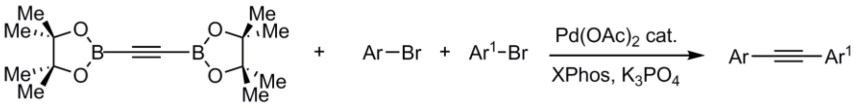


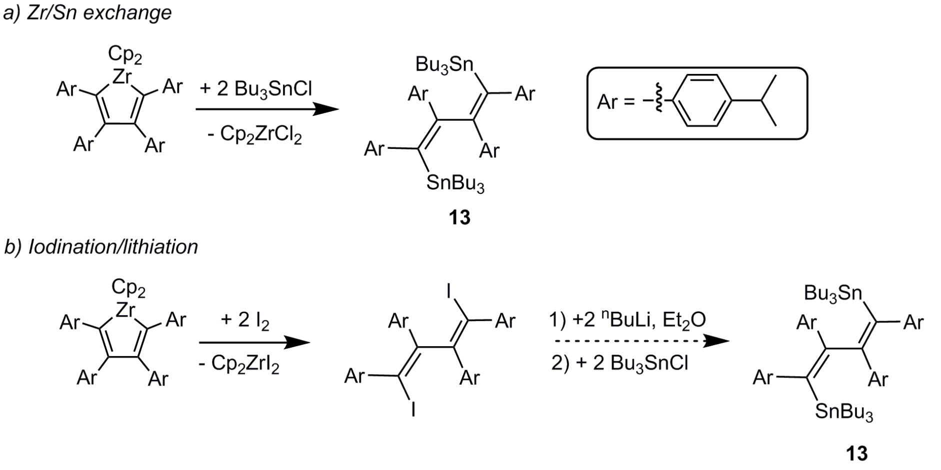
Figure 5.4. White-light-emitting compound reported by Chi and co-workers.

Chapter 3 described development of Suzuki-Miyaura protocol to obtain symmetrical diarylalkynes. They were further converted into the tetraarylbutadienes with tunable luminescent properties, and moderate quantum yields (*e.g.*, 24.8 % in the solid state) as well as thermal and photooxidative stability. Future work could involve expanding of the protocol towards the one-pot synthesis of asymmetric diarylalkynes (Equation 5.2).



(5.2)

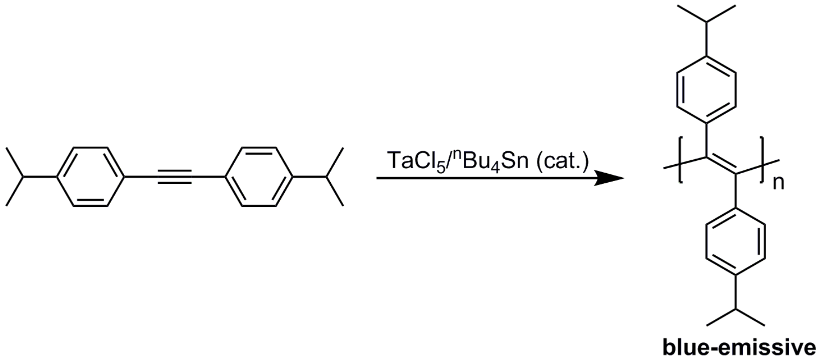
In order to incorporate blue-emissive tetracumylbutadiene into polymeric structures, synthesis of the tributyltin-capped tetracumylbutadiene monomer **13** was attempted *via* transmetallation with Bu_3SnCl; however it did not yield the desired product (Scheme 5.3).



Scheme 5.3. Synthetic approaches towards the monomer **13**.

Hence synthetic route through iodination/lithiation of zirconacycle was tested, but synthesis of 1,4-diiodo-1,3-butadiene was not successful. Interestingly, Takahashi and co-workers showed remarkable effect of copper chloride on diiodination of zirconacyclopentadienes as well the effectiveness of iodine monochloride as an iodinating agent,[8] thus improvement of the synthesis of 1,4-diiodo-1,3-butadiene could be potentially made by using CuCl as a catalyst or ICl as a source of iodine. A third approach towards halogenated 1,3-butadienes could be one-pot oxidation of diarylalkyne by HSO_3F/PbO_2 system, followed by quenching with hydrochloric (or hydrobromic) acid to yield 1,4-dihalo-1,3-butadiene, although extreme care has to be taken when working with fluorosulfuric acid (HSO_3F).[9]

Another approach to blue-emissive polymers (Equation 5.3) is using $TaCl_5/^nBu_4Sn$ catalytic system[10] to convert diarylalkynes into fluorescent polyacetylenes,[11] which are used for nitroaromatic sensing. For example, Schanze group studied poly[1-phenyl-2-(4-trimethylsilylphenyl)ethyne] as thin-film fluorescence sensor for dinitrotoluene.[12]



(5.3)

Chapter 4 outlined the preparation of (a)symmetric tellurophenes. The triphenylamine-capped symmetrical tellurium heterocycles (**14** and **15**; Figure 5.5) exhibited green fluorescence in the solid state, arising from restriction of molecular motion of appended amine substituents.

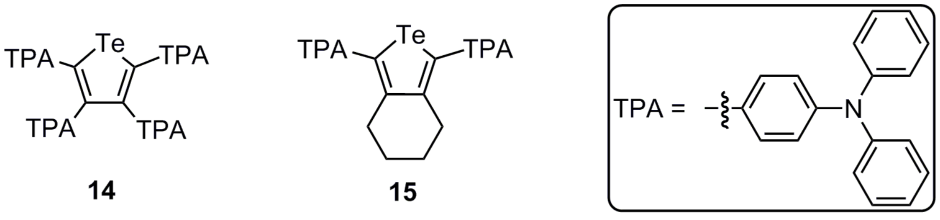
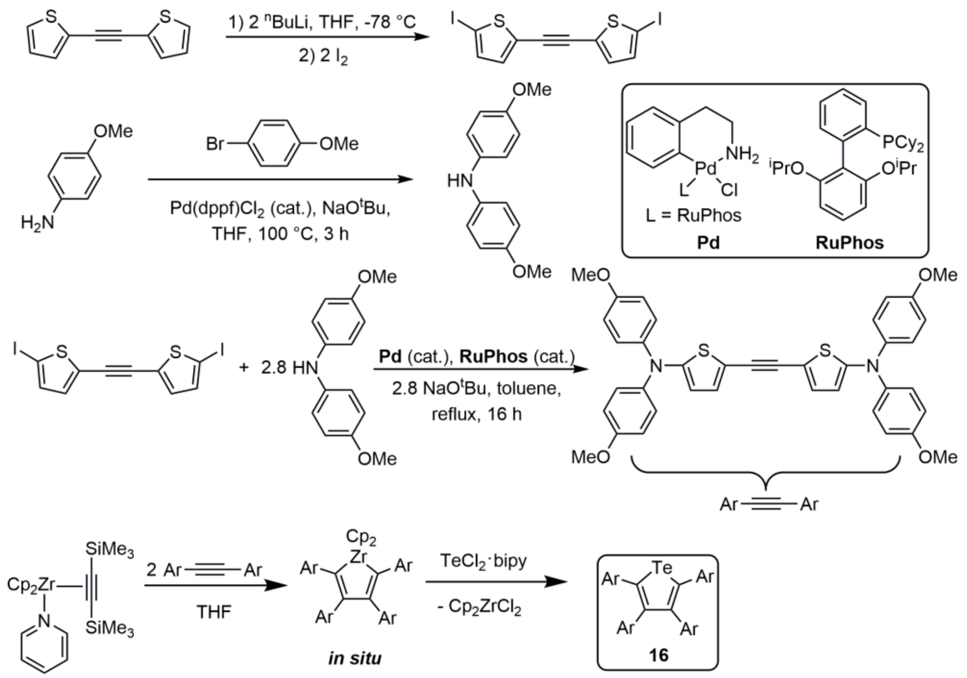


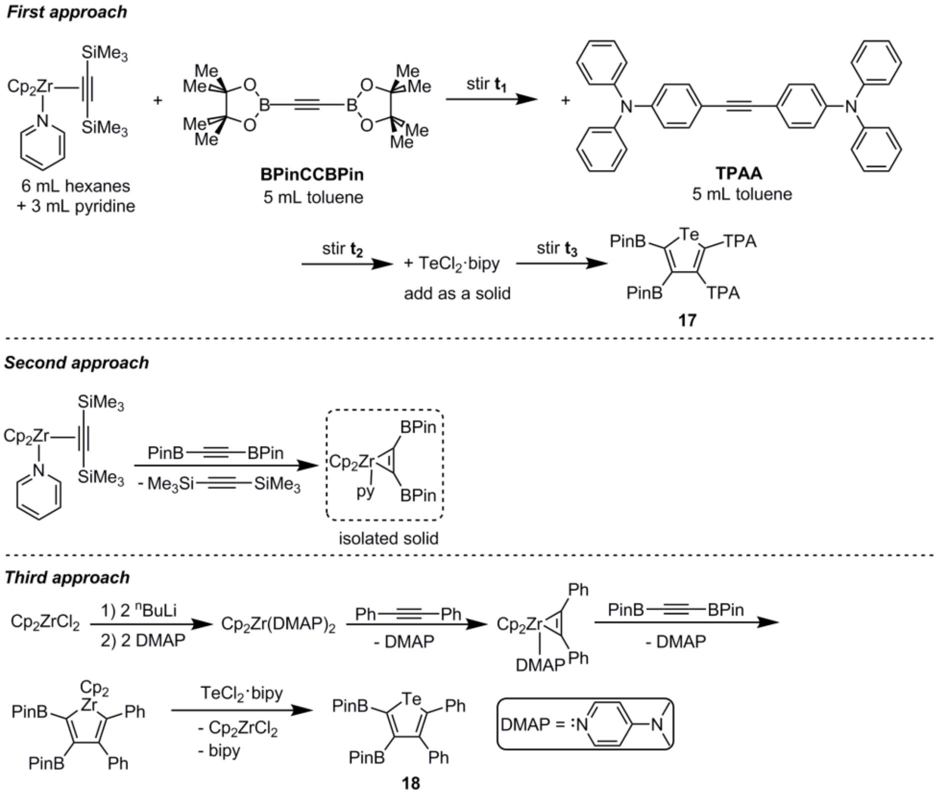
Figure 5.5. Structures of tellurophenes **14** and **15**.

Their electron and hole mobilities are currently under investigation through the collaboration with the Müller-Buschbaum group (TU Munich). Furthermore, in collaboration with Dr. Mike Boone (UofA) and the Wakamiya group (Kyoto University), their HOMO and LUMO levels were computed by DFT as well as by photoelectron spectroscopy. Based on these results, these compounds were determined to be unsuitable candidates for hole transport layers in perovskite solar cells, so a new system (**16**) with suitable HOMO level (≈ -5.0 eV) was designed; however the synthetic route towards **16** failed at the one step prior to the final. Thus, future work includes modification of the synthesis by using RuPhos-based catalyst/ligand system and an iodide-capped 1,2-bis(thiophen-2-yl)ethyne[13] for Buchwald-Hartwig amination in place of the bromide-substituted reagent used in the current study. The proposed synthetic pathway is outlined on the Scheme 5.4.



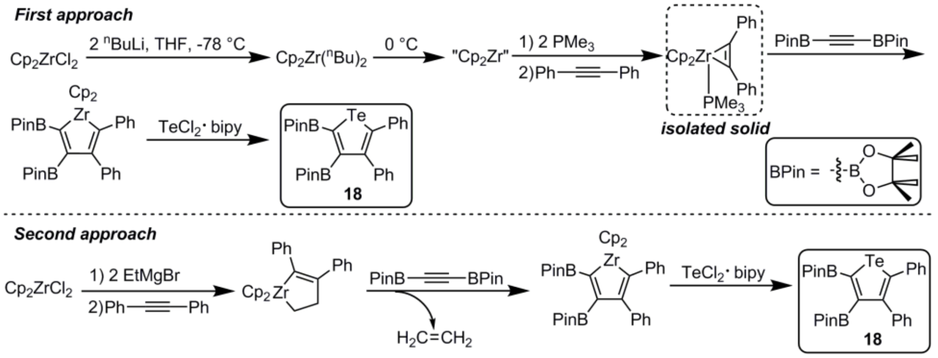
Scheme 5.4. Proposed synthesis of a tellurophene **16** for use as a hole transport layer in perovskite solar cells.

Moreover, asymmetric tellurophenes with a pinacolborane group (BPin) at the 2-position are of interest due to their efficient colour tunable phosphorescence in the solid state.[14] In this chapter synthetic attempts (summarized in Scheme 5.5) towards the abovementioned tellurophenes (**17** and **18**) were reported, including the step-wise addition of alkynes to Rosenthal's reagent $Cp_2Zr(pyridine)(Me_3SiCCSiMe_3)$,[15] followed by transmetallation with $TeCl_2$•bipy; however only symmetric derivatives were obtained.



Scheme 5.5. Synthetic approaches towards asymmetric tellurophenes **17** and **18**.

The second approach was isolation of previously reported[16] pyridine-stabilized zirconacyclopropene intermediate capped with BPin groups, however the procedure could not be reproduced. In 2000 Gouygou and co-workers reported synthesis of asymmetrically-substituted phospholes from *in situ* generated zirconacyclopropenes stabilized by dimethylaminopyridine.[17] These conditions were probed for the step-wise coupling of tolan (PhC≡CPh) and BPin-C≡C-BPin, but only starting alkynes were identified as major products at the end of the reaction. Future work would be based on the report by Negishi and co-workers, where they isolated zirconacyclopropene-phosphine intermediate (in the dashed box in Scheme 5.6 below) as a thermally stable solid.[18] With this in mind, the isolated intermediate could further react with PinB-C≡C-BPin and $TeCl_2$•bipy to form the desired phosphorescent tellurophenes. Moreover, a second approach would involve the synthesis of an asymmetrically-susbstituted zirconacycle using methodology developed by the Takahashi group (Scheme 5.6).[19]



Scheme 5.6. Proposed synthesis of the asymmetric tellurophene **18**.

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Chapter Five

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