

**Synthesis of Purine-Containing Conjugated Polymers and their Optoelectronic
Characteristics**

**A Dissertation Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville**

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August 2022**

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DEDICATION

This dissertation is dedicated to all the friends and family who have helped me along the way. Their relentless support has made my successes possible.

“I had the time of my life fighting dragons with you.” -T. Swift

ACKNOWLEDGEMENTS

Pursuing a Ph.D. has been one of my most life-changing experiences so far, and it would not have been possible without the support and advice from many people. I would first like to thank my advisors, Prof. S. Michael Kilbey II and Prof. Brian K. Long, for their guidance and continued encouragement during my time at the University of Tennessee – Knoxville. There are few things I can imagine that are as challenging as guiding students through a graduate career, and I am grateful to you both for advising me. I am so proud of the successes we accomplished together and the inspiration you provided. A special thanks goes to the other members of my doctoral committee, Prof. Gila Stein and Prof. John Brantley. Thank you for your guidance, analyses, and critiques, which helped make me a better scientist.

I am also thankful for the scientists I have been able to work with along the way. To Will Ledford, Justin Burroughs, Xinyi Wang, and Ashley Stark, I was honored to join the Chemistry Department at the same time as all of you. I cannot imagine what classes and research would have been like without each of you being there. To Graham Collier and Sina Sabury, your guidance and encouragement with my project cannot be understated. My successes during graduate school are because of the support I received from both of you. I would also like to recognize Dayton Street, Rachel Ramirez, Morgan Higgins, Nia Parker, Dani Chun, Trevor Wilson, Cameron Workman, Maggie Powell, and Nick Shawver for their camaraderie over the years.

I would also like to thank my family and friends whose unrelenting encouragement got me through the hardest and greatest days. To my friends, Sarah, Hannah, Ashley, Jensie, Chelsea, Nicole, Stephanie, Mary Kate, Katie, Lizzie, and Jeffrey, I'm not sure how

I got lucky enough to know each of you, but I am so excited to see how our friendships grow and change. Thank you for all of the late-night calls, chaotic texts, weekend visits, Zoom chats, and a special thank you for allowing me to send sporadic TikToks all of which helped get me here. I am evermore appreciative for the adventures your friendships have brought into my life. To my parents, Mitzi and Dan O’Connell, and sisters, Cherise Hurt and Olivia O’Connell, I can never express how important your love and support has been to me. My parents worked to open as many doors as possible and I’m so glad each time one of us can walk through one, and I’m excited to see the opportunities we will work to give to my nieces, Elaina and Maddie. You are all, simply put, fabulous. Finally, to my partner in all things, Andrew Chancellor, who has always encouraged me, your love and support has allowed me to struggle and achieve things I would have never thought possible, and I am grateful every day that graduate school brought us together.

ABSTRACT

Understanding the relationships between conjugated polymer properties and monomer design is vital when targeting specific properties for specific technologies. Purines are multifunctional heterocycles that have hardly been studied as building blocks for conjugated polymers because of synthetic challenges. The overarching goal for my dissertation was to design a viable synthetic route for purine-containing π -conjugated polymers and characterize their optoelectronic properties. Herein, purine-containing monomers containing thienyl flanking groups were synthesized, which enables fully conjugated, purine-containing polymers to be created and studied. Monomers were synthesized via Suzuki-Miyaura cross-coupling reactions, and connectivity across the purine scaffold was varied to synthesize conjugated copolymers. In this vein, the purine-containing units were copolymerized with a variety of comonomers, including electron accepting monomers, highly fluorescent monomers, electron donating monomers, and monomers that extend the conjugation. These copolymers were synthesized via direct arylation polymerization or, in a few cases, microwave-assisted Suzuki-Miyaura cross-coupling polymerizations. In addition, purine-containing homopolymers made via AB and AA+BB step-growth polymerizations were analyzed to understand how sequence regularity effects optoelectronic and physical properties. My work highlights the functionality of purine as a building block for conjugated polymers and describes fundamental properties of a series of purine-containing copolymers.

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CHAPTER I: INTRODUCTION

1.1 Motivation

Purines are the most abundant type of nitrogen-containing heterocycles in nature, and amongst these, the most recognized variants are adenine, guanine, and caffeine. (See **Figure 1.1.**) Purines are aromatic heterocycles consisting of a pyrimidine ring fused to an imidazole ring. In addition to being naturally abundant, purines are also highly tailorable, having four distinct sites available for synthetic modification. These sites are the *C2*, *C6*, *C8*, and *N9* positions, as shown in **Figure 1.1**. Because purines can participate in π -stacking and in hydrogen bonding, as demonstrated by the helical structure of DNA, purines have been used for myriad purposes in the field of polymer chemistry. Examples include the use of purines as templates for conjugated polymer synthesis,¹ as polymer adhesives,^{2–4} and to promote control of self-assembly.^{5–7} They have also been used to create highly fluorescent materials.^{8–10} Various computational studies indicate that the electronic properties of purines can be altered through functionalization at various sites of the purine scaffold^{11–14} and that the hydrogen bonding properties of purines can be used to promote morphology organization.^{11–15} As examples, purine and its derivatives have been used as components in “push-pull” designs for molecular electronics,¹⁶ emitters,^{17,18} chromophores,^{17,19} and sensors,²⁰ and also as templates for nanomaterials.^{21,22} Because purines are of biological and chemical interest, their use in polymer-based materials has steadily increased; however, the incorporation of purine-containing heterocycles into the main chain of conjugated polymers has thus far remained elusive.

The research presented in this dissertation describes how the purine scaffold has been incorporated as a central structural motif in conjugated polymer materials. The

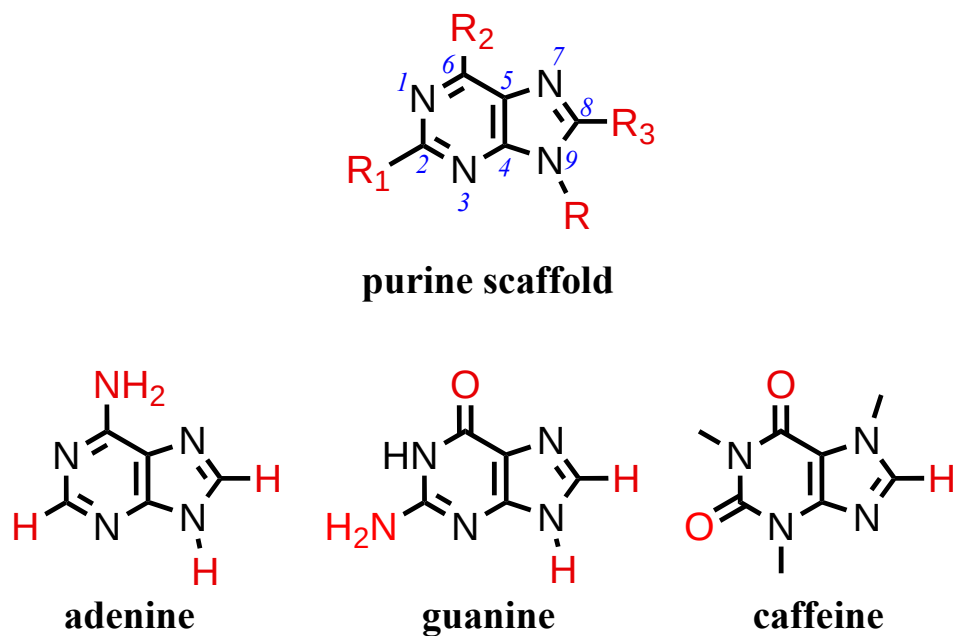


Figure 1.1 Top) The purine scaffold (blue numbers identify the carbon and nitrogen atoms on the heterocycle, while the substituents in red indicate sites that can be synthetically accessed). Bottom) Purine derivatives from left to right: adenine, guanine, and caffeine.

primary goal of my dissertation research was to elucidate structure-property relationships between chemical design and the optoelectronic properties of conjugated polymers containing the purine scaffold within the main chain. As a result, my research focuses on the synthesis and characterization of conjugated purine-containing polymers. To understand how comonomer design and connectivity across the heterocyclic purine scaffold influence polymer optoelectronic properties, my work strives to design purine-containing monomers that can be readily copolymerized with various conjugated comonomers. Previous attempts to integrate purinyl units into polymer backbones were based on copolymerizations involving the dihalogenated purine, 2,6-dibromo-9*H*-alkylpurine, but polymerization was largely unsuccessful due to reactivity differences between the C2 and C6 sites on the purine scaffold. These attempts are presented in **Figure 1.2a**. The first successful synthesis of “poly(purine)s” resulted from copolymerization of a dibromopurine comonomer with a benzodithiophene comonomer, as shown in **Figure 1.2b**. The resultant purine-containing polymers had molecular weights in the range of 7-10 kg/mol. These poly(purine)s showed how variations in the main chain design lead to distinct changes in the thermostability and glass transition temperature, as well as changes in photophysical behaviors, which were affected by the substitution pattern of main chain aromatic units. However, these purine-containing copolymers did not have continuous π -orbital overlap due to the presence of a methylene unit within the backbone and were therefore not fully conjugated. Additionally, these purine-containing copolymers had relatively low molecular weights and were regiorandom because of the asymmetry of the purine-containing comonomer.¹⁹

The key aspect that distinguishes the research presented herein from prior efforts

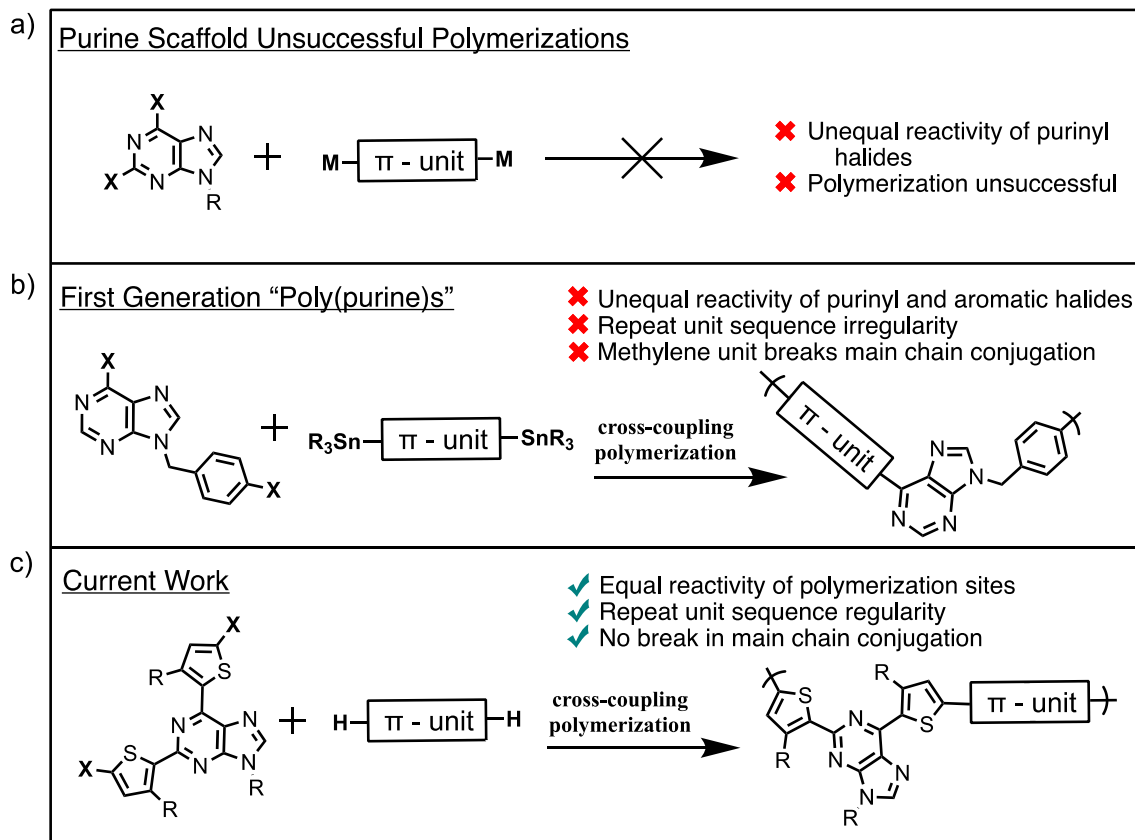


Figure 1.2 Previous and current research of purine-containing polymers. a) Early polymerization attempts with the a dihalogenated purine scaffold did not result in polymers due to unequal reactivity across the purine heterocycle. b) The first generation of “poly(purine)s” had broken conjugation in the main chain broken because of a methylene unit from the N9 functionalization. c) The first generation of purine-containing conjugated polymers made via cross-coupling polymerization reactions.

to synthesize purine-containing conjugated polymers is the design of purine-containing monomers, which are flanked by an alkyl-thiophene at the C2 and C6 positions to facilitate the synthesis of fully conjugated purine-containing polymers. The thienyl groups are advantageous in that they are known to efficiently participate in cross-coupling reactions and are designed to promote equal reactivity for cross-coupling polymerization by positioning the coupling sites farther from the asymmetric purine core, as is shown in **Figure 1.2c**.

1.2 Design of Donor-Acceptor Copolymers

Since the discovery of polyacetylene almost 50 years ago,^{23,24} conjugated polymers have been of interest because of their semiconducting properties.²⁵ As synthetic methods and characterization techniques have developed, so has our understanding of the chemical structure of conjugated polymers. The polyunsaturated main chain consisting of aromatic or conjugated monomers allows π -orbital overlap along the backbone of a conjugated polymer, which gives rise to charge transport and optoelectronic properties, enabling innovative organic electronic devices that are not possible with conjugated small molecules.^{25–27} While early conjugated polymers were mostly homopolymers with limited functionalization, researchers have used monomer design to improve processability and optoelectronic properties such as bandgap, fluorescence, quantum yield, and absorbance. Conjugated polymers have advanced from their simplest form (polyacetylene) (**Figure 1.3a**) to aromatic homopolymers such as polythiophenes (**Figure 1.3b**), which were then made processible by the addition of alkyl side chains (**Figure 1.3c**). Most recently, researchers have shifted their focus to donor-acceptor or “push-pull” systems in which the

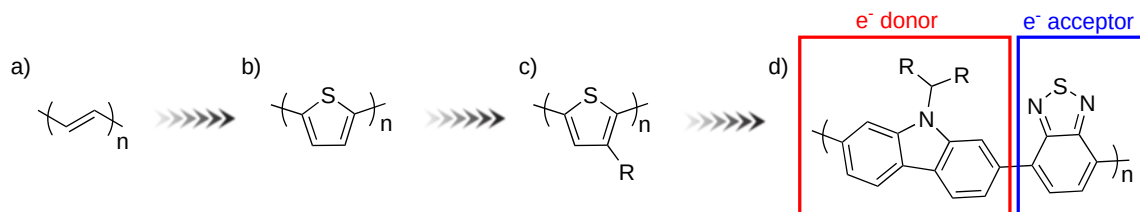


Figure 1.3 The evolution of conjugated polymers from a) polyacetylene to homopolymers that include b) polythiophene, and alkylated homopolymers including c) poly(alkylthiophene)s, and finally to d) acceptor-donor copolymers.

optical and electrical bandgaps can be modulated through further monomer/comonomer design (**Figure 1.3d**).²⁵

While polymers are widely used in an immense number of applications because of their processability and low-cost of synthesis, the aromatic structures of conjugated polymers can often cause them to be plagued by issues of low solubility and rigidity that renders them difficult to process.^{28,29} Efforts to modify the processability and properties of conjugated polymers are predominately focused on altering the main chain structure or through side chain design. For example, optoelectronic properties are commonly tuned through the main chain design, whereas solubility and processability of conjugated polymers are generally modified with side chain functionality. In the latter example, long alkyl side chains are typically used to increase solubility and processability in organic solvents such as tetrahydrofuran (THF), chloroform (CHCl_3) *N,N*-dimethylformamide (DMF) and *N,N*-dimethylacetamide (DMAc), which are commonly used for cross-coupling polymerizations and polymer characterization. As a result of these many advances, conjugated polymer materials have gained tremendous interest for their potential use in organic devices, including organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), organic photovoltaics (OPVs), and biomedical sensors.^{25,27,30} Tailoring the optoelectronic properties of conjugated polymers for such devices is most often done by modifying the main chain to vary the optoelectronic properties, such as lowering the bandgap, which improves functioning as a component of an OPV or OFET,^{31–34} increasing the quantum yield and emission efficiency for improved OLED devices,^{35–38} or facilitating charge separation for increased efficiency of OPVs.^{39–41}

Conjugated polymers have conjugation lengths longer than those of small molecules, and extending their conjugation typically narrows the bandgap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) by delocalization of electrons across the main chain, as shown in **Figure 1.4**. The bandgap continues to narrow as conjugation is increased until the effective conjugation length (ECL) is reached. Thus, the ECL is defined as the chain size at which increases in the number of repeat units no longer influence the optoelectronic properties.^{3826,31,42–44}

Excitation of electrons from the HOMO to the LUMO occurs when energy is absorbed, and relaxation from this excited state may occur via emission or by non-radiative losses. Molecular perturbation theory has been used to describe how the HOMOs of the electron donor and acceptor give rise to two new hybrid HOMOs while the LUMOs of the donor and acceptor give rise to two hybrid LUMOs. The HOMO energy level created by band mixing is influenced by the characteristics of the electron donor, leading to a higher energy level, while and the energy level of the LUMO is largely set by the electron acceptor, which leads to a lower energy LUMO, as shown in **Figure 1.5**.⁴⁵ This redistribution of electrons to raise the copolymer's HOMO energy level with a simultaneous lowering of its LUMO results in a lower overall bandgap between, which is the difference between HOMO and LUMO energy levels. Understanding how monomer design affects the molecular energy levels provides the capability to modify the bandgap of donor-acceptor type conjugated polymers to

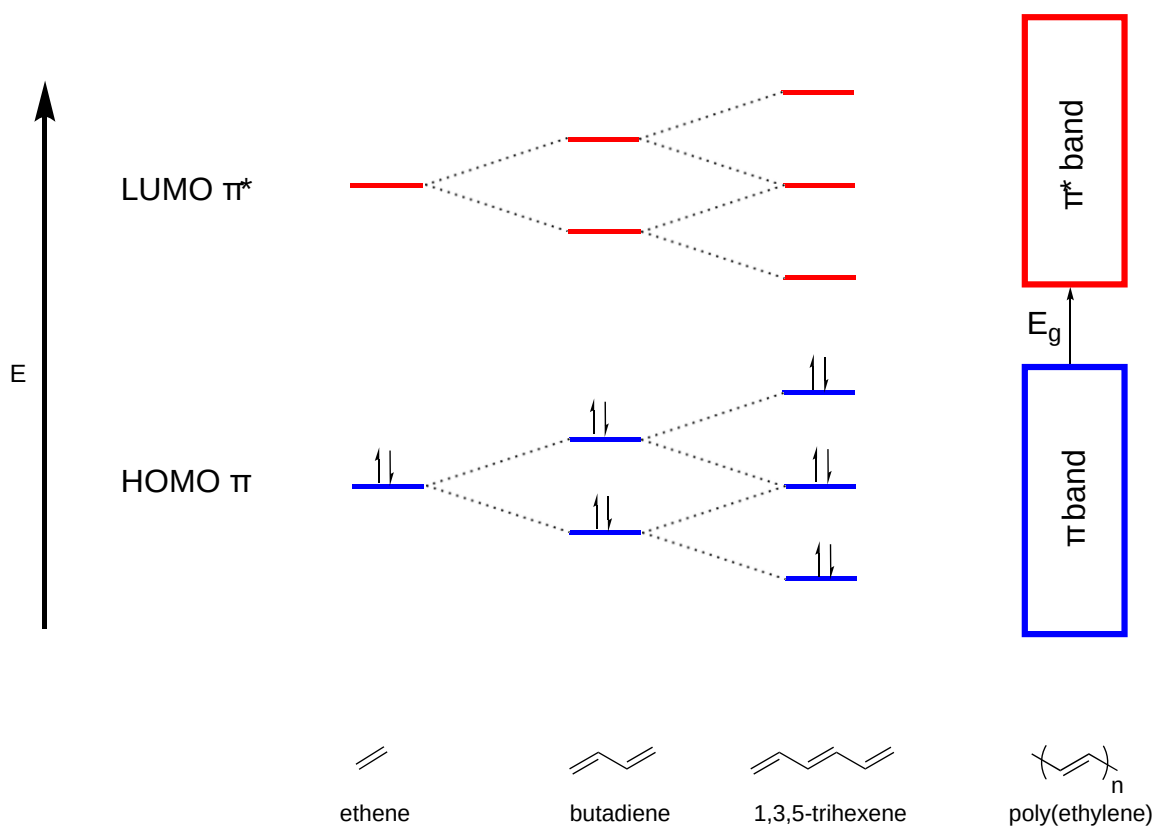


Figure 1.4 Generic narrowing of bandgap by extending the conjugation length from small molecules to polymers. Left to right: ethene, butadiene, 1,3,5-hexatriene, and polyacetylene.

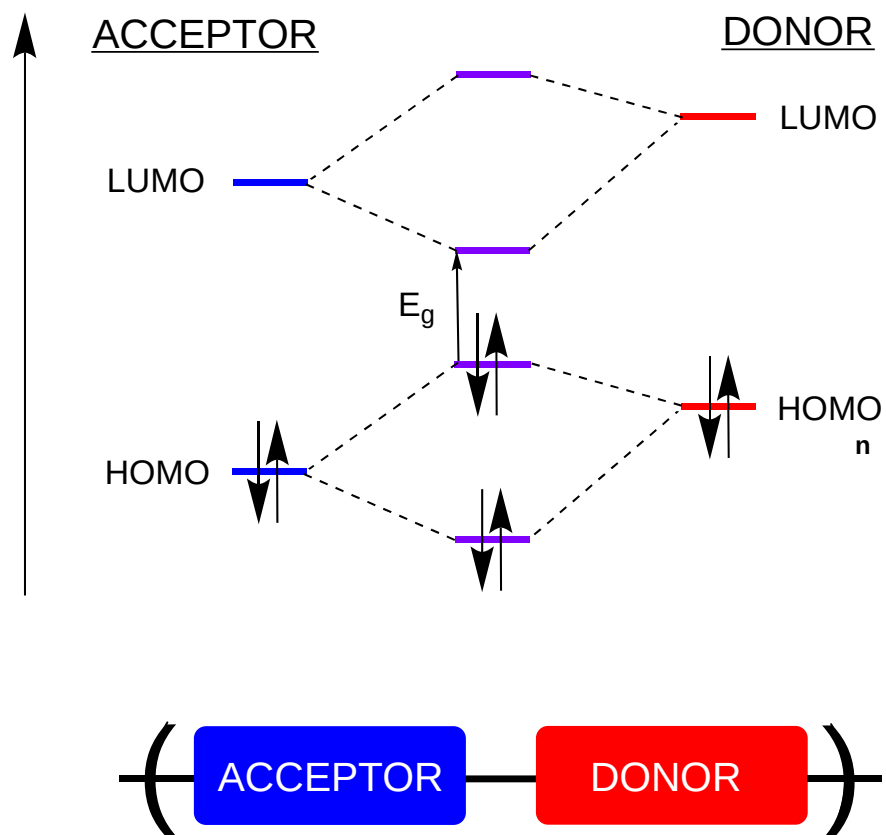


Figure 1.5 Schematic showing how band mixing in conjugated polymers that contain electron acceptors and electron donors result in new frontier energy levels and lower bandgap.

exchange device functionality. For example, it has been suggested that in OPVs, charge dissociation is facilitated when the LUMO of the electron transport layer is ~ 0.35 eV below the LUMO of the conjugated polymer.^{31,46} The use of electron acceptors and donors in the main chain of conjugated polymers has been used to control the optical absorbance/emission spectra of the corresponding conjugated polymers in order to achieve charge dissociation.^{47–49} Purines are of particular interest because they are both highly fluorescent and have been previously reported to act as either an electron acceptor or an electron donor in small molecule donor-acceptor systems, depending on the aromatic unit coupled to the purine.^{50,51}

1.3 Synthesis of Purine-Containing Monomers and Polymers

1.3.1 Cross-Coupling Reactions and Purines

Cross-coupling reactions are a type of organic synthesis where a carbon-carbon bond is formed with the assistance of a metal catalyst. Cross-coupling generally occurs via reaction of an organometallic compound that is typically comprised of a main group metal (M) bound to a carbon-based fragment (M–C), which then undergoes reaction with an organohalide (C–X) in the presence of a transition metal-based catalyst, thereby yielding a metallic byproduct (M–X) and a new organic compound. There are many types of cross-coupling reactions, but three elementary steps are inherent to most metal catalyzed cross-coupling reactions, and these mechanistic steps are shown in **Figure 1.6**. The steps include: 1) oxidative addition, where the metal catalyst (usually palladium-based) is oxidized from

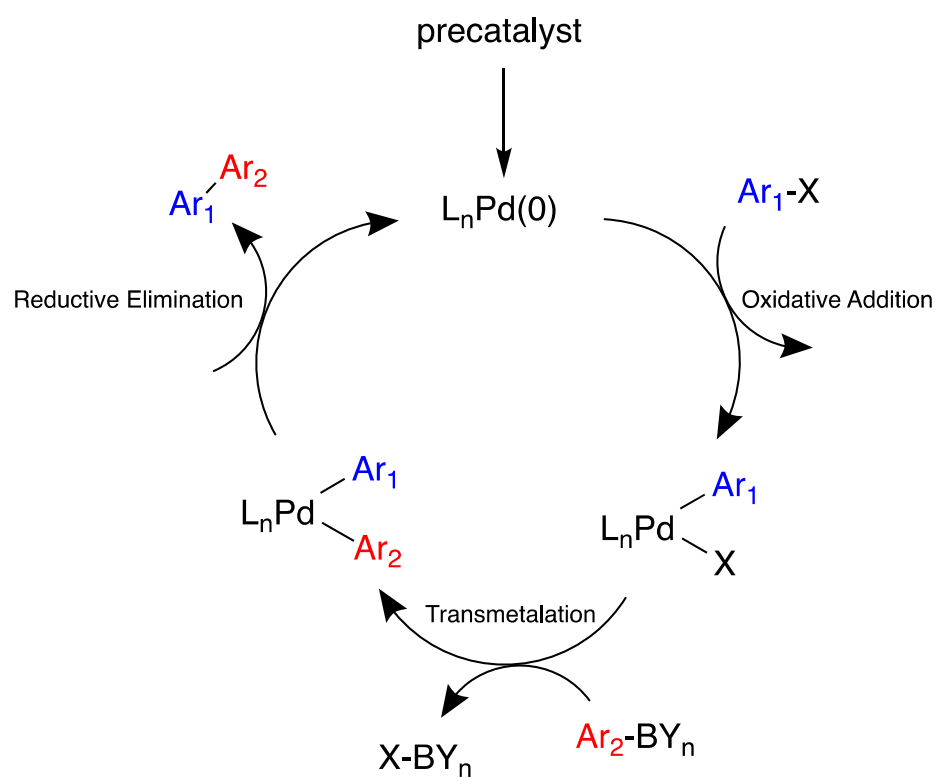


Figure 1.6 The general catalytic mechanism for Suzuki-Miyaura cross-coupling reactions.

palladium(0) L_n to palladium(II)ArX upon reaction of an Ar₁-X with a palladium precursor, 2) transmetallation, where a second metal bound to the other carbon unit (Ar₂-BY_n) exchanges the aromatic unit for the halogen, thereby producing a metallic byproduct (X-BY_n), and 3) reductive elimination, where the palladium is reduced from palladium(II)Ar₁Ar₂ to palladium(0) L_n , releasing a newly formed organic molecule and starting the catalytic process over again. Cross-coupling reactions, including Suzuki, Stille, direct arylation, and others, have been used to functionalize small molecules, polymers, and conjugated monomers. In this research, the purine scaffold has been functionalized at the C2, C6, and C8 positions via several different cross-coupling reactions.^{52–55} These are known strategies, as early work by Gunderson and coworkers showed how halogenated purines can form a carbon-carbon bond selectively at the C6 or C2 position via Stille cross-coupling reactions.^{56,57} These initial findings sparked a variety of new endeavors focused on functionalization of purines at different positions of the scaffold by cross-coupling reactions, including Stille and Suzuki-Miyaura cross-couplings.^{52,52–55,57} The knowledge from these studies has provided a way to functionalize purines to enable polymerization.

1.3.2 Flanking of Purines with Thienyl Groups: For Efficient Coupling of π -Conjugated Comonomers

Because previous studies have shown that purines cannot be directly incorporated into the backbone of conjugated polymers through copolymerization, our work establishes a monomer with sites for efficient cross-coupling polymerization. To make purine-containing monomers with sites of efficient reactivity for cross-coupling polymerizations, I hypothesize that flanking thienyl units will allow purine-containing copolymers to be synthesized. In addition, this strategy will allow a variety of alternating copolymers to be

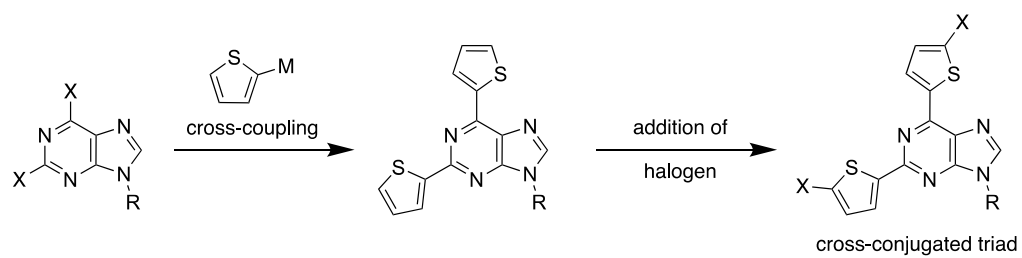
generated with properties that are varied based on comonomer choice. Thienyl units, which are widely used in cross-coupling polymerizations, can be added onto a purine core to make monomeric triads comprised of thiophene-purine-thiophene (TPT). These designs should diminish problems of inefficient cross-coupling reactivity previously observed for purines while also providing sites of similar reactivity on both sides of the purine, as shown in **Scheme 1.1**. The triad also retains conjugation and can be brominated at specific sites to make a di-halogenated aromatic molecule that will also participate in cross-coupling reactions with another conjugated monomer to create conjugated copolymers. Further, because the thienyl unit is commonly used in cross-coupling polymerizations, the monomer should have efficient reactivity for copolymerization. This route is appealing because it provides purine-containing triads with functional groups that are highly efficient in cross-coupling and are essentially of equal reactivity. Moreover, it allows design-structure-property relationships of the polymer and monomeric units to be developed, as described in later chapters.

1.3.3 Step-Growth Cross-Coupling Polymerizations

In order to attain high molecular weight polymers via step-growth polymerizations, exceptionally high conversion is required. This is embodied in the simplified Carothers equation for step-growth polymerizations, which expresses the relation between conversion (p) and number-average degree of polymerization (X_n):

$$X_n = \frac{1}{(1-p)} \quad (1.1)$$

There are three general criteria that must be met to achieve high molecular weight



Scheme 1.1 Strategy for synthesizing thiophene-purine-thiophene (TPT) triads from purine analogues. R = hexyl.

in cross-coupling polymerizations. i.) Monomers must be of high purity because impurities will lead to stoichiometric imbalance; ii.) Comonomers must be added in perfect stoichiometric balance because, again, unequal numbers of reactive groups limits the ability to achieve high conversion; and iii.) Nearly complete conversion of reactive groups in chain-making reactions must be achieved. The first two criteria emphasize monomer purification and reaction formulation. The last criteria, maximizing conversion, relies also on highly active catalysts and the reactivity of the selected monomers.

Conjugated polymers can be synthesized through reactions in which carbon-carbon bonds are made, including cross-coupling reactions. In these polymerizations, complementary functional groups on the same substrate or on pairs of difunctional substrates are needed. **Figure 1.7** shows five types of cross-coupling reactions that have been used for polymerization of conjugated monomers. Each type of cross-coupling reaction used for polymerization has advantages and disadvantages. Stille and Suzuki-Miyaura have larger substrate scopes than Kumada or Negishi cross-couplings, but they are also less reactive and generally give little to no control over molecular weight of the resulting polymer. Direct arylation differs from these cross-coupling reactions both in mechanism and in reagents used. The key chemical difference between previously discussed cross-coupling reactions and direct arylation is that direct arylation does not use starting materials functionalized with organometallics. Organometallics used for cross-coupling may contain starting materials that lead to unwanted byproducts, specifically, in the case of Stille cross-coupling reactions, toxic tin-based byproducts.^{62–67} Instead, direct arylation reactions activate the bond between carbon and hydrogen (C-H activation). While there is some debate over the exact mechanism of direct arylation, most researchers

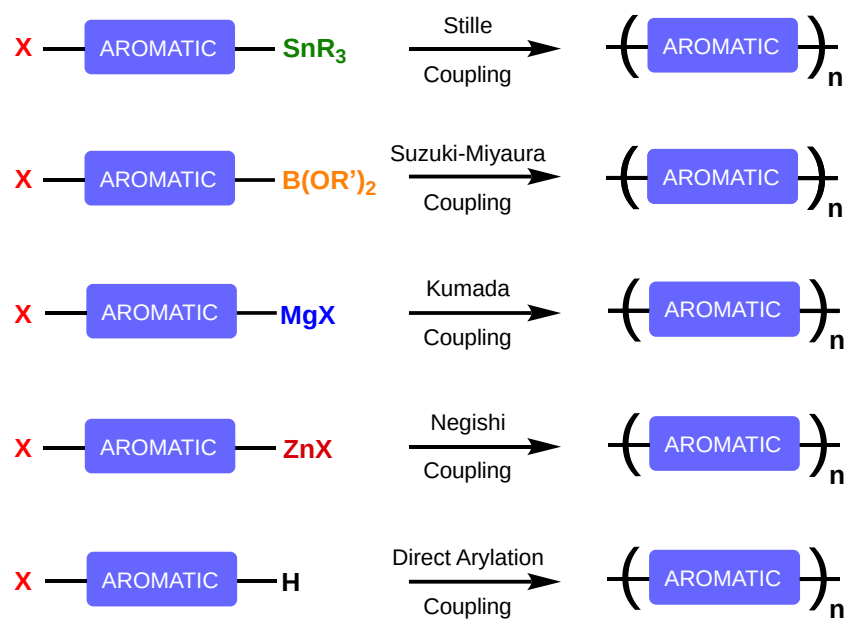


Figure 1.7 Cross-coupling polycondensation reactions used to synthesize conjugated polymers.

agree that concerted metalation-deprotonation (CMD) is the most accurate description of the catalytic cycle. As shown in **Figure 1.8**, the mechanism begins with the same oxidative addition as other cross-coupling reactions, but is followed by a ligand exchange in which the halide leaves the metal center and the carboxylate anion coordinates to the catalytic metal. C-H activation then occurs through a six-membered ring where the anionic oxygen coordinates to the hydrogen to make a carboxylic acid. Finally, reductive elimination occurs, and the catalytic cycle starts over again.^{63,64,68,69}

1.4 Characterization of Physical Properties

All small molecules, monomers, and polymers have been thoroughly characterized. ¹H and ¹³C NMR (nuclear magnetic resonance) spectroscopy was used to monitor conversion in reactions used to produce monomers and polymers. 2-D NMR techniques, including heteronuclear single quantum coherence (HSQC), heteronuclear multiple bond correlation (HMBC), and nuclear Overhauser effect spectroscopy (NOESY), were also used for further characterization of select monomers and polymers. Direct analysis in real time mass spectroscopy (DART-MS) was used to determine the mass of small molecule intermediates and monomers. UV-Vis and photoluminescence measurements were used to investigate the photophysical properties of the conjugated polymers and corresponding monomers, including absorbance and emissions profile, optical bandgap, Stokes shift, and photoluminescence quantum yield. Gel permeation chromatography (GPC) was used to determine number-average molecular weight (M_n) and dispersity (M_w/M_n) of the copolymers. Cyclic voltammetry was used to determine the molecular energy levels of our conjugated polymers and corresponding monomers through measurements of the oxidation

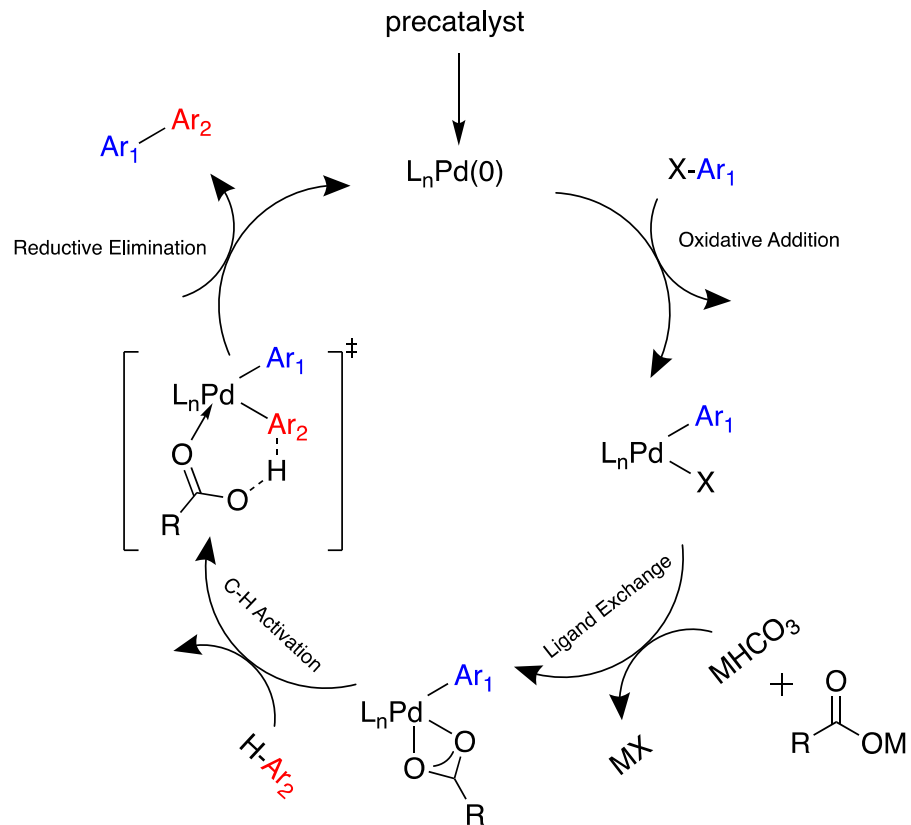


Figure 1.8 The catalytic cycle proposed for direct arylation cross-coupling via concerted-metalation deprotonation.

1.5 Optoelectronic Characterization of Materials

Because the optical bandgap and absorbance behavior establish the utility of a conjugated polymer, an absorbance profile was acquired both in solution and as thin films. When a molecule absorbs light, an electron can be excited from the ground state into an excited state. This movement of the electron into the excited state leaves a hole in the ground state and this electron-hole pair is called an exciton. The amount of energy required to free an electron from its bound hole is described as the exciton binding energy. Exciton binding energy can be determined from the difference between the electrochemical and optical bandgaps, as the electrochemical bandgap is larger than the optical bandgap by the amount of energy required to remove an electron from the hole created upon absorbance.^{70–72} After the electron is excited, it can undergo radiative or nonradiative transitions to return to the ground state. Radiative transitions include fluorescence and phosphorescence, which occur when an electron moves from an excited singlet or triplet state to the ground state, respectively. Nonradiative decays, which can occur include vibrational progressions, internal conversion, and intersystem crossing, as shown in **Figure 1.9**. Absorbance transitions of organic-based molecules are used to assess the optical character of materials for optoelectronic device applications. Molar absorptivity (ϵ) of organic materials is an important parameter for optoelectronic devices, and it can be calculated from the relationship between absorbance and concentration, known as Beer's Law, which is shown in Equation 1.2.

$$A = \epsilon bc \quad (1.2)$$

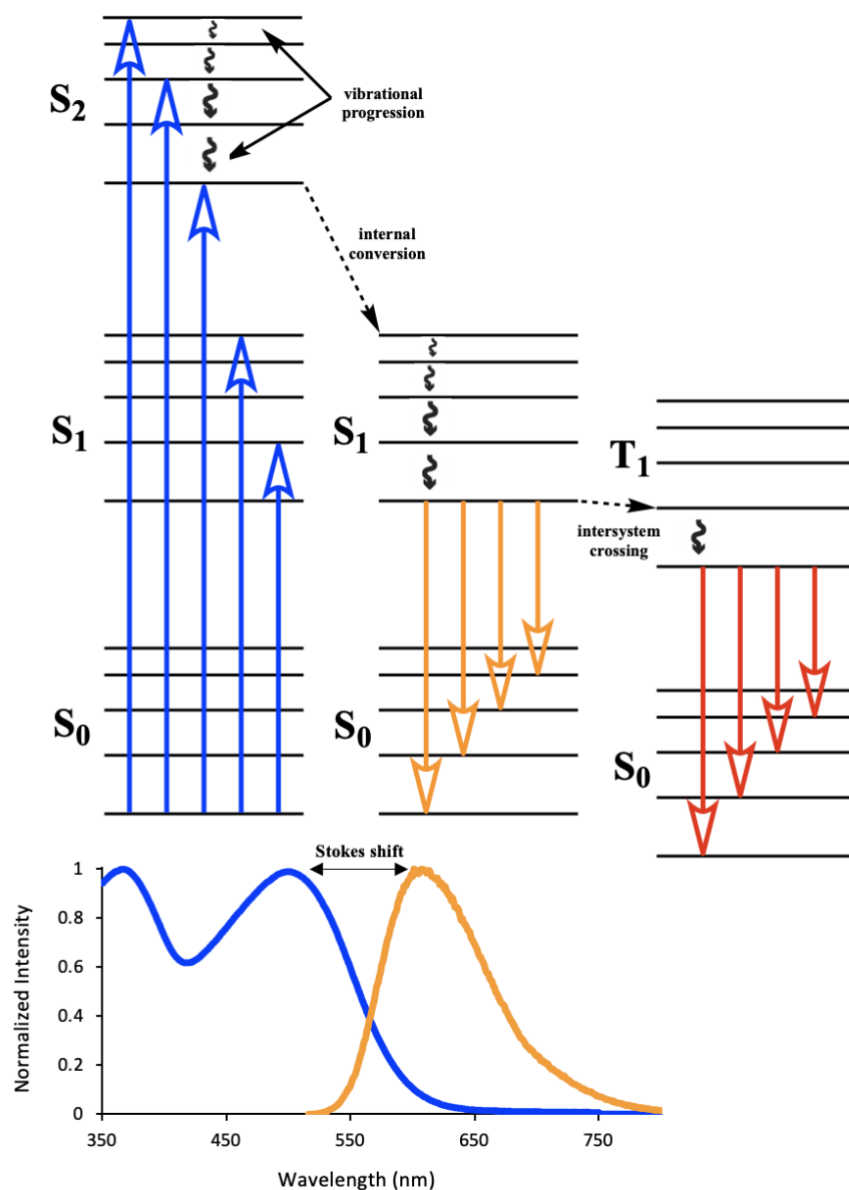


Figure 1.9 Jablonski diagram (top) and absorbance/emission spectra of copoly(4-(4-hexyl-5-(9-hexyl-2-(3-hexylthiophen-2-yl)-9*H*-purin-6-yl)thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole) illustrating the following photophysical processes: blue represents the absorbance of photons from the ground state to the excited singlet states (S_1 and S_2). Orange represents the emission of photons through fluorescence from the lowest excited state to the ground electronic states (S_0). Red represents the emission of photons through phosphorescence from the excited triplet state (T_1) to the ground triplet state (T_0). Dashed arrow from S_2 to S_1 represents internal conversion and dashed arrow from S_1 to T_1 represents intersystem crossing. Vibrational progressions are represented with black squiggled arrows.

A is the absorbance at a specific wavelength (typically the absorbance maximum), b is the pathlength of the cell, and c is the concentration of the material in solution. Absorbance measurements taken at various concentrations can be used to determine ϵ .

Fluorescence is another important characteristic of conjugated chromophores and polymers. While the relationship between absorbance maximum and emission maximum can signify energy differences in absorbed and emitted photons, generally the emitted photon has less energy than the absorbed photon. The change in photon energy is normally due to some nonradiative loss such as solvent reorganization or vibrational progressions.^{17,51} These losses shift the emission spectra to higher wavelengths, as seen in **Figure 1.9**. The difference between the absorbance maximum and emission maximum is called Stokes shift, which describes the energy loss due to structural reorganization.

A key characteristic for OLEDs is the photoluminescent quantum yield (PLQY), which is defined as the number of photons emitted divided by the number of photons absorbed. While there are multiple ways to determine photoluminescent quantum yield, the comparative method in solution was used in our studies. To measure this, the integrated fluorescence intensity versus absorbance of a standard (Rhodamine 101 in ethanol with +0.01 wt% HCl) with a known quantum yield ($\phi = 1.00$) is compared to that of the chromophore and polymer samples. This is done by measuring the absorbance and fluorescence of a set of solutions at different concentrations. Equation 1.3 is used to calculate the quantum yield of the sample (ϕ_s) by using the slope of the best fit line (m) for integrated fluorescence intensity versus absorbance intensity of the reference (r) and

sample (s) and (n) is the refractive index of the solvents used for fluorescence measurements.

$$\phi_s = \phi_r \left(\frac{m_s}{m_r} \right) \left(\frac{n_s}{n_r} \right)^2 \quad (1.3)$$

The UV-Vis spectra of the copolymers as thin films were used to determine optical properties of our fully conjugated copolymers in the solid state. Key changes from solution to solid states can be inferred from changes in the absorbance profile, including the packing of the conjugated copolymers. In solution, poly(3-hexylthiophene) has a featureless absorbance profile, but as a thin film the absorbance profile is red shifted with two shoulders. These shoulders are attributed to vibronic coupling between lamellar stacks of chains, which are organized by π - π interactions.⁷³ When a conjugated polymer has better π - π stacking as a thin film, a red shift is generally observed and secondary shoulder or peaks can arise due to vibronic coupling, which is known to promote charge delocalization and transport.^{40,74} On the other hand, some copolymers have bulky alkyl chains that are designed to disrupt π - π stacking of copolymers as thin films. Specifically, the 9,9-dioctylfluorene comonomers can be used to synthesize copolymers that interrupt π -stacking as thin films. Because of the sensitivity of UV-Vis to organization due to π -interactions and the overall design of the conjugated copolymers and monomers, it is a good technique for understanding how comonomer selection affects photophysical properties. Absorbance and emission behaviors as a function of solvent type (solvatochromism) and temperature (thermochromism) were also investigated.

1.6 Research Objectives

The central goal of my doctoral research is to develop a synthesis for purine-containing conjugated polymers and characterize them to discover relationships between monomer design and the properties of the corresponding polymers. A key goal of my research is to better understand relationships between the main chain design of purine-containing copolymers and their optoelectronic properties. This will be accomplished by using purine-containing comonomers flanked with alkythiophenes and copolymerizing them with various comonomers. In this vein, I have successfully designed a synthesis for a thienyl flanked, purine-containing monomers using Suzuki-Miyaura cross-coupling reactions. Direct arylation cross-coupling polymerizations are used to synthesize the purine-containing polymers. The specific goals addressed in each of the following chapters include:

1. Design and synthesize purine-containing comonomers flanked with thienyl groups, and use these to create a series of fully conjugated purine-containing copolymers, examining how comonomer selection and main chain design relate to optoelectronic properties observed, including absorbance, bandgap, molecular energy levels, fluorescence, etc;
2. Elucidate how regioregularity and noncovalent interactions in the main chain purine-containing polymers affect backbone rigidity and the optoelectronic properties; and

3. Investigate how the incorporation of additional thienyl linkers in the main chain affects the electronic and optical properties of the purine-containing thienyl copolymers;

In Chapter II, a set of six purine-containing conjugated polymers consisting of the thienyl-purine-thienyl (TPT) comonomer and various comonomers that include a good electron donor (ProDOT) and a good electron acceptor (TBTT) were synthesized and characterized. We utilized Suzuki-Miyaura cross coupling reactions to make the purine containing comonomer, and DArP was used to make the six copolymers. Comonomer selection affects optoelectronic properties, such as bandgap, which varied from 2.46 to 1.96 eV, and some copolymers demonstrated exceptional emissive properties because of the cross-conjugated design and having purines within the main chain. Chapter III then expands upon the work from Chapter II by focusing on the differences between regioregular AB and regiorandom AA+BB polymerizations of the TPT purine-containing triads. While the optoelectronic properties are similar, key differences are discussed and 2-D NMR techniques (HMBC, HSQC, and NOESY) are used to disentangle polymer conformation. Signatures that suggest there are noncovalent conformational locks in the monomer and corresponding polymers are observed. Work described in Chapter IV examines the relationships between the cross-conjugated TPT comonomer and the effect of additional thienyl groups placed between the electron acceptor and electron donor monomers. Specifically, I demonstrated how additional π -linkers can reduce the coplanarity of the main chain, affecting the “push-pull” electronic communication in conjugated copolymers containing the purine scaffold. Emissive behavior was also affected

by the increased thienyl group content of the repeat unit, as the quantum yield dropped significantly as more thienyl groups were incorporated. Finally, my conclusions and a summary of my main findings are presented in Chapter V. This also outlines some preliminary studies that may be the basis for future work. Preliminary data for this future work includes comparing polymerization methods and the resulting copolymer properties in cases where the copolymers are made via different cross-coupling reactions (for example, DArP and microwave-assisted Suzuki-Miyaura). The appendices can be found at the end of the document, and they provide supporting information for each chapter, including procedures and characterizations.

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**CHAPTER II: HIGHLY FLUORESCENT PURINE-CONTAINING
CONJUGATED COPOLYMERS WITH TAILORED
OPTOELECTRONIC PROPERTIES**

A version of this chapter was originally submitted for publication in Polymer Chemistry. In addition to C. Elizabeth O’Connell, other coauthors are Sina Sabury, J. Elias Jenkins, Graham S. Collier, Brian K. Long, and S. Michael Kilbey II. This article was titled “Direct Arylation Polymerization of Highly Fluorescent Purine-Containing Conjugated Copolymers with Tailored Optoelectronic Properties.” I synthesized all the monomers and copolymers and performed all physical and optoelectronic characterizations. Coauthors Sina Sabury and Graham S. Collier assisted with the synthetic design of monomers and polymers and contributed to manuscript generation. Coauthor J. Elias Jenkins assisted with the purification and fluorescence characterization of the copolymers. Brian K. Long and S. Michael Kilbey II advised this work and participated in the writing of the manuscript.

2.1 Abstract

Conjugated copolymers containing electron donor and acceptor units in their main chain have emerged as promising materials for organic electronic devices due to their tunable optoelectronic properties. Herein, we describe the use of direct arylation polymerization to create a series of fully π -conjugated copolymers containing the highly tailorable purine scaffold as a key design element. To create efficient coupling sites, dihalopurines are flanked by alkyl-thiophenes to create a monomer that is readily copolymerized with a variety of conjugated comonomers, ranging from electron-donating 3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine (ProDOT) to electron-accepting 4,7-bis(5-bromo-3-hexylthiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (TBTT). The comonomer choice and electronic nature of the purine scaffold allow the photophysical properties of the purine-containing copolymers to be widely varied, with optical bandgaps ranging from

1.96 – 2.46 eV, and photoluminescent quantum yields as high as $\phi = 0.61$. The utility of direct arylation polymerization and intrinsic tailorability of the purine scaffold highlights the potential of these fully conjugated polymers to establish structure-property relationships based on connectivity pattern and comonomer type, which may broadly inform efforts to advance purine-containing conjugated copolymers for various applications.

2.2 Introduction

Purines are naturally abundant materials, with adenine and guanine being perhaps the most familiar examples. While purines are routinely used in the creation of drugs or therapeutic agents, they have recently gained traction in materials applications. These efforts generally benefit from the distinctive, fused-ring heterocyclic structure of purines, which features four spatially defined sites that can be readily and specifically functionalized.¹ Computational studies of purines and their derivatives show that their electronic properties may be tailored by functionalization or expansion of the purine scaffold,^{2–5} and their hydrogen bonding properties can promote molecular alignment and influence morphological organization.^{2–6} The potential use of hydrogen bonding to direct or enhance the nanoscale structure in organic electronic devices has recently been explored,⁷ with various researchers demonstrating the importance of purines in the molecular engineering of nucleobase-derived nanoscale materials.^{8–15}

Purines are also highly fluorescent, which stimulates their use as photoactive conjugated components in the form of oligomers and small molecule “push-pull” chromophores.^{16–23} In these cases, site-specific synthetic modification of the purine

scaffold has been used to manipulate their optical properties, resulting in highly luminescent compounds.^{16–20,24,25} Castellano and coworkers examined the impact of adding DNA or RNA bases (e.g., adenine and guanine, which are purines, as well as thymine and uracil which are pyrimidines) to the ends of π -conjugated small molecules. In those studies, telechelic small molecules were accessed by coupling nucleobases onto 2,2':5',2''-terthiophene (TTT) and 4,7-bis(2-thienyl)-2,1,3-benzothiadiazole (TBTT). They showed that the terminal nucleobases on these oligomers retained their ability to participate in hydrogen bonding,²⁵ as well as altered their frontier molecular orbital energy levels and bandgaps. The telechelic oligomers made with a TBTT core showed intramolecular charge transfer (ICT), with the purine unit acting as the electron donor and the benzothiadiazole unit acting as the electron acceptor. However, when purines were coupled to TTT, which is a good donor, no ICT was observed because the purine is not a strong enough acceptor.²⁰ Similarly, our recent studies of purine-containing chromophores featuring either the strong donor 4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT), the conjugated linker thiophene (T), or the strong acceptor TBTT (**Figure 2.1a**, top) indicated that the purine unit acts as an electron acceptor when coupled to BDT, but acts as an electron donor when coupled to TBTT.¹⁹

The impressive optoelectronic properties of purines as small molecules along with the ability of halopurines to participate in metal-mediated cross-coupling reactions,^{26–28} motivated our prior efforts to synthesize polymers containing purines in the main chain.²⁹ In that endeavor, two different purine-containing monomers were synthesized and those dihalo-monomers were copolymerized via Stille cross-coupling polymerization with two different bis-stannane benzodithiophenes (BDT) to create purine-containing copolymers

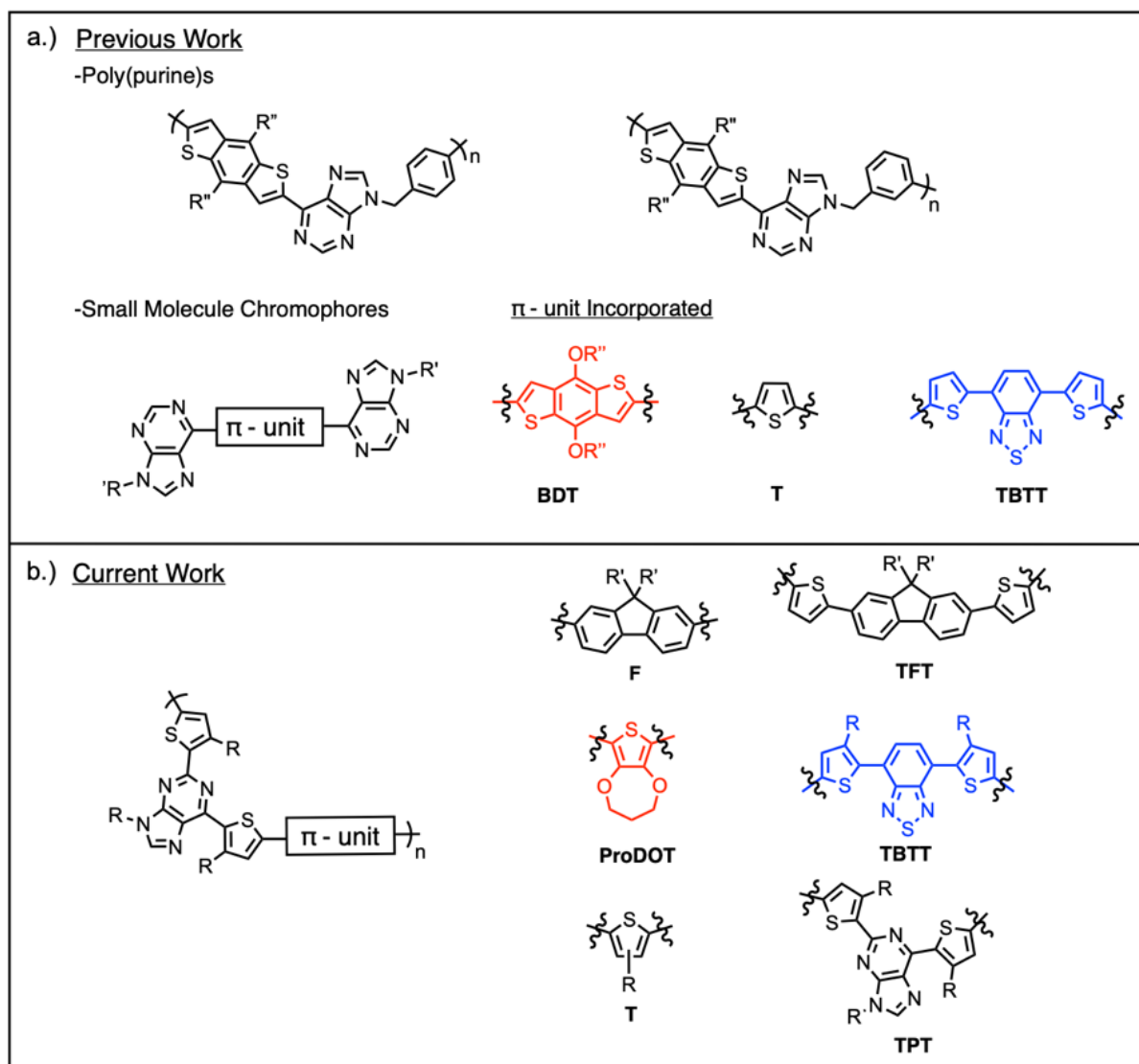


Figure 2.1 a) Previously reported purine-containing chromophores and copolymers, and b) conjugated purine-containing copolymers described in this work. Comonomer units are color-coded, blue for electron acceptor units, red for electron donor units, and black for linkers that extend the conjugation. In these structures R = hexyl, R' = octyl, and R'' = ethylhexyl.

(**Figure 2.1a**, top). While these alternating copolymers displayed ICT, they were regiorandom, of lower molecular weight, and conjugation along their main chain was broken by the methylene unit attached at the *N9* position of the purine.²⁹

Herein, we report the synthesis of a series of fully conjugated purine-containing copolymers that address previous issues of broken conjugation and unequal reactivity of coupling sites, and we describe the optoelectronic properties of the resulting copolymers. Because the different sites on the purine scaffold exhibit differential reactivity toward C-C bond formation by metal-mediated cross-coupling ($C6 > C8 > C2$),^{26,27,30} a monomeric unit consisting of a purine core with flanking aromatic units that promote efficient coupling was created. Direct arylation polymerization (DArP) of the monomer triads with various conjugated comonomers allowed several π -conjugated alternating copolymers to be synthesized, as can be seen in **Figure 2.1b**. Complementary comonomers were selected based on their proven ability to participate in DArP and solubility in common organic solvents.^{19,31–35} These copolymers displayed a range of optoelectronic properties, including decreased bandgaps due to the design of donor-acceptor conjugated polymers, high quantum yields for fluorene-containing copolymers, and fluorescent emission across a wide spectral range.

2.3 Experimental Methods

2.3.1 Methods and Materials

N-Bromosuccinimide (NBS, 99%, Aldrich) was recrystallized from water and dried under vacuum before use. 2,6-dichloropurine (97%, Ark Pharm), 3-hexylthiophene-2-boronic acid pinacol ester (95%, Aldrich), 1-bromohexane (96%, Aldrich), glacial acetic

acid, (Fisher Chemical), potassium carbonate (99%, Aldrich), Pd(PPh₃)₄ (98%, Aldrich), Pd(OAc)₂ (98%, Aldrich), pivalic acid (PivOH, 99%, Aldrich), anhydrous *N,N*-dimethylacetamide (DMAc, 99%, Sigma Millipore) anhydrous *N,N*-dimethylformamide (DMF, 99.8%, Acros Organics), anhydrous toluene (99.8%, Acros Organics), anhydrous tetrahydrofuran (THF, 99.9%, Fisher), hexanes (95%, Fisher), methanol (99%, Fisher), and chloroform (98%, Fisher) were used as received unless stated otherwise. 3,4-Dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine (ProDOT) was synthesized according to previously published procedures.⁴⁶ Monomers and polymers were synthesized using standard Schlenk technique under an argon atmosphere.

¹³C and ¹H NMR spectra of synthesized monomers were acquired at room temperature in CDCl₃ using a Varian VNMRs 500 MHz NMR. Time-of-flight direct analysis in real time mass spectrometry (using a JEOL AccuTOF DART mass spectrometer) was used to make high-resolution mass measurements of **M1** and **M2**. ¹H NMR spectra of the copolymers were acquired at room temperature in CDCl₃ using a Varian Mercury Vx 300 MHz NMR. Chemical shifts are referenced to residual solvent peaks. Number-average molecular weights, *M_n*, and dispersity, *D*, were determined via gel permeation chromatography (GPC). Measurements were made using an Agilent 1260 Infinity II system that used THF as the mobile phase at a flow rate of 1 mL/min at 25 °C and are reported relative to polystyrene standards. The system was equipped with a guard column and two PLgel Mixed-C columns (300 mm length) with a lower limit of 200 g/mol and an upper limit of 2×10⁶ g/mol. Polymer solutions for GPC analysis were prepared at 5 mg/mL in THF and passed through a 0.2 μm PTFE filter prior to injection. Optical absorbance spectra of the copolymers and **M1** in CHCl₃ were acquired using a Thermo

Scientific Evolution 600 spectrophotometer by scanning from 275 nm to 425 nm for **M1** and from 350 nm to 600 nm for the purine-containing copolymers. A Cary 5000 UV-Vis-NIR spectrometer was used for thin film measurements, and spectra were acquired by scanning from 350 nm to 900 nm. Beer-Lambert plots for **M1** and all copolymers were constructed from measurements of samples in CHCl₃, and the results are reported in **Figures A.25-A.31** of Appendix A. Fluorescence emission spectra were measured in CHCl₃ using a Cary Eclipse fluorescence spectrophotometer. Samples were excited at the absorbance maximum of each sample and spectra were recorded by scanning from ($\lambda_{max}^{abs} + 10$) nm to 700 nm for **M1**, **P1_{TPT}**, **P2_F**, **P3_{TFT}**, **P4_T**, and **P5_{ProDOT}**, and 850 nm for **P6_{TBT}**. Cyclic voltammetry was performed in acetonitrile at a scan rate of 150 mV s⁻¹ using a Biological VSP3 potentiostat. Films were drop cast onto a 3 mm Au working electrode from a 1 mg/mL dichloromethane solution. The supporting electrolyte was (nBu)₄NPF₆ with Ag/AgCl as the reference electrode and a tungsten wire as the counter electrode. Thin films for optical images were painted on wax-coated paper from a CHCl₃ solution constituted at 1 mg/mL.

2.3.2 Synthesis of 2,6-Dichloro-9-hexyl-9H-purine

A solution of 2,6-dichloropurine (5.00 g, 26.4 mmol) and potassium carbonate (9.57 g, 122 mmol) in DMF (150 mL) was added to a 500 mL round bottom flask equipped with a stir bar, and the resulting mixture was stirred for 5 minutes at room temperature under argon. 6-bromohexane (6.55 mL, 46.6 mmol) was added via syringe and the mixture was stirred for 20 h at room temperature. After 20 h, the reaction mixture was poured into 40 mL of dichloromethane and washed with brine (3×50 mL). If the aqueous layer

remained turbid after the third wash, 10 mL of DI water were added, and the mixture was extracted with dichloromethane. This process was repeated until the aqueous layer was colorless. The organic layers were combined, and the solvent was removed via rotary evaporation under reduced pressure. *N9* and *N7* substituted isomers were separated via flash column chromatography using dichloromethane with 1% methanol (by volume). The *N9* product was recovered at a 60% yield. ¹H NMR and ¹³C NMR spectra were consistent with data previously reported by Sabury *et al.*³⁶

2.3.3 Synthesis of Monomer Triads **M1** and **M2**

Synthesis of 9-hexyl-2,6-bis(3-hexylthiophen-2-yl)-9*H*-purine (**M1**).

An oven-dried 100 mL round bottom flask containing a stir bar was flushed with argon. After it cooled to ambient temperature, 2,6-dichloro-9-hexyl-9*H*-purine (0.313 g, 1.15 mmol) and dried/degassed toluene (30 mL) were added to the flask. The catalyst, Pd(PPh₃)₄ (55.1 mg, 0.0476 mmol), was added, followed by 3-hexylthiophene-2-boronic acid pinacol ester (0.710 mL, 2.37 mmol). Then, 11 mL of a previously-sparged aqueous solution of K₂CO₃ (2 M) were added. The reaction mixture was placed in an oil bath that was preheated to 95 °C. Conversion was monitored by TLC. After 48 h, the reaction flask was removed from the oil bath and allowed to cool to room temperature. Diethyl ether was added, and the mixture was extracted with brine (3×). The organic layers were combined, filtered, and dried. Flash column chromatography using a solvent mixture consisting of 1:3 ethyl acetate:hexanes was used to separate mono- and di-brominated products. The isolated yield of **M1** was 92%. ¹H and ¹³C NMR spectra and the high-resolution mass spectrum (HRMS) are presented in Appendix A (**Figures A.2, A.3, and A.6**). ¹H NMR (500 MHz,

25 °C, CDCl₃). δ , ppm: 0.88 (t, 6H, CH₃), 1.19-1.52 (m, 18H, CH₂), 1.75 (p, 4H, CH₂), 1.96 (p, 2H, CH₂), 3.31 (t, 2H, ArCH₂), 3.44 (t, 2H, ArCH₂), 4.28 (t, 2H, NCH₂), 7.00 (d, 1H, ArH), 7.09 (d, 1H, ArH), 7.31 (d, 1H, ArH), 7.54 (d, 1H, ArH), 8.02 (s, 1H, C8-H). HRMS: calc'd [M+H⁺]: 537.3080, found: 537.2793.

Synthesis of 2,6-bis(5-bromo-3-hexylthiophen-2-yl)-9-hexyl-9H-purine (**M2**).

9-hexyl-2,6-bis(3-hexylthiophen-2-yl)-9H-purine (0.316 g, 0.589 mmol) was added to a 25 mL round bottom flask along with tetrahydrofuran (10 mL) and glacial acetic acid (10 mL). The mixture was stirred at room temperature for 30 min. *N*-Bromosuccinimide (0.227 g, 1.27 mmol) was then added gradually over 5 min. The reaction conversion was monitored via TLC. After 16 h, the solvents were removed via rotary evaporation under reduced pressure. Flash column chromatography using a solvent mixture consisting of 1:1 ethyl acetate:hexanes was used to separate mono- and di-brominated products. The di-brominated product was collected as a pale, yellow powder, and the isolated yield of **M2** was 43%. ¹H and ¹³C NMR spectra and the HRMS spectrum are presented in the Appendix A (**Figures A.4, A.5, and A.7**). ¹H NMR (500 MHz, 25 °C, CDCl₃). δ , ppm: 0.89 (m, 6H, CH₃), 1.17-1.54 (m, 18H, CH₂), 1.70 (p, 4H, CH₂), 1.95 (p, 2H, CH₂), 3.24 (t, 2H, ArCH₂), 3.34 (t, 2H, ArCH₂), 4.24 (t, 2H, NCH₂), 6.95 (s, 1H, ArH), 7.05 (s, 1H, ArH), 8.01 (s, 1H, C8-H). HRMS: calc'd [M+H⁺]: 693.1290, found: 695.0925.

2.3.4 General Procedure for Direct Arylation Polymerization of Comonomers

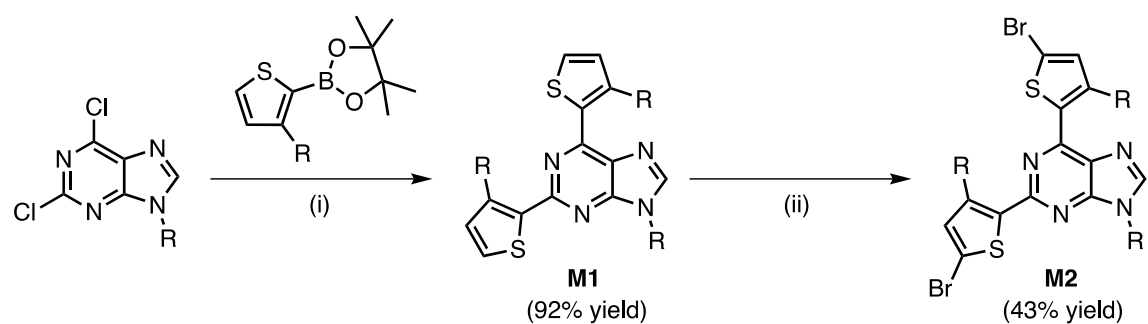
The purine-containing monomer (either **M1** or **M2**) and desired comonomer were added (in a 1:1 stoichiometric ratio, 0.15 mmol of each monomer) to a 25 mL round bottom flask equipped with a Teflon stir bar. All DArP reactions were performed in 5 mL of DMAc

at 95 °C with 4-5 mol% Pd(OAc)₂ as the catalyst, 3.0 equiv. of K₂CO₃ as the base, and 0.3 equiv. of PivOH as the proton shuttle, which has proven to be effective at limiting defects in DArP of monomers based on 3-hexylthiophene.³⁷ All reagents were added under a positive pressure of argon. Dry DMAc was sparged with argon for 15 min before it was added to the reaction vessel. After 18 h, the reaction was cooled to room temperature and added dropwise to cold methanol (MeOH, ~50 mL) to precipitate the copolymer. To isolate the copolymer, the recovered solid precipitate was washed with methanol (25 mL × 3) and acetone (25 mL × 3), followed by centrifugation for 10 min after each wash. The final isolated and purified polymer was dried and collected as a solid powder. ¹H NMR spectra and GPC traces of the copolymers are presented in Appendix A. (**Figure A.9-13** and **Figures A.14-19**, respectively).

2.4 Results and Discussion

2.4.1 Synthesis of Monomer Triads M1 and M2

Based on insights from our prior work,²⁹ we hypothesized that cross-coupling polymerizations involving purines would benefit from monomer designs that feature efficient coupling sites of equal reactivity. For this reason, **M1** was synthesized from the dihalopurine, 2,6-dichloro-9-hexyl-9*H*-purine, by *N*9-alkylation of 2,6-dichloropurine according to previously reported methods,³⁶ followed by Suzuki-Miyaura cross-coupling between 3-hexylthiophene-2-boronic acid pinacol ester and 2,6-dichloro-9-hexyl-9*H*-purine. (See **Scheme 2.1**.) Based on previous studies of alternating copolymers containing terthiophene, hexyl side chains on the thiophene-purine-thiophene (TPT) triad were expected to enhance the solubility of the conjugated copolymer.³⁶ ¹H NMR spectroscopy



Scheme 2.1 Synthesis of thiophene-purine-thiophene triads, M1 and M2, which have 2,6-connectivity due to the use of 2,6-dichloro-9-hexyl-9*H*-purine. R = hexyl. Synthetic conditions are (i) Pd(PPh₃)₄, 2 M K₂CO₃, toluene, reflux 110 °C for 48 h; (ii) 2 eq. NBS, THF/acetic acid, rt for 6 h.

confirmed coupling at both the 2- and 6-positions of the purine scaffold, respectively (**Figure A.2**). After purification and isolation of **M1**, *N*-bromosuccinimide (NBS) was used to synthesize the dibromo-substituted monomer **M2**, as shown in **Scheme 2.1**, and functionalization was confirmed by ¹H NMR spectroscopy. Specifically, the spectrum of **M1** (**Figure 2.2**, bottom) shows two sets of doublets associated with the C-H bonds of the thienyl rings coupled at the C2 and C6 positions of the purine, as well as the singlet associated with the proton from C8 of the purine scaffold ($\delta = 8.03$ ppm). After bromination, the four doublets are lost and replaced by two singlets, as seen in the spectrum for **M2** (**Figure 2.2**, top).

2.4.2 Synthesis of Purine-Containing Copolymers

A series of fully conjugated, alternating copolymers containing the alkylated thiophene-purine-thiophene triads (**M1** or **M2**) were synthesized by DArP, as shown in **Scheme 2.2**. Two variations of AA + BB copolymerizations were used: First, **M1** was copolymerized with four different dibromo-monomers: **M2**, 2,5-dibromo-3-hexylthiophene (T), 4,7-bis(5-bromo-3-hexylthiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (TBTT), or 2,7-dibromo-9,9-dioctyl-9*H*-fluorene (F). Second, the dibrominated triad **M2** was copolymerized with either 2,2'-(9,9-dioctyl-9*H*-fluorene-2,7-diyl)dithiophene (TFT) or 3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine (ProDOT). These polymerizations generated a series of alternating, purine-containing copolymers that are designated as **P1_{TPT}**, **P2_F**, **P4_T**, **P6_{TBTT}** (**Scheme 2.2a**), and **P3_{TFT}** and **P5_{ProDOT}** (**Scheme 2.2b**), where the subscript designates the comonomer used. After each copolymerization, the resultant copolymer was precipitated into cold methanol and isolated after washing the recovered

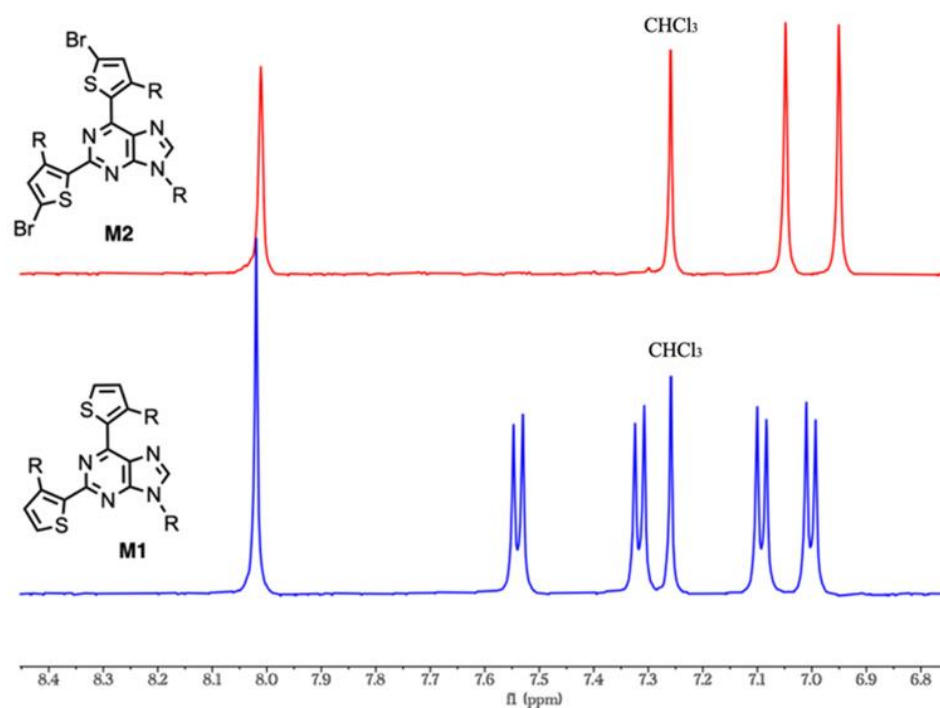
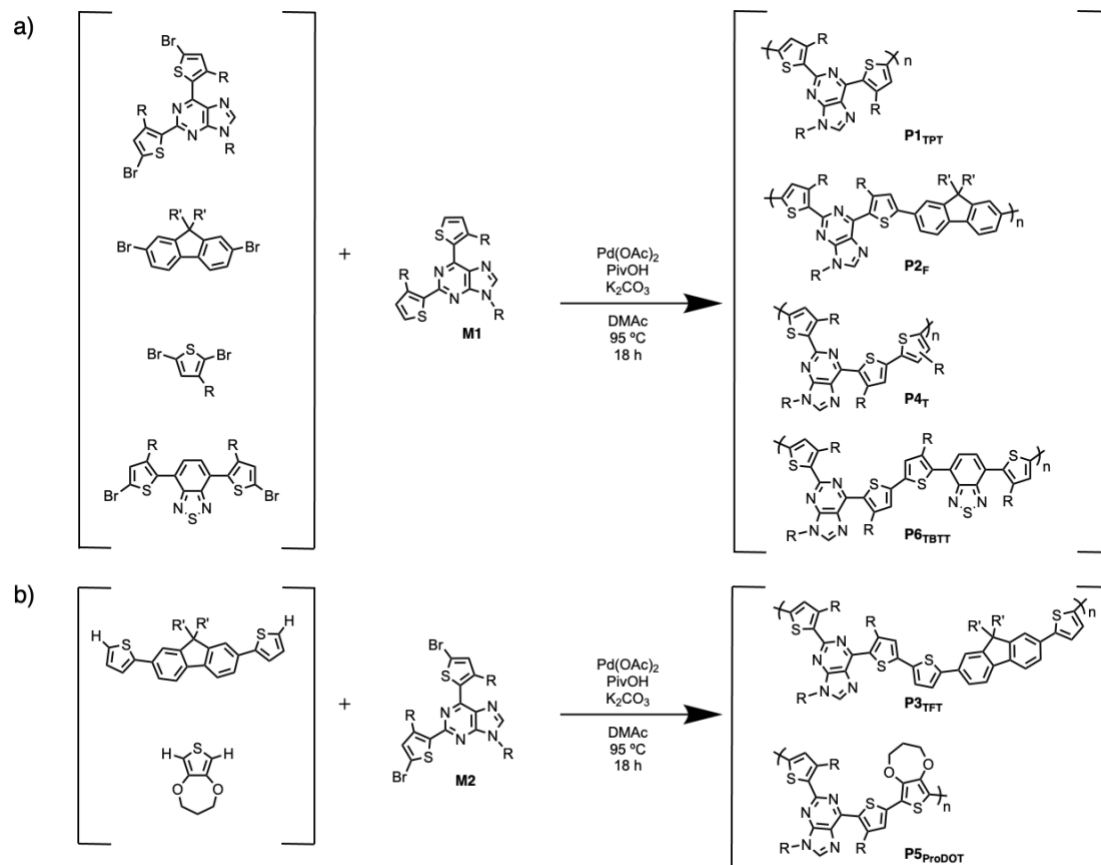


Figure 2.2 Aromatic region of the ^1H NMR spectra (in CDCl_3) confirming the conversion from M1 (blue spectrum, bottom) to M2 (red spectrum, top). R = hexyl.



Scheme 2.2 Synthesis of purine-containing copolymers by DArP by copolymerization of a) **M1** with **M2**, **F**, **T**, or **TBTT** to form **P1_{TPT}**, **P2_F**, **P4_T**, and **P6_{TBTT}**, and of b) **M2** with **TFT** or **ProDOT** to form **P3_{TFT}** and **P5_{ProDOT}**. In all structures, **R** = hexyl while **R'** = octyl.

precipitate with methanol (×3) and acetone (×3), followed by centrifugation after each wash. Copolymers with number-average molecular weights ranging from 4 – 18 kg/mol were synthesized with yields ranging from 42 – 86%, as reported in **Table A.1**. The conditions used for polymerization were selected based on a variety of studies in which the synthesis of poly(3-hexylthiophene) by DArP was optimized to avoid regioerrors (or “defects”).^{38–41} Specifically, Thompson *et al*, demonstrated that bulky carboxylic acids (such as PivOH) effectively reduce β -activation,³⁷ while our previous study shows that a reaction temperature of 95 °C avoids activation of the proton at C8 position of the purine and undesired C-H activation on thienyl monomers.⁴² Because of the influence of molecular weight on polymer properties and as elaborated in the following section, we chose to focus characterization studies on purine-containing copolymers having $M_n = 10$ kg/mol (nominal value). The macromolecular characteristics of this set of copolymers are summarized in **Table 2.1**, and their ¹H NMR spectra are presented in **Figures A.8-A.13**. All resonances show the broadening expected for polymers as well as the characteristic signature of the C8-H proton (at $\delta = 8.0$ ppm).

2.4.3 Optical Properties of Copolymers

To investigate the dependence of optical properties on molecular weight, absorbance spectra were acquired for all copolymers. (See **Figures A.20-A.24** and **Table A.1** for data.) These studies provide some insight into the effective conjugation length (ECL) of these copolymers, as optoelectronic properties are expected to be independent of molecular weight above the ECL. For example, studies of oligothiophenes and poly(alkylthiophene)s showed that when the number of repeat units (N) in the chain exceeded 9-12

Table 2.1 Yield and macromolecular characteristics of purine-containing copolymers synthesized by DArP.

	Yield (%)	M_n (kg/mol)^a	$\bar{D}$	X_n^b
P1_{TPT}	71%	9.0	2.2	9
P2_F	80%	9.4	1.9	10
P3_{TFT}	48%	12.1	3.2	11
P4_T	53%	9.8	1.7	14
P5_{ProDOT}	42%	9.8	2.1	13
P6_{TBTT}	47%	12.5	2.5	12

^aNumber-average molecular weights (M_n) were measured by GPC (mobile phase of THF at 25 °C) using universal calibration analysis based on polystyrene (PS) standards. ^b X_n is the average degree of polymerization based on M_n .

units, there were no observable changes in the absorbance spectrum.^{43–46} Similarly, homopolymers of 9,9-dialkyl-substituted fluorenes, which have a fused aromatic ring structure, have an effective conjugation length of 12 repeat units.^{34,47} In both of these cases, the bulky alkyl side chains lead to out-of-plane deformation that reduce the conjugation length in comparison to highly planar polythiophenes, such as those made by Otsubo *et al.* They demonstrated that blocking β sites using a 2,2-bis(butoxymethyl)-1,3-propanediyl group allowed highly conjugated polythiophenes to be made, and those materials exhibited changes in optical absorption maxima up to chain lengths of $N = 96$.⁴⁸ Although our copolymers are disperse, the optical absorbance of our purine-containing copolymers becomes independent of molecular weight at $M_n \approx 9$ kg/mol. As an example, **Figure A.23** shows that for **P4T**, there is a 5 nm red-shift in the absorbance maximum as the molecular weight is increased from 5.0 kg/mol (~ 7 repeat units) to 9.8 kg/mol (~ 14 repeat units); however, there are essentially no changes in the absorbance maxima and onsets as molecular weight is increased from 9.8 kg/mol to 18 kg/mol (~ 25 repeating units). The spectra of the other copolymers reflect the same pattern of behavior: There were no changes in absorbance maximum and onset above $M_n \approx 9$ kg/mol, which is reflected in absorbance maxima and onset values presented in **Table A.1**. For this reason, optical and electronic properties reported in **Table 2.2** were extracted from experiments that used copolymers where $M_n = 9.0 - 12.5$ kg/mol.

As shown in **Table 2.2** and **Figure 2.3**, the absorbance maximum (λ_{max}^{abs}) of all of the copolymers is between 400 – 460 nm, which is attributed to the π - π^* transition.⁴⁹ Except

Table 2.2 Optoelectronic data for purine-containing copolymers and M1.

	$\lambda_{\text{max}}^{\text{abs}^a}$	$\lambda_{\text{onset}}^{\text{abs}^a}$	$\lambda_{\text{max}}^{\text{em}^a}$	$\lambda_{\text{onset}}^{\text{em}^a}$	Stokes shift ^a (nm)	Φ^a	Opt E _{gap} ^b (eV)
M1	309	377	405	488	96	0.12	--
P1_{TPT}	424	492	514	630	90	0.19	2.41
P2_F	416	479	475	606	59	0.61	2.46
P3_{TFT}	441	500	530	627	104	0.22	2.41
P4_T	426	514	515	637	98	0.17	2.24
P5_{ProDOT}	458	532	534	650	76	0.09	2.17
P6_{TBT}	400	569	648	797	248	0.02	1.96

^aUV-Vis and fluorescence spectra were acquired from CHCl₃ solutions. ^bBased on UV-Vis spectra acquired from drop cast thin films on glass slides.

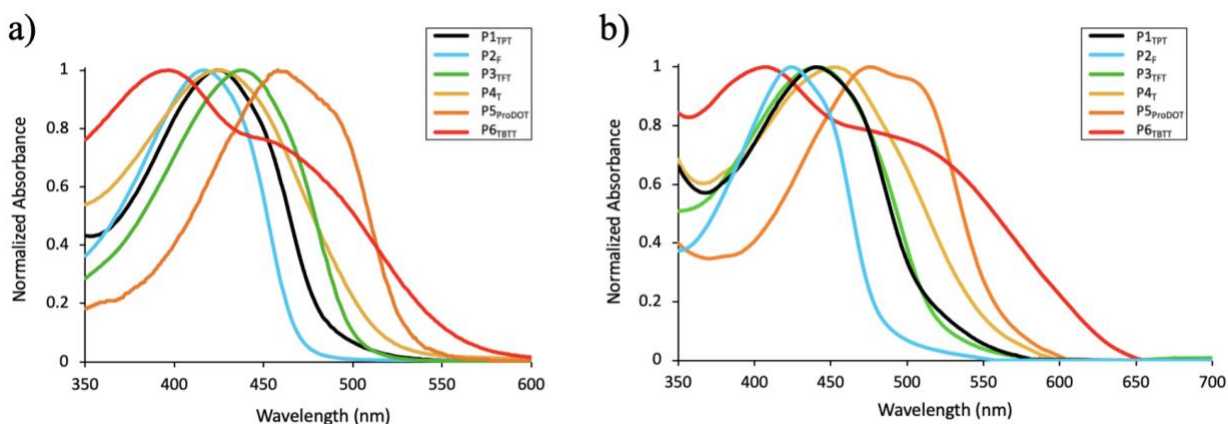


Figure 2.3 Normalized UV-Vis spectra for the various purine-containing copolymers: Spectra for P1_{TPT} (black), P2_F (blue), P3_{TFT} (green), P4_T (yellow), P5_{ProDOT} (orange), and P6_{TBT} (red) were acquired a) at 0.01 mg/mL in CHCl₃ and b) as thin films.

for **P5_{ProDOT}** and **P6_{TBT}**, broad and featureless absorbance spectra with $\lambda_{max}^{abs} \approx 420$ nm are observed relative to the other copolymers, **P5_{ProDOT}** has a red-shifted absorbance maximum, which was expected due to the electron-rich nature of ProDOT and its high degree of planarity. **P6_{TBT}** has the most blue-shifted absorbance maximum ($\lambda_{max}^{abs} = 400$ nm) and the highest (bathochromic) absorbance onset ($\lambda_{onset}^{abs} = 569$ nm). The spectra of **P5_{ProDOT}** and **P6_{TBT}** also exhibit distinctive shoulders or secondary absorbance peaks at 500 and 463 nm, respectively, which could be attributed to ICT and indicative of a donor-acceptor relationship for these copolymers. A titration study using sequential additions of methanol to a chloroform solution of **P5_{ProDOT}** was completed to investigate whether the absorbance shoulder at 500 nm arose due to polymer aggregation. It is known that ProDOT homopolymers often exhibit dual-band absorbance profiles in solution caused by aggregation that is brought on by the planarity of the ProDOT monomer.⁵⁰ If the vibronic shoulder were a product of aggregation, an increase in the shoulder and a corresponding decrease in the main peak at $\lambda = 458$ nm with sequential additions of the poor solvent methanol would be expected. However, as seen in **Figure A.32**, decreasing the solvent quality by adding methanol did not lead to an increase in the shoulder, which suggests that the shoulder in **P5_{ProDOT}** is not due to aggregation. Thus, this vibronic shoulder in the absorbance profile of **P5_{ProDOT}** is likely due to complementary S $\cdots$ O interactions that result in a more rigid backbone.⁵¹ The absorbance maxima of **P6_{TBT}** (400 nm and 463 nm) are similar to those reported previously for BT-containing chromophores^{19,20} and alternating donor-acceptor copolymers where BT acts as the electron acceptor.^{35,52} As discussed

below, we hypothesize that this dual-band behavior arises due to ICT between the purine and the strong electron acceptor, BT.

Within this set of results, there are other aspects worth highlighting. For example, in comparison to **P1_{TPT}**, which is synthesized by an AA + BB copolymerization of **M1** and **M2**, the breadth of the absorbance peak of **P4_T** is larger while the absorbance maximum is basically unchanged. The differences in peak breadth may be attributed to **P4_T** being more flexible due to the additional hexylthiophene in the repeat unit, which provides more conformational freedom. This manifests as a broadening of the absorbance profile, which is a phenomenon that has been reported for other conjugated polymer systems.^{53,54} Amongst the purine-containing copolymers, **P2_F** exhibits the highest onset energy (lowest λ_{onset}^{abs}) due to the high energy LUMO from the fluorene unit. The high energy onset of **P2_F** is similar to copolymers containing fluorene units in the main chain.^{34,55,56} The absorbance data also show that when fluorene monomers are flanked with thiophenes (to create TFT) and then copolymerized with **M2** to produce **P3_{TFT}**, the absorbance onset and maximum are both lower in energy than **P2_F**. In addition to being soluble in chloroform, the purine-containing copolymers were soluble in tetrahydrofuran (THF) and *N,N*-dimethylformamide (DMF), which allowed solvatochromic properties to be examined in more polar solvents. (Adsorption spectra are presented in **Figures A.33-A.38**.) The absorbance profiles acquired for **P1_{TPT}** and **P4_T** show essentially no changes as solvent polarity is increased, while the λ_{onset}^{abs} of **P2_F**, **P5_{ProDOT}** and **P6_{TBTT}** are at lower energies in the most polar aprotic solvent, DMF. This change in λ_{onset}^{abs} is attributed to the excited state of **P2_F**, **P5_{ProDOT}**, and **P6_{TBTT}** being more polar than the ground state, and the polar solvent

(DMF) assists in stabilization of the excited state.⁵⁷ **P3_{TFT}** exhibits a different pattern of behavior, showing a hypsochromic shift in λ_{onset}^{abs} and λ_{max}^{abs} with increasing solvent polarity, indicating a less polar excited state than ground state.⁵⁸

To understand how optical properties change from solution to thin film, absorbance spectra were acquired from drop cast thin films, and are presented in **Figure 2.3b**. The absorbance maximum for films of **P6_{TBTT}**, **P5_{ProDOT}**, **P4_T**, and **P1_{TPT}** are red-shifted relative to those measured in chloroform (CHCl₃). This pattern of behavior is consistent with a larger degree of π -orbital overlap as well as a higher degree of ordering in the solid-state (as compared to solution-state measurements).⁵⁹ **P2_F** showed no appreciable shift in absorbance maximum from solution to a thin film, ostensibly because the octyl groups on the sp^3 -carbon of 9,9-dioctyl-9H-fluorene (F) disrupt packing in the solid state.^{59,60} All of the purine-containing copolymers synthesized in this work are fluorescent, and as seen from **Figure 2.4**, they show visible emissions as solutions in CHCl₃, as thin films, and as powders. The emission spectra of the conjugated copolymers in CHCl₃ were measured by exciting at the λ_{max}^{abs} measured for each copolymer, and those values are tabulated in **Table 2.2**. As shown in **Figure 2.5**, the photoluminescence emission maximum and onset change significantly for each copolymer, with the emission spectrum of **P6_{TBTT}** approaching the near-IR region of the electromagnetic spectrum. Compared to **P1_{TPT}**, the fluorene-containing copolymer, **P2_F**, has a hypsochromic shift, while **P4_T**, **P5_{ProDOT}**, and **P6_{TBTT}** exhibit increasingly bathochromic shifts. **P3_{TFT}** has the same absorbance maximum and onset as **P1_{TPT}** as thin films. While these traits are also reflected in the values of optical bandgap determined from the UV-Vis measurements (**Table 2.2**), it is not possible at this juncture to discern whether the pattern of behavior is due to solvatochromic effects,

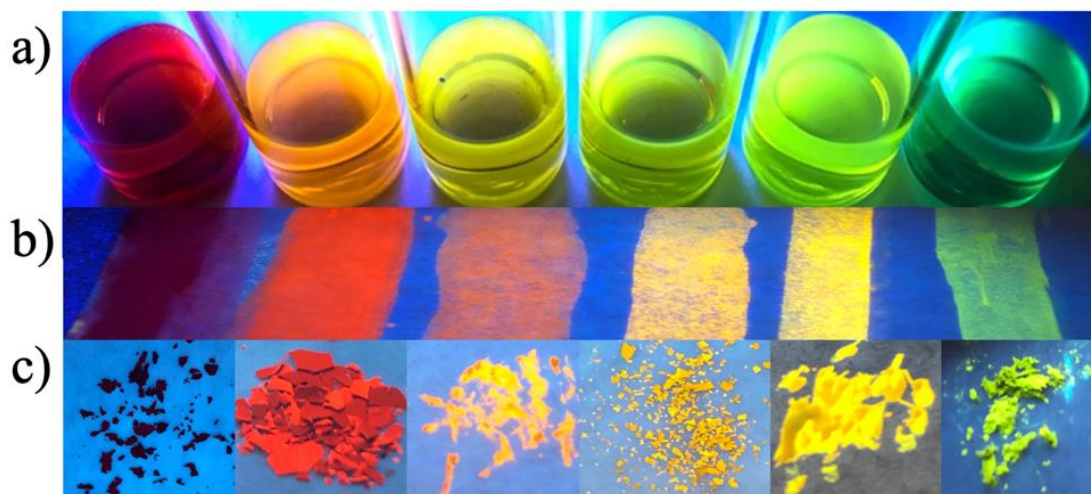


Figure 2.4 Images highlighting the emission behavior of purine-containing copolymers, from left to right, P6_{TBTT}, P5_{ProDOT}, P4_T, P1_{TPT}, P3_{TFT}, and P2_F in a) CHCl₃ solution at 1 mg/mL, b) the solid-state (thin films on wax paper), and c) as powders. Images were acquired by illuminating samples with a 365 nm UV lamp.

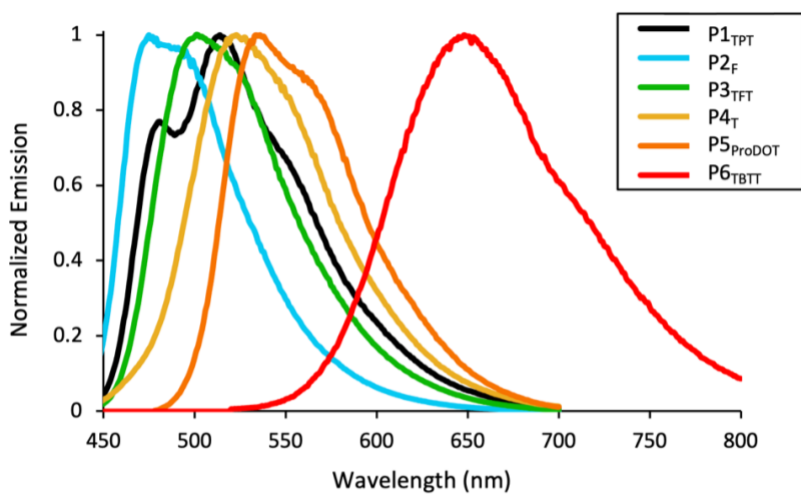


Figure 2.5 Normalized photoluminescence spectra of P1_{TPT} (black), P2_F (blue), P3_{TFT} (green), P4_T (yellow), P5_{ProDOT} (orange), and P6_{TBTT} (red). All emission spectra were acquired from chloroform solutions 0.001 mg/mL.

difference in stacking or organization due to inherent solubility of the chains, or a result of changes in conjugation. We note that both absorbance and emission patterns for **P6_{TBTT}** are consistent with previous reports of related small molecule chromophores.^{19,20} Because **P6_{TBTT}** has dual-band character with localized maxima (red trace in **Figure 2.3a**), emission spectra were acquired at excitation wavelengths of 400 nm and 463 nm. Both excitation energies resulted in the same featureless emission spectra, which confirms ICT in **P6_{TBTT}**. The other purine-containing copolymers have fine-structure vibrational progressions in their emission spectra, which are consistent with the absence of ICT. **P1_{TFT}**, **P3_{TFT}**, and **P4_T** have emission maximums within 15 nm of each other and emission onsets within 10 nm of each other. (See **Figure 2.5** and **Table 2.2**.) **P6_{TBTT}**, which contains the strong electron acceptor BT, displays a large Stokes shift of 248 nm, which indicates a large degree of structural reorganization upon photoexcitation. The other copolymers show less structural reorganization, with Stokes shifts ranging from 59-104 nm.

The extinction coefficient for each copolymer was determined from a series of absorption measurements at various concentrations, and the resulting Beer-Lambert plots are presented in **Figures A.25-A.31**. The fluorescence quantum yield (ϕ) was determined relative to Rhodamine 101 in ethanol (+0.01 wt.% HCl) by the comparative method.

$$\phi = \phi_r \left(\frac{m_s}{m_r} \right) \left(\frac{n_s}{n_r} \right)^2 \quad (2.1)$$

In this expression, m_s and m_r are the slopes of the lines relating integrated fluorescence and absorbance intensities, respectively, with subscripts r and s referring to the reference

and sample, and n_s and n_r are the refractive indices of the sample and reference solvents, respectively. ϕ_r is the fractional quantum yield of the reference, Rhodamine 101 in ethanol, which has a $\phi_r = 1.00$.⁶¹ As reflected in results presented in **Table 2.2**, the purine-containing copolymers exhibit quantum yields that range widely, from $\phi = 0.02 - 0.61$. **M1** has a modest quantum yield of $\phi = 0.12$, which is lower than purine-containing chromophores reported in our previous study,¹⁹ as well as those studied by Bou Zerdan *et al.*²⁰ Given that purines have vibrant photoemission characteristics, the lower quantum yield determined for **M1** may be the result of having only one purine unit in the structure, compared to small molecule chromophores capped at each end by a purine.^{17,34} **P1_{TFT}** has a slightly higher quantum yield of $\phi = 0.19$, which is similar to that of copolymer **P4_T**, which has an additional thiophene interposed between the TPT triads. Most notably, **P2_F** has the highest fractional quantum yield at $\phi = 0.61$ while **P3_{TFT}** follows at $\phi = 0.22$, and these results are consistent with many studies demonstrating that small molecule chromophores and conjugated polymers containing fluorene are highly fluorescent.^{16–20,24,25,62–64} These results also show that the increase in sulfur content from **P2_F** to **P3_{TFT}** leads to a decrease in fluorescence quantum yield, from $\phi = 0.61$ to $\phi = 0.22$, which is consistent with an internal heavy atom effect that facilitates intersystem crossing via spin orbit coupling.^{65,66} Nevertheless, **P2_F** has a higher photoluminescent quantum yield than values reported for homopolymers of poly(alkylfluorene)s in chloroform⁶⁷ and a significantly higher quantum yield compared to thiophene-alkylfluorene copolymers,⁶⁸ suggesting that the purine unit contributes strongly to the highly fluorescent behavior. The quantum yields of these four purine-containing copolymers are notable, as a benchmark value of $\phi \geq 0.1$ is typically viewed as sufficient for use in organic light-emitting diodes

and polymer dots.^{69,70} Both **P5_{ProDOT}** and **P6_{TBT}** have quantum yields below $\phi = 0.1$: **P5_{ProDOT}** has a modest quantum yield of $\phi = 0.09$ and **P6_{TBT}** is significantly lower with a quantum yield of $\phi = 0.02$, which we hypothesize is due to non-radiative decay accompanying ICT.⁷¹ While it is tempting to compare the quantum yield of these purine-containing copolymers against one another, it is possible that the solvation state of each copolymer in chloroform is different, which brings solvation effects into play that are known to impact fluorescent emission.

2.4.4 Bandgaps and Energy Levels (HOMO-LUMO)

Oxidation and reduction behavior of the copolymers as thin films (created by drop-casting on a gold button electrode) were measured via cyclic voltammetry (CV). Oxidation and reduction onsets, E_{onset}^{ox} and E_{onset}^{red} , were used to estimate the HOMO and LUMO energy levels using Equations 2.2 and 2.3, respectively. Ferrocene was used as the reference and assuming that the Fc/Fc⁺ redox couple is 5.1 eV relative to a vacuum.^{20,72,73}

$$E_{HOMO} (eV) = -(E_{onset}^{ox} + 5.1) eV \quad (2.2)$$

$$E_{LUMO} (eV) = -(E_{onset}^{red} + 5.1) eV \quad (2.3)$$

Cyclic voltammetry experiments show that **M1**, **P1_{TPT}**, **P3_{TFT}**, **P4_T**, **P5_{ProDOT}**, and **P6_{TBT}** exhibit quasi-reversible oxidations within the acetonitrile solvent window (**Figures A.39-A.44**). The values of HOMO and LUMO for each polymer are tabulated in **Table 2.3** and compared graphically in **Figure 2.6**. The redox onset potentials from CV were assigned from the intersection of the tangent line of the redox peak at half height to the baseline

Table 2.3 Redox onsets and molecular energy levels for purine-containing copolymers and M1.

	Oxidation Onset (V)	HOMO ^{CV^a} (eV)	Reduction Onset (V)	LUMO ^{CV^a} (eV)
M1	0.88	-5.98	-- ^c	-2.70 ^b
P1_{TPT}	0.60	-5.70	-1.85	-3.25
P2_F	-- ^c	-- ^c	-- ^c	-- ^c
P3_{TFT}	0.59	-5.69	-2.16	-2.94
P4_T	0.59	-5.69	-1.81	-3.29
P5_{ProDOT}	0.29	-5.39	-1.96	-3.14
P6_{TBTT}	0.50	-5.60	-1.62	-3.48

^aBased on the onset of oxidation/reduction potentials that were measured by CV (c.f. equations 2 and 3). ^bValue is calculated based on absorbance onset. ^cNot measured because oxidation and reduction potentials were outside the potential window of acetonitrile.

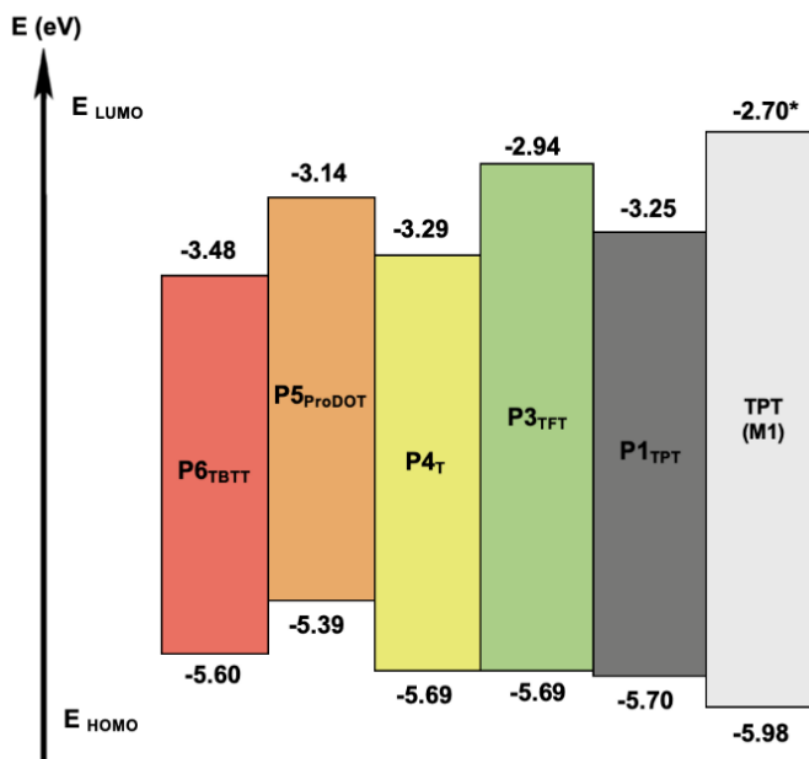


Figure 2.6 HOMO/LUMO energy level diagram of conjugated purine-containing copolymers obtained via cyclic voltammetry. The symbol * indicates that the LUMO for M1 was calculated from the UV-Vis absorbance onset.

current, as has been described by Janssen *et al.*⁷⁴ Data for **P2F** is not included because oxidation and reduction were not observed in the potential window of acetonitrile. Also, although the oxidation onset for **M1** was observed in CV, no reduction wave was observed. Thus, the LUMO for **M1** was calculated using the HOMO measured by CV and the optical bandgap (which was reported in **Table 2.2**). **P1TPT** has a HOMO of -5.70 eV and a LUMO of -3.25 eV. When ProDOT is copolymerized (with **M2**), an increase in the HOMO level is observed for **P5ProDOT** (-5.39 eV) due to the electron-rich nature of ProDOT. The LUMO energy of **P5ProDOT** (-3.14 eV) is similar to that of **P1TPT** (-3.25 eV), which suggests that it is dictated primarily by the TPT triad. These frontier energy levels indicate a donor-acceptor relationship for **P5ProDOT**, with the TPT unit serving as the electron acceptor and ProDOT functioning as the electron donor, which leads to an optical bandgap of 2.17 eV. **P6TBTT** has the smallest optical bandgap of 1.96 eV and a low lying LUMO at -3.48 eV (compared to **P1TPT**), suggesting a “weak donor-strong acceptor” relationship between the BT and purine-containing units. This character in which BT functions as the strong acceptor is consistent with the behavior reported for P-TBTT-P small molecule chromophores and corresponding DFT calculations.^{19,20} These examples in which the purine unit acts either as the electron acceptor (i.e., **P5ProDOT**) or as the electron donor (i.e., **P6TBTT**) confirm the versatility of the purine monomer.^{19,29} **P1TPT**, **P3TFT**, and **P4T** all have bandgaps and molecular energy levels that suggest the comonomers TFT and T function as conjugated linkers between the aryl units of the main chain.

Finally, we would like to note the cross-conjugated nature of these copolymers, which arises because of the 2,6-pattern connectivity across the purine scaffold. As reported by Matsumoto *et al.*⁷⁵ and Janssen *et al.*⁷⁶ in their studies of donor-acceptor systems, cross-

conjugation tends to weaken delocalization along the backbone, which lowers the HOMO energy. However, our TPT-based copolymers are different from typical alternating conjugated copolymers because **M1** and **M2** are comprised of triads that possess a cross-conjugated meta-linkage across the pyrimidine ring of the purine scaffold. Because of this design, a specific purine unit in the chain will have conjugated orbital overlap with one of the various comonomers used to construct the alternating copolymer, as evidenced by ICT observed for **P6_{TBTT}**. Although electronic communication throughout the main chain is likely weakened due to cross-conjugation, linearly conjugated subunits within the main chain consisting of P-T-comonomer-T-P units essentially act like oligomeric chromophores. Thus, these linearly conjugated, multi-ring subunits readily allow radiative decay, resulting in high quantum yields. This can be observed in the case of **P2_F**, where the copolymer benefits from the highly emissive nature of purines and fluorenes, and in the case of **P1_{TPT}** where the quantum yield of the copolymer is higher than its equivalent monomeric unit even though the ratio of heavy atoms (thiophene-based units) is the same. Thus, while cross-conjugation is typically deleterious to optoelectronic properties, preserving electronic communication within a well-defined subunit of the chain appears to be a viable way to maintain properties and performance of conjugated polymers.

2.5 Conclusions

The synthesis and fundamental optoelectronic characteristics of fully conjugated copolymers incorporating 2,6-disubstituted purines in the main chain are described. Flanking the 2,6-dihalopurine with alkyl-thiophene units overcomes issues of unequal reactivity of coupling sites on the purine scaffold toward metal-mediated cross-coupling,

allowing purine-containing copolymers with molecular weights up to 18 kg/mol to be synthesized by DArP. Naturally, the optical and electrochemical properties of these conjugated copolymers depend on comonomer selection, with properties being invariant of molecular weight above $M_n \approx 9$ kg/mol. Molecular orbital energy levels from cyclic voltammetry and optical bandgaps show how the TPT triad can participate as an electron-accepting unit in **P5_{ProDOT}** and as a donating unit in **P6_{TBTT}**. Although the 2,6-connectivity across the pyrimidine ring of the purine results in cross-conjugation, these cross-conjugated designs with extended repeat unit structures are intriguing because of the possibility of tailoring electronic communication along the backbone. Finally, we note that the synthetic accessibility of specific sites on the purine scaffold enables design-structure-property relationships to be developed for other structural isomers, thereby engendering opportunities to enhance the properties of purine-containing conjugated materials.

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**CHAPTER III: TWO-DIMENSIONAL NUCLEAR MAGNETIC
RESONANCE ANALYSIS AND OPTOELECTRONIC PROPERTIES
OF AA+BB AND AB PURINE-CONTAINING CONJUGATED
POLYMERS**

3.1 Abstract

Precise control over monomer conformation and regiorchemistry is crucial when designing conjugated polymers. Herein, we make comparisons between purine-containing copolymers polymerized in a way that creates a regioregular “AB” polymer and a regiorandom “AA+BB” copolymer derived from the thienyl-purine-thienyl (TPT) repeating units that were described in Chapter II. The AB polymerization uses an AB monomer, 2-(5-bromo-3-hexylthiophen-2-yl)-9-hexyl-6-(3-hexylthiophen-2-yl)-9*H*-purine, to make the homopolymer via direct arylation polymerization (DArP). The other copolymer is made by copolymerizing AA and BB monomers, 9-hexyl-2,6-bis(3-hexylthiophen-2-yl)-9*H*-purine and 2,6-bis(5-bromo-3-hexylthiophen-2-yl)-9-hexyl-9*H*-purine. The syntheses of the AA and BB monomers were previously described in Chapter II. Direct arylation polymerization was found to be robust for these polymerizations, allowing various comparisons between the regioregular and regiorandom copolymers to be made. Specifically, 2-D NMR techniques, including HSQC, HMBC, and NOESY, were used to assign the protons and carbons of the monomers and the resulting conjugated polymers. These 2-D NMR experiments suggest that there is a noncovalent conformational lock in the AA monomer, 9-hexyl-2,6-bis(3-hexylthiophen-2-yl)-9*H*-purine, that is due to S $\cdots$ N interactions. The crystal structure deduced for the di-hydro (AA) monomer corroborated this finding, and 2-D NMR experiments of the AB and AA+BB polymers also showed the presence of the same S $\cdots$ N interactions. The AA+BB and AB polymers have very similar optical bandgaps and quantum yields, but the emissions profiles and thin

film absorbance profiles show distinct differences, which could be due to the impact of chain configuration on assembly, which is dictated by π -stacking interactions.

3.2 Introduction

Conjugated polymers are useful for their ability to transport charge along the polymer main-chain and between chains; therefore, designing monomers to improve electron delocalization has been a topic of continued interest in conjugated polymer research.^{1,2} One way to improve electron delocalization is by increasing the planarity of the main chain.³⁻⁵ While alkyl side chains are generally needed to improve the solubility of conjugated polymers, they can induce twist along the backbone due to steric crowding, which decreases the planarity of the chain and changes the morphological organization in the solid state, thereby impacting charge carrier transport.⁶⁻⁹ Thus, a key consideration in designing conjugated polymers is balancing polymer solubility and main chain planarity.^{7,10,11} While fused ring aromatic structures generally increase the planarity, this comes at a cost of decreasing solubility. Another approach used to enhance the planarity of conjugated polymers is to introduce noncovalent conformational locks.¹²⁻¹⁴ For example, S $\cdots$ N conformational locks have been observed in small organosulfur compounds and in their corresponding polymers, and they tend to induce planarity in the conjugated unit.¹⁵⁻²² These noncovalent S $\cdots$ N conformational locks can be observed in solution with 2-D NMR experiments and in the solid-state with X-ray crystallography. Specifically and as shown in **Figure 3.1**, Bazan *et al.* used noncovalent S $\cdots$ N conformational locks in chromophores to narrow the bandgap and increase bulk organization.¹⁹

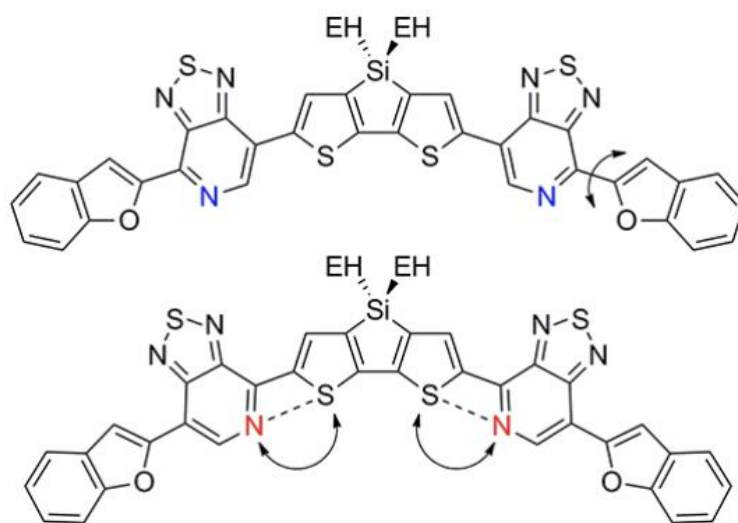


Figure 3.1 Small molecules studied by Bazan *et al.* that feature S...N interactions that accentuate bending of the molecular framework and induce planarity. Picture reproduced from reference 19.

Additionally, it has been shown that planarity of the main chain and charge carrier transport can be increased in conjugated polymers through sequence control or regioregularity.^{2,23–25} 2-D NMR experiments, including heteronuclear single quantum coherence (HSQC) and heteronuclear multiple bond correlation (HMBC), can be used to assign proton and carbon peaks of regioregular and regiorandom conjugated polymers, and nuclear Overhauser effect (NOESY) can be used to assign configuration and preferred conformation of molecules.^{26–28} By investigating the relationship between regioregularity and optoelectronic properties of the purine-containing polymers, I find that the thin film properties are influenced by the regioregularity of the polymers. The different orientation of monomers in the main chain affect the regioregularity, which can impact conformation of the chain and aggregation behavior, leading to changes in optoelectronic properties.²³ For example, Yu *et al.* demonstrated that the charge transport pathways of conjugated polymers were directly affected by the primary sequence of the polymer main chain.²⁹

Herein, a new thienyl-purine-thienyl AB-type monomer (2-(5-bromo-3-hexylthiophen-2-yl)-9-hexyl-6-(3-hexylthiophen-2-yl)-9*H*-purine) and previously reported AA+BB comonomers are studied to assess whether S $\cdots$ N noncovalent conformational locks are present in the monomer and polymers. Particularly, 2-D NMR techniques are used to accurately assign protons and carbons of the monomers and their corresponding polymers. These analyses, along with X-ray crystallography, confirm that S $\cdots$ N conformational locks are present in these purine-containing compounds. Further, the use of an AB monomer to synthesize the purine-containing copolymer allows me to study changes in optoelectronic properties of the polymer as a function of regioregularity. 2-D

NMR experiments show that the AA+BB copolymer has more magnetically inequivalent protons than the AB polymer. While the polymer regioregularity can impact conformation of the main chain and aggregation, leading to changes in bandgap, Stokes shift, thin film absorbance profiles, and emission profiles, the differences observed in the AB and AA+BB purine-containing polymers are surprisingly trivial, likely due to the presence of noncovalent conformational locks in the monomers. Specifically, the bandgap and quantum yield are unchanged, while the Stokes shift is greater in the regioregular AB polymer. In addition, thin film absorbance results show changes in absorbance profile which have been associated with the increased regioregularity of the polymer main chain.

3.3 Experimental Methods

3.3.1 Methods and Materials

N-Bromosuccinimide (NBS, 99%, Aldrich) was recrystallized from water and dried under vacuum before use. 2,6-dichloropurine (97%, Ark Pharm), 3-hexylthiophene-2-boronic acid pinacol ester (95%, Aldrich), 1-bromohexane (96%, Aldrich), glacial acetic acid, (Fisher Chemical), potassium carbonate (99%, Aldrich), Pd(PPh₃)₄ (98%, Aldrich), Pd(OAc)₂ (98%, Aldrich), pivalic acid (PivOH, 99%, Aldrich), anhydrous *N,N*-dimethylacetamide (DMAc, 99%, Sigma Millipore) anhydrous *N,N*-dimethylformamide (DMF, 99.8%, Acros Organics), anhydrous toluene (99.8%, Acros Organics), hexanes (95%, Fisher), methanol (99%, Fisher), and chloroform (98%, Fisher) were used as received, unless stated otherwise. Monomers and polymers were synthesized using standard Schlenk technique under an argon atmosphere.

^{13}C and ^1H NMR spectra of synthesized monomers were acquired at room temperature in CDCl_3 using a Varian VNMRS 500 MHz NMR spectrometer. Spectra needed for 2-D NMR studies, including HSQC, HMBC, and NOESY, were acquired at room temperature using a Varian VNMRS 600 MHz NMR spectrometer. Chemical shifts are referenced to the residual chloroform peak. Number-average molecular weights, M_n , and dispersity, $\bar{D}$, were determined via gel permeation chromatography (GPC), and are reported relative to polystyrene standards. Measurements were made using an Agilent 1260 Infinity II system that used THF as the mobile phase at a flow rate of 1 mL/min at 25 °C. The system was equipped with a guard column and two PLgel Mixed-C columns (300 mm length) with a lower limit of 200 g/mol and an upper limit of 2×10^6 g/mol. Polymer solutions for GPC analysis were prepared at 5 mg/mL in THF and passed through a 0.2 μm PTFE filter prior to injection. Optical absorbance spectra of the copolymers and monomers in chloroform were acquired using a Thermo Scientific Evolution 600 spectrophotometer by scanning from 300 nm to 500 nm for monomers and from 350 nm to 750 nm for the purine-containing copolymers. A Cary 5000 UV-Vis-NIR spectrometer was used for thin film measurements, and spectra were acquired by scanning from 350 nm to 800 nm. Fluorescence emission spectra were measured in CHCl_3 using a Cary Eclipse fluorescence spectrophotometer. Samples were excited at the absorbance maximum of each sample and spectra were recorded by scanning from $(\lambda_{\text{max}}^{\text{abs}} + 10)$ nm to 700 nm for monomers and polymers. Starting materials and monomers **M1**, **M2**, and **M3** were synthesized by methods previously described in Chapter II. ^1H NMR peaks and yields are reported in Appendix B. **M3** ^1H NMR and ^{13}C NMR spectra are presented in Appendix B as **Figure B.1** and **Figure B.2**, respectively.

General Procedure for AA+BB Direct Arylation Polymerization of Comonomers. As described in Chapter II, the purine-containing monomer **M1** and the dibrominated analog **M2** were added to a 25 mL round bottom flask equipped with a stir bar. The stoichiometric ratio was set at 1:1 using 0.15 mmol of each monomer. All DArP reactions were performed in 5 mL of DMAc at 95 °C with 4-5 mol% Pd(OAc)₂ as the catalyst, 3.0 equiv. of K₂CO₃ as the base, and 0.3 equiv. of PivOH as the proton shuttle. All reagents were added under a positive pressure of argon. Dry DMAc was sparged with argon for 15 minutes before being added to the reaction vessel. After 18 h, the reaction was cooled to room temperature and added dropwise to cold methanol (MeOH, ~50 mL) to precipitate the copolymer. To isolate the copolymer, the recovered solid product was washed with methanol (25 mL ×3) and acetone (25 mL ×3), followed by centrifugation for 10 minutes after each wash. The final isolated and purified polymer was dried and collected as a solid powder.

General Procedure for Direct Arylation Polymerization of the AB Monomer. The AB purine-containing monomer (**M3**, 0.3 mmol) was added to a 25 mL round bottom flask equipped with a stir bar. The polymerization was performed in 5 mL of DMAc at 95 °C with 4-5 mol% Pd(OAc)₂ as the catalyst, 3.0 equiv. of K₂CO₃ as the base, and 0.3 equiv. of PivOH as the proton shuttle. As with the AA + BB copolymerization, all reagents were added under a positive pressure of argon. Dry DMAc was sparged with argon for 15 minutes before being added to the reaction vessel. After 18 h, the reaction was cooled to

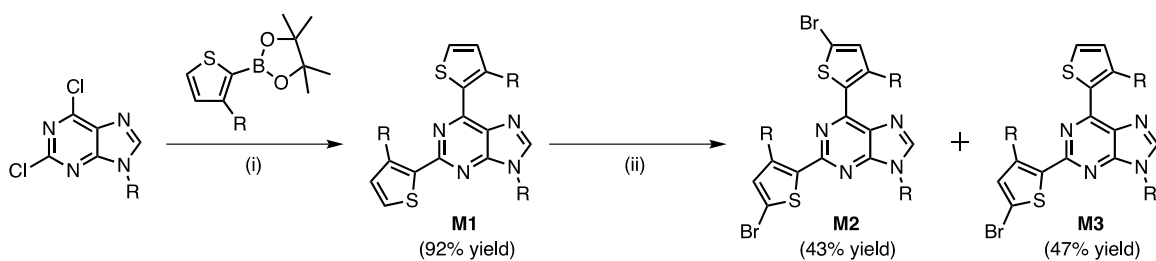
room temperature and the copolymer purified and isolated using the work-up procedures described for the AA+BB copolymer.

3.4 Results and Discussion

3.4.1 Synthesis of the Purine-Containing Monomers **M1**, **M2**, and **M3**

The cross-conjugated monomers **M1**, **M2**, and **M3** were synthesized from the dihalopurine, 2,6-dichloro-9-hexyl-9*H*-purine, as described in Chapter II. ¹H NMR spectroscopy was used to confirm coupling of the thienyl group at both the 2- and 6-positions of the purine scaffold. After purification of **M1**, *N*-bromosuccinimide (NBS) was used to synthesize the dibromo-substituted monomer **M2** and the monobromo-substituted monomer (**M3**). These preparations are shown in **Scheme 3.1**, and functionalization was confirmed by ¹H NMR spectroscopy. The ¹H NMR spectrum of **M1** has two sets of doublets associated with the protons of the thienyl rings that are coupled at the C2 and C6 positions of the purine. The singlet at ~ 8 ppm is associated with the proton at C8 of the purine motif. After a single bromination, the doublets at 7.32 ppm and 7.00 ppm are lost, and a new singlet is observed at 6.95 ppm. These changes confirm that the monobrominated purine monomer **M3** has been synthesized. The formation of the dibrominated monomer, **M2**, is evidenced by disappearance of the doublets at 7.55 ppm and 7.09 ppm, which are replaced by a new singlet at 7.05 ppm, as seen in **Figure 3.2**. Column chromatography (using 90% hexanes and 10% ethyl acetate as the mobile phase) is found to be effective for the separation of **M2** and **M3**.

According to ¹H NMR spectroscopy, the synthesis of the monobrominated purine triad **M3** from **M1** yields only one product, which indicates that there is a reaction bias for



Scheme 3.1 Synthesis of thiophene-purine-thiophene triads, M1, M2, and M3, which have 2,6- connectivity due to the use of 2,6-dichloro-9-hexyl-9*H*-purine. R = hexyl. Synthetic conditions are (i) Pd(PPh₃)₄, 2 M K₂CO₃, toluene, reflux 110 °C for 48 h; (ii) 2 eq. NBS, THF/acetic acid, rt for 6 h.

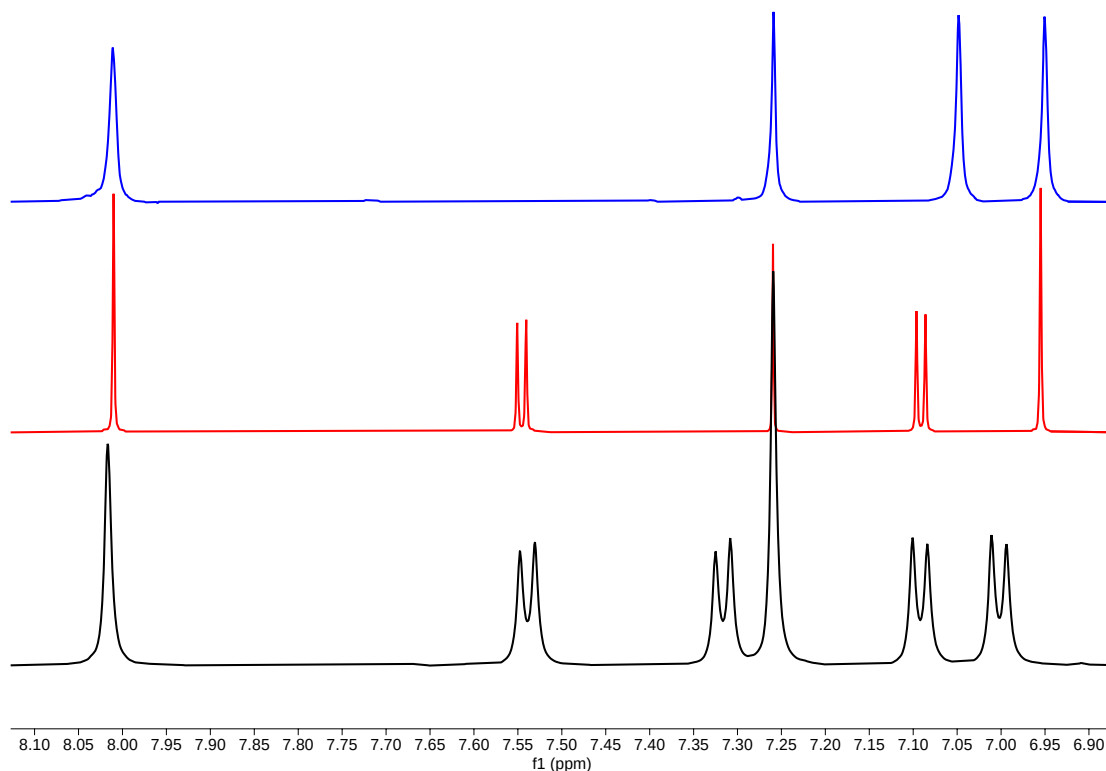


Figure 3.2 Aromatic region of the ¹H NMR spectra (in CDCl₃) confirming the conversion from M1 (black spectrum, bottom) to the monobrominated monomer, M3 (red spectrum, middle), to the dibrominated monomer, M2 (blue spectrum, top).

halogenation of one of the thienyl groups flanking the purine monomer. I hypothesized that while the thienyl groups at the *C2* and *C6* sites of the pyrimidine ring should have similar reactivity, differences in orbital overlap with the purine scaffold changes their reactivity towards electrophilic aromatic substitution making the thienyl group at the *C2* position of the purine more reactive toward aromatic electrophilic bromination. The ^1H NMR spectra of **M3** in **Figure 3.2** (red, middle) shows that only one monobrominated product is produced during the electrophilic aromatic bromination. This can be appreciated by recognizing that the carbons on the thienyl rings at the *C2* and *C6* positions are not magnetically equivalent.

3.4.2 2-D NMR Characterization of Monomers

2-D NMR was used to confirm the electrophilic substitution on the thienyl ring coupled at the *C2* position on the purine scaffold. The conclusion that the *C2* thienyl ring undergoes electrophilic aromatic bromination first was established by examining multi-bond correlations between carbons and protons of the **M3** monomer, and comparing these to spectra for **M2** and **M1**. After standard ^1H and ^{13}C NMR spectra were acquired, heteronuclear single-quantum coherence (HSQC) and heteronuclear multiple-bond correlation (HMBC) experiments were done for each monomer. $^1\text{H} - ^{13}\text{C}$ HSQC is used to determine single bond proton-carbon correlations, and the results are presented in a 2-D spectrum comprised of the ^1H NMR spectrum along the horizontal axis and the ^{13}C spectrum along the vertical axis. The HSQC spectrum shows the correlations between each proton attached to the purine scaffold or thienyl rings and the carbon atom to which they

are directly bound. These spectra can be found in Appendix B. (See **Figures B.4, B.5, and B.6** for the HSQC spectra of **M1**, **M2**, and **M3**, respectively.)

The $^1\text{H} - ^{13}\text{C}$ HMBC experiment correlates chemical shifts of protons and carbons separated by two or more chemical bonds. Generally $^1\text{H} - ^{13}\text{C}$ HMBC can show protons correlating to carbons at a distance of two to three bonds, but long-range $^1\text{H} - ^{13}\text{C}$ HMBC correlations have been observed between carbons and protons that are four or even five bonds apart.³⁰⁻³² Specifically, $^1\text{H} - ^{13}\text{C}$ HMBC has been used to observe long-range correlations between the aromatic protons and carbons of 2,6-disubstituted purines.³³ $^1\text{H} - ^{13}\text{C}$ HMBC spectra of the **M1**, **M2**, and **M3** monomers show useful long-range correlations that aid in distinguishing which site (carbon atom) on the TPT triad is brominated first via aromatic electrophilic bromination. Full $^1\text{H} - ^{13}\text{C}$ HMBC spectra for the monomers can be found in Appendix C, **Figures B.7-B.9**. The $^1\text{H} - ^{13}\text{C}$ HMBC 2 – 3 bond correlations can be used to assign many of the carbon and proton peaks in the NMR spectra. Specifically, in the $^1\text{H} - ^{13}\text{C}$ HMBC spectra of **M1**, C8 and C4 of the purine scaffold both have strong 3-bond correlations to the first methylene protons of the hexyl chain added by alkylation at the N9 position of the purine. **Figure 3.3** shows this correlation outlined with a pink box, and carbons on the purine scaffold are labeled. The ^{13}C NMR peaks for C8 and C4 are at 143.5 ppm and 153.4 ppm, respectively. Similarly, we expect C5 and C4 to each have a three-bond correlation with the proton bound to C8 of the purine ring, which is within the purple box in **Figure 3.3**. This expectation assigns the carbon peak at 127.5 ppm to C5. Once the resonances due to C4, C5, and C8 of the purine scaffold are assigned, thienyl proton – carbon correlation peaks may be assigned. While it is not possible to directly assign C2 or C6 from these correlations, after assigning C4, C5, and

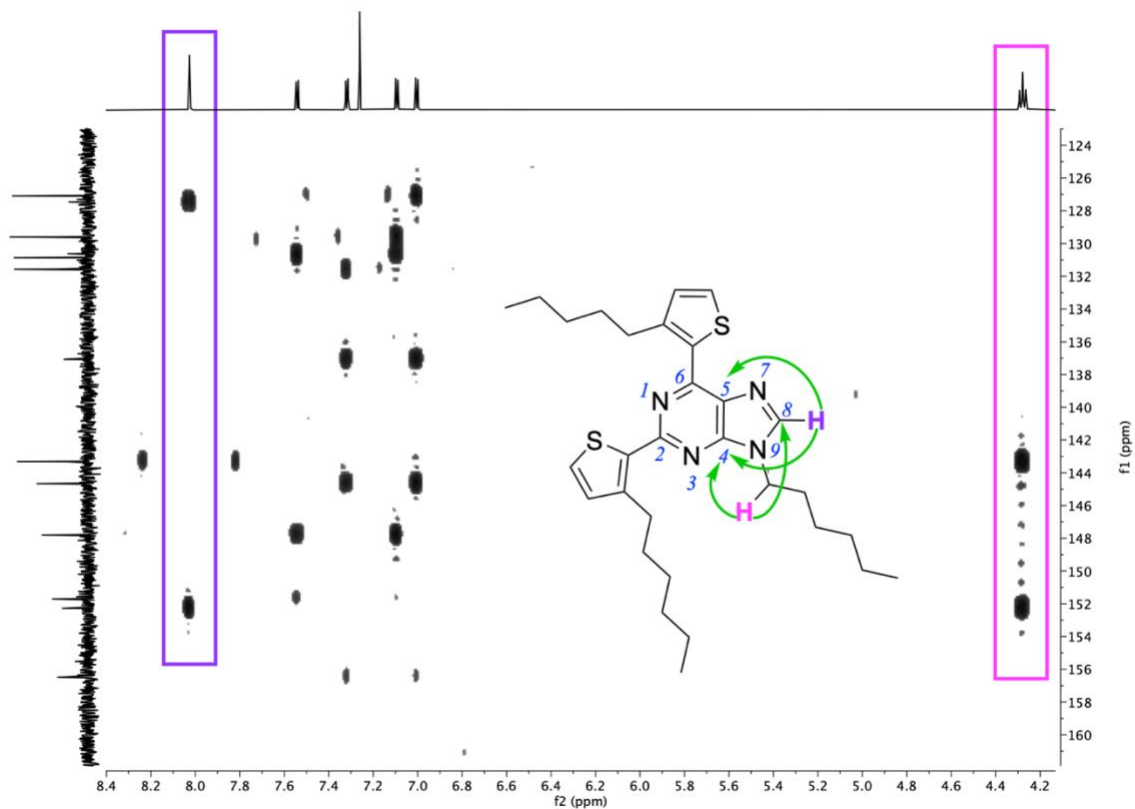


Figure 3.3 Selected region of 2-D $^1\text{H} - ^{13}\text{C}$ HMBC NMR spectra of M1 (in CDCl_3). Blue numbers label the carbons on the purine scaffold. The pink box represents correlations between the protons of the first methylene (pink) on the alkyl chain at $N9$ with $C4$ and $C8$. The purple box highlights correlations between the $C8$ proton (purple) with $C4$ and $C5$. Correlations are indicated by green arrows.

C8, there are only two aromatic carbon peaks of the purine scaffold C2 and C6, left to assign. Those carbon peaks are at 151.7 ppm and 156.5 ppm for **M1**. The other aromatic peaks are associated with the thienyl rings. Because the purine scaffold has been widely studied via 2-D NMR, it is generally accepted that the C2 peak will be further downfield than the C6 peak.^{33–37} Specifically, Hocek *et al.* found that when phenyl groups were substituted at the C2 and C6 positions, the carbon NMR peaks for C2 and C6 were at 157.6 ppm and 152.5 ppm, respectively.³⁷ Thus, with this in mind, the ¹³C NMR peak at 156.5 ppm is assigned to C2 and the ¹³C NMR peak at 151.7 ppm is assigned to C6.

To confirm the carbon peak assignments for C2 and C6, a proton-proton nuclear Overhauser effect spectra (¹H – ¹H NOESY) was acquired for **M1**. NOESY is a 2-D NMR spectroscopy method that can be used to determine signals between two equivalent atoms that are close to each other in space even when not directly bonded.^{38,39} NOESY is most commonly used for ¹H – ¹H bond correlations, but it can be used for other magnetically active atoms (including ¹³C).⁴⁰ The ¹H – ¹H NOESY spectra of **M1**, which is presented in **Figure 3.4**, shows a correlation between protons that are on the first two methylene (CH₂) groups on the N9 hexyl chain and protons on the first two methylenes of one of the hexyl chains attached to a thienyl ring. These correlation peaks are outlined in orange boxes in **Figure 3.4**. Because of the rigidity of the fused ring heteroaromatic purine scaffold and the spatial distance between the C6-thienyl ring and the N9 hexyl chain, we conclude that the only hexyl group in proximity to the first sets of methylene protons (labeled H_a and H_b) of the N9 hexyl chain are those belonging to the hexyl chain on the C2-thienyl ring (labeled H_c and H_d). Additionally, ¹H – ¹H NOESY spectra of **M1** shows no

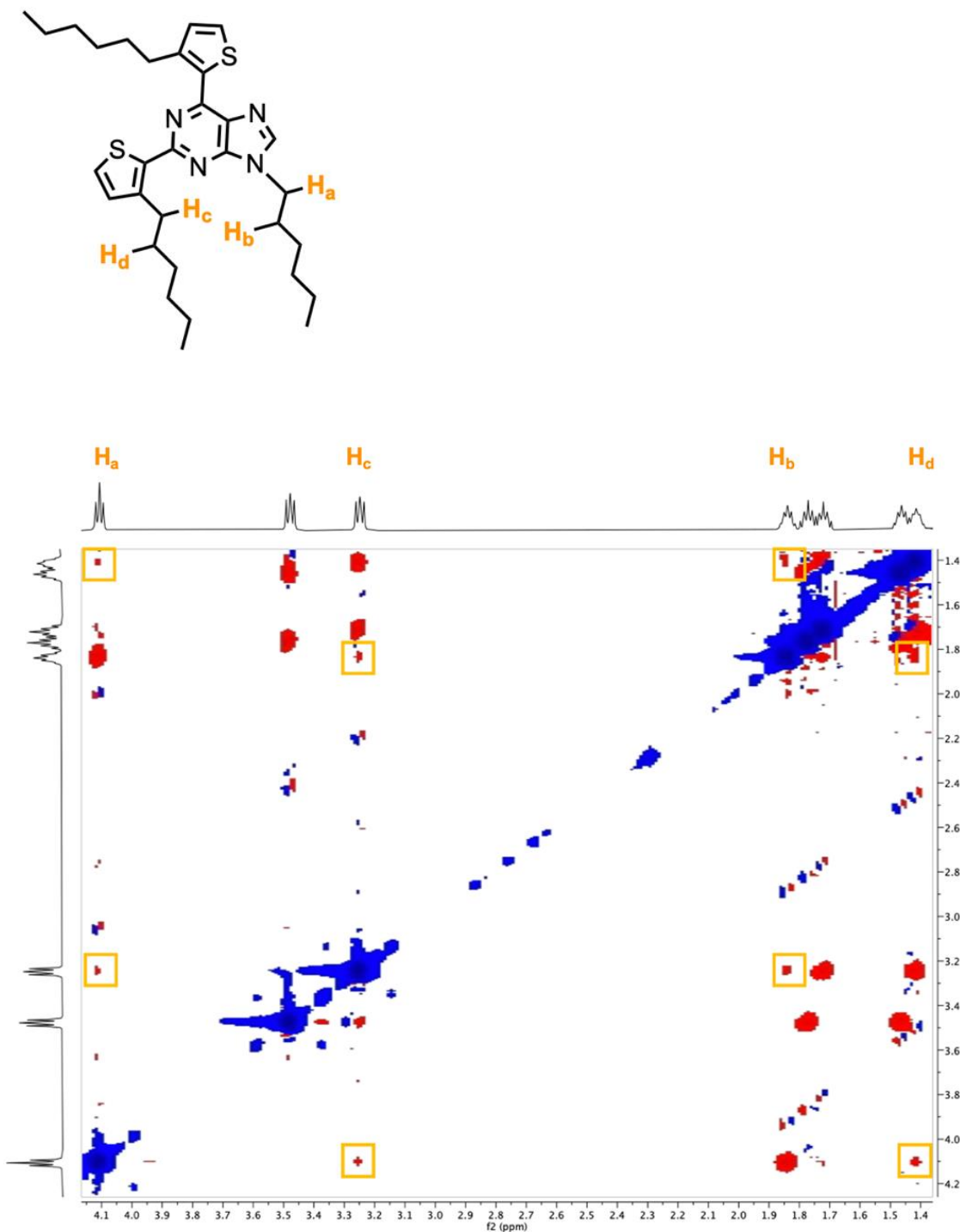


Figure 3.4 Selected region of 2-D ^1H – ^1H NOESY NMR spectra of M1 (in CDCl_3). The orange boxes represent correlations between the protons of the first methylene of the *N*9 alkyl chain with the protons of the first methylene of the alkyl chain of the *C*2 thienyl ring. The protons discussed are also colored orange.

correlation between the C8-proton and the hexyl chain attached to the C6-thienyl ring. Because of these insights, we are able to settle the ambiguity remaining from the $^1\text{H} - ^{13}\text{C}$ HMBC experiment, confirming the ^{13}C peak assignments for C6 and C2 of **M1** as being 151.7 ppm and 156.5 ppm, respectively.

The same sets of 2-D NMR experiments were completed and analyzed for each of the three monomers and their $^1\text{H} - ^{13}\text{C}$ HSQC and $^1\text{H} - ^{13}\text{C}$ HMBC spectra can be found in **Figures B.4-B.9** of Appendix B. **Figure 3.5** shows a stacked image of the 2-D $^1\text{H} - ^{13}\text{C}$ HMBC NMR spectra of **M1** (black, bottom), **M2** (blue, top), and **M3** (red, middle) covering the region from 3.0 ppm – 8.35 ppm. The pink boxes highlight correlations between the C2 or C6 carbons, which are now unambiguously assigned, and the aromatic protons of the thienyl ring that are four bonds apart, as indicated by the green arrows in **Figure 3.5**. The 2-D $^1\text{H} - ^{13}\text{C}$ HMBC NMR spectra of **M1** (bottom) shows correlations between the C2 carbon on the purine scaffold and the protons on the thienyl ring coupled at C2, as well as correlations between C6 and the protons on the thienyl ring coupled at C6. These result in four long-range correlation peaks. The long-range correlations seen in the monobrominated species (**M3**) and the dibromo monomer (**M2**) are compared to realize that under the conditions selected for bromination, bromination is selective for the thienyl at C2. The spectra also settle where on the thienyl ring the bromination occurs. **Figure 3.6** shows a selected region of the 2-D $^1\text{H} - ^{13}\text{C}$ HMBC NMR spectra for the monobrominated, purine-containing triad **M3**. The spectra are labeled to identify important proton and carbon peaks.

As discussed earlier, noncovalent conformational locks can be used to increase the planarity of small molecules and polymers.^{17–22,41–43} The 2-D NMR spectra of **M1**, **M2**,

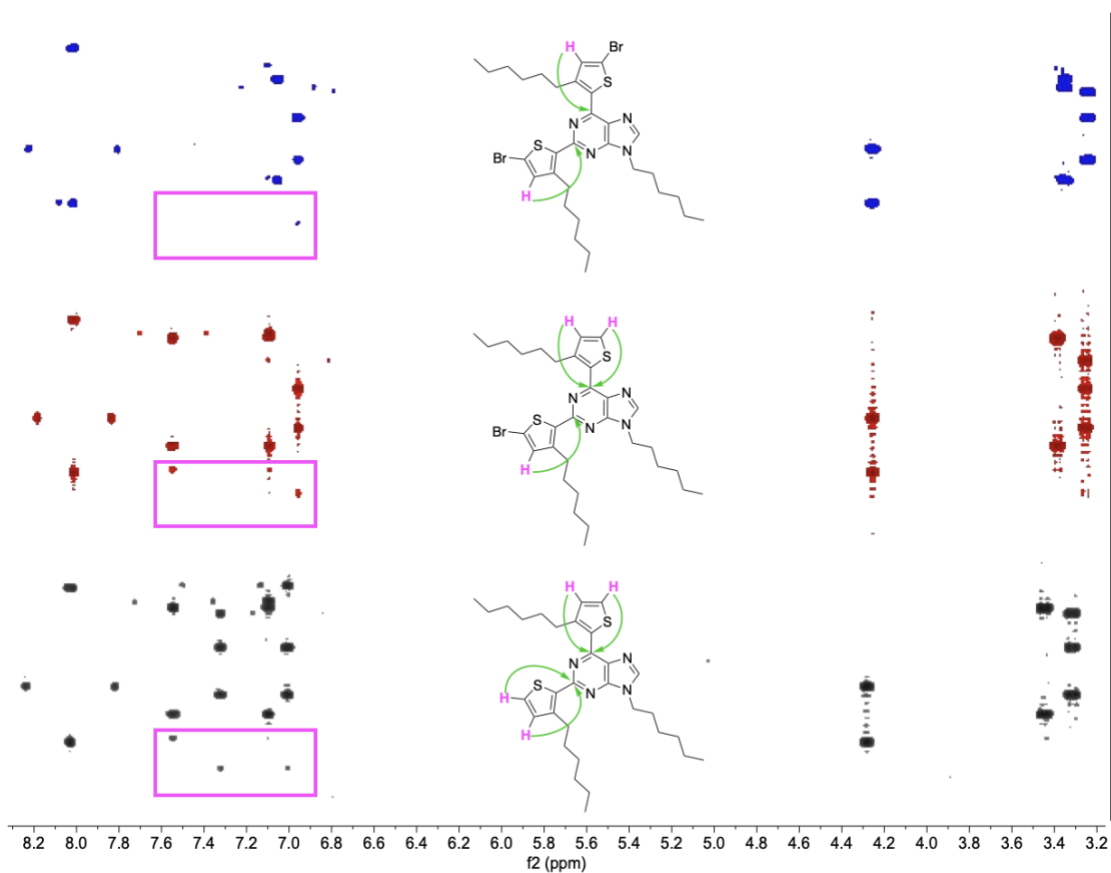


Figure 3.5 Comparison of the 2-D ^1H – ^{13}C HMBC NMR spectra (in CDCl_3) of M1 (bottom), M2 (top), and M3 (middle). The pink boxes represent four-bond correlations between the thienyl protons (colored in pink in the inset structures) and the carbon (C2 or C6) of the purine scaffold to which these thienyl rings are attached. The proton-carbon correlations are indicated by green arrows on the inset structures.

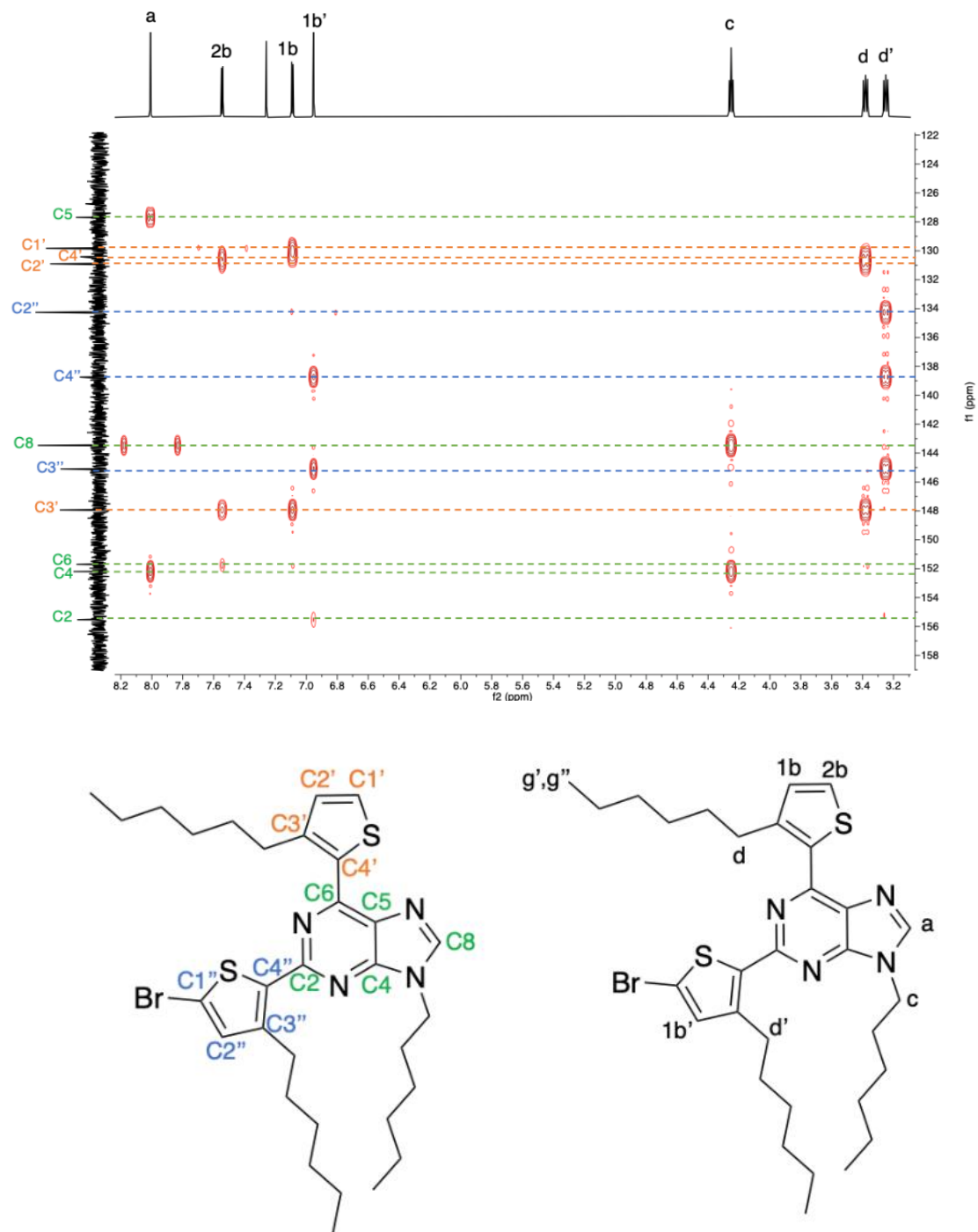


Figure 3.6 Selected region of 2-D ^1H – ^{13}C HMBC NMR spectra of M3 (in CDCl_3). Each proton and carbon indicated in the figures below the spectra are labeled to correspond to peaks in the spectra.

and **M3** reveal a specific conformation of the thienyl groups that are attached to the purine scaffold. This conformation can be seen in any of the figures along with the 2-D spectra, and **Figure 3.7** reproduces the conformation with the S $\cdots$ N conformational locks denoted by dashed lines. We arrive at this structure by emphasizing two points made earlier: First, the 2-D $^1\text{H} - ^1\text{H}$ NOESY NMR spectra specifically suggests that the hexyl chain of the C2-thienyl group and the N9 hexyl chain are in close proximity to each other – protons from each chain interact. Second, the lack of correlation between C8-H and the protons of the hexyl chain of the thienyl ring attached at C6 indicates that the hexyl chain on the C6 thienyl ring is not in close proximity to the C8-H of the purine ring. In addition, the hexyl chains of both thienyl rings have no $^1\text{H} - ^1\text{H}$ NOESY correlation peaks, which means that those hexyl chains are not in spatial proximity (not interacting with one another). With all of these points in mind, there is only one conformation of the thiophene-purine-thiophene monomers that would have the indicated magnetic environments and interactions, and this structure is depicted in **Figure 3.7**. Because the peaks observed in the 2-D HMBC and NOESY NMR spectra of the monomers suggest a noncovalent conformational lock for purine monomers, a crystal structure was acquired for **M1**. The conformation deduced via NMR for **M1** is also the only conformation observed in the solid-state crystal structure of **M1**, which can be found in Appendix B, **Figure B.22**. Because this conformation is the only one observed in solution and in the solid state, it is likely the dominant conformation of monomers **M1-M3**.

3.4.3 Synthesis of Purine-Containing Copolymers

Direct arylation cross-coupling copolymerization for the AA+BB polymer was

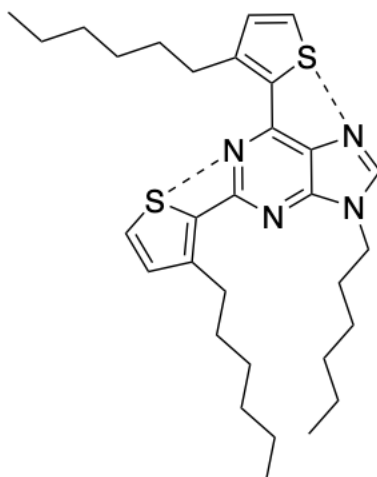


Figure 3.7 Observed conformation of M1 in solution and solid state. Noncovalent conformation S···N locks are indicated with dashed lines.

performed by combining comonomers (**M1** and **M2**) in a 1:1 stoichiometric ratio (0.15 mmol of each comonomer) with Pd(OAc)₂, PivOH, and K₂CO₃ in N,N-dimethylacetamide at 95 °C, as described in Chapter II. The resulting AA+BB copolymers had number-average molecular weights ranging from 4.5 – 10.1 kg/mol with yields ranging from 68 – 83%, as reported in **Table 3.1**. The AB polymer synthesized using **M3** was made under similar conditions, but instead of equimolar ratios of the two comonomers at 0.15 mmol each, twice as much of the AB monomer was added (0.3 mmol). The AB polymers had number-average molecular weights ranging from 5.0 – 18.4 kg/mol with yields ranging from 29 – 81%, as reported in **Table 3.1**. The conditions used for polymerization were selected based on a variety of studies in which the synthesis of poly(3-hexylthiophene) by DArP was optimized to avoid regioerrors (or “defects”), as discussed in Chapter II.^{44–47}

Because of the influence molecular weight has on optoelectronic properties (which was previously discussed in Chapter II), we used AB and AA+BB polymers that had a similar number of purines within the main chain and that were above the effective conjugation length, which for our purposes was identified as the molecular weight at which optical properties became insensitive to chain size. This means we studied the purine-containing AB and AA+BB polymers having $M_n = 9$ kg/mol (nominal value). These polymers are indicated by boldfaced text in **Table 3.1**. The macromolecular characteristics of the entire set of copolymers are summarized in **Table 3.1**, and their ¹H NMR spectra are presented in **Figure A.8** and **Figure B.11**. All ¹H NMR resonances show the broadening expected for polymers, as well as the characteristic signature of the C8-H proton (at $\delta = 8.0$ ppm). **Figure 3.8** shows ¹H HMR spectra for the AA+BB copolymer (bottom, blue) and AB polymer (top, red) in the region from 3.0-8.5 ppm. The aromatic region of these

Table 3.1 Yield and macromolecular characteristics of purine-containing polymers (AA+BB and AB) synthesized by DArP.

	Yield (%)	M_n (kg/mol) ^a	$\bar{D}$
AA+BB			
1	68%	4.5	1.8
2	71%	9.0	2.2
3	83%	10.1	1.7
AB			
1	29%	5.0	1.4
2	81%	9.2	1.4
3	73%	18.4	1.9

^aNumber-average molecular weights (M_n) were measured by GPC (mobile phase of THF at 25 °C) using universal calibration analysis based on polystyrene (PS) standards. ^b X_n is the average degree of polymerization based on M_n . *Data in bold identifies the copolymer that was used for optoelectronic characterizations.

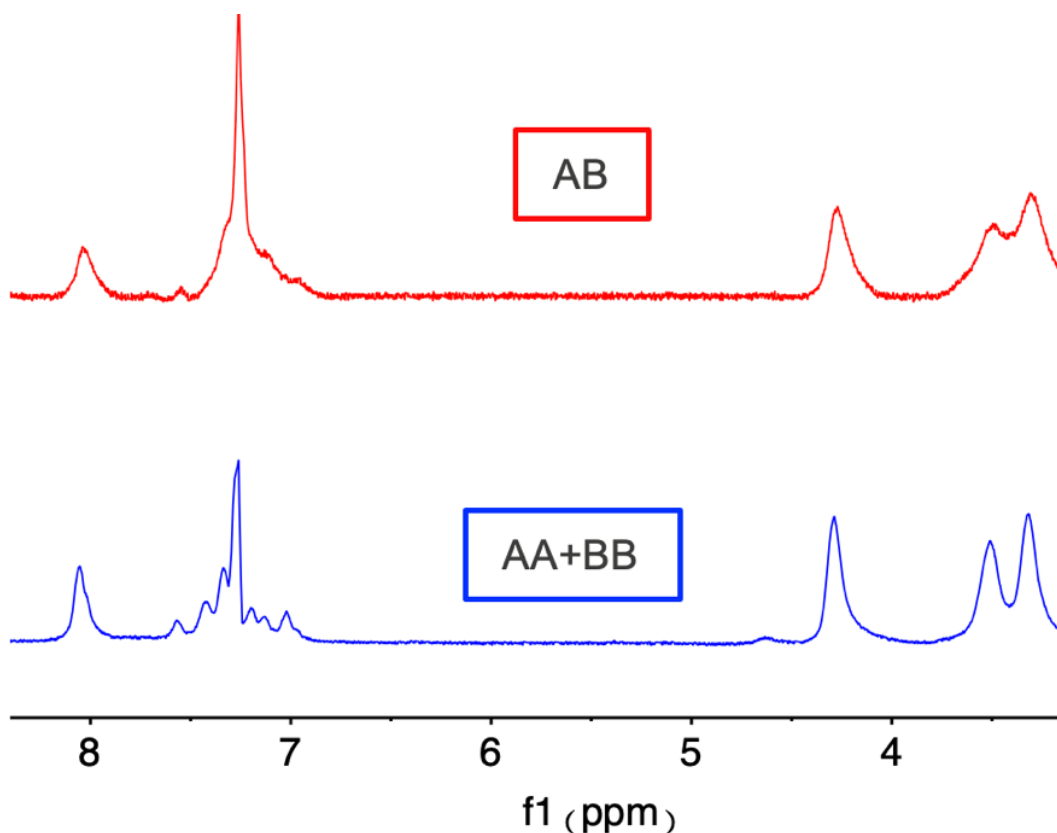


Figure 3.8 Comparison of ¹H NMR spectra of purine-containing polymers AB (top) and AA+BB (bottom) from 3.0 ppm to 8.3 ppm.

NMR spectra shows that the AA+BB copolymer has additional resonances compared to the AB polymer, which is likely due to the AB polymer being more regioregular than the AA+BB counterpart. We anticipate that in the cross-coupling between the AA monomer **M1** and the BB monomer **M2** (AA+BB copolymerization), the second monomer can add either the thienyl ring on the C2 carbon of the purine or through the thienyl ring on the C6 carbon of the purine, which will lead to a higher number of magnetically inequivalent protons. This is discussed in more depth in the following section.

3.4.4 Characterization of Purine-Containing Polymers (AA+BB and AB)

2-D NMR studies, including HSQC, HMBC, and NOESY, were used to examine the AA+BB and AB purine-containing polymers. The $^1\text{H} - ^{13}\text{C}$ HSQC NMR spectra for the AA+BB copolymer has more single bond carbon – proton correlations than what is observed for the AB purine-containing polymer. These additional correlations are due to the asymmetry of the **M1** and **M2** comonomers, which leads to head-to-head or tail-to-tail additions and results in additional magnetically inequivalent carbon – proton correlations. On the other hand, the AB monomer (**M3**) should undergo head-to-tail additions, leading to a simpler spectrum. This is, in fact, reflected in the spectra presented in **Figure 3.9**, with **Figure 3.10** showing the configurations resulting from idealized coupling due to the transition metal-catalyzed C-H activation mechanism proposed for DArP. The $^1\text{H} - ^{13}\text{C}$ HSQC NMR spectra for the AA+BB copolymer (**Figure 3.9**, bottom) has 13 peaks in the aromatic region, with the peaks at 6.93 ppm and 7.03 ppm being attributed to the end group of the BB (-dibromo) monomer, **M2**. The $^1\text{H} - ^{13}\text{C}$ HSQC NMR spectra for the AB polymer (**Figure 3.9**, top) has 8 carbon – proton correlations in the aromatic region, with the peak

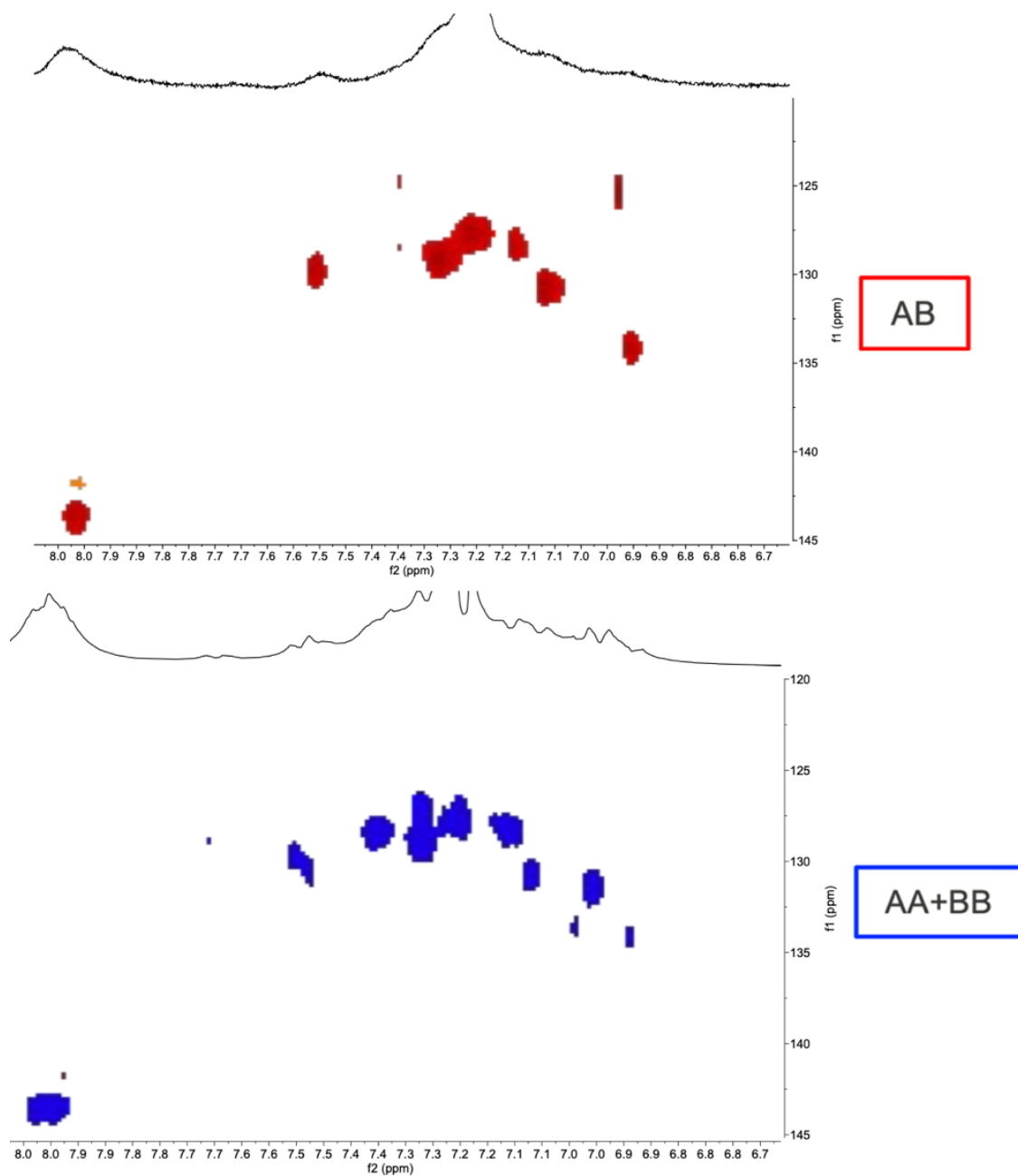
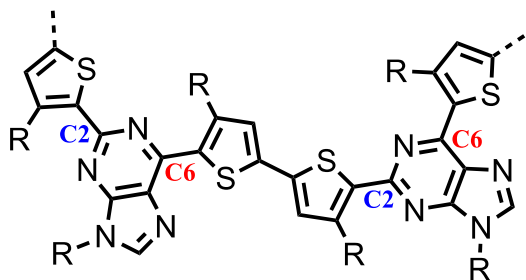


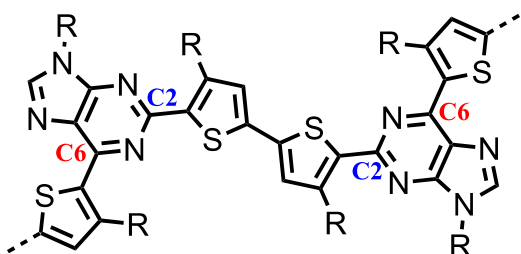
Figure 3.9 Selected region of 2-D ^1H – ^{13}C HSQC NMR spectra (acquired in CDCl_3). The top spectra (red) is derived from the AB polymer and the bottom spectra (blue) is derived from the AA+BB copolymer.

Head-to-Tail Addition:



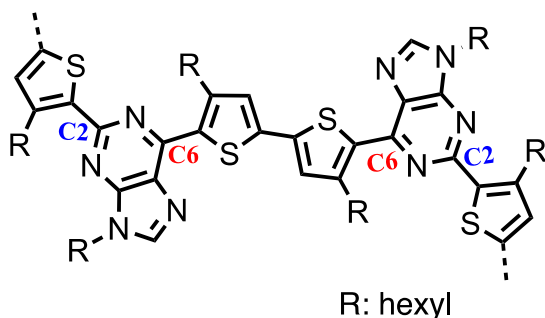
-DArP of **M3** should result in head-to-tail addition. Head-to-tail additions can also occur in copolymerization of **M1** and **M2**.

Head-to-Head Addition:



-Could result from copolymerization of **M1** and **M2**.

Tail-to-Tail Addition:



R: hexyl

-Could result from copolymerization of **M1** and **M2**.

Figure 3.10 Possible additions of AA and BB comonomers, including head-to-tail (top), head-to-head (middle), and tail-to-tail (bottom) addition. The C2 and C6 carbons on the purine ring are labelled with blue and red, respectively. In these depictions, defects due to homocoupling of H/H monomers or due to activation of other aromatic hydrogens are ignored.

at 6.97 ppm being attributed the bromine from a thienyl-ring end group proton. All the other peaks in the aromatic region of the $^1\text{H} - ^{13}\text{C}$ HSQC NMR spectra of the AB polymer are also observed in the $^1\text{H} - ^{13}\text{C}$ HSQC NMR spectra acquired for the AA+BB copolymer.

The $^1\text{H} - ^{13}\text{C}$ HMBC NMR spectra for the AA+BB copolymer also has more two- and three- bond correlations compared to the AB polymer. (See **Figure 3.11.**) While some of the peaks in the AA+BB $^1\text{H} - ^{13}\text{C}$ HMBC NMR spectra may be attributed to end groups, the new proton correlations at 7.40 ppm and 7.36 ppm are attributed to either head-to-head or tail-to-tail coupling. While there is not enough information to discern which coupling is occurring, it is likely that the tail-to-tail coupling is dominant compared to head-to-head coupling because the C6 position on the purine is more reactive toward cross-coupling reactions.^{48–52} **Figure 3.9** depicts the various structures that may be formed from cross-couplings. The full $^1\text{H} - ^{13}\text{C}$ HSQC and $^1\text{H} - ^{13}\text{C}$ HMBC NMR spectra for the AA+BB and AB polymers are presented in **Figures B.12 – B.15** of Appendix B.

The 2-D $^1\text{H} - ^1\text{H}$ NOESY NMR spectra of the AA+BB copolymer and the AB polymer, which are shown in Appendix B, **Figure B.16** and **Figure B.17**, show where the endgroup NMR peaks for each polymer are and show differences in the number of correlation peaks observed. Specifically, the 2-D $^1\text{H} - ^1\text{H}$ NOESY NMR spectra generated from the AA+BB copolymer shows four $^1\text{H} - ^1\text{H}$ NOESY correlations in the aromatic region, which result from the AA (-dihydro) monomer, while the spectra generated from the AB polymer only shows two aromatic NOESY proton – proton correlations. Further, the 2-D $^1\text{H} - ^1\text{H}$ NOESY NMR spectra of both polymers have correlations that are similar to those that defined the conformation of monomer **M1**. Specifically, proton-proton correlations in the spectra indicates that the hexyl chains of the thienyl group on C2 and

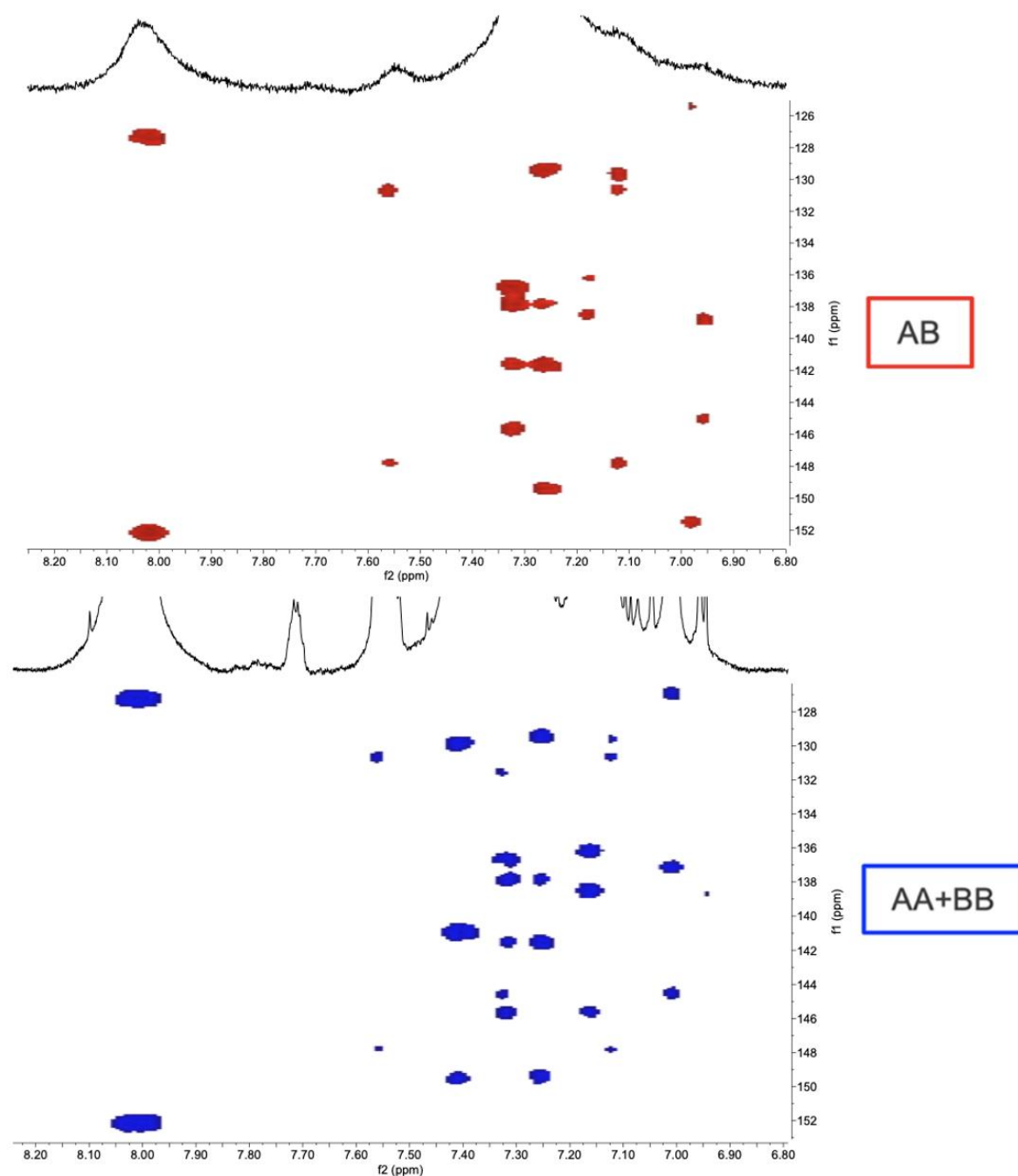


Figure 3.11 Selected aromatic region of 2-D ^1H – ^{13}C HMBC NMR spectra (acquired in CDCl_3). The top spectrum (red) is the AB polymer and the bottom spectra (blue) is the AA+BB copolymer.

the N9 hexyl chain are near each other, which indicates that the noncovalent conformational lock is not lost during polymerization. (See **Figure B.16** and **Figure B.17**.) Previous reports also describe noncovalent S $\cdots$ N conformational locks being maintained during the synthesis of conjugated polymers and oligomers.^{16–18,20,43}

The optoelectronic characteristics of the AA+BB and AB polymers in solution have a few key differences. As seen in **Figure 3.12** and listed in **Table 3.2**, the absorbance onsets and absorbance maxima are within 5 nm of one another, but the AB polymer has a red-shifted shoulder. We suspect this is due to the regioregular structure, which enables π -stacking (which is typically why a vibronic shoulder appears). **Figure 3.12** also presents the emission spectra acquired from the AA+BB and AB polymers. (The Beer-Lambert plot for the AB polymer is in Appendix B, **Figure B.21**, while the Beer-Lambert plot for the AA+BB copolymer was presented in Appendix A, **Figure A.26**) The emission spectra of the AB polymer is red shifted compared to the AA+BB copolymer, which results in a larger Stokes shift (103 nm) for the AB polymer compared to that of the AA+BB copolymer (90 nm). This larger Stokes shift for the AB polymer is attributed to a higher degree of structural reorganization upon photoexcitation, which agrees with the idea of the chain having a more regioregular structure for the AB polymer. Conversely, the AA+BB copolymer is more regiorandom, leading to a less pronounced reorganization upon photoexcitation. The photoluminescent quantum yield (Φ) was measured to be the same for both polymers ($\Phi = 0.19$). As seen in **Figure 3.13**, the absorbance spectrum acquired from the AA+BB copolymer thin film is red-shifted compared to the spectrum acquired in solution, which is consistent with the behavior observed for the AA+BB copolymer (reported in Chapter II). While the spectrum acquired for the AA+BB copolymer as a solid

Table 3.2 Optoelectronic data for purine-containing AA+BB and AB polymers and the M1 monomer.

	$\lambda_{\text{max}}^{\text{abs}^a}$	$\lambda_{\text{onset}}^{\text{abs}^a}$	$\lambda_{\text{max}}^{\text{em}^a}$	$\lambda_{\text{onset}}^{\text{em}^a}$	Stokes shift ^a (nm)	Φ	Opt E _{gap} ^b (eV)
M1	309	377	405	488	96	0.12	--
AA+BB	424	492	514	630	90	0.19	2.41
AB	425	497	528	647	103	0.19	2.41

^aUV-Vis and fluorescence spectra were acquired from CHCl₃ solutions. ^bBased on UV-Vis spectra acquired from drop cast thin films on glass slides.

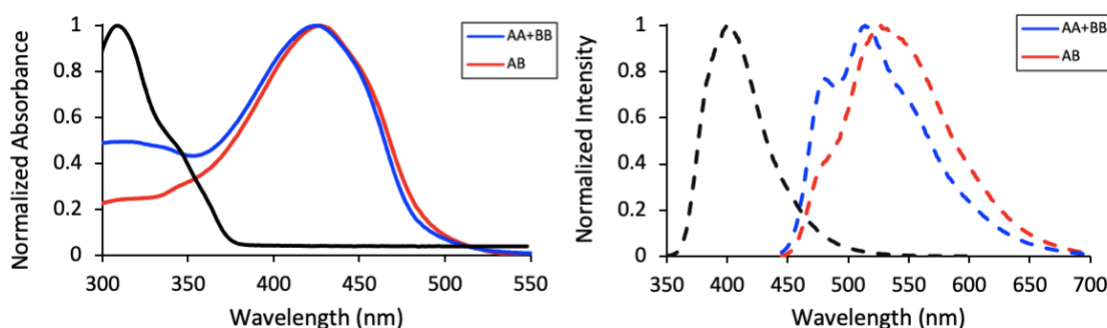


Figure 3.12 Normalized absorbance spectra (left) and normalized emission spectra (right) of M1 (black) and the purine-containing polymers synthesized by DArP of AA+BB comonomers M1 and M2 (blue) and an AB monomer (M3) AA+BB (red). All spectra were measured at a concentration of 0.01 mg/mL in chloroform.

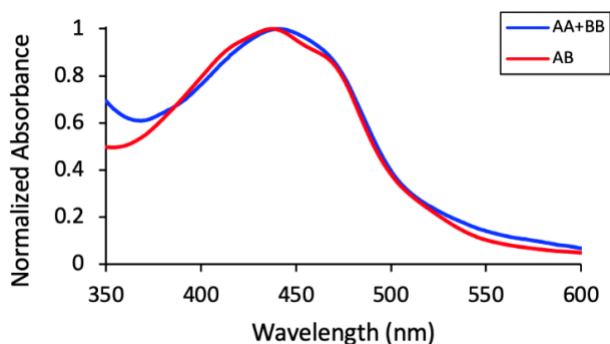


Figure 3.13 Normalized absorbance spectra the purine-containing polymers synthesized by DArP of AA+BB comonomers M1 and M2 (blue) and an AB monomer (M3) AA+BB (red). Films were drop cast from a chloroform solution at 1.0 mg/mL.

film is monomodal, the absorbance spectrum for a film of the AB polymer has the same absorbance maxima as the AA+BB copolymer but vibronic shoulders on either side of the absorbance maxima are observed. These are characteristics of enhanced chain packing that also facilitate transitions related to inter-chain exciton delocalization.⁵³ Although there is a subtle difference in the shapes of thin film absorbance spectra, as reported in **Table 3.2**, the optical bandgaps for the AA+BB copolymer and the AB polymer are the same (2.41 eV).

3.5 Conclusions

Regioregularity and conformation play important roles in the organization and properties of conjugated polymers. This work described in this chapter examines the synthesis and basic optoelectronic properties of two purine-containing, fully conjugated polymers derived from the TPT repeat units. One is made by DArP of an AB monomer, which ideally produces a regioregular polymer, and one is made by an AA+BB copolymerization, which because of the asymmetry of the purine scaffold, is likely to yield regiorandom copolymers. 2-D NMR techniques – HSQC, HMBC, and NOESY – were used to assign proton and carbon resonances of the monomers and their corresponding polymers. Noncovalent S $\cdots$ N conformational locks are observed in the crystal structure of monomer **M1**, the AA monomer, and 2-D NMR confirms that the conformational lock is maintained in both the AB and AA+BB polymers. While NMR characterizations suggest that there are differences in the regioregularity of the AB and AA+BB polymers, the optoelectronic properties of the two purine-containing polymers are largely unchanged. The thin film absorbance spectra of the AB polymer have characteristics attributed to close

packing brought about by π -stacking interactions, but these are not observed in the AA+BB, likely due to its regiorandom configuration.

3.6 References

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**CHAPTER IV: IMPACT OF RIGID COMONOMER DESIGN AND
THIENYL π -LINKERS ON THE OPTOELECTRONIC PROPERTIES
OF CONJUGATED PURINE-CONTAINING COPOLYMERS**

A version of this chapter is in preparation for submission to *ACS Omega*. It is authored by C. Elizabeth O’Connell with coauthors Samantha M. Cahill, Brian K. Long, and S. Michael Kilbey II. “Impact of Rigid Comonomer Design and Thienyl π -Linkers on the Optoelectronic Properties of Cross-conjugated Purine-Containing Copolymers.” I synthesized all of the monomers and copolymers described in this work and performed all physical and optoelectronic characterizations. Coauthor Samantha M. Cahill assisted with the purification and characterization of the monomers and copolymers. Brian K. Long and S. Michael Kilbey II advised this work.

4.1 Abstract

Highly emissive conjugated polymers are of interest for their application in photonic devices and sensors, and generally require conjugated polymers with highly rigid main chains. Herein, we describe how extending the conjugation by adding thienyl π -linkers between comonomers affects the optoelectronic properties such as quantum yield, bandgap, and exciton binding energy of cross-conjugated purine-containing copolymers. Noncovalent S $\cdots$ N conformational locks in the purine-containing comonomer, 9-hexyl-2,6-bis(3-hexylthiophen-2-yl)-9*H*-purine, observed via $^1\text{H} - ^1\text{H}$ NOESY NMR experiments are present, leading to highly rigid, coplanar conjugated polymer main chains. Direct arylation polymerization is used to access purine-containing copolymers containing either 2,1,3-benzothiadiazole (BT), 2,7-dibromo-9-hexyl-9*H*-carbazole (Cz), 4,7-bis(5-bromothiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (TBTT), or 9-hexyl-2,7-bis(3-hexylthiophen-2-yl)-9*H*-carbazole (TCzT) as comonomers. Addition of a second thienyl π -linkers between the purine and the comonomer (BT or Cz) reduces the rigidity of the

polymer main chain, which leads to a decreased quantum yield and increased effective exciton binding energies. Optical bandgaps range from 1.95 to 2.41 eV, photoluminescent quantum yields vary from $\phi = 0.02$ to 0.95, and the effective exciton binding energies also vary widely, ranging from 0.01 to 0.46 eV.

4.2 Introduction

Conjugated polymers are integral to organic electronic devices such as light-emitting diodes, photovoltaic cells, sensors, and field-effect transistors,¹⁻³ and efforts devoted to altering monomer design to enhance solubility, optimize optoelectronic properties, and tailor morphological structures have been key themes in the pursuit of high-performing conjugated polymers.⁴⁻⁹ As with all synthetic polymers, properties and performance are strongly controlled by the chemical identity of the constituent monomers and how they are enchain. The issues are especially complex in conjugated polymer systems because optoelectronic properties are highly sensitive to modifications in molecular design, as they affect chain configuration, planarity, electronic structure, and organization over multiple length scales.¹⁰⁻¹⁵ For these reasons, it is rather difficult to predict properties and performance from the molecular structure of the repeating units.

Designing monomers to improve electronic delocalization along the π -conjugated main chain has been at the forefront of conjugated polymer research.^{16,17} One way to improve electron delocalization is through increased planarity of the polymer main chain.¹⁸⁻²⁰ Increasing the rigidity of the main chain of conjugated polymers has been shown to increase charge carrier mobility,²¹⁻²³ intramolecular charge transport,^{24,25} and emissivity.^{15,26} Noncovalent conformational locks have been used to enhance the rigidity

of the main chain of conjugated polymers.^{21,27,28} In this vein, noncovalent S $\cdots$ N conformational locks have been observed in small molecules and polymers containing organosulfur compounds,^{29–36} and these noncovalent S $\cdots$ N conformational locks have been shown to improve the planarity of the conjugated repeat unit.^{29–36} Specifically, Bazan *et al.* have installed noncovalent S $\cdots$ N conformational locks in chromophores to narrow bandgap and increase bulk organization.³³ Janssen *et al.* used noncovalent conformational locks in oligo(2,3-alkylthieno[3,4-b]pyrazine)s to decrease the optical bandgap.³²

In addition to exploiting molecular design, a common and frequently used approach to tune properties of conjugated polymers is by integrating comonomers in an alternating fashion.^{37,38} Particularly relevant to this work, we recently described the synthesis of fully conjugated copolymers containing purines in their main chain. The integration of purines was motivated by their use as small molecule chromophores with “push-pull” designs, which benefits from the highly fluorescent behavior of purines.^{39–41} Nucleobases like adenine and guanine (both of which are purines) have been studied as side chain functionality in vinyl and conjugated polymers,^{42–47} but the impact of these conjugated heteroaromatic structures as components of the polymer main chain has only recently been investigated. From that work, two examples of highly emissive, cross-conjugated copolymers having purine-containing monomers emerged. Alternating copolymers of the purine-containing comonomer 9-hexyl-2,6-bis(3-hexylthiophen-2-yl)-9*H*-purine or 2,6-bis(5-bromo-3-hexylthiophen-2-yl)-9-hexyl-9*H*-purine and either 9,9-dioctyl-2,7-diboromfluorene or 2,2'-(9,9-dioctyl-9*H*-fluorene-2,7-diyl)dithiophene, respectively, resulted in copolymers that had higher quantum yields than the corresponding fluorene-

based homopolymers⁴⁸ and fluorene-thienyl copolymers.⁴⁹ The high fluorescent quantum yield was attributed to the cross-conjugated nature and use of the highly fluorescent purine core.

Beyond molecular design and comonomer selection, optoelectronic properties can be varied by changing electronic communication along the main chain. As an example, van Pruissen *et al.* examined how cross-conjugation affects electronic properties in donor-acceptor alternating copolymers created from isoindigos with different substitution patterns (either 6,6' or the 5,5' connectivity) and either thieno[2,3-*b*]thiophene or thieno[3,2-*b*]thiophene. They showed that optical and electrochemical bandgaps did not change significantly when cross-conjugation was located in the thienothiophene or in the isoindigo repeat units or in both the donor and acceptor units; however, a blue shift in the optical absorbance spectra was observed when the cross-conjugated thieno[2,3-*b*]thiophene was incorporated into the chain.⁵¹ They demonstrated that the cross-conjugated designs limited the delocalization of the HOMO and LUMO to the donor and acceptor units, respectively, due to weakened electronic communication between the electron acceptor and electron donor units. This resulted in a decrease in the highest molecular energy level (HOMO).⁵¹ Huang *et al.* reported similar behaviors in studies of benzothiophene-flanked diketopyrrolopyrrole polymers in which the connectivity was varied to access linearly- and cross-conjugated materials.⁵² While cross-conjugation similarly resulted in localization of frontier orbitals and a blue-shift in optical absorption characteristics, the hole mobility measured for field effect transistors was significantly lower for devices made using the cross-conjugated polymer.⁵² These studies suggest that

utilizing cross-conjugation may allow optoelectronic properties to be manipulated, but the overall effect depends on the specific molecular entity.

Herein, we describe the synthesis of highly emissive, purine-containing copolymers that are cross-conjugated due to their pattern of connectivity across the purine and investigate how thienyl π -linkers and selected comonomers effect the optoelectronic properties. Comonomers were selected for their optoelectronic properties, specifically, the 2,7-dibromo-9-hexyl-9*H*-carbazole (Cz) comonomer was selected for this study because it is highly emissive, while the BT comonomer is an archetypal acceptor unit in donor-acceptor copolymers used in organic solar cells.^{39,42,53–58} In addition, we examine how the conjugated thienyl π -linker between the electron acceptor benzo[*c*][1,2,5]thiadiazole (BT) and electron donor purine (P) on photophysical properties, including quantum yield, effective exciton binding energy, and intramolecular charge transfer. The copolymers with fewer noncovalent conformational locks will likely result in a less rigid main chain, leading to lower quantum yields and higher effective exciton binding energies. This study shows how planarity of the main chain in conjugated copolymers can be altered to promote high quantum yields and low effective exciton binding energies.

4.3 Experimental Methods

4.3.1 Materials and Methods

N-Bromosuccinimide (NBS, 99%, Aldrich) was recrystallized from water and dried under vacuum before use. 2,6-dichloropurine (97%, Ark Pharm), 2,7-dibromo-9*H*-carbazole (97%, Fisher), 4,7-dibromobenzo[*c*]-1,2,5-thiadiazole (95%, Aldrich), 3-hexylthiophene-2-boronic acid pinacol ester (95%, Aldrich), 1-bromohexane (96%,

Aldrich), glacial acetic acid, (Fisher Chemical), potassium carbonate (99%, Aldrich), Pd(PPh₃)₄ (98%, Aldrich), Pd(OAc)₂ (98%, Aldrich), pivalic acid, PivOH (99%, Aldrich), anhydrous *N,N*-dimethylacetamide (DMAc, 99%, Sigma Millipore) anhydrous *N,N*-dimethylformamide (DMF, 99.8%, Acros Organics), anhydrous toluene (99.8%, Acros Organics), anhydrous tetrahydrofuran (THF, 99.9%, Fisher), hexanes (95%, Fisher), methanol (99%, Fisher), and chloroform (98%, Fisher) were used as received unless stated otherwise. 2,6-dichloro-9-hexyl-9*H*-purine was used to synthesize two monomers, designated as **M1**, and **M2**, according to previous reports, and Chapters II and III.⁵⁸ Monomers and polymers were synthesized using standard Schlenk line techniques under an argon atmosphere.

¹H NMR spectra of the copolymers and monomers were acquired at room temperature in CDCl₃ using a Varian Mercury Vx 300 MHz NMR. Chemical shifts are referenced to residual solvent peaks. Number-average molecular weights, *M_n*, and dispersity, *D*, were determined via gel permeation chromatography (GPC). Measurements were made using an Agilent 1260 Infinity II system that used tetrahydrofuran (THF) as the mobile phase at a flow rate of 1 mL/min at 25 °C, and molecular weights are reported based on universal calibration. The system was equipped with a guard column and two PLgel Mixed-C columns (300 mm length), which have a lower limit of 200 g/mol and an upper limit of 2×10⁶ g/mol. Polymer solutions for GPC analysis were prepared at 5 mg/mL in THF and passed through a 0.2 μm PTFE filter prior to injection. Optical absorbance spectra of the copolymers in CHCl₃ were acquired using a Thermo Scientific Evolution 600 spectrophotometer by scanning from 350 nm to 600 nm. A Cary 5000 UV-Vis-NIR spectrometer was used for thin film measurements, and spectra were acquired by scanning

from 350 nm to 650 nm. Beer-Lambert plots for the copolymers were constructed from measurements of samples of known concentration in CHCl_3 . Fluorescence emission spectra were measured in CHCl_3 using a Cary Eclipse fluorescence spectrophotometer. Samples were excited at the absorbance maximum, $\lambda_{\text{max}}^{\text{abs}}$, measured for each copolymer and spectra were recorded by scanning from $(\lambda_{\text{max}}^{\text{abs}} + 10)$ nm to 700 nm. Cyclic voltammetry was performed in acetonitrile (99.9%, Aldrich) at a scan rate of 150 mV s^{-1} using a CHI 900B Scanning Electrochemical Microscope Bipotentiostat. Films were drop cast onto a 3 mm Au working electrode from a 1 mg/mL dichloromethane solution. The supporting electrolyte was $(n\text{Bu})_4\text{NPF}_6$ (99%, Aldrich) with Ag/AgCl as the reference electrode and a tungsten wire as the counter electrode.

4.3.2 Synthesis of Monomers and Purine-Containing Copolymers

2,6-dichloro-9-hexyl-9H-purine, 9-hexyl-2,6-bis(3-hexylthiophen-2-yl)-9H-purine (**M1**), and 2,6-bis(5-bromo-3-hexylthiophen-2-yl)-9-hexyl-9H-purine (**M2**) were synthesized by previously reported methods.⁵⁸ The ^1H NMR shifts observed and other characterization results were consistent with previous reports⁵⁸ and are available in Appendix C.

4.3.3 Synthesis of 2,7-Dibromo-9-hexyl-9H-carbazole

2,7-dibromo-9H-carbazole (1.001 g, 3.081 mmol) and potassium carbonate (2.190 g, 15.87 mmol) were added to 250 mL round bottom flask equipped with a stir bar. Dried and sparged DMF (70 mL) was added to the round bottom flask under a positive pressure of argon, and the resulting mixture was stirred for 5 minutes at room temperature. Then, 6-

bromohexane (1.10 mL, 7.837 mmol) was added via syringe and the mixture stirred for 15 h at room temperature. After 15 h, the reaction mixture was poured into 20 mL of dichloromethane and washed with brine (3×25 mL). The organic layers were combined, and solvent was removed via rotary evaporation under reduced pressure. The product was recovered at a yield of 88%. ¹H NMR spectrum of 2,7-dibromo-9-hexyl-9*H*-carbazole (300 MHz, 25 °C, CDCl₃) δ (ppm): 0.77-0.99 (m, 9H, CH₃), 1.18-1.50 (m, 18H, CH₂), 1.67 (p, 4H, CH₂), 1.91 (p, 2H, CH₂), 2.76 (t, 4H, ArCH₂), 4.33 (t, 2H, NCH₂), 7.05 (d, 2H, ArH), 7.28 (d, 2H, ArH), 7.34 (d, 2H, ArH), 7.47 (s, 2H, ArH), 8.11 (d, 2H, ArH). (See **Figure C.1** in Appendix C.)

4.3.4 Synthesis of 9-hexyl-2,7-bis(3-hexylthiophen-2-yl)-9H-carbazole

An oven-dried 100 mL round bottom flask equipped with a stir bar was flushed with inert gas. After it cooled room temperature, 2,7-dibromo-9-hexyl-9*H*-carbazole (350.1 mg, 0.8554 mmol) and dried/degassed toluene (25 mL) were added to the flask under a positive pressure of argon. The catalyst, Pd(PPh₃)₄ (108.16 mg, 0.0919 mmol), was added, followed by 3-hexylthiophene-2-boronic acid pinacol ester (0.540 mL, 1.80 mmol). Then, 8.5 mL of a degassed aqueous solution 2M K₂CO₃ were added. The reaction mixture was placed in an oil bath preheated to 95 °C. After 40 h, thin layer chromatography (TLC) showed no presence of starting material, so the reaction flask was removed from the oil bath and allowed to cool to ambient temperature. Diethyl ether was added (50 mL), and the mixture was extracted with brine (3×30 mL). The organic layers were combined, filtered, and dried. Flash chromatography using a solvent mixture consisting of 1:100 ethyl acetate:hexanes was used to separate mono- and di-functionalized products. The product

was recovered at an 81% yield. ^1H NMR spectrum of 9-hexyl-2,7-bis(3-hexylthiophen-2-yl)-9H-carbazole (300 MHz, 25 °C, CDCl_3). δ (ppm): 0.77-0.99 (m, 9H, CH_3), 1.18-1.50 (m, 18H, CH_2), 1.67 (p, 4H, CH_2), 1.91 (p, 2H, CH_2), 2.76 (t, 4H, ArCH_2), 4.33 (t, 2H, NCH_2), 7.05 (d, 2H, ArH), 7.28 (d, 2H, ArH), 7.34 (d, 2H, ArH), 7.47 (s, 2H, ArH), 8.11 (d, 2H, ArH). (See **Figure C.2**.)

4.3.5 General Procedure for Direct Arylation Polymerization of Comonomers

As described in the previous chapters, the purine-containing monomer (either **M1** or **M2**) and the desired comonomer were added in a 1:1 stoichiometric ratio (0.15 mmol of each monomer) to a 25 mL round bottom flask equipped with a stir bar. All DArP reactions were performed in 5 mL of DMAc at 95 °C with 4-5 mol% $\text{Pd}(\text{OAc})_2$ as the catalyst, 3.0 equiv. of K_2CO_3 as the base, and 0.3 equiv. of PivOH as the proton shuttle, unless otherwise specified. All reagents were added under a positive pressure of argon. Dry DMAc was sparged with argon for 15 minutes before being added to the reaction vessel. After 18 h, the reaction was cooled to room temperature and added dropwise to cold methanol (MeOH, ~50 mL) to precipitate the copolymer. To isolate the copolymer, the recovered solid product was washed with methanol (25 mL $\times$ 3) and acetone (25 mL $\times$ 3), followed by centrifugation for 10 minutes after each wash. The final isolated and purified copolymer was dried and collected as a solid powder.

4.4 Results and Discussion

4.4.1 Synthesis of Monomers and Copolymers

Because the different sites on the purine scaffold have different reactivities toward cross-coupling reactions, the use of an unfunctionalized purine for polymerization has been

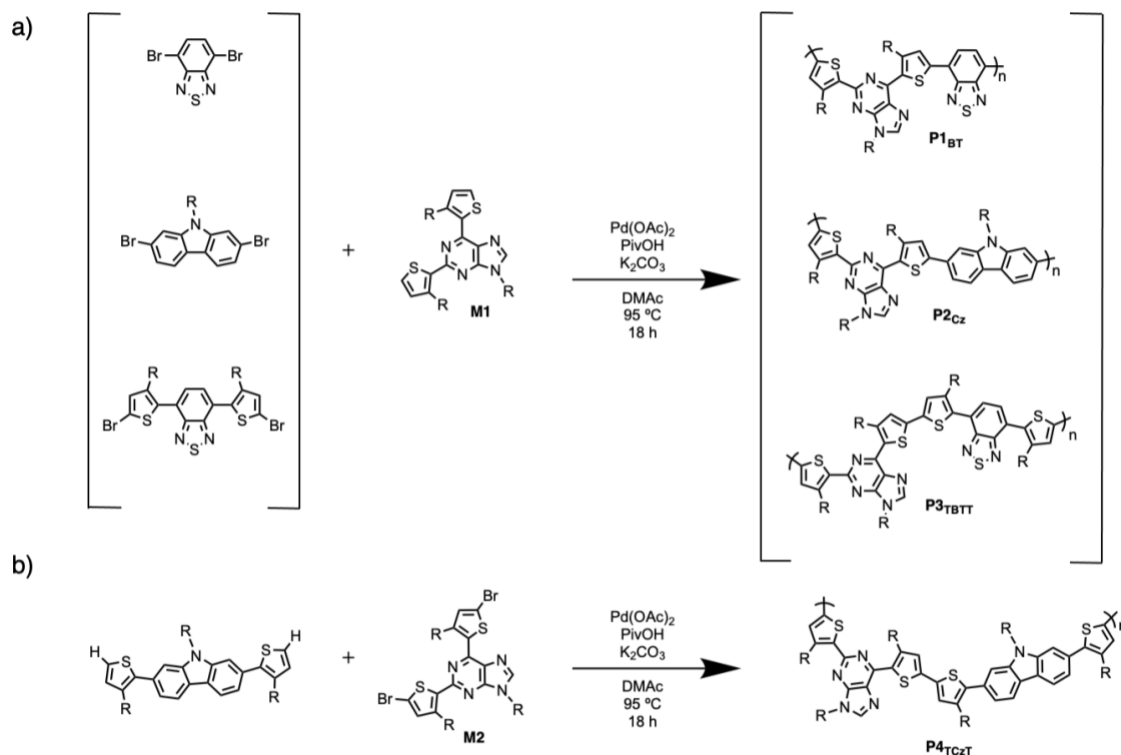
unsuccessful.³⁹ To circumvent this limitation, the purine was flanked with alkyl thiophenes at C6 and C2 of the purine scaffold, as shown by structures labeled **M1** and **M2** within **Scheme 4.1**. The syntheses of **M1** and **M2** followed procedures described in our previous work that proved to be successful. Hexyl chains were chosen to enhance solubility of the conjugated polymers in *N,N*-dimethylacetamide and other common solvents used in the syntheses. Similarly, alkylation at the N9 positions of 2,6-dichloropurine and 2,7-dibromocarbazole was used to add hexyl side chains, using methods described previously.⁵⁸ Suzuki-Miyaura cross-coupling involving 2,7-dibromo-9-hexyl-9*H*-carbazole (Cz) and 3-hexylthiophene-2-boronic acid pinacol ester was used to flank the carbazole units with thienyl groups, yielding 9-hexyl-2,7-bis(3-hexylthiophen-2-yl)-9*H*-carbazole (TCzT), respectively. (See Appendix C, **Figures C.1-C.2**).

The alternating copolymers were synthesized by DArP, as shown in **Scheme 4.1**. The subscript denotes the comonomer used for copolymerization with **M1** or **M2**. As seen in the **Scheme 4.1**, **M1** was copolymerized with two different dihalogenated comonomers, 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (BT) or 2,7-dibromo-9-hexyl-9*H*-carbazole (Cz), to generate **P1_{BT}** and **P2_{Cz}**. As described in Chapter II, **M1** also was copolymerized with 4,7-bis(5-bromo-3-hexylthiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (TBTT) to create **P3_{TBTT}**, which as reported previously had a $M_n = 12.5$ kg/mol. The dibrominated triad **M2** was copolymerized with 9-hexyl-2,7-bis(3-hexylthiophen-2-yl)-9*H*-carbazole (TCzT) to yield **P4_{TCzT}**. These copolymerizations generated cross-conjugated copolymers with either one or two alkyl-thienyl groups between the purine and the Cz or BT. As reported in **Table 4.1**, polymerizations were robust, creating copolymers having number average molecular weights (M_n) ranging from 12.4 kg/mol to 21.5 kg/mol and yields ranging from 47-76%.

Table 4.1 Molecular weights and yields of copolymers synthesized by DArP.

Polymer	yield (%)	M_n (kg/mol)	M_w (kg/mol)	$\bar{D}$
P1_{BT}	65%	25.0	95.1	3.8
P2_{Cz}	76%	12.4	18.8	1.5
P3_{TBTT} ^a	47%	12.5	31.8	2.5
P4_{TCzT}	55%	21.4	30.2	1.4

^aThe P3_{TBTT} used in this study was previously reported in Chapter II.



Scheme 4.1 Synthesis of the purine-containing copolymers via DArP by copolymerization of a) M1 with 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (BT), 2,7-dibromo-9-hexyl-9*H*-carbazole (Cz), or 4,7-bis(5-bromo-3-hexylthiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (TBTT) to form P1_{BT}, P2_{Cz}, and P3_{TBTT}, and b) M2 with 9-hexyl-2,7-bis(3-hexylthiophen-2-yl)-9*H*-carbazole (TCzT) to form P4_{TCzT}. In all structures, R = hexyl.

Based on our previous study of purine-containing conjugated copolymers that showed there to be no changes in optical absorbance behavior above $M_n \approx 9$ kg/mol (or $N \approx 9$ repeat units), the four conjugated copolymers listed in **Table 4.1** are similarly expected to be above their effective conjugation length (where optoelectronic properties become independent of molecular weight).

Because **P1BT** had a higher dispersity ($\mathcal{D}$) than the other copolymers, the copolymerization of **P1BT** was repeated three times under the conditions presented above to check the robustness of the reaction conditions. In addition, a polymerization was done at a lower temperature, 90 °C (instead of 95 °C), which resulted in lower M_n and higher dispersity, and one copolymerization was run for 9 h (instead of 18 h), which also resulted in a lower M_n but high dispersity. The results of these five polymerizations are documented in **Table C.1** and **Figure C.6**. Decreasing the temperature resulted in a M_n below the effective conjugation length, as evidenced by the absorbance profile having a blue-shifted absorbance maximum and onset compared to the other **P1BT** copolymers. The absorbance profiles of the other **P1BT** copolymers show that despite changes in molecular weight and dispersity, the optical properties do not change once $M_n > 9.6$ kg/mol, which supports the contention that molecular weights above $M_n \approx 9$ kg/mol exceed the effective conjugation length.

4.4.2 Optical Properties of Copolymers

The photophysical properties of these copolymers were studied using UV-Vis and fluorescence spectroscopies. Previous studies show that incorporating π -linkers in small molecules^{59–61} and polymers^{62,63} can improve optoelectronic properties such as reducing

optical bandgap ($E_{\text{gap}}^{\text{Opt}}$) by increasing conjugation length of the repeat unit, but such changes in the structural design can also change the rigidity, resulting in changes in organization behavior and optoelectronic properties. As shown in **Table 4.2**, the absorbance maximum ($\lambda_{\text{max}}^{\text{abs}}$) corresponding to the π - π^* transition⁶⁴ of the copolymers containing the 2,1,3-benzothiadiazole conjugated unit, **P1_{BT}** and **P3_{TBTT}**, are blue-shifted compared to the $\lambda_{\text{max}}^{\text{abs}}$ of the carbazole-containing copolymers, **P2_{Cz}** and **P4_{TCzT}**. Specifically, **P1_{BT}** and **P3_{TBTT}** have $\lambda_{\text{max}}^{\text{abs}} = 375$ nm and $\lambda_{\text{max}}^{\text{abs}} = 400$ nm, and **P2_{Cz}** and **P4_{TCzT}** have $\lambda_{\text{max}}^{\text{abs}} = 416$ nm and $\lambda_{\text{max}}^{\text{abs}} = 411$ nm, respectively. The redshift in absorbance maximum observed from **P1_{BT}** to **P3_{TBTT}** is likely the result of a more flexible main chain with additional rotational states due to the second thienyl π -linker between the electron acceptor (BT) and electron donor (P). In addition and as seen in **Figure 4.1a**, the absorbance spectra of **P1_{BT}** and **P3_{TBTT}** in solution have distinctive, red-shifted secondary peaks that are attributed to intramolecular charge transfer (ICT). These dual-band absorbance profiles suggest a donor-acceptor behavior.^{65,66} This behavior is consistent with the behavior exhibited by small molecule chromophores constructed by Stille cross-coupling of 6-bromo-*N*9 alkylated purines to 4,7-bis(5-(trimethylstannyl)thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole.^{40,41} **P2_{Cz}** and **P4_{TCzT}** have monomodal absorbance peaks with no ICT observed between the purine and carbazole units.

Emission profiles for **P1_{BT}**, **P3_{TBTT}**, and **P4_{TCzT}** in solution are broad and featureless, and **P2_{Cz}** has a fine-structure vibrational progression. (See **Figure 4.1a,b**.) **P2_{Cz}** and **P4_{TCzT}** have smaller Stokes shifts compared to **P1_{BT}** and **P3_{TBTT}**, which indicates that

Table 4.2 Optoelectronic data and molecular energy levels for copolymers.

Polymer	$\lambda_{\max}^{\text{abs}^a}$ (nm)	$\lambda_{\text{onset}}^{\text{abs}^a}$ (nm)	$\lambda_{\max}^{\text{em}^a}$ (nm)	$\lambda_{\text{onset}}^{\text{em}^a}$ (nm)	Stokes shift ^a (nm)	Φ^a	Opt E_{gap}^b (eV)
P1_{BT}	375,503	620	611	723	236,108	0.16	1.95
P2_{Cz}	416	477	488	650	72	0.95	2.40
P3_{TBTT}	400 ^c	569 ^c	648 ^c	797 ^c	248 ^c	0.02 ^c	1.96 ^c
P4_{TCzT}	411	488	513	640	102	0.26	2.41

^aUV-Vis and fluorescence spectra were acquired in CHCl₃ solutions. ^bBased on absorbance onset of UV-Vis spectra acquired from spin cast thin films on glass slides. ^cThe data for P3_{TBTT} has been previously reported.³⁹

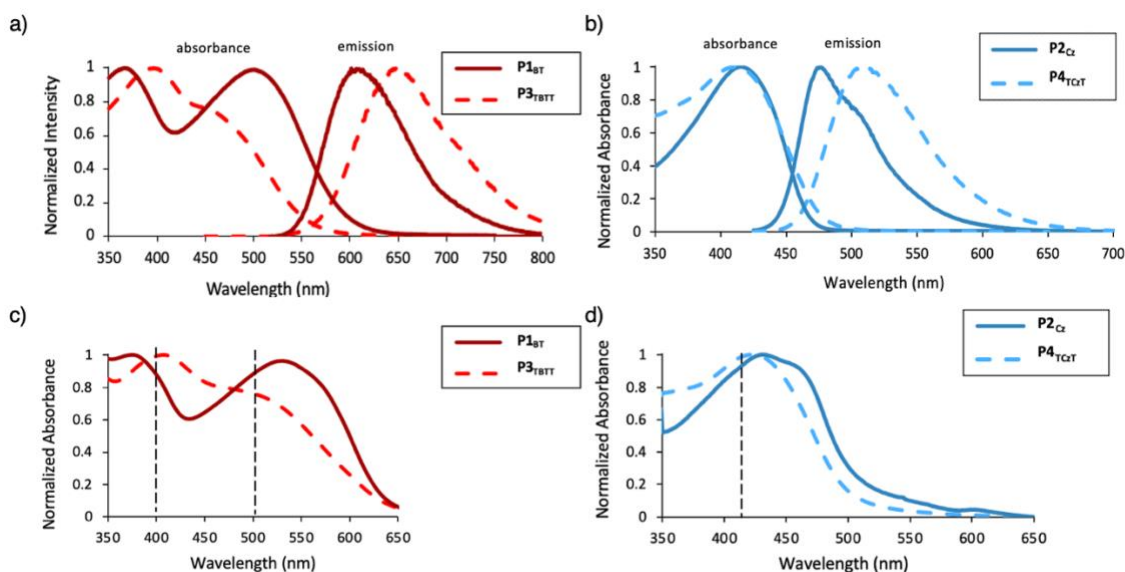


Figure 4.1 Normalized absorbance and emission spectra for purine-containing copolymers in chloroform: a) P1_{BT} and P3_{TBTT}, and b) P2_{Cz} and P4_{TCzT}. Normalized UV-Vis spectra for copolymer thin films: c) P1_{BT} and P3_{TBTT}, d) P2_{Cz} and P4_{TCzT}. Black dotted lines in c) and d) indicate values of the $\lambda_{\max}^{\text{abs}}$ of copolymers in chloroform solution.

the addition of the π -linker in the carbazole-containing copolymers, **P2_{Cz}** and **P4_{TCzT}**, causes less structural reorganization upon photoexcitation. (Values of Stokes shift are presented in **Table 4.2**.) **P1_{BT}** has a Stokes shift of 236 nm while **P3_{TBTT}** has a larger Stokes shift of 248 nm. The same trend is seen for **P2_{Cz}** and **P4_{TCzT}**, where the Stokes shift is larger for **P4_{TCzT}** (102 nm) than for **P2_{Cz}** (72 nm). The larger Stokes shift for **P3_{TBTT}** and **P4_{TCzT}** compared to **P1_{BT}** and **P2_{Cz}** respectively is attributed to an increase in structural reorganization upon photoexcitation that is caused by the additional thienyl groups along the main chain. The additional conformational states results in less rigidity of the copolymer backbone, as recently observed in a study of boryl-thiophene-BODIPY oligomers.⁶⁸ The smaller increase in Stokes shift observed from **P1_{BT}** to **P3_{TBTT}** (12 nm) compared to **P2_{Cz}** to **P4_{TCzT}** (30 nm) is likely the result of the noncovalent S $\cdots$ N conformational locks between the thiophenes flanking the benzothiadiazole unit, which has been previously observed in conjugated polymers containing BT units flanked with thiophenes.³⁵ In comparison, there are no noncovalent conformational locks within the carbazole comonomers.

To investigate the change in optical properties from solution to thin film, absorbance spectra were acquired for all copolymers as thin films created by spin casting onto a glass slide (from a solution of 0.5 mg/mL in chloroform). As seen from **Figure 4.1c,d**, thin film absorbance profiles of **P1_{BT}**, **P3_{TBTT}**, and **P4_{TCzT}** are similar in shape but red-shifted compared to their absorbance profile in solution. This change is expected, as it is associated with a higher degree of order in the solid state and a larger degree of π -orbital overlap.⁶⁹ **P2_{Cz}** is also slightly red-shifted compared to solution state, but a vibronic

shoulder at longer wavelength is also observed in **Figure 4.1d**. The appearance of this feature, which is not seen for **P1_{BT}**, **P3_{TBTT}**, and **P4_{TCzT}**, is attributed to crystalline domains formed by π -stacking interactions of chains. The thin film $E_{\text{gap}}^{\text{Opt}}$, which is calculated based on $\lambda_{\text{onset}}^{\text{abs}}$ for the copolymers as thin films, for **P1_{BT}** and **P2_{TBTT}** are similar (1.96 eV and 1.95 eV respectively). **P2_{Cz}** and **P4_{TCzT}** also have similar bandgaps as thin films (2.40 eV and 2.41 eV, respectively).

Because all copolymers were soluble in tetrahydrofuran (THF), chloroform and toluene, solvatochromic properties were studied using these solvents. **P1_{BT}** and **P2_{Cz}** have essentially no change in their absorbance profile based on solvent polarity, which increases from toluene to chloroform to THF while **P3_{TBTT}** and **P4_{TCzT}** show a minimal red-shift with decreasing solvent polarity. (See Appendix C, **Figures C.10-C.13**.) The emission profiles for **P1_{BT}** (**Figure 4.2a**), **P2_{Cz}** (**Figure 4.2b**), and **P4_{TCzT}** (**Figure 4.2d**) in the three different solvents show no substantial changes as solvent polarity is increased from toluene to chloroform to THF. This behavior suggests that there the ground- and excited-state dipole moments are essentially the same. As seen in **Figure 4.2c**, **P3_{TBTT}** has a distinct blue-shift in toluene which indicates that **P3_{TBTT}** has a more polar ground state than the other copolymers.⁷⁰

The temperature dependance of the absorbance profile for these purine-containing copolymers was investigated in toluene because it has a higher boiling point (110 °C) than chloroform, which allows a wider range of temperatures to be studied. Temperature-dependent absorbance studies for each copolymer were measured using solution concentrations of 0.01 mg/mL, and an absorbance spectrum was acquired every 10 °C from

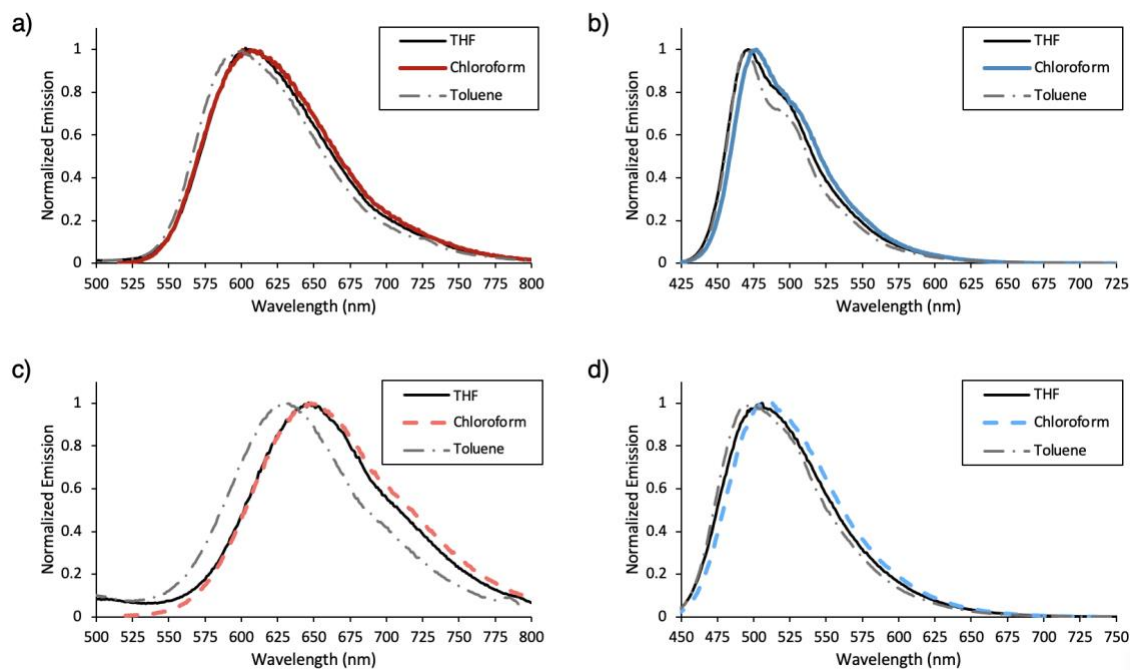


Figure 4.2 Normalized emission spectra for the four purine-containing copolymers in THF, chloroform, and toluene. a) P1_{BT}, and b) P2_{Cz}, c) P3_{TBTT}, and d) P4_{TCzT}. Only the emission spectrum of P3_{TBTT} changes when the solvent is changed to toluene. The colors and style of the lines used for spectra in chloroform are consistent with those used in Figure 4.1.

10 to 80 °C. (The data are presented in **Figures C.14-C.17.**) The temperature-dependent absorbance spectra for each copolymer show a blue shift as temperature increases and a decrease in overall absorption intensity. For all copolymers, the gradual decrease in absorbance maximums and onsets is attributed to a decrease in the twisting of the copolymer as temperature decreases. This behavior has been previously observed in fused heterocycles copolymerized with thienyl units.⁷¹ The increase in absorbance intensity at lower temperatures is attributed to the thermal contraction of the solvent toluene at low temperatures. This phenomena has been previously reported for conjugated copolymers, including copolymers containing fused heterocycles and thienyl units.⁷²

Highly fluorescent polymers are generally made with monomeric units of fluorene or carbazole, which yield highly emissive electroluminescent layers for OLEDs.^{52,72-74} As previously discussed, purines are known to be highly fluorescent and, when copolymerized with fluorene, leads to highly fluorescent conjugated polymers. The quantum yield (ϕ) of the four purine-containing copolymers in chloroform solution were determined via the comparative method (relative to Rhodamine 101 in ethanol (+0.01 wt% HCl), as expressed by Eq 4.1.

$$\phi = \phi_r \left(\frac{m_s}{m_r} \right) \left(\frac{n_s}{n_r} \right)^2 \quad (4.1)$$

In this expression, m_s and m_r are the slopes of the lines relating the integrated fluorescence and absorbance intensities, respectively, with the subscripts r and s refer to the reference and sample, and n_s and n_r are the refractive indices of the sample and

reference solvents, respectively. ϕ_r is the fractional quantum yield of the reference, Rhodamine 101 in ethanol, which has a $\phi_r = 1.00$.⁷⁶

P1_{BT} has a quantum yield of $\phi = 0.16$, which is significantly higher than **P3_{TBT}**, for which a quantum yield of $\phi = 0.02$ has been reported. **P3_{TBT}** has a lower quantum yield compared to **P1_{BT}** likely due to the additional thienyl groups that increase torsional states (flexibility) of the main chain and an increase in the number of heavy atoms in the repeat unit, which are known to increase the efficiency of intersystem crossing, leading to a decrease in quantum yield.^{76,77} The same trend is observed for **P2_{Cz}** and **P4_{TCzT}**, where the observed quantum yield for the copolymer **P2_{Cz}**, $\phi = 0.95$, is higher than the quantum yield of **P4_{TCzT}**, $\phi = 0.26$. **P2_{Cz}** has a remarkably high quantum yield ($\phi = 0.95$), which is significantly higher than the quantum yields of corresponding carbazole-based homopolymer, poly(*N*-octyl-2,7-carbazolediyl), and the alternating, thiophene-containing copolymer, poly(*N*-octyl-2,7-carbazolediyl-*alt*-2,5-thiophene). The quantum yields reported for these carbazole-containing copolymers are $\phi = 0.80$ and $\phi = 0.63$, respectively.⁷² We attribute the exceptional quantum yield of **P2_{Cz}** to the combination of the integration of the highly fluorescent purine with carbazole, the cross-conjugated copolymer design, which limits the delocalization of the frontier orbitals,⁵⁰ and the rigidity of the main chain subunit consisting of the conformationally-locked thiophene-purine-thiophene triad and carbazole unit. This is similar to previously observed highly fluorescent conjugated polymers comprising fluorene and the thienyl-purine-thienyl triad described in Chapter II.

4.4.3 Molecular Energy Levels, Bandgaps, and Effective Exciton Binding Energy

Electrical bandgaps and molecular energy levels were calculated from the oxidation and reduction potentials of the conjugated copolymers as thin films created by drop-casting onto a 3 mm gold button electrode. Cyclic voltammetry (CV) was used to determine the oxidation and reduction onsets, E_{onset}^{ox} and E_{onset}^{red} . The molecular energy levels, HOMO and LUMO, were estimated from equations 4.2 and 4.3, respectively, which are based on the assumption that reduction/oxidation of Fc/Fc⁺ is at 5.1 eV (relative to a vacuum).^{79,80}

$$E_{HOMO} (eV) = -(E_{onset}^{ox} + 5.1) eV \quad (4.2)$$

$$E_{LUMO} (eV) = -(E_{onset}^{red} + 5.1) eV \quad (4.3)$$

The values of E_{HOMO} and E_{LUMO} for each copolymer are listed in **Table 4.3** and their corresponding cyclic voltammograms and molecular energy levels are presented in **Figure 4.3**. **P1_{BT}** and **P2_{TBTT}** have two quasi-reversible reduction events which are common for polymers and small molecules containing the BT unit.^{41,66,72,81} The oxidation peaks for **P1_{BT}** and **P3_{TBTT}** also appear to be quasi reversible while the oxidation peaks for **P2_{Cz}** and **P4_{TCzT}** are irreversible. We note that while the E_{gap}^{Opt} for copolymers (**Table 4.2**) did not change when an additional thienyl group was enchainned between the purine and either the Cz or the BT units, the E_{gap} determined by cyclic voltammetry increases when the additional thienyl groups are interposed between the purine and Cz or BT.

The difference between the E_{gap}^{Opt} and the electrochemical bandgap (E_{gap}^{CV}) is described as the effective exciton binding energy (E_b). The optical bandgaps, E_{gap}^{Opt} , for our copolymers as thin films are given in **Table 4.2**. When the purine-containing triad is cross-

Table 4.3 Molecular energy levels and effective exciton binding energy for copolymers.

Polymer	E_{HOMO}^a (eV)	E_{LUMO}^a (eV)	CV E_{gap}^a (eV)	E_b^b (eV)
P1_{BT}	-5.63	-3.67	1.96	0.01
P2_{Cz}	-5.56	-2.91	2.65	0.25
P3_{TBTT}	-5.60 ^c	-3.48 ^c	2.12	0.16
P4_{TCzT}	-5.78	-2.91	2.87	0.46

^aBased on the oxidation/reduction onset potentials measured via CV and calculated from Eq 2 and 3. ^bDifference between E_{gap}^{CV} and E_{gap}^{Opt} . ^cThe data for P3_{TBTT} have been reported in Chapter II.

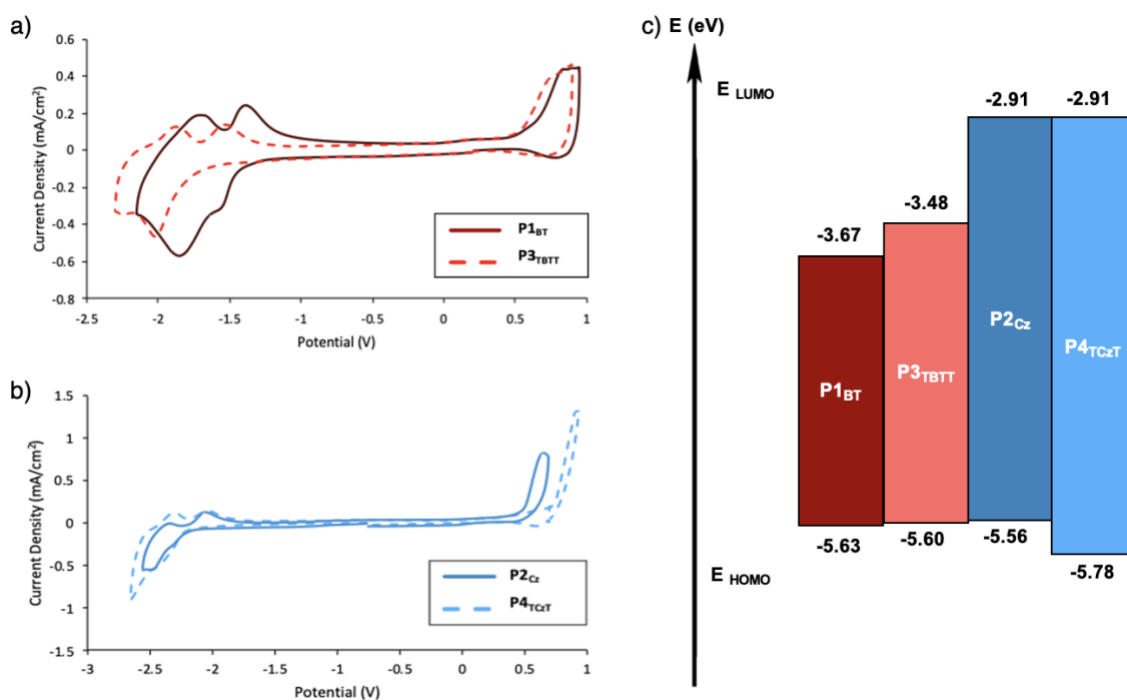


Figure 4.3 Cyclic voltammogram for a) P1_{BT} and P3_{TBTT}, and b) P2_{Cz} and P4_{TCzT}. c) HOMO/LUMO energy level diagram obtained via cyclic voltammetry measurements of the purine-containing copolymers.

coupled to the BT comonomer to create **P1_{BT}**, E_b is negligible (0.01 eV), but the **P3_{TBTT}** copolymer, which has the additional thienyl, has a higher E_b of 0.16 eV. The same pattern of behavior is observed for **P2_{Cz}** and **P4_{TCzT}**, where E_b for **P2_{Cz}** is 0.25 eV and **P4_{TCzT}** is 0.46 eV. A lower E_b is associated with an increase in the yield of charge-carrier generation and improved charge dissociation. Structurally, E_b is known to decrease as the rigidity of the main chain of the conjugated polymer increases.^{63,82,83} Specifically, Lan *et al.* has shown that for fused heterocycles, increasing the rigidity of the conjugated polymer main chain can minimize E_b .⁸² The small exciton binding energies observed for **P1_{BT}** and **P3_{TBTT}** compared to **P2_{Cz}** and **P4_{TCzT}** could be the result of the rigidity of the copolymer main chain. **P3_{TBTT}** has noncovalent S $\cdots$ N conformational locks between the thienyl unit and BT that results in two relatively planar comonomers being coupled.

4.5 Conclusions

To-date, this is one of a handful of studies that use cross-conjugation and main chain rigidity to improve optoelectronic properties, and our study demonstrates how these design features can be used to tailor optoelectronic properties including quantum yield and exciton binding energy. Specifically, our research shows how thienyl π -linkers between comonomers can increase effective exciton binding, resulting in higher electrical bandgap without changing the optical bandgap. Additionally, the use of highly fluorescent chromophores, like purine and carbazole, within the main chain results in exceptionally high quantum yields, up to $\phi = 0.95$, but additional thienyl π -linkers vastly reduce the quantum yield due to the increase in heavy atoms within the repeat unit and additional conformational states. Noncovalent S $\cdots$ N conformational locks in the purine-containing

repeat unit contribute rigidity to the polymer main chain, which when cross-coupled with TBTT, which is also planar due to S $\cdots$ N conformational locks, leads to small effective exciton binding energies.

4.6 References

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CHAPTER V: SUMMARY, CONCLUSIONS, AND FUTURE WORK

5.1 Summary and Conclusions

Designing thienyl-flanked purine-core monomers was crucial for integration of the purine scaffold into the main chain of conjugated polymers. The work described in my dissertation provides a simple synthetic route to making purine-containing monomers and comonomers that can be cross-coupled with comonomers of varied aromatic structures. The synthesis and structure-property relationships described in this dissertation will be a useful guide for future endeavors to incorporate the purine scaffold or other asymmetric conjugated units into the main chain of conjugated polymers. The first main accomplishment of my work was synthesizing purine-containing monomers that proved to have high efficiency toward cross-coupling polymerizations, specifically DArP. Optoelectronic properties of the resulting polymers show a dependence on repeat unit design and suggest that cross-conjugation may be a design element that can be used to make conjugated polymers with high photoluminescent quantum yields while maintaining lower bandgaps. These accomplishments are noteworthy because a simple synthesis yields purine-containing monomers that can be copolymerized with a wide range of comonomers through direct arylation and shows how incorporation of purines in the main chain can participate in donor/acceptor interactions.

With this in mind, Chapter III investigates the structure of the purine-containing monomers and their corresponding AA+BB and AB polymers. Through 2-D NMR and crystallography, S $\cdots$ N conformational locks are observed, and these noncovalent conformational locks persist after polymerization. Specifically, $^1\text{H} - ^1\text{H}$ NOESY is used to show interactions between the *N9* hexyl chain protons and the hexyl chain of the thienyl

ring coupled at C2. $^1\text{H} - ^{13}\text{C}$ HSQC and $^1\text{H} - ^{13}\text{C}$ HMBC are then used to assist in assigning signals observed in proton and carbon NMR spectra of the monomers and polymers, as well as to monitor which correlations are due to head-to-tail coupling versus head-to-head or tail-to-tail couplings. Following efforts to understand configuration and conformation, the optoelectronic properties of the AB polymer and AA+BB copolymer were studied. While bandgap and quantum yield are the same for the two polymers, the thin-film absorbance profile and emission profile show changes based on regioregularity. Due to its regioregularity, the AB polymer has two shoulders in the thin film absorbance spectra due to increased $\pi - \pi$ stacking.

Finally, I investigated the impact of thienyl π -linker units in the main chain of purine-containing conjugated polymers on photophysical properties. I found that while thienyl π -linkers are highly efficient aromatic sites for cross-coupling polymerizations, they can negatively affect the optoelectronic properties when multiple thienyl units are placed between the electron donor and acceptor. The effect is especially pronounced if the comonomer does not have noncovalent conformational locks, which increase the rigidity of the conjugated copolymer. While copolymerization of highly fluorescent conjugated monomers, including fluorene and carbazole, with the purine-containing monomer result in conjugated copolymers with exceptionally high photoluminescent quantum yields, additional thienyl units between the purine triad and the comonomer significantly lower the quantum yield. This is attributed to the heavy atom effect due to sulfur atoms in the additional thienyl rings and a loss in rigidity of the main chain. Additionally, it was shown that the effective exciton binding energies of the purine-containing copolymers were greater for copolymers having additional thienyl rings in their repeat unit. The additional

thienyl rings decrease the rigidity of the main chain, resulting in less optimal optoelectronic properties.

5.2 Future Work

The work described in my dissertation focused on synthesizing and studying polymers with purine-containing monomeric units, which are highly tailorable conjugated building blocks. Specifically, this dissertation focused on the incorporation of a cross-conjugated purine-containing monomer into the main chain via direct arylation polymerization. Follow-on studies that examine other polymerization techniques, as well as other patterns of connectivity across the purine to create linearly conjugated polymers, would be very compelling. Given the versatility of the purine scaffold, efforts to introduce electron donors or electron acceptors and study design-structure-property relationships may also be intriguing for the potential to widely vary optoelectronic properties.

5.2.1 Microwave-Assisted Suzuki-Miyaura Cross-Coupling Polymerization versus DArP of Purine-Containing Monomers

Because direct arylation polymerization can be used to form purine-containing conjugated polymers, it would be compelling to make copolymers having the same repeat units through different cross-coupling polymerization reactions and compare their optoelectronic properties. While Stille and Suzuki-Miyaura polymerizations are of interest, early attempts to polymerize the dibromo-purine comonomer (2,6-bis(5-bromo-3-hexylthiophen-2-yl)-9-hexyl-9H-purine (**M2**)) with other comonomers via Stille or Suzuki cross-coupling polymerizations were unsuccessful. However, a microwave-assisted

Suzuki-Miyaura cross-coupling polymerization involving **M2** and (9,9-dioctyl-9H-fluorene-2,7-diyl)diboronic acid (**F**) to form **P(M2-F)** was successful. This copolymer has the same repeat unit as **P2_F** from Chapter II. (See **Scheme 5.1**.) The polymerization was performed three times, and the results are available in **Table 5.1**. **Figure 5.1** shows that there are slight differences in the absorbance and emission profiles of the copolymers made via direct arylation polymerization (**P2_F**) and microwave-assisted Suzuki-Miyaura polymerization (**P(M2-F)**). Although the absorbance and emission profiles are similar, there are striking differences in quantum yield in both in solution and solid state. In solution, **P2_F** has a photoluminescent quantum yield (PLQY) of $\phi = 0.61$, while **P(M2-F)** has a PLQY of $\phi = 0.41$. In the solid state the PLQY for **P2_F** and **P(M2-F)** are $\phi = 0.34$ and $\phi = 0.13$, respectively. While both copolymers are highly fluorescent, the quantum yield of **P2_F** is significantly higher than the quantum yield of **P(M2-F)** both in solution and as thin films. Because Suzuki-Miyaura is generally associated with improved optoelectronic properties in comparison to polymers with the same repeat unit made by direct arylation polymerization, the preliminary results for copolymers **P2_F** compared to **P(M2-F)** of similar number-average molecular weights are particularly interesting and require further investigation. To identify how the polymerization method affects optoelectronic properties.

5.2.2 Linearly-Conjugated Purine-Containing Monomers and Polymers

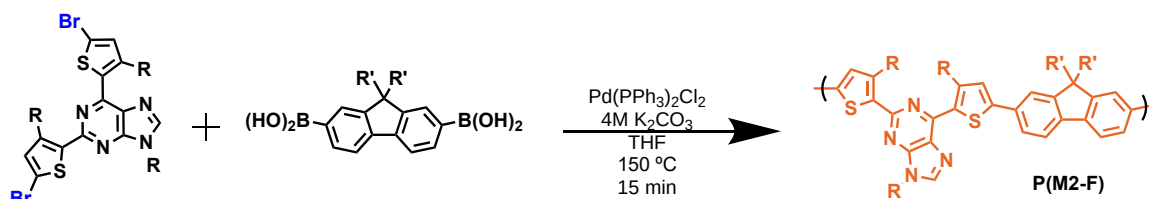
Because the work described in this dissertation show that purine-containing conjugated polymers can be made via direct arylation polymerization, it stands to reason that changing the connection pattern on the purine should not inhibit polymerization. A

Table 5.1 Yield and macromolecular characteristics of purine-containing copolymers synthesized by microwave-assisted Suzuki-Miyaura cross-coupling polymerizations of P(M2-F).

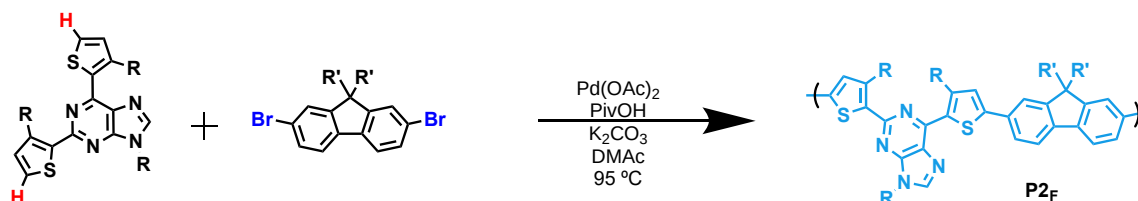
P(M2-F)	Yield (%)	M_n (kg/mol) ^a	$\bar{D}$
1	58%	8.9	1.7
2	66%	9.5	1.8
3	69%	15.4	2.4

^aNumber-average molecular weights (M_n) were measured by GPC (mobile phase of THF at 25 °C) using universal calibration analysis based on polystyrene (PS) standards. *Data in bold identifies the copolymer that was used for optoelectronic characterizations.

Microwave-Assisted Suzuki-Miyaura Polymerization



Direct Arylation Polymerization



Scheme 5.1 Microwave-assisted Suzuki-Miyaura polymerization conditions for P(M2-F) (top), and the direct arylation polymerization conditions for P2F (bottom). *P2F was reported in Chapter II.

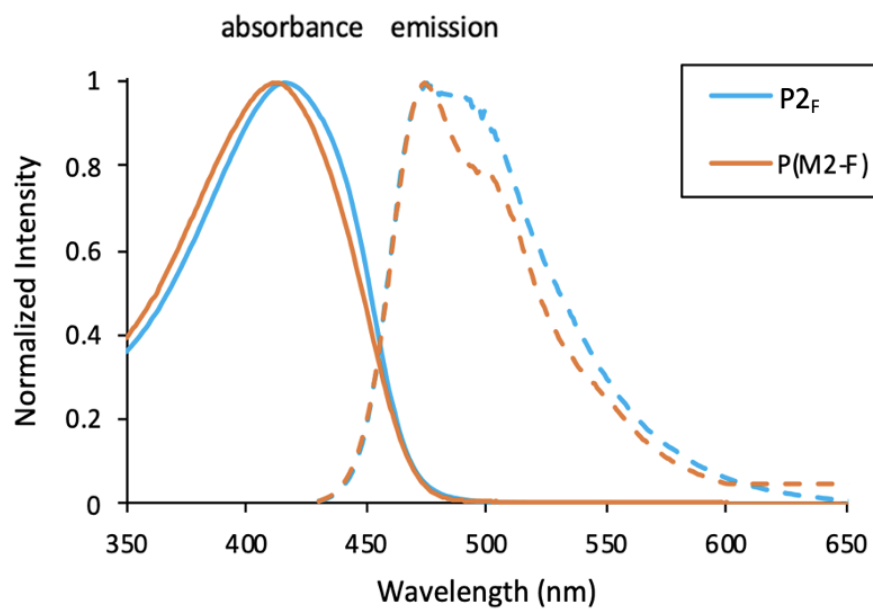


Figure 5.1 Normalized absorbance and emission profiles for P(M2-F) (orange), and P2_F (P2(F)) (blue). *P2_F was reported in Chapter II.

linearly-conjugated purine-containing monomer (9-hexyl-6,8-bis(3-hexylthiophen-2-yl)-9*H*-purine (**M4**)) was synthesized as described in Appendix D. **Figure 5.2** shows the linearly-conjugated monomer (**M4**, right) next to the cross-conjugated monomer used in this dissertation (**M1**, left). To synthesize **M4**, 6-bromopurine was initially alkylated under the same conditions described in Appendix B for 2,6-dichloro-9-hexyl-9*H*-purine to yield 6-bromo-9-hexyl-9*H*-purine. Then, aromatic bromination was done to yield 6,8-dibromo-9-hexyl-9*H*-purine. Finally, a Suzuki-Miyaura cross-coupling reaction was completed to add the thienyl units to the purine at C6 and C8, yielding **M4**. The full synthetic conditions can be found in Appendix D along with yields and ¹H NMR spectra. (See Appendix D, Figures **D.2-D.4**.) Bromination of **M4** followed the same protocol as was used to synthesize **M1** to **M2**, and these are described in Appendix A.

Early attempts to polymerize 9-hexyl-6,8-bis(3-hexylthiophen-2-yl)-9*H*-purine (**M4**) comonomer under the same conditions described in Chapters II, III, and IV with either (9,9-dioctyl-2,7-dibromofluorene or 6,8-bis(5-bromo-3-hexylthiophen-2-yl)-9-hexyl-9*H*-purine (**M5**)) as comonomers did not result in a copolymer. While this study was not exhaustive, it does show that **M4** and **M5** do not easily polymerize by direct arylation polymerization, so direct arylation conditions need to be optimized. Microwave-assisted Suzuki-Miyaura of **M5** and 9,9-dioctyl-9*H*-fluorene-2,7-diyl)diboronic acid was attempted three times as described in Section 5.2.1 and Appendix D. This resulted in copolymers with number-average molecular weights between 16.1 kg/mol and 27.8 kg/mol. **Table 5.2** presents the yield, M_n , and $\bar{D}$ of these copolymers. As seen in **Figure 5.3** and **Table 5.3**, the $\lambda_{\text{max}}^{\text{abs}}$ of the linear and cross-conjugated purine-containing copolymers – **P(M5-F)** and

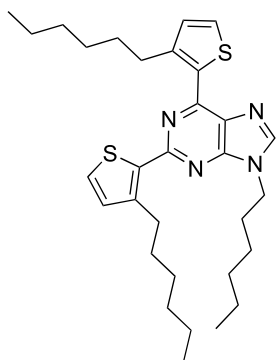
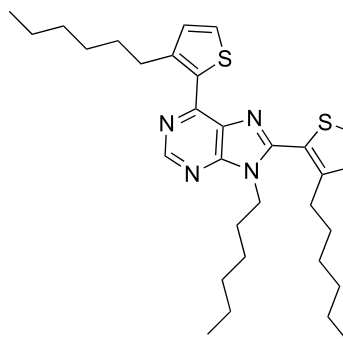
Cross-Conjugated Monomer (This Work)**Linearly-Conjugated Monomer (Future Work)**9-hexyl-2,6-bis(3-hexylthiophen-2-yl)-9*H*-purine (**M1**)9-hexyl-6,8-bis(3-hexylthiophen-2-yl)-9*H*-purine (**M4**)

Figure 5.2 The cross-conjugated purine-containing monomer (**M1**, left) and the linear-conjugated purine-containing monomer (**M4**, right).

Table 5.2 Yield and macromolecular characteristics of purine-containing copolymers synthesized by microwave-assisted Suzuki-Miyaura cross-coupling polymerization to yield P(**M5-F**).

P(M5-F)	Yield (%)	M_n (kg/mol)^a	$\bar{D}$
1	73%	16.1	1.3
2	81%	22.1	1.4
3	68%	27.8	1.3

^aNumber-average molecular weights (M_n) were measured by GPC (mobile phase of THF at 25 °C) using universal calibration analysis based on polystyrene (PS) standards. *Data in bold identifies the copolymer that was used for optoelectronic characterizations.

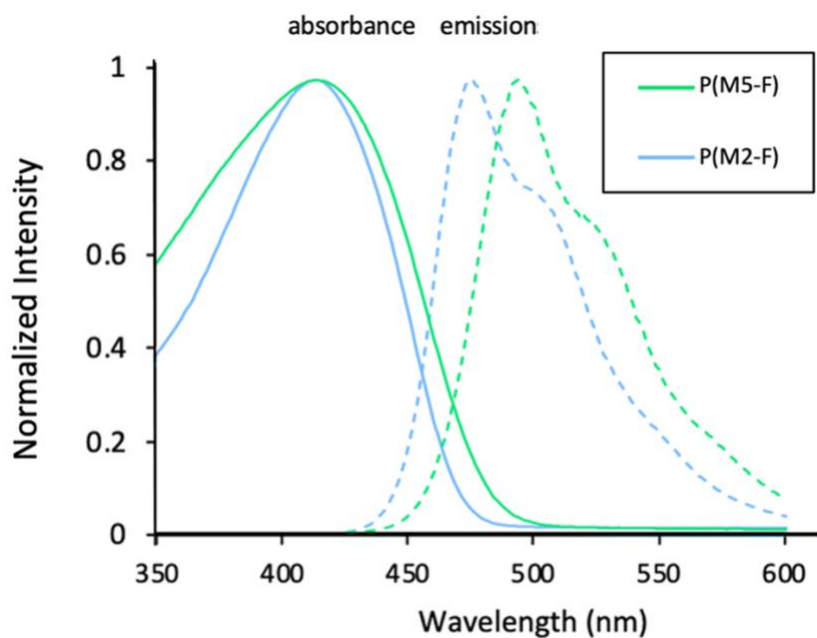


Figure 5.3 Normalized absorbance and emissions profiles for P(M2-F) (blue), and P(M5-F) (green).

Table 5.3 Optoelectronic data for purine-containing copolymers with the same repeat unit made via different cross-coupling polymerizations.

	$\lambda_{\text{max}}^{\text{abs}^a}$	$\lambda_{\text{onset}}^{\text{abs}^a}$	$\lambda_{\text{max}}^{\text{em}}$	$\lambda_{\text{onset}}^{\text{em}^a}$	Stokes shift ^a (nm)	Sol'n. Φ^a	Thin film Φ
P(M2-F)	411	478	475	603	64	0.41	0.13
P(M5-F)	413	499	495	612	82	0.35	-

^aUV-Vis and fluorescence spectra were acquired from CHCl₃ solutions.

P(M2-F) respectively – are within 2 nm of each other, but the $\lambda_{\text{onset}}^{\text{abs}}$ is red shifted for the linearly conjugated copolymer. The Stokes shift of the **P(M5-F)** is also larger than that of **P(M2-F)**, and this is likely due to an increase in reorganization upon photoexcitation. This could be an indication that the noncovalent S $\cdots$ N conformational locks that are present in the cross-conjugated copolymer **P(M2-F)** lead to a more rigid copolymer main chain that undergoes less structural reorganization when excited. This may also be why **P(M2-F)** has a higher quantum yield ($\phi = 0.41$) compared to **P(M5-F)** ($\phi = 0.35$). While there is still much work to be done in order to adequately study cross- and linear-conjugation in purine-containing conjugated copolymers, this data indicates that there are optoelectronic changes based on connectivity along the main chain.

APPENDICES

Appendix A

A.1 NMR Spectra of Small Molecules and Monomers

2,6-dichloro-9-hexyl-9H-purine:

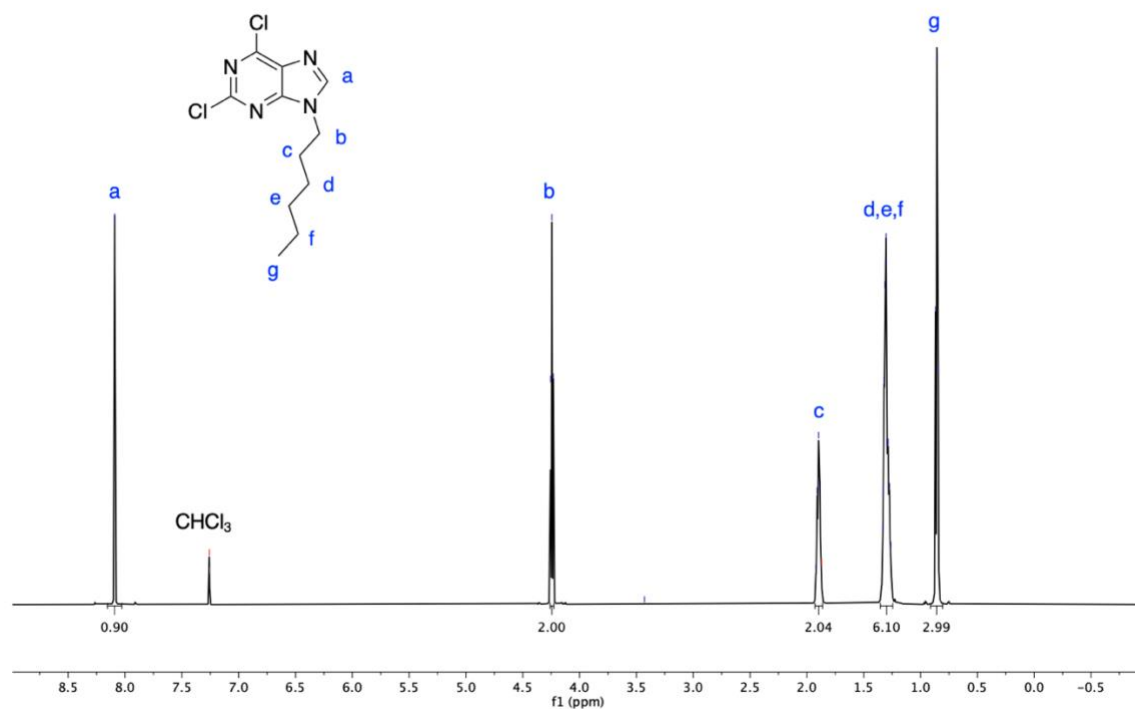


Figure A.1 ¹H NMR spectrum of 2,6-dichloro-9-hexyl-9H-purine (500 MHz, 25 °C, CDCl₃). δ, ppm: 0.87 (t, 3H, CH₃), 1.31 (m, 6H, CH₂), 1.91 (p, 2H, CH₂), 4.25 (t, 2H, NCH₂), 8.09 (s, 1H, C8H).

9-hexyl-2,6-bis(3-hexylthiophen-2-yl)-9H-purine (M1)

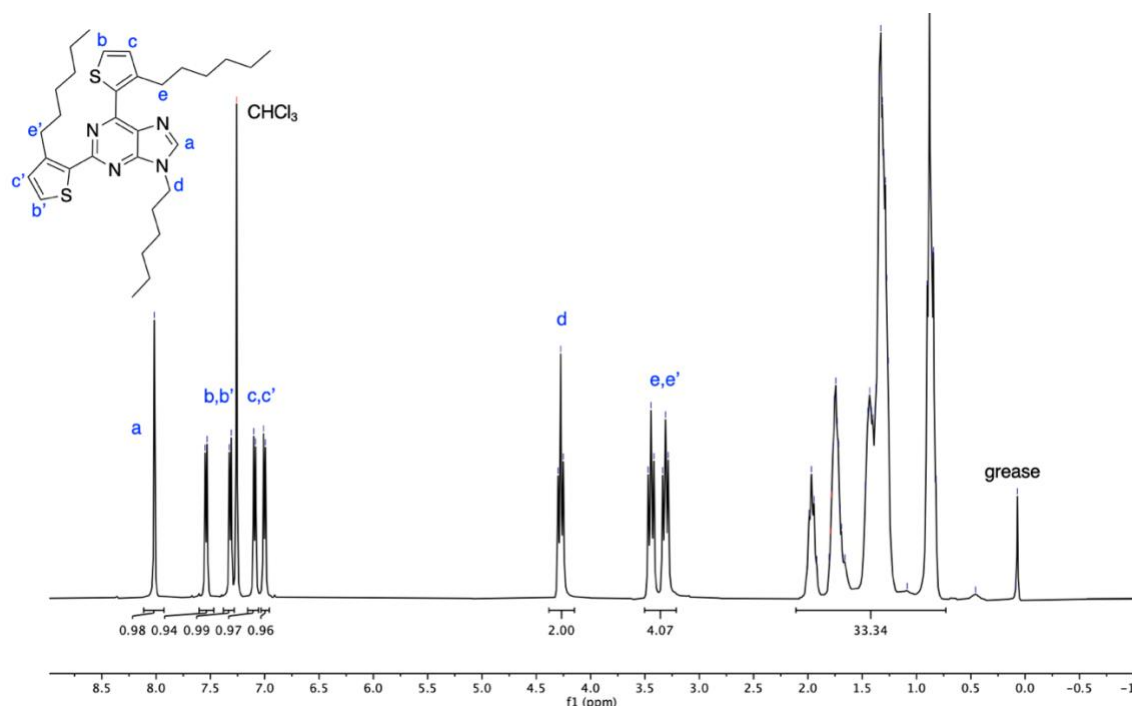


Figure A.2 ^1H NMR spectrum of 9-hexyl-2,6-bis(3-hexylthiophen-2-yl)-9H-purine (M1) (500 MHz, 25 °C, CDCl_3). δ , ppm: 0.88 (t, 6H, CH_3), 1.19-1.52 (m, 18H, CH_2), 1.75 (p, 4H, CH_2), 1.96 (p, 2H, CH_2), 3.31 (t, 2H, ArCH_2), 3.44 (t, 2H, ArCH_2), 4.28 (t, 2H, NCH_2), 7.00 (d, 1H, ArH), 7.09 (d, 1H, ArH), 7.31 (d, 1H, ArH), 7.54 (d, 1H, ArH), 8.02 (s, 1H, C8-H).

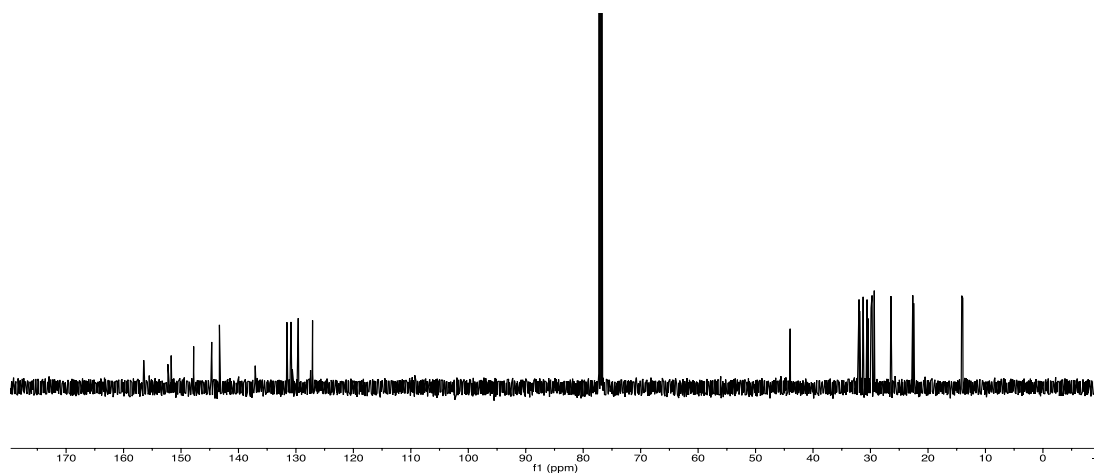


Figure A.3 ^{13}C NMR spectrum (500 MHz, 25 °C, CDCl_3) of 9-hexyl-2,6-bis(3-hexylthiophen-2-yl)-9H-purine (M1).

2,6-bis(5-bromo-3-hexylthiophen-2-yl)-9-hexyl-9H-purine (M2):

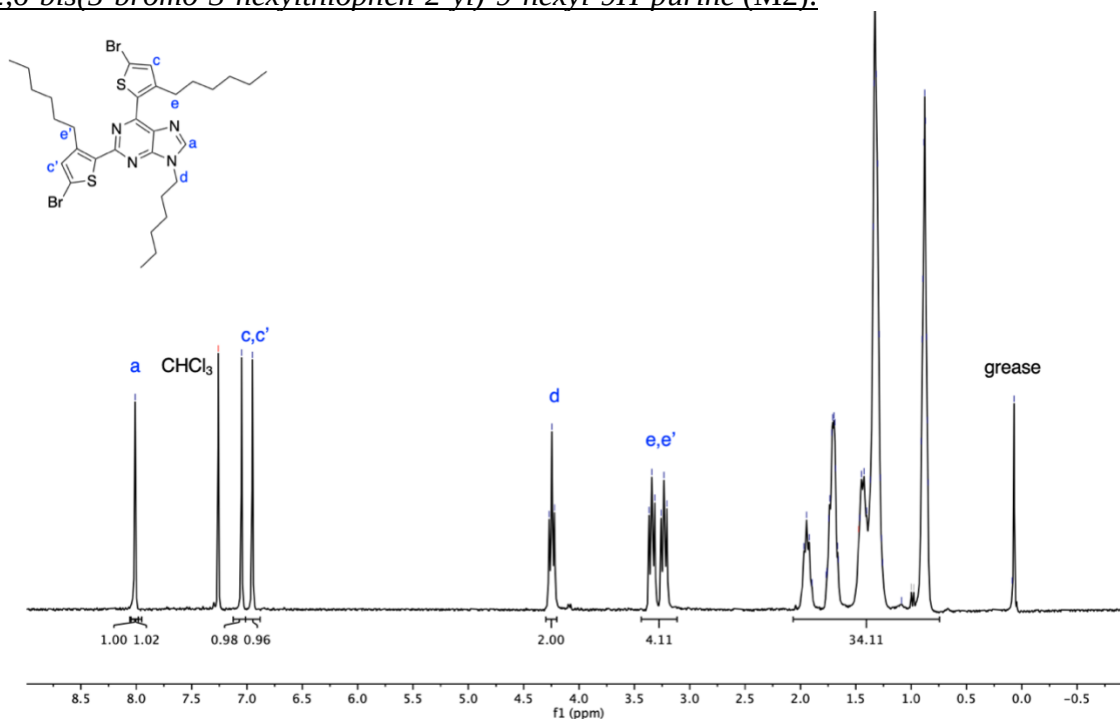


Figure A.4 ^1H NMR spectrum of 2,6-bis(5-bromo-3-hexylthiophen-2-yl)-9-hexyl-9H-purine (M2) (500 MHz, 25 °C, CDCl_3). δ , ppm: 0.89 (m, 6H, CH_3), 1.17-1.54 (m, 18H, CH_2), 1.70 (p, 4H, CH_2), 1.95 (p, 2H, CH_2), 3.24 (t, 2H, ArCH_2), 3.34 (t, 2H, ArCH_2), 4.24 (t, 2H, NCH_2), 6.95 (s, 1H, ArH), 7.05 (s, 1H, ArH), 8.01 (s, 1H, C8-H).

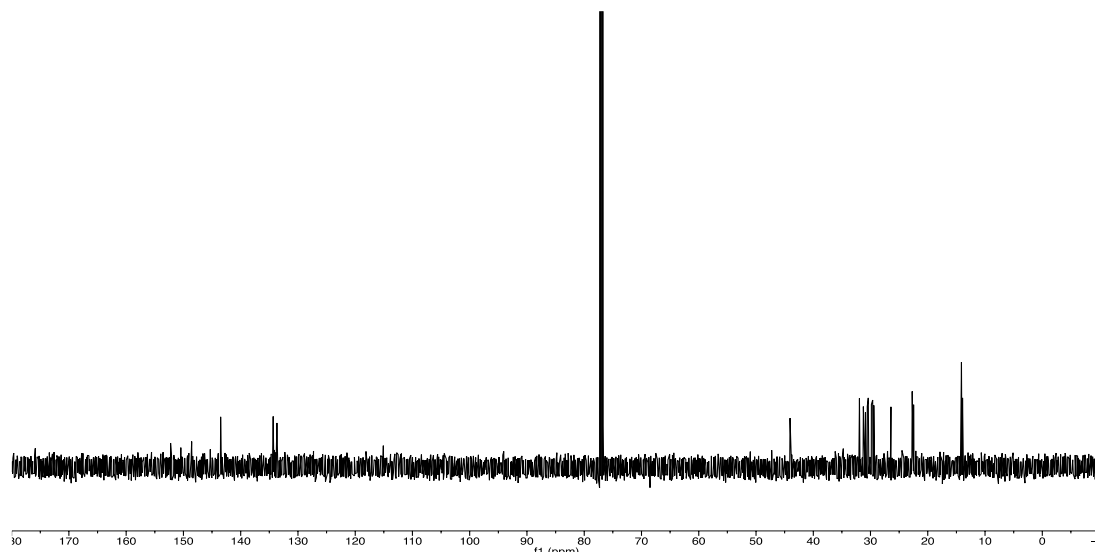


Figure A.5 ^{13}C NMR spectrum (500 MHz, 25 °C, CDCl_3) of 2,6-bis(5-bromo-3-hexylthiophen-2-yl)-9-hexyl-9H-purine (M2).

A.2 Direct Analysis in Real Time - Mass Spectrometry of M1 and M2

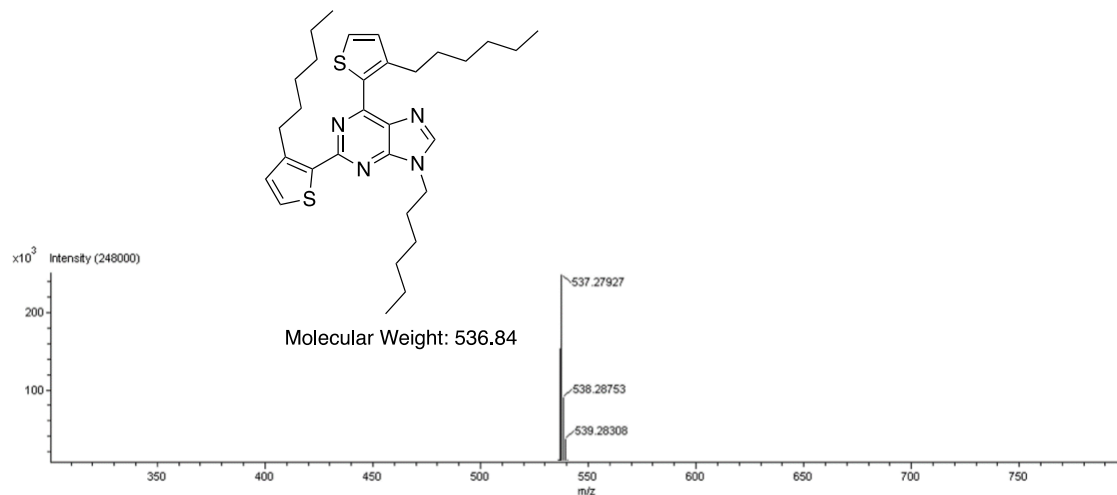


Figure A.6 AccuTOF DART-MS analysis of M1. calc'd $[M+H]^+$: 537.3080, found: 537.2793.

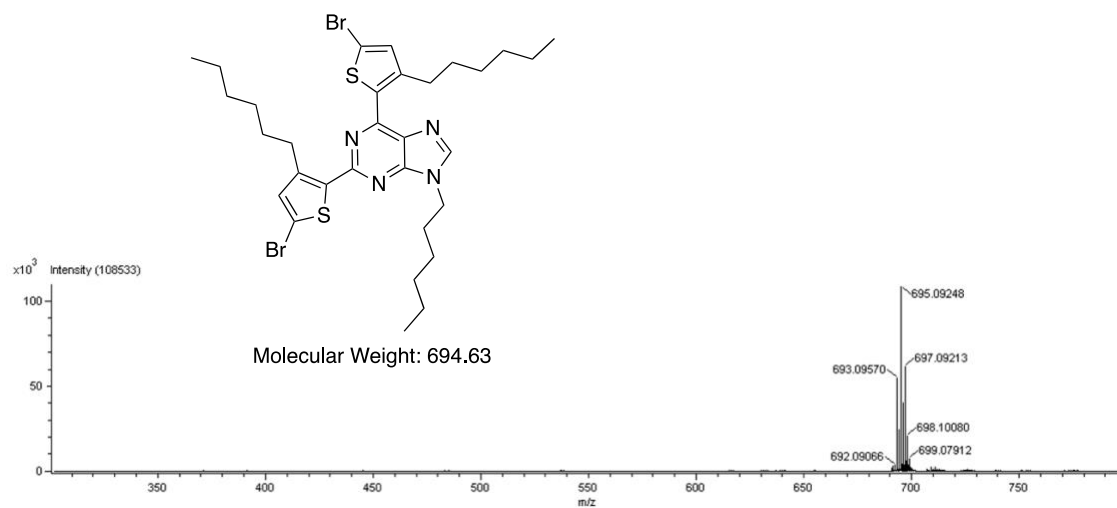


Figure A.7 AccuTOF DART-MS analysis for M2. calc'd $[M+H]^+$: 693.1290, found: 695.0957.

Table A.1 Molecular weights, yields, and absorption characteristics of purine-containing copolymers synthesized via DArP.

Sample	Yield (%)	M_n (kg/mol)	M_w (kg/mol)	$\bar{D}$	$\lambda_{\text{max}}^{\text{abs}}$	$\lambda_{\text{onset}}^{\text{abs}}$
P1_{TPT}	68%	4.5	7.9	1.8	424	491
	71%	9.0	19.5	2.2	424	492
	83%	10.1	16.7	1.7	423	492
P2_F	57%	4.6	6.0	1.3	412	459
	80%	9.4	17.5	1.9	416	479
P3_{TFT}	42%	5.0	16.7	3.3	423	477
	55%	5.3	7.4	1.4	425	482
	48%	12.1	38.5	3.2	441	500
P4_T	50%	5.0	7.6	1.5	423	494
	53%	9.8	16.9	1.7	426	514
	61%	18.0	37.8	2.1	425	514
P5_{ProDOT}	69%	4.4	6.8	1.5	455	531
	42%	9.8	20.5	2.1	458	532
	86%	18.3	38.5	2.1	458	533
P6_{TBTT}	47%	12.5	31.8	2.5	400	569

*Data in bold identifies the copolymer that was used for optoelectronic characterizations.

A.3 ¹H NMR spectra of Purine-Containing Copolymers

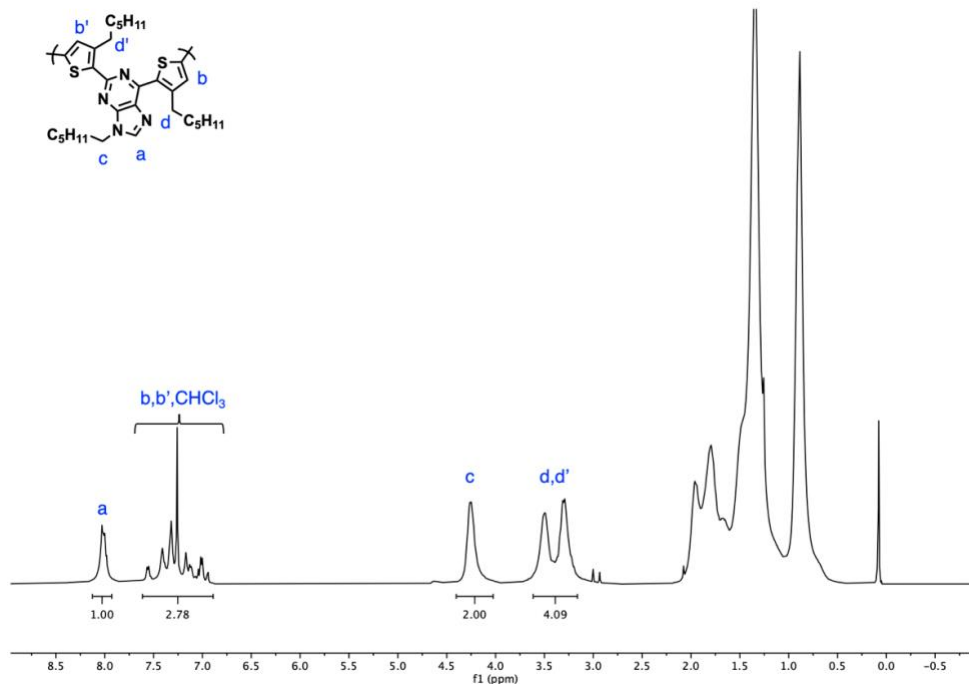


Figure A.8 ¹H NMR spectrum of P1_{TPT} (300 MHz, 25 °C, CDCl₃). δ (ppm): 0.50-2.15, 3.21-3.63, 4.02-4.45, 6.89-7.70, 7.87-8.20. The copolymer was obtained as an orange solid.

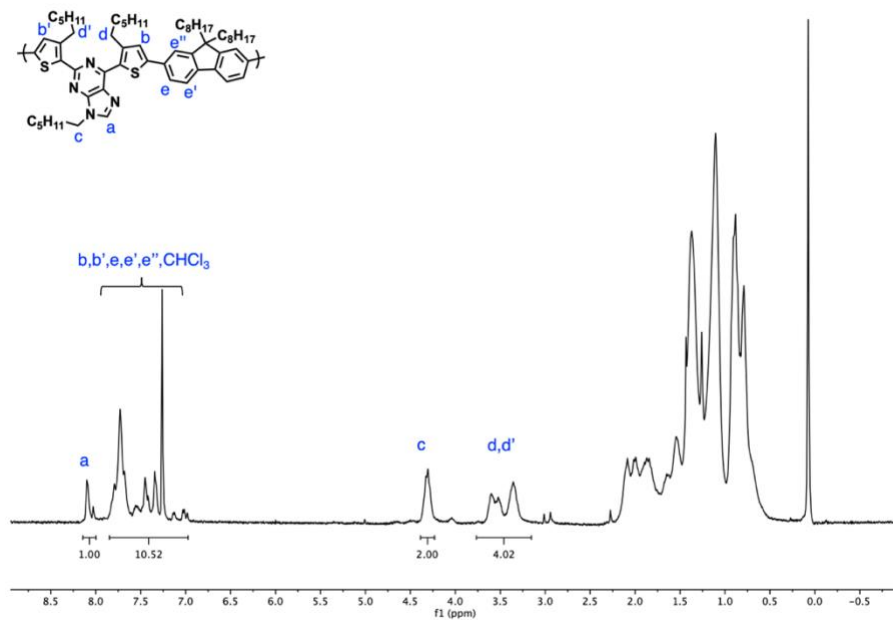


Figure A.9 ^1H NMR spectrum of P2_F (300 MHz, 25 °C, CDCl₃). δ (ppm): 0.51-2.19, 3.17-3.72, 4.95-5.25, 6.86-7.88, 8.00-8.18. The copolymer was obtained as a dark green solid.

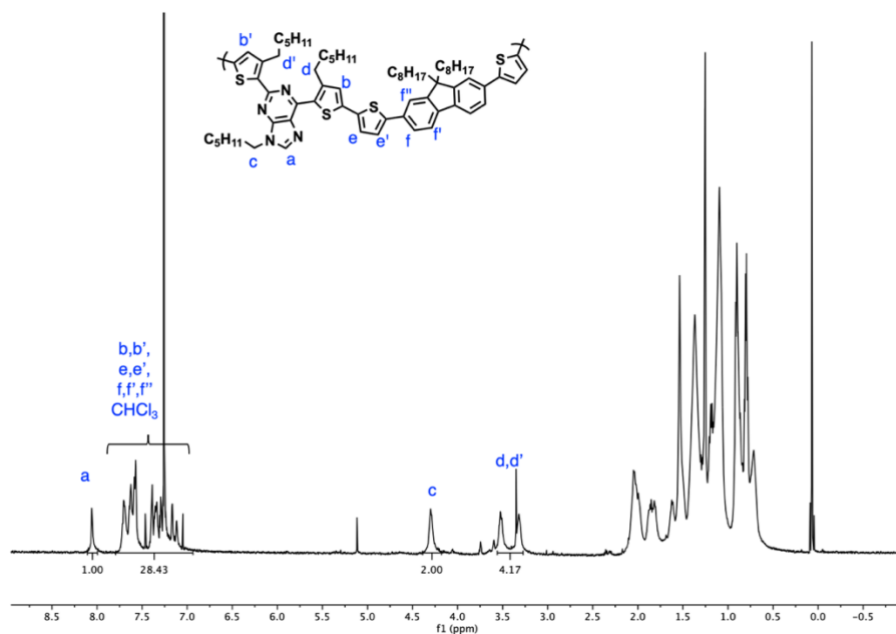


Figure A.10 ^1H NMR spectrum of P3_{TFT} (300 MHz, 25 °C, CDCl₃). δ (ppm): 0.61-2.19, 3.23-3.79, 4.16-5.37, 7.01-7.73, 8.03-8.13. The copolymer was obtained as a green solid.

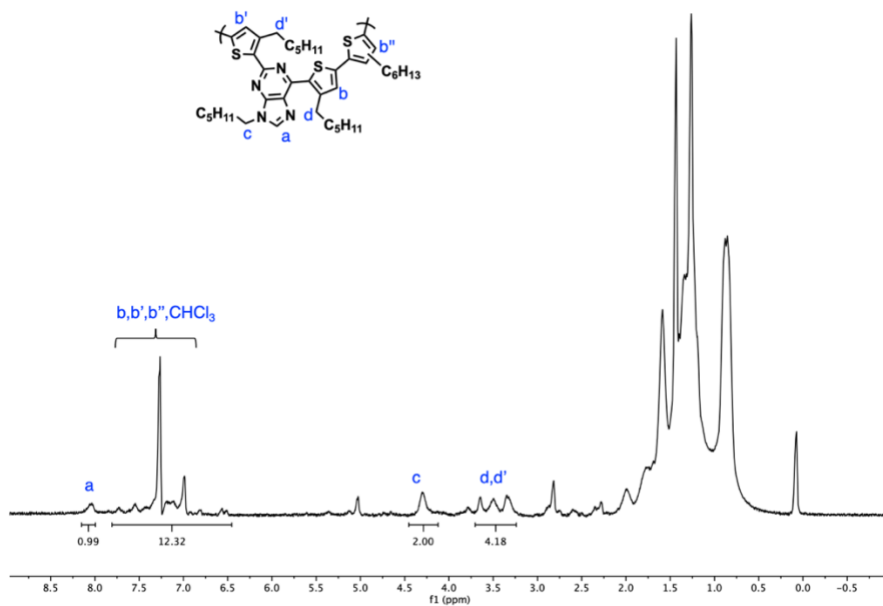


Figure A.11 ^1H NMR spectrum of P4_T (300 MHz, 25 °C, CDCl_3). δ (ppm): 0.46-2.98, 3.21-3.95, 4.11-4.38, 6.43-7.74, 7.81-8.13. The copolymer was obtained as a dark orange solid.

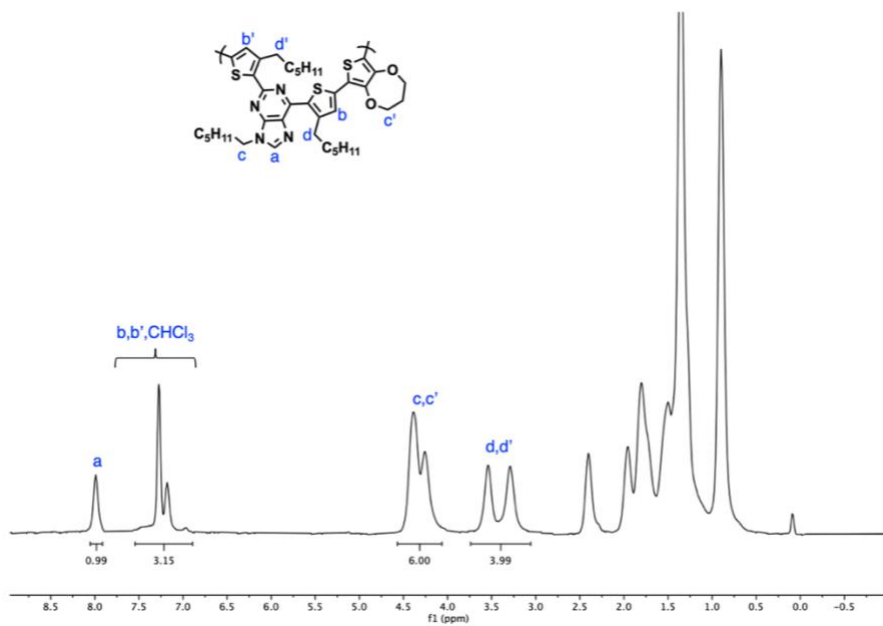


Figure A.12 ^1H NMR spectrum of P5_{ProDOT} (300 MHz, 25 °C, CDCl_3). δ (ppm): 0.53-2.15, 2.21-2.53, 3.11-3.67, 4.02-4.58, 6.91-7.44, 7.87-8.08. The copolymer was obtained as a red solid.

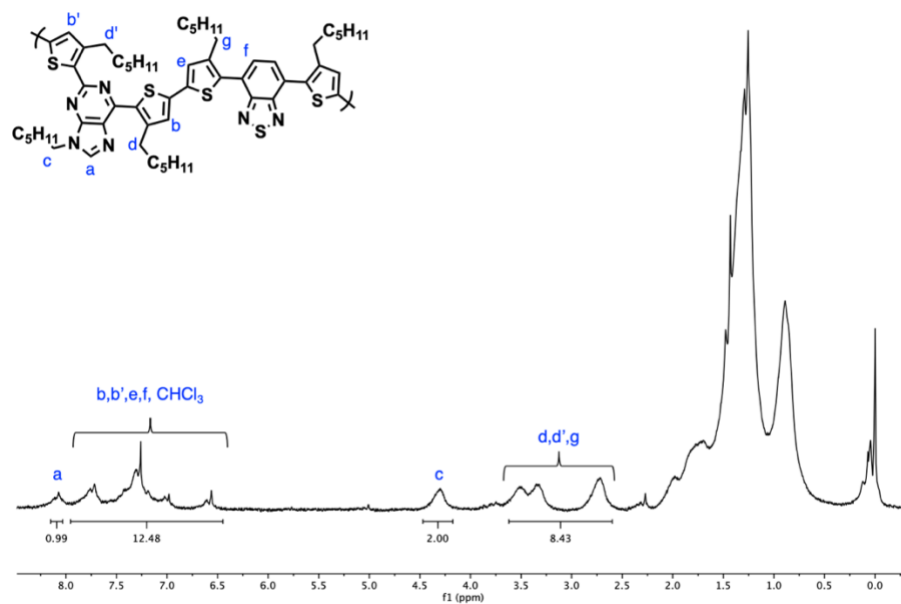


Figure A.13 ^1H NMR spectrum of P6_{TBTT} (300 MHz, 25 °C, CDCl_3). δ (ppm): 0.31-2.95, 3.12-3.99, 4.20-4.51, 6.52-8.27. The copolymer was obtained as a dark purple solid.

A.4 GPC Traces of Purine-Containing Copolymers

The following elugrams are from the copolymers presented in **Table 2.1**. All samples were measured using THF at 25 °C as the mobile phase at a flow rate of 1 mL/min, and molecular weight values are reported relative to PS standards. The concentration of samples was nominally 5 mg/mL.

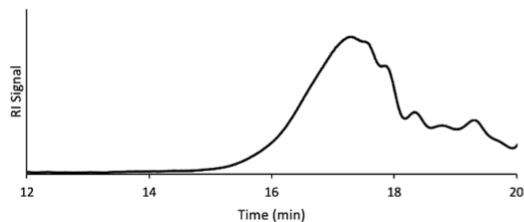


Figure A.14 GPC trace of P1_{TPT}.
P1_{TPT} has an $M_n = 9.03$ kg/mol and $\mathcal{D} = 2.16$.

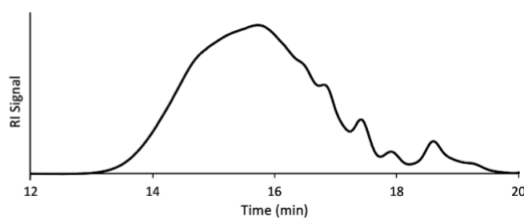


Figure A.15 GPC trace of P2_F.
P2_F has an $M_n = 9.46$ kg/mol and $\mathcal{D} = 1.81$.

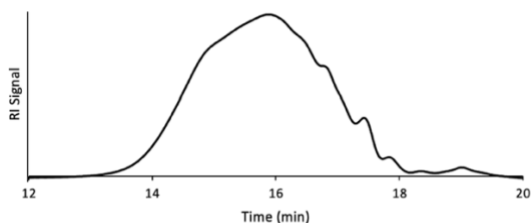


Figure A.16 GPC trace of P3_{TFT}.
P3_{TFT} has an $M_n = 12.1$ kg/mol and $\mathcal{D} = 3.18$.

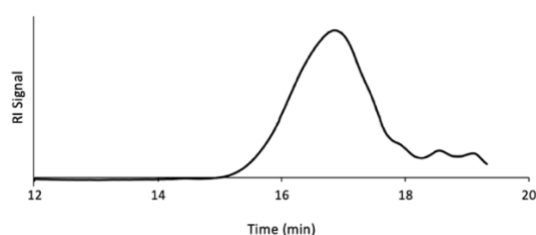


Figure A.17 GPC trace of P4_T.
P4_T has an $M_n = 9.82$ kg/mol and $\mathcal{D} = 1.72$.

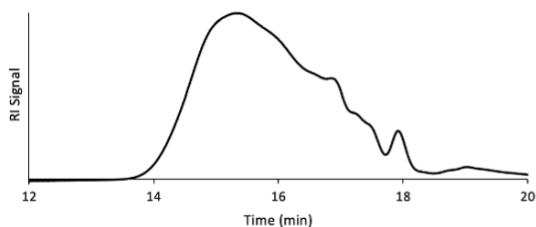


Figure A.18 GPC trace of P5_{ProDOT}.
P5_{ProDOT} has an $M_n = 9.79$ kg/mol and $\mathcal{D} = 2.06$.

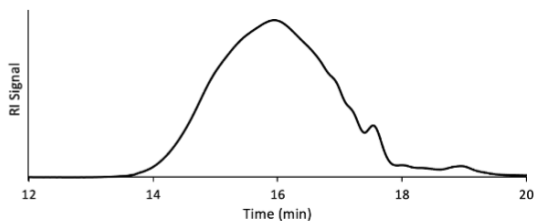


Figure A.19 GPC trace of P6_{TBTT}.
P6_{TBTT} has an $M_n = 12.5$ kg/mol and $\mathcal{D} = 2.54$.

A.5 Absorption Spectra as a Function of Copolymer Molecular Weight

The following UV/Vis spectra provide insight into changes in absorption behaviors of the various purine-containing copolymers as a function of copolymer molecular weight. All spectra were acquired at a nominal concentration of 0.01 mg/mL in CHCl_3 . Absorption maxima and onsets are summarized in **Table A.1**.

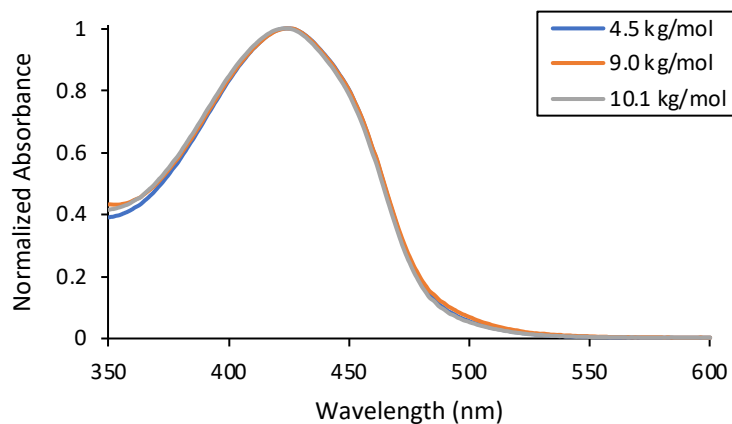


Figure A.20 Normalized UV-Vis spectra of P1_{TPT} copolymers synthesized at $M_n = 4.5$ g/mol, 9.0 g/mol, and 10.1 g/mol, as indicated in the legend.

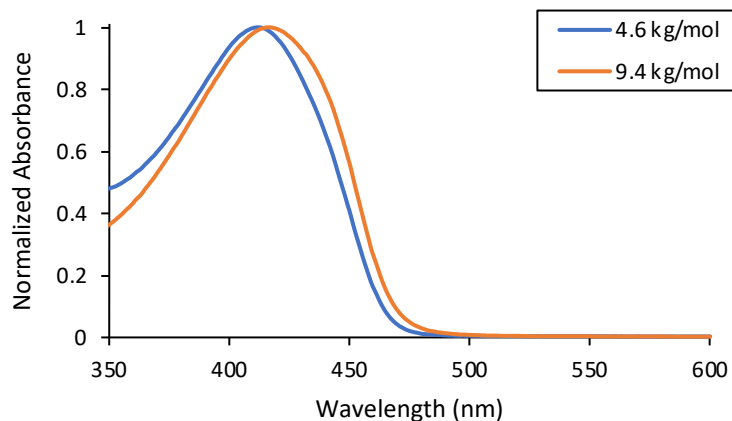


Figure A.21 Normalized UV-Vis spectra of P2_F copolymers synthesized at $M_n = 4.6$ g/mol and 9.4 g/mol, as indicated in the legend.

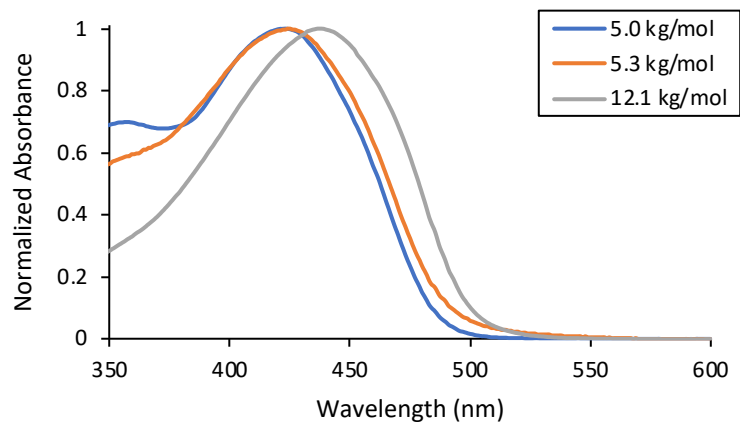


Figure A.22 Normalized UV-Vis spectra of P3_{TFT} copolymers synthesized at $M_n = 5.0$ g/mol, 5.3 g/mol, and 12.1 g/mol, as indicated in the legend.

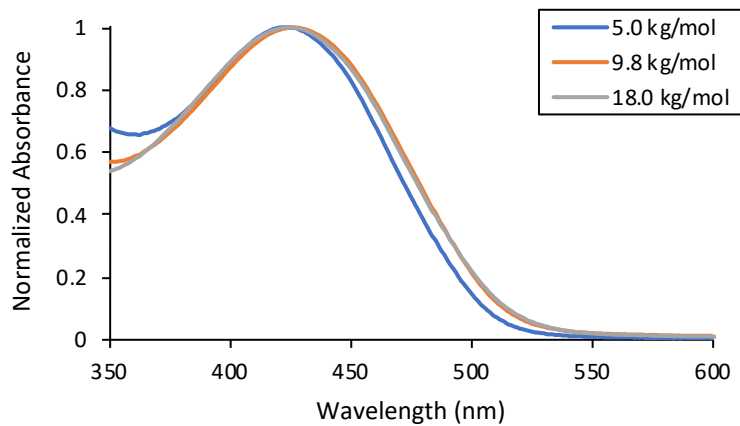


Figure A.23 Normalized UV-Vis spectra of P4_T copolymers synthesized at $M_n = 5.0$ g/mol, 9.8 g/mol, and 18.0 g/mol, as indicated in the legend.

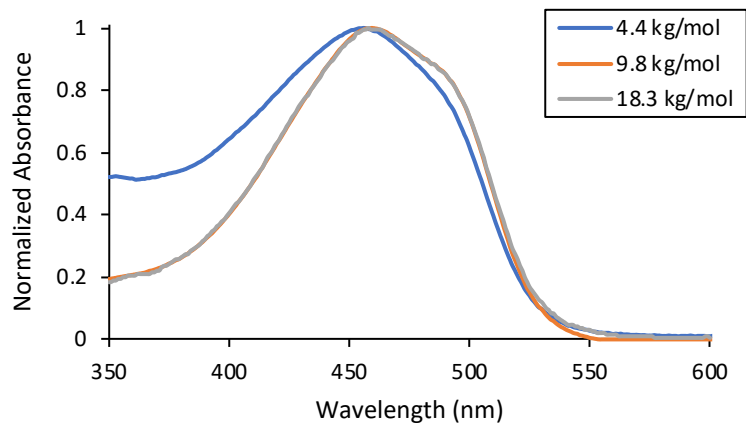


Figure A.24 Normalized UV-Vis spectra of P5_{ProDOT} copolymers synthesized at $M_n = 4.4$ g/mol, 9.8 g/mol, 18.3 g/mol, as indicated in the legend.

A.6 Absorbance Spectra and Corresponding Beer-Lambert Plots

The following plots present concentration dependent optical absorption data and Beer-Lambert plots for **M1** and for the purine-containing polymers presented in **Table 2.1** of Chapter II.

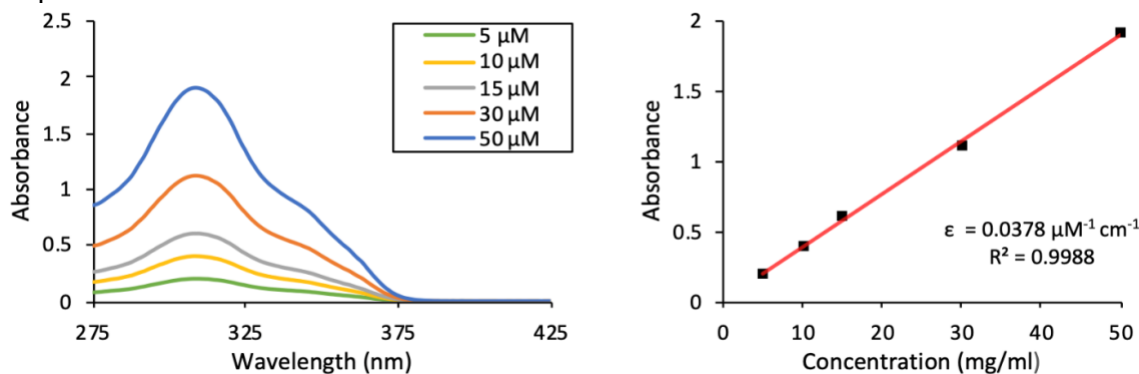


Figure A.25 UV-Vis spectra of TPT (M1) at various concentrations in chloroform (left) and the corresponding Beer-Lambert plot (right) with best-fit line.

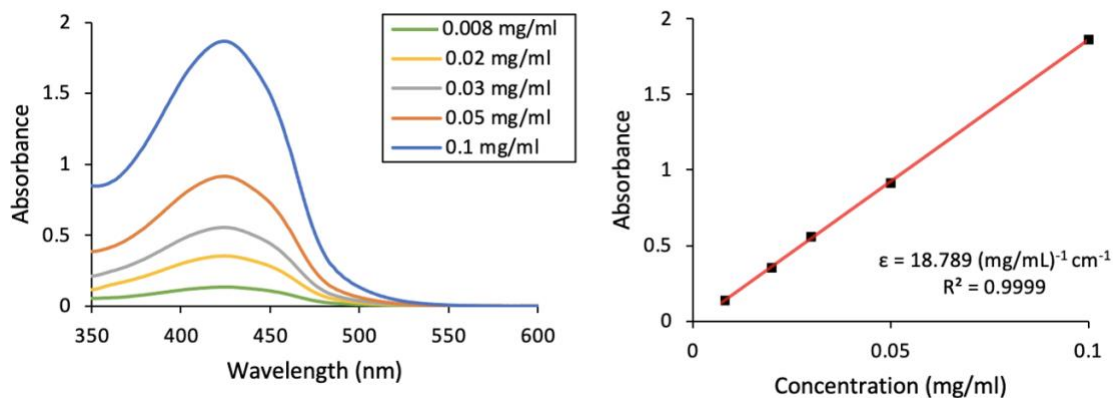


Figure A.26 UV-Vis spectra of P1_{TPT} at various concentrations in chloroform (left) and the corresponding Beer-Lambert plot (right) with best-fit line.

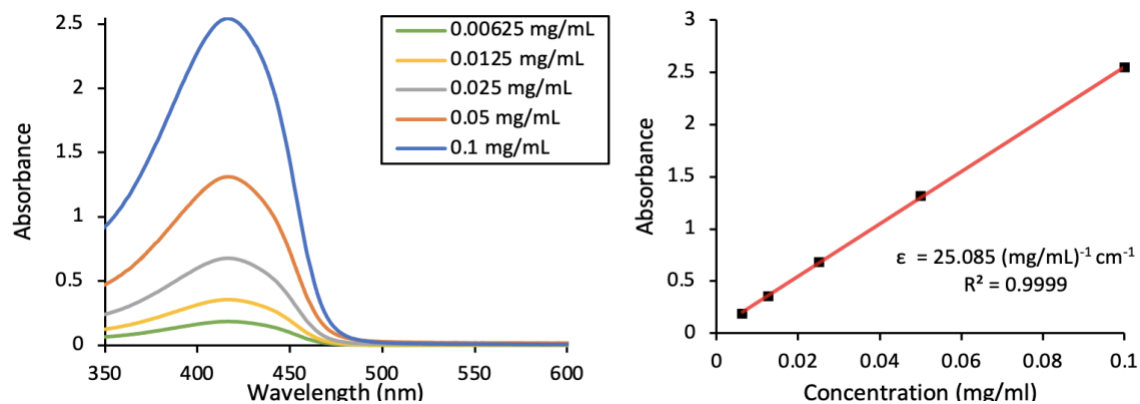


Figure A.27 UV-Vis spectra of P2_F at various concentrations in chloroform (left) and the corresponding Beer-Lambert plot (right) with best-fit line.

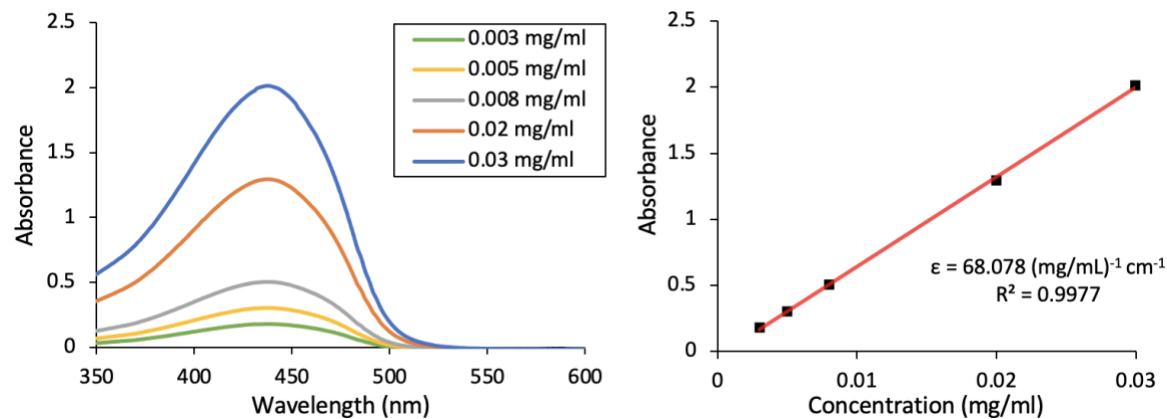


Figure A.28 UV-Vis spectra of P3_{TFT} at various concentrations in chloroform (left) and the corresponding Beer-Lambert plot (right) with best-fit line.

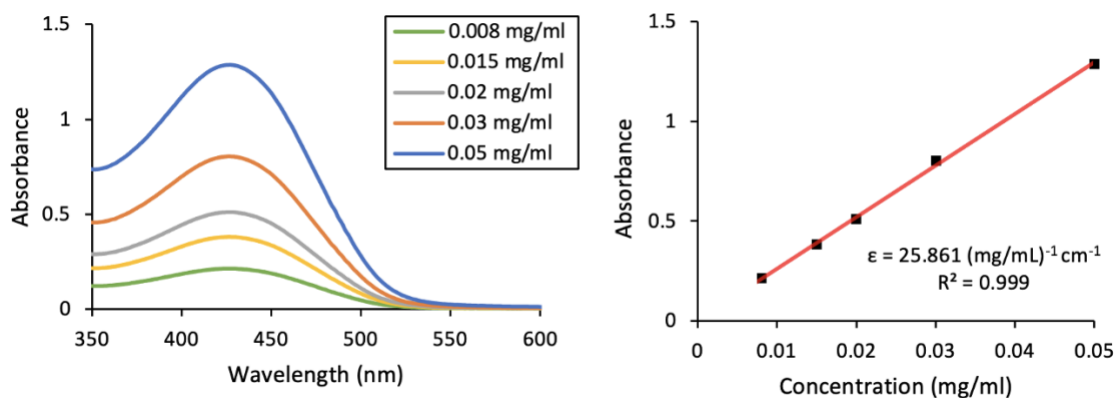


Figure A.29 UV-Vis spectra of P4_T at various concentrations in chloroform (left) and the corresponding Beer-Lambert plot (right) with best-fit line.

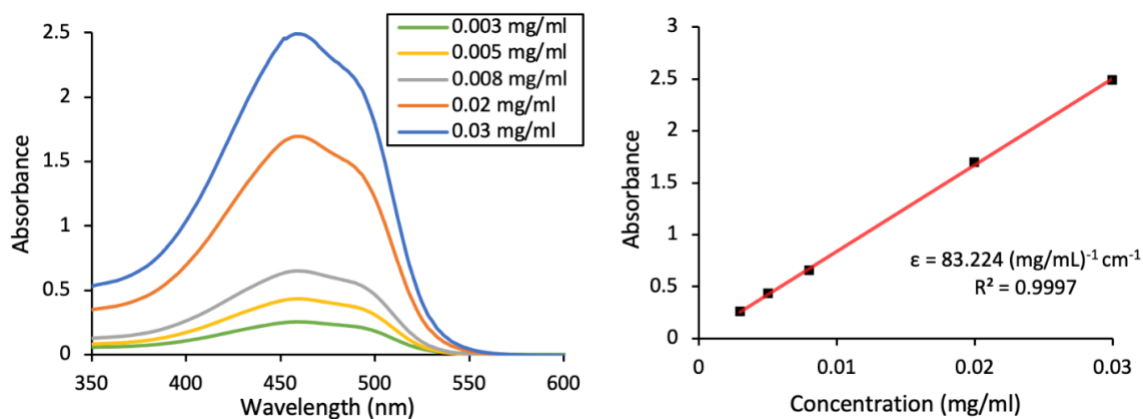


Figure A.30 UV-Vis spectra of P5_{ProDOT} at various concentrations in chloroform (left) and corresponding the Beer-Lambert plot (right) with best-fit line.

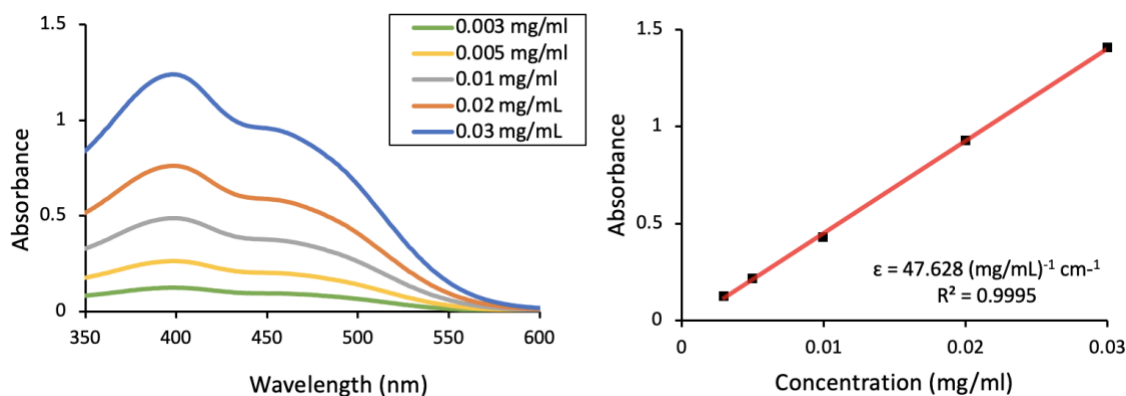


Figure A.31 UV-Vis spectra of P6_{TBTT} at various concentrations in chloroform (left) and the corresponding Beer-Lambert plot (right) with best-fit line.

A.7 Methanol Titration Study of P5_{ProDOT} in Chloroform

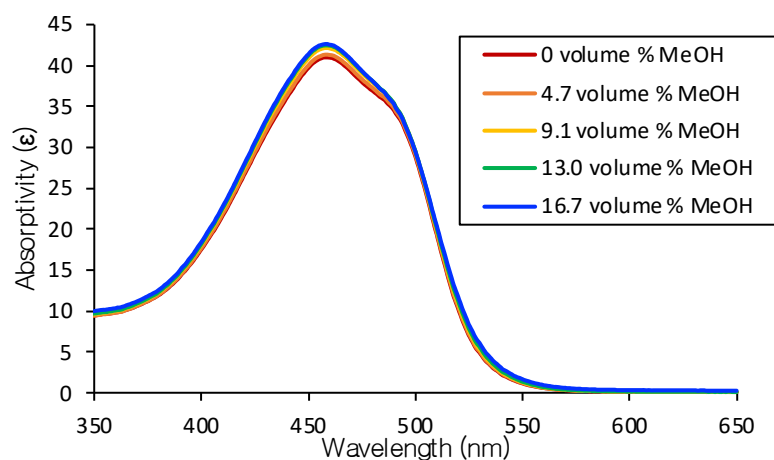


Figure A.32 UV-Vis spectra of P5_{ProDOT} in CHCl₃ acquired after sequential additions of methanol are used to investigate whether shoulder at 500 nm is due to aggregation. The fact that the absorbance maximum and shape remain unchanged suggests that the shoulder is not due to increased aggregation.

A.8 Solvatochromic Behavior of Purine-Containing Copolymers

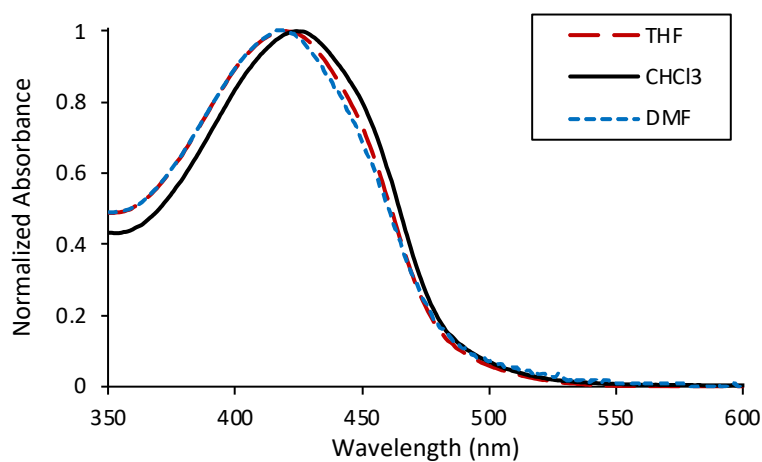


Figure A.33 UV-Vis spectra of P1_{TPT} in THF, DMF, and CHCl₃.

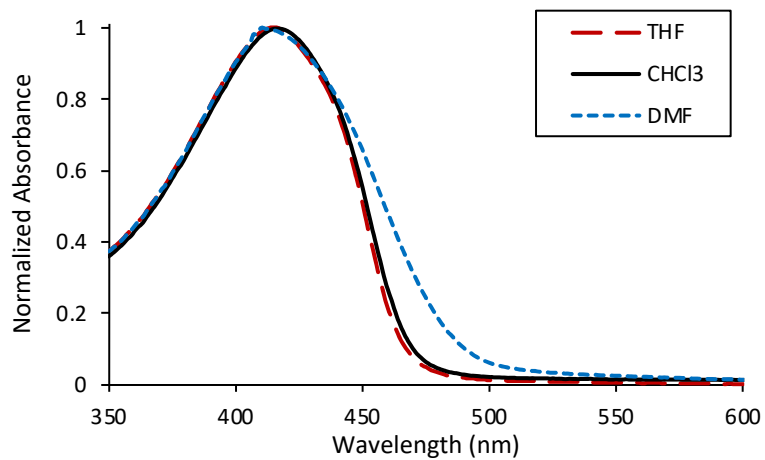


Figure A.34 UV-Vis spectra of P2_F in THF, DMF, and CHCl₃.

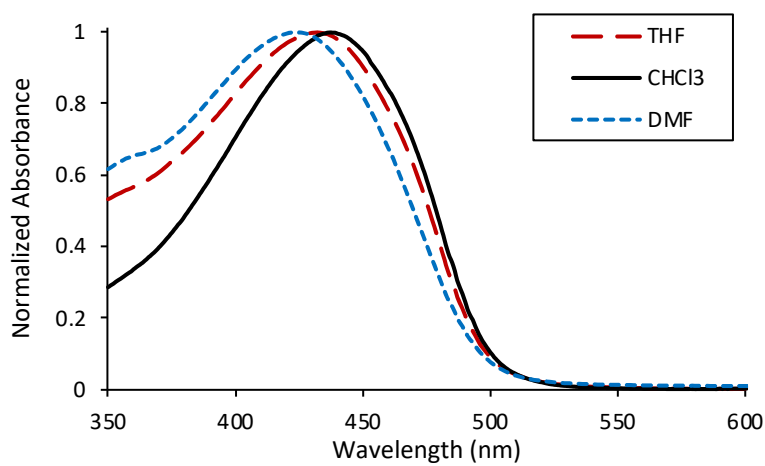


Figure A.35 UV-Vis spectra of P3_{TFT} in THF, DMF, and CHCl₃.

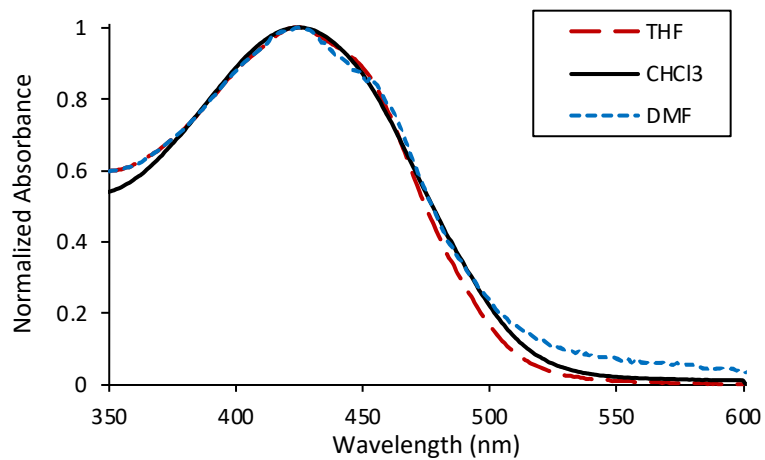


Figure A.36 UV-Vis spectra of P4_T in THF, DMF, and CHCl₃.

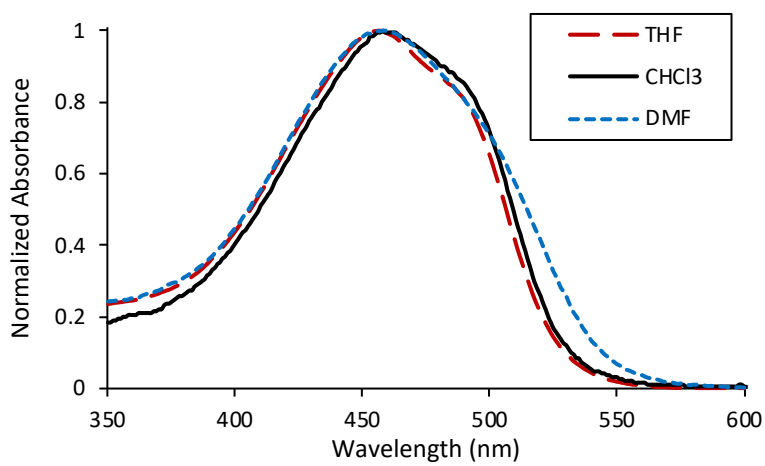


Figure A.37 UV-Vis spectra of P5_{ProDOT} in THF, DMF, and CHCl₃.

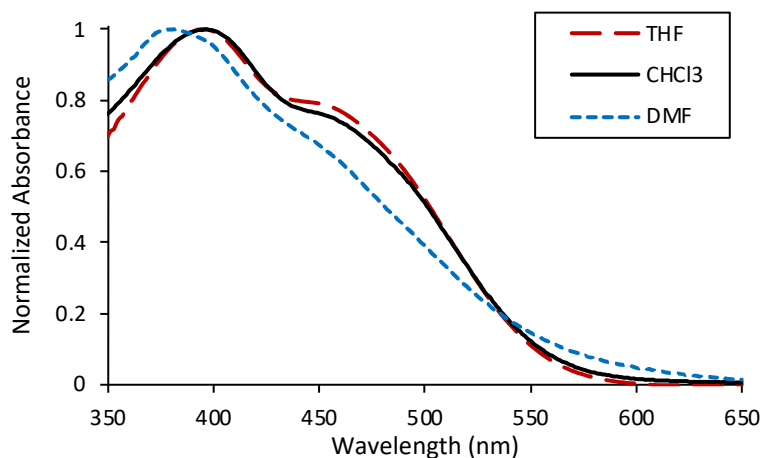


Figure A.38 UV-Vis spectra of P6_{TBTT} in THF, DMF, and CHCl₃.

A.9 Cyclic Voltammograms of Purine-Containing Copolymers

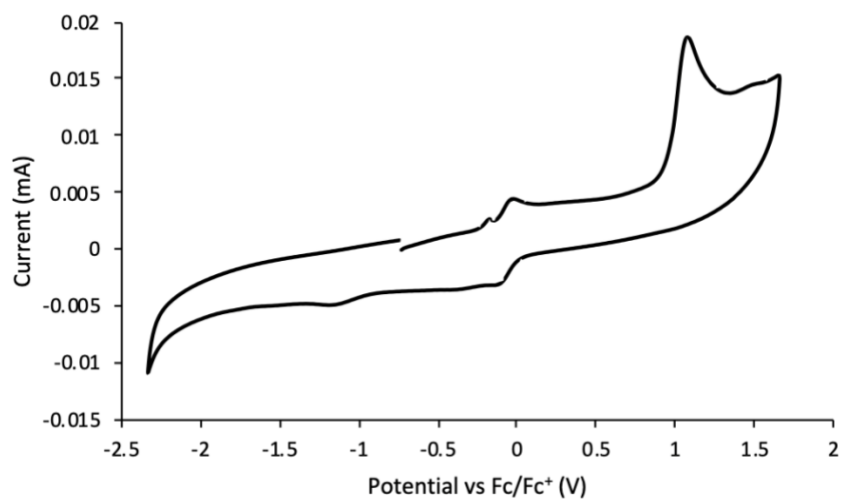


Figure A.39 Cyclic voltammogram of TPT (M1) in solution. Measured in dichloromethane using a scan rate of 150 mV/s with (*n*Bu)₄NPF₆ (at 0.20 M) as the supporting electrolyte. Potential is set relative to Fc/Fc⁺.

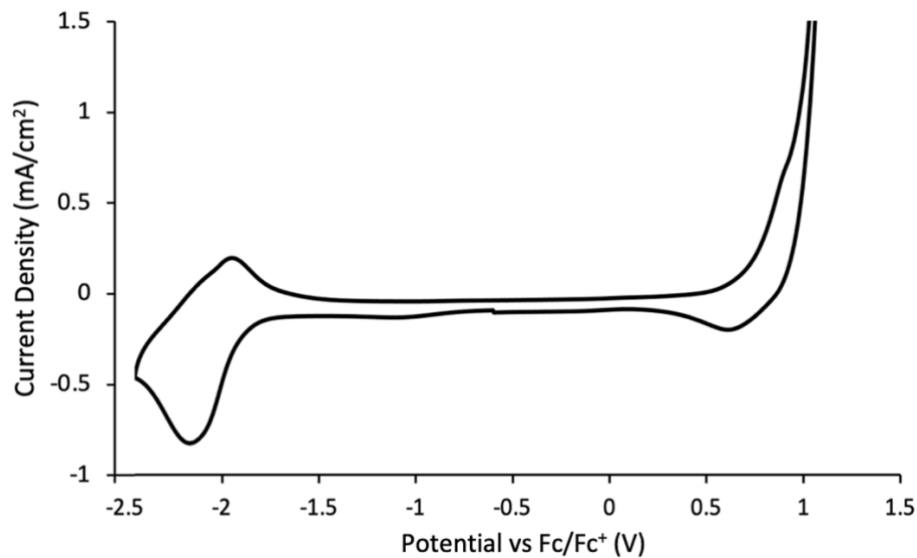


Figure A.40 Cyclic voltammogram of P1_{TPT} as a thin film. Measured in acetonitrile using a scan rate of 150 mV/s with (*n*Bu)₄NPF₆ (at 0.20 M) as the supporting electrolyte. Potential is set relative to Fc/Fc⁺.

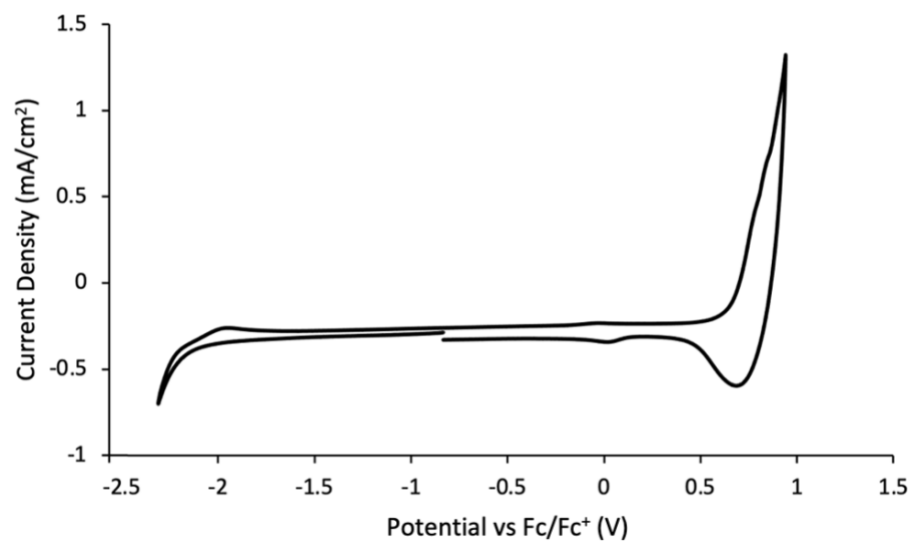


Figure A.41 Cyclic voltammogram of P3_{TFT} as a thin film. Measured in acetonitrile using a scan rate of 150 mV/s with (*n*Bu)₄NPF₆ (at 0.20 M) as the supporting electrolyte. Potential is set relative to Fc/Fc⁺.

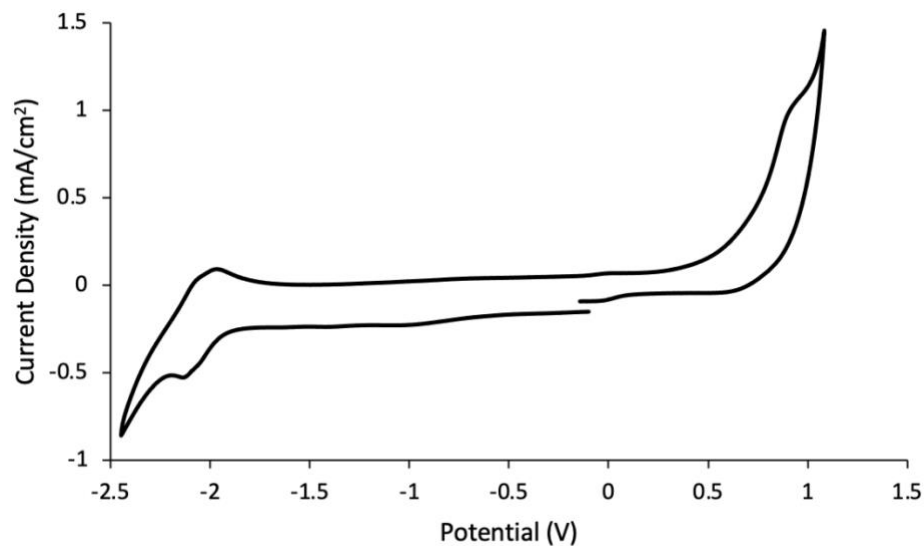


Figure A.42 Cyclic voltammogram of P4_T as a thin film. Measured in acetonitrile using a scan rate of 150 mV/s with (*n*Bu)₄NPF₆ (at 0.20 M) as the supporting electrolyte. Potential is set relative to Fc/Fc⁺.

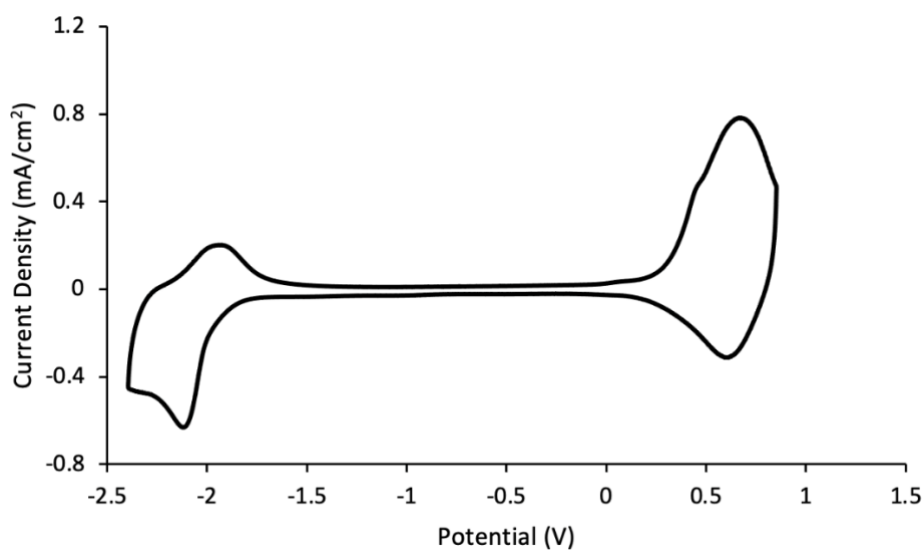


Figure A.43 Cyclic voltammogram of P5_{ProDOT} as a thin film. Measured in acetonitrile using a scan rate of 150 mV/s with (*n*Bu)₄NPF₆ (at 0.20 M) as the supporting electrolyte. Potential is set relative to Fc/Fc⁺.

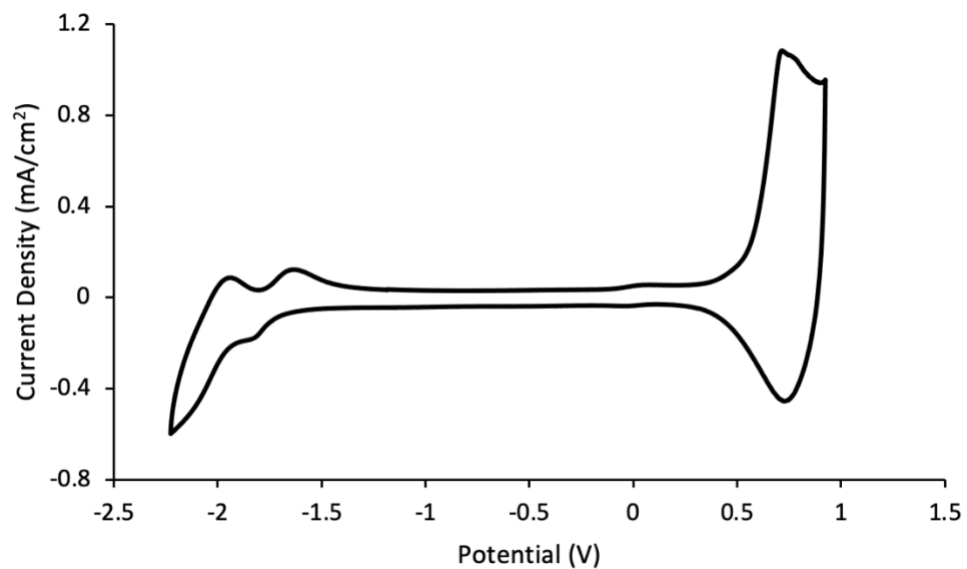


Figure A.44 Cyclic voltammogram of P6_{TBT} as a thin film. Measured in acetonitrile using a scan rate of 150 mV/s with (*n*Bu)₄NPF₆ (at 0.20 M) as the supporting electrolyte. Potential is set relative to Fc/Fc⁺.

Appendix B

B.1 Synthesis and Characterization of Monomers

Synthesis of 9-hexyl-2,6-bis(3-hexylthiophen-2-yl)-9H-purine (M1). Reaction conditions have been previously reported in Chapter II. **M1** was recovered at an 87% yield. ¹H NMR spectrum was consistent with the peaks reported in Chapter II: (500 MHz, 25 °C, CDCl₃). δ, ppm: 0.88 (t, 6H, CH₃), 1.19-1.52 (m, 18H, CH₂), 1.75 (p, 4H, CH₂), 1.96 (p, 2H, CH₂), 3.31 (t, 2H, ArCH₂), 3.43 (t, 2H, ArCH₂), 4.28 (t, 2H, NCH₂), 7.00 (d, 1H, ArH), 7.09 (d, 1H, ArH), 7.31 (d, 1H, ArH), 7.54 (d, 1H, ArH), 8.01 (s, 1H, C8-H).

Synthesis of 2,6-bis(5-bromo-3-hexylthiophen-2-yl)-9-hexyl-9H-purine (M2) and 2-(5-bromo-3-hexylthiophen-2-yl)-9-hexyl-6-(3-hexylthiophen-2-yl)-9H-purine (M3). Reaction conditions have been reported in Chapter II. **M2** was recovered at a 43%. ¹H NMR spectrum was consistent with the peaks reported in Chapter II: (500 MHz, 25 °C, CDCl₃). δ, ppm: 0.90 (m, 6H, CH₃), 1.17-1.56 (m, 18H, CH₂), 1.70 (p, 4H, CH₂), 1.95 (p, 2H, CH₂), 3.24 (t, 2H, ArCH₂), 3.35 (t, 2H, ArCH₂), 4.24 (t, 2H, NCH₂), 6.96 (s, 1H, ArH), 7.05 (s, 1H, ArH), 8.02 (s, 1H, C8-H). The mono-brominated product **M3** was also recovered at a 47% yield. ¹H NMR spectrum recorded for 2-(5-bromo-3-hexylthiophen-2-yl)-9-hexyl-6-(3-hexylthiophen-2-yl)-9H-purine (**M3**) (500 MHz, 25 °C, CDCl₃). δ, ppm: 0.86 (t, 9H, CH₃), 1.14-1.50 (m, 18H, CH₂), 1.73 (p, 4H, CH₂), 1.95 (p, 2H, CH₂), 3.24 (t, 2H, ArCH₂), 3.38 (t, 2H, ArCH₂), 4.25 (t, 2H, NCH₂), 6.95 (s, 1H, ArH), 7.09 (d, 1H, ArH), 7.54 (d, 1H, ArH), 8.00 (s, 1H, C8-H).

B.2 ^1H and ^{13}C NMR of 2-(5-bromo-3-hexylthiophen-2-yl)-9-hexyl-6-(3-hexylthiophen-2-yl)-9H-purine (M3)

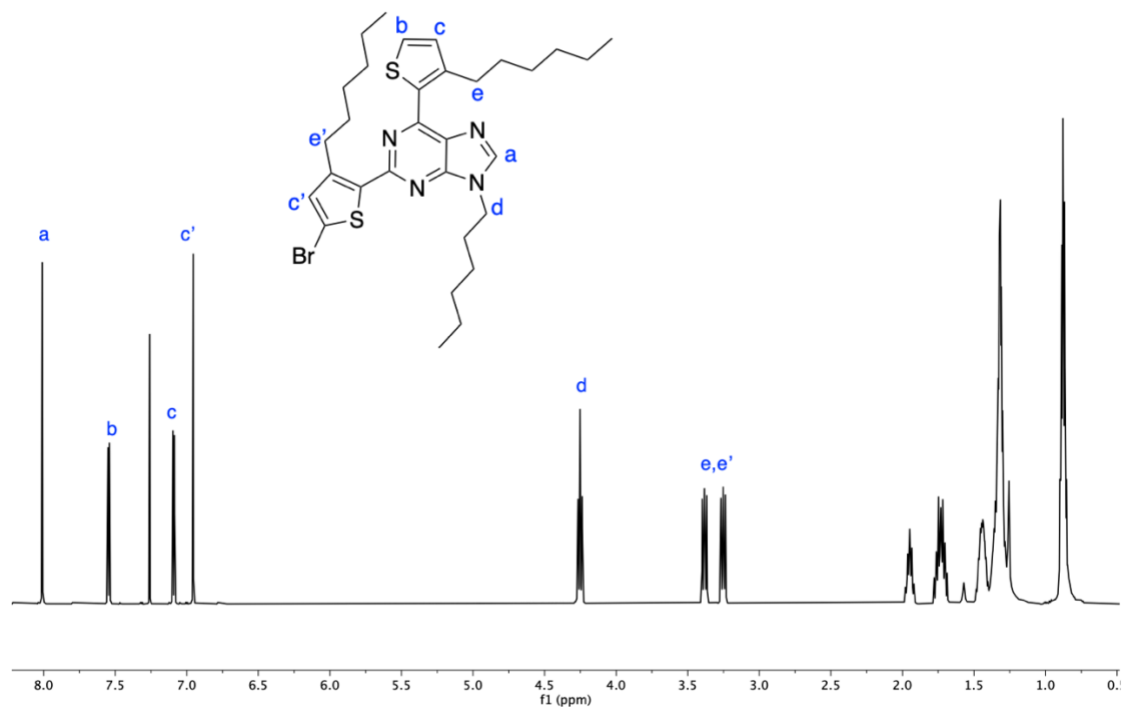


Figure B.1 ^1H NMR spectrum of 2-(5-bromo-3-hexylthiophen-2-yl)-9-hexyl-6-(3-hexylthiophen-2-yl)-9H-purine (M3) (600 MHz, 25 °C, CDCl_3). δ , ppm: 0.86 (t, 9H, CH_3), 1.14-1.50 (m, 18H, CH_2), 1.73 (p, 4H, CH_2), 1.95 (p, 2H, CH_2), 3.24 (t, 2H, ArCH_2), 3.38 (t, 2H, ArCH_2), 4.25 (t, 2H, NCH_2), 6.95 (s, 1H, ArH), 7.09 (d, 1H, ArH), 7.54 (d, 1H, ArH), 8.00 (s, 1H, C8-H).

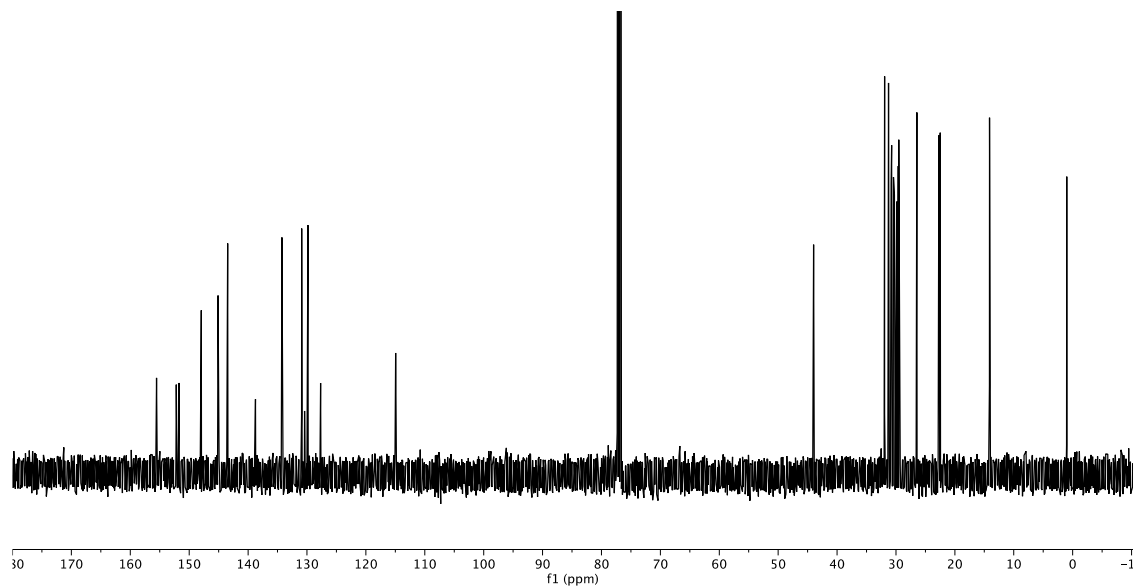


Figure B.2 ^{13}C NMR spectrum (600 MHz, 25 °C, CDCl_3) of 2-(5-bromo-3-hexylthiophen-2-yl)-9-hexyl-6-(3-hexylthiophen-2-yl)-9*H*-purine (M3).

B.3 Stacked ^1H NMR Spectra of M1, M2, and M3

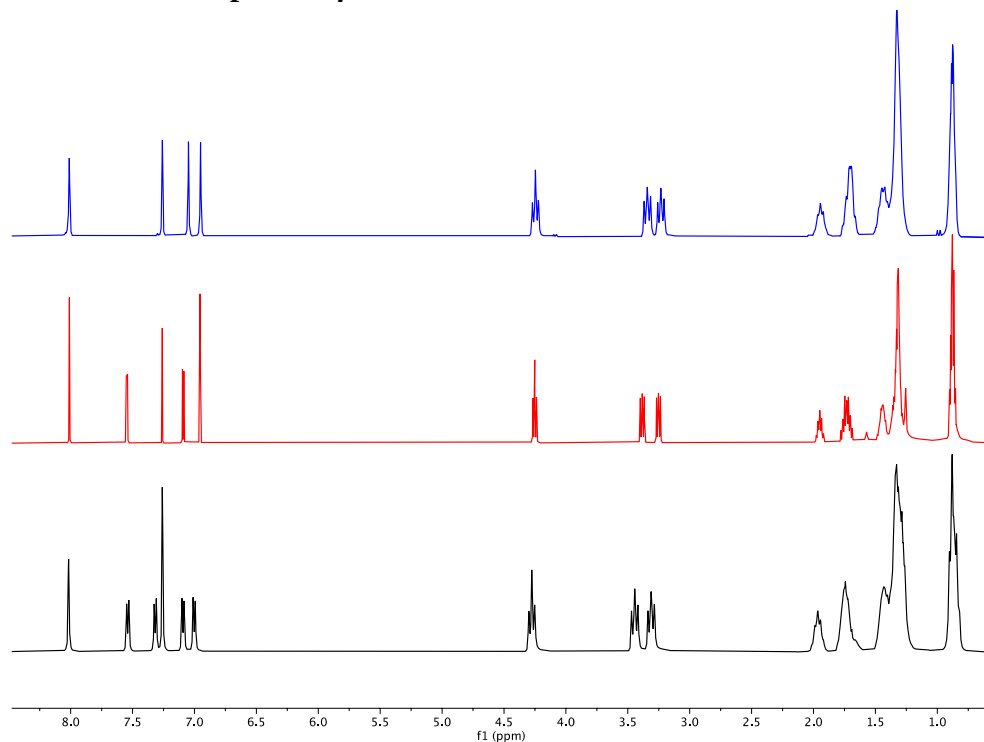


Figure B.3 Complete ^1H NMR spectra (in CDCl_3) confirming the conversion from M1 (black spectrum, bottom) to M3 (red spectrum, middle) to M2 (blue spectrum, top). R = hexyl.

B.4 2-D ^1H - ^{13}C HSQC NMR Spectra of M1, M2, and M3

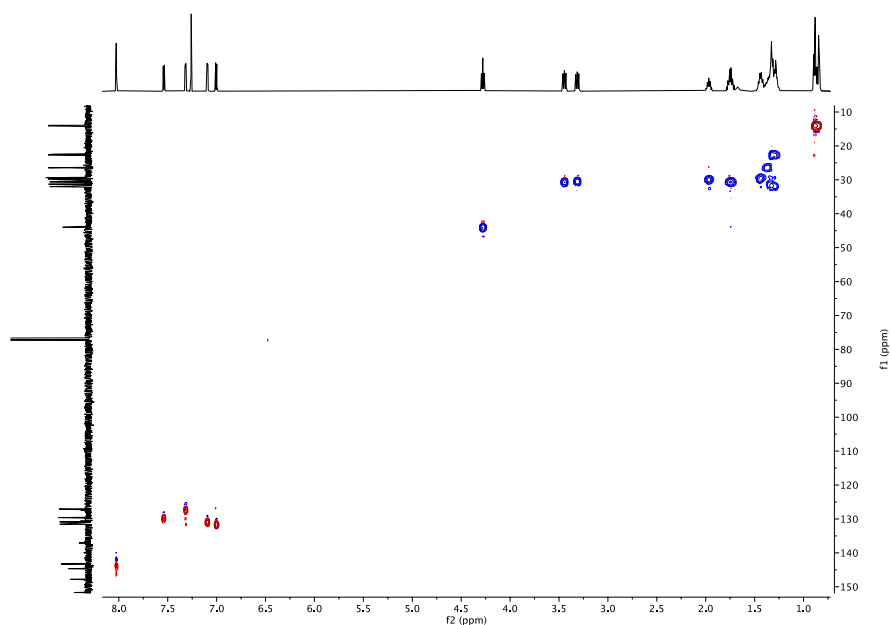


Figure B.4 ^1H - ^{13}C HSQC NMR spectra of 9-hexyl-2,6-bis(3-hexylthiophen-2-yl)-9H-purine (M1) (600 MHz, 25 $^{\circ}\text{C}$, CDCl_3).

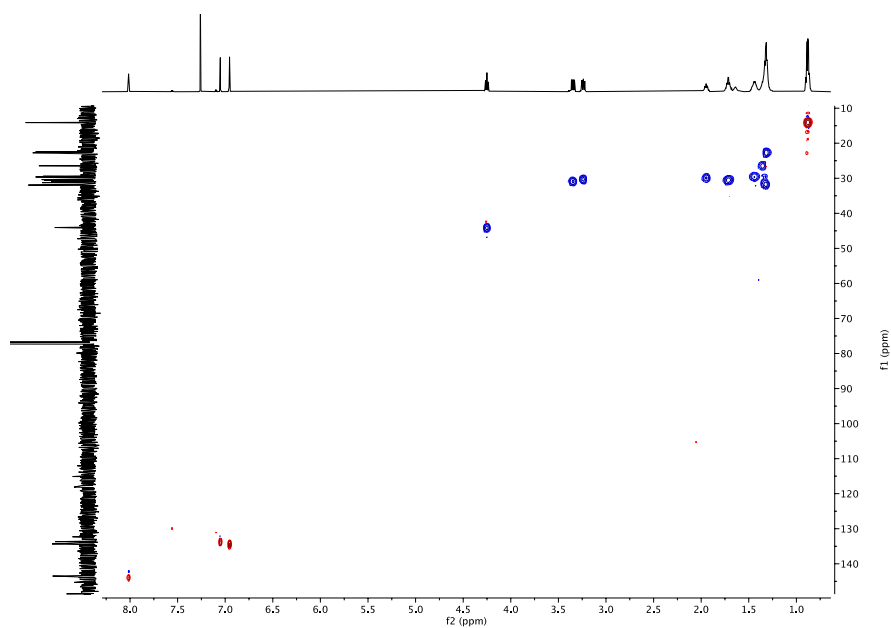


Figure B.5 ^1H - ^{13}C HSQC NMR spectra of 2,6-bis(5-bromo-3-hexylthiophen-2-yl)-9-hexyl-9H-purine (M2) (600 MHz, 25 $^{\circ}\text{C}$, CDCl_3).

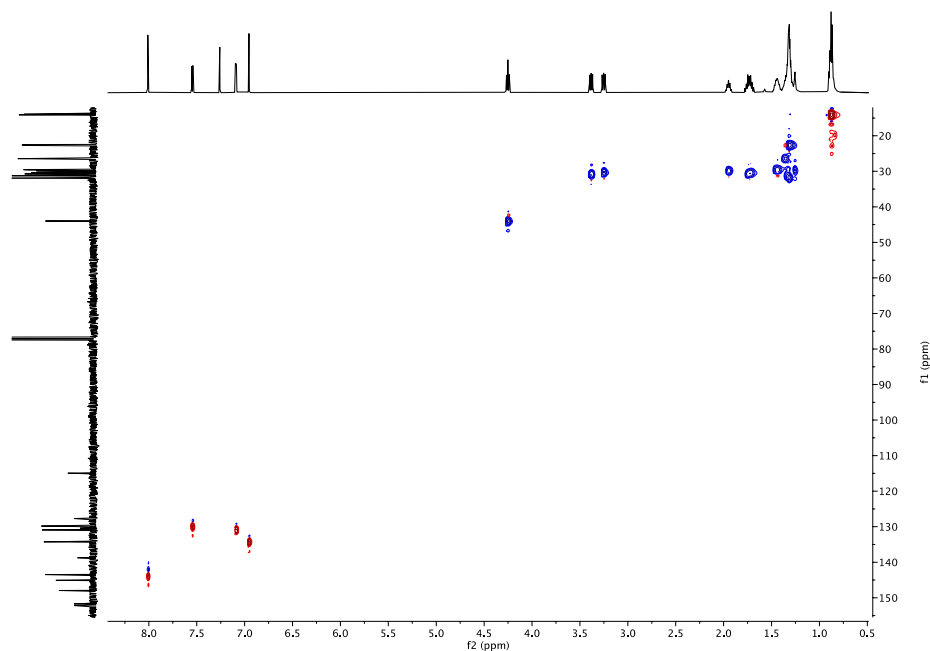


Figure B.6 $^1\text{H} - ^{13}\text{C}$ HSQC NMR spectra of 2-(5-bromo-3-hexylthiophen-2-yl)-9-hexyl-6-(3-hexylthiophen-2-yl)-9H-purine (M3) (600 MHz, 25 °C, CDCl_3).

B.5 2-D $^1\text{H} - ^{13}\text{C}$ HMBC NMR Spectra of Monomers

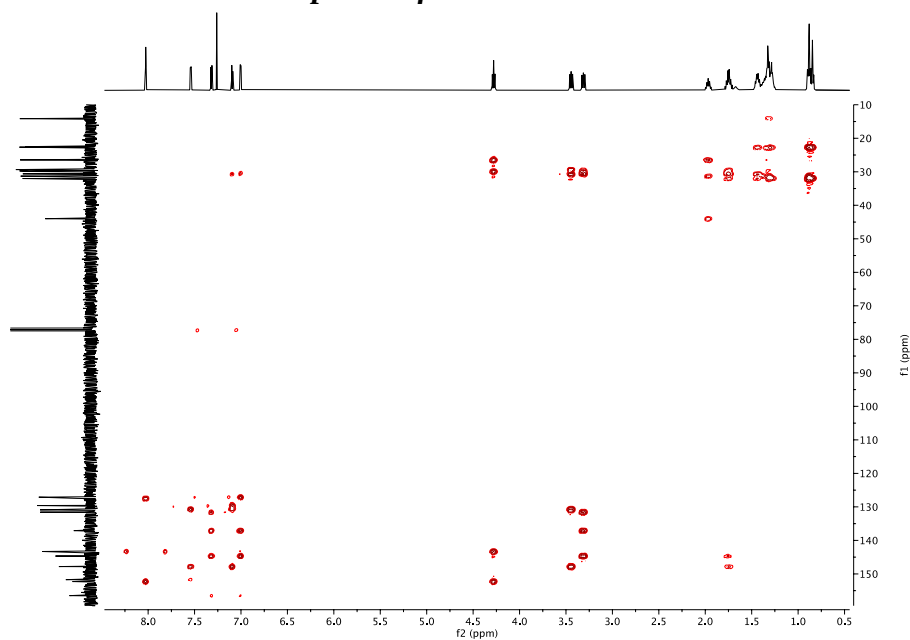


Figure B.7 $^1\text{H} - ^{13}\text{C}$ HMBC NMR spectra of 9-hexyl-2,6-bis(3-hexylthiophen-2-yl)-9H-purine (M1) (600 MHz, 25 °C, CDCl_3).

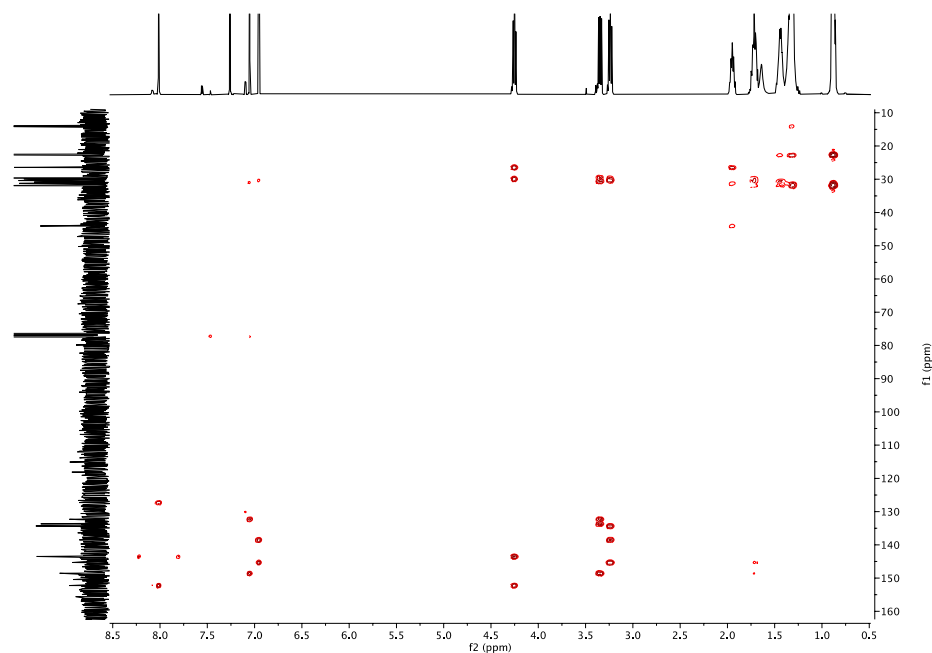


Figure B.8 ^1H – ^{13}C HMBC NMR spectra of 2,6-bis(5-bromo-3-hexylthiophen-2-yl)-9-hexyl-9*H*-purine (M2) (600 MHz, 25 °C, CDCl_3).

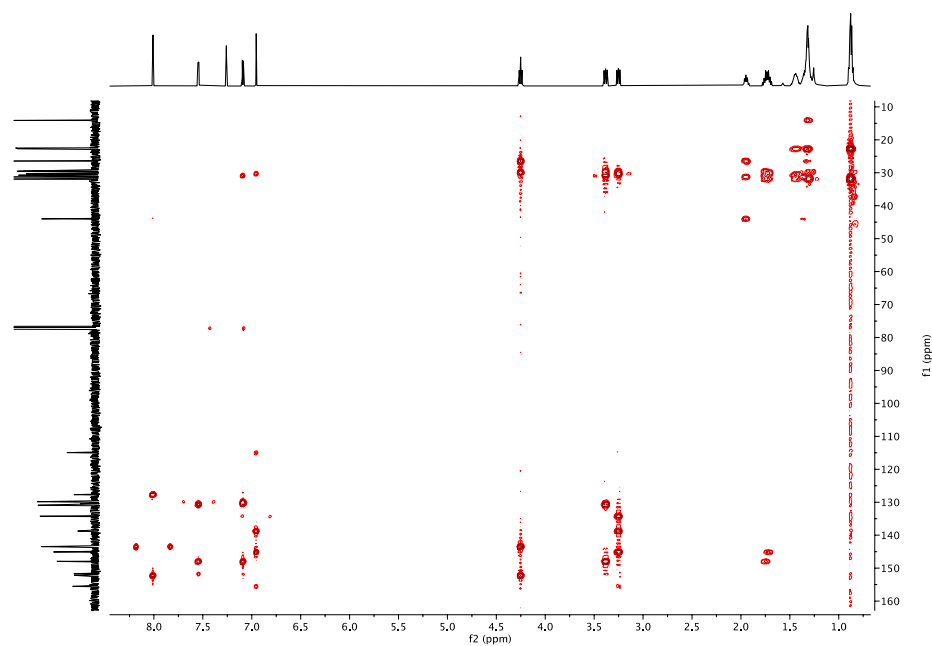


Figure B.9 ^1H – ^{13}C HMBC NMR spectra of 2-(5-bromo-3-hexylthiophen-2-yl)-9-hexyl-6-(3-hexylthiophen-2-yl)-9*H*-purine (M3) (600 MHz, 25 °C, CDCl_3).

B.6 2-D ^1H – ^1H NOESY NMR Spectra of M1

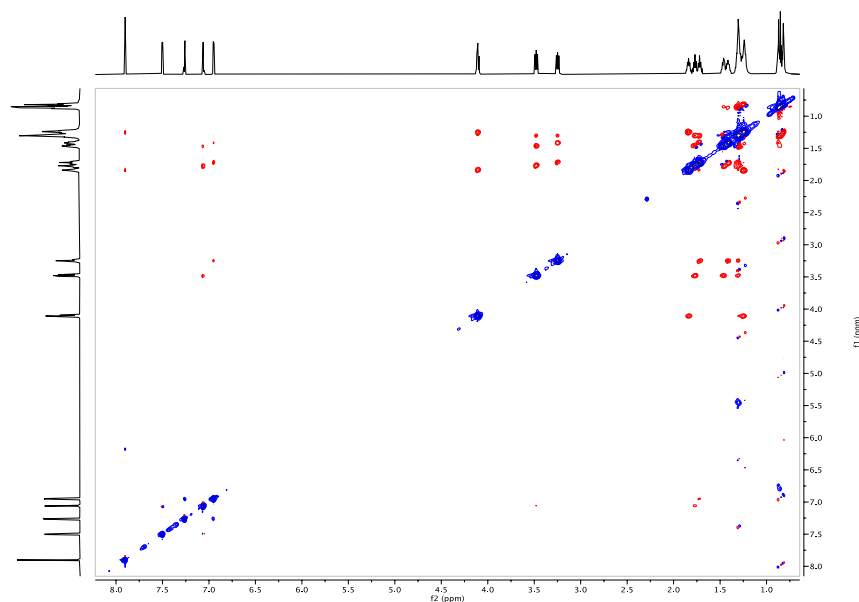


Figure B.10 ^1H – ^1H NOESY NMR spectra of 9-hexyl-2,6-bis(3-hexylthiophen-2-yl)-9H-purine (M1) (600 MHz, 25 °C, CDCl_3).

B.7 NMR spectra of Purine-Containing Copolymers

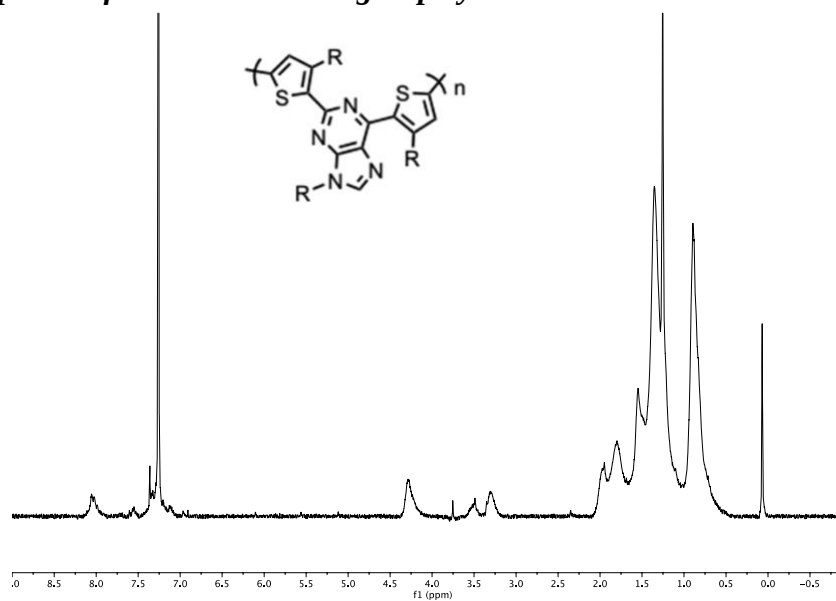


Figure B.11 ^1H NMR spectrum of the polymer created by DArP using the AB monomer (M3) (300 MHz, 25 °C, CDCl_3). δ (ppm): 0.42-2.11, 3.14-3.39, 3.42-3.65, 4.02-4.39, 6.86-7.68, 7.87-8.17. The copolymer was obtained as a dark orange solid.

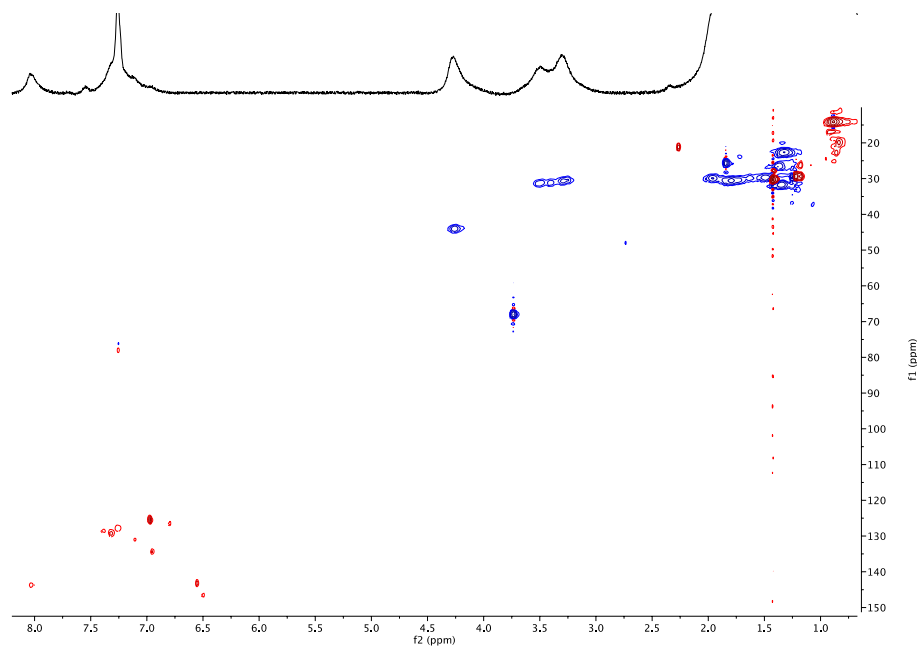


Figure B.12 $^1\text{H} - ^{13}\text{C}$ HSQC NMR spectra of the polymer created by DArP using the AB monomer (M3) (600 MHz, 25 °C, CDCl_3). Correlations indicate a single bond between carbon and corresponding protons.

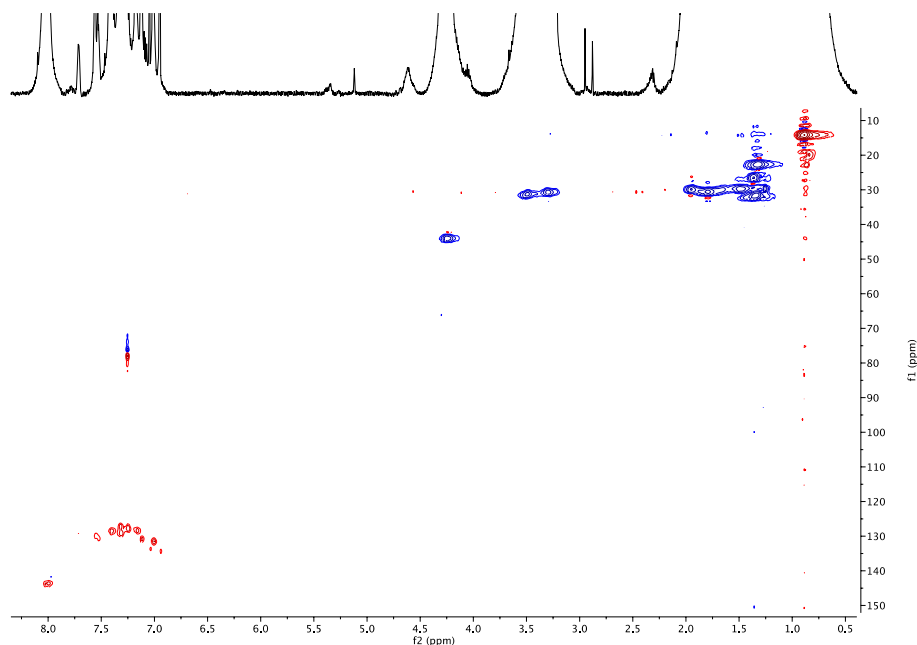


Figure B.13 $^1\text{H} - ^{13}\text{C}$ HSQC NMR spectra of the copolymer created by DArP using the AA+BB monomers (M1 and M2) (600 MHz, 25 °C, CDCl_3). Correlations indicate a single bond between carbon and corresponding protons.

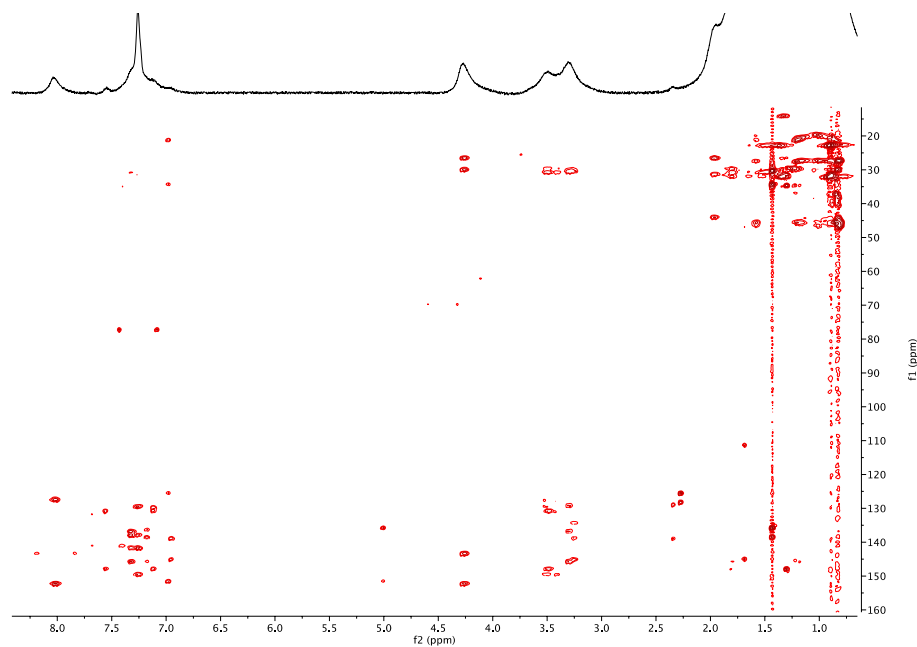


Figure B.14 $^1\text{H} - ^{13}\text{C}$ HMBC NMR spectra of the polymer created by DArP using the AB monomer (M3) (600 MHz, 25 °C, CDCl_3). Correlations indicate 2-3 bonds between carbon and corresponding protons.

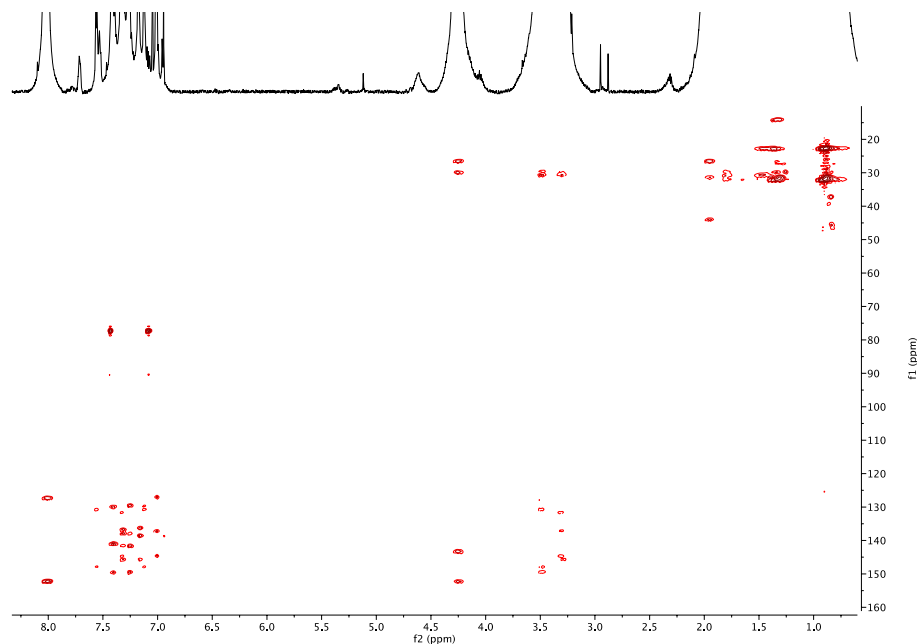


Figure B.15 $^1\text{H} - ^{13}\text{C}$ HMBC NMR spectra of the copolymer created by DArP using the AA+BB monomers (M1 and M2) (600 MHz, 25 °C, CDCl_3). Correlations indicate 2-3 bonds between carbon and corresponding protons.

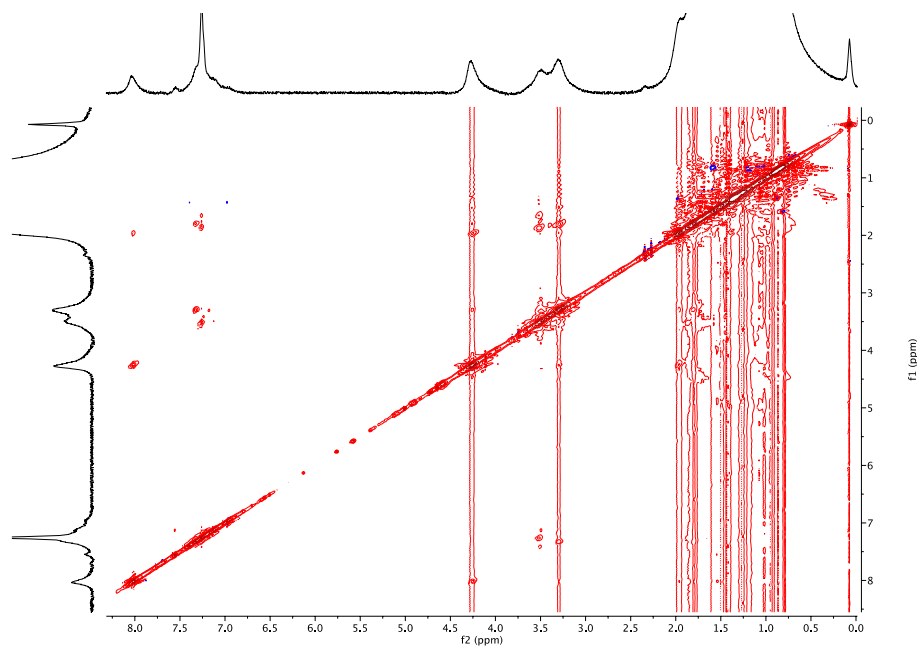


Figure B.16 2-D ^1H – ^1H NOESY NMR spectra of the polymer created by DArP using the AB monomer (M3) (600 MHz, 25 °C, CDCl_3). Correlations indicates two hydrogens within 2-5 Å.

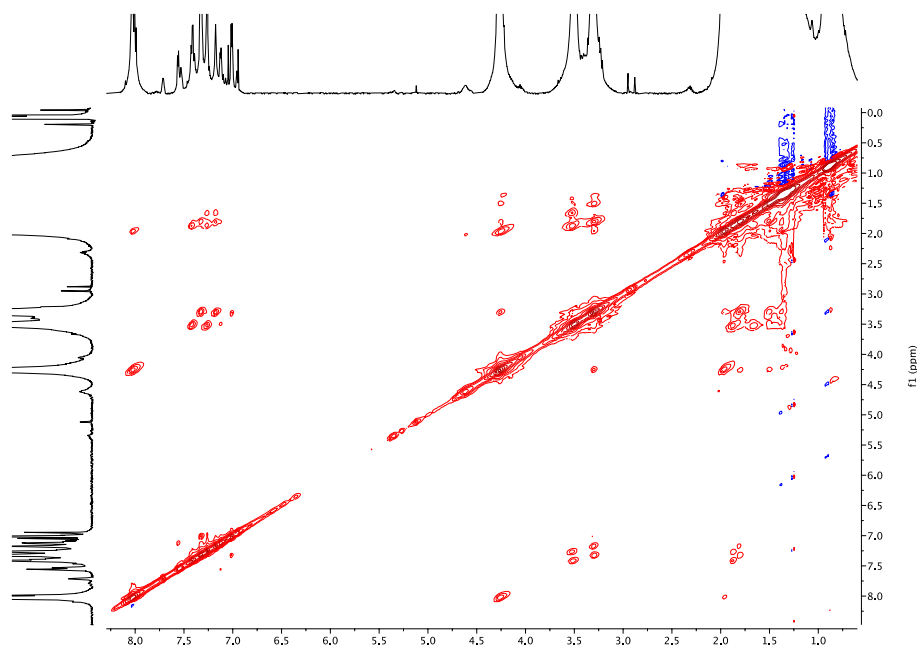


Figure B.17 ^1H – ^1H NOESY NMR spectra of the copolymer created by DArP using the AA+BB monomers (M1 and M2) (600 MHz, 25 °C, CDCl_3). Correlations indicates two hydrogens within 2-5 Å.

B.8 GPC Traces of the Polymer Created by DArP using the AB Monomer (M3)

Samples were measured using THF at 25 °C as the mobile phase at a flow rate of 1 mL/min, and molecular weight values are reported relative to PS standards. The solution concentration was nominally 5 mg/mL for all polymers studied.

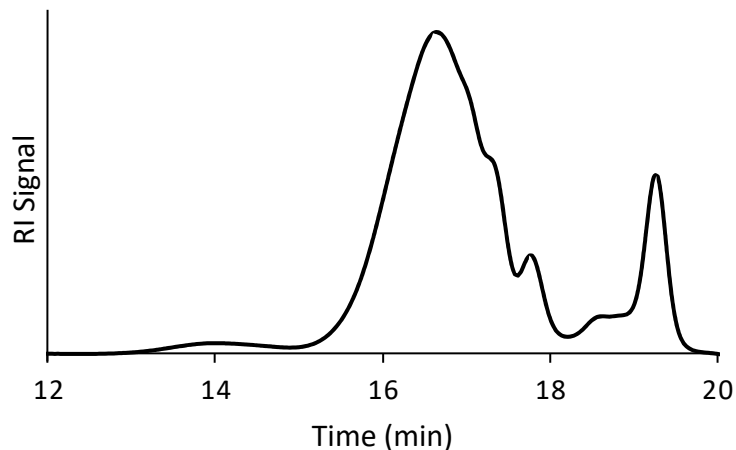


Figure B.18 GPC trace of the polymer created by DArP using the AB monomer (M3) – Sample 1. The polymer has an $M_n = 5.0$ kg/mol and $\mathcal{D} = 1.4$.

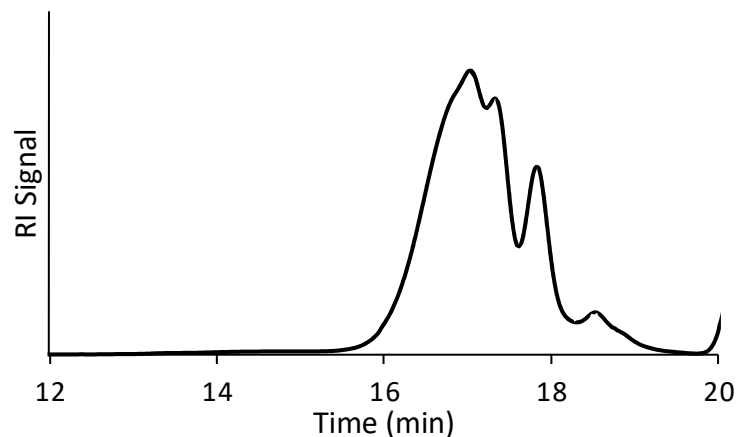


Figure B.19 GPC trace of the polymer created by DArP using the AB monomer (M3) – Sample 2. The polymer has an $M_n = 9.2$ kg/mol and $\mathcal{D} = 1.4$.

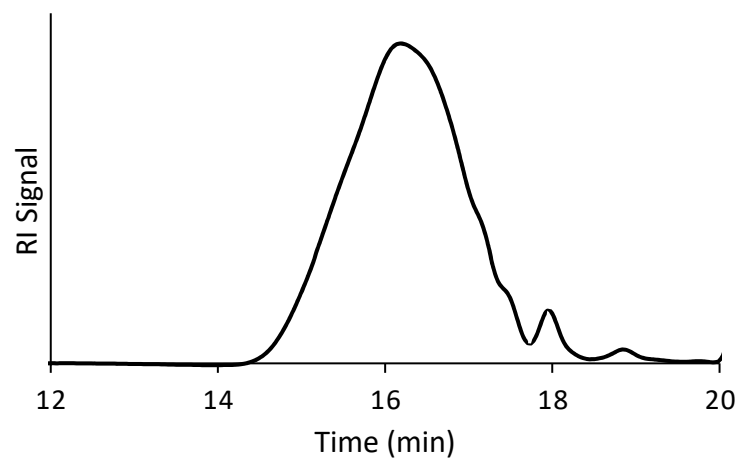


Figure B.20 GPC trace of the polymer created by DArP using the AB monomer (M3) – Sample 3. The polymer has an $M_n = 18.4$ kg/mol and $\bar{D} = 1.9$.

B.9 Concentration-Dependent Absorbance Spectra and Corresponding Beer-Lambert Plots

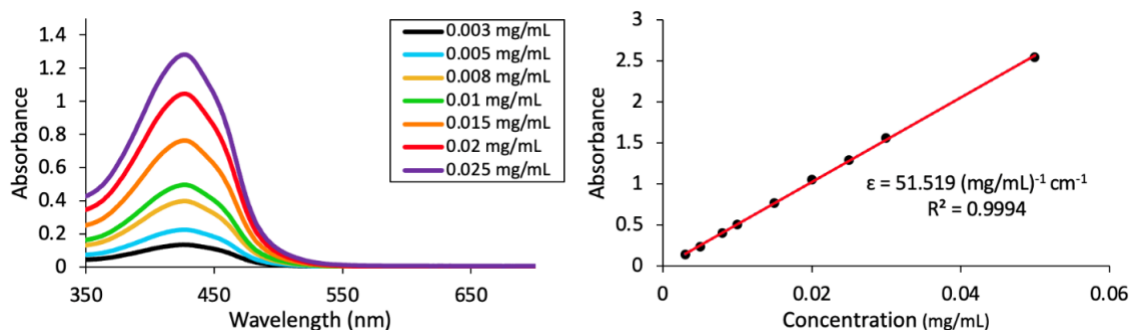


Figure B.21 UV-Vis spectra of the the polymer created by DArP using the AB monomer (M3) at various concentrations in chloroform (left) and the corresponding Beer-Lambert plot (right) with best-fit line. The concentration-dependent absorbance and Beer-Lambert plot of AA+BB copolymer was shown in Appendix A, Figure A.14.

B.10 X-ray Crystal Structure of M1

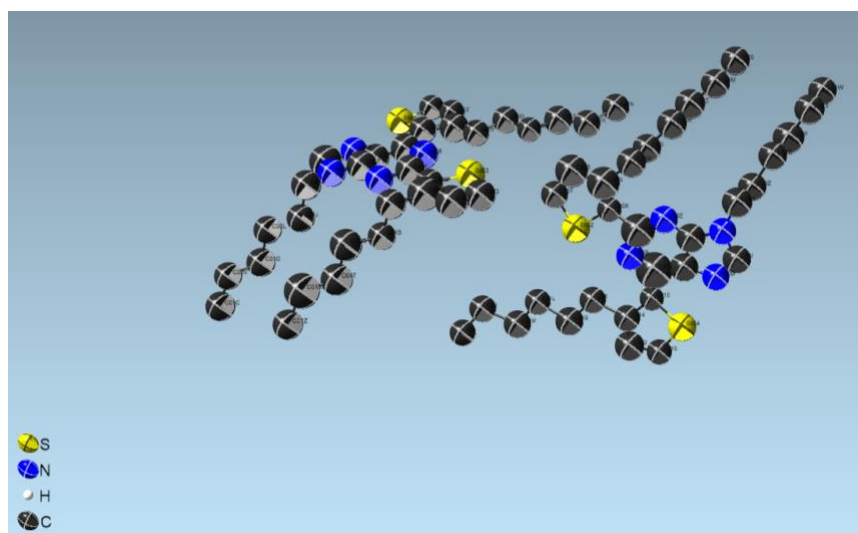


Figure B.22 ShelXle representation of M1. Hydrogens were omitted for clarity. X-ray quality crystals of M1 were obtained via recrystallization from pentane upon cooling to 0 °C. ShelXle representation shows only one conformation of M1 present, indicating noncovalent S···N conformational locks.

Appendix C

C.1 Synthesis and Characterization of Previously Reported Starting Materials and Monomers

Synthesis of 2,6-dichloro-9-hexyl-9H-purine. The N9-alkylated product was recovered at a 63% yield. The ¹H NMR spectrum was consistent with data previously reported by Sabury *et al.*⁴⁵ (500 MHz, 25 °C, CDCl₃). δ, ppm: 0.87 (t, 3H, CH₃), 1.31 (m, 6H, CH₂), 1.91 (p, 2H, CH₂), 4.25 (t, 2H, NCH₂), 8.09 (t, 2H, C8-H).

Synthesis of 9-hexyl-2,6-bis(3-hexylthiophen-2-yl)-9H-purine (M1). **M1** was recovered at a 87% yield. ¹H NMR spectrum was consistent with data previously reported in Chapter II. ¹H NMR spectrum of 9-hexyl-2,6-bis(3-hexylthiophen-2-yl)-9H-purine (**M1**) (500 MHz, 25 °C, CDCl₃). δ, ppm: 0.88 (t, 6H, CH₃), 1.19-1.52 (m, 18H, CH₂), 1.75 (p, 4H, CH₂), 1.96 (p, 2H, CH₂), 3.31 (t, 2H, ArCH₂), 3.43 (t, 2H, ArCH₂), 4.28 (t, 2H, NCH₂), 7.00 (d, 1H, ArH), 7.09 (d, 1H, ArH), 7.31 (d, 1H, ArH), 7.54 (d, 1H, ArH), 8.01 (s, 1H, C8-H).

Synthesis of 2,6-bis(5-bromo-3-hexylthiophen-2-yl)-9-hexyl-9H-purine (M2). **M2** was recovered at a 47% yield. ¹H NMR spectrum was consistent with data previously reported in Chapter II. ¹H NMR spectrum of 2,6-bis(5-bromo-3-hexylthiophen-2-yl)-9-hexyl-9H-purine (**M2**) (500 MHz, 25 °C, CDCl₃). δ, ppm: 0.90 (m, 6H, CH₃), 1.17-1.56 (m, 18H, CH₂), 1.70 (p, 4H, CH₂), 1.95 (p, 2H, CH₂), 3.24 (t, 2H, ArCH₂), 3.35 (t, 2H, ArCH₂), 4.24 (t, 2H, NCH₂), 6.96 (s, 1H, ArH), 7.05 (s, 1H, ArH), 8.02 (s, 1H, C8-H).

C.2 ^1H NMR Spectra of Starting Materials and Monomers

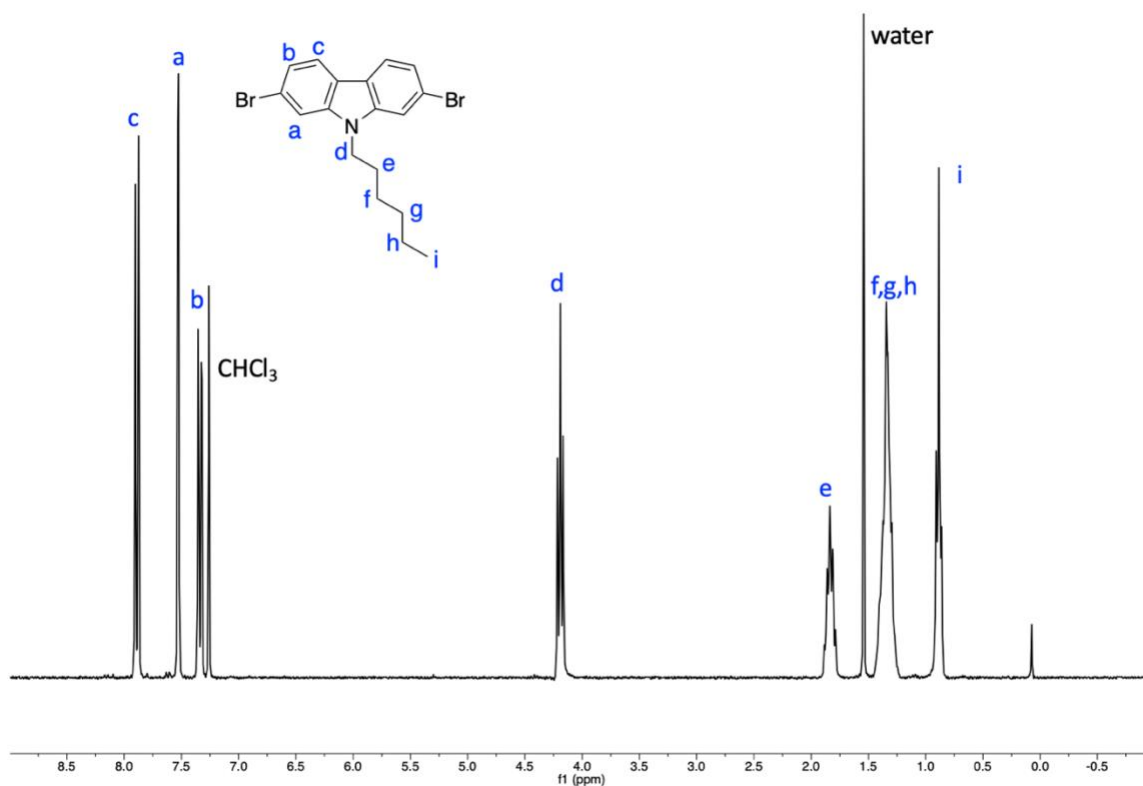


Figure C.1 ^1H NMR spectrum of 2,7-dibromo-9-hexyl-9H-carbazole (300 MHz, 25 °C, CDCl_3). δ (ppm): 0.77-0.99 (m, 9H, CH_3), 1.18-1.50 (m, 18H, CH_2), 1.67 (p, 4H, CH_2), 1.91 (p, 2H, CH_2), 2.76 (t, 4H, ArCH_2), 4.33 (t, 2H, NCH_2), 7.05 (d, 2H, ArH), 7.28 (d, 2H, ArH), 7.34 (d, 2H, ArH), 7.47 (s, 2H, ArH), 8.11 (d, 2H, ArH).

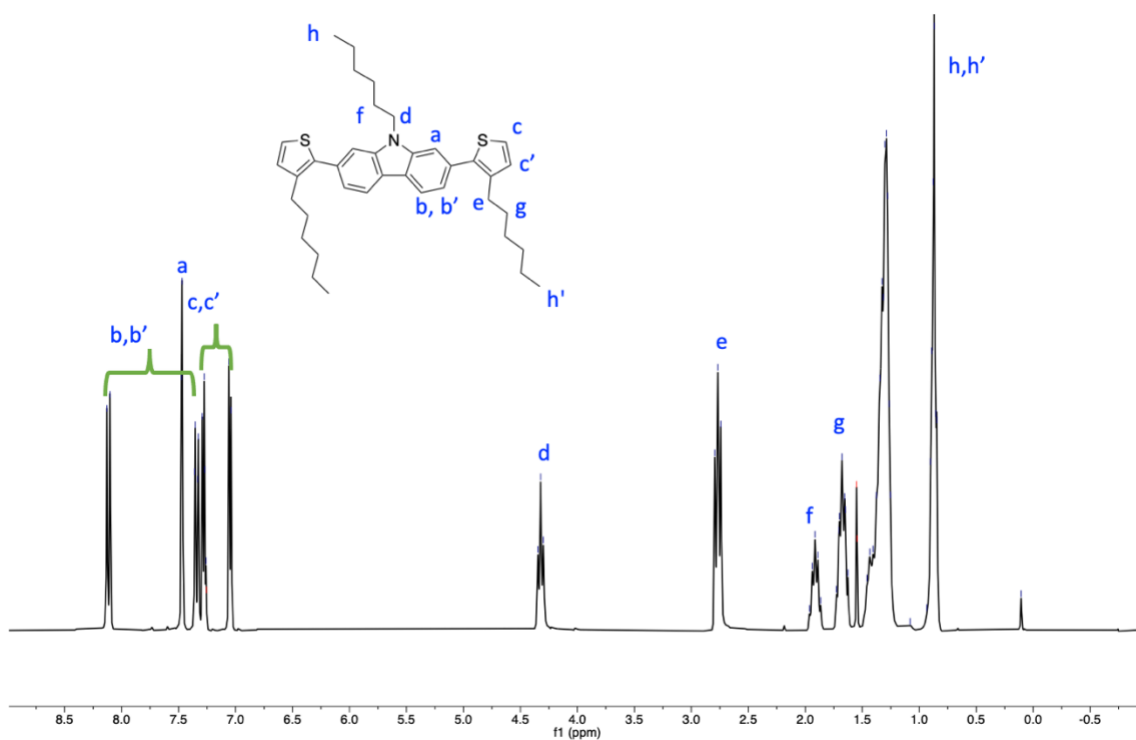


Figure C.2 ^1H NMR spectrum of 9-hexyl-2,7-bis(3-hexylthiophen-2-yl)-9H-carbazole (300 MHz, 25 °C, CDCl_3). δ (ppm): 0.77-0.99 (m, 9H, CH_3), 1.18-1.50 (m, 18H, CH_2), 1.67 (p, 4H, CH_2), 1.91 (p, 2H, CH_2), 2.76 (t, 4H, ArCH_2), 4.33 (t, 2H, NCH_2), 7.05 (d, 2H, ArH), 7.28 (d, 2H, ArH), 7.34 (d, 2H, ArH), 7.47 (s, 2H, ArH), 8.11 (d, 2H, ArH).

C.3 ^1H NMR spectra of Purine-Containing Copolymers

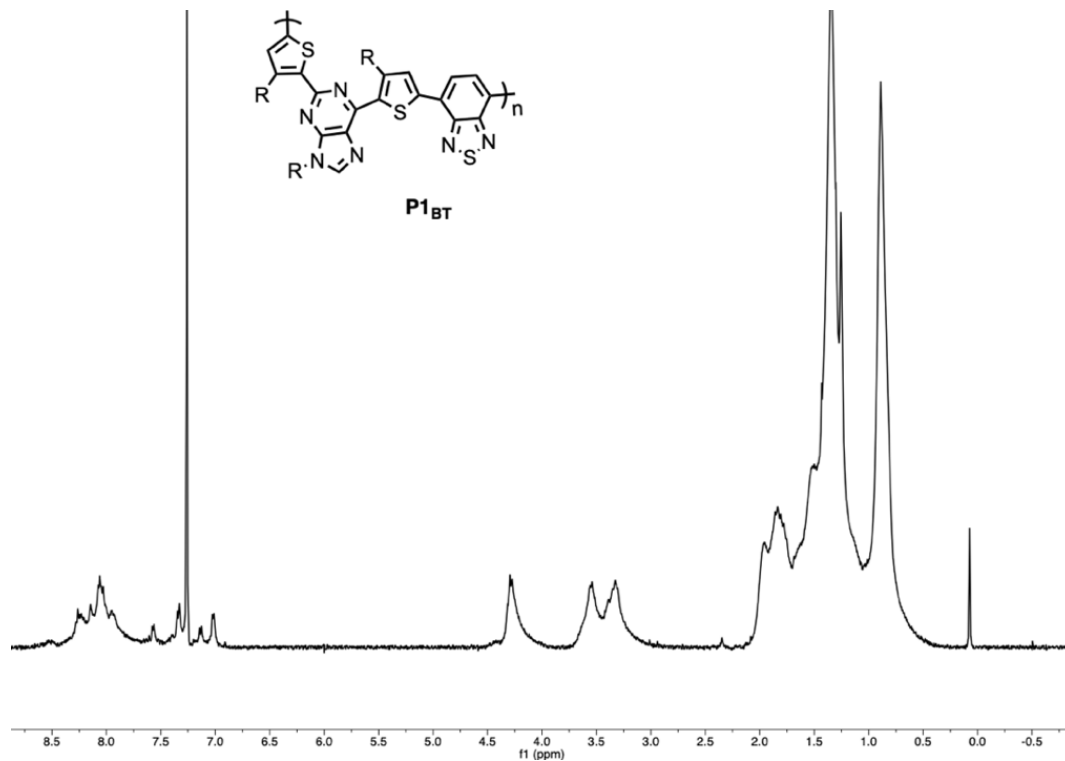


Figure C.3 ^1H NMR spectrum of P1_{BT} (500 MHz, 25 °C, CDCl_3). δ (ppm): 0.34-2.15, 2.98-3.73, 3.92-4.52, 6.87-7.67, 7.69-8.73. The copolymer was obtained as a dark purple solid.

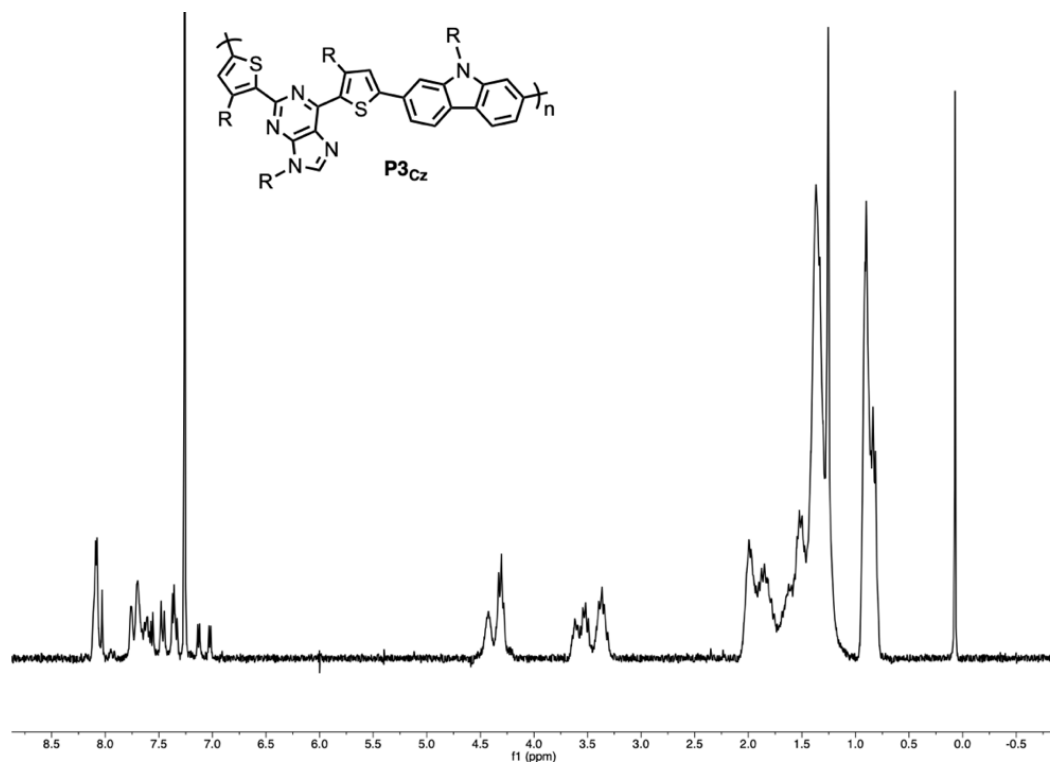


Figure C.4 ^1H NMR spectrum of P3Cz (500 MHz, 25 $^\circ\text{C}$, CDCl_3). δ (ppm): 0.67-0.98, 1.00-2.11, 3.22-3.70, 4.14-4.53, 6.96-7.82, 7.87-8.18. The copolymer was obtained as a green solid.

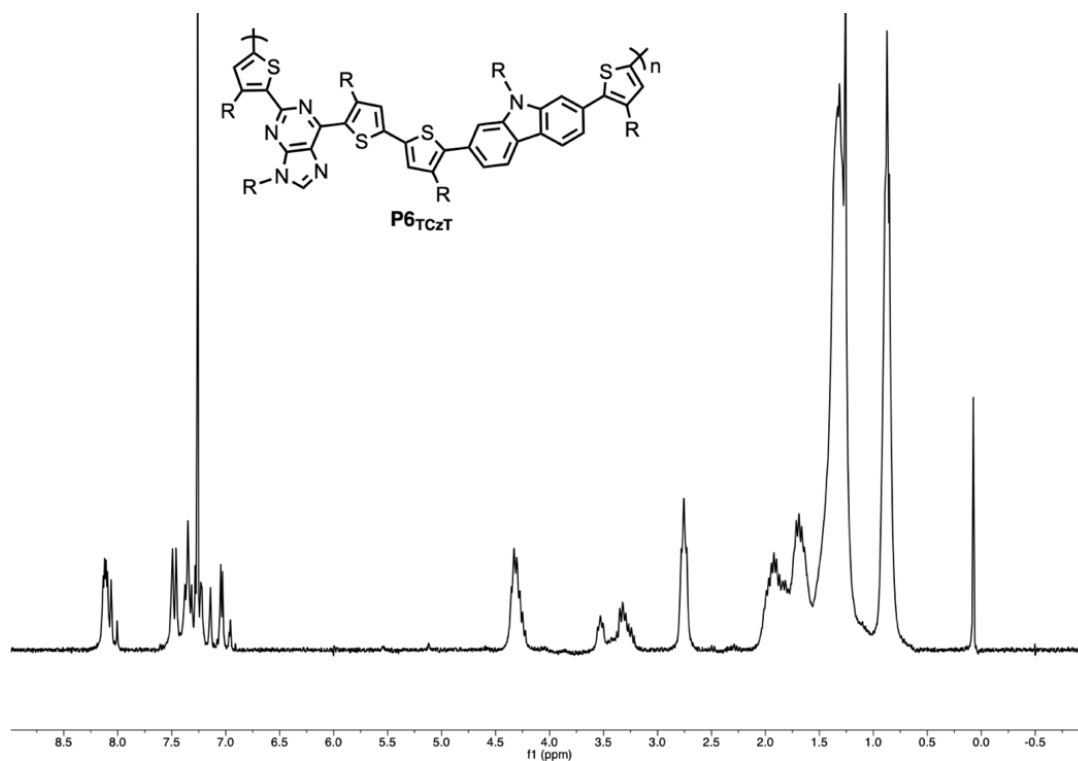


Figure C.5 ^1H NMR spectrum of P6_{TCzT} (500 MHz, 25 $^{\circ}\text{C}$, CDCl_3). δ (ppm): 0.57-2.95, 2.64-2.86, 3.17-3.62, 4.16-4.44, 6.89-7.62, 7.96-8.25. The copolymer was obtained as a dark purple solid.

C.4 Absorbance Study of P1_{BT} at Varied Molecular Weights and Dispersities

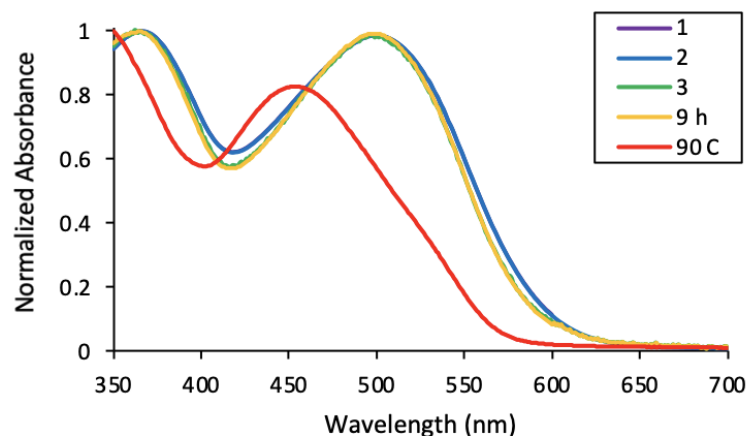


Figure C.6 UV-Vis spectra of P1_{BT} copolymers. Copolymers 1-3 (purple, blue, and green) were made via the conditions provided in the general copolymerization procedure in the Experimental Methods of Chapter IV. The 9 h copolymerization (yellow) was run under the same conditions, but for 9 h instead of 18 h. The copolymerization labeled 90 C was run at 90 °C instead of 95 °C for 18 h. Molecular weight and yield of each of these copolymerizations are provided in Table C.1, below.

Table C.1 Molecular weight and yields of copolymers (P1_{BT}).

P1 _{BT}	yield (%)	M_n (kg/mol)	M_w (kg/mol)	M_w/M_n
1	53%	25.5	136.7	5.4
2	65%	25.0	95.2	3.8
3	71%	9.7	77.4	7.9
9 h	42%	9.6	62.2	6.4
90 C	26%	4.6	47.3	10.1

*Data in bold identifies the copolymer that was used for optoelectronic characterizations.

C.5 GPC Traces of Purine-Containing Copolymers

All samples were measured using THF at 25 °C as the mobile phase at a flow rate of 1 mL/min, and molecular weight values are reported relative to PS standards. The concentration of samples was nominally 5 mg/mL.

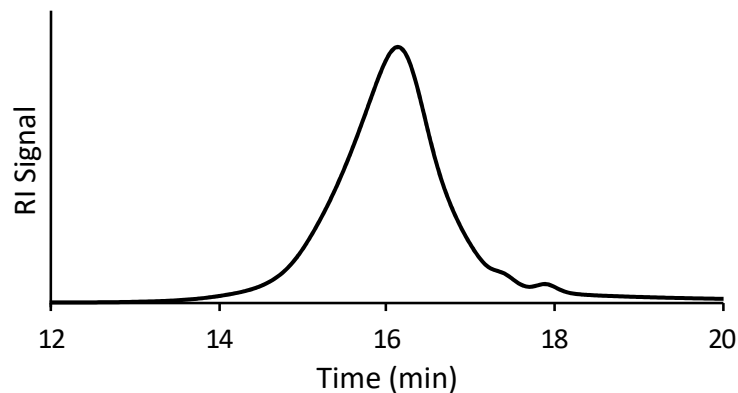


Figure C.7 GPC trace of P1_{BT}. P1_{BT} has an $M_n = 25.0$ kg/mol and $\mathcal{D} = 3.8$.

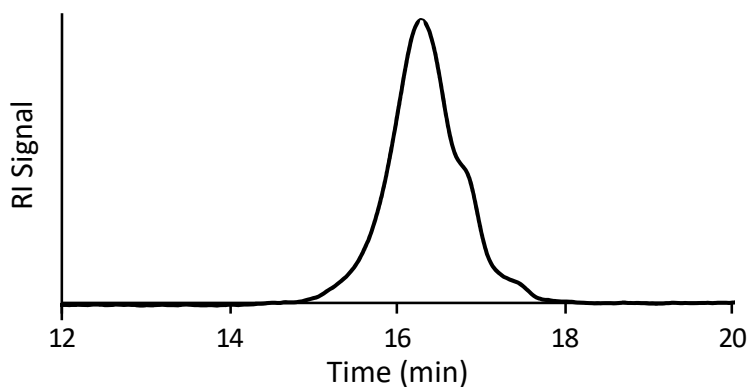


Figure C.8 GPC trace of P2_{Cz}. P2_{Cz} has an $M_n = 12.4$ kg/mol and $\mathcal{D} = 1.5$.

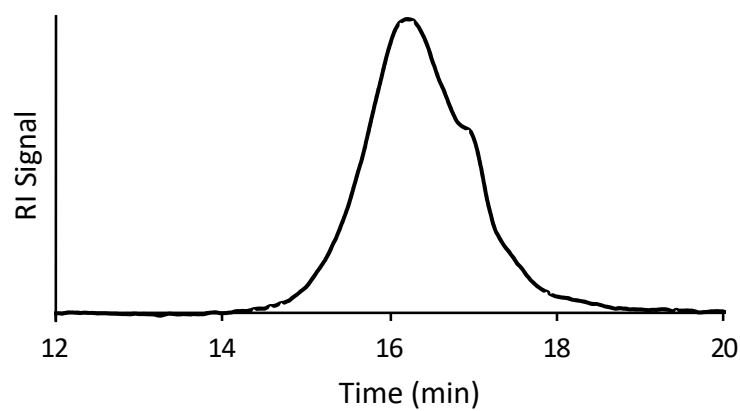


Figure C.9 GPC trace of P4_{TCzT}. P4_{TCzT} has an $M_n = 21.4$ kg/mol and $\bar{D} = 1.4$.

C.6 Solvatochromic Behavior of Purine-Containing Copolymers

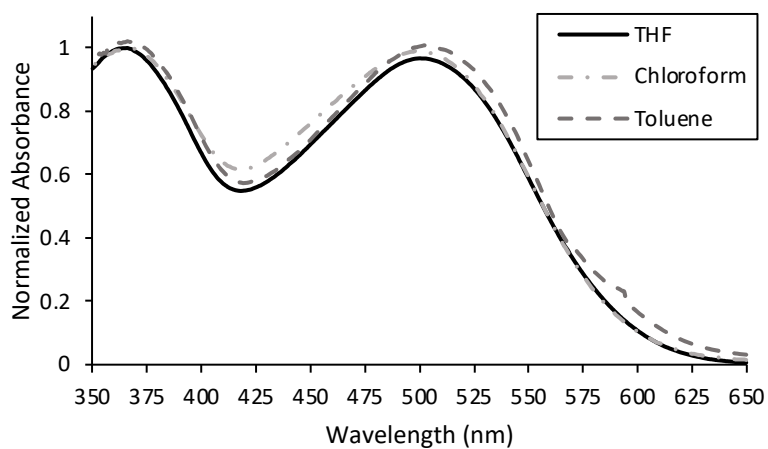


Figure C.10 UV-Vis spectra of P1_{BT} at 0.01 mg/mL in THF, chloroform, and toluene. The spectra show no change as solvent polarity is increased from toluene to chloroform to THF.

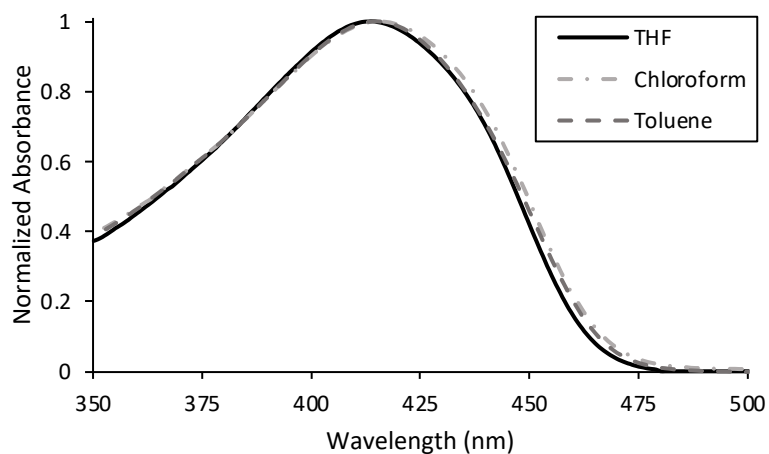


Figure C.11 UV-Vis spectra of P2_{Cz} at 0.01 mg/mL in THF, chloroform, and toluene. The spectra show no change as solvent polarity is increased from toluene to chloroform to THF.

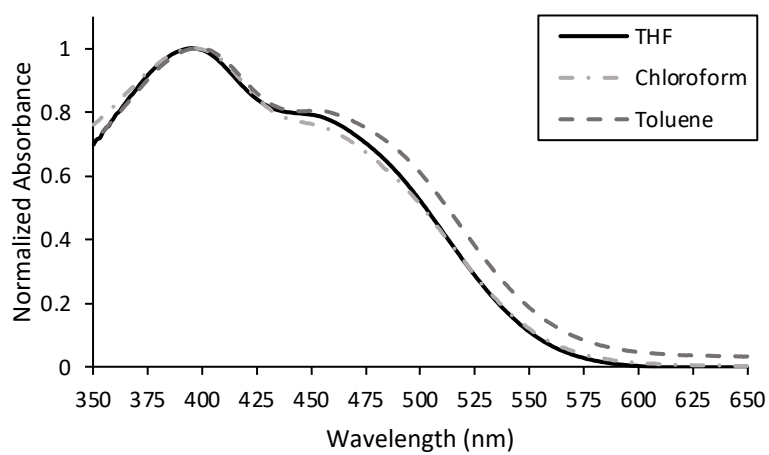


Figure C.12 UV-Vis spectra of P3_{TBTT} at 0.01 mg/mL in THF, chloroform, and toluene. The spectra show a blueshift in the absorbance onset as solvent polarity is increased from toluene to chloroform but no change in absorbance max when solvent polarity is increased from toluene to chloroform to THF.

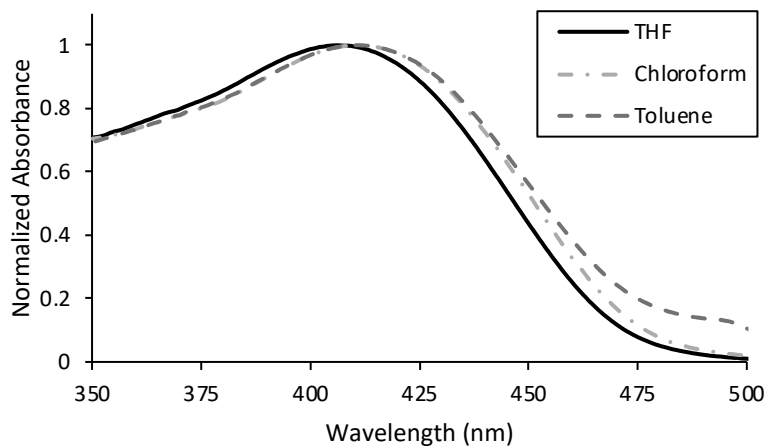


Figure C.13 UV-Vis spectra of P4_{TCzT} at 0.01 mg/mL in THF, chloroform, and toluene. The spectra show a blueshift in absorbance max and onset as solvent polarity is increased from toluene to chloroform to THF.

C.7 Thermochromic Behavior of Purine-Containing Copolymers

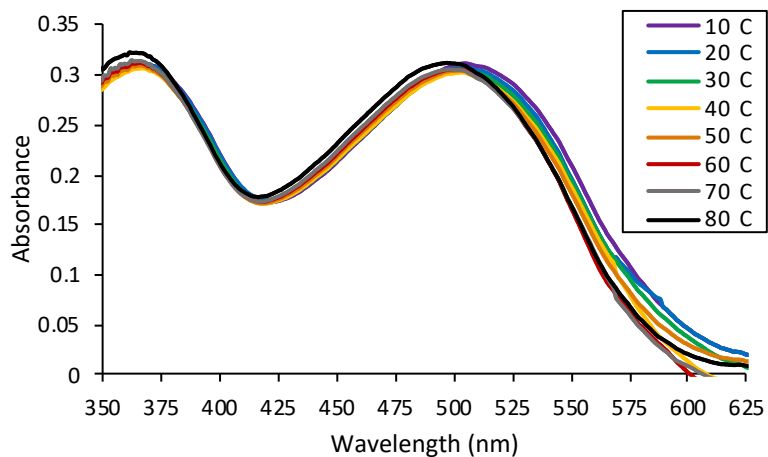


Figure C.14 UV-Vis spectra of P1_{BT} measured at various temperatures in toluene. The solution concentration was 0.01 mg/mL.

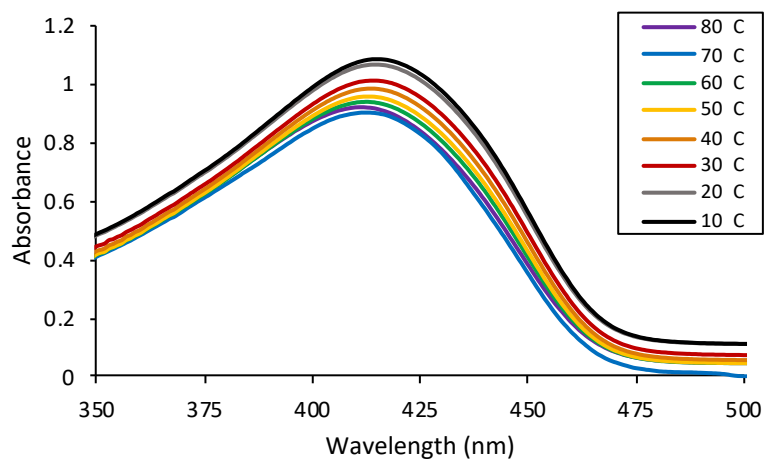


Figure C.15 UV-Vis spectra of P2_{Cz} measured at various temperatures in toluene. The solution concentration was 0.01 mg/mL.

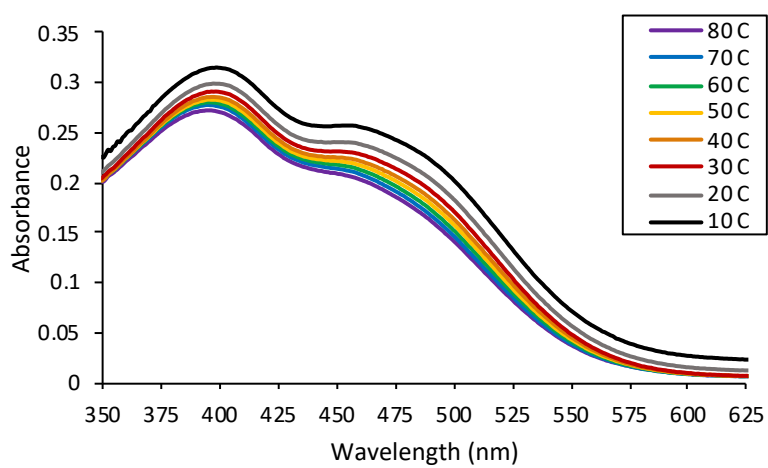


Figure C.16 UV-Vis spectra of P3_{TBTT} measured at various temperatures in toluene. The solution concentration was 0.01 mg/mL.

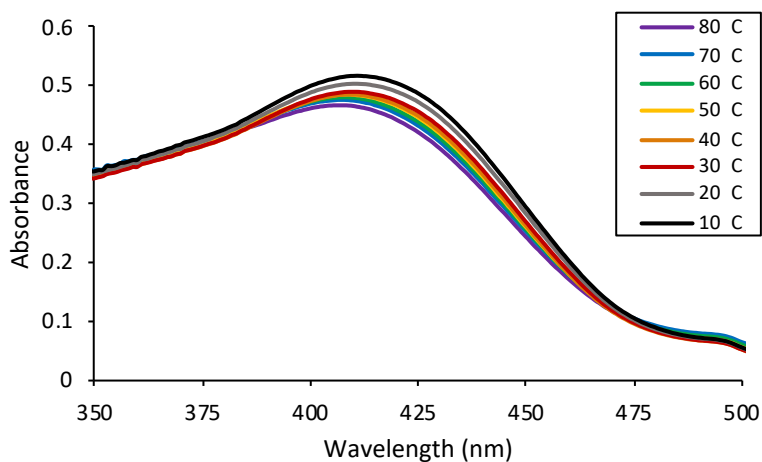


Figure C.17 UV-Vis spectra of P4_{TCzT} measured at various temperatures in toluene. The solution concentration was 0.01 mg/mL.

C.8 Absorbance Spectra and Corresponding Beer-Lambert Plots of Purine-Containing Copolymers

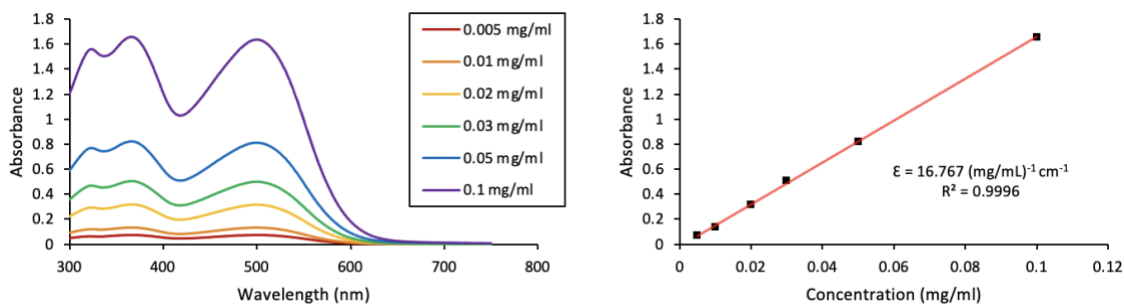


Figure C.18 UV-Vis spectra of P1_{BT} at various concentrations in chloroform (left) and the corresponding Beer-Lambert plot (right) with best-fit line.

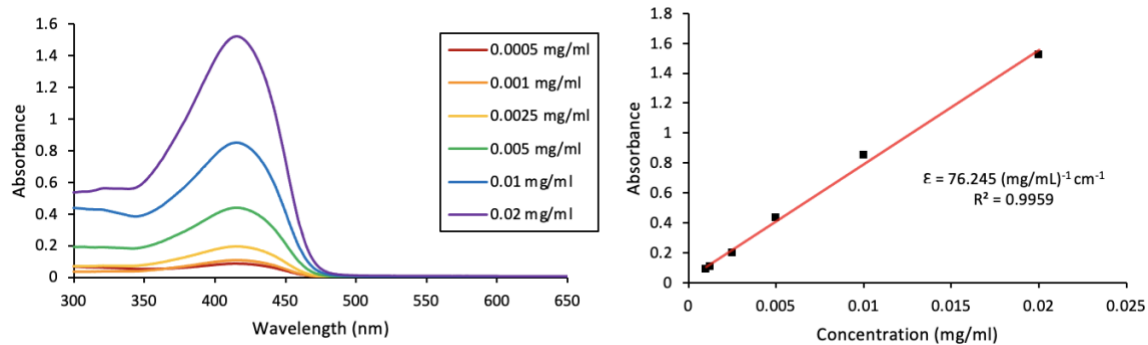


Figure C.19 UV-Vis spectra of P3Cz at various concentrations in chloroform (left) and the corresponding Beer-Lambert plot (right) with best-fit line.

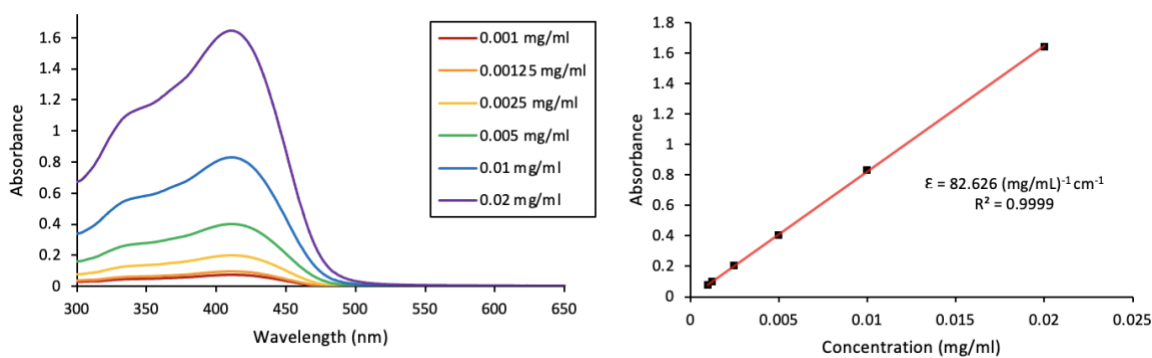


Figure C.20 UV-Vis spectra of P4TCzT at various concentrations in chloroform (left) and the corresponding Beer-Lambert plot (right) with best-fit line.

Appendix D

D.1 Methods and Materials

N-Bromosuccinimide (NBS, 99%, Aldrich) was recrystallized from water and dried under vacuum before use. 6-dichloropurine (97%, Aldrich), 3-hexylthiophene-2-boronic acid pinacol ester (95%, Aldrich), 1-bromohexane (96%, Aldrich), glacial acetic acid, (Fisher Chemical), potassium carbonate (99%, Aldrich), Pd(PPh₃)₄ (98%, Aldrich), Pd(PPh₃)₂ Cl₂ (97%, Aldrich), anhydrous *N,N*-dimethylformamide (DMF, 99.8%, Acros Organics), anhydrous tetrahydrofuran (THF, 99.9%, Fisher), hexanes (95%, Fisher), methanol (99%, Fisher), and chloroform (98%, Fisher) were used as received unless stated otherwise. Monomers and polymers were synthesized using standard Schlenk technique under an argon atmosphere.

¹³C and ¹H NMR spectra of synthesized monomers were acquired at room temperature in CDCl₃ using a Varian VNMRS 500 MHz NMR. Chemical shifts are referenced to residual chloroform peak. Number-average molecular weight, M_n , and dispersity, D , were determined via gel permeation chromatography (GPC). Measurements were made using an Agilent 1260 Infinity II system that used THF as the mobile phase at a flow rate of 1 mL/min at 25 °C and are reported using universal calibration. The system was equipped with a guard column and two PLgel Mixed-C columns (300 mm length) with a lower limit of 200 g/mol and an upper limit of 2×10^6 g/mol. Polymer solutions for GPC analysis were prepared at 5 mg/mL in THF and passed through a 0.2 µm PTFE filter prior to injection. Optical absorbance spectra of the copolymers and monomers in chloroform were acquired using a Thermo Scientific Evolution 600 spectrophotometer by scanning from 250 nm to 450 nm for monomers and from 350 nm to 750 nm for the purine-

containing copolymers. Fluorescence emission spectra were measured in CHCl₃ using a Cary Eclipse fluorescence spectrophotometer. Samples were excited at the absorbance maximum of each sample and spectra were recorded by scanning from ($\lambda_{max}^{abs} + 10$) nm to 700 nm for monomers and polymers. Organic samples were drop cast on precleaned silicon substrates and illuminated in an integrating sphere using a 400 nm, 10 mW laser to collect fluorescence quantum yield in solid state. Light intensities scattered within the sphere were measured using Ocean Optics Spectrometer QE65000.

D.2 Synthesis of 6-bromo-9-hexyl-9H-purine

A solution of 6-bromopurine (1.02 g, 5.13 mmol) and potassium carbonate (2.02 g, 15.5 mmol) in DMF (30 mL) was added to a 100 mL round bottom flask equipped with a stir bar, and the resulting mixture was stirred for 5 minutes at room temperature under argon. 1-bromohexane (0.820 mL, 5.84 mmol) was added via syringe and the mixture was stirred for 18 h at room temperature. After 18 h, the reaction mixture was poured into 15 mL of dichloromethane and washed with brine (3×20 mL). The organic layers were combined, and the solvent was removed via rotary evaporation under reduced pressure. *N9* and *N7* substituted isomers were separated via flash column chromatography using 10% ethyl acetate in 90% hexanes (by volume). The *N9* product was recovered at a 52% yield. ¹H NMR (500 MHz, 25 °C, CDCl₃). δ , ppm: 0.89 (t, 6H, CH₃), 1.19-1.43 (m, 18H, CH₂), 1.92 (p, 4H, CH₂), 4.27 (t, 2H, NCH₂), 8.11 (s, 1H, ArH), 8.69 (s, 1H, ArH).

D.3 Synthesis of 6,8-dibromo-9-hexyl-9H-purine

A solution of 6-bromo-9-hexyl-9H-purine (0.285 g, 1.01 mmol) in THF (2 mL) was added dropwise over 10 minutes to a 25 mL round bottom flask containing 0.5 M LDA in

THF (2.8 mL) equipped with a stir bar at -78 °C. The resulting mixture was stirred for 1 hour at room -78 °C under argon. After 1 h, a solution of 1,2-dibromotetrachloroethane (0.634 g, 1.95 mmol) in THF (1 mL) was added via syringe dropwise over 5 minutes. After addition of 1,2-dibromotetrachloroethane, the reaction mixture was allowed to warm slowly to room temperature and stirred for 16 h. After 16 h, the reaction mixture was poured into 10 mL of diethyl ether and washed with DI water (3×10 mL). The organic layers were combined, and the solvent was removed via rotary evaporation under reduced pressure. The product was recovered at an 86% yield. ¹H NMR spectrum of 6,8-dibromo-9-hexyl-9*H*-purine (300 MHz, 25 °C, CDCl₃). δ, ppm: 0.88 (t, 3H, CH₃), 1.13-1.48 (m, 6H, CH₂), 1.87 (p, 2H, CH₂), 4.31 (t, 2H, NCH₂), 8.71 (s, 1H, ArH).

D.4 Synthesis of 9-hexyl-6,8-bis(3-hexylthiophen-2-yl)-9H-purine

An oven-dried 50 mL round bottom flask containing a stir bar was flushed with argon. After it cooled to ambient temperature, 6,8-dibromo-9-hexyl-9*H*-purine (0.471 g, 1.30 mmol) and dried/degassed dimethyloxyethane (40 mL) were added to the flask. The catalyst, Pd(PPh₃)₄ (195.08 mg, 0.169 mmol), was added, followed by 3-hexylthiophene-2-boronic acid pinacol ester (0.915 mL, 3.06 mmol). Then, 13.5 mL of a previously-sparged aqueous solution of K₂CO₃ (4 M) were added. The reaction mixture was placed in an oil bath that was preheated to 110 °C. Conversion was monitored by TLC. After 20 h, the reaction flask was removed from the oil bath and allowed to cool to room temperature. Chloroform was added (30 mL), and the mixture was extracted with brine (3×). The organic layers were combined, filtered, and dried. Flash column chromatography using a solvent mixture consisting of 1:4 ethyl acetate:hexanes was used to separate mono- and di-

brominated products. The isolated yield of 9-hexyl-6,8-bis(3-hexylthiophen-2-yl)-9H-purine was 63%. (500 MHz, 25 °C, CDCl₃). δ , ppm: 0.84 (t, 9H, CH₃), 1.15-1.41 (m, 18H, CH₂), 1.66 (p, 4H, CH₂), 1.81 (p, 2H, CH₂), 2.88 (t, 2H, ArCH₂), 3.33 (t, 2H, ArCH₂), 4.25 (t, 2H, NCH₂), 7.05 (s, 1H, ArH), 7.10 (d, 1H, ArH), 7.50 (d, 1H, ArH), 8.95 (s, 1H, C8-H).

D.5 General Procedure for Microwave-Assisted Suzuki-Miyaura Polymerization

The purine-containing monomer (either **M2** or **M5**) and comonomer – (9,9-dioctyl-9H-fluorene-2,7-diyl)diboronic acid) – were added (in a 1:1 stoichiometric ratio, 0.06 mmol of each monomer) to a 5 mL microwave reaction vial equipped with a Teflon stir bar. Suzuki-Miyaura microwave assisted cross-coupling reactions were performed in 3 mL of THF and 0.75 mL of 4M K₂CO₃ at 150 °C with 4-5 mol% Pd(PPh₃)₂Cl₂ as the catalyst. All reagents were added under a positive pressure of argon. Dry THF was sparged with argon for 15 min before it was added to the microwave reaction vial. After 15 min, the reaction was cooled to room temperature and added dropwise to cold methanol (MeOH, ~50 mL) to precipitate the copolymer. To isolate the copolymer, the recovered solid precipitate was washed with methanol (25 mL $\times$ 3) and acetone (25 mL $\times$ 3), followed by centrifugation for 10 min after each wash. The final isolated and purified polymer was dried and collected as a solid powder. The microwave used was a Biotage Initiator⁺ Microwave System with Robot 8.

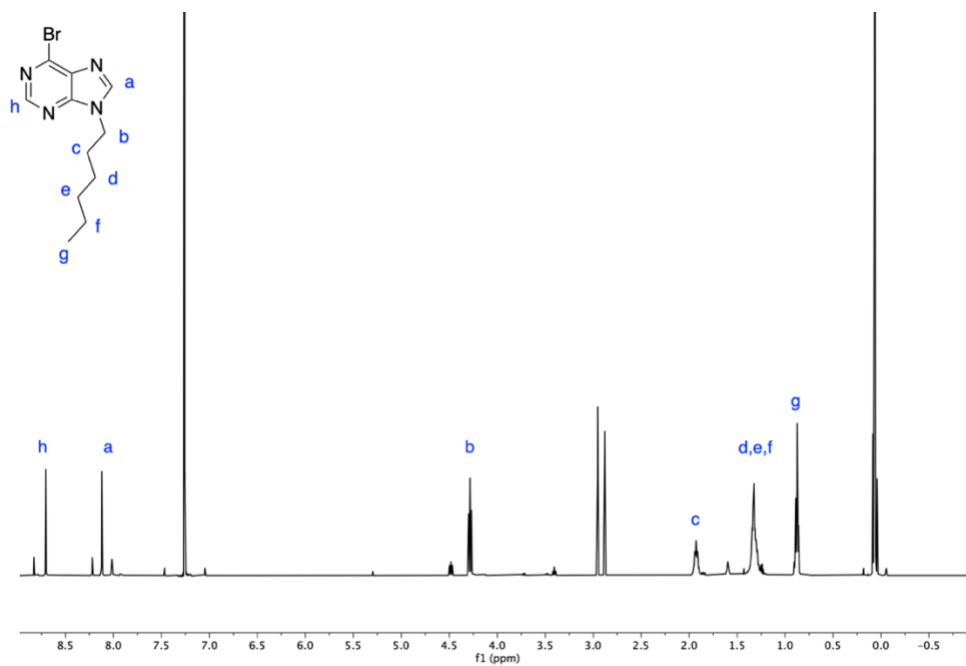


Figure D.1 ¹H NMR spectrum of 6-bromo-9-hexyl-9H-purine (500 MHz, 25 °C, CDCl₃).
δ, ppm: 0.89 (t, 3H, CH₃), 1.19-1.43 (m, 6H, CH₂), 1.92 (p, 2H, CH₂), 4.27 (t, 2H, NCH₂),
8.11 (s, 1H, ArH), 8.69 (s, 1H, ArH).

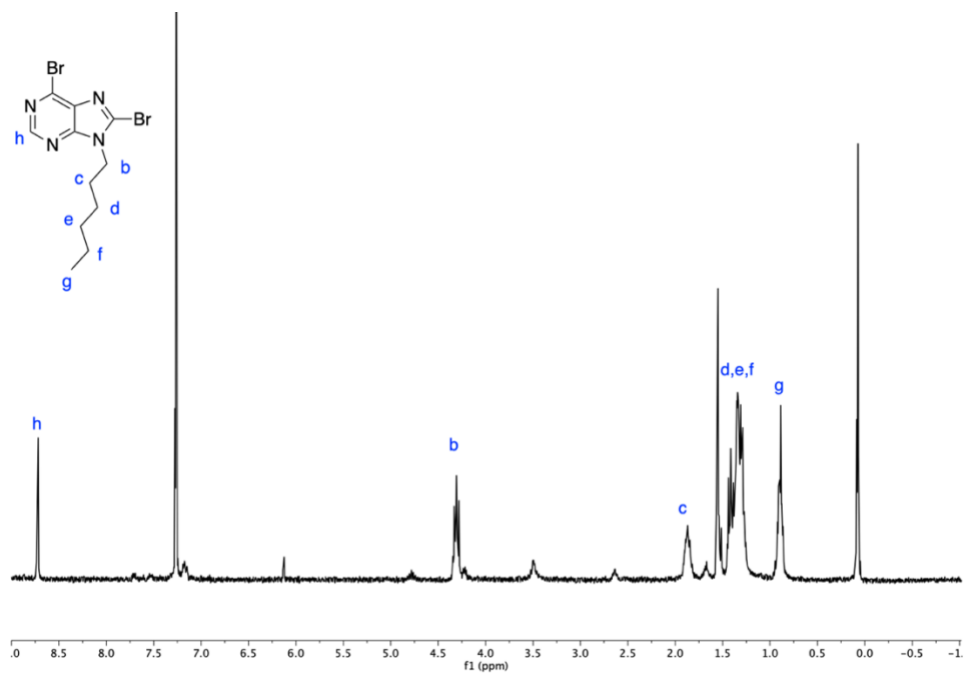


Figure D.2 ^1H NMR spectrum of 6,8-dibromo-9-hexyl-9H-purine (300 MHz, 25 °C, CDCl_3). δ , ppm: 0.88 (t, 3H, CH_3), 1.13-1.48 (m, 6H, CH_2), 1.87 (p, 2H, CH_2), 4.31 (t, 2H, NCH_2), 8.71 (s, 1H, ArH).

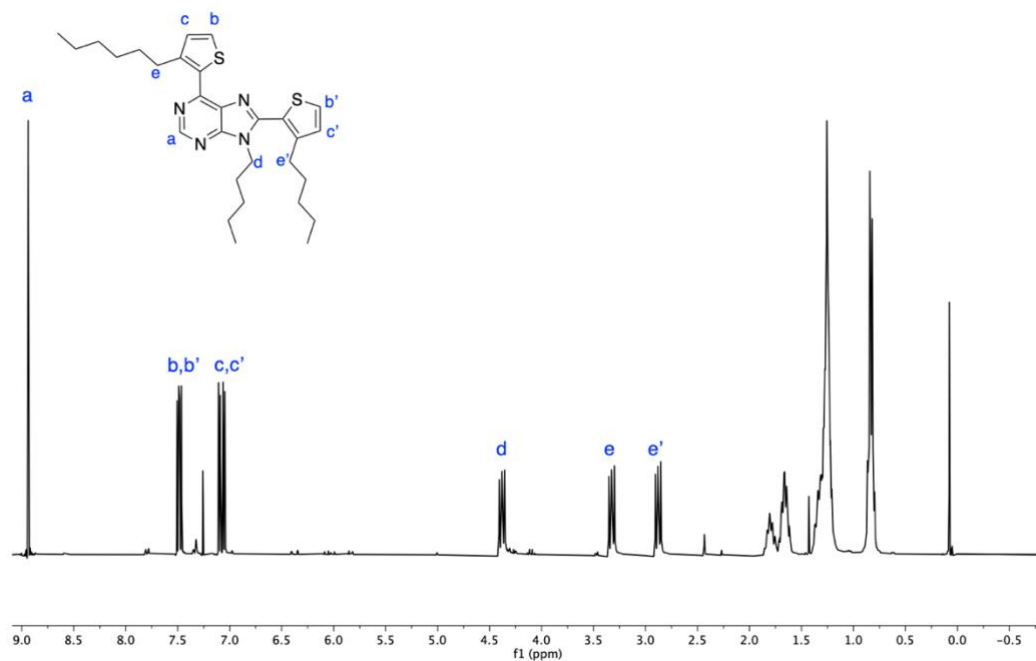


Figure D.3 ¹H NMR spectrum of 9-hexyl-6,8-bis(3-hexylthiophen-2-yl)-9H-purine (M4) (500 MHz, 25 °C, CDCl₃). δ, ppm: 0.84 (t, 9H, CH₃), 1.15-1.41 (m, 18H, CH₂), 1.66 (p, 4H, CH₂), 1.81 (p, 2H, CH₂), 2.88 (t, 2H, ArCH₂), 3.33 (t, 2H, ArCH₂), 4.25 (t, 2H, NCH₂), 7.05 (s, 1H, ArH), 7.10 (d, 1H, ArH), 7.50 (d, 1H, ArH), 8.95 (s, 1H, C2-H).

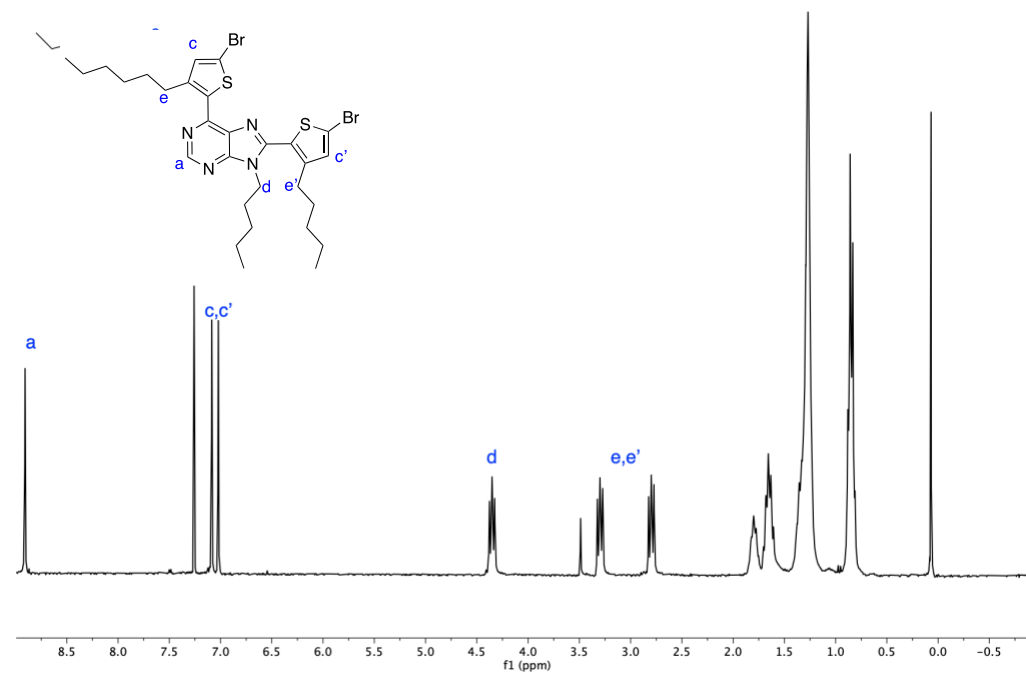


Figure D.4 ^1H NMR spectrum of 6,8-bis(5-bromo-3-hexylthiophen-2-yl)-9-hexyl-9H-purine (M5) (300 MHz, 25 °C, CDCl_3). δ , ppm: 0.85 (t, 9H, CH_3), 1.15-1.45 (m, 18H, CH_2), 1.65 (p, 4H, CH_2), 1.80 (p, 2H, CH_2), 2.80 (t, 2H, ArCH_2), 3.30 (t, 2H, ArCH_2), 4.35 (t, 2H, NCH_2), 7.02 (s, 1H, ArH), 7.08 (d, 1H, ArH), 7.50 (d, 1H, ArH), 8.91 (s, 1H, C2-H).

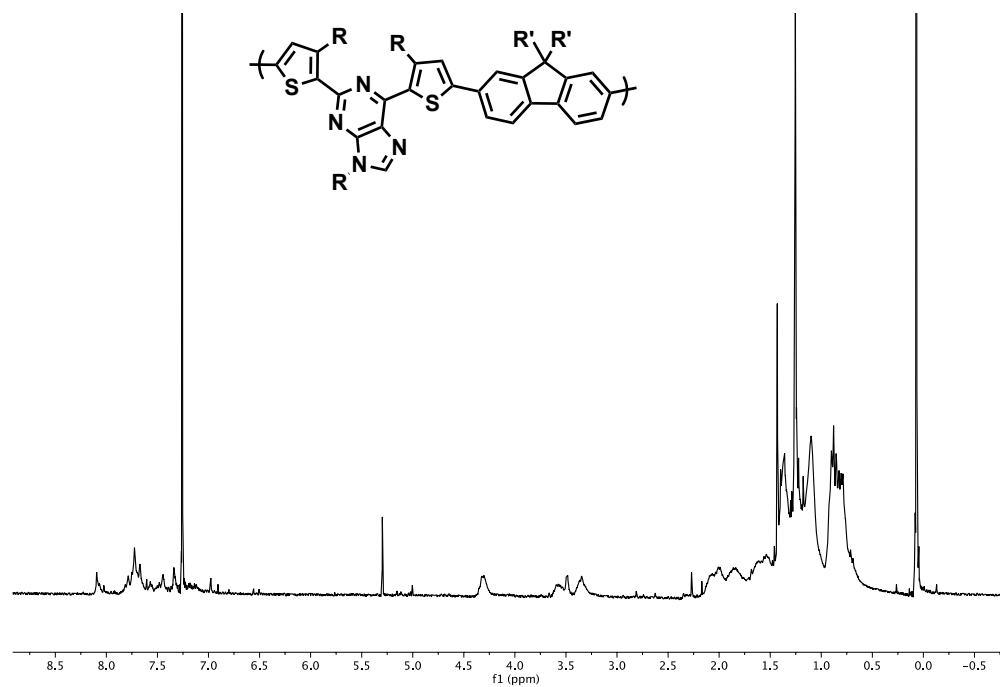


Figure D.5 ¹H NMR spectrum of P(M2-F) (300 MHz, 25 °C, CDCl₃). δ (ppm): 0.60-2.27, 3.15-3.70, 4.19-4.46, 6.82-7.86, 8.00-8.18. The copolymer was obtained as a dark green solid.

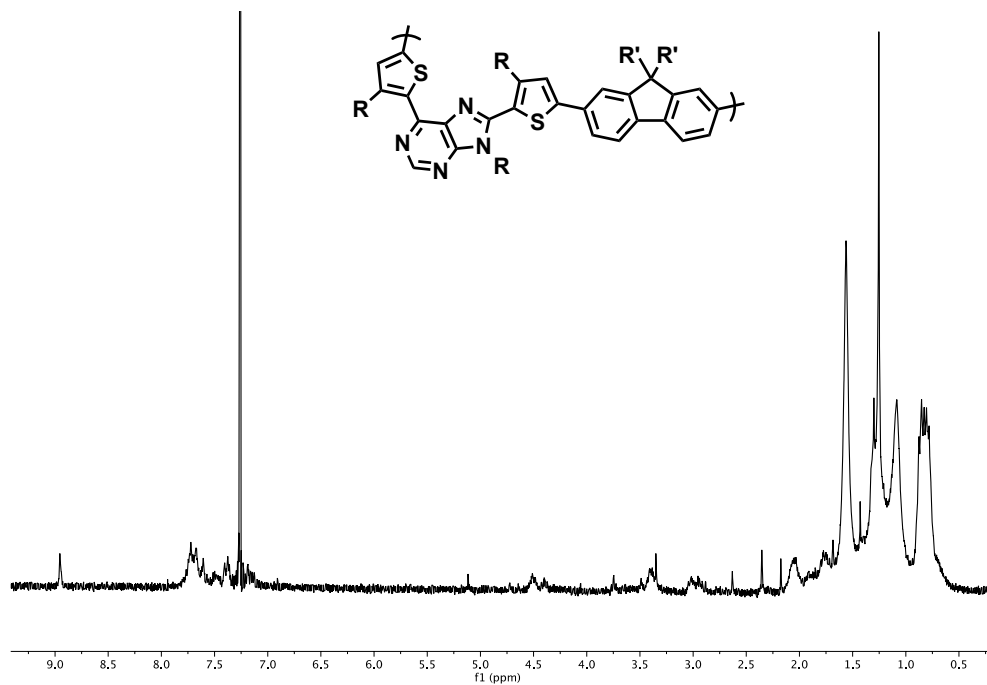


Figure D.6 ¹H NMR spectrum of P(M5-F) (300 MHz, 25 °C, CDCl₃). δ (ppm): 0.42-2.23, 2.76-3.82, 4.27-4.63, 6.93-7.86, 8.84-9.01. The copolymer was obtained as a green solid.

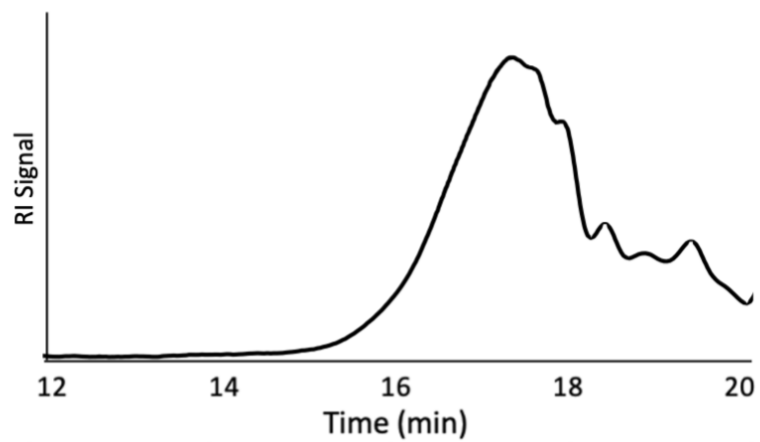


Figure D.7 GPC trace of P2_F. P2_F has an $M_n = 9.5$ kg/mol and $\mathcal{D} = 1.8$.

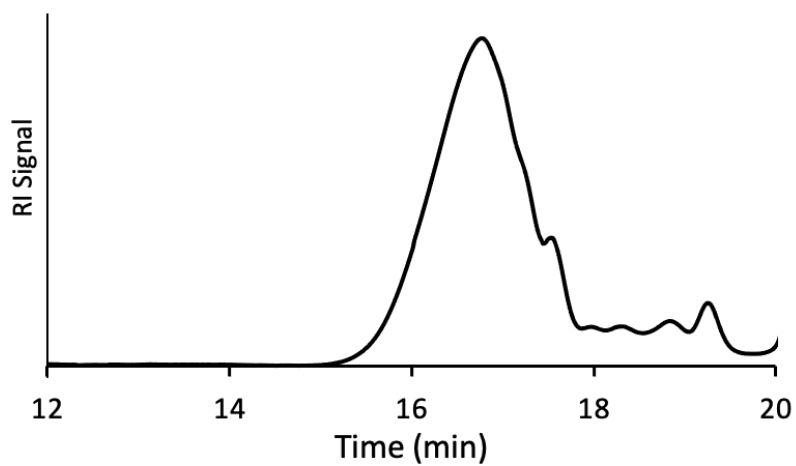


Figure D.8 GPC trace of P2(M5-F). P2(M5-F) has an $M_n = 16.1$ kg/mol and $\mathcal{D} = 1.3$.

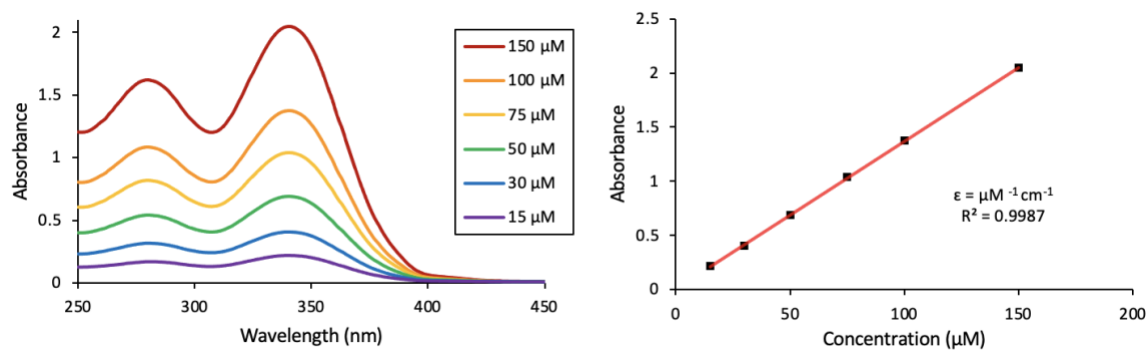


Figure D.9 UV-Vis spectra of the M4 purine-containing monomer at various concentrations in chloroform (left) and the corresponding Beer-Lambert plot (right) with best-fit line.

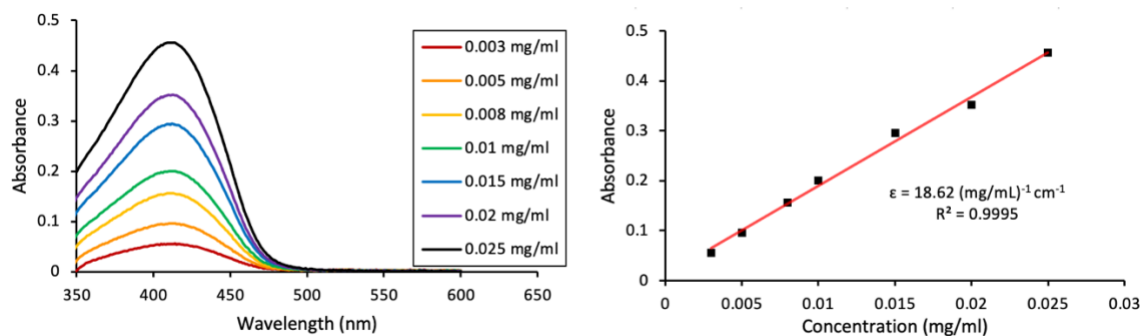


Figure D.10 UV-Vis spectra of the P(M2-F) purine-containing polymer at various concentrations in chloroform (left) and the corresponding Beer-Lambert plot (right) with best-fit line.

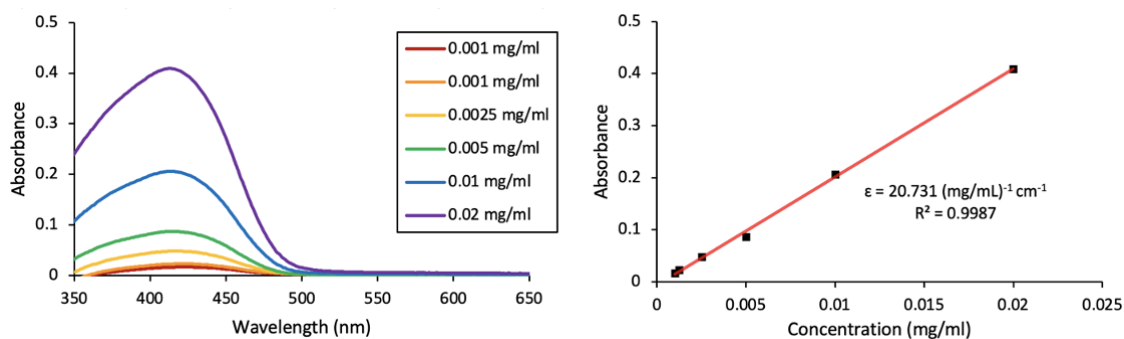


Figure D.11 UV-Vis spectra of the P(M5-F) purine-containing polymer at various concentrations in chloroform (left) and the corresponding Beer-Lambert plot (right) with best-fit line.

VITA

Elizabeth O'Connell was born near Nashville, Tennessee on February 28th, 1992. She attended K-12 school in Dickson County before moving to Cookeville, where she attended Tennessee Technological University and earned her Bachelor of Science degree in Chemistry. While at Tennessee Technological University, she completed research in the Biology Department, studying invertebrates of different cave settings and depths. Elizabeth was granted a summer fellowship to work on organometallic synthesis with Dr. Ted Burkey at the University of Memphis. After graduating in 2014, Elizabeth moved to Memphis to study Z-type bonds at the University of Memphis, where she earned a degree in Inorganic Chemistry under the mentorship of Dr. Tim Brewster. She graduated with her Master of Science degree in May of 2017, shortly before moving to Knoxville to pursue a Doctor of Philosophy in Polymer Chemistry. At the University of Tennessee – Knoxville, she was advised by Prof. S. Michael Kilbey and Prof. Brian K. Long. Her research involved studying the synthetic development and structure-property relationships of purine-containing conjugated polymers.