

SYNTHESIS OF PYRROLE FUNCTIONALIZED MATERIALS FOR ORGANIC
ELECTRONIC APPLICATIONS

by

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This dissertation and my academic achievements are dedicated to my wife and family, whose unconditional devotion and support laid the foundation for completing this work.

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Pyrrole is a well-known class of blocks used for conductive polymers and semiconducting materials applied in organic electronics. Pyrroles were initially involved in developing conducting polymer-based materials and relevant applications due to their high electron-rich properties and doping ability. Lately, pyrroles got involved in the synthesis of organic semiconducting materials. However, due to their high electron richness and elevated highest occupied molecular orbitals (HOMO), pyrrole compounds were prone to oxidize in the air; Thus, it was hard to work with pyrrole chemistry initially. Recently, scientists started to demonstrate an effective way of using electron-rich pyrrole moieties in organic semiconductors by synthesizing pyrrole-fused aromatic heterocyclic ring systems. Fusing pyrrole moieties with other stable aromatic ring systems such as thiophene has assisted pyrroles with air stability by lowering HOMO and providing an opportunity to fine-tune the bandgap. Following this, several different pyrrole-fused heterocyclic aromatic blocks such as thienopyrrole, dithienopyrrole, and thienodipyrrole were introduced and incorporated in organic semiconductors to apply them in organic electronics later. Pyrrole moieties of these blocks paved the path to perform various structural modifications through N-

functionalization, leading to the development of solution-processable semiconducting materials from insoluble fused blocks. Solubilizing unit modifications on pyrrole N atoms improved the solvent compatibility of fused-ring semiconducting materials, leading to a low-cost solvent processing of such organic semiconductors. Even though pyrrole-containing fused-ring blocks are advantageous in developing hole-transporting semiconductors due to their electron richness, there are still not many studies performed to identify various other potential fused-pyrrole blocks that can be used in the hole transporting semiconductors. Thus, it is necessary to systematically design various pyrrole-functionalized blocks and materials for applying them in organic electronics to fully understand their structure-property relationship with regards to the development of hole transporting solution processable materials. In this study, such pyrrole functionalized organic small molecular materials were systematically investigated to reveal their structure-property relationship and OFETs application potentials. In regards to this, Chapter 1 summarizes the evolution of organic semiconductors, pyrrole-based semiconducting materials applied in organic electronics, and other related potential donors & acceptor blocks. In Chapter 2, we have demonstrated synthesis and OFETs applications of thiophene or furan spacers flanked siloxane side-chain modified diketopyrrolopyrrole (DPP) acceptors and thienopyrrole donors containing small molecules. This is the first-time report of DPP and thienopyrrole containing small molecules applied in OFETs. In Chapter 3, understudied 1*H*-indole and pyrrolopyridine potential donor blocks were incorporated in thiophene spacers flanked benzothiadiazole-based donor-acceptor small molecules for applying them in OFETs to understand the potential of these pyrrole-based materials in OFETs. In Chapter 4, an extension to the study in chapter 3 was performed by systematically varying the chalcogenophene spacer flanked to benzothiadiazole in 1*H*-indole-benzothiadiazole-based

donor-acceptor small molecular design to further investigate the structure-property relationship of the fused-pyrrole containing small molecular systems and their OFETs application potentials.

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CHAPTER 1

THE EVOLUTION OF ORGANIC SEMICONDUCTORS AND THE CONTRIBUTION OF PYRROLE- AND DIKETOPYRROLOPYRROLE-BASED DERIVATIVES IN ORGANIC FIELD-EFFECT TRANSISTORS

1.1 Abstract

In this chapter, we report an introduction to organic semiconductors and their development. Furthermore, basic principles of organic field-effect transistors' device architecture, its basic operational principle, and charge transport mechanisms are briefly discussed. In addition, the contribution of pyrroles and their derivatives to the field of organic field-effect transistors and their evolution are discussed. Pyrrole derivatives such as thienopyrrole, thienodipyrrole, dithionopyrrole, indole, and pyrrolopyridine are included in this discussion. Apart from that, diketopyrrolopyrrole (DPP), a widely occupied acceptor block in organic electronics, is also briefly introduced, and its contribution in the field of organic transistors is discussed. Siloxane substituted DPP-based semiconducting materials have shown a significant improvement in thin-film crystallinity and OFETs mobilities. The aspects of siloxane side-chains and their DPP derivatives are also briefly stated in this report.

1.2 Introduction to organic semiconductors

The history of organic semiconducting materials begins with the invention of doped polyacetylene films by Alan G. MacDiarmid, Alan J. Heeger, and Hideki Shirakawa in the 1970s.^{1–}

⁴ Previously, in the 1960s, Donald Weiss René reported polypyrrole as a potential candidate for organic-based conducting material for the first time. In parallel to that, René Buvet and Marcel

Jozefowicz introduced polyaniline as a comparable candidate for conducting polymers.⁵⁻⁸ However, the actual application of organic conjugated molecules in the semiconducting field started to blossom with the invention of doped polyacetylene. The specific properties of organic semiconductors, such as solution processability, mechanical flexibility, optical tunability, higher absorption coefficients, compared to inorganic silicon, paved the path to get them involved in a wide variety of electronic applications while experimenting on developing their properties. Among the fields of organic semiconductors' involvement, organic field-effect transistors (OFETs), organic photovoltaics (OPV), organic light-emitting diodes (OLEDs), organic electrochromic devices, and biological or chemical sensors have shown great importance in electronics.⁹⁻¹⁵ Even though organic semiconductors still require some development in electronic performance to be eligible for broad commercial applications, the synthetically adaptable nature of these materials to fine-tune optical and electronic properties kept those fields running until now. When developing organic semiconductors, there are several criteria to be considered in material selection, such as thermal stability, chemical stability, π -electron richness, frontier energy levels, electrical conductivity, aromaticity, and dipole moments.¹⁶⁻¹⁸ Since thiophene seemed to meet most of the above requirements, thiophene-based derivatives, including polythiophenes, have dominated the organic electronic field in the last few decades. Depending on the variation upon the development of semiconductors, they can be categorized into three generations. Those generations are given below.

1. First-generation semiconductors – Under the first generation of semiconductors, polythiophenes have become the widely studied material. This was primarily used in the 1970s due to their greater conductivity under the doped state closer to 1 S cm^{-1} . But lately, the

utilization of polythiophene was drastically reduced due to their lack of mechanical properties, crystallinity, and solubility required in electronic applications.^{19–21}

2. **Second-generation semiconductors** – the second generation was also based on thiophene materials. To overcome observed drawbacks in first-generation, alkyl-chain substituted thiophene derivatives were introduced. For example, poly(3-hexylthiophene) derivatives exhibit hole mobilities over $1 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$, proving excellent semiconductor properties.^{22–24} However, optical and energy level tunability was restricted in these materials due to limited possible structural modification and conjugation length-dependent bandgap.
3. **Third-generation semiconductors** – To overcome limitations found in previous-generation, donor-acceptor (DA) semiconducting material architecture was introduced. This strategy introduced the orbital mixing between donor and acceptor counterparts, leading to better bandgap tunability.²⁵ Alternating DA type polymers were developed by polymerizing different electron-rich and electron-deficient monomers, which allow the bandgap to tune by adjusting frontier orbitals through careful selection of blocks and design of polymers. However, DA polymers showed less control over molecular weight and polydispersity, leading to batch-to-batch performance variation. Therefore, DA small molecules with exact molecular weights were applied in OFETs but lately, acene-based small molecules exhibited mobilities over $10 \text{ cm}^2 \text{ V}^{-1}$, indicating potential in high-performing materials.²⁶ However, acene-based small molecules require harsh processing conditions; thus, experimentalists had to perform modifications on conventional acene to develop other heterocyclic analogous blocks such as fused-pyrrole blocks, thieno[3,2-*b*]pyrrole (TP).^{27–29}

Third-generation DA-type polymers and small molecules created a new direction in field-effect transistors, becoming a strong candidate and a competitor to silicon semiconductors. Since then, organic semiconductors have started to move forward with inorganic counterparts as a significant component, specifically in flexible electronic devices and related applications such as e-papers, flexible displays, and wearable electronic technologies.^{30–32} In this process, OFETs also contributed to developing organic semiconductors, along with OPVs and OLEDs.

1.3 Working principle of OFETs

OFETs architecture contains three components. The semiconducting layer, a dielectric layer, and metallic or other conductive contacts (source, drain, and gate) are the parts of OFET. The semiconducting layer, also called the active layer, is a conjugated polymer or small molecule. An insulator material is used as the dielectric layer, holding an applied electric field across the layer while maintaining zero or extremely low current. The commonly used dielectrics include SiO₂ and organic plastic materials such as polymethyl methacrylate (PMMA), CYTOP, polystyrene (PS), and poly(4-vinylphenol) (PVP).³³ Contacts consist of conductive metals (in most cases), metal oxides, or graphene, based on device structure.³⁴ The above-described components can be arranged differently based on device architecture, but the source and drain contacts must be in contact with the active layer. In contrast, gate contact must only be in contact with the dielectric layer. An applied voltage across the source and drain forces them to inject chargers into the semiconducting layer at the semiconductor-metal interface. These chargers move between two electrodes parallel to the dielectric layer passing through the channel region.

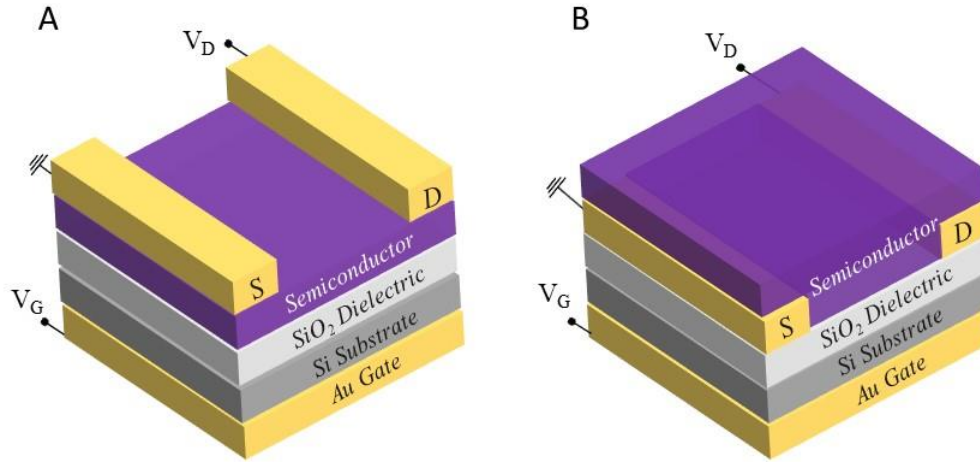


Figure 1.1: OFET device architectures (A) bottom-gate-top-contact (BGTC) and (B) bottom-gate-bottom-contact (BGBC)

In OFETs, BGBC and BGTC configurations are the two most common device architectures used in the field (see Figure 1.1). The major charge carrier of the OFETs is decided by the chemical nature of the active layer component. It can be either electrons or holes, making them n-type or p-type semiconductors, respectively. If the active layer is p-type, a negative bias voltage is necessary to apply across the gate dielectric (V_G), which accumulates positive charges at the vicinity of the semiconductor-dielectric interface. Under the applied V_G , if another negative voltage (V_D) is applied across the source and drain contacts, holes begin to move from source to drain, leading to a source-drain current (I_D). Under a constant V_D , I_D values can be recorded by applying a linear-sweep V_G , leading to a plot called transfer curve (see Figure 1.2 a). On the other hand, when V_D is swept to recorded I_D under a constant V_G , I_D reaches a saturation point with higher V_D , leading to a plot called output curve. (see Figure 1.2 b)

Three major parameters can be obtained from transfer curves for evaluating OFETs' performance. They are charge carrier mobility (μ), threshold voltage (V_T), and current on-to-off ratio ($I_{on/off}$). μ can be calculated from the slope of the square root I_D Vs. V_G curve of the transfer

plot. V_T can be extracted from the same curve by extrapolating it to meet the X-axis and obtaining the corresponding voltage (V_G) at the intercept. V_T is the minimum V_G required to switch an OFET to on-state. $I_{on/off}$ is the ratio of I_D at on-state (higher V_G) and off-state (ideal case $V_G = 0$ V).

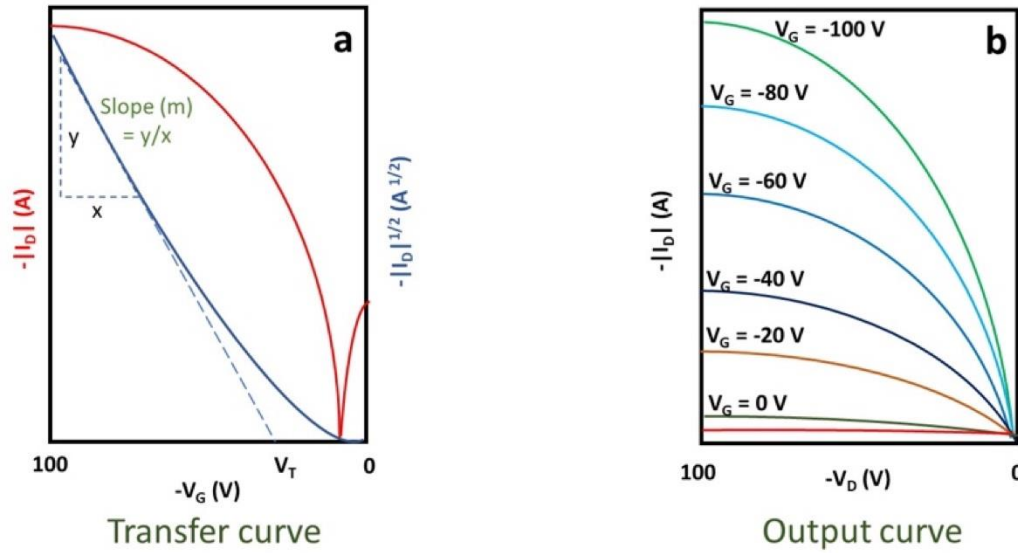


Figure 1.2: OFETs a) transfer curve and b) output curve

Using OFETs parameters, charge carrier mobilities are calculated from transfer curves. A constant V_D extracted from two different regions of output curves, namely linear and saturation regions, can be used to obtain transfer curves. When a $V_D \ll V_G - V_T$ is used to obtain the transfer curve, it is obtained from the linear region. In the linear region, I_D varies linearly with the V_D , which is also called the ohmic region. At a greater V_D where $V_D \gg V_G - V_T$, OFETs operates in saturation region with the formation of a depletion zone at the drain contact, and I_D becomes independent from V_D and varies only with V_G sweep.

Charge carrier mobilities can be extracted from transfer curves using linear and saturation regions, and corresponding equations are given below.

$$I_D = \frac{W}{L} \mu C_i V_D (V_G - V_T) \quad V_D < V_G - V_T \text{ (Linear Region)}$$

$$I_D = \frac{W}{2L} \mu C_i (V_G - V_T)^2 \quad V_D > V_G - V_T \text{ (Saturation Region)}$$

Where,

W = channel width, L = length, μ = charge carrier mobility, and C_i = capacitance per unit area

1.4 Charge transport in π -conjugated systems

Semiconducting materials used in organic electronics are conjugated organic molecules in which single and double/triple bonds are positioned alternatively in the backbone. Single bonds comprise sigma-bond formed by overlapped sp^3 , sp^2 , or sp hybridized orbitals, and double/triple bonds consist of π -bonds made of lateral overlap of unhybridized p-orbitals perpendicular to the sigma bond.

When the atomic orbitals are involved in covalent bonding in a molecule, a series of molecular orbitals are formed due to atomic orbital mixing. The energy gap between HOMO and LUMO defines the molecular bandgap. π -bonded electrons are strongly delocalized throughout the sigma-bonded covalent backbone to form an extended electron cloud.

There are two major theories to explain charge transportation.³⁵⁻³⁸

1. Band-like transport for single crystal and conjugated polymer
2. Hopping mechanism for highly disordered semiconductors (see Figure 1.3)

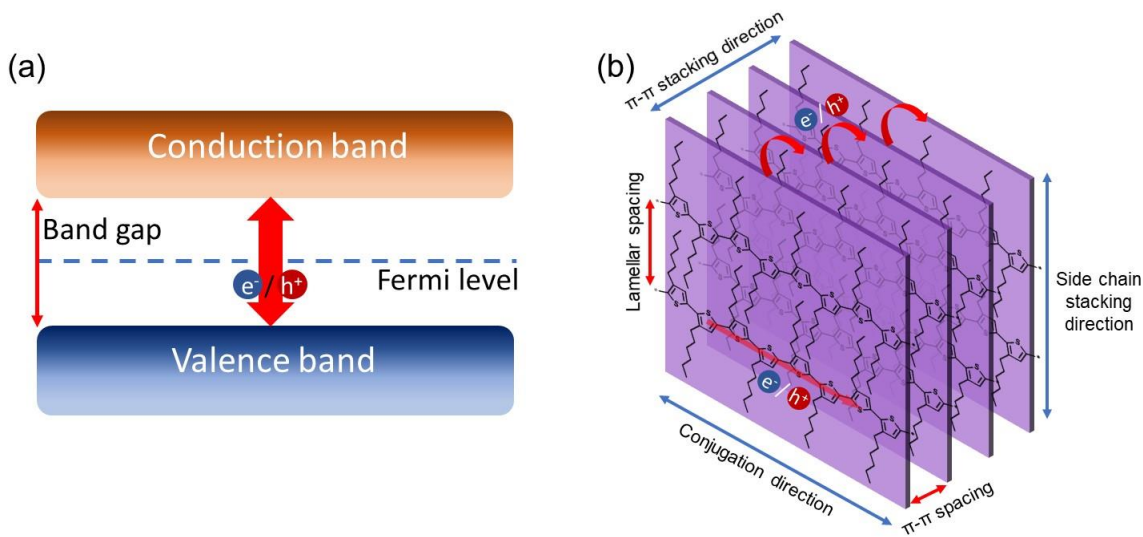


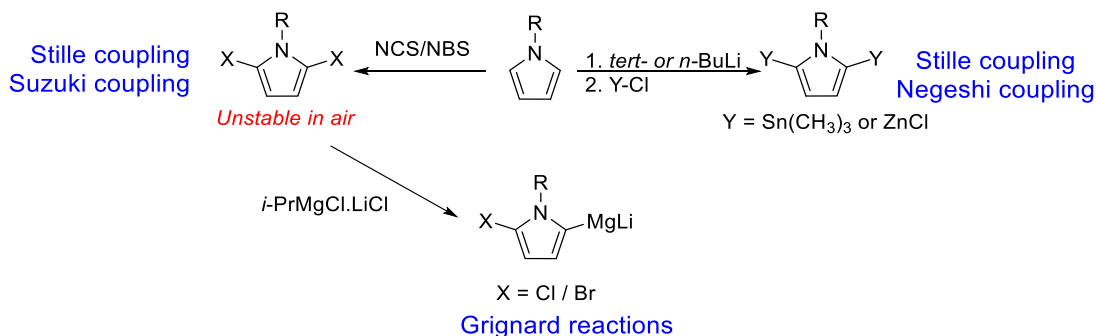
Figure 1.3: Charge transportation mechanisms in organic conjugated molecules; (a) Band transport and (b) hopping mechanism

Among these models, the hopping mechanism is widely used to explain charge transport in organic semiconducting materials since they are mostly polycrystalline or amorphous with less ordering. According to the above theory, charge transportation of the organic semiconductors mainly depend on electron tunneling and electron hopping. At lower temperatures, the charge tunneling effect dominates and, at higher temperatures, thermally driven charge hopping becomes more significant.^{37,39,40} In most cases, OFETs are operated at ambient temperatures and above; Hence, it is believed that the hopping transport of charges mainly contributes to total charge carrier mobility in organic semiconductors.

1.5 Pyrroles in OFETs applications

Pyrrole is an electron-rich nitrogen heteroatom-containing five-membered ring system. Pyrrole can contribute as a donor moiety in organic semiconductors. While incorporating pyrroles

in other aromatic systems, functionalization through 2- and 5- positions is the most popular. Several different coupling methods such as Grignard coupling, Negishi coupling, Stille coupling, and Suzuki coupling were involved in coupling pyrroles with other moieties in literature. Those different synthesis methods followed in the literature are summarized in Scheme 1.1.



Scheme 1.1: Coupling synthesis methods applied for *N*-alkylated pyrroles⁴¹

When coupling with thiophenes, the halogenated pyrrole derivative is mainly used as it can be introduced into any of the above coupling reaction systems as a precursor.^{42–45} Thionyl or *N*-chlorosuccinimide (NCS) is used to chlorinate a pyrrole, while bromination is performed with cupric bromide, pyridinium tribromide, and *N*-bromosuccinimide (NBS).^{42,45–47} Both 2,5-brominated or chlorinated derivatives of pyrroles have demonstrated less stability in air and are prone to decompose upon removal of the solvent. Also, halogenation reactions are hard to perform selectively on pyrrole rings and produce mixtures of substituted products at multiple sites.⁴⁵ Purification of these mixtures to separate individual products is also a bit challenging due to air oxidation. However, storing these compounds with adequate stability is possible at cold temperatures in hexane or diethyl ether under the presence of an organic base such as triethylamine or tributylamine. By introducing electron-withdrawing protecting groups such as Boc (tert-butyloxycarbonyl) to *N*-substituent, stable halogen derivatives can be synthesized.⁴⁸ After

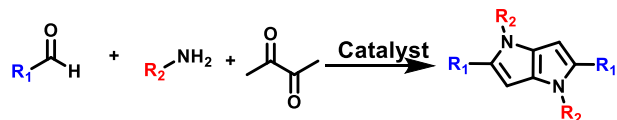
coupling Boc substituted pyrrole derivatives with another electron-withdrawing block. Deprotection can be performed to recover the previous form of coupled pyrrole moiety.^{49,50}

Pyrrole can be installed into molecules using mono- or di-stannylated forms, as single units, through the Stille coupling method. In the above process, α - position of pyrrole can be lithiated by *n*-BuLi at reflux conditions with N, N, N', N'-tetramethylethylenediamine (TMEDA).^{48,49,51–55} Synthesis of boronic acid and ester derivatives of pyrroles is also possible, enabling the use of Suzuki-Miyura and Suzuki cross-coupling reactions.^{56–58} Analogous to this, organozinc complexes can also be made by lithiation of pyrroles followed by adding ZnCl₂ for transmetallation. These complexes are utilized with Kumada and Negishi coupling reactions.^{59,60} In recent literature by He et al., synthesis of Grignard reagent from an *N*-alkylated iodinated pyrrole derivative was reported.⁶¹ However, due to the extreme sensitivity of pyrrole derivatives to the ambient atmosphere, all the above synthesis methods and related purification, characterization, and storage should be performed with care. To overcome issues caused by halogenated and other unstable pyrrole derivatives, Sadighi and coworkers have demonstrated that the direct hetero arylation method can be used with pyrroles.⁶² In this method, rhodium or palladium-based catalysts are used in combining with cesium pivalate or ZnCl₂, respectively, also with a support of a suitable ligand.⁶³

1.5.1 Pyrrolo[3,2-b]pyrrole

Pyrrolo[3,2-b]pyrrole scaffolds were first discovered in 1972 by Hemetsberger and Knittel. Among the 10 π -electron heterocycles, 1,4-dihydropyrrolo[3,2-b]pyrrole is an unstable material with excessive π -electron density and not often studied. However, lately, molecules comprise pyrrolo[3,2-b]pyrrole moieties were reported with lower overall yields in multi-step synthesis routes.^{64,65} But recently, a one-pot synthesis method was developed for 1,4-dihydropyrrolo[3,2-

b]pyrrole with yields ranging from 5-34% without time-consuming multiple column purifications, involving commercially readily available and inexpensive starting materials (see Scheme 1.2).⁶⁶ For this synthesis method, a few catalysts such as NbCl₅, *p*-toluenesulfonic acid, acetic acid, and trifluoroacetic acid have been applied to improve the efficacy.^{67–70}



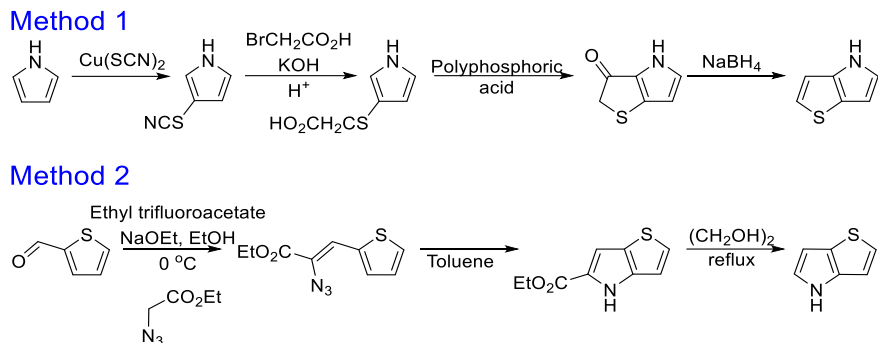
Scheme 1.2: Synthesis of *N*-functionalized pyrrolo[3,2-*b*]pyrrole small molecules with one-pot method⁴¹

Lately, even though a library of compounds with pyrrolo[3,2-*b*]pyrrole as the central core were reported,^{67,68,70–72} a few molecules were found relevant to OFETs application. Two fused heteroacenes carrying core pyrrolo[3,2-*b*]pyrrole were reported by Qiu et al. and applied in OFETs. These two molecules yielded hole mobilities of 0.001 cm² V⁻¹ s⁻¹ and 0.01 cm² V⁻¹ s⁻¹, respectively. However, based on the ease of synthesizing 1,4-dihydropyrrolo[3,2-*b*]pyrrole derivatives with no column chromatography, more attention should be paid to prepare more compound libraries and apply them in OFETs to extend the studies further.

1.5.2 Thieno[3,2-*b*]pyrrole

Matteson and Snyder first reported thieno [3,2-*b*]pyrrole block in 1957 with a relatively lower yield.⁷³ Later, a different method involving a Knoevenagel condensation reaction between thiophen-2-carboxyaldehyde and ethyl or methyl azidoacetate to yield thienylacrylate followed by Hemetsberger cyclization reaction was reported. Additional ester group remaining after this method can be removed or modified later depending on the needs in the application.^{74,75} In contrast with pyrrolo[3,2-*b*]pyrrole, thieno[3,2-*b*]pyrrole possesses a low lying HOMO level benefitting

long-term stability in OFETs materials. The above discussed different synthetic methods for thieno[3,2-*b*]pyrrole are given in Scheme 1.3.



Scheme 1.3: Thieno[3,2-*b*]pyrrole synthesis methods with different precursors⁴¹

Relatively, thieno[3,2-*b*]pyrrole has the potential of broader structure tunability and stability for electronic applications.^{73,76} The thieno[3,2-*b*]pyrrole block was first applied for OFETs testing by Jones et al. In that experiment, thieno[3,2-*b*]pyrrole (TP) was put in TP-Ar-TP (Ar = aromatic) type sandwich configuration structures and hole mobilities were measured with bottom-gate/top-contact device architecture.⁷⁷ In all of these molecules, ester linkage at 5-position was conserved after determining that it helped to stabilize the HOMO level by 0.3-0.5 eV. In this study, starting from TP dimer, the middle aromatic group was systematically changed from phenyl, anthracene, 9,9-didodecylfluorene, 2,1,3-benzothiadiazole, and bithiophene while the N-alkyl substituent of TP was kept as dodecane.⁷⁷ Reported hole mobilities for these molecules were 0.03 cm² V⁻¹ s⁻¹ (**TP-dimer**), 0.1 cm² V⁻¹ s⁻¹ (**S1**), 0.04 cm² V⁻¹ s⁻¹ (**S2**), 0.00003 cm² V⁻¹ s⁻¹ (**S3**), 0.28 cm² V⁻¹ s⁻¹ (**S4**), and 0.004 cm² V⁻¹ s⁻¹ (**S5**), respectively, as measured through OFETs after thermally annealing at 110 °C for 5 minutes in air.

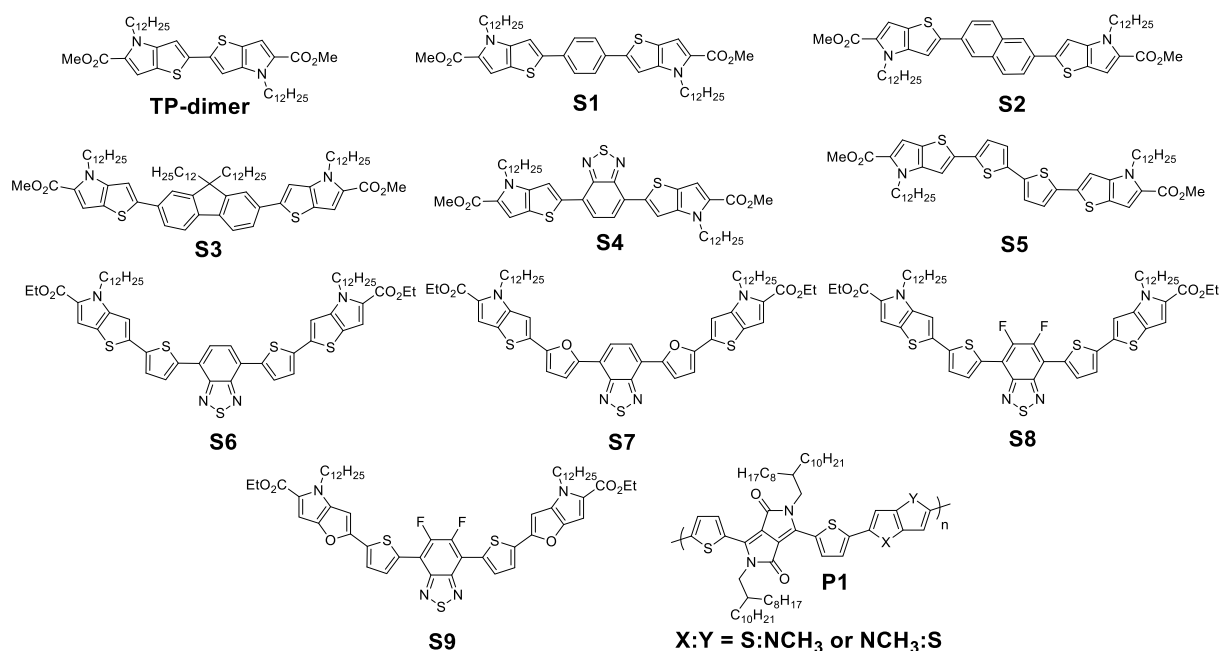


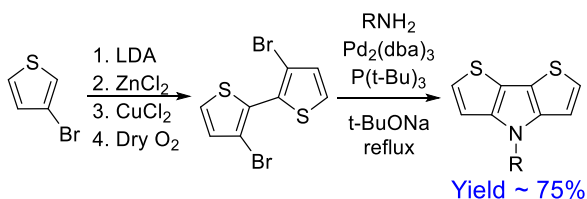
Figure 1.4: TP- and furo[3,2-*b*]pyrrole-based Organic semiconducting materials in OFETs⁴¹

In 2018, two small molecules (**S6** and **S7**) analogous to **S4** but with thiophene and furan spacers, respectively, were reported by Stefan et al.⁷⁴ In this experiment, **S6** exhibited a hole mobility maximum of $0.08 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ while **S7** showed a maximum of $7.1 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with BGBC devices upon annealing at 120 °C for 5 minutes, indicating that thiophene works better than furan as a spacer in this molecular design. Lately, thiophene flanked 5,6-difluorobenzo[*c*][1,2,5]thiadiazole was introduced as the acceptor moiety to yield **S8** and **S9**, respectively, with thieno[3,2-*b*]pyrrole and Furo[3,2-*b*]pyrrole as the donors and two molecules were tested in OFETs.⁷⁸ **S8** showed moderate hole mobilities around $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, regardless of the annealing temperatures, while **S9** was OFET inactive. TMAFM performed for these molecules revealed that **S8** has larger crystallites while no significant crystallites formation was observed for **S9**, supporting the mobility trend. As an extension to the pyrrole-based work, Stefan et al. synthesized an *N*-methyl substituted thieno[3,2-*b*] pyrrole-based alternative copolymer with

thiophene flanked diketopyrrolopyrrole as the acceptor to yield more conjugation length.⁷⁵ In this study, thieno[3,2-*b*]pyrrole ester functionality was removed to have a stannylated end on both sides of the block, to be able to polymerize it with brominated thiophene flanked DPP via the Stille method. The copolymer obtained (**P1**) exhibits average hole mobility of $0.12 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for BGTC devices annealed at 200 °C. **P1** was non-regioregular due to the presence of an asymmetric pyrrole donor monomer. These small molecules and polymers reported by Stefan et al. showed “kink” free linear transfer characteristics, limiting chances for overestimated mobilities. In a recently reported study, molecular modeling methods were used to predict OFETs activity of a series of TP containing potential molecular structures. These tools will be useful to eliminate the necessity to synthesize a library of molecules to determine applicability in OFETs.

1.5.3 Dithieno[3,2-*b*: 2',3'-*d*]pyrrole (DTP)

Among all the pyrrole-based blocks, DTP is the most studied and widely applied block to yield efficient OPV and OFETs devices. Berlin et al. reported a redox potential measurement and conductivity study on poly(dithieno[3,2-*b*: 2',3'-*d*]pyrrole), after which utilizing DTP as a monomer is increased progressively.⁷⁹



Scheme 1.4: A synthesis method for *N*-functionalized dithieno[3,2-*b*: 2',3'-*d*]pyrrole with higher yield⁴¹

Compared with other pyrrole-based blocks, DTP has a low lying HOMO making it stable to ambient conditions. N-alkylation modifications can also be performed on these units to enhance solubility. Apart from that, DTP as a monomer for a copolymer can produce regioregular backbone structures owing to its symmetric nature. This block also produces a slight torsion angle when combined with other monomers because more bulky *N*-substituents are placed in the middle ring of the structure and away from monomer binding sites.

In 1983, the synthesis of unfunctionalized DTP was reported by Zanirato et al. After about a decade, Berline and coworkers performed alkyl functionalization with linear and branched side chains on DTP to improve the solubility of the material.⁷⁹ Synthesis of the precursor DTP block required a four-step route with low overall yields. Hence, Rasmussen and Ogawa developed a method involving Buchwald-Hartwig amination of 3-bromothiophene followed by a one-pot bromination-cyclization via Ullmann coupling to generate *N*-functionalized DTPs.⁴¹ 3,3'-dibromo-2,2'-bithiophene was used to convert to *N*-functionalized DTP via a reactive intermediate, aminothiophene, in this method.⁸⁰⁻⁸³ Lately, Rasmussen and Evenson developed a synthesis method to effectively synthesize 3,3'-dibromo-2,2'-bithiophene via 3-bromothiophene, leading to a higher DTP yield of 75% (see Figure 1.4).⁸⁴

Some of the DTP-based structures involved in OFETs applications are summarized in Figure 1.5. Among the few DTP containing small molecules and polymers, maximum mobilities reported were $1.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $1.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively, for holes and electrons. In 2008, McCullough's group first reported *N*-alkylated DTP in copolymers with alkylated thiophenes and bithiophenes comonomers (**P2-P4**), applied in OFETs.⁸⁵ These polymers exhibited hole mobilities of $0.026 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $0.13 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and $0.0035 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively with a higher

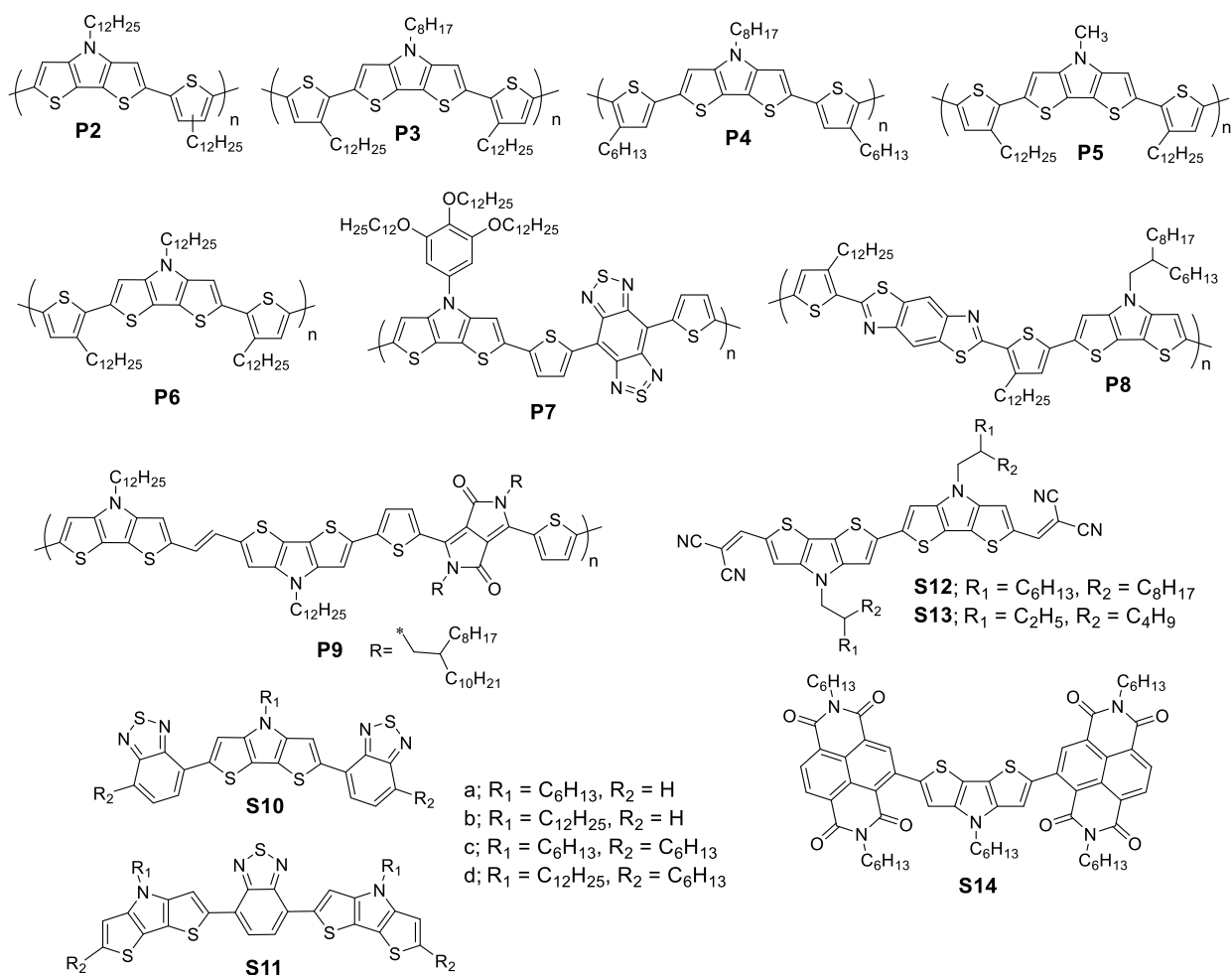


Figure 1.5: DTP-based polymers and small molecules in OFETs⁴¹

reproducibility but suffered from small $I_{\text{on/off}}$ current ratios (4-120). Thermal annealing of the OFETs based on these polymers didn't show improving hole mobilities; Instead, they were further reduced due to the thermally induced face-on orientation of polymer chains. In parallel to this work, Zhang and coworkers reported two polymers analogous to **P3**.⁸⁶ In these polymers, *N*-alkylation on DTP was changed to methyl and dodecyl to obtain **P5** and **P6**, respectively. Hole mobility extracted from the saturation regime for devices prepared using **P5** and **P6** were $0.08 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ($I_{\text{on/off}} = 10^3$) and $0.11 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ($I_{\text{on/off}} = 10^4$), respectively. In addition, an ambipolar

copolymer (**P7**) containing DTP and benzobisthiadiazole copolymer blocks was reported in 2009 by Reynolds et al.⁸¹ It has shown mobilities of $1.2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $5.8 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively, for holes and electrons for devices fabricated on octadecyltrichlorosilane modified silicon dioxide surface. In the same year, Marder et al. published a study on perylene diimide and DTP-based copolymer and tested the material in n-type OFETs. Reported mobility for this polymer was $1.2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with $I_{\text{on/off}} = 10^3$.⁸⁷ Jenekhe's group synthesized two polymers with benzobisthiadiazole and DTP monomers which are different in molecular weights (**P8**(1): $M_n = 10.3 \text{ kDa}$, $\text{PDI} = 3.12$ and **P8**(2): $M_n = 52.4 \text{ kDa}$, $\text{PDI} = 2.82$).⁸⁸ Both polymers exhibit similar hole mobilities ($\sim 5.0 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) despite the difference in molecular weights. The highest hole mobility reported for a DTP-containing polymer (**P9**) in OFETs was obtained by Hsu et al. recently. This group synthesized a DPP acceptor and DTP-vinylene donor-based copolymer to achieve hole mobility of $1.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.⁸⁹

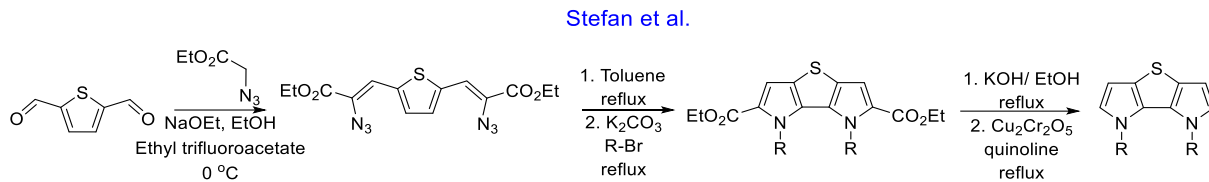
A few small molecules based on DTP blocks are also reported relevant to OFETs applications. The first set of small molecules tested in OFETs incorporating DTP were reported by Marder et al. This series of molecules consist of acceptor-donor-acceptor (A-D-A)-(S10a-S10d) and donor-acceptor-donor (D-A-D)-(S11a-S11d) molecular design, four different molecules from each type. In both architectures, benzothiadiazole acceptor and DTP donor were used and alkyl chains were varied within each architecture to yield four different molecules from each (Figure 1.5).⁹⁰ OFETs measurements obtained for these molecules indicate that longer alkyl chains with D-A-D architecture performed better with mobilities between 10^{-2} and $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Introducing terminal alkyl chains on R_2 of molecules caused reduced hole mobilities by almost ten folds.

Recently, Zhu and the team synthesized two small molecules (S12 and S13) comprise dicyanovinylene terminated DTP dimer with different branched side chains and applied them in OFETs to yield $1.1 \times 10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $7.0 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively.⁹¹ Recorded significant differences between mobilities attribute to the drastic morphological differences in thin films. So far, the only high-performing DTP-based small molecule having electron carrier mobilities was reported by Kippelen and coworkers. This molecule (S14) consists of terminal naphthalene diimide units and a center DTP unit and produced electron mobility of $1.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in OFETs with small batch-to-batch variation.⁹²

1.5.4 Thieno[3,2-b:4,5-b']dipyrrole (TDP)

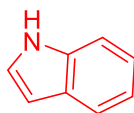
In 1976, Fournari and co-workers reported the synthesis of TDP monomer for the first time.⁹³ TDP was found to be relatively unstable in ambient conditions and possess properties equivalent to pyrrole. However, this block was first incorporated in a polymer by Sannicolo and co-workers. They demonstrated excellent resistance of the material to the oxidation process.⁹⁴ Lately, a study using electrochemistry was performed on polypyrrole (PP) and poly(thieno[3,2-b:4,5-b']dipyrrole) by Zotti et al. to investigate the oxidation potentials of monomers (bipyrrole and TDP) and redox potentials of polymers.⁹⁵ Fusing thiophene between the two pyrrole rings has not altered electrochemical properties compared to PP. Oxidation potentials of 0.55 V and 0.42 V were reported for PP and TDP, respectively, while polymers made out of these monomers showed redox potentials of -0.20 V and -0.19 V, respectively. There was a drastic drop, however, in conductivity measurement observed for TDP-based polymer (2 S cm^{-1}) compared to PP incorporated polymer (100 S cm^{-1}). Stefan et al. have attempted to perform polymerization with TDP using both oxidative polymerization with FeCl_3 and metal-catalyzed polymerization.⁵⁴

Oxidative polymerization yielded molecular weights of 6.5 kDa while metal-catalyzed Stille coupling polymerization produced only oligomers.

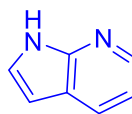


Scheme 1.5: Synthesis of *N*-alkylated TDP⁴¹

1.5.5 Indole and pyrrolopyridine



1*H*-indole



1*H*-pyrrolo[2,3-*b*]pyridine

Figure 1.6: Structures of 1*H*-indole and 1*H*-pyrrolo[2,3-*b*]pyridine

Indole and pyrrolopyridenes are the simplest phenyl- and pyridine-fused pyrrole-based ring systems analog to TP, respectively (see Figure 1.6). Indole is a widely known organic block that has been used in a wide variety of applications. Indole derivatives have become important in the medicinal field due to their biological and pharmaceutical activity.^{96,97} Even though there are not many reports of indole used in its simplest form in organic electronics, some derivatives, such as fused indole (Indolo[3,2-*b*]indole (II)) and indole fused with other aromatic units, were reported. For example, Indolo[3,2-*b*]indole has been reported in a set of small molecules with malononitrile substituted thiophene or bithiophene derivatives applied in ambipolar OFETs, which provided both hole and electron mobilities between 10^{-2} – 10^{-1} cm² V⁻¹ s⁻¹.⁹⁸ In another study, a similar fluorinated II derivative without a malononitrile substitution was applied in perovskite solar cell as the hole transporting material to yield optimal performance of 19%.⁹⁹ A series of fluoro-, chloro-, cyano-,

and trifluoromethyl-substituted II derivatives were synthesized and applied in OFETs by Chetti et al. They were able to demonstrate hole mobilities in the range of 0.11 to $0.85 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for these molecules.¹⁰⁰ Apart from that, indole-based derivatives are reported in OLEDs applications. A triindole-based single crystal and thin films were involved in OLEDs and OFETs by García-Frutos et al. in 2009. This material exhibited photoluminescence activity and OFETs prepared out of the materials gained hole mobility of $0.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.¹⁰¹ Recently, in 2020, Irgashev & Tameev et al. reported a set of thieno[3,2-*b*]indole-based blocks as hole-transporting materials with reported hole mobilities in the range between 10^{-5} and $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, as determined by Charge Carrier Extraction by Linearly Increasing Voltage (CELIV) method.¹⁰² Even though a few reports are found for indole derivatives involved in electronics, there is still plenty of studies to be explored relevant to organic electronics, especially OFETs.

Pyrrolopyridines are an analogous heterocyclic fused-ring system to indole, but they have different physical properties. They are typically colorless and odorless compounds with higher melting points and stability in a range of pHs than indole. Pyrrolopyridine derivatives have also been used in medicinal and biological applications, such as kinase enzyme inhibitors.^{103–105} However, there is no significant involvement of pyrrolopyridine blocks in organic electronics except for one report. In this report, fused pyrrolopyridine- and fluorinated-BT-based DA copolymers were synthesized and applied in solar cells. In this study, they were able to obtain short circuit current and power conversion efficiency of 11.32 mA cm^{-2} and 5.68% , respectively.¹⁰⁶ In conclusion, there is still plenty of room to explore the potential of pyrrolopyridine in organic electronics.

1.6 DPP-based materials

DPP is one of the most common and extensively studied acceptor blocks among the organic electronics community due to some specific properties such as excellent electronic properties, higher photo/thermal- stability, and strong aggregation potential (assists for thin film crystallinity).^{107,108} Its desirable properties observed in the semiconducting materials originated from unique features, such as electron deficiency, extended π -conjugation system, and extreme coplanarity.¹⁰⁹ DPP was first commercialized in the 1980s as a red dye or pigment and applied in producing colored plastic, inks, and paints.^{109,110} There were only a few reports found for DPP-based pigments in history and no application of DPP in OFETs was reported until 2008. In 2008, thiophene flanked DPP-based polymer was synthesized and applied in OFETs to yield electron mobility of $0.09 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and hole mobility of $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,¹¹¹ after which huge attention was applied to DPP from scientists all over the world.

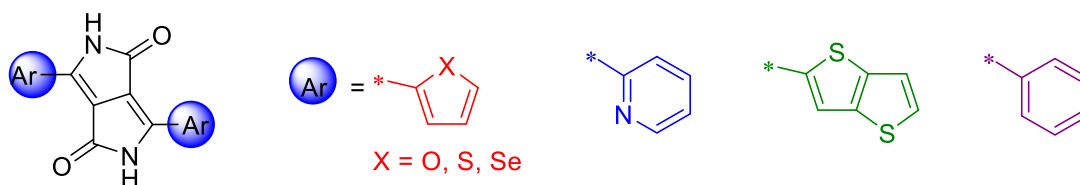


Figure 1.7: DPP derivatives with different aromatic substituents

DPP core flanked with two phenyl spacers was the first reported DPP-based block by Farnum et al. in 1974, but it suffered from low yield.¹¹² Product was brilliant red-colored and mostly insoluble in common organic solvents. Lately, Iqbal developed a new synthesis route with a single step involving dialkyl succinate and aromatic nitriles in a basic medium to produce higher yields. After this, a series of DPP derivatives with various aromatic flanks were synthesized, among them furanyl, thienyl, selenyl, pyridyl, thienothiophenyl, and phenyl derivatives were the

most common (Figure 1.7). Many modifications with distinctive side chains such as linear-, branched-, and functionalized-alkyls have also been performed on DPP-derivatives based on different applications, which further expands the library of the compound. Side chain substitution on DPP assists in reducing stronger hydrogen bonding interactions, making them more soluble in common organic solvents.

Lately, these soluble DPP derivatives with dibromine functionality on aromatic-flank groups were involved in synthesizing DA-type polymers using standard coupling methods such as Stille, Suzuki, and Buchwald.^{108,113} Subsequently, electrochemical polymerization methods were also developed and reported for DPP-based derivatives.¹¹³ Compared to DPP-containing polymer-based materials reported, fewer studies are reported for small molecules and oligomers.¹⁰⁹ Among reported small molecules, most of them are involved in OPV applications rather than OFETs.^{114,115} However, compared to other acceptors-based organic semiconductors, DPP-based materials, especially polymers, often show high hole mobilities over $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

1.7 Siloxane side chains

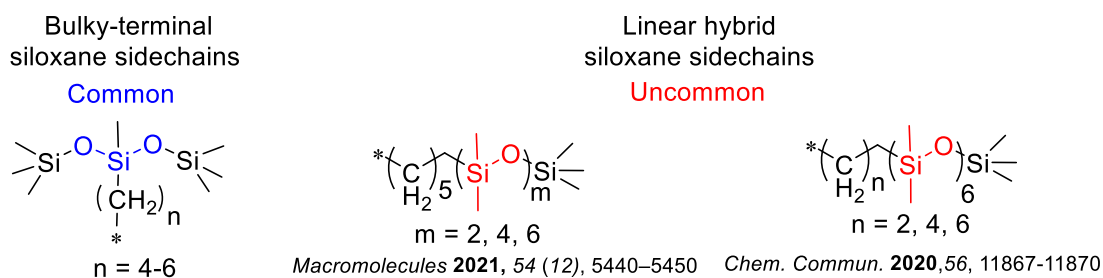


Figure 1.8: Siloxane side chains in the literature

Siloxane side chains are alkyl side chains with bulky or linear siloxane functionalized terminals (see Figure 1.8). These siloxane terminals consist of several -Si-O- units resembling the

mostly known polyorganosiloxanes repeating units.¹¹⁶ One of the most significant properties of polydimethylsiloxane is its very low surface tension (21-22 mN/m).¹¹⁷ Introduction of siloxane side chains into semiconducting materials has caused lower surface energy of polymer material surfaces, leading to reduced phase separation when blending with other materials, which is advantageous in OPV applications.¹¹⁶ In OFETs applications, siloxane side chains substituted copolymer materials have shown closer backbone assembly in thin films. Bao et al. has demonstrated that siloxane side chain substituted isoindigo based copolymer with bithiophene comonomer, packed closer than reference polymer with branched alkyl chains.¹¹⁸ Siloxane counterparts on side chain also help to improve the solubility of conjugated polymers and small molecular materials in common organic solvents.^{119,120} Ding and coworkers recently published the use of linear alkyl-siloxane hybrid side chains in isoindigo and bithiophene-based conjugated polymers varying side-chain lengths and demonstrated high solubility of these materials even in non-halogenated solvents such as aromatic hydrocarbons, ether, alkanes, and esters.¹¹⁹ On the other hand, siloxane side chains have demonstrated their ability to make OFETs materials more ambient and moisture stable when incorporated in isoindigo- and DPP-based polymers, creating an opportunity to use the polymers for more practical applications and in moisture environments.^{121,122} Although physical and thin film microstructure property changes occur, no significant optoelectronic property changes were observed due to the incorporation of siloxane side chains in place of alkyl side chains in semiconducting materials.

1.8 Siloxane substituted DPP-based materials in OFETs

Siloxane side chains substituted DPP (see Figure 1.9) have gained attention due to their contribution in improving organic electronic materials performance compared to their alkyl-

substituted analogous. Although a significant number of studies have been conducted incorporating siloxane substituted DPP in conjugated polymer backbones, there are no adequate studies reported for small molecules. In 2012, Yang's group synthesized a siloxane side chain modified thiophene-flanked DPP containing copolymer with selenophene comonomer and managed to yield significantly high hole and electron mobilities (3.97 and $2.20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively).¹²³ This polymer has exhibited better mobilities for the solution-shearing method than both spin-coating and drop-casting methods.

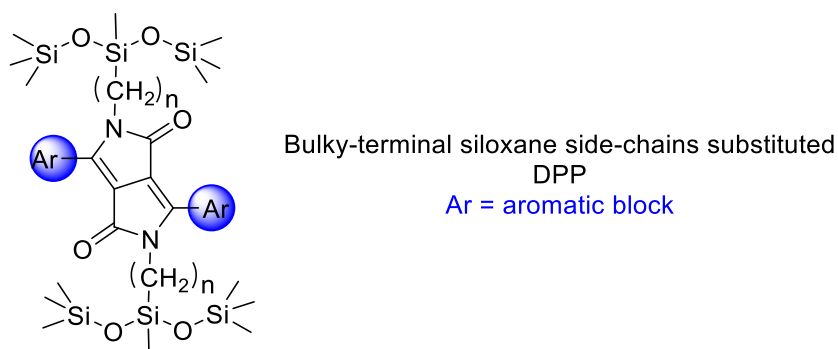


Figure 1.9: An example for terminal bulky siloxane side chain substituted DPP derivatives

Further, according to the literature, incorporating siloxane side chains in DPP polymers has provided opportunities to improve several material properties such as thin film morphology, ambient stability, and wettability of thin films. In a relevant study, Yang et al. has demonstrated that the distant branching point of siloxane side chains improves OFETs hole mobility (from 0.54 to $4.55 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) by one order of magnitude compared to typical branched side chains with branching point at carbon-2.¹²² In this study, they further noticed that siloxane side chains had improved the ambient stability of the material showing high stability in OFETs devices over an extended time in a moisture environment. Furthermore, they have found that siloxane-modified DPP polymer in solution has provided better wettability and compatibility with

octadecyltrimethoxysilane (OTMS) modified SiO₂ wafer surfaces, indicating more favorability with solution-processing. In 2017, Yang et al. reported two polymers with siloxane-DPP block and thiophene vinyl thiophene comonomers (with hexyl chains at different positions). These polymers showed hole mobilities of 1.69 and 0.90 cm² V⁻¹ s⁻¹ in OFETs.¹²⁴ In another study, Yang and the group demonstrated synthesis and OFETs application of siloxane-DPP and thienothiophene comonomer based copolymers having thiophene and furan DPP-flanks units. Both polymers exhibited high hole mobilities, 3.57 and 2.40 cm² V⁻¹ s⁻¹, respectively, for thiophene and furan incorporated polymers. They have further observed relatively enhanced solubility of furan incorporated polymer in various solvents and used it in halogen-free solvents processing to yield mobility of 1.87 cm² V⁻¹ s⁻¹.¹²⁵

1.9 Conclusion

Evaluation of organic semiconductors began with the discovery of organic conducting polymers such as polypyrrole and polyaniline. Pyrrole was a major block in the early history of semiconductors, but most of the early pyrrole-based derivatives such as pyrrolopyrrole and TDP were relatively unstable in air. However, later, relatively stable pyrrole-based derivatives such as DTP and thienopyrrole were introduced and since then, the contribution of pyrrole derivatives for OFETs has become convenient and abundant. However, other pyrrole derivatives, apart from thiophene-based, such as indole and pyrrolopyridine so far, have an insignificant contribution to the field of OFETs. Somehow, indole and pyrrolopyridine derivatives were able to expose their potentials of being used in organic electronics by exhibiting moderate performances in a few OPVs, OLEDs, and OFETs-based studies. Therefore, further studies should be done to reveal the full potentials of such pyrrole blocks. On the other hand, DPP was one of the major acceptor

candidates in recently reported high-performing semiconductors. However, the involvement of DPP in pyrrole-based materials is not very common, and the potential of this combination should be further investigated. However, among the DPP-based semiconducting materials, siloxane side-chains substituted DPP-involved cases showed improved hole mobilities than their branched side chains derivatives. Therefore, it is noteworthy to mention that engagement of siloxane side-chains is also vital in enhancing pyrrole-based semiconducting materials with the contribution of DPP. However, other acceptor materials such as benzothiadiazole should also be involved in developing pyrrole-based materials since it has already revealed compatibility with pyrrole derivatives, as discussed in this chapter.

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CHAPTER 2

**SILOXANE SIDE-CHAIN MODIFIED DIKETOPYRROLOPYRROLE AND
THIENOPYRROLE CONTAINING SMALL MOLECULES FOR ORGANIC FIELD-
EFFECT TRANSISTORS**

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2.1 Abstract

Siloxane side chain substituted diketopyrrolopyrrole (DPP)-based semiconducting materials have shown significantly improved charge carrier mobilities in organic field-effect transistors (OFETs), compared to branched or linear alkyl-substituted DPP material. So far, a considerable number of studies have been expanded towards siloxane-DPP-containing donor-acceptor (DA) type semiconducting polymers and have demonstrated significantly improved results in OFETs properties and solubility in various solvents, including halogen-free solvents. However, the commitment of siloxane side chain containing DPP in designing and synthesis of semiconducting small molecules for OFETs, is not that significant. A few studies have demonstrated that the siloxane-DPP combination can be used in developing well-performing small molecules. Thieno[3,2-b]pyrrole (TP) has been demonstrated to be a well-performing donor moiety, which is isoelectronic to widely used thieno[3,2-b]thiophene (TT), in both semiconducting small molecules and polymers. Among the TT containing small molecules, benzo[*c*][1,2,5]thiadiazole (BT) acceptor-based DA type materials have shown significant mobilities closer to $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. However, TT fused-ring donor system was never studied in a DPP-acceptor-based system for small molecules. In this study, we have demonstrated the synthesis, characterization, and OFETs application of two DA-type small molecules, namely DPP-2T-2TP and DPP-2F-2TP, which contain siloxane-DPP acceptor with thiophene or furan spacers and TP donors, respectively. Both molecules showed OFETs activity with a maximum hole mobility of $4.10 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $6.40 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. DPP-2T-2TP showed typical mobility enhancement upon thermal annealing as most organic semiconductors, but surprisingly, a reduction in hole mobility

was observed for DPP-2F-2TP. Both molecules were stable enough to perform all the OFETs thin film treatments at ambient conditions.

2.2 Introduction

Organic semiconducting materials (OSMs) have gained attention within the last few decades due to several reasons, such as low-cost, light-weight, flexibility, and more tunable optoelectronic properties compared with their inorganic alternatives.¹ OSMs are often found in organic field-effect transistors (OFETs), light-emitting diodes, solar cells, photodetectors, memory devices, chemical sensors, logic circuits, etc.¹ Among organic electronic devices, OFETs are a vital component in various analog and digital integrated circuits.^{2–4} OSMs are mainly categorized into two components depending on their complexity of molecular backbone structure and molecular weight; those are semiconducting small molecules and semiconducting polymers. Solvent processible semiconducting polymers are often well-performing compared to solvent processible small molecules. However, their large-scale real-world applications have been limited due to batch-to-batch variation of the OFETs performances caused by molecular weight-dependent charge carrier mobilities. Semiconducting small molecules are found in both thermal and solvent processible forms.^{5,6} Thermally processed and single-crystal semiconducting small molecules such as fused-ring acenes have exhibited high hole mobilities^{6–9} exceeding hole mobilities reported for amorphous silicon ($0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)¹⁰ and approaching polycrystalline silicon ($100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).^{11,12} However, thermally processible small molecular materials require harsh processing conditions such as ultrahigh vacuum conditions and high temperatures, making large-scale application processes hard and less cost-effective. On the other hand, due to the harsh conditions applied, it has been incapable of conducting extensive structural modifications on thermal

processable materials since electron-rich hole conducting materials could be intolerant to the harsh conditions. In addition, solvent-processable small molecules have shown relatively underdeveloped hole mobilities due to the introduction of various side-chains, which makes the materials soluble in common solvents but influences the thin film crystallinity and thus carrier mobility.^{13,14} However, with the ambient conditions used in solution processing, structural modifications become possible to get versatile designs for both small molecular backbones and solubilizing side-chains.^{1,15} Introduction of electron-rich counterparts such as thiophene and pyrrole-based fused-ring systems has become feasible with solvent processing conditions, leading to an additional electron-richness in hole-transporting materials. These facts associated with the small molecular semiconducting materials has led experimentalist to focus on developing solvent processable small molecules with better performances.

TP which is isoelectronic to a widely occupied electron-rich TT moiety in semiconducting materials, has started to gain attention due to its better electron richness compared to TT. TP also provides an additional site to perform side-chain modification through *N*-alkylation which is advantageous in fine-tuning solubility and thin film properties. In some recent literature, TP has been utilized within donor counterparts of donor-acceptor type small molecules and polymers.^{16–19} Usually, pyrrole materials are less stable in ambient conditions but once pyrrole is fused with other stable aromatic rings, they provide much more stable materials with low-lying HOMO. Even though TP is a stable electron-rich fused-pyrrole moiety, fewer studies have been performed so far in the semiconducting field on it; thus, its full potential is yet to be understood.

The major challenge of designing solvent-processable semiconducting materials with solubilizing side chains is to compromise between solubility, which is critical in thin film

processing, and crystallinity, which is critical in optimizing OFETs performance.^{20,21} Hence, side-chain engineering has become a crucial area when developing high-performance solvent processable small molecules. Siloxane terminated side-chains are found to be an excellent candidate in some of the high-performing semiconducting polymers.^{20,22–27} These shorter length alkyl chains containing 4-6 carbons with solubilizing bulky siloxane terminals provide less crowdedness around *N*-alkyl sites especially due to the placement of the chain branching point at a fair distance from the backbone.^{28,29} This will provide more room for backbone counterparts to pack well, effectively improving crystallinity in thin films via π – π interactions.²⁵ In addition, bulky siloxane terminals interact with most of the commonly used solvents to provide adequate solubility during solution processing.^{21,24} Siloxane side chains also provide additional ambient stability to thin films which offer an opportunity to attempt processing in ambient conditions.²⁹

In the recent past, our group reported TP-based semiconducting materials with reasonable hole mobilities for small molecules¹⁸ ($\sim 0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). BT and TP based small molecules with different spacer units are reported among them with hole mobilities between 10^{-1} - $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.^{17,18,30} Apart from that, diketopyrrolo[3,4-*c*]pyrrole (DPP)-TP based copolymer was also reported with hole mobility over $10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.¹⁹ In the process of understanding the behavior of TP in semiconductors, especially in small molecules, there is more room to expand our studies incorporating other excellent acceptors reported in the literature such as DPP. There is a vast variety of high-performing donor-acceptor polymers reported with DPP acceptors which shows excellent hole mobilities. DPP-based small molecules are also reported with moderately fair hole mobilities (10^{-1} - $10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) in OFETs but most of the times, cases are reported relevant to applications in organic photovoltaics (OPV).^{1,31} In the recent past, in 2017, DPP-based small

molecule containing siloxane terminated side chains was reported with a high hole mobility ($3.04 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) by Noh et al.²¹ Since then, there is not any recent reports of such higher mobilities found in the literature for donor-acceptor small molecules in OFETs. Therefore, it is important to further study structure-property relationships of different structural models to fully understand design strategies for high-performing donor-acceptor small molecules.

In this study, for the first time, we report DPP- and TP-based small molecules with siloxane side chains to further understand the structure-property relationship of these blocks towards its OFETs performance and gain more understanding about pyrrole based small molecules in OFETs. Two DA-type small molecules, DPP-2T-2TP and DPP-2F-2TP, respectively, with thiophene or furan spacer containing DPP acceptor block and an ester mono-capped *N*-methylated TP donor blocks were synthesized (see Figure 2.1). The design objectives of these molecules include investigation of the effect of change in heteroatom on chalcogenophene spacer towards the optoelectronic, thermal, and OFETs properties. Furthermore, how the overall backbone design, its linearity and planarity affect the OFETs performance was investigated. These molecules were characterized and analyzed for optoelectronic and thermal properties to understand the structure-property relationship.

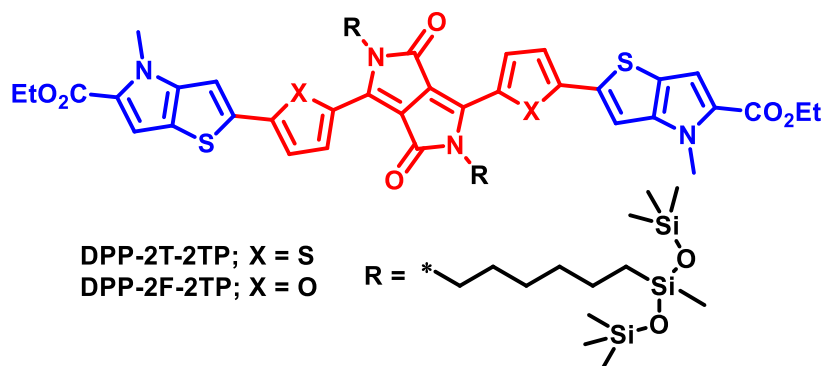


Figure 2.1: Structures of suggested DPP and TP containing donor-acceptor-donor small molecules

2.3 Materials and methods

2.3.1 Materials

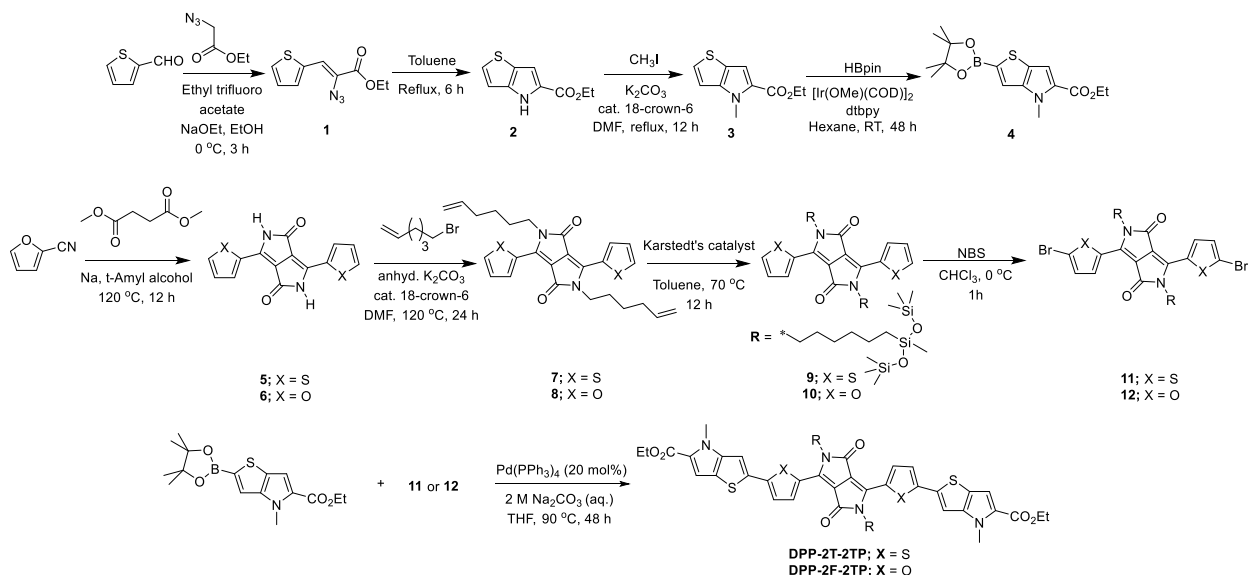
All the chemicals are purchased from Sigma Aldrich and Fisher Scientifics except for methoxy(cyclooctadiene)iridium(I) dimer ($\text{Ir}[(\mu_2\text{-OMe})(\text{COD})]_2$) (Alfa Aesar), pinacolborane (Acros Organics) and used without any further purifications. Toluene and tetrahydrofuran (THF) were used in reactions immediately after distilling over the sodium-benzophenone ketyl. *N,N*-Dimethylformamide (DMF) was used after distillation over calcium hydride and stored over the anhydrous molecular sieves.

2.3.2 General Methods

500 MHz Bruker AVANCE III spectrometer was used to obtain ^1H and ^{13}C NMR spectra. Agilent 8453 UV-vis spectrometer was used to obtain UV-visible spectra in both solution and thin film. BAS CV-50W voltammetry analyzer (with Pt wire auxiliary electrode, Pt inert working electrode, and Ag/Ag^+ reference electrode system; electrolyte - 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile) was used to perform electrochemical analysis. Mettler Toledo

TGA/DSC-1 analyzer was used to examine thermal properties of the final products. Shimadzu Biotech Axima Confidence under high-resolution mode was used to perform MALDI-TOF (Matrix-assisted laser desorption ionization time-of-flight) spectra using dithranol matrix. GIXRD measurements were collected with a Rigaku III SmartLab XRD instrument. Tapping mode atomic force microscopy (TMAFM) images were obtained with a Nanoscope IV Multimode Veeco instrument by scanning the OFETs channel region. Keithley 4200-SCS parameter analyzer was used to obtain electrical parameters. OFETs devices were fabricated according to a previously reported method under a cleanroom facility with typical photolithographic techniques (deposited electrodes consist of 100 nm Au layer over 5 nm Cr layer on SiO₂/Si substrate).¹⁸

2.3.3 Synthesis of small molecules



Scheme 2.1: Synthesis of small molecules DPP-2T-2TP and DPP-2F-2TP

Synthesis of DPP-2T-2TP and DPP-2F-2TP is depicted in Scheme 2.1. Ethyl 4-methyl-4H-thieno[3,2-b]pyrrole-5-carboxylate (3) was synthesized according to a previously published

procedure.¹⁹ Briefly, commercial thiophene-2-carbaldehyde was reacted through a Knoevenagel condensation at 0 °C to obtain the corresponding acrylate, ethyl (Z)-2-azido-3-(thiophen-2-yl)acrylate (**1**). Ethyl 4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate (**2**) was synthesized via Hemetsberger cyclization of (**1**) by refluxing in toluene. Compound (**2**) was alkylated with methyl iodide in the presence of anhydrous potassium carbonate and a catalytic amount of 18-crown-6 in anhydrous *N,N*-dimethylformamide (DMF) at 120 °C to obtain compound (**3**). Compound (**3**) was then treated with 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (HBPin) in the presence of 4,4'-di-*tert*-butyl-2,2'-dipyridyl (dtbpy) ligand and methoxy(cyclooctadiene)iridium(I) dimer (Ir[(μ₂-OMe)(COD)]₂) catalyst in dry hexane to obtain ethyl 4-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate (**4**). 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(6-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)hexyl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (**11**) and 3,6-bis(5-bromofuran-2-yl)-2,5-bis(6-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)hexyl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (**12**) were synthesized according to procedures given below in section 2.3.3. In brief, thiophene-2-carbonitrile and furan-2-carbonitrile were converted in to their corresponding DPP derivatives by reacting with dimethyl succinate in the presence of a base (Sodium *tert*-amylate) in *tert*-amyl alcohol at 120 °C. Then the alkylation was performed with 6-bromohex-1-ene in the presence of anhydrous potassium carbonate as the base and catalytic amount of 18-crown-6 in DMF at 120 °C to obtain 2,5-di(hex-5-en-1-yl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (**7**) and 2,5-di(hex-5-en-1-yl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (**8**), respectively. Terminal allyl functionality in side chains of compound **7** and **8** were then converted into their corresponding siloxane terminated derivatives (**9** and **10**) by reacting with 1,1,1,3,5,5,5-heptamethyltrisiloxane

in toluene at 70 °C under the catalytic activity of Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Karstedt's catalyst). Siloxane derivatives were then brominated with *N*-bromosuccinimide to get their dibrominated derivatives (**11** and **12**) which were subsequently reacted with compound (**4**) using Suzuki cross coupling to yield the final small molecules DPP-2T-2TP and DPP-2F-2TP, respectively. The detailed synthesis procedures for all steps are provided below and NMR spectra (see Figure A.1 – A.28) are provided in Appendix A.

2.3.4 Synthesis procedure

2.3.4.1 Synthesis of ethyl (*Z*)-2-azido-3-(thiophen-2-yl)acrylate (**1**)

Ethyl (*Z*)-2-azido-3-(thiophen-2-yl)acrylate was prepared according to a previously reported procedure.¹⁹ Product was recovered as a yellowish-brown solid (5.25 g, yield = 88%). ¹H NMR (CDCl₃, 500 MHz): δ_{H} 1.39 (t, 7.5 Hz, 3H), 4.35 (q, 7.0 Hz, 2H), 7.06(dd, 1H), 7.16 (s, 1H), 7.33 (d, 1H), 7.49 (d, 1H). ¹³C NMR (CDCl₃, 125 MHz); δ_{C} 14.35, 62.23, 119.38, 122.84, 127.16, 130.50, 132.07, 136.74, 163.29.

2.3.4.2 Synthesis of ethyl 4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate (**2**)

Ethyl (*Z*)-2-azido-3-(thiophen-2-yl)acrylate (2.50 g, 11.2 mmol) was refluxed in toluene (8 mL) in a round bottom flask (50 mL). After 6 hours, reaction mixture was cooled to room temperature and solvent was removed under vacuum. Recovered crude solid was further washed with cold hexane to obtain pure product as reddish-brown crystalline solid (1.84 g, yield = 84%). ¹H NMR (CDCl₃, 500 MHz): δ_{H} 1.39 (t, 7.0 Hz, 3H), 4.36 (q, 7.0 Hz, 2H), 6.95 (d, 5.0 Hz, 1H), 7.14 (s, 1H), 7.33 (d, 5 Hz, 1H), 9.11 (s, 1H). ¹³C NMR (CDCl₃, 125 MHz); δ_{C} 14.60, 60.81, 107.68, 111.19, 124.96, 127.24, 129.57, 141.33, 161.75.

2.3.4.3 Synthesis of ethyl 4-methyl-4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate (3)

Ethyl 4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate (0.50 g, 2.56 mmol) and anhydrous K₂CO₃ (1.27 g, 9.19 mmol) were dissolved in dimethylformamide (DMF, 8 mL) under nitrogen conditions in a round bottom flask while stirring and heating at 100°C for 40 minutes. Then methyl iodide (1.23 g, 8.71 mmol) was injected into the reaction flask and further stirred at 120°C for 24 hours. The reaction was quenched by pouring into the water and extracted with diethyl ether (3 times). Then the combined organic layer was washed thoroughly with deionized water to remove DMF and dried over magnesium sulfate. The solvent was removed under vacuum-evaporator and high vacuum to recover the product as a viscous brown-liquid (0.49 g, yield = 91%) at room temperature (note: solidifying upon refrigeration). The product was utilized for the next step without further purification. ¹H NMR (CDCl₃, 500 MHz): δ_{H} 1.38 (t, 3H), 4.06 (s, 3H) 4.33 (q, 2H), 6.93 (d, 1H), 7.18 (s, 1H), 7.32 (d, 1H) ¹³C NMR (CDCl₃, 125 MHz); δ_{C} 14.57, 34.70, 60.21, 109.06, 110.19, 121.85, 127.05, 129.11, 145.72, 161.94.

2.3.4.4 Synthesis of ethyl 4-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate (4)

Ir[(μ_2 -OMe)(COD)]₂ (0.057 g, 0.086 mmol), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (dtbpy) (0.046 g, 0.17 mmol), and ethyl 4-methyl-4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate (0.36 g, 1.72 mmol) were added to a 25 mL single-neck round bottomed flask, under nitrogen. Then dry hexane (5.0 mL) and pinacolborane (0.5 mL) were added to the flask and stirred for 48 h under nitrogen conditions at room temperature. Then the solvent was removed under vacuum and pure product was recovered by performing a silica flash column using 5% ethyl acetate in hexane as the eluent. (0.45 g, yield

= 78%). ^1H NMR (CDCl_3 , 500 MHz): δ_{H} 1.35-1.39 (m, 15H), 4.04 (s, 3H), 4.33 (q, 2H), 7.17 (s, 1H), 7.45 (s, 1H). ^{13}C NMR (CDCl_3 , 125 MHz): δ_{C} 14.55, 24.92, 34.59, 84.43, 108.81, 119.31, 127.91, 129.01, 128.34, 147.01, 161.96.

2.3.4.5 Synthesis of 3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (5)

Metallic Sodium (1.28 g, 54 mmol) was dissolved in t-amyl alcohol (80 mL) at 120 °C in a 3-neck round bottom flask (250 mL) equipped with a reflux condenser connected to a bubbler until all the sodium metal disappears. After cooling down to 60°C, thiophene-2-carbonitrile (5.95 g, 54 mmol) was slowly injected into the reaction flask through the septum followed by drop-wise addition of dimethyl succinate (2.65 g, 18 mmol). The reaction mixture was turned red and stirred at 100 °C for 12 h until completed. The resulted red solution was left to cool to room temperature and poured into deionized water. pH of the solution was adjusted to 2-3 to obtain a precipitate was filtered and dried in air. The recovered solid was further washed with cold-methanol and dried to afford the pure product as a dark-red solid (4.35 g, 79%). ^1H NMR (DMSO-d_6 , 500 MHz): δ_{H} 7.29 (dd, 1H), 7.96 (dd, 1H), 8.21 (dd, 1H), 11.23 (s, 1H). ^{13}C NMR (DMSO-d_6 , 125 MHz): δ_{C} 109.55, 128.71, 130.79, 131.27, 132.65, 136.15, 161.62.

2.3.4.6 Synthesis of 3,6-di(furan-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (6)

A similar synthetic procedure was used as described for 5. The product was isolated as a reddish-brown solid (3.50 g, 73%). ^1H NMR (DMSO-d_6 , 500 MHz): δ_{H} 6.83 (dd, 1H), 7.66 (d, 1H), 8.04 (d, 1H), 11.17 (s, 1H). ^{13}C NMR (DMSO-d_6 , 125 MHz): δ_{C} 107.57, 113.68, 116.76, 131.26, 143.75, 146.87, 161.25.

2.3.4.7 Synthesis of 2,5-di(hex-5-en-1-yl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (7)

3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (1.00 g, 3.32 mmol), anhydrous potassium carbonate (1.01 g, 7.34 mmol), 18-crown-6 (cat. amount) was dissolved in anhydrous dimethylformamide (15 mL) in a 2-neck round-bottom flask (100 mL) under nitrogen conditions and stirred for 40 minutes at 100°C. 6-bromohex-1-ene (1.12 g, 7.34 mmol) was slowly injected into the reaction flask and further stirred at 120°C for 24 hours. After that, the reaction mixture was cooled to room temperature and the solution was concentrated under a vacuum using a rotor-evaporator. The concentrated solution was added into water (100 mL), stirred for 30 minutes, and filtered to afford a brown solid. The solid was further washed with deionized water and air-dried. Resulted solid was further washed with cold hexane to afford reddish-brown solid (1.25 g, 81%). ¹H NMR (CDCl₃, 500 MHz): δ_{H} 1.52 (m, 2H), 1.76 (m, 2H), 2.11 (q, 2H), 4.09 (t, 2H), 4.98 (m, 2H), 5.79 (m, 1H), 7.28 (dd, 1H), 7.64 (dd, 1H), 8.91 (dd, 1H). ¹³C NMR (CDCl₃, 125 MHz); δ_{C} 26.29, 29.61, 33.48, 42.18, 107.87, 115.04, 128.79, 129.87, 130.84, 135.41, 138.43, 140.16, 161.53.

2.3.4.8 Synthesis of 3,6-di(furan-2-yl)-2,5-di(hex-5-en-1-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (8)

A similar synthetic procedure was used as described for 7. The product was isolated as a reddish-brown solid (1.09 g, 76%) ¹H NMR (CDCl₃, 500 MHz): δ_{H} 1.49 (m, 2H), 1.71 (m, 2H), 2.10 (q, 2H), 4.13 (t, 2H), 4.95 (m, 2H), 5.79 (m, 1H), 6.70 (dd, 1H), 7.64 (d, 1H), 8.30 (d, 1H). ¹³C NMR (CDCl₃, 125 MHz); δ_{C} 26.27, 29.83, 33.51, 42.38, 106.58, 113.62, 114.84, 120.32, 133.78, 138.63, 144.78, 145.36, 162.01.

2.3.4.9 Synthesis of 2,5-bis(6-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)hexyl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (9)

2,5-di(hex-5-en-1-yl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (0.400 g, 0.98 mmol) was dissolved in freshly distilled anhydrous toluene (10 mL) under nitrogen conditions in a 2-neck round-bottom flask (50 mL). 1,1,1,3,5,5,5-heptamethyltrisiloxane (0.480 g, 2.15 mmol) was slowly injected into the flask through the septum followed by addition of a drop of Karstedt's catalyst (Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution in xylene, Pt ~3%) at room temperature while stirring. Reaction mixture was further stirred at 70°C for 12 hours. After completion, reaction mixture was cooled to room temperature and solvent was removed under vacuum. Resulted solid was further purified using silica column chromatography (8:2 = dichloromethane: hexane) to afford pure compound as purple crystalline solid (0.450 g, 57%). ¹H NMR (CDCl₃, 500 MHz): δ_{H} -0.02(s, 3H), 0.07 (s, 18H), 0.44 (t, 2H), 1.32-1.41 (m, br, 6H), 1.74 (m, 2H), 4.07 (t, 2H), 7.28 (dd, 1H), 7.63 (d, 1H), 8.93 (d, 1H). ¹³C NMR (CDCl₃, 125 MHz); δ_{C} -0.13, 2.02, 17.71, 23.20, 26.80, 30.11, 32.99, 42.40, 107.86, 128.74, 129.94, 130.77, 135.39, 140.17, 161.52.

2.3.4.10 Synthesis of 3,6-di(furan-2-yl)-2,5-bis(6-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)hexyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (10)

A similar synthetic procedure was used as described for **9**. Purification was performed using silica column chromatography (9:1 = dichloromethane: hexane) to isolate the product as a reddish-purple crystalline solid (0.438 g, 51%). ¹H NMR (CDCl₃, 500 MHz): δ_{H} -0.02(s, 3H), 0.07 (s, 18H), 0.44 (t, 2H), 1.29-1.39 (m, br, 6H), 1.69 (m, 2H), 4.11 (t, 2H), 6.69 (dd, 1H), 7.63 (d, 1H), 8.30 (d,

1H). ¹³C NMR (CDCl₃, 125 MHz); δ_C -0.13, 2.01, 17.74, 23.17, 26.76, 30.36, 33.05, 42.59, 106.61, 113.59, 120.23, 133.80, 144.84, 145.29, 161.02.

2.3.4.11 Synthesis of 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(6-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)hexyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (11)

2,5-bis(6-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)hexyl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (0.150 g, 0.17 mmol) was dissolved in chloroform (20 mL) at 0°C under nitrogen conditions. N-bromosuccinimide (0.064 g, 0.36 mmol) was dissolved in chloroform (5 mL) and slowly injected into the reaction mixture over 10 minutes at 0°C while stirring. The reaction mixture was further stirred for an additional 1 hour at 0°C and completion of the reaction was confirmed by thin-layer chromatography. The reaction mixture was poured on to deionized water, extract with two more chloroform portions (50 mL ×3), washed with deionized water, and dried over anhydrous magnesium sulfate. Then the solvent was removed under vacuum to obtain the crude product. Crude was purified by column chromatography using silica and 75% dichloromethane in hexane as eluent to obtain a dark-purple solid product (0.147 g, 86%). ¹H NMR (CDCl₃, 500 MHz): δ_H -0.01(s, 3H), 0.07 (s, 18H), 0.44 (t, 2H), 1.28-1.44 (m, br, 6H), 1.69-1.72 (m, 2H), 3.98 (t, 2H), 7.24 (d, 1H), 8.67 (d, 1H). ¹³C NMR (CDCl₃, 125 MHz): δ_C -0.11, 2.02, 17.71, 23.17, 26.76, 30.16, 32.95, 42.46, 108.00, 119.28, 131.28, 131.80, 135.48, 139.16, 161.21.

2.3.4.12 Synthesis of 3,6-bis(5-bromofuran-2-yl)-2,5-bis(6-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)hexyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (12)

A similar synthetic procedure was used as described for **11**. Purification was performed using silica column chromatography (8:2 = dichloromethane: hexane) to isolate the product as a dark reddish-

purple solid (0.137 g, 78%). ^1H NMR (CDCl_3 , 500 MHz): δ_{H} -0.02(s, 3H), 0.07 (s, 18H), 0.45 (t, 2H), 1.33-1.44 (m, br, 6H), 1.66-1.70 (m, 2H), 4.05 (t, 2H), 6.63 (d, 1H), 8.25 (d, 1H). ^{13}C NMR (CDCl_3 , 125 MHz); δ_{C} -0.14, 2.02, 17.74, 23.23, 26.76, 30.36, 33.08, 42.67, 106.46, 115.65, 122.24, 126.54, 132.67, 146.34, 160.68.

2.3.4.13 Synthesis of diethyl 2,2'-((2,5-bis(6-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)hexyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)bis(thiophene-5,2-diyl))bis(4-methyl-4H-thieno[3,2-b]pyrrole-5-carboxylate) (DPP-2T-2TP)

Compound **11** (0.140 g, 0.132 mmol), Ethyl 4-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4H-thieno[3,2-b]pyrrole-5-carboxylate (0.108 g, mmol), and $\text{Pd}(\text{PPh}_3)_4$ (0.032 g, 0.026 mmol) added into a pressure flask with a magnetic stir bar under nitrogen environment. THF (5.0 mL) and 2 M Na_2CO_3 solution (0.90 mL) was added to the same flask before tightly seal the system under inert conditions. Then the reaction mixture was heated at 90°C while stirring for 48 hours. After cooling to room temperature, the reaction mixture was added into cold methanol (200 mL) and the resulting precipitate was separated by a Soxhlet-thimble. Solid was washed with additional methanol (100 mL) and hexane (50 mL) to remove the mono-coupled product and further purified by Soxhlet extraction with methanol for 72 hours. The pure product was recovered as a dark-purple solid (0.110 g, 63%). ^1H NMR (CDCl_3 , 500 MHz): δ_{H} -0.01(s, 3H), 0.07 (s, 18H), 0.47 (t, 2H), 1.36-1.46 (m, br, 9H), 1.76 (m, 2H), 4.03 (s, 3H), 4.08 (t, 2H), 4.31 (q, 2H), 7.09 (s, 1H), 7.11 (s, 1H), 7.29 (d, 1H), 8.87 (d, 1H). ^{13}C NMR (CDCl_3 , 125 MHz); δ_{C} -0.11, 2.02, 14.55, 17.80, 23.30, 26.93, 30.25, 33.14, 34.73, 42.47, 60.45, 107.76, 108.49, 109.10, 122.32, 125.00, 127.80, 129.57, 136.41, 138.71, 138.76, 143.75, 145.40, 161.24, 161.43. MALDI mass $m/z = 1324.84 \text{ g mol}^{-1}$; calculated mass = $1324.15 \text{ g mol}^{-1}$

2.3.4.14 Synthesis of diethyl 2,2'-((2,5-bis(6-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)hexyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)bis(furan-5,2-diyl))bis(4-methyl-4H-thieno[3,2-b]pyrrole-5-carboxylate) (DPP-2F-2TP)

Compound **12** (0.120 g, 0.116 mmol), Ethyl 4-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4H-thieno[3,2-b]pyrrole-5-carboxylate (0.97 g, 0.290 mmol), and Pd(PPh₃)₄ (0.028 g, 0.023 mmol) added into a pressure flask with a magnetic stir bar under nitrogen environment. THF (5.0 mL) and 2 M Na₂CO₃ solution (0.80 mL) was added to the same flask before tightly seal the system under inert conditions. Then the reaction mixture was heated at 90°C while stirring for 48 hours. After cooling to room temperature, the reaction mixture was added into cold methanol (150 mL) and the resulted precipitate was separated by a Soxhlet-thimble. Solid was washed with additional hexane (50-100 mL) to remove the mono-coupled product and further purified by Soxhlet extraction with hexane for 2 hours. The remaining solid was extracted into chloroform and solvent was evaporated under vacuum. The pure product was recovered as a purple-blue solid (0.072 g, 48%). ¹H NMR (CDCl₃, 500 MHz): δ_H -0.04(s, 3H), 0.05 (s, 18H), 0.43 (t, 2H), 1.35-1.37 (m, 7H), 1.49 (m, 2H), 1.76 (m, 2H), 4.00 (s, 3H), 4.12 (t, 2H), 4.29 (q, 2H), 6.79 (d, 1H), 7.07 (s, br, 1H), 7.11 (s, 1H), 8.38 (s, br, 1H). ¹³C NMR (CDCl₃, 125 MHz): δ_C -0.18, 1.99, 14.51, 17.79, 23.29, 27.16, 29.85, 33.36, 34.62, 42.91, 60.44, 106.76, 107.29, 109.11, 109.51, 122.53, 122.81, 128.02, 131.64, 134.43, 143.78, 145.32, 152.62, 160.62, 161.33. MALDI mass m/z = 1292.52 g mol⁻¹; calculated mass = 1292.03 g mol⁻¹

2.4 Results and discussion

2.4.1 Optoelectronic properties

Optoelectronic properties were analyzed with UV-Vis spectroscopy and Cyclic voltammetry (CV). UV-vis spectra of DPP-2T-2TP and DPP-2F-2TP were obtained for both solution (chloroform) and thin film forms of the materials (see Figure 2.2A & 2.2B). The typical dual-band nature of the donor-acceptor semiconducting materials was observed for both small molecules. The CV plots obtained are provided in Appendix A (see Figure A.30). All the extracted optoelectronic data from UV-Vis and CV are summarized in Table 2.1.

Table 2.1: Summary of optoelectronic properties of small molecules

Small molecule	^a HOMO (eV)	^b LUMO (eV)	^c E _g ^{ec} (eV)	^d E _g ^{opt} (eV)	λ _{max} ^{sol} (nm)	λ _{max} ^{film} (nm)	λ _{onset} (nm)
DPP-2T-2TP	-4.80	-3.24	1.56	1.53	376, 612, 650	398, 620, 713	809
DPP-2F-2TP	-4.90	-3.16	1.74	1.72	379, 600, 652	400, 575, 612, 682	721

^a Calculated from onset of oxidation peak of CV; ^b Calculated from onset of reduction peak of CV; ^c Calculated with HOMO and LUMO energies; ^d Calculated from onset of lowest energy band

In solution, π - π^* electron transitions occur at high-energy wavelength maxima of 376 nm and 379 nm whereas delocalized HOMO to acceptor-centered LUMO charge transfer band appears at lower energy wavelength maxima of 650 nm and 652 nm, respectively, for DPP-2T-2TP and DPP-2F-2TP. Moreover, a low energy charge transfer band is associated with a 0 $\rightarrow$ 1 vibronic hump at 612 nm and 600 nm, respectively, for DPP-2T-2TP and DPP-2F-2TP small molecules. In

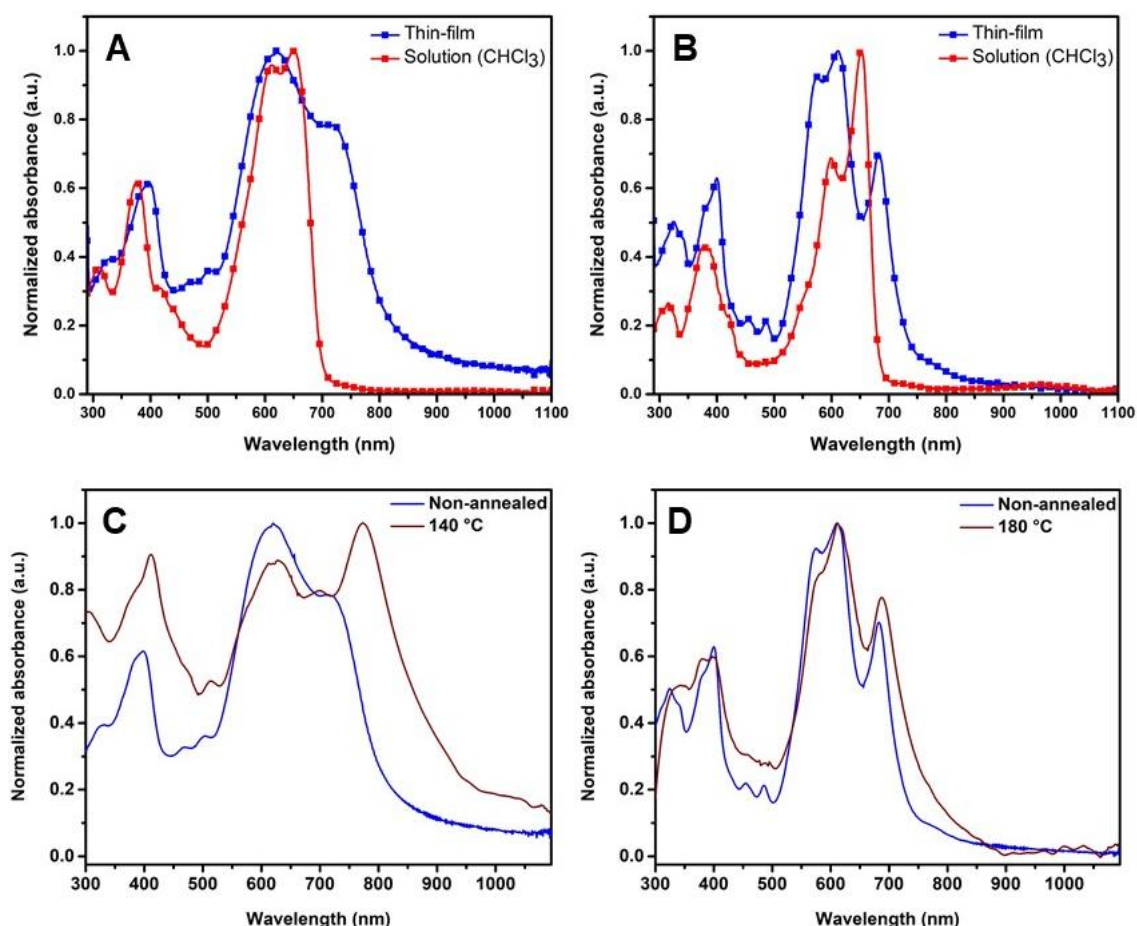


Figure 2.2: UV-Vis spectra of A) DPP-2T-2TP and B) DPP-2F-2TP in solution (CHCl₃) and thin films; alteration in UV-Vis spectra of annealed thin films for C) DPP-2T-2TP (at 140 °C) and D) DPP-2F-2TP (at 180 °C) relative to non-annealed.

the thin film, compared to in solution, DPP-2T-2TP shows a bathochromic shift of 22 nm in the high energy band, appearing at a wavelength maximum of 398 nm. A similar trend was observed for DPP-2F-2TP exhibiting a 21 nm shift to appear at a wavelength maximum of 400 nm. An opposite trend was observed for the low energy charge transfer peaks of both molecules in thin films. Compared to in solution, DPP-2T-TP showed a hypsochromic shift of 32 nm with a peak maximum at 620 nm in thin film. The associated 0→1 vibronic hump of the charge transfer band disappeared when moving from solution to thin film. A similar trend was seen for DPP-2F-2TP with a peak shift of 40 nm and a peak maximum at 612 nm. Associated 0→1 vibronic hump was

also shifted by 25 nm but the vibronic energy splitting gap was reduced compared to the solution. The disappearance of vibronic splitting or the reduced splitting gap of vibronic spectral counterparts is an indication of a restricted vibrational motion of the molecules in solid-state thin films. On the other hand, for both molecules in thin film, a new low energy peak has arisen in each UV-Vis at 713 nm (DPP-2T-2TP) and 682 nm (DPP-2F-2TP). These peaks might have arisen due to strong intermolecular π - π orbital stacking interactions between closely packed small molecular counterparts in thin films. Although there is no significant difference between wavelength maxima of charge transfer bands of both molecules in solution, distinctive red-shifts were observed for both charge transfer peak (8 nm) and π - π stacking peak (31 nm) for DPP-2T-2TP compared with DPP-2F-2TP, in thin films. Calculated optical bandgaps (E_g^{opt}) from the onset of each lowest energy band of DPP-2T-2TP and DPP-2F-2TP in thin films were found to be 1.53 eV and 1.72 eV, respectively. DPP-2T-2TP seems to have a significantly lower E_g^{opt} compared to DPP-2F-2TP which also aligns with the relative red-shift in the corresponding peaks of DPP-2T-2TP in thin film. For both molecules, UV-Vis spectra of thin films at different annealing temperatures are given and overlayed to compare in Appendix A (see Figure A.31). A significant red-shift and intensity enhancement in the lowest energy band was observed for DPP-2T-2TP thin films upon annealing at temperatures over 60 °C, but such a drastic change was not observed for DPP-2T-2TP thin films.

Electrochemical properties were obtained using onset potentials of the oxidation (E_{ox}) and reduction (E_{red}) bands of the cyclic voltammogram. HOMO and LUMO energies (E_{HOMO} and E_{LUMO}) were calculated with E_{ox} and E_{red} potentials using the following equations.

$$E_{\text{HOMO}} = -(E_{\text{ox}} + 4.4) \text{ eV}$$

$$E_{LUMO} = -(E_{red} + 4.4) \text{ eV}$$

Electrochemical bandgap (E_g^{ec}) was calculated with HOMO and LUMO energy values using the following equation.

$$E_g^{ec} = (E_{LUMO} - E_{HOMO}) \text{ eV}$$

For DPP-2T-2TP, HOMO and LUMO were found to be -4.80 and -3.24 eV, respectively. Similarly, HOMO and LUMO energies were obtained for DPP-2F-2TP which were -4.90 and -3.16 eV, respectively. E_g^{ec} for both molecules were calculated to be 1.56 and 1.74 eV, respectively, which are also well aligned with the E_g^{opt} values obtained from UV-Vis (refer to Table 1). A slight discrepancy between E_g^{opt} and E_g^{ec} might be due to exciton binding energy associated with the electrochemical method used for thin films.

2.4.2 Thermal Analysis

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) experiments were performed on both small molecules (Figure 2.3). TGA analysis suggests that both molecules are stable under nitrogen flow up to slightly over 300 °C, where a significant drop in the mass occurs afterward. 5% weight loss can be observed at 357.4 °C and 336.1 °C, respectively, for DPP-2T-2TP and DPP-2F-2TP, indicating significant thermal stability. DSC analysis indicates two melting points corresponding to siloxane side-chains (T_{m1}) and backbone (T_{m2}) regions of small molecules. T_{m1} was recorded to be 75.3 °C for DPP-2T-2TP, indicating an occurrence of strong lamellar interactions among DPP-2F-2TP molecules compared to DPP-2T-2TP. However, surprisingly, there was no clear T_{m1} observed for DPP-2F-2TP even after three cycles of DSC scanning. On the other hand, T_{m2} was recorded as 276.8 °C and 240.4 °C, respectively, for DPP-2T-2TP and DPP-2F-2TP. Both small molecules, DPP-2T-2TP and DPP-

2F-2TP, show sharp crystallization temperatures (T_c) at 262.7 °C and 219.4 °C, respectively, indicating the crystalline nature of both materials.

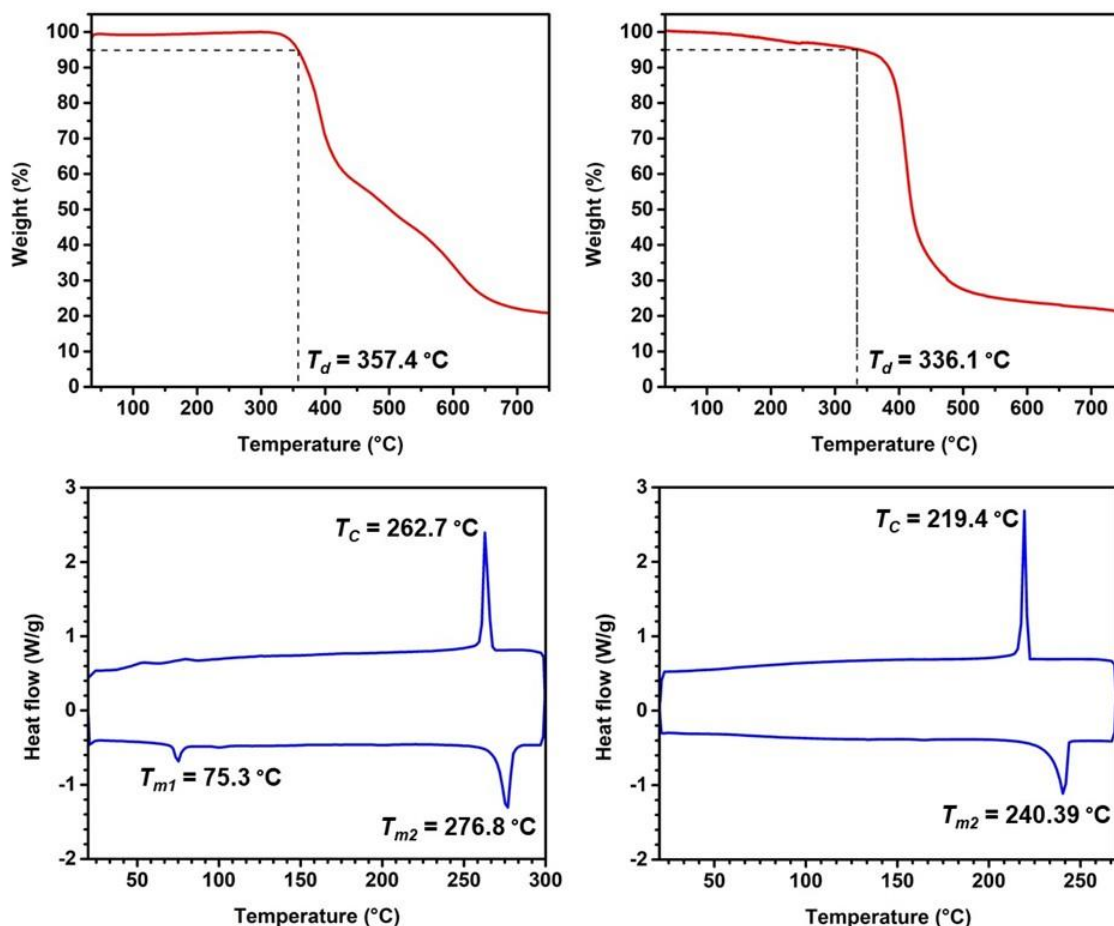


Figure 2.3: Thermal properties of small molecules; TGA (top) and DSC (bottom) thermograms of DPP-2T-2TP (left) and DPP-2F-2TP (right)

2.4.3 OFETs Performance

Bottom-gate/bottom contact (BGBC) device configuration was used to determine the charge transport properties of the small molecules. All the measurements were collected under ambient conditions. A significant difference in hole mobilities between the two materials was found in thin films. A significant increment in hole mobilities was observed for DPP-2T-2TP,

while no improvement in hole mobility was observed for DPP-2F-2TP upon thermal annealing. For DPP-2T-2TP, non-annealed devices showed average hole mobility of $4.67 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with a maximum of $7.39 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. All the transfer and output curves for DPP-2T-2TP are given below (Figure 2.4).

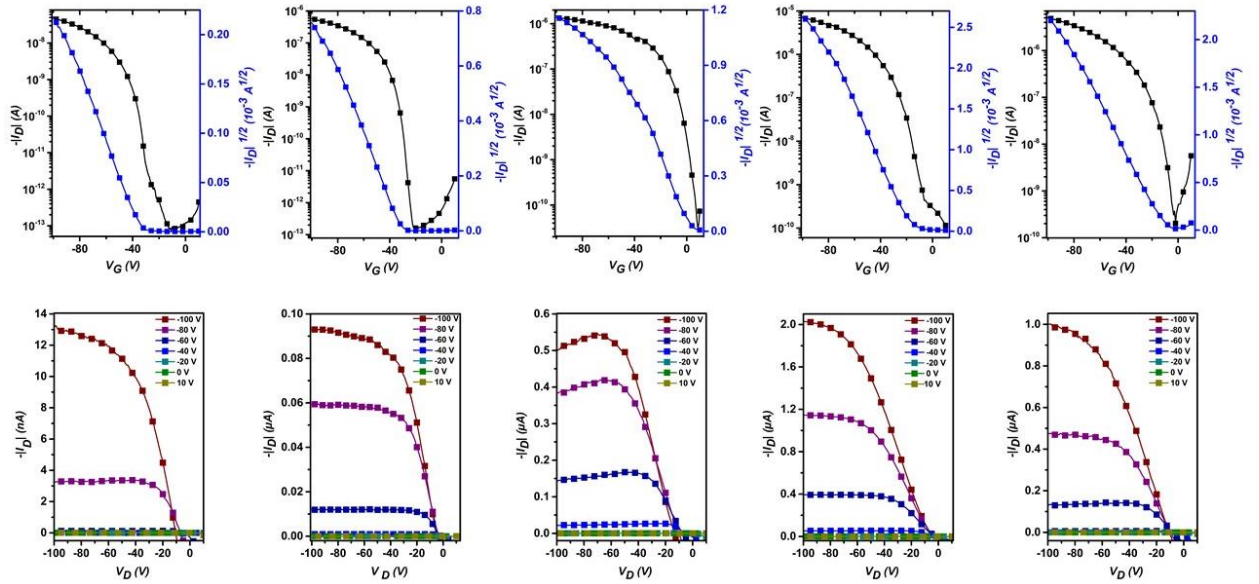


Figure 2.4: Transfer (top) and output (bottom) characteristics of DPP-2T-2TP at different annealing temperatures (left to right – non-annealed, 60 °C, 100 °C, 140 °C, 180 °C)

A gradual increase of hole-mobility was observed up to an annealing temperature of 140 °C but a drop was seen with further annealing to 180 °C. The maximum hole mobility of $4.10 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was observed with average mobility of $1.62 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for devices annealed at 140 °C. A significant on-off current ratio ($I_{\text{on/off}}$) values between 10^4 - 10^5 were obtained at all annealing temperatures for DPP-2T-2TP, but a drop in $I_{\text{on/off}}$ to 10^3 was detected at higher annealing temperatures (140 °C and 180 °C) in some devices. Threshold voltage (V_T) values from -19.6 to -7.4 V were observed at 140 °C. All OFETs parameters obtained for DPP-2T-2TP at different annealing temperatures are summarized in Table 2.2.

Table 2.2: Summary of OFETs parameters at different annealing temperatures for DPP-2T-2TP based devices.

Temperature/ °C	^a Maximum hole mobility /cm ² V ⁻¹ s ⁻¹	^a Average hole mobility /cm ² V ⁻¹ s ⁻¹	Threshold Voltage/ V	On/off ratio
Non-annealed	7.39×10^{-4}	4.67×10^{-4}	-34.9 to 4.7	$10^4 - 10^5$
60	3.80×10^{-3}	1.80×10^{-3}	-31.3 to 2.4	$10^4 - 10^5$
100	8.41×10^{-3}	3.84×10^{-3}	-13.3 to 2.5	$10^4 - 10^5$
140	4.10×10^{-2}	1.62×10^{-2}	-19.6 to -7.4	$10^3 - 10^5$
180	2.21×10^{-2}	7.81×10^{-3}	-12.0 to -5.12	$10^3 - 10^5$

^a Calculated from measurements obtained for 15 devices; Measurements were obtained for BGBC devices with channel width (W) = 457 μm and channel length (L) = 20 μm (applied $V_d = -100$ V). Thin films were deposited under ambient conditions at 300 rpm from 5 mg/mL solutions in chloroform. Thermal annealing was performed under ambient conditions.

DPP-2F-2TP showed its maximum average mobilities for non-annealed devices, exhibiting a gradual decrease in mobilities upon increasing annealing temperature. Maximum hole mobility of $6.33 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was reported for non-annealed devices with an average hole mobility of $3.12 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. In DPP-2F-2TP, annealing at 60 °C did not induce a drastic difference in average hole mobilities compared to non-annealed devices but produces the maximum hole mobility of $6.40 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. However, annealing temperatures over 100 °C cause a reduction in hole mobility in DPP-2F-2TP. $I_{\text{on/off}}$ also exhibited a drop from 10^4 to 10^2 when annealing temperature increased to 180 °C. Upon thermal annealing at 180 °C, V_T values have moved to a narrower range around 1.0 to 1.6 V compared to non-annealed devices, which shows a broader range from -32.1 to 19.5 V. All the OFETs characteristic curves are given in Figure 2.5 and OFETs parameters obtained for DPP-2F-2TP at different annealing temperatures are summarized in Table 2.3.

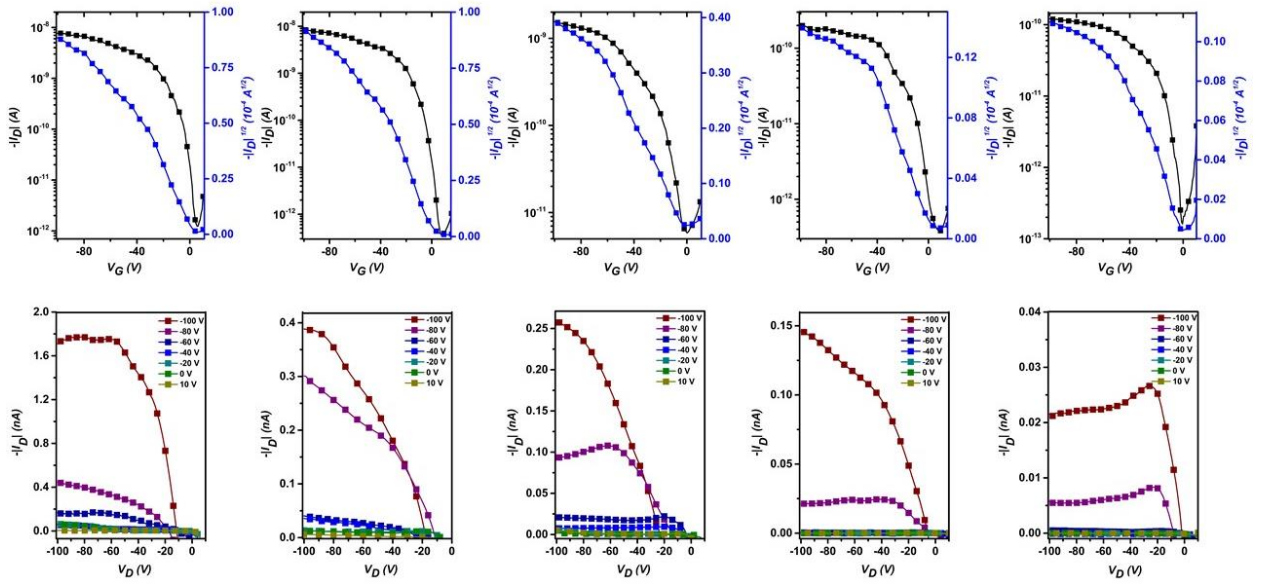


Figure 2.5: Transfer (top) and output (bottom) characteristics of DPP-2F-2TP at different annealing temperatures (left to right – non-annealed, 60 °C, 100 °C, 140 °C, 180 °C)

Table 2.3: Summary of OFETs parameters at different annealing temperatures for DPP-2F-2TP based devices.

Temperature/ °C	^a Maximum hole mobility / cm ² V ⁻¹ s ⁻¹	^a Average hole mobility / cm ² V ⁻¹ s ⁻¹	Threshold Voltage/ V	On/off ratio
Non-annealed	6.33×10^{-5}	3.12×10^{-5}	-32.1 to 19.5	$\sim 10^4$
60	6.40×10^{-5}	2.80×10^{-5}	-14.5 to 1.6	$\sim 10^4$
100	2.29×10^{-6}	1.29×10^{-6}	-30.2 to 1.2	$\sim 10^3$
140	1.65×10^{-6}	4.40×10^{-7}	-1 to 7.62	$\sim 10^3$
180	2.99×10^{-7}	1.08×10^{-7}	-1 to 1.6	$\sim 10^2$

^a Calculated from measurements obtained for 15 devices; Measurements were obtained for BGBC devices with $W = 457 \mu\text{m}$ and $L = 20 \mu\text{m}$ (applied $V_d = -100 \text{ V}$). Thin film were deposited under ambient conditions at 300 rpm from 5 mg/mL solutions in chloroform. Thermal annealing was performed under ambient conditions.

2.4.4 Surface morphology

Thin film morphologies for the highest and the lowest mobility conditions of each material were depicted in Figure 6. Both DPP-2T-2TP and DPP-2F-2TP exhibited crystallinity in non-annealed thin films (See Figure 2.6a & 2.6e), as observed by TMAFM imaging technique.

Compared with non-annealed thin films, a significant change in the surface morphology was observed for DPP-2T-2TP upon annealing to 140 °C (Figure 2.6b) but no significant difference in

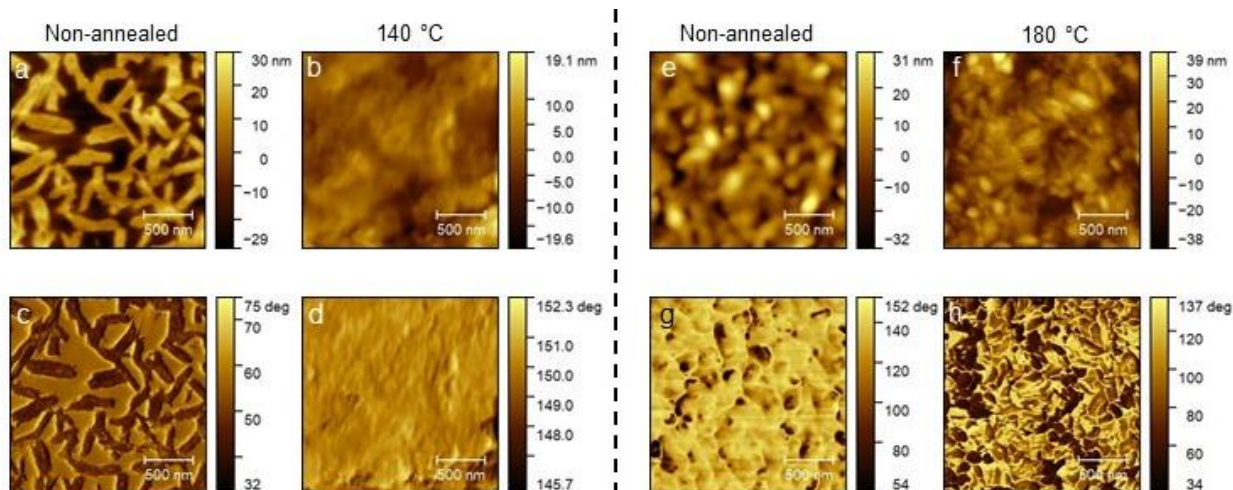


Figure 2.6: Height (top) and phase (bottom) TMAFM images of DPP-2T-2TP (left) and DPP-2F-2TP (right) thin films for non-annealed (a, c, e, & g) and annealed at 140 °C (b & d) and 180 °C (f & h); scanned area in each case is 2 $\mu\text{m} \times 2 \mu\text{m}$

grain size was observed for DPP-2F-2TP annealed at 180 °C (Figure 2.6f). Height images for all the annealing temperatures are provided in Figure A.32 in Appendix A. Upon annealing to 60 °C, for DPP-2T-2TP, a significant change in the film surface morphology was noticed with an increment in root mean square roughness (S_q) from 11.76 to 15.24 nm. This observation is due to the growth of crystalline domains upon annealing (Figure A.32). Thermal annealing to 140 °C causes a gradual decrease in S_q to 4.05 nm but further annealing at 180 °C increases S_q to 8.65 nm. In here, the decrease in the surface roughness was observed upon annealing at 140 °C since domain sizes begin to be comparable in size with the scanned area. Further annealing to a higher temperature might cause formation of thermally induced cracks in domains which could lead to enhanced S_q . In DPP-2F-2TP, non-annealed films show a higher S_q of 10.24 nm, which changes to 6.77 nm upon annealing at 60 °C. Further annealing at 100 °C and 140 °C induced no significant

changes in the surface morphology, but a significant increase of S_q to 10.02 nm was detected at 180 °C. This is an evidence of slight growth in crystalline domains at 60 °C but no significant growth was detected for higher temperatures. Surface roughness data are summarized in Table A.1 (Appendix A).

When further analyzing TMAFM images, for DPP-2T-2TP, non-annealed thin films showed grain domains with significantly sharper and clear grain boundaries. These crystalline domains in non-annealed thin films were observed due to possible random aggregates formed while spin-coating. Upon annealing to 60 °C, domain sizes improved but at annealing temperatures over T_{m1} , side-chain phase started to melt and backbone-interaction-based crystallinity started to improve. At a higher annealing temperature of 180 °C, the abundance of gaps between grain domains might increase, creating more trapping sites for charge carriers. This trend is well-aligned with the mobility trend in OFETs. In order to verify this behavior, we performed additional experiments to measure thin film UV-Vis at different annealing temperatures (Figure A.31 in Appendix A). The behavior of thin film UV-Vis upon annealing also well explained these morphologies and mobility trends in thin films.

In contrast, DPP-2F-2TP show no significant changes in thin film morphology upon thermal annealing over 100 °C, but OFETs mobilities were decreased significantly. This might be due to the formation of more charge trapping sites through increased sharpness of crystalline domain boundaries upon thermal annealing without any significant improvement in domain sizes. Such a decline in charge carrier mobility was reported for a siloxane side chain containing small molecules in literature upon annealing at higher temperatures due to the aforementioned reason.²¹ In another study, copolymers consisting of siloxane side chains substituted DPP and TT, with

thiophene or furan spacers, have demonstrated that thiophene-spacer containing polymer is superior with the growth of thin film crystalline domains compared to its furan containing analogous, upon thermal annealing.²⁴ UV-Vis analysis data for annealed DPP-2F-2TP thin films also follow the same trend and show no significant change, indicating no considerable change in molecular π - π interactions upon annealing (see Figure A.31 in Appendix A). In addition to the above reason, smaller grain formation of thin film on gold contacts, especially in BGBC architecture, could cause significantly greater contact resistance which might lead to “kink” behavior of the OFETs transfer curves and also restricted hole mobility for DPP-2F-2TP.³²

2.4.5 GIXRD analysis

GIXRD experiment was performed for non-annealed and annealed thin films of both molecules to better understand the crystallinity. Thin film annealing conditions for GIXRD, 2 θ angle, and d-spacing values extracted from GIXRD patterns are depicted in Table 4. In GIXRD studies, both molecules showed a significant crystallinity even in non-annealed thin films (see Figure 2.7). Both GIXRD spectra showed apparent enhancement in intensity for (100) plane suggesting an improvement in out-of-plane crystalline grain size upon annealing. According to a previously published work, siloxane side chains containing small molecular thin film has also exhibited a significant crystallinity in non-annealed state which was further developed upon thermal annealing.²¹ In this GIXRD study, DPP-2T-2TP demonstrated a significant ordering of molecules, including an ordered bulk crystallinity, which was indicated by the presence of several orders of out-of-plane GIXRD peaks even for non-annealed thin films. DPP-2F-2TP also indicated an enhancement in crystallinity upon thermal annealing at 180 °C with appearances of diffraction peaks up to 4 order. However, DPP-2T-2TP thin films seemed to have relatively lower lamellar d-

spacings in both non-annealed and annealed conditions, indicating a closely packed out-of-plane molecular arrangement compared to DPP-2F-2TP. Furthermore, annealing showed no change in d-spacing for DPP-2F-2TP while a slight decrease was detected for DPP-2T-2TP (see Table 2.4). These GIXRD data also well-aligned with both UV-Vis and TMAFM experimental results obtained for thermally annealed films.

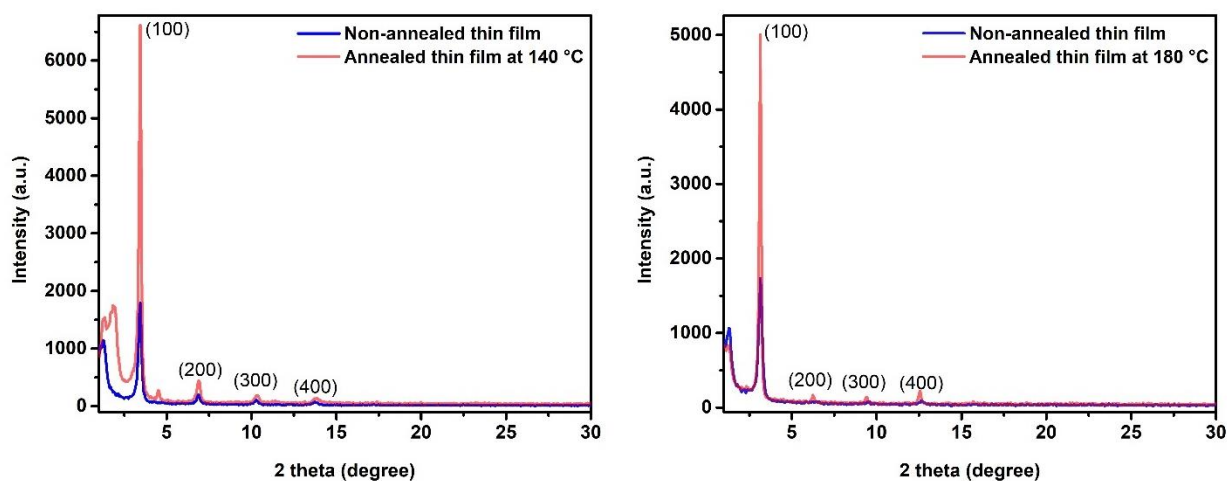


Figure 2.7: GIXRD spectra of DPP-2T-2TP and DPP-2F-2TP

Table 2.4: Summary of out-of-plane GIXRD data extracted for (100) crystalline plane for non-annealed and annealed at 140 °C thin films

Small Molecule	Thermal annealing temperature/ °C	2 θ / degree	d-spacing/ Å
DPP-2T-2TP	Non-annealed	3.43	25.8
	140	3.45	25.6
DPP-2F-2TP	Non-annealed	3.15	28.0
	180	3.15	28.0

2.5 Conclusion

DPP acceptor and TP donor containing two solution-processable novel donor-acceptor-donor type small molecules with thiophene (in DPP-2T-2TP) or furan (in DPP-2F-2TP) spacers were successfully synthesized and characterized by NMR spectroscopy and MALDI-TOF mass

spectroscopy. Optoelectronic properties were characterized by UV-Vis and CV techniques while thermal properties were characterized with TGA and DSC techniques. OFETs parameters were obtained for both small molecules by fabricating organic thin film transistors and annealing at different temperatures to obtain optimum conditions. Thin film morphology and properties were further investigated with TMAFM and GIXRD. Both small molecules show OFET activity and thiophene spacer containing DPP-2T-2TP seems superior to DPP-2F-2TP in OFETs performances. DPP-2T-2TP shows maximum hole mobility of $4.10 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with an average of $1.62 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at annealing temperature 140°C . Upon thermal annealing, DPP-2T-2TP exhibits a gradual increase in reported hole mobility up to 140°C , which decreased with further annealing. DPP-2F-2TP shows its maximum hole mobility of $6.33 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for non-annealed thin films with an average of $3.12 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which gradually decreases by two order of magnitude upon thermal annealing, probably due to creating charge carrier trapping sites by isolated small domain grain boundaries as observed by TMAFM. Furthermore, “kink” behavior in transfer curves was observed for DPP-2F-2TP might be due to high contact resistance of the material at metal-thin film interface. TMAFM and UV-Vis analysis performed for annealed thin films provided evidence for the hole mobility trend in both molecules. Red-shift and peak-intensity enhancement observed for the lowest energy band of DPP-2T-2TP upon annealing indicates improved backbone π - π interaction compared to DPP-2F-2TP which didn’t show such a significant change in UV-Vis spectra. GIXRD data further confirms the presence of much closer out-of-plane lamellar packing in DPP-2T-2TP than DPP-2F-2TP, which may cause more compact and long-range ordered larger grains in thin films. The combined effect of optoelectronic bandgap

difference (~ 0.2 eV) and thin film morphology must have affected the observed drastic difference in OFETs performances of tested small molecules.

Even though sufficient work is done for siloxane side-chain-based donor-acceptor copolymers to investigate the structure-property relationship, inadequate work is done to investigate siloxane side chains containing small molecules which is applied in OFETs, so far. This work will be helpful for those who are interested in designing DPP-siloxane side chain containing small molecules with further structural optimization of side-chain length, spacer, and donor to improve OFETs performances. Siloxane side chain length will be varied to systematically to study the effect side chain length on OFET performance of analogous small molecules in the future.

2.6 Acknowledgment

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CHAPTER 3
1*H*-INDOLE AND PYRROLO[2,3-*B*]PYRIDINE AS PYRROLE-FUSED DONORS IN
DONOR-ACCEPTER SMALL MOLECULES FOR ORGANIC FIELD-EFFECT
TRANSISTORS

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3.1 Abstract

Pyrrole blocks have been used in conductive polymers and semiconducting materials in the history of organic semiconductors. Even though pyrrole-based materials showed promising semiconducting properties, it was challenging to work with pyrrole-based materials due to their lower stability in ambient conditions. Since elevated HOMO levels seemed to be the reason behind this, lately, pyrrole was fused with other stable aromatic rings to build electron-rich but ambient-stable blocks for hole transporting semiconductors. These blocks were capable of being a donor in most donor-acceptor (D-A) type semiconducting materials, providing more electron density to the backbone promoting hole transportation. Thienopyrrole (TP) is among the fused-pyrrole ring systems which has demonstrated promising potential in both D-A type polymers and small molecules. In this study, 1*H*-indole (IN) and pyrrolo[2,3-*b*]pyridine (PP), analogous to TP, were examined for their capability to work as an effective donor block in organic semiconducting materials, considering their comparable HOMO and LUMO to TP. Bezoethadiazole acceptor-based two D-A small molecules, IN-BT2T-IN and PP-BT2T-PP, were synthesized using each donor block and tested for hole-transporting properties by fabricating organic field-effect transistors (OFETs). Both molecules exhibit moderate hole-transporting properties with maximum hole mobilities of 4.83×10^{-3} and $3.81 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively, for IN-BT2T-IN and PP-BT2T-PP. Thermally-induced crystallinity of thin films has enhanced hole mobilities of both small molecules in OFETs as determined by AFM and XRD methods.

3.2 Introduction

Solution processable organic semiconducting materials have become popular due to their several positive potentials such as low-cost processing, large area applicability, mechanical flexibility, and reasonably high charge carrier mobilities ($> 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).^{1,2} Among them, organic semiconducting small molecules have gained attention in solution-processable organic electronics due to various reasons such as their high purities, well-defined structures, precise molecular weights, and a high degree of order.³⁻⁶ On the other hand, relatively more promising organic polymers with higher conjugation lengths and good film-forming ability which are desirable with large area applications⁷⁻⁹ exhibit molecular weight dependency in charge carrier mobilities¹⁰⁻¹⁴ due to irreproducible molecular weights and broad molecular weight distribution leading to display batch-to-batch variations in organic field-effect transistors (OFETs). The potential of producing more reproducible results with small molecules has paved a path to further explore for improving OFETs properties such as charge-carrier mobility to make them competitive with polymers. So far, solvent processable organic polymers have reached hole mobilities exceeding amorphous silicon ($0.1\text{-}1.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)¹⁵⁻¹⁷ and approaching polycrystalline silicon ($> 10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)¹⁸⁻²⁰ in OFETs. High-performing organic small molecules often involve vacuum deposition techniques that require ultra-high vacuum conditions,²¹⁻²³ leading to practical difficulties and less cost-effectiveness, making the real-world applications more challenging. These molecules require vacuum deposition due to the absence of any solubilizing alkyl chains that are insulating by its nature. Therefore, designing solution-processable small molecules without compromising charge carrier mobility is highly challenging. However, solvent processable small molecules have recently started to surpass hole mobilities of amorphous silicon approaching hole mobility $3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.²⁴

Thus, there is still plenty of space to explore for new small molecular designs and blocks to understand the structure-property relationship and improve OFETs properties.

High-performing solution-processable small molecules, in most cases, comprise donor-acceptor architecture involving acenes or fused ring systems.^{23,25–28} Fused ring systems are comparatively more stable than individual aromatic rings due to their low-lying HOMO energy levels owing to resonance stabilization and provide larger π – π overlapping areas that assisting charge transportation through the hopping mechanism.^{7,17,29} Among fused ring systems, thieno[3,2-*b*]thiophene (TT),^{7,8,17} dithieno[3,2-*b*:2',3'-*d*]pyrrole (DTP),^{30,31} thieno[3,2-*b*]pyrrole (TP)^{32–35}, dithienosilole,^{6,36} and cyclopentadithiophene^{37,38} blocks are commonly used in organic electronics. Pyrroles are expected to possess more electron density than their isoelectronic five-membered aromatic rings, such as thiophene and furan, thus exhibiting better donor properties. Even though pyrrole systems possess rich donor properties, they are comparatively understudied because of challenges in synthesis owing to high electron density.^{39–41} Designing pyrrole ring systems fused with other stable aromatic rings produces relatively air-stable donors. DTP is such a fused pyrrole system that has been studied relative to TP. However, there is inadequate attention paid to other various pyrrole fused-ring systems as potential candidates in OFETs materials.

Recently, our group has published a few donor-acceptor-donor (DAD) type small molecules which include relatively understudied TP donors and benzo[*c*][1,2,5]thiadiazole (BT) acceptor units combined through various spacers such as thiophene, furan,³² bithiophene, and TT.⁴² Some of these molecules showed hole mobilities between 10^{-1} – 10^{-2} cm² V⁻¹ s⁻¹ magnitude range. Following the same strategy, our focus was to investigate more versatile nonconventional pyrrole fused ring systems comparable with TP to further understand the structure-property relationships

of fused-pyrroles in OFETs. 1*H*-indole (IN) and pyrrolo[2,3-*b*]pyridine (PP) are also pyrrole-based fused ring systems that are not often involved in OFETs materials. IN units have been reported seldomly in a few squaric-acid-pyrroles-based conjugated polymers which were applied in organic photovoltaics (OPV).⁴³ On the other hand, to the best of our knowledge, PP is not yet reported in organic electronics-related applications. Thus, in this study, 1*H*-indole and pyrrolo[2,3-*b*]pyridine donor systems will be combined with BT acceptor via thiophene spacer since thiophene was the best performing spacer as observed by the previous studies.³² To study the donor potential of the candidates mentioned above, their HOMO/LUMO levels were compared with TP using DFT with the basis set B3LYP/6-31G* (see Figure 3.1). With the comparable results found, we synthesized and reported two BT-based small molecules containing ester-mono-capped 1*H*-indole (IN) and pyrrolo[2,3-*b*]pyridine (PP) donors. With this study, we attempted to understand the structure-property relationship of the suggested fused-pyrrole donor-blocks in BT-acceptor-based donor-acceptor semiconducting small molecules and compare their potentials with the existing analogous TP-based small molecule in literature.

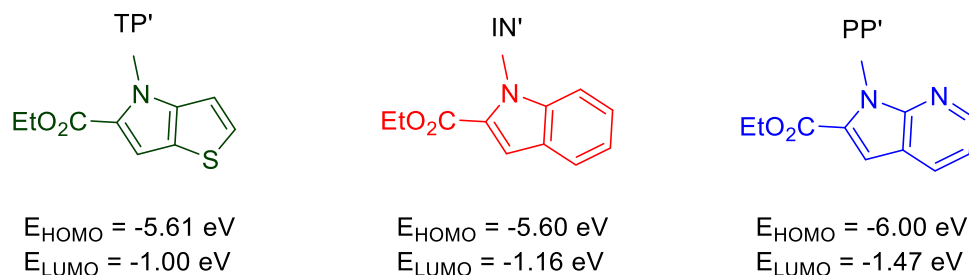


Figure 3.1: DFT calculated HOMO-LUMO energies of pyrrole-based donor blocks; calculated under basis set B3LYP/6-31G* using Spartan'16 software (used methyl as N-alkylated substituent for the simplification of DFT calculations and denoted with prime symbol)

3.3 Materials and methods

3.3.1 Materials

All the chemicals were obtained from Sigma-Aldrich or Fisher-Scientific and used in reactions without additional purifications unless stated otherwise. 4,7-dibromobenzo[c][1,2,5]thiadiazole, trimethyl(thiophen-2-yl)stannane, 4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole, and 4,7-bis(5-(trimethylstannyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole were synthesized according to procedures in literature.³² All the reactions were performed under a nitrogen atmosphere in oven-dried glassware. Toluene and tetrahydrofuran (THF) were distilled over sodium-benzophenone ketyl under a nitrogen atmosphere immediately before use. *N,N*-dimethylformamide (DMF) was distilled over calcium hydride prior to use in reactions.

3.3.2 General Methods

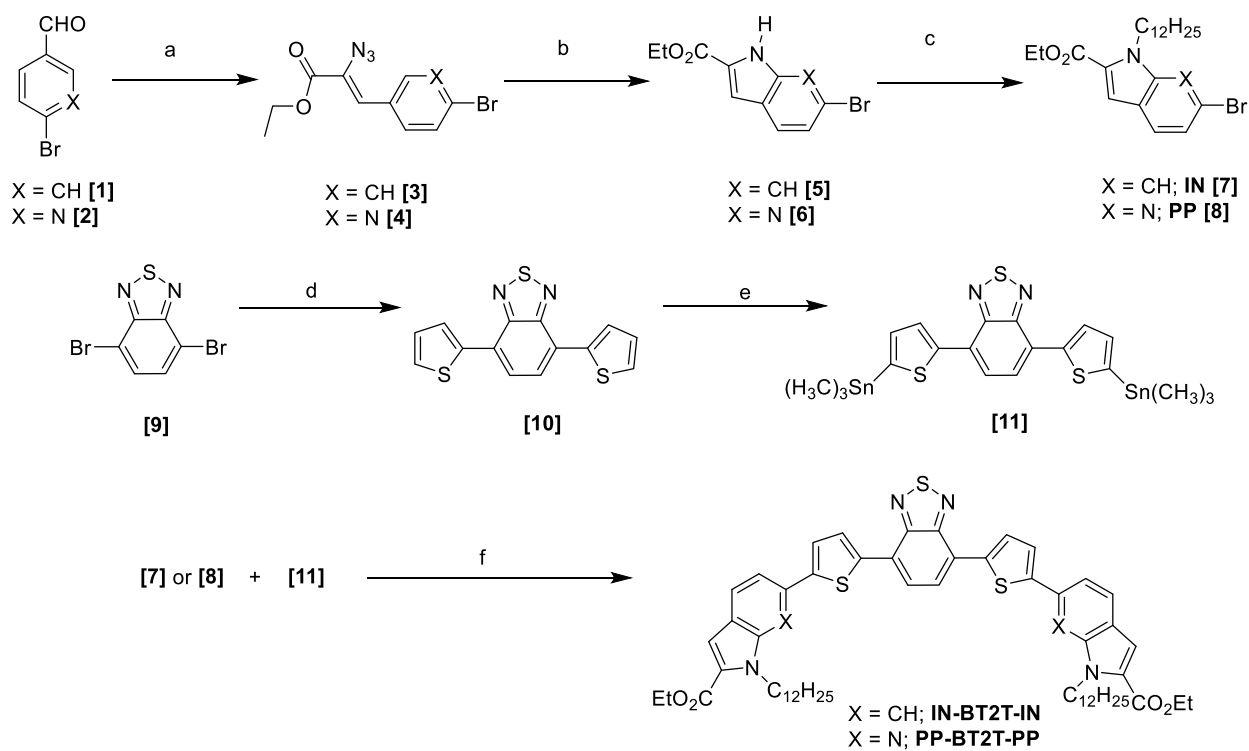
Structure characterization of the materials was done with ¹H and ¹³C NMRs using 500 MHz Bruker AVANCE III spectrometer. Shimadzu Biotech Axima Confidence in reflectron HiRes mode was used to obtain matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) spectra using dithranol as the matrix. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed using Mettler Toledo TGA/DSC-1 system with heating/cooling rates of 10/-10 °C min⁻¹ respectively under a nitrogen flow (40 mL min⁻¹). UV-vis optical analysis was performed both in solution (chloroform) and thin film (drop-casted on a cleaned glass-slide) with Agilent 8453 UV-vis spectrometer. Electrochemical analysis with cyclic voltammetry (CV) was done using a BAS CV-50W voltammetry analyzer by engaging a 0.1 M

tetrabutylammonium hexafluorophosphate electrolyte in acetonitrile and three-electrode system (Ag/Ag⁺ reference electrode, Pt inert working electrode, and Pt wire auxiliary electrode).

3.3.3 OFET device fabrication and characterization

A highly doped n⁺⁺ Si wafer consisting of a thermally grown 200 nm SiO₂ dielectric layer was employed as the substrate for bottom-gate/bottom-contact (BGBC) device configuration to test the OFETs for small molecules. SiO₂ layer was masked with 5 nm Cr layer and 100 nm Au layers, respectively, using Temescal e-beam evaporator prior to pattern source-drain electrodes (Cr/Au) with different channel lengths on the substrate by standard photolithographic procedures in a cleanroom. Fabricated contacts were covered with a photoresist before the opposite side of the substrate was etched with 7:1 BOE solution and deposit a gold layer (100 nm) was thermally deposited on the etched surface as contacts for the silicon gate electrode. Subsequently, acetone, toluene, and 2-propanol were used to rinse the OFETs substrate. Electrode deposited Si/SiO₂ substrate was further cleaned by piranha solution (3:7 = 30% H₂O₂: conc. H₂SO₄) for 10 minutes followed by thorough rinsing with a plentiful amount of deionized (DI) water and dried with a pressured N₂ flow. UV-ozone treatment was later carried out for 10 minutes, followed by rinsing with DI water and acetone, respectively, and dried with an N₂ flow. Octadecyltrimethoxysilane (OTMS) treatment was performed to form a self-assembled monolayer of octadecylsilane (OTS) on the Si/SiO₂ substrate by base vapor-catalyzed hydrolysis of OTMS according to a reported procedure in literature.⁴⁴ Thin films were deposited using a spin-coating method at 300 rpm from 5 mg/mL solutions in chloroform. Annealing of thin films was performed in a nitrogen environment for 5 minutes. Keithley 4200-SCS parameter analyzer was used for OFETs electrical characterization. All of the OFETs electrical parameters were measured in air at room temperature.

3.3.4 Synthesis methods



Scheme 3.1: General synthesis route for IN-BT2T-IN and PP-BT2T-PP; Reaction conditions: (a) ethyl azidoacetate (2 equiv.), ethyl trifluoroacetate (2 equiv.), metal-sodium (2 equiv.), ethanol, 0 °C, 6 h; (b) toluene, reflux, 24 h; (c) anhydrous K_2CO_3 (2.1 equiv.), 18-crown-6 (cat.), 1-bromododecane (2 equiv.), DMF, 120 °C, 24 h, N_2 ; (d) trimethyl(thiophen-2-yl)stannane (2.2 equiv.), $\text{Pd}_2(\text{dba})_3$ (3 mlo%), $\text{P}(p\text{-tol})_3$ (12 mol%), toluene, reflux, 12 h; (e) (i) $n\text{-BuLi}$ (> 2 equiv.), THF, -78 °C, 1 h; (ii) trimethylstannylchloride (> 2 equiv.), THF, -78 °C, 3 h, RT; (f) **[11]** (1 equiv.), **[7]** or **[8]** (>2 equiv.), $\text{Pd}_2(\text{dba})_3$ (10 mlo%), $\text{P}(p\text{-tol})_3$ (40 mol%), toluene, reflux, 24 h

The synthesis of **IN-BT2T-IN** and **PP-BT2T-PP** is shown in Scheme 3.1. Briefly, commercially purchased 4-bromo benzaldehyde **[1]** and 6-bromonicotinaldehyde **[2]** were subjected to Knoevenagel condensation with ethyl azidoacetate, consuming ethyl trifluoroacetate as the “sacrificial electrophile”, using sodium ethanolate base to synthesize their corresponding acrylates **[3]** and **[4]**, respectively. Resulted acrylates were then converted into ethyl 6-bromo-1*H*-indole-2-carboxylate **[5]** and ethyl 6-bromo-1*H*-pyrrolo[2,3-*b*]pyridine-2-carboxylate **[6]**, respectively by employing Hemetsberger cyclization in toluene. Cyclized products **[5]** and **[6]**

were undergone through *N*-alkylation steps in which deprotonation of pyrrolic hydrogens with K_2CO_3 followed by addition of 1-bromododecane to yield pyrrolic monomers, ethyl 6-bromo-1-dodecyl-1*H*-indole-2-carboxylate [7] and ethyl 6-bromo-1-dodecyl-1*H*-pyrrolo[2,3-*b*]pyridine-2-carboxylate [8]. BT2T [10] was synthesized by Stille coupling reaction between 4,7-dibromobenzo[*c*][1,2,5]thiadiazole [9] and trimethyl(thiophen-2-yl)stannane. BT2T [10] was, later, employed in stannylation step by addition of *n*-BuLi at -78 °C followed by trimethylstannyl chloride solution to produce acceptor monomer, 4,7-bis(5-(trimethylstannyl)thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole [11], for small molecules. **IN-BT2T-IN** and **PP-BT2T-PP** were then synthesized by Stille coupling reaction between [11] and [7] or [8] respectively in the presence of tris(dibenzylideneacetone)dipalladium(0) catalyst and tri(*o*-tolyl)phosphine ligand. Detailed experimental procedures are provided below.

3.3.4.1 Synthesis of ethyl (*Z*)-2-azido-3-(4-bromophenyl)acrylate [3]

Sodium (1.20 g, 52.34 mmol) was slowly added to 200 proof ethanol (50 mL) in a 250 mL round bottom flask equipped with a gas bubbler while stirring at room temperature. Once the sodium disappeared, the solution was cooled to 0°C under nitrogen conditions. Ethyl azidoacetate (6.75 g, 52.34 mmol), ethyl trifluoroacetate (7.38 g, 52.34 mmol), and 4-bromo benzaldehyde (4.84 g, 26.17 mmol) were dissolved in ethanol (10 mL) in a separate vial and slowly injected into the above mixture under nitrogen at 0 °C. Then the reaction mixture was further stirred for over 6 hours while leaving the temperature to elevate to room temperature slowly. After that, the reaction mixture was transferred into a saturated ammonium chloride solution and stirred for 5 minutes. It was extracted three times with ethyl ether (50 mL) and collected ether layers were washed with brine (50 mL × 2), dried with anhydrous magnesium sulfate. The solvent was removed under a

vacuum to recover the crude product. Then the pure product was recovered by column chromatography (Silica and 2:8 = ethyl acetate: hexane) as a pale-yellow oil (3.53 g, 46%). ^1H NMR (CDCl_3 , 500 MHz): δ_{H} – 1.40 (t, 3H), 4.37 (q, 2H), 6.82 (s, 1H), 7.50 (d, 2H), 7.69 (d, 2H). ^{13}C NMR (CDCl_3 , 125 MHz); δ_{C} – 14.22, 62.43, 123.50, 123.72, 126.25, 131.69, 131.96, 132.13, 163.33.

3.3.4.2 Synthesis of ethyl (Z)-2-azido-3-(6-bromopyridin-3-yl)acrylate [4]

A similar procedure to [3] was followed except for different amounts of materials used. Sodium (0.68 g, 29.57) was dissolved in ethanol (40 mL). Ethyl azidoacetate (3.47 g, 26.88 mmol), ethyl trifluoroacetate (3.82 g, 26.88 mmol), and 6-bromonicotinaldehyde (2.50 g, 13.44 mmol) were dissolved in ethanol (5 mL) before injecting into the reaction flask. After running the reaction for 3 hours, the reaction mixture was quenched into saturated ammonium chloride solution to yield a yellow precipitate which was later filtered and washed with plenty of water under suction to recover the pure compound as a yellow solid (2.58 g, 65%). ^1H NMR (CDCl_3 , 500 MHz): δ_{H} – 1.41 (t, 3H), 4.39 (q, 2H), 6.77 (s, 1H), 7.49 (d, 1H), 8.20 (dd, 1H), 8.56 (d, 1H). ^{13}C NMR (CDCl_3 , 125 MHz); δ_{C} – 14.32, 62.87, 119.46, 128.03, 128.70, 128.80, 138.92, 142.24, 151.89, 162.88.

3.3.4.3 Synthesis of ethyl 6-bromo-1H-indole-2-carboxylate [5]

Ethyl (Z)-2-azido-3-(4-bromophenyl)acrylate (2.50 g, 8.44 mmol) was dissolved in toluene (15 mL) in a round bottom flask equipped with a condenser. Then the reaction mixture was rapidly refluxed with an air bubbler connected to the top of the condenser to release evolving nitrogen. After 24 h, the reaction mixture was allowed to cool and the solvent was removed under vacuum to recover yellow solid crude. Crude was later washed with hexane a few times to obtain the pure

solid as a crystalline yellow solid (1.76 g, 78%). ^1H NMR (CDCl_3 , 500 MHz): δ_{H} – 1.42 (t, 3H), 4.41 (q, 2H), 7.19 (d, 1H), 7.25 (d), 7.55 (d, 1H), 7.59 (s, 1H), 8.87 (s, br, 1H). ^{13}C NMR (CDCl_3 , 125 MHz); δ_{C} – 14.52, 61.37, 108.76, 114.87, 119.25, 123.96, 124.57, 126.48, 137.48, 161.78.

3.3.4.4 Synthesis of ethyl 6-bromo-1*H*-pyrrolo[2,3-*b*]pyridine-2-carboxylate [6]

A similar procedure to [5] was used. Briefly, ethyl (Z)-2-azido-3-(6-bromopyridin-3-yl)acrylate (0.80 g, 2.69 mmol) was refluxed in toluene (15 mL) for 3 hours. The solvent was concentrated to a minimum volume under vacuum and quenched into hexane (200 mL). Then the deposited solid precipitate was separated and hexane-filtrate was concentrated under vacuum to recover a yellow solid (0.41 g, 56%). The recovered solid was used in the next step without any further purifications. ^1H NMR (CDCl_3 , 500 MHz): δ_{H} – 1.40 (t, 3H), 4.42 (q, 2H), 7.15 (d, 1H), 7.28 (d, 1H), 7.85 (d, 1H), 9.46 (s, br, 1H). ^{13}C NMR (CDCl_3 , 125 MHz); δ_{C} – 14.46, 61.69, 107.23, 118.69, 121.46, 128.03, 133.15, 139.09, 147.55, 161.16.

3.3.4.5 Synthesis of ethyl 6-bromo-1-dodecyl-1*H*-indole-2-carboxylate [7]

Ethyl 6-bromo-1*H*-indole-2-carboxylate (1.00 g, 3.73 mmol), anhydrous potassium carbonate (1.08 g, 7.83 mmol), and 18-crown-6 (cat.) were dissolved in *N,N*-dimethyl formamide (DMF, 10 mL) in a 50 mL round bottom flask and stirred under nitrogen at 100°C for 1 h. Then 1-bromododecane (1.86 g, 7.46 mmol) was added to the reaction vessel and continued stirring at 120 °C for 24 h. After that, the reaction was quenched into deionized water and extracted with dichloromethane (100 mL $\times$ 3). The organic layer was thoroughly washed with deionized water (100 mL $\times$ 3) to remove DMF. Then the solvent was removed under vacuum to obtain crude as a pale-yellow oil. Crude was further purified with a silica column using hexane followed by 1%

ethyl acetate (in hexane) eluents to obtain pure product as a yellow oil (1.57 g, 96%). ^1H NMR (CDCl_3 , 500 MHz): δ_{H} – 0.88 (t, 3H), 1.25 (m, 18H), 1.41 (t, 3H), 1.77 (m, 2H), 4.37 (q, 2H), 4.49 (t, 2H), 7.22 (m, 2H), 7.53 (m, 2H). ^{13}C NMR (CDCl_3 , 125 MHz); δ_{C} – 14.32, 62.87, 119.46, 128.03, 128.70, 128.80, 138.92, 142.24, 151.89, 162.82

3.3.4.6 Synthesis of ethyl 6-bromo-1-dodecyl-1H-pyrrolo[2,3-b]pyridine-2-carboxylate [8]

A similar procedure to [7] was used. Ethyl 6-bromo-1H-pyrrolo[2,3-b]pyridine-2-carboxylate (0.61 g, 2.26 mmol), anhydrous potassium carbonate (0.47 g, 3.39 mmol), and 18-crown-6 (cat.) were dissolved in DMF (8 mL). 1-bromododecane (0.68 g, 2.71 mmol) was added to the reaction vessel and continued stirring at room temperature under nitrogen conditions for 17 hours. The reaction mixture was quenched into ammonium chloride solution (100 mL), extracted with diethyl ether (30 mL $\times$ 4), washed with deionized water, dried over MgSO_4 , and solution removed under vacuum to get the crude. The crude was purified using silica column chromatography (1:9 = Ethyl acetate: hexane) to recover pure product as yellow oil (0.612 g, 62%). ^1H NMR (CDCl_3 , 500 MHz): δ_{H} – 0.88 (t, 3H), 1.24 (m, 18H), 1.41 (t, 3H), 1.76 (m, 2H), 4.39 (q, 2H), 4.67 (t, 2H), 7.22 (s, 1H), 7.24 (d, 1H), 7.80 (d, 1H). ^{13}C NMR (CDCl_3 , 125 MHz); δ_{C} – 14.26, 14.46, 22.84, 26.87, 29.43, 29.49, 29.72, 29.74, 29.77, 29.80, 30.85, 32.07, 43.72, 61.08, 108.52, 117.16, 121.03, 128.28, 132.70, 138.60, 148.69, 161.47.

3.3.4.7 Synthesis of 4,7-dibromobenzo[c][1,2,5]thiadiazole [9]

Synthesis of [9] was performed according to a previously reported procedure.⁴⁵ The product was obtained as off-white solid (1.93 g, 90%). (^1H NMR (CDCl_3 , 500 MHz) δ_{H} 7.73 (s, 1H). ^{13}C NMR (CDCl_3 , 125 MHz); δ_{C} 114.07, 132.50, 153.14)

3.3.4.8 Synthesis of 4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole [10]

4,7-dibromobenzo[c][1,2,5]thiadiazole (0.750 g, 2.55 mmol), tris(dibenzylideneacetone)dipalladium(0) (0.072 g, 3 mol%), and Tri(*o*-tolyl)phosphine (0.093 g, 12 mol%) were placed in a round bottom flask (50 mL) and dissolved in toluene (10 mL) under nitrogen conditions. Later, tributyl(thiophen-2-yl)stannane (2.095 g, 5.61 mmol) was injected into the reaction mixture and reaction mixture was refluxed while stirring for 12 hours. After the completion of the reaction, the solvent was removed under vacuum to recover a reddish solid and the solid was further purified using silica column chromatography (6:4 = Hexane: DCM) to recover the pure product as a reddish crystalline solid (0.656 g, 86%). (^1H NMR (CDCl_3 , 500 MHz): δ_{H} 7.21 (dd, 1H), 7.46 (d, 1H), 7.87 (s, 1H), 8.12 (d, 1H). ^{13}C NMR (CDCl_3 , 125 MHz): δ_{C} 125.91, 126.15, 126.92, 127.64, 128.13, 139.49, 152.78)

3.3.4.9 Synthesis of 4,7-bis(5-(trimethylstannyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole [11]

4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (0.200 g, 0.66 mmol) was dissolved in freshly distilled THF (20 mL) under nitrogen conditions. Temperature was adjusted to $-78\text{ }^\circ\text{C}$ and *n*-butyl lithium (2.5 M, 1.3 mL) was added drop-wise while stirring at $-78\text{ }^\circ\text{C}$. Reaction mixture was stirred for 1 hour while allowing temperature to rise slowly. After 1 hour, reaction mixture was cooled to $-78\text{ }^\circ\text{C}$ again and trimethylstannylchloride (1 M, 3.6 mL) was injected. Later reaction mixture was further stirred for 3 hours while temperature was allowed to rise over the time. The reaction mixture was quenched into deionized water (100 mL) and extracted with diethyl ether (100 mL $\times$ 3). Combined organic fractions were washed with deionized water (50 mL $\times$ 3) and dried over anhydrous magnesium sulfate. Solvent was removed under vacuum to recover the product as a reddish solid (0.352 g, 84%). This solid was used for the next reaction without any further

purification. (^1H NMR (CDCl_3 , 500 MHz): δ_{H} 0.43 (s, 9H), 7.29 (d, 1H), 7.87 (s, 1H), 8.18 (d, 1H); ^{13}C NMR (CDCl_3 , 125 MHz); δ_{C} -8.03, 125.96, 125.99, 128.54, 136.23, 140.39, 145.19, 152.82)

3.3.4.10 Synthesis of diethyl 6,6'-(benzo[c][1,2,5]thiadiazole-4,7-diylbis(thiophene-5,2-diyl))bis(1-dodecyl-1H-indole-2-carboxylate) [IN-BT2T-IN]

Ethyl 6-bromo-1-dodecyl-1H-indole-2-carboxylate (0.340 g, 0.78 mmol), 4,7-bis(5-(trimethylstannyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (0.175 g, 0.28 mmol), tris(dibenzylideneacetone)dipalladium(0) (0.026 g, 10 mol%), and tri(*o*-tolyl)phosphine (0.034 g, 40 mol%) were dissolved in toluene (10 mL) under nitrogen in a 50 mL round bottom flask and refluxed for 24 h. Upon completion, the reaction mixture was quenched into methanol (250 mL) and the resulting red solid was separated under gravity filtration. Solid was collected and purified with column chromatography (silica and Hexane: Dichloromethane (DCM) = 1:1) to obtain a dark-purple amorphous solid (0.158 g, 56%). ^1H NMR (CDCl_3 , 500 MHz): δ_{H} - 0.85 (t, 3H), 1.23 (m, 18H), 1.43 (t, 3H), 1.85 (m, 2H), 4.39 (q, 2H), 4.62 (t, 2H), 7.31 (s, 1H), 7.49 (d, 1H), 7.54 (d, 1H), 7.69 (m, 2H), 7.93 (s, 1H), 8.17 (d, 1H). ^{13}C NMR (CDCl_3 , 125 MHz); δ_{C} - 14.26, 14.54, 22.83, 27.12, 29.50, 29.56, 29.76, 29.79, 29.83, 30.85, 32.07, 44.98, 60.73, 107.58, 110.68, 119.61, 123.22, 124.33, 125.47, 125.96, 126.02, 128.66, 128.92, 131.83, 138.63, 139.54, 146.88, 152.82, 161.96. MALDI-TOF m/z = 1012.12; calculated M.W. = 1011.46 g/ mol $^{-1}$

3.3.4.11 Synthesis of diethyl 6,6'-(benzo[c][1,2,5]thiadiazole-4,7-diylbis(thiophene-5,2-diyl))bis(1-dodecyl-1H-pyrrolo[2,3-b]pyridine-2-carboxylate) [PP-BT2T-PP]

Ethyl 6-bromo-1-dodecyl-1H-pyrrolo[2,3-b]pyridine-2-carboxylate (0.341 g, 0.78 mmol), 4,7-bis(5-(trimethylstannyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (0.175 g, 0.28 mmol),

tris(dibenzylideneacetone)dipalladium(0) (0.026 g, 10 mol%), and tri(*o*-tolyl)phosphine (0.034 g, 40 mol%) were dissolved in toluene (10 mL) under nitrogen in a 50 mL round bottom flask and refluxed for 24 h. Upon completion, the reaction mixture was quenched into methanol (250 mL) and the resulting red solid was separated under gravity filtration. Solid was collected and purified with column chromatography (silica and Hexane:DCM = 4:6) to obtain a crystalline shiny dark-purple solid (0.128 g, 45%). (^1H NMR (CDCl_3 , 500 MHz): δ_{H} – 0.82 (t, 3H), 1.27-1.40 (m, 16H), 1.43 (m, 5H), 1.88 (m, 2H), 4.41 (q, 2H), 4.81 (t, 2H), 7.23 (s, 1H), 7.58 (d, 1H), 7.74 (d, 1H), 7.97 (m, 2H), 8.32 (d, 1H). ^{13}C NMR (CDCl_3 , 125 MHz): δ_{C} –14.24, 14.52, 22.82, 27.00, 29.46, 29.61, 29.83, 29.86, 29.89, 30.86, 32.06, 43.41, 60.88, 108.66, 113.37, 117.54, 125.90, 126.31, 128.39, 129.17, 131.05, 141.22, 147.06, 149.17, 149.20, 152.87, 161.74. MALDI-TOF m/z = 1014.88; calculated M.W. = 1013.43 g/ mol $^{-1}$)

3.4 Results and discussion

3.3.1 Density functional theoretical (DFT) calculations

Theoretical conformational calculations were performed for both **IN-BT2T-IN** and **PP-BT2T-PP** backbones at the B3LYP/6-31G* level of theory and basis set using Spartan'16 software to predict HOMO/LUMO energy levels and optimized conformations. Dodecyl- and ethyl-alkyl chains were replaced with methyl to get **IN-BT2T-IN'** and **PP-BT2T-PP'** to avoid complications during the calculation. Optimized geometries, HOMO-LUMO energies, and frontier molecular orbitals are represented in Figure 3.2. Both molecules produce almost planer backbones in energy minimized geometries. **IN-BT2T-IN'** showed a relatively larger dihedral angle between IN and thiophene blocks (27.2°) due to possible repulsive interactions between H atoms on each block,

facing each other. The dihedral angle between BT and thiophene spacer showed a relatively lower value (7.4°). On the other hand, **PP-BT2T-PP'** exhibits almost zero dihedral angles ($\approx 0.5^\circ$) between all the major counterparts, leading to almost perfect backbone-planarity.

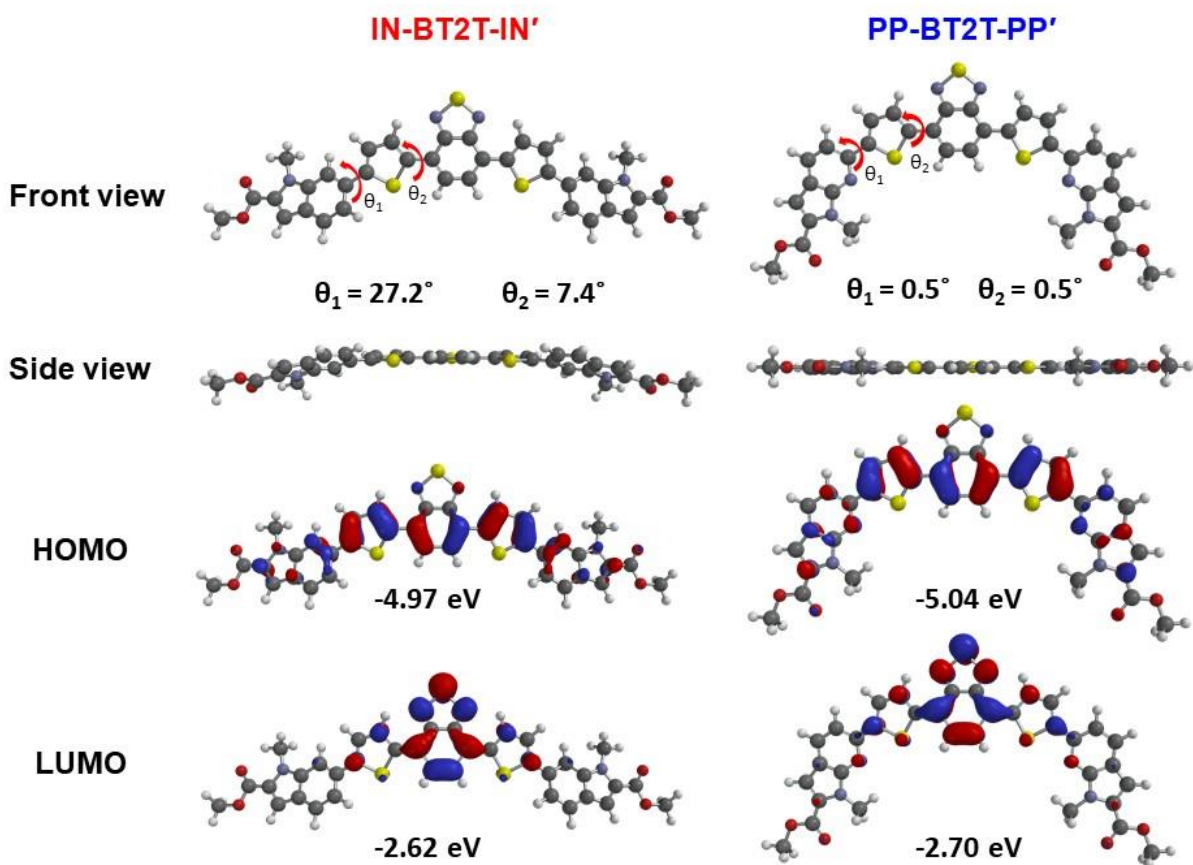


Figure 3.2: DFT analysis of small molecules performed to predict HOMO-LUMO energies and molecular planarity.

Introducing PP into **PP-BT2T-PP'** structure, compared to **IN-BT2T-IN'**, leads to forming additional S-N intramolecular interactions between C-S antibonding orbitals in thiophene and lone pair on pyridinic N atom on PP. In addition, a shorter pyridinic C-N bond ($1.33 \text{ \AA}$) in PP than the benzoic C-C ($1.40 \text{ \AA}$) bond in IN leads to a further curved backbone, which increases the distance between H atoms of PP and thiophene units, on the same plane, eliminating repulsive interactions.

When considering HOMO-LUMO orbital distribution, in both small molecules, LUMO is only delocalized in the core BT2T unit while HOMO is delocalized all along the backbone. For both molecules, corresponding calculated HOMO and LUMO energy values showed no significant differences.

3.3.2 Optoelectronic properties

Ultraviolet-visible (Uv-vis) spectra for **IN-BT2T-IN** and **PP-BT2T-PP** were obtained both in solution (chloroform) and thin films. For both small molecules, UV-vis spectra showed the typical dual-band nature corresponds to donor-acceptor organic semiconductors. The absorption spectra for both molecules are shown in Figure 3.3 and a summary of optoelectronic properties is included in Table 3.1.

Table 3.1: Optical and electrochemical properties of **IN-BT2T-IN** and **PP-BT2T-PP**

Small molecule	HOMO (eV)	LUMO (eV)	E_g^{ec} (eV)	E_g^{opt} (eV)	λ_{max}^{sol} (nm)	λ_{max}^{film} (nm)	λ_{onset} (nm)
IN-BT2T-IN	-4.83	-2.86	1.97	1.97	369, 510	379, 525	629
PP-BT2T-PP	-5.10	-3.19	1.92	1.91	386, 507	395, 528	650

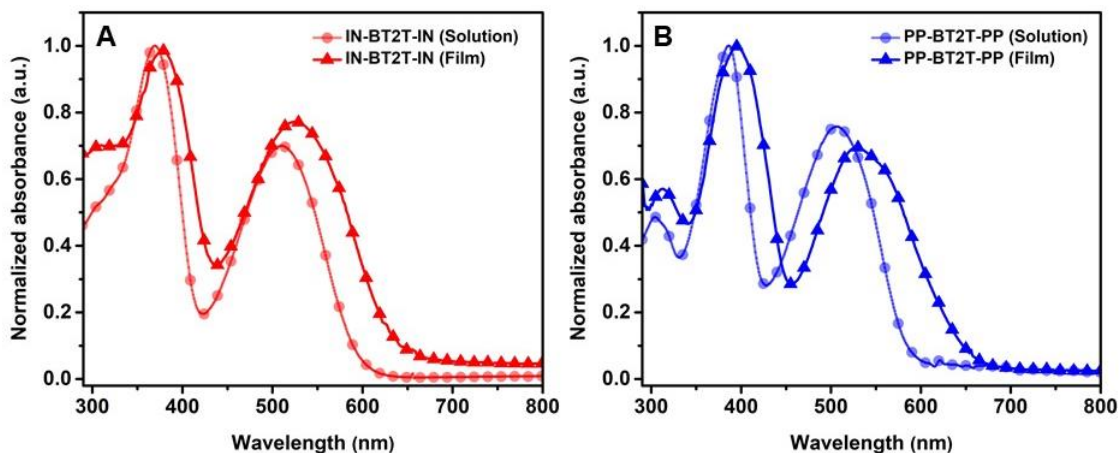


Figure 3.3: UV-Vis spectra of small molecules

In solution, higher energy bands corresponding to $\pi-\pi^*$ transitions appeared with an absorption maximum at 369 nm (**IN-BT2T-IN**) and 386 nm (**PP-BT2T-PP**) while lower energy bands corresponding to intramolecular charge transfer from backbone-delocalized HOMO to acceptor-centered LUMO, as depicted from DFT, appeared with a peak maximum at 510 nm (**IN-BT2T-IN**) and 507 nm (**PP-BT2T-PP**). According to results, compared with **IN-BT2T-IN**, **PP-BT2T-PP** has a slight redshift (17 nm) in the low-energy band while no significant difference in peak position was found for the higher-energy band. When moving to thin films, both small molecules show bathochromic shifts in both characteristic bands with the high energy bands appearing at the absorption maximum 379 nm (**IN-BT2T-IN**) and 395 nm (**PP-BT2T-PP**) while charge transfer bands show-up with the maximum at 525 nm (**IN-BT2T-IN**) and 528 nm (**PP-BT2T-PP**). High energy bands show a small red-shift with ≈ 10 nm difference for both small molecules while charge transfer bands show a red-shift with 15 nm and 21 nm difference respectively for **IN-BT2T-IN** and **PP-BT2T-PP**. The above results indicate that intermolecular $\pi-\pi$ interactions occur when moving from solution to thin film, for both small molecules. The optical bandgap (E_g^{opt}) was calculated using the on-set of the charge transfer band in the absorption profile for both small molecules.

Cyclic voltammetry (CV) was used to obtain electrochemical bandgap (E_g^{ec}) and HOMO/LUMO energies (Figure 3.4). For that, a thin film of the molecule was deposited on the working electrode of the three-electrode setup, and on-set potentials of the oxidation and reduction peaks (E_{ox} and E_{red}) in the voltammogram were used to calculate HOMO and LUMO energy levels, respectively. The following equations were used to calculate HOMO and LUMO energies respectively: $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.4)$ eV and $E_{\text{LUMO}} = -(E_{\text{red}} + 4.4)$ eV. HOMO/LUMO energies for

IN-BT2T-IN and **PP-BT2T-PP** were found to be -4.83/-2.86 eV and -5.10/-3.19 eV resulting in calculated electrochemical bandgaps to be 1.97 eV and 1.91 eV, respectively.

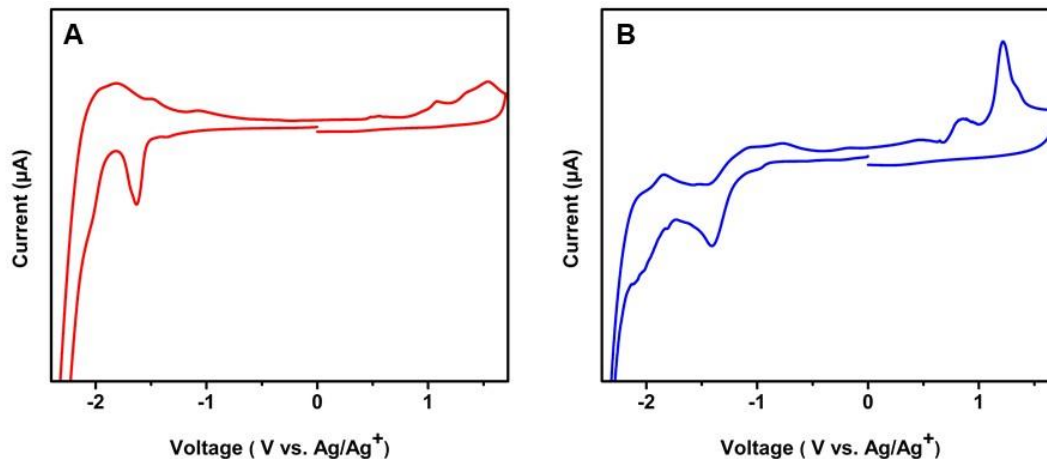


Figure 3.4: Cyclic voltammogram of small molecules; (A) **IN-BT2T-IN** and (B) **PP-BT2T-PP**

Relatively more deep-lying HOMO and LUMO levels were observed for **PP-BT2T-PP**, probably due to more electronegative extra nitrogen atom on PP than IN moieties in **IN-BT2T-IN**. Surprisingly, there was no significant discrepancy between E_g^{opt} and E_g^{ec} observed for both small molecules, which is typically observed due to associated exciton binding energy. However, both small molecules showed E_g^{ec} comparable with observed E_g^{ec} (= 1.90 eV) for thiophene-based analogs in the literature (**TP-BT2T-TP**).³² But, **TP-BT2T-TP** indicates a little elevated HOMO compared to **IN-BT2T-IN**, attributing to the presence of relatively electron-rich fused-thiophene in **TP-BT2T-TP**. Meanwhile, **PP-BT2T-PP** exhibited significantly deep-lying HOMO compared to the other two small molecules mentioned above. This significant change is due to the presence of an electron-withdrawing sp^2 hybridized nitrogen atom in the fused-pyridine moiety.

3.4.3 Thermal properties

Small molecules were tested for their thermal properties using TGA and DSC techniques and corresponding curves are shown in Figure 3.5. TGA results indicate reasonable thermal stability in both small molecules with decomposition temperatures (T_d , 5% weight loss) at 338.5 °C (**IN-BT2T-IN**) at 395.5 °C (**PP-BT2T-PP**).

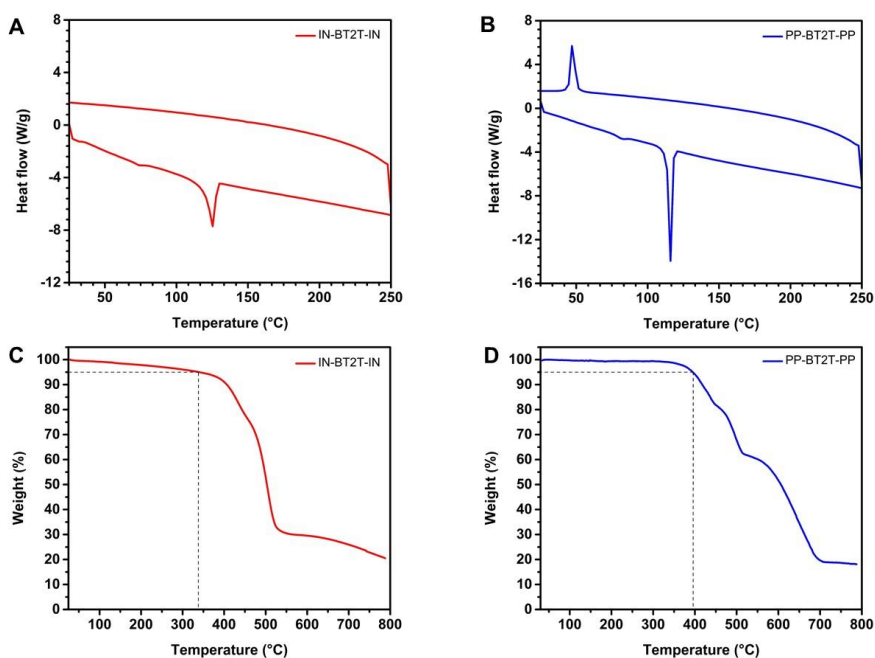


Figure 3.5: DSC (A & B) and TGA (C & D) thermograms of IN-BT2T-IN and PP-BT2T-PP, respectively

However, **IN-BT2T-IN** showed relatively less thermal stability while **PP-BT2T-PP** showed similar stability compared with previously reported **TP-BT2T-TP** ($T_d = 385$ °C). DSC experiments were performed to get additional thermal properties such as phase transition temperatures. For both small molecules, sharp first-order melting temperatures (T_m) were observed at 125.3 °C (**IN-BT2T-IN**) and 116.0 °C (**PP-BT2T-PP**). First-order crystallization temperature (T_c) was only observed for **PP-BT2T-PP** at 47.0 °C in the cooling curves. However, **TT-BT2T-**

TT have shown relatively higher T_m ($=160.5$ °C) than both molecules tested in this study. Regardless of almost closer molecular weights (see Figure B.23 in Appendix B) to the other two molecules, **TT-BT2T-TT** (M.W.= 1022.8 g mol⁻¹) have exhibited relatively higher molecular weight, indicating the presence of stronger intermolecular interactions.

3.4.4 OFETs Properties

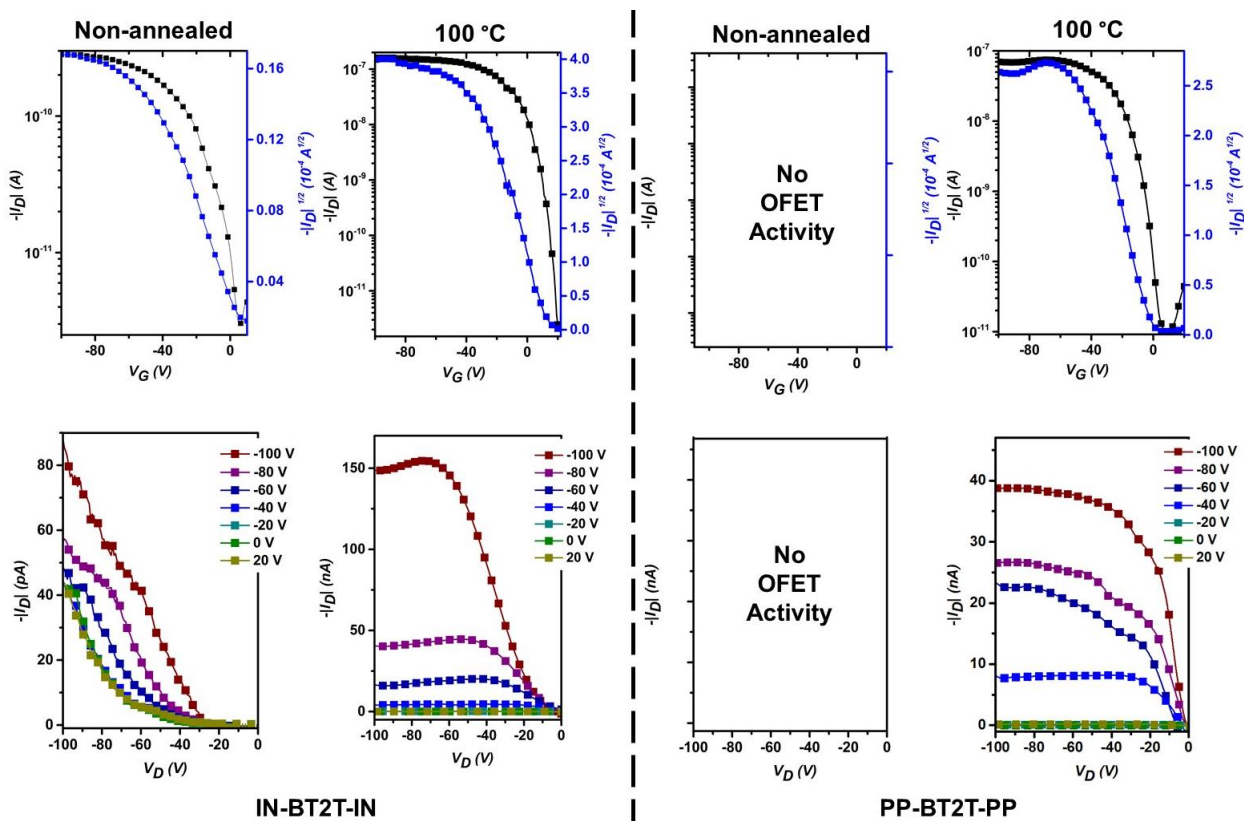


Figure 3.6: OFETs transfer (top) and output curves (bottom) of **IN-BT2T-IN** (left) and **PP-BT2T-PP** (right) at non-annealed and annealed (at 100 °C) devices.

OFETs parameters were obtained using bottom-gate/bottom-contact (BGBC) device configuration (see Figure 3.6). Both small molecules exhibited similar average hole mobilities for annealed thin films at 100 °C with a maximum hole mobility of 4.83×10^{-3} and 3.81×10^{-3} cm² V⁻¹

¹ s⁻¹, respectively, for **IN-BT2T-IN** and **PP-BT2T-PP**. However, these numbers are relatively one order of magnitude less than the mobilities reported for **TP-BT2T-TP** ($\mu_h = 0.08 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) in literature. For non-annealed thin films, **PP-BT2T-PP** showed no significant OFETs activity, while **IN-BT2T-IN** demonstrated average hole mobility of $4.85 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with a maximum of $1.12 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

Thermal annealing at different temperatures indicates a gradual increase in hole mobility as temperature increases, but temperatures over 100 °C caused thermal degradation of thin films. A similar trend was observed for **TP-BT2T-TP** in the literature, previously.³² Both small molecules based devices displayed a drastic change in the on-off current ratio ($I_{\text{on/off}}$) upon thermal annealing. $I_{\text{on/off}}$ has changed from 10^2 to 10^6 and 10^2 to 10^5 for **IN-BT2T-IN** and **PP-BT2T-PP**, respectively. **IN-BT2T-IN** showed threshold voltages (V_T) varying from negative to positive values while **PP-BT2T-PP** remained with positive values for all annealing temperatures. All the OFETs parameters recorded are summarized in Table 3.2.

Table 3.2: OFETs parameters obtained from BGBC configuration

Small molecule	Annealing Temperature/ °C	Maximum hole mobility/ $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	^a Average hole mobility (μ_h)/ $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	Threshold voltage	On/off current ratio
IN-BT2T-IN	Non-annealed	1.12×10^{-4}	4.85×10^{-5}	(-2.1) – 11.0 V	10^2
	60	8.90×10^{-4}	4.67×10^{-4}	(-6.9) – 4.5 V	10^3 – 10^4
	100	4.83×10^{-3}	2.61×10^{-3}	(-1.2) – 13.4 V	10^5 – 10^6
PP-BT2T-PP	Non-annealed	-	-	-	-
	60	4.48×10^{-4}	9.84×10^{-5}	10.6 – 15.9 V	10^2 – 10^3
	100	3.81×10^{-3}	2.33×10^{-3}	11.7 – 22.2 V	10^4 – 10^5

^a Calculated from mobilities obtained for 6 devices

3.4.5 TMAFM imaging

TMAFM images were taken to understand surface morphology behavior upon thermal annealing. Both **IN-BT2T-IN** and **PP-BT2T-PP** showed smoother morphology for non-annealed thin films, providing root mean square roughness (RMS) of 2.10 nm and 1.41 nm, respectively.

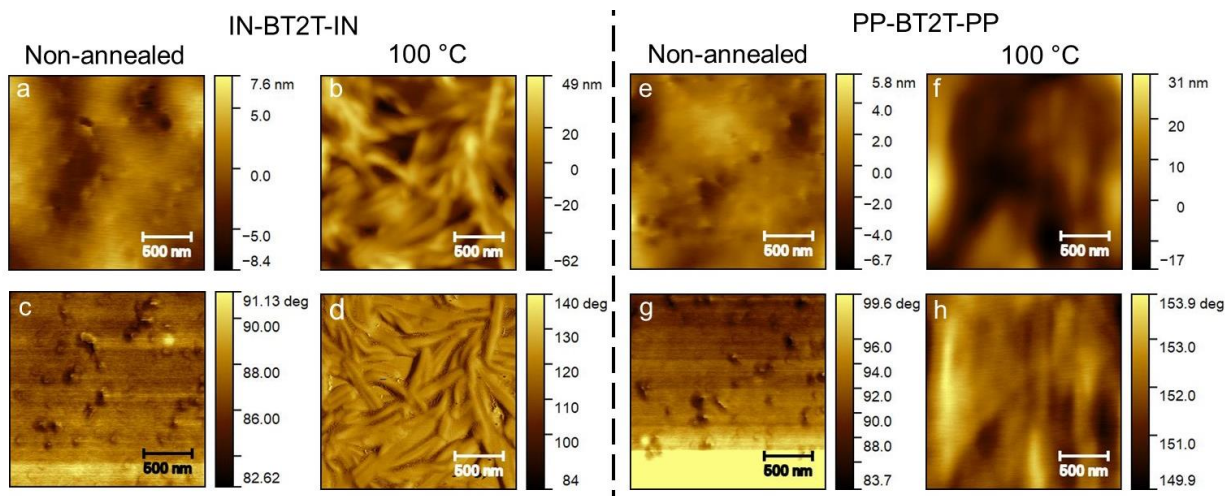


Figure 3.7: Height (top) and phase (bottom) images of **IN-BT2T-IN** (left-half) and **PP-BT2T-PP** (right-half) for non-annealed (a-c & e-g) and annealed thin films at 100 °C (b-d & f-h), obtained from TMAFM; scale bar indicates 500 nm length.

Upon annealing at 100 °C, the roughness of the thin film surface has been drastically increased in each material, showing RMS of 16.96 nm and 8.78 nm, respectively (see Figure 3.7b & 3.7f). In comparison, **TP-BT2T-TP**, in literature, has shown RMS of 7.24 nm with improved granular morphology for annealed thin films. **IN-BT2T-IN** exhibited a fibrils nature (Figure 3.7b & 3.7d), providing more roughness to the surface morphology compared to **PP-BT2T-PP** with grainy morphology at the annealing temperature of 100 °C (Figure 3.7f & 3.7h). Both fibrils and grainy morphologies provided better aggregation of small molecules with reduced molecular distances to

form significantly larger crystallites. This morphology change must have assisted in enhancing hole mobilities in each material upon thermal annealing.

3.4.6 GIXRD data

GIXRD parameters calculated from (100) diffraction peak showed that **IN-BT2T-IN** has considerably lower d-spacing (see Table 3.3). However, **IN-BT2T-IN** showed no significant change in lamellar packing distances upon annealing, but **PP-BT2T-PP** showed a reduction by 3.8 Å. **PP-BT2T-PP** provided a low intense peak which was enhanced significantly upon annealing, attributing to the apparent change in d-spacing values upon annealing. This observation aligns with the apparent drastic improvement of hole mobility in **PP-BT2T-PP** OFETs when annealing to 100 °C, from no hole mobility to $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ magnitude. The relatively visible broadness of (100) diffraction peak of **PP-BT2T-PP** (Figure 3.8 - right) indicates the presence of smaller out-of-plane crystallites in thin film compared to **IN-BT2T-IN** which could be attributed to relatively large out-of-plane lamellar d-spacing values of **PP-BT2T-PP**. In comparison, lamellar packing distance calculated from (100) peak for **TP-BT2T-TP** has shown a moderate value (30.96 Å) to those two molecules studied in this case. Apart from that, **TP-BT2T-TP** showed several orders of Braggs reflection peaks, indicating the highly ordered nature of films.

Table 3.3: Summary of GIXRD data extracted from (100) diffraction peak

Small Molecule	Thermal annealing temperature/ °C	2θ/ degree	d-spacing/ Å
IN-BT2T-IN	Non-annealed	3.43	25.7
	100	3.41	25.9
PP-BT2T-PP	Non-annealed	2.55	34.6
	100	2.30	38.4

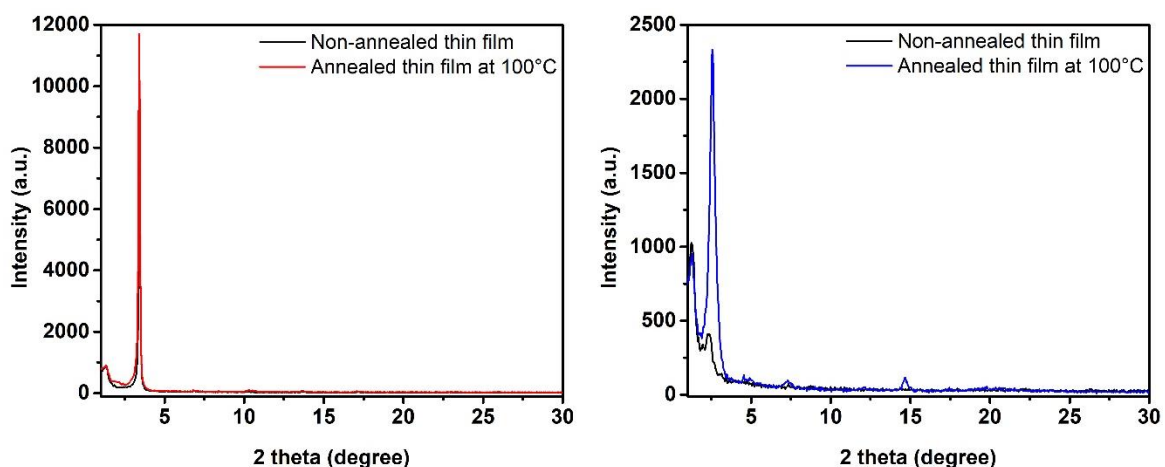


Figure 3.8: GIXRD spectra of **IN-BT2T-IN** (left) and **PP-BT2T-PP** (right) for non-annealed and annealed (at 100 °C) thin films on OTMS modified silicon substrate

3.5 Conclusions

In this study, synthesis of novel fused-pyrrole ring systems, **IN** and **PP**, containing two small molecules was successfully accomplished and they were characterized for their purity, optoelectronic, thermal, and OFETs properties. DFT calculations showed more planarity in **PP-BT2T-PP** than **IN-BT2T-IN**, possibly due to the intramolecular S-N interactions between **PP** donor and spacer thiophene, which reduces torsion angle through conformational locking. Despite the backbone planarity difference, both small molecules showed comparable optoelectronic properties with similar electrochemical and optical bandgaps. These values were also comparable with **TP-BT2T-TP** in literature. The lower difference between electrochemical and optical bandgaps for both molecules is an indication of ease of charge injection at the thin film electrode interface in the CV method. Both small molecules showed significant thermal stability with degradation temperatures over 200 °C but relatively lower than **TP-BT2T-TP**. On the other hand, the relatively higher melting point of **TP-BT2T-TP** compared to two small molecules tested in this study suggests strong molecular interaction in solid-state. OFETs properties seem comparable

at optimized annealing conditions of each small molecule in this study, aligning with their similar optoelectronic properties. However, these mobilities were one order of magnitude lower compared with **TP-BT2T-TP**. However, surface morphology studies showed increased crystallinity in annealed thin films compared to non-annealed, which is also well supported by GIXRD experiments data in this study. In comparison, **TP-BT2T-TP** has shown highly ordered thin film morphology as explained by both TMAFM and GIXRD data in the previous study. Overall, despite the planarity difference in DFT results, both small molecules exhibited comparable optoelectronic properties, indicating a similar effective conjugation effect. Thermally-induced crystallinity of thin films at optimized annealing conditions helped to improve intermolecular interactions enhancing hole mobility in both materials. Even though some comparable optoelectronics properties were observed, **IN-BT2T-IN** and **PP-BT2T-PP** underperformed in OFETs, compared to previously reported **TP-BT2T-TP**, probably due to their lower ordering in thin films.

3.6 Acknowledgment

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3.7 References

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CHAPTER 4

EFFECT OF VARYING CHALCOGENOPHENE-SPACERS IN INDOLE- AND BENZOTHIADIAZOLE-BASED DONOR-ACCEPTOR SMALL MOLECULES: REDUCED BANDGAP BY LOWERING LUMO WITH SELENOPHENE SPACER

4.1 Abstract

The introduction of selenophene analogs in place of widely used thiophene derivatives has been of great interest in the semiconducting field to improve optoelectronic properties and performance in electronic applications. In recent reports, selenium-based small molecule derivatives have proved to improve power conversion efficiencies and current densities in organic photovoltaics (OPVs) compared to thiophene analogs. Even though some studies have been conducted relevant to organic field-effect transistors (OFETs) involving selenium-based semiconducting small molecules with improved properties compared to sulfur-based analogs, they are still fewer in number. In this study, we report indole (IN)- and benzo[c][1,2,5]thiadiazole (BT)-based small molecule with selenophene spacer and applied in OFETs. Further, to systematically investigate structure-property relationship, an analogous furan-spacer-containing molecule was also synthesized and compared with the selenophene-based molecule. Selenophene-based material has shown average hole mobility of $1.92 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with a maximum of $2.57 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 100 °C annealing temperature while furan analog was OFETs inactive even after thermal annealing. To further accomplish a systematic investigation, previously reported thiophene analog (IN-BT2T-IN in Chapter 3) was compared with two molecules reported in this study.

4.2 Introduction

Organic semiconductors (OS) have been gaining significant attention within the last few decades due to their unique characteristics compared to conventional inorganic semiconductors, such as lightweight, mechanical flexibility, higher absorption coefficients, low-cost processability, and large area applicability.¹⁻⁵ Even though the inorganic semiconductors exhibited better charge transfer properties, the above mentioned specific properties of organic semiconducting materials have kept the field alive, and experiments were continued to develop charge-transporting properties of OS. As a result of significant efforts and contributions to developing charge-transporting properties lately, OS materials with relatively high hole and electron mobilities⁶⁻⁹ exceeding mobility of amorphous silicon ($> 0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)¹⁰ approaching mobilities of polycrystalline silicon ($100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)^{11,12} were introduced. In achieving such high mobilities, fused-acenes and donor-acceptor (DA) type copolymers have provided a greater contribution to the field.^{13,14} Properties such as high coplanarity, electron richness, and thin film crystallinity resulted in achieving high hole mobilities with fused-acenes.¹⁵⁻¹⁷ On the other hand, DA polymers provided an opportunity to fine-tune bandgap and position of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) by varying the donor-acceptor combination which was also important to develop charge-transporting properties. However, large-scale applications of acenes were limited due to their solvent incompatibilities and required costly thermal processing procedures.¹⁸⁻²⁰ In contrast, even though polymer materials are solvent processable with the capability of large-area applications through methods such as roll-to-roll and printing methods,²¹⁻²⁴ molecular weight dependence batch-to-batch variation has limited their applicability in large scale production.

In order to address these issues, experimentalists focused on developing solvent processable DA small molecules due to their well-defined molecular weights, possible functionalization, and the ability to produce with high purity.²⁵ Small molecules can also be used to achieve thin films with better crystallinity.^{25,26} Even though these small molecules possess some improved properties compared to acenes and DA polymers, they still lag in achieving higher mobilities. However, there are some recent reports of solvent processable small molecules possessing high mobilities ($3.04 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)²⁵ exceeding mobilities of amorphous silicon semiconductors. However, these small molecules consist of lengthy backbones with multiple complicated steps which may also cause problems in real-world applications. So it should be a vital interest to develop more simple but better performing small molecules. In recent years, the introduction of Selenium-based counterparts into organic semiconducting materials has been of greater interest in developing optoelectronic properties and performance in electronic applications.^{27–32} Scientists have shown that replacing some of the widely occupied thiophene-based counterparts in OS with corresponding selenium-based analogs improved optoelectronic properties and application performance.^{27–30} Although there are significant numbers of reported polymers^{33–35} and small molecules^{36–38} containing selenium counterparts with better performance in OPVs applications, a small number of literature can be found for such small molecules in OFETs applications.³⁹

In one of our previous studies (Chapter 3), we developed a non-conventional IN- and BT-based small molecule with thiophene spacer (IN-BT2T-IN). With that molecular design, we achieved moderate hole mobilities over $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. In this study, we synthesized a small molecule (**IN-BT2Se-IN**) by replacing thiophene spacer with selenophene to vary the involved

chalcogen atom (Figure 4.1) to investigate the structure-property relationship, improve charge-transporting potential, and study in OFETs applications. The introduction of selenophene has proved to improve optoelectronic properties, thin film properties, and performance in OFETs. In order to further understand the structure-property relationship relevant to the chalcogenophene spacers involved in this design, furan spacer containing small molecule analog (**IN-BT2F-IN**) was also synthesized and its properties were compared with its thiophene and selenophene derivatives.

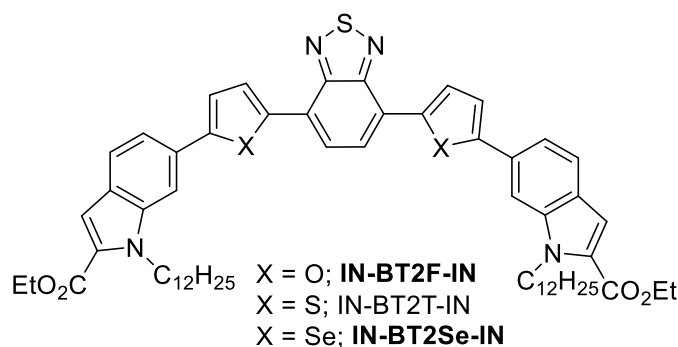


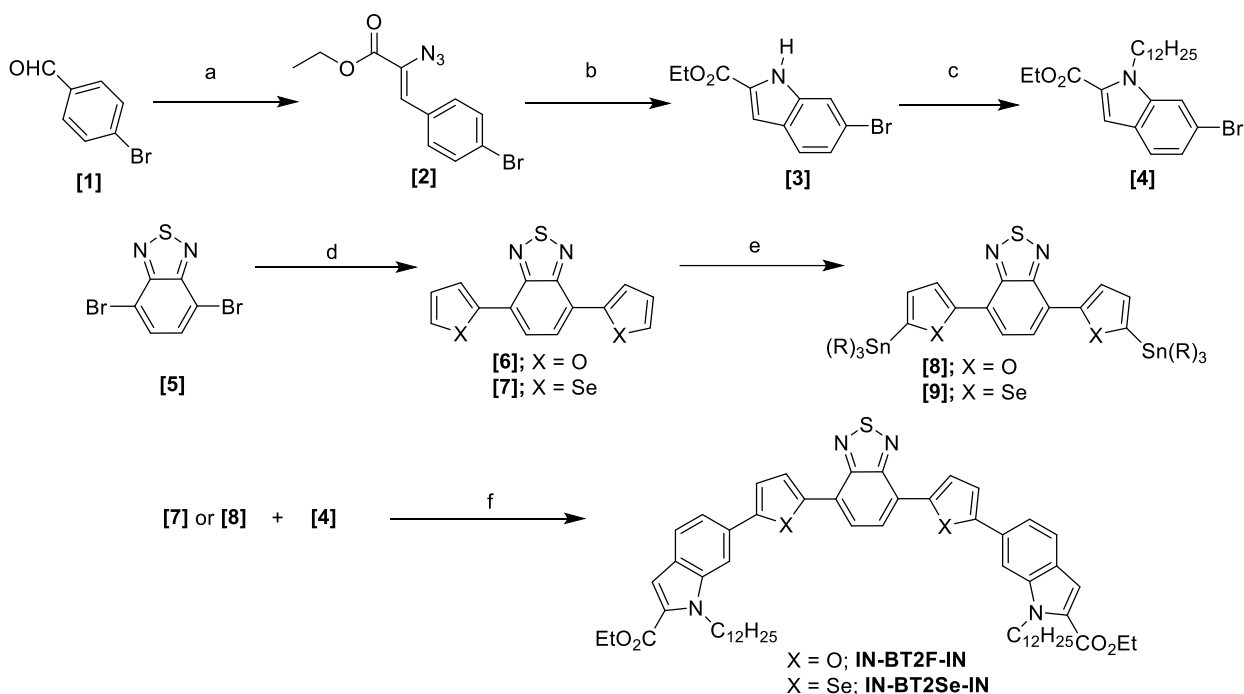
Figure 4.1: Design of suggested small molecules (**IN-BT2F-IN** & **IN-BT2Se-IN**) and previously reported molecule (**IN-BT2T-IN**)

4.3 Materials and methods

4.3.1 Materials and general methods

All the chemicals were purchased from Sigma-Aldrich and Fisher Scientifics and used without any further purifications unless otherwise noted. Freshly distilled anhydrous toluene and previously distilled N,N-dimethylformamide (DMF) stored under nitrogen over activated molecular sieves were used in reactions. OFETs devices were fabricated using a previously published method under a cleanroom facility using general lithographic methods.²⁶

4.3.2 Synthesis of small molecules



Scheme 4.1: General synthesis route for **IN-BT2Se-IN** and **IN-BT2F-IN**; Reaction conditions: (a) ethyl azidoacetate (2 equiv.), ethyl trifluoroacetate (2 equiv.), metal-sodium (2 equiv.), ethanol (50 mL), 0 °C, 6 h, 46%; (b) toluene (15 mL), reflux, 24 h, 78%; (c) anhydrous K₂CO₃ (2.1 equiv.), 18-crown-6 (cat.), 1-bromododecane (2 equiv.), DMF (10 mL), 120 °C, 24 h, N₂, 96%; (d) [8] or [9] (≥ 2 equiv.), Pd₂(dba)₃, P(*p*-tol)₃, toluene, reflux; (e)-(i) *n*-BuLi (> 2 equiv.), THF, -78 °C: - (ii) trimethylstannylchloride (> 2 equiv.), THF, -78 °C; (f) [11] (1 equiv.), [7] or [8] (> 2 equiv.), Pd₂(dba)₃ (5-10 mlo%), P(*p*-tol)₃ (20-40 mol%), toluene, reflux, 24 h; Detailed procedures and/or references for steps d, e, and f are provided in section 4.3.3.

4.3.3 Synthesis procedures

4.3.3.1 Synthesis of ethyl 6-bromo-1-dodecyl-1H-indole-2-carboxylate

Synthesis was accomplished according to previously reported method (see Chapter 3). Pure product was obtained as a yellow oil (1.57 g, 96%). ¹H NMR (CDCl₃, 500 MHz): δ_{H} – 0.88 (t, 3H), 1.25 (m, 18H), 1.41 (t, 3H), 1.77 (m, 2H), 4.37 (q, 2H), 4.49 (t, 2H), 7.22 (m, 2H), 7.53 (m, 2H). ¹³C NMR (CDCl₃, 125 MHz): δ_{C} – 14.32, 62.87, 119.46, 128.03, 128.70, 128.80, 138.92, 142.24, 151.89, 162.82

4.3.3.2 Synthesis of 4,7-di(furan-2-yl)benzo[c][1,2,5]thiadiazole [6]

Synthesis was done according to a previously published method.⁴⁰ Product was obtained as a red solid (0.455 g, 67.2%). NMR data matched with previously reported spectra.^{40,41} ¹H NMR (CDCl₃, 500 MHz): δ_{H} – 6.63 (dd, 1H), 7.59 (d, 1H), 7.69 (d, 1H), 8.06 (s, 1H)

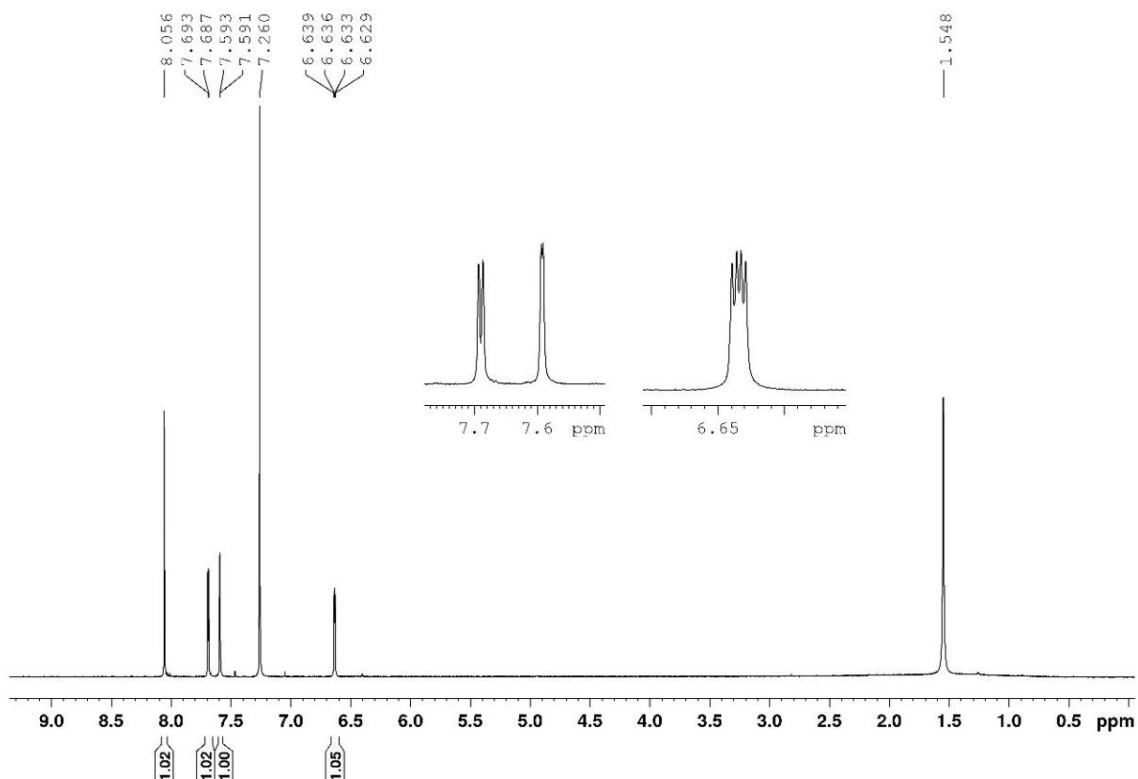


Figure 4.2: ¹H NMR of 4,7-di(furan-2-yl)benzo[c][1,2,5]thiadiazole

4.3.3.3 Synthesis of 4,7-di(selenophen-2-yl)benzo[c][1,2,5]thiadiazole [7]

Synthesis was accomplished using a previously published method.⁴² One-tenth of the amounts of materials and solvents from the original procedure were used for the reaction. The product was obtained as a crystalline red-orange solid (0.350 g, 90%). ¹H NMR (CDCl₃, 500 MHz): δ_{H} – 7.45(dd, 1H), 7.90(s, 1H), 8.17 (dd, 1H), 8.20 (dd, 1H); ¹³C NMR (CDCl₃, 125 MHz): δ_{C} – 125.32, 127.85, 128.44, 130.29, 133.62, 144.24, 152.66

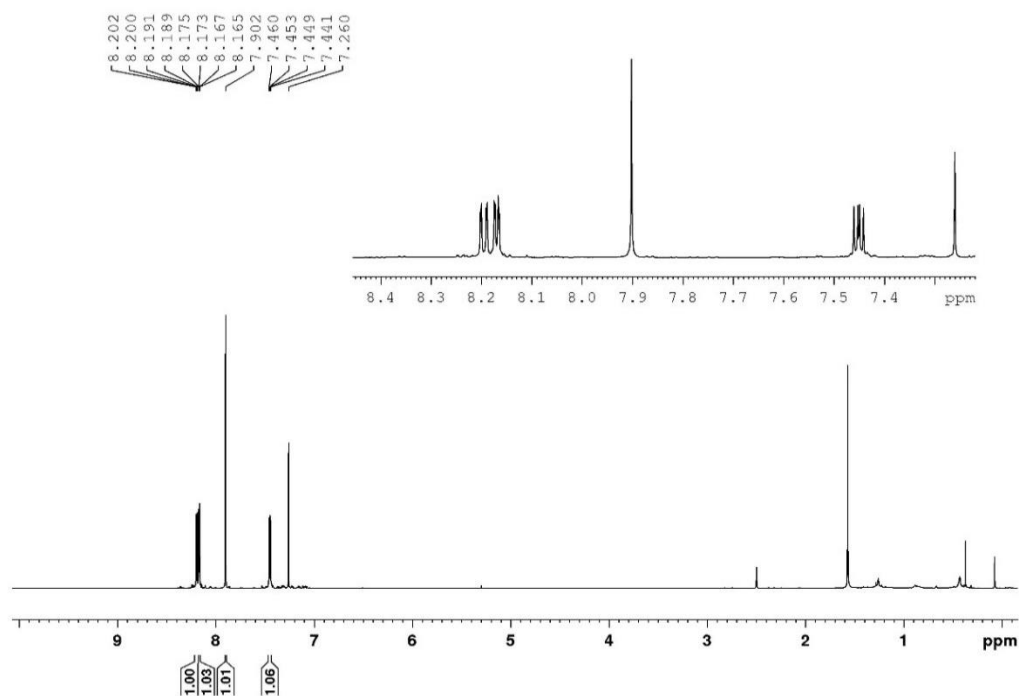


Figure 4.3: ¹H NMR of 4,7-di(selenophen-2-yl)benzo[c][1,2,5]thiadiazole

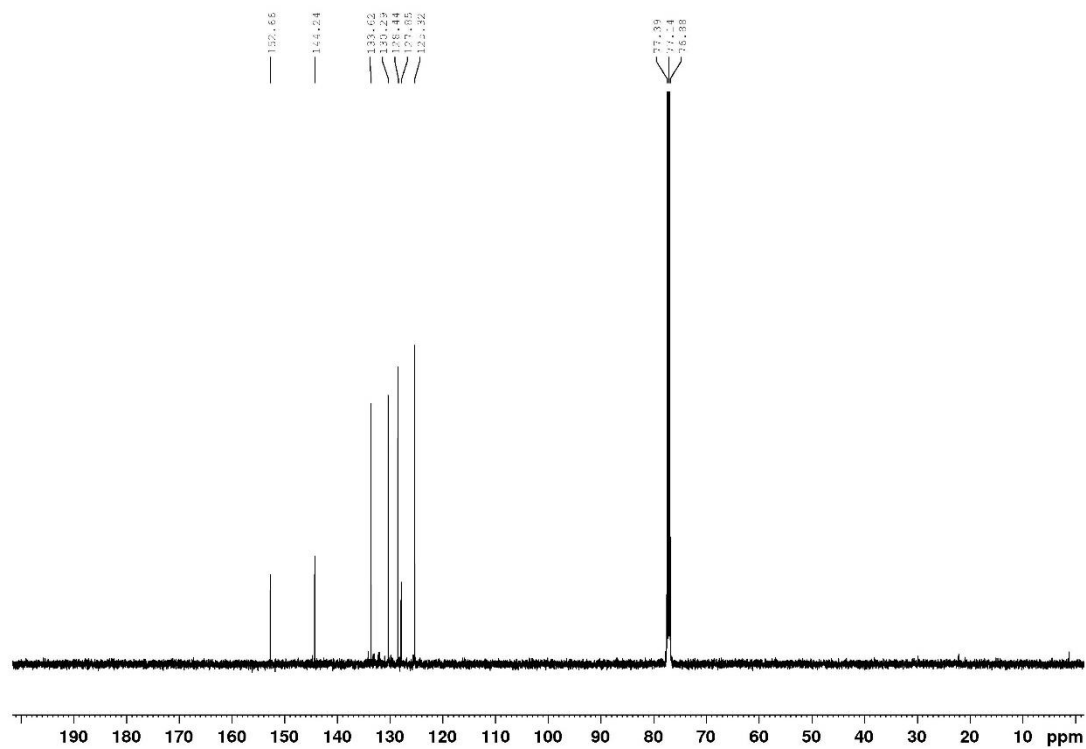


Figure 4.4: ¹³C NMR of 4,7-di(selenophen-2-yl)benzo[c][1,2,5]thiadiazole

4.3.3.4 Synthesis of 4,7-bis(5-(trimethylstannyl)furan-2-yl)benzo[c][1,2,5]thiadiazole [8]

Synthesis and purification of this block was done according to a previously published method.⁴⁰ Instead of tributylstannyl chloride, the same numbers of moles from trimethylstannyl chloride was used as stannylating agent. The product was obtained as red solid (0.360 g, 74.7%). Material was used in the next step without further purifications. ¹H NMR (CDCl₃, 500 MHz): δ_{H} – 0.93(t, 5.0Hz, 9H), 1.17 (m, 6H), 1.39 (m, 6H), 1.64 (m, 6H), 6.79 (d, 1H), 7.71 (d, 1H), 8.06 (s, 1H); ¹³C NMR (CDCl₃, 125 MHz): δ_{C} – 10.48, 13.86, 27.35, 29.16, 112.15, 121.95, 123.51, 124.44, 151.51, 154.73, 162.57

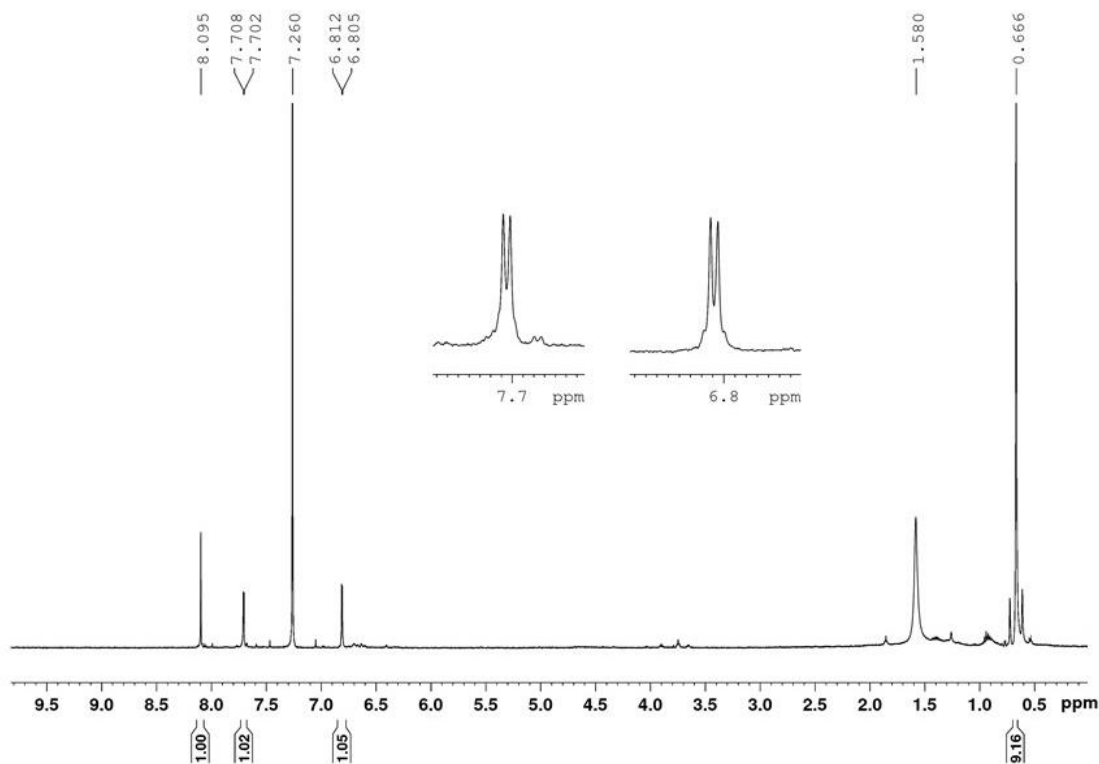


Figure 4.5: ¹H NMR of 4,7-bis(5-(trimethylstannyl)furan-2-yl)benzo[c][1,2,5]thiadiazole

4.3.3.5 Synthesis of 4,7-bis(5-(trimethylstannyl)selenophen-2-yl)benzo[c][1,2,5]thiadiazole

[9]

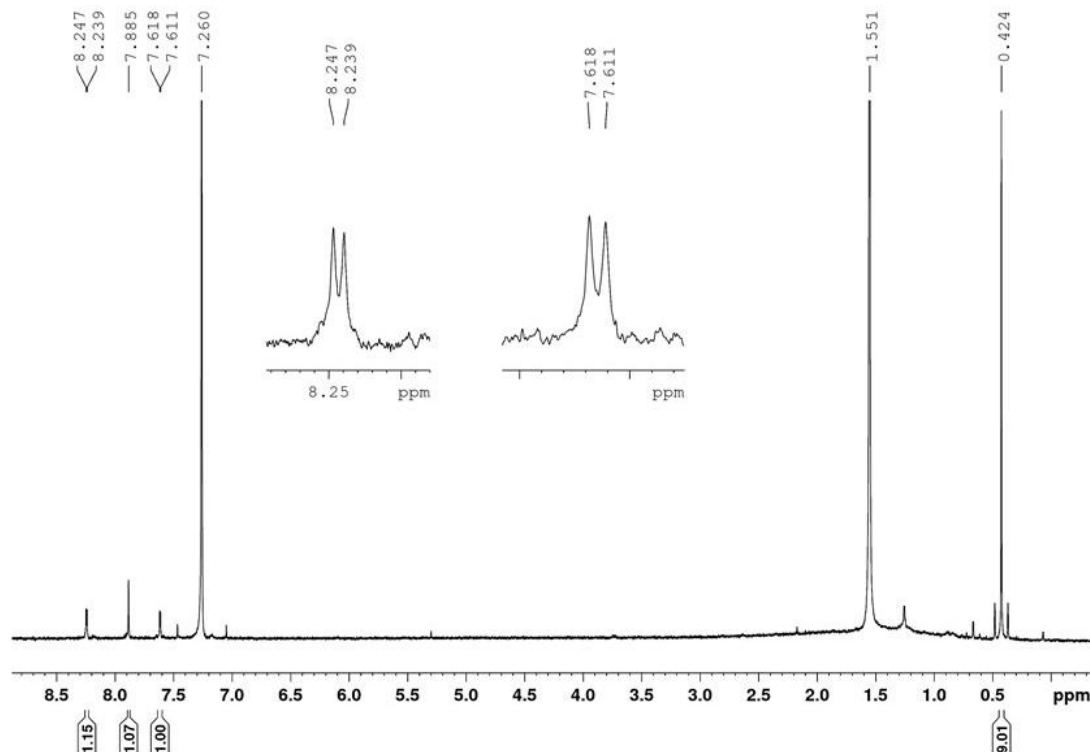


Figure 4.6: ^1H NMR of 4,7-bis(5-(trimethylstannyl)selenophen-2-yl)benzo[c][1,2,5]thiadiazole

4,7-di(selenophen-2-yl)benzo[c][1,2,5]thiadiazole (0.100 g, 0.25 mmol) was dissolved in freshly distilled tetrahydrofuran (20 mL) under nitrogen conditions with minimum moisture. The temperature of the reaction mixture was brought to $-78\text{ }^\circ\text{C}$ and lithium diisopropylamide (0.51 mL, 2M) was slowly added and stirred for 40 minutes. Completion of the lithiation step was confirmed by quenching in D_2O and ^1H NMR analysis. Chlorotrimethylstannane (1.14 mL, 1M) was added at $-78\text{ }^\circ\text{C}$ and slowly allowed to come to room temperature while stirring. After 3 hours reaction mixture was again tested with NMR analysis for completion and quenched in cold water. The product was extracted with diethyl ether ($3 \times 50\text{ mL}$) and washed with deionized water (3×50

mL). Later organic solvent was dried with anhydrous MgSO_4 and removed under vacuum to obtain the product as a deep-red solid (0.169 g, 92.5%). Product was used in the next step without further purifications. NMR data matched with reported literature.⁴² ^1H NMR (CDCl_3 , 500 MHz): δ_{H} 0.42 (s, 9H), 7.61 (s, 1H), 7.89 (s, 1H), 8.24 (s, 1H). ^{13}C NMR (CDCl_3 , 125 MHz)

4.3.3.6 Synthesis of IN-BT2F-IN

4,7-bis(5-(trimethylstannyl)furan-2-yl)benzo[c][1,2,5]thiadiazole (0.250 g, 0.30 mmol), ethyl 6-bromo-1-dodecyl-1*H*-indole-2-carboxylate (0.300 g, 0.69 mmol), tris(benzylideneacetone)dipalladium(0) (28 mg, 0.03 mmol) tri(*o*-tolyl)phosphine, (37 mg, 0.12 mmol) was dissolved in freshly distilled toluene (15 mL) under a nitrogen environment in a round bottom flask (100 mL) equipped with a reflux condenser. The reaction mixture was then refluxed under nitrogen for 24 hours. Later, the reaction flask was allowed to come to room temperature and toluene volume was reduced under vacuum. Then the reaction mixture was crashed into methanol (200 mL) and the resulted precipitate was filtered to recover a red solid. The solid was further washed with methanol (~50 mL) and hexane (~100 mL) to recover the pure solid (0.192 g, 65%). ^1H NMR (CDCl_3 , 500 MHz): δ_{H} – 0.81 (t, 3H), 1.21 (m, 18H), 1.43 (t, 3H), 1.88 (m, 2H), 4.40 (q, 2H), 4.66 (t, 2H), 6.97 (d, 1H), 7.31 (s, 1H), 7.61(d, 2H), 7.72(d, 1H), 7.84 (m, 2H), 8.24 (s, 1H); ^{13}C NMR (CDCl_3 , 125 MHz); δ_{C} – 14.21, 14.54, 22.79, 27.13, 29.48, 29.59, 29.78, 29.82, 29.85, 30.87, 32.02, 44.95, 60.71, 105.76, 108.52, 110.77, 115.12, 117.81, 121.53, 123.15, 123.27, 125.97, 127.34, 128.66, 139.49, 149.85, 151.64, 155.19, 161.95

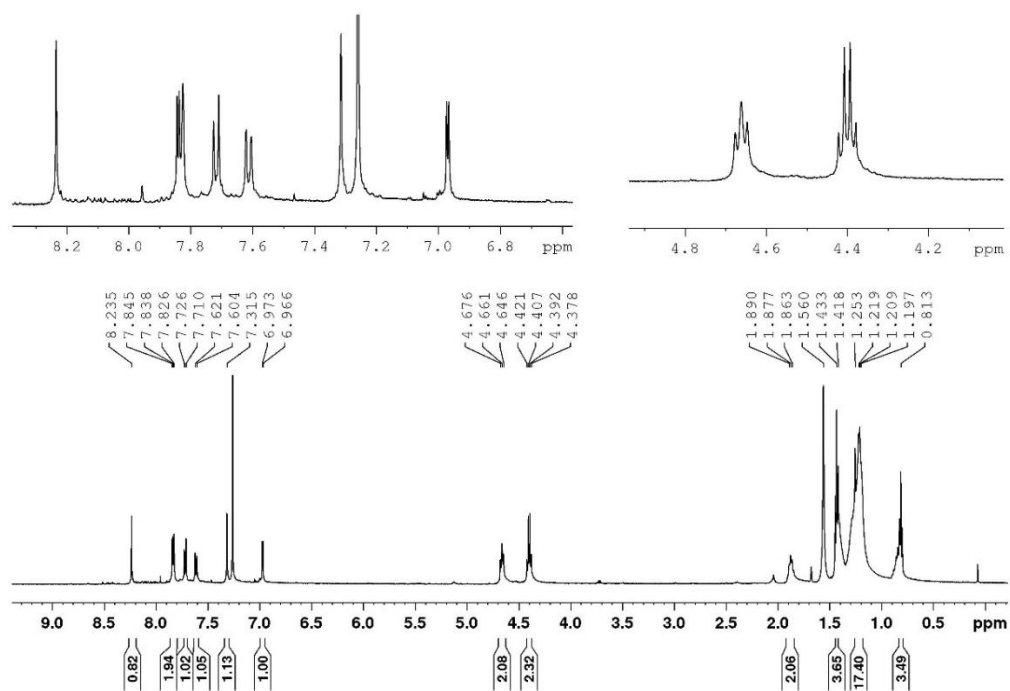


Figure 4.7: ^1H NMR of IN-BT2F-IN

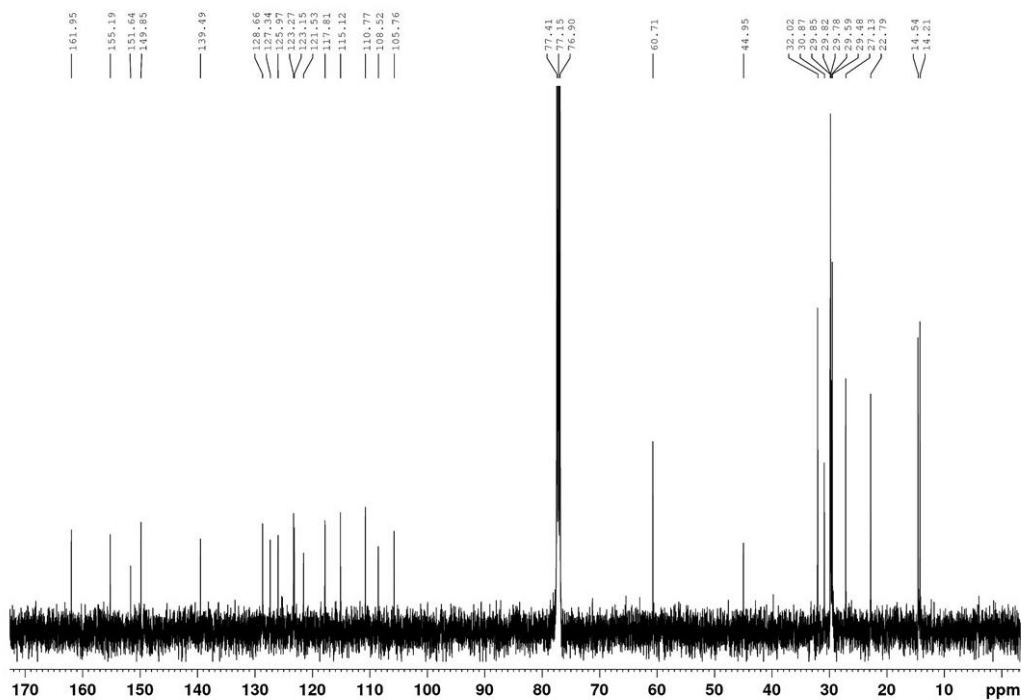


Figure 4.8: ^{13}C NMR of IN-BT2F-IN

4.3.3.7 Synthesis of IN-BT2Se-IN

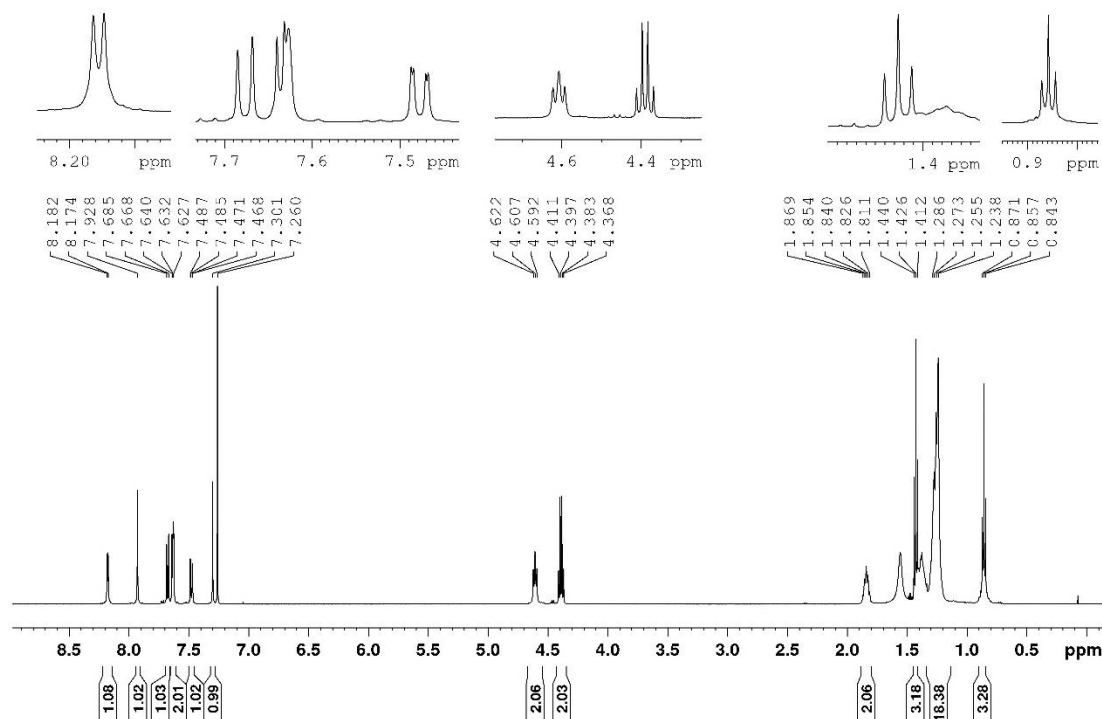


Figure 4.9: ^1H NMR of **IN-BT2Se-IN**

4,7-bis(5-(trimethylstannyl)selenophen-2-yl)benzo[c][1,2,5]thiadiazole (0.108 g, 0.15 mmol), ethyl 6-bromo-1-dodecyl-1*H*-indole-2-carboxylate (0.196 g, 0.45 mmol), tris(benzylideneacetone)dipalladium(0) (7 mg, 7.5 μmol), tri(*o*-tolyl)phosphine (9.2 mg, 30.0 μmol) was dissolved in freshly distilled toluene (15 mL) under a nitrogen environment in a round bottom flask (50 mL) equipped with a reflux condenser and refluxed for 24 hours under inert atmosphere. The reaction flask was allowed to cool to room temperature and solvent was removed under vacuum. The solid obtained was directly purified using silica column chromatography with dichloromethane(DCM)-hexane (40-50% DCM) solvent system. The pure solid was recovered as a magenta solid (0.092 g, 55%). ^1H NMR (CDCl_3 , 500 MHz): δ_{H} – 0.86 (t, 3H), 1.26 (m, 18H), 1.43 (t, 3H), 1.84 (m, 2H), 4.39 (q, 2H), 4.61 (t, 2H), 7.31 (s, 1H), 7.48 (dd, 1H), 7.63(m, 2H),

7.68(d, 1H), 7.93 (s, 1H), 8.18 (d, 1H); ^{13}C NMR (CDCl_3 , 125 MHz); δ_{C} – 14.25, 14.53, 22.83, 27.13, 29.50, 29.56, 29.75, 29.78, 29.83, 30.84, 32.07, 44.79, 60.73, 107.83, 110.69, 119.90, 123.19, 124.72, 126.06, 127.64, 128.67, 129.55, 133.40, 139.59, 142.97, 152.70, 154.46, 161.95

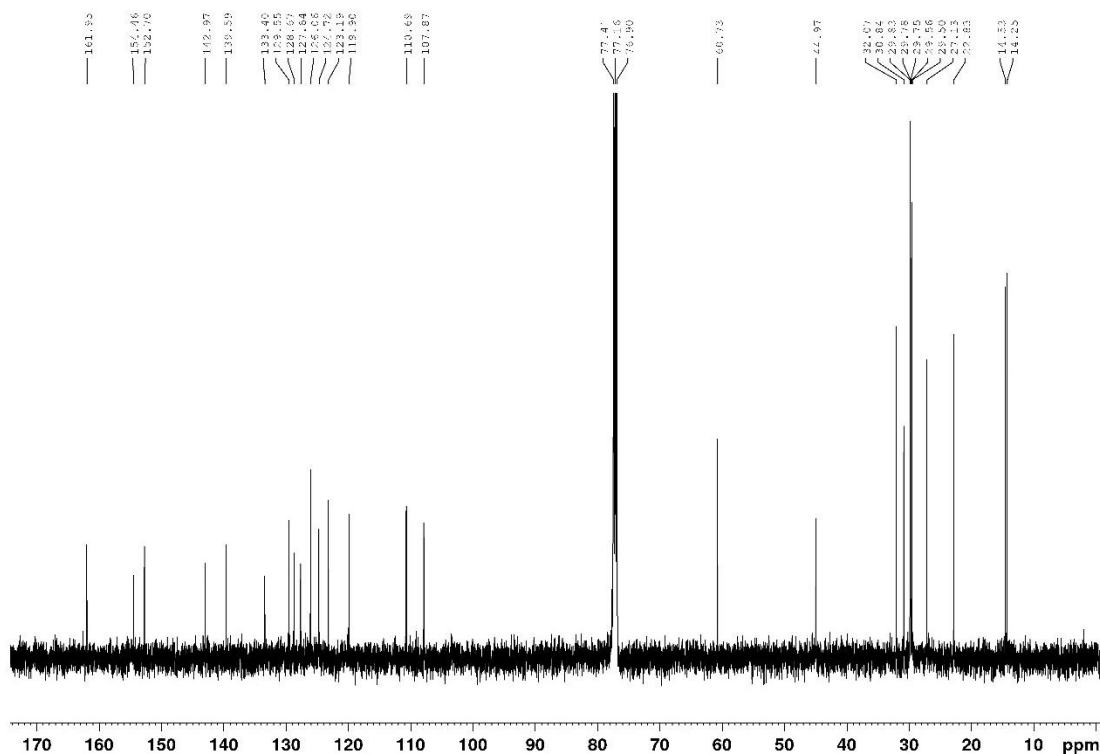


Figure 4.10: ^{13}C NMR of IN-BT2Se-IN

4.4 Results and discussion

4.4.1 Optoelectronic properties

UV-Vis experiment was performed to get an insight into the optical properties of synthesized molecules. Since both small molecules possess donor-acceptor molecular architecture, both spectra exhibit the typical dual-band nature in solution and thin film. π - π^* electron transfer (ET)

bands were visible at 300-450 nm for both molecules in solution and thin film except for **IN-BT2Se-IN** thin film, which expanded from 300-500 nm (see Figure 4.11).

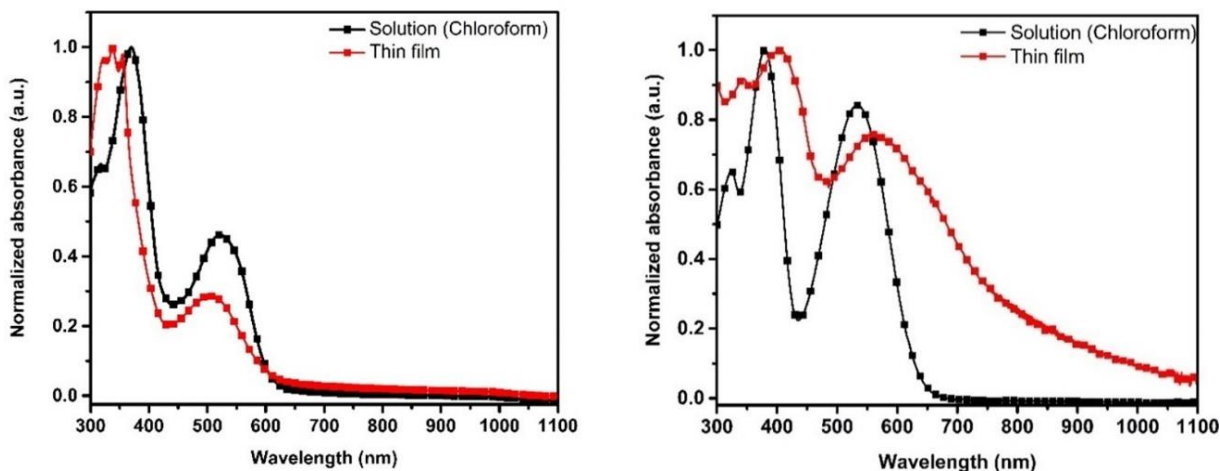


Figure 4.11: UV-Vis spectra of BP-BT2F-BP (left) and BP-BT2Se-BP (right)

IN-BT2F-IN exhibits π - π^* electron transfer band at a peak maximum of 369 nm in solution and 337 nm in the thin film, indicating a relative blueshift in the thin film state. On the other hand, **IN-BT2Se-IN** showed a UV-Vis peak maximum of 380 nm and 404 nm, respectively, for the solution and thin film, exhibiting a relative redshift in thin films. **IN-BT2Se-IN**, in both solution and thin films, signifies a relative redshift compared to **IN-BT2F-IN**. When comparing two molecules, there is a redshift by 11 nm in solution while 67 nm shift was observed for thin film of **IN-BT2Se-IN**, relative to **IN-BT2F-IN**. On the other hand, the donor-accepter charge transfer (DACT) band also exhibited a similar trend and peak maxima were reported at 521 nm and 499 nm, respectively, for **IN-BT2F-IN** solution and thin films, notifying a blue shift. However, **IN-BT2Se-IN** exhibited peak maxima at 533 nm and 560 nm, respectively, for the solution and thin films, which showed a redshift of 27 nm in thin films. Compared with **IN-BT2F-IN**, in solution, it showed 12 nm red shift while, in thin film state, a significant 60 nm shift was observed.

When observing intensities, **IN-BT2F-IN** exhibited a lower intense DACT band than the ET band, indicating a restricted DACT ability. On the other hand, **IN-BT2Se-IN** illustrates a comparably intense DACT band to ET band, with a significant area under the curve, explaining an occurrence of a large population of DACT electron transitions. This is also a probable indication of a significantly lower bandgap in **IN-BT2Se-IN**, compared to **IN-BT2F-IN**. To further confirm this, the onset wavelength of DACT band was extracted and used to calculate the optical bandgap (E_g^{opt}). **IN-BT2Se-IN** showed E_g^{opt} of 1.57 eV, which is significantly lower than **IN-BT2F-IN** ($E_g^{opt} = 2.03$ eV).

The cyclic voltametric method was involved to further investigate HOMO and LUMO energy levels and electrochemical bandgap (E_g^{ec}) of small molecules. Corresponding cyclic voltammograms are depicted in Figure 4.12. The HOMO was calculated using the onset of oxidation peak of the voltammogram while LUMO was determined by the onset of reduction peak. Following equations were involved in calculating the HOMO, LUMO, and E_g^{ec} ($E_{HOMO} = -(E_{ox} + 4.4)$ eV and $E_{LUMO} = -(E_{red} + 4.4)$ eV). Calculated HOMO/LUMO energy levels of molecules were -4.98/-2.94 eV and -4.89/-3.28 eV, respectively, for **IN-BT2F-IN** and **IN-BT2Se-IN**. Obtained correspondingly E_g^{ec} values for these molecules were 2.04 eV and 1.61 eV. The observed discrepancies between E_g^{opt} and E_g^{ec} for two molecules were determined to be 0.01 eV and 0.03 eV, respectively. A summary of all the optoelectronic properties of both molecules is provided in Table 4.1.

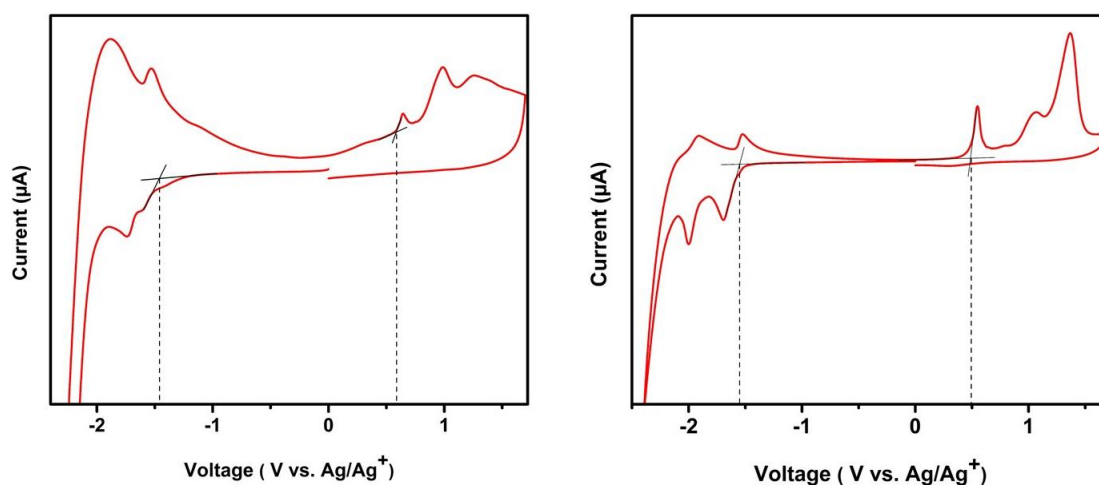


Figure 4.12: Cyclic voltammograms of **IN-BT2F-IN** (left) and **IN-BT2Se-IN** (right)

Table 4.1: Summary of optoelectronic properties all analog small molecules

Small molecule	HOMO (eV)	LUMO (eV)	E_g^{ec} (eV)	E_g^{opt} (eV)	λ_{max}^{sol} (nm)	λ_{max}^{film} (nm)	λ_{onset} (nm)
IN-BT2F-IN	-4.98	-2.94	2.04	2.03	369, 521	337, 499	609
IN-BT2T-BT	-4.83	-2.86	1.97	1.97	369, 510	379, 525	629
IN-BT2Se-IN	-4.89	-3.28	1.61	1.57	380, 533	404, 560	771

When optoelectronic properties of IN-BT2T-BT were compared with this study, moderate properties were observed. For example, both E_g^{ec} and E_g^{opt} were found to be in between the corresponding values of the other two small molecules. Somehow, IN-BT2T-BT also exhibited a redshift when moving from solution to thin film state, indicating improved intermolecular interaction in solid-state but overall redshift was only by 15 nm, which is about half of the value for IN-BT2Se-BT. The thiophene and selenophene derivatives have similar HOMO levels, but the LUMO level was drastically lowered by about ~ 0.4 eV with introducing selenophene. A similar trend of lowering LUMO without altering HOMO due to introduction of selenophene counterparts

can be seen in some of the literature.^{43–45} The introduction of selenophene counterparts has also caused in reduction of the bandgap compared to thiophene derivatives in this literature.

4.4.2 Thermal Properties

Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC) techniques were involved in determining the thermal properties of the two small molecules. TGA analysis was performed under a nitrogen flow to get an insight into the thermal degradation temperatures of synthesized molecules. In this experiment, any rapid thermal degradation was observed only after 350 °C for both small molecules. Degradation temperatures (T_d) at which 5% weight loss occurred were determined to be 288.1 °C and 295.3 °C, respectively, for **IN-BT2F-IN** and **IN-BT2Se-IN**. (See Figure 4.13) Both small molecules seemed adequately stable to perform any thermal treatments without any significant degradation. Observed degradation temperatures over 250 °C allowed to perform DSC scanning for a more comprehensive temperature range.

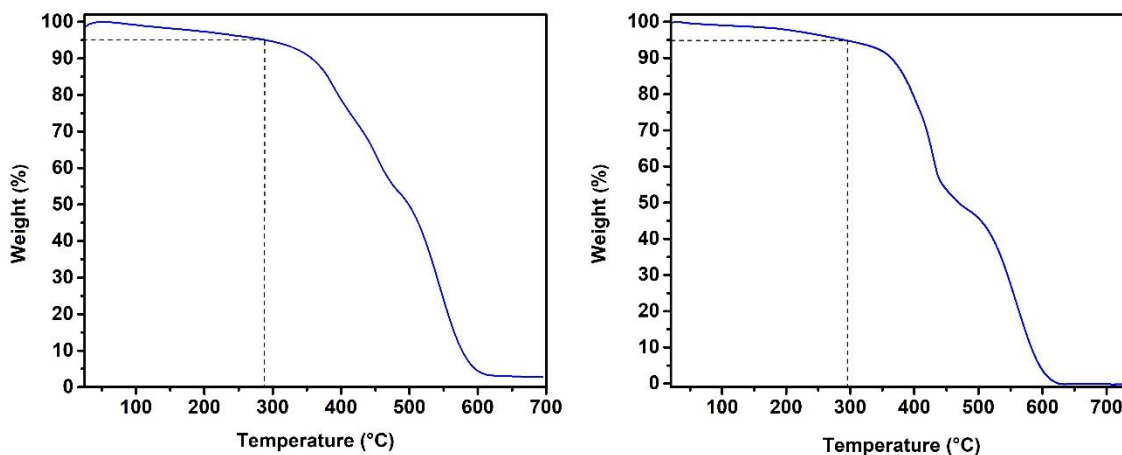


Figure 4.13: TGA thermograms of **IN-BT2F-IN** (Left) and **IN-BT2Se-IN** (right)

In order to determine thermal transitions associated with the two small molecules, DSC analysis was performed. Corresponding DSC thermograms are given in Figure 4.14. **IN-BT2F-IN**

indicated a melting point (T_m) at 129.9 °C while no crystallization temperature (T_c) was observed. Meanwhile, for **IN-BT2Se-IN**, both T_m and T_c were observed at 138.1 °C and 94.6 °C. The relatively higher melting point observed for **IN-BT2Se-IN** attributes to the presence of a heavier selenium chalcogen atom than oxygen in the structure and associated stronger intermolecular interactions.

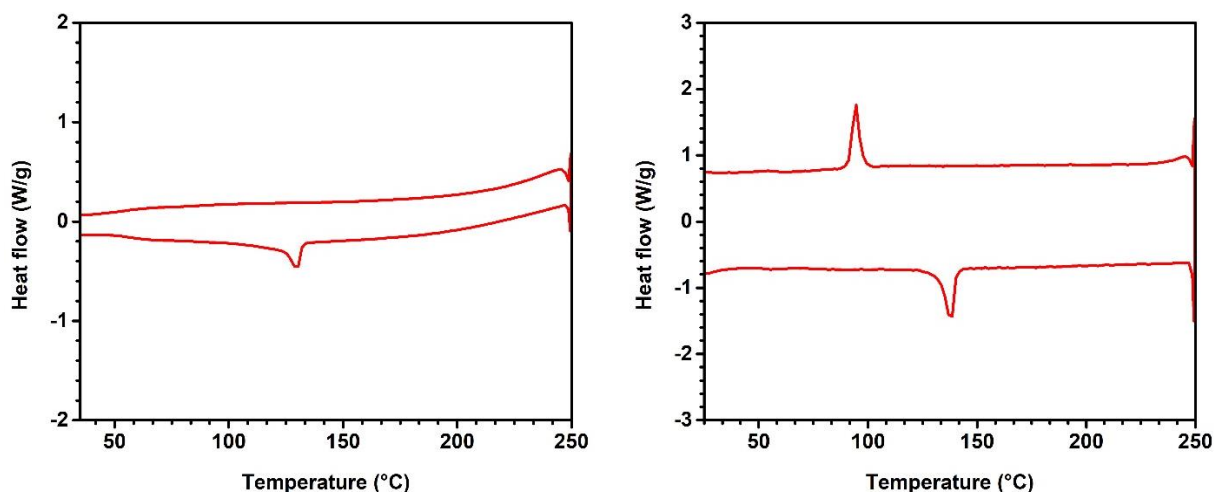


Figure 4.14: DSC thermograms of **IN-BT2F-IN** (left) and **IN-BT2Se-IN** (right)

4.4.3 OFETs Properties

OFETs properties were determined using bottom-gate-bottom contact (BGBC) device configuration. Both small molecules were tested under open-air after fabricating them on OTMS treated SiO₂/n⁺⁺-Si substrate. Extracted OFETs parameters from transfer and output curves are depicted in Table 4.2. **IN-BT2Se-IN** showed OFETs activity for non-annealed thin films which later improved upon thermal annealing. Annealing at 80 °C, which is below its crystallization temperature, slightly improved average hole mobility of the devices by a factor of ~4. However, annealing at 100 °C, a temperature slightly

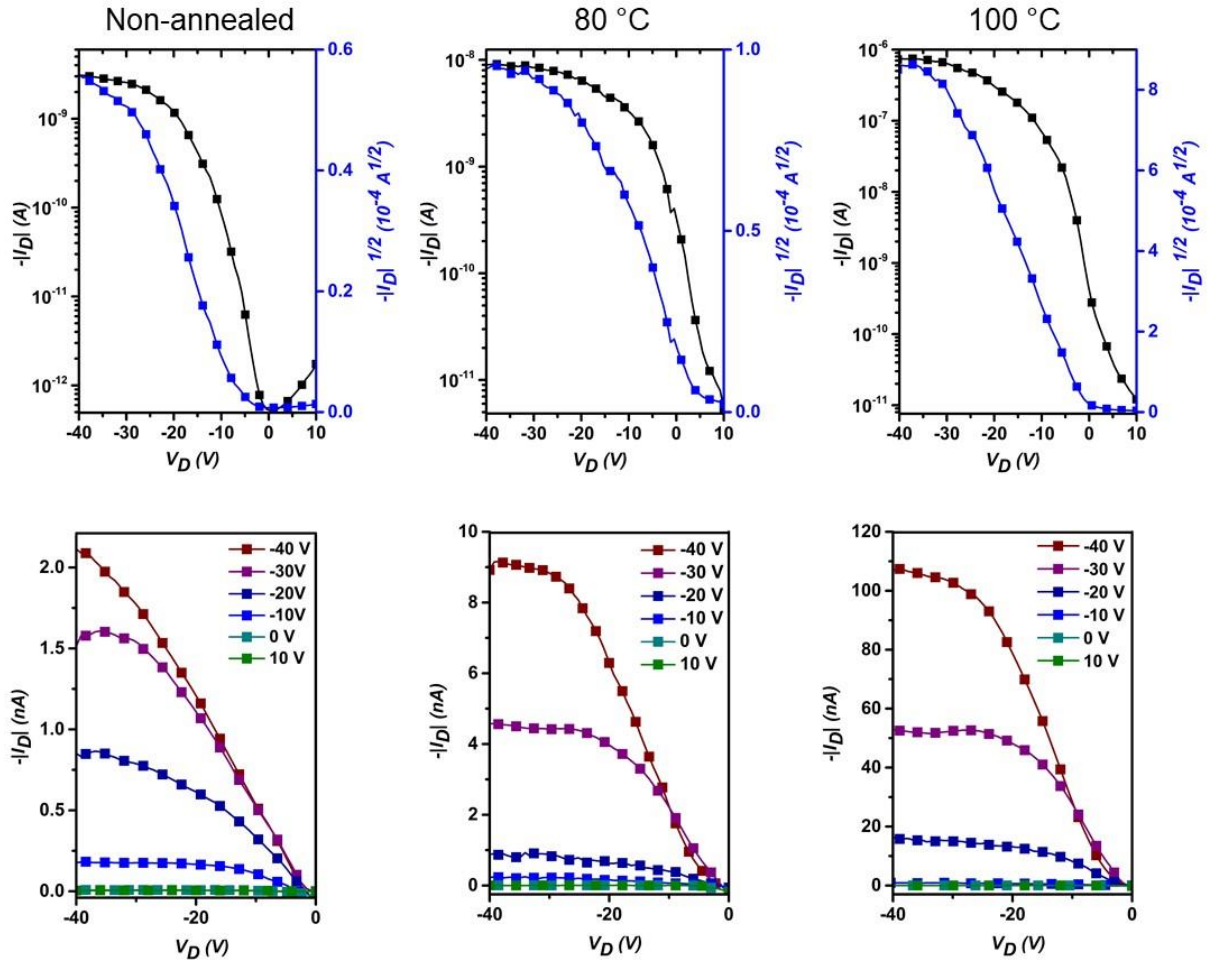


Figure 4.15: Transfer (top) and output (bottom) curves for IN-BT2Se-IGFET at different thermal annealing conditions; annealed for 1 hour under nitrogen atmosphere

Table 4.2: OFETs parameters of IN-BT2Se-IGFET

Annealing Temperature / °C	Maximum hole mobility / $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$	^a Average hole mobility / $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$	Threshold Voltage (V_T) / V	$I_{\text{on/off}}$
Non-annealed	3.28×10^{-4}	1.56×10^{-4}	12.7-(-7.1)	10^3
80	9.30×10^{-4}	6.50×10^{-4}	10.5-(-6.3)	10^3
100	2.57×10^{-2}	1.92×10^{-2}	6.7 – (-8.9)	10^5 - 10^6

^aCalculated from the measurements of 6 devices; Measurements were obtained for BGBC devices with $W = 457 \mu\text{m}$ and $L = 20 \mu\text{m}$ (applied $V_D = -40 \text{ V}$). Thin film were deposited under ambient conditions at 300 rpm from 5 mg/mL solutions in chloroform. Thermal annealing was performed under nitrogen conditions for 1 h.

over its cold crystallization temperature, improved hole mobility of the devices by two orders of magnitude. Maximum hole mobility obtained at optimized conditions was $2.57 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with an average of $1.92 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Threshold voltage (V_T) values ranged from 6.7 – (-8.9) V for the optimized conditions, annealing at 100 °C. V_T has shown a bit narrower range for devices at 100 °C annealing temperature. Moreover, the on-off current ratio ($I_{\text{on/off}}$) was drastically improved from 10^3 to the range of 10^5 - 10^6 for optimized devices at this condition. On the other hand, **IN-BT2F-IN** showed no OFETs-active nature at all. Devices prepared out of **IN-BT2F-IN** showed flat lines with lower currents around 10^{-13} to 10^{-12} A upon increasing V_G at $V_D = -40$ V. **IN-BT2Se-IN** showed one order of magnitude improvement in hole mobility with relatively lower operating voltages and similar $I_{\text{on/off}}$, compared with its thiophene spacer based analog (IN-BT2T-IN; $V_D = -100$ V, $V_G = -100$ V, and $I_{\text{on/off}} = 10^5$ - 10^6).

4.4.4 Surface morphology

Tapping-mode atomic force microscopy (TMAFM) was involved in determining the surface properties of fabricated thin films. Analysis was done for non-annealed thin films and annealed thin films at 100 °C in the channel region with the best-reported mobilities. TMAFM analysis mainly provided an insight into surface topological features of thin films and surface root means square roughness (RMS) data. Collected height and phase images at corresponding annealing temperatures are given in Figure 4.16a. For **IN-BT2F-IN**, there were not any detailed topological features observed for non-annealed thin films except for small bubbles on the surface formed probably due to trapped air between the thin film and silicon substrate. Upon thermal annealing at 100 °C, there was not much improvement seen in crystallinity features, but trapped air might have expanded to provide existing widely spread bubble-like features in the scanned

area. However, due to the expanded bubble-like features on the thin film surface, RMS increased from 5.54 nm to 27.60 nm upon thermal annealing. On the other hand, **IN-BT2Se-IN** exhibited small crystalline domain features on the thin film surface for non-annealed films which were further developed into relatively significantly larger long-plate-like crystalline domains. In this case, RMS increased from 10.60 nm to 32.70 nm upon thermal annealing at 100 °C relative to non-annealed films. In order to further investigate long-range ordered plate-like features on the thin film surface, the scanning area was further expanded, expecting to see more features (see Figure 4.16b). In expanded area scanning proved the existence of more long-range driven crystalline boundaries. When the scanned area was getting larger, calculated RMS values increased correspondingly from 31.79 nm, 62.82 nm, to 78.30 nm (refer to Figure 4.16b). To clearly visualize how the thin film topology is structured in thin films, 3D versions of the height data images are shown in Figure 4.16c. A regular image of the thin film captured under TMAFM focusing camera is also provided in Figure 4.16d to further demonstrate how the annealed thin film displayed its crystalline features. Somehow, compared with the previously reported thiophene derivative, **IN-BT2Se-IN** has shown better crystalline thin film morphology at optimized conditions. These results are well-aligned with mobility data trends observed for compared small molecules.

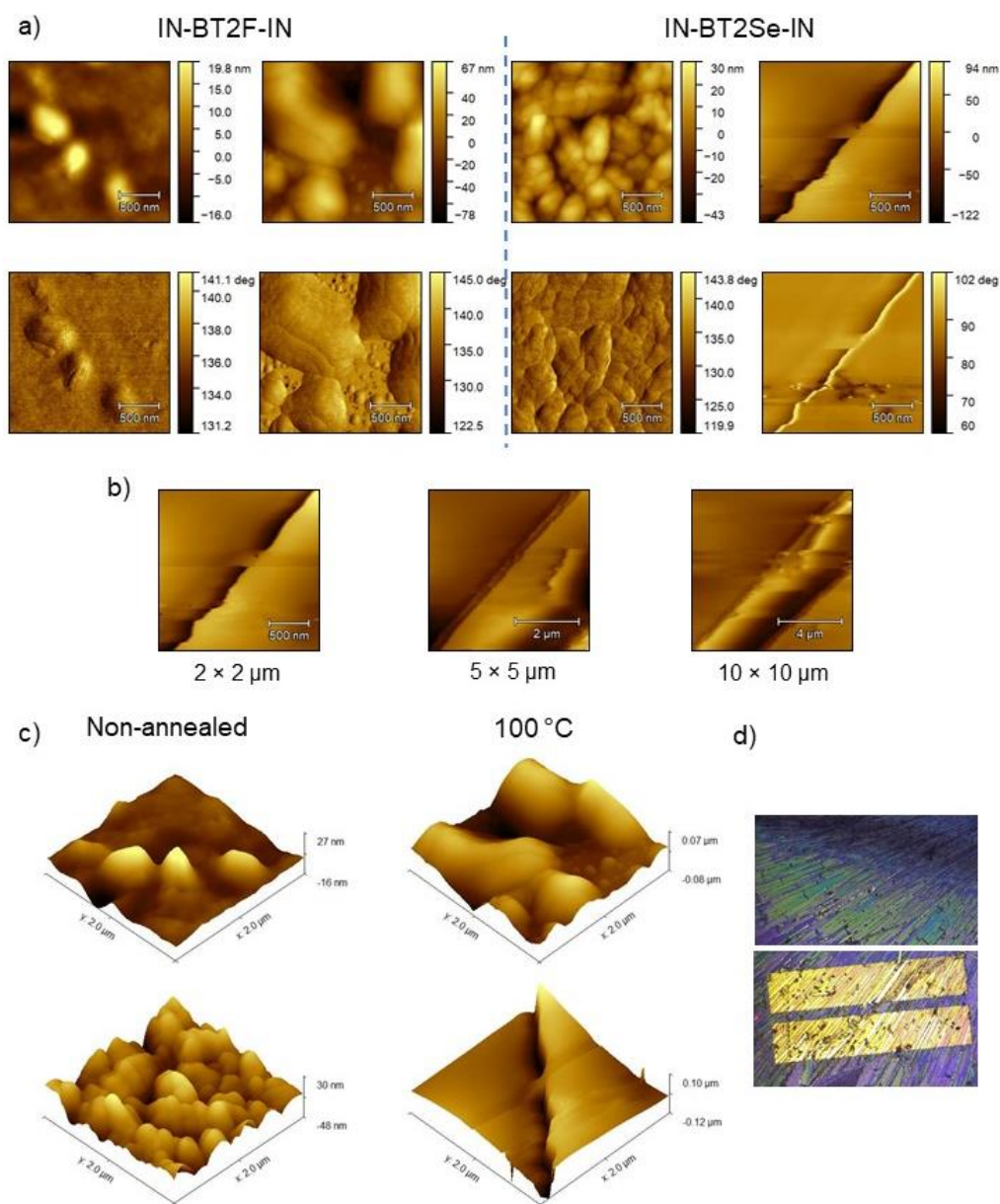


Figure 4.16: a) Height (top) and phase (bottom) TMAFM images of **IN-BT2F-IN** (left) and **IN-BT2Se-IN** (right); In each side, the first column depicted images of non-annealed thin films while the second column include images of annealed thin films at 100 °C. b) TMAFM height images taken for **IN-BT2Se-IN** annealed thin film (at 100 °C); scanned for different window sizes (left to right - $2 \times 2 \mu\text{m}$, $5 \times 5 \mu\text{m}$, and $10 \times 10 \mu\text{m}$) to obtain apparent morphological features; c) 3D-images for TMAFM height data of both **IN-BT2F-IN** (top) and **IN-BT2Se-IN** (bottom) small molecules at non-annealed (left) and annealed at 100 °C (right) conditions; d) Images of thin films fabricated on transistor devices (thin film on OTMS modified silica (top) & gold electrode with the channel region (bottom)) as captured by TMAFM instrument's focusing camera.

4.4.5 Grating incident X-ray diffraction (GIXRD) analysis

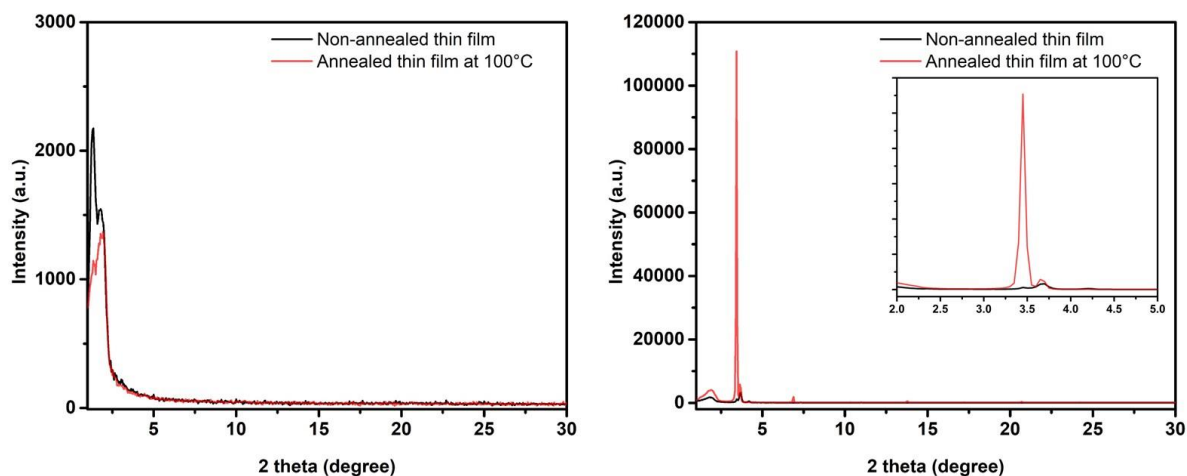


Figure 4.17. Out-of-plane GIXRD spectra of **IN-BT2F-IN** (left) and **IN-BT2Se-IN** (right)

Out of plane GIXRD analysis was performed on both non-annealed and annealed thin films at 100 °C to further analyze the crystalline features. Obtained GIXRD spectra for both small molecules are depicted in Figure 4.17. GIXRD spectra taken for both non-annealed and annealed thin films of **IN-BT2F-IN** showed no distinctive diffraction peaks, indicating no significant crystallinity in both conditions. This data further confirmed that the observed topological features in TMAFM images of both non-annealed and annealed thin films of **IN-BT2T-IN** were not crystalline. However, compared to non-annealed thin films of **IN-BT2Se-IN**, annealed thin films at 100 °C exhibited a highly intense narrower peak arising from the first order (100) crystalline plane, implying highly ordered long-range dispersed crystalline domains in thin films. The annealed thin film of **IN-BT2Se-IN** displayed the corresponding (100) Bragg's reflection peak at $2\theta = 3.45^\circ$ from which the lamellar d-spacing value was determined to be 25.6 Å. This data also provided a clue about existing highly ordered edge-on oriented small molecules in thin films as they were forced to be arranged by the OTMS modified silicon dioxide surfaces. Compared with

previously reported IN-BT2T-IN, **IN-BT2Se-IN** showed almost comparable lamellar d-spacing values (25.9 Å, IN-BT2T-IN) but with ~10 times of intensity in (100) peak.

4.5 Conclusion

In summary, indole- and BT-based two DA small molecules with furan and selenophene spacers were synthesized and characterized for optoelectronic properties and thin film properties following OFETs applications. Further, results were compared with previously reported thiophene analogs to understand the structure-property relationship by varying the chalcogenophene in indole-based DA small molecules. Optoelectronic studies indicated that the introduction of selenophene (**IN-BT2Se-IN**) into the small molecular design drastically reduced the bandgap via lowering the LUMO level by ~0.4 eV compared with its thiophene derivative (IN-BT2T-IN). Both furan and thiophene derivatives showed an almost identical bandgap but with more elevated HOMO and LUMO for thiophene analogous. OFETs data obtained for **IN-BT2Se-IN** showed average hole mobility of $1.92 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with a maximum of $2.57 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Meanwhile, **IN-BT2F-IN** displayed no OFETs activity. Acquired average mobility data for **IN-BT2Se-IN** was about one order of magnitude higher than that of IN-BT2T-IN with lower operational voltages. TMAFM experiments clearly indicated the presence of highly ordered thin film morphology in **IN-BT2Se-IN** compared to its furan derivative. When compared with previously reported thiophene derivatives, **IN-BT2Se-IN** has long-range-ordered crystalline domains as indicated by topological height data and RMS values. The presence of highly ordered **IN-BT2Se-IN** thin films was also confirmed by GIXRD analysis. In conclusion, observed mobility

trends were well-supported by optoelectronic, morphological, and GIXRD experimental results in this study.

4.6 References

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APPENDIX A

**SILOXANE SIDE-CHAIN MODIFIED DIKETOPYRROLOPYRROLE AND
THIENOPYRROLE CONTAINING SMALL MOLECULES FOR ORGANIC FIELD-
EFFECT TRANSISTORS**

^1H and ^{13}C NMR Spectra

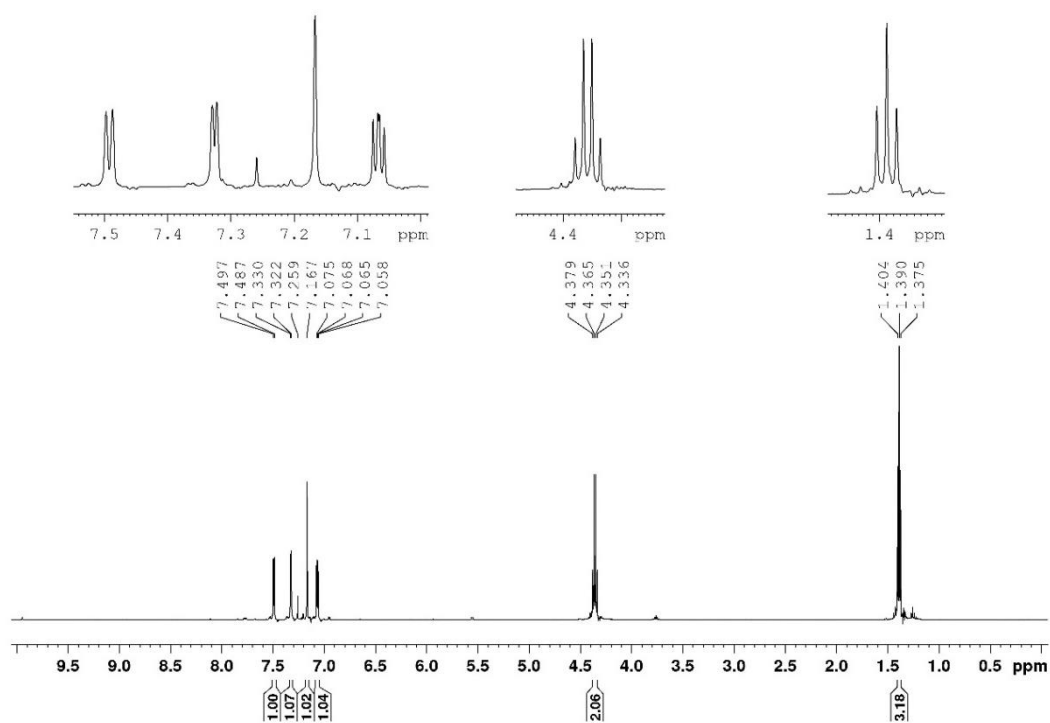


Figure A.1: ^1H NMR of ethyl (Z)-2-azido-3-(thiophen-2-yl)acrylate (**1**)

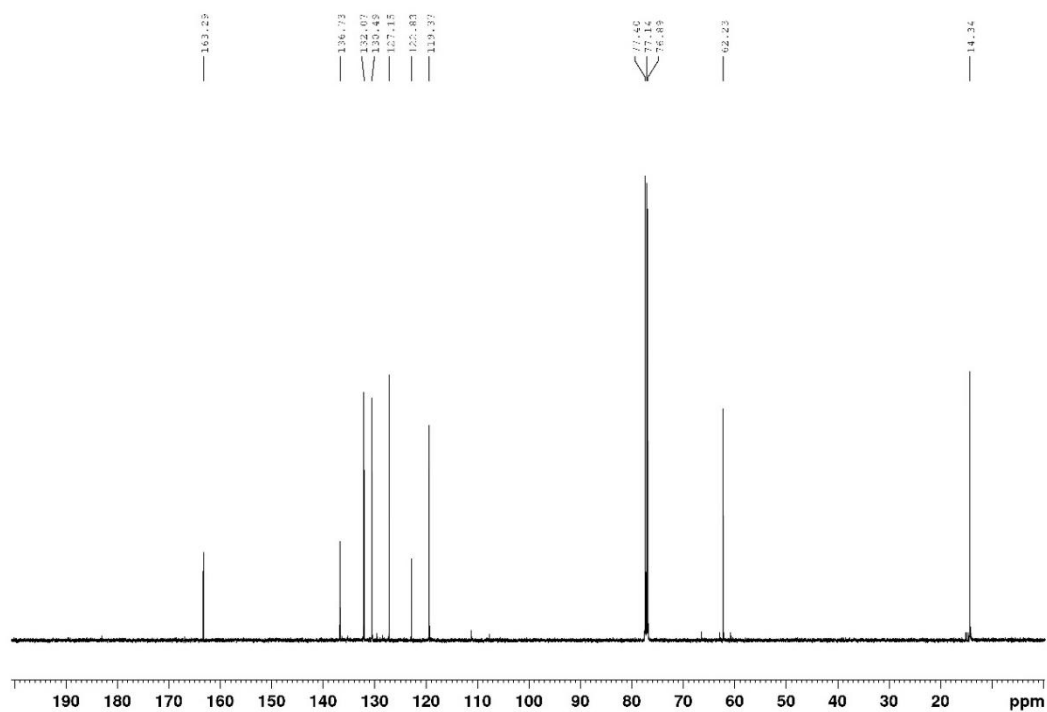


Figure A.2: ^{13}C NMR of ethyl (Z)-2-azido-3-(thiophen-2-yl)acrylate (**1**)

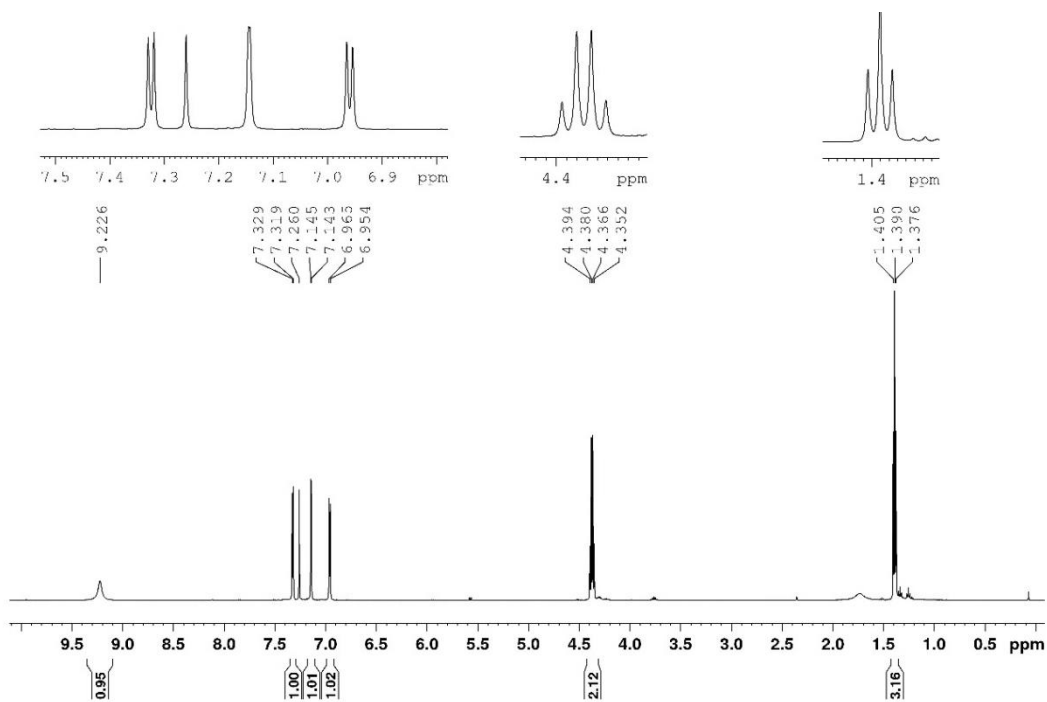


Figure A.3: ^1H NMR of ethyl 4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate (**2**)

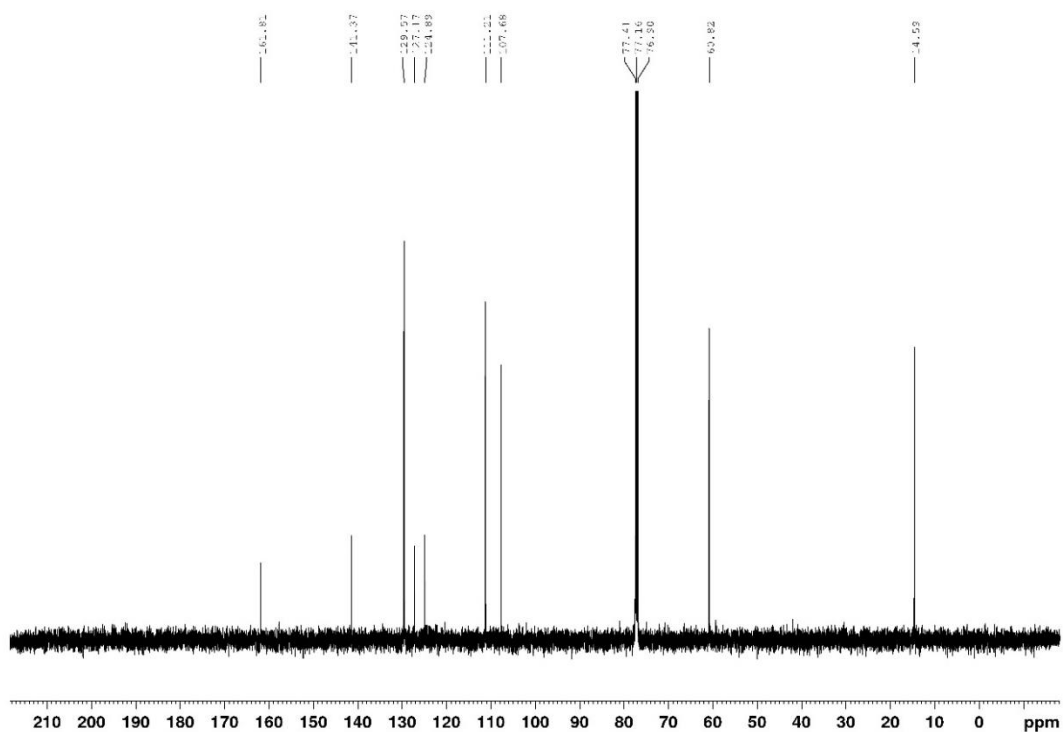


Figure A.4: ¹³C NMR of ethyl 4H-thieno[3,2-b]pyrrole-5-carboxylate (2)

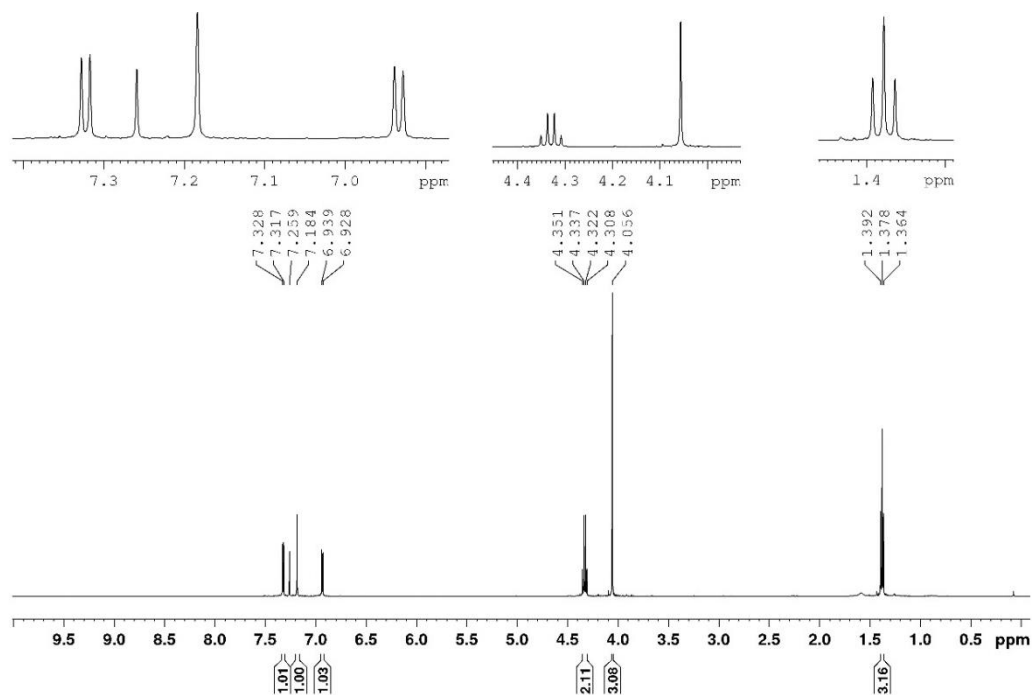


Figure A.5: ¹H NMR of ethyl 4-methyl-4H-thieno[3,2-b]pyrrole-5-carboxylate (3)

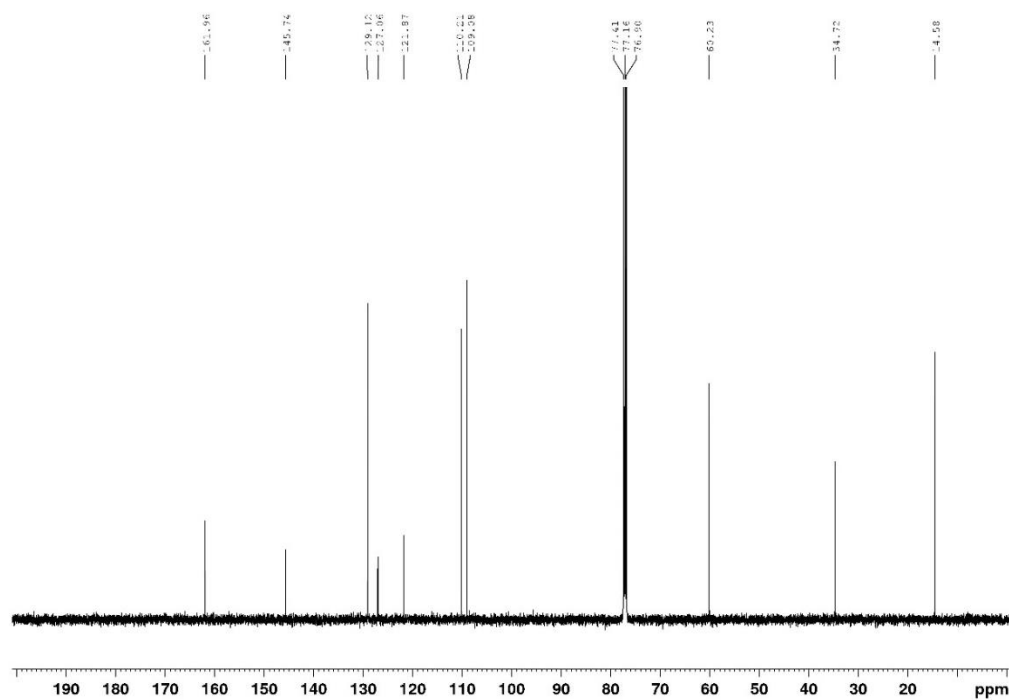


Figure A.6: ¹³C NMR of ethyl 4-methyl-4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate (**3**)

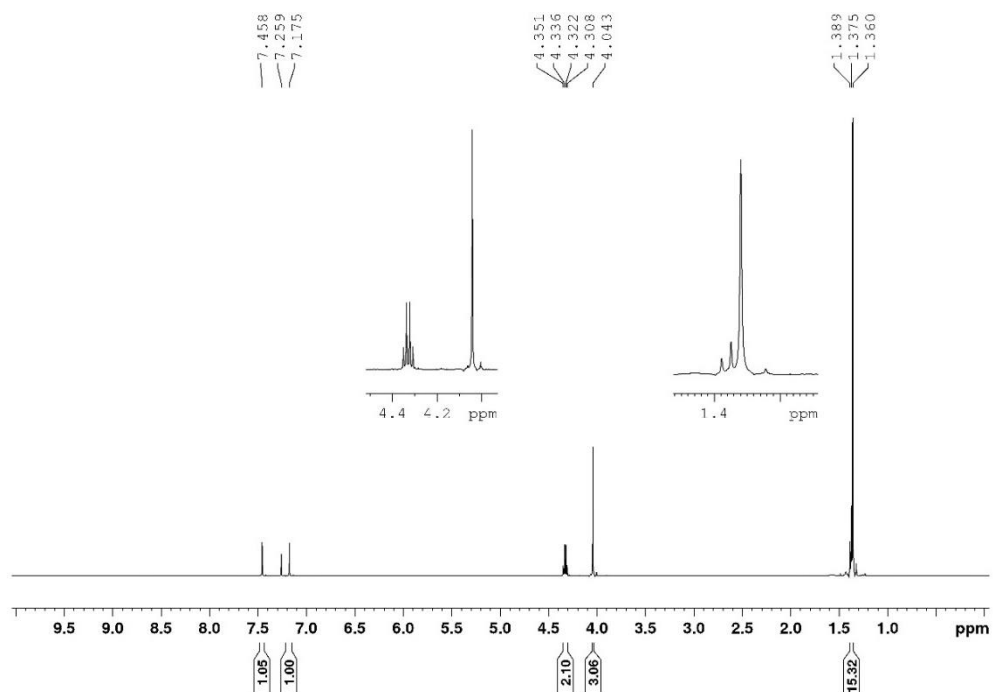


Figure A.7: ¹H NMR of ethyl 4-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate (**4**)

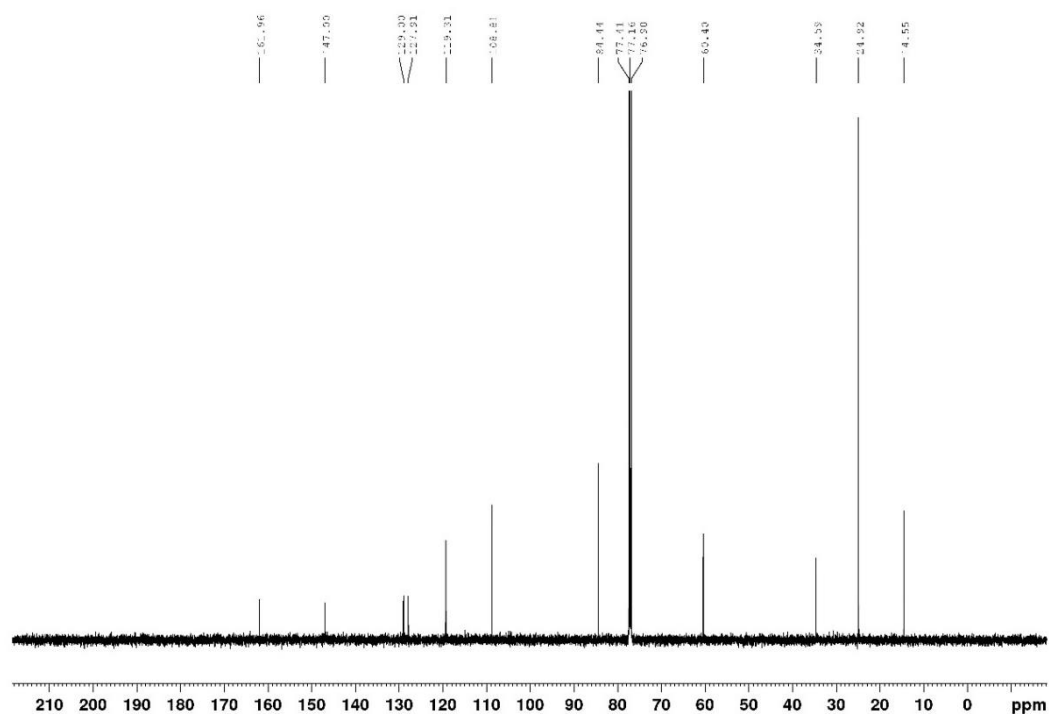


Figure A.8: ^{13}C NMR of ethyl 4-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4H-thieno[3,2-*b*]pyrrole-5-carboxylate (**4**)

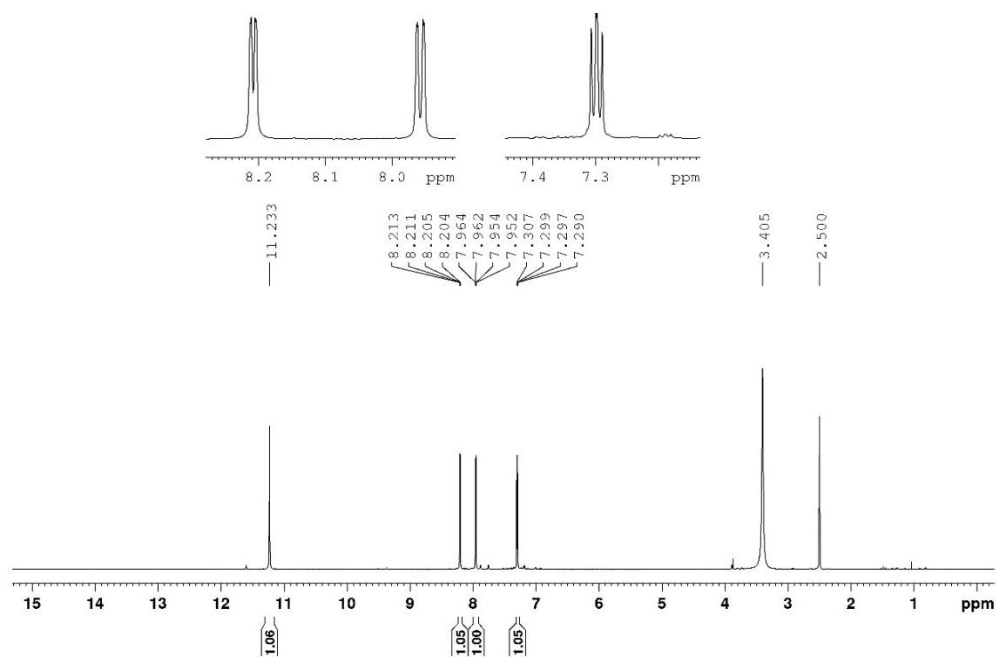


Figure A.9: ^1H NMR of 3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (**5**)

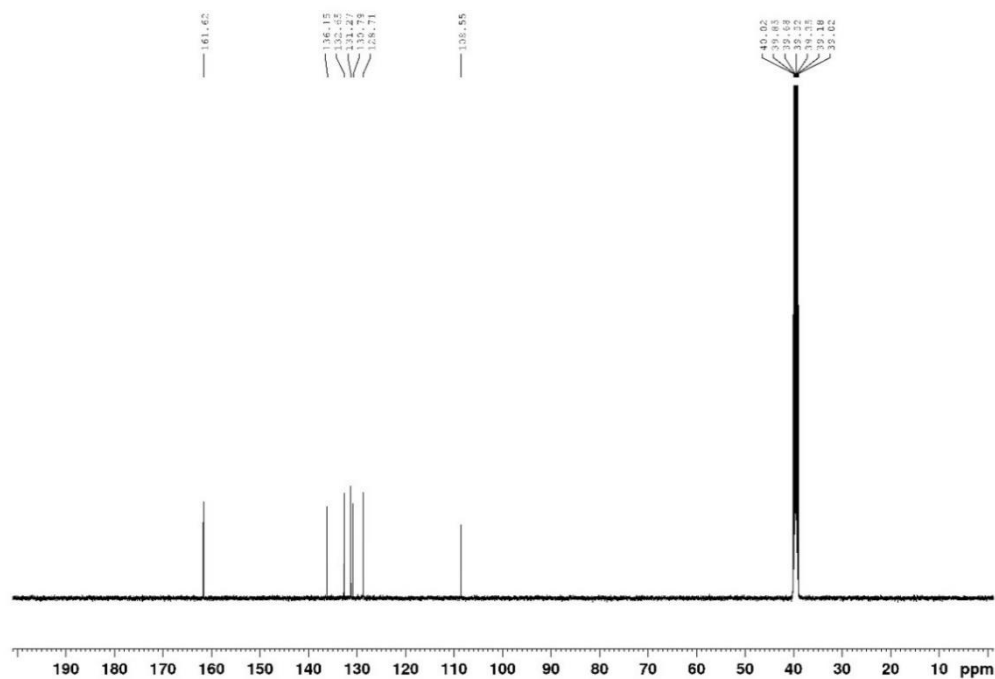


Figure A.10: ¹³C NMR of 3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (5)

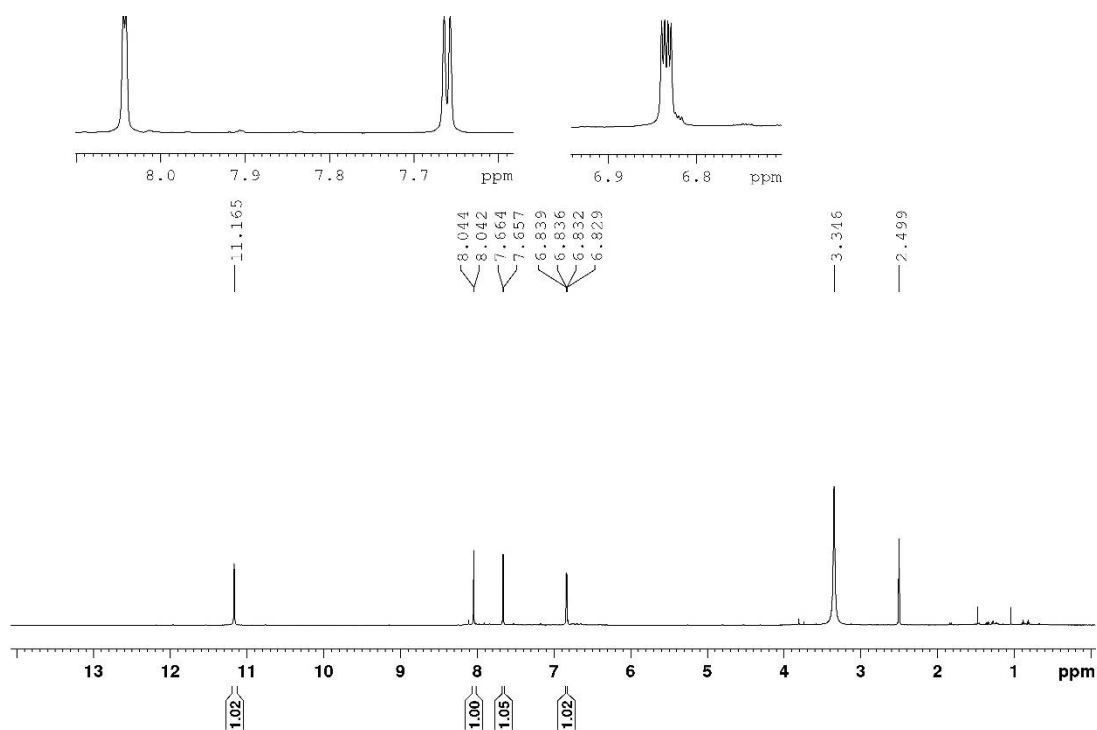


Figure A.11: ¹H NMR of 3,6-di(furan-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (6)

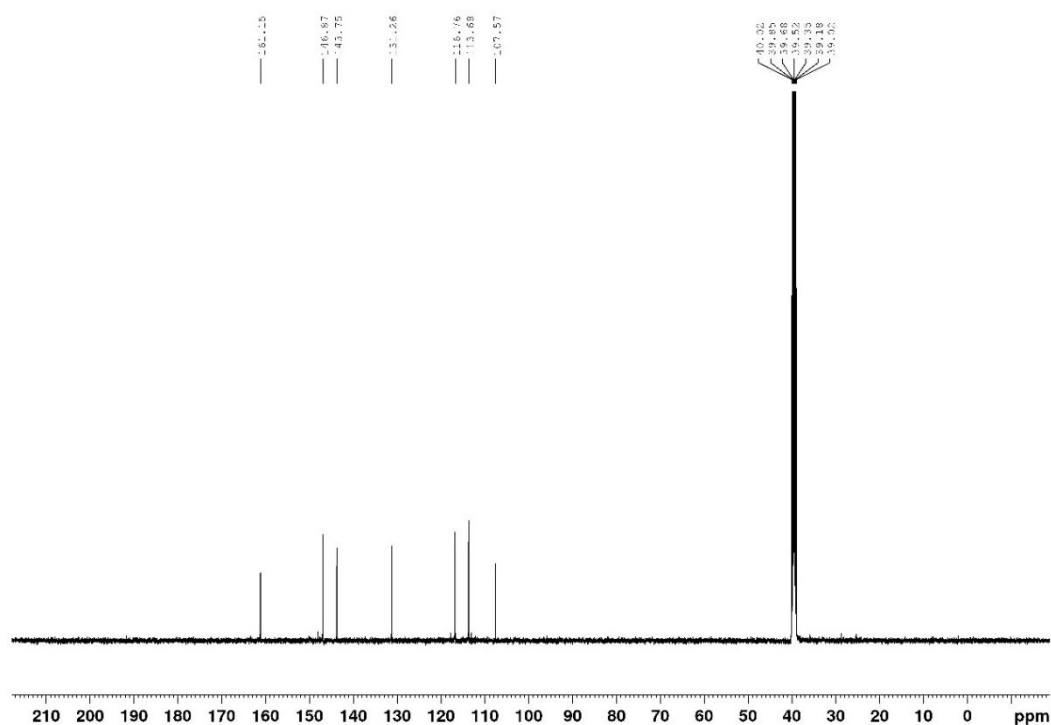


Figure A.12: ^{13}C NMR of 3,6-di(furan-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**6**)

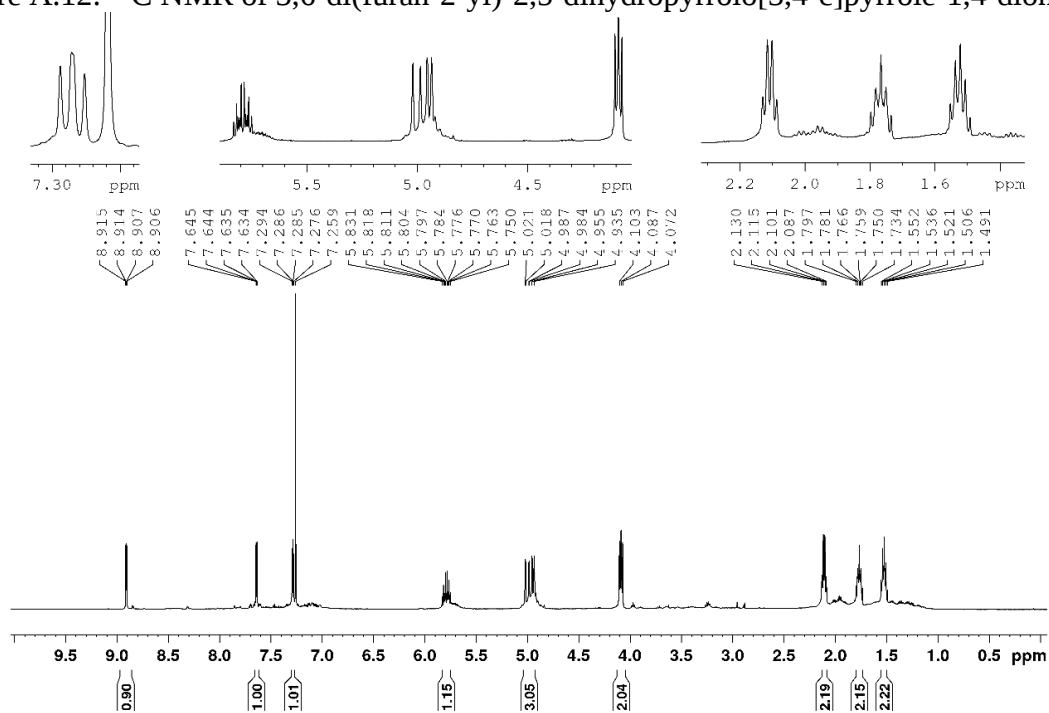


Figure A.13: ^1H NMR of 2,5-di(hex-5-en-1-yl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**7**)

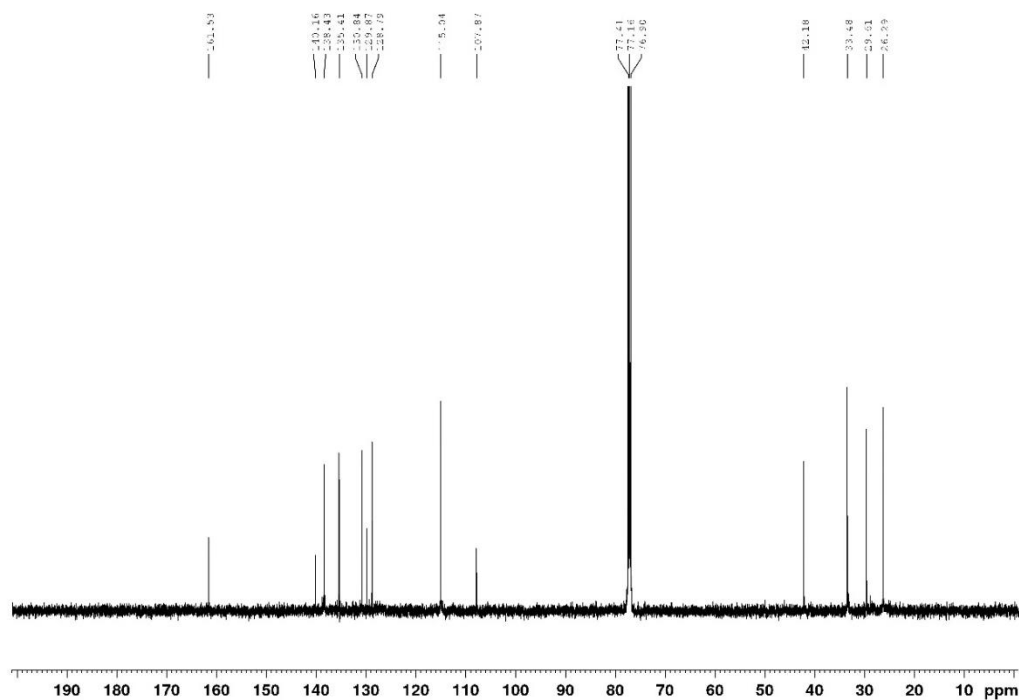


Figure A.14: ^{13}C NMR of 2,5-di(hex-5-en-1-yl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**7**)

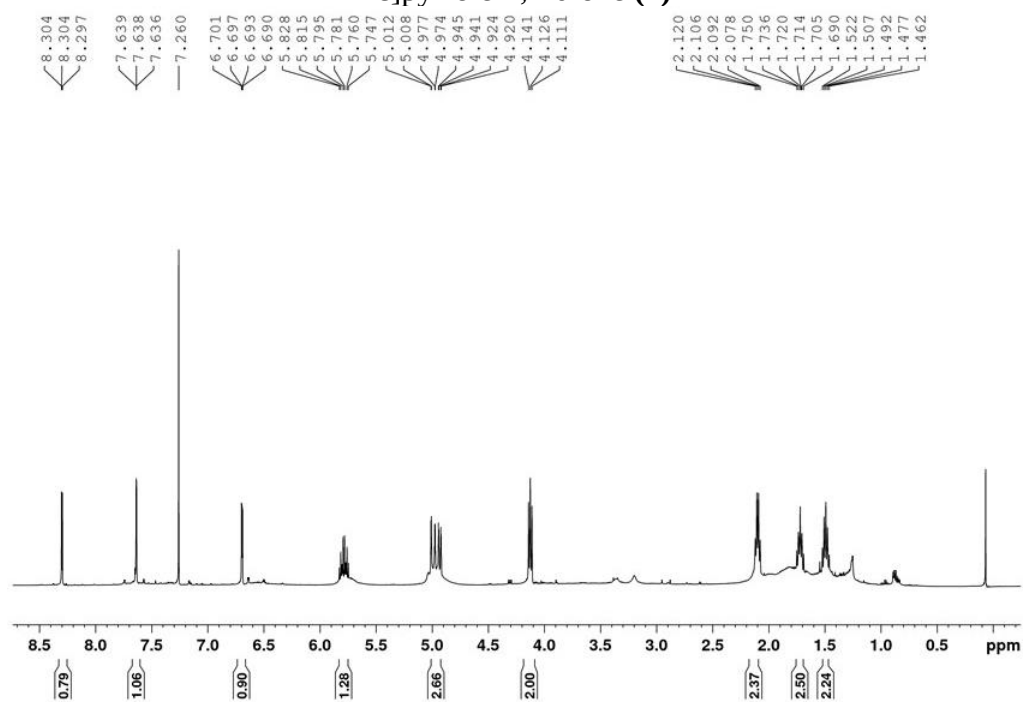


Figure A.15: ^1H NMR of 3,6-di(furan-2-yl)-2,5-di(hex-5-en-1-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**8**)

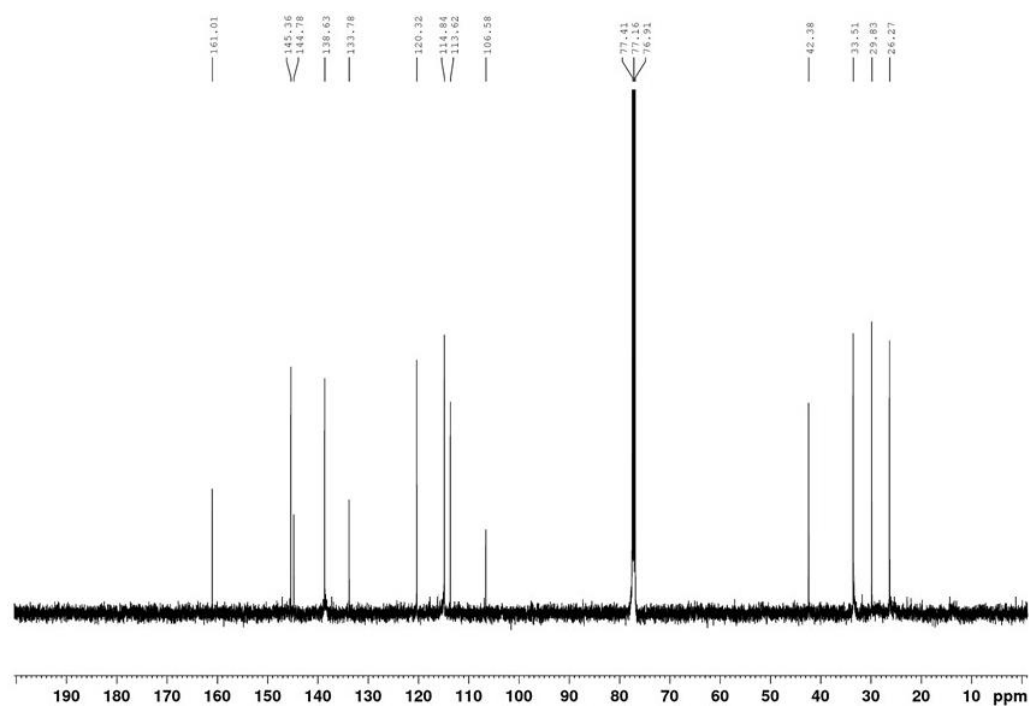


Figure A.16: ^{13}C NMR of 3,6-di(furan-2-yl)-2,5-di(hex-5-en-1-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**8**)

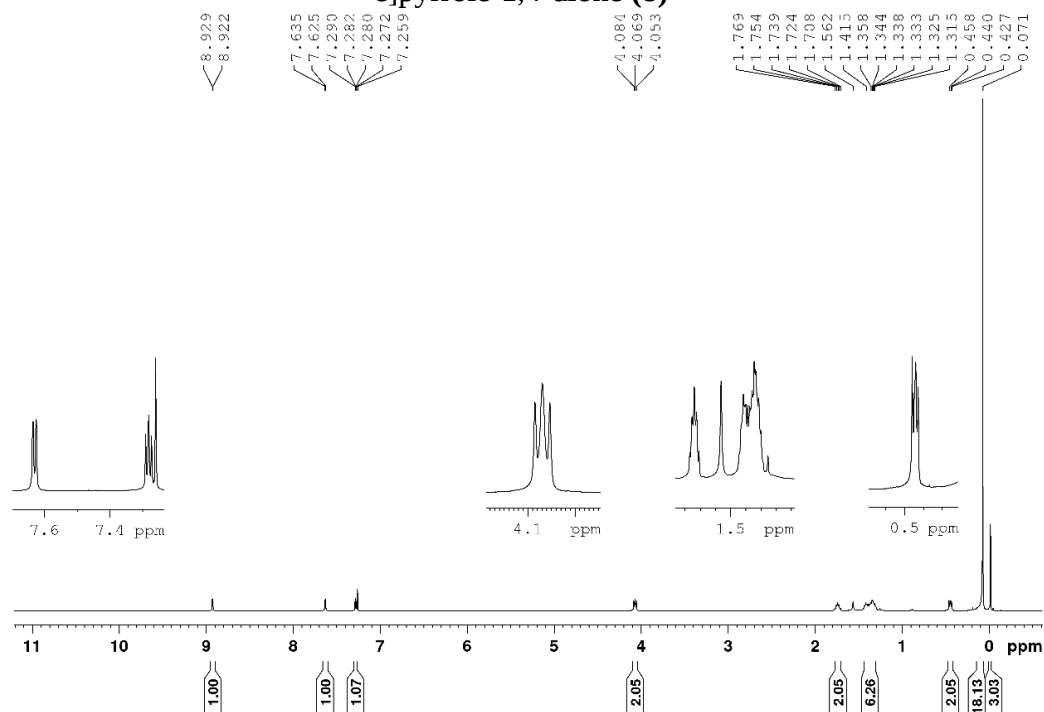


Figure A.17: ^1H NMR of 2,5-bis(6-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)hexyl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**9**)

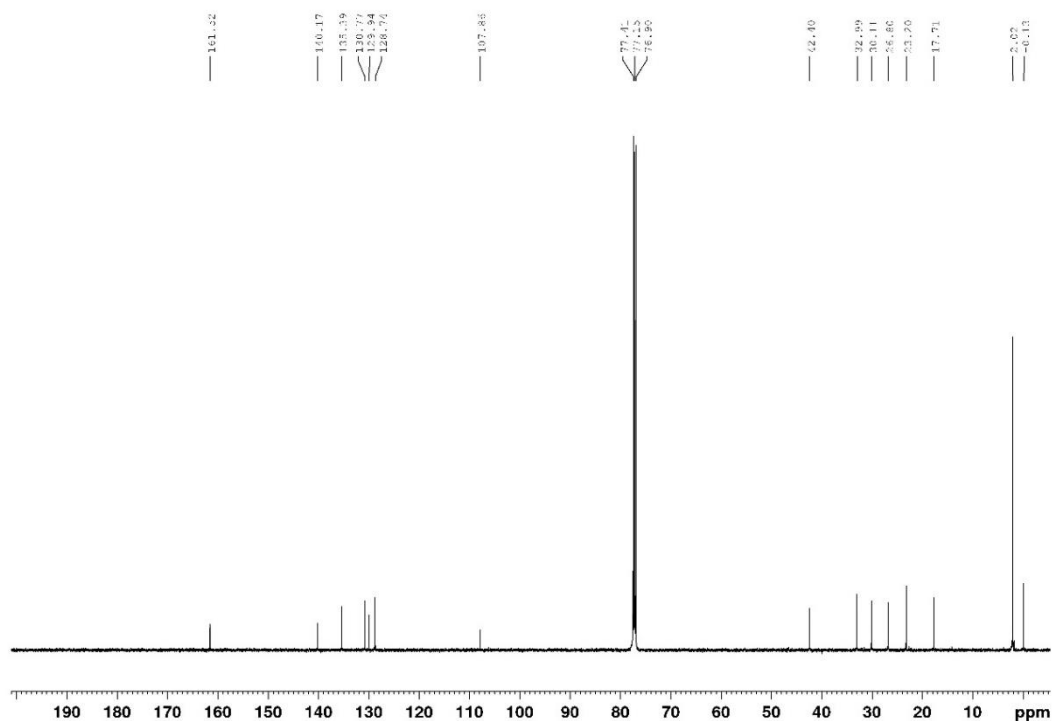


Figure A.18: ^{13}C NMR of 2,5-bis(6-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)hexyl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**9**)

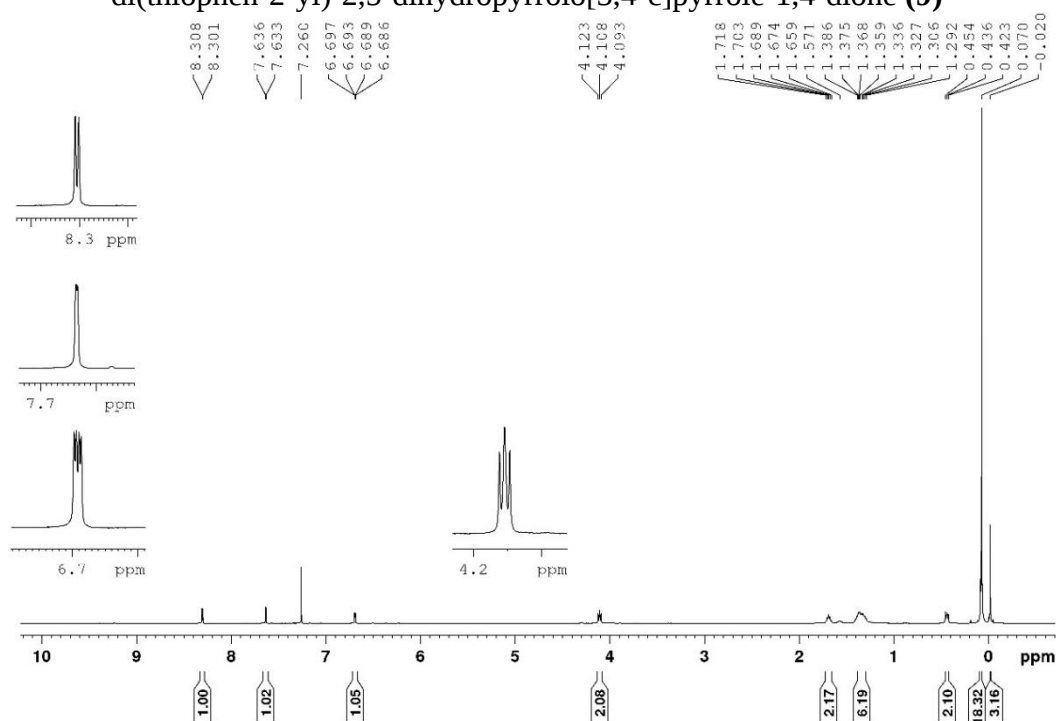


Figure A.19: ^1H NMR of 3,6-di(furan-2-yl)-2,5-bis(6-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)hexyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**10**)

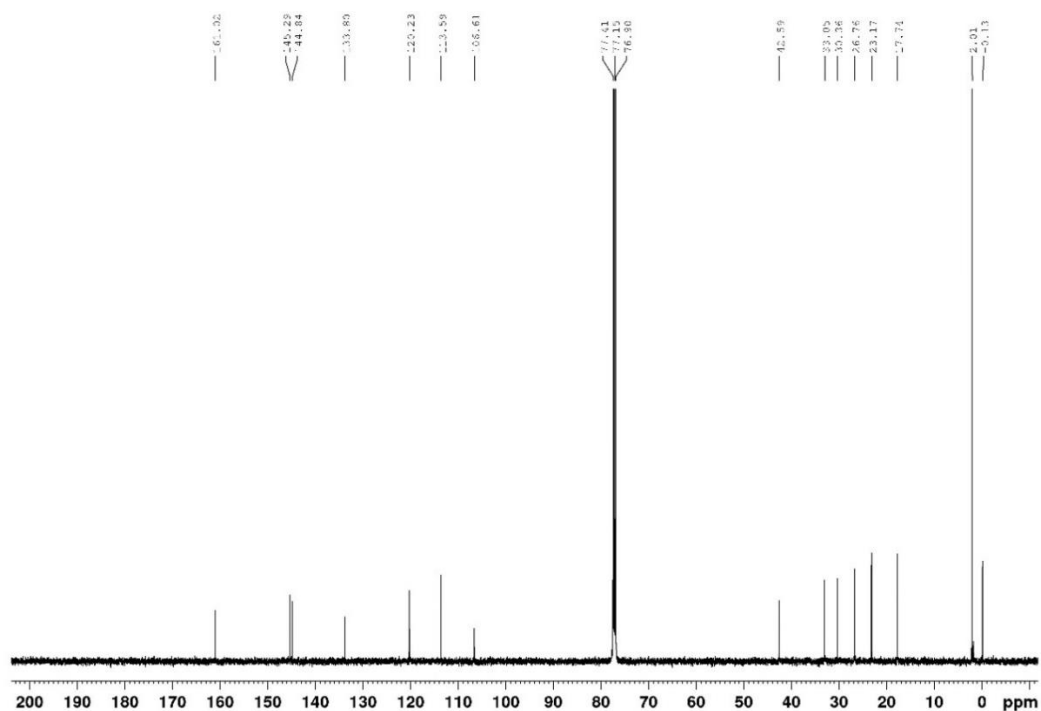


Figure A.20: ^{13}C NMR of 3,6-di(furan-2-yl)-2,5-bis(6-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)hexyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**10**)

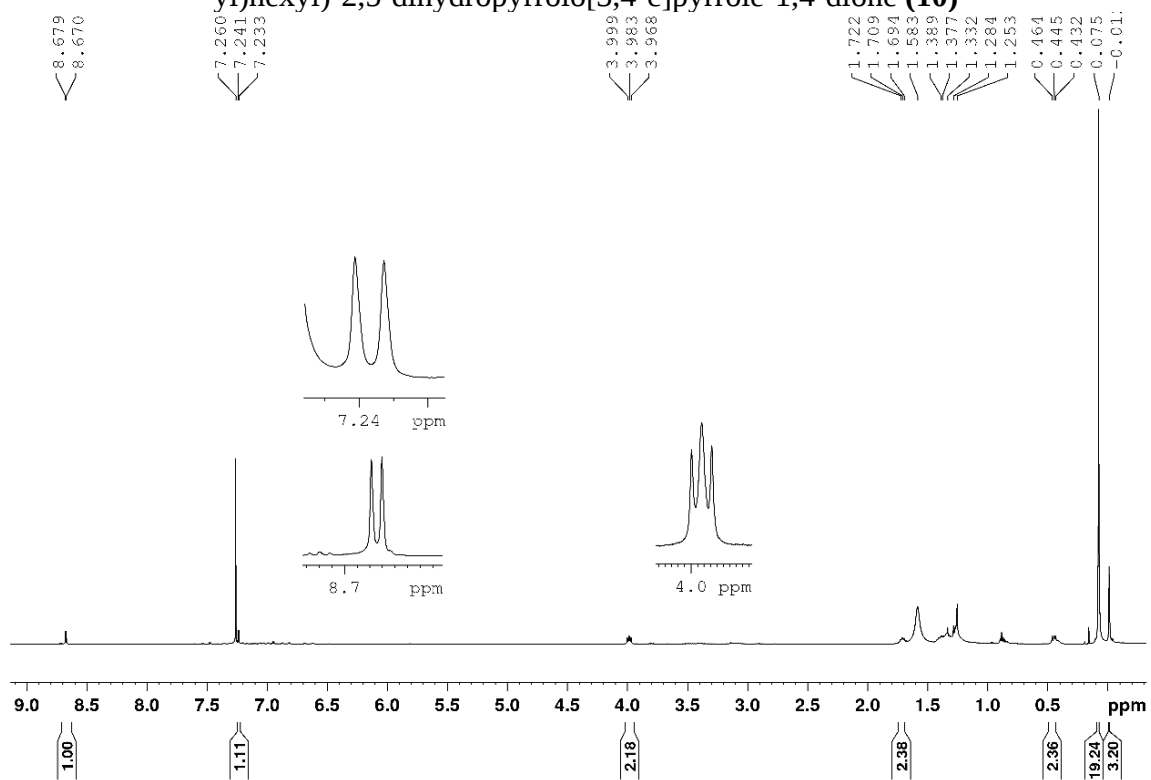


Figure A.21: ^1H NMR of 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(6-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)hexyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**11**)

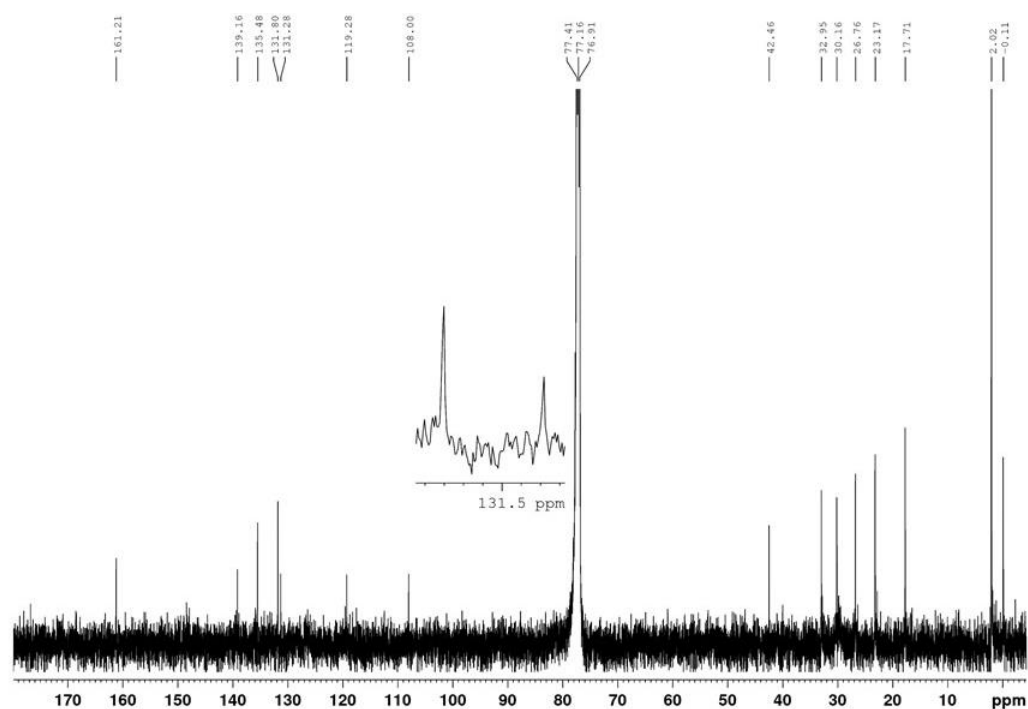


Figure A.22: ^{13}C NMR of 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(6-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)hexyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**11**)

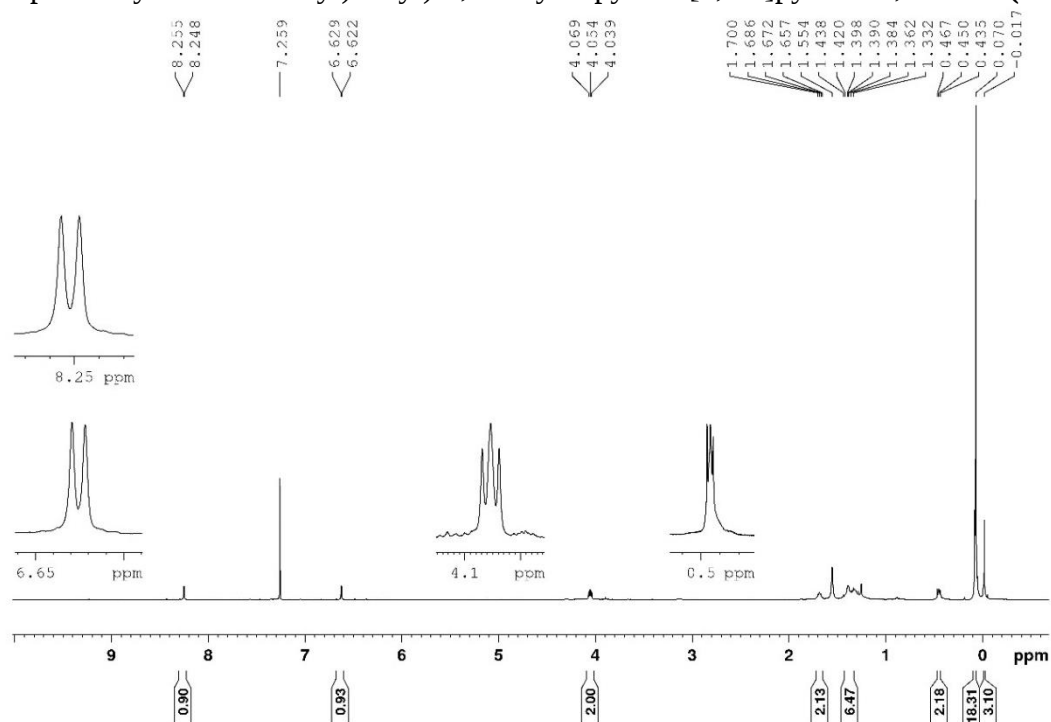


Figure A.23: ^1H NMR of 3,6-bis(5-bromofuran-2-yl)-2,5-bis(6-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)hexyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**12**)

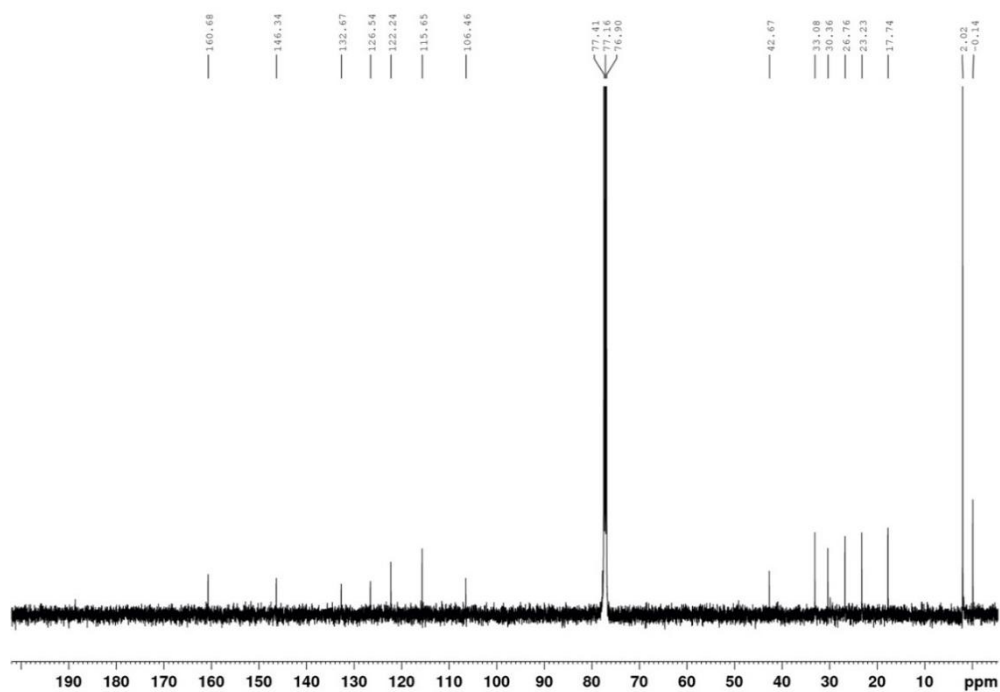


Figure A.24: ^{13}C NMR of 3,6-bis(5-bromofuran-2-yl)-2,5-bis(6-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)hexyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**12**)

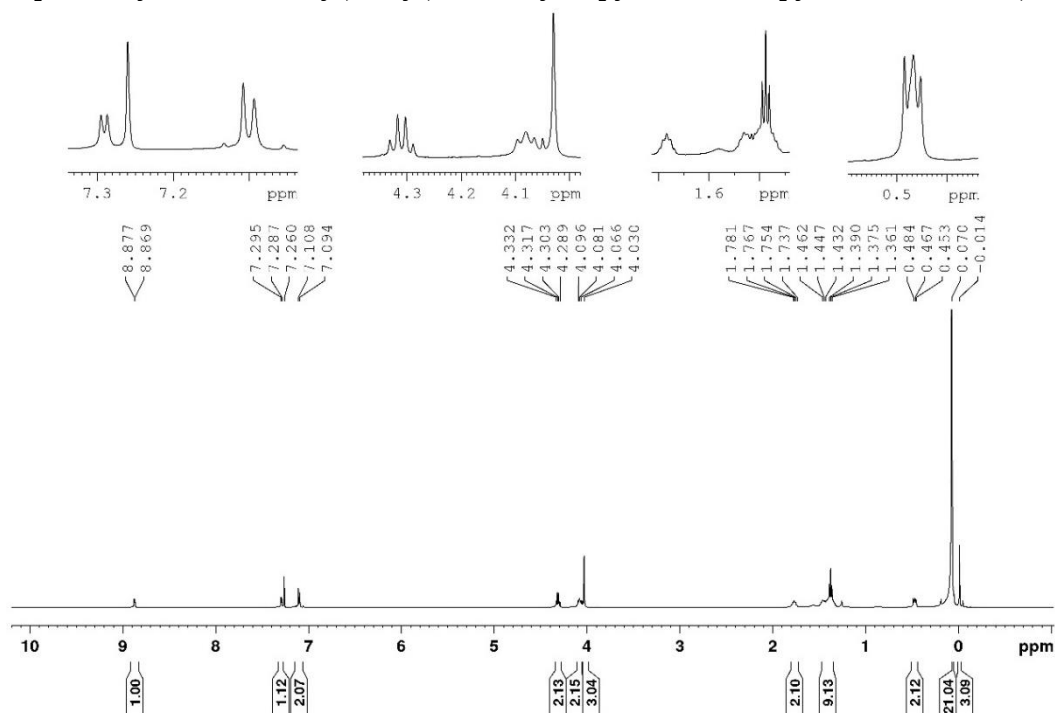


Figure A.25: ^1H NMR of DPP-2T-2TP

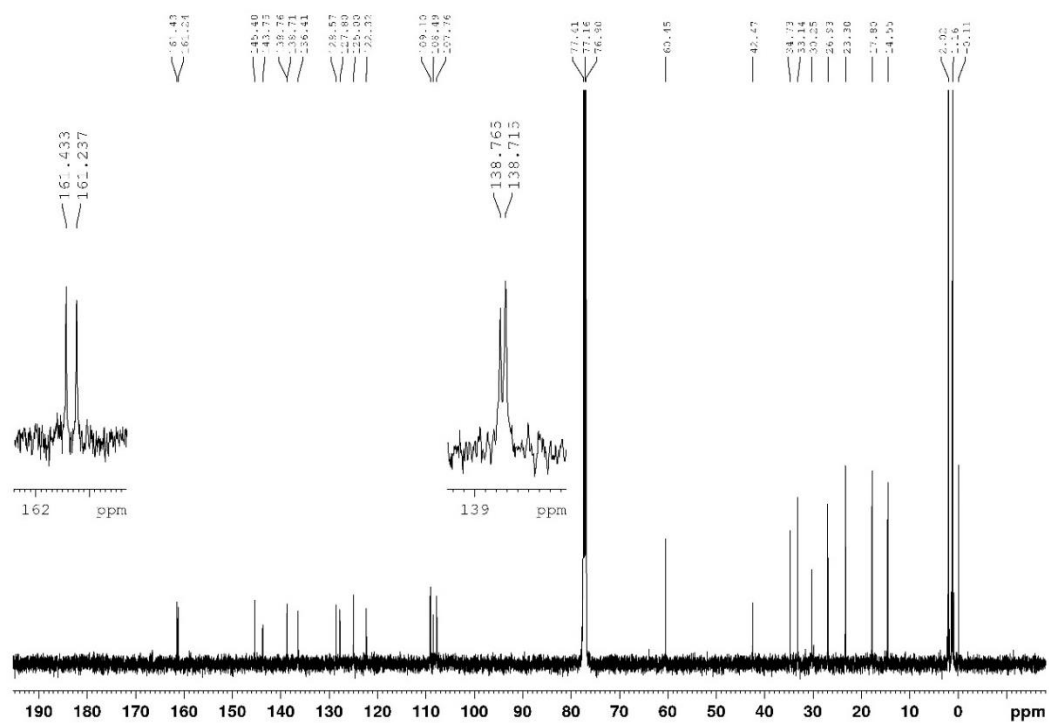


Figure A.26: ^{13}C NMR of DPP-2T-2TP

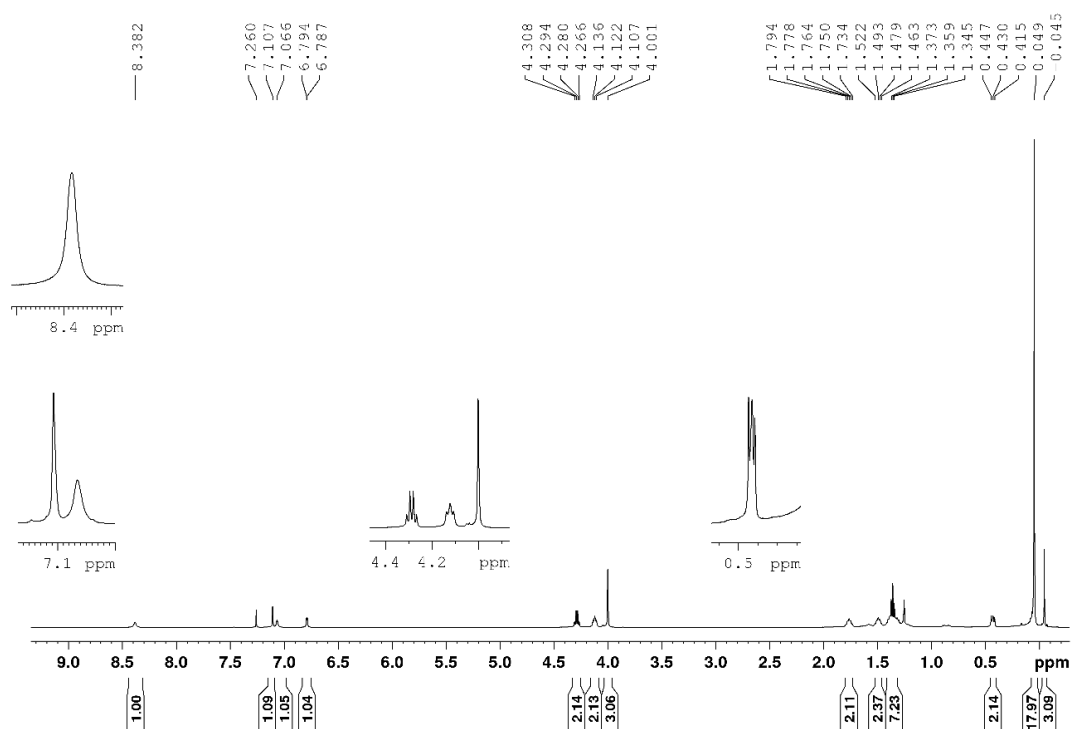


Figure A.27: ^1H NMR of DPP-2F-2TP

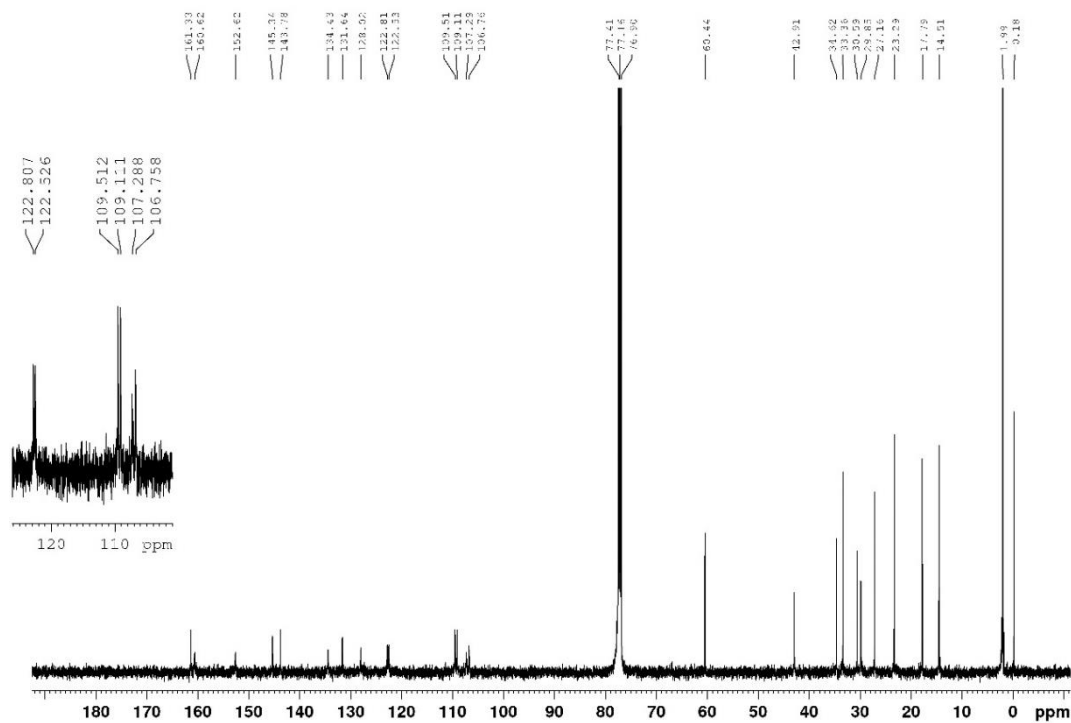


Figure A.28: ^{13}C NMR of DPP-2F-2TP

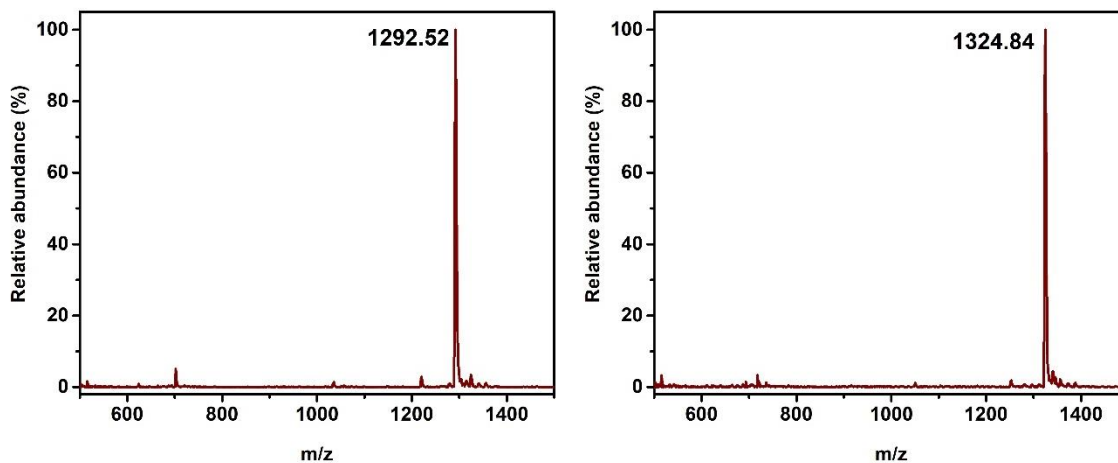


Figure A.29: MALDI-TOF mass spectra of DPP-2T-2TP (left) and DPP-2F-2TP (right)

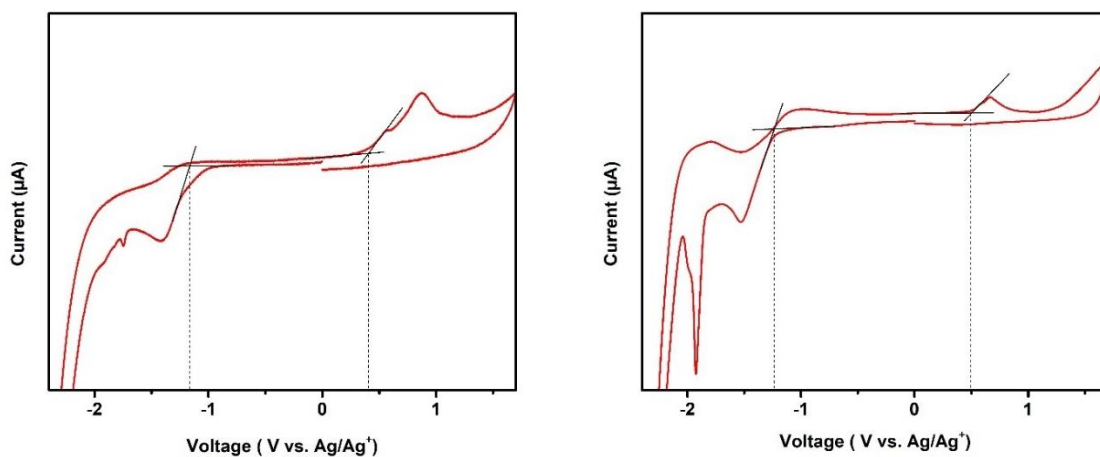


Figure A.30: Cyclic voltammograms of DPP-2T-2TP (left) and DPP-2F-2TP (right)

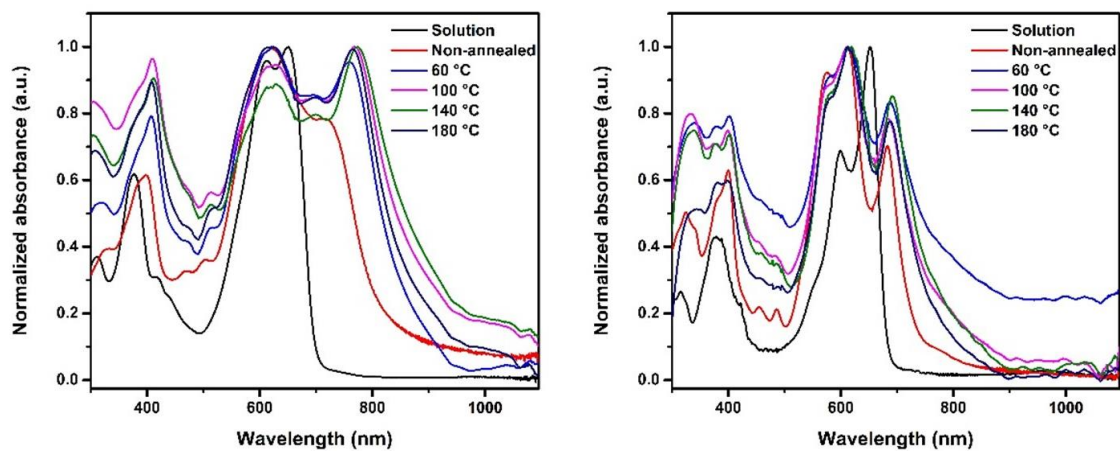


Figure A.31: UV-Vis spectral behavior of thin films upon annealing at different temperatures compared with in-solution (CHCl_3) for DPP-2T-2TP (left) and DPP-2T-2TP (right), respectively

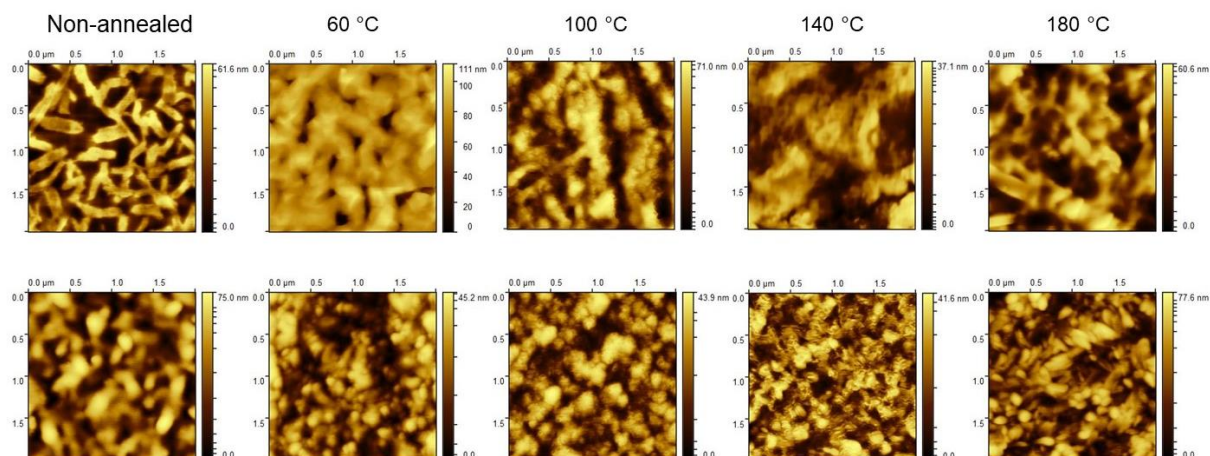


Figure A.32: TMAFM height images of DPP-2T-2TP (top) and DPP-2F-2TP (bottom) at different annealing temperatures. scanned area in each case is $2 \mu\text{m} \times 2 \mu\text{m}$

Table A.1: Root mean square roughness (S_q) values for thermally annealed thin films

Small molecule	Annealing temperature/ $^{\circ}\text{C}$	S_q / nm
DPP-2T-2TP	Non-annealed	11.76
	60	15.24
	100	10.54
	140	4.05
	180	8.65
DPP-2F-2TP	Non-annealed	10.24
	60	6.77
	100	5.54
	140	5.06
	180	10.02

APPENDIX B

1H-INDOLE AND PYRROLO[2,3-B]PYRIDINE AS PYRROLE-FUSED DONORS IN DONOR-ACCEPTER SMALL MOLECULES FOR ORGANIC FIELD-EFFECT TRANSISTORS

¹H and ¹³C NMR spectra of synthesized materials

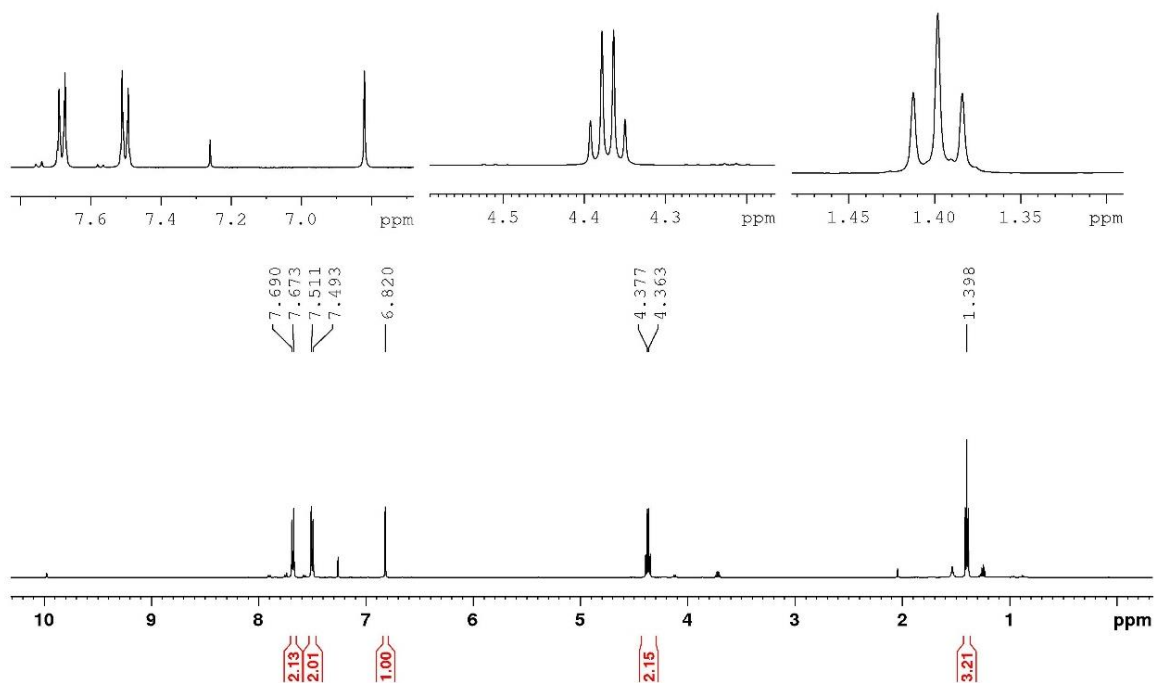


Figure B.1: ¹H NMR Ethyl (Z)-2-azido-3-(4-bromophenyl)acrylate [3]

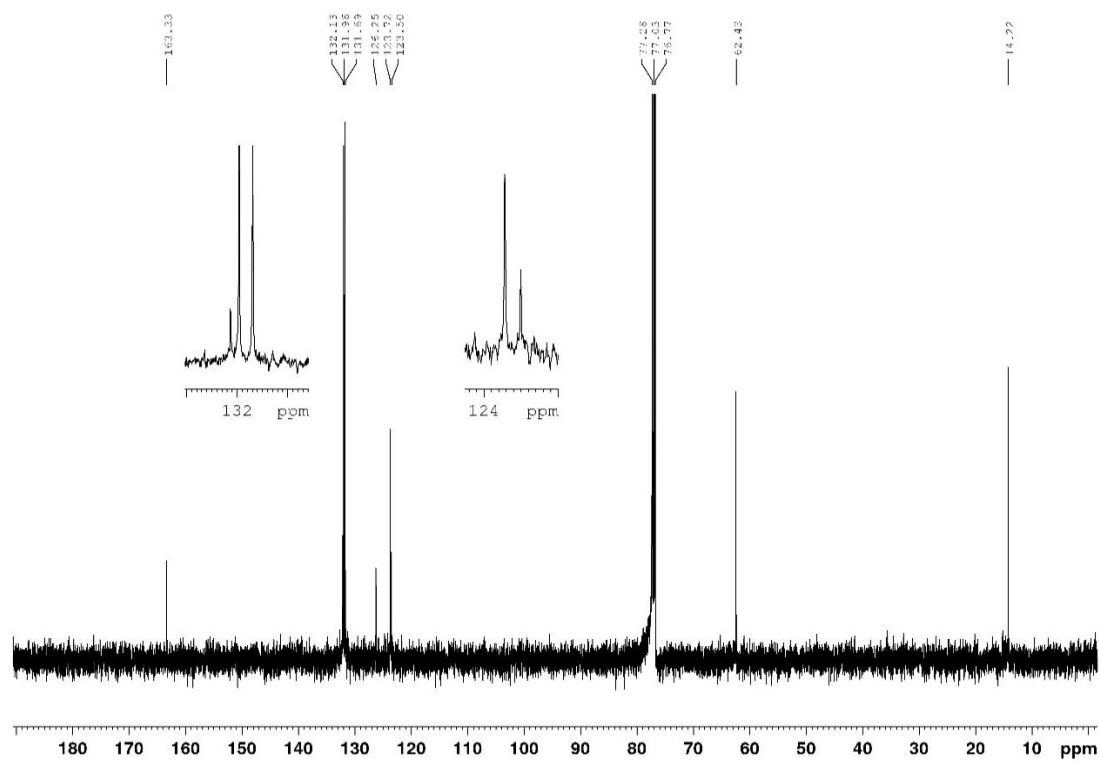


Figure B.2: ¹³C NMR Ethyl (Z)-2-azido-3-(4-bromophenyl)acrylate [3]

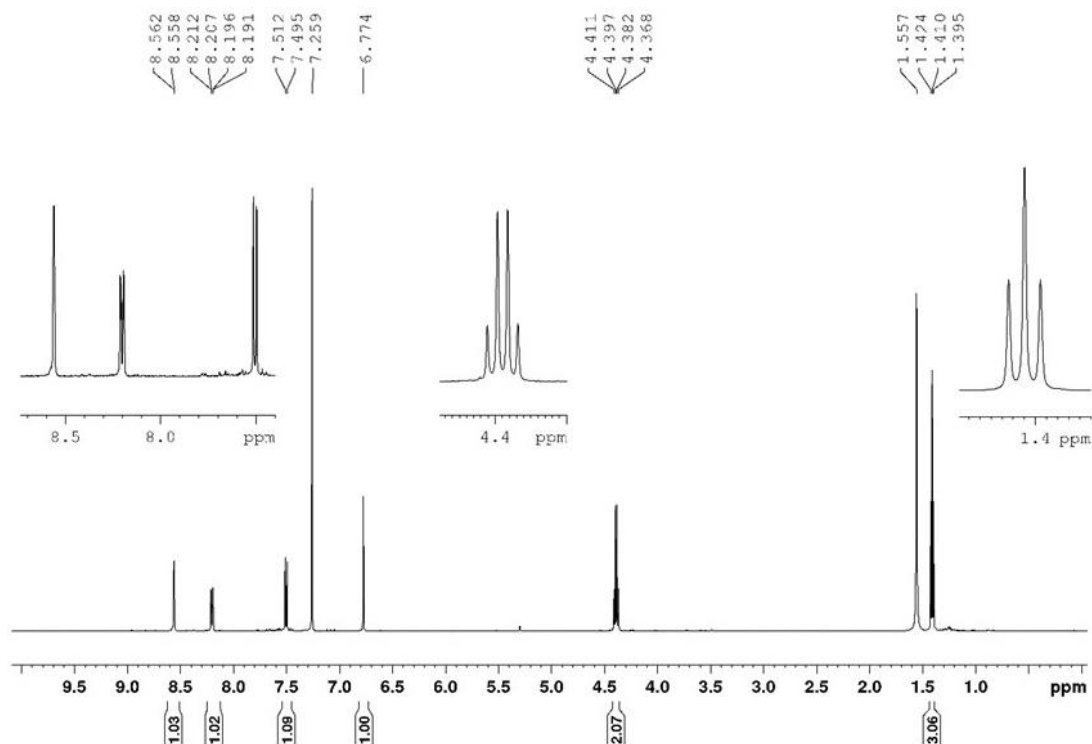


Figure B.3: ¹H NMR Ethyl (Z)-2-azido-3-(6-bromopyridin-3-yl)acrylate [4]

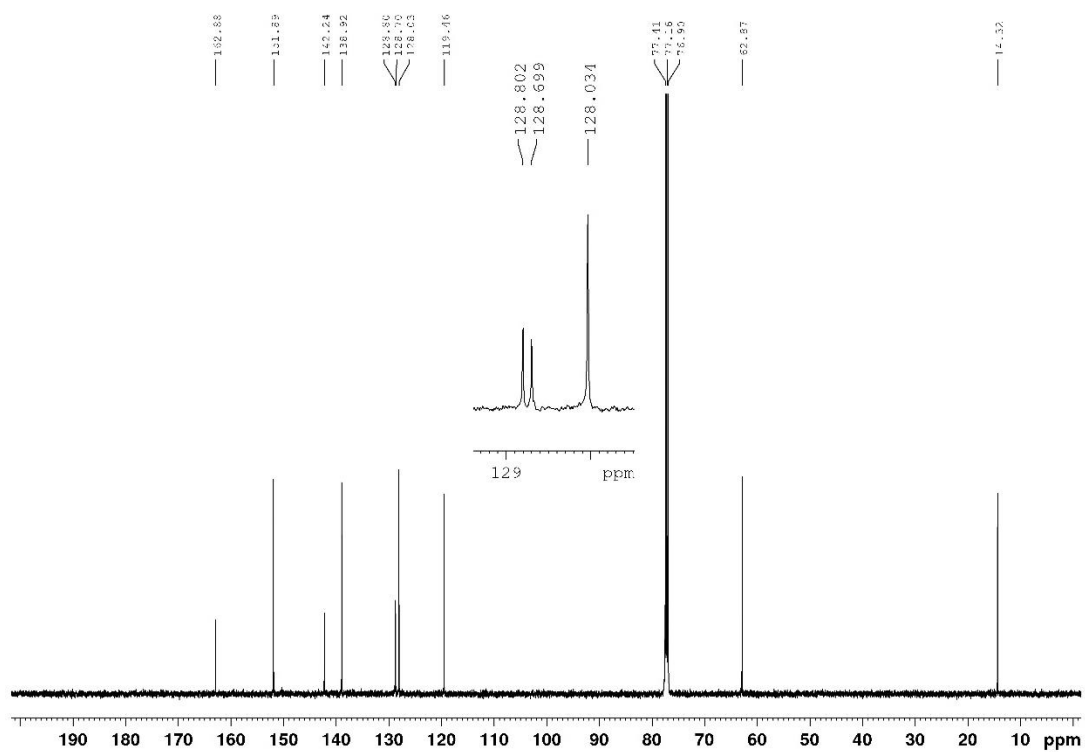


Figure B.4: ^{13}C NMR Ethyl (Z)-2-azido-3-(6-bromopyridin-3-yl)acrylate [4]

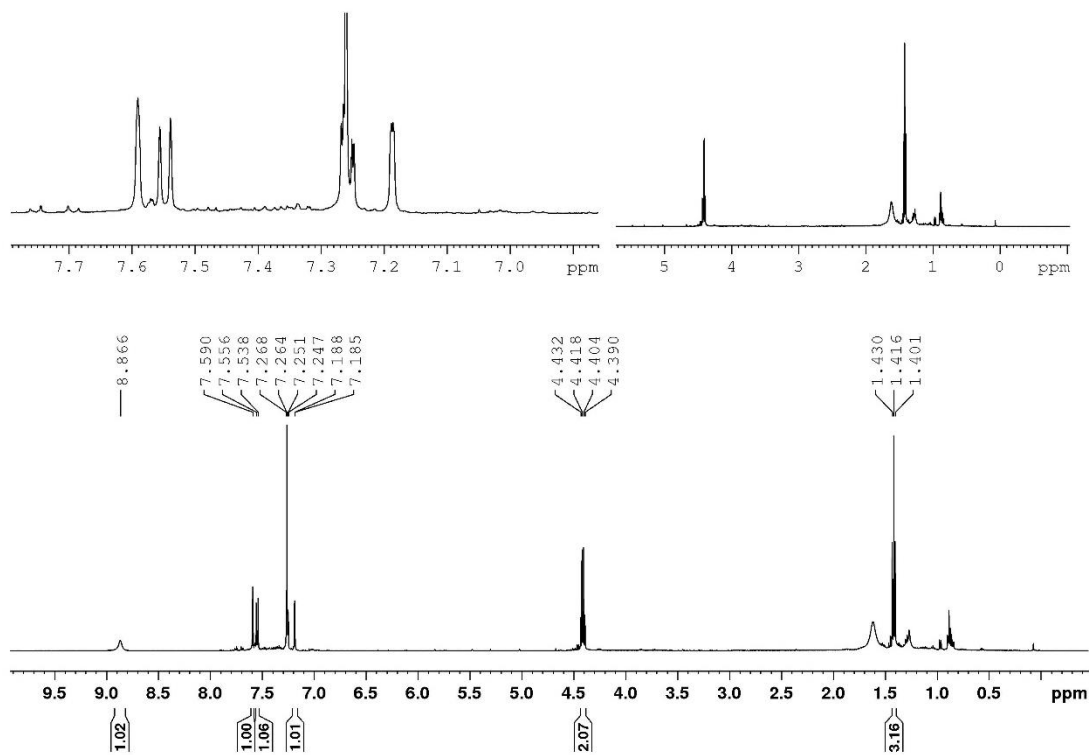


Figure B.5: ^1H NMR of Ethyl 6-bromo-1H-indole-2-carboxylate [5]

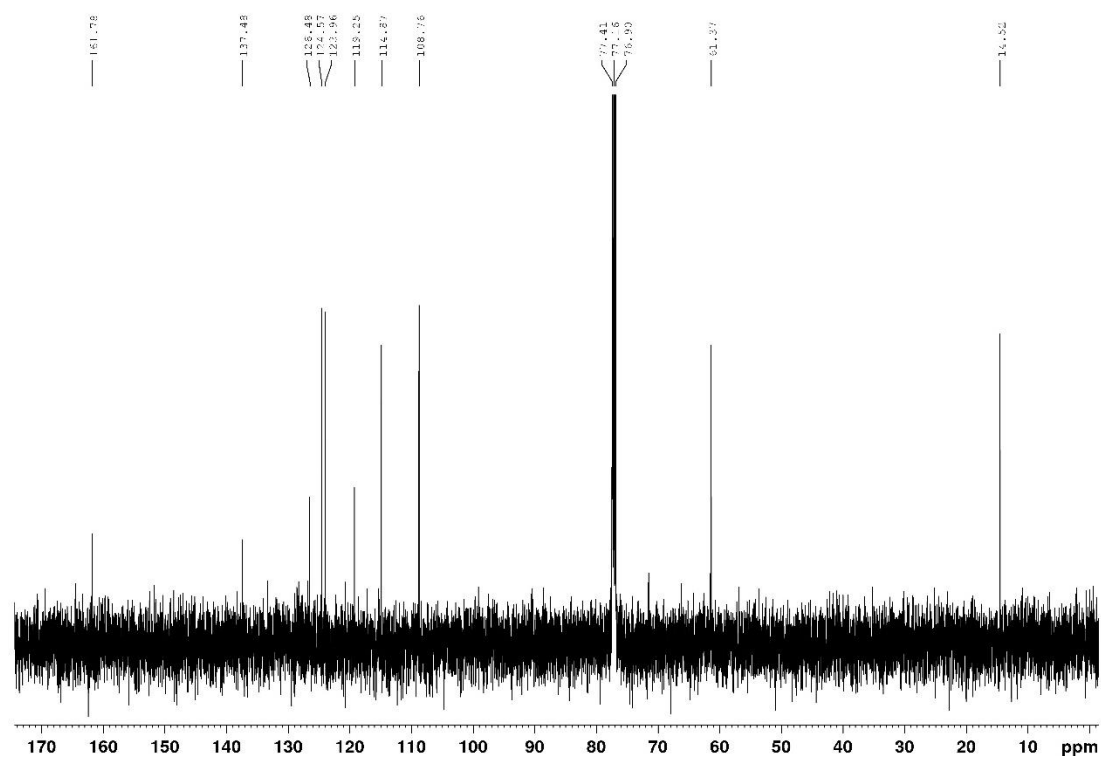


Figure B.6: ^{13}C NMR of Ethyl 6-bromo-1H-indole-2-carboxylate [5]

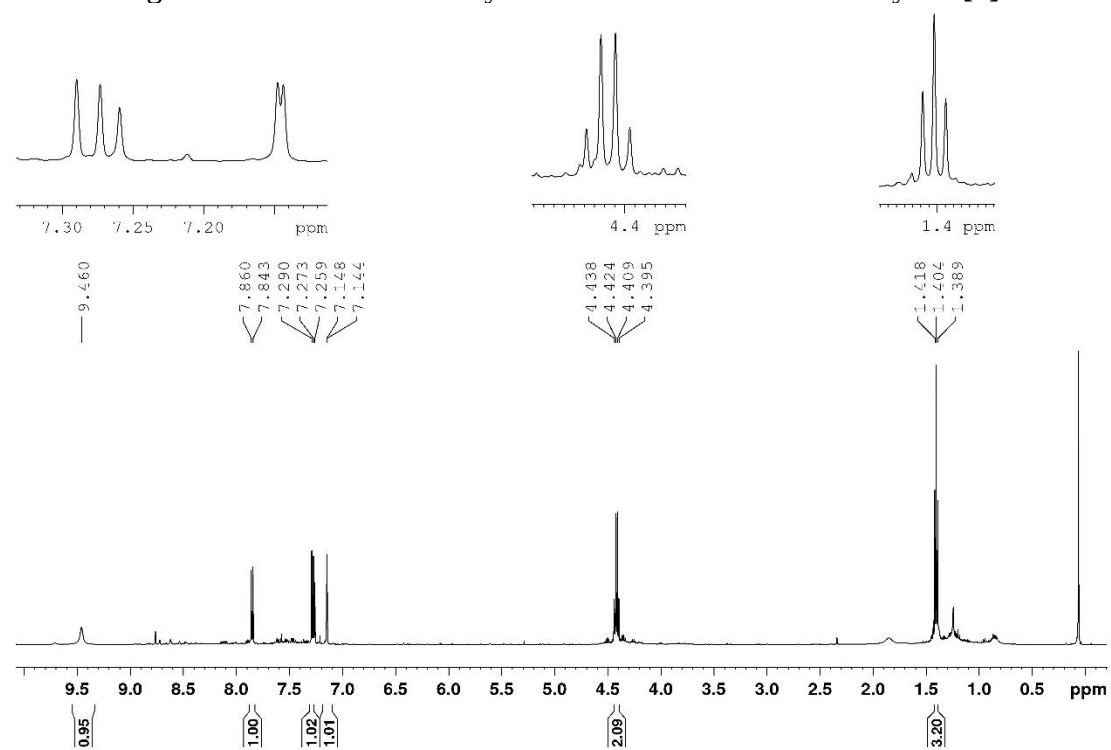


Figure B.7: ^1H NMR of Ethyl 6-bromo-1H-pyrrolo[2,3-b]pyridine-2-carboxylate [6]

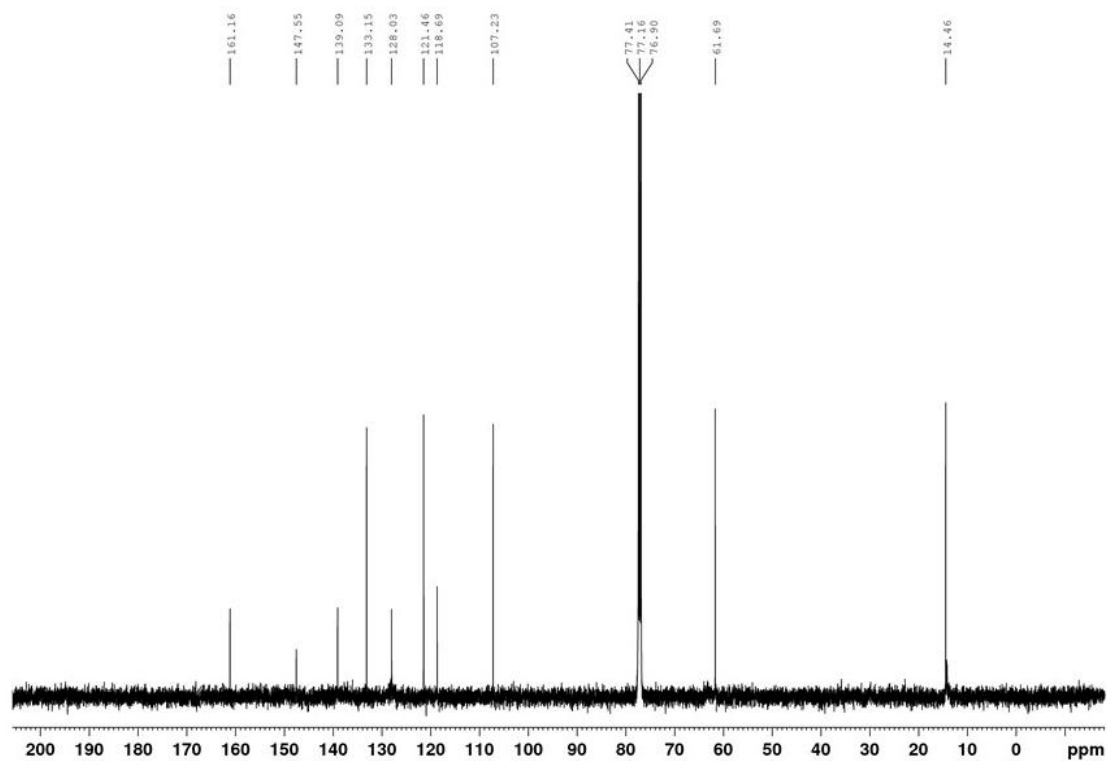


Figure B.8: ^{13}C NMR of Ethyl 6-bromo-1H-pyrrolo[2,3-b]pyridine-2-carboxylate [6]

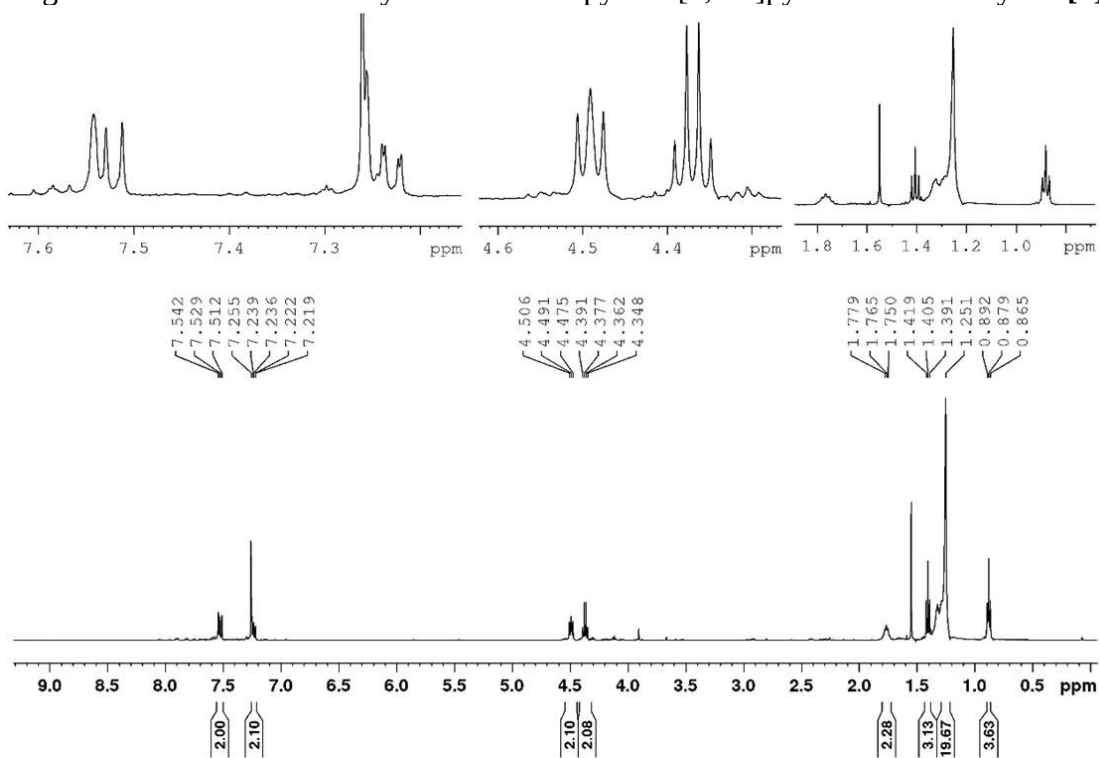


Figure B.9: ^1H NMR of Ethyl 6-bromo-1H-dodecyl-1H-indole-2-carboxylate [7]

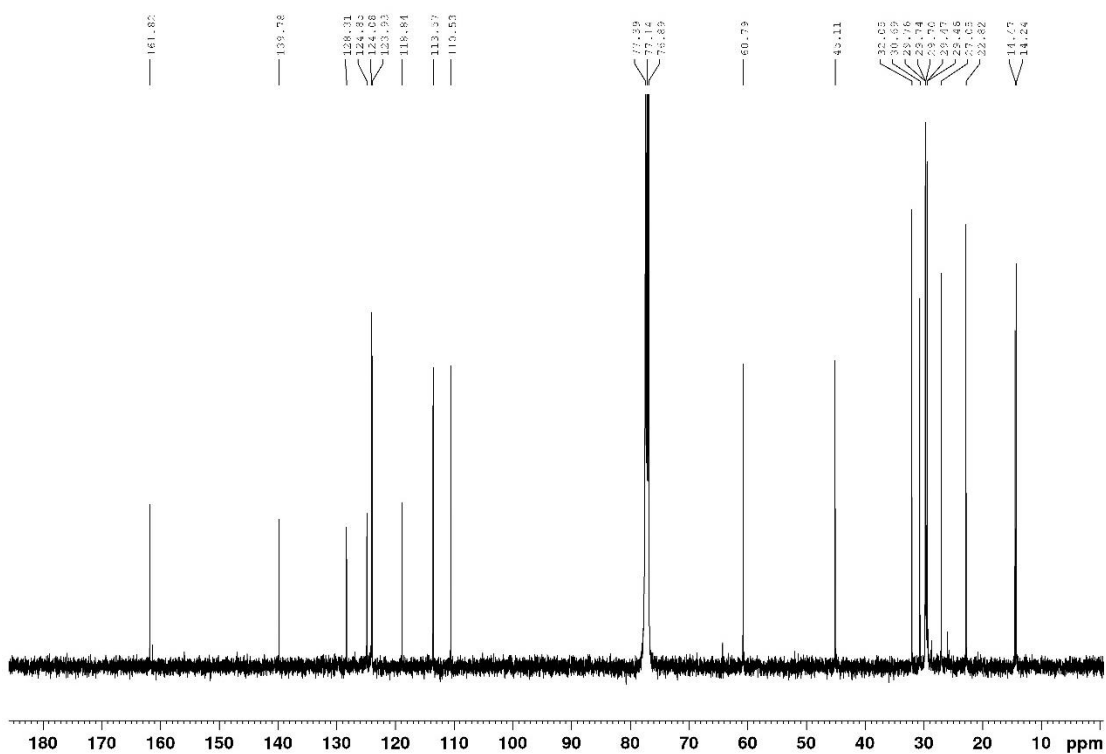


Figure B.10: ^{13}C NMR of Ethyl 6-bromo-1-dodecyl-1H-indole-2-carboxylate [7]

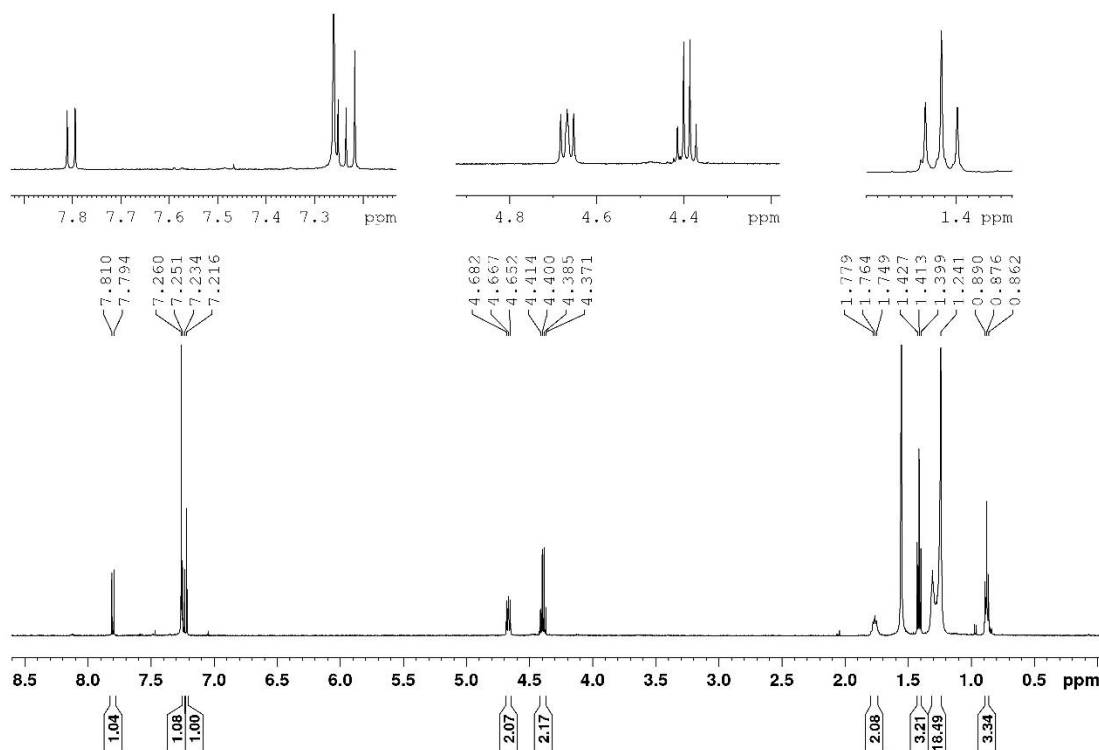


Figure B.11: ^1H NMR of Ethyl 6-bromo-1-dodecyl-1H-pyrrolo[2,3-b]pyridine-2-carboxylate [8]

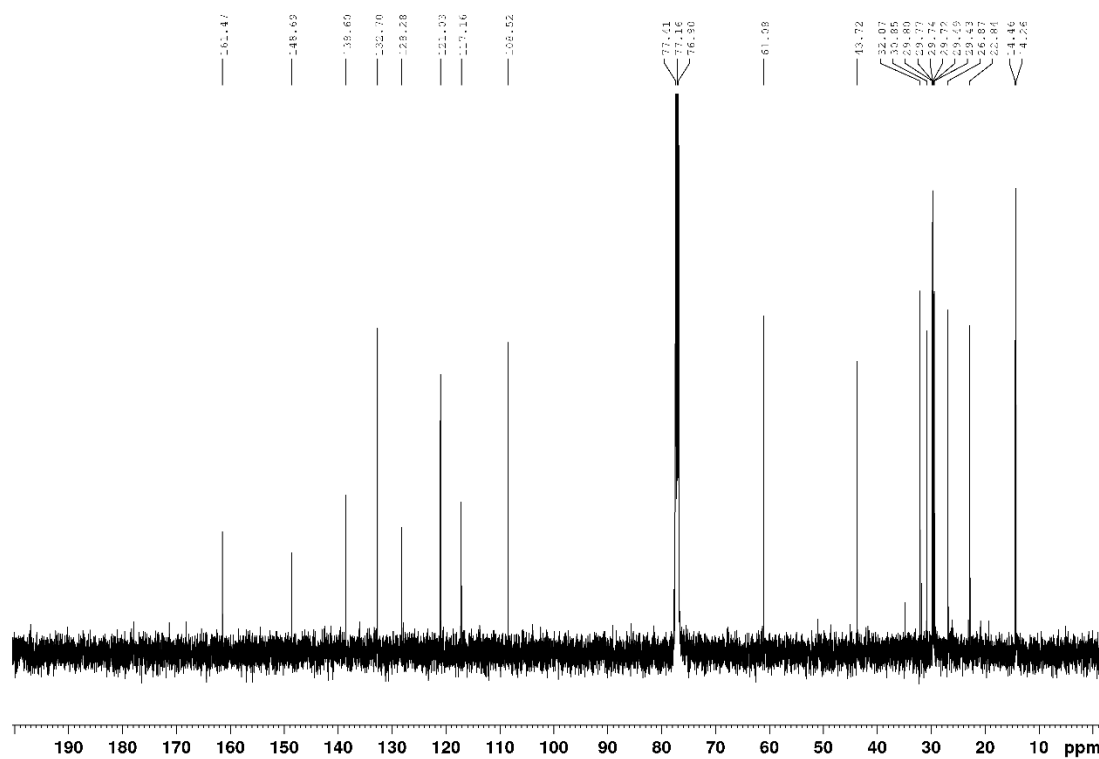


Figure B.12: ^{13}C NMR of Ethyl 6-bromo-1-dodecyl-1H-pyrrolo[2,3-b]pyridine-2-carboxylate [8]

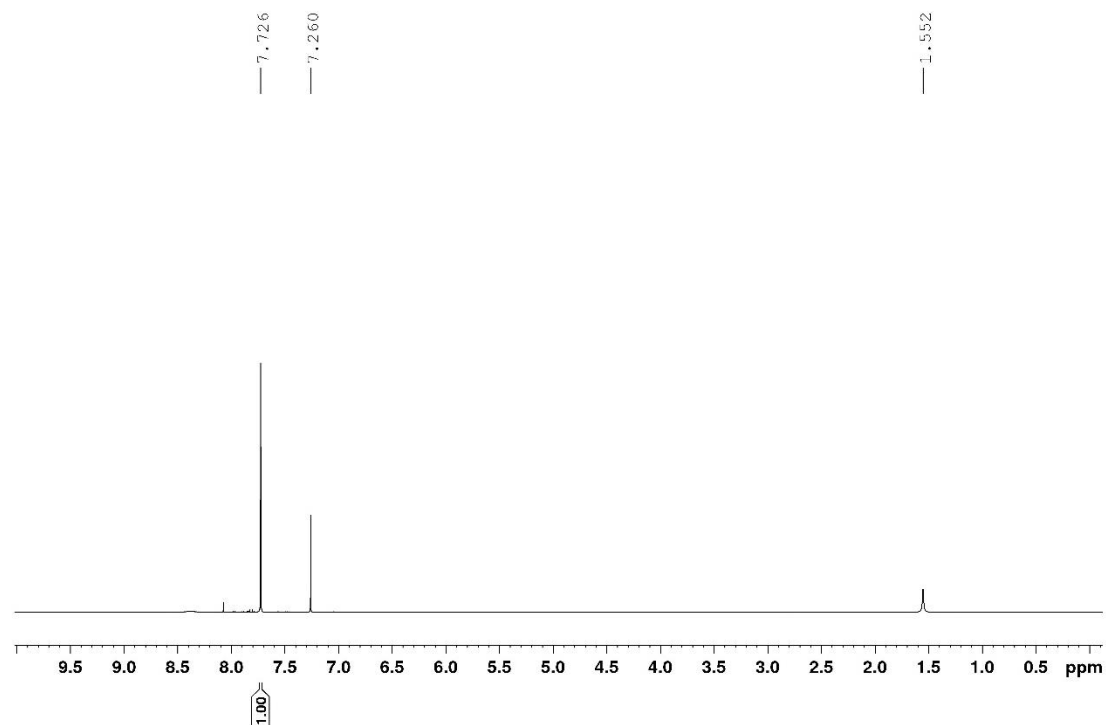


Figure B.13: ^1H NMR of 4,7-dibromobenzo[c][1,2,5]thiadiazole [9]

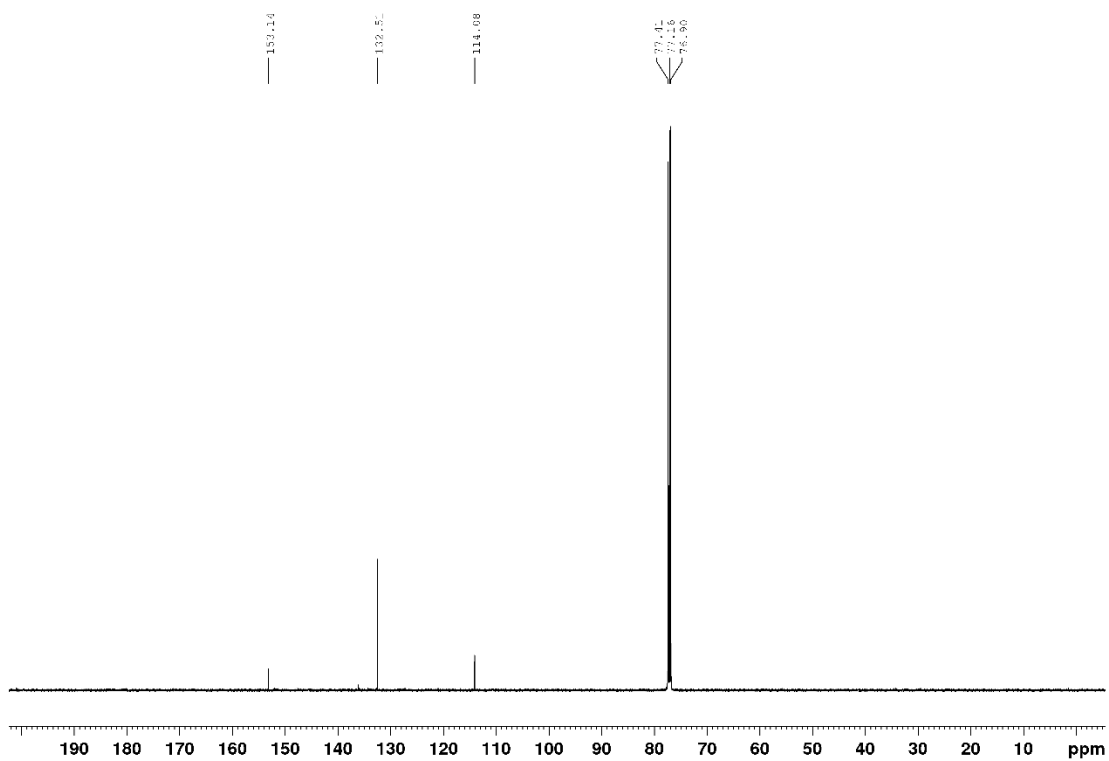


Figure B.14: ^{13}C NMR of 4,7-dibromobenzo[c][1,2,5]thiadiazole **[9]**

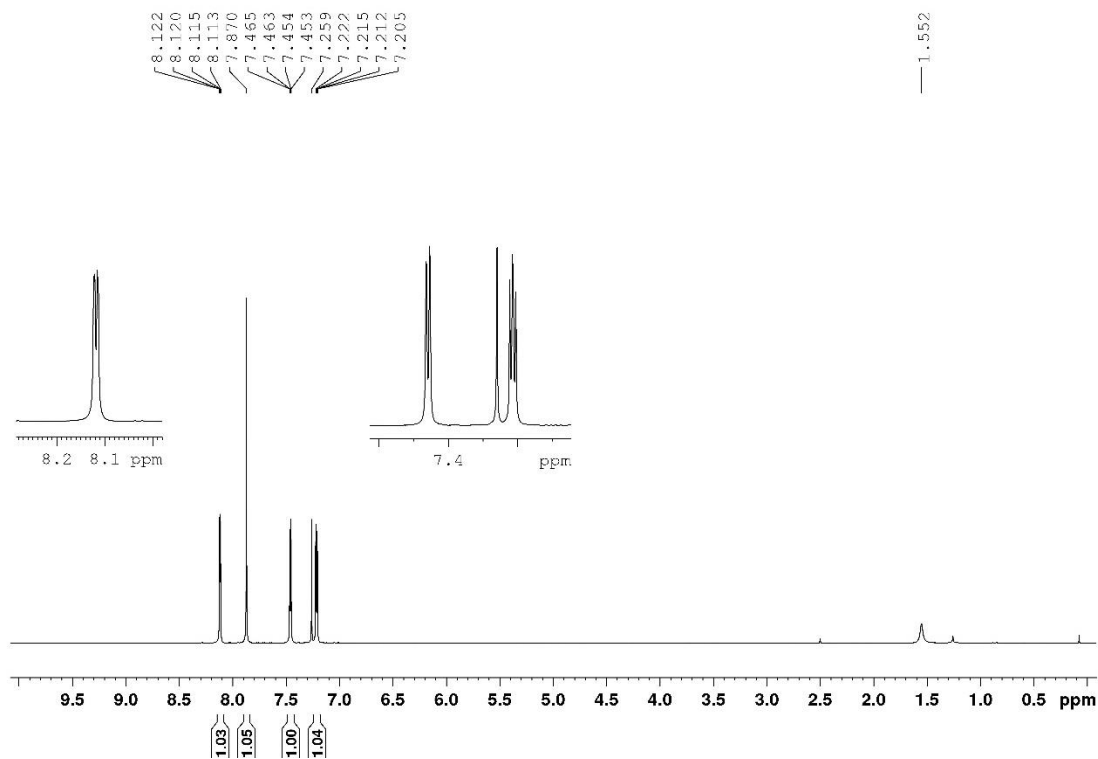


Figure B.15: ^1H NMR of 4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole **[10]**

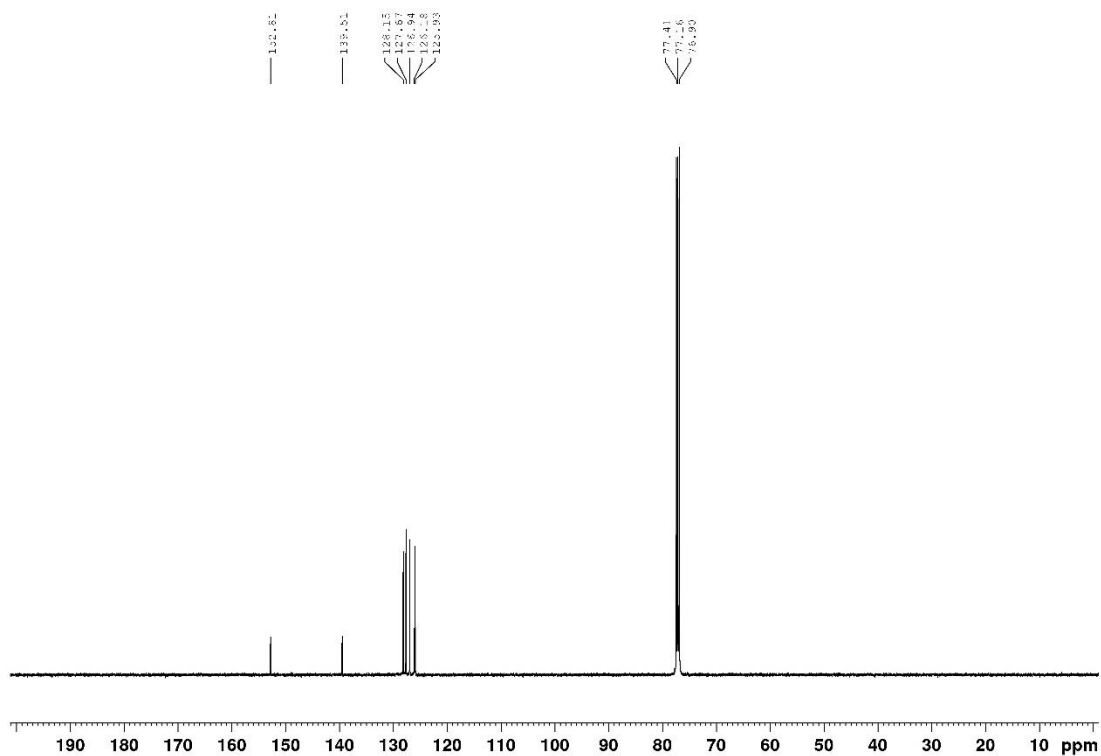


Figure B.16: ¹³C NMR of 4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole [10]

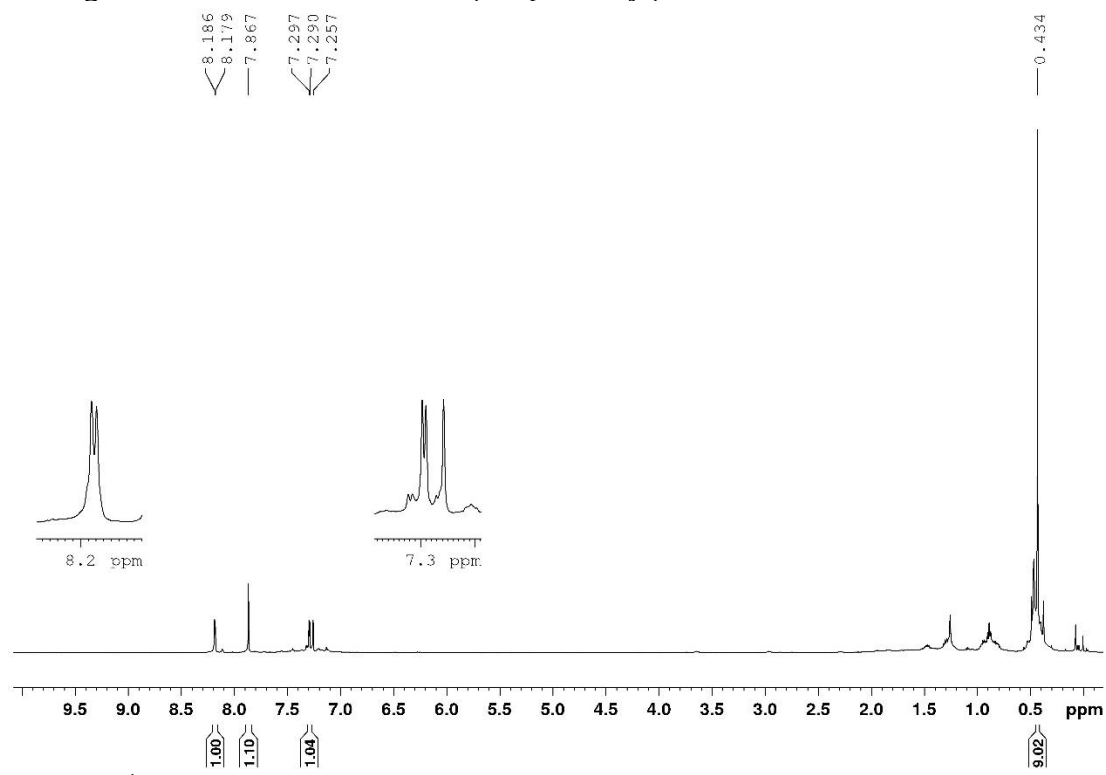


Figure B.17: ¹H NMR of 4,7-bis(5-(trimethylstannyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole [11]

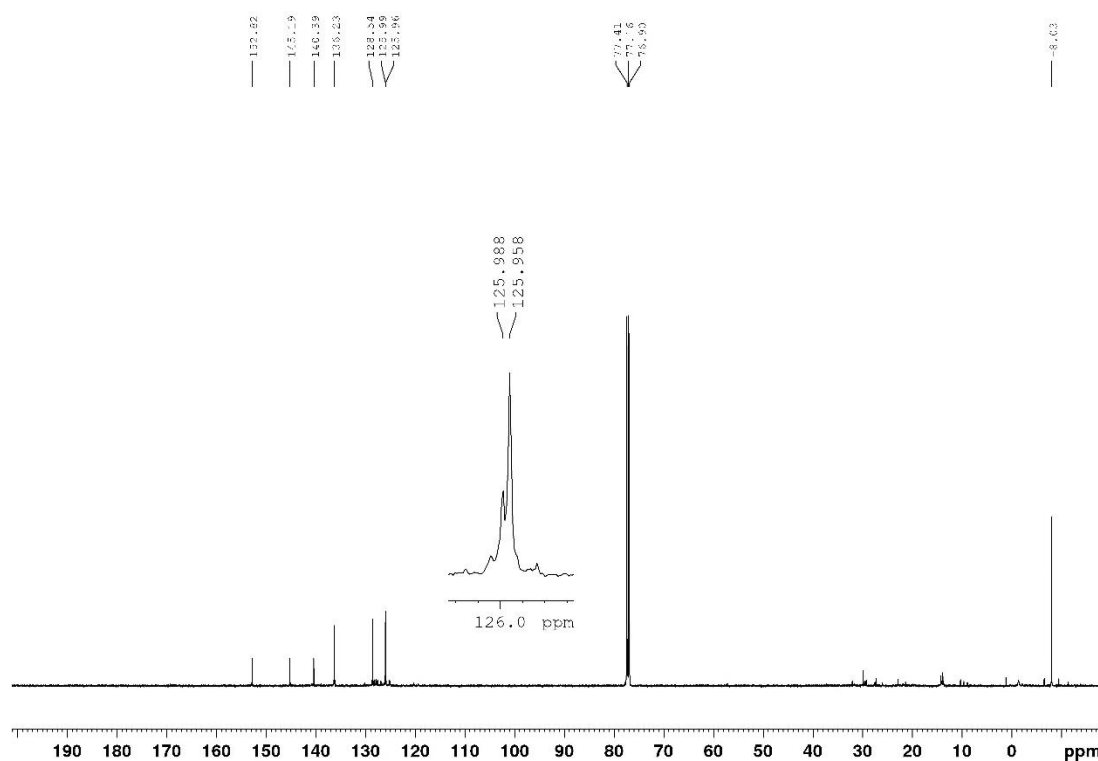


Figure B.18: ^{13}C NMR of 4,7-bis(5-(trimethylstannyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole [11]

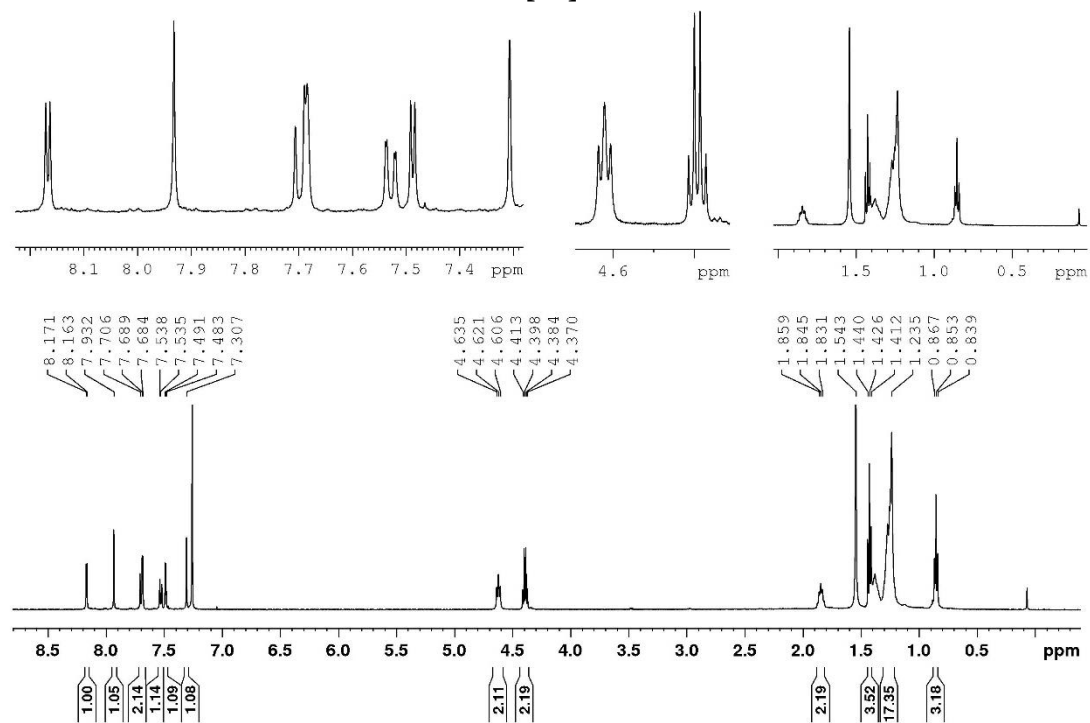


Figure B.19: ^1H NMR of IN-BT2T-IN

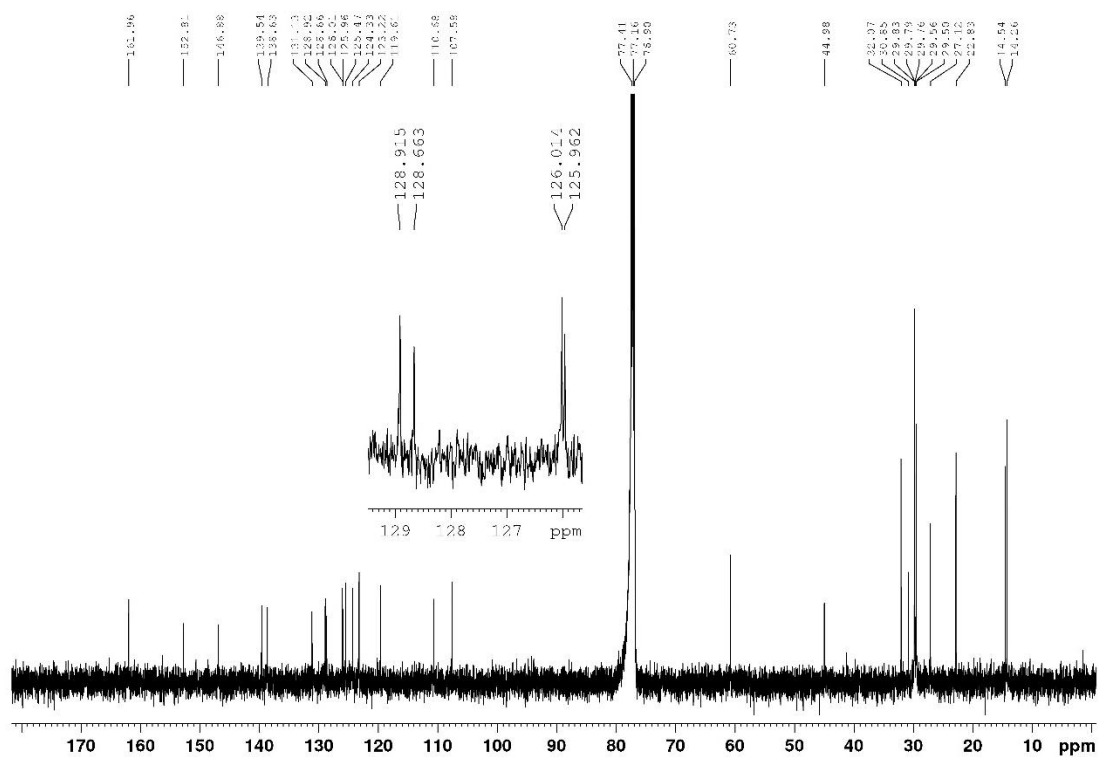


Figure B.20: ^{13}C NMR of IN-BT2T-IN

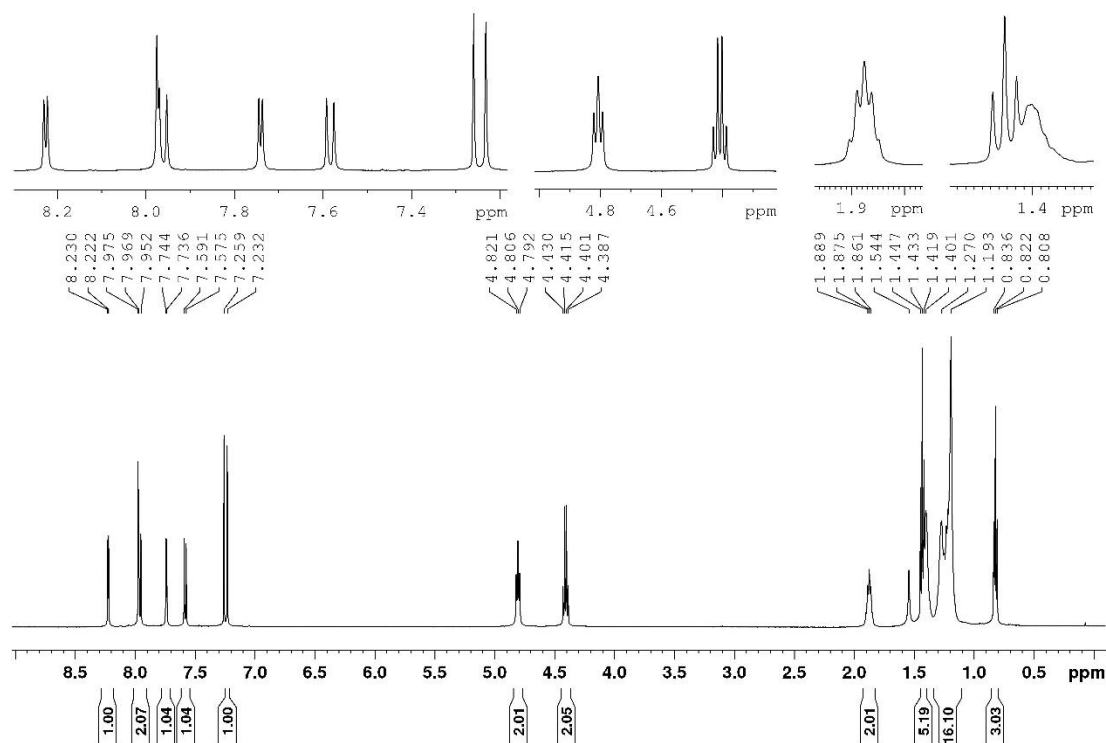


Figure B.21: ^1H NMR of PP-BT2T-PP

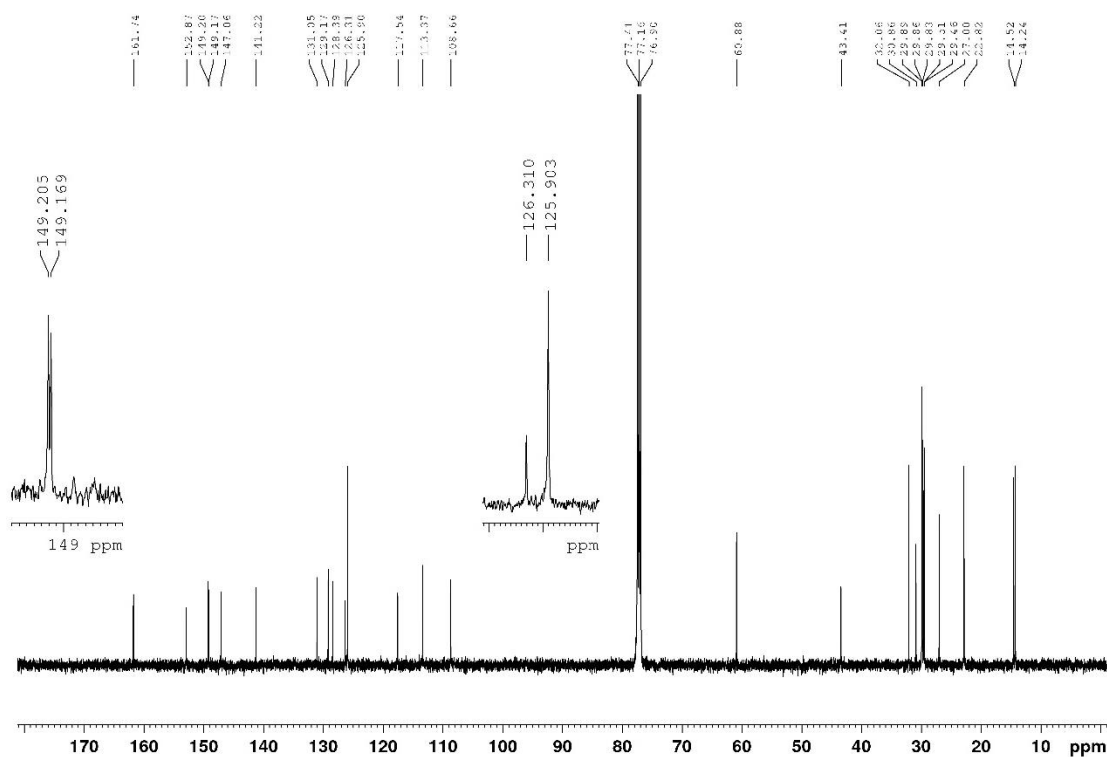


Figure B.22: ¹³C NMR of PP-BT2T-PP

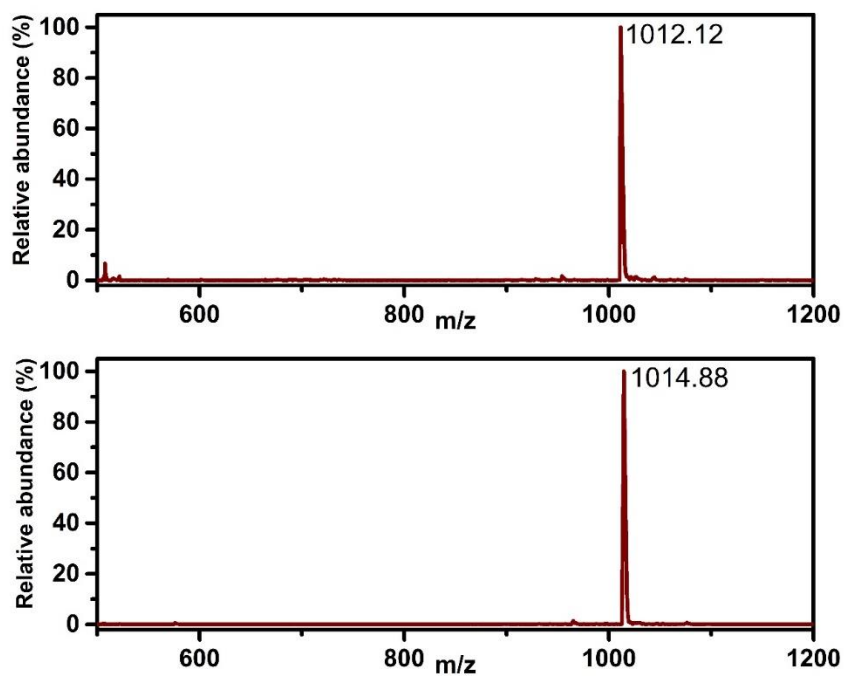


Figure B.23: MALDI-TOF mass spectra of IN-BT2T-IN (top) and PP-BT2T-PP

BIOGRAPHICAL SKETCH

Chinthaka Mahesh Kumara Senarath Udamulle Gedara was born and raised in Nawalapitiya City, Sri Lanka. He attended Anuruddha Kumara National College, Nawalapitiya, and Ranabima Royal College, Gannoruwa. In 2009, he pursued higher education at the University of Peradeniya (UOP), Peradeniya, to obtain a BS degree in Chemistry in 2014. After graduating from UOP, he worked in the same university as a teaching assistant for one year. In 2015, he joined The Open University of Sri Lanka as a teaching assistant and worked there for one and a half years. Then, in 2016, he moved to the USA to pursue graduate school at The University of Texas at Dallas and joined Dr. Biewer's Group. In collaborating with Dr. Mihaela C. Stefan, he worked on synthesizing pyrrole functionalized materials for organic electronic applications.

CURRICULUM VITAE

Chinthaka Mahesh Kumara Senarath Udamulle Gedara
cxu160230@utdallas.edu

EDUCATION

- **Ph.D.** in Synthetic Organic & Polymer Chemistry 05/2016 – 07/2021
The University of Texas at Dallas, Richardson, Texas, USA
- **B.Sc.** Special honors degree in Chemistry 07/2009 – 01/2014
University of Peradeniya, Sri Lanka
Second Class (Upper Division)
Major - Chemistry; Minor - Computer Science, Molecular Biology

PROJECTS

- **Diketopyrrolopyrrole and thienopyrrole based donor-acceptor small molecules and polymers for Organic Field-effect transistors (OFETs)**
Conceptualization, design, synthesis, and characterization of thienopyrrole-based novel donor-acceptor small molecules and polymers; Fabrication of devices and thin films for OFETs applications; Testing OFETs for organic electronics applications
- **Indole and pyrrollopyridine containing benzothiadiazole-based donor-acceptor small molecules for OFETs**
Conceptualization, design, synthesis, and characterization of novel donor-acceptor small molecules for OFETs
- **Incorporation of photochromic moieties into organic semiconducting materials to develop stimuli-responsive electronic materials**
Design, synthesis, and characterization of photochromic small molecular blocks for smart organic electronic materials.

RESEARCH AND DEVELOPMENT

- Graduate Research Assistants**, The University of Texas at Dallas 2016 – Present
- Multi-step organic synthesis and problem-solving skills as demonstrated by optimizing reaction conditions and purification methods for synthesis of novel organic semiconducting and photochromic materials; Expertise in the characterization of semiconducting and photochromic materials
 - Expertise in spectroscopic techniques (UV-Vis, Fluorescence, FTIR, and NMR), surface analytical & imaging techniques (Optical tensiometer and AFM), microscopic techniques (Polarization-microscope), thermal analytical techniques (TGA and DSC), chromatographic & mass spectrometric techniques (GPC/SEC, HPLC, GC-MS, and MALDI-TOF), organic

semiconductor-property characterization (4-point probe and probe-station), thin film fabrication, and photolithography

- Experience in cleanroom utilities, protocols, and safety
- Practice in setting up experiments, maintaining, and troubleshooting instruments such as GPC/SEC, HPLC, and GC-MS
- Experience in training and maintaining general lab safety protocols, including storing and handling hazardous chemicals and chemical waste

TECHNICAL SKILLS, SOFTWARE, AND INSTRUMENTATION

- UV-Vis, Fluorescence, FTIR, and NMR spectroscopy for molecular characterization
- Column chromatography, GPC/SEC, HPLC, GC-MS, LC-MS and MALDI-TOF for molecular separation and characterization
- TGA and DSC techniques for thermal-property analysis
- AFM and optical tensiometer for surface imaging and characterization
- Photolithography, ultra-high vacuum deposition, and thin film fabrication for OFETs
- Origin lab and Prism software for data analysis; Spartan software for molecular modeling; Adobe Photoshop, Illustrate, Premier, and Audition for visualization and recording; MS-Office and Endnote/Mendeley for data-managing, writing, and referencing

MENTORING AND TEACHING

Graduate Teaching Assistant

08/2016 – Present

Department of Chemistry and Biochemistry, The University of Texas at Dallas

- Conducting advanced organic synthesis laboratory classes for senior undergraduate students
- Mentoring and training first-year graduate students for organic thin film fabrication and lab safety protocols
- Conducted organic chemistry laboratory classes for sophomore and junior undergraduate students
- Mentored and trained four undergraduate students on the synthesis of photochromic and semiconducting materials and characterization

Teaching Assistant

01/2015 – 07/2016

Department of Chemistry, Faculty of Natural Sciences, The Open University of Sri Lanka, Sri Lanka

- Organized, arranged and conducted laboratory sessions for undergraduate students helping them with their experiments
- Evaluated quizzes, examination papers and laboratory reports
- Performed Day-schools (tutorial discussions) and Workshops for 1st year and 2nd year students

Teaching Assistant

02/2014 – 12/2014

Department of Chemistry, Faculty of Science, University of Peradeniya, Sri Lanka

- Arranged and conducted laboratory sessions for undergraduate students helping them with their experiments

- Evaluated quizzes, examination papers and laboratory reports
- Performed tutorial discussions for 1st year and 2nd year students

Teaching Assistant (visiting)

2014

Post Graduate Institute of Science - University of Peradeniya, Sri Lanka

- Arranged and conducted laboratory sessions for postgraduate student

MEMBERSHIPS

- American chemical society (ACS) 2018 – Present

AWARDS

- Ph.D. research small grant award in 2019 from the University of Texas at Dallas (UTD)

CONFERENCE PROCEEDINGS

- **Udamulle Gedara, C. M.**; Stefan, M. C.; Biewer, M. C. Aziridine-based photochromic monomers for conductive polymers. Abstracts of Papers, 258th ACS National Meeting & Exposition, San Diego, CA, United States, August 25-29, 2019. 2019, p ORGN-0156.
- **Udamulle Gedara, C. M.**; Gunawardhana, R.; Gamage, P. L.; Nguyen, K. M.; Biewer, M. C.; Stefan, M. C. Banana-shaped donor-acceptor-donor (DAD) type small molecules for organic field-effect transistors (OFETs). In Abstracts of Papers, 260th ACS National Meeting & Exposition, San Francisco, CA, United States, August 23-27, 2020; American Chemical Society, 2020; p ORGN-0132.

PUBLICATIONS

- Karmegam, V.; **Udamulle Gedara, C. M.**; Biewer, M. C.; Stefan, M. C. Synthesis and optoelectronic properties of functionalized pyrimidine-based conjugated polymers. *J. Polym. Sci. Part A Polym. Chem.* **2018**, 56 (22).
- Dissanayake, D. S.; Gunathilake, S. S.; **Udamulle Gedara, C. M.**; Du, J.; Yoo, S. H.; Lee, Y.; Wang, Q.; Gomez, E. D.; Biewer, M. C.; Stefan, M. C. Conductive triethylene glycol monomethyl ether substituted polythiophenes with high stability in the doped state. *J. Polym. Sci. Part A Polym. Chem.* **2019**, 57 (10).
- Gunawardhana, R.; Bulumulla, C.; Gamage, P. L.; Timmerman, A. J.; **Udamulle, C. M.**; Biewer, M. C.; Stefan, M. C. Thieno[3,2-b]pyrrole and Benzo[c][1,2,5]thiadiazole Donor-acceptor semiconductors for organic field-effect transistors. *ACS Omega* **2019**, 4 (22), 19676–19682.
- Talukder, M. M.; Miller, J. T.; Cue, J. M. O.; **Udamulle, C. M.**; Bhadrar, A.; Biewer, M. C.; Stefan, M. C. Mono- and dinuclear α -diimine nickel(II) and palladium(II) complexes in C–S cross-coupling. *Organometallics* **2021**, 40 (1), 83–94.
- Gamage, P. L.; Gunawardhana, R.; Bulumulla, C.; Kularatne, R. N.; **Gedara, C. M. U.**; Ma, Z.; Biewer, M. C.; Stefan, M. C. An Ester Functionalized Wide Bandgap Polythiophene for Organic Field-Effect Transistors. *Synth. Met.* **2021**, 277, 116767.

- Pathirana, T. M. S. K.; Ma, Z.; **Udamulle Gedara, C. M.**; Pan, X.; Lee, Y.; Gomez, E.; Biewer, M. C.; Matyjaszewski, K.; Stefan, M. C. Improved Self-Assembly of P3HT with Pyrene-Functionalized Methacrylates. *ACS Omega* (in press), **2021**.
- Karmegam, V.; Kuruppu, S. S.; **Udamulle Gedara, C. M.**; Biewer, M. C.; Stefan, M. C. Enhanced DOX Loading in Benzyl Functionalized-Polycaprolactone Micelles Based on Star-Polymer Architecture. Manuscript submitted for publication, **2021**.
- **Udamulle Gedara, C. M.**; Gamage, P. L.; Ma, Z.; Bhadrar, A.; Gunawardhana, R.; Bulumulla, C.; Biewer, M. C.; Stefan, M. C. Incorporation of Selenopheno[3,2-b]Pyrrole into Benzothiadiazole-Based Small Molecules for Organic Field-Effect Transistors. Manuscript submitted for publication, **2021**.
- Talukder, M. M.; Miller, J. T.; Cue, J. M. O.; **Udamulle Gedara, C. M.**; Arche, P. D. E.; Biewer, M. C.; Stefan, M. C. Iminopyridine-Based A-Diimine Nickel (II) and Palladium (II) Com-Plexes in Direct C-H Bond (Hetero)Arylation of Thiazoles and Thio-Phenes. Manuscript submitted for publication, **2021**.
- **Udamulle Gedara, C. M.**; Ma, Z.; Mukhtadir, T.; Gunawardhana, R.; Biewer, M. C.; Stefan, M. C. (2021). Siloxane Side-Chain Modified Diketopyrrolopyrrole and Thienopyrrole Containing Small Molecules for Organic Field-Effect Transistors. Manuscript in preparation, **2021**.
- **Udamulle Gedara, C. M.**; Ma, Z.; Gamage, P. L.; Gunawardhana, R.; Bulumulla, C.; Mukhtadir, T.; Karmegam, V.; Stefan, M. C.; Biewer, M. C. (2021). 1H-Indole and Pyrrolo[2,3-b]Pyridine as Pyrrole-Fused Donors in Donor-Acceptor Small Molecules for Organic Field-Effect Transistors. Manuscript in preparation, **2021**.

EXTRACURRICULAR ACTIVITIES

- Member of chemistry graduate student association at UTD 2016 – Present

REFERENCES

- | | |
|--|--|
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