Synthesis and Characterization of Segmented Fluorescent Conjugated Polymers via Acyclic Diene Metathesis (ADMET)

Gagandeep Singh

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SYNTHESIS AND CHARACTERIZATION OF SEGMENTED FLUORESCENT CONJUGATED POLYMERS VIA ACYCLIC DIENE METATHESIS (ADMET)

by

GAGANDEEP SINGH

Adviser: Professor Ralf M. Peetz

A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York

2016
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This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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Abstract

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by

GAGANDEEP SINGH

Adviser: Professor Ralf M. Peetz

This doctoral thesis is focused on the novel and facile synthesis and characterization of segmented conjugated polymers featuring various electro-optically active segments, with or without heteroatom linkages. The polymers were synthesized, via acyclic diene metathesis (ADMET) using ruthenium-based Grubbs-type catalysts. All products are soluble, and have a well-defined all-trans microstructure without defects. Some of the polymers were also synthesized via Suzuki polycondensation for comparison purposes. All monomers utilized were designed and synthesized in the laboratory.

Segmented conjugated polymers have received a great deal of attention in organic electronics, such as organic light emitting-diodes, organic field-effect transistors and organic solar cells due to that fact they are more flexible, lightweight and processable than their inorganic counterparts. ADMET allowed us access to luminescent conjugated polymers exhibiting different emission characteristics by systematically varying electro-optically active segments in the polymer backbone. The effects of alternating segments (incl. donor-acceptor systems), directly linked and bridged by heteroatoms or vinylene groups, were studied with regard to opto-electronic properties of the polymers. Characterizations included UV-vis, fluorescence spectroscopy, and cyclic voltammetry. Si was found to effectively disrupt the π-conjugation resulting in a well-defined blue emission. The HOMO-LUMO energy levels could be tuned by careful selection of aromatic segments in the
polymer backbone. E.g. systems with alternating functionalized phenylene vinylene and benzothiadiazole segments exhibited strong electronic interactions between segments, resulting in broad absorptions and lower HOMO-LUMO band gaps, which are important for higher power conversion efficiencies in solar cells. The experimental results obtained were consistent with calculated data obtained from density functional theory (DFT) calculations.
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This dissertation is dedicated to my fiancé Manjinder Kaur
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1. Introduction

1.1 Conjugated polymers

The growing demand for low-cost, light weight, and flexible electronics continues to drive the development of next generation organic electronics.\textsuperscript{1} Conjugated polymers have received a great deal of attention in organic electronics since they exhibit semiconducting properties along with the mechanical properties, and processing benefits of plastics. This synergy make these functional materials useful in devices, such as organic light emitting-diodes (OLEDs), organic field-effect transistors (OFETs) and organic solar cells (PSCs).\textsuperscript{1,6,20} The semiconducting behavior of the conjugated polymers is due to the presence of delocalized $\pi$ electrons along the polymer chain. The efficient transport of excitons along the polymer chain plays a major role in the electronic properties of the conjugated polymers.\textsuperscript{1} Research on conjugated polymers was refueled since the Nobel Prize for Chemistry in 2000 was awarded to Professors Heeger, Shirakwa, and MacDiamrid for their discovery of “doped” polyacetylene as a highly conducting polymer.\textsuperscript{2,3} Another major breakthrough in the field of conjugated polymers includes the discovery of electroluminescence observed in these polymers reported by Burroughes et al. in 1990.\textsuperscript{4} Scheme 1.1 shows some examples of typical conjugated polymers such poly (para-phenylene) (PPP), poly (para-phenylene ethynylene) (PPE) polypyrrole (PP) and polythiophene (PT).

\begin{center}
\includegraphics[width=0.8\textwidth]{scheme.png}
\end{center}

**Scheme 1.1.** Chemical structures of early examples of conjugated polymers
1.2 Applications of conjugated polymers

**Organic Photovoltaics**

Solar cells have been recognized as one of the most important renewable energy source. However, the large scale use of this technology is limited by high manufacturing cost, which are mostly fabricated from inorganic materials and requires high-temperature fabrication techniques and expensive vacuum systems. Polymer solar cells have become an active area of research due to their potential advantages over inorganic counterparts, including low cost, light weight, and fast roll to roll production. In particular, bulk heterojunction solar cells have demonstrated remarkable power conversion efficiency, now reaching values ~10%. Donor-acceptor polymers are one of the promising architectures for use in polymer solar cells.

**Field effect transistors**

Field-effect transistors (FETs) are electronic switches applied in electronic devices such as displays and computer logics. Charge mobility is a key parameter in FETs which decides on/off switching speed of the device. Although crystalline and amorphous silicon compounds are widely used in FETs, they cannot be used on flexible electronic devices. On the other hand, conjugated polymers offer solution processability and can be easily coated onto flexible devices. Conjugated polymers should have some critical characteristics in order to be used for organic field-effect transistors applications. The semiconducting polymer should possess a HOMO energy level lower than 5.2 eV to be air stable, and it should be able to form well organized film in order to achieve high mobility. The polymer should also have alkyl chains in the backbone in order to make it soluble and processable.
Light-emitting diodes

Light-emitting diodes (LEDs) are used in various electronic devices acting as electronic displays or light indicators. Since first polymer organic LED was discovered by Friend and coworkers, large number of conjugated polymers have been investigated for light-emitting applications. Various conjugated polymers and small molecules have been applied in electronic devices made of organic LEDs such as smartphones, high definition displays and digital cameras.
1.3 Monomer/Polymer design

While designing the monomer/polymer for optoelectronic applications, several principles have to be taken into account, including i) side chain engineering ii) molecular weights iii) HOMO and LUMO energy levels iv) absorption profile and the band gap v) morphology. These factors are interrelated and must be comprehensively considered while designing the polymers for optoelectronic applications. Tuning the HOMO-LUMO energy levels will also affect the band gap, absorption profile, and thus change the emitting color in OLED or alters the open-circuit voltage in polymer solar cell. To address these issues, various molecular engineering strategies have been explored to tune the optoelectronic properties of conjugated polymers. Some of the methodologies applied include increased conjugation and rigidity in polymer backbone, stabilization of quinoidal resonance structure, planarization of aromatic units, incorporation of heteroatoms, and the use of donor-acceptor strategy.

1.4 Aromatic Conjugated Systems

Early research on conjugated polymers was focused on poly-para-phenylenes (PPPs) and its derivatives. Some of polyphenylene derivatives include ladder-type poly-para-phenylenes (Scheme 1.2a), which are composed of linear fused fluorenes or heteroatom bridged phenylenes such as polycarbazoles. Further extension to polyphenylenevinylenes (PPVs) lead to the development of semiconducting polymers, widely applied in polymer light-emitting diodes and polymer solar cells. Unsubstituted PPV (Scheme 1.2b) emits in green-yellow region of visible spectrum. Later on, the solubility of PPVs was improved by introducing side chains in polymer backbone. Most PPV derivatives are used as donor materials in solar cells. The cyano substitution on vinlylenes led to narrow band gap material emitting in red region. Polyfluorenes (Scheme 1.2c) are also one of the most promising candidates for various optoelectronic devices due to its highly
efficient emission. Moreover, various functional groups could be introduced at 9-position carbon atom of fluorene unit enabling the engineering of photophysical properties.

Another representative class of rigid π-conjugated systems are polycyclic aromatic hydrocarbons (PAHs) (Scheme 1.2d) which were found to be blue emitters and p-type semiconductors. Thiophenes are also another important class of conjugated polymers used in organic field-effect transistors and polymer solar cells. High polarizability of sulfur atoms in thiophenes leads to excellent charge transport which is quite important for optoelectronic applications. Fusion of another electron rich moieties with thiophenes resulted in polymers which exhibit interesting optoelectronic properties due to enlargement of π-conjugated system. In general polythiophenones demonstrates hole transport characteristics, and have been used as p-type semiconductor for organic field-effect transistors and polymer solar cells.

![Scheme 1.2](image)

**Scheme 1.2** Aromatic conjugated systems: a) Ladder-type PPV b) PPVs c) Polyfluorenes d) PAHs
1.5 Heteroatom containing Conjugated polymers

Although the above mentioned polymers are of paramount importance in organic electronics, the development of new materials to further tune the HOMO and LUMO energy levels is an active area of research for the next generation light-emitting and solar cell devices.\textsuperscript{20,21,22} The incorporation of main-group elements (Se-, Te-, P-, Si-, Ge- and B-) in the polymer backbone (Scheme 1.3) represents a promising way to engineer the optoelectronic properties due to their unique structural and electronic properties.\textsuperscript{20} These elements have been found to impact the photophysical properties of the resulting polymers considerably and have been used with many conjugated polymers for optoelectronic devices. Polyselenophenes (Scheme 1.3a) have been reported to exhibit excellent electrochomic properties.\textsuperscript{23,24} Similarly, tellurium has also been demonstrated to narrow down the energy gap and offer post-polymerization in conjugated polymers.\textsuperscript{20} Phosphorus containing conjugated polymers (Scheme 1.3b) have attracted considerable attention\textsuperscript{25} especially due to increased electron acceptability owing to pyramidal nature of phosphorus. These polymers have been used in development of n-type semiconducting materials. In 2010, Leclerc et al. reported germanium containing conjugated polymers (Scheme 1.3c) as well as their applications in FETs and bulk heterojunction solar cells.\textsuperscript{26} Theoretical calculations on similar systems revealed that longer Ge-C bonds relieve the steric stress of the side chains thereby allowing efficient \( \pi \)-\( \pi \) stacking resulting in lower band gaps as compared to carbon analogues.\textsuperscript{27} On the other hand, Boron-containing \( \pi \)-conjugated polymers ((Scheme 1.3d) have attracted increasing attention owing to their distinct optoelectronic properties due to \( \pi \)-\( \pi^* \)conjugation between vacant p orbital on the boron atom with the \( \pi^* \) orbital of the \( \pi \)-conjugated system. Boron-containing polymers have found applications in light-emitting diodes and sensors.\textsuperscript{28,29}
In particular, Si-containing conjugated polymers have received considerable attention as conductors, semiconductors, light emitters and photovoltaic systems. In 2008, series of silole containing thiophene and benzene polymers were prepared by Facchetti, Ratner, and coworkers (Scheme 1.3e). They found out that the polymers absorb strongly in green region and emit in orange-red region of visible spectrum. Polymers exhibited blue-shift in both absorption and emission spectrum. Conjugated organosilicon polymers are also used in solar cells. In 2008, Yang et al. reported donor-acceptor polymer based on dithienosiloles and benzothiadiazole (Scheme 1.3f). Increased hole mobility was observed as compared to carbon analogues showing the advantage of incorporating Si in the conjugated back bone. Polymer exhibited power conversion efficiency up to 5.1% and $J_{sc}$ of 12.7 mA cm$^{-2}$ when blended with PCBM ([6,6]-phenyl-C$_{61}$-butyric
acid methyl ester). Similarly, dibenzosililole based polymer exhibited 20 nm red-shifted absorption maximum and 0.1 eV lower band gap as compared to carbon counterpart. PCE of 5.4 % was achieved with this polymer/PCBM blend. Another dithienosililole and theionopyrrole-dione based polymer showed deep HOMO level (5.57 eV) and low band gap (1.7 eV). Polymer showed a high PCE of 7.3% in a photovoltaic device when blended with PCBM.

Silicon when placed as a spacer group in conjugated polymers, results in quite different electronic structure as compared to that of carbon analogues. The uniqueness of silicon-carbon copolymers arises from a discrete size and structure of said aromatic segments with well-defined electro-optical properties, compared to their polymeric analogues with average distributions of conjugated systems. The polymers may exhibit σ*-π* conjugation between the σ orbitals of the silicon atoms and π orbitals of the double bonds along the polymer chain. There are various reports on incorporation of silicon into the conjugated backbone. In 2005, Luh et al. reported phenylene and biphenylene based Si-containing conjugated polymers via hydrosilation (Scheme 1.4). Kim et al. also reported synthesis of thiophene and phenylene based silylene copolymers via Heck coupling. (Scheme 1.5). Hadziioannou et al. also reported oligothiophene-dibutylsilanylene copolymer whose emission maxima could be tuned by varying the number of thiophene and silanylene units. Silylene copolymers with electro-optically active units have been prepared by a similar route.
While all the synthetic strategies to access this useful class of polymers are important as they allow to tune their electro-optical properties, acyclic diene metathesis (ADMET) is of significant interest because the reaction conditions are quite mild, ethylene formed as only byproduct is easily removed, and the polymer architectures are well defined. Moreover, various functional groups
could be incorporated in the polymer backbone owing to the selectivity of highly sophisticated catalysts, developed by Grubbs, Shrock and Hoveyda.

**1.6 Donor-acceptor polymers**

Another important strategy to tailor the optoelectronic properties of conjugated polymers is to integrate electron donor and electron acceptor moieties in one polymer system. The electron push/pull ability, structure, geometry and the interaction determine the resulting properties of the polymer. Intra- and Intermolecular interactions between donor and acceptor moieties may lead to self-assembly into ordered structures and \( \pi-\pi \) stacking leading to charge carrier transport in organic field-effect transistors.\(^8\) Another important feature of donor-acceptor polymers is that it allows us to tune HOMO and LUMO energy levels and hence provides an ability to control the band gap. Control over the HOMO-LUMO band gap is crucial for effective material development for polymer solar cells.\(^{54,55}\) Incorporation of electron-rich and electron deficient unit in the polymer chain favors internal charge transfer and has been widely used to prepare low band gap donor-acceptor conjugated polymers.\(^{56,57,58}\) In such polymers, HOMO is localized on donor segment whereas acceptor is localized on acceptor block, enabling us to individually tune the energy levels and hence the band gap.\(^{6,59}\)

Numerous donors based on benzene and thiophene have been employed as donors. There are several principles which guides the strength of the donors. In general thiophene donors are stronger than benzene, similarly bridged bithiophenes are usually regarded as strong donors while bridged biphenyls are weak donors.\(^8\) Most acceptor units possess at least one or more strong electron withdrawing unit. Most common examples are based on thiazole-, pyrrole, thiazole-, pyrazine, imide-, and carboxylic group. The electron-accepting abilities of these acceptors can be determined theoretically through Density Functional Theory (DFT) calculations and experimentally through Cyclic Voltammetry (CV) characterization. In general low HOMO levels
(5.2 eV-5.4 eV) are important for high open circuit voltage and the narrow band gap is beneficial for high short-circuit current in photovoltaic devices. So an optimum balance is required between HOMO level and the band gap to yield higher power conversion efficiencies.

The most common synthetic strategies to access donor-acceptor polymers are palladium-catalyzed Suzuki and Stille coupling. These coupling strategies are significant as they are applicable to wide variety of monomers producing library of donor-acceptor polymers with high power conversion efficiencies. However, there are also considerable limitations associated with these strategies. Stille polymerization requires the use of toxin tin derivatives whereas Suzuki polycondensation involves use of AA (boronic acid/esters) and BB (halogens) monomers which are susceptible to undesired processes such as protodeboronation, oxidation, homocoupling, and dehydration. Besides, Suzuki polycondensation often requires end-capping to remove boron and bromo end functionality at the polymer chain ends and palladium removal from the polymer is always a challenge. On the other hand, ADMET provides a convenient route to access these polymers due to mild reaction conditions employed. The functional group tolerance of the ADMET catalysts, allow to polymerize large variety of monomers to access precise donor-acceptor architectures. End capping is not required in ADMET and the catalyst removal is comparatively easy.
1.7 Olefin Metathesis: ADMET

Olefin metathesis is defined as a chemical reaction which involves the exchange of bond (or bonds) between related chemical species resulting in the product formation with similar bonding patterns as reactants. In Olefin metathesis, two carbon-carbon double bonded species transforms into two new olefins as shown in scheme 1.6.

Scheme 1.6 Olefin metathesis

Acyclic Diene Metathesis (ADMET) is a mode of metathesis reaction which involves divinyl functional monomers in a condensation reaction to make oligomeric/polymeric materials using either Schrock or Grubbs type complexes. Reaction proceeds in forward reaction forming metathesis products by the release of condensate generally ethylene as shown in Scheme 1.7. ADMET is carried out under reduced pressures to remove the ethylene gas so that the reaction can be driven to forward direction. Although the term ADMET was first coined by Wagner and coworkers in 1980’s, Dall’Asta et al. reported the metathetic polycondensation of alpha-omega-dienes. ADMET is a convenient route to access various polymer architectures which would not be possible by other methods. Chauvin and Herisson proposed the ADMET mechanism in 1972, which is widely accepted. The key steps of mechanism are shown in Scheme 1.8. The first step involves the formation of metallocyclobutane ring (intermediate) by the coordination of metal carbene catalyst with the double bond of olefin. The intermediate can then either proceeds in forward direction and breaks apart forming new alkylidene complex (productive) or go backwards producing reactants (non-productive). The productive alkylidene complex will then react with
monomer forming a dimer and methyldiene catalyst. Methyldiene complex will act as a true catalyst, forming a new metallocyclobutane ring and forming oligomers/polymer.

Scheme 1.7 ADMET reaction

Scheme 1.8 ADMET mechanism (Reprinted with permission from ref. 92 Copyright (2013) American Chemical Society )
1.8 ADMET in Synthesis of silicon containing conjugated polymers

The first quantitative synthesis of polymers by homopolymerization and copolymerization of 1,5-hexadiene and 1,9-decadiene via ADMET, using Shrock’s catalysts, was reported by Wagener and coworkers. Since then, Wagener et al. synthesized various heteroatom (silicon/germanium/tin) containing polymers using ADMET. However, hardly any attention has been focused on synthesis of silicon containing conjugated polymers because the vinyl derivatives of silicon compounds are very unreactive towards homometathesis due to steric and electronic effects originating from the silyl group, stimulating non-productive cleavage of the metallacyclobutane intermediate containing two silyl groups attached to adjacent carbonatoms. Marciniec et al. reported organosilicon conjugated polymers via ADMET but it was dominated by side reaction, silylative coupling (Scheme 1.9). Bazan and coworkers also reported cross-linked polymeric side products in the ADMET of thiophene containing silane conjugated polymers problematic side-reactions. In silicon conjugated polymers, the organo-silicon moiety acts as a “spacer group” between the conjugated units, generating a well-defined conjugation unit, usually with a band gap ~3 eV, corresponding to a blue emission (difficult to make from inorganic counterparts).
In 2008, Mukherjee and Peetz reported silylene and siloxane functional conjugated polymers and macrocycle via ADMET (Scheme 1.10). The siloxane based monomers under investigated experimental conditions exclusively yielded dimeric rings while silylene type monomers resulted in linear conjugated polymers with no significant side reactions. In a follow up report, Interrante et al. synthesized cyclolinar carbosilane polymers via ADMET (Scheme 1.11). Recently, Peetz et al. reported synthesis of Boron- and silicon-containing conjugated homo- and copolymers using ADMET (Scheme 1.12). The copolymer with tri-coordinate boron exhibited highly efficient fluorescence quenching in the presence of fluoride ions demonstrating its potential as anion sensor.
Scheme 1.10 Silylene and siloxane functional conjugated polymers and macrocycle via ADMET

Scheme 1.11 Synthesis of cycloliner carbosilane polymers via ADMET by Interrante et al.
Scheme 1.12 Synthesis of Boron- and silicon-containing conjugated homo- and copolymers using ADMET reported by Peetz et al.\textsuperscript{90} (reproduced by the permission of John Wiley and sons)

The scope of this thesis lies in extending the ADMET approach to produce various segmented conjugated polymers exhibiting different photo-physical characteristics by systematically varying electro-optically active segments in the polymer backbone. In the first part using ADMET in a unified approach, we synthesized homologous luminescent conjugated polymers with two aromatic segments based on thiophene and substituted phenylene, either alternating or randomly distributed, either directly connected or separated by Si-linkers. We then studied their interaction in terms of photophysical properties. This unified synthetic strategy could
be applied to prepare a wide range of useful organosilicon polymers. UV-vis and fluorescence studies along with cyclic voltammetry data provide important insights into the effect of silicon on the photo physical properties. Experimental data is supported by Density functional theory (DFT) calculations.

1.9 ADMET in donor-acceptor conjugated polymers

Recently, ADMET has emerged as a convenient route to precise polymer architectures that would not be possible by any other methods.\textsuperscript{80} It has been applied to synthesize conjugated polymers including polyenes and poly(arylene vinylene)s.\textsuperscript{81} Furthermore, various functional groups could be incorporated in the polymer backbone owing to the selectivity of highly sophisticated catalysts developed by Grubbs, Shrock and Hoveyda. In 2013, Hillmeyer et al. have successfully employed ADMET to synthesize polyIthienylene vinylene- (PTV-) based polymer series (Scheme 1.13) where they studied the impact of tuning the olefin content in the repeating unit, on optical and polymer solar cell behavior.\textsuperscript{82} Hillmeyer et al. also prepared PTVs based D-A polymers (Scheme 1.14) with distinct optoelectronic properties via ADMET.\textsuperscript{83}

\begin{center}
\textbf{Scheme 1.13} PolyIthienylene vinylene based polymers prepared via ADMET by Hillmeyer et al.\textsuperscript{82}
\end{center}
Scheme 1.14 PTV based D-A polymers prepared via ADMET by Hillmeyer et al.\textsuperscript{83}

We have previously demonstrated the use of ADMET for the preparation of various heteroatom containing macromolecules.\textsuperscript{40,84,90} Based on these results, we proceeded to make a systematic series of donor acceptor polymers of significant interest for potential use in polymer solar cells. We tuned the energy levels by careful selection of aromatic segments in the polymer backbone, and then compared their electro-optical properties based on structural variation. Polymer structures
are based on hexyl thiophene, benzothiadiazole and phenylene vinylene. We chose these aromatic components, as polyphenylenevinylenes\textsuperscript{85,56} have shown interesting electronic properties, poly3-hexylthiophenes\textsuperscript{2,86,87,88} remains one of the main efficient donor and benzothiadiazole has been used as an acceptor for constructing low band-gap polymers\textsuperscript{89,37} For comparison, we have also synthesized the analogous polymers via Suzuki polycondensation. ADMET polymers differs from Suzuki polymers in terms of alkoxy phenylene vinylene content in the repeating unit. The polymers are characterized and the optoelectronic properties are compared.
1.10 References


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2. Studies on Homologous Random and Alternating Segmented Conjugated Polymers With and Without Silicon Synthesized by ADMET

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2.1 Introduction

The developments of next generation light weight, flexible and printed electronics have revolutionized the field of conjugated polymers. Consequently, a multitude of conjugated polymeric materials have been reported and incorporated into organic photovoltaics (OPVs), organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs), and other applications. The class of Si-containing conjugated polymers have received particular attention as conductors, semiconductors, light emitters, light harvesters in photoelectrics and photovoltaic systems. The photophysical properties of such materials can be tailored by careful selection of electro-optically active conjugated aromatic segments, particularly in the polymer backbone. The uniqueness of silicon containing segmented conjugated polymers is due to the discrete size and structure of said aromatic segments with well-defined electro-optical properties, compared to polymeric analogues with average distributions of conjugated segments. While the conjugated segments electronically interact through space, due to their vicinity to each other, the polymers may also feature σ*-π* conjugation between the σ orbitals of the silicon atoms and π orbitals of the organic segment in the polymer chain. Along with the electronic effects, silylene spacers, especially dialkylsilylenes, have also been shown to introduce significant flexibility into the polymeric chain, making such otherwise typically rigid-rod like polymers soluble and processable. Furthermore, intramolecular energy transfer from photoexcited states reported for organosilicon polymers may present alternatives donor-acceptor systems.
The most common techniques to access conjugated polymer systems containing silicon are condensation-based syntheses\textsuperscript{7,8,26} and hydrosilylation techniques.\textsuperscript{19,25,27-37} We and others have reported using acyclic diene metathesis (ADMET) as a convenient route to precise polymer architectures that would not be accessible by any other methods, including silicon containing systems.\textsuperscript{18,23,38-44} Such control over polymer architecture is highly beneficial for varying material properties and determining potential applications.\textsuperscript{41} Various functional groups can be incorporated into the polymer backbone owing to the reactivities of catalysts developed by Grubbs, Schrock, and Hoveyda.

In 2008, we reported ADMET as a convenient route to yield silylene- and siloxane-containing conjugated polymers and macrocycles featuring alternating aromatic and silicon segments.\textsuperscript{18} The resulting polymers emitted at wavelengths in the blue region with quantum efficiencies ~0.24-0.28. Later, we used ADMET for the controlled synthesis of fluorescent macrocycles consisting of aromatic segments linked by germanium containing segments.\textsuperscript{42} Interrante et al. reported on using a related ADMET approach for the synthesis of photocurable, photoluminescent polycarbosilanes.\textsuperscript{23} Recently, we reported on conjugated homo- and co-polymers containing both silicon and tri- or tetra-coordinated boron in the main chain. These polymers exhibited intriguing electro-optical properties. E.g., the copolymer with tri-coordinated boron served as a highly sensitive Lewis-donor sensor, as demonstrated by very efficient fluorescence quenching by fluoride ion binding.\textsuperscript{39}

We hereby report the extension of the ADMET strategy to synthesize structurally related segmented conjugated polymers that feature two different electro-optically active aromatic segments, linked by a flexible silylene group or connected directly to each other. The segments in the silylene-containing systems were either distributed randomly along the chain or strictly alternating. The aromatic segments were based on thiophene and diheptyloxy substituted
phenylene. To this end, three distinct bis-vinyl functional monomers were synthesized and subjected to ADMET polycondensation. The Si-containing systems were found to be emitting at blue wavelengths, whereas homologous systems without Si-linkages emitted at longer wavelengths. Blue-light-emitting polymers are of significant interest as energy transfer host materials in the presence of lower energy fluorophores. Furthermore, the synthesized polymers were observed to exhibit energy transfer from one segment to another. Such intramolecular energy transfers along macromolecular organosilicon systems have received attention as they may serve as a useful model to mimic the natural light harvesting process. The observations could be explained using results from electrochemical measurements and theoretical calculations of the HOMO/LUMO levels.
2.2 EXPERIMENTAL SECTION

General Information. All experiments involving air/moisture sensitive materials were carried out using standard Schlenk techniques with a dry nitrogen - filled dual manifold (inert gas/vacuum).

Materials. 5-Bromo-2-thiophenecarboxaldehyde (98%), n-butyllithium solution (BuLi, 2.5 M in hexane), methyltriphenylphosphonium bromide (98%), dichlorodimethylsilane (>99.5%), Grubbs’ catalyst (2nd Generation), Hoveyda-Grubbs catalyst (2nd Generation), and diethyl ether (anhydrous) were obtained from Sigma-Aldrich. 1-bromo-2,5-bis(heptyloxy)-4-vinylbenzene and 2-bromo-5-vinylthiophene were prepared according to previous work. Column chromatography was carried out on silica gel 60 (70-230 or 230-400 mesh) from EMD Chemicals. Solvents such as tetrahydrofuran (THF), toluene, hexane, and dichloromethane were purchased as HPLC grade from Fisher Scientific. Solvents were dried and degassed by a “Pure Solv” solvent purification system (using activated alumina, copper catalyst, molecular sieves column) by Innovative Technology Inc. before use. Deuterated solvents for NMR spectroscopy were from Cambridge Isotope laboratories.

Analytical Methods. 600 MHz 1H-NMR, 125 MHz 13C NMR spectra, and 120 MHz 29Si NMR were recorded in CDCl3 on Varian Unity NMR instruments. All signals in the 1H NMR spectra are reported in ppm relative to the solvent’s residual 1H signal (CDCl3; 7.24 ppm) and with multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, dd = doublet of doublet). 13C NMR and 29Si NMR spectra were referenced to CDCl3 (77 ppm) and tetramethylsilane (TMS) respectively. Thermogravimetric analysis was carried out on a Hi-Res TGA 2950 thermogravimetric analyzer from TA Instruments using a platinum pan with a heating rate 10 °C/min under continuous nitrogen flow.
UV-Visible absorption spectroscopy was performed on Perkin Elmer Model 650 UV Spectrophotometer with 1-cm path length cells in hexane. Photoluminescence spectra were recorded using a Varian spectrofluorometer with 1-cm path length cells in hexane. Gel permeation chromatography (GPC) analysis in THF was performed on an Alliance GPCV 2000 (Waters) instrument equipped with four Waters Styragel HR columns, i.e. HR-1, HR-3, HR-4, and HR-5E. The flow rate of THF was kept at 1.0 mL/min at 40°C throughout the analysis. Molecular weights are recorded relative to polystyrene standards. Results were processed using the Empower Pro Multidetection GPC software. Absolute molecular weight and structural studies were performed on Viskotek TDA max (Model 305) equipped with advanced temperature controlled, triple-detector GPC system with Refractive Index, Viscometer and Light scattering detectors. Cyclic voltammetry (CV) experiments were carried out on a CV-50W analyzer from BAS. The three electrode system consisted of an Au disk as working electrode, a Pt wire as secondary electrode and an Ag wire as the reference electrode. The voltammograms were recorded with ~ 10^{-3} - 10^{-4} M solutions in THF and 0.1 M Bu4N[Pf6] as supporting electrolyte. The scans were referenced to ferrocene as internal standard. The potentials are reported relative to the ferrocene/ferrocenium couple.

**Calculations.** Density functional theory calculations were carried out on dimer models of the polymers and diheptyloxy were replaced with methyloxy for the sake of simplicity of calculations. The input files were prepared via Gaussview 3.07. First, the geometries of the dimer models were optimized in the ground state using basis set DFT/B3LYP/6-31G(d,p) in Gaussian 09 with CUNY high performance computers. The calculations were carried out in gas phase to neglect the solvent effect.

**Procedures.**
Synthesis of 1 [(2,5-bis(heptyloxy)-4-vinylphenyl)dimethyl(5-vinylthiophen-2-yl)silane] 1-bromo-2,5-bis(heptyloxy)-4-vinylbenzene (700 mg, 1.70 mmol) was dissolved in a mixture of 5.4 mL dry THF and 0.6 mL of dry diethyl ether. This first solution was cooled to -78°C and n-BuLi (0.70 mL, 2.5 M in hexanes, 1.70 mmol) was added through a syringe. The mixture (solution 1) was stirred at -78°C for 3 hours. Dichlorodimethylsilane (0.20 mL, 1.70 mmol) dissolved in 1 mL THF (solution 2) and cooled to -78°C. Solution 1 then was transferred via cannula to solution 2, and the resulting mixture stirred at -78°C for 4 additional hours to form a monochloro-substituted silane intermediate (solution 3). In a separate reaction tube, 2-bromo-5-vinylthiophene (322 mg, 1.70 mmol) in 5.4 mL dry THF and 0.6 mL dry diethyl ether was cooled to -78°C, and then n-BuLi (0.70 mL, 2.5 M in hexanes, 1.70 mmol) was added via syringe. This mixture was stirred at -78°C for 3 hours to form lithiated vinylthiophene (solution 4). Solution 3 was then transferred drop-wise via cannula to solution 4 and the resulting mixtures stirred at -78°C for 2.5 hours to yield monomer 1. The solvent was evaporated, and the dry mixture was dissolved in hexane/toluene (1:1). The mixture was washed with water. After evaporating the solvent, the crude product was purified using a 70-230 mesh size silica gel column using hexane/toluene (4:1) as an eluent. Monomer 1 was yielded as a light green viscous liquid (650 mg, 76%). 1H NMR (600 MHz, CDCl3): 7.14 (d, 3J = 3.43 Hz, 1H), 7.07-7.02 (dd, 4J = 11.40 Hz, 3J = 18.00 Hz, 1H), 7.02 (d, 3J = 3.24 Hz, 1H), 6.92 (s, 1H), 6.84-6.80 (dd, 4J = 11.40 Hz, 3J = 17.40 Hz, 1H), 6.83 (s, 1H), 5.74 (d, 3J = 17.89 Hz, 1H), 5.57 (d, 3J = 17.47 Hz, 1H), 5.26 (d, 3J = 11.31 Hz, 1H), 5.12 (d, 3J = 10.94 Hz, 1H), 3.92 (t, 3J = 6.59 Hz, 2H), 3.85 (t, 3J = 6.48 Hz, 2H), 1.77-1.24 (m, 20H), 0.89 (m, 6H), 0.59 (s, 6H). 13C NMR (125 MHz, CDCl3): 158.96, 151.11, 149.31, 139.08, 136.35, 132.87, 130.75, 130.31, 127.89, 126.83, 121.72, 115.46, 114.40, 108.62, 70.58, 69.15, 32.76, 30.39, 30.05, 27.04, 23.63, 15.10, 0.04. Elemental analysis: calculated C 72.23, H 9.30, S 6.43; found C 72.21, H 9.33, S 6.65.
Synthesis of [(E)-1,2-bis(5-bromothiophen-2-yl)ethene] 2-bromo 5-vinylthiophene (395 mg, 2.09 mmol) was dissolved in 10 mL dry toluene and Grubbs second generation catalyst (87 mg, 0.10 mmol) was added. The mixture was heated to 65°C and stirred for 72 hours under reduced pressure at this temperature. The solvent was evaporated, and the crude product purified using column chromatography with silica gel. A bright yellow solid was yielded (260 mg, 71%). ¹H NMR (600 MHz, CDCl₃): 6.92 (d, ³J = 3.62 Hz, 2H), 6.78 (s, 2H), 6.75 (d, ³J = 3.64 Hz, 2H). Elemental analysis: calculated C 34.31, H 1.73, S 18.32; found C 35.15, H 1.95, S 18.16.

Synthesis of 2 [(E)-1,2-bis(5-((2,5-bis(heptyloxy)-4-vinylphenyl)dimethylsilyl) thiophen-2-yl)ethane]. 1-bromo-2,5-bis(heptyloxy)-4-vinylbenzene (672 mg, 1.64 mmol) was dissolved in 5.4 mL dry THF and 0.6 mL dry diethyl ether. The solution was cooled to -78°C and n-BuLi (654 µL, 2.5 M in hexanes, 1.64 mmol) was added via syringe. The mixture was stirred at -78°C for 3 hours (solution 1). Dichlorodimethylsilylane (197 µL, 1.64 mmol) dissolved in 1 mL THF was cooled to -78°C (solution 2). Solution 1 was then transferred via cannula to solution 2 at -78°C. The mixture was stirred at -78°C for four additional hours to form monochlorosubstituted methylsilane (solution 3). In separate reaction tube, to a solution of (E)-1,2-bis(5-bromothiophen-2-yl)ethene (286 mg, 0.82 mmol) dissolved in 5.4 mL dry THF and 0.6 mL dry diethyl ether, cooled to -78°C, n-BuLi (654 µL, 2.5 M in hexanes, 1.64 mmol) was added via syringe. This mixture was stirred at -78°C for 3 hours to form lithiated thiophene “dimer” (solution 4). Solution 3 was then added to solution 4 via cannula transfer and stirred at -78°C for 3 hours and then allowed to warm up to room temperature overnight resulting in the formation of monomer 2. The reaction mixture was dried, dissolved in a minimum amount of chloroform and precipitated into methanol. It was then filtered and passed through silica gel column using hexane/toluene (4:1) as an eluent to yield monomer 2 as a light green, viscous liquid (475 mg, 60%). ¹H NMR (600 MHz, CDCl₃): 7.15 (d, ³J = 3.13 Hz, 2H), 7.06 (s, 2H), 7.05 (d, ³J = 3.10 Hz, 2H), 7.05-7.01 (dd, ⁴J = 11.10 Hz,
\(^3\text{J} = 17.71 \text{ Hz}, 2\text{H}), 6.92 \text{ (s, 2H), 6.83 \text{ (s, 2H), 5.72 \text{ (d, } ^3\text{J} = 17.90 \text{ Hz, 2H), 5.25 \text{ (d, } ^3\text{J} = 11.20 \text{ Hz, 2H), 3.92 \text{ (t, } ^3\text{J} = 6.42 \text{ Hz, 4H), 3.84 \text{ (t, } ^3\text{J} = 6.42 \text{ Hz, 4H), 1.76-1.23 \text{ (m, 40H), 0.87 \text{ (m, 12H), 0.58 \text{ (s, 12H).} \text{^13C NMR (125 MHz, CDCl}_3): 158.95, 151.16, 148.80, 139.17, 136.66, 132.86, 130.33, 128.13, 126.84, 122.57, 121.75, 115.49, 108.64, 70.57, 69.21, 32.79, 30.43, 30.08, 27.07, 23.63, 15.11, 0.06. Elemental analysis: calculated C 71.85, H 9.15, S 6.61; found C 71.58, H 9.17, S 6.57.

**Synthesis of 3** \((-2,(2,5\text{-bis(heptyloxy)}-4\text{-vinylphenyl})-4,4,5,5\text{-tetramethyl-1,3,2 dioxaborolane})\) (2-(2,5-bis(heptyloxy)-4-vinylphenyl)-4,4,5,5-tetramethyl-1,3,2 dioxaborolane) (320 mg, 0.70 mmol) was dissolved in 3 mL dry THF and ((E)-1,2-bis(5-bromothiophen-2-yl)ethane) dimer (110 mg, 0.32 mmol was added to it. Tetrakis(triphenylphosphine)palladium catalyst (20 mg, 4 mol%) was added to the reaction mixture followed by the addition of 0.35 ml 4M K\(_3\)PO\(_4\) solution. The reaction mixture was purged with nitrogen and stirred at 55\(^\circ\)C for 24h under nitrogen. The solvent was evaporated, and the dry mixture was dissolved in dichloromethane and washed with brine solution. After evaporating the solvent, the crude product is passed through 230-400 mesh size silica gel column using hexane/toluene (2:1) as an eluent to obtain pure monomer 3 as an orange solid (170 mg, yield 61%). \(^1\text{H NMR (300 MHz, CDCl}_3): 7.42 \text{ (d, } ^3\text{J} = 3.64 \text{ Hz, 2H), 7.12 \text{ (s, 2H), 7.05 \text{ (s, 2H), 7.02 \text{ (s, 2H), 6.98 \text{ (d, } ^3\text{J} = 3.50 \text{ Hz, 2H), 6.98-7.05 \text{ (dd, 2H), 5.74 \text{ (d, } ^3\text{J} = 17.60 \text{ Hz, 2H), 5.26 \text{ (d, } ^3\text{J} = 11.10 \text{ Hz, 2H), 4.06 \text{ (t, } ^3\text{J} = 6.52 \text{ Hz, 4H), 3.97 \text{ (t, } ^3\text{J} = 6.26 \text{ Hz, 4H), 1.91-1.78 \text{ (m, 8H), 1.54-1.23 \text{ (m, 32H), 0.87 \text{ (t, } ^3\text{J} = 6.53 \text{ Hz, 12H).}} \text{^13C NMR (125 MHz, CDCl}_3): 150.66, 149.53, 142.35, 138.50, 131.40, 126.72, 126.20, 126.68, 123.42, 121.26, 114.29, 122.21, 110.81, 69.68, 69.42, 31.85, 29.49, 29.12, 26.18, 26.16, 22.67, 14.14. MALDI-TOF (pos.) m/z: calcd. for C\(_{54}\)H\(_{76}\)O\(_4\)S\(_2\) [M-H\(^+\)] 852.52 found 853.74.

**Typical Synthesis of P1 (random copolymers):** (2,5-bis(heptyloxy)-4-vinylphenyl)dimethyl(5-vinylthiophen-2-yl)silane (monomer 1) (200 mg, 0.40 mmol) was dissolved in 4 mL dry toluene
and Grubbs’ second generation catalyst (34 mg, 0.04 mmol) or Hoveyda-Grubbs second generation catalyst (25.4 mg, 0.04 mmol) was added. The mixture was heated to 70°C and stirred for 72 hours at this temperature under reduced pressure. The solvent was evaporated and the crude product was dissolved in dichloromethane and passed through silica gel plug. After solvent evaporation, P1 was obtained as a viscous, sticky green liquid (120 mg, 60%).$^1$H NMR (600 MHz, CDCl$_3$): 7.44 (s), 7.32-7.25 (m), 7.17(s), 7.10(s), 7.06-7.04 (m), 6.93 (s), 6.84 (s), 3.94 (t), 3.87 (t), 1.84-1.12 (m), 0.86 (m), 0.59 (s). $^{13}$C NMR (125 MHz, CDCl$_3$): 159.10, 151.41, 148.98, 138.93, 136.67, 129.54, 127.90, 127.47, 127.20, 123.41, 123.26, 122.11, 121.90, 70.72, 69.06, 32.55, 31.23, 30.12, 27.13, 23.59, 15.13, 0.05. $^{29}$Si NMR (120 MHz, CDCl$_3$): 12.95. UV-Vis (hexane, 1.87 x 10$^{-6}$ M): $\lambda_{\text{max}} = 363$ nm ($\varepsilon = 49727$); fluorescence (hexane, 1.87 x 10$^{-8}$ M): $\lambda_{\text{max}} = 410$ nm, 432 nm; $\Phi = 0.51$ ($\lambda_{\text{exc}} = 363$ nm), $M_n$ (polystyrene standards) = 3705 g/mol; $M_w/M_n = 1.58$.

Typical Synthesis of P2 (segmented copolymers). To (E)-1,2-bis(5-((2,5bis-(heptyloxy)-4-vinylphenyl)dimethylsilyl)thiophen-2-yl)ethene (monomer 2) (160 mg, 0.170 mmol) dissolved in 2.5 mL dry toluene, Hoveyda-Grubbs second generation catalyst (11 mg, 0.017 mmol) or Grubbs’ second generation catalyst (13 mg, 0.016 mmol) was added. The mixture was heated to 70°C and stirred for 72 hours at this temperature under reduced pressure. The reaction mixture was then dried and purified in small fractions, by passing it through a small silica gel column using toluene as an eluent. The solvent was evaporated, the crude product was then re-dissolved in toluene and passed through silica gel plug to yield polymer P2 as viscous, sticky yellow liquid (105 mg, 65%).$^1$H NMR (600 MHz, CDCl$_3$): 7.44 (s, 2H), 7.15 (d, $^3$J = 3.38 Hz, 2H), 7.06 (s, 2H), 7.05 (d, $^3$J = 3.46 Hz, 2H), 7.04 (s, 2H), 6.85 (s, 2H), 3.95 (t, $^3$J = 6.52 Hz, 4H), 3.86 (t, $^3$J = 6.44 Hz, 4H), 1.78-1.21 (m, 40H), 0.85 (m, 12H), 0.58 (s, 12H).$^{13}$C NMR (125 MHz, CDCl$_3$): 159.10, 151.40, 148.76, 139.20, 136.66, 130.80, 128.11, 126.50, 125.10, 122.57, 122.14, 108.44, 70.85, 69.11, 32.99,
30.53, 30.08, 27.17, 23.53, 15.21, 0.05. $^{29}$Si NMR (120 MHz, CDCl$_3$): 12.95. UV-Vis (hexane, $1.27 \times 10^{-6}$ M): $\lambda_{\text{max}} = 363\text{nm} (\varepsilon = 57,454)$; fluorescence (hexane, $1.27 \times 10^{-8}$ M): $\lambda_{\text{max}} = 411\text{ nm}$, 434 nm, $\Phi = 0.57 (\lambda_{\text{exc}} = 363\text{ nm})$. $M_n$ (polystyrene standards) = 4330 g/mol; $M_w/M_n = 1.42$.

**Typical Synthesis of P3.** (170 mg, 0.20 mmol) of 3 was dissolved in 2.5 mL dry toluene and Grubbs’ second generation catalyst (8.5 mg, 0.01 mmol) was added. The mixture was heated to 70°C and stirred for 72 hours at this temperature under reduced pressure. The reaction mixture was brought to room temperature and 0.5 mL of ethyl vinyl ether was added and stirred for 0.5h. The resulting solution was precipitated into 100 mL cold methanol and filtered to obtain P3 as reddish brown powder (120 mg, 70% yield). $^1$H NMR ( 600 MHz, CDCl$_3$): 7.48 (s, 2H), 7.46 (d, $^3$J = 3.71 Hz, 2H), 7.20 (s, 2H), 7.18 (s, 2H), 7.06 (s, 2H), 7.02 (d, $^3$J = 3.98 Hz, 2H), 4.13 (t, $^3$J = 5.78 Hz, 4H), 4.04 (t, $^3$J = 6.37 Hz, 4H), 1.97-1.84 (m, 4 H), 1.59-1.46 (m, 4 H), 1.44-1.29 (m, 32 H), 0.89 (t, $^3$J = 5.96 Hz, 12H. $^{13}$C NMR (125 MHz, CDCl$_3$): 150.88, 149.69, 142.31, 138.58, 128.64, 127.23, 126.53, 125.96, 123.47, 121.21, 122.32, 110.56, 69.59, 69.42, 31.87, 29.51, 29.10, 26.20, 26.12, 22.63, 14.18. UV-Vis (dichloromethane, $5.87 \times 10^{-6}$ M): $\lambda_{\text{max}} = 490\text{ nm} (\varepsilon = 43541)$; fluorescence (dichloromethane, $5.87 \times 10^{-7}$ M): $\lambda_{\text{max}} = 556\text{ nm}$, $\Phi = 0.40 (\lambda_{\text{exc}} = 490\text{ nm})$. $M_n$ (polystyrene standards) = 3139 g/mol; $M_w/M_n = 2.01$.

**2.3 RESULTS AND DISCUSSION**

We were interested in using ADMET to synthesize segmented conjugated polymers that feature two conjugated aromatic segments. The segments were placed either in direct conjugation with each other or separated by silicon linkages, randomly distributed or strictly alternating (Scheme 2.1). The influence of structure on the opto-electronic properties was then investigated. Precise sequence control in copolymerizations enables control of many properties of the copolymers,
including thermal, crystalline, and as in our case opto-electronic. The aromatic segments chosen are based on thiophene and para-phenylenevinylene because of their ubiquitous use as functional materials in applications based on conducting polymers, e.g. light-emitting diodes, plastic solar cells, etc. We were specifically interested in the cooperative properties of the two conjugated segments. The inclusion of aliphatic chains in the polymer structure ensures solubility and thus access to higher molecular weights, as well as processability. ADMET has been shown to successfully polymerize a wide variety of divinyl functional monomers. To that end we synthesized two systems in which the segments would be separated by silicon linkage, one in which the segments are statistically distributed over the macromolecule, and another in which the segments strictly alternate. A third, homologous system was designed, featuring strictly alternating segments but lacking the silicon linkages, thus allowing for effective electronic conjugation between the segments. The three macromolecular systems are each required specially designed monomers.

2.3.1 Synthesis of monomers. Scheme 2.1 details the synthetic strategies for monomers 1, 2 and 3. A key intermediate in the syntheses of 1 and 2 consisted of a chloro-silane functional bis(heptyloxy)vinylbenzene (Si-IM). Si-IM was synthesized from 1-bromo-2,5-bis(heptyloxy)-4-vinylbenzene (see Supporting Information) by lithiating and subsequently coupling it with one equivalent of dichloro-dimethyl silane. To yield 1, a lithiated vinylthiophene (IM1) was combined in a 1/1 molar ratio with Si-IM. To yield 2, a dilitiated (E)-1,2-bis(5-bromothiophen-2-yl)ethene (IM2) was coupled with Si-IM using a 1/2 molar ratio. (E)-1,2-bis(5-bromothiophen-2-yl)ethene had been previously prepared by homo-coupling two bromovinylthiophenes using olefin metathesis. (E)-1,2-bis(5-bromothiophen-2-yl)ethene was also used as a starting point for the
synthesis of 3, i.e. by coupling it with a boronic ester made from the above mentioned, 1-bromo-2,5-bis(heptyloxy)-4-vinylbenzene.

**Scheme 2.1.** Synthesis of monomers 1 - 3
Figure 2.1. $^1$H NMR spectra of 1, 2, 3
The $^1$H NMR spectra of 1, 2 and 3 with assignments are shown in figure 2.1. In 1, the formation of two chemically different vinyl functions (one attached to a thiophene ring and the other to benzene ring) is indicated by four doublet signals a, b, j, k in the region of 5.12-5.74 ppm. In 2 and 3 only one type of vinyl function is present, resulting in two doublet proton resonances a and b for 2 at 5.25 and 5.72 ppm (3: 5.26 and 5.74 ppm) respectively. In all cases, the -CH=CH$_2$ resonances are observed as double doublets at 6.98 - 7.07 ppm. The aromatic protons H$_f$ and H$_g$ from thiophene show resonances at ~6.98 - 7.15 and ~ 7.02 – 7.48 ppm respectively, the protons H$_d$ and H$_e$ from the benzene resonate at ~6.92-7.02 and ~6.83-7.12 ppm respectively. The proton resonances from –OCH$_2$– from the heptyloxy chains are observed as triplets at ~3.92 - 4.06 and ~3.84 - 3.97 ppm. The remaining protons of the side chains result in multiplets at 1.91 - 0.87 ppm. In 1 the protons i from the –CH$_3$ connected to Si formed a singlet at 0.58 ppm. Structure, purity, and composition were further supported by $^{13}$C NMR (see Supporting Information), liquid chromatography, mass spectrometry, and elemental analysis.

2.3.2 Polymerization. Two catalysts were used for the ADMET polycondensations (Scheme 2.2), the ruthenium-based alkylidenes “Grubbs-Hoveyda second generation” [(1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(o-isopropoxy phenyl-methylene)ruthenium] (C$_{31}$H$_{38}$Cl$_2$N$_2$ORu) and “Grubbs second generation” [1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene) dichloro(phenyl methylene) (tricyclohexylphosphine) ruthenium] (C$_{46}$H$_{65}$Cl$_2$N$_2$PRu).$^{53,54}$
Optimizing the ADMET involved varying reaction temperature, time, catalyst, catalyst concentration, as well as ratio catalyst/monomer. Typical reactions were carried out at 70 °C for the duration of 72 h under reduced pressure to shift the equilibrium towards the polymer with the removal of ethylene gas. Table 2.1 summarizes representative ADMET results for monomers and both catalysts. Under said conditions, and using \([1]/[\text{Catalyst}]=1.0 \times 10^{-1} \text{M}/1.0 \times 10^{-2} \text{M}\), \(M_n\) of 3705 and 3163 g/mol (GPC with PS standard) were reached using Grubbs second generation and Grubbs-Hoveyda second generation catalysts respectively. Compared to the GPC results, NMR end group analysis indicated higher degrees of polymerization with respective \(M_n\) of 8829 and 7888 g/mol.

**Scheme 2.2** Synthesis of polymers P1 – P3 via ADMET
Table 2.1 Representative ADMET polycondensations and polymer characteristics

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Catalyst</th>
<th>M (mol/L)</th>
<th>NMR</th>
<th>GPC</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>1.0 x 10⁻¹</td>
<td>1.0 x 10⁻²</td>
<td>8829</td>
<td>7888</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td></td>
<td>3705</td>
<td>3163</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.59</td>
<td>1.54</td>
</tr>
<tr>
<td>P2</td>
<td>6.6 x 10⁻²</td>
<td>6.6 x 10⁻³</td>
<td>10713</td>
<td>14589</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td></td>
<td>3868</td>
<td>4330</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.38</td>
<td>1.42</td>
</tr>
<tr>
<td>P3</td>
<td>8.0 x 10⁻²</td>
<td>8.0 x 10⁻³</td>
<td>4982</td>
<td>4982</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3139</td>
<td>3139</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.01</td>
<td>2.01</td>
</tr>
</tbody>
</table>

a Grubbs 2nd generation catalyst; b Hoveyda – Grubbs 2nd generation catalyst; c t = 72h and T = 70 °C; d Decomposition temperature at 5% weight loss in N₂/O₂; e between -60 and 200 °C.

Earlier studies indicated significantly different conditions for the ADMET coupling of vinyl-functional thiophenes and benzenes. This was not observed for the two different vinyl functions in 1. Attempts to first selectively homo-couple the vinyl-thiophene side of 1 and then subsequently the vinyl-benzene function did not yield success. In fact, under all conditions investigated both vinyl functions seemed to have the same reactivity toward the catalyst systems at all stages of the reaction. As a result, the coupling was completely random as indicated by H-NMR analysis of P1 (vide infra).

In the case of 2, Grubbs 2nd generation and Hoveyda – Grubbs 2nd generation catalysts yielded polymers P2 with respective Mn of 3868 and 4330 g/mol per GPC (PS standards) (10,713 and 14,589 g/mol via H-NMR). P3 was achieved using Grubbs 2nd Gen. catalyst with respective Mn of 3139 g/mol as per GPC (PS standards) (4982 g/mol with H-NMR end group analysis). The GPC
chromatograms are shown in figure 2.2. The higher degrees of polymerization for P1 and P2 are most likely due to their higher solubilities due to the presence of flexible silylene linkages.

The thermal stabilities of P1 and P2 are very similar. In N₂, 5% weight loss was observed at 276 °C whereas in O₂ this was reduced to 216 °C. Comparatively, P3 is thermally more stable and exhibited 5% weight loss at 363 °C in N₂ and 324 °C in O₂. Differential scanning calorimetry (DSC) yielded glass transition temperatures for P1 and P2 at -18 °C and -13 °C respectively. Tg was not detected in DSC analysis of P3 in the tested temperature range of -60 °C – 200 °C.

![Figure 2.2. GPC chromatograms of 1-3 and P1-P3](image)

### 2.3.3. Microstructure of ADMET Polymers

Figure 2.3 shows ¹H-NMR spectra of P1 – P3 with relevant assignments. In P1 three types of vinylene functions arise from the three possible coupling modes. Homo coupling between vinyl-thiophene functions yields vinylene assigned with 1. Homo coupling between vinyl-benzene functions yields vinylene assigned as 12. “Hetero” coupling between the two functions yields vinylene with two protons assigned as 13 and 14. These three vinylene types are part of three
distinct aromatic segments present in the polymer chain. As a result, resonances from protons on the aromatic rings also depend on the type of segment they are part of, i.e. protons 3 vs. 3’ and 10 vs. 10’. Integration of the relevant resonance signals with integrated signal intensities of 1 / 12/ (13+14) ~ 1/ 1/ 2 indicates statistical ADMET coupling. This ratio was independent of reaction time and temperature, indicating similar reactivities of the two different vinyl functions in 1 under the conditions used (also: vide supra).

Figure 2.3. $^1$H NMR spectra of P1, P2, P3
To produce strictly alternating segmented blocks in the polymer chain, we designed monomers 2 and 3 which already contain the preformed thiophene segment. ADMET polycondensation yields the second aromatic, phenylene containing block. The spectra of the segmented polymers P2 and P3 are very similar to that of P1 (Figure 2.3), e.g. when comparing vinylene proton resonances 1 and 12. But they lack the resonances from the imixed aromatic segment containing both a thiophene and benzene part, i.e. the resonances of the vinylene protons 13 and 14. As mentioned above, 1H NMR end group analysis of P2 yielded molecular weights of 10,713 – 14,589 g/mol, indicating degrees of polymerization between 11 and 15. The progress of the polycondensation can easily be monitored by following a select few 1H NMR resonance: The signal intensity of the vinyl end groups decreases with increasing degree of polymerization, while the intensities from the newly formed vinylene groups grows, i.e. 12 in the case of P2 and P3 and 1,12,13, and 14 in the case of P1. Residual signal intensity at ~4.0 ppm in the spectra of P2 and P3 arises from methylene protons –OCH2– in the outermost heptyloxy side chains next to unreacted vinyl end groups. Especially at longer chain lengths, the polycondensation equilibrium can be expected to show evidence of macrocycles as a result of “back biting”, potentially rendering NMR end group analysis for size-determination inappropriate. To probe for the presence of cyclic polycondensates we performed Mark-Houwink analyses of the polymers (see Supporting Information). We did not detect the presence of cyclic structures in the product distributions, therefore validating our NMR determinations.

The structures of P1, P2, and P3 are further confirmed by 13C NMR (Supporting Information), most characteristically showing clearly the formation of the new vinylene functions. 2D NMR experiments (Supporting Information) helped to unequivocally assign every C and H resonance to the structures discussed. 29Si NMR analysis for both P2 and P1 (Figure 2) showed a single resonance around -12.9 ppm for both systems, indicating both facts, that the chemical
environments at the Si are very similar in both systems, and that no side reactions occurred at the Si during polycondensation. Furthermore, the shift corresponds to earlier results on related system.\textsuperscript{18}

\begin{figure}[h]
\centering
\includegraphics[width=\linewidth]{figures/si_nmr.png}
\caption{\textsuperscript{29}Si NMR spectra of P2 and P1}
\end{figure}

2.3.4. Optical properties. Figure 2.5 illustrates absorption and emission spectra of monomers and polymers. The measurements were performed using hexane solutions. In general, P1 and P2 absorbed in the UV and emitted in blue region. Earlier studies on optical properties of polymers containing trans-stilbene segments linked by silicon suggested that the Si linkages only allow for a weak electron delocalization between segments, thus resulting in polymer properties very similar to those of the isolated stilbene, albeit somewhat shifted to longer wavelengths, but still blue emission.\textsuperscript{51}
**Figure 2.5** Absorption (right) and the emission spectra (left) of 1-3 and P1 – P3

1 showed three distinct absorptions at 259 nm, 292 nm and 336 nm. The absorption of P1 is red shifted compared to 1 due to the aromatic segments with π – delocalization formed during ADMET. It showed a $\lambda_{\text{max}}$ at ~ 363 nm with “shoulders” in the range of ~ 300 and 390 nm. Absorption of 2 showed a $\lambda_{\text{max}}$ at ~ 359 nm with shoulders at ~ 344 and 377 nm, whereas P2 displayed a $\lambda_{\text{max}}$ at ~ 363 nm with shoulders at ~ 300 and 382 nm. The red shift of the P2 vs. 2 is not as strong as in case of P1 vs. 1 because 2 already contains one of the two extended conjugated
aromatic segments. \( \textbf{P2} \) and \( \textbf{P1} \) absorb at the same wavelength maximum, and very similar to \( \textbf{2} \). However, the absorption of \( \textbf{P1} \) is broader and seems to contain more transitions than \( \textbf{P2} \) as evidenced in the line shape. This is to be expected as \( \textbf{P1} \) contains an additional type or extended conjugated aromatic segment not present in \( \textbf{P2} \). Furthermore, the absorption seems to be dominated by the segment containing thiophene, as it is present in both polymer systems, as well as monomer \( \textbf{2} \), leading to similar major absorptions. In comparison, the absorptions of \( \textbf{3} \) and \( \textbf{P3} \) are found at lower energies, i.e. at \( \lambda_{\text{max}} \approx 436 \) and 490 nm respectively. They lack the Si-linkage, thus enabling effective direct electron delocalization between the different aromatic segments of the monomer and then the polymer chain, resulting in a significant red shift.

The contribution of the stilbene-containing segment to the optical properties of \( \textbf{P1} \), \( \textbf{P2} \), and \( \textbf{2} \) is seen in the emission characteristics, as the emission maxima are observed at \( \lambda_{\text{max}} \approx 410, 411, \) and 414 nm respectively (with respective shoulders at \( \approx 432 \) and 434 nm for \( \textbf{P1} \) and \( \textbf{P2} \)). Another (weak) shoulder at \( \approx 470 \) nm is present regardless of concentration. \( \textbf{2} \) features an additional emission at \( \approx 394 \) nm and a weaker shoulder at \( \approx 440 \) nm. \( \textbf{1} \) is very different in its emission characteristics with \( \lambda_{\text{max}} \approx 376 \) nm and a shoulder at \( \approx 360 \) nm. The fact that \( \textbf{P1} \) with randomly distributed aromatic segments and \( \textbf{P2} \) with strictly alternating segments (and lacking the “mixed” segment containing both parts benzene and thiophene) show such similarities in absorption and emission is no coincidence. There are two potential explanations: (1) the excited state electronic interactions between thiophene and benzene units linked via internal vinylene bond are negligible, or (2) the emission process was quenched.

We compared the data of \( \textbf{P2} \) and \( \textbf{P1} \) with earlier results from polymers systems \( \textbf{A} \) and \( \textbf{B} \) (Scheme 2.3), each containing only one of the two aromatic segments found in \( \textbf{P2} \), and connected similarly by a silylene linkage.\(^{59,39}\) The absorption and emission spectra of \( \textbf{A} \) and \( \textbf{B} \) are overlayed with those of systems \( \textbf{P1} \) and \( \textbf{P2} \) in Figure 2.6. There is a significant overlap between the absorption of \( \textbf{B} \) and
the emission of A. Also, the emission of P2 closely resembles that of B, indicating the emission in P2 (and in P1) is mainly emanating from the stilbene segment. This could be explained through possible fluorescence resonance energy transfer (FRET) from the thiophene containing segments in P1 and P2, resulting also in a quenching of emission from these segments. This is supported by observations of FRET in earlier reports on silylene containing copolymers featuring alternating chromophores.\textsuperscript{19,21,25,28,33} Fluorescence quantum efficiencies of P1, P2, and P3 were determined as 0.51, 0.57, and 0.40 respectively (relative to trans-stilbene and anthracene). These values are significantly higher compared to related silicon-containing polymers having fluorophores such as phenylenevinylene, biphenylene and phenylene.\textsuperscript{8,18,23} It appears that FRET from that bithiophenevinylene segment to the biphenylenevinylene segment is the reason for these higher quantum efficiencies.

As in the absorption, the emission of P3 at $\lambda_{\text{max}} \sim 556$ nm is strongly red-shifted, compared to the other systems. Also, the emission characteristics cannot be associated with either of the two aromatic segments. The emission is the result of more extended conjugated electron systems, containing both segments. This conjugation is possible due to the absence of the Si linkers. Figure 2.7 illustrates the solutions of P2 and P3 in solution, irradiated with a UV lamp clearly indicating the blue shift caused by silicon. Table 2.2 summarizes the absorption and the emission results of the monomers and the polymers.
Scheme 2.3. Model polymers A, B

Figure 2.6. Absorption (Abs) and emission (Em) of A, B, p1 and p2

Figure 2.7 Solutions of P2 and P3 in solution, irradiated with a UV lamp
Table 2.2. Optical Properties of Monomers and Polymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\lambda_{\text{max,abs}}$ (nm)</th>
<th>$\lambda_{\text{max,em}}$ (nm)</th>
<th>$\varepsilon$ (L mol$^{-1}$ cm$^{-1}$)</th>
<th>$\Phi_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>259, 292, 335</td>
<td>376</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>344, 359</td>
<td>394, 414</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>436</td>
<td>485, 517</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P1</td>
<td>363</td>
<td>410, 432</td>
<td>49727</td>
<td>0.51</td>
</tr>
<tr>
<td>P2</td>
<td>363</td>
<td>411, 434</td>
<td>57454</td>
<td>0.57</td>
</tr>
<tr>
<td>P3</td>
<td>490</td>
<td>556</td>
<td>43541</td>
<td>0.40</td>
</tr>
</tbody>
</table>

$^1$excited at absorption maximum

2.3.5 Cyclic Voltammetry (CV). The HOMO and LUMO levels of the polymers were estimated experimentally by cyclic voltammetry (CV) and theoretically using density functional theory (DFT). The redox potentials are reported relative to the ferrocene/ferrocenium (Fc/Fc$^+$) couple at 298 K. The HOMO levels of P1, P2, and P3 were found to be -5.29, -5.29 and -4.75 eV respectively, whereas LUMO levels of P1, P2, and P3 were found to be -2.29 eV, -2.22 eV and -2.54 eV respectively. Confirming results from the optical characterizations, the lack of the Si-linkages in P3 also leads to a markedly smaller HOMO-LUMO gap. In P3 the backbone lacks the flexible Si linkage enabling more electron delocalization, and resulting in a destabilized HOMO energy but a lower energy LUMO compared to systems P1 and P2, thus lowering the band gap from ~ 3.0 eV to ~2.2 eV. Electrochemical parameters are summarized in Table 2.3 and the CV graphs are shown in Figure 2.8.
### Table 2.3 Summary of Results from Cyclic voltammetry experiment

<table>
<thead>
<tr>
<th>Polymer</th>
<th>HOMO&lt;sup&gt;a&lt;/sup&gt; (eV)</th>
<th>LUMO&lt;sup&gt;a&lt;/sup&gt; (eV)</th>
<th>Bandgap&lt;sup&gt;a&lt;/sup&gt; (eV)</th>
<th>HOMO&lt;sup&gt;b&lt;/sup&gt; (eV)</th>
<th>LUMO&lt;sup&gt;b&lt;/sup&gt; (eV)</th>
<th>Bandgap&lt;sup&gt;b&lt;/sup&gt; (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>-5.29</td>
<td>-2.29</td>
<td>3.00</td>
<td>n.d.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P2</td>
<td>-5.29</td>
<td>-2.22</td>
<td>3.07</td>
<td>-4.92</td>
<td>-1.55</td>
<td>3.37</td>
</tr>
<tr>
<td>P3</td>
<td>-4.75</td>
<td>-2.54</td>
<td>2.21</td>
<td>-4.39</td>
<td>-1.98</td>
<td>2.41</td>
</tr>
</tbody>
</table>

<sup>a</sup> Energy levels determined by CV; <sup>b</sup> Energy levels determined by theoretical calculation

**Figure 2.8** CV curves of polymers: Oxidation (top, in CH<sub>2</sub>Cl<sub>2</sub>) and reduction (bottom, in THF) with Bu<sub>4</sub>N<sup>+</sup>PF<sub>6</sub><sup>-</sup> (0.1M) as a supporting electrolyte recorded vs Fc/Fc<sup>+</sup> (Fc=[(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Fe ] as an internal reference (marked as *) at a scan rate of 100 mV/s

**2.3.6. DFT calculations.** In order to further understand the effect of silicon on the HOMO-LUMO levels of the resulting polymers, we performed a computational study on the dimer models of **P2** and **P3**. Geometries were optimized using density functional theory (DFT) in the Gaussian 09
package at the DFT/B3LYP/6-31G(d,p) level. The HOMO-LUMO orbital plots for the dimer models for P2 and P3 are shown in Figure 2.9 along with the calculated energy levels. Confirming experimental results, silicon is disrupting the planarity and conjugation of the polymer backbone resulting in more locally confined HOMO and LUMO orbitals. The calculated HOMO and LUMO energy levels of the P2 model are found at -4.92 eV and -1.55 eV respectively, with a band gap of 3.37 eV. In P3, the molecular orbitals are much more extensive due to the effective electron conjugation without the Si-interruption. As a result, the HOMO energy is raised by ~ 0.5 eV and the LUMO energy lowered by ~ 0.4 eV, resulting in a smaller band gap. The calculated HOMO and LUMO energy levels of the P3 dimer model are -4.39 eV and -1.98 eV respectively, with a band gap of 2.41 eV. The calculated energy levels for P3 vs. P2 strongly support the experimental observations in the CV experiments.

![HOMO/LUMO orbital plots of p2 and p3, simulated by DFT/B3LYP/6-31g(d), which were carried out with a chain length of n=2](image)

**Figure 2.9** HOMO/LUMO orbital plots of p2 and p3, simulated by DFT/B3LYP/6-31g(d), which were carried out with a chain length of n=2

### 2.3.7. Thermal Analysis

The thermal stabilities of P1 and P2 are very similar. In N2, 5% weight loss was observed at 276 °C whereas in O2 this was reduced to 216 °C. Comparatively, P3 is thermally more stable and exhibited 5% weight loss at 363 °C in N2 and 324 °C in O2. Differential
scanning calorimetry (DSC) yielded glass transition temperatures for P1 and P2 at -18 °C and -13 °C respectively. T_g was not detected in DSC analysis of P3 in the tested temperature range of -60 °C – 200 °C probably due to the rigid backbone of P3 limiting chain mobility. TGA and DSC curves are shown in supporting information.

2.4 Conclusion. Using ADMET, we synthesized homologous luminescent conjugated polymers with two different aromatic segments, either alternating or randomly distributed along the polymer chain, either directly connected or separated by a Si-linker. Molecular weights Mn (NMR – endgroup analysis) ranged from 4982 g/mol (P3), 8829 g/mol (P1) to 14600 g/mol (P2). The systems were studied experimentally as well as theoretically to learn about specific interactions between the aromatic units that might provide guidance for future designs. It was observed that silicon limited the π-conjugation to the defined segments, resulting in shorter wavelength emission. Random or alternating placement of the two segments did not seem to influence the absorption and emission energies much (λ_max at 363 nm and ~ 411 nm respectively), although P2 with its alternating segments showed a slightly more defined absorption with slightly higher absorptivity and emission efficiency (57% vs. 51%). P3 with alternating segments directly conjugated (without a Si-linkers) resulted in longer wavelength absorption and emission (λ_max at 490 nm and ~ 556 nm respectively), and slightly lower emission efficiencies (40%), most likely due to more non-radiative relaxation pathways due to the extended electron conjugation. Electrochemical measurements confirmed the optical findings and showed a smaller HOMO-LUMO bandgap for the more delocalized P3 without Si-linkers (2.21 eV vs. 3.00-3.07 eV). DFT calculations could support the above results and analyses, as calculated model structures of P2 also showed silicon disrupting the co-planarity and conjugation of aromatic segments, resulting in a larger HOMO-LUMO gap compared to P3.
2.5 References


(2) Thompson, B. C.; Frechet, J. M. *Angew Chem Int Ed Engl* **2008**, *47*, 58.


2.6 Appendix

Precursor Synthesis

Synthetic route to 1-bromo-2,5-bis(heptyloxy)-4-vinylbenzene

**Synthesis of 1,4-bis(heptyloxy)benzene**

40 g of potassium hydroxide pellets were suspended in 200 ml of dimethylsulfoxide and stirred at room temperature for 0.5h. Hydroquinone (9.35 g, 85 mmol) was added to the solution and stirred for another 0.5 h. 1-Bromoheptane (50 mL, 318 mmol) was transferred via syringe and the resulting mixture was stirred at room temperature for 2h. The reaction mixture was then poured into ice cold water (500 mL). The solid product was filtered, washed twice with ethanol and further purified by recrystallization from ethanol to obtain 1,4-bis(heptyloxy)benzene as white crystals (22 g, 85 %). $^1$H NMR (600 MHz, CDCl$_3$): 0.86 (t, 6H, $^3$J = 7.02 Hz), 1.20-1.48 (m, 16H), 1.64-1.80 (m, 4H), 3.87 (t, 4H, $^3$J = 6.64 Hz), 6.79 (s, 4H).

**Synthesis of 1,4-dibromo-2,5-bis(heptyloxy)benzene**

1,4-bis(heptyloxy)benzene (1.90 g, 6.21 mmol) was dissolved in 40 mL of glacial acetic acid and the solution is immersed in an ice bath. Bromine (0.83 mL, 16.14 mmol) was added drop wise and the ice bath was removed after bromine addition. The resulting mixture was stirred overnight at room temperature. The reaction mixture was then poured into 100 mL of ice cold water, stirred for
10 minutes followed by solvent extraction with chloroform. After evaporating the solvent, the compound was further purified by recrystallization from cyclohexane. 1,4-dibromo-2,5-bis(heptyloxy)benzene was obtained as white crystals (3.5 g, 75 % yield). $^1$H NMR (600 MHz, CDCl$_3$): 0.87 (t, 6H, $^3$J = 7.09 Hz), 1.25-1.37 (m, 12H), 1.42-1.48 (m, 4H), 1.75-1.81 (m, 4H), 3.92 (t, 4H, $^3$J = 6.57 Hz), 7.06 (s, 2H).

**Synthesis of 4-bromo-2,5-bis(heptyloxy)benzaldehyde**

1,4-dibromo-2,5-bis(heptyloxy)benzene (2.72 g, 5.87 mmol) was dissolved in 30 mL of anhydrous diethyl ether. The solution was cooled to -50°C and n-BuLi (2.35 mL, 2.5 M in hexanes, 5.87 mmol) was added through a syringe. The mixture was stirred at -50°C for 0.5h and $N,N$-Dimethylformamide (0.55 mL, 7.05 mmol) was added. The resulting mixture was stirred at -50°C for additional 1.5h. 10% HCl (20 mL) was then poured into reaction mixture and stirred for 0.5h. The product was extracted by solvent extraction with diethyl ether. After evaporating the solvent, the crude product was purified using a 70-230 mesh size silica gel column in hexane:toluene (2:1) mixture. 4-bromo-2,5-bis(heptyloxy)benzaldehyde was yielded as a yellowish white solid (1.95 mg, 80% yield). $^1$H NMR (600 MHz, CDCl$_3$): 0.87 (t, $^3$J = 6.54 Hz, 6H), 1.21-1.51 (m, 16H), 1.72-1.87 (m, 4H), 3.95-4.04 (m, 4H), 7.20 (s, 1H), 7.29 (s, 1H), 10.39 (s, 1H).

**Synthesis of 1-bromo-2,5-bis(heptyloxy)-4-vinylbenzene**

Methyltriphenylphosphonium bromide (2.39 g, 6.68 mmol) was suspended in 50 ml dry THF. To this suspension n-BuLi (2.54 mL, 2.5 M in hexanes, 6.35 mmol) was added dropwise at 0°C. The reaction mixture was stirred at 0°C for 3h. To this resulting solution 4-bromo-2,5-bis(heptyloxy)benzaldehyde (2.76 g, 6.68 mmol) dissolved in 10ml of dry THF, was added slowly at 0°C. The resulting solution was allowed to reach room temperature and stirred overnight. The reaction mixture was then concentrated under reduced pressure followed by washing with hexane. The hexane layer was treated with sodium sulfate and then filtered. The organic phase was then
concentrated under reduced pressure to give the crude product. Further purification was carried by column chromatography with hexane-toluene (1:1) solvent mixture as the eluent to obtain a greenish white solid (2.1 g, 76% yield). $^1$H NMR (600 MHz, CDCl$_3$): 0.88 (t, $^3$J = 6.85 Hz, 6H), 1.22-1.51 (m, 16H), 1.73-1.85 (m, 4H), 3.88 (t, $^3$J = 6.54 Hz, 2H) 3.96 (t, $^3$J = 6.50 Hz, 2H) 5.25 (d, $^3$J = 11.36 Hz, 1H), 5.70 (d, $^3$J = 17.88 Hz, 1H), 6.92-6.97 (dd, $^4$J = 11.35 Hz, $^3$J = 17.88 Hz, 1H), 6.99 (s, 1H), 7.02 (s, 1H).

Synthesis of 2-bromo 5-vinylthiophene

Methyltriphenylphosphonium bromide (3.01 g, 8.41 mmol) was suspended in 40 ml dry THF. To this suspension n-BuLi (3.20 mL, 2.5 M in hexanes, 7.99 mmol) was added dropwise at 0°C. The reaction mixture was stirred for 3h. To this resulting solution 2-bromo 5-thiophene carbaldehyde (1.00 mL, 8.41 mmol) dissolved in 10 mL of dry THF was added slowly at 0°C. The resulting solution was allowed to reach room temperature, stirred overnight at and then concentrated under reduced pressure followed by washing with hexane. The hexane layer was treated with sodium sulfate and then filtered. The organic phase was then concentrated under reduced pressure to give the crude product. Further purification was carried by column chromatography with hexane-dichloromethane (7:3) solvent mixture as the eluent to obtain a reddish yellow liquid (0.95 g, 60% yield). $^1$H NMR (600MHz, CDCl$_3$): 6.89 (d, $^3$J = 3.70 Hz, 1H), 6.69 (d, $^3$J = 3.70 Hz, 1H), 6.67 (dd, $^4$J = 10.64 Hz, $^3$J = 17.74 Hz, 1H), 5.45 (d, $^3$J = 17.43 Hz, 1H), 5.13 (d, $^3$J = 11.10 Hz, 1H).
Monomers: $^{13}$C-NMR Spectra (125 MHz) in CDCl$_3$
Mark-Howink Analyses

P1:

P2:
Polymers: $^{13}\text{C}$-NMR Spectra (125 MHz) of p1-p3 in CDCl$_3$
HSQC spectrum of **p1**:

HSQC spectrum of **p2**:
HSQC spectrum of p3:
HMBC spectrum of **p1**:

![HMBC spectrum of p1](image)

HMBC spectrum of **p2**:

![HMBC spectrum of p2](image)
HMBC spectrum of \textbf{p3}:
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Absorption (left) and emission spectra (right) of p2 in solution (hexanes) and film

PL spectra of p2 at different concentrations (normalized)
TGA curves of $p_1$ and $p_2$ under nitrogen and air

DSC curves of $p_1$ and $p_2$ under nitrogen
TGA curves of p3 under nitrogen and air

DSC curve of p3 under nitrogen
Additional Details from DFT calculations

Selected orbital plots and results summary of P2 models calculated at the DFT/B3LYP/6-31g(d,p) level.

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Selected orbital plots and results summary of P3 models calculated at the DFT/B3LYP/6-31g(d,p) level.

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3. Experimental and theoretical Structural/Property Studies: Donor-Acceptor polymers synthesized via Acyclic Diene Metathesis and Suzuki polycondensation

3.1 Introduction

In recent years, conjugated polymers have been the focus of great research activity, owing to their unique electronic and optoelectronic properties. Conjugated polymers offer advantages over inorganic counterparts, including flexibility, light weight and cost-effective solution processability.\(^1\) As a result, they are being investigated for various applications such as organic light-emitting diodes, field-effective transistors, sensors and polymer solar cells.\(^2\) In particular, polymer solar cells have attracted an increasing amount of attention due to their potential use for next generation renewable energy sources.\(^3,4,5,6,7\) Typically conjugated polymer (electron donor) and fullerene derivative (electron acceptor) are blended in a bulk heterojunction configuration as the core component for polymer solar cell.\(^8,9\) It is clear that tuning of HOMO and LUMO energy levels and controlling the band gap are essential for effective material development for polymer solar cells.\(^1,10,11\) Incorporation of electron-rich and electron deficient unit in the polymer chain favors internal charge transfer and has been extensively used to prepare low band gap donor-acceptor conjugated polymers.\(^12,13,14\) One of the unique feature of these polymers is that the HOMO and LUMO are localized on donor and acceptor moiety respectively, offering an advantage to individually tune the energy levels and hence the band gap.\(^8\)

The strategies that allow access to donor-acceptor polymers are of significant interest as they play a crucial role in engineering the photo-physical properties of these polymers. The widely used synthetic strategies to access donor-acceptor polymers make use of palladium-catalyzed Suzuki and Stille coupling.\(^15\) These coupling strategies are mainstay in this field as they are applicable to
wide variety of monomers producing library of donor-acceptor polymers with high power conversion efficiencies. However, there are also considerable limitations associated with these strategies. Stille polymerization involves the use of tin derivatives whereas Suzuki polycondensation requires exact stoichiometric balance between the AA (boronic acid/esters) and BB (halogens) monomers to yield high molecular weight polymers.\textsuperscript{16} Realization of certain stoichiometry becomes a challenge as the boron reagents are susceptible to undesired processes such as protodeboronation, oxidation, homocoupling, and dehydration.\textsuperscript{19,17} On the other hand AB monomers used in Suzuki polycondensation are intrinsically non-symmetric and often difficult to synthesize. Finally it should be pointed out that Suzuki polycondensation often requires end-capping to remove boron and bromo end functionality at the polymer chain ends and palladium removal from the polymer is always a challenge. However, these limitations are not a problem for synthesis of monomeric multi-aryls, but for polymer synthesis.\textsuperscript{18} One of the approaches to circumvent this problem is to synthesize the donor-acceptor symmetrical diene monomer which have in built stoichiometric balance by Suzuki coupling and then polymerize it via acyclic diene metathesis (ADMET).

Recently, ADMET has been employed as a convenient route to precise and well-defined polymer architectures that would not be possible by any other methods.\textsuperscript{19} It has been applied to synthesize conjugated polymers including polyenes and poly(arylene vinylene)s.\textsuperscript{20} Furthermore, various functional groups could be incorporated in the polymer backbone owing to the selectivity of highly sophisticated catalysts developed by Grubbs, Shrock and Hoveyda. In 2013, Hillmeyer et al. have successfully employed ADMET to synthesize polyIthienylene vinylene)- (PTV-) based polymer series where they studied the impact of tuning the olefin content in the repeating unit, on optical and polymer solar cell behavior.\textsuperscript{21} Hillmeyer et al. also prepared PTVs based donor-acceptor polymers with distinct optoelectronic properties via ADMET.\textsuperscript{22}
We have previously demonstrated the use of ADMET for the preparation of various heteroatom containing macromolecules$^{23,24}$ and report here its further extension to access donor-acceptor polymers. Polymer structures are based on hexyl thiophene, benzothiadiazole and phenylene vinylene. We chose these electro-optically active segments, as polyphenylen vinylenes$^{25,12}$ have shown interesting electronic properties, poly3-hexythiophenes$^{2,26, 27,28}$ remain one of the prominent efficient donor and benzothiadiazole has been used as an acceptor for constructing low band-gap polymers$^{29,30}$ For comparison, we have also synthesized the analogous polymers via Suzuki polycondensation. ADMET polymers differ from Suzuki polymers in terms of alkoxy phenylene vinylene content in the repeating unit. The polymers are characterized via analytical techniques such as UV-Vis spectroscopy, fluorescence spectroscopy and cyclic voltammetry. The optoelectronic properties of the polymers are compared emphasizing effect of structural variation.
3.2 EXPERIMENTAL SECTION

General Information. All experiments involving air/moisture sensitive materials were carried out using standard Schlenk techniques with a dry nitrogen - filled dual manifold (inert gas/vacuum).

Materials. Hydroquinone, n-butyllithium solution (BuLi, 2.5 M in hexane), 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, Grubbs 2\textsuperscript{nd} generation catalyst, tetrakis (triphenylphosphine)palladium catalyst, and diethyl ether (anhydrous) were obtained from Sigma Aldrich. 4,7-Dibromobenzothiadiazole (1) and 3-hexyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene were obtained from TCI America. 1-Bromo-2,5-bis(heptyloxy)-4-vinylbenzene was prepared from hydroquinone (see Supporting Information). Column chromatography was carried out on silica gel 60 (230-400 mesh) from EMD Chemicals and Sephadex\textsuperscript{TM} LH-20 from GE healthcare. Solvents such as tetrahydrofuran (THF), toluene, hexane, ethyl acetate and dichloromethane were purchased as ACS grade from Fisher Scientific. THF was dried and degassed by a “Pure Solv” solvent purification system by Innovative Technology Inc. before use. Deuterated solvents for NMR spectroscopy were from Cambridge Isotope Laboratories.

Analytical Methods. 600 MHz $^1$H NMR, 300 MHz $^1$H NMR and 125 MHz $^{13}$C NMR spectra were recorded in CDCl\textsubscript{3}, CD\textsubscript{2}Cl\textsubscript{2} and C\textsubscript{6}D\textsubscript{6} on Varian Unity NMR instruments. All signals in the $^1$H NMR spectra are reported in ppm relative to the solvent’s residual $^1$H signal (CDCl\textsubscript{3}: 7.24 ppm) and with multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, dd = doublet of doublet). $^{13}$C NMR spectra were referenced to CDCl\textsubscript{3} (77 ppm). Thermogravimetric analysis was carried out on a Hi-Res TGA 2950 thermogravimetric analyzer from TA Instruments using a platinum pan with a heating rate 10 °C/min under continuous nitrogen flow.
UV-Visible absorption spectroscopy was performed on a Perkin Elmer Model 650 UV Spectrophotometer with 1-cm path length cells in dichloromethane. Photoluminescence spectra were recorded using a Varian spectrofluorometer with 1-cm path length cells in dichloromethane. Gel permeation chromatography (GPC) analysis in THF was performed on an Alliance GPCV 2000 (Waters) instrument equipped with four Waters Styragel HR columns, i.e. HR-1, HR-3, HR-4, and HR-5E. The flow rate of THF was kept at 1.0 mL/min at 40°C throughout the analysis. Molecular weights are recorded relative to polystyrene standards. Results were processed using the Empower Pro Multidetection GPC software. Cyclic voltammetry (CV) experiments were carried out on a CV-50W analyzer from BAS. The three electrode system consisted of an Au disk as working electrode, a Pt wire as secondary electrode and an Ag wire as the reference electrode. The voltammograms were recorded with ~ 10^{-3} - 10^{-4} M solutions in THF and 0.1 M Bu4N[Pf6] as supporting electrolyte. The scans were referenced to ferrocene as internal standard. The potentials are reported relative to the ferrocene/ferrocenium couple. Density functional theory calculations were carried out on dimer models of the polymers and diheptyloxy and hexyl chains were replaced with methyloxy and methyl groups respectively for the sake of simplicity of calculations. The input files were prepared via Gaussview 3.07. First, the geometries of the dimer models were optimized in the ground state using basis set DFT/B3LYP/6-31G(d,p) in Gaussian 09 on the CUNY High Performance Computer facility. The calculations were carried out in the gas phase to neglect the solvent effect.32

Procedures. (2-(2,5-bis(heptyloxy)-4-vinylphenyl)-4,4,5,5-tetramethyl-1,3,2 dioxaborolane) (2). 1-bromo-2,5-bis(heptyloxy)-4-vinylbenzene (640 mg, 1.53 mmol) was dissolved in a mixture of 7.2 mL dry THF and 0.8 mL dry diethyl ether. The solution was cooled to -78°C and n-BuLi (0.64 mL, 2.5 M in hexanes, 1.56 mmol) was added through a syringe. The mixture was stirred at -78°C for 3 hours. 2-isoproxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.35 mL, 1.69 mmol)
was added at -78°C drop-wise through a dropping funnel. The mixture was allowed to reach room temperature and stirred for 24 hours. The reaction was quenched by exposing the mixture to air. The reaction mixture was treated with brine solution and extracted with ethyl acetate. The solvent was removed and the crude product was purified by re-dissolving in hexane, subsequent filtration and final solvent evaporation. The pure product was collected as a viscous green liquid (492 mg, yield 70%).

$^1$H NMR (600 MHz, CDCl$_3$): 7.10 (s, 1H), 7.06-7.02 (dd, $^4$J = 11.34 Hz, $^3$J = 15.32 Hz, 1H), 6.95 (s, 1H), 5.74 (d, $^3$J = 17.87 Hz, 1H), 5.26 (d, $^3$J = 10.95 Hz, 1H), 3.94 (t, $^3$J = 5.81 Hz, 2H), 3.91 (t, $^3$J = 6.64 Hz, 2H), 1.79-1.69 (m, 4H), 1.52-1.24 (m, 16H), 1.32 (s, 12H), 0.90 (td, $^4$J = 2.15 Hz, $^3$J = 6.89 Hz, 6H). MALDI-TOF (neg.) m/z: calcd. for C$_{28}$H$_{47}$BO$_4$ [M $^-$] 458.36 found 458.48

(4,7-bis(3-hexylthiophen-2-yl)benzo[1,2,5]thiadiazole) (4). 4, 7-Dibromo-2, 1, 3-benzothiadiazole (1) (411 mg, 1.40 mmol) and 3-Hexyl-2- (4, 4, 5, 5-tetramethyl-1, 3, 2-dioxaborolan2-yl)-thiophene (988 mg, 3.36 mmol) were dissolved in 14 mL dry dimethoxyethane. The solution was purged with nitrogen and 5.6 mL 2.0 M aqueous potassium carbonate was added. After the addition of tetrakis (triphenyl phosphine) palladium (0) catalyst (32 mg, 1.8%), the mixture was purged with nitrogen again. It was then stirred at 90°C for 24 hours. The reaction mixture was dissolved in 15 mL dichloromethane and extracted with 15 mL 2.0 M aqueous NaOH solution. The organic layer was collected and placed under reduced pressure to remove the solvent. The resulting viscous liquid was purified using a 230-400 mesh silica gel column in a hexane/toluene mixture to obtain the pure product as a yellow viscous liquid (745 mg, yield 73%). $^1$H NMR (600 MHz, CDCl$_3$): 0.80 (t, 6H, $^3$J = 6.90 Hz), 1.132-1.264 (m, 12H), 1.58-1.64 (m, 4H), 2.65 (t, 4H, $^3$J = 7.74 Hz), 7.09 (d, 2H, $^3$J = 5.34 Hz), 7.42 (d, 2H, $^3$J = 5.22 Hz), 7.63 (s, 2H). MALDI-TOF (neg.) m/z: calcd. for C$_{28}$H$_{32}$N$_{2}$S$_{3}$ [M-H$^+$] 468.17 found 468.85.
**Monomer (m1).** 2-(2,5-Bis(heptyloxy)-4-vinylphenyl)-4,4,5,5-tetramethyl-1,3,2 dioxaborolane) (2) (440 mg, 0.96 mmol) was dissolved in 8 mL THF (from “Pure Solv” solvent purification system), together with 4,7-dibromobenzothiadiazole (1) (128 mg, 0.44 mmol). Tetrakis(triphenylphosphine)palladium catalyst (33 mg, 3 mol%) was added to the reaction mixture followed by 0.5 ml 4M aqueous K$_3$PO$_4$ solution. The reaction mixture was purged with nitrogen and stirred at 55$^\circ$C for 24h. The solvent was evaporated, and the dry mixture was dissolved in dichloromethane and washed with brine solution. After removing the solvent, the crude product was passed through 230-400 mesh size silica gel column in a hexane/toluene mixture to isolate pure monomer m1 as an orange solid (224 mg, yield 64%). $^1$H NMR ( 600 MHz, CDCl$_3$): 7.74 (s, 2H), 7.18 (s, 2H), 7.15 (s, 2H), 7.14-7.08 (dd, $^3$J = 11.23 Hz, $^3$J = 17.82 Hz, 2H), 5.80 (d, $^3$J = 17.81 Hz, 2H), 5.30 (d, $^3$J = 11.10 Hz, 2H), 3.96 (t, $^3$J = 6.59 Hz, 4H), 3.92 (t, $^3$J = 6.57 Hz, 4H), 1.82-1.75 (m, 6H), 1.49-1.08 (m, 34 H), 0.87 (t, $^3$J = 6.92 Hz, 6H), 0.80 (t, $^3$J = 7.22 Hz, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$): 155.20, 151.64, 151.39, 132.59, 131.44, 131.44, 130.08, 128.64, 128.09, 117.32, 115.50, 112.36, 70.45, 70.24, 32.74, 32.63, 30.39, 30.19, 30.04, 29.75, 27.06, 26.81, 23.60, 23.46, 15.00, 14.98. MALDI-TOF (neg.) m/z: calcd. for C$_{50}$H$_{72}$N$_2$O$_4$S [M-H$^+$] 796.52 found 797.16.

2,2'-(2,5-bis(heptyloxy)-1,4-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (m2). 1,4-dibromo-2,5-bis(heptyloxy)benzene (3, see Supporting Information) (2g, 4.31 mmol) was dissolved in 25 mL dry THF. The solution was cooled to -78 $^\circ$C and n-BuLi (3.72 mL, 2.5 M in hexanes, 9.32 mmol) was added through a syringe. The mixture was stirred at -78$^\circ$C for 3 hours. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.90 mL, 9.32 mmol) was added at -78$^\circ$C drop wise through a dropping funnel. The mixture was allowed to reach room temperature and stirred for 24 hours. The reaction mixture was treated with brine solution and extracted with ethyl acetate. The solvent was evaporated and the crude product was re-dissolved in 5 mL THF and
precipitated in hexanes. Precipitates were filtered out and the solvent was evaporated from the filtrate. Pure compound m2 was obtained in the form of white crystals by recrystallizing from ethyl acetate (1.3 g, yield 55%). 1H NMR (300 MHz, CDCl3): 7.06 (s, 2H), 3.91 (t, J = 6.31 Hz, 4H), 1.79-1.65 (m, 4H), 1.52-1.21 (m, 16H), 1.31 (s, 24H), 0.86 (t, J = 2.15 Hz, J = 6.66 Hz, 6H). MALDI-TOF (neg.) m/z: calcd. for C32H56B2O6 [M-H+] 558.43 found 558.99.

Monomer (m3). 2-(2,5-bis(heptyloxy)-4-vinylphenyl)-4,4,5,5-tetramethyl-1,3,2 dioxa-borolane (2) (403 mg, 0.88 mmol) was dissolved in 2.5 mL THF (from “Pure Solv” solvent purification system) and m4 (240 mg, 0.38 mmol was added to it. Tetrakis(triphenylphosphine)palladium catalyst (17 mg, 3 mol%) was added to the reaction mixture followed by the addition of 0.38 ml 4M aqueous K3PO4 solution. The reaction mixture was purged with nitrogen and stirred at 55 °C for 24h. The solvent was evaporated, and the dry mixture was dissolved in dichloromethane and washed with brine solution. After evaporating the solvent, the crude product is passed through 230-400 mesh size silica gel column in a hexane/dichloromethane mixture to isolate pure monomer m3 as red semi-solid (289 mg, yield 66%). 1H NMR (600 MHz, CDCl3): 7.66 (s, 2H), 7.52 (s, 2H), 7.19 (s, 2H), 7.07 (s, 2H), 7.06-7.02 (dd, J = 11.55 Hz, J = 17.68 Hz, 2H), 5.76 (d, J = 17.92 Hz, 2H), 5.27 (d, J = 11.10 Hz, 2H), 4.07 (t, J = 6.31 Hz, 4H), 4.00 (t, J = 6.94 Hz, 4H), 2.68 (t, J = 7.79 Hz, 4H), 1.91-1.86 (m, 4H), 1.83-1.79 (m, 4H), 1.56-1.45 (m, 4H), 1.41-1.18 (m, 44 H), 0.88 (t, J = 6.73 Hz, 6H), 0.81 (dt, J = 6.94 Hz, J = 10.10 Hz, 12H). 13C NMR (125 MHz, CDCl3): 154.25, 150.57, 149.58, 141.49, 139.76, 132.49, 131.41, 129.61, 129.01, 128.19, 127.77, 127.38, 126.64, 125.26, 123.38, 112.36, 110.61, 69.55, 69.50, 31.80, 31.60, 30.73, 29.60, 29.49, 29.46, 29.21, 29.15, 29.01, 26.32, 26.12, 22.61, 22.60, 22.55, 32.74, 32.63, 30.39, 30.19, 30.04, 29.75, 27.06, 26.81, 23.60, 23.46, 14.08, 14.04. MALDI-TOF (neg.) m/z: calcd. for C70H100N2O4S3 [M-H+] 1128.68 found 1129.31.
4,7-bis(5-bromo-3-hexylthiophen-2-yl)benzo[1,2,5]thiadiazole(m4).

Dithiophenebenzothiodiazole(4,7-bis(3-hexylthiophen-2-yl)benzo[1,2,5]thiadiazole (4) (290 mg, 0.62 mmol) and N-bromosuccinamide (264 mg, 1.48 mmol) were dissolved in 7.7 mL chloroform. The reaction mixture was refluxed at 55°C for 24 hours. The reaction mixture was then diluted with 20 mL chloroform and treated with 20 mL, 10% HCl solution. The organic layer was collected and filtered into a round bottom flask and placed under reduced pressure to remove the remaining solvent. The resulting viscous liquid was passed through a 230-400 mesh silica gel column using a hexane/chloroform mixture to isolate pure product m4 in the form of a red viscous liquid (280 mg, yield 72%). \(^1\)H NMR (600 MHz, CDCl\(_3\)): 0.79 (t, 6H, \(^3\)J = 6.90 Hz), 1.12-1.26 (m, 12H), 1.55-1.61 (m, 4H), 2.59 (t, 4H, \(^3\)J = 7.86 Hz), 7.04 (s, 2H), 7.58 (s, 2H). \(^1\)C NMR (125 MHz, CDCl\(_3\)): 153.83, 142.36, 133.48, 131.91, 129.62, 126.52, 113.13, 31.46, 30.44, 29.36, 28.97, 22.45, 13.99.

MALDI-TOF (neg.) m/z: calcd. for C\(_{26}\)H\(_{30}\)Br\(_2\)N\(_2\)S\(_3\) [M-H] 625.99 found 624.78.

Typical Synthesis of Polymer (P1). Monomer m1 (200 mg, 0.25 mmol) was dissolved in 2.5 mL dry toluene and Grubbs second generation catalyst (10.6 mg, 0.0125 mmol) was added. The mixture was heated to 70°C and stirred for 48 hours at this temperature under reduced pressure. The reaction was quenched by adding few drops of ethyl vinyl ether after bringing the reaction mixture to room temperature. The solvent was evaporated; the crude product was then re-dissolved in 1.5 mL chloroform and precipitated into 200 mL cold methanol. The polymer was collected by filtration and passed through a short sephadex column to obtain the pure polymer p1 as reddish-brown solid (140 mg, yield 70 %). \(^1\)H NMR (600 MHz, CDCl\(_3\)): 7.81 (s, 2H), 7.62 (s, 2H), 7.38 (s, 2H), 7.24 (s, 2H), 4.03 (t, \(^3\)J = 6.56 Hz, 8H), 1.86 (s, 6H), 1.53-1.15 (m, 34H), 0.84 (t, \(^3\)J = 7.44 Hz, 12H). \(^1\)C NMR (125 MHz, CDCl\(_3\)): 155.22, 151.72, 151.67, 130.71, 129.50, 129.20, 127.53,
Polymer \((P2)\). 4, 7-Dibromo-2, 1, 3-benzothiadiazole (92 mg, 0.47 mmol) and \(m2\) (260 mg, 0.47 mmol) were dissolved in 4 ml THF (from “Pure Solv” solvent purification system). The solution was purged with nitrogen and 0.5 mL 4M aqueous \(K_3PO_4\) solution was added. After the addition of tetrakis (triphenyl phosphine) palladium (0) catalyst (8 mg, 2 mol%), the solution was purged with nitrogen again. The mixture was then stirred for 48 hours at 55°C. Then 10 mL dichloromethane were added and the mixture was treated with brine solution and organic layer was collected. The solvent was evaporated and the crude product was purified by soxhlet extraction using acetone, methanol, hexanes and chloroform as solvents. The pure product \(p2\) was obtained from the chloroform fraction as yellowish green powder (138 mg, yield 68%).

\(^1H\) NMR (600 MHz, CDCl\(_3\)): 7.91 (s, 2H), 7.43 (s, 2H), 3.97 (t, \(^3J = 6.5\) Hz, 4H), 1.88-1.48 (m, 4H), 1.32-1.09 (m, 16H), 0.82 (t, \(^3J = 6.40\) Hz, 6H). UV-Vis (dichloromethane, 1.7 x \(10^{-4}\) M): \(\lambda_{\text{max}} = 414\) nm \((\varepsilon = 28416)\); fluorescence (dichloromethane, 1.7 x \(10^{-6}\) M): \(\lambda_{\text{max}} = 576\) nm; \(\Phi = 0.43\) \((\lambda_{\text{exc}} = 364\) nm), \(M_n\) (polystyrene standards) = 2788 g/mol; \(M_w/M_n = 1.81\).

Polymer \((P3)\). Monomer \(m3\) (350 mg, 0.31 mmol) was dissolved in 2.5 mL dry toluene and Grubbs second generation catalyst (26 mg, 0.03 mmol) was added. The mixture was heated to 70°C and stirred for 48 hours at this temperature under reduced pressure. The reaction was quenched by adding few drops of ethyl vinyl ether after bringing the reaction mixture to room temperature. Then the solvent was evaporated, the crude product re-dissolved in 2 mL chloroform and precipitated into 200 mL cold methanol. The polymer was collected by filtration and passed through a short sephadex column to obtain pure polymer \(p3\) as dark red solid (289 mg, yield 75%).
1H NMR (300 MHz, CDCl₃): 7.70 (s, 2H), 7.58 (s, 2H), 7.51 (s, 2H), 7.24 (s, 4H), 4.12 (t, ³J = 6.60 Hz, 4H), 4.06 (t, ³J = 6.40 Hz, 4H), 2.80-2.60 (m, 4H), 1.99-1.05 (m, 56H), 0.84 (m, 18H).

13C NMR (125 MHz, CDCl₃): 154.22, 150.84, 149.79, 141.52, 129.58, 128.64, 127.71, 127.39, 126.51, 123.04, 112.56, 69.75, 69.53, 31.76, 31.60, 30.76, 29.64, 29.17, 26.41, 26.21, 22.58, 14.06. UV-Vis (dichloromethane, 4.2 x 10⁻⁶ M): λmax = 400 nm (ε = 50767); fluorescence (dichloromethane, 4.2 x 10⁻⁷ M): λmax = 656 nm; Φ = 0.47 (λexc = 400 nm), Mₙ (polystyrene standards) = 10289 g/mol; Mₘ/Mₙ = 1.58.

**Polymer(P4):** Co-monomers m4 (269 mg, 0.43 mmol) and m2 (239 mg, 0.43 mmol) were dissolved in 3.5 mL THF (from “Pure Solv” solvent purification system). The solution was purged with nitrogen and 0.42 mL of 4M aqueous K₃PO₄ solution was added. After the addition of tetrakis (triphenyl phosphine) palladium (0) catalyst (14 mg, 3%), the mixture was purged with nitrogen again and then stirred for 48 hours at 55°C. The reaction mixture was diluted by adding 10 mL dichloromethane and subsequently treated with brine solution. The solvent was evaporated and the crude product purified by soxhlet extraction using acetone, methanol, hexanes and chloroform as solvents. The pure product p4 was isolated from the chloroform fraction as a reddish brown solid (248 mg Yield 72 %). 1H NMR (600 MHz, CDCl₃): 7.70 (s, 2H), 7.59 (s, 2H), 7.31 (s, 2H), 4.14 (t, ³J = 6.44 Hz, 4H), 2.75-2.66 (m, 4H), 1.96-1.55 (m, 8H), 1.41-1.17 (m, 28H), 0.82 (m, 12H).

13C NMR (125 MHz, CDCl₃): 155.27, 150.51, 142.59, 140.63, 133.62, 130.58, 123.87, 128.85, 128.39, 113.31, 70.70, 32.82, 32.63, 31.77, 30.55, 30.19, 27.36, 23.58, 15.06. UV-Vis (dichloromethane, 6.4 x 10⁻⁶ M): λmax = 376 nm (ε = 51339); fluorescence (dichloromethane, 6.4 x 10⁻⁷ M): λmax = 651 nm; Φ = 0.52 (λexc = 376 nm), Mₙ (polystyrene standards) = 18785 g/mol; Mₘ/Mₙ = 1.76.
3.3 Results and discussion

We were interested in utilizing ADMET to make a systematic series of donor-acceptor polymers of significant interest for potential use in polymer solar cells.\textsuperscript{10} We then prepared the analogous polymers via Suzuki polycondensation for comparison and studied the structure-property relationship of these polymers in terms of photophysical and electrochemical properties. ADMET and Suzuki polymers differ in terms of diheptyloxyphenylene vinylene content in their repeating unit and our results indicate that this structural difference has a significant effect on the overall polymer properties. Additionally the ADMET is a very simple method to access various precise architectures. We circumvented the typical Suzuki polycondensation synthetic route to access donor-acceptor polymers by preparing the monomer by Suzuki coupling, purifying it by column chromatography (which is not realistic in high $M_n$ Suzuki polymers) and then using the monomer having intrinsic donor-acceptor stoichiometry to produce corresponding polymers via ADMET. We tested substituted phenylene vinylene and phenylene vinylene-hexyl thiophene as donor components and benzothiadiazole as an acceptor in our donor-acceptor architectures. Throughout our discussion, we will be pointing out the effect on polymer properties arising from 1) difference in heptyloxyphenylene vinylene unit in polymer backbone between ADMET (p1,p3) and Suzuki polymers (p2, p4) 2) difference in hexylthiophene (HT) unit in polymer backbone among ADMET polymers (p1 and p3) and Suzuki polymers (p2 and p4).

3.3.1 Monomer Synthesis

Monomer design is very important to access precision polymers through ADMET. By designing and synthesizing symmetrical diene monomers incorporating donor and acceptor moiety, the symmetry of monomer is carried directly into the polymer, resulting in precisely controlled donor-acceptor architectures.\textsuperscript{19} The synthetic strategies for the monomer units used are illustrated in
Scheme 3.1. Monomers m1 and m3 are made using the same precursor, a boronic ester derivative (2). 2 was synthesized from 1-bromo-2,5-bis(heptyloxy)-4-vinylbenzene by lithiation, followed by boronation (see Supporting information). Suzuki coupling reaction of 2 with 4,7-dibromobenzothiadiazole (1) at 55 °C using Pd(PPh₃)₄ as a catalyst in THF and 4M aqueous K₃PO₄ as a base yielded m1 with a 64% yield. Similarly, m3 was prepared by reacting 2 with m4 via Suzuki coupling under similar conditions. Diboronic ester monomer m2 and dibromo monomer m4 were prepared by adapting published recipes to our systems. The use of diboronic ester precursors is found to be advantageous as compared to diacid ones owing to the possibility of self-dehydration of boronic acid derivatives into anhydride trimers. Monomer m2 was prepared from 1,4-dibromo-2,5-bis(heptyloxy)benzene (3) via lithiation followed by boronation with 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. To synthesize monomer m4, (4,7-bis(3-hexylthiophen-2-yl)benzo[1,2,5]thiadiazole (4) was first prepared from Suzuki coupling reaction of a borolane derivative of hexylthiophene with 4,7 dibromobenzothiadiazole (see Supporting information), followed by bromination with N-bromosuccinimide. The ¹H NMR spectra of monomers are shown in figure 3.1-3.4. In the case of ADMET diene monomers m1 and m3, the formation of terminal vinyl functionality is indicated by two doublet signals in the region of 5.20-5.85 ppm. These resonances will progressively lose intensity as the polycondensation proceeds. In m1, proton resonance from benzothiadiazole moiety was observed at ~7.74 ppm whereas those from phenylene at ~7.18 and at ~7.15 ppm. In m3, where there is hexylthiophene coupled with phenylenevinlyne as a donor, singlet proton resonance from hexylthiophene block also appeared at ~7.52 ppm along with the additional signals in aliphatic region (0.8-2.8 ppm). In m2, a singlet was observed at ~7.06 ppm from phenylene component along with the high intensity peak at ~1.31 ppm resulting from 24 ester protons. In dibromo monomer m4, singlet resonance from
benzothiadiazole component was observed at \(~7.58\) ppm while that from hexylthiophene at \(~7.04\) ppm.

Scheme 3.1 Synthesis of monomers
Figure 3.1 $^1$H NMR spectrum of m1 in CDCl$_3$

Figure 3.2 $^1$H NMR spectrum of m2 in CDCl$_3$
Figure 3.3 $^1$H NMR spectrum of m3 in CDCl$_3$

Figure 3.4 $^1$H NMR spectrum of m4 in CDCl$_3$
3.3.2 Polymerization

The monomers m1-4 were subjected to polycondensations using either homocoupling or heterocoupling (Scheme 3.2). For ADMET polycondensations of m1 and m3, the ruthenium-based alkylidene complex “Grubbs second generation” \([1,3\text{-bis}(2,4,6\text{-trimethylphenyl})-2\text{-imidazolidinylidene}) \text{dichloro(phenyl methylene)} \text{(tricyclohexylphosphine) ruthenium}] (\text{C}_{46}\text{H}_{65}\text{Cl}_{2}\text{N}_{2}\text{PRu})\) was used. Typical reactions were carried out at 70 °C in toluene for the duration of 48h under reduced pressure to shift the equilibrium towards the formation of polymers through the removal of ethylene gas.\(^{36}\) The reaction was quenched by adding ethyl vinyl ether and the polymers p1 and p3, were purified by precipitating into methanol.\(^{37}\) For Suzuki polycondensations of m2 and m4, a palladium based catalyst tetrakis(triphenylphosphine)palladium(0), \(\text{Pd(PPh}_3)_4\), was used. Typical reactions were carried out at 55 °C in THF for the duration of 48h to yield polymers p2 and p4. At the end of the reaction, the mixture was diluted with dichloromethane and treated with brine solution. The organic layer was collected and the solvent was removed. To remove the palladium catalyst,\(^{27,38}\) the polymers p2 and p4 were further purified by Soxhlet extraction successively with methanol, acetone, hexane and chloroform. Pure polymers were recovered from chloroform fraction.

Table 3.1 summarizes representative polycondensation results and Figure 3.5 illustrates representative GPC chromatograms for the polymers p1-p4. GPC number average molecular weights of 7385 g/mol and 2788 g/mol were reached with polydispersities \(\text{Mn/Mw} \sim 1.69\) and 1.81 for p1 and p2 respectively. In the case of p2, precipitation was observed during the polymerization indicating the poor solubility in THF resulting in lower molecular weight. We tried to increase the molecular weight of p2 by varying polymerization conditions such as monomer concentration, reaction time, solvent, catalyst,\(^{37}\) base, and temperature but only slight increase (\(\text{Mn} \sim 3500\) g/mol) was achieved (see Supporting Information). The varied parameters include monomers’
concentrations (100 mM, 150 mM and 200 mM), reaction times (24h, 48h and 72h) and temperatures (55 °C, 65 °C, 75 °C and 85 °C). Solvents which were tested, include THF, toluene, dioxane and THF/toluene (1:1 mixture) whereas bases include aqueous solutions of K₃PO₄, K₂CO₃ and KF. The catalysts tested were tetrakis(triphenylphosphine)palladium(0), and [2′-(amino-kN)[1,1′-biphenyl]-2-yl-kC]chboro(trit-butyolphosphine)-palladium. P1 and p2 differ structurally, among others, in terms of numbers of diheptyloxy side chains per repeat unit. The additional side chains in p1 significantly increase the polymer solubility, despite of the fact that p1 structurally features on large coplanar trans-stilbene unit per repeat unit compared to the single phenylene unit in p2. GPC results yielded Mn of p3 and p4 ~ 10289 g/mol and 18785 g/mol with polydispersities Mn/Mw ~ 1.58 and 1.76 respectively. Comparing Mn of p2 and p4 it is evident that the incorporation of a hexyl-substituted thienyl unit on either side of the benzothiodiazole unit in the p4 backbone resulted in increased solubility with higher molecular weights.
Scheme 3.2 Synthesis of polymers
Table 3.1. Representative ADMET and SPC polycondensation results

<table>
<thead>
<tr>
<th>Entry</th>
<th>M (mol/L) [Monomer]</th>
<th>(g/mol) [Catalyst]</th>
<th>PDI</th>
<th>Mn</th>
<th>Mw</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.00 x 10&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>5.00 x 10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>7385</td>
<td>12480</td>
<td>1.69</td>
</tr>
<tr>
<td>P2&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.04 x 10&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>2.08 x 10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>2788</td>
<td>5046</td>
<td>1.81</td>
</tr>
<tr>
<td>P3&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.24 x 10&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>1.24 x 10&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>10289</td>
<td>17388</td>
<td>1.58</td>
</tr>
<tr>
<td>P4&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.10 x 10&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>3.30 x 10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>18785</td>
<td>33061</td>
<td>1.76</td>
</tr>
</tbody>
</table>

<sup>a</sup>Typical reaction conditions: Grubbs II Catalyst, t = 48h, T = 70 °C; <sup>b</sup>both monomers are in 1:1 molar ratio; Pd(PPh<sub>3</sub>)<sub>4</sub> catalyst, t = 48h, T = 55 °C

Figure 3.5 GPC chromatograms p1, p2, p3 and p4

The <sup>1</sup>H NMR spectra of the polymers along with relevant assignments, are shown in Figure 3.6-3.9. In the ADMET polymers p1 and p3, the substituted trans-stilbene component formed during polymerization is same arising from homo coupling between vinyl-phenylene functions. During the polymerization, the signal intensity of the resonances attributed to the terminal vinyl groups
in the monomers decreases while that of newly formed vinylene groups (h) grows with increasing chain length during the polycondensation (vide supra). The singlet resonance from said vinylene in p1 and p3 is observed at ~7.6 ppm for both systems, indicating similar chemical environments, including exclusively trans-configuration of the double bond. In both p1 and p3, some resonances overlapped with the chloroform resonance, therefore NMR measurements were also performed in CD$_2$Cl$_2$ and benzene-D$_6$ for p1 and p3 respectively (Figure 3.10 and Figure 3.11). Resonances from benzothiadazole, hexylthiophene and phenylene ring protons are assigned with labels f, g, d and e. Compared to p1, p3 shows an additional resonance g at 7.24 ppm in CDCl$_3$ (7.61 ppm in C$_6$D$_6$) due to the presence of the hexylthiophene unit. In The $^1$H NMR spectra of p2, integration of resonance signals in the aromatic region is ~1:1, which is the indicative of two distinct aromatic protons of each type in the structure. As we were only able to achieve low molecular weight in p2, significant signals from the oligomeric units and end groups were also observed. In p4 there are three distinct protons resonances between ~7.25 – 7.80 ppm arising from protons in phenylene, hexylthiophene, and benzothiadiazole units, marked e, g and f respectively and observed with ~1:1:1 integral ratios. Compared to p2, p4 has the additional resonance g due to the presence of the hexylthiophene unit in its backbone. Similarly comparing polymers p1 and p3 with polymers p2 and p4, the additional two resonances in the former arise from phenylene vinylene segment vs. only a phenylene in the latter. In addition, the resonance of the protons f on the benzothiadiazole unit shows a diamagnetic shift in systems p3 and p4 vis-à-vis p1 and p2, indicating a different chemical environment due to the thiophene unit in the vicinity and evidenced electronically in the lowering of the LUMO energies (vide infra). All structures and assignments were confirmed by $^{13}$C NMR and 2D NMR experiments (see Appendix)
Figure 3.6 $^1$H NMR spectrum of p1 in CDCl$_3$

Figure 3.7 $^1$H NMR spectrum of p2 in CDCl$_3$
Figure 3.8 $^1$H NMR spectrum of p3 in CDCl$_3$

Figure 3.9 $^1$H NMR spectrum of p4 in CDCl$_3$
Figure 3.10 $^1$H NMR spectrum of p1 in CD$_2$Cl$_2$

Figure 3.11 $^1$H NMR spectrum of p3 in C$_6$D$_6$
3.3.3 Optical properties

Figure 3.12 details absorption and emission spectra of polymers solutions and films. The results are summarized in Table 3.2. The measurements were performed in solution using dichloromethane and as thin films spincast from toluene solutions. The absorption of p1 in solution shows three distinct transitions at 316, 364 and 440 nm with $\lambda_{\text{max,ab}}$ at 316 nm. The absorption of p1 in thin film showed bathochromic shift due to enhanced $\pi$-$\pi$ stacking. The polymer p2 shows a maximum absorption at 307 nm with additional absorption at 414 nm. In case of p2, the film was not formed due to lower molecular weight. Comparing p1 and p2 spectra in solution it is clear that phenylene vinylene segment in the p1 backbone is causing additional transition at 364 nm and the overall red-shift in the spectrum. The reason could be attributed to the increasing donor strength with phenylene vinylene segment which in turn could raise the HOMO energy level decreasing the band gap and causing red shift in absorption of p1 as compared to that of p2. The extinction coefficient of p1 and p2 was found to be 43230 and 28416 Lmol$^{-1}$cm$^{-1}$ at 316 and 307 nm respectively. The absorption spectrum of p3 in dichloromethane solution shows three distinct transitions at 321, 400 and 468 nm. These transitions are red shifted in absorption of p3 thin film exhibiting peaks at 324, 424 and 514 nm. The polymer p4 also exhibits three absorption peaks at 321, 376 and 470 nm in dichloromethane solution. In this case also p4 in thin film showed red shift in absorption due to extended $\pi$-$\pi$ stacking. Comparing the absorptions of p3 and p4, transition at 376 nm in p4 solution (388 nm in film) is attributed to phenylene component which is red shifted to 400 nm (424 nm in film) in case of p3 owing to additional phenylenevinylene unit in its structure. Both p3 and p4 exhibit high extinction coefficients of 50767 Lmol$^{-1}$cm$^{-1}$ and 51339 Lmol$^{-1}$cm$^{-1}$ at 400 nm and 376 nm respectively. Comparing absorptions of ADMET polymers (p1 with p3) and SPC polymers (p2 with p4), it is evident that hexylthiophene unit present in p3 and p4 is causing a significant red shift in their absorptions, reducing the band gap as compared to p1.
and p2 respectively. The reason is attributed to the fact that hexylthiophene unit contributes in raising the HOMO energy level and lowering the LUMO energy level and hence reducing the band gap causing the red shift in the spectrum. The HOMO-LUMO band gaps were estimated by UV-spectroscopy and by cyclic voltammetry.

The polymers were found to be light-emitting in solution as well as thin films (except p2). In the contrast to several transitions in absorption, all the polymers exhibited only one distinct emission transition in dichloromethane solution as well as in thin films spin casted from toluene. The maximum emissions of p1, p2, p3 and p4 are observed at 592, 576, 656 and 651 nm respectively. These results also indicate that there is only slight red shift caused by phenylenevinylene segment from p2 to p1 (16 nm) and p4 to p3 (4 nm). On the other hand hexylthiophene unit has caused significant red shift in the emission from p1 to p3 (64 nm) and p2 to p4 (75 nm) which clearly shows it influence on excited state transitions of these polymers. The polymers p1, p3 and p4 exhibited emission maxima at 582, 665 and 665 nm respectively in film. The quantum efficiencies of p1, p2, p3 and p4 were found to be 0.40, 0.43, 0.47 and 0.52 relative to anthracene standard. Figure 3.13 illustrates the solutions of P1-P4 in solution, irradiated with a UV lamp.
Figure 3.12 Absorption (top) and the emission spectra (bottom) of p1, p2, p3, and p4
Table 3.2. Summary of absorption and emission data of the polymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\lambda_{\text{max,ab}}$ (nm) solution</th>
<th>$\lambda_{\text{max,ab}}$ (nm) film</th>
<th>$\lambda_{\text{max,em}}$ (nm)$^1$</th>
<th>$\Phi_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>316, 364, 440</td>
<td>310, 369, 465</td>
<td>592</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>582</td>
<td></td>
</tr>
<tr>
<td>P2</td>
<td>307, 414</td>
<td>n.a.</td>
<td>576</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>n.a.</td>
<td></td>
</tr>
<tr>
<td>P3</td>
<td>321, 400, 468</td>
<td>324, 424, 514</td>
<td>656</td>
<td>0.47</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>665</td>
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<td>P4</td>
<td>321, 376, 470</td>
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<td></td>
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<td>665</td>
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</table>

$^1$excitation wavelength for P1, P2, P3 and P4 are 364, 414, 400 and 376 nm respectively and the spectra is recorded in dichloromethane, $^2$value at 316 nm, $^3$at 307 nm, $^4$at 400 nm, $^5$at 376 nm

Figure 3.13 P1-P4 in dichloromethane solution, irradiated with a UV lamp

3.3.4 Cyclic Voltammetry: Electrochemical experiments were carried out in tetrahydrofuran for reduction and dichloromethane for oxidation processes by cyclic voltammetry. The polymers are reversibly reduced and the redox potentials are reported relative to Fc/Fc$^+$ couple at 298 K$^{39,40}$ in Figure 4. The first reduction wave for P1 was observed at $E_{1/2} = -1.93$ V and the second one at -2.43 V whereas the reduction wave for P2 was detected at $E_{1/2} = -1.98$ V. Similarly, two reduction waves were also observed for P3 at $E_{1/2} = -1.78$ V and -2.28 V. P4 exhibited reduction peaks at
$E_{1/2} = -1.81$ V and -2.36 V. The polymers also exhibit reversible oxidation waves at $E_{1/2} = 1.10$ V, 1.40 V, 0.91 V and 1.02 V for P1-P4 respectively. The HOMO and LUMO energy levels were estimated from oxidation and reduction plots of the polymers. For P1, HOMO and LUMO energy levels were found to be -5.31 eV and -2.87 eV respectively with a band gap of 2.44 eV. HOMO and LUMO energy levels for P2 were determined to be -5.61 eV and -2.82 eV with a band gap of 2.79 eV. As the acceptor is benzothiadiazole in both the polymers and LUMO is acceptor centered, LUMO energy levels are close in both the cases. On the other hand phenylenevinylene segment has a significant effect on HOMO orbital raising its energy from -5.61 eV in P2 to -5.31 eV in P1. In P3 and P4, hexylthiophene 1 unit seems to affect both HOMO and LUMO energy levels. The contribution of hexylthiophene on both the orbitals was also evident from the orbital plots obtained by DFT calculations. Due to this fact, P3 and P4 have lower band gaps as compared to P1 and P2. Furthermore, with phenylenevinylene segment in P3, HOMO energy level was raised to $– 5.12$ eV as compared to $– 5.23$ eV in P4 resulting in reduced band gap (2.10 eV vs 2.24 eV). LUMO energy levels for P3 and P4 were found to be $-3.02$ eV and $-2.99$ eV respectively. The results from CV are consistent with those of DFT calculations. Table 3.3 summarizes the electrochemical data of the polymers.
Figure 3.14 Cyclic voltammetry plots: Reduction (top) of p1, p2, p3 and p4 in THF and oxidation (bottom) of p1, p2, p3 and p4 in CH$_2$Cl$_2$ and with Bu$_4$N$^+$PF$_6^-$ (0.1M) as a supporting electrolyte recorded vs Fc/Fc$^+$ (Fc=[(η-C$_5$H$_5$)$_2$Fe]) as an internal reference at a scan rate of 100 mV/s
Table 3.3 Summary of electrochemical data of the polymers

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<th>Entry</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>Band Gap (eV) CV</th>
<th>Band Gap (eV) DFT*</th>
<th>Band Gap (eV) UV-Vis #</th>
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<tr>
<td>P1</td>
<td>-5.31</td>
<td>-2.87</td>
<td>2.44</td>
<td>2.43</td>
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<tr>
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<td>-2.82</td>
<td>2.79</td>
<td>2.93</td>
<td>2.43##</td>
</tr>
<tr>
<td>P3</td>
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<td>-3.02</td>
<td>2.10</td>
<td>2.16</td>
<td>1.81</td>
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<td>P4</td>
<td>-5.23</td>
<td>-2.99</td>
<td>2.24</td>
<td>2.32</td>
<td>1.95</td>
</tr>
</tbody>
</table>

*calculated for optimized structure of a trimer using basis set: B3LYP/6-31g(d)

Figure 3.15 Optimized geometry, HOMO/LUMO orbital plots of p1, p2, p3, and p4 simulated by DFT/B3LYP/6-31g(d), which were carried out with a chain length of n=2
3.3.5 DFT calculations: The interesting differences in the electro optical properties of the polymers with structural differences encouraged us to perform a computational study to deepen our understanding. Geometries of the dimer models of the polymers were optimized using density functional theory (DFT) in the Gaussian 09 software at the DFT/B3LYP/6-31G(d,p) level of theory, which have been widely used in such calculations. The optimized geometry and HOMO-LUMO orbital plots for the dimer models for all the polymers are shown in Figure 3.15 along with the energy levels and the band gap. It appears that in general HOMO levels of all the polymers are well localized along the conjugated backbone while LUMO is mainly localized on benzothiadiazole block. These results further demonstrates the alternating donor-acceptor character of the polymers. However the delocalization in HOMO is more extended in p3 and p4 due to additional hexylthiophene unit. The structural effects are prominent on HOMO and LUMO energy levels. The HOMO energy levels of P1 and P2 are -4.68 eV and -5.18 eV respectively. The HOMO energy level of p1 is elevated about 0.5 eV compared to that of p2 because of the contribution by donor phenylenevinylene segment in the backbone of p1. On the other hand LUMO energy level of p1 and p2 is same i.e. -2.25 eV because LUMO is acceptor localized and both have benzothiadiazole block as an acceptor. Similarly, comparing HOMO energy levels of p3 and p4 which are -4.56 eV and -4.75 eV, it appears that HOMO energy is elevated about 0.19 eV because of the presence of additional phenylenevinylene unit in p3. LUMO levels of p3 and p4 are -2.43 and -2.40 eV, which are quite close due to same acceptor in both. Also comparing the energy levels and orbital plots of ADMET polymers (p1 and p3) and Suzuzki polycondensation polymers (p2 and p4), it is observed that HT has a significant contribution in HOMO and LUMO orbitals. HOMO energy levels were raised from -5.18 to -4.75 eV from p2 to p4 and -4.68 to -4.56 eV from p1 to p3. LUMO energy levels were also affected by hexylthiophene unit lowering it from
-2.25 to -2.43 eV (p2 to p4) and -2.25 to -2.40 eV in p1 to p3. These results suggest that the structural differences in the backbone of the polymer affects the electron distribution severely, consequently leading to the variation of the energy levels.\(^\text{40}\)

3.4 References


(2) Lei, T., Wang, J. Y., Pei, J. Accounts of chemical research 2014, 47, 1117-1126.


3.5 Appendix

Polymers (p1, p3 and p4): $^{13}$C-NMR Spectra (125 MHz) in CDCl$_3$
HSQC spectrum of p1:

HSQC spectrum of p3:
HSQC spectrum of \textbf{p4}:
DFT studies on models of donor-acceptor polymers based on substituted trans-stilbene donor

4.1 Introduction

Features such as cost-effective cell fabrication, flexibility, and tunable band gap have made polymer solar cells an emerging renewable energy source.\textsuperscript{1-3} The power conversion efficiency of polymer solar cells has increased substantially to above 10% recently.\textsuperscript{4} As \textasciitilde{}54.3\% of the solar energy is confined to the wavelength range of 380-800 nm, the active layer of the polymer solar cells should have a broad and strong absorption in this range for high efficiencies.\textsuperscript{5} Although, there is a crucial role played by device optimization and morphology profile, the essential driving force for the high efficiencies of polymer solar cells is control of HOMO and LUMO energy levels and hence the band gap. In this regard, donor-acceptor polymers are usually employed to tune these energy levels individually, hence optimizing the HOMO-LUMO band gap for wide absorption range in the visible light region.\textsuperscript{6,7} Moreover, donor-acceptor architectures also favors charge separation in photoexcited states thereby enhancing carrier density of the photovoltaic cells.

The rational design of donor-acceptor polymers is a challenging issue that involves experimental and theoretical chemistry and physics.\textsuperscript{8} In the process of designing novel polymer materials for solar cells, theoretical tools play a crucial role in predicting their electronic and optical properties.\textsuperscript{9} Density functional theory (DFT) calculations are widely used to predict these properties and hence aids in design of the polymers by choosing appropriate donor and acceptor moieties. Through the DFT calculations at the B3LYP/6-31G(d,p) level on model compounds, the HOMO-LUMO

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energy levels and the band gap could be estimated. In these studies, solvent effect is usually neglected as solvent corrections are not significant to study neutral oligomers.\textsuperscript{9}

According to the rational design principles for donor-acceptor type solar cell fabrication, the ideal polymer should have a HOMO-LUMO band gap of ~1.5 eV (Scheme 4.1) with HOMO energy level of ~ -5.4 eV and LUMO of ~ -3.9 eV.\textsuperscript{10,11} Weak donor-strong acceptor strategy has been proposed to achieve low lying HOMO energy level via the “weak donor” and to obtain low band gap by using “strong acceptor” via internal charge transfer.\textsuperscript{11} In order to achieve the proposed ideal polymer of band gap around 1.5 eV, the HOMO should be still maintained ~ -5.4 eV whereas the LUMO should be lowered to narrow the band gap. Generally, a donor component with moderate electron donating ability is required to create donor-acceptor polymer with HOMO energy levels around -5.4 eV.\textsuperscript{10} Several donor moieties, such as carbazole, fluorene, dithienosilole and benzodithiophene while other acceptors such as benzothiadiazole, pyridine and diketopyrrolopyrro have been employed in synthesis of low band gap polymers.\textsuperscript{3} It is very important to investigate more donor-acceptor pairs via theoretical and experimental studies to guide the design of future polymer architectures.

In the previous studies we found that we can tune HOMO to ~ -5.4 eV using substituted trans-stilbene based donors. Here, we investigated various strong acceptors via DFT calculations to tune LUMO energy levels and hence design lower band gap polymers. Acceptors investigated were oxadiazolo[3,4-c]pyridine (OP), thiadiazolo[3,4-c]pyridine (TP), thiadiazolo[3,4-g]quinoxaline (TQ), benzo[c][1,2,5]oxadiazole (BO), benzo[d][1,2,3]triazole (BT), benzo[c][1,2,5]selenadiazole (BSD), and thieno[3,4-c]pyrrole-4,6(5H)-dione (TPD). These acceptors are selected because of their interesting properties in photovoltaic devices.\textsuperscript{10} The second set of acceptors inculde thienyl unit on either side of an acceptor block. Dithiophene substituted acceptors are also reported to
enhance the power conversion efficiencies as it contributes in raising HOMO level and lowering LUMO energy level thereby decreasing HOMO-LUMO band gap.\textsuperscript{12-14} The advantages offered by thienyl units include the relief of steric hindrance between the donor and the acceptor units\textsuperscript{10,15} thereby making conjugated backbone more planar thereby reducing the band gap by enhancing donor-acceptor interaction. Secondly, the electron rich thienyl units could improve the hole mobility of the polymers.\textsuperscript{16} It also introduces the solubility in otherwise rigid acceptor blocks. Through the DFT calculations at the B3LYP/6-31G(d,p) level on oligomeric model compounds, it was found that the HOMO-LUMO band gap is highly dependent on the type of donor and the acceptor moiety incorporated. The planarity of the backbone also plays a crucial role in deciding electronic distribution in these architectures. The presence and position of side chains on neighboring segments in the structure significantly alter the torsion angles between these blocks and hence affect the energy levels of the frontier orbitals.
4.2 Results and Discussion

In order to design new donor-acceptor polymers for solar cells, it is very important to predict their HOMO and LUMO energy levels and the band gaps. We are interested in using theoretical calculations to predict the HOMO-LUMO band gap of selected donor-acceptor polymer models and guide their design. In our earlier studies using BT as an acceptor and substituted trans-stilbene as a donor, we synthesized a series of donor-acceptor polymers in the band gap range of ~2.1 eV to ~2.7 eV (determined by cyclic voltammetry). In order to further lower the band gap, we selected various strong acceptors and carried out DFT calculations on donor-acceptor models to predict the band gap. These results would aid us in designing the appropriate systems which could result in lower band gaps. In that pursuit, we have systematically investigated the segmented structures...
containing bisphenylene as a donor and varying the acceptors to estimate the HOMO-LUMO band gap via DFT calculations. The calculations were carried out on dimer models of the polymers and diheptyloxy chain on trans-stilbene were replaced with methyloxy and hexyl chain on thiophene with methyl to simplify the calculations. The input files were prepared via Gaussview 3.07. First, the geometries of the dimer models were optimized in the ground state using basis set DFT/B3LYP/6-31G(d,p) in Gaussian 09 with CUNY high performance computers. The calculations were carried out in gas phase to neglect the solvent effect.3

4.2.1 DFT Studies on first set of acceptors

In this report we investigated two sets of acceptors (seven each) and predicted the energy levels of their frontier orbitals using DFT/B3LYP/6-31G* method which has been found accurate in predicting the electro-optical properties of several electronic systems. First set includes seven acceptors: oxadiazolo[3,4-c]pyridine (OP), thiaziazolo[3,4-c]pyridine (TP), thiaziazolo[3,4-g]quinoxaline (TQ), benzo[c][1,2,5]oxadiazole (BO), benzo[d][1,2,3]triazole (BT), benzo[c][1,2,5]selenadiazole (BD) I (160,164), and thieno[3,4-c]pyrrole-4,6(5H)-dione (TP). The donor employed was tetraheptyloxy substituted trans-stilbene because of its low-lying HOMO energy level. Second set of dimer models incorporates thiophene ring on either side of the acceptor and tetraheptyloxy substituted trans-stilbene as a donor. The optimized geometries along with the structures for the first set for the dimer models of donor-acceptor polymers are shown in Figure 4.1.
Figure 4.1 The optimized geometries and the structures for the dimer models of D-A polymers
Figure 4.2 HOMO/LUMO orbital plots D-A systems simulated by DFT/B3LYP/6-31g(d), which were carried out with a chain length of n=2.

The HOMO-LUMO orbital plots along with the associated energy levels are shown in figure 4.2. It appears that in general HOMO levels of all the polymers are well delocalized along the conjugated backbone while LUMO is mainly localized on acceptor blocks except in the system using BT as an acceptor. The electronic distribution further demonstrates the alternating donor-acceptor character of the investigated structures. In OP containing system, HOMO is delocalized throughout the conjugated backbone while LUMO is localized on OP which is an acceptor. The
HOMO and the LUMO energy levels are -4.84 eV and -2.75 eV with a band gap of 2.09 eV. Using TP as an acceptor, where oxygen atom is replaced by S, both the HOMO and LUMO energy levels are raised to -4.76 eV and -2.64 eV yielding a band gap of 2.12 eV. The reason for the destabilization of the molecular orbitals might be attributed to the distortion of planarity in the latter case as evident from the optimized structure (Figure 4.1). In the third system, using TQ as an acceptor, LUMO energy level is lowered substantially to -2.97 eV resulting in decreased band gap of 1.74 eV. However, the LUMO orbital was only localized on the external TQ unit of the dimer model. Employing BO acceptor, the geometries were found much planar, resulting in HOMO energy level of -4.71 eV and LUMO energy level of -2.61 eV. The band gap was found to be 2.10 eV. In BT containing system, HOMO and LUMO energy levels are much more destabilized, -4.52 eV and -1.69 eV respectively, resulting in higher band gap of 2.83 eV. From the orbital plots, it appears that the electronic distribution in both the orbitals is extended throughout the backbone which might have caused elevated energy levels hence yielding much higher band gap as compared to the other models. In BS containing system where oxygen from benzoxadiazone is replaced by selenium, resulted in higher LUMO energy level of -2.34 eV clearly indicating the effect of acceptor on the LUMO. On the other hand HOMO energy level, which is decided by trans-stilbene donor was found to be -4.65 eV. System containing TP as an acceptor, yielded HOMO of -4.76 eV and LUMO of -2.26 with a band gap of 2.50 eV. The HOMO-LUMO energy levels along with the band gap are summarized in Scheme 4.2.
4.2.2 DFT Studies on thiophene incorporated acceptors

Second set of donor-acceptor systems investigated incorporates respective acceptor moiety between two thiophene units and tetraheptyloxy substituted trans-stilbene as a donor. Thiophene unit is selected because it is reported to further tune the energy levels and the band gap. Thienyl units offer advantages such as reduced steric hindrance between donor and acceptor molecules and reduced band gaps. This set includes seven acceptors incorporated between thiophene blocks:
dithienyloxadiazolo[3,4-c]pyridine (DTOP), dithienylthiadiazolo[3,4-c]pyridine (DTTP),
dithienylthiadiazolo[3,4-g]quinoxaline (DTTQ), dithienylbenzo[c][1,2,5]oxadiazole (DTBO),
dithienylbenzo[d][1,2,3]triazole (DTBT), dithienylbenzo[c][1,2,5]selenadiazole (DTBD), and
dithienylthieno[3,4-c]pyrrole-4,6(5H)-dione (DTTP). The optimized geometries along with the
structures for the dimer models of D-A polymers are shown in Figure 4.3.

**Figure 4.3** Optimized geometries of the dimer models and the structures of D-A polymers
**Figure 4.4** HOMO/LUMO orbital plots D-A systems simulated by DFT/B3LYP/6-31g(d), which were carried out with a chain length of n=2

The HOMO-LUMO orbital plots along with the associated energy levels for the systems containing dithienyl based acceptors are shown in Figure 4.4. In general, the effect of thiophene blocks on the band gap and the energy levels is evident from substantial lowering of band gaps as compared to first set of models. It appears from the results that thienyl units seem to raise the HOMO levels and lower the LUMO levels resulting in lower band gaps. The band gap trend is
quite similar to the results obtained from previous set of systems without thienyl units. Dimer model based on DTOP resulted in the HOMO and the LUMO energy levels of -4.63 eV and -2.78 eV with a band gap of 1.85 eV. Using DTTP as an acceptor, where oxygen atom is replaced by S, both the HOMO and LUMO energy levels are elevated to -4.57 eV and -2.72 eV yielding a band gap of 1.85 eV. These results are consistent with the calculated data on the first set of architectures. As seen before, employing DTTQ as an acceptor, LUMO is lowered to -3.08 eV yielding band gap of 1.49 eV. DTBO based systems resulted in HOMO energy level of -4.60 eV and LUMO of -2.65 eV with band gap of 1.95 eV. Systems based on DTBT, DTBS, and DTTP yielded higher band gaps with their raised LUMO energy levels, yielding much higher band gap as compared to the other models. These results clearly show the role of thienyl units in tuning HOMO-LUMO energy levels and hence the band gap. The HOMO-LUMO energy levels along with the band gap are summarized in Scheme 4.3. These results also suggest that the structural differences in the backbone of the polymer affects the electron distribution severely, consequently leading to the variation of the energy levels. Based on the results and the ease of synthesis we selected systems based on BO, TP, DTBO and DTTP for polymer design. We propose the polymers and the monomers design in Scheme 4.4 and Scheme 4.5 respectively.
Scheme 4.3 Schematic of theoretical HOMO LUMO energy levels of the D-A systems calculated by DFT/B3LYP/6-31g(d), which were carried out with a chain length of n=2
4.3 Monomer/Polymer Design

Scheme 4.4 Design of polymers
Scheme 4.4 Design of monomers

2.5 References


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