

***Sulphur- & Nitrogen-Containing π -Conjugated Organic
Molecules as Potential Semiconductors for Optoelectronic
Devices***

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Thesis submitted to the
Faculty of Graduate and Postdoctoral Studies
In partial fulfillment of the requirements for the degree of

Doctor of Science

In
Chemistry

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Abstract

Organic semiconductors (OSCs), compared to the more traditional silicon, are enticing materials for the fabrication of optoelectronic devices (*e.g.*, transistors, photovoltaic cells, light-emitting diodes) due notably to the lower cost associated with their preparation and purification, as well as their increased solubility in solvents which can accommodate large-scale fabrication. However, a higher degree of molecular disorder typically results in lower performance than silicon and remains an issue to be addressed. As the structure of an OSC is crucial to its performance, understanding the nature of this structure-property relationship is key to further the field of OSCs. In this regard, this thesis explores the optoelectronic properties of different π -conjugated organic frameworks which incorporate sulphur and nitrogen atoms along the rigid conjugated backbone for their desirable impacts on charge mobilities and stability.

After a brief review of both small-molecule OSCs as well as key experimental techniques employed in the course of this work, chapter three covers the synthesis and characterization of dithiatetrazocines (DTTA), electron-deficient sulphur-nitrogen heterocycles, which were functionalized with various (oligo)thienyls pendants. The impact of both the substitution patterns and the degree of conjugation on the optoelectronic and solid-state properties of the ring system was investigated.

The fourth chapter expands on previous work from the Brusso group that focused on extending the 2D conjugation of tetrathienoanthracene. While oligothienyls were previously shown to effectively increase the degree of conjugation, little to no change in device performance were observed, which was ascribed to disorder of the rotatable pendants. Here, rigid thieno[3,2-b]thiophene was used instead to increase both the degree of conjugation while maintaining structural rigidity, as assessed by optical, electrochemical and theoretical studies.

The fifth chapter introduces preliminary work toward expanding the electron-deficient hexaazatrinaphthylene core with thiophene rings. The resulting concentric donor-acceptor structure promotes luminescent behavior with pronounced emission solvatochromism. Optical measurements were performed before and after intramolecular cyclization of the thiophene rings, to study the impact of aromatization on the optoelectronic properties of the system.

Acknowledgments

This is not the greatest acknowledgment in the world, no. This is a tribute. If anything, a tribute to the patience of my friends and colleagues, which goes to show that even under enduring circumstances, I can be, at the very least, tolerated as a person and as a coworker.

I am truly grateful to my supervisor Jaclyn Brusso for taking me under her wing and showing me that being both a good scientist and a balanced human being are not mutually exclusive. Thank you for your guidance and patience, and for all trust you've shown with chemistry projects and lab responsibilities. Again, all my apologies for that butt picture and for the grey hairs that I may or may not have caused.

I am also particularly grateful to my doctoral committee members (Pr. Muralee Murugesu, Pr. Darrin Richeson, Pr. Wayne Z.Y. Wang and Pr. Joe Gilroy) for taking the time to read my thesis and to sit on its oral defense. I appreciate all the feedback and comments, and this work is all the better for it.

All my thanks to our many scientific collaborators (Dr. Ilia Korobkov, Dr. Bulat Gabidullin, Pr. Benoît Lessard and his group, namely Dr. Nicole Rice and Owen Manville), whose expertise and help were invaluable in the course of this work. I also need to thank the most excellent personnel and supporting staff from the University of Ottawa (including Dave, Armstrong, Pierre Bisson and all the staff from the scientific store, Annette Campeau, Dr. Glenn Facey, Don Hopkins, Dr. Wendy Pell, Josée Rouleau, Dr. Eric Yu) whose professionalism and ever-helpful presence made my stay here a breeze. Further thanks to the crew of the undergraduate teaching lab, namely Robert Nadon and Dan Lafleur, for their familial spirit. While I could probably blame a few of my extra pounds on Bob and all the extra-bacon breakfasts, let it be known that I have no regrets.

A particular nod to members of the Brusso Bunch, both past and present, who have made my stay through grad school memorable to say the least. This includes Nathan, who despite me having been in the group for what seemed like an eternity, has managed to be around for even longer. Thank you for being a rainbow in this group: without you, there would be little to no photographic evidence of my tenure at OttawaU. Keep on sipping on your IPAs and ignore the haters. Alicea, you were the adult presence I needed early on in my work. Thank you again for the wolf shirt; it remains to this day the best gift I never got. Sean, thank you for being my wingman through the *danger zone* that was early grad school. Soofieh, despite your short stay in the group, you have taught me that you can never be too careful when it comes to labwork. Andrew, you showed me that, sometimes, you gotta do what you wanna do. You truly are the salt of the earth. Elizabeth, thanks for all the coffee breaks: I would had gone crazy without them. Irina; while I remain convinced that the German Purity Law of 1516 is the worst thing to happen to the world of beer, I still miss our summer night drinks and arguments. Raül, your

unique insight into chemistry has been invaluable through and through. Thank you again for introducing me to the Quentin Tarantino-school of scientific presentations. Jamie, you have been a most excellent lab roommate in a time I needed one the most; that said, don't quit chemistry for a singing career! Finally, Yousaf, you showed me that I can really, *really*, love my TLC lamp (sorry again!). A final shout-out to all the undergraduate interns that populated the lab over the years and made the group livelier.

Obviously, my time in grad school does not limit itself to my group and research, and was shaped by many people in the department. A particular shout out to my BFFs Terry "TPain" McCallum and Thomas "100" Charlton: without you guys, I would have been done over a year ago (but what a boring experience it would have been)! You two may have wisened up a bit since but, to me, you'll always be the young disreputable whipper-snappers you were in the summer of 2014. Remember boys, if we ever get bored of chemistry, we can always brew some beer.

Maykon, thank you for reminding me that, sometimes, *tequila is the answer*. Katie, you showed me that the simplest of words can be totally naughty, and that is just totally *wizard*. Tom L., keep on bringing the Guns, both in science and to the (drinking) table. Paul, you may or may not be the new daddy of your group: have fun with that! But don't forget to go out a bit more and have real fun too. Ryan, you showed me that you don't need alcohol to have fun (although it sure can't hurt). So long, and thanks for all the (raw) fish. To everyone else (Lauren, McKinsey, Camillo, Dr. Nick, Virginie, Josh, JP, Mathieu, Spencer, Maddie, Lauren, Steven, Yixin, and so many more), keep on fighting the good fight.

I am eternally grateful to my family, particularly my parents, who supported me throughout the years. Indubitably, I wouldn't be here today without your constant support and the values of hard work and of inquisitiveness that you transmitted to me at an early age.

A last quick acknowledgment to the University of Ottawa, which has provided me with both a salary and essentially free tuition, allowing me to live a decent life, (more or less) free to pursue my academic interests. Luckily enough, I was able to make it through the bureaucratic gears relatively intact! This gratitude would also have to extend to the governments of Canada and Ontario; while your many funding organisms have never dared to give me a single penny directly, the money provided to the University and my supervisor has made my graduate experience reality. As always, I would like to finish by recognizing Costco's excellent hot-dog/poutine combos; despite the 25¢ increase in cost that occurred over my time in grad school, you guys truly are doing God's work.

*No. No.
Be of good cheer.
If science teaches us anything,
it teaches us to accept our failures,
as well as our successes,
with quiet dignity and grace.*

...

*Son of a %\$#@^! Bastard!
I'll get you for this! What did you do to me?
I don't want to live!
I do not want to live!
-Gene Wilder
(Dr. Frederick Frankenstein)*

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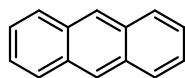
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List of Abbreviations

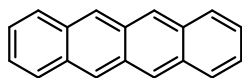
A	Absorbance
Å	Angstrom
Anal. Cald.	Calculated Elemental Analysis
B3LYP	Becke's 3-parameter exchange Lee-Yang-Parr functional
cm ⁻¹	Reciprocal centimeters
CV	Cyclic Voltammetry
dba	Dibenzylideneacetone
DCE	1,2-Dichloroethane
DCM	Dichloromethane
DDQ	4,5-Dichloro-3,6-dioxo-1,4-cyclohexadiene-1,2-dicarbonitrile
Δf	Orientation Polarizability
DFT	Density Functional Theory
dppf	1,1'-Ferrocenediyl-bis(diphenylphosphine)
DPV	Differential Pulse Voltammetry
DTTA	1,5-Dithia-2,4,6,8-tetrazocine
E	Energy
<i>E</i>	Potential
E _{gap} ^{opt}	Optical Energy Gap
ε	Molar Coefficient of Extinction
Eq.	Equivalents
eV	Electronvolt
<i>f</i>	Oscillator Strength
Fc/Fc ⁺	Ferrocene/Ferrocenium
FET	Field-Effect Transistor
fw	Formula Weight
h	Hours
HAT	1,4,5,8,9,12-hexaazatriphenylene or 1,4,5,8,9,12-hexaazatrinaphthylene
HATN	1,4,5,8,9,12-hexaazatrinaphthylene
HATP	1,4,5,8,9,12-hexaazatriphenylene
HOMO	Highest Occupied Molecular Orbital
HQ-GC	High Quality-Gas Chromatography
I	Current
IR	Infrared
LDA	Lithium Diisopropylamide
LUMO	Lowest Unoccupied Molecular Orbital
min	Minutes
MO	Molecular Orbital
ν	Frequency
NBS	<i>N</i> -bromosuccinimide
nm	Nanometers
NMP	<i>N</i> -methylpyrrolidone
NMR	Nuclear Magnetic Resonance
OLED	Organic Light-Emitting Diode

OSC	Organic Semiconductor
PCBM	Phenyl-C61-Butyric Acid Methyl Ester
PCM	Polarized Continuum Model
ppm	Parts per million
Φ	Quantum Yield of Fluorescence
r.t.	Room Temperature
SCE	Standard Calomel Electrode
S _N 1	Unimolecular Nucleophilic Substitution
S _N 2	Bimolecular Nucleophilic Substitution
S _N Ar	Aromatic Nucleophilic Substitution
TCE	1,1,2,2-Tetrachloroethane
TDDFT	Time Dependent Density Functional Theory
TFA	2,2,2-Trifluoroacetic Acid
TMS	Trimethylsilyl
TT	Thieno[3,2-b]thiophene
TTAn	Tetrathienoanthracene
UV-Vis	Ultraviolet-Visible
XRD	X-ray Diffraction

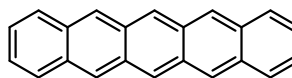
Summary of Chemical Structures



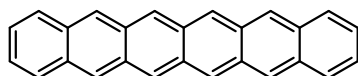
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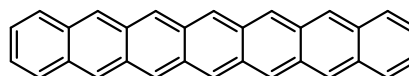
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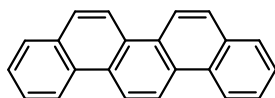
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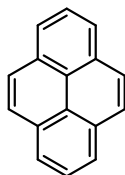
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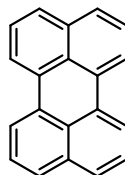
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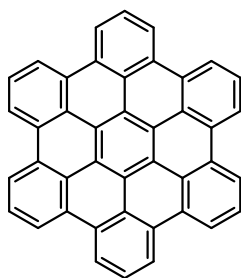
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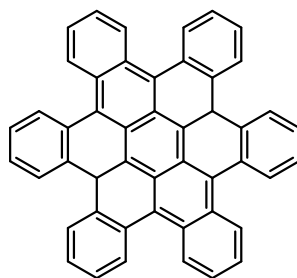
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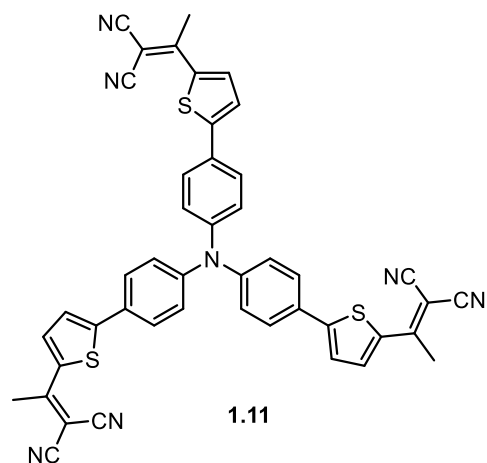
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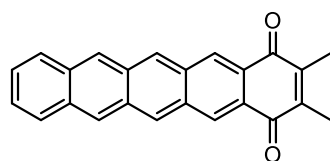
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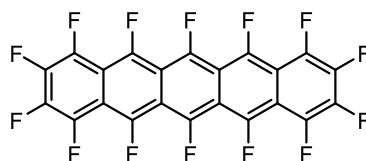
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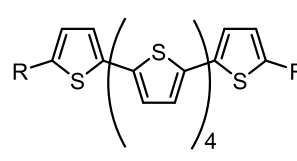
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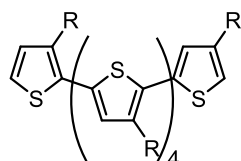
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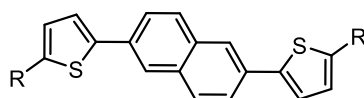
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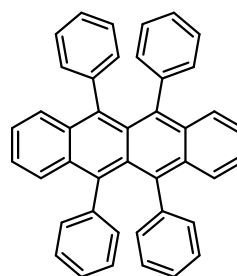
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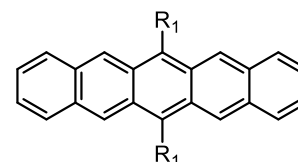
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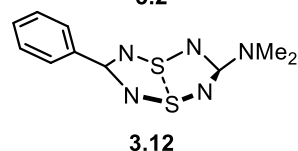
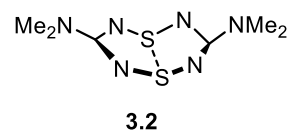
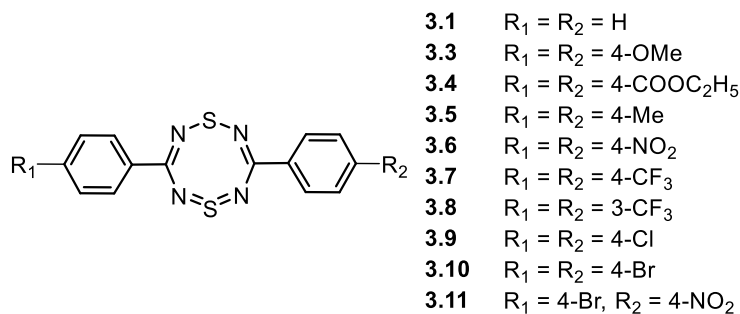
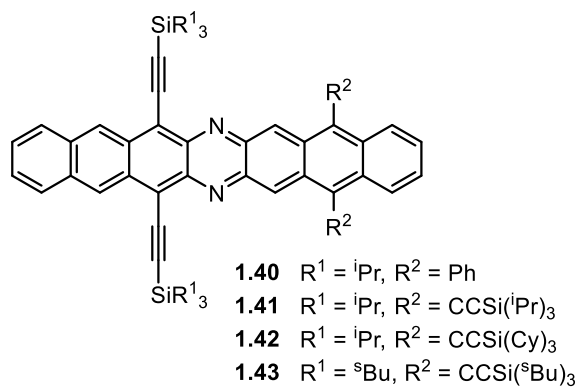
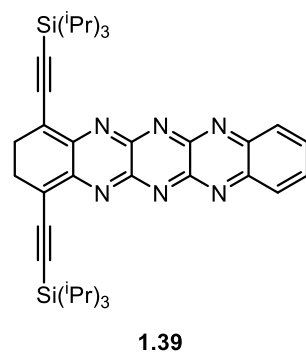
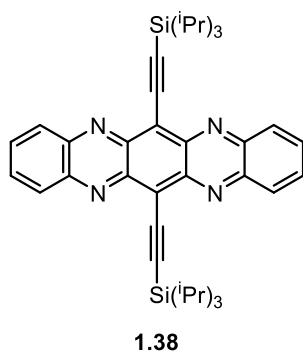
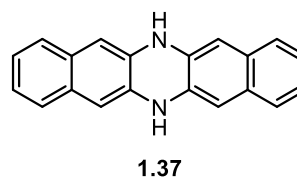
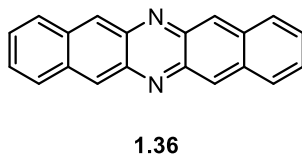
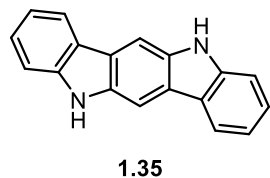
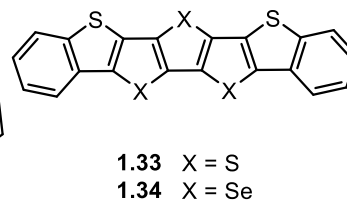
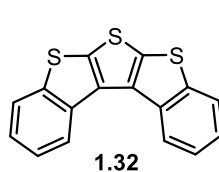
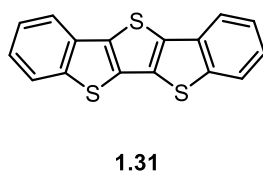
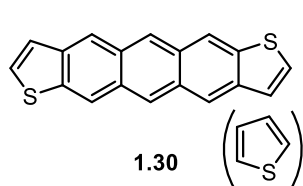
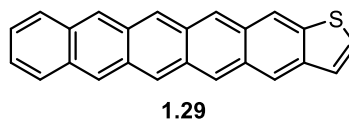
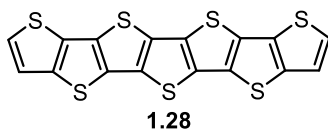
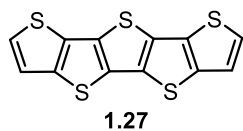
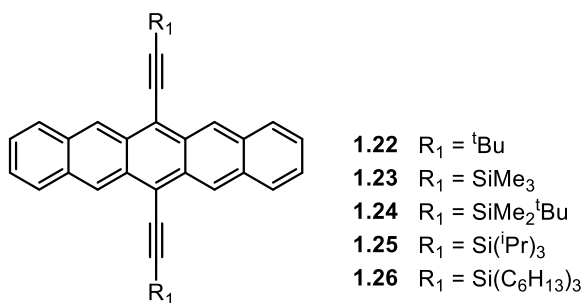
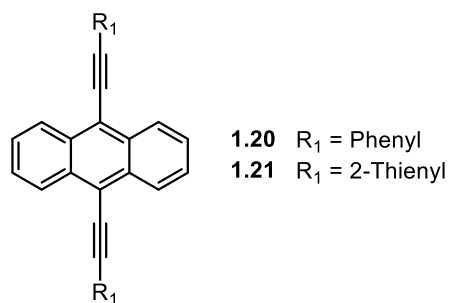


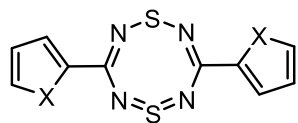
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1.18 R₁ = Phenyl

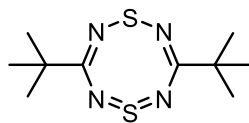
1.19 R₁ = 2-Thienyl



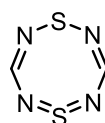


3.13 X = O

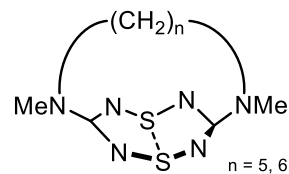
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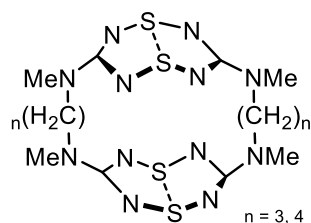
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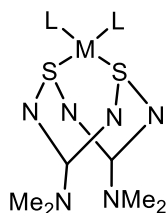
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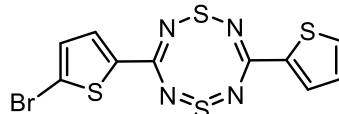
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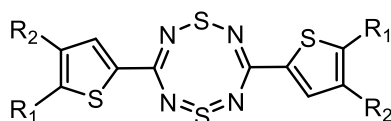
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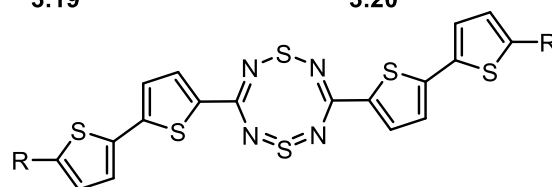
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3.22 R₁ = C₆H₁₃, R₂ = H

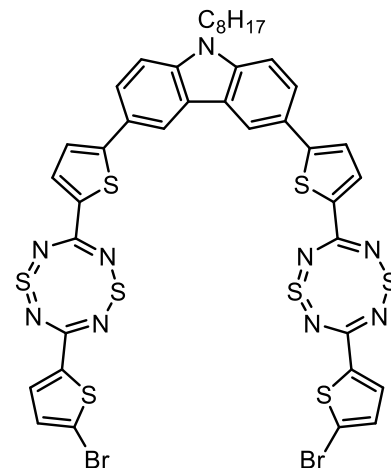
3.23 R₁ = Br, R₂ = H

3.24 R₁ = H, R₂ = C₆H₁₃

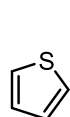


3.25 R = H

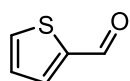
3.26 R = C₆H₁₃



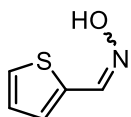
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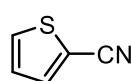
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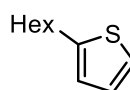
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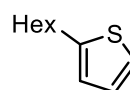
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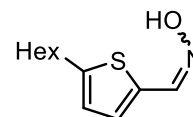
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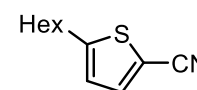
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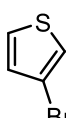
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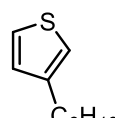
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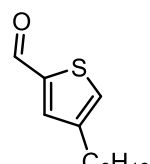
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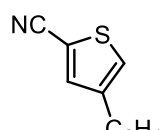
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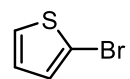
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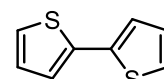
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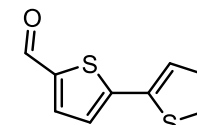
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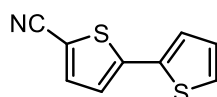
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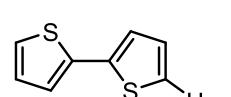
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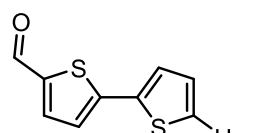
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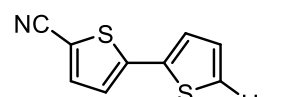
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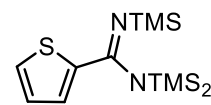
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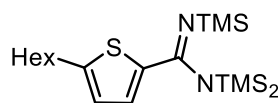
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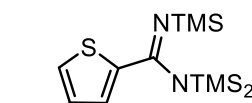
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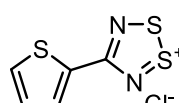
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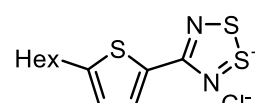
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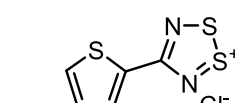
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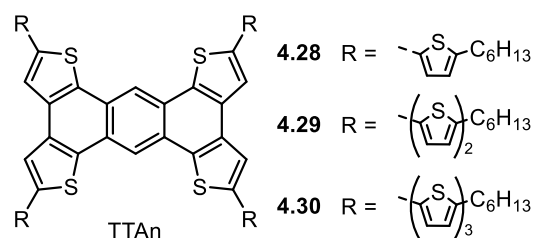
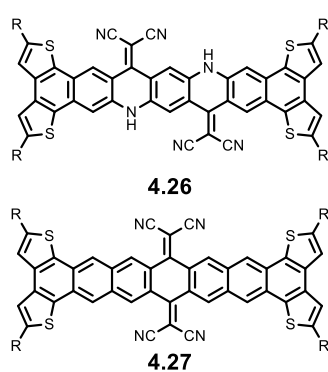
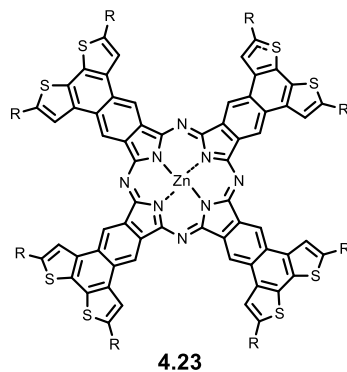
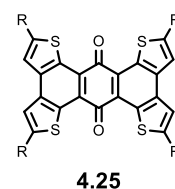
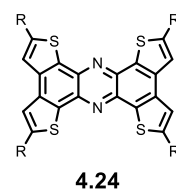
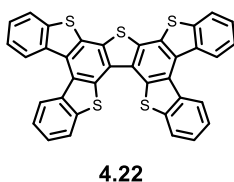
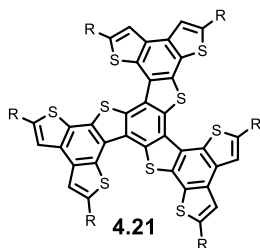
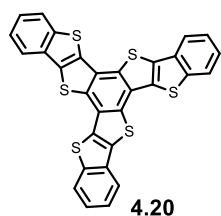
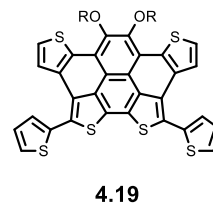
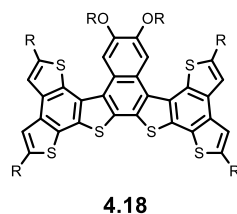
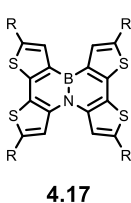
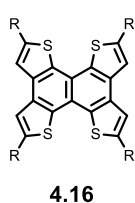
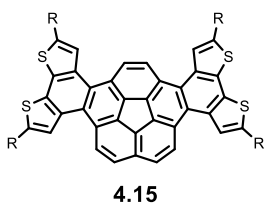
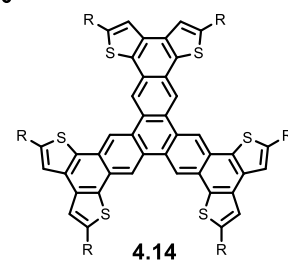
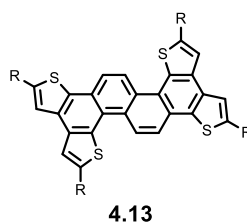
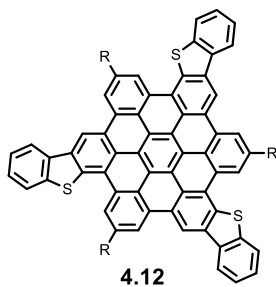
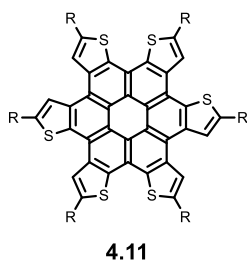
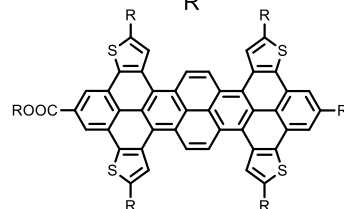
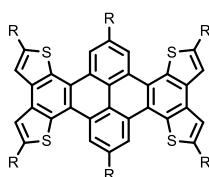
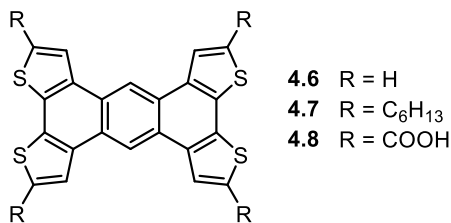
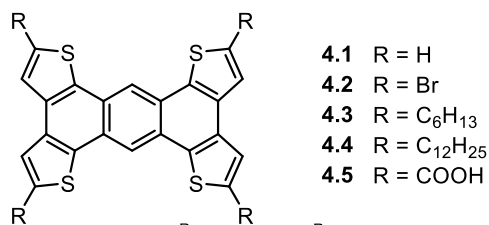
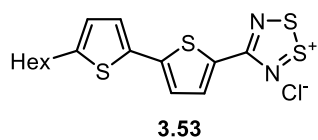
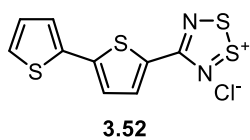
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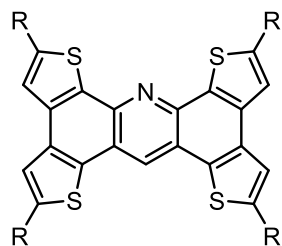


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3.51

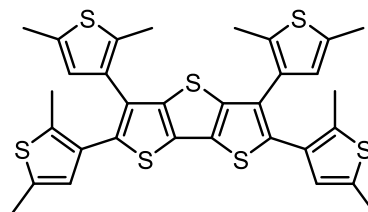




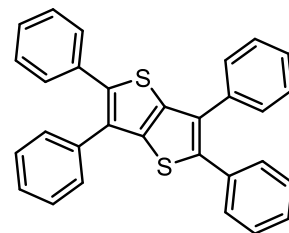
4.31 R = Br

4.32 R = C₆H₁₃

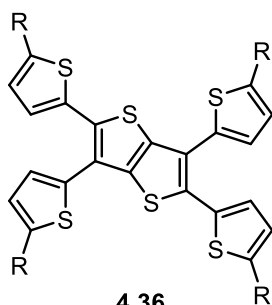
4.33 R =



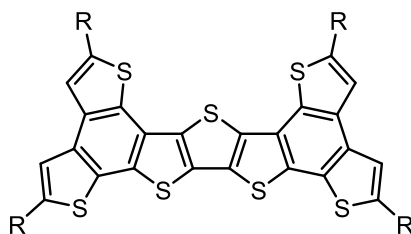
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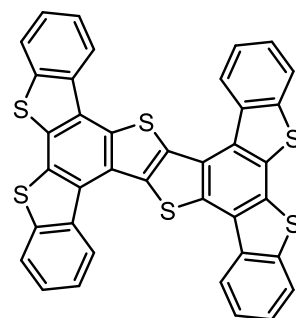
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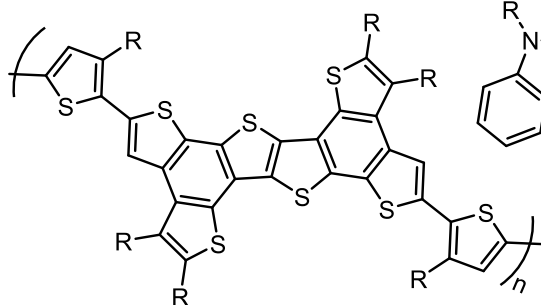
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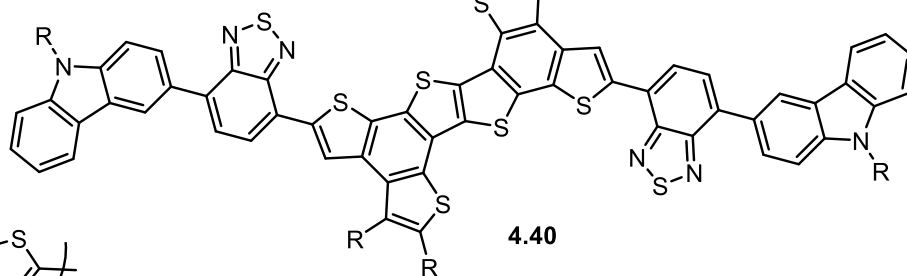
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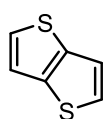
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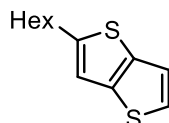
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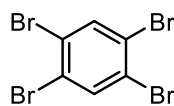
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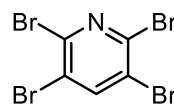
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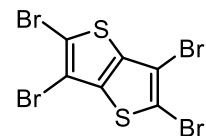
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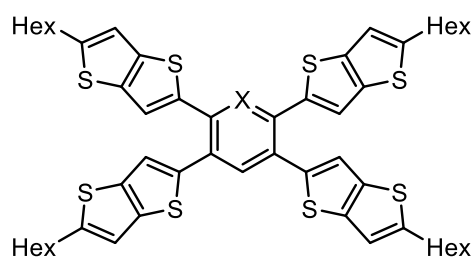
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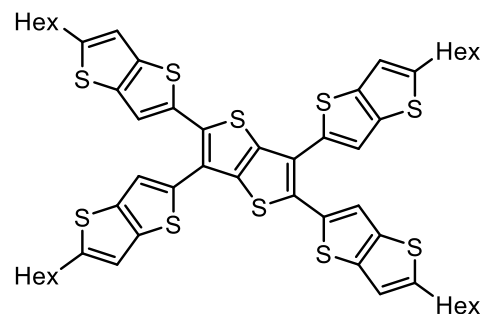


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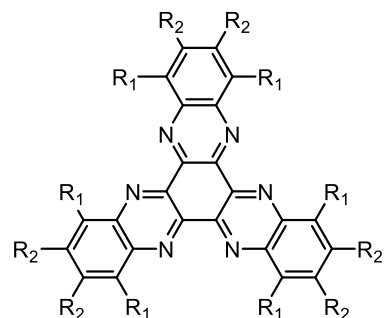
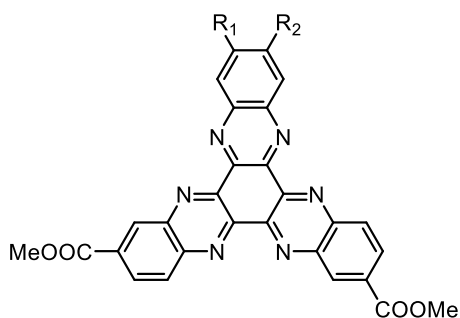
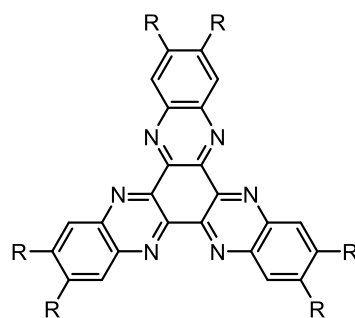
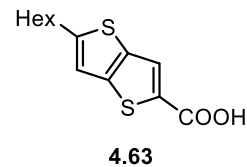
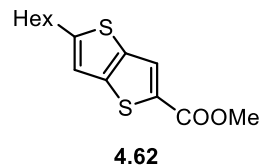
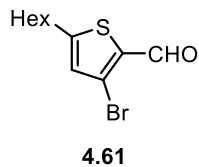
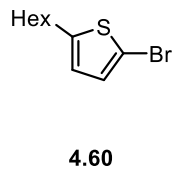
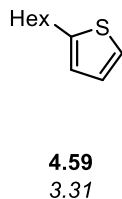
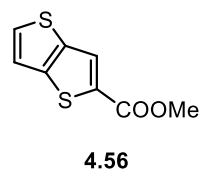
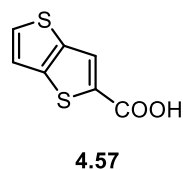
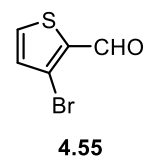
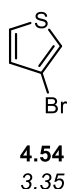
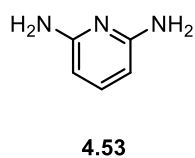
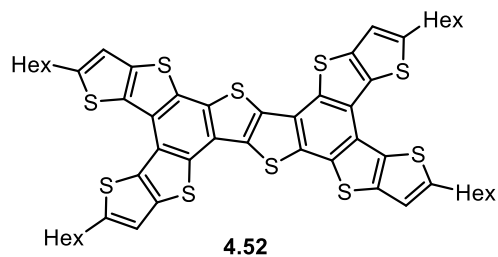
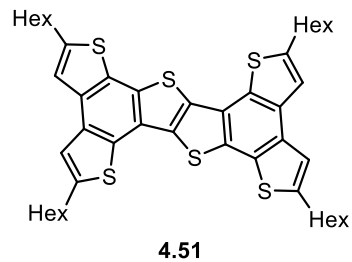
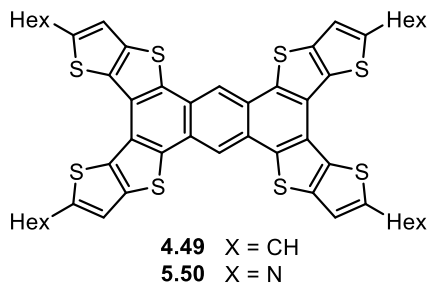


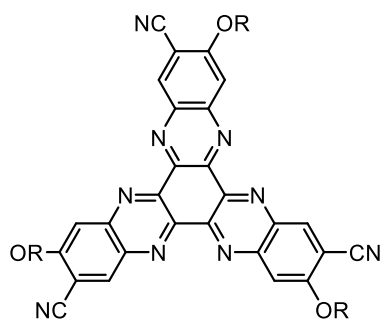
4.46 X = CH

4.47 X = N

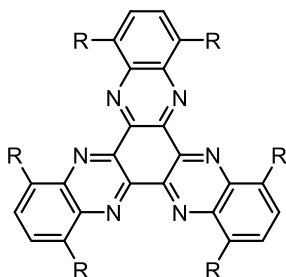


4.48





5.9 $R = OC_nH_{2n+1}$, $n = 1, 6$



5.10 $R = C_nH_{2n+1}$, $n = 4-14$

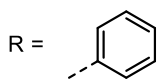
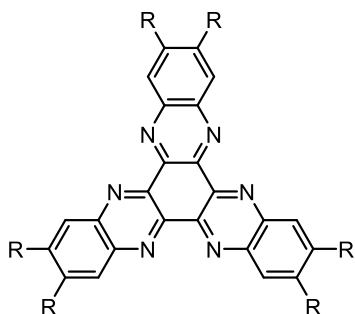
5.11 $R = SC_nH_{2n+1}$, $n = 6-8$

5.12 $R = CCC_nH_{2n+1}$, $n = 6-8$

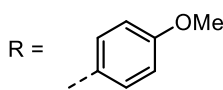
5.13 $R_2 = CCSiEt_3$

5.14 $R_2 = CCSi^iBu_3$

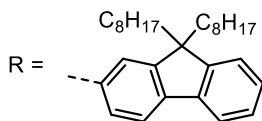
5.15 $R_2 = CCSi^iPr_3$



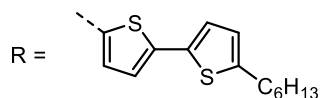
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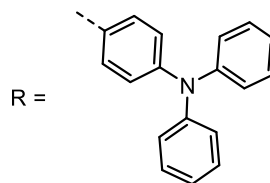
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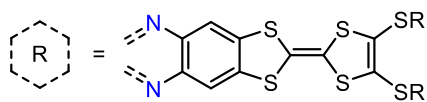
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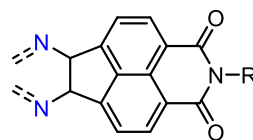
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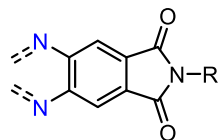
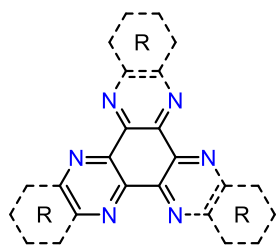
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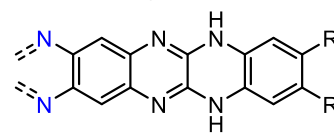
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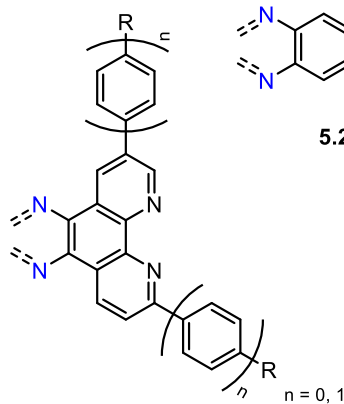
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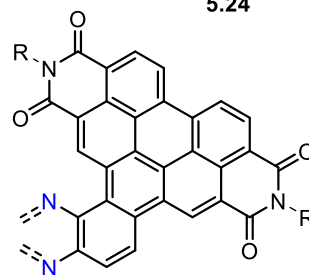
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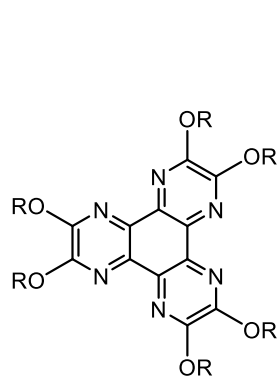
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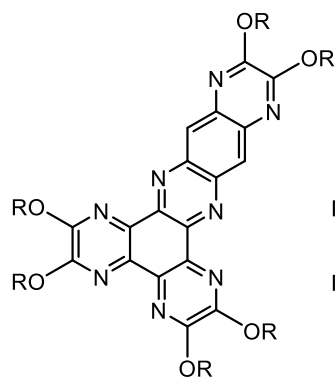
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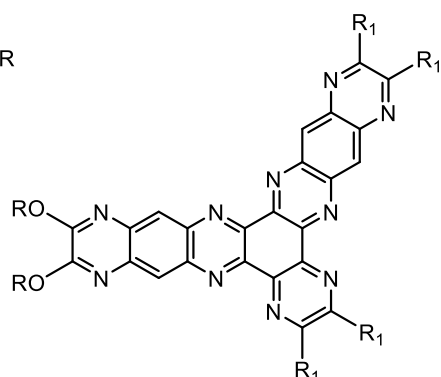
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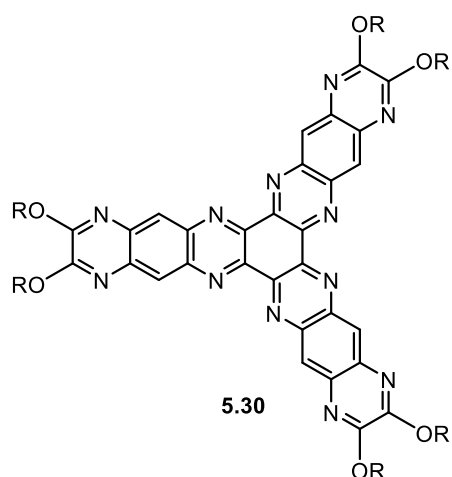
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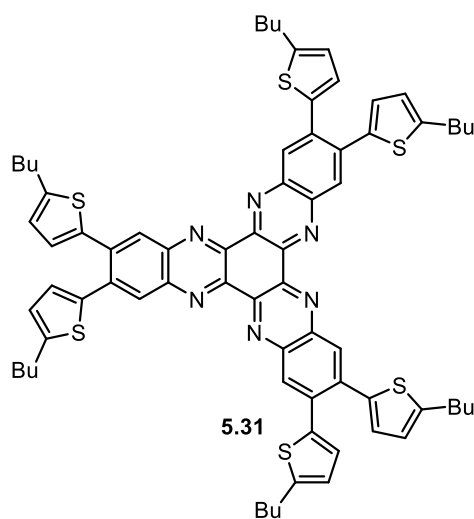
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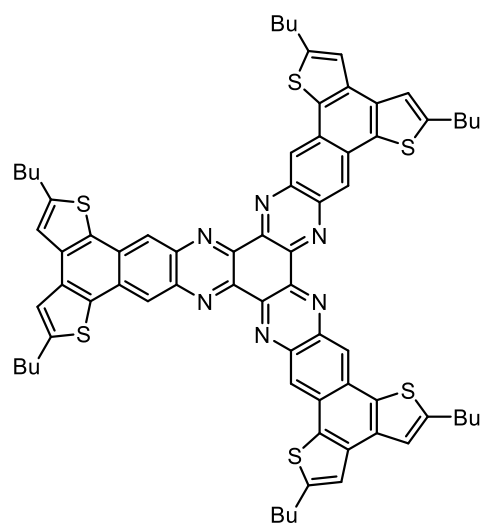
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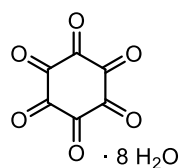
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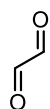
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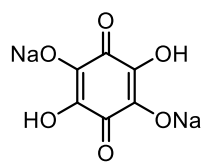
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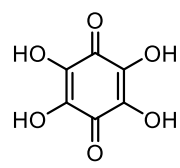
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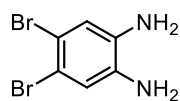
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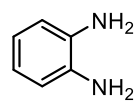
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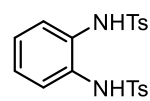
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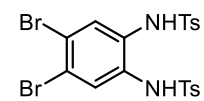
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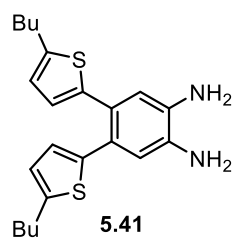
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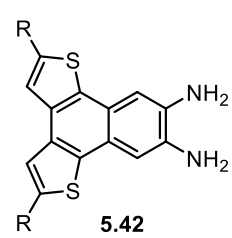
5.39



5.40



5.41



5.42

Chapter 1

Introduction

1.1 Transistors: Applications and Architectures

Solid-state transistors are fundamental building blocks in electronic devices whose miniaturization has paved the way to a dramatic shrinking of computerized systems, along with an equally impressive expansion in their processing power.¹ Comprised of a three electrode setup bridged by a semiconductor, applying a voltage (input) to one pair of electrodes (source-gate) allows control over current (output) flowing through the second pair of electrode (source-drain). Since the current used in the input is typically much smaller than that in the output, the transistor can act as both a signal amplifier and a switch, both of which are crucial in the design of logic gates and in signal processing for modern-day electronics. Of particular relevance is the field-effect transistor (FET), which requires less current to turn on while providing a higher current output. FETs are constructed from the same three electrodes (the source, the drain and the gate), which can be arranged in different configurations (Fig. 1.1).² In all instances, the source and the drain electrodes, through which the output current flows, are in contact with the semiconductor, while the gate electrode is separated from the other electrodes by a dielectric insulator.

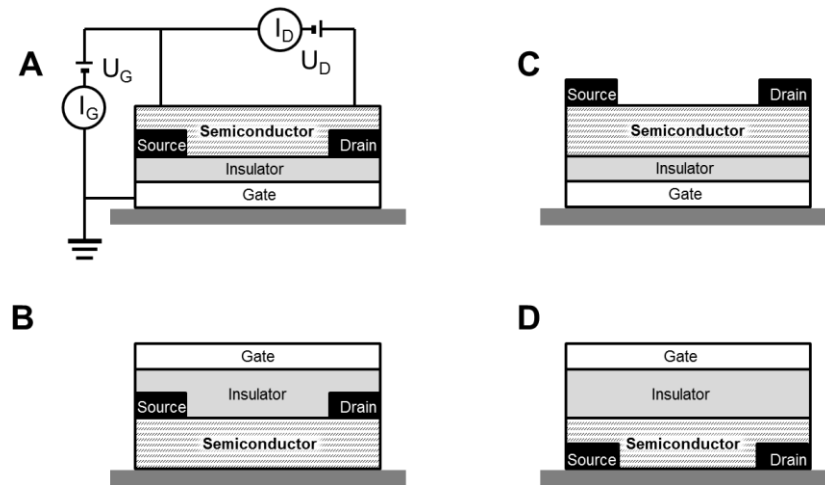


Figure 1.1 - Schematic view of common FET configurations. **A)** Bottom gate/Bottom contact. **B)** Top gate/Top contact. **C)** Bottom gate/Top contact. **D)** Top gate/Bottom contact. The schematic for A also displays the electrical circuit involved in the FET's functioning (similar circuits for B-D are omitted for clarity). Legend: Dark gray: Substrate; White: Gate electrode; Light gray: Insulator; Black: Source/Drain electrodes; Dashed: Semiconductor. U_G : gate voltage; I_G : gate current; U_D : drain voltage; I_D : drain current.

If no input voltage is applied between the gate and the source, (ideally) no output current can flow from the source to the drain, and the device is in its *off-state*. By applying a positive voltage to the gate, negative charge carriers will accumulate at the semiconductor/insulator interface (and vice-versa for a negative voltage and positive charge carriers), which allows the output current to flow between the source and the drain. By tuning both the gate voltage (U_G) and the source/drain voltage (U_D), the current (I_D) can be controlled. This conductive state is referred to as the *on-state*. The performance of FETs can be characterized using three important parameters:¹

Threshold voltage - The minimal gate voltage that needs to be applied for the transistor to display conductivity. Defects in the semiconductor act as charge traps, which inhibits current between the source and drain. Applying a gate voltage first fill these traps, after which current can start circulating. Although this value is ideally low, it shouldn't be quite 0, as the FET needs a true *off-state* for a proper logic-gate application.³

On-off ratio - The ratio of the output current in the *on* and *off* states. A high value is ideal for easily distinguishing the two states in electronic circuits and logic gates, with 10^5 being competitive with amorphous silicon.

Charge-carrier mobility - The charge mobility is the drift velocity of the charge carrier for a given potential. As a high charge-mobility implies faster charge transport for a given potential, the mobility determines the power consumption of the transistors, and as such a high value is also desirable (a mobility of $0.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ is comparable to that of amorphous silicon).

The electronic structure of the semiconductor plays the most determinant role in its device performance. Firstly, a judicious choice of materials for all the transistor's elements (*i.e.*, the semiconductor, but also electrodes and insulator) and their energy level alignment plays a crucial role in obtaining optimal charge transport.⁴

1.2 Semiconductors from an Atomic Point-of-view

Although the use of semiconductors to transport electrical current in lieu of metals might seem counter-intuitive, one must remember that the key aspect of transistors is their capacity to be turned *on* and *off*. The conductivity of metals is hardly tunable, at least in a practical fashion.

The electronic properties of semiconductors, on the other hand, can be carefully controlled by doping with impurities. This behaviour can be rationalized by taking a closer look at what is happening at the atomic level.⁵ Interaction between n atomic orbitals results in the formation of n molecular orbitals through constructive and destructive interference. Constructive interference between the atomic orbitals leads to a stabilizing interaction, which lowers the energy of the resulting molecular orbitals, while the opposite occurs for destructive interference (*i.e.*, destabilization, thus raising the energy of the resulting orbitals). As more and more atoms, and thus atomic orbitals, are added, the energetic difference between the resulting molecular orbitals grows progressively smaller. Where adding a few atoms together to form discrete molecules will yield well defined energy levels, the mixing of a large quantity of atoms generates many closely-spaced orbitals that form a continuous band rather than discrete orbitals, as illustrated in Figure 1.2. Two bands of interest result: the valence band, which is analogous to the HOMO and contains electrons, and the conduction band, which is analogous to the LUMO and is empty. The level of electron occupancy in the band structure is described with the Fermi level, which can be treated as a hypothetical energy level with a 50% probability of being occupied.⁶

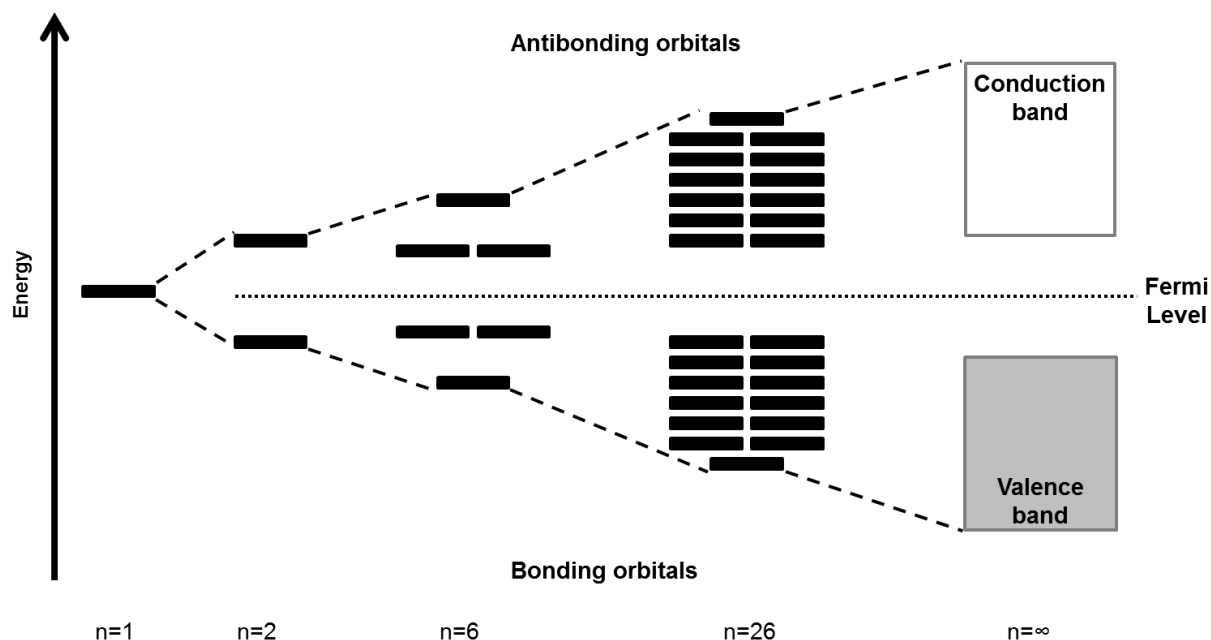


Figure 1.2 - Energy level diagram of a theoretical solid system that shows the evolution of the MOs as more and more atoms are added. In a continuous solid (where the number of atoms n is considered as infinite) the closely spaced MOs result in a band structure.

Because of this minimal energy difference in the levels constituting bands, intraband electron movement is technically uninhibited at room temperature.² In that regard, the excellent thermal and electric conductivity of metals can be rationalized by their partially filled valence band (Fig. 1.3), where electrons are freely delocalized throughout the metal. Compounds with filled bands and no overlapping of the bands are poor conductors, as electrons have no room to move about, *per* Pauli's exclusion principle. They can, however, be made conductive by chemical oxidation, which depletes electrons from the valence band, or reduction, which inserts electrons into the conduction band. In both cases, a partially filled band results, and metallic behavior occurs. Otherwise, insulators make for poor active materials from a device application point-of-view, as the energy difference between the two bands (*i.e.*, the band gap) is too large to allow efficient promotion of electrons (Fig. 1.3) and induce conductivity.

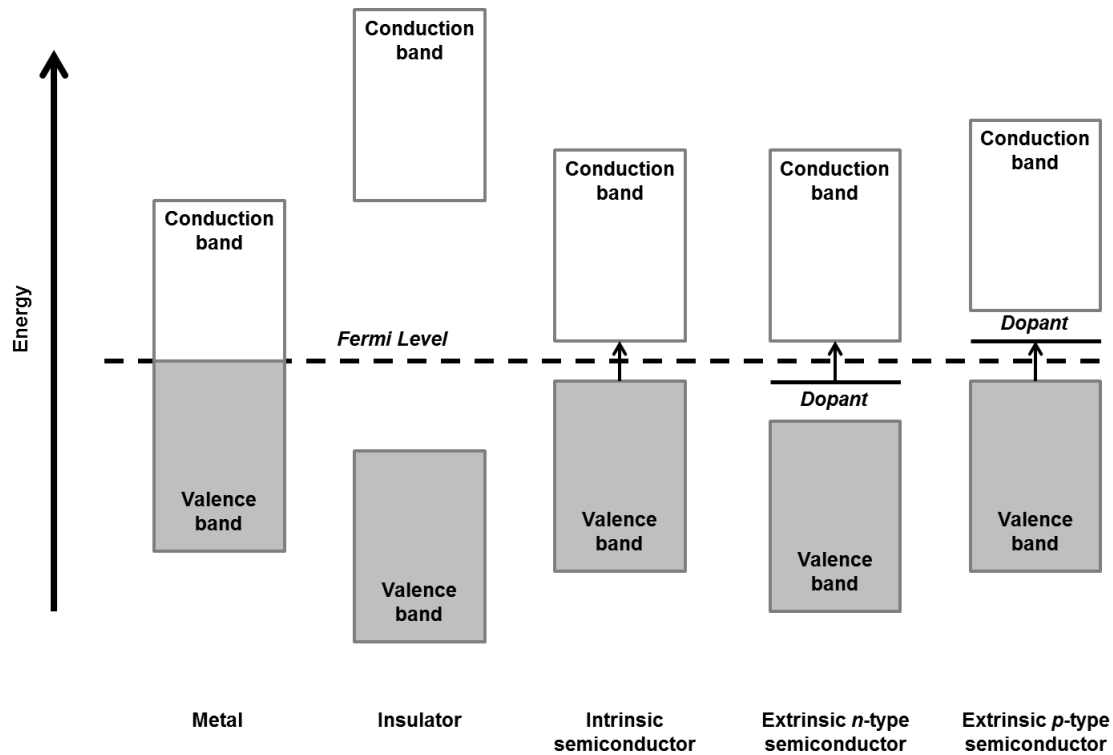


Figure 1.3 - Band energy diagram for metals, insulators and various types of semiconductors. Figure adapted from [2].

Intrinsic semiconductors, on the other hand, exhibit a non-null band gap that is sufficiently small to allow electron promotion from the valence band to the conduction band through thermal activation at room temperature. The use of light or electric potentials can also efficiently promote electrons (Fig. 1.3). Frequently, high purity inorganic semiconductors will be

carefully doped to introduce charge carriers and localized energy levels within the band gap, effectively narrowing the latter and enabling thermal activation.² While *n*-type doping introduces electron-rich impurities that facilitate the promotion of electrons to the conduction band (and thus electron transport), *p*-type doping favours hole transport, as electron-deficient impurities can accept electrons from the filled valence band (Fig. 3). In combination with the limited scattering of the charge carriers by the solid lattice, this doping can lead to fairly high mobilities (*e.g.*, up to $\sim 1400 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for electron transport in single crystalline silicon).⁷

1.3 Organic Semiconductors in Device Applications

Although the materials used in transistors have historically been inorganic semiconductors,⁶ such as silicon, germanium or gallium arsenide (GaAs), organic semiconductors (OSCs) have emerged as a potential alternative. Levels of purity like those obtained in inorganic semiconductors is however seldom achieved in organic molecules, and, until recently,^{8–11} doping could not be relied on as a strategy to further control the semiconductive behaviour of organic compounds, as it afforded instead a fully conductive state.² Additionally, the greater degree of structural disorder typically found in OSC is not conducive to band conductivity as the mean free path of charge carriers is on the order of magnitude of the molecular length. As a result, conductivity takes place instead *via* charge-hopping mechanism, and lower mobilities are observed in this class of semiconductors.¹²

While the mechanism at play with OSCs differs from its inorganic brethren, and typically doping is not employed, the *n*-type and *p*-type terminology still applies, whether the charge carrier is negative (electron) or positive (hole), respectively. Considering that holes are quasi-particles that are electrons migrating in the opposite direction as the carrier, one could expect organic molecules to conduct both charges equally well. This is rarely the case, however, as a result of the charge hopping mechanism at play.¹² To minimize the operating voltage and obtain efficient charge injection at the electrodes, the energy level of the OSC's appropriate frontier molecular orbital has to closely match the work function of the electrode material.⁴ The frontier orbitals of most organic compounds are sufficiently separated that they seldom are efficient for both hole- and electron- injection. Moreover, the molecule undergoes structural reorganization upon ionization. Since different reorganization typically occurs whether an electron is being

introduced or removed, the overall energetic cost of charge transport can differ whether the carrier is negative or positive.¹³ Finally, depending on the geometry of the molecule and the layout of the respective frontier orbitals, the packing motif might favor one carrier over another, depending on how the orbitals interact.

Organic *p*-type semiconductors remain more common than their *n*-type counterparts due to issues with stability toward ambient oxygen and water.⁴ The radical anion formed for *n*-type carriers can potentially reduce either oxygen and water or both. For an *n*-type OSC to be air-stable, the energy level of the LUMO has to be low lying (ideally below -4 eV), as to minimize the reducing potential of the anion. As low LUMO levels are difficult to achieve, efficient *n*-type OSC lag behind.¹⁴ *P*-type OSCs, on the other hand, are easier to achieve due to the key orbital, the HOMO, being by nature lower in energy to the LUMO. Still, the energy level of the HOMO in a *p*-type OSC should be below -5.2 eV to prevent oxidation by ambient oxygen. Shown in Figure 1.4 are a few examples of some of the key motifs frequently seen for *p*-type and *n*-type carriers.

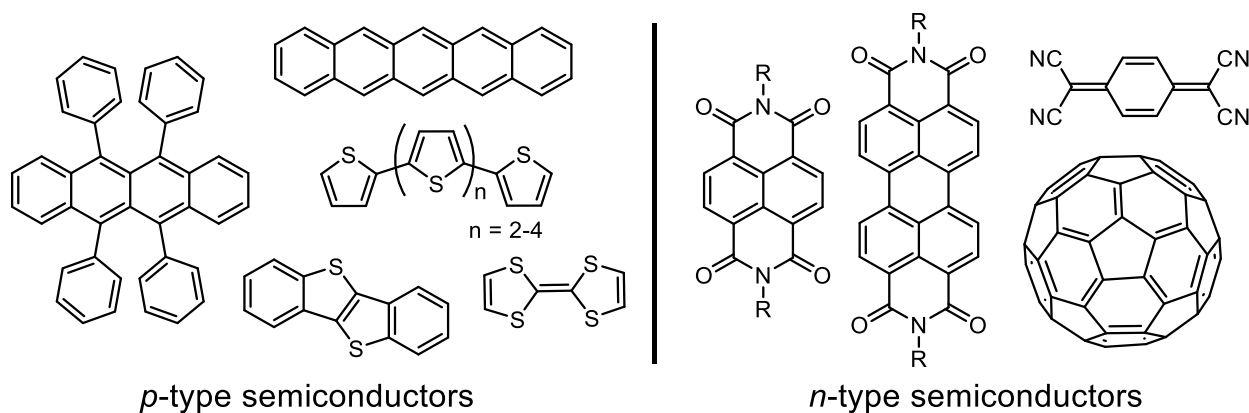


Figure 1.4 – Examples of common motifs observed in the construction of small-molecule *p*-type and *n*-type organic semiconductors.

As mentioned above, inorganic semiconductors typically exhibit higher mobilities than organic molecules due to the difference in the charge-carrying mechanism and the higher degree of structural order. Additionally, silicon devices tend to be more robust toward decomposition, unlike organic molecules, which can degrade either by reacting with oxygen/water or through decomposition of the excited-state intermediate. Both are important drawbacks, and much work

is geared toward solving them. Nonetheless, OSCs offer undeniable advantages over inorganic materials to warrant further research and usage in specific applications:¹

High processability - While some organic compounds lend themselves well to vacuum deposition techniques already common with inorganic semiconductors, the increased solubility of OSCs opens up the door to new processing and fabrication techniques that would be impossible with silicon, such as ink-jet and roll-to-roll printing techniques. These also have the advantage of being easily scaled-up, which means large areas devices can be rapidly fabricated

Low cost - In addition to being potentially cheaper to synthesize and purify, the printing techniques mentioned above also contribute to driving down the cost of mass-producing devices. This can open the way to new applications, such as radio-frequency identification chips as substitutes to optical barcodes employed today on consumer goods, low-cost sensors, flexible displays, plastic solar cells and single-use electronics.

Mechanical flexibility - Organic thin films are more tolerant to mechanical deformation than their silicon counterparts. In addition, the low temperature required for printing and film-forming techniques permits the use of plastic substrates which, in combination with the organic material's own mechanical advantages, allows for flexible devices.

Versatility of chemical synthesis - As chemists, we have access to the whole toolbox of organic synthetic methodology that allows control over the molecular structure of a material. This enables fine-tuning of both the electronic character of a single molecule and the 3D solid-state packing, parameters that have been showed to be determinant to device performance, and which are inherently unique for each molecule. Nonetheless, a lack of knowledge regarding structure-property relationship is one of the key challenges hindering further progress on OSCs. The remainder of this chapter is intended as a small review which will focus on some of the key aspects used in influencing and tuning the properties of molecules to afford better performance in device-applications.

Structure-wise, conjugated organic molecules can be divided in two large families: small-molecules and polymers. Small-molecule conductors carry several undeniable advantages over polymers.¹ Unlike polymers, which are prepared with a certain polydispersity, the synthesis of small-molecules is unambiguous, as all molecules are identical. Furthermore, defects along the

polymer chain, as a result of varying synthetic conditions, can lead to different levels of regio-regularity within the same backbone. Both of these issues contribute to lower batch-to-batch reproducibility. Small molecules may lend themselves to both solution and thermal deposition methods, but polymers are exclusively solution-processable. Due to their excellent film-forming characteristics, issues with film uniformity are uncommon for polymers. However, low crystallinity typically leads to limited charge carrier mobility. For all these reasons, the performance of small-molecule conductors remains higher than polymers.² Accordingly, work in the Brusso group has focused exclusively on small-molecules thus far.

1.4

Influence of the Solid-state Morphology on Device Performance

The packing morphology of organic molecules in the solid-state governs the extent of intermolecular interactions at play, and is therefore a crucial element to consider in the fabrication of devices. To maximise charge mobility in the solid-state, the molecular packing should be as dense as possible to maximise intermolecular orbital overlap. Shown in Figure 1.5 are examples of commonly observed packing motifs for planar π -conjugated molecules, in increasing order of intermolecular interactions.

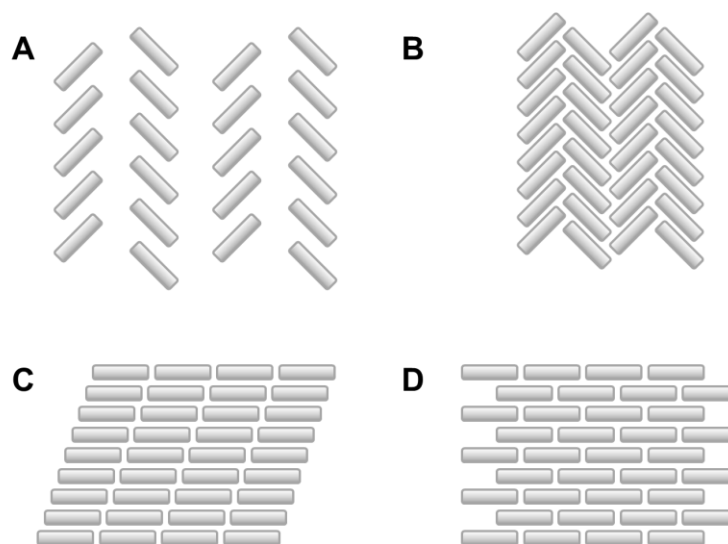


Figure 1.5 - Common packing motifs for 2D planar π -conjugated molecules, in increasing order of intermolecular contacts. **A)** Herringbone packing without $\pi \cdots \pi$ overlap. **B)** Herringbone packing with $\pi \cdots \pi$ overlap. **C)** Lamellar 1D π -stacking. **D)** Brick-like 2D π -stacking. Figure adapted from [15].

The herringbone motif (**A-B**), the least efficient packing covered here, displays face-to-edge interactions between neighbouring molecules. Albeit π -overlap can still occur, it is typically weak, depending on the molecular density. Once face-to-face interactions dominate, lamellar packing occurs, with a significant improvement in π -orbital overlap. This lamellar stacking can be columnar (C) or brick-like (D); the latter being highly desirable, as it promotes both a higher number of intermolecular interactions and higher degree of dimensionality to charge transfer. In addition to packing density, the spatial alignment of the semiconductor in regards to the electrodes can be determinant in device performance, as charge mobility is anisotropic in space. This is due to the charge-carriers moving about the π orbitals of the aromatic molecules, which are perpendicular to the plane of the framework. Finally, as molecular order tends to promote charge mobility, higher levels of crystallinity are desirable for enhanced performance. Everything else unchanged, single-crystal OSCs tend to exhibit better charge mobility than thin films.¹⁶ Minimizing grain boundaries in the latter will help in promoting continuous films and minimizing localized charge traps, thus enhancing the mobility.

1.5

Parent Molecular Structures of Organic Semiconductors

While it is well known that there is an intimate relationship between a molecule's structure and its properties and performance in device applications, there is yet much to be learned regarding this structure-property relationship to allow for total control in the design of materials. For this reason, the remainder of this chapter is devoted to successful strategies previously reported in literature for controlling the morphology and/or performance of small organic molecules in devices. These examples will be divided into two broad families: linear acenes and oligothiophenes.

1.5.1 Linear Acenes

Linear acenes (Fig. 1.6), composed of linearly fused benzene rings, hold a somewhat special place in the field of OSCs. Indeed, research on the photoconductivity of anthracene (**1.1**) over a century ago kick-started the study of the optoelectronic properties of organic molecules that continues to this day.⁶ Acenes of increasing lengths (**1.1-1.3**) have shown improved charge mobility by approximately one order of magnitude per extra ring, with typical mobilities ranging

from ~ 0.02 to $0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ between **1.1**¹⁷ and **1.2**.¹⁸ and with values of $1.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ having been reported for films of pentacene **1.3**.¹⁹

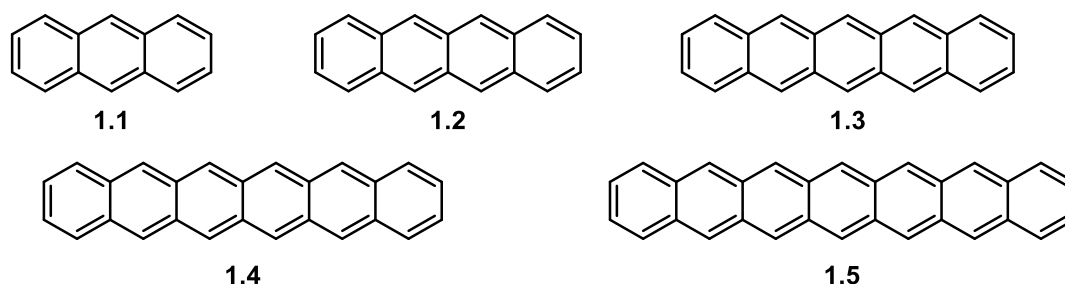


Figure 1.6 – Molecular structures of unfunctionalized linear acenes.

These values should be taken as a trend rather than at face value, as they can fluctuate from trial to trial depending on differing parameters, such as device configuration and fabrication techniques, purity and/or crystallinity. For instance, mobilities as high as $5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ have been reported for polycrystalline pentacene²⁰ as a result of increased molecular order, which facilitates charge hopping in the solid-state. This increase in charge mobility with increased conjugation length can be attributed to both an increase in intermolecular overlap and a decrease in structural reorganization energy.²¹ Considering this trend, the logical extension would be to push the conjugation toward longer systems, such as hexacene **1.4** and heptacene **1.5**; however, two major issues have hindered progress toward such derivatives, both of which are illustrated in Figure 1.7.

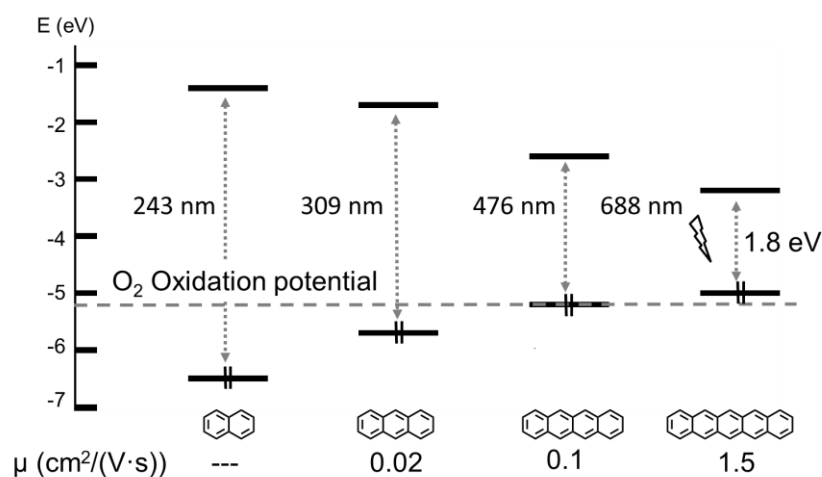


Figure 1.7 – Energy level diagram for the frontier molecular orbitals of short linear acenes that shows the impact of the extension of conjugation on the orbitals.

Firstly, increasing the length of linear acenes leads to a steady increase of the HOMO level, which makes the molecules more and more susceptible to oxidation from ambient oxygen (as mentioned in Section 1.3). While the HOMO energy levels for acenes from benzene through tetracene are located below the oxidation potential of oxygen (-5.2 eV), the HOMO of pentacene is already above this potential. As a result, pentacene is prone to decomposition to 6,13-pentacenequinone through an endoperoxide intermediate upon exposure to oxygen.²² On the other hand, increasing the length of conjugation leads to a decrease in the band gap of the molecule, which therefore lowers the amount of energy required to promote an electron to an unoccupied orbital. In the case of pentacene, this gap is only 1.8 eV, which corresponds to a photon with a wavelength of 688 nm. The entire visible light spectrum is thus sufficiently energetic to photoexcite the ground-state pentacene, which can lead to decomposition as a butterfly dimer.²³ Consequently, pentacene has to be stored away from both air and light to prevent decomposition, and simple extension of the conjugation can be expected to worsen these issues. Finally, an increase in the conjugation length is associated with a concomitant decrease in solubility. Although these issues certainly haven't stopped adventurous chemists of succeeding at preparing higher acenes, their reports remain scarce, as a result of their limited stability.^{24–27}

1.5.2 Oligothiophenes

Whereas acenes were the first types of organic molecules whose photophysical properties were investigated, oligothiophenes hold the distinction of being the first organic molecules employed in FETs.²⁸ In fact, the thiophene heterocycle, whose electron-rich nature promotes *p*-type behaviour, is almost ubiquitous with the field of OSCs, and for many good reasons. While aromatic and stable to ambient conditions, they tend to be more chemically reactive than benzene derivatives, with improved regioselectivities. In combination with the fact that many thiophene derivatives are commercially available at modest prices, this amounts to a facilitated synthetic customization and makes the preparation of a library of thiophene derivatives fairly straightforward. The sulphur atom also contributes to the solid-state and conductive properties. Its incorporation introduces the potential for additional intermolecular contacts (*e.g.*, S $\cdots$ S, S $\cdots$ H, S $\cdots$ π), which can disrupt the typical edge-to-face interactions found in all-carbon acenes in favour of a more desirable face-to-face packing motif. The larger, more diffuse orbitals associated with sulphur (compared to carbon), also permits a greater potential for intermolecular

interactions, which can be favourable to enhanced electronic communication, and thus charge transport in the solid-state.

Contrary to acenes, which are rigid planar molecules, oligothiophenes can adopt a twisted shape, as the individual cycles are free to rotate with respect to one another, the result of being linked together through a single carbon-carbon sigma bond. Unlike oligophenylenes, whose monomers favor an orthogonal arrangement to avoid steric clash between the hydrogen atoms, oligothiophenes maintain planarity in the solid-state more efficiently thanks to both interchain sulphur-sulphur interactions and the less sterically demanding five-membered ring geometry. This flat geometry allows the conjugation to be more efficiently maintained throughout the oligomer and a tighter, more efficient packing results. While sulphur is more favorable toward efficient intermolecular orbital overlap and charge-carrier mobility, the HOMO levels of oligothiophenes are generally higher in energy than their phenylene counterparts as a result of the electron-rich core, which lowers their ambient stability. One strategy to overcome this has been to prepare thiophene-phenylene co-oligomers, which has been shown to successfully combine the best of both derivatives.^{29–31}

1.6

Tuning the Molecular Structure of Organic Semiconductors

Both linear acenes and oligothiophenes tend to be plagued with stability and solubility issues, which arise with extension of the conjugation. Thankfully, this isn't the end of the line, as multiple strategies have been shown to effectively stabilize OSCs and fine-tune their properties, both at the molecular and at the solid level, some of which will be discussed in the following sections.

1.6.1 Bent, Discotic and 2D Acenes

Simply deviating from linearity in acenes (Fig. 1.8) can have an important impact on the molecular properties. Perhaps the most obvious case of this is picene **1.6**, a bent isomer of pentacene. Stable to both air and light (unlike pentacene) as a result of a higher HOMO and a wider bandgap, **1.6** has exhibited comparable mobilities in devices ($\sim 1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$).³² Extension of the conjugation in 2D is also a viable strategy to maximise intermolecular interactions in the solid-state and provide more pathways for charge hopping. Additional contacts between

neighbouring molecules also reinforces the solid network, and prevents disruptions in the packing that can occur from molecular reorganization that occurs as charge carriers move through the molecules. Discotic 2D molecules that possess a higher C/H ratio tend to prefer columnar aggregates over herringbone packing arrangements, as a consequence of diminished $\text{CH}\cdots\pi$ interactions. Pyrene **1.7** and perylene **1.8**, 2D counterparts to tetracene and pentacene, are both examples of this change of morphology.³³ Isomers of hexabenzocoronene **1.9** and **1.10** have also exhibited interesting morphological differences in the solid state.^{34,35} While **1.9** is fully planar, its structural isomer **1.10** adopts a twisted conformation as a result of steric congestion between the outer benzene rings.³⁵

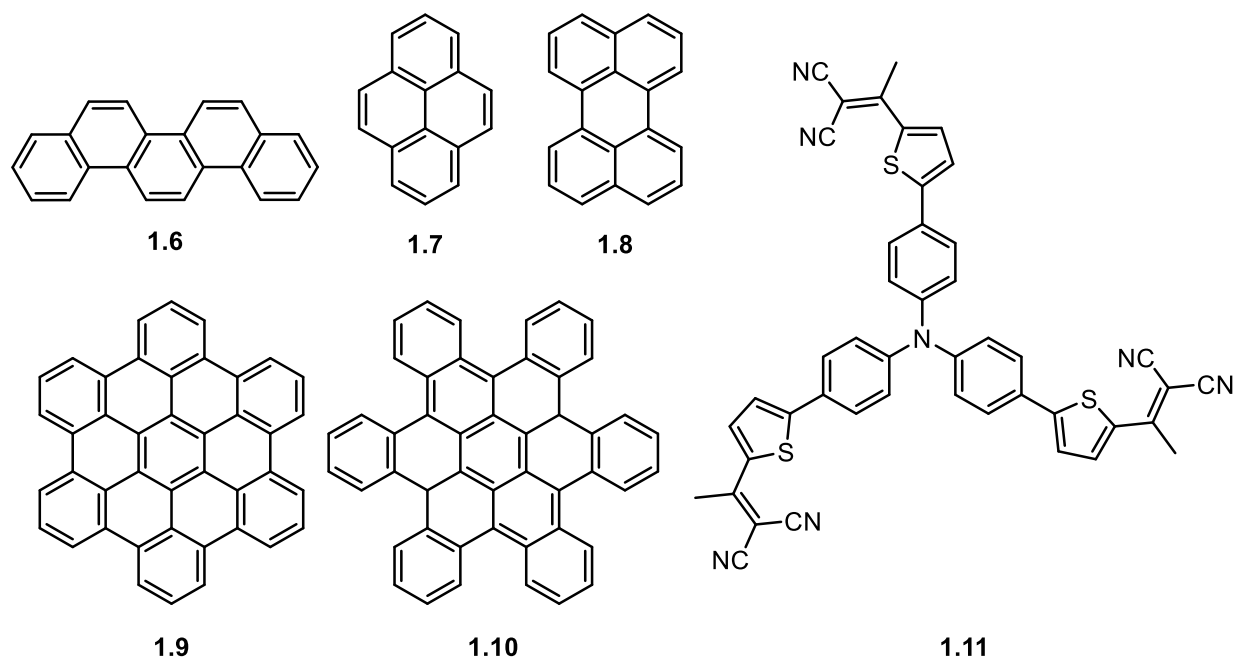


Figure 1.8 – Molecular structures of bent and discotic acenes and oligothiophenes.

Additionally, star-shaped oligomers are structures with linear branches extending from a common core. While the nature of the core can range from a single atom (*e.g.*, carbon, silicon) to an aromatic system of varying length and dimensionality, it is attached to its arms through a single sigma bond, which implies a degree of rotational freedom for the arms. Star-shaped molecules with oligothiophenes arms, a frequent sight for OSC applications, can be viewed as 2D analogues to linear oligothiophenes (*e.g.*, **1.11**). Compared to oligothiophenes, they typically exhibit higher solubility, better film-forming qualities, enhanced optical absorption, and isotropic

charge-transport and optical properties. Conversely, their synthesis is often more complex than both small molecules and linear polymers and typically involve repeated synthetic steps.^{36,37}

1.6.2 Substitution and its Effect on Molecular and Solid-state Properties

Solid-state packing of molecule plays a key role in the performance of OSCs, as it accounts for intermolecular orbital overlap and thus bandwidth for charge transport. All of the components of an organic molecule play a role in the way a molecule will stack in the solid-state, whether it be major or subtle (Fig. 1.9). Planar aromatic molecules, such as pentacene **1.3**, have a tendency to assemble in a herringbone fashion as a result of a balance between $\pi \cdots \pi$ interactions and electrostatic repulsion, but this balance can be easily disturbed to yield different packing geometries. For instance, the addition of polar groups to the rigid framework, such as carbonyls (**1.12**),³⁸ has been shown as a successful strategy to induce lamellar stacking in the solid-state, thanks to the resulting dipole moment that acts as a templating interaction to guide the solid assembly of the molecules.

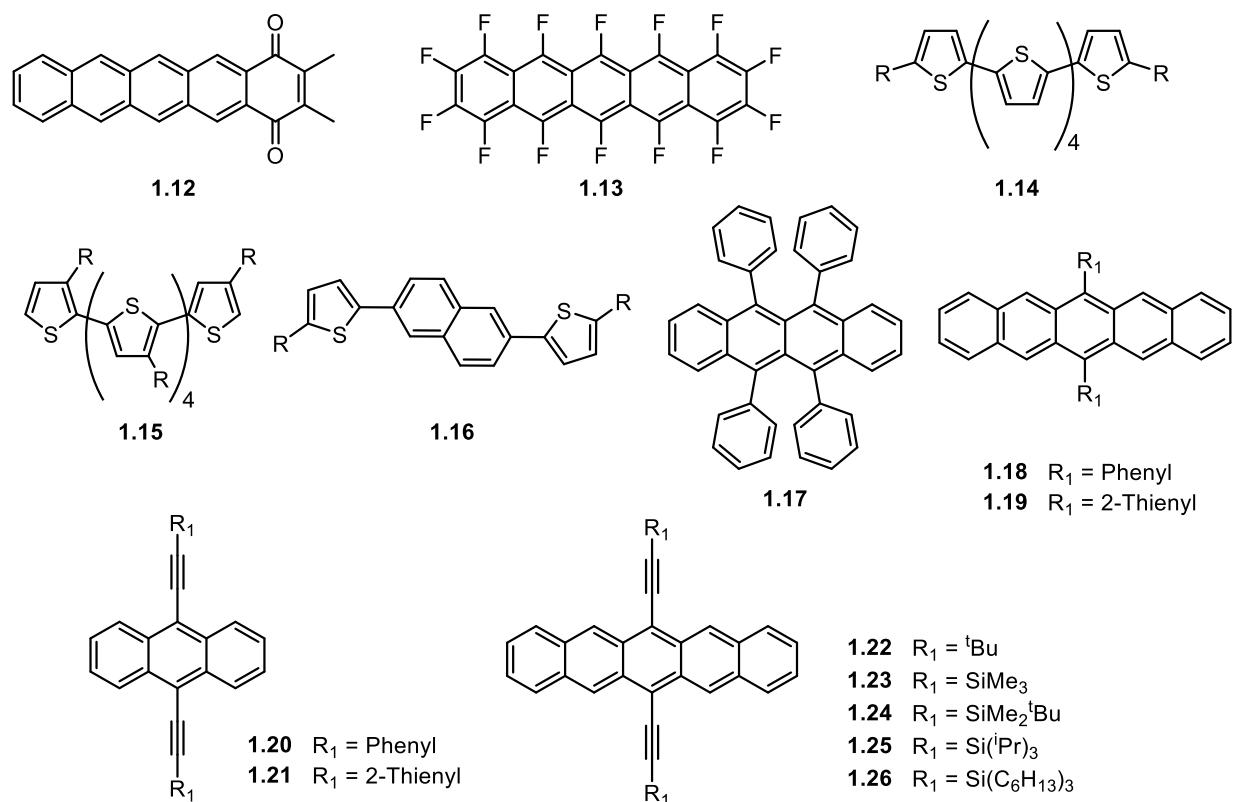


Figure 1.9 – Molecular structures of substituted acenes and oligothiophenes. Unspecified R groups correspond to alkyl chains of various lengths and geometries.

A more obvious impact that substituents can have on an aromatic framework is their capacity to influence its electronic structure. While electron donating groups increase the electron density in the ring and raise the MO energy levels, electron withdrawing groups have the opposite effect. As mentioned in Section 1.3, *n*-type OSCs remain more scarce than their *p*-type cousins due to the requirement of low lying LUMOs for stable and efficient operation. As a result, most successful *n*-type OSCs possess strongly electron withdrawing groups, notably halogens, cyanos and carbonyls. One somewhat less obvious influence of substituting groups, however, is their ability to direct solid-state packing through intermolecular contacts, such as van der Waals interactions or hydrogen bonding, in the presence of appropriate substituents (*e.g.*, amines, imines, alcohols). Halogens, in addition to being electron-withdrawing, are also an important templating moiety thanks to halogen bonding, which is a result of the anisotropic electron distribution around the halogen atom.³⁹ For instance, perfluorinating pentacene (**1.13**) has been shown to promote a tighter herringbone packing in the solid state, as all the CH $\cdots\pi$ interactions are substituted for halogen bonding.⁴⁰ Furthermore, the combined power of all the electron-withdrawing fluorine atoms were sufficient to reverse the charge-carrier polarity of pentacene, making it an *n*-type semiconductor.

Alkyl chains of various lengths and geometries are another type of substituent commonly employed. As unsubstituted acenes and oligothiophenes tend to be poorly soluble due to strong $\pi\cdots\pi$ interactions, these chains are useful to impart not only solubility (a necessary characteristic for solution-based processing) but have also been shown to promote self-assembling character in the solid-state.⁴¹ Both solubility and packing are highly dependant on the size and geometry of the alkyl moiety. While linear chains allow for more efficient interdigitation of the substituents and tighter packing in the solid-state, branched chains yield enhanced solubility through increased steric repulsion, at the cost of reduced contacts between molecules. The pattern of substitution for a given core framework can also play an important role on the way the molecules pack in the solid-state. For instance, alpha substitution of oligothiophenes (**1.14**) barely affects solubility of the oligomer, as the monomers prefer to keep a planar structure, but has the advantage of promoting a more intimate packing. Beta substitution (**1.15**), on the other hand, has an opposite effect, as twisting in the chain is prone to occur to minimize steric repulsion between carbon chains. In the case of linear acenes, side-substitution is more efficient at disrupting edge-to-face

intermolecular interactions, and promotes the more desirable face-to-face stacking in the solid-state.

Functionalization can also be achieved with aryl groups. As aromatic systems, they can extend the conjugation of the framework and offer additional active surface area for molecular interactions. For instance, a thienyl substituted naphthalene derivative (**1.16**) has been shown to exhibit mobilities on-par with tetracene, with which it shares a comparable π surface area.⁴² Again, the position of functionalization in regards to the core dictates the impact on the properties. In the case of linear acenes, functionalizing the end positions with aryl groups is more conducive to extending the conjugation than functionalizing the side positions. Although substitution at *peri* positions (perpendicular to the main conjugation axis) can still lead to enhanced intermolecular interactions and $\pi\cdots\pi$ overlap, such side-substituents with rotational freedom tend to be non-planar, to minimise steric clashing with the core system. This translates to capricious, typically unsatisfactory, performance in amorphous films, but excellent performance in single-crystals. Perhaps the most famous example of this contrast can be seen with rubrene (**1.17**), a tetracene core substituted with four phenyl rings.⁴³ While single-crystals of rubrene have repeatedly exhibited among the best measured mobilities for organic compounds ($\sim 13 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$), amorphous thin films make for poor active layers ($\sim 0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$).⁴⁴ This difference is due to the well-ordered structure, which shows multiple close contacts between the benzene rings and neighbouring tetracene cores, and consequently facilitates orbital overlap between neighbours. The choice of the aryl substituent also impacts the solid-state structure. A diphenyl substituted pentacene (**1.18**) exhibited an orthogonal cage-like arrangement due to $\text{CH}\cdots\pi$ interactions between the hydrogen atoms in the phenyl group and the neighbouring acene. Substituting the phenyl to a thienyl (**1.19**) led to a cofacial arrangement of neighbouring acenes due to the disappearance of the aforementioned $\text{CH}\cdots\pi$ interaction, along with a concomitant increase in charge mobility.⁴⁵

One successful strategy to promote co-planarity of the side aryl substituent with the acene core, and thus promote $\pi\cdots\pi$ stacking with multiple intermolecular interactions, is the use of acetylene π -bridges (*e.g.*, **1.20-1.21**). The sterically undemanding alkyne prevents repulsion between the two aromatic systems, while still allowing for the conjugation to be maintained between the two substituents. As a result, the aryl substituents tend to remain co-planar to the

acene core, which promotes both film uniformity and charge mobility compared to the non-bridged analogues. Perhaps the most well known application of this strategy is the use of alkyne-bridged silyl substituents (**1.22-1.26**) pioneered by Anthony and coworkers to control the solid-state packing of pentacene derivatives.^{46–48} Although crystalline pentacene exhibits commendable mobility for an OSC, it crystallizes preferentially in a herringbone fashion, a less-than-ideal scenario for charge transport. Varying the relative size of the silyl group relative to the pentacene core introduced important changes in film morphology. Whereas small silyl groups (less than half the length of pentacene in diameter; *e.g.*, **1.22**) led to one dimensional π -stacks, larger substituents (about half the length; *e.g.*, **1.23-1.26**) promoted a 2D brick-like arrangement, a highly desirable structure for efficient charge-transport. The functionalization of pentacene disrupts its electronic properties to a point that even with the improved packing structure, mobilities remain at best on-par with the pristine acene. Nevertheless, substitution of the reactive central positions greatly stabilizes the core against both oxidation and photodegradation and imparts it with higher solubility, which are both important factors for successful device applications.³

1.6.3 The Incorporation of Heteroatoms

Another commonly employed strategy in the design of OSCs is the incorporation of heteroatoms, which has already been addressed in Section 1.5.2 with the use of sulphur in oligothiophenes. In addition to oligothiophenes, sulphur can also be integrated into rigid conjugated aromatic backbones to yield thienoacenes, a particularly important class of chalcogen-containing OSCs (Fig. 1.10). As mentioned above, the extra intermolecular interactions afforded by sulphur allows for compact packing in the solid state. But, unlike oligothiophenes, the thiophene ring in thienoacenes has a stabilizing effect on the HOMO as a result of slightly reduced π -delocalization, resulting in higher ambient stability. For instance, pentathienoacene **1.27** is both air- and light-stable and adopts a slipped π -stacking motif in the solid-state.⁴⁹ Unlike linear all-carbon acenes, which exhibit poor ambient stability with five consecutive rings, an unsubstituted thienoacene with seven consecutive units (**1.28**) has been reported.⁵⁰ Even a pentacene core extended by one thieno unit **1.29** has shown increased stability with respect to pentacene, with a slightly diminished mobility (*i.e.*, $0.574 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, vs $1.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for **1.3**).⁵¹ Considering that a single sulphur atom with one participating lone pair substitutes

two CH units that both provide one electron, **1.27** might be regarded more accurately as an equivalent to picene, itself stable to ambient conditions. Nonetheless, dithienoanthracene **1.30**, which can be viewed as a proper thienoacene equivalent of pentacene, also exhibited enhanced stability with respect to the all-carbon **1.3**.^{52,53} Many of the reported thienoacenes mix thiophene and benzene subunits to yield cores with varying properties. However, the presence of sulphur can potentially lead to isomerism in the thienoacenes and, as a result, important structural and chemical differences. For instance, **1.31** adopts a herringbone arrangement in the solid-state, while isomer **1.32** favours columnar packing, which leads to enhanced charge mobility for single-crystals of the latter (1.8 vs $0.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$).^{54,55} In some cases, such as **1.30**, pure isomers are seldom obtained, and the resulting sample is typically reported as a mixture of both isomers. This might very well be detrimental to packing (and thus performance) as isomerically pure anti-isomer **1.30** has been shown to display charge mobility up to three times higher ($0.3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) than the racemic mixture ($0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$).⁵⁶ Although this can be avoided by limiting the number of heterocycles, this isomerism can be a potential strategy to further tune device performance.

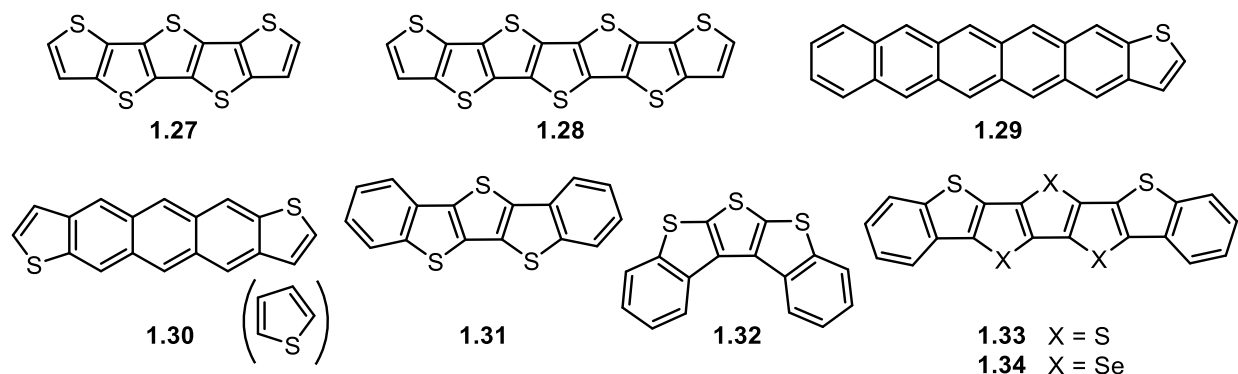


Figure 1.10 – Molecular structures of thienoacenes derivatives.

The rest of the chalcogen family has also found room in charge-transport materials. Typically, the use of heavier chalcogens favours enhanced mobilities (*e.g.*, **1.33/1.34**, 0.5 vs 1.1 cm²V⁻¹s⁻¹ respectively) as a consequence of the larger orbitals of the heteroatom.^{57,58} This trend does not automatically preclude the use of oxygen in OSCs, as the smaller size of oxygen's orbitals can be off-set by a tighter solid-state packing. Such a finding is of great importance in a context of energetic sustainability, as many short furan derivatives can be obtained from biomass-derived renewable feedstocks.⁵⁹

Chalcogens are certainly not the only heteroatoms to be incorporated within π -conjugated frameworks. Boron, silicon and phosphorus have all shown fairly widespread usage in the literature.^{60–65} Of particular interest in the context of this work is nitrogen, which can be integrated in aromatic frameworks without disturbing the aromaticity (Fig. 1.11). Building blocks for azaarenes can be divided in two categories, depending on the formal hybridization of the nitrogen atoms. An sp^3 -type nitrogen (**1.35**), such as in a pyrrole unit, contributes its lone pair to the π -system, enriching it in electron and resulting in an increase in the energy level of the MOs. On the other hand, sp^2 -type nitrogens (**1.36**), whose electronegativity is left unchecked by its lone pair orthogonal to the ring system, features lowered energy levels for its MOs. In addition to tuning the energy of the MOs, nitrogen atoms add the potential for hydrogen bonding as an additional intermolecular interaction that can regulate the solid-state packing, particularly in the case of hydrogenated sp^3 -type nitrogens. Again, the impact of such interactions on packing morphology and device performance cannot be overstated. For instance, **1.37** was shown to exhibit three polymorphic crystal structures, between which up to a 5000 fold difference in charge mobility was observed.⁶⁶ Finally, sp^3 -type nitrogen atoms are also valuable as reactive positions, to strategically functionalize the aromatic framework.

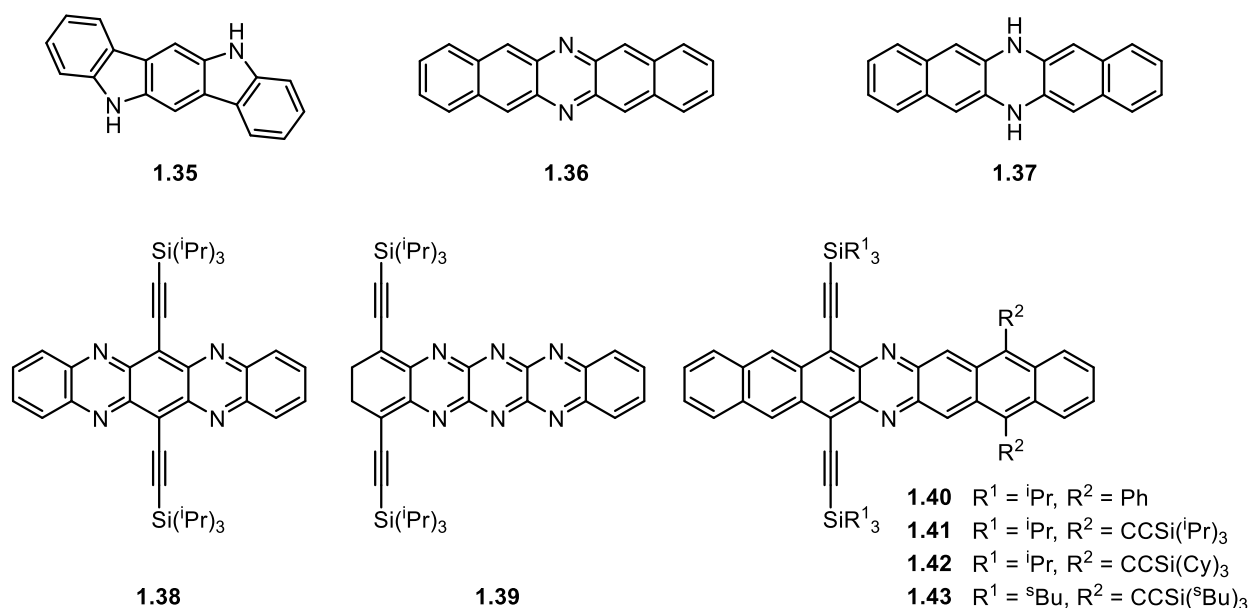


Figure 1.11 - Molecular structures of representative N-containing acenes.

Azaacenes, acenes with at least one CH fragment substituted by a sp^2 -type nitrogen atom, have been investigated for both *p*-type and *n*-type OSCs. First generation azaacenes, such as **1.36** and **1.37**, have shown rather modest hole mobilities ($\sim 10^{-5}$ - $0.4 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$).⁶⁶⁻⁶⁸ The use of alkyne-bridged silyl substituents, a tried-and-tested strategy with pentacene derivatives (see Section 1.6.2), has also been applied to azaacenes. This has led to a four order of magnitude increase in device performance thanks to the resulting brick-like arrangement in the solid state, with **1.38** being one of the best performing azaacene-based *n*-type OSC ($\sim 2.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$).⁶⁹ Incorporating more and more nitrogen atoms within the framework can result in a drastic lowering of the energy levels of the MOs. For instance, **1.39**, with three consecutive pyrazine rings, has shown a particularly low lying LUMO at -4.50 eV.⁷⁰ This allows, much like in the case of thienoacenes, the preparation of longer π -system that remain stable toward ambient conditions. For instance, extended azaacenes with as as much as seven consecutive rings **1.40-1.43** have also been reported. While they do exhibit some degree of dimerization in solution, as observed for **1.3**, this instability could be similarly controlled by the use of trialkylsilyl side substituents, with bulkier alkyls promoting enhanced stability (*i.e.*, the stability trend goes **1.43**>**1.42**>**1.41**>>**1.40**).⁷¹

1.7

Outline of the Thesis

The goal of this work was to design, prepare and characterize novel organic semiconductors with potential applicability as active materials in organic devices, namely transistors, and study the relationship between their structure and their properties. To achieve this goal, the strategies elaborated in this chapter, notably the incorporation of sulphur and nitrogen, for their beneficial effect on intermolecular contacts and energy levels, were applied in the construction of novel OSCs. The basic core structure of the compounds considered in this work are highlighted in Figure 1.12.

The second chapter of this thesis provides a brief theoretical description of the characterization techniques used in the course of this work. Admittedly, the OSCs are to be applied in the construction of devices as solid-state thin films. As the packing morphology is highly dependant on preparation techniques (*e.g.*, deposition methodology, nature of the substrate, surface pretreatment, annealing steps, etc.), solid-state data should ideally be obtained from similarly prepared films. Nonetheless, valuable data specific to the OSCs can still be

obtained *a priori* via solution-state measurements. As such, the characterization methods presented herein were chosen to extract valuable information (*e.g.*, energy levels, HOMO-LUMO gap, Stokes shift) that can be later employed toward the fabrication of said devices. In addition to describing the type of information provided by each technique, experimental methods, as well as data analysis protocols, are presented. Techniques such as optical absorption, photoluminescence measurements, cyclic voltammetry, X-ray diffraction and computational calculations are briefly covered therein.

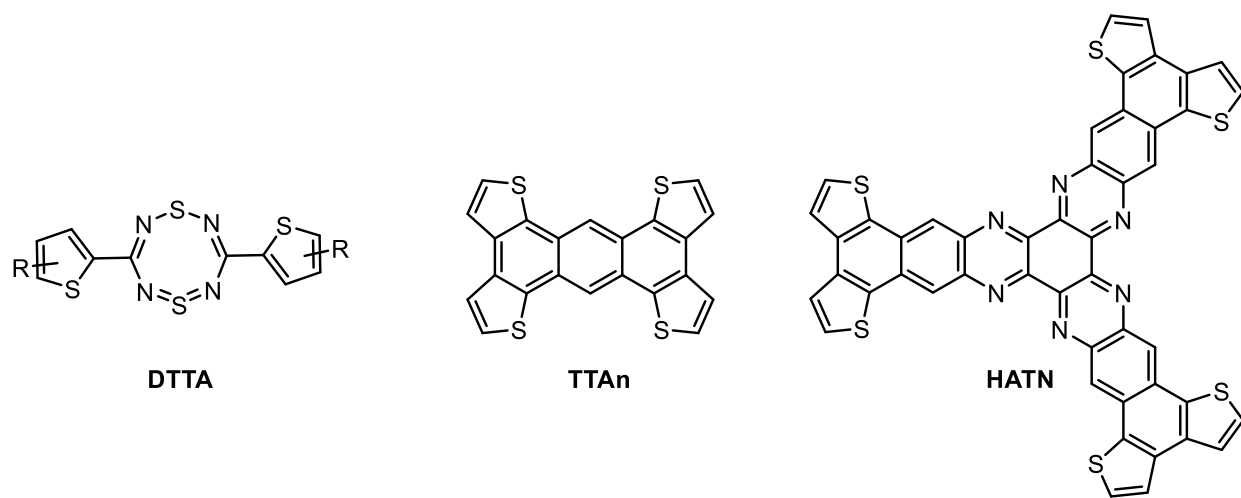


Figure 1.12 - Molecular structures of the core frameworks covered by this work. a) 1,5-Dithia-2,4,6,8-tetrazocine. b) 2D thienoacene. c) Hexaazatrinaphthylene.

The third chapter covers the synthesis and characterization of 1,5-dithia-2,4,6,8-tetrazocines (**DTTA**), relatively electron-deficient sulphur-nitrogen heterocycles, to promote intermolecular charge transfer. These rarely reported heterocycles were functionalized with various (oligo)thienyls pendants, and the influence of the degree of conjugation, as well as the substitution patterns, on the optoelectronic and solid-state properties of the parent ring system was investigated.

The fourth chapter focuses on the preparation of novel 2D fused aromatic thienoanthracenes (**TTAn**) which incorporates thieno[3,2-b]thiophene as a key building block, as the core and/or as the arm moieties of the molecule. These novel rigid derivatives were compared to both oligothienyl-appended analogues and their propeller-shaped uncyclized precursors in

terms of substitution pattern, effective rigidity and degree of conjugation as means to study the impact of these parameters on molecular properties.

The fifth chapter introduces unpublished results on the extension of the electron deficient discotic core hexaazatrinaphthylene (**HATN**) with rotatable thienyl pendants or rigid π -fused benzodithiophenes, with an emphasis on the synthetic steps required to prepare such frameworks. Due to the core-shell donor-acceptor geometry of these derivatives, emission solvatochromic effects were observed in both types of structures.

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Chapter 2

Experimental Methodology

This chapter describes the methodology used throughout the course of this work. The synthetic procedures employed in this work involve commonplace organic reactions and techniques, and as a result are not covered here. Similarly, details on more traditional organic characterization techniques, such as nuclear magnetic resonance (NMR) and infrared (IR) spectroscopies, and elemental analysis, are not included. Relevant reaction-specific details are, however, included in the appropriate chapters. Instead, this chapter focuses on more project-specific instrumental techniques used throughout this work to characterize the different materials prepared. For each technique, the underlying theory, the way the data was analyzed, as well as the type of information that can be obtained and how it lends itself to organic semiconductors (OSC), are addressed. Characterization methods included in this chapter are optical spectroscopy (both absorption and emission), electrochemistry and X-ray diffraction. Finally, the methodology and results obtained by computational methods are described.

2.1

Optical Spectroscopy

2.1.1 Absorption Spectroscopy

As a result of spatial confinement, electrons can only display discrete values of energy, as imposed by the structure of the molecule and are referred to as molecular orbitals (MOs). By default, electrons occupy the lowest energy orbitals of a molecule to yield the most stable configuration possible. This electronic configuration, however, is far from static, and electrons can transit to higher energy orbitals, provided of course that the energetic cost be provided. As a result of the aforementioned quantization of the MOs, the magnitude of the energy input has to match the exact value of a given transition for it to occur.¹

The energy associated with the HOMO-LUMO transition, the smallest allowed electronic transition for a given molecule, typically falls in the 2-6 eVs range for organic molecules, which concords well with the energy carried by ultraviolet and visible light (UV-Vis, 190-700 nm).

Accordingly, photoexcitation of a molecule can lead to the promotion of an electron from a lower to a higher energy MO, again if the energy of the photon matches exactly the energy difference between the two MOs.² Instrumentally speaking, one can thus observe electronic transitions by the use of a spectrophotometer, which measures absorbance (A) as the attenuation of a light beam by a sample throughout a range of wavelengths:

$$A = -\log \left(\frac{I}{I_0} \right) \quad (2.1)$$

$$A = \epsilon b C \quad (2.2)$$

where I_0 and I correspond to the intensity of the light beam before and after passing through the sample; b is the length of the sample cell (in cm, typically 1 cm); ϵ is the molar absorptivity coefficient of the compound at a given wavelength (in $M^{-1} \cdot cm^{-1}$ for solution samples), and C is the concentration (in M). Equation 2.2, Beer-Lambert's Law, states that absorbance is proportional to concentration. To ensure this proportionality holds true, A is typically maintained below a numerical value of 1, otherwise self-absorption artefacts can occur and lead to deviation from linearity.

Based on the above explanation on quantized energy levels, one could expect sharp absorption bands. The presence of both vibrational relaxation modes and solvent interactions in solution-state measurements however causes a broadening of the absorption signal, and as a result larger bands are typically seen. The width of the peaks can provide qualitative information on the rigidity of the studied molecule: while a rigid molecule will display sharper bands, the presence of additional vibrational freedom will favour instead broader peaks. One can also infer from the absorption peak's wavelength the corresponding transition's energy value through this equation:

$$E(J) = \frac{hc}{\lambda} \quad (2.3)$$

Where E is the energy (in Joules); h is Planck's constant ($6.626 \times 10^{-34} J \cdot s$); c is the speed of light in a vacuum ($2.998 \times 10^8 m \cdot s^{-1}$), and λ is the wavelength (in m). By rearranging constants h and c and the unit sets, one can obtain:

$$E(eV) = \frac{1240}{\lambda} \quad (2.4)$$

Where E is the energy (in eV) and λ is the wavelength in nanometers. Similarly, the band gap, the smallest possible electronic transition (HOMO-LUMO) and thus the minimal amount of energy required to promote an electron to a higher energy MO, can be measured with optical absorption. Consequently, the wavelength of the onset of absorption, as shown in Figure 2.1 (rather than the peak of the lowest energy absorption band), is used to measure the band gap through Equation 2.4. Knowledge of the band gap's value is of importance to device fabrication. For instance, the photoactive layer in a solar cell should display a low band gap to maximize the quantity of photons that are sufficiently energetic to effectively promote charge generation.³ On the other hand, the band gap of the active material in a light-emitting diode dictates the color of the emitted photon, and as such its value should reflect the targeted hue.⁴

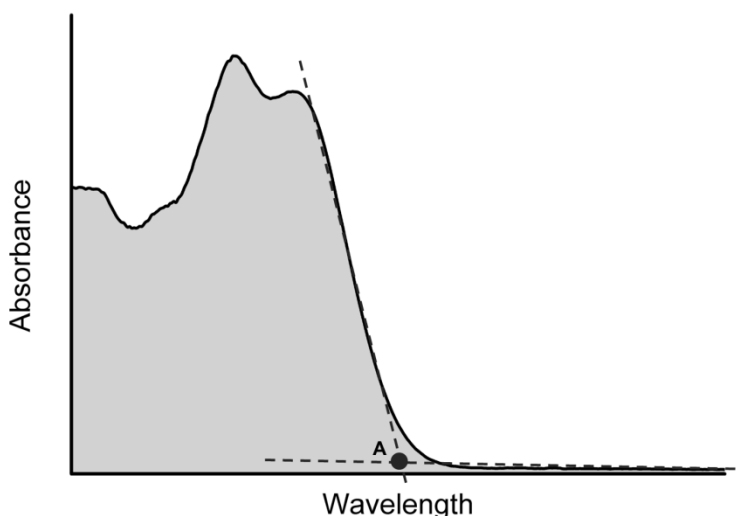


Figure 2.1 - Absorption spectrum of a hypothetical OSC. The band gap is measured from the onset of absorption, the wavelength corresponding to point A, found by extrapolating the tangent of the absorption curve and the baseline.

Finally, the molar extinction coefficient of each band can be obtained by measuring the absorption of solutions of increasing concentrations and plotting, for each peak, the absorption as a function of concentration. Following Beer-Lambert's law (Equation 2.2), the slope of the linear regression corresponds to the product of the extinction coefficient ϵ and the length b . Throughout the experiments reported in this thesis, one centimeter-wide cuvettes were used, meaning that the slope of the linear fit is directly equivalent to the coefficient ϵ . In all measurements, absorbance

values were maintained below 1 to ensure the validity of Beer-Lambert's law. A high absorptivity can be a desirable trait for applications where high light absorption correlates with high performance, notably photovoltaics.

2.1.2 Emission Spectroscopy

Absorption of a photon by a molecule leads to promotion of an electron from a lower energy orbital to a higher energy one. The molecule in the excited state will quickly shed the extra energy to return to its more stable ground state.⁵ While this is typically achieved by non-radiative vibrational relaxation or solvent collisions, some molecules cannot fully discard the acquired energy in such manners. The remaining energy can then be eliminated by emission of a photon. As part of the initial energy was already non-radiatively lost, the emitted photon is of lower energy than the absorbed one, or red-shifted. In addition to fluorescence, phosphorescence is another photoluminescence process that can potentially occur for OSCs. Compounds studied in this work were characterized under both aerobic and anaerobic conditions, and showed no spectral differences. As phosphorescence involves a triplet-state intermediate, the lack of influence of oxygen on the luminescent properties rules out phosphorescence as a major contributor to the emission properties. As in the case of absorption spectroscopy, the process is highly dependent on the photophysical properties of the analyte, which derives from the specific structure of the molecule. In the case of rigid molecules, the emission profile is generally a mirror image of the absorption spectrum, as the electronic transition barely affects the nuclear geometry within the allotted timeframe. The presence of rotational and vibrational freedom can however lead to deviation to this "mirror-image rule", which results in a broader featureless emission spectrum (and vice-versa for structured excited states). One key parameter is the Stokes shift, the difference between the maximum emission wavelength ($\lambda_{\text{max}}^{\text{em}}$), and the absorption wavelength ($\lambda_{\text{max}}^{\text{abs}}$) of an electronic transition, usually reported in cm^{-1} (Fig. 2.2).⁶ The Stokes shift can be indicative of a compound's performance toward charge mobility, as it represents the amount of energy lost by molecular rearrangement over the course of the excitation-deexcitation process. An ideal semiconductor exhibits minimal rearrangement during the charge-transfer process, and accordingly should display a minimal Stokes shift.

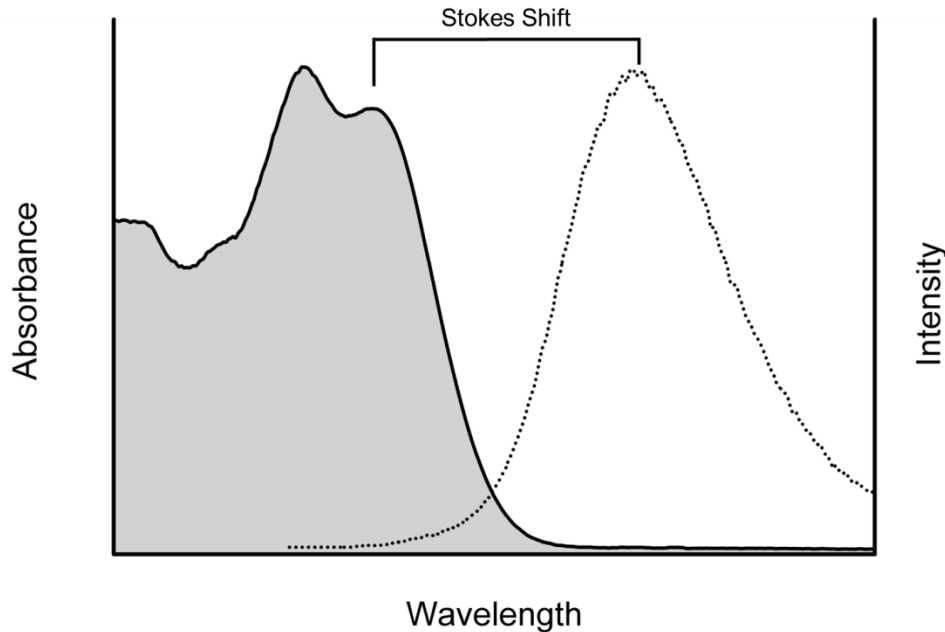


Figure 2.2 – Absorption (left, solid line) and emission (right, dotted line) spectra of a hypothetical OSC. The Stokes shift corresponds to the energy difference between the absorption and emission maxima of the same electronic transition.

The efficiency of the photoluminescence process can be described by the quantum yield, essentially the ratio of emitted photons to absorbed photons. In the context of this work, quantum yields measurements were performed by a comparative method, which involves correlating the total integrated intensity of photoluminescence to the absorbance value at the excitation wavelength. By performing the same measurement on a standard of known quantum yield, the unknown yield could be measured using the following equation:⁷

$$\Phi_U = \Phi_{ST} \left(\frac{m_U}{m_{ST}} \right) \left(\frac{\eta_U^2}{\eta_{ST}^2} \right) \quad (2.5)$$

where Φ is the fluorescence quantum yield, m is the slope of the linear fit of integrated fluorescence intensity vs optical absorbance, and η is the refractive index of the solvent employed in the measurements. The subscript U and ST refer to the unknown and the standard, respectively. For this characterization to be valid, the measurements for both the unknown and the standard have to be performed in the same conditions (*i.e.*, excitation wavelength, slit widths, the use of filters). Moreover, the absorbance at and above the excitation wavelength was maintained below 0.1 to avoid inner-filter effects (the absorption of an emitted photon by a second molecule) and assure linearity. Finally, both the standard and the analyte have to be

excited using the same wavelength while their emission profile should ideally (although not necessarily) match as closely as possible. As relatively few molecules are fluorescent, and since fluorescence spectroscopy is rapid and sensitive, fluorescence is a useful diagnostic and reaction-monitoring tool to determine the presence (or absence) of a given luminogen in a complex reaction medium using little sample.

2.2 Electrochemistry

Charge transfer processes are key aspects of organic semiconductors and can be directly related to the frontier MOs. The energy of the HOMO represents the energy required to oxidise, or remove an electron, while the LUMO represents the energy required to reduce, or inject an electron. Knowing the energy levels of a material's frontier molecular orbitals is primordial in ensuring the proper and optimal functioning of a device, as energy levels of a device's components have to properly match to allow proper charge transport. These processes can be measured using electrochemistry, a useful technique for determining, among others, the redox potentials for the charge transfer events, as well as the stability of the resulting ionic species.⁸

The most commonly employed electrochemical experiment in this work was cyclic voltammetry (CV), which involves sweeping the potential between two electrodes back and forth at a constant rate (Fig. 2.3-i). When the potential of the electrode reaches the potential of the analyte's own redox potential, electron transfer occurs between the electrode and the molecule. The resulting current can be measured and plotted as a function of the electrode's potential. A fully-reversible redox event displays two peaks per event, for the anodic and cathodic reverse reactions (Fig. 2.3-ii). Since the same number of electrons should be involved in both processes, the measured current for both peaks should be the same, but of opposite signs. The absence of a second peak implies rapid decomposition of the charged intermediate, before it can be converted back to the neutral state (Fig. 2.3-iii). Typically, the two peaks will not occur at the exact same potential because of ionic diffusion in solution. However, peaks should be closely spaced to be considered fully-reversible (<59 mV for one-electron processes). A larger separation between two peaks is interpreted as an increased stability of the ionic form, which requires a larger energy input to be converted back to the neutral state.

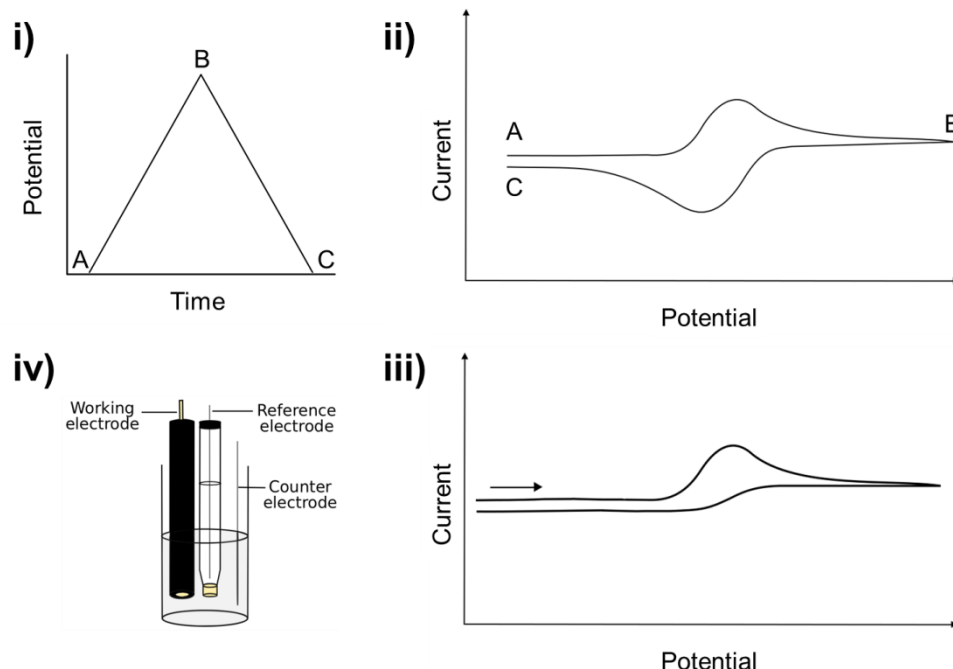


Figure 2.3 - **i)** Linear sweep of the potential between the working and reference electrodes over time in a CV experiment. **ii)** Hypothetical fully reversible cyclic voltammogram. Points A, B and C refer to the corresponding points on graph i. **iii)** Hypothetical irreversible cyclic voltammogram. **iv)** Typical CV setup employed, comprised of a working, a counter and a reference electrodes in an undivided cell.

The typical CV experimental setup employed in the course of this thesis involves a closed undivided glass cell with three electrodes: the working, the reference and the counter electrodes (Fig. 2.3-iv). The measured redox processes occur at the working electrode, which is connected to the reference electrode through a high resistance connection, to insure little to no current circulates between them. The reference electrode is typically made of a material whose redox properties are well known and well-behaved: examples of commonly employed materials in the literature include H^+/H_2 (Standard Hydrogen Electrode), Hg/HgCl_2 (Standard Calomel Electrode) and Ag/AgCl . As a result, the potential of the working electrode is measured as a function of the reference electrode, whose potential is constant for given conditions. The counter electrode only acts to close the circuit and inject the counter charge carrier back in the solution to maintain electrical parity. As the aforementioned reference electrodes are aqueous-based and the measurements in this work were performed in organic media, all three electrodes here consisted of platinum wire, meaning the reference electrode acted only as a *pseudo*-reference. Instead, ferrocene was employed as an internal reference, since it well-known and well-behaved, inexpensive, and unreactive with the analytes.⁸

Data acquisition starts by insuring the cleanliness of the setup by measuring the blank. If satisfactory results are achieved, the analyte is added, and appropriate measurements are performed. Finally, ferrocene is added, and the electrograph is reacquired. The new ferrocene redox event is then calibrated to its appropriate value in the conditions employed to provide the proper redox potentials of the analyte. From these results, the energy levels of the frontier molecular orbitals can be calculated using the following equations:⁹

$$E_{\text{HOMO}}(\text{eV}) = -e((E_{\text{ox}} - E_{\text{Fc/Fc}^+}) + 4.8) \quad (2.6)$$

$$E_{\text{LUMO}}(\text{eV}) = -e((E_{\text{red}} - E_{\text{Fc/Fc}^+}) + 4.8) \quad (2.7)$$

Where E_{HOMO} and E_{LUMO} are the energy levels (in eV) of the HOMO and LUMO, respectively; e is the number of electrons involved in the redox process (typically 1), and E_{ox} and E_{red} are the potentials at which the corresponding redox process is occurring (in V), after calibration of the ferrocene signal (+0.48 V vs SCE for DCM solutions using 0.1 M $^n\text{Bu}_4\text{PF}_6$ as supporting electrolyte). If a redox event is fully- or quasi-reversible, then the average potential between its cathodic and anodic peaks is employed. Otherwise, the onset potential is used, which is measured similarly to the way the band gap was measured in absorption spectroscopy (See section 2.1.1). Being able to measure both HOMO and LUMO in CV experiments alone is a fairly rare occurrence. In this case, the missing orbital energy can be deduced from both the electrochemically obtained MO energy and the optically-measured band gap ($E_{\text{band gap}}$) in the following fashion:

$$E_{\text{LUMO}}(\text{eV}) = E_{\text{HOMO}} + E_{\text{band gap}} \quad (2.8)$$

2.3

Single-crystal X-ray diffraction

The structural morphology that a semiconductor adopts in the solid-state is critical to its performance in device applications, as it dictates the intermolecular overlap through which charge-transfer can occur. Different parameters (*e.g.*, crystallinity, grain size, crystal orientation and polymorphism) will have a direct impact on performance: while these will vary depending on device preparation techniques, an estimate of the intermolecular overlap can be obtained by acquiring the crystalline-state structure of the OSC. This is achieved by directing a beam of X-

rays onto a crystal of sufficient quality, whose well-ordered and periodic molecular arrangement allows for the diffraction of the X-rays onto a detector to form structure-specific diffraction patterns. By measuring the angles and the intensities of the resulting spots, a map of the electronic density in 3D space can be constructed. Combined with chemical acuity and some prior knowledge of the molecular structure, the mean atomic positions of the crystal's constituents can be ascertained. Further data analysis and measurements on the resulting structure can be performed using specialized software. For the sake of discussion, interactions between two atoms separated by a distance smaller than the sum of their respective van der Waals radii plus 0.1 Ångström are considered as nominal intermolecular contacts. However, contacts involving alkyl chains, while important to the assembly and packing of the crystal, are neglected, as they are not conducive to charge-transport. In all cases reported in this thesis, crystals of good quality were obtained from suitable methods, then entrusted to in-house crystallographers (Dr. Ilia Korobkov or Dr. Bulat Gabidullin) for data acquisition.

2.4 Computational Chemistry

Computational chemistry is a very powerful tool to predict, correlate and explain the properties of organic materials. Calculations for this thesis were performed using Density Functional Theory (DFT), a type of calculations designated to shorten calculation time while still providing accurate data. To do so, the method foregoes the calculations of electronic wavefunctions, substituting it instead for overall electronic density.^{10,11} In doing so, the calculations are shortened from 3N elements (where N corresponds to the number of atoms) to simply three elements. As such, every electron is considered as residing in an average electric field, the interaction with which leads to calculating the energy of the system. In all cases, calculations were done using the Gaussian09 software.¹² A Becke, three-parameter, Lee-Yang-Parr (B3LYP) hybrid functional, performed at the 6-31G* level of theory or above, was chosen as it is a good compromise between computational cost and accuracy of results.¹³ Its widespread use in the literature also makes comparison of obtained results more direct.

The first step is the optimization of the structure, which is performed by an iterative process in which the computer calculates, for a given inputted molecular structure, electronic

potentials for each electron in regard to the mean electric field. From the results, the computer generates new molecular orbitals and a corresponding intermediate structure. These steps are repeated with each new intermediate structure until minimal changes in overall energy are observed and a stable structure with a minimum energy is obtained. This optimized structure is then used as the starting point in subsequent calculations.

The converged structure can be used to calculate the energy and the spatial distribution of molecular orbitals. As mentioned in Section 2.2, the energy levels of the molecular orbitals are a key aspect of charge transport, as they have to properly match to optimize charge hopping. The distribution of the orbitals throughout the molecule's framework is also important, since maximal intermolecular orbital overlap is optimal for charge mobility. Time-Dependent Density Functional Theory (TDDFT) can also be performed on optimized structure as to provide a theoretical absorption spectrum. To do so, calculations are performed using a polarized continuum model, which simulates the effect of solvent on optical properties. TDDFT calculations provide data on electronic transitions, including orbitals involved in a given transition, its energy (and thus corresponding wavelength) and oscillator strength, an indication of the absorption intensity, which can be correlated to the extinction coefficient.

Finally, DFT calculations have been used to estimate the charge transport properties of a compound. As mentioned above (see Section 2.1.2), ionization of a molecule leads to structural rearrangement, both internal and external. External reorganization of the solvent molecule is often considered to be trivial when compared to internal reorganization, and as such is typically not considered in the literature,¹⁴ including the present work. The internal reorganization energy λ , which is minimal for an ideal OSC, was calculated using the adiabatic potential energy surface method:

$$\lambda_+ = (E_+^* - E_+) + (E^* - E) \quad (2.9)$$

$$\lambda_- = (E_-^* - E_-) + (E^* - E) \quad (2.10)$$

where E and E_+ (E_-) represent the energies of the neutral and cationic (anionic) species at their respective equilibrium geometries. E^* corresponds to the energy of the neutral compound with the equilibrium geometry of the cation/anion, while $E_{(\pm)}^*$ is the energy of the cation/anion with the equilibrium geometry of the neutral structure (Fig. 2.4). Commonly, the reorganization

energy for holes and electron charge-carriers won't be equivalent due to different processes occurring upon oxidation/reduction, and is one of the reasons behind the varying performance of a given molecule toward p-type and n-type behaviour (See Section 1.3).

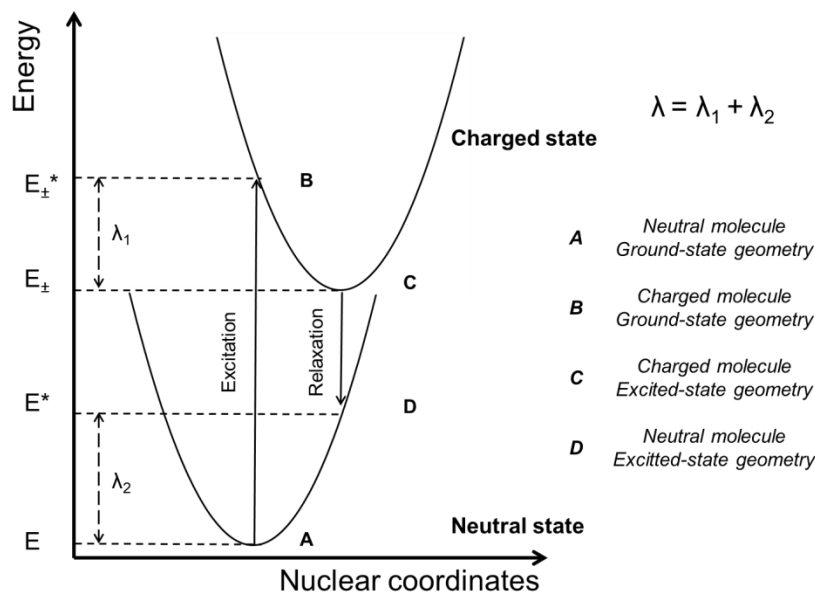


Figure 2.4 - Calculation of the internal reorganization energy (λ) via the adiabatic potential energy surface method. Values of molecular energies E , E^* , $E_{(\pm)}$ and $E_{(\pm)}^*$ were obtained on pre-optimized structures in Gaussian09, then used in Equations 2.9/2.10 to yield λ .

2.4

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Chapter 3

Influence of Substitution Pattern and Enhanced π -conjugation on a Family of Thiophene Functionalized 1,5-Dithia-2,4,6,8-tetrazocines

Authorship disclosure: A version of this work was published in *New Journal of Chemistry* as “Influence of substitution pattern and enhanced π -conjugation on a family of thiophene functionalized 1,5-dithia-2,4,6,8-tetrazocines” **Magnan, F**, Korobkov, I. and Brusso, J.L. *New J. Chem.* (2015), **39**, 7272-7280. As it is the direct continuation from a previous study (“Optoelectronic and structural properties of a family of thiophene functionalized 1,5-dithia-2,4,6,8-tetrazocines” Afjeh, S.S., Leitch, A.A., Korobkov, I., Brusso, J.L. *RSC Adv.* (2013), **3**, 23438-23444.), results from that publication were included in this chapter for the sake of comparison. Synthesis and characterization of compounds **3.14**, **3.22** and **3.23** (and their respective precursors) were performed by Soofieh Afjeh and Dr. Alicea Leitch, whereas **3.24-3.26** were prepared and studied by François Magnan. In all cases, XRD characterization was performed by Dr. Ilia Korobkov.

3.1 Introduction

Electroactive organic molecules have seen significant development over the past two decades owing to their potential use in next-generation electronic devices.¹⁻³ Low-cost, miniaturization, tunable optoelectronic properties, mechanical flexibility and processability are a few of the key advantages organic based materials offer compared to their more traditional inorganic counterparts.⁴⁻⁶ In regards to tuning the optoelectronic properties in organic semiconductors (OSC), this may be achieved *via* modulating the substituents or by introduction of heteroatoms into the conjugated core. To that end, sulphur and nitrogen containing heterocycles are commonly observed motifs in OSCs as incorporating these atoms into planar π -conjugated frameworks provides several benefits over their all carbon variants (*e.g.*, acenes). For example, S-N heterocycles have been shown to demonstrate: i) improved stability towards air oxidation due to the presence of the electronegative atoms, which lowers the energy of the highest occupied molecular orbital (HOMO); ii) the potential for structural control through S $\cdots$ N and N $\cdots$ HC interactions; and iii) the possibility of strong orbital overlap between the larger π -

orbitals of sulphur leading to enhanced electronic communication between molecules.^{7–13} With respect to the rational design of electroactive materials, organization in the solid-state is of utmost importance as their electronic properties are critically dependent on the extent of molecular order. Thus the packing arrangements afforded by planar π -conjugated molecules, in addition to the intermolecular interactions exhibited by sulphur and nitrogen moieties, are key to the implementation of S-N heterocycles into molecular electronics. As such, ideal systems should exhibit π - π stacking in the solid-state, strong intermolecular communication, as well as high thermal and ambient stability.

In that regard, 1,5,2,4,6,8-dithiatetrazocine (DTTA) is an attractive building block for electroactive substrates as not only does it meet these criteria, but it can also be modulated by virtue of the 3,7-susbtituent. First serendipitously discovered in 1981 by Woodward and coworkers as a minor product in the reaction between benzamidine and sulphur dichloride (SCl_2),¹⁴ various DTTA derivatives with different electro-active groups were initially prepared (**3.1-3.4**). The molecular structure of DTTA has been shown to be highly dependent on the nature of the substituents. For example, the $\text{C}_2\text{N}_4\text{S}_2$ ring can exist in either a planar, 10π electron aromatic structure (*e.g.*, **3.1**) or in a bent conformation (*e.g.*, **3.2**) where the ring is folded about the axis of the two sulphur atoms with a transannular $\text{S}\cdots\text{S}$ contact, as shown in Figure 3.1. Although this structural dichotomy is substituent dependent, the planar structure is most commonly observed except when strongly electron-donating substituents are employed (*e.g.*, $-\text{NMe}_2$).¹⁵

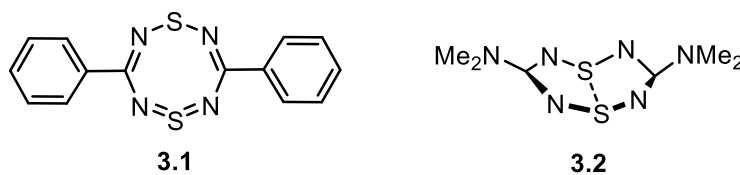


Figure 3.1 - Planar and bent configurations of 1,5-dithia-2,4,6,8-tetrazocine.

The stability of the eight-membered ring can be rationalized as a result of a delicate balance between counteracting bonding and antibonding interactions joining the two sulphur atoms. The strong electron-donating amino groups disturb this equilibrium and weaken the π -system by raising the energy level of the HOMO, making the molecule more susceptible to a pseudo-Jahn-Teller distortion. Consequently, bending of the ring occurs in order to stabilize the

structure through an in-plane interaction, which results overall in a widening of the HOMO-LUMO gap. A single amino group is in fact sufficiently electron donating to buckle the ring system, as witnessed for the asymmetrically substituted **3.12**.¹⁶ In the solid-state, planar DTTAs commonly form π -stacked structures with close intermolecular contacts and tend to be incredibly robust with high tolerance to acidic, basic, oxidizing and thermal conditions.^{14,16} Thus, incorporation of the DTTA framework in the design of OSCs, either polymeric or molecular in nature, offers many potential avenues to explore.

One of the major issues that plagued initial research into DTTA was the poor reaction yield, which typically hovered around 5-10% for planar derivatives. As a result, much attention was devoted to optimizing the reaction conditions. While slow addition of SCl_2 , lower reaction temperature and higher dilution were not found to influence the yield, changing the sulphur transfer reagent to a mixture of bis(phthalimido sulphide) and tosyl di-imide led to a small but consistent increase in the yield of **3.1**. This improvement, however, still led to a disappointingly low yield to only 9% (from 7%).^{16,17} In the same report, it was noted that replacing the benzamidine with its persilylated equivalent led instead of DTTA to the preferential preparation of a dithiadiazolium salt in moderate yields. This eventually proved fruitful, as shortly thereafter Boéré and coworkers discovered that a dithiadiazolyl-type radical could be converted into a DTTA ring in comparable yields (8-20%) when heated in the presence of dry oxygen. More importantly, it was found that reducing a dithiadiazolium salt with triphenylantimony (SbPh_3) in an oxygen-saturated solution would directly provide the eight-membered ring in largely increased yields (30-60%).¹⁸ Combining this discovery with the aforementioned usage of persilylated amidines to produce dithiadiazoliums, the authors went on to demonstrate the substrate scope of their method by reproducing the synthesis of previously known DTTAs (**3.1**, **3.3**, **3.5-3.7**, Fig. 3.2) in improved yields, or by producing novel DTTAs (**3.8-3.9**).^{19,20}

The majority of research reported on DTTA focuses on the synthesis of phenyl- and amino-functionalized derivatives and their crystal structures, with very little emphasis on their optoelectronic properties or potential as electroactive substrates. Almost no side-groups other than phenyl and amines have been researched, with furyl/thienyl (**3.13-3.14**),^{16,21} tert-butyl (**3.15**)^{15,22} and unsubstituted (**3.16**)²³ analogues (which all exhibited a planar aromatic structure) being the rare exceptions. Woodward's seminal work¹⁴ also investigated the optical absorption

spectra for both the planar and bent structures. As a result of the bent shape, the eight-membered ring essentially behaves as two fused five-membered 4π -electron rings, and accordingly displays low wavelength absorption. On the other hand, the planar system, which possesses a higher degree of conjugation, exhibits a distinctive absorption pattern, with longer wavelength absorption up to 400 nm, which is highly typical of all planar eight-membered ring derivatives.

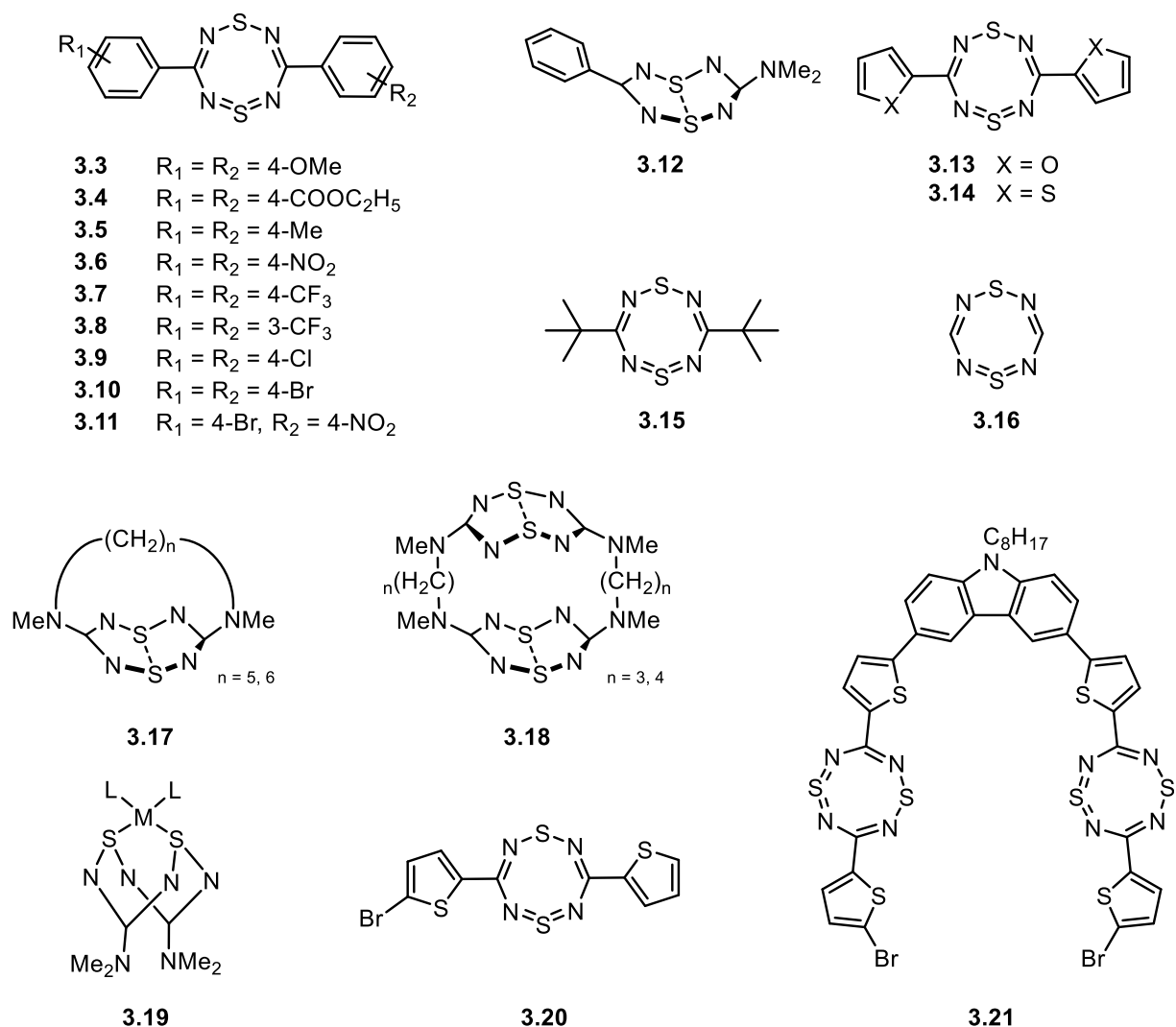


Figure 3.2 - Structures of known 1,5-dithia-2,4,6,8-tetrazocine derivatives.

Cyclic voltammetry (CV) experiments by Boéré and coworkers have shown that planar DTTAs exhibit either fully- or quasi-reversible reductions and non-reversible oxidations in solution.²⁰ While the reduction process might be fully reversible on a CV time scale, an isolated radical anion sample remains elusive. Simultaneous electrochemical electron-paramagnetic

resonance spectroscopy studies by the same group demonstrated that while the reduction process indeed forms a radical species, its half-life is too short (below 30 seconds) to allow the anion to be isolated,²⁴ likely due to a lack of steric bulk to protect the ring system.

Since 1981, research into DTTA rings has included work by Pascal and coworkers who prepared a series of cyclophanes using a bent diamino functionalized eight-membered ring bridged by alkyl chains of various lengths. While longer chains promote monomeric cyclophanes (**3.17**), shorter chains resulted in a dimeric species (**3.18**) instead, due to the high strain that would result in a monomeric cyclophane.^{25,26} As well, the Chivers group studied the transannular sulphur-sulphur interaction of bent DTTA rings by preparing a series of platinum and palladium adducts (**3.19**) in which metal insertion occurs in said interaction.^{27–29} Rawson and coworkers investigated the structural impact of symmetrical and asymmetrical substitution of the phenyl pendants (**3.6**, **3.10** and **3.11**) as a way to produce macroscopically polar materials that could exhibit non-linear optical properties.³⁰ Since the publication of the works presented in this chapter, Zhang and coworkers have similarly suggested thienyl- and phenyl-appended DTTAs (**3.1**, **3.10**, **3.14**, **3.20** and **3.23**) as potential electroactive materials, and proposed, based on fluorescence quenching experiments, that they could act as good acceptors in the solid-state.³¹ Further work by the same group has focused on synthesizing and characterizing the first DTTA dimeric derivative (**3.21**) of the eight-membered ring, where two rings were connected to a carbazole core through thienyl π -bridges to form an acceptor-donor-acceptor type structure that could act as an efficient substitute for fullerenes in optoelectronic devices.³²

In light of the favourable properties of DTTA for potential OSCs, one of the axes of research in the Brusso group has been on the eventual applications of this unique ring system in optoelectronic devices. To this end, thienyl pendant groups were chosen over phenyls for their enhanced conductivity. While thienyl groups are stronger π -donors than phenyl substituents, thienyl derivatives have been shown to be planar, π -conjugated aromatic molecules.^{16,21} To investigate the role of the substitution pattern on the optoelectronic and solid-state properties, the synthesis and characterization of **3.22–3.25** are reported herein, and compared to the previously known **3.14** (Fig. 3.3). As well, in order to enhance the intermolecular interactions, we sought to increase the degree of conjugation. As such, the first examples of bithienyl-substituted DTTAs 3,7-bis([5-(thiophen-2-yl)thiophen-2-yl])-1,5,2,4,6,8-dithiatetrazocine (**3.25**) and 3,7-bis([5-(5'-

hexylthiophen-2-yl)thiophen-2-yl]]-1,5,2,4,6,8-dithiatetrazocine (**3.26**) are also presented. These studies demonstrate the versatility of the synthetic procedure in the development of DTTAs functionalized with thienyl moieties. As well, comparative electrochemical, optical, computational and single crystal X-ray diffraction (XRD) studies were performed on this family of thienyl (**3.14**, **3.22-3.24**) and bithienyl (**3.25-3.26**) functionalized DTTAs to probe the influence that both the substitution pattern and extension of the conjugation have on the optoelectronic and solid-state properties.

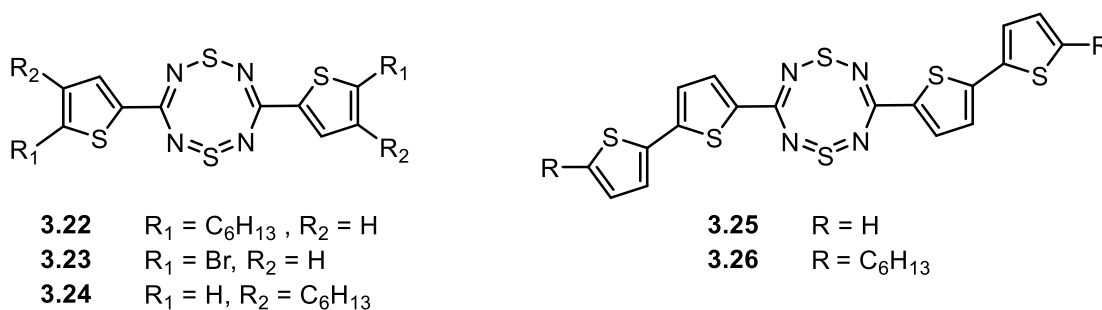


Figure 3.3 – Structures of novel thienyl-appended 1,5-dithia-2,4,6,8-tetrazocines reported in this chapter.

3.2

Results and Discussion

3.2.1 Synthesis of Carbonitrile Precursors

Examples of thienyl-substituted derivatives of DTTA remain scarce,^{16,21} with the first established synthetic route, the reaction of 2-thienylamidine with sulphur dichloride, affording 1,5-bisthieryl-2,4,6,8-dithiatetrazocine (**3.14**) in a paltry 7% yield.¹⁶ Instead, the Boeré reduction protocol (as described in the previous section) was chosen for its enhanced reaction yields. The thienyl carbonitriles required by this procedure were synthesized beforehand as described in Figures 3.4-3.6.

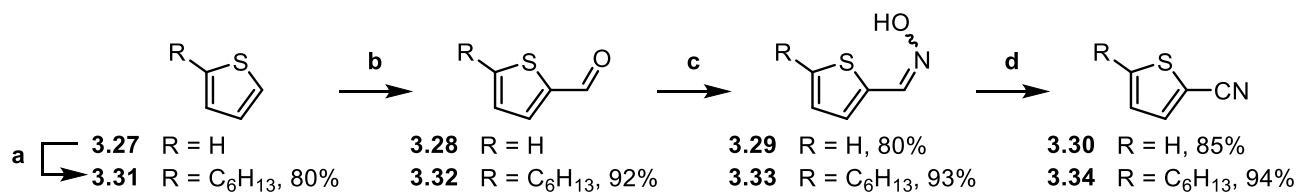


Figure 3.4 - Synthesis of unfunctionalized or 5-functionalized thienyl carbonitriles. Reagents and conditions: **(a)** $^n\text{BuLi}$, $\text{C}_6\text{H}_{13}\text{Br}/\text{THF}/-78^\circ\text{C}$. **(b)** $^n\text{BuLi}$, $\text{DMF}/\text{THF}/0^\circ\text{C}$. **(c)** $\text{NH}_2\text{OH}\cdot\text{HCl}$, $\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}/\text{EtOH}-\text{H}_2\text{O}/\text{reflux}$. **(d)** $\text{Ac}_2\text{O}/\text{DCE}/\text{reflux}$.

Shortly, **3.30** and **3.34** were obtained in 69-83% overall yield from the treatment of the corresponding aldehyde (commercially available (**3.28**) or prepared by subsequent alkylation and formylation of the thiophene ring (**3.32**)) with hydroxylamine hydrochloride to form the oxime intermediate (**3.29/3.33**), followed by reduction to the nitriles with acetic anhydride, as outlined in Figure 3.5. Although preparing the 4-alkyl-thienyl analogue (**3.38**) proved somewhat more problematic from a synthetic point of view (Fig. 3.5), it could still be obtained in 75% yield over three steps. While 3-hexylthiophene (**3.36**) was straightforwardly prepared from commercially available 3-bromothiophene (**3.35**) using Kumada coupling, formylation by consecutive lithiation with *n*-butyllithium and quenching with dimethylformamide (DMF) afforded 4-hexyl-2-thienylcarbaldehyde **3.37** in a 6:4 mixture with its isomer 3-hexyl-2-thienylcarbaldehyde. Unfortunately, distillation and chromatography couldn't efficiently separate the two products, and converting the aldehydes to their nitriles also failed to facilitate the purification step. Instead, by employing a bulkier base, improved ratios of the desired 4-isomer were obtained by virtue of the steric effect of the hexyl group on the asymmetric thiophene ring. Whereas lithium diisopropylamide (LDA) improved the ratio to roughly 9:1 in favour of the desired isomer, the even bulkier lithium 2,2',6,6'-tetramethylpiperidide exclusively afforded the target isomer. A different route, both faster and higher yielding, was employed to directly convert the aldehyde into the corresponding nitrile (**3.38**). Refluxing the aldehyde with hydroxylamine hydrochloride in *N*-methylpyrrolidone (NMP) produced the nitrile in an hour, and could be easily purified by vacuum distillation.

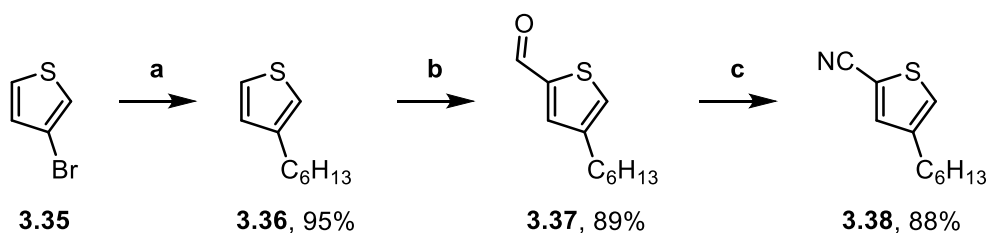


Figure 3.5 - Synthesis of 3-hexyl-2-thienylcarbonitrile. Reagents and conditions: **(a)** $\text{C}_6\text{H}_{13}\text{MgBr}$, $\text{NiCl}_2\cdot\text{dppp}/\text{Et}_2\text{O}/\text{Reflux}$. **(b)** $\text{LiTMP}/\text{THF}/-78\text{ }^\circ\text{C}$. **(c)** $\text{NH}_2\text{OH}\cdot\text{HCl}/\text{NMP}/\text{reflux}$.

The bithienyl carbonitriles were achieved in an analogous manner (Fig. 3.6). Firstly, the bithienyl cores (**3.40/3.43**) were prepared in almost quantitative yield by Kumada coupling between **3.39** and the appropriate Grignard reagent (2-thienyl magnesium bromide or 5-hexyl-2-thienyl magnesium bromide). Subsequent formylation, employing either a Vilsmeier-Haack

methodology or the usual lithiation-DMF quench, afforded the corresponding aldehydes (**3.41/3.44**). Without further purification, these aldehydes were directly converted to the equivalent nitriles (**3.42/3.45**) by refluxing in NMP with hydroxylamine hydrochloride. Purification by aqueous work-up, followed by filtration through a short silica gel column yielded clean nitriles in 65-75% yield over two steps.

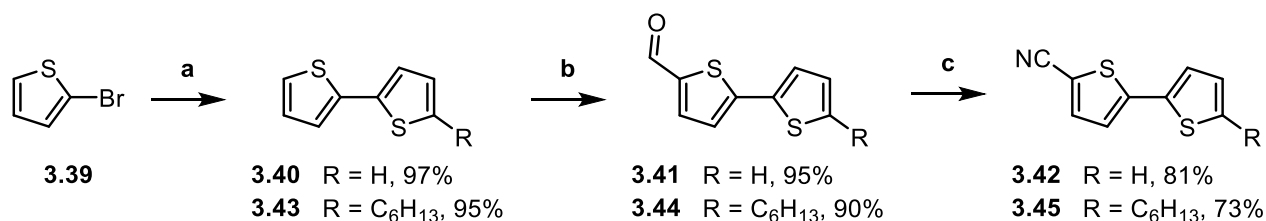


Figure 3.6 – Synthesis of bithienyl carbonitrile derivatives. Reagents and conditions: **(a)** 2-ThMgBr (R = H) or 5-Hex-2-ThMgBr (R = C₆H₁₃), NiCl₂dppp/Et₂O/reflux. **(b)** POCl₃, DMF/DCE/0 ° to r.t. (R = H) or ⁿBuLi, DMF/THF/-78 °C to r.t. (R = C₆H₁₃). **(c)** NH₂OH·HCl/NMP/reflux.

3.2.2 Synthesis of the Eight-membered Rings

Gratifyingly, Boéré's reduction protocol (Route A, Fig. 3.7) translated well to the preparation of thienyl functionalized DTTAs, with yields ranging between 13-50% for **3.14**, **3.22** and **3.24**, all as bright yellow solids following recrystallization from hot chloroform, ethyl acetate and chlorobenzene, respectively. By contrast, the bromo derivative **3.23** could not be directly synthesized in an analogous fashion, and were instead obtained by bromination of **3.14** using *N*-bromosuccinimide as a mild brominating agent. Following recrystallization from hot toluene, **3.23** was obtained as an orange solid in 87% yield. While route A was more efficient than the original synthetic procedure, it required isolation and purification of silylated amidines *via* vacuum distillation. This would unfortunately lead to varying yields due to the instability of the intermediate, especially with respect to moisture. In order to alleviate these issues, a slightly different procedure was explored in the course of this work (Route B, Fig. 3.7), inspired by the work of Rawson and coworkers.³³ Following treatment of **3.38** with LiN(TMS)₂·Et₂O, the reaction was quenched *in-situ* with sulphur monochloride to afford the dithiadiazolium salt **3.51** directly without isolation of the silylated amidine intermediate. Subsequent treatment of the dithiadiazolium cation with SbPh₃ in the presence of oxygen provided **3.24** as bright yellow needles in 15-20% yield following recrystallization from hot chlorobenzene. Although the yields

for the one-pot synthesis of **3.24** were admittedly lower than that of Route A, the latter route carried the advantage of higher throughput as it eliminated the need of isolating the persilylated amidine intermediate, where purification tend to be difficult. Thus following Route B outlined in Figure 3.7, compounds **3.24-3.26** could be prepared from the corresponding nitrile (*i.e.*, **3.38**, **3.42** and **3.45**). Compared to the yellow single-thienyl derivatives of DTTA, the π -extended systems **3.25** and **3.26** are copper-coloured and red, respectively, indicative of the expected bathochromic shift associated with extension of the conjugation. While **3.25** was recrystallized as copper-like flakes from hot toluene, recrystallization from chloroform afforded **3.26** as red shards.

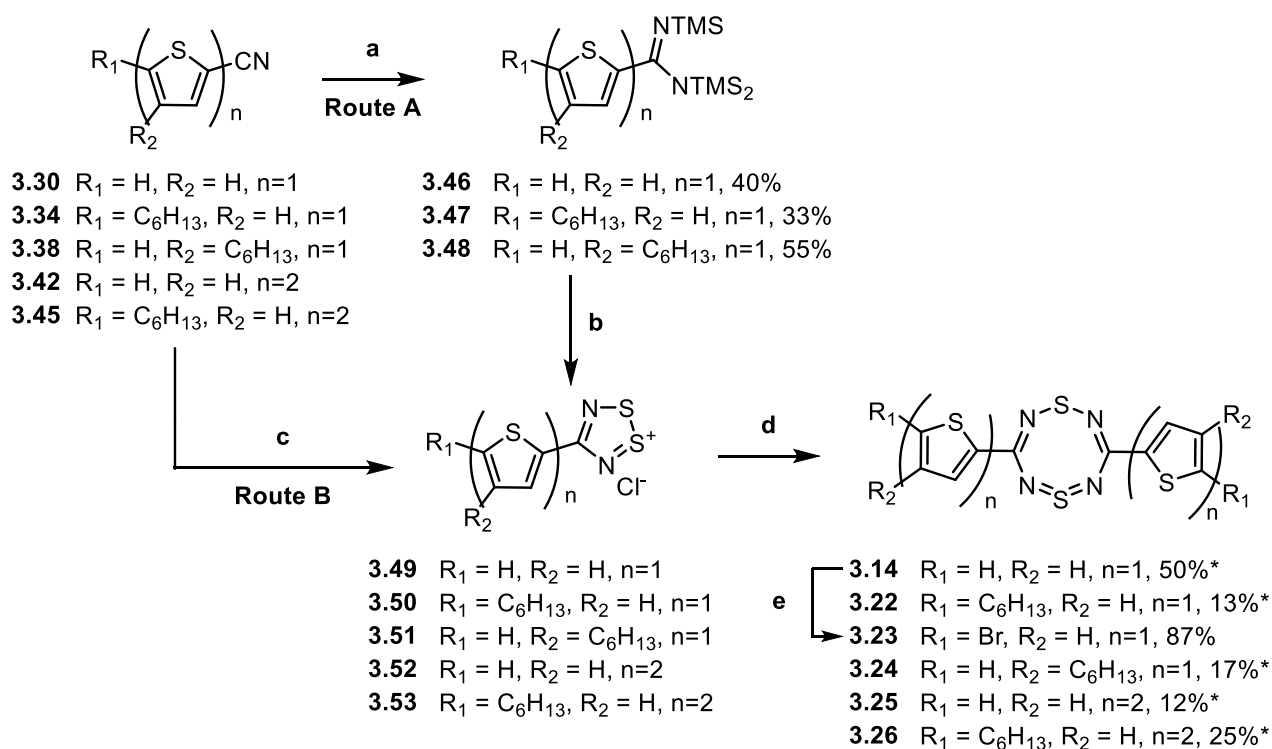


Figure 3.7 - Synthesis of thienyl functionalized dithiatetrazocines. Reagents and conditions: **(a)** $LiN(TMS)_2 \cdot Et_2O$, $TMSCl/PhMe/r.t.$ to reflux. **(b)** $S_2Cl_2/MeCN/0^\circ C$ to $r.t.$ **(c)** $LiN(TMS)_2 \cdot Et_2O$, $S_2Cl_2/Et_2O/0^\circ C$ to $r.t.$ **(d)** $SbPh_3$, $O_2/MeCN/60^\circ C$. **(e)** $NBS/CHCl_3$, $AcOH/50^\circ C$. *Yields calculated from corresponding nitrile or silylated amidine.

3.2.3 Electrochemical, Spectroscopic and Computational studies

In order to probe the optoelectronic properties of thienyl-substituted DTTA derivatives, along with the substituent effect (*e.g.*, 5-hexyl vs. 4-hexylthiophene) on the optoelectronic

properties of DTTAs, electrochemical, computational and optical studies were performed, the results of which are listed in Table 3.1. The redox behaviour of **3.14**, **3.22** and **3.23** were probed by cyclic voltammetry (Fig. 3.8).

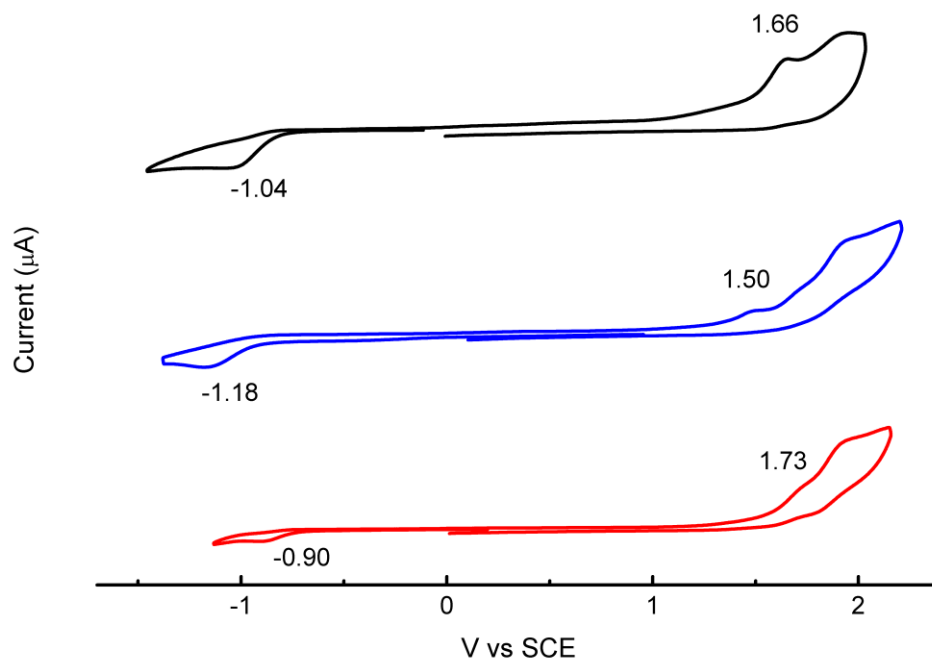


Figure 3.8 - Cyclic voltammograms of **3.14** (black), **3.22** (blue) and **3.23** (red) in dilute DCM solutions with 0.1M $n\text{Bu}_4\text{NPF}_6$ as supporting electrolyte.

In order to observe the oxidation processes, the solutions were scanned to the limit of the solvent window, as witnessed by the intense peak at 1.95V for each derivative. In all cases, both reduction and oxidation processes were observed, all irreversible regardless of conditions. Oxidation to a radical cation occurred at 1.66 V, 1.50 V and 1.73 V for **3.14**, **3.22** and **3.23** respectively. All of the derivatives were stable toward electropolymerization, as witnessed by the lack of changes upon cycling. The shift in oxidation potential between **3.14** and **3.22** or **3.23** is in line with what could be expected by the addition of an electron-donating or –withdrawing group, respectively. Overall, the oxidation events are cathodically shifted (~400 mV) when compared to phenyl-substituted DTTAs, indicative of the stronger electron donating character of the thiophene ring. On the other hand, the reduction processes for **3.14**, **3.22** and **3.23** were all observed at a potential of approximately -1 V, regardless of the substituent. This value is very

similar to the reduction potential of several phenyl derivatives. From the electrochemical data, a LUMO of approximately -3.5 eV can be obtained, which is on par with S-N heterocycles used as acceptor molecules.

Table 3.1 – Electrochemical,^a photophysical^b and theoretical^c properties of DTTAs **3.14**, **3.22**-**3.26**

	3.14	3.22	3.23	3.24	3.25	3.26
E^{ox1} (V)	1.66	1.50	1.73	- ^d	- ^d	- ^d
E^{red1} (V)	-1.04	-1.18	-0.90	- ^d	- ^d	- ^d
$E_{\text{LUMO}}^{\text{exp}}$ (eV)	-3.50	-3.40	-3.60	- ^d	- ^d	- ^d
$E_{\text{LUMO}}^{\text{calcd}}$ (eV)	-3.26	-3.12	-3.48	-3.22	-3.28	-3.20
$\lambda_{\text{max}}^{\text{abs}}$ (nm)	337	349	349	343	395	404
ϵ^{f} ($\times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$)	3.25	4.22	4.30	3.94	5.94	6.62
$\lambda_{\text{edge}}^{\text{abs}}$ (nm)	490	515	500	504	547	564
$E_{\text{gap}}^{\text{opt}}$ (eV)	2.53	2.40	2.47	2.45	2.27	2.19
$\lambda_{\text{max}}^{\text{calcdh}}$ (nm)	339	349	359	345	415	426
$f^{\text{h,i}}$	1.0472	1.1787	0.8468	1.0581	1.5882	1.6323
$\lambda_{\text{edge}}^{\text{calcdh}}$ (nm)	540	570	550	565	644	676
$E_{\text{gap}}^{\text{calcdg,h}}$ (eV)	2.29	2.17	2.25	2.19	1.92	1.84

^aDCM solutions with 0.1 M Bu₄NPF₆ as supporting electrolyte with a scan rate of 100mV/s, referenced to the Fc/Fc⁺ couple of ferrocene at +0.48 V vs. SCE. ^bSolution measurements performed in HQ-GC grade DCM. ^cDFT/B3LYP/6-311+G(d,p) calculations. ^dMeasurements not performed. ^eDerived from the onset of reduction. ^fMolar extinction coefficient for $\lambda_{\text{max}}^{\text{abs}}$. ^gCalculated from corresponding λ_{edge} . ^hFrom TDDFT calculations performed on optimized geometries. ⁱOscillator strength of the corresponding transition.

DFT calculations, performed at the B3LYP/6-311+G(d,p) level of theory, revealed that the LUMO in **3.14**, **3.22**, **3.23** and **3.24** (where R = Me for **3.22** and **3.24**) is centered on the eight-membered ring with a nodal plane that bisects the DTTA ring through the two carbon atoms and, as a result, no electron density resides on the thienyl groups (Fig. 3.9-3.10). Consequently, substituent modification should have little effect on the energy level of this orbital. By contrast, electron density in the HOMO is spread over the entire tricyclic ring system; thus any variation in the substituents (*e.g.*, alkylation) should influence these orbital energies. Both of these predictions reflect well the trends observed in cyclic voltammetry.

The photophysical properties of **3.14**, **3.22**, **3.23**, and **3.24** were investigated *via* absorption studies on dichloromethane (DCM) solutions; the results of which are presented in Figure 3.11. All of their UV-Vis spectra are comprised of two regions; one consisting of intense bands absorbing at 300-380 nm, while the other contained a weaker broad band centred at 450

nm. Such an absorption profile is consistent with a planar, aromatic structure, as the bent configuration leads to absorption restricted to the UV region of the electromagnetic spectrum (*i.e.*, below 270 nm).¹⁴ In general, the absorption profiles of thiophene DTTAs are red shifted when compared to their phenyl analogues due to the electron donating character of the heterocycle. The small red shift of λ_{max} for **3.22** and **3.23** in regards to **3.14** are consistent to those observed for similarly *para*-substituted phenyl compounds (**3.5/3.9** vs. **3.1**). Furthermore, the band gaps experimentally calculated from the respective onsets of absorption are consistent with the values predicted by DFT calculations. Compared to the 5-hexylthienyl derivative **3.22**, the main absorption band of the 4-hexyl **3.24** is shifted hypsochromically by 11 nm, from 472 to 461 nm, which is consistent with the 5 nm blue shift predicted by TDDFT calculations (*vide infra*).

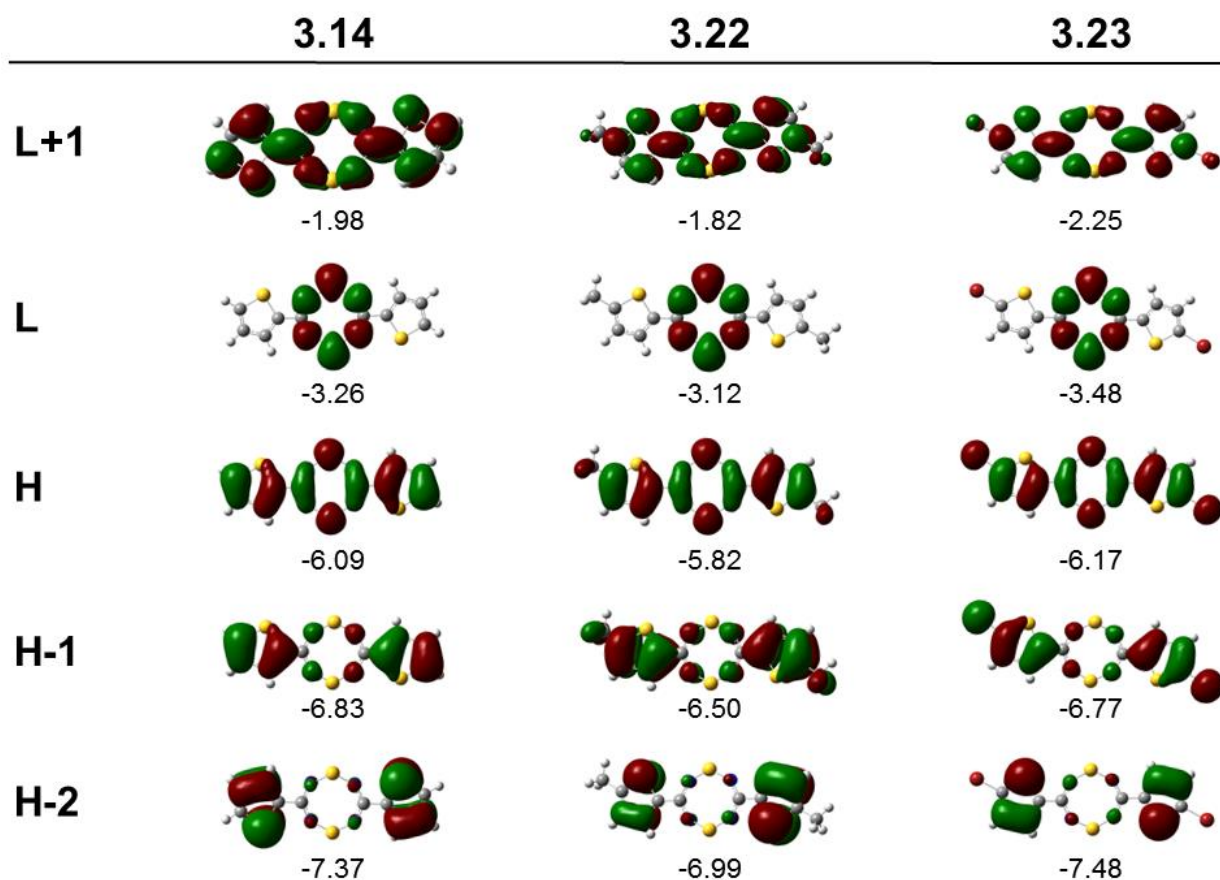


Figure 3.9 - Frontier molecular orbitals and corresponding energies (in eV) for **3.14**, **3.22** and **3.23**.

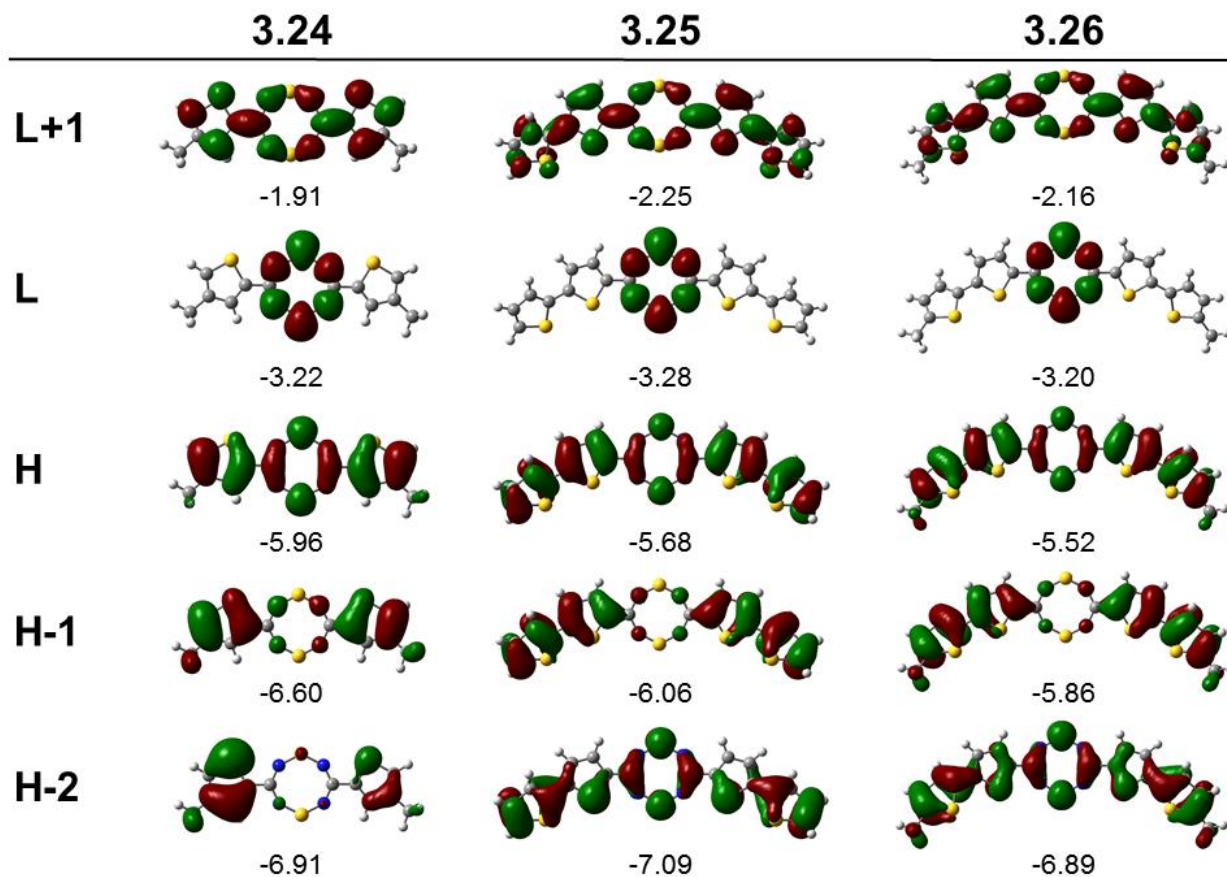


Figure 3.10 - Frontier molecular orbitals and corresponding energies (in eV) for **3.24**, **3.25** and **3.26**.

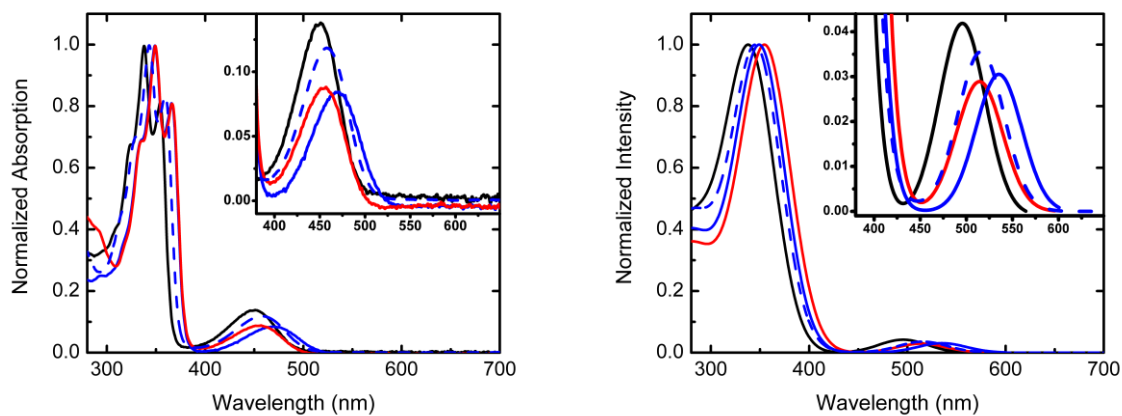


Figure 3.11 - Experimental absorption spectra (left) and TDDFT calculated absorption spectra (right) of **3.14** (black), **3.22** (blue), **3.23** (red) and **3.24** (dashed blue) in dichloromethane solutions/solvent cavities. Insets: zoom-in on the low energy absorptions between 400-700 nm.

The absorption profiles of the π -extended complexes **3.25** and **3.26** are similar to the single thienyl compounds; however, a much less defined vibronic structure is observed (Fig. 3.12). This may be attributed to a less rigid structure resulting from flexibility of the peripheral thienyl substituents.³⁴ Furthermore, the spectrum of **3.25** and **3.26** are bathochromically shifted with respect to shorter analogues **3.14** and **3.22** by 58 and 55 nm, respectively, as is expected due to the increased conjugation afforded by the additional thiophene moieties.^{35–37} Based on the onset of UV-Vis absorption, extension of conjugation from **3.14** to **3.25** and **3.22** to **3.26** leads to a decrease in the optical energy gap of 0.26 eV and 0.21 eV, respectively. DFT calculations show concordant results, with a decrease in the HOMO-LUMO energy gap of 0.37 and 0.33 eV with increased conjugation (*i.e.*, for **3.14** $\rightarrow$ **3.25** and **3.22** $\rightarrow$ **3.26**, respectively).

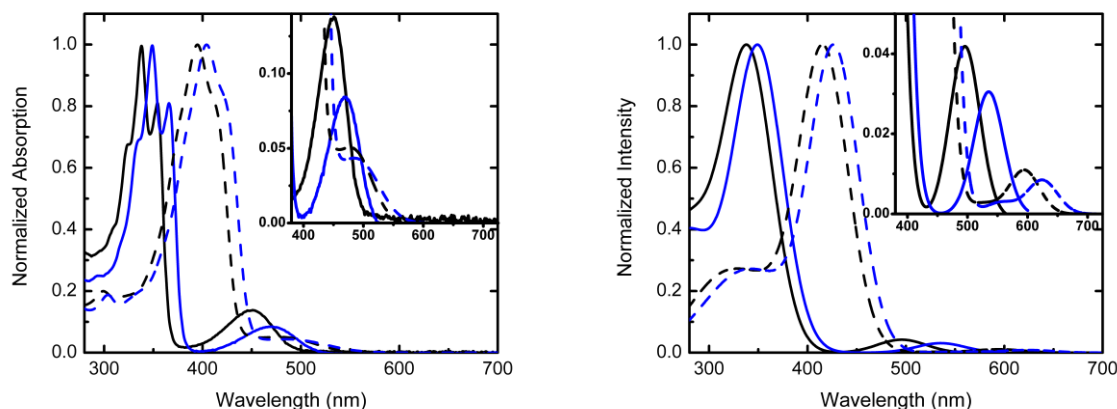


Figure 3.12 - Experimental absorption spectra (left) and TDDFT calculated absorption spectra (right) of **3.14** (black), **3.22** (blue), **3.25** (dashed black) and **3.26** (dashed blue) in dichloromethane solutions/solvent cavities. Insets: zoom-in on the low energy absorptions between 400-700 nm.

DFT calculations, performed at the B3LYP/6-311+G(d,p) level of theory for **3.25** and **3.26**, revealed that the HOMO and LUMO behave similarly to the shorter analogues **3.14/3.22-3.24** (Fig. 3.13, where R = Me for alkylated derivatives). Consequently, the observed shifts in the absorption profiles within this family of compounds all stem mainly from a change in the HOMO level upon variation in the substituents (*e.g.* alkylation, bromination). Interestingly, geometry optimization for the pentacyclic derivatives, **3.25** and **3.26**, revealed a degree of rotation about the peripheral thienyl moieties away from planarity, contrary to the tricyclic derivatives (**3.14/3.22-3.24**), which were calculated to be planar (Fig. 3.14).

TDDFT calculations were performed on optimized geometries of **3.14/3.22-3.26** (where R = Me for **3.22**, **3.24** and **3.26**) in order to probe the optical transitions; the results are presented in Figures 3.11-3.12 and the twenty vertical excitation energies calculated for each compound are listed in Appendix Tables A.3 and A.4. Overall, the calculated absorption profiles are consistent with those experimentally obtained; the calculated maximum absorption wavelengths and bathochromic shifts associated with functionalization or extension of the conjugation match the experimental behaviour well. Energy gaps obtained from these calculations are shifted by 0.25-0.52 eV compared to those determined from optical measurements, but the trends are consistent such that E_{gap} is largest for **3.14** and smallest for **3.26**. The highest wavelength absorption, which is associated with the HOMO to LUMO transition, has relatively low oscillator strength ($f \sim 0.02$) for all derivatives. The band with the largest oscillator strength ($f > 1$) corresponds to excitation of the HOMO to LUMO+1 for each compound and, in the case of **3.14**, **3.22**, **3.23** and **3.25**, also includes contribution from the HOMO-2 to LUMO transition. Furthermore, the oscillator strength predicted by computational methods for each derivative correlates well with the measured molar extinction coefficients (Table 3.2).

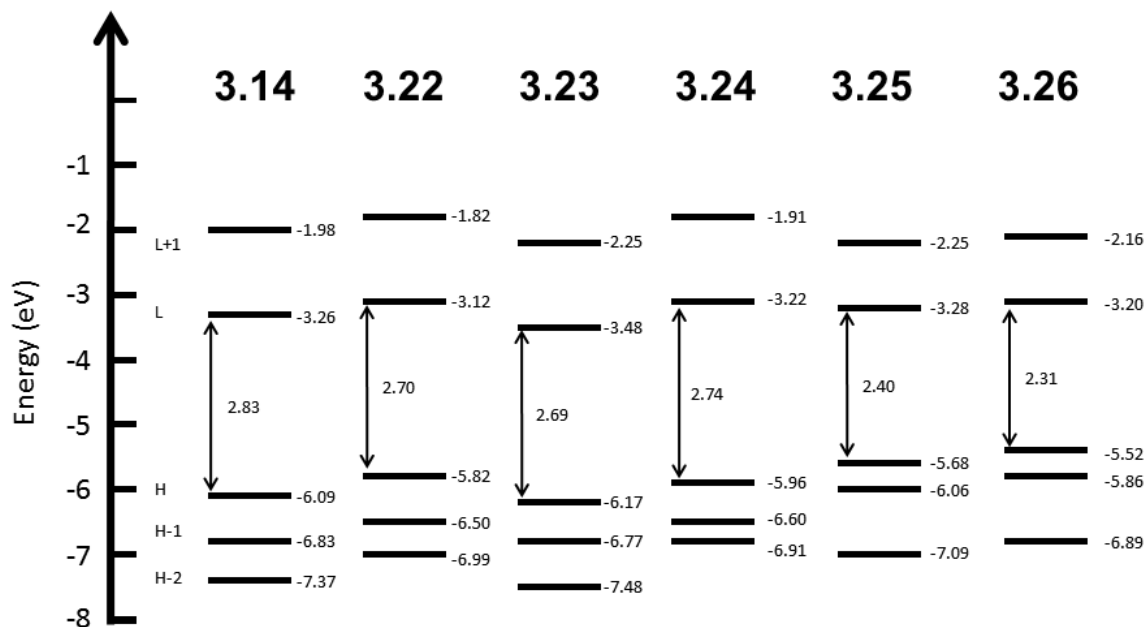


Figure 3.13 – Energy level diagram for the frontier orbitals of **3.14**, **3.22-3.26**.

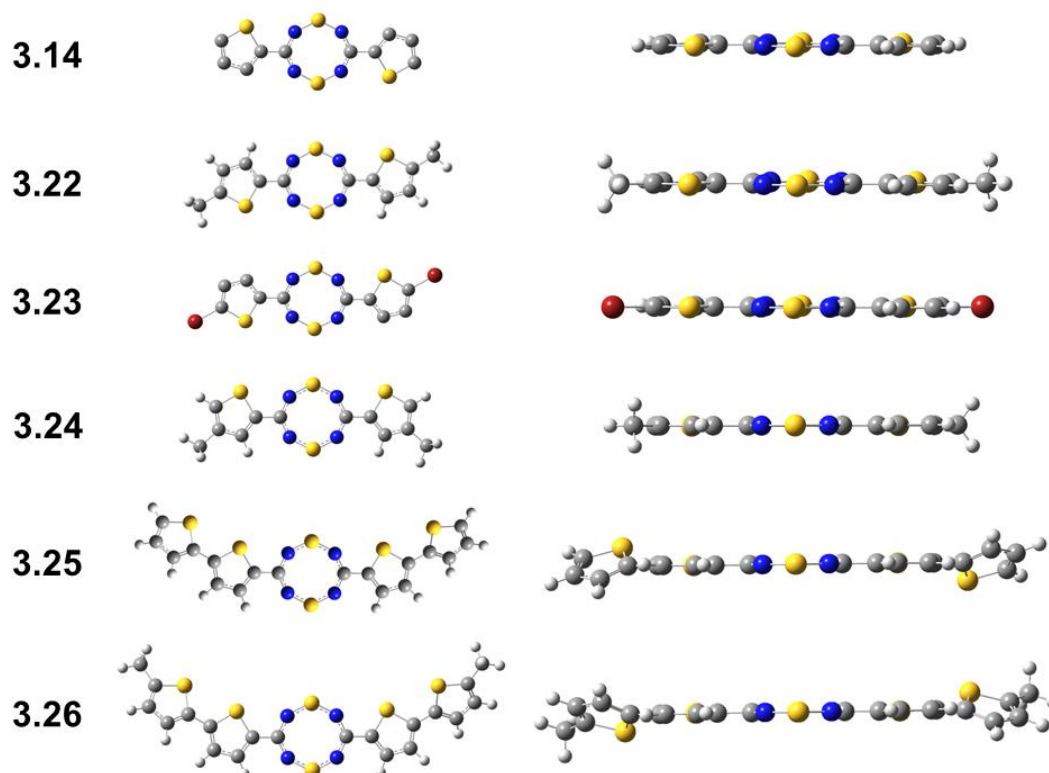


Figure 3.14 - Top view (left) and side view (right) of geometry optimized structures of (from top to bottom) **3.14**, **3.22**, **3.23**, **3.24**, **3.25** and **3.26**, where R=Me for **3.22**, **3.24** and **3.26**.

Table 3.2 - Comparative table for the measured molar coefficients of extinction^a with the corresponding calculated oscillator strengths.^b

	λ (nm)	ϵ (M ⁻¹ cm ⁻¹)	Calculated λ (nm)	f
3.14	338	32500	339	1.0472
	450	4440	495	.0458
3.22	349	42200	350	1.1787
	470	3560	535	0.0366
3.23	349	43000	359	0.8468
	455	3750	514	0.0365
3.24	343	39396	346	1.0581
	458	4563	516	0.0382
3.25	395	59436	415	1.5882
	477	3056	594	0.0175
3.26	404	66223	426	1.6323
	485	2944	624	0.0139

^aOptical measurements were performed on dilute DCM solutions. ^bTDDFT/B3LYP/6-311+G(d,p) level of theory on geometry optimized structures (where R = Me for **3.22**, **3.24** and **3.26**) where f = oscillator strength).

3.2.4 X-ray Crystallography Characterization of DTTA Derivatives

Since long-range molecular order and π -orbital overlap are crucial to semiconductor efficiency as they provide a pathway for electronic communication, structures consisting of π -stacked planar molecules are often considered ideal. To confirm the planarity of the DTTA ring and to investigate the effect of the substitution pattern on intermolecular interactions, the solid-state structure of **3.14** and **3.22-3.26** were studied by single crystal X-ray diffraction. Pertinent crystallographic data for all six derivatives is given in Appendix Table A.1. In each compound, the planarity of the eight-membered heterocyclic ring coupled with the symmetrical bond lengths, which correlate well to previously reported DTTAs,²⁰⁻²² is indicative of the 10π electron aromatic system. Thus, as expected, thienyl-functionalization affords essentially planar tricyclic (**3.14/3.22-3.24**) and pentacyclic (**3.25** and **3.26**) frameworks, which is consistent with the photophysical properties.

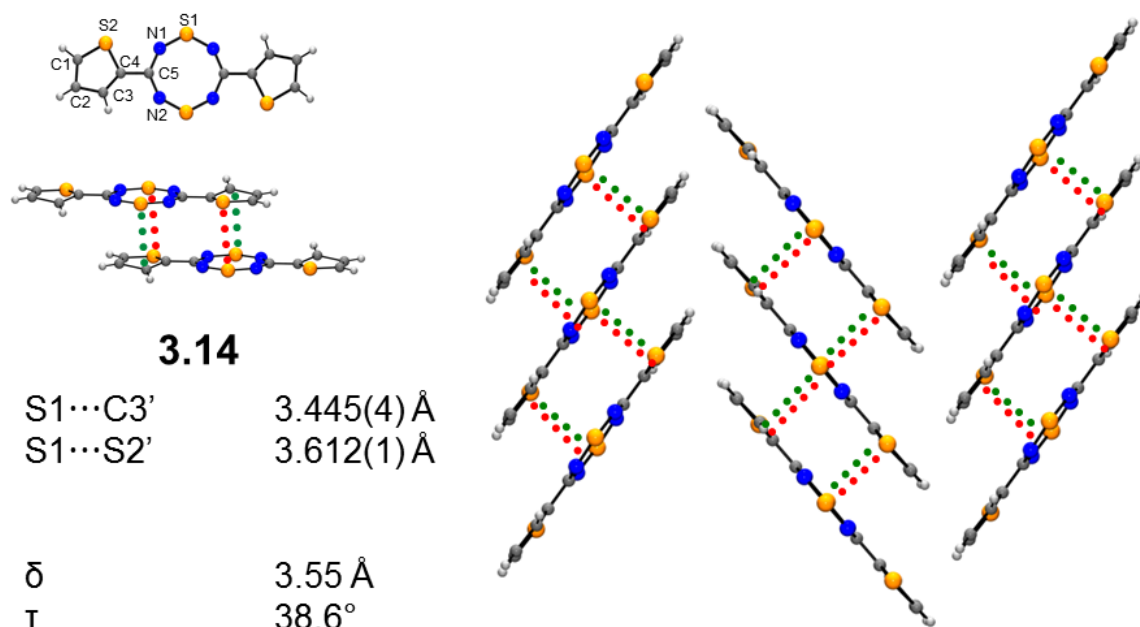


Figure 3.15 - (top left) Crystal structures of **3.14** showing atom numbering. **(bottom left)** Close intermolecular contacts along the π -stack. **(right)** Slipped π -stacks. Close intermolecular contacts are shown: S...S (red); S...C (green).

The effect of the substituents on the packing arrangement was probed by analyzing the single-crystal structure of **3.14/3.22-3.24**. The thiophene derivative **3.14**'s structure (Fig. 3.15) corresponds to a monoclinic $P2_1/c$ space group and is formed of herringbone arrays of slipped π -

stacks with close (within or nominally above the sum of van der Waals radii) S...S' (3.590(6) Å) intra-stack contacts between thienyls and DTTAs. The crystal structure of the 5-hexyl derivative **3.22** (Fig. 3.16) belongs to the triclinic space group P-1 and consists of slipped π -stacks. Within the molecular framework, disorder is present about the thienyl substituents, in the same vein as **3.14**, and involves a 180° rotation about the C2-C13 bond. This disorder here was modelled with 0.65/0.35 occupancy, and the most favoured *cis* isomer is presented in Figure 3.16. On the other hand, crystals of the tricyclic 4-hexyl derivative **3.24** belong to the monoclinic space group P2₁/n and consist of slipped π -stacks that align in a herringbone arrangement (Fig. 3.17). In both cases, the structures also reveal that the hexyl chains interdigitate between stacks and are relatively planar to the tricyclic framework, allowing for tight π -stacking while limiting inter-stack communication. Consequently, the only close contacts observed for **3.22** are intra-stack (S1...S4' = 3.564(6) Å, S3...S1' = 3.560(2) Å, S2...C14' = 3.444(30) Å, C4...S2' = 3.471(5) Å). This type of effect has been noted in other alkyl-substituted π -conjugated systems, in which the long hydrocarbon chains act as buffer that effectively isolate the π -stacked molecules from one another. Similarly, the only close contacts observed in the structure of **3.24** are those within the π -stacks (*e.g.*, S1...S2' = 3.613(2) Å; C3...S1' = 3.482(4) Å; C1...C1' = 3.429(6) Å). Comparison to **3.22**, which crystallizes in the triclinic space group P-1, reveals that switching the hexyl chain from the 5- to the 4-position of the thienyl substituent leads to enhanced symmetry for **3.24**.

Crystals of **3.23** belong to the monoclinic P2₁/c space group and consist of slipped π -stacks in a herringbone arrangement that, when viewed along the z-direction, form a cross-braced structure (Fig. 3.18). Within the herringbone structure, molecules are linked by close Br...Br' interactions (3.687(1) Å) that lace π -stacks together along the 2₁ rotation axis. No intra-stack contacts less than the sum of the van der Waals radii are observed; the closest interactions are between bromine and carbon (Br1...C4' = 3.679(4) Å, Br1...C5' = 3.730(3) Å). Although it has been suggested that Br...Br' interactions play a role in crystal packing of molecular systems, the herringbone array observed for **3.23** is also observed in the parent derivative **3.14**, signifying that these interactions may not be the dominant structure-making forces for this system. However, within the molecular framework they may contribute to locking the thienyl substituents in a *trans*-conformation, as there is no disorder observed for **3.23**.

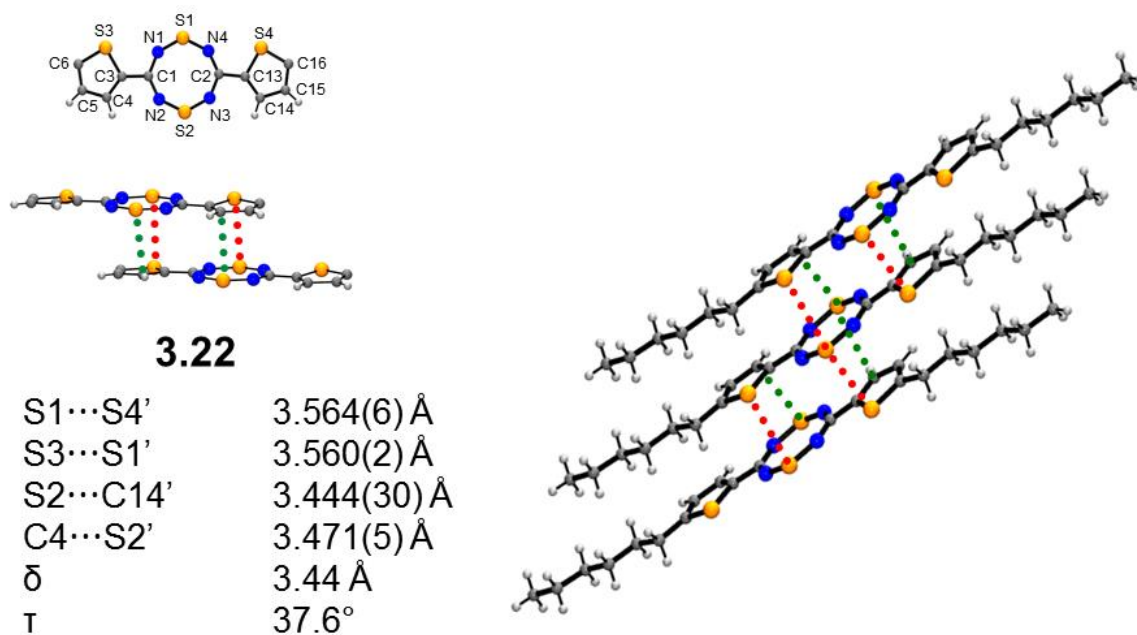


Figure 3.16 - (top left) Crystal structures of **3.22** showing atom numbering. **(bottom left)** Close intermolecular contacts along the π -stack. Hexyl chains were omitted for clarity **(right)** Slipped π -stacks. Close intermolecular contacts are shown: S...S (red); S...C (green).

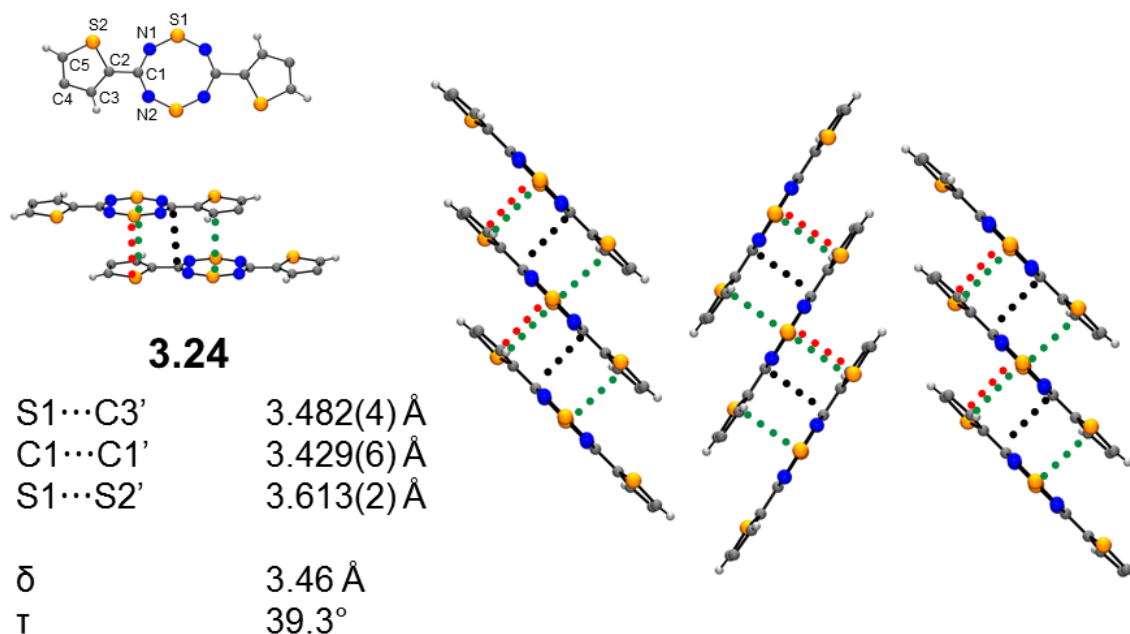


Figure 3.17 - (top left) Crystal structures of **3.24** showing atom numbering. **(bottom left)** Close intermolecular contacts along the π -stack. **(right)** Slipped π -stacks. Hexyl chains were omitted for clarity. Close intermolecular contacts are shown: S...S (red); S...C (green); C...C (black).

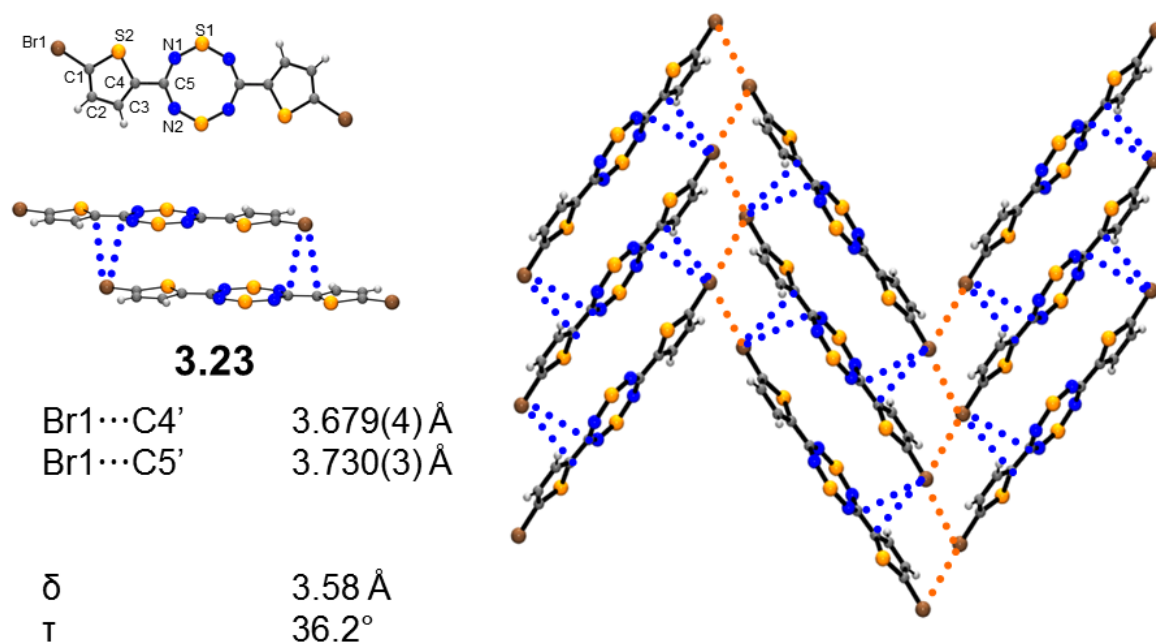


Figure 3.18 - (top left) Crystal structures of **3.23** showing atom numbering. (bottom left) Close intermolecular contacts along the π -stack. (right) Slipped π -stacks. Close intermolecular contacts are shown: Br...Br (orange); Br...C (blue).

Regardless of the differences in the packing motifs, a number of similarities exist between the four structures, especially when looking down the perpendicular direction to the π -conjugated core. For example, in all structures a thiophene moiety on one molecule overlaps with the DTTA ring of a neighbouring molecule below. This degree of slippage within the π -stacked structure, which can be quantified in terms of the slippage angle τ , is nearly identical (cf. 37.6°, 36.2° and 39.3° for **3.22**, **3.23** and **3.24**, respectively). While this leads to a relatively consistent interplanar separation (δ) between molecules **3.22** and **3.24** (3.44 Å vs. 3.46 Å, respectively), a slight difference in δ is observed for **3.23** (3.58 Å), potentially as a result of the additional halogen bonding interactions. While it has been observed in other π -conjugated molecules^{35,38} and heterocycles³⁹ that minor changes in substituents result in dramatic changes in slippage angle, here it appears the interaction between the donor thienyl groups with the acceptor DTTA core dominates the packing arrangement.

The crystal structure of the extended bithienyl derivative **3.25** also corresponds to the monoclinic space group $P2_1/n$ and consists of herringbone arrays of slipped π -stacks (Fig. 3.19).

Within the molecular framework, there is disorder about the outer thienyl substituents, similar to that of **3.14** and **3.22**, in addition to other thiophene-substituted heterocycles.^{9,21,40} This disorder involves a 180° rotation about the C5-C6 bond that affects the positions of the C7 and S3 atoms and was modelled as 0.60 and 0.40 occupancy of the two positions. The major contributor in **3.25**, presented in Figure 3.19, is comprised of a cis-bithiophene in a trans-conformation about the DTTA ring. As well, while the central tricyclic core is essentially planar, with a torsion angle of only 5.25° between the DTTA ring and the inner thienyl moieties, the outer thienyl groups twist at a torsion angle of 29.55° reducing the planarity of the pentacyclic framework. Nonetheless, numerous close π - π interactions exist within the π -stacked structure (*e.g.*, C7...S2' = 3.44(2) Å; C3...S1' = 3.424(6) Å; S1...S1' = 3.463(2) Å). This increase in the number of close contacts, compared to **3.14**, is likely due to the enhanced π -conjugation while maintaining a relatively close interplanar separation (3.53 Å for **3.25** vs. 3.55 Å for **3.14**).

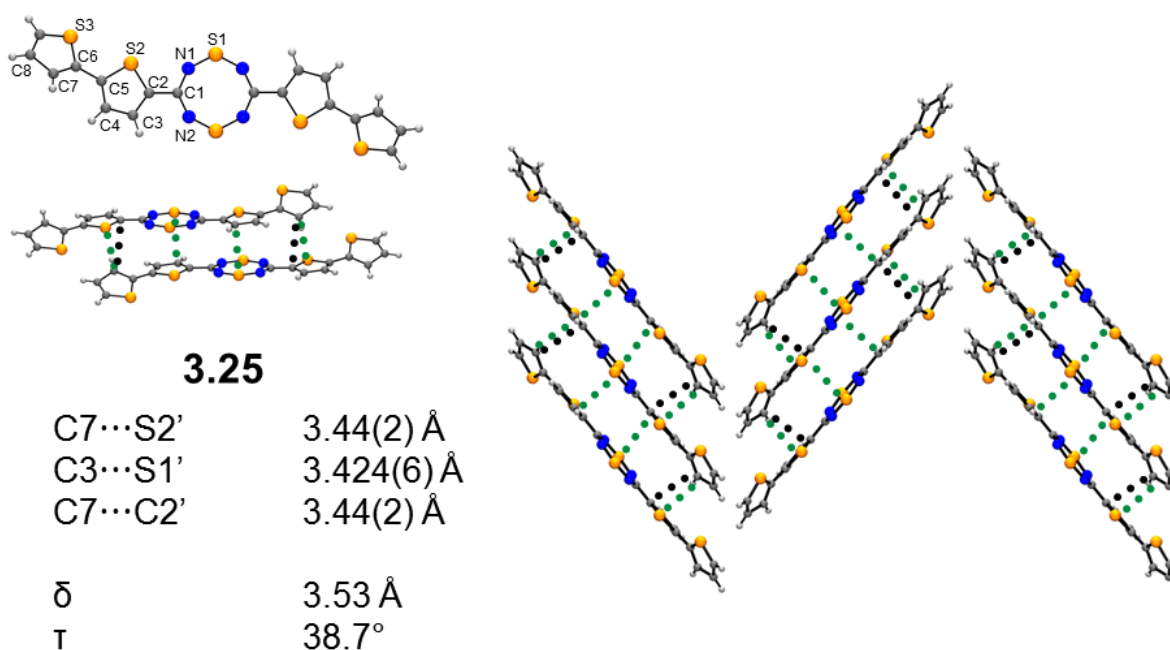


Figure 3.19 - (top left) Crystal structures of **3.25** showing atom numbering. **(bottom left)** Close intermolecular contacts along the π -stack. **(right)** Slipped π -stacks. Close intermolecular contacts are shown: S...C (green); C...C (black).

Similar to the 5-hexylthienyl derivative **3.22**, crystals of its π -extended analogue **3.26** belong to the triclinic space group P-1 and consist of slipped π -stacks (Fig. 3.20). However, contrary to the former, in which numerous close π - π interactions exist within the slipped π -stack,

the structure of **3.26** reveals only two close intra-stack contacts ($S2\cdots S2' = 3.5686(6)$ Å; $C1\cdots C7' = 3.415(2)$ Å). Interestingly, these interactions occur between neighbouring thienyl moieties, which is inconsistent with the other thienyl substituted DTTAs where the structure is dominated by the donor-acceptor interaction between the DTTA ring on one molecule and the thienyl groups of another. This dichotomy is exemplified by considering the slippage angle τ , which is significantly altered in **3.26** (21.7°) compared to the other thienyl functionalized DTTAs ($\tau = 36^\circ - 39^\circ$). This may be attributed to alkyl-alkyl interactions dominating the packing arrangement in **3.26**, compared to the other thienyl substituted DTTA derivatives (*i.e.*, **3.14**, **3.22-3.25**) where the π - π interactions between the donor thienyl groups and central DTTA acceptor appear to dictate the solid-state structure. Overall, the pentacyclic framework in **3.26** is more planar than in the case of **3.25**, with torsion angles of only 1.8° and 8.7° for the inner and outer thienyl moieties, respectively. As well, while there are limited contacts within the slipped π -stacks, additional inter-stack contacts exist between carbon atoms of the thienyl substituents on neighbouring stacks ($C7\cdots C3' = 3.568(6)$ Å).

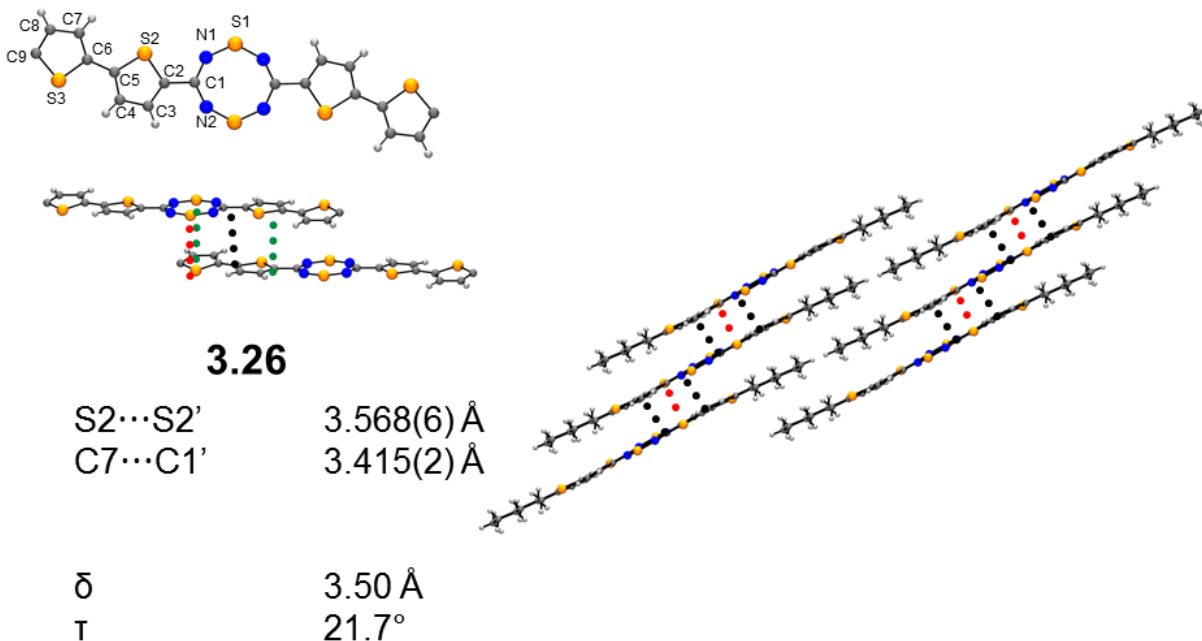


Figure 3.20 - (top left) Crystal structures of **3.26** showing atom numbering. **(bottom left)** Close intermolecular contacts along the π -stack. Hexyl chains were omitted for clarity. **(right)** Slipped π -stacks. Close intermolecular contacts are shown: $S\cdots S$ (red); $C\cdots C$ (black).

3.3 Conclusions

To summarize, a family of dithiatetrazocines functionalized with thienyl (**3.14**), 5-hexylthienyl (**3.22**), 5-bromothienyl (**3.23**), 4-hexylthiophen-2-yl (**3.24**), 5-(thiophen-2-yl)thiophen-2-yl (**3.25**) and 5-(5'-hexyl-thiophen-2-yl)thiophen-2-yl (**3.26**) substituents were prepared using either Boeré's reduction protocol, or a modified one pot variant thereof, from the corresponding nitrile, demonstrating the versatility of the synthetic procedure described here. The latter two compounds (*i.e.*, **3.25** and **3.26**) mark the first published examples of π -extended DTTA systems. Comparative electrochemical, optical, computational and X-ray diffraction studies were carried out on this family of heterocycles to investigate the influence of the substitution pattern, in addition to enhanced conjugation, on the optoelectronic and solid-state properties. More specifically, the shorter derivatives **3.14/3.22-3.24** exhibit irreversible redox behaviour, with a wide electrochemical window and low-lying LUMO levels. In all cases, substitution leads to small red-shifts in the absorption spectra, which points to a decreased HOMO-LUMO gap in regard to the protonated analogue. Displacement of the alkyl chain from the 5- to the 4-position in hexylthienyl functionalized DTTA (*i.e.*, **3.22** vs. **3.24**) results in a relatively small hypsochromic shift in the absorption profile, indicative of a slight increase in the optical energy gap. Single crystal X-ray diffraction shows π -stacks for all derivatives in the solid state, with close intermolecular contacts within the stacks for all compounds except **3.23**, where inter-stack halogen-halogen interactions prevail. At the same time, variations in the placement of the alkyl substituent on the π -conjugated core (*i.e.*, **3.22** vs. **3.24**) leads to enhanced symmetry in the solid-state affording a herringbone arrangement of slipped π -stacks. Extension of the conjugation *via* additional thienyl moieties on either side of the central DTTA ring leads to a decrease of the HOMO-LUMO gap, as witnessed by the bathochromic shifts in the absorption profiles for **3.25** and **3.26** with respect to their mono-thienyl analogues (*i.e.*, **3.14** and **3.22**, respectively). As is expected, enhanced conjugation afforded by the presence of additional thienyl groups in **3.25** also results in an increase in the number of intermolecular contacts in the solid-state, which bodes well for its implementation into optoelectronic devices. On the other hand, comparison of the structures between **3.22** and **3.26** reveal a decrease in the number of π - π interactions with increasing conjugation. This may be attributed to alkyl-alkyl interactions dominating the packing arrangement in **3.26**, whereas in all the other thienyl substituted DTTA

derivatives (*i.e.*, **3.14**, **3.22**, **3.24** and **3.25**) the π - π interactions between the donor thienyl groups and central DTTA acceptor appear to dictate the solid-state structure.

3.4 Experimental Methods

3.4.1 General Procedures

The reagents acetic acid sodium salt trihydrate, acetic anhydride, *n*-Butyllithium (ⁿBuLi), hydroxylamine hydrochloride, 1-iodohexane, lithium bis(trimethylsilyl)amide, *N*-bromosuccinimide (NBS), *N*-methylpyrrolidone (NMP), sulphur monochloride, 2-thienylcarboxaldehyde (**3.28**), thiophene, trimethylsilyl chloride (TMSCl) and triphenylantimony (SbPh₃) and were obtained commercially from Aldrich/Fisher/VWR and used as received. LiN(TMS)₂·Et₂O,⁴¹ 2-formyl-4-hexylthiophene (made with ⁿBuLi in-lieu of ^tBuLi),⁴² 5-formyl-2,2'-bithiophene⁴³ and 5-formyl-5'-hexyl-2,2'-bithiophene⁴⁴ were prepared as previously reported. All solvents were ACS grade; dry solvents were obtained by passing them through activated alumina on a J.C. Meyer solvent purification system. Melting points were taken using a Mel-Temp apparatus and were uncorrected. NMR spectra were run in CDCl₃ solutions at room temperature on a Bruker Avance 400 MHz spectrometer. All spectra were referenced to the deuterated solvent peak at 7.26 ppm. IR spectra were recorded on an Agilent Technologies Cary 630 FT-IR spectrometer. Elemental analyses were performed by G.G. Hatch Stable Isotope Laboratory, Ottawa, ON, K1N 6N5.

3.4.2 Spectroscopy

UV-visible absorption spectra were measured with a Varian Cary Series 6000 UV-Vis-NIR spectrophotometer. UV-Visible spectra were measured in HQGC-grade DCM solutions with 1 cm precision quartz cuvettes.

3.4.3 Electrochemistry

Cyclic voltammetry was performed using a Princeton Applied Research (PAR) VersaSTAT 3 potentiostat/galvanostat/frequency response analyser and V3-Studio electrochemical software (V 1.0.281 (c) 2008 PAR) employing a glass cell fitted with platinum electrodes. The measurements were carried out on dichloromethane solutions (dried by distillation over CaH₂) containing 0.1M tetrabutylammonium hexafluorophosphate (Aldrich) as supporting electrolyte with a scan rate of 100 mV/s. The experiments were referenced to the Fc/Fc⁺ couple of ferrocene at +0.48 V vs. SCE.⁴⁵

3.4.4 Crystal Growth

Single crystals of **3.22** suitable for X-ray diffraction were obtained through vapor diffusion of acetonitrile into toluene solutions. Crystals of **3.23-3.26** suitable for X-ray analysis were grown by slowly cooling saturated solutions. **3.23** and **3.25** were both obtained from toluene solution; **3.24**, from chlorobenzene and **3.26** from chloroform.

3.4.5 X-ray Measurements

Data collection results for compounds **3.22-3.26** represent the best data sets obtained in several trials for each sample. The crystals **3.22/3.24-3.26** were mounted on thin glass fibers using paraffin oil, **3.23** was glued to a glass fibre with epoxy. Prior to data collection crystals were cooled to 200.15 K. Data were collected on a Bruker AXS KAPPA single crystal diffractometer equipped with a sealed Mo tube source (wavelength 0.71073 Å) APEX II CCD detector. Raw data collection and processing were performed with APEX II software package from BRUKER AXS.⁴⁶ Diffraction data for **1c** and **2a** samples were collected as a sequence of 0.3° ω scans at 0, 120, and 240° in ϕ . Due to lower unit cell symmetry, diffraction data for **2b** were collected as a sequence of 0.3° ω scans at 0, 90, 180 and 270° in ϕ , in order to ensure adequate data redundancy. Initial unit cell parameters were determined from 60 data frames with 0.3° ω scan each collected at the different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied.⁴⁷ Systematic absences in the diffraction data-set and unit-cell parameters were consistent with triclinic P-1 (№2) for compound **3.22** and **3.26**, monoclinic P21/c (№14) for compound **3.23** and **3.24**, monoclinic

P21/n (№14, alternative settings) for compound **3.25**. Solutions in the centrosymmetric space groups for all three compounds yielded chemically reasonable and computationally stable refinement results. The structures were solved by direct methods, completed with difference Fourier synthesis, and refined with full-matrix least-squares procedures based on F^2 .

Refinement of the original molecular model of **3.22** revealed additional strong electron density peaks around the C(13)-C(22) fragment. To accommodate the positions and intensity of those peaks a disorder model was introduced in the refinement. The structural model was updated with positional disorder of the C(13)-C(22) fragment, caused by the nominal rotation of this fragment around C(2)-C(13). The quality of the collected data allowed full anisotropic refinement of the full molecule including the disordered parts. However, to achieve satisfactory geometry of the disordered fragments and acceptable thermal motion parameters as well as to improve refinement results, several sets of the self-converging geometry constraints (SAME) and thermal motion constraints (SIMU, DELU) were applied. Diffraction data for the crystal of the complex **3.24** was collected to 0.75 Å resolution, however due to small crystal size and weak diffraction it was discovered that both $R(\text{int})$ and $R(\text{sigma})$ exceeded 35% for the data below 0.95 Å resolution. Based on $R(\text{sigma})$, value data were truncated to 0.90 Å resolution for refinement. Asymmetric unit for crystallographic model of **3.24** consists of one target molecule located in the inversion center of the space group. Structural model of **3.25** consists of one molecule of compound located in the inversion center of the space group. On the final refinement stages, unusual values of thermal parameters for sulphur atoms as well as several carbon atoms in the model indicated the presence of disorder in the orientation of 5-membered ring S(3) – C(6) to C(8). Such disorder unrelated to symmetry was interpreted as an 180° rotation of the fragment around the C(5) – C(6) bond. Initial value of the occupancies for disordered fragment was refined. However, at the final refinement cycles occupancies of the fragment were fixed at a 60:40 ratio. Several sets of geometry constraints (SADI) and thermal motion parameters constraints (SIMU, RIGU) were introduced to ensure reasonable molecular geometry and acceptable thermal motion values for these fragments. Solution of structure for **3.26** revealed that one molecule of target compound was located in the inversion center of the space group.

For all five compounds all non-hydrogen atoms were refined in anisotropic thermal motion approximation. All hydrogen atomic positions were calculated based on the geometry of

related non-hydrogen atoms. All hydrogen atoms were treated as idealized contributions during the refinement. All scattering factors are contained in several versions of the SHELXTL program library, with the latest version used being v.6.12.⁴⁸

3.4.6 Computational Chemistry

All calculations were carried out using the Gaussian09 program package.⁴⁹ The geometries of the studied compounds were investigated using the hybrid density functional B3LYP with the 6-311+G(d,p) basis set. Optimized structures were used to examine the orbital energies and HOMO-LUMO gaps. Archival files for the optimized geometries of **3.14**, **3.22-3.26** can be found in the Appendix Section A.3. The calculated UV-Vis spectra and excitation energies were determined using TDDFT which employed the optimized B3LYP ground states. A polarized continuum solvent model was employed with DCM as the solvent, and twenty excited states were considered.

3.4.7 Synthetic Procedures

Preparation of (3,7)-bis(thienyl)-1,5,2,4,6,8-dithiatetrazocine (3.14). Oxygen was bubbled through a slurry solution of **3.49** (1.95 g, 8.75 mmol based on amidine) in MeCN (25 mL) for 15 min, at which time SbPh₃ (1.54 g, 4.36 mmol) was added. The bubbling of O₂ was continued for another 30 min. The light brown precipitate of **3.14** was filtered and dried in air. Yield 1.36 g (4.38 mmol, 50 %). This material was recrystallized from chloroform to afford yellow crystals. mp = 290 °C. The product was identified by comparison to the ¹H NMR spectrum reported in the literature.¹⁶ ¹H NMR (δ, CDCl₃, r.t., 400 MHz): 7.94 (dd, J = 1.2, 3.7 Hz, 2H), 7.44 (dd, J = 1.2, 5.1 Hz, 2H), 7.14 (dd, J = 3.7, 5.2 Hz, 2H). IR ν_{max} (cm⁻¹): 622.17(w), 629.16(w), 645.60(w), 658.79(w), 701.09(s), 816.92(m), 840.16(m), 853.56(w), 892.93(w), 1033.06(w), 1076.27(w), 1193.93(w), 1225.51(w), 1245.97(w), 1274.51(w), 1345.24(w), 1368.29(m), 1426.63(s), 1523.28(w), 1548.74(w), 1608.72(w), 1682.25(w), 1809.51(w), 1980.09(w), 2116.18(w), 2465.09(w), 3117.83(w). Given the low solubility of this compound, ¹³C NMR spectroscopy was not possible.

Preparation of 3,7-bis(5-hexylthiophene)-1,5,2,4,6,8-dithiatetrazocine (3.22). Oxygen was bubbled through a slurry solution of **3.50** (1.98 g, 6.45 mmol) in MeCN (30 mL) for 15 min, at

which time SbPh_3 (2.53 g, 7.15 mmol) was added. The bubbling of O_2 was continued for another 30 min. The yellow precipitate of **3.22** was filtered and dried in air. Crude yield 0.93 g (1.88 mmol, 30 %). This material was recrystallized from ethyl acetate to afford light yellow crystals. Yield 0.46 g (0.96 mmol, 13 %). m.p = 134 °C. ^1H NMR (δ , CDCl_3 , r.t., 400 MHz): 7.73 (d, J = 3.6 Hz, 2H), 6.80 (d, J = 3.6 Hz, 2H), 2.84 (t, J = 7.8 Hz, 4H), 1.73 (t, J = 6.5 Hz, 4H), 1.32 (m, 12H), 0.9 (m, 6H). IR ν_{max} (cm^{-1}): 576.61(w), 607.14(w), 637.06(m), 658.36(m), 722.12(w), 781.79(w), 804.46(s), 829.03(w), 871.69(w), 1039.00(w), 1103.02(w), 1206.65(w), 1246.13(w), 1368.24(s), 1426.19(m), 1466.96(w), 2853.40(w), 2924.78(w), 2956.04(w). Anal. calcd for $\text{C}_{22}\text{H}_{30}\text{N}_4\text{S}_4$: C, 55.19; H, 6.32; N, 11.70. Found: C, 55.64; H, 6.44; N, 11.50. Given the low solubility of this compound, ^{13}C NMR spectroscopy was not possible. The identity of this compound was confirmed through ^1H NMR spectroscopy, elemental analysis and X-ray crystallography.

Preparation of 3,7-bis(5-bromothiophene)-1,5,2,4,6,8-dithiatetrazocine (3.23). In a flask covered by aluminum foil, NBS (0.459 g, 2.58 mmol) was added to a slurry of **3.14** (0.320 g, 1.03 mmol) in 135 mL of a 2:1 solution of CH_3Cl /acetic acid. The reaction mixture was heated at 50 °C for 48 h in the absence of light. After cooling to r.t. the orange precipitate of **3.23** was filtered, washed with water and methanol and dried in air. Yield 0.42 g (0.90 mmol, 87 %). This material was recrystallized from toluene to afford orange crystals. mp = 260 °C. ^1H NMR (δ , CDCl_3 , r.t., 400 MHz): 7.68 (d, J = 4.0 Hz, 2H), 7.09 (d, J = 4.0 Hz, 2H). IR ν_{max} (cm^{-1}): 629.16(m), 647.53(w), 658.95(w), 702.16(w), 720.77(w), 798.97(s), 830.12(w), 878.75(w), 967.57(m), 1046.57(w), 1046.49(w), 1197.95(w), 1209.60(w), 1238.75(w), 1361.56(s), 1424.48(s), 1531.88(w), 1607.85(w), 1767.42(w), 1981.24(w), 247.95(w), 3093.35(w). Anal. calcd for $\text{C}_{10}\text{H}_4\text{Br}_2\text{N}_4\text{S}_4$: C, 25.65; H, 0.86; N, 11.97. Found: C, 25.70; H, 0.90; N, 11.75. Given the low solubility of this compound, ^{13}C NMR spectroscopy was not possible. The identity of this compound was confirmed through ^1H NMR spectroscopy, elemental analysis and X-ray crystallography.

Preparation of 3,7-bis(4-hexylthiophen-2-yl)-1,5,2,4,6,8-dithiatetrazocine (3.24): **3.38** (10.54 g, 54.5 mmol) was added dropwise to a stirring slurry of $\text{LiN}(\text{TMS})_2 \cdot \text{Et}_2\text{O}$ (13.40 g, 55.5 mmol) in dry ether (150 mL) under nitrogen to yield a cloudy orange solution. After stirring overnight, a solution of sulphur monochloride (8.50 mL, 106 mmol) in dry diethyl ether (25 mL) was added

to the reaction mixture at 0 °C over 30 min. After stirring for 3 h at 0 °C, the resulting orange solid was filtered under inert atmosphere. Washing with diethyl ether and carbon disulfide followed by drying *in vacuo* afforded 4-(4-hexylthienyl)-1,2,3,5-dithiadiazolylium chloride (**3.51**) as a bright orange solid, which was used without further purification. Crude yield 17.7 g (57.6 mmol, > 100 %). IR ν_{max} (cm⁻¹): 3385.57(w), 3040.48(m), 3002.24(w), 2952.65(m), 2920.91(m), 2843.88(m), 1632.52(w), 1549.21(m), 1461.64(s), 1373.32(m), 1230.65(m), 1211.37(m), 1154.68(m), 1103.21(m), 957.08(w), 908.21(m), 874.25(m), 839.39(s), 825.70(s), 722.17(m), 699.40(s). Dry oxygen was bubbled through a slurry of **3.51** in dry acetonitrile (130 mL) for 30 min, after which SbPh₃ (11.80 g, 33.4 mmol) was added to the reaction. The solution was stirred for 2 h at 60 °C with oxygen bubbling, then hot-filtered to isolate a brown-yellow solid. The solid was refluxed in chloroform (250 mL) then hot-filtered over Celite to afford a clear amber filtrate. The filtrate was concentrated to 200 mL, cooled to room temperature and added to 200 mL of methanol. After stirring for 1h, the resulting slurry was filtered, washed with methanol, then dried in air to afford the target product as a bright yellow solid (2.34 g, 17% yield). Recrystallization from hot chlorobenzene afforded the target product as yellow needles. m.p. = 126-128 °C. ¹H NMR (δ , CDCl₃, r.t., 400 MHz): 7.80 (d, J=1.55 Hz, 2H), 7.05 (m, 2H), 2.65 (t, J = 7.70 Hz, 4H), 1.69 (m, 4H), 1.36 (m, 12H), 0.90 (t, J = 6.90 Hz, 3H). IR ν_{max} (cm⁻¹): 2963.18(w), 2922.11(m), 2910.87(m), 2851.30(m), 1467.40(w), 1452.36(m), 1437.92(m), 1424.18(m), 1363.23(s), 1276.94(w), 1244.76(m), 1220.72(m), 1187.54(m), 1129.98(w), 1111.70(w), 863.92(m), 851.77(s), 823.02(m), 794.77(w), 751.56(s), 734.64(s), 660.92(s). Anal. calcd for C₂₂H₃₀N₄S₄: C, 55.19; H, 6.32; N, 11.70. Found: C, 54.78; H, 6.15; N, 11.58. Given the low solubility of this compound, ¹³C NMR spectroscopy was not possible. The identity of this compound was confirmed through ¹H NMR spectroscopy, elemental analysis and X-ray crystallography.

Preparation of 3,7-bis([5-(thiophen-2-yl)thiophen-2-yl])-1,5,2,4,6,8-dithiatetrazocine (3.25): **3.42** (4.20 g, 22.0 mmol) and LiN(TMS)₂·Et₂O (5.45 g, 22.6 mmol) were stirred overnight in dry ether (100 mL) under nitrogen to yield a cloudy orange solution. A solution of sulphur monochloride (3.50 mL, 43.8 mmol) in dry diethyl ether (25 mL) was added to the reaction mixture at 0 °C over 30 min. After stirring at 0 °C for 3 h, the resulting green solid was filtered under inert atmosphere. Washing with diethyl ether and carbon disulfide followed by drying *in vacuo* afforded 4-[5-(thiophen-2-yl)thienyl]-1,2,3,5-dithiadiazolylium chloride (**3.52**) as a green

solid, which was used without further purification. Crude yield 8.05 g (26.4 mmol, >100% yield). IR $\nu_{\max}$ (cm⁻¹): 3384.68(w), 3081.76(w), 1654.86(w), 1550.12(w), 1512.71(s), 1457.43(s), 1397.22(s), 1362.81(m), 1210.62(w), 1130.68(s), 1080.10(w), 1056.93(w), 893.61(w), 868.09(w), 839.88(s), 798.73(s), 740.65(s), 704.37(s). Dry oxygen was bubbled through a slurry of **3.52** in dry acetonitrile (150 mL) for 30 min, after which SbPh₃ (11.80 g, 33.4 mmol) dissolved in dry MeCN (30 mL) was added dropwise to the reaction over 15 min. The solution was stirred for 2.5 h at 60 °C with oxygen bubbling, then hot-filtered to isolate a rust-orange solid. Recrystallization from toluene afforded target product as copper flakes. (612 mg, 12% yield). m.p. = 259-262 °C. ¹H NMR (δ , CDCl₃, r.t., 400 MHz) 7.85 (d, J=3.90 Hz, 2H), 7.28 (m, 4H), 7.22 (d, J=3.90 Hz, 2H), 7.07 (dd, J₁=5.10 Hz, J₂=3.70 Hz, 2H). IR $\nu_{\max}$ (cm⁻¹): 3097.17(m), 3069.47(m), 1456.13(s), 1417.31(m), 1371.03(s), 1250.00(m), 1223.15(m), 1197.09(m), 1156.87(w), 1077.34(m), 1035.31(m), 915.32(w), 880.58(w), 841.23(m), 826.62(m), 802.19(s), 745.70(w), 705.64(s), 686.08(s), 660.14(s). Anal. calcd for C₁₈H₁₀N₄S₆: C, 45.55; H, 2.12; N, 11.80. Found: C, 45.49; H, 2.05; N, 8.75. Given the low solubility of this compound, ¹³C NMR spectroscopy was not possible. The identity of this compound was confirmed through ¹H NMR spectroscopy, elemental analysis and X-ray crystallography.

Preparation of 3,7-bis[5-(5'-hexylthiophen-2-yl)thiophen-2-yl]-1,5,2,4,6,8-dithiatetrazocine (3.26): **3.45** (9.93 g, 36.0 mmol) and LiN(TMS)₂·Et₂O (8.79 g, 36.4 mmol) were stirred overnight in dry ether (120 mL) under nitrogen to yield a cloudy orange solution. A solution of sulphur monochloride (5.80 mL, 72.5 mmol) in dry diethyl ether (30 mL) was added at 0 °C over 30 min. After stirring at 0 °C for 3 h, the resulting green solid was filtered under inert atmosphere. Washing with dry diethyl ether and carbon disulfide followed by drying *in vacuo* afforded 4-[5-(5-hexylthiophen-2-yl)thienyl]-1,2,3,5-dithiadiazolylum chloride (**3.53**) as a green solid, which was used without further purification. Crude yield 12.57 g (32.3 mmol, 90% yield). IR $\nu_{\max}$ (cm⁻¹): 2953.41(w), 2920.62(m), 2852.06(m), 1551.93(w), 1525.74(m), 1466.72(s), 1441.59(s), 1390.23(s), 1353.22(m), 1259.62(m), 1216.62(m), 1132.14(s), 1047.10(m), 888.96(m), 854.84(m), 833.82(m), 801.84(s), 725.29(w), 701.10(s). Dry oxygen was bubbled through a slurry of **3.53** in dry acetonitrile (180 mL) for 30 min, after which SbPh₃ (12.74 g, 36.0 mmol) dissolved in dry MeCN (30 mL) was added dropwise to the reaction over 15 min. The solution was further stirred for 2 h at 60 °C with oxygen bubbling, then hot-filtered to isolate a dark orange solid. Recrystallization from chloroform afforded the target product as a red-orange

solid (2.92 g, 25% yield). m.p. = 182-184 °C. ^1H NMR (δ , CDCl_3 , r.t., 400 MHz): 7.80 (d, $J=3.90$ Hz, 2H), 7.11 (d, $J=3.90$ Hz, 2H), 7.09 (d, $J=3.60$ Hz, 2H), 6.72 (d, $J=3.60$ Hz, 2H), 2.81 (t, $J = 7.70$ Hz, 4H), 1.70 (m, 4H), 1.36 (m, 12H), 0.90 (t, $J = 6.90$ Hz, 3H). IR ν_{max} (cm^{-1}): 3071.75(w), 2917.59(m), 2847.49(m), 1478.10(m), 1465.62(m), 1445.13(m), 1430.37(m), 1368.00(s), 1235.22(m), 1196.93(m), 1101.82(m), 1050.39(m), 890.67(m), 864.42(m), 825.16(m), 792.26(s), 723.42(m), 660.17(s). Anal. calcd for $\text{C}_{30}\text{H}_{34}\text{N}_4\text{S}_6$: C, 56.04; H, 5.33; N, 8.71. Found: C, 55.55; H, 5.29; N, 8.45. Given the low solubility of this compound, ^{13}C NMR spectroscopy was not possible. The identity of this compound was confirmed through ^1H NMR spectroscopy, elemental analysis and X-ray crystallography

Preparation of 2-thiophenecarbonitrile (3.30). Sodium acetate trihydrate (36.4 g, 268 mmol) and hydroxylamine hydrochloride (18.6 g, 268 mmol) were added to a solution of 2-thiophenecarboxaldehyde **3.28** (20.0 g, 178 mmol) in 20% EtOH in H_2O (120 mL), which was then set to heat at reflux for 16 h. After cooling to room temperature, the yellow solution was further cooled to 0 °C. The resulting precipitate of **3.29** was filtered off and recrystallized from EtOH/ H_2O . Yield 18.3 g (142 mmol, 80 %). The product was a mixture of two isomers, and was identified by comparison to the ^1H NMR spectrum reported in the literature.⁵⁰ ^1H NMR (δ , CDCl_3 , r.t., 400 MHz) : First isomer; 7.72 (s, 1H), 7.56 (dt, $J = 1.1, 5.1$ Hz, 1H), 7.39 (dd, $J = 1.2, 3.8$ Hz, 1H), 7.09 (dd, $J = 3.7, 5.1$ Hz, 1H). Second isomer; 8.27 (s, 1H), 7.31 (dt, $J = 1.1, 5.1$ Hz, 1H), 7.19 (dd, $J = 1.2, 3.8$ Hz, 1H), 7.02 (dd, $J = 3.7, 5.1$ Hz, 1H). A mixture of **3.29** (18.3 g, 142 mmol) and acetic anhydride (56.0 mL, 592 mmol) in DCE (125 mL) were set to reflux for 16 h. After cooling to r.t., the reaction mixture was neutralized using a saturated aq. Na_2CO_3 solution (1.2 L) until pH = 10-11 was obtained. The biphasic mixture was separated and the aqueous phase was extracted with DCM. The organic phase was dried over K_2CO_3 and concentrated to give the target product, which was further dried over 4 Å molecular sieves. Yield 12.6 g (121 mmol, 85 %). The product was identified by comparison to the ^1H NMR spectrum reported in the literature.⁵⁰ ^1H NMR (δ , CDCl_3 , r.t., 400 MHz): 7.62 (dd, $J = 1.0, 3.8$ Hz, 1H), 7.59 (dd, $J = 1.2, 5.0$ Hz, 1H), 7.12 (dd, $J = 3.7, 5.0$ Hz, 1H).

Preparation of 5-hexylthiophene-2-carboxaldehyde (3.32). Thiophene **3.27** (4.20 g, 49.9 mmol) was dissolved in THF (30 mL) under a N_2 atmosphere. The reaction vessel was cooled to 0 °C and $^n\text{BuLi}$ (10 M, 5.90 mL, 59.0 mmol) was added dropwise. After 16 h 1-iodohexane (7.40

mL, 50.1 mmol) was added and the mixture was stirred for another 16 h. The solution was poured onto H₂O, the aqueous phase was washed with hexanes and the combined organic phases were washed with brine, dried over MgSO₄, and concentrated to afford 2-hexylthiophene **3.31** as an oil, crude yield 7.56 g (44.9 mmol, 90 %). This material was purified by distillation under reduced pressure (85 °C and 0.07 mmHg). Yield 5.20 g (30.9 mmol, 61 %). The product was identified by comparison to the ¹H NMR spectrum reported in the literature.⁵¹ ¹H NMR (δ, CDCl₃, r.t., 400 MHz): 7.09 (dd, J = 1.2, 5.1 Hz, 1H), 6.91 (m, 1H), 6.77 (m, 1H), 2.82 (t, J = 7.5 Hz, 2H), 1.67 (m, 2H), 1.32 (m, 6H), 0.89 (t, J = 6.5 Hz, 3H). Pure **3.31** (5.10 g, 30.3 mmol) was dissolved in dry THF (70 mL) under an inert atmosphere and cooled to 0 °C, at which time ⁿBuLi (10M, 4.40 mL, 44.0 mmol) was added. After 15 min, dry DMF (3.50 mL, 45.4 mmol) was added and the reaction mixture was stirred for 1 h. The reaction was quenched by the addition of an aqueous NH₄Cl solution (1M, 100 mL). The aqueous phase was extracted with hexanes and the combined organic phases were washed with H₂O, dried over MgSO₄, and concentrated to afford the target product. Yield 5.51 g (28.1 mmol, 92%). The product was identified by comparison to the ¹H NMR spectrum reported in the literature.⁵² ¹H NMR (δ, CDCl₃, r.t., 400 MHz): 9.78 (s, 1H), 7.58 (d, J = 3.8 Hz, 1H), 6.87 (d, J = 3.7 Hz, 1H), 2.85 (t, J = 7.5 Hz, 2H), 1.68 (m, 2H), 1.30 (m, 6H), 0.86 (t, J = 6.5 Hz, 3H).

Preparation of 5-hexylthiophene-2-carbonitrile (3.34). Sodium acetate trihydrate (6.86 g, 50.4 mmol) and hydroxylamine hydrochloride (3.50 g, 50.4 mmol) were added to a solution of **3.32** (8.24 g, 42.0 mmol) in 50:50 EtOH/H₂O (60 mL), which was refluxed for 16 h. After cooling to r.t., the product was extracted into DCM, washed with H₂O, dried over MgSO₄ and concentrated to obtain 5-hexylthiophene-2-carboxime **3.33** as an oil. This product was a mixture of two isomers. Yield 8.26 g (39.1 mmol, 93%). ¹H NMR (δ, CDCl₃, r.t., 400 MHz): First isomer; 7.59 (s, 1H), 7.20 (d, J = 3.7 Hz, 1H), 6.76 (d, J = 3.6 Hz, 1H), 2.82 (t, J = 7.5 Hz, 1H), 1.67 (m, 2H), 1.31 (m, 6H), 0.86 (t, J = 6.5 Hz, 3H). Second isomer; 8.18 (s, 1H), 6.98 (d, J = 3.7 Hz, 1H), 6.68 (d, J = 3.6 Hz, 1H), 2.82 (t, J = 7.5 Hz, 2H), 1.67 (m, 2H), 1.31 (m, 6H), 0.86 (t, J = 6.5 Hz, 3H). A mixture of **3.33** (5.00 g, 23.7 mmol) and acetic anhydride (9.94 mL, 105 mmol) in DCE (33 mL) were set to reflux for 16 h. After cooling to r.t., the reaction mixture was neutralized using a saturated aq. Na₂CO₃ solution (200 mL) until pH = 11-12 was obtained. The biphasic mixture was separated and the aqueous phase was washed with DCM. The organic phase was dried over K₂CO₃ and concentrated to give **3.34**. Yield 4.31 g (22.3 mmol, 94 %). The product was

identified by comparison to the ^1H NMR spectrum reported in the literature.⁵³ ^1H NMR (δ , CDCl_3 , r.t., 400 MHz): 7.43 (d, $J = 3.8$ Hz, 1H), 6.76 (d, $J = 3.6$ Hz, 1H), 2.81 (t, $J = 7.8$ Hz, 2H), 1.66 (m, 2H), 1.29 (m, 6H), 0.86 (t, $J = 6.9$ Hz, 3H).

Preparation of 2-cyano-4-hexylthiophene (3.38): 3.37 (17.7 g, 91.6 mmol), hydroxylamine hydrochloride (9.5 g, 136 mmol) and NMP (100 mL) were refluxed under nitrogen for 2 h then cooled to r.t.. The resulting dark brown mixture was poured into water, extracted with hexanes, washed with brine then dried over MgSO_4 . Removal of volatiles under reduced pressure afforded a brown oil. Vacuum distillation was performed in two-steps: first at 105 °C (0.6 mmHg) to eliminate volatile impurities, then at 165 °C (0.6 mmHg) to yield the target product as a yellow oil (15.1 g, 85% yield). The product was identified by comparison to the ^1H NMR spectrum reported in literature.⁵⁴ ^1H NMR (δ , CDCl_3 , r.t., 400 MHz): 7.43 (bs, 1H), 7.18 (bs, 1H), 2.60 (t, $J=7.65\text{Hz}$, 2H), 1.59 (m, 2H), 1.29 (m, 6H), 0.88 (t, $J=6.75\text{Hz}$, 3H).

Preparation of 5-cyano-2,2'-bithiophene (3.42): 3.41 (28 g, 144 mmol), hydroxylamine hydrochloride (15.34 g, 221 mmol) and NMP (140 mL) were refluxed under nitrogen for 2 h, then cooled to r.t. The resulting brown solution was poured into water, extracted with diethyl ether, washed with brine then dried over MgSO_4 . Two-fold dilution with hexanes, followed by elution through a short silica gel plug yielded the target product as a sand-coloured solid (13.12 g, 81% yield). The product was identified by comparison to the ^1H NMR spectrum reported in literature.⁵³ ^1H NMR (δ , CDCl_3 , r.t., 400 MHz): 7.52 (d, $J=3.93$ Hz, 1H), 7.35 (dd, $J_1=5.10$ Hz, $J_2=1.15$ Hz, 1H), 7.29 (dd, $J_1=3.70$ Hz, $J_2=1.15$ Hz, 1H), 7.13 (d, $J=3.90$ Hz, 1H), 7.07 (dd, $J_1=5.10$ Hz, $J_2=3.70$ Hz, 1H).

Preparation of 5-cyano-5'-hexyl-2,2'-bithiophene (3.45): 3.44 (18.40 g, 66.1 mmol), hydroxylamine hydrochloride (6.89 g, 99.2 mmol) and NMP (100 mL) were refluxed under nitrogen for 2 h, then cooled to r.t. The brown solution was poured into water, extracted with ethyl acetate, washed with water and brine then dried over MgSO_4 . Removal of the volatiles under reduced pressure afforded a brown oil. Purification by short-column chromatography (1:1 DCM/Hexanes) yielded the target product as a red oil which crystallized upon standing (6.06 g, 73% yield). The product was identified by comparison to the ^1H NMR spectrum reported in literature.⁵³ ^1H NMR (δ , CDCl_3 , r.t., 400 MHz): 7.47 (d, $J=3.95$ Hz, 1H), 7.08 (d, $J = 3.65$ Hz,

1H), 7.02 (d, $J = 3.95$ Hz, 1H), 6.71 (dt, $J_1 = 3.65$ Hz, $J_2 = 0.95$ Hz, 1H), 2.79 (t, $J = 7.70$ Hz, 2H), 1.66 (m, 2H), 1.32 (m, 6H), 0.88 (t, $J = 6.80$ Hz, 3H).

Preparation of Thiophene-2-*N,N,N'*-tris(trimethylsilyl)carboximidamide (3.46). Under an inert atmosphere, **3.30** (4.00 g, 36.7 mmol) was added to a slurry of $\text{LiN}(\text{TMS})_2 \cdot \text{Et}_2\text{O}$ (9.66 g, 40.0 mmol) in toluene (38 mL) and the reaction mixture turned black. After 20 h of stirring at room temperature, TMSCl (5.5 mL, 43.3 mmol) was added and the reaction mixture was refluxed for 1 h. The LiCl byproduct was filtered off as a white precipitate. Toluene was removed from the filtrate by distillation under N_2 . The crude product was distilled under reduced pressure (100 °C at 0.07 mmHg) to afford target product as a yellow oil. The product is a mixture of two isomers. Yield 5.00 g (14.6 mmol, 40 %). ^1H NMR (δ , CDCl_3 , r.t., 400 MHz): First isomer; 7.25 (dd, $J = 1.2, 5.0$ Hz, 1H), 7.12 (dd, $J = 1.2, 3.6$ Hz, 1H), 6.92 (dd, $J = 3.6, 5.0$ Hz, 1H), 0.11 (s, 21H), 0.05 (s, 6H). Second isomer; 7.23 (dd, $J = 1.2, 5.0$ Hz, 1H), 7.10 (dd, $J = 1.2, 3.6$ Hz, 1H), 6.94 (dd, $J = 3.6, 5.0$ Hz, 1H), 0.11 (s, 21H), 0.05 (s, 6H).

Preparation of 5-hexylthiophene-2-*N,N,N'*-tris(trimethylsilyl)carboximidamide (3.47). **3.34** (10.0 g, 51.7 mmol) was added to a slurry solution of $\text{LiN}(\text{TMS})_2 \cdot \text{Et}_2\text{O}$ (12.49 g, 51.7 mmol) in dry toluene (62 mL) under an inert atmosphere to give a brown solution. After 2 days of stirring at r.t., TMSCl (8.90 mL, 70.1 mmol) was added and the mixture was refluxed for 18 h. The LiCl byproduct was filtered off as a white precipitate. Toluene was removed from the filtrate by distillation under N_2 . The crude product was purified by fractional distillation under reduced pressure to afford target product as a mixture of two isomers. In addition, after careful distillation, the distillate contained starting reagent **3.34** (~ 14%). As this impurity did not interfere in subsequent reactions, this material was used without further purification. Yield 7.28 g (17.05 mmol, 33 %). ^1H NMR (δ , CDCl_3 , r.t., 400 MHz): First isomer; 6.91 (d, $J = 3.6$ Hz, 1H), 6.59 (d, $J = 3.7$ Hz, 1H), 2.74 (t, $J = 6.5$ Hz, 2H), 1.63 (m, 2H), 1.28 (m, 6H), 0.86 (m, 2H), 0.11 (s, 19H), 0.04 (s, 6H). Second isomer; 6.94 (d, $J = 3.6$ Hz, 1H), 6.61 (d, $J = 3.7$ Hz, 1H), 2.74 (t, $J = 6.5$ Hz, 2H), 1.63 (m, 2H), 1.28 (m, 6H), 0.86 (m, 2H), 0.11 (s, 19H), 0.04 (s, 6H).

Preparation of 4-thienyl-1,2,3,5-dithiadiazolylum chloride (3.49). Under an inert atmosphere, a solution of sulphur monochloride (1.2 mL, 15.0 mmol) in MeCN (10 mL) was added dropwise to a solution of **3.46** (3.00 g, 8.75 mmol) in MeCN (40 mL) at 0 °C. Once the ice bath had warmed to room temperature, the resulting orange precipitate was filtered, washed with MeCN

and dried in vacuo to afford the target compound, which was used without further purification. Crude yield 1.95 g (8.75 mmol, 100 %). IR ν_{max} (cm^{-1}): 3085 (w), 3070 (w), 1654 (w), 1560 (w), 1530 (w), 1508 (m), 1425 (s), 1392 (s), 1335 (m), 1244 (m), 1122 (m), 1066 (w), 1043 (w), 891 (s), 875 (s), 849 (s), 830 (s), 759 (s), 705 (s).

Preparation of 4-(5-hexylthiophene)-1,2,3,5-dithiadiazolylium chloride (3.50). A solution of sulphur monochloride (1.8 mL, 22.5 mmol) in MeCN (10 mL) under an inert atmosphere was added dropwise to a solution of **3.47** (4.30 g, 10.1 mmol) in MeCN (40 mL) at 0 °C. Once the ice bath had warmed to room temperature, the resulting orange-red solid was filtered, washed with MeCN and dried in vacuo to afford the target compound, which was used without further purification. Crude yield 1.98 g (6.45 mmol, 64 %). IR ν_{max} (cm^{-1}): 3048 (w), 2954 (w), 2927 (w), 2847 (w), 1655 (w), 1648 (w), 1637 (w), 1549 (m), 1501 (w), 1467 (s), 1426 (w), 1383 (s), 1323 (w), 1244 (w), 1227 (w), 1116 (s), 1100 (s), 1046 (m), 890 (s), 867 (s), 833 (s), 783 (w), 722 (w), 697 (s).

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Chapter 4

Applying Thieno[3,2-b]thiophene as a Building Block in the Design of Rigid Extended Thienoacenes.

Authorship disclosure: A version of this work was published in *RSC Advances* as “Applying thieno[3,2-b]thiophene as a building block in the design of rigid extended thienoacenes” **Magnan, F.**, Gabidullin, B.M., and Brusso, J.L. *RSC Advances*, (2016), 6, 97420-97429. The synthesis and characterization of all compounds reported in this chapter were performed by François Magnan. X-ray diffraction measurements on **4.50** were performed by Dr. Bulat Gabidullin. Device fabrication and characterization were performed by Dr. Nicole Rice and Owen Manville, from Professor Benoît Lessard’s group in the Faculty of Engineering at the University of Ottawa.

4.1 Introduction

Rational design of organic semiconductors (OSCs), both polymeric and molecular, continues to draw a great deal of attention due in part to their potential application as active components in optoelectronic devices (*e.g.*, solar cells, light emitting diodes, field effect transistors).¹⁻³ Inherent mechanical flexibility, tuneable optoelectronic properties, miniaturization and solution processability are just some of the key advantages that OSCs possess over their inorganic counterparts.⁴⁻⁷ Within the broad family of OSCs, molecular-based semiconductors, notably oligoacenes, are enticing alternatives to their polymeric analogues due to their well-defined structure, which allows for higher purity, enhanced reproducibility, and better control of the solid state packing.^{6,8,9} Possessing a well-defined structure also facilitates a greater understanding of the relationship between a molecule’s structure and its solid state properties, thus providing insight applicable to OSC design.^{10,11} Device efficiency and stability, however, continue to plague OSC-based optoelectronic devices compared to their silicon-based counterparts.

To that end, extended π -conjugated frameworks that exhibit tight $\pi\cdots\pi$ interactions in the solid state have been shown to possess enhanced charge mobility in molecular OSCs;¹² however, ambient stability is often lost upon lengthening acenes along one-dimension.¹³ Pentacene, for instance, which is a benchmark for thin-film molecular electronics, is air and light sensitive, thus requiring devices to be encapsulated in order to avoid degradation and obtain optimal performance.^{8,14} Further extension of the conjugation to longer acenes is doomed to exacerbate the problem, unless further precautions are taken. To enhance molecular OSCs, heteroatom incorporation has proven to be a successful design strategy. For example, the presence of electronegative nitrogen in the conjugated framework of OSCs can improve stability against air oxidation by lowering the energy of the HOMO.¹⁵ Likewise, the usage of electron-withdrawing groups has been shown to have a similar effect on HOMO levels; for instance, perfluorination of pentacene has been shown to transform the otherwise p-type semiconductor into an n-type one. Inclusion of sulphur atoms can lead to enhanced electronic communication between molecules due to its larger π -orbitals. Furthermore, intermolecular contacts, notably $S\cdots N$ and $N\cdots HC$ interactions, and more recently hydrogen bonding, have been shown to allow structural control in the solid state.^{12,16,17} Two dimensional (2D) structures also tend to exhibit increased stability compared to their linear analogues. For instance, picene, a “bent” isomer of pentacene, possesses both a lower HOMO energy level and a wider band gap than its isomer, making it respectively more oxygen- and photostable.¹⁸ In that regard, the development of π -conjugated two dimensional (2D) molecules can also be expected to be a viable strategy to bring about enhanced stability and intermolecular interactions through the increased dimensionality.^{19,20}

Hexabenzocoronene and triphenylene are two such examples of 2D aromatic frameworks that have been successfully applied in device fabrication.^{21–26} Combining this strategy with the incorporation of sulphur, one obtains 2D thienoacenes. One of the first forays into the field came about in the form of two independent reports of tetrathienoanthracene (TTAn, **4.1**), by the Pei²⁷ and Perepichka²⁸ groups, respectively (Fig. 4.1). By appending four thienyl arms to a benzene core through cross-coupling chemistry, followed by oxidative cyclodehydrogenation, the target products were obtained in moderate yields. In particular, Perepichka and coworkers reported both isomers **4.1–4.3** and **4.6–4.7**, functionalized with different side-arms (*i.e.*, hydrogen, bromide and hexyl chains). XRD data has shown that the frameworks are indeed planar and exhibit multiple intermolecular contacts, a desirable aspect for charge mobility. In both reports, similar

moderate charge mobilities were observed (*i.e.*, $0.02 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ vs $0.08 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for **4.3** and **4.7**, respectively).

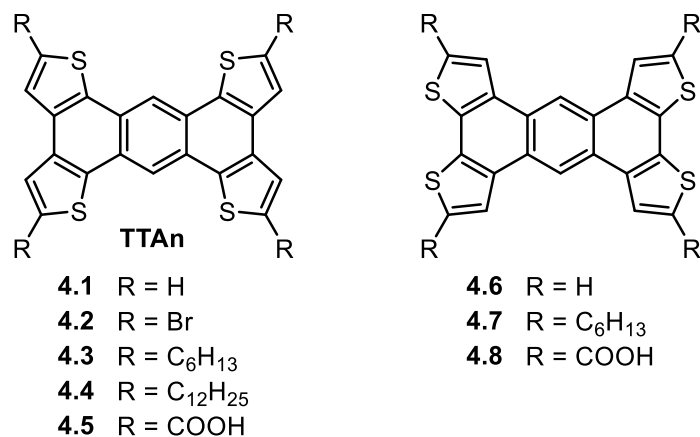


Figure 4.1 – Molecular structures of isomeric tetrathienoanthracenes.

The favorable attributes associated with the TTAn framework (*e.g.*, large 2D delocalized system, planarity, facile synthesis and modular structure) have made it, or derivatives thereof, a prime candidate for further studies. Further work^{29–36} by the Perepichka group has focused on studying the 2D self-assembly and reactivity of TTAn derivatives, particularly the proto (**4.1**), bromo (**4.2**) and carboxylic acid (**4.5**) derivatives, on surfaces by Scanning Tunneling Microscopy. The TTAn motif has also attracted some attention in the design of high-mobility photovoltaic materials, both in small-molecule³⁷ and polymer semiconductors.^{20,38} As in small-molecules, strong cofacial interactions between the planar structures reinforces $\pi\cdots\pi$ stacking in the polymers' thin films, and as a result a reduction in conformational strain of the polymer strand and a concomitant increase in charge transport efficiency is observed. These advantages have also made TTAn an attractive framework for application in perovskite solar cells as hole transport materials.^{39,40} Finally, the TTAn framework has been the focus of several theoretical studies dedicated to ascertaining and predicting the effects of heteroatoms, substituents and molecular structure on solid-state packing and their (opto)electronic and transport properties.^{41–44}

Since the initial communications of TTAn by Pei and Perepichka, more reports of 2D thienoacenes have come to light in the literature (Fig. 4.2). Polyaromatic hydrocarbons, popular frameworks for printed electronics due to their structural rigidity, large π -system and enhanced π -contacts, are prime candidates as starting cores for further 2D expansion. Examples of such

cores that have been reported include pyrene (**4.9/4.10**),^{45–49} coronene (**4.11**),^{50,51} hexabenzocoronene (**4.12**),⁵² chrysene (**4.13**),⁵³ triphenylene(**4.14**)⁵⁴ and corranulene (**4.15**).⁵⁵ Whereas most of these studies focused on the optoelectronic and structural properties of the target compounds, only a handful reported device fabrication. Among them, **4.13**, an extended bent analogue of **4.3**, showed a 10-fold increase in mobility (*i.e.*, $\sim 0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ vs $0.02 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively) for similarly built devices. Considering the similar crystal packing observed in both cases, the enhancement was likely due to the enlargement of the acene, which promoted intermolecular interactions and reduced reorganization energy. Furthermore, the enhancement in mobilities was on par with what is seen in the case of unfunctionalized linear acenes (See Section 1.5.1). On the other hand, shorter analogue tetrathienonaphthalene (**4.16**) has also been the focus of studies.^{56–58} Incorporation into a polymer backbone showed a marked dependence on the structure of the isomer, with mobilities on par with those seen for tetrathienoanthracenes (*i.e.*, 10^{-4} – $10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$). Substitution of the middle C=C bond of the naphthalene analogue with the isoelectronic BN unit (**4.17**)^{59,60} has been shown to tune the electronic properties of the π -system and to provide intermolecular dipole-dipole interactions, a valuable tool for crystal engineering.

Further incorporation of heteroatoms in the aromatic core has also drawn attention from several groups. Liu and coworkers devised extended dithienonaphthalenes isomers **4.18** and **4.19**, which exhibited marked differences in mobilities (*i.e.*, $0.07 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ vs $10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively), despite the similar structures and likely as a result of rotational freedom in **4.19** that disrupts solid-state packing.⁶¹ Starphenes that incorporate sulphur (*e.g.*, **4.20/4.21**) into their rigid cores combine the propensity of discotic molecules to form columnar stacks with the presence of intermolecular S $\cdots$ S contacts, which promotes good intermolecular interactions and strengthens the columnar aggregates. The presence of long alkyl chains in **4.21** leads to a liquid-crystalline mesophase with a wide temperature range, and a concomitant increase in mobilities in regards to the shorter **4.20** (*i.e.*, $0.02 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for vacuum-processed **4.20**⁶² vs $0.2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for spin-coated **4.21**).⁶³ Hu and coworkers prepared thiophene-based **4.22** and exploited its strong intermolecular interactions to grow crystalline microribbons that exhibited excellent hole mobilities, on the order of $1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.⁶⁴ The presence of nitrogen has also been the target of investigation for 2D thienoacenes with the use, for example, of metallophthalocyanine (**4.23**)⁶⁵ and phenazine (**4.24**)⁶⁶ cores, due to the beneficial impact of the electronegative heteroatom on energy levels. Finally, modification of the core with functional electroactive groups, such as

carbonyls (4.25)⁶⁷ or dicyanoquinomethane (4.26/4.27),^{68,69} has been achieved to further decrease the energy levels of the molecular orbitals and narrow the band gap of the compounds.

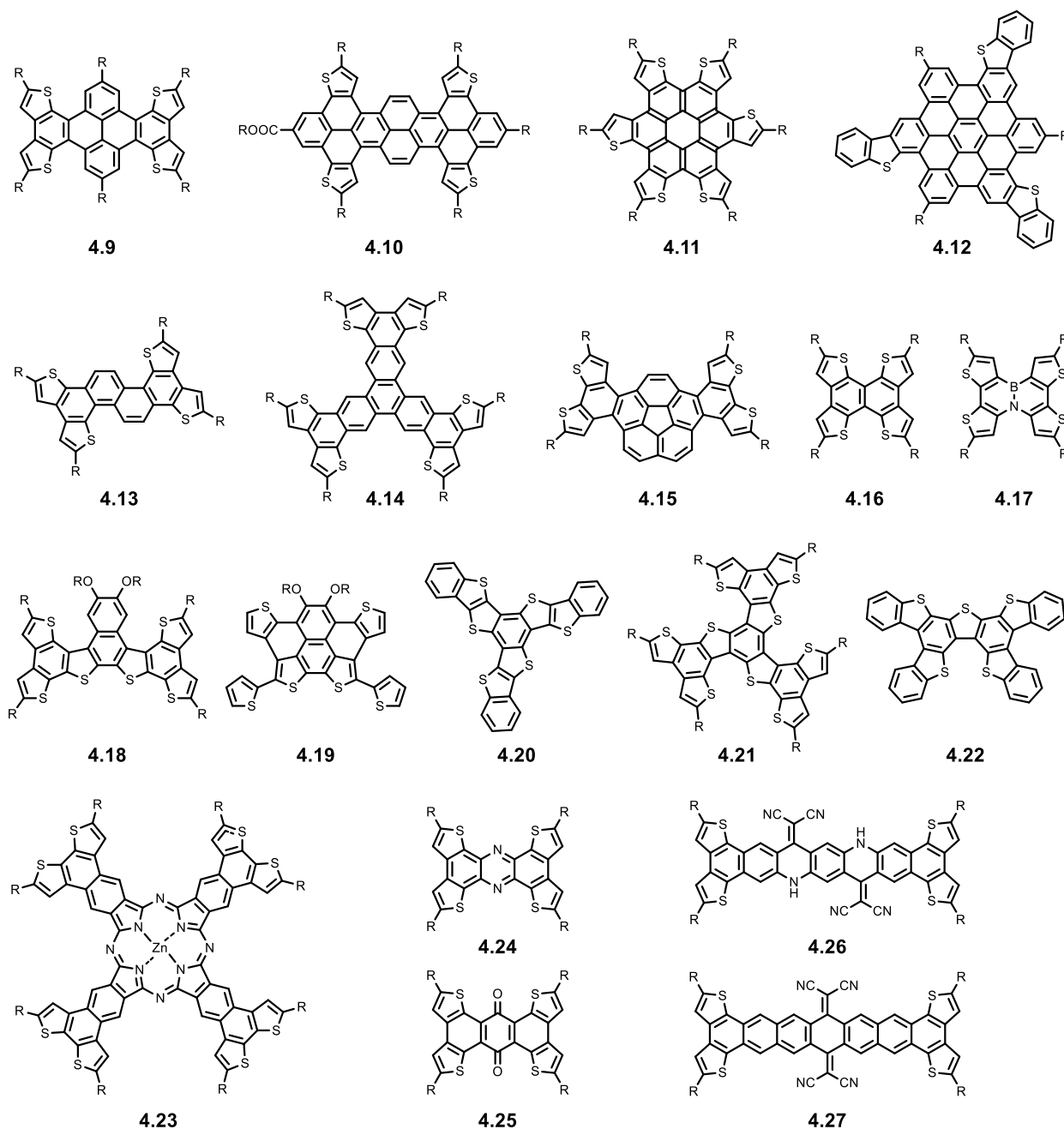


Figure 4.2 - Examples of core molecular structures of reported 2D thienoacenes derivatives.

In parallel to these reports, work in the Brusso group on 2D thienoacenes has focused on two key aspects (Fig. 4.3). The first and foremost is the elongation of conjugation in 2D to enhance $\pi\cdots\pi$ contact and maximize charge transport in the solid-state. Appending the TTAn framework with four oligothieryl chains through Stille coupling successfully resulted in extension of the conjugation (**4.28-4.30**), as assessed by optical, electrochemical and theoretical characterizations.⁷⁰ Single-crystal diffraction measurements showed that only minimal propeller-like distortion was observed in the crystalline phase, regardless of the freely rotatable moiety that one could expect to introduce distortion in the lattice. While transistors were successfully constructed from the molecules, the expanded molecules showed hole mobilities on the same order of magnitude as similarly-built devices of **4.3** (*i.e.*, 10^{-4} cm²V⁻¹s⁻¹ vs 10^{-4} - 10^{-2} cm²V⁻¹s⁻¹ for **4.28/4.29** and **4.3**, respectively)^{28,71} and was hypothesized as being a result of poor packing of molecules in the solution-processed devices, which would hinder intermolecular charge transport.

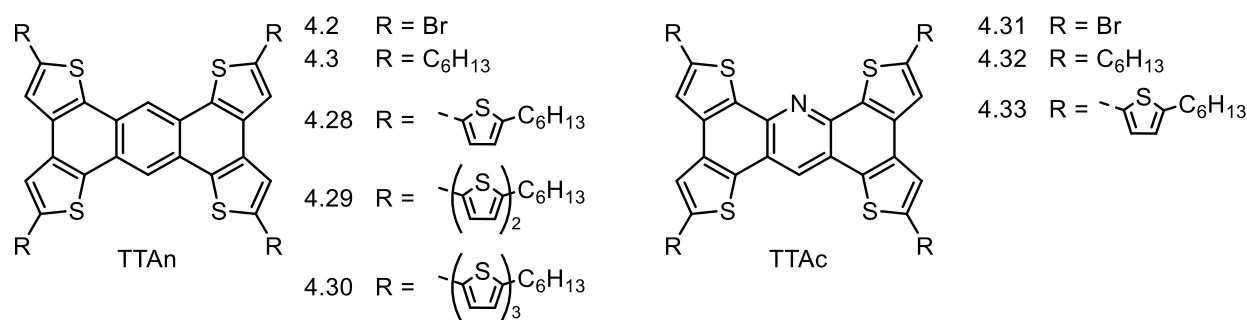


Figure 4.3 - Molecular structures of TTAn derivatives previously explored in the Brusso group.

Another strategy that has been the topic of investigation in the Brusso group is the incorporation of nitrogen in the core framework (*e.g.*, **4.31-4.33**).⁷² The presence of the more electronegative heteroatom leads to a lowering of the HOMO-LUMO levels, with a slight decrease in the overall energy gap of the molecule. Furthermore, the presence of nitrogen was shown to lead to a permanent dipole in the molecule, affording additional intermolecular interactions and even inducing thermochromic behavior in the solid-state.

Combining the aforementioned design strategies for molecular OSCs, and building on our previous studies, we set to investigate the effect of thieno[3,2-b]thiophene (TT) moieties, which are known to have a stabilized quinoidal structure that have been shown to promote lowered

bandgap in polymers.⁷³ Contrary to oligothiophenes, fused thiophenes are much more rigid, which can lead to increased intermolecular interactions in the solid state, better π -electron delocalization and enhanced light absorptivity and charge conductivity,^{74,75} while simultaneously offering a more electron rich core to further influence the frontier energy levels.⁷⁶ To that end, the TT moiety was incorporated either as the “arms” and/or the “core” of the star-shaped frameworks, thus influencing the overall optoelectronic and solid state properties of thienoacenes in which the conjugation can be extended in 2D.

Examples of symmetrically and asymmetrically substituted thieno[3,2-b]thiophene-materials (Fig. 4.4) have been reported, although those studies remain scarce. Some relevant cases include the uncyclized tetrathienyl dithienothiophene (**4.34**), which can act as a potential photochromic switch⁷⁷ through the photocyclization of the pendant thienyls. Uncyclized derivatives of thienothiophene, with pendant phenyl (**4.35**) and thienyls arms (**4.36**), have also been reported.⁷⁸ The cyclized equivalent of **4.34**, **4.37**, has been produced and showed self-assembly into nanoribbons in solution, with an up to twenty-fold increase in mobility with respect to **4.3** (*i.e.*, $0.42 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ vs $0.019 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively).⁷⁹ A cyclized thieno[3,2-b]thiophene core with benzothiophene arms (**4.38**), an extended analogue of **4.22**, has been shown to display excellent hole-mobility ($\sim 5.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) in the single-crystal state, owing to strong $\pi\cdots\pi$ stacking and $\text{S}\cdots\text{S}$ interactions.⁸⁰ Asymmetrically-substituted cyclized thienothiophenes with thienyl arms have been employed in the construction of both polymeric (**4.39**) and small-molecule (**4.40**) photovoltaic materials. In these last cases, little to no attention was given to the 2D thienoacene itself. In all cases, the thieno[3,2-b]thiophene motif was employed exclusively as a core and not as an arm.

In that regard, we herein report the synthesis and characterization of a number of TT-based star shaped OSCs. More specifically, derivatives in which the thieno[3,2-b]thiophene moiety is attached as the arm (*i.e.*, tetra(5-hexyl)thieno[3,2-b]thieno)anthracene, **4.49**, and its acridine analogue tetra(5-hexylthieno[3,2-b]thieno)acridine, **4.50**), the core (*i.e.*, tetra(5-hexylthieno)benzothieno[3,2-b]benzothiophene **4.51**), and as both the arm and core moieties (tetra(5-hexylthieno[3,2-b]thieno)benzothieno[3,2-b]benzothiophene, **4.52**) are described. Comparative electrochemical, optical, computational and single crystal X-ray diffraction (XRD) studies were performed on this family of star-shaped thieno[3,2-b]thiophene based OSCs to

probe the influence that the substitution pattern, rigidity and effective degree of conjugation have on the optoelectronic and solid state properties. This work represents a fundamental study of heteroatom substitution in 2-D conjugated small molecules and investigates how thieno[3,2-b]thiophene moieties in fused heterocyclic compounds can influence the physical properties.

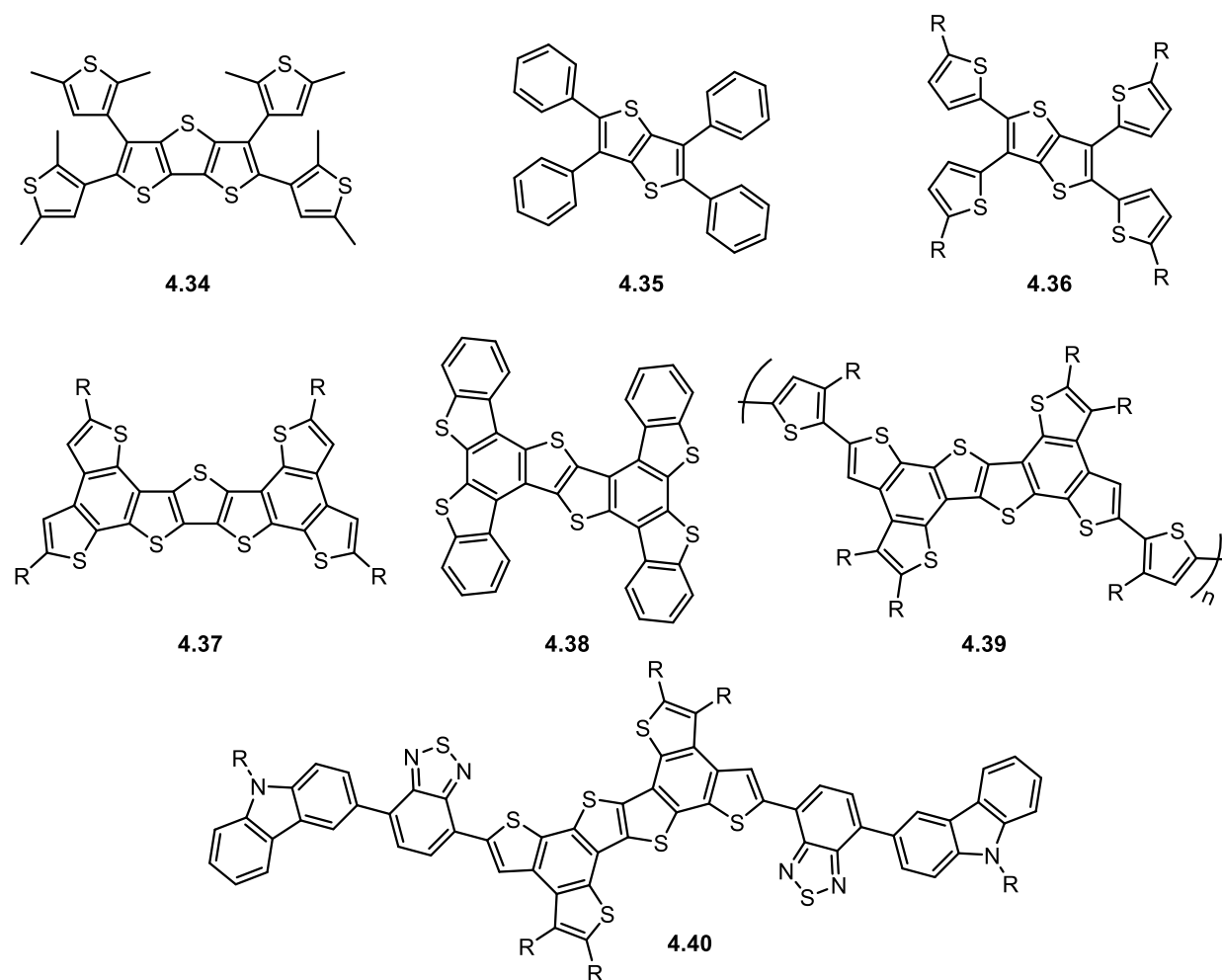


Figure 4.4 – Molecular structures of previously reported thieno[3,2-b]thiophene-based thienoacenes.

4.2

Results and Discussion

4.2.1 General Synthetic Plan

The strategy toward constructing the desired 2D thienoacenes is a relatively simple one. Four-fold cross coupling between metallated thiophene-based arm moieties (derived from **4.42** or **4.59**) and a tetrahalogenated core (**4.43-4.45**) yielded propeller-shaped molecules **4.36/4.46-4.48**.

Oxidative ring-closing between the 3 position of neighboring arms led to planarization and aromatization of the molecule and afforded the fully conjugated thienoacene frameworks **4.49-4.52**. The compounds of interest prepared throughout this chapter are shown in Figure 4.5.

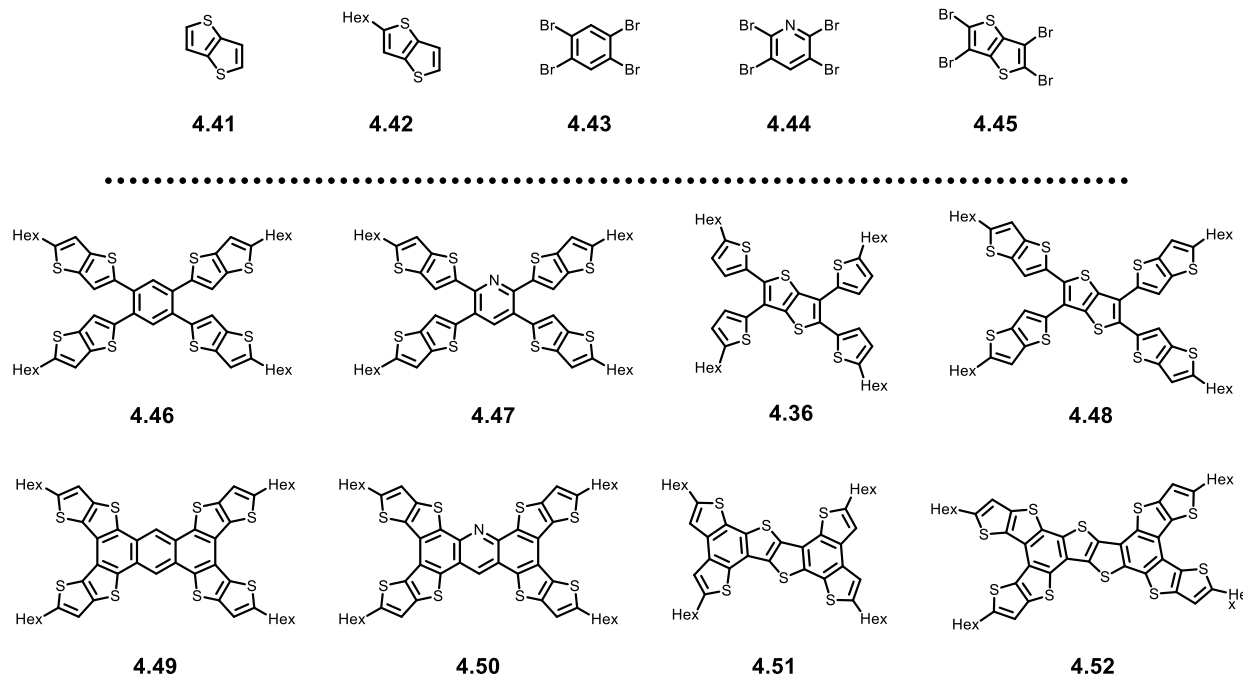


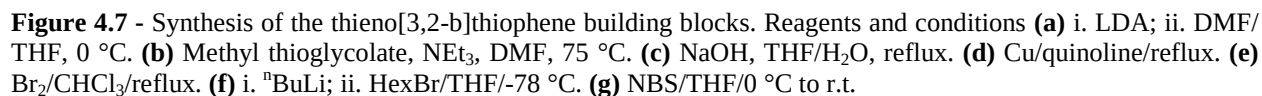
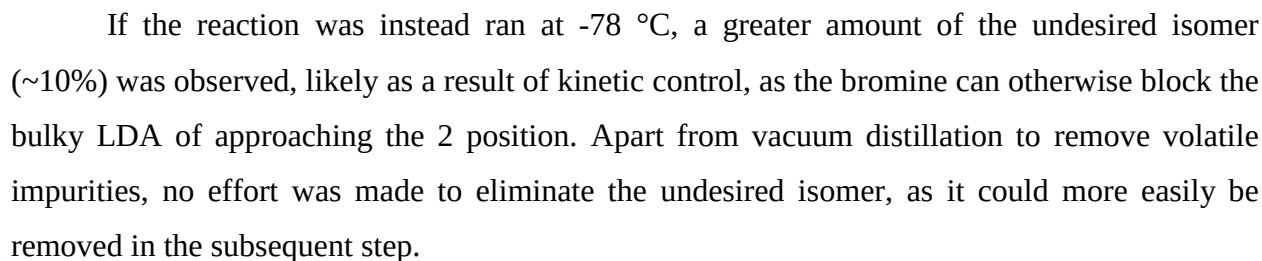
Figure 4.5 – (top) Building blocks employed in the present work for the construction of 2D thienoacenes. **(bottom)** Novel 2D thienoacenes reported here, along with their propeller-shaped precursor.

4.2.2 Obtaining the Tetrahalogenated Cores

Whereas 1,2,4,5-tetrabromobenzene **4.43** was commercially available, 2,3,5,6-tetrabromopyridine **4.44** was prepared in a one-pot procedure involving a sequential electrophilic aromatic substitution and diazotization (Fig. 4.6).⁷² Adding four equivalents of bromine to a suspension of 2,6-diaminopyridine **4.53** in 48% HBr at 0 °C led to the *in-situ* formation of 2,6-diamino-3,5-dibromopyridine. Addition of an aqueous sodium nitrite solution to the reaction resulted in the diazotization of the amino groups, who then underwent substitution with remaining bromine while eliminating N₂ to afford the target product after basic work-up and recrystallization from hexanes.

Preparation of the brominated thieno[3,2-b]thiophene building block (**4.45**, Fig. 4.7), although more laborious, was nonetheless straightforward and could be prepared following a route similar to that reported by Iddon and coworkers.⁸¹ Shortly, treatment of 3-bromothiophene

Figure 4.6 – Synthesis of the 2,3,5,6-tetrabromopyridine building block. Reagents and conditions: **(a)** Br₂/48% HBr/ 0 °C. **(b)** NaNO₂, Br₂/48% HBr/ 0 °C.



Following formylation, the reaction of **4.55** with methyl thioglycolate in DMF in the presence of a base afforded **4.56**. This reaction occurs over three consecutive steps (Fig. 4.8). First, the thiolate that results from deprotonation can substitute the bromine in an S_NAr fashion, which is stabilized by the neighboring electron-accepting aldehyde moiety (Step A). Next, deprotonation of the carbon alpha to the ester (Step B), followed by attack of the resulting anion on the near-by aldehyde (Step C) forms the second sulfur-containing five-membered ring, as the alkoxide produced by the opening of the aldehyde protonates itself to form an alcohol. Finally, an $E1_{CB}$ step leads to loss of the remaining hydrogen alpha to the ester (Step D), followed with the concerted elimination of the hydroxyl to aromatize the newly created ring and produce the second thiophene ring.

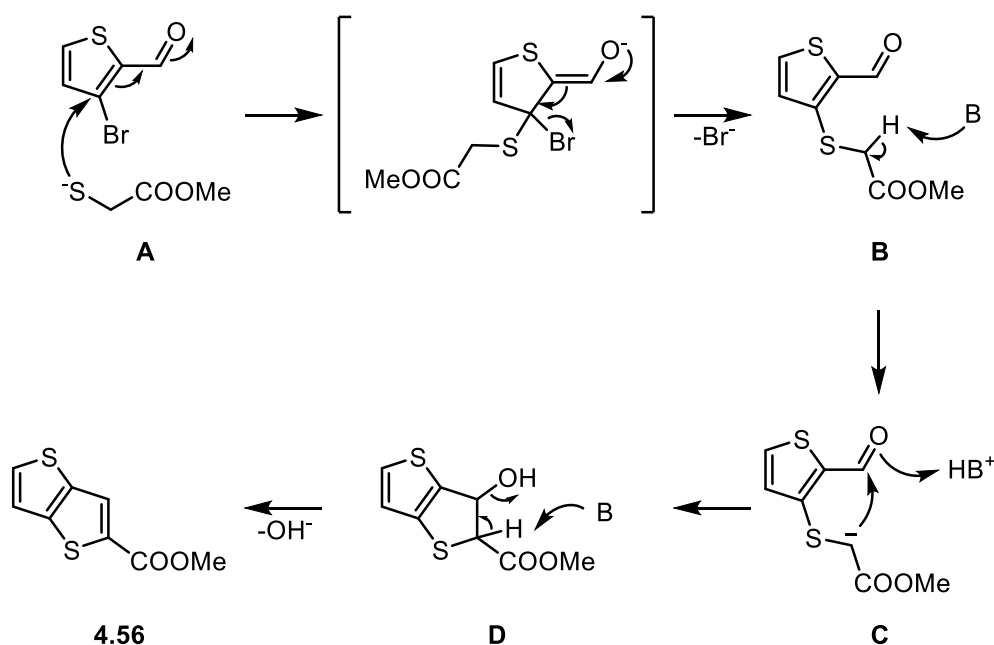


Figure 4.8 - Mechanism for the formation of the thieno[3,2-b]thiophene core from a 3-bromo-2-thienylcarbaldehyde framework.

Iddon's original procedure for this step called for the use of potassium carbonate as a base.⁸¹ While the reaction here did proceed as described, the presence of this insoluble solid made scaling the reaction up a challenge, as efficient stirring quickly became an issue. To overcome this, triethylamine was considered as a suitable substitute, as it is fully miscible with the reaction solvent, inexpensive and displays comparable basicity to potassium carbonate (pK_a of $HNEt_3^+ \sim 10.75$ vs pK_a of $HCO_3^- \sim 10.33$).⁸² To our delight, replacing the carbonate with

triethylamine yielded the product in similar yield and purity while greatly facilitating the synthesis of the ester on larger scales. Following mild heating (*i.e.*, 70°C) of a DMF solution of **4.55**, triethylamine and methyl thioglycolate overnight, the cooled reaction was poured in ice water to precipitate the product as a light yellow solid that was filtered off and copiously rinsed with water. With no further purification, the ester was hydrolyzed under basic conditions in a mixture of water and THF to produce the carboxylate, then extracted in basified water and washed with diethyl ether. Acidification of the resulting aqueous phase followed by extraction into diethyl ether, drying and removal of volatiles yielded the acid **4.57** as a white solid. Finally, decarboxylation was achieved by refluxing the acid over copper powder in quinoline. After aqueous work-up and removal of volatiles, the crude mixture was dissolved in hexanes and filtered through a silica plug to remove leftover quinoline, which afforded **4.41** upon removal of the solvent. Finally, **4.41** could be brominated by an excess of elemental bromine in refluxing chloroform over 48 hours. Upon cooling, a white solid precipitated, which was recrystallized from toluene to afford **4.45** as fine white needles.

4.2.3 Synthetic Work Toward the Thiophene-based Arms

Since the solubility of fused aromatics is typically low, the TT arm moieties were functionalized with an hexyl chain to impart solubility, and, by extension, processability to the target small molecules. While the synthesis of **4.59** is trivial and requires lithiation of thiophene **4.58** using *n*-butyllithium at -78 °C followed by addition of 1-bromohexane as an electrophile, attempts at preparing **4.42** in a similar way afforded a mixture of starting material, mono- and dialkylated products that could not be conveniently separated. Previous reports achieved the synthesis of **4.42** by Friedel-Craft acylation of **4.41** using hexanoic acid and AlCl₃ to yield the hexyl ketone, followed by a Wolff-Kishner reduction.⁸³ While the reaction afforded the target product, this method was found to be poor-yielding (*i.e.*, ~40%). Instead, **4.42** was synthesized in an analogous manner to **4.41** (Fig. 4.7). Firstly, **4.59** was brominated with NBS to afford **4.60**. Upon reaction with LDA, lithiation occurred at the 3 position; however, rapid lithium-halogen exchange led to isomerization of the intermediate, forming 3-bromo-5-hexyl-2-lithiothiophene. Quenching the intermediate *in-situ* with DMF yielded **4.61**, which was purified by vacuum distillation. Subsequent treatment with methyl thioglycolate in the presence of base produced **4.62** as an off-white solid after precipitation in water. While the pure ester could be obtained by

recrystallization from methanol, the crude material was of sufficient purity to be directly hydrolyzed to the carboxylate in basic conditions, similarly to the non-alkylated equivalent. Due to the solubilizing hexyl chain, complete dissolution of the carboxylate in basic aqueous solution couldn't be conveniently achieved. Instead, the reaction mixture was directly acidified, and the neutral acid was extracted into diethyl ether. Removal of volatiles yielded the crude acid **4.63** as an off-white solid, which was recrystallized from a 3:7 ethyl acetate/hexanes solvent mixture to yield the product as a white solid. Decarboxylation over copper in quinoline produced **4.42**, which could be obtained as a clear golden oil following vacuum distillation.

4.2.4 Preparing the Uncyclized Intermediates

Once the core moieties (Section 4.2.2) and the arm fragments (Section 4.2.3) were prepared, they were assembled together into the paddlewheel-shaped precursors using cross-coupling methodologies. Previous work in the Brusso group favoured Stille coupling between a halogenated (hetero)aryl core and an organotin (hetero)aryl arm.^{70–72} While Stille coupling is a robust reaction with an excellent success rate, the usage of the heavy tributyltin moiety requires the production and consumption of large amounts of organotins, which are nefarious for their health hazards. As a result, greener and safer alternatives were explored, namely Kumada and Negishi couplings, to achieve the desired end products. Optimization attempts were first done on **4.3**, as the starting materials are easily obtained and characterization for the product was already known.²⁸ Whereas the Kumada coupling failed to afford anything but a mixture of poly-substituted products, Negishi couplings were much more effective at successfully coupling all four arms substituents to the core. Lithiation of 2-hexylthiophene afforded 2-hexyl-5-lithiothiophene, to which solid ZnCl_2 was added at $-78\text{ }^\circ\text{C}$. Upon warming to room temperature, transmetallation occurred between the zinc salt and the lithiated thiophene to afford the organozinc. Addition of the organozinc solution to a mixture of **4.43**, PdCl_2 and PPh_3 in dry THF, followed by refluxing overnight, successfully generated **4.3**. While this strategy worked equally well for **4.42** and **4.59** with both the phenyl and pyridyl cores, it was less successful when the thieno[3,2-b]thiophene core was employed, usually leaving an inseparable mixture of poly-substituted thieno[3,2-b]thiophenes. While factors such as increased ratio of arm to core moieties, increased reaction time and increased catalyst loading were unsuccessful, simply switching the catalytic system from $\text{PdCl}_2/\text{PPh}_3$ to tris(dibenzylideneacetone) dipalladium/1,1'-

bis(diphenylphosphino)ferrocene ($\text{Pd}_2\text{dba}_3/\text{dppf}$) proved to be the key in completely coupling the core. In all cases, pouring the cooled reaction mixture in an excess of methanol and stirring for an hour afforded a yellow slurry, which could be filtered off and rinsed with methanol and ethyl acetate. Filtration through a short silica plug, followed by recrystallization of the crude dark yellow solid from either a mixture of ethyl acetate and chloroform or from isopropanol provided **4.36/4.46-4.48** as bright yellow solids.

4.2.5 Oxidative Cyclodehydrogenation

Typical ring closing and aromatization of the thienoacene framework can be achieved by treating the acyclic system with an appropriate dehydrogenative coupling reagent (*e.g.*, AlCl_3 , FeCl_3 , $\text{K}_3[\text{Fe}(\text{CN})_6]$, phenyliodine bis(trifluoroacetate), MoCl_5 and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)). In the course of this work, both FeCl_3 and DDQ have been successfully applied to synthesize 2D thienoacenes. Two possible mechanisms have been proposed for the oxidative cyclodehydrogenation,⁸⁴ and are presented in Figure 4.9.

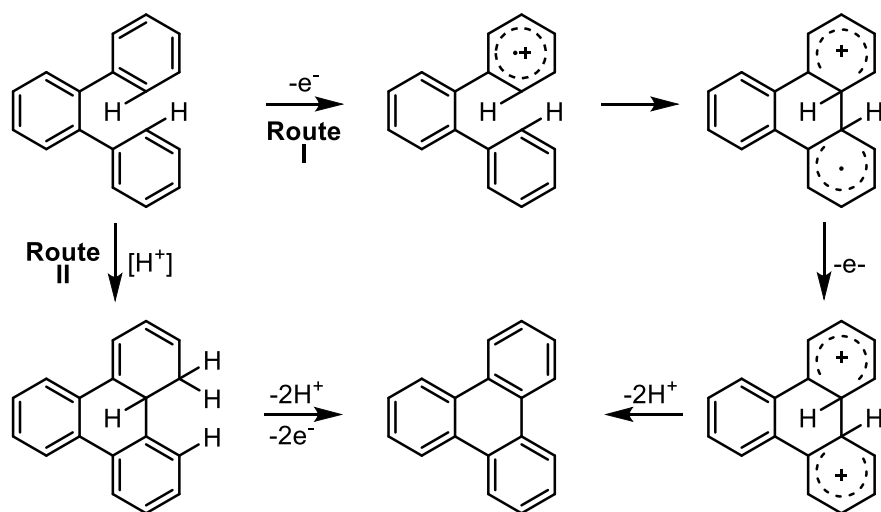


Figure 4.9 - Proposed reactional pathways for the dehydrogenative coupling of aryl systems, with triphenylene as a model system. Route I - Radical cation pathway. Route II - Arenium pathway. While a proton is shown in the arenium pathway, a Lewis acid can also successfully activate the ring system. Figure adapted from Ref. [84].

The radical cation pathway (**Route I**) proposes, successively, oxidation of the aromatic ring to form a radical cation, attack of the radical on the neighboring ring, a second oxidation step to the dication and finally the loss of acidic protons to produce the intended target. On the other hand, the arenium pathway (**Route II**) starts with the formation of a sigma complex

between the aromatic ring and the Lewis acid to form an arenium system. Electrophilic attack of the arenium ring on a neighboring aromatic system, followed by loss of H^+ to restore aromaticity yields the target product. Distinguishing between the two mechanisms is not an easy task, as the reagents commonly employed can act as both Lewis acids and oxidizing agents. In the case of the DDQ oxidation, experimental observations (*i.e.*, the lack of reactivity in acidic conditions with no oxidant) heavily hinted at a radical cation pathway. The mechanism at play in the case of $FeCl_3$ is harder to determine. While some computational studies have been published supporting the arenium pathway,^{85–87} many experimental results favor the radical cation pathway based on oxidation potential requirements for the substrate. Discrepancies from the computational studies could be explained, in part, by the fact that intermolecular interactions between the substrate and the reagent were not taken into account, which could account for a significant energy difference. For the systems at hand, a radical cation pathway was assumed, due to the lack of reactivity in strongly acidic conditions. At this step, it is very important that the 2 position on thiophene rings, which bears higher charge density, be functionalized to avoid undesired polymerization at this position and enforce instead the desired intramolecular cyclization. Here, hexyl chains were employed to that end, in addition to provide enhanced solubility. Bromine atoms have also been shown in the past to be effective protecting groups.^{28,70}

Oxidative cyclodehydrogenation in chlorobenzene using anhydrous ferric chloride as an oxidant yields the corresponding thienoacenes **4.49** and **4.50**, respectively. Recrystallization from chlorobenzene afforded **4.49** as a microcrystalline yellow solid. In the case of **4.50**, pure material could be realized following treatment with base to remove iron from the coordination pocket in the form of iron hydroxide. Subsequent recrystallization with hot chlorobenzene afforded the product, albeit in a paltry 30% yield. Fortunately, this relatively low yield could be improved by replacing the ferric chloride oxidant with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in acidic conditions. Using methodology pioneered by Rathore and coworkers,^{88–90} a two-fold increase in the yield of **4.50** was achieved, while also simplifying the workup for the reaction by removing the need for an aqueous work-up and a basic wash step. Oxidative cyclodehydrogenation with DDQ was also successful at improving the yield of **4.49** (*i.e.*, 60% rather than 30%). Oxidative cyclodehydrogenation of **4.51** and **4.52** was initially attempted using DDQ, as this provided better results in the preparation of **4.49** and **4.50**; however, in the case of the thieno[3,2-b]thiophene core derivatives, this methodology failed to lead to any reaction.

Nonetheless, oxidative cyclodehydrogenation using ferric chloride was successful at affording the target molecules **4.51** and **4.52**. Purification of **4.51** was achieved via washing a dichloromethane solution with ammonium hydroxide, filtering through silica and triturating with methanol. Due to its limited solubility in comparison to **4.51**, purification of **4.52** was accomplished via recrystallization from hot chlorobenzene.

4.2.6 Electrochemical, Optical and Theoretical Studies of the Thienoacenes

The redox behavior of **4.49-4.52** probed by cyclic voltammetry (CV) and differential pulse voltammetry (DPV), and referenced to the ferrocene/ferrocenium redox couple as an internal standard; the results of which are presented in Table 4.1 and Figures 4.10 and 4.11.

Table 4.1 – Photophysical^a, electrochemical^b and theoretical^c properties of **4.49-4.52**.

	4.49	4.50	4.51	4.52
λ_{max}^{abs} (nm)	377	372	390	421
ϵ^d (M ⁻¹ ·cm ⁻¹)	253200	178200	47200	85700
λ_{edge}^{abs} (nm)	481	511	435	433
E_{gap}^{opte} (eV)	2.58	2.43	2.85	2.86
λ_{max}^{em} (nm)	474	506	421	428
Stokes shift (cm ⁻¹)	270	480	1890	390
$E_{1/2}^{ox}$ (mV)	949	1066	1023	856 ⁱ
$E_{HOMO}^{exp f}$ (eV)	-5.12	-5.25	-5.17	-5.01 ⁱ
λ_{max}^{calcdg} (nm)	390	378	393	430
$f^{g,h}$	2.1559	1.7656	1.0053	1.3623
E_{HOMO}^{calc} (eV)	-5.20	-5.37	-5.26	-5.19
E_{gap}^{calc} (eV)	3.03	2.98	3.59	3.30

^aSolution measurements performed in HQ-GC grade PhCl. ^bMeasurements performed at 50 mV/s in dry PhCl with 0.1M nBu₄NPF₆ as supporting electrolyte. ^cDFT/B3LYP/6-311+G(2d,p) calculations. ^dMolar extinction coefficient for λ_{max}^{abs} . ^eCalculated from corresponding λ_{edge} . ^fCalculated from the onset of oxidation. ^gFrom TDDFT calculations performed on optimized geometries. ^hOscillator strength of the reported transition. ⁱMeasurements performed at 60 °C due to limited solubility.

In all cases, two anodic processes were observed, which correspond to the sequential oxidation of the neutral molecule to the radical cation, then to the dication. While these two processes may be unambiguously identified in the CV for **4.49**, **4.50** and **4.52**, due to the overlap between the first and second oxidation process for **4.51**, the second oxidation was more easily ascertained from the DPV scan (Fig. 4.11). From the onset of oxidation for each compound, the

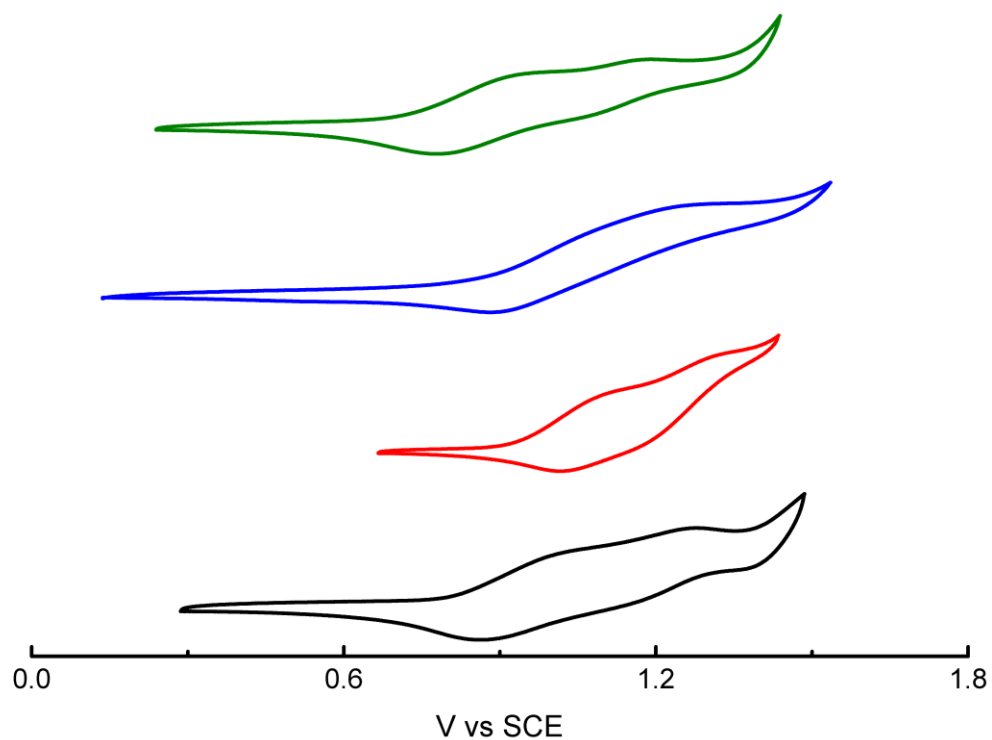


Figure 4.10 - Cyclic voltammogram of **4.49** (black), **4.50** (red), **4.51** (blue) and **4.52** (green) in PhCl at 50 mV s^{-1} with $0.1\text{M } ^n\text{Bu}_4\text{NPF}_6$ as supporting electrolyte.

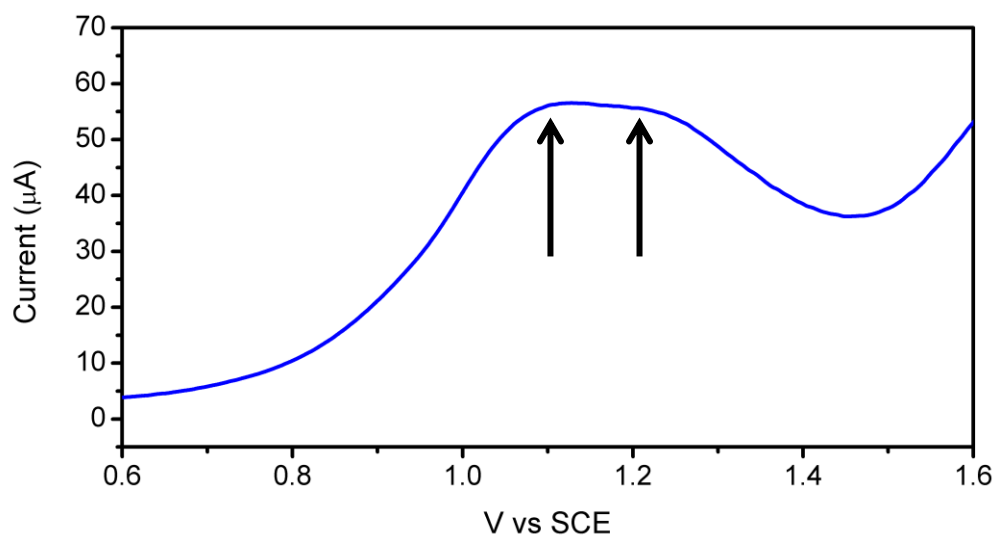


Figure 4.11 - Differential pulse voltammetry (DPV) scan of **4.51** (Arrows have been added to indicate the two oxidation events).

HOMO energy levels were estimated to be -5.12, -5.25, -5.17 and -5.01 eV for **4.49**, **4.50**, **4.51** and **4.52**, respectively. It should be noted that due to the limited solubility of **4.52** at room temperature, the electrochemical experiments were performed at 60 °C, which prevents any direct comparisons to **4.49**, **4.50** and **4.51**. The oxidation potential of **4.49** and **4.50** were cathodically shifted with respect to their previously reported congeners **4.3** and **4.32**, respectively, which can be attributed to the increased degree of conjugation afforded by the TT arm moiety. Furthermore, the oxidation potential of **4.50** is cathodically shifted compared to **4.49**, due to the more electronegative nitrogen atom in the acridine core. The electrochemical behavior demonstrated by this family of star-shaped molecules, that is, the shift in HOMO energy level with increasing degree of conjugation, correlates well with what is predicted by computational calculations. DFT calculations using the B3LYP functional and 6-311+G(2d,p) basis set were performed on **4.49**, **4.50**, **4.51** and **4.52** (where R = Me); optimized geometries, molecular orbitals and orbital energetics are provided in the Figures 4.12 and 4.13.

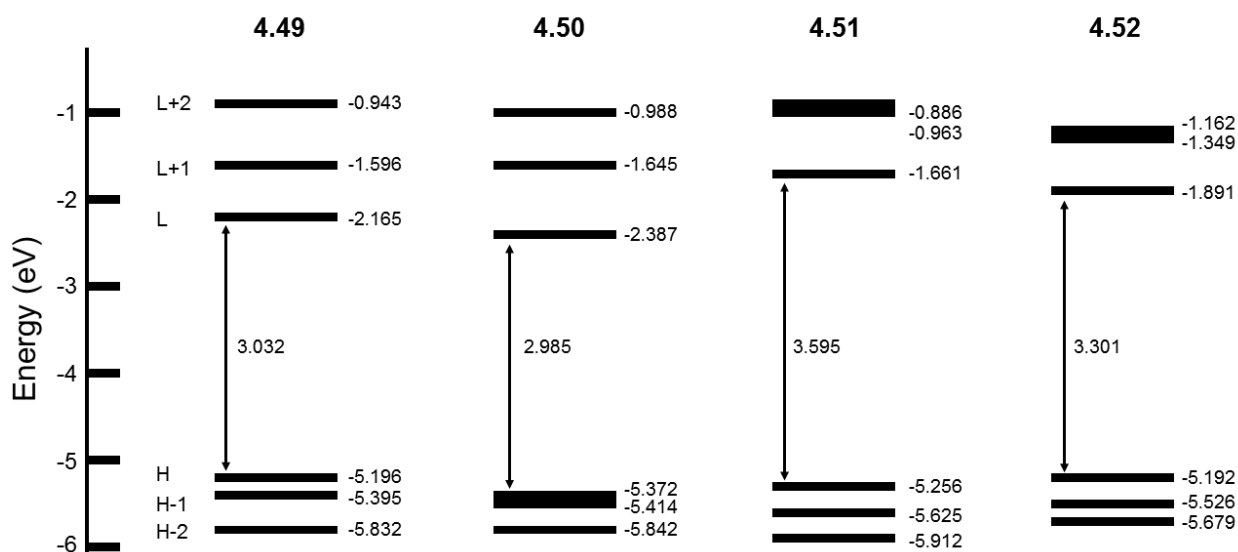


Figure 4.12 - Energy level diagram for the frontier molecular orbitals of **4.49**, **4.50**, **4.51** and **4.52**.

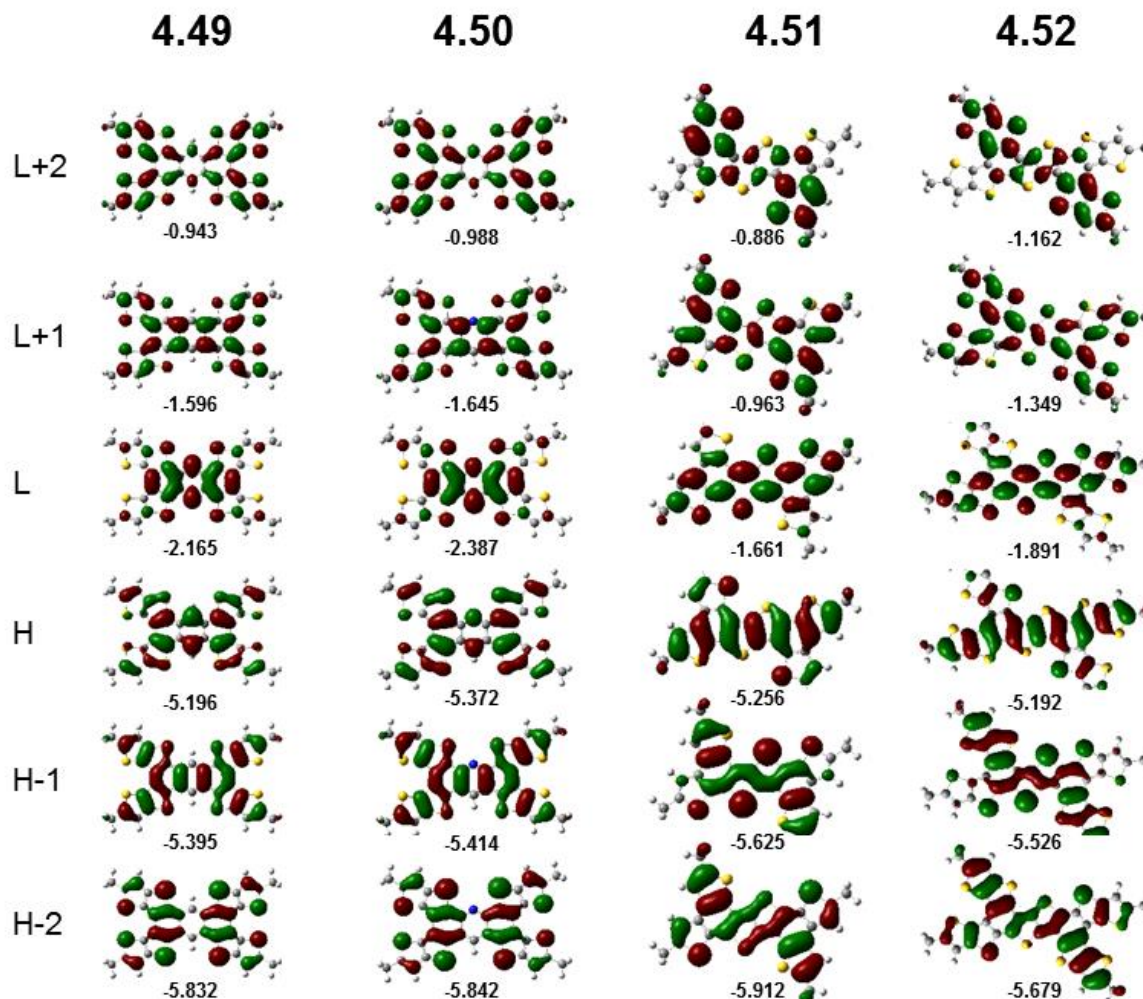


Figure 4.13 - Frontier molecular orbitals and their corresponding energies (eV) for **4.49**, **4.50**, **4.51** and **4.52**.

The internal reorganization energy associated with charge transport were calculated for both hole (λ_h) and electron transport (λ_e) in all thienoacenes by the adiabatic potential energy surface method,⁹¹ the values of which can be found in Table 4.2. Interestingly, **4.3/4.32/4.28/4.33** have smaller λ_e value, indicative of favorable electron transport, while **4.49** and **4.50** are expected to favour hole transport. In contrast, **4.51** displays the potential to exhibit ambipolar charge transfer based on these calculations (*i.e.*, 0.202 and 0.203 eV for hole and electron transport, respectively), and **4.52** shows only a slight preference for electron transport. These calculations also suggest that OSCs containing the TT core would exhibit inferior charge transport properties compared with the other analogues reported here – *i.e.* **4.51** and **4.52** possess greater overall reorganization energies than the other thienoacenes. However, these values

should be taken lightly since charge mobility depends on much more than just reorganization energy (*e.g.*, the charge transfer integral in the solid state, thin-film morphology, etc.). While the electron density of the HOMO and LUMO for **4.49** and **4.50** were calculated to be distributed fairly homogeneously across the entire molecule, in the case of **4.51** and **4.52** the electron density is preferentially located along the TT core and the 2,2' arms (alpha axis) rather than the 3,3' arms (beta axis). It is therefore likely that substituents located along this axis would have a greater impact on the overall optoelectronic properties of the resulting acene than those along the beta axis. This could be applied toward the design of asymmetric acenes, where judicious choice of substituents and their location could lead to careful tuning of the optoelectronic properties and charge-transport efficiency.

Table 4.2 – DFT-calculated internal reorganization energy for oxidation (hole transfer, λ_{hole}) and reduction (electron transfer, $\lambda_{\text{electron}}$) processes of 2D thienoacenes.

	λ_{hole} (eV)	$\lambda_{\text{electron}}$ (eV)
4.3	0.122	0.109
4.32	0.132	0.125
4.28	0.148	0.108
4.33	0.100	0.078
4.49	0.113	0.125
4.50	0.114	0.138
4.51	0.202	0.203
4.52	0.179	0.172

To probe the impact of increased rigidity and conjugation on the optoelectronic properties of thienoacene frameworks, photophysical studies were carried out on **4.49**, **4.50**, **4.51** and **4.52**, the results of which are presented in Tables 4.1 and 4.3. In the case of **4.49** and **4.50**, their optoelectronic properties were also compared to their previously reported counterparts (**4.3** and **4.28** for **4.49**, and **4.32** and **4.33** for **4.50**; see Figure 4.14). As anticipated, cyclization of **4.46** and **4.47** to afford **4.49** and **4.50**, respectively, resulted in a red-shift of the absorption edge consistent with the expected reduction in the HOMO-LUMO energy gap associated with

increased effective π -conjugation. As well, a more defined vibronic structure was observed, which can be attributed to the more rigid molecular framework as the rotational freedom of the pendant thieno[3,2-b]thiophene moieties is inhibited upon cyclization. Furthermore, an approximately four-fold increase in the extinction coefficient is seen upon ring-closing, as a result of the planar conjugated structures being stronger absorbers. The UV-Vis spectra for both **4.49** and **4.50** are comprised of two regions, one consisting of a weak, broad band that spans between 400 – 490 nm and 400 – 530 nm, respectively, and another containing a cluster of three more intense bands centred near 356 nm (Fig. 4.15). Comparison of the absorption spectra of **4.3**, **4.28** and **4.49** provides evidence for the increased conjugation brought upon via replacing thienyl substituents with thieno[3,2-b]thiophene moieties. More specifically, the relatively intense UV absorption bands in **4.49** are bathochromically shifted to 358 and 377 nm (cf. 321 nm and 337 nm for **4.3**), as is the broad absorption band between 400 – 470 nm (cf. 350 - 430 nm for **4.3**). Aside from the bathochromic shift, the overall spectroscopic signatures for the two analogues are in fact quite similar (Fig. 4.14).

Table 4.3 – Molar extinction coefficients of **4.49**, **4.50**, **4.51** and **4.52**.

4.49		4.50		4.51		4.52	
λ (nm)	ϵ (M ⁻¹ cm ⁻¹)	λ (nm)	ϵ (M ⁻¹ cm ⁻¹)	λ (nm)	ϵ (M ⁻¹ cm ⁻¹)	λ (nm)	ϵ (M ⁻¹ cm ⁻¹)
341	57712	354	94162	296	39349	325	71705
358	114394	372	178201	308	34555	340	50598
377	253227	464	19918	352	25100	375	37404
405	19292	496	34997	369	43649	396	76133
430	17909	--	--	390	47195	421	85755
440	18466	--	--	--	--	--	--
471	18899	--	--	--	--	--	--

Considering the thienoanthracene derivative **4.28**, which contains an additional thienyl pendant on each arm of the fused star-shaped core, a much less defined vibronic structure was obtained. Here, the retention of the sharp absorption peaks for **4.49** confirms the rigidity of the molecule vis-à-vis the thienoanthracene core, and bodes well for strong $\pi \cdots \pi$ interactions in the solid state. Interestingly, the onset of absorption for **4.49** is intermediate to those of **4.3** and **4.28**, an indication that the latter does exhibit larger effective π -conjugation, regardless of the rotational freedom of the pendant thienyl groups. Such observations are supported by DFT calculations.

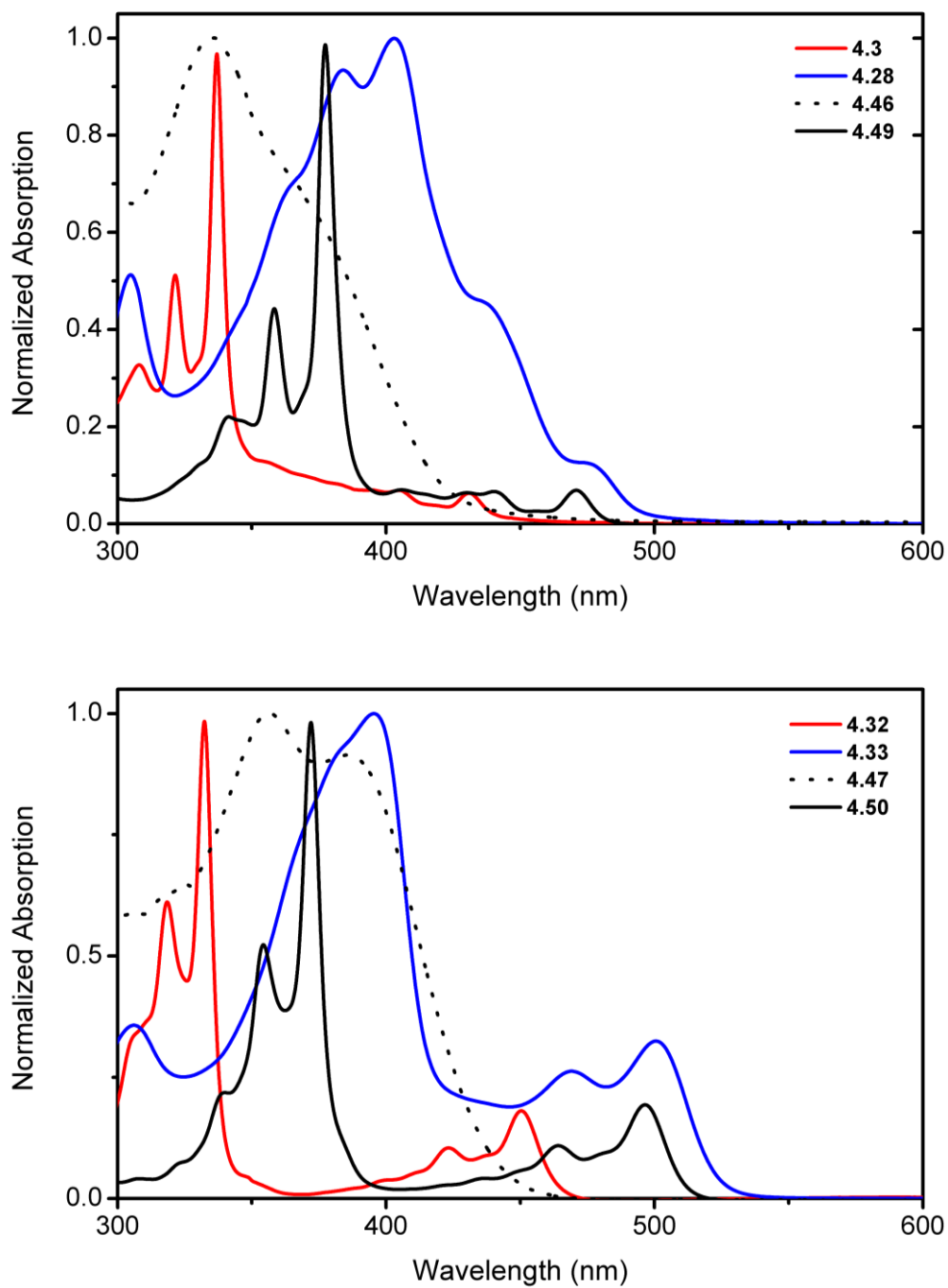


Figure 4.14 - (top) Normalized absorption spectra for 4.3, 4.28, 4.46 and 4.49 (top) and 4.32, 4.33, 4.47 and 4.50 (bottom) Data for 4.3/4.28/4.32/4.33 was taken from Robertson et al.;⁷² these spectra were recorded in DCM and are provided here for comparison purposes.

Incorporation of nitrogen into the thienoacene core (*i.e.*, **4.50**) has little impact on the overall spectroscopic signature (Fig. 4.15); however, the lower energy broad absorption band, corresponding to the HOMO-LUMO transition, is red-shifted to 494 nm (cf. 468 nm for **4.49**), as are the more intense UV absorptions. These bathochromic shifts in the absorption profile can be attributed to the more electronegative nitrogen atom in the thienoacene core, which is expected to lower the energy level of the LUMO resulting in a diminished energy gap. As well, the same trends that were observed between **4.3**, **4.28** and **4.49** are also exhibited by **4.32**, **4.33** and **4.50**.

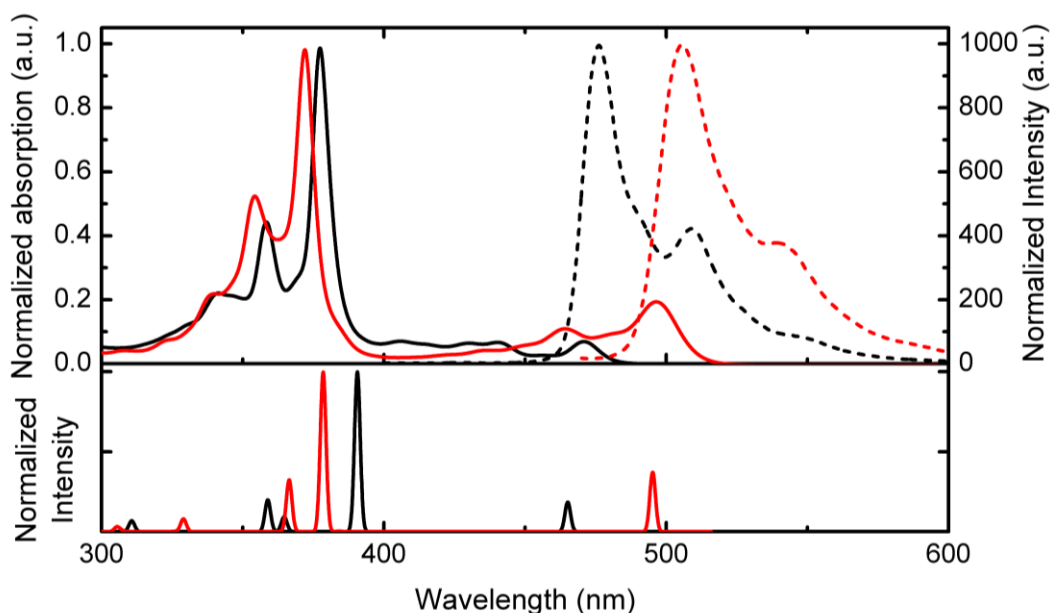


Figure 4.15 - (top) Experimental absorption (solid) and PL (dashed) spectra of **4.49** (black) and **4.50** (red) in PhCl solutions. **(bottom)** TDDFT calculated absorption spectra of **4.49** (black) and **4.50** (red).

In order to probe the optical transitions, TDDFT calculations were performed on optimized geometries of **4.49** and **4.50**; the results are presented in Figure 4.15 and the twenty vertical excitation energies calculated for each compound are listed in Appendix Tables A.5 (a summary can be found in Table 4.4). Overall, the predicted absorption profiles concord well with those measured experimentally. In both cases, the strong features found in the UV region correspond to a mix of the HOMO-1 to LUMO and HOMO to LUMO+1 transitions, with fairly strong oscillator strengths ($f \sim 1.7$ -2). While the HOMO to LUMO transition is of correct energy for the highest wavelength absorption, the corresponding oscillator strength is very weak ($f=0.0012$ and $f=0.0017$ for **4.49** and **4.50**, respectively). Based on TDDFT, in addition to the

HOMO to LUMO transition, this absorption also results from a mixture of the HOMO-1 to LUMO and HOMO to LUMO+1 transitions, albeit with a different ratio of contributions compared to the UV absorption.

Switching the core moiety to a fused thieno[3,2-b]thiophene leads to more drastic changes in the optical properties, with a spectroscopic signature unlike what was obtained for **4.49** and **4.50** (Fig. 4.16). While a sharp vibronic structure is still discerned, a good indication of molecular rigidity, in the case of **4.51** and **4.52** the absorption profiles are shifted hypsochromically by ~80 nm compared to **4.49** and **4.50**. This therefore suggests that **4.51** and **4.52** possess a larger HOMO-LUMO energy gap than **4.49** and **4.50**. As well, for **4.51** and **4.52** the longer wavelength absorption has a much larger molar absorptivity (cf. 47200 and 85700 M⁻¹ • cm⁻¹ for **4.51** and **4.52**, respectively, vs. 18900 and 35000 M⁻¹ • cm⁻¹ for **4.49** and **4.50**, respectively), with strong absorption bands at 295 and 380 nm for **4.51** and 330 and 410 nm for **4.52**. The bathochromic shift between the absorption profile of **4.51** with respect to **4.52** is consistent with the expected increase in effective π -conjugation. TDDFT calculations for **4.51** and **4.52** are also in good agreement with what is observed experimentally. Here, the HOMO to LUMO transition is responsible for the most intense transitions, centered at 393 ($f \sim 1.0053$) and 430 nm ($f \sim 1.3623$) for **4.51** and **4.52**, respectively. The energy levels of the frontier molecular orbitals, particularly the LUMOs, are increased with respect to **4.49** and **4.50**, which results in a widening of the energy gap, thus explaining the blue-shifted absorption profiles.

All the thienoacene derivatives described here fluoresce, emitting blue or green in solution and yellow to orange luminescence in the solid state; photoluminescence (PL) measurements were performed in chlorobenzene solutions, and the results are presented in Figures 4.15 and 4.16. In all cases, photoluminescence excitation scans for all derivatives are in good agreement with their respective absorption spectrum. Furthermore, the emission profiles are mirror images of the absorption spectra, which is consistent with the rigid structure of the molecules (See Section 2.1.2). Similar trends to what was observed for the absorption profiles of **4.3**, **4.28** and **4.49** are also displayed in their PL spectra. Namely, the luminescence profile for **4.3** and **4.49** are alike in appearance, but red-shifted by ~40 nm, from 436 to 475 nm; again an indication of the decreased energy gap. As well, the maximum emission wavelength for **4.49** is intermediate to those of **4.3** and **4.28**. Interestingly, the precursor to **4.49** (*i.e.*, **4.46**) also

exhibited fluorescence in both the solid state and solution, unlike the previously reported unfused analogues, which did not fluoresce in either form. Much like the absorption profile, the PL profile of **4.46** is broader than its fused counterpart, an indication of the rotational freedom of the pendant thieno[3,2-b]thiophene “arm” moieties. Analogous trends are noted for **4.50**; namely a bathochromic shift of the emission profile upon extension of the conjugation ($\lambda_{\text{max}} = 474$ nm for **4.32** vs. 506 nm for **4.50**) as well as fluorescence of the uncyclized precursor **4.47**.

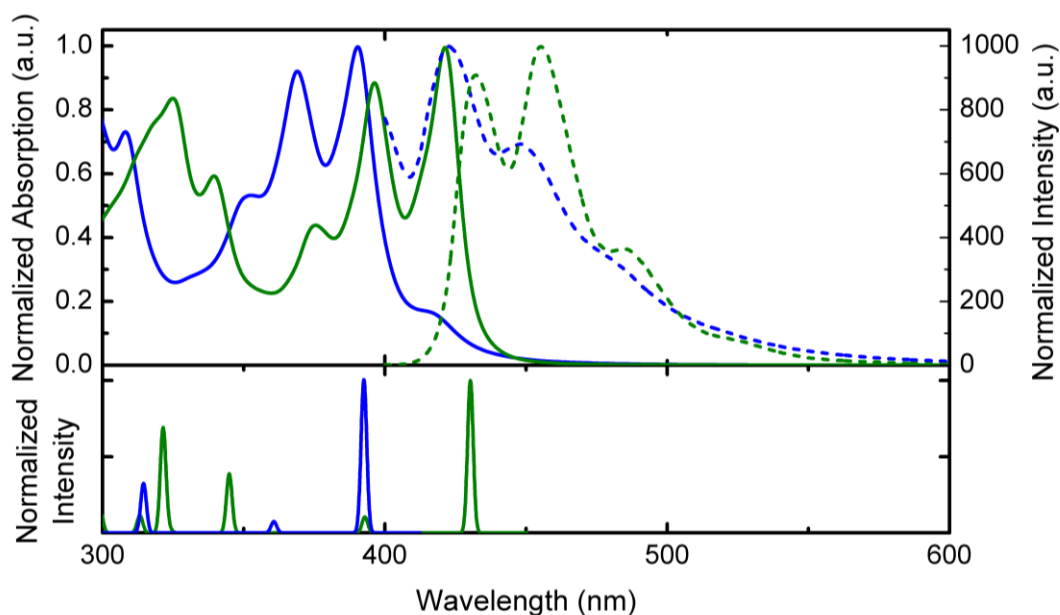


Figure 4.16 - (top) Experimental absorption (solid) and PL (dashed) spectra of **4.51** (blue) and **4.52** (green) in PhCl solutions. **(bottom)** TDDFT calculated absorption spectra of **4.51** (blue) and **4.52** (green).

PL studies of **4.51** and **4.52** are also in good agreement with both absorption measurements and computational studies. Their increased energy gap with respect to **4.49** and **4.50** is translated as a blueshift in the emission spectra, with the two maxima centered at 425 and 450 nm for **4.51** and **4.52**, respectively. As well, the emission profile of **4.52** is bathochromically shifted with respect to **4.51**, further supporting the lower energy gap of the frontier molecular orbitals expected upon extension of the conjugation.

In summary, replacing the benzene core with the electron-deficient pyridine or the electron-rich thieno[3,2-b]thiophene has the respective effect of diminishing and increasing the band gap of the resulting acene. On the other hand, increasing the conjugation, either with oligothiényls or fused thiophenes, leads in both cases to an expanded conjugated network, thus

Table 4.4 – Selected TDDFT transitions with highest oscillator strengths for **4.49**, **4.50**, **4.51** and **4.52**.

Compound	Calculated λ (nm)	Transition	Oscillator Strength (f)
4.49	390	HOMO-1 $\rightarrow$ LUMO+0	2.1559
		HOMO-0 $\rightarrow$ LUMO+1	
	359	HOMO-4 $\rightarrow$ LUMO+0	0.4282
		HOMO-1 $\rightarrow$ LUMO+1	
	465	HOMO-1 $\rightarrow$ LUMO+0	0.3982
		HOMO-0 $\rightarrow$ LUMO+1	
	365	HOMO-4 $\rightarrow$ LUMO+0	0.1994
		HOMO-1 $\rightarrow$ LUMO+1	
4.50	379	HOMO-1 $\rightarrow$ LUMO+0	1.7656
		HOMO-0 $\rightarrow$ LUMO+1	
	495	HOMO-1 $\rightarrow$ LUMO+0	0.6708
		HOMO-0 $\rightarrow$ LUMO+1	
	366	HOMO-4 $\rightarrow$ LUMO+0	0.5855
		HOMO-1 $\rightarrow$ LUMO+1	
	329	HOMO-6 $\rightarrow$ LUMO+0	0.1446
4.51	393	HOMO-0 $\rightarrow$ LUMO+0	1.0053
	292	HOMO-1 $\rightarrow$ LUMO+2	0.5398
	276	HOMO-2 $\rightarrow$ LUMO+1	0.3821
	315	HOMO-1 $\rightarrow$ LUMO+0	0.3250
		HOMO-0 $\rightarrow$ LUMO+2	
4.52	430	HOMO-0 $\rightarrow$ LUMO+0	1.3623
	321	HOMO-2 $\rightarrow$ LUMO+1	0.9390
		HOMO-1 $\rightarrow$ LUMO+2	
	345	HOMO-1 $\rightarrow$ LUMO+0	0.5281
		HOMO-0 $\rightarrow$ LUMO+2	
	299	HOMO-4 $\rightarrow$ LUMO+0	0.2407
		HOMO-3 $\rightarrow$ LUMO+1	

yielding a decreased bandgap. The presence of rotational freedom from the pendant thienyls can however disrupt solid-state packing, a problem that should be avoided by the use of fused thiophene.

4.2.7 Structural Analysis of the Acridine Compound

Crystals of sufficient quality for single crystal X-ray analysis were obtained for **4.50**, allowing for the elucidation of its crystal structure. Two views of the crystal structure, that of the unit cell and the slipped π -stacked motif, are provided in Figure 4.17 (for crystallographic data, see Appendix Table A.6). Crystals of **4.50** belong to the triclinic space group P-1 and consists of slipped π -stacks. While the molecules are essentially planar, as the core atoms show minimal displacement from the mean plane formed by the 38-atom core (≤ 0.1092 Å), the hexyl substituents deviate from planarity with respect to the aromatic core by $\sim 42^\circ$. Furthermore, as is apparent from Figure 4.17, the hexyl substituents in **4.50** form an interdigitated network between slipped π -stacks and, consequently, the degree of lateral communication is diminished. Nonetheless, close intra-stack C $\cdots$ S' (S3 $\cdots$ C14': 3.597(2) Å) and C $\cdots$ C' (C26-C27': 3.468(3) Å, C26 $\cdots$ C1': 3.475(3) Å) contacts exist. Since **4.50** contains an acridine core, and therefore a dipole moment resulting from replacement of CH with N along the middle of the molecular framework, it is expected that the molecules in the slipped π -stacks will pack in such a way that their dipoles alternate. However, since CH and N groups are isoelectronic, and the molecule sits on a center of inversion, these sites are virtually indistinguishable. Therefore, the model used involves disorder of the nitrogen atom over two positions about the acridine core with 0.5 occupancy in the unit cell.

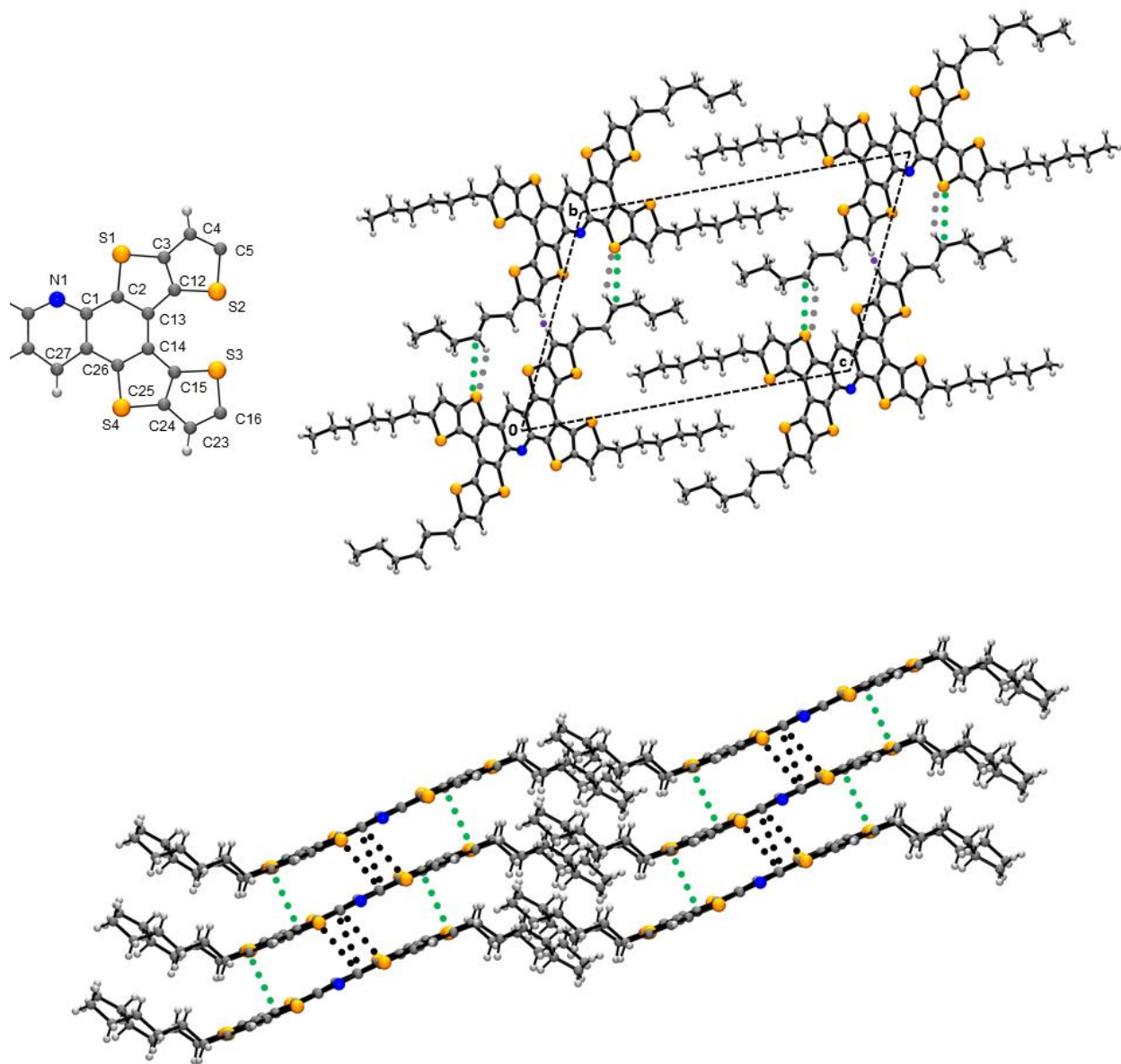


Figure 4.17 – Atom numbering (top left), unit cell (top right) and slipped π -stack (bottom) drawings of **4.50** with close intermolecular contacts highlighted with dotted lines. $C \cdots C'$ contacts are shown in black, $C \cdots S'$ in green, $S \cdots H'$ in gray and $H \cdots H'$ in purple.

4.2.8 Device fabrication and characterization

Bottom-gate bottom-contact (BGBC) OTFTs were constructed by spin coating a thin film of each thienoacenes on pre-fabricated chips purchased from Fraunhofer IPMS (further fabrication details can be found in the section 4.4.7). All devices were characterized first in vacuum then in air, using identical experimental parameters in both cases. Initial devices were prepared from chlorobenzene solutions, and exhibited *p*-type behavior in both vacuum and air conditions, which is consistent with what was previously observed for similar derivatives. Due to low solubility, poor quality films were formed, and as a result low mobilities ($\sim 10^{-6} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$) and inconsistent performances were observed. Switching to carbon disulfide (CS_2), which showed enhanced solvation of the thienoacenes, as the spin-casting solvent alleviated these issues and led to an order of magnitude increase in device mobilities ($\sim 10^{-5} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$). However, uneven film formation remained an issue, likely as a result of the high volatility of CS_2 .

In an effort to further improve device performance, molecules **4.49-4.52** were each blended with poly(styrene) (PS). Several reports demonstrate that blending OSC small molecules with insulating polymers can be an advantageous route to enhance the performance of OTFTs, combining the excellent semiconducting properties of small molecules with the ease of processing and film uniformity of polymers.^{92,93} The two-component films phase segregate during the deposition process, with the small molecules accumulating at either the air-thin film or thin film-dielectric interface. Microstructural control of this vertical phase separation has been demonstrated to be dependent on a wide range of processing conditions, including blend ratio, concentrations, solvent, polymer molecular weight and post-thermal treatment. For the device configurations at hand, it is essential that the small molecules segregate to the dielectric interface to allow charge transport. Yoon and coworkers demonstrated that the utilization of a high-molecular weight polymer allows for the small molecules to accumulate adjacent to the dielectric, whereas a combination of a smaller-molecular weight polymer and thermal annealing promoted segregation of the small molecules to the air-thin film interface.⁹⁴ Accordingly, a high-molecular weight PS ($M_n = 194 \text{ kDa}$) was used to assist in the formation of the semiconducting layer at the dielectric interface. Samples were prepared with each of the thienoacenes in a 1:1 wt/wt ratio of PS to small molecule, with CS_2 again employed as the solvent. Blending with PS resulted in further improvement in OTFT performance, with hole mobilities increased by an

additional order of magnitude ($\sim 10^{-4}$ - 10^{-3} $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$). Additionally, device variability decreased significantly, and the devices were found to be more robust when tested in air, likely due to the improved film forming characteristics of the polymer-small molecule blend. However, this strategy makes characterization of the OSC morphology a challenge, as many techniques probe the air-thin film interface. X-ray analysis of the thin films obtained in this work indicated they were amorphous, and no further solid-state characterization on the films were performed .

In general, devices prepared with **4.52**/PS blend demonstrated superior performance in air compared to vacuum, with a 20 – 125 % increase in mobility. The highest mobility of all the devices tested was obtained for a **4.52**/PS device in air, with a maximum mobility of 9.2×10^{-3} $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ (Table 4.5).

Table 4.5 – Comparison of best-obtained mobility data for devices built from **4.49-4.52** tested in vacuum and air.

	Vacuum				Air			
	μ_{average} ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) $\times 10^{-4}$	μ_{best} ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) $\times 10^{-4}$	$I_{\text{on/off}}$	V_T (V)	μ_{average} ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) $\times 10^{-4}$	μ_{best} ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) $\times 10^{-4}$	$I_{\text{on/off}}$	V_T (V)
4.49	7.7 ± 1.6	23	10^3	-8 ± 2	9.6 ± 3.6	46	10^3	-4.0 ± 5
4.50	3.0 ± 0.82	25	10^4	-23 ± 0.9	17 ± 5.2	62	10^4	-16 ± 2
4.51	1.9 ± 0.4	5.5	10^3	-23 ± 2	2.6 ± 0.33	5.3	10^3	-13 ± 1
4.52	12 ± 1.7	31	10^4	-32 ± 0.6	20 ± 3.8	92	10^4	-28 ± 1

While these values remain lower than previously reported TT-containing molecules, these molecules were incorporated into devices as single-crystals or using deposition/nanoribbon mask methodologies, all methods that produce higher quality active layers, at the expense of decreased scalability. A more apt comparison would be their shorter analogues, which were fashioned into devices through similar solvent-casting techniques. The highest mobility obtained for molecule **4.49** (2.3×10^{-3} $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) represents a 1740 % increase over previously-reported solution-processed anthracene molecules, whereas the highest mobility of 6.2×10^{-3} $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for molecule **4.50** represents a 2380 % increase in mobility (Table 5). **4.49** exhibited comparable to slightly-decreased mobilities upon switching from vacuum to ambient condition; conversely **4.50** showed an increase in charge mobility (400-700%) when characterized in air. We surmise the

enhanced performance for **4.50** is attributed to the presence of the nitrogen atom in the acridine core, which makes this molecule more stable in air compared to derivatives with an anthracene core.

Out of the four compounds investigated in this study, devices prepared using **4.51**/PS were consistently the least performing, for both vacuum and air experiments, with average mobilities typically two orders of magnitude lower compared to the other thienoacenes. Ranking the OTFT performance of the four thienoacenes in terms of mobility can be partially rationalized by the conjugation length of the four molecules considered. With the shortest conjugation path, **4.51** consistently underperformed compared to the others under all studied processing conditions, whereas **4.49** and **4.50** have similar conjugation lengths and show average mobilities that are on the same order of magnitude under vacuum. However, in air the increased stability of **4.50** compared to **4.49** enables devices containing the former to outperform those prepared with the latter. Finally, **4.52**, the longest conjugated system, exhibited the highest mobility observed in this work.

4.3 Conclusions

To summarize, a family of thienoacenes containing the thieno[3,2-b]thiophene building block incorporated either within the “core” of the molecule, attached as the “arm” moiety, or functionalized in both positions, have been prepared and isolated. Comparative studies of their electrochemical, optical, computational and solid state properties were carried out to probe the influence the thieno[3,2-b]thiophene moiety has on the optoelectronic and structural behavior of this family of heterocycles. These studies demonstrate that extension of the conjugation leads to narrowing of the energy gap of the frontier molecular orbitals, as evidenced by the bathochromic shifts in the absorption profiles and reduced oxidation potentials when compared with their previously reported analogues (*e.g.*, **4.49** vs. **4.3** and **4.50** vs. **4.32**). These results are further supported by DFT studies. At the same time, incorporation of thieno[3,2-b]thiophene into the molecular framework affords a more rigid material, as deduced from their defined vibronic absorption patterns and XRD measurements. Such features bode well for the use of this family of compounds in device applications. In that regard, further studies to investigate the thin film morphology of these TT-based compounds are currently being pursued.

4.4 Experimental Methods

4.4.1 General Procedures

n-Butyllithium (ⁿBuLi), triphenylphosphine (PPh₃), 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), iron trichloride (FeCl₃), methyl thioglycolate (Sigma); diisopropylamine, anhydrous zinc chloride (ZnCl₂), 1,2,4,5-tetrabromobenzene (VWR); trifluoroacetic acid (TFA), quinoline, triethylamine (NEt₃), palladium dichloride (PdCl₂), Tris(dibenzylideneacetone) dipalladium(0) (Pd₂dba₃) and 1,1'-Bis(diphenylphosphino)ferrocene (dppf) (Oakwood) were commercially obtained and used as received. 2-bromo-5-hexyl-thiophene (**4.60**),⁹⁵ 2,3,5,6-tetrabromopyridine (**4.44**)⁷² and tetrabromothieno[3,2-*b*]thiophene (**4.45**)⁹⁶ were prepared as previously reported. All solvents were ACS grade; dry solvents were obtained by passing them through activated alumina on a J.C. Meyer solvent purification system. Unless specified otherwise, NMR spectra were run in CDCl₃ solutions at room temperature on a Bruker Avance 400 MHz spectrometer and spectra were referenced to the residual solvent peak at 7.26 and 77.16 ppm for proton and carbon respectively. Owing to their limited solubility, spectra of **4.49**, **4.50** and **4.52** were recorded in carbon disulfide, with some CDCl₃ added to assist in the locking and shimming process. Measured integrations vary from expected values: purity of compounds were confirmed by elemental analysis. IR spectra were recorded on an Agilent Technologies Cary 630 FT-IR spectrometer. Elemental analyses were performed by G.G. Hatch Stable Isotope Laboratory, Ottawa, ON, K1N 6N5.

4.4.2 Optical Spectroscopy

UV-visible spectra were measured with a Varian Cary Series 6000 UV-Vis-NIR spectrophotometer and the fluorescence spectra were obtained using a Varian Cary Eclipse fluorescence spectrometer. UV-Visible and fluorescence spectra were measured in HQGC-grade chlorobenzene solutions with 1 cm precision quartz cuvettes.

4.4.3 Electrochemistry

Cyclic voltammetry was performed using a Bioanalytical Systems Inc. (BASi) Epsilon potentiostat with C3 cell stand, BASi Epsilon EC software (V 2.13.77 (c) 2013BASi) employing

a glass cell and platinum wires for working, counter and *pseudo*-reference electrodes. The measurements were carried out on chlorobenzene solutions (dried by distilling over P₂O₅ under inert atmosphere) containing 0.1 M tetrabutylammonium hexafluorophosphate (Aldrich) as supporting electrolyte with a scan rate of 50 mV/s. The experiments were referenced to the Fc/Fc⁺ redox couple of ferrocene at +0.48 V vs. SCE.

4.4.4 Crystal Growth

Orange plates of **4.50** suitable for X-Ray analysis were grown by slowly evaporating a saturated chloroform solution.

4.4.5 X-ray Measurements

The X-ray data was collected at 200(2) K on a Bruker Kappa Apex II CCD diffractometer with graphite-monochromatised Mo-K α radiation ($\lambda = 0.71073$ Å). Data collection and processing were performed with the Bruker APEX II software package.⁹⁷ Semi-empirical absorption corrections based on equivalent reflections were applied.⁹⁸ The structure was solved by direct methods and refined with full-matrix least-squares procedures using SHELXL⁹⁹41 and WinGX.¹⁰⁰ All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated based on the geometry of related non-hydrogen atoms. A disorder of the molecule's central pyridine ring was modelled over two positions with equal occupancies (0.5: 0.5). Two of four alkyl groups are disordered over two positions with 0.414(8):0.586(8) occupancies, starting from C28. The compound crystallizes in P-1 triclinic space group: the molecule lies on the center of symmetry with half of the molecule being symmetrically independent.

4.4.6 Computational Chemistry

All calculations were carried out using the Gaussian09 program package.¹⁰¹ The geometries of the studied compounds were investigated using the hybrid density functional B3LYP with the 6-311+G(d,p) basis set. Optimized structures were used to examine the orbital energies and HOMO-LUMO gaps. The archival files for the geometry optimized structures of **4.49-4.52** can be found in the Appendix Section A.3. The calculated UV-Vis spectra and excitation energies were determined using TDDFT which employed the optimized B3LYP

ground states. The solvent model and solvent was chlorobenzene, and twenty excited states were considered.

4.4.7 Device Preparation

Bottom-gate bottom-contact devices were constructed using pre-fabricated OTFT chips (Generation 5) purchased from Fraunhofer Institute for Photonic Microsystems (IPMS). The gate was n-doped Si, with a 230 nm SiO₂ dielectric; the drain and source electrodes were Au (30 nm), with a 10 nm ITO adhesion layer. Each chip contained 16 transistors, four each of the four different channel lengths: 2.5, 5, 10 and 20 μm . The width of all the devices was 2000 μm . Device data was averaged for a minimum of 8 devices, with the exception of **4.50** which experienced some device degradation in air. All device preparation was performed in air. Pre-fabricated chips were rinsed well with acetone (to remove the resist) and plasma treated (Harrick Plasma Cleaner PDC-32G) for 15 min. The chips were rinsed with water and isopropanol and dried with N₂ before being submerged in a 1% solution of octyltrichlorosilane (OTS) in toluene to form a monolayer on the surface. The chips were left sitting in the OTS/toluene mixture for 1 h at 70 °C, rinsed well with toluene and dried in a vacuum oven at 70 °C, again for 1h.

For the devices prepared using chlorobenzene or CS₂ (no poly(styrene)), 5 mg of each molecule was weighed out and dissolved in 1 mL of either chlorobenzene or CS₂. The solutions were heated to either 90 °C (for chlorobenzene) or 60 °C (for CS₂) before being filtered through a 0.2 μm PTFE membrane. Thin films were prepared by static spin coating (Laurell Spin Coater, Model WS-650MZ-23NPPB; 500 rpm for 1 min) 200 μL of solution at room temperature in air.

A 5 mg/mL stock solution of poly(styrene) (PS, $M_n = 194$ kDa) in CS₂ was prepared. 5 mg of each of the four thienoacenes was weighed out into separate vials, and 1 mL of the PS/CS₂ solution was added to each of the vials (final ratio of thienoacene:PS in solution was 1:1 wt/wt). The solutions were heated at 60 °C for 10 minutes, allowed to cool to room temperature and then filtered through PTFE membranes (pore size of 0.2 μm). Thin films were prepared by static spin coating (2500 rpm for one minute) 200 μL of each of the small molecule solutions at room temperature in air. The chips were dried in a vacuum oven for 1 h before testing in both vacuum and air.

Electrical measurements were performed on a custom electrical probe station with environmental chamber with controlled atmosphere, oesProbe A10000-P290 (Element Instrumentation Inc. & Kreus Design Inc.) using a Keithley 2614B to set V_{DS} and V_{GS} and to measure I_{DS} . Voltages were increased in a step-wise manner, rather than pulsed, with a delay of 100 ms between measurements. Each device was tested four times. Transfer curves were measured in the saturation regime and were modeled using the following equation:

$$I_{DS} = \frac{\mu C_i W}{2L} (V_{GS} - V_T)^2 \quad (4.1)$$

where L and W are the channel length and width, respectively. C_i is the capacitance density of the gate dielectric, calculated using $C_i = \frac{\epsilon_0 \epsilon_r}{t}$, where t is the thickness of the dielectric (230 nm) and ϵ_r is the relative dielectric constant of SiO_2 (3.9). μ is the field-effect mobility and is calculated from the slope of best fit through the most linear region of $\sqrt{I_{DS}}$ plotted against V_{GS} . The threshold voltage V_T is calculated as the x-intercept of the same line fitting.

4.4.8 Synthetic Procedures

Preparation of 4.36. $n\text{BuLi}$ (2.5M, 10.4 mL, 26.1 mmol) was added to a solution of **4.59** (4.00 g, 23.7 mmol) in dry THF (25 mL) under nitrogen at 0 °C. After stirring for 2 h at 0 °C, the brown solution was cooled to -78 °C in a dry ice bath, and anhydrous ZnCl_2 (4.84 g, 35.5 mmol) was added in one portion. After stirring at -78 °C 5 min, the solution was stirred for 1 h at r.t., then added to a solution of **4.45** (1.80 g, 3.96 mmol), Pd_2dba_3 (101 mg, 6 mol% Pd) and dppf (124 mg, 6 mol%) in dry THF (10 mL) under nitrogen. After refluxing overnight, the reaction was cooled, then quenched by adding MeOH. The resulting slurry was filtered and the precipitate washed with MeOH and EtOAc to yield a dark yellow solid. Recrystallization (iPrOH) afforded the target product as a vibrant yellow solid (2.00 g, 63% yield). ^1H NMR (δ , CDCl_3 , r.t., 400 MHz): 7.08 (d, $J=3.50$ Hz, 2H), 7.01 (d, $J=3.50$ Hz, 2H), 6.76 (d, $J=3.50$ Hz, 2H), 6.70 (d, $J=3.50$ Hz, 2H), 2.82 (m, 8H), 1.70 (m, 8H), 1.37 (m, 24H), 0.92 (m, 12H). ^{13}C NMR (δ , CDCl_3 , r.t., 400 MHz): 148.1, 147.0, 137.9, 133.0, 132.9, 132.7, 127.9, 127.2, 124.8, 124.4, 124.3, 31.7, 31.6, 30.3, 30.3, 28.9, 28.9, 22.7, 14.2. IR ν_{max} (cm^{-1}): 3061.30(w), 2955.56(m), 2924.08(s), 2853.48(m), 1466.00(m), 1212.65(m), 1028.52(m), 844.34(m), 802.78(s), 756.44(m)

Preparation of 2-hexylthieno[3,2-b]thiophene (4.42). A solution of **4.63** (30.73 g, 114 mmol) and copper powder (3.05 g, 48 mmol) in quinoline (100 mL) was refluxed for 2 h. After cooling, the solution was poured in acidified water and filtered. The filtrate was extracted with hexanes, washed with 10% HCl, saturated sodium bicarbonate and brine, and then dried over magnesium sulfate. Removal of volatiles under reduced pressure afforded a brown oil. Vacuum distillation (0.6 mmHg) was performed in two-steps: first at 130 °C to eliminate volatile impurities, then at 210 °C to yield the target product as a golden oil (20.47 g, 80% yield). The product was identified by comparison to the ¹H NMR spectrum reported in literature.⁸³ ¹H NMR (δ, CDCl₃, r.t., 400 MHz): 7.27 (d, J = 5.20 Hz, 1H), 7.19 (dd J1=5.20 Hz, J2 = 0.70 Hz, 1H), 6.96 (m, 1H), 2.89 (t, J=7.60 Hz, 2H), 1.73 (m, 2H), 1.37 (m, 6H), 0.90 (t, J=7.00 Hz, 3H)

Preparation of 4.46. ⁿBuLi (2.5M, 9.7 mL, 24.2 mmol) was added to a solution of **4.42** (4.58 g, 20.4 mmol) in dry THF (25 mL) under nitrogen at 0 °C. After stirring for 2 h at 0 °C, the brown solution was cooled to -78 °C and anhydrous ZnCl₂ (4.26 g, 31.2 mmol) was added in one portion. After stirring at -78 °C for 5 min, the solution stirred for 1 h at r.t., then added to a solution of **4.43** (1.36 g, 3.44 mmol), PdCl₂ (36 mg, 6 mol%) and PPh₃ (118 mg, 13 mol%) in dry THF (10 mL) under nitrogen. After refluxing overnight, the solution was cooled, and then quenched by pouring in MeOH. The resulting slurry was filtered and the precipitate washed with MeOH and EtOAc to yield a dark yellow solid. Recrystallization (3:2 EtOAc/CHCl₃) afforded the target product as a vibrant yellow solid (2.41 g, 73% yield). ¹H NMR (δ, CDCl₃, r.t., 400 MHz): 7.71 (s, 2H), 7.13 (s, 4H), 6.89 (s, 4H), 2.86 (t, J=7.60 Hz, 8H), 1.71 (m, 8H), 1.37 (m, 24H), 0.90 (t, J=7.00 Hz, 12H). ¹³C NMR (δ, CDCl₃, r.t., 400 MHz): 148.6, 141.4, 139.8, 137.3, 134.1, 133.6, 120.1, 116.5, 31.7, 31.7, 31.3, 28.9, 22.8, 14.3. IR ν_{max} (cm⁻¹): 3082.93(w), 2950.52(m), 2920.26(s), 2849.94(s), 1522.83(m), 1466.24(m), 1424.60(m), 1162.22(m), 903.52(m), 833.60(s), 818.06(s).

Preparation of 4.47. ⁿBuLi (2.5M, 7.2 mL, 17.9 mmol) was added to a solution of **4.42** (3.60 g, 16.0 mmol) in dry THF (15 mL) under nitrogen at 0 °C. After stirring for 2 h at 0 °C, the brown solution was cooled to -78 °C in a dry ice bath, and anhydrous ZnCl₂ (3.32 g, 24.4 mmol) was added in one portion. After stirring at -78 °C for 5 min, the solution was further stirred for 1 h at r.t., then added to a solution of **4.44** (1.08 g, 2.73 mmol), PdCl₂ (25 mg, 5 mol%) and PPh₃ (74 mg, 10 mol%) in dry THF (10 mL) under nitrogen. After refluxing overnight, the reaction was

cooled, then quenched by pouring in MeOH. The resulting slurry was filtered and the precipitate washed with MeOH and EtOAc to yield a dark yellow solid. Recrystallization (5:3 EtOAc/CHCl₃) afforded the target product as a vibrant yellow solid (2.00 g, 76% yield). ¹H NMR (δ, CDCl₃, r.t., 400 MHz): 7.66 (s, 1H), 7.25 (s, 2H), 7.19 (s, 2H), 6.99 (s, 2H), 6.92 (s, 2H), 2.89 (m, 8H), 1.72 (m, 8H), 1.37 (m, 24H), 0.90 (m, 12H). ¹³C NMR (δ, CDCl₃, r.t., 400 MHz): 150.4, 150.1, 149.0, 144.3, 143.7, 141.8, 139.8, 139.3, 137.9, 137.4, 124.1, 121.2, 120.3, 116.8, 116.6, 31.7, 31.7, 31.7, 31.6, 31.4, 29., 28.9, 22.7, 14.2, 14.2. IR $\nu_{\max}$ (cm⁻¹): 2951.03(w), 2920.41(m), 2849.31(m), 1514.44(m), 1414.98(s), 1159.98(m), 835.14(s), 817.06(s)

Preparation of 4.48. ⁿBuLi (2.5M, 7.7 mL, 19.2 mmol) was added to a solution of **4.42** (3.74 g, 16.7 mmol) in dry THF (10 mL) under nitrogen at 0 °C. After stirring for 2 h at 0 °C, the brown solution was cooled to -78 °C in a dry ice bath, and anhydrous ZnCl₂ (3.44 g, 25.2 mmol) was added in one portion. After stirring at -78 °C for 5 min, the solution stirred for 1 h at r.t., then added to a solution of **4.45** (1.32 g, 2.89 mmol), Pd₂dba₃ (90 mg, 7 mol% Pd) and dppf (106 mg, 7 mol%) in dry THF (10 mL) under nitrogen. After refluxing overnight, the reaction was cooled, then quenched by adding MeOH. The resulting slurry was filtered and the precipitate washed with MeOH and EtOAc to yield a dark yellow solid. Recrystallization (1:1 CHCl₃/EtOAc) afforded the target product as a vibrant yellow solid (1.84 g, 62% yield). ¹H NMR (δ, CDCl₃, r.t., 400 MHz): 7.38 (d, J=0.60 Hz, 2H), 7.30 (d, J=0.60 Hz, 2H), 6.94 (d, J=0.60 Hz, 2H), 6.88 (d, J=0.60 Hz, 2H), 2.88 (m, 8H), 1.72 (m, 8H), 1.35 (m, 24H), 0.90 (m, 12H). ¹³C NMR (δ, CDCl₃, r.t., 400 MHz): 149.6, 149.3, 140.2, 139.6, 138.6, 137.3, 135.0, 134.9, 133.8, 125.0, 120.5, 120.2, 116.5, 116.5, 31.7, 31.7, 31.6, 31.4, 29.0, 28.9, 22.7, 22.7, 14.2. IR $\nu_{\max}$ (cm⁻¹): 3084.42(w), 2951.75(m), 2921.00(s), 2850.24(s), 1453.66(m), 1421.32(m), 1169.27(m), 802.07(s), 724.37(m).

Preparation of 4.49. DDQ (853 mg, 3.76 mmol) was added in one portion to a degassed solution of **4.46** (1.20 g, 1.24 mmol) in dry DCM/TFA (55 mL, 10:1 ratio) at 0 °C. The reaction was stirred 2 h, then quenched by the addition of a saturated aqueous sodium bicarbonate solution, followed by filtration to yield a rust-coloured solid. Recrystallization (PhMe) afforded the target product as a bright orange powder (785 mg, 65% yield). ¹H NMR (δ, CS₂/CDCl₃, r.t., 400 MHz): 8.58 (s, 2H), 7.08 (s, 4H), 3.04 (m, 8H), 1.89 (m, 8H), 1.48 (m, 24H), 0.99 (m, 12H). IR $\nu_{\max}$ (cm⁻¹): 2951.60(m), 2925.68(s), 2850.42(s), 1527.38(w), 1406.91(m), 991.07(m),

844.24(s), 805.87(s), 724.02(m). Anal. calcd. for $C_{54}H_{58}S_8$: C, 67.31; H, 6.07; N, 0.00. Found C, 67.34; H, 6.14; N, 0.00. Given the low solubility of this compound ^{13}C NMR spectroscopy was not possible. The identity of this compound was confirmed by 1H NMR spectroscopy and elemental analysis.

Preparation of 4.50. DDQ (851 mg, 3.75 mmol) was added in one portion to a degassed solution of **4.47** (1.20 g, 1.24 mmol) in dry DCM/TFA (55 mL, 10:1 ratio) at 0 °C. The reaction was stirred for 90 min, then quenched by the addition of MeOH and triethylamine. Removal of volatiles under partial vacuum yields a yellow slurry. Recrystallization ($CHCl_3$) afforded the target product as a microcrystalline orange powder (640 mg, 53% yield). 1H NMR (δ , $CS_2/CDCl_3$, r.t., 400 MHz): 8.76 (s, 1H), 7.11 (s, 2H), 7.04 (s, 2H), 3.03 (m, 8H), 1.89 (m, 8H), 1.48 (m, 24H), 0.99 (m, 12H). IR ν_{max} (cm^{-1}): 3092.17(w), 2953.72(m), 2921.14(s), 2850.29(s), 1560.35(m), 1508.61(s), 1430.51(m), 1394.69(s), 996.34(m), 981.23(m), 875.40(m), 807.39(s), 783.88(m). Anal. calcd. for $C_{53}H_{57}NS_8$: C, 66.00; H, 5.96; N, 1.45. Found C, 66.42; H, 5.59; N, 1.47. Given the low solubility of this compound ^{13}C NMR spectroscopy was not possible. The identity of this compound was confirmed by 1H NMR spectroscopy, elemental analysis and X-ray crystallography.

Preparation of 4.51. A degassed solution of $FeCl_3$ (2.46 g, 15.2 mmol) in $MeNO_2$ (10 mL) was added dropwise to a solution of **4.36** (1.43 g, 1.77 mmol) in dry degassed DCM (100 mL) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C, then another 60 min at r.t. The reaction was quenched by the addition of 25 mL of MeOH and stirred 15 min, following which volatiles were removed under reduced pressure. The residue was slurried in MeOH and filtered to yield a light green solid. The solid was dissolved in DCM, washed twice with ammonium hydroxide, sodium bicarbonate and brine, and volatiles were removed under reduced pressure. The residue was eluted through a short silica plug using 1:3 DCM/hexanes to yield a clear yellow solution. Addition of MeOH precipitated the pure product as a yellow powder (417 mg, 30% yield). 1H NMR (δ , $CDCl_3$, r.t., 400 MHz): 7.28 (s, 2H), 7.23 (s, 2H), 2.99 (t, $J=7.5$ Hz, 4H), 2.92 (t, $J=7.5$ Hz, 4H), 1.82 (m, 8H), 1.40 (m, 24H), 0.93 (m, 12H). ^{13}C NMR (δ , $CDCl_3$, r.t., 400 MHz): 146.1, 145.4, 132.6, 132.6, 132.4, 130.4, 130.3, 129.0, 123.8, 119.5, 119.1, 31.8, 31.8, 31.6, 31.4, 31.0, 30.9, 29.1, 29.1, 22.8, 22.8, 14.3, 14.3. Note: The positions of the aromatic protons in the NMR spectrum are highly concentration dependent. IR ν_{max} (cm^{-1}): 3065.44(w), 2952.86(m),

2922.77(s), 2852.00(s), 1458.69(m), 1364.75(m), 1294.96(m), 1089.79(m), 873.70(m), 816.67(s), 800.55(m), 725.51(m). Anal. calcd. for $C_{46}H_{56}S_6$: C, 68.95; H, 7.04; N, 0.00. Found C, 69.18; H, 7.08; N, 0.00.

Preparation of 4.52. A degassed solution of $FeCl_3$ (1.56 g, 9.59 mmol) in $MeNO_2$ (8 mL) was added dropwise to a solution of **4.48** (1.07g, 1.04 mmol) in degassed PhCl (80 mL) at 0 °C. The reaction was stirred for 60 min, then diluted with MeOH. The resulting precipitate was filtered, rinsed with MeOH and dried in air to yield a greenish-yellow solid. Recrystallization (PhCl) afforded the target product as a yellow powder (567 mg, 53% yield). 1H NMR (δ , $CS_2/CDCl_3$, r.t., 400 MHz): 7.09 (s, 2H), 7.02 (s, 2H), 3.01 (m, 8H), 1.88 (m, 8H), 1.48 (m, 24H), 0.99 (m, 12H). IR ν_{max} (cm^{-1}): 2953.64 (m), 2921.50(s), 2850.20(s), 1458.69(m), 1345.48(m), 1189.67(m), 867.44(m), 808.44(s), 771.47(m), 724.57(m). Anal. calcd. for $C_{54}H_{56}S_{10}$: C, 63.24; H, 5.50; N, 0.00. Found C, 63.03; H, 5.64; N, 0.01. Given the low solubility of this compound ^{13}C NMR spectroscopy was not possible. The identity of this compound was confirmed by 1H NMR spectroscopy and elemental analysis.

Preparation of 3-bromo-5-hexylthiophene-2-carbaldehyde (4.61). $nBuLi$ (2.5M, 92 mL, 230 mmol) was added to a solution of diisopropylamine (37 mL, 264 mmol) in dry THF (240 mL) under nitrogen at 0 °C. After 15 min, **4.60** (52.98 g, 214 mmol) was added. After stirring the resulting brown solution for 2 h at 0 °C, dry DMF (34 mL, 439 mmol) was added. After stirring for an additional 2 h at 0 °C, the solution was poured into 10% HCl, extracted with Et_2O , washed with 10% HCl, saturated sodium bicarbonate and brine, then dried over magnesium sulfate. Removal of volatiles under reduced pressure afforded a brown oil. Vacuum distillation (0.6 mmHg) was performed in two-steps: first at 130 °C to eliminate volatile impurities, then at 170 °C to yield the target product as a golden oil (45.6 g, 78% yield). 1H NMR (δ , $CDCl_3$, r.t., 400 MHz): 9.87 (s, 1H), 6.85 (t, $J = 0.88$ Hz, 1H), 2.83 (t, $J = 7.60$ Hz, 2H), 1.68 (m, 2H), 1.34 (m, 6H), 0.89 (t, $J = 6.85$ Hz, 3H). ^{13}C NMR (δ , $CDCl_3$, r.t., 400 MHz): 182.7, 157.2, 134.6, 129.5, 120.4, 31.5, 31.0, 30.9, 28.7, 22.6, 14.1.

Preparation of methyl 5-hexylthieno[3,2-b]thiophene-2-carboxylate (4.62). A solution of **4.61** (45.6 g, 166 mmol), triethylamine (52 mL, 368 mmol) and methyl thioglycolate (19 mL, 208 mmol) in dry DMF (120 mL) was stirred overnight under nitrogen at 70 °C. After cooling to r.t., the solution was poured into an ice/water mixture and stirred for 30 min. The resulting

yellow slurry was filtered, the precipitate was rinsed with deionized water and dried in air to yield crude methyl 5-hexylthieno[3,2-b]thiophene-2-carboxylate as an off-white solid, which could be used without further purification. Crude yield 60g (>100% yield). Pure target compound could be obtained by recrystallization (MeOH) as a white solid. (28.5 g, 60% yield). ¹H NMR (δ, CDCl₃, r.t., 400 MHz): 7.90 (d, J=0.55 Hz, 1H), 6.97 (d, J = 0.55 Hz, 1H), 3.90 (s, 3H), 2.89 (t, J=7.65 Hz, 2H), 1.72 (m, 2H), 1.32 (m, 6H), 0.89 (t, J=7.00 Hz, 3H). ¹³C NMR (δ, CDCl₃, r.t., 400 MHz): 163.3, 153.8, 144.2, 137.0, 132.7, 126.1, 117.7, 52.3, 31.6, 31.5, 31.4, 28.8, 22.7, 14.2.

Preparation of 5-hexylthieno[3,2-b]thiophene-2-carboxylic acid (4.63). The ester **4.62** (28.5 g, 101 mmol) and sodium hydroxide (8.14 g, 203 mmol) were refluxed overnight in THF/water (300 mL, 2:1 ratio). After cooling, the mixture was acidified with concentrated HCl, extracted with Et₂O, washed with 10% HCl and brine, then dried over magnesium sulfate. Removal of volatiles under reduced pressure followed by recrystallization (3:7 EtOAc/Hex) afforded the target product as a white solid (24.89 g, 92% yield). ¹H NMR (δ, CDCl₃, r.t., 400 MHz): 11.70 (bs, 1H), 8.00 (d, J=0.55 Hz, 1H), 7.00 (d, J = 0.55 Hz, 1H), 2.91 (t, J=7.60 Hz, 2H), 1.74 (m, 2H), 1.35 (m, 6H), 0.90 (t, J=7.00 Hz, 3H). ¹³C NMR (δ, CDCl₃, r.t., 400 MHz): 168.7, 154.9, 145.6, 137.3, 131.8, 127.7, 116.8, 31.6, 31.6, 31.4, 28.9, 22.7, 14.2.

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Chapter 5

Design of Thiophene-expanded Hexaazatrinaphthylenes & the Study of their Photoluminescence

Authorship disclosure: This work has not yet been published. All of the synthesis and characterization work in this chapter were performed by François Magnan. X-ray diffraction measurements on **5.31** were performed by Raül Castañeda, and further refined by Dr. Bulat Gabidullin.

5.1 Introduction

Self-assembly of organic molecules to yield nanostructures with novel properties is an enticing strategy for the fabrication of well-defined nano- or micro-architectures.^{1,2} This “bottom-up” approach is particularly well-suited for optoelectronic device applications, where the production of such architectures over large-areas is crucial for widespread application. Whereas “top-down” approaches afford a more direct control of the nanomorphology, they are generally slow, expensive and limited to small surface-areas. Self-assembly, on the other hand, relies on non-covalent intermolecular interactions and their high directionality to guide the formation of supramolecular arrangements.³ The exact self-assembling behavior is difficult to predict beforehand, as different types of interactions, cooperative or antagonistic, are simultaneously at play. A well-known strategy is the use discotic molecules, whose planar π -conjugated 2D systems tend to promote stacking in a columnar fashion.⁴ This increased molecular order brought forth by the columnar arrangement can be beneficial to charge mobilities due to the resulting large anisotropic π -orbital overlap. The majority of discotic mesogens reported in the literature are *p*-type organic semiconductors (OSCs) rather than *n*-type.^{4,5} Derivatives of 1,4,5,8,9,12-hexaazatriphenylene (HATP) and its extended version, hexaazatrinaphthylene (HATN, Fig. 5.1) are such examples of discotic molecules that can exhibit *n*-type performance. The six sp^2 -type nitrogen atoms give the heterocyclic core an electron-deficient character, making it a good electron-acceptor.⁵ This, in concert with their rigid and

planar structure, makes HATP/HATN (or HATs, when referring to either frameworks) enticing building blocks for a variety of organic materials and applications.

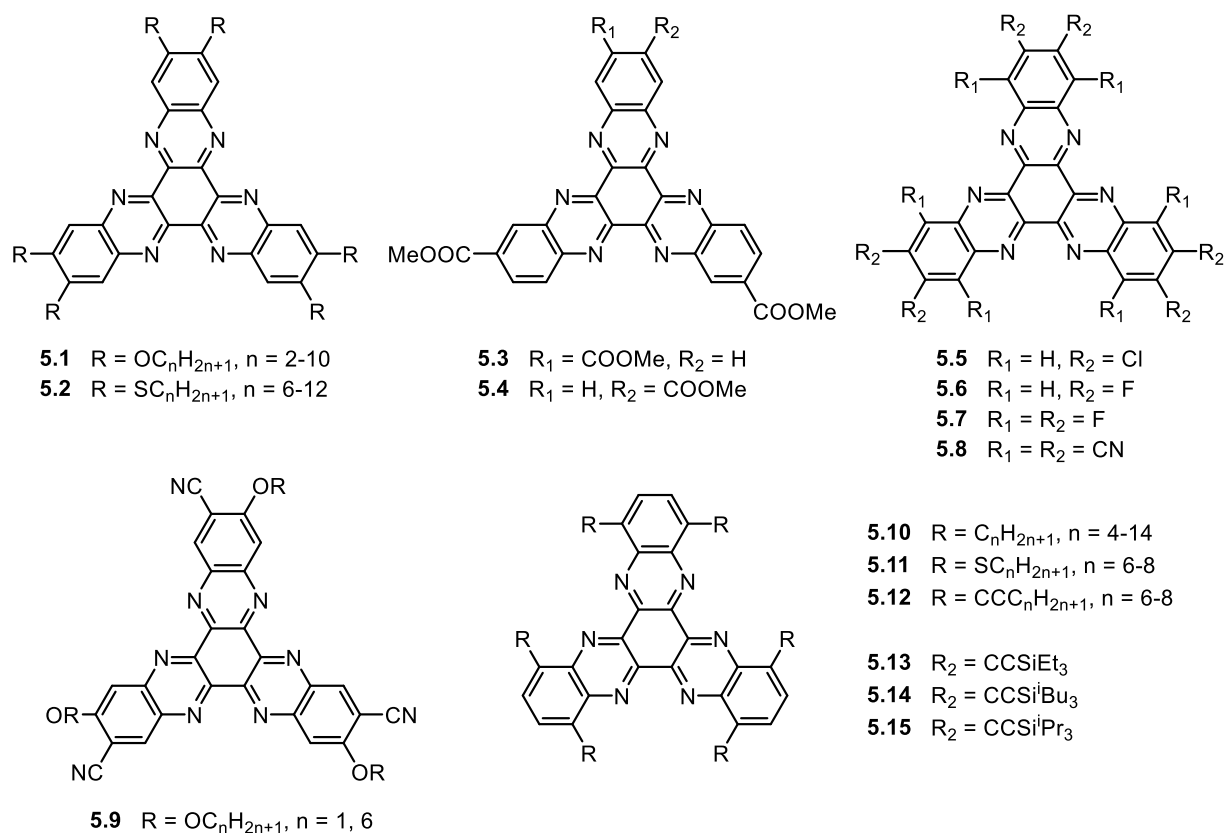


Figure 5.1 – Molecular structures of previously reported short functionalized HATN derivatives

HATs are tris-bidentate ligands with non-innocent redox behavior, and accordingly much of the research on these structures has been dedicated toward their use as ligands for metal coordination chemistry, notably molecular magnetism and luminescence, metal-ion sensors and catalysis.^{6–14} When functionalized with solubilizing alkyl chains, these discotic molecules will typically exhibit liquid crystalline behaviour,^{15–20} as a result of a balance between π - π interactions and thermal motion of the alkyl chains. Early work on these building blocks as charge carriers for organic electronics has focused on the preparation of derivatives functionalized with alkoxy (**5.1**) and alkylthio (**5.2**) chains of various lengths and their impact on liquid-crystalline behavior.^{15,18,20,21} In all cases, the transition to the liquid-crystalline phase typically occurred at lower temperature with increasing chain lengths. Whereas oxy derivatives pack more tightly in the columnar phase and are more thermally stable,¹⁵ sulphur substituents are

better suited to stabilize the radical anions produced.²² Geerts and coworkers further elaborated on the studies of liquid-crystal charge carriers by measuring the mobilities of HATN derivatives as a function of the molecular ordering.¹⁷ While respectable mobilities ($0.07\text{--}0.6\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) were observed in pristine materials, transitioning to the liquid crystalline phase led to a decrease of performance due to an increase in intracolumnar disorder.

Further work has explored the effects of peripheral substituents on the stacking and electronic properties of HATs. Marder and coworkers showed that the solid-state ionization potential and electron affinity of HATN core could be tuned over ranges of approximately 2 eV by substitution with electroactive groups (*i.e.*, alkyloxys **5.1**, alkylthios **5.2**, esters **5.3–5.4**, halogens **5.5–5.7**).^{23,24} Reaction of cyanated derivative **5.8** with alcohols was shown to regioselectively substitute half of the electron-withdrawing cyano groups for electron-donating alkoxys.¹⁶ Whereas **5.8**, and other electron-deficient HATN derivatives, avoid π -stacking in the solid state, the resulting electron-enriched compound **5.9** showed smaller intermolecular distance, a desirable trait for enhanced semiconducting behavior. Bay-substitution of HATN has been shown to induce twisting in the heterocyclic core and a deviation from planarity as a result of steric hindrance between the neighboring chains, the extent of twisting was directly related to the size and rigidity of the bay-substituent (**5.10–5.15**). This could lead to further tuning of electronic properties, such as redox potential, as a result of the distorted molecular structure and packing arrangement.^{25–28}

The creation of new π -expanded HAT-based systems has been a topic of research for several years, and has targeted both their self-assembling properties and the tuning of the energy levels of their molecular orbitals. In both aspects, increasing the π surface-area can be seen as beneficial for charge-mobility, due notably to enhanced bandwidth, lowered reorganization energy and a higher number of directing intermolecular interactions. One of the strategies explored has been to append the HAT core with (hetero)aryl substituents. Gao and coworkers published a series of hexa-substituted HATN (Fig. 5.2), with aryl substituents ranging from phenyl to triphenylamine (**5.16–5.20**), and found that the photophysical properties (*i.e.*, emission wavelength, fluorescence quantum yield) could be tuned by the electron-donating ability of the substituents.²⁹ Such donor-acceptor dyads are worthwhile structures for certain optoelectronic applications, namely light-emitting diodes and solar cells, as the energy levels of their frontier

molecular orbitals can be tuned relatively independently with each block. Furthermore, a reduction in the energy level of the LUMO was reported for all derivatives in regard to the HATN core, due to the extension of the conjugation.

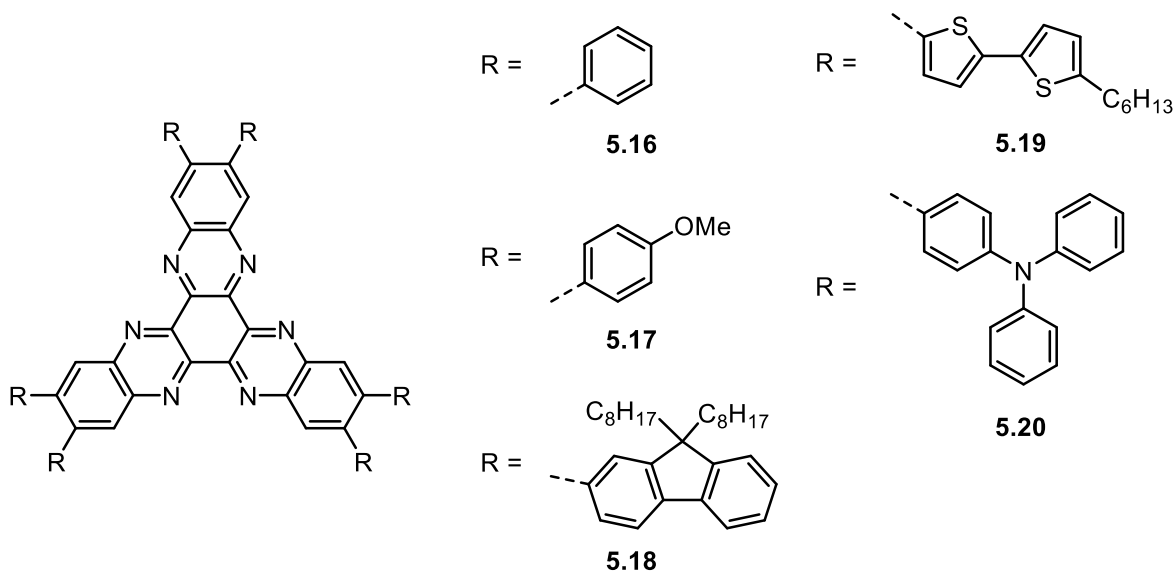


Figure 5.2 – Molecular structures of a family of π -extended HATN functionalized with aryl groups of increasing electron-donating behavior.

Admittedly, functionalization of the HAT core with (hetero)aryl substituents is not the most efficient way to extend the degree of conjugation, due to the rotational freedom of the aryl groups which can lead to less-than-optimal π -overlap. For this reason, fusing the HAT core with electron-rich systems (Fig. 5.3), notably tetrathiafulvalenes (5.21),^{30,31} has also been the subject of investigation for designing new donor-acceptor dyads. Owing to their rigid backbone, the resulting molecule displays long-range self-assembly and strong intramolecular charge-transfer between the peripheral tetrathiafulvalenes and the central HATN. The opposite strategy, the combination of the HATN core with additional electron-deficient structures, has been performed either by the fusion of three HAT molecules,³² or by combining with different electron-deficient systems, such as naphthalimide (5.22),³³ dicarboximides (5.23),³⁴ dihydrotetrazatetracene (5.24),³⁵ phenanthroline (5.25)^{36,37} or perylene bisimides (5.26).³⁸ In all cases, the fusion of the HATN core with the additional electron-poor structures leads to a further increase in the electron affinity of the resulting framework, which is desirable for better *n*-type semiconducting performance. A LUMO with an energy level as low as -3.93 eV was observed for the perylene bisimide

derivative, which is near the ideal value of -4 eV, and below that of PCBM (-3.8 eV), a commonly employed *n*-type OSC. Whereas the electron mobility ($\sim 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) is comparable to that of PCBM, the hybrid compound exhibited a two orders of magnitude enhancement in charge mobility in regard to the individual perylene bisimide units due to enhanced molecular order in thin films. In a similar vein, Wang and coworkers characterized the expansion of the HAT's branches with more pyrazine units to promote *n*-type behavior.³⁹ Upon step-wise growth of an alkoxy phenyl substituted HATP core (5.27) along one (5.28), two (5.29) and three (5.30) branches, the energy levels of the frontier molecular orbitals steadily decreases, reaching a low value of -4.02 eV for the tri-fold expanded system.

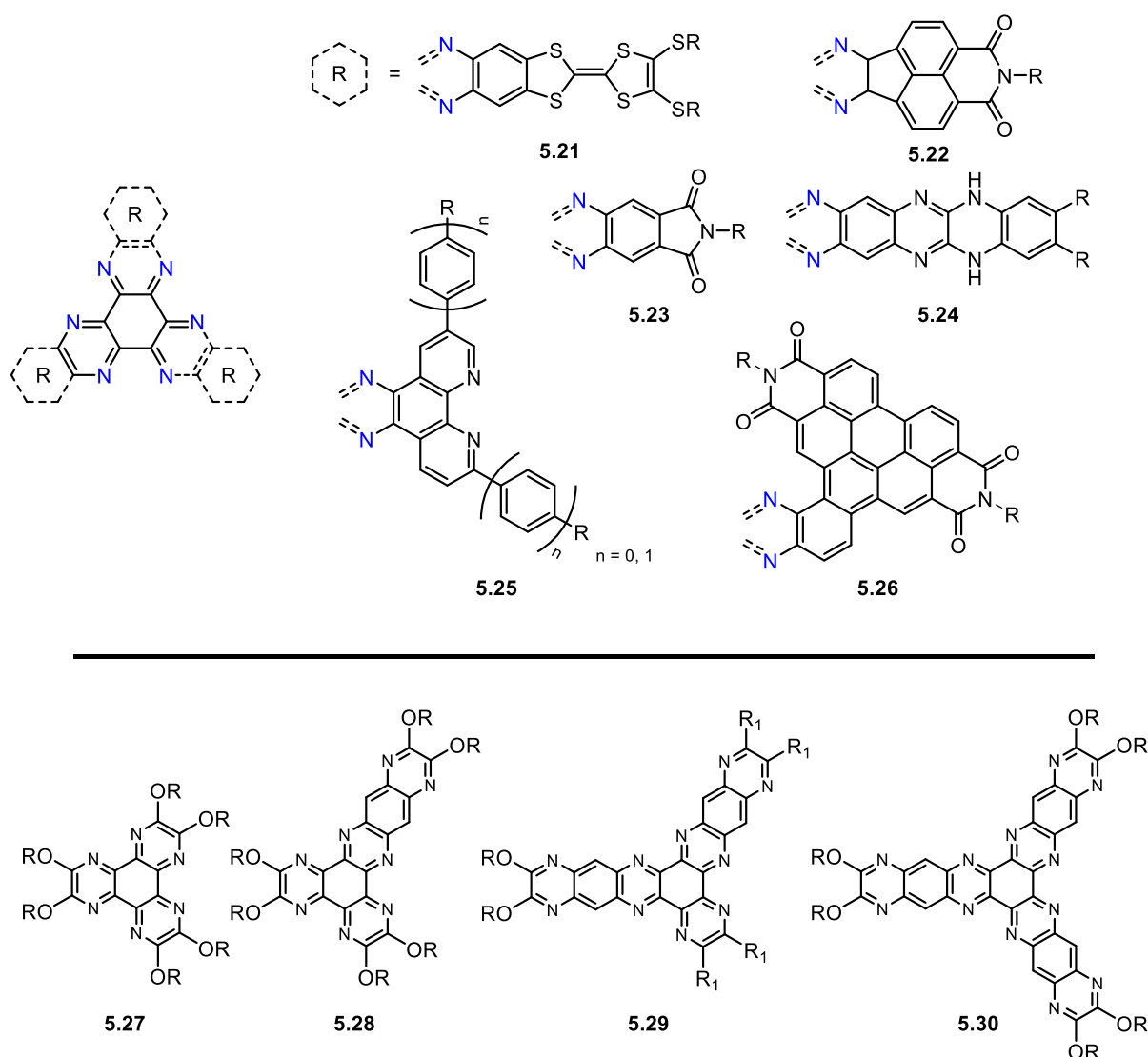


Figure 5.3 - Molecular structures of HAT-based compounds with rigid extension of the π -framework. (R = Alkyl)

Considering the benefits of discotic molecules on charge mobility and the extent of tuning that can be achieved by rational extension of the conjugation, reported herein are preliminary results toward extended HATN systems that were first conceived as potential active layers for optoelectronic devices (Fig. 5.4). The thiophene heterocycle, largely ignored in the context of HATs, was chosen for its positive impact on charge mobility, as well as its electron-donating character that can lead to donor-acceptor systems with interesting optical properties. Enlargement of the conjugation was performed by appending thienyl rings to the heterocyclic core and produce **5.31**, which upon oxidative cyclodehydrogenation could be fully aromatized to form **5.32**. The resulting system was studied by a combination of optical, computational and single X-ray diffraction (XRD) studies before and after cyclization of the thienyls to further assess the impact of planarity and extended conjugation on the HATN's properties.

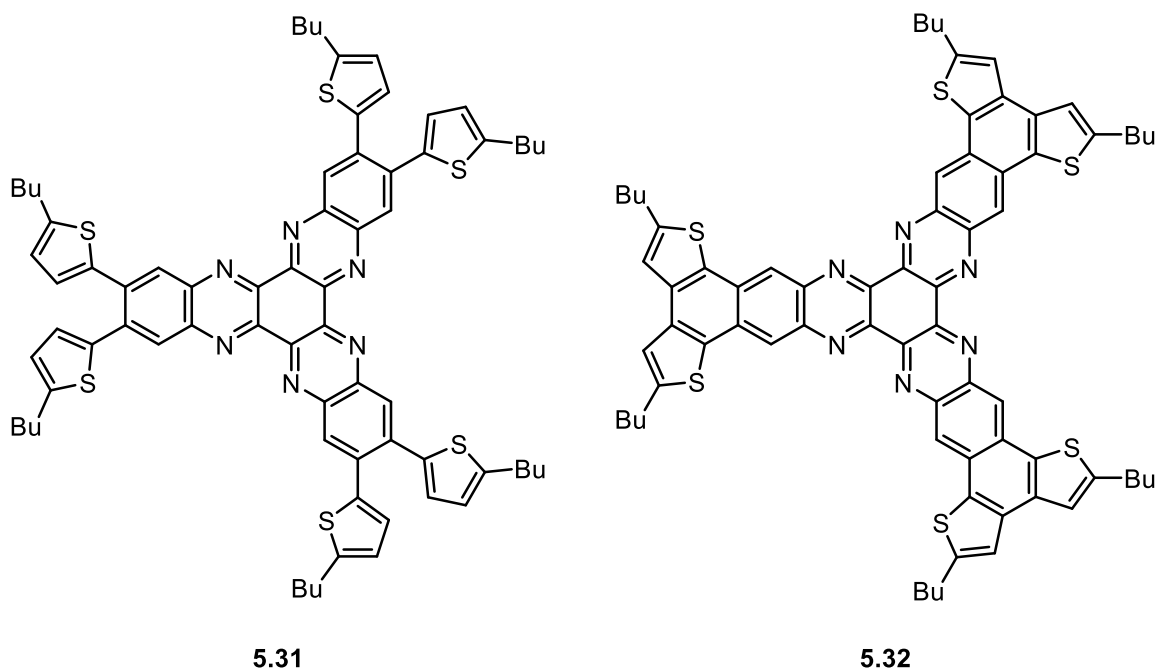


Figure 5.4 – Molecular structures of novel HATN derivatives **5.31** and **5.32** investigated in this work.

5.2 Results and Discussion

5.2.1 Obtaining the Building Blocks

Azaacenes are mainly obtained by the condensation between α -diketones and α -diamines in the presence of an acid catalyst. In that regard, hexaketocyclohexane **5.33** was required to generate the trigonal HATN system and was prepared using a procedure pioneered by Sager and coworkers (Fig. 5.5).^{40,41} It should be noted that the product, while identified (and even sold) as hexaketocyclohexane octahydrate, is really dodecahydroxycyclohexane dihydrate, as confirmed by IR and XRD measurements.^{42,43} A reversible equilibrium in solution, however, allows for the geminal diols to revert back to carbonyls, which can further react with amines by nucleophilic addition. For the sake of the reactions at hand, this compound behaves essentially as hexaketocyclohexane, and will be referred to as such for the sake of simplicity.

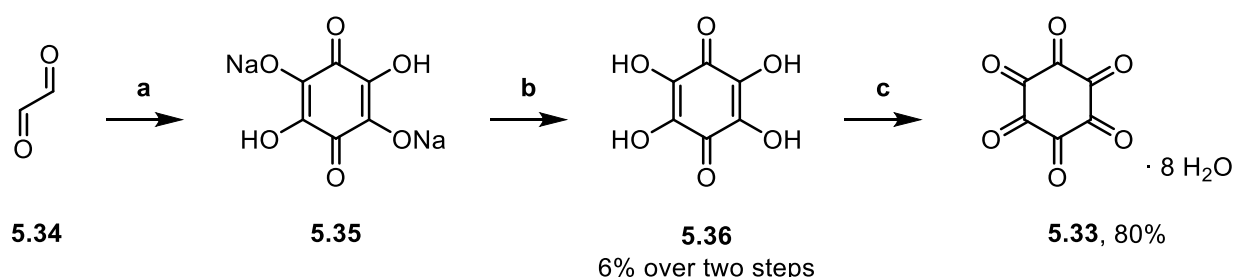


Figure 5.5 – Reaction pathway for the preparation of **5.33**. Reagents and conditions: **(a)** Na_2SO_3 , NaHCO_3 , air/water/45-100 °C. **(b)** HCl 2M/Reflux. **(c)** HNO_3 13M/0 °C.

Reaction of glyoxal **5.34**, sodium sulfite and sodium bicarbonate in a hot air-saturated aqueous solution leads to the formation of glyoxal's bisulfite addition compound. *In-situ* trimerization afforded the disodium salt of tetrahydroxyquinone **5.35** as a green powder that could be recuperated by filtration and rinsed with cold water and methanol. Although the yield for this step was low (~10%), this was offset by the low cost and toxicity of the reagents involved, along with the overall synthetic simplicity. Protonation of the salt in boiling dilute hydrochloric acid afforded glistening black plates of tetrahydroxyquinone **5.36** in almost quantitative yield upon cooling. Adding this quinone to an ice-cold concentrated nitric acid solution led to almost immediate formation of **5.33**, which precipitated as white microcrystals. Filtration, followed by rinsing with water and an acetone/diethyl ether mixture, provided clean

starting material, which could be used in combination with α -diamines to form hexaazatrinaphthylene derivatives.

The second building block for the preparation of the HATN framework was obtained from 1,2-dibromo-4,5-diaminobenzene **5.37**, itself prepared following a modified previously reported route (Fig. 5.6).³⁴ Briefly, commercially available 1,2-phenylenediamine **5.38** was tosylated using tosyl chloride. The original procedure called for the use of neat anhydrous pyridine as solvent to soak up the hydrochloric acid formed as a by-product in the reaction. It was found however that running the reaction in anhydrous DCM, with a slight stoichiometric excess of pyridine, was sufficient to enable the reaction to run to completion, which is advantageous considering pyridine's increased toxicity and cost. Substituting pyridine for triethylamine as an even cheaper, safer alternative, failed to afford the product, most likely as a result of the steric hindrance of the base that forbids its direct approach to the active site. Considering the difference in basicity between pyridine and triethylamine (*i.e.*, pK_a of pyridinium 5.25 vs 9.0 for triethylammonium),^{44,45} the use of a catalytic amount of pyridine in tandem with a stoichiometric amount of the amine was also explored. The rationale for this choice was that pyridine could fit in the reaction pocket, abstract the proton, diffuse back to solution and transfer the proton to the triethylamine, thus freeing it for further reaction. This however also failed to afford more than an intractable mixture of products. A stoichiometric amount of pyridine was thus employed in the preparation of the precursor **5.39**. Upon recrystallizing the obtained solid in ethanol, crystalline **5.39** was obtained in 90% overall yield.

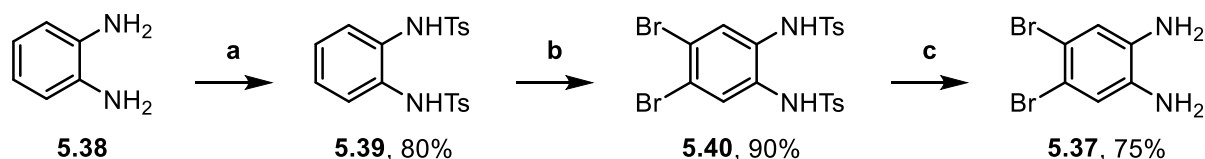


Figure 5.6 - Reaction pathway for the preparation of **5.37**. Reagents and conditions: **(a)** TsCl, Pyridine/DCM/0 °C to r.t. **(b)** Br₂, NaOAc/AcOH/0 °C to 70 °C. **(c)** concentrated H₂SO₄/110 °C.

The goal of the tosyl protecting group was to ensure a proper degree of reactivity in the next step, the bromination of the aromatic ring at the para positions to each amino group. As amino groups are strong activating groups toward electrophilic aromatic substitution, the starting 1,2-phenylenediamine employed as-is would result in over-bromination. The formation of the

sulfamate greatly reduced the extent of electron donation into the aromatic ring, allowing a better control over the reactivity. Bromination of the protected diamine was achieved in hot acetic acid with elemental bromine in the presence of sodium acetate as a base to neutralize the hydrobromic acid formed during the reaction. Pouring the reaction mixture into water and ethanol formed a slurry, which was then filtered and rinsed with water to yield a white solid. In-lieu of a proper recrystallization, the solid was slurried in isopropanol and stirred until all aggregates were broken loose, then filtered and air-dried to yield intermediate **5.40** in good purity, which could be directly employed in the deprotection step. Heating the intermediate in concentrated sulfuric acid at 110 °C for 20 minutes was sufficient to remove the tosyl protecting groups and afford the free diamine. Longer reaction times could lead to decomposition of the product and were avoided. Quenching the reaction in an ice-water mixture, followed by neutralization of the acid, extraction and recrystallization of the crude in a 2:1 mixture of water and isopropanol produced **5.37**, with yields of 60% over three steps.

5.37 could be used as a starting point to attach the thienyl moieties, thanks to cross-coupling chemistry (Fig. 5.7). The amino groups precluded the use of Negishi or Kumada couplings due to the strong basicity of Grignards and organozinc reagents employed for both reactions. Stille coupling reactions, which make use of neutral tributylstannyl derivatives, face no such limitation and directly afforded target product in moderate yields (~70-80%).

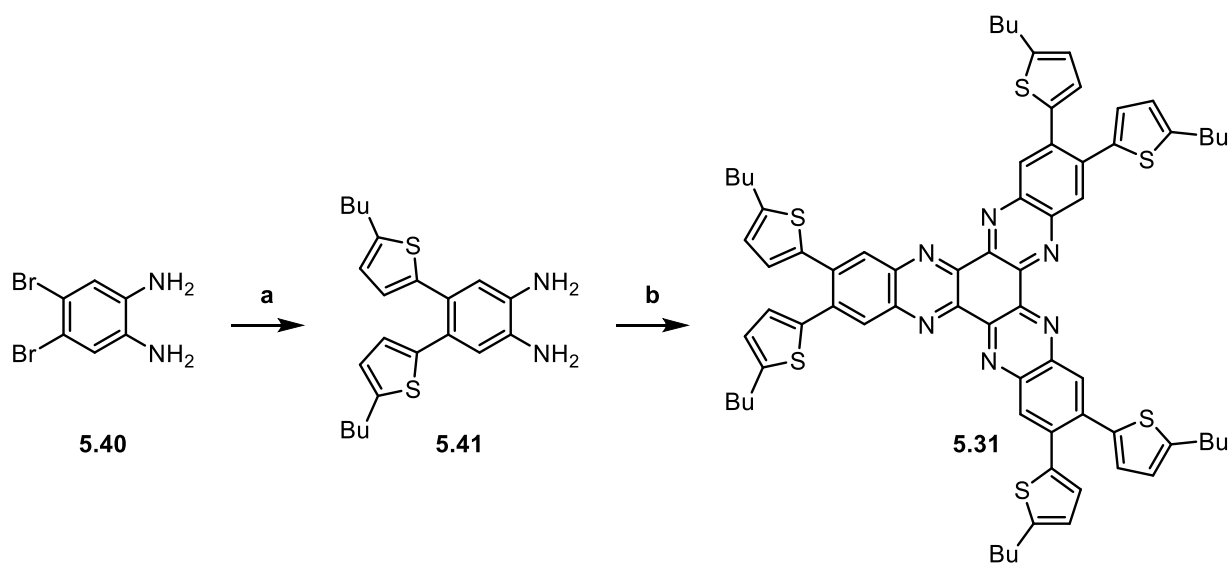


Figure 5.7 - Reaction pathway for the preparation of **5.31**. Reagents and conditions **(a)** 2-tributylstannyl-5-butythiophene, PdCl₂, PPh₃/PhMe/reflux. **(b)** **5.33**/EtOH, AcOH/reflux.

The corresponding Stille tin reagents were prepared in-house beforehand by lithiation of the corresponding thienyl derivative, followed by *in-situ* transmetallation with tributylstannyl chloride. Coupling between the Stille reagents and **5.37** was performed in refluxing toluene along with PdCl₂/PPh₃ to form the active catalyst *in-situ* and were complete within 12 hours. The cooled reaction mixture was subjected to vacuum distillation to remove volatile impurities (*i.e.*, the solvent, the Stille reagent, tin by-products) and afford a thick dark brown oil. Filtration of this oil through a short silica gel plug with a 1:1 ethyl acetate/hexanes solvent mixture as eluent removed a dark impurity and yielded, upon removal of volatiles, **5.41** as a syrupy light brown oil. While this oil could be directly used in subsequent steps, its high viscosity made smaller scale reactions problematic as it couldn't be efficiently transferred without avoiding important losses. As a solution, the diamine could be dissolved in hot toluene and protonated with concentrated hydrochloric acid to generate the dichloride salt, which was smoothly filtered after cooling and rinsed with diethyl ether to afford a convenient powder.

5.2.2 Assembling the HATN Framework

Refluxing three equivalents of diamines with **5.33** under acidic conditions led to the formation of the HATN framework **5.31** through consecutive imine condensations. Whereas many reported procedures are performed under inert atmosphere in degassed solvents,^{21,24,46} these derivatives were found to form in similar yields and purities regardless of the exclusion of oxygen from the reaction. Furthermore, most reports indicate the reaction is allowed to react for upwards of 24 h before terminating the reaction. In the present case, thirty minutes was typically sufficient for complete reaction of the starting diamine, as witnessed by both TLC and optical spectroscopy monitoring. As such, the reactions were refluxed for one hour to ensure full reaction and repeatability. No partial substitution product of the hexaketone was observed, most likely as each substitution steps makes the resulting intermediate more soluble than its predecessor, and thus more reactive. In addition to the use of anaerobic conditions, previous reports similarly indicated the use of neat glacial acetic acid as reaction solvent.^{24,29} While the reactions studied here performed well in acetic acid, the subsequent work-up was initially found to be troublesome and hardly reproducible. Indeed, while in some fortuitous cases the product would precipitate as a pure vibrant orange solid which could simply be filtered off and rinsed, for the most part a thick black oil coating the reaction flask was obtained. This discrepancy

originated from the concentration of the reagents during the reaction, where fairly dilute conditions were required to avoid immediate oiling out of the product upon cooling. As such a high level of dilution with glacial acetic acid as a solvent is non-practical for larger scale synthesis, a different solvent system was chosen, namely a 9:1 mixture of ethanol and acetic acid. While clean precipitation of the product was seldom achieved in this solvent mixture, the work up was greatly facilitated by the reduced amount of acetic acid, which facilitated extraction into dichloromethane. Purification of the crude HATN **5.31** was then achieved by filtering through a short silica gel plug to remove polar impurities. Bulk recrystallization could also be achieved by diluting a concentrated dichloromethane solution with acetic acid and allowing to stand overnight.

As mentioned above, the diamine can be converted to its dichloride salt for synthetic ease. While the freebase form reacts straightforwardly with the hexaketone, the dichloride salt exhibited lowered reactivity as a result of the reduced nucleophilicity of the protonated amino groups. Accordingly, a slight excess of triethylamine was added to the ethanolic solution of the dichloride salt to liberate the freebase *in-situ*, following which the ketone and the acetic acid were added and the mixture refluxed, as usual. Similar results and purities were obtained with this method compared to the use of the freebase.

5.2.3 Oxidative Cyclization of the HATN Framework

Two different strategies were explored to obtain the fully conjugated and planarized HATN **5.32** (Fig. 5.8); namely, performing the oxidative cyclodehydrogenation between the two pendant thienyl rings before and after the formation of the HATN core. In both scenarios, the use of anhydrous iron trichloride (FeCl_3),⁴⁷ 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in acidic conditions⁴⁸ or photocyclization⁴⁹ were considered as ring-closing methodologies. Photocyclization was attempted by exposing a dilute toluene solution of the reagent to 365 nm light in the presence of catalytic iodine and solid potassium carbonate for 24 hours. Attempts at photocyclizing the preformed **5.31** were unfruitful, and only starting material was recovered. **5.41** on the other hand could be cleanly converted to the cyclized **5.42** in such a fashion. However, low concentrations were required, lest a mixture of starting material, product and side-

products be recovered. As the experimental setup available to perform such a reaction was limited to small volumes, this route was not further explored.

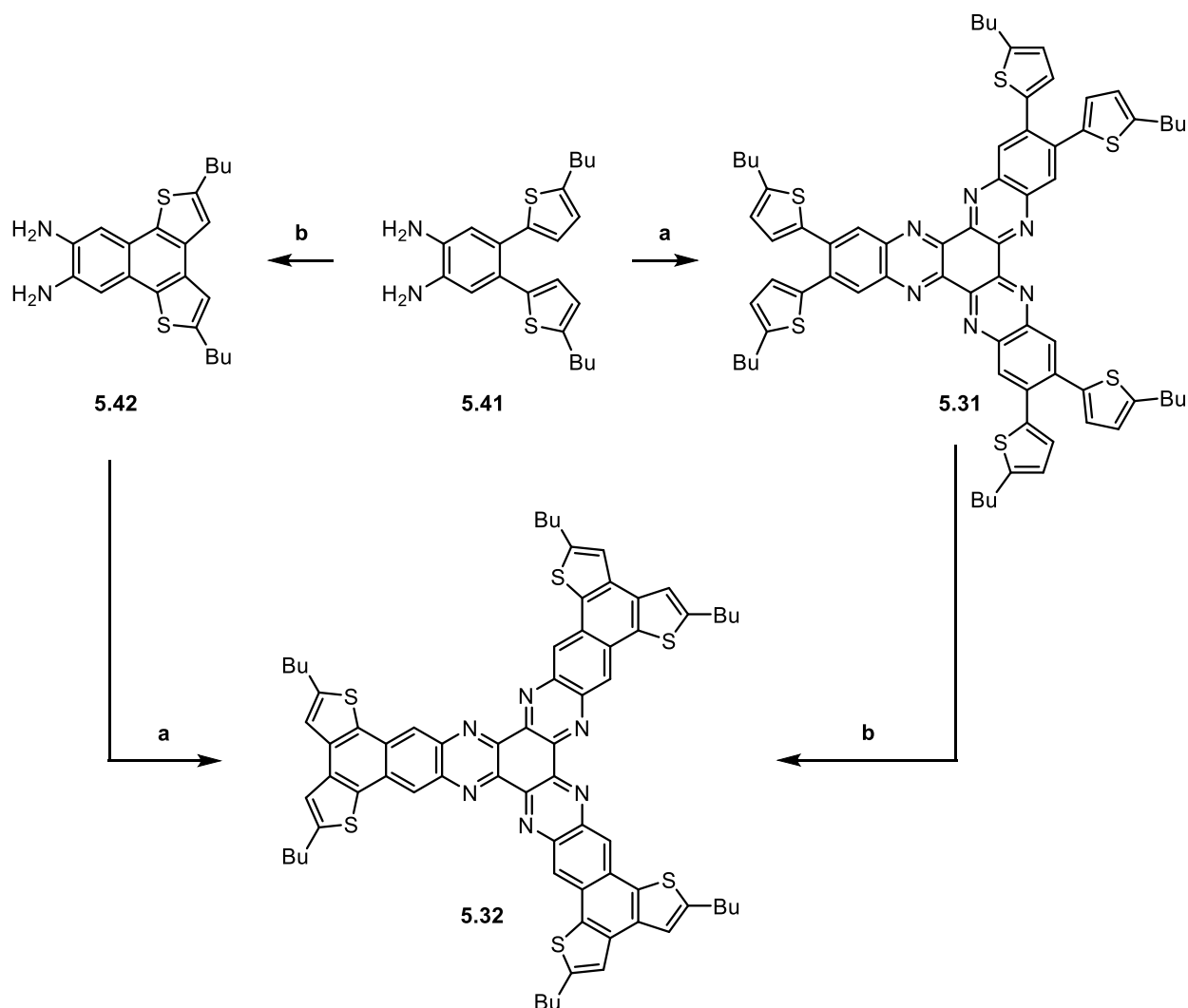


Figure 5.8 – Generic reaction scheme for the preparation of fully planarized thieno derivatives of **5.32**. Reagents and conditions: **(a)** **5.33**/EtOH,AcOH/reflux. **(b)** Oxidative cyclodehydrogenation step (e.g., anhydrous FeCl₃, DDQ/TFA or *hν*).

The use of DDQ in acidic conditions, which previously showed success in the preparation of 2D thienoacenes (Chapter 4) was also attempted for both routes. Again, the preformed **5.31** failed to react, leaving in all cases intact starting material. Increasing the temperature and the amount of DDQ failed to promote reactivity, in most likelihood due to the limited oxidizing power of DDQ, which can only react with substrates that possess oxidation potentials below 1.7 V.⁴⁸ On the other hand, **5.41** could undergo oxidative cyclodehydrogenation under these

conditions to give **5.42**, albeit in a wildly irreproducible fashion. Interestingly enough, a side product was formed during the reaction that could be isolated during the work-up. Whereas this solid was fully soluble in chloroform, no peaks were observed in the corresponding NMR spectrum. While it was originally speculated that this could simply be either DDQ or its reduction product, this couldn't be the case here, as both molecules are soluble in basic aqueous conditions and would have been removed during the work-up. The oxidative conditions and the presence of the free amino groups could lead to a complicated mixture of heterocycles. While **5.42** was unambiguously produced in these conditions, the reaction yields were fairly low, averaging 30%. For these reasons, this methodology was not explored further.

Finally, anhydrous iron trichloride was investigated for the ring-closing reaction, and displayed reactivity for both **5.42** and **5.31**. Although target **5.32** was obtained by starting with **5.42**, low crude yields and several side-products made this route poorly enticing. While FeCl₃ was successful at producing **5.32**, an issue facing the use of **5.31** as the starting material is the presence of the HATN core, which can potentially coordinate the iron ion. Accordingly, nine equivalents of iron trichloride (three for the coordinating pockets plus two per bond formed) were used as a starting point for the reaction. Whereas this stoichiometric ratio typically afforded the cyclized product, employing less iron led to an intractable mixture of fully and partially cyclized compounds. To ensure complete reaction, fifteen equivalents of FeCl₃ were instead used. Furthermore, as the reaction was slow at room temperature, moderate heating (60 °C) was required for a timely reaction (*i.e.*, less than an hour). The addition of iron trichloride to a warm solution of **5.31** turned the initially red-orange solution a dark royal blue; while this could potentially be due to the coordination of the iron, such a drastic color change was typically observed in similar oxidative scenarios with no coordinating pockets. Quenching of the reaction was performed with methanol, which immediately dissipated the blue color to afford a brown-red solution. Removal of volatiles, followed by slurrying the residue in methanol and filtering eliminated excess soluble iron salts. Particularly broad peaks in the NMR characterization of the crude solid seemed to be indicative of paramagnetic species, likely iron being coordinated in the bidentate pockets. As a result, the solid was dissolved in dichloromethane and treated with ammonium hydroxide to form solid iron hydroxide, which was filtered off. Upon evaporation of the dried solvent, a brown-red solid was obtained. Recrystallization from concentrated solutions of 1,1,2,2-tetrachloroethane and acetic acid yielded a dark red solid in 50% yield.

5.2.4 Spectroscopic and Computational Studies of the Uncyclized Framework

The optical behavior of **5.31** and **5.32** were investigated by optical spectroscopy and computational studies to probe the effect of rigidity and aromatization of the expanded HATN. The uncyclized **5.31** was fairly soluble in a wide-range of solvents, due to the rotational freedom of the thienyl rings that disrupts solid-state packing. As a result, its absorptive properties could be quantitatively investigated in various solvents. Regardless of the solvent employed, the absorption profile remains similar and consists of two high absorption regions of comparable intensities (Fig. 5.9). The first, centered around 300-400 nm, is attributed to HATN-centered π - π^* transitions, while the second region at lower energy (430-570 nm) is ascribed to charge-transfer between the peripheral electron-donating thienyls and the central electron-accepting HATN core. This assignment of a charge-transfer character to the lower energy transitions was supported by DFT calculations performed on geometry optimized **5.31** (with methyls *in-lieu* of butyl chains) at the B3LYP/6-31G(d,p) level of theory, which show the HOMO and the LUMO to reside almost exclusively on the thienyls and the HATN core, respectively (Fig. 5.10). Additionally, the overall absorption profile correlates well with both previously reported **5.19** derivative²⁹ and TDDFT calculations performed on geometry optimized **5.31** at the same level of theory (a comparison of the experimental and predicted spectra in DCM is shown in Figure 5.11, and the twenty calculated excitation energies are listed in Appendix Table A.6).

Quantitative measurements were performed on stock solutions of known concentrations, and from such studies the molar extinction coefficients were measured for each peak observed. In all solvents, the absorption patterns were found to be independent of concentration in the range investigated, which implies the molecules were either isolated or aggregated at all concentrations. Considering that well-defined NMR spectra could be obtained for **5.31** at much higher concentrations than the ones employed in this optical study (typically 1-10 μ M), it is reasonable to assume that no aggregation is occurring and that the results observed were indeed for individual molecules. The measured extinction coefficients were found to be similar in magnitude throughout the different solvents investigated (Table 5.1). For instance, the coefficient for the charge-transfer band ranged from 59000 to 71000 $\text{M}^{-1}\text{cm}^{-1}$, with a more typical average value of 66000 $\text{M}^{-1}\text{cm}^{-1}$. This value compares favorably to shorter HATN derivatives,^{50,51} and is

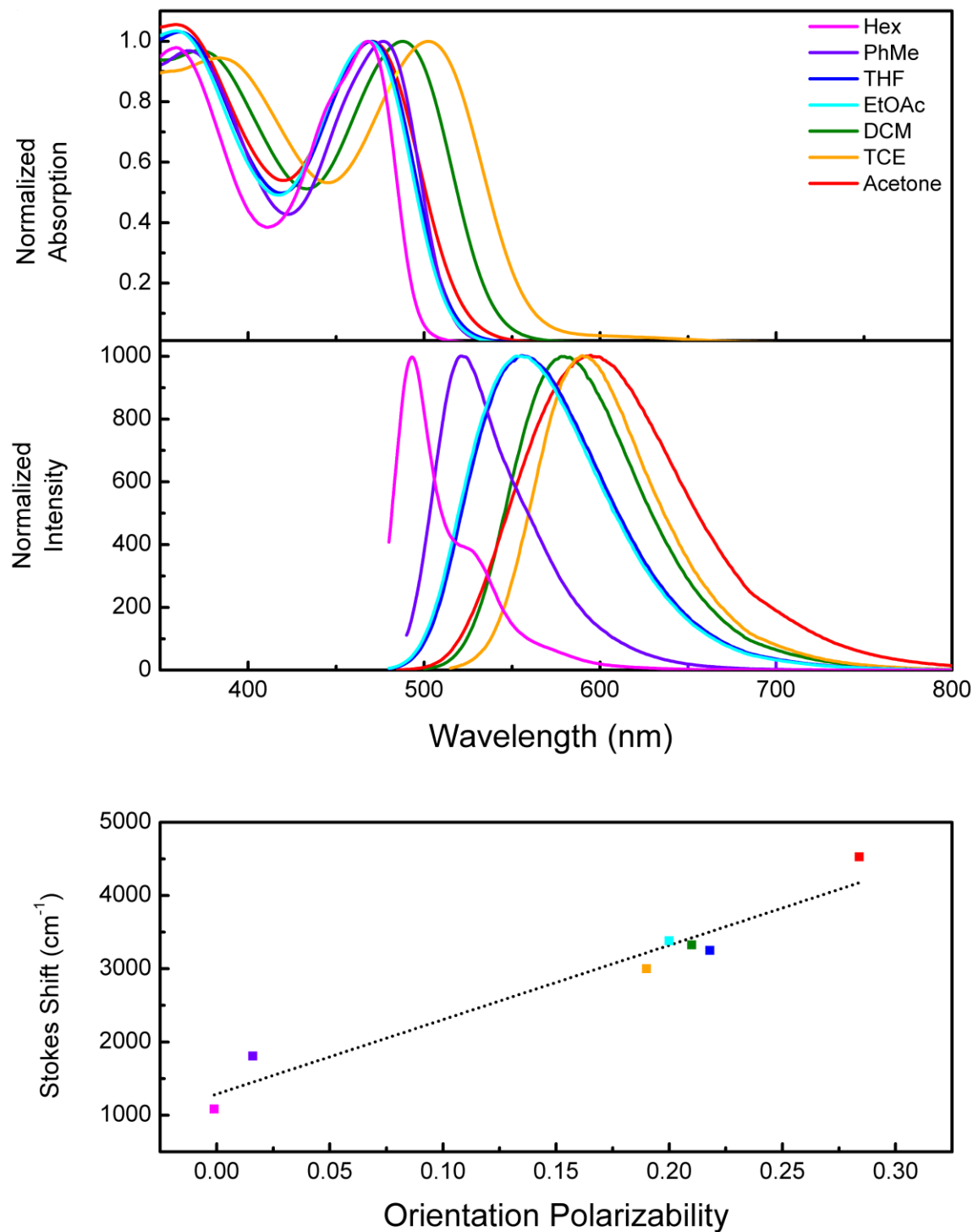


Figure 5.9 - (top) Normalized experimental absorption and (middle) photoluminescence spectra of **5.31** in solvents of various polarities. (bottom) Lippert-Mataga plot that shows the dependence of **5.31**'s Stokes shift on solvent polarity parameter "Orientation polarizability". Linear fit: $m = 10159$, $b = 1289$ ($R^2 = 0.9461$)

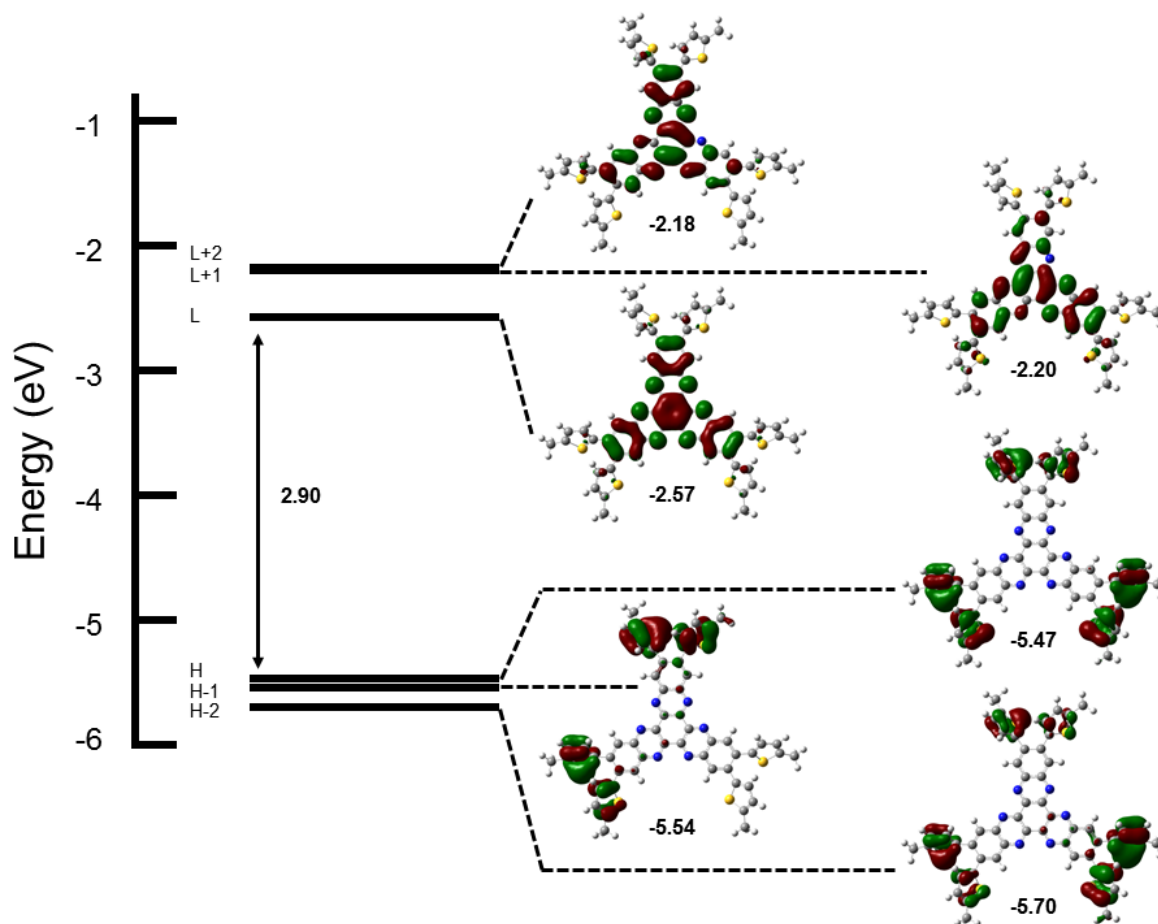


Figure 5.10 – Energy level diagram and frontier molecular orbitals of **5.31**.

indicative of the positive effect of the additional π -surface provided by the thiophene rings on light capture.

Furthermore, shifts were observed in the charge-transfer bands upon varying solvents. At the simplest level, solvatochromism can be rationalized by differences in the degree of stabilization of the excited- and ground-state by the solvent shell, where polar solvents stabilize more efficiently molecules with large dipole moments. As a result, solvatochromic effects will be typically stronger for dyes that exhibit a drastic change in the net dipole moment upon electron transitions. If the dipole moment becomes stronger upon excitation, the resulting state will be better stabilized than the ground-state, and a red-shift of the absorption maximum is observed upon increasing solvent polarity. On the other hand, a diminishing dipole moment upon

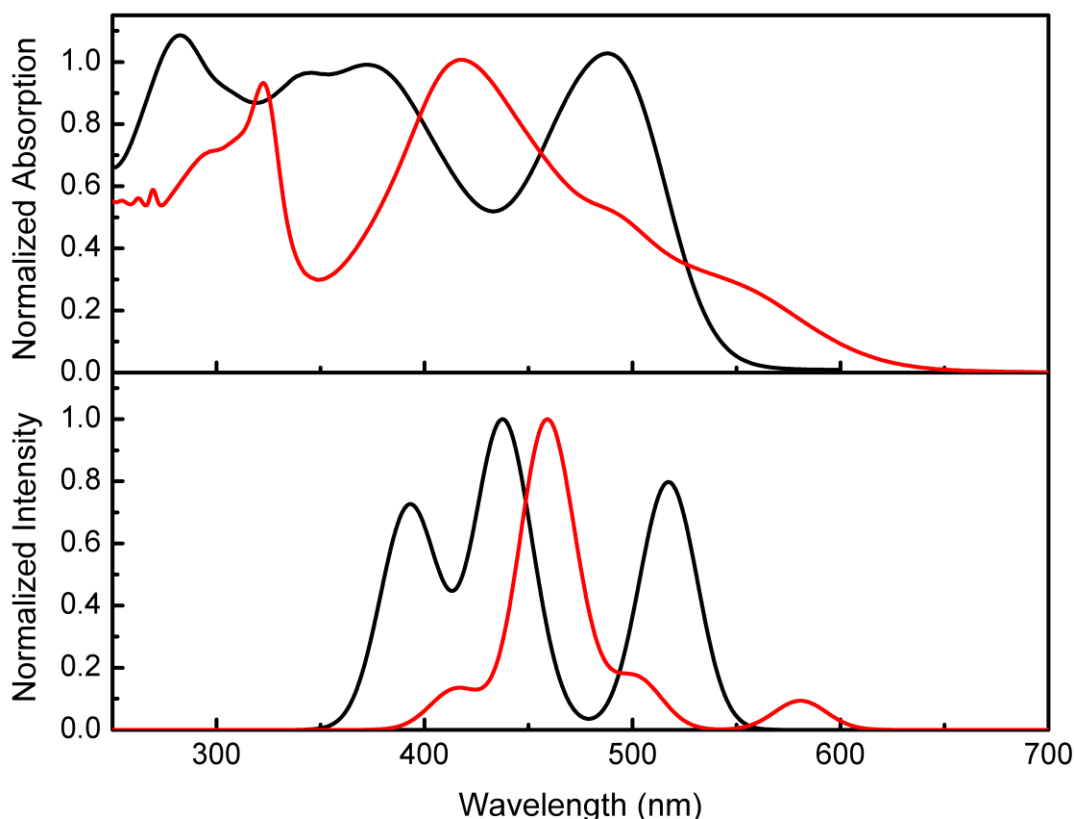


Figure 5.11 – **(top)** Experimental absorption spectra of **5.31** (black) and **5.32** (red). **(bottom)** TDDFT calculated absorption spectra of **5.31** (black) and **5.32** (red).

excitation means the ground-state is better stabilized by polar solvent, and a blue-shift would occur upon increasing solvent polarity. The orientation was chosen as a simple scale to account for the polarity of the solvent medium, and is a function of the dielectric constant (ϵ) and refractive index (n) of the solvent:

$$\Delta f = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \quad (5.1)$$

The first term of the equation, dependent on ϵ , is the nuclear polarizability, and quantifies the relatively slow motion of the solvent's molecular dipole in response to the dye's electric field. The second term, a function of n , accounts for the electrons' polarization in response to the local electric field. The difference between the two terms yields the impact of molecular reorientation around the excited dye.⁵³ Absorption of a photon is a fast process, occurring within a few femtoseconds (10^{-15} seconds). Within that time frame, atomic nuclei can be considered immobile

Table 5.1 – Molar extinction coefficients of **5.31** and **5.32**^a in various solvents.

Solvent	5.31		5.32	
	λ (nm)	ϵ^b (M ⁻¹ cm ⁻¹)	λ (nm)	ϵ^b (M ⁻¹ cm ⁻¹)
Hexanes	468	67700	-	-
	358	70500	-	-
	331	65900	-	-
	274	64100	-	-
Toluene	477	67000	-	-
	366	65000	-	-
	341	61200	-	-
1,1,2,2-tetrachloroethane	502	59000	500	54000
	383	56800	426	90700
	354	54400	324	90000
Ethyl acetate	468	67300	-	-
	359	69900	-	-
	335	69200	-	-
	276	67500	-	-
Tetrahydrofuran	470	71200	-	-
	361	73200	-	-
	338	70700	-	-
	277	67500	-	-
DCM	488	64300	-	-
	372	62400	-	-
	345	60800	-	-
	282	68600	-	-
Acetone	470	66200	-	-
	359	69300	-	-

^aDue to solubility issues, accurate measurements for **5.32** could only be performed in 1,1,2,2-tetrachloroethane.^bMolar extinction coefficient.

per the Born-Oppenheimer approximation. As a result, the solvation shell is considered static and cannot rearrange itself to respond to the newly formed dipole (*i.e.*, the Franck-Condon principle).⁵⁴ Only the polarization of electrons on solvent molecules is sufficiently fast to react to the excitation process. This model of polarizability is universal, or independent of the solute, and can essentially be viewed as a dipole (chromophore) sitting in a continuous medium of uniform

dielectric constant (the solvent medium). Specific interactions, namely hydrogen-bonding and charge-transfer complexes with solvent molecules, are not covered by this model. Absorption measurements showed no linear dependence between the maximum absorption wavelength of the lowest energy transition and the polarity of the solvent. In contrast, TDDFT calculations performed in simulated solvent cavities predict a bathochromic shift of the charge-transfer band with increasing solvent polarity. However, the computational model treats the system exactly as described above (*i.e.*, a dipole sitting in a continuous medium) and does not include solvent-specific interactions. As such, the almost perfect correlation observed between the predicted absorption wavelength and the solvent's orientation polarizability and the discrepancy with the experimental results are unsurprising.

5.31 displays photoemissive properties in solution-state that are strong-enough to be appreciated by the naked eye. It became rapidly apparent that this emission was also highly solvent dependent, and gradually ranged from green to orange upon increasing the polarity of the solvent. While HATN derivatives have been shown to exhibit fluorescence, few reports have been published on their solvatochromic behavior. Excluding cases where the spectral shifts with different solvents were due to aggregation rather than a true polarity effect, the only reported cases for such behavior are for shorter HATP cores who all possess a donor-acceptor structure,^{19,55–57} as is the case here. Solution emission measurements confirmed the sensitivity of the fluorophore in regards to the solvent (Table 5.2), and showed the excitation spectrum to be in good agreement with its absorption profile. As observed in Figure 5.9, a bathochromic shift of the emission band occurs with increasing solvent polarity. This marked dependence of fluorescence on its environment in regards to absorption can be explained by the photophysical processes occurring at the molecular level.⁵⁸ Unlike absorption, which occurs very rapidly, photoluminescence is relatively slow, typically exhibiting lifetimes on the order of nanoseconds (10^{-9} seconds). Comparatively, molecular movements and vibrations are 10-1000 times faster, signifying that solvent molecules, which were considered immobile during the absorption process, now have ample time to move and rearrange themselves in a more stable fashion in response to the excited dye. Intermolecular interactions between the solvent molecules and the emitter at equilibrium can lead to enhanced stabilization/destabilization of the excited state, which translates as a shift in the emission profile. This behavior can be modeled in terms of the Lippert-Mataga model,⁵³ which linearly relates the Stokes shift of a fluorophore (the energy

difference between the maximum absorption and emission wavelengths of a given transition) to the orientation polarizability of the solvent, the ability of the solvent to stabilize a dipole moment. **5.31** was found to follow a Lippert-Mataga relationship (Fig. 5.9), and exhibits Stokes shifts ranging between approximately 1000 cm⁻¹ (0.124 eV) in non-polar hexanes to 4500 cm⁻¹ (0.558 eV) in polar acetone.

Table 5.2 – Spectroscopic^a properties of **5.31** and **5.32**.

Solvent	Δf^b	5.31				5.32			
		$\lambda_{\max}^A$ (nm)	$\lambda_{\max}^{em}$ (nm)	S.S. ^c (cm ⁻¹)	QY ^{d,e} (%)	$\lambda_{\max}^A$ (nm)	$\lambda_{\max}^{em}$ (nm)	S.S. ^c (cm ⁻¹)	QY ^{d,e} (%)
Hexanes	0.0011	468	493	1084	17	--	--	--	--
Toluene	0.016	477	522	1807	19	410	577	2277	7.0
TCE	0.19	502	591	3000	9	426	664	3056	1.4
EtOAc	0.20	468	556	3382	13	--	--	--	--
THF	0.21	470	557	3323	12	401	625	3493	2.4
DCM	0.218	488	580	3250	9	417	656	3696	0.5
Acetone	0.284	470	597	4526	7	--	--	--	--

^aSolution measurements performed by exciting at 480 nm. ^bOrientation polarizability. ^cStokes shift. ^dQuantum yield of fluorescence. ^eAverage determined relative to fluorescein in 0.1 M NaOH ($\Phi = 0.91$) and Rhodamine G in EtOH ($\Phi = 0.95$).

Furthermore, it can be seen that the emission profile in hexanes is narrower and better defined than that for other solvents, where a structure-less emission profile is observed. This is justified by the donor-acceptor structure of the molecule, which is composed of an electron-accepting HATN core with electron-donating thienyl rings on the periphery.¹⁹ Since the molecule is not fused and the thienyls can rotate about the C-C bond, the conformation of the heterocyclic rings can twist between fully coplanar and orthogonal to the core. In non-polar solvents, the planar conformation of the luminogen is stabilized by conjugation, and as a result only partial charges form on the framework, yielding a locally excited (LE) state. If a complete charge-transfer from the donor (D) to the acceptor (A) occurs, D-A twisting generally occurs, and a perpendicular structure ensues. This internal charge-transfer (ICT) state yields a charged intermediate, and it is thus favored in polar solvents, which stabilize the resulting dipole more efficiently.^{59,60} The ICT state, by virtue of the increased energy level of its non-conjugated HOMO,⁶¹ displays a narrower band gap than the LE state, which contributes, in addition to the

effect of the dielectric medium, to the red-shift of the emission maximum.⁶² The broader signature observed in more polar solvents can then be ascribed to stabilization of the ICT state and the greater degree of vibrational freedom of the resulting structure.^{63,64} Relative quantum yield measurements were performed on **5.31** in the different solvents, and showed that the efficiency steadily grows weaker with increasing solvent polarity, ranging from 19% in toluene to 7% in acetone. While the increased solvent polarity in itself can be at cause due to interactions with the excited-state,⁶⁵ the additional degree of torsional freedom found in the ICT state, itself promoted by more polar solvents, can also be held accountable for the lower quantum yield of emission, as rotational motions of the thienyl groups act as non-radiative relaxation pathways.⁶⁶

5.2.5 The Effects of Ring Cyclization on the Optical Properties of Thienyl-appended HATN

Similar spectroscopic measurements were performed on fused derivative **5.32**, albeit in fewer solvents due to solubility issues. Of the seven solvents investigated for **5.31**, only toluene, tetrahydrofuran, dichloromethane and 1,1,2,2-tetrachloroethane solvated the fused HATN sufficiently to permit partial characterization. Again, the absorption patterns, although shifted, are similar throughout the different solvents (Fig. 5.12) and correlate well with what was predicted by TDDFT (Fig. 5.11). These shifts do not particularly correlate with solvent polarity, positively or negatively, similarly to uncyclized **5.31**. TCE solvated **5.32** sufficiently well to allow precise measurement of the molar extinction coefficient which revealed increased absorptivity ($\epsilon_{\text{max}} = 90\,700\text{ M}^{-1}\text{cm}^{-1}$) in regard to the uncyclized derivative, as a result of the complete conjugation of the HATN core with the thienyl moieties. Fluorescence measurements (Fig. 5.12) are also found to follow Lippert-Mataga behavior (Fig. 5.12), a linear trend between the Stokes shift and the solvent polarity, with slightly increased Stokes shifts ranging between 2300 and 3700 cm^{-1} . This increased Stokes shift was accompanied by an overall decrease in quantum yield of emission upon cyclization. Again, the trend between the quantum yield and the orientation polarizability is similar to what was observed pre-cyclization (*i.e.*, a decrease in emission intensity with increasing solvent polarity), and ranges from 7% in toluene to 0.5% in DCM. Unlike **5.31**, **5.32** is devoid of flexibility, and no extensive twisting can occur upon excitation. Although the HOMO and LUMO are found to be centered mostly on the outer dithienobenzene systems and the central HATN core respectively (Fig. 5.13), a true ICT state is

unlikely due to the full conjugation of the framework. In that case, the steady drop in quantum yield with increasing polarity would be due entirely to solvent polarity effects. Overall, the increased Stokes shift and diminished quantum yields upon cyclization of the thienyl rings are likely a result of the fully planar discotic structure of the luminogen that can facilitate head-on aggregation in solution and which has been shown to have similar effects on luminescence.⁶⁷

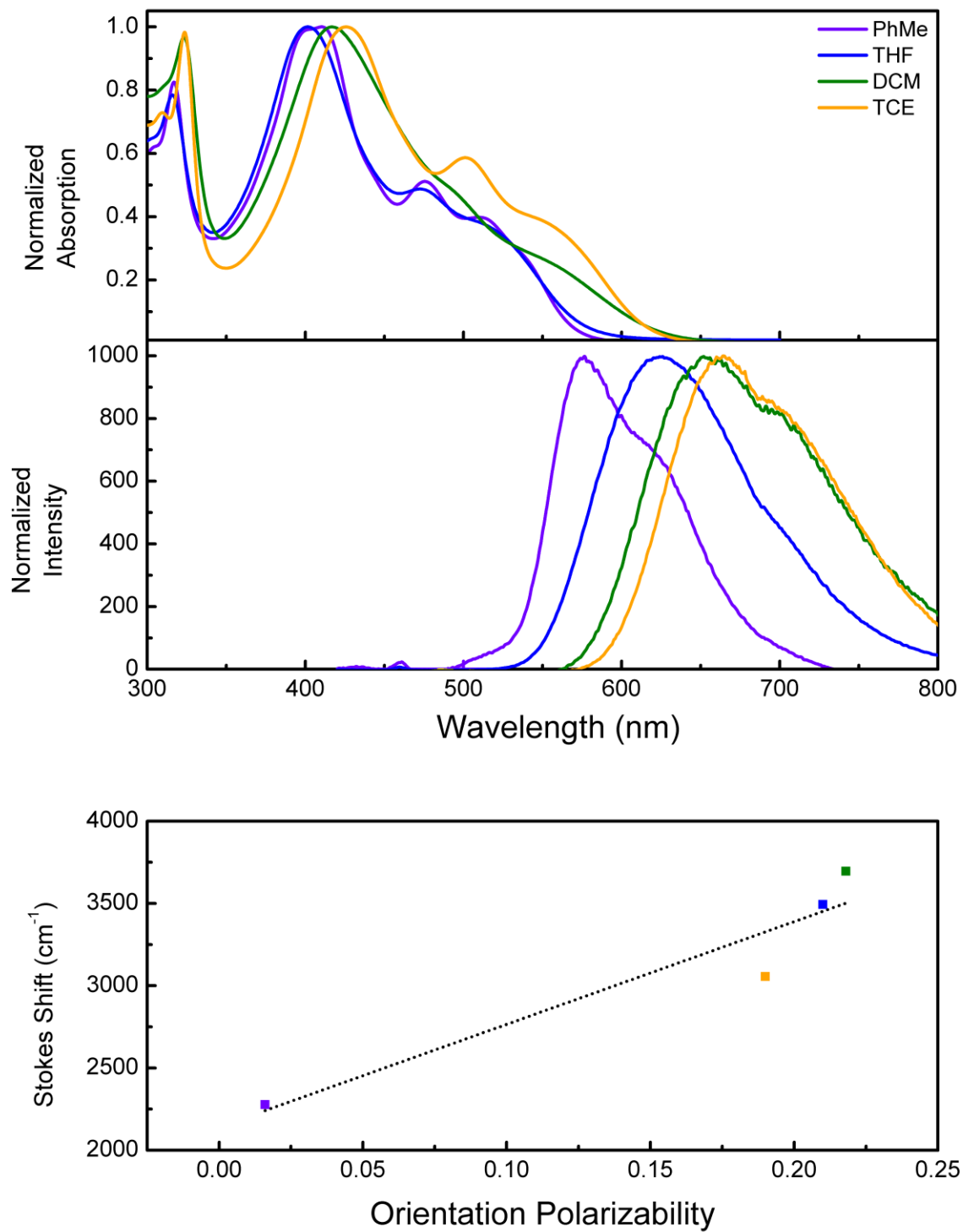


Figure 5.12 - **(top)** Normalized experimental absorption and **(middle)** photoluminescence spectra of **5.32** in solvents of various polarities. **(bottom)** Lippert-Mataga plot that shows the dependence of **5.32** Stokes shift on solvent polarity parameter Orientation polarizability. Linear fit: $m = 6242$, $b = 2141$ ($R^2 = 0.9037$)

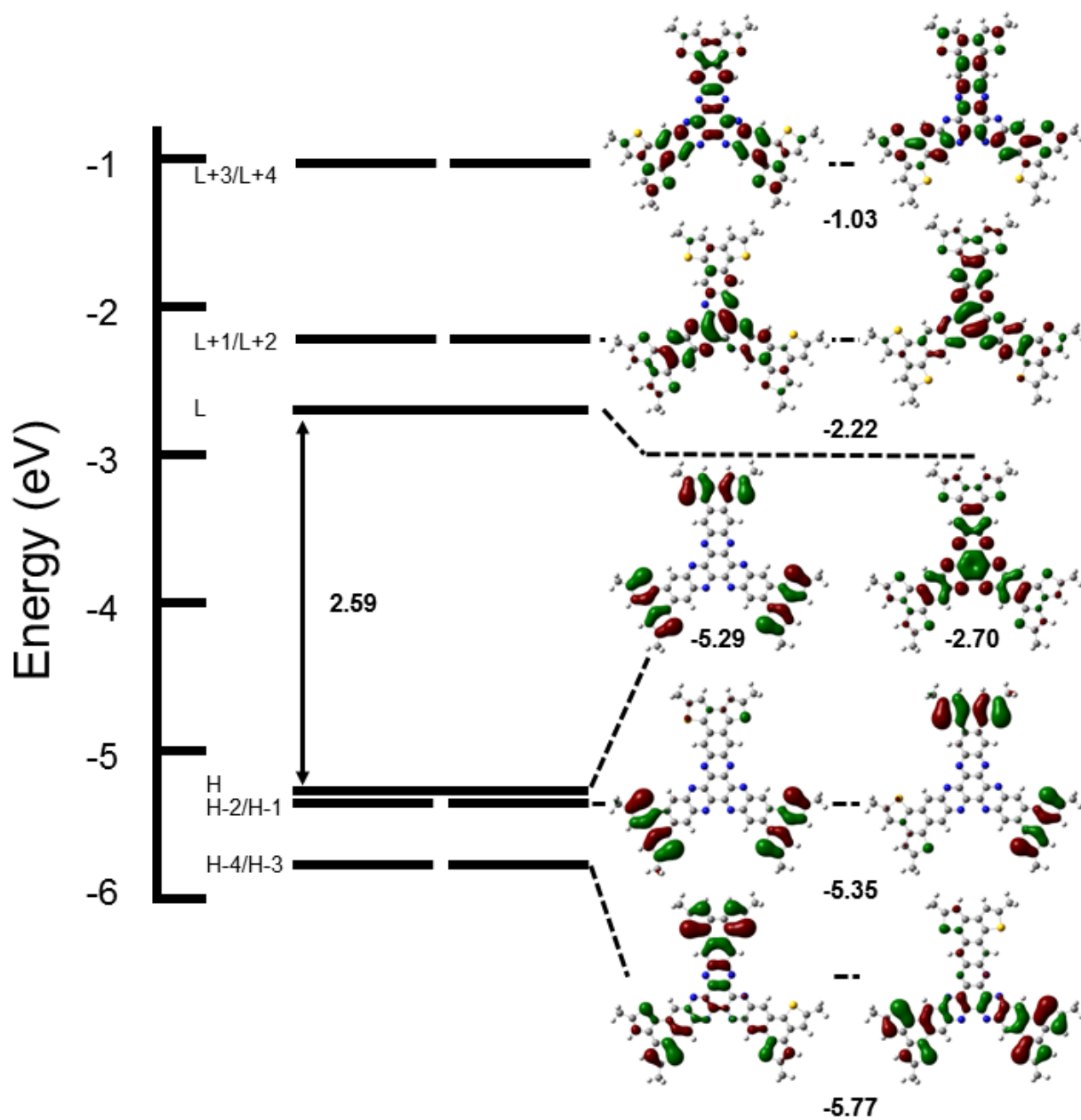


Figure 5.13 – Energy level diagram and frontier molecular orbitals of 5.32.

5.2.6 X-ray Diffraction Study of the Uncyclized HATN

Crystals of sufficient quality for single crystal X-ray diffraction analysis were obtained for **5.31** as bright red needles by slow cooling and evaporation of a dilute 5:1 dichloromethane/methanol solvent mixture. Despite our best efforts, crystals for **5.32** could not be obtained. Crystallographic data for the obtained solid can be found in Appendix Table A.2.

5.31 crystallized in the triclinic P-1 space group, and the unit cell is composed of six molecules: two product and four co-crystallized dichloromethane molecules (Fig. 5.14). While disorder is observed in the butyl chains due to their rotational freedom, an acceptable degree of disorder is found in the HATN core and thienyl rings. The core is mostly planar, with an average deviation from the mean plane of 0.110 Å. A slight twisting of approximately 2° occurs between the outermost and central carbons of the HATN core, mainly on two of the three outer branches. The aromaticity of the system is confirmed by the C-N and C-C bond lengths, which fall between 1.316-1.372 and 1.367-1.468 Å, respectively, and are both on-par with aromatic C-N and C-C bonds. While the HATN core is fairly planar, the thienyl rings are twisted with respect to the heterocyclic core, with angles varying from 21-54°, due to steric constraints.

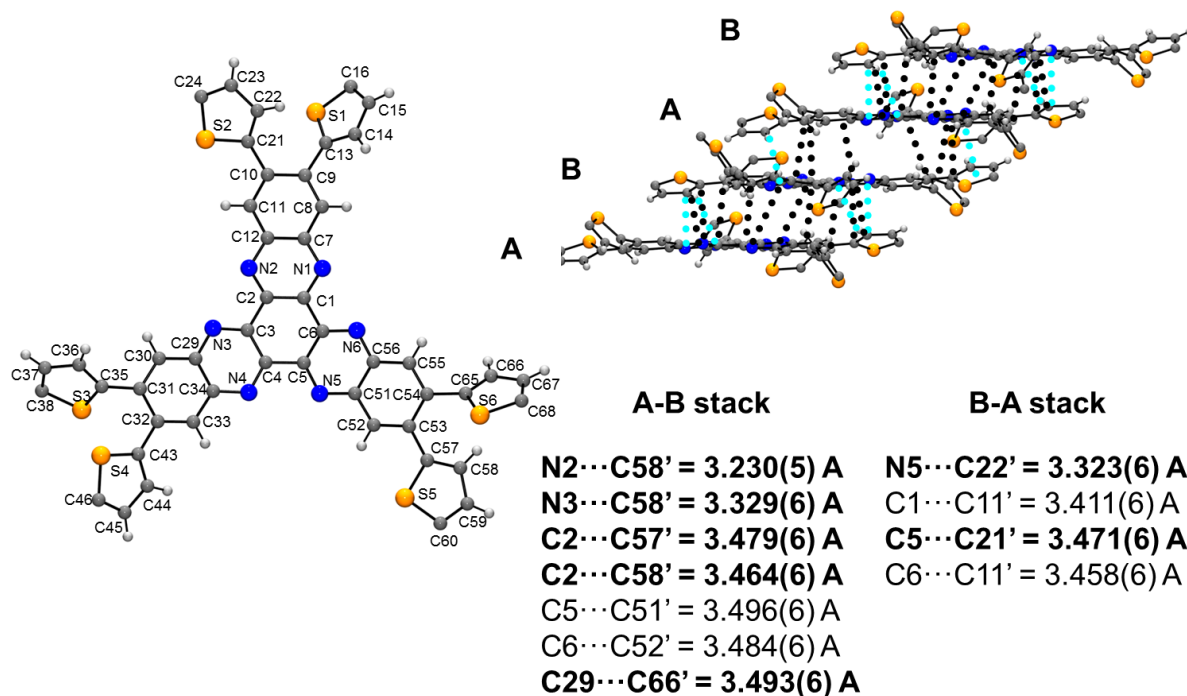


Figure 5.14 - (left) Crystal structure of **5.31** showing atom numbering. **(top right)** Side view of the vertical stacking and the resulting ABAB stacking motif with close intermolecular contacts highlighted with dotted lines. C...C' contacts are shown in black, C...N' in cyan. In both cases, butyl chains were omitted for clarity. (*n.b.* the butyl chains are still included in the numbering of the atoms). **(bottom right)**. Close intermolecular contacts along the π -stack. Bolded contacts denote donor-acceptor(thienyl-HATN) interactions.

Multiple close-contacts between neighboring molecules are observed and give the crystal a brick-like arrangement, where the “walls” are held together by interdigitation of butyl chains. Within a given slice, lateral contacts occur between hydrogens on the thienyl rings and butyl chains ($\text{H40}\cdots\text{H18}' = 2.366 \text{ \AA}$, $\text{H39}\cdots\text{C14}' = 2.851 \text{ \AA}$, $\text{H47}\cdots\text{C66}' = 2.980 \text{ \AA}$, $\text{H45}\cdots\text{H67}' = 2.458 \text{ \AA}$). Although important to crystal packing, these contacts, along with the interdigitation of the butyl chains and the interactions with solvent molecules, are not conducive to charge mobility, such that charge transport should occur preferentially vertically along the stacking axis. Upon this vertical axis, stacking occurs in an ABAB fashion, with two non-equivalent dimers (and contacts) formed between AB and BA, and is dominated by donor-acceptor interactions between the thiophene rings and the HATN core, respectively.

5.3 Conclusions

To conclude, the HATN core was successfully π -extended with thienyl arms, and characterized using optical spectroscopy, computational calculations and single crystal X-ray diffraction to investigate the impact of π -extension on the heterocyclic core's optoelectronic and structural properties. Results showed an improvement in light absorptivity and the apparition of a charge-transfer band upon conjugating the electron-deficient core with electron-donating thienyl rings. The resulting fluorescence exhibited noticeable solvatochromism that followed Lippert-Mataga's behavior (*i.e.*, a linear increase in the Stokes shift with increasing solvent polarity) along with pronounced internal charge transfer character in more polar solvents. Furthermore, the expended HATN system crystallized in a brick-like fashion in the solid state, and exhibited a structure dominated by numerous intermolecular contacts along the π -stacking axis. Cyclization of **5.31** to yield **5.32** was also achieved *via* oxidative cyclodehydrogenation. While a solid-state structure could not be obtained, optical studies show similar trends to what was observed in the uncyclized precursor, albeit with lower emission efficiency, likely due to enhanced aggregation of the fully planar molecule. While still preliminary, this work lays the groundwork for the preparation and study of a library of π -extended HATN derivatives that could exhibit interesting device performance, namely for transistors, light-emitting diodes and sensors.

5.4

Experimental methods

5.4.1 General Procedures

Triphenylphosphine (PPh_3), 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), iron trichloride (FeCl_3) (Sigma); trifluoroacetic acid (TFA), palladium dichloride (PdCl_2) (Oakwood) were commercially obtained and used as received. 5-tributyl(5-butylthiophen-2-yl)stannane,⁶⁸ hexaketocyclohexane,⁴¹ 4,5-dibromo-1,2-phenylenediamine³⁴ were prepared as previously reported. All solvents were ACS grade; dry solvents were obtained by passing them through activated alumina on a J.C. Meyer solvent purification system. Unless specified otherwise, NMR spectra were run in CDCl_3 solutions at room temperature on a Bruker Avance 400 MHz spectrometer and spectra were referenced to the deuterated solvent peak at 7.26 and 77.16 ppm for proton and carbon respectively. IR spectra were recorded on an Agilent Technologies Cary 630 FT-IR spectrometer.

5.4.2 Optical Spectroscopy

UV-visible absorption spectra were measured with a Varian Cary Series 6000 UV-Vis-NIR spectrophotometer and the fluorescence spectra were obtained using a Varian Cary Eclipse fluorescence spectrometer. UV-Visible and fluorescence spectra were measured in HQGC-grade chlorobenzene solutions with 1 cm precision quartz cuvettes.

5.4.3 Crystal Growth

Red needles of **5.31** suitable for X-ray analysis were grown by slowly evaporating a saturated dichloromethane/methanol solution at room temperature.

5.4.4 X-ray Measurements

The crystal of **5.31** was mounted on a thin glass fiber using paraffin oil. Prior to data collection, the crystal was cooled to 200(2) K. The data was collected on a Bruker AXS single-crystal diffractometer equipped with a sealed Mo tube (wavelength 0.71073 Å) and APEX II CCD detector. The raw data collection and reduction were done with Bruker APEX II software package.⁶⁹ Semi-empirical absorption corrections based on equivalent reflections were applied.⁷⁰

Systematic absences in the diffraction dataset and unit-cell parameters were consistent with triclinic P-1(#2) space group. The structure was solved by direct methods and refined with full-matrix least-squares procedures based on F^2 , using SHELXL⁷¹ and WinGX⁷². All non-H atoms were refined anisotropically. The positions of hydrogen atoms were calculated based on the geometry of related non-hydrogen atoms.

One of the chloroform molecules is disordered over two positions Cl(1A), Cl(1B) with 0.77(3) : 0.23(3) occupancy ratio. The C(17)-C(20) butyl group is disordered over two positions with 0.703(14) : 0.297(14) occupancy ratio. The C(39)-C(42) butyl group is disordered over two positions with 0.780(11) : 0.220(11) occupancy ratio. The C(47)-C(50) butyl group is disordered over two positions with 0.654(16) : 0.346(16) occupancy ratio. The C(61)-C(64) butyl group is disordered over two positions with 0.735(18) : 0.265(18) occupancy ratio. The C(69)-C(72) butyl group is disordered over two positions with 0.617(16) : 0.383(16) occupancy ratio.

A combination of restraints was applied to these disordered groups. The atomic displacement parameters were refined using RIGU enhanced rigid-bond restraints and selectively SIMU. The bond distances and angles (1,3-distances) of butyl groups were restrained using SADI and DFIX commands. All hydrogen atoms were placed in calculated positions. Displacement ellipsoid plots were produced using ORTEP,⁷³ and uncertainties were estimated using PLATON.⁷⁴

5.4.5 Computational Chemistry

All calculations were carried out using the Gaussian09 program package.⁷⁵ The geometries of the studied compounds were investigated using the hybrid density functional B3LYP with the 6-31G(d,p) basis set. Optimized structures were used to examine the orbital energies and HOMO-LUMO gaps. The archival files for the optimized structures of **5.31** and **5.32** can be found in the Appendix Section A.3. The calculated UV-Vis absorption spectra and excitation energies were determined using TDDFT which employed the optimized B3LYP ground states. A polarized continuum solvent model with various solvents was employed, and twenty excited states were considered.

5.4.6 Synthetic Procedures

Preparation of 5.31. **5.33** (783 mg, 2.51 mmol) and **5.41** (3.60 g, 7.87 mmol) were refluxed for 1 h in EtOH/AcOH (100mL, 9:1 ratio) to afford a dark red solution. After removal of volatiles under reduced pressure, the residue was poured onto H₂O, and the product was extracted into EtOAc, washed with sodium bicarbonate and brine, dried over MgSO₄ and concentrated to afford the crude product as a black-red solid. The crude was dissolved in a 3:1 hexanes/ethyl acetate solvent mixture and filtered through a short silica plug. Elution with a 1:1 hexanes/ethyl acetate solvent mixture yielded a clear orange filtrate, which was concentrated to produce the target product as a red-orange solid (2.50 g, 82% yield). ¹H NMR (δ, CDCl₃, r.t., 400 MHz): 8.70 (s, 6H), 6.94 (d, J=3.40 Hz, 6H), 6.73 (d, J=3.40 Hz, 6H), 2.86 (t, J=7.5Hz, 12H), 1.70 (m, 12H), 1.44 (m, 12H), 0.97 (t, J=7.30 Hz, 6H). ¹³C NMR (δ, CDCl₃, r.t., 400 MHz): 148.8, 143.8, 142.8, 139.1, 138.4, 131.2, 128.6, 124.7, 33.8, 30.0, 22.3, 14.0. IR $\nu_{\max}$ (cm⁻¹): 3421.00(w), 2954.70(m), 2924.97(m), 2855.74(m), 1453.18(s), 1361.84(m), 1245.06(m), 1087.56(s), 1031.29(m), 887.28(m), 794.98(s).

Preparation of 5.32. A degassed solution of anhydrous FeCl₃ (615 mg, 3.79 mmol) in MeNO₂ (2 mL) was added dropwise to a solution of **5.31** (304 mg, 0.250 mmol) in dry degassed DCE (40 mL) at 60 °C. The reaction mixture was stirred for 45 min at 60 °C. The reaction was quenched by the addition of 5 mL of MeOH and stirred 15 min, following which volatiles were removed under reduced pressure. The residue was slurried in MeOH and filtered to yield a red-brown solid. The solid was dissolved in DCM, washed twice with ammonium hydroxide (including filtration over Celite to remove insoluble iron hydroxide), sodium bicarbonate and brine, and volatiles were removed under reduced pressure to afford a dark brown solid. Double recrystallization from a 1:1 TCE/AcOH solvent mixture produced the target product as a dark red powder (150 mg, 50% yield). ¹H NMR (δ, C₂D₂Cl₄, r.t., 300 MHz): 8.54 (s, 6H), 7.06 (s, 6H), 2.91 (t, J=7.5Hz, 12H), 1.86 (m, 12H), 1.58 (m, 12H), 1.12 (t, J=7.30 Hz, 6H). IR $\nu_{\max}$ (cm⁻¹): 2951.51(m), 2925.57(m), 2854.67(m), 1409.70(s), 1360.99(s), 1282.93(m), 1078.79(s), 868.42(m), 821.86(m).

Preparation of 4,5-bis(5-butylthiophen-2-yl)benzene-1,2-diamine (5.41). PdCl₂ (100 mg, 0.564 mmol) and PPh₃ (300 mg, 1.14 mmol) were added to a degassed solution of 5-butyl-2-tributylstannyl-thiophene (23.5 g, 54.8 mmol) and **5.37** (6.31 g, 23.7 mmol) in dry toluene (35

mL) under nitrogen, and refluxed overnight. Upon cooling, the reaction mixture was filtered to eliminate solid impurities, and the removal of volatiles under reduced pressure afforded a black oil. Vacuum distillation (0.6 mmHg, 180 °C) removed tin by-products and leftover Stille reagent as a clear golden distillate and left a black oil that thickened upon cooling. The residue was dissolved in a 3:1 hexanes/ethyl acetate solvent mixture, filtered through a short silica plug and eluted with a 1:1 hexanes/ethyl acetate solvent mixture to afford a clear amber filtrate. Removal of volatiles under reduced pressure afforded the target product as a brown oil (7.64g, 83% yield). ¹H NMR (δ, CDCl₃, r.t., 400 MHz): 6.81 (s, 2H), 6.59(d J=3.50 Hz, 2H), 6.57(d J=3.50 Hz, 2H), 3.44 (bs, 4H), 2.75 (t, J=7.5Hz, 4H), 1.62 (m, 4H), 1.37 (m, 4H), 0.92 (t, J=7.40 Hz, 6H). ¹³C NMR (δ, CDCl₃, r.t., 400 MHz): 145.6, 140.7, 134.2, 126.1, 125.9, 123.7, 118.9, 33.9, 29.9, 22.2, 14.0. IR ν_{max} (cm⁻¹): 3330.62(w), 3065.38(w), 2954.62(s), 2926.21(s), 2855.51(s), 1621.87(s), 1560.37(s), 1508.76(s), 1466.30(s), 1458.76(s), 1438.38(m), 1279.07(s), 1235.08(m), 1156.44(m), 969.62(w), 868.24(m), 799.41(s).

The free base **5.41** (5.11 g) could be converted to the hydrochloride salt by dissolving in refluxing toluene and slowly adding concentrated HCl (5mL). Upon cooling to r.t., the resulting solid was filtered off and copiously rinsed with diethyl ether to afford a tan powder (6.19 g, 80% yield). ¹H NMR (δ, CDCl₃, r.t., 400 MHz): 7.52 (s, 2H), 6.56(m, 10H), 2.62 (t, J=7.6Hz, 4H), 1.48 (m, 4H), 1.23 (m, 4H), 0.78(t, J=7.30 Hz, 6H). IR ν_{max} (cm⁻¹): 3443.08(w), 3341.15(w), 2924.42(s), 2848.41(s), 2562.34(s), 1622.79(m), 1582.10(m), 1501.48(s), 1481.35(s), 1232.04(m), 1141.59(m), 1115.36(s), 895.14(m), 804.40(s). Before use in preparing **5.31**, the free base could be regenerated by adding three equivalents of triethylamine to an ethanolic solution of the salt and stirring for 5 min before acidifying with excess acetic acid.

5.5

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Chapter 6

Conclusion

6.1

Conclusions

The overarching theme of this thesis was the study of structure-property relationships in organic molecules as potential active materials in electronic devices. To this end, the preparation and characterization of novel compounds comprised of various frameworks was achieved and reported therein.

Chapter 3 introduced analogues of the heterocyclic eight-membered ring 1,5-dithia-2,4,6,8-tetrazocine (DTTA) appended with thienyl rings as side-substituents, which included the first π -extended DTTAs ever reported. The impacts of both substitution pattern and conjugation length on the optoelectronic and solid-state properties of the resulting compounds were investigated. Substitution of single-thienyl derivatives led to minor but consistent changes in the electronic structure with varying substituents, as predicted *via* computational methods and confirmed by optical spectroscopy and electrochemistry. A more drastic effect (*i.e.*, reduced band gap, increased light absorption) was seen upon extension of the conjugation with an additional thienyl ring on both sides of the DTTA, owing in both cases to the increased π -surface. Single-crystal X-ray diffraction measurements were also performed to analyze the impact of the molecular structure on intermolecular contacts. In all cases, lamellar π -stacking was observed, and intra-stack contacts dominated the packing in all derivatives save for the brominated analogue, where instead inter-stack halogen-halogen interactions prevailed. This preference for intra-stack interactions can be rationalized by both the strong intermolecular donor-acceptor interactions present, as well as the use (in some cases) of solubilizing hexyl chains that act as insulating sheaths surrounding the conductive aromatic systems.

Chapter 4 followed up on work previously established in the Brusso group, specifically the design of π -expanded 2D thienoacenes. While 2D extension of conjugation of the core tetrathienoanthracene (TTAn) with oligothieryl chains of increasing lengths was previously achieved, device performance remained on-par with the parent thienoacene. This was rationalized in terms of the rotational freedom of the oligothieryl substituents, which could

disrupt packing in solution-processed thin films. Consequently, we turned toward the use of thieno[3,2-b]thiophene (TT) as a building block for the construction of rigid π -expanded thienoacenes. The TT moiety was incorporated either as the “arms” and/or the “core” of the star-shaped frameworks, thus influencing the overall optoelectronic and solid state properties. Comparative studies of the different derivatives’ optoelectronic properties were performed by optical, electrochemical and computational methods. Cyclization of the paddle-wheel shaped precursor into the planar and rigid product was corroborated by a concomitant sharpening and bathochromic shift of the absorption band. A sharpening of the absorption band also confirmed the increased rigidity of the novel thienacenes in regards to the previous oligothiényls analogues. The use of TT arms was also combined with incorporation of electronegative nitrogen in the core, which was shown by electrochemical methods to stabilize the HOMO, a desirable outcome for enhanced air-stability. Conversely, the use of the electron-rich TT core resulted in a widened band gap. This, along with the asymmetry of the molecular orbital distribution of these derivatives, could be exploited in the strategic design of organic semiconductors (*vide infra*).

Chapter 5 consisted of preliminary work toward extending the discotic electron-deficient hexaazatrinaphthylene (HATN) core with fused benzodithiophene π -systems. Both the cyclized derivative and its uncyclized precursor were prepared and characterized to study the impact of aromatization on the material’s properties. It was rapidly recognized that the uncyclized **5.31** exhibited noticeable positive emission solvatochromism as a result of the concentric donor-acceptor structure. Furthermore, the derivative was found to crystallize in a brick-like arrangement dominated by numerous intra-stack donor-acceptor contacts. While crystals of sufficient quality for an X-ray diffraction could not be obtained to confirm the structure of the final cyclized product, NMR and optical characterization were congruent with the target product. A concomitant increase in the Stokes shift and decrease in quantum yield upon cyclization were consistent with aggregation in solution, as one could expect from a rigid discotic π -conjugated molecule.

6.2 Future Work

The emphasis of this work has been to study the relationship between the molecular structure of novel OSCs and their electronic and solid-state properties. While these molecular studies reveal important data about the OSCs, the ultimate gauge of the structure-property

relationship remains their incorporation into devices, as-well as the study of their solid-state properties (*e.g.*, absorbance, photoluminescence, film morphology, etc.). In that regard, collaborative work with the Lessard group from the Faculty of Engineering at the University of Ottawa, which has already been initiated on employing the 2D thienoacenes (Chapter 4) as active materials in organic field-effect transistors (OFETs), should be particularly fruitful. HATN derivatives (Chapter 5) remain to be tested for their OFET applicability. In both cases, device testing should provide valuable feedback toward further refining the molecular structure of OSCs. In the meantime, different avenues of research can be probed for each framework investigated in this work, and will be covered below.

Expanding the π -system of the DTTA ring by conjugating with a myriad of electron donors and acceptors has been a long-standing goal of this project. Considering the synthetic complexity of DTTA, this should be achieved through cross-coupling chemistry, hence the preparation of brominated thienyl derivatives. Unfortunately, thus far cross-coupling attempts remain unsuccessful; however, recently a successful Stille coupling reaction on a thienyl-functionalized DTTA has been reported by Zhang and coworkers using a modified catalytic system.¹ While in our hands such reactions could not be replicated, such results provide motivation that perhaps a library of DTTA derivatives may yet be realized.

The design of 2D thienoacenes can be explored in various ways. One approach would be the development of asymmetric structures. As mentioned above, thienoacenes with a TT core exhibit a preferential distribution of the frontier molecular orbitals along the alpha axis of the thienoacene, due to increased electron density of the core at these positions. Accordingly, electro-active substituents on arms at these positions should have a more pronounced effect on the optoelectronic properties, while the beta positions could be utilized for solubilizing alkyl chains. The marked difference in reactivity between the alpha and beta positions of 2,3,4,5-tetrabromothieno[3,2-b]thiophene in regards to cross-coupling reactions would contribute to make the preparation of asymmetric derivatives a straightforward achievement. Asymmetric tetrathienoanthracenes can also be realized by substituting the starting 1,2,4,5-tetrabromobenzene reagent with an appropriate tetra(iodo-bromo)benzene isomer and exploiting the enhanced reactivity of iodine atoms toward cross-coupling to selectively attach desired arms at select locations. Among others, this could be applied to the formation of thienoacene dimers.

Finally, the HATN project is still in its infancy and several avenues of research lie ahead. This includes the original goal, the use of the discotic nature of the cyclized derivatives to obtain OSC with enhanced stacking in the solid-state and, ideally, improved charge mobilities. Additionally, the uncyclized HATNs precursors are moderately strong luminescent structures with marked environmental sensitivity and could be employed in fabricating sensors and light-emitting devices. Finally, the presence of three bidentate coordination pockets within a conjugated frame makes HATN an interesting ligand for the preparation of complexes with magnetic properties, as it should promote magnetic coupling between the metals. In this regard, collaborative work with the Murugesu group has recently begun to further explore this aspect of HATN's chemistry.

6.3 Bibliography

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Appendix

A.1 Crystallographic Data

Table A.1 - Crystallographic data for DTTA derivatives from Chapter 3

	3.14^a	3.22	3.23	3.24	3.25	3.26
Formula	C ₁₀ H ₆ N ₄ S ₄	C ₂₂ H ₃₀ N ₄ S ₄	C ₁₀ H ₄ Br ₂ N ₄ S ₄	C ₂₂ H ₃₀ N ₄ S ₄	C ₁₇ H ₁₀ N ₄ S ₆	C ₃₀ H ₃₄ N ₄ S ₆
fw	310.42	478.74	468.23	478.74	474.66	642.96
Crystal System	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space Group	P2 ₁ /c	P-1	P2 ₁ /c	P2 ₁ /n	P2 ₁ /n	P-1
<i>a</i> (Å)	6.9888(10)	5.6375(5)	11.23430(10)	11.837(4)	5.6479(6)	6.6627(4)
<i>b</i> (Å)	5.6836(5)	13.6973(12)	6.04950(10)	5.482(2)	28.280(3)	9.3450(6)
<i>c</i> (Å)	16.019(2)	15.9263(14)	11.38010(10)	18.312(6)	6.4275(7)	13.5348(7)
α (°)	90	87.350(4)	90	90	90	98.497(3)
β (°)	101.822(11)	81.484(3)	106.9430(10)	92.953(12)	110.342(6)	102.934(4)
γ (°)	90	79.921(3)	90	90	90	107.792(3)
<i>V</i> (Å ³)	622.80(13)	1197.22(18)	739.843(15)	1186.8(7)	962.58(18)	760.54(8)
<i>Z</i>	2	2	2	2	2	2
<i>D</i> _{calc} (Mg·m ⁻³)	1.66	1.328	2.102	1.340	1.638	1.404
<i>T</i> (K)	293	200(2)	296(2)	200	200	200
<i>u</i> (mm ⁻¹)	0.72	0.414	6.035	0.418	0.724	0.478
2 Θ _{max} (°)	49.82	46.72	56.00	56.728	56.662	56.688
No. of total reflections	2245	9026	11597	13302	11549	7798
No. of unique reflections	1094	3309	1771	2886	2354	3723
<i>R</i> _{int}	0.016	0.0772	0.0315	0.1728	0.0722	0.0199
<i>R</i> _I , <i>wR</i> ₂ (on <i>F</i> ²)	0.035, 0.059	0.0546, 0.0831	0.0397, 0.0774	0.0746, 0.1580	0.1155, 0.1987	0.0424, 0.0853
δ^b (Å)	3.55	3.438	3.577	3.46	3.53	3.50
τ^c (°)	38.65	37.57	36.25	39.3	38.7	21.7

^aData obtained from Ref.[1]. ^b δ is the mean interplanar separation between molecules along the π -stack. ^c τ is the tilt angle between the mean molecular plane and the stacking axis.

Table A.2 – Crystallographic data for thienoacene and HATN derivatives **4.50** and **5.31** from Chapters 4 & 5.

	4.50	5.31
Formula	C ₅₃ H ₅₇ NS ₄₈	C ₇₄ H ₇₆ Cl ₄ N ₆ S ₆
fw	964.48	1383.56
Crystal System	Triclinic	Triclinic
Space Group	P-1	P-1
<i>a</i> (Å)	4.6484(2)	5.6375(5)
<i>b</i> (Å)	13.9788(7)	12.3274(10)
<i>c</i> (Å)	19.2908(9)	16.7475(14)
α (°)	105.132(2)	18.3983(15)
β (°)	90.170(3)	76.4290(10)
γ (°)	98.420(3)	88.8690(10)
<i>V</i> (Å ³)	1195.88(10)	3522.7(15)
<i>Z</i>	1	2
<i>D</i> _{calc} (Mg·m ⁻³)	1.339	1.304
<i>T</i> (K)	200	200
<i>u</i> (mm ⁻¹)	0.411	0.393
2 Θ _{max} (°)	56.924	25.250
No. of total reflections	6037	39320
No. of unique reflections	4764	12732
<i>R</i> _{int}	0.0519	0.1865
<i>R</i> _I , <i>wR</i> ₂ (on <i>F</i> ²)	0.0725, 0.1330	0.0629, 0.1421
δ^b (Å)	3.4811	-
τ^c (°)	49.777	-

A.2

TDDFT Calculated Optical Transitions

Table A.3 - TDDFT calculated optical transitions and oscillator strengths for DTTA derivatives **3.14**, **3.22** and **3.23** from Chapter 3.^a

<i>k</i>	3.14		3.22		3.23	
	E (eV)	<i>f</i>	E (eV)	<i>f</i>	E (eV)	<i>f</i>
1	2.5023	0.0458	2.3162	0.0366	2.4119	0.0365
2	3.0225	0.0000	2.7823	0.0001	2.8419	0.0000
3	3.2041	0.0000	3.1962	0.0000	3.2265	0.0000
4	3.3913	0.0000	3.3485	0.0042	3.4512	0.8468
5	3.4271	0.0000	3.3879	0.0007	3.5712	0.4388
6	3.6567	1.0472	3.5456	1.1787	3.5834	0.0000
7	4.0159	0.0000	4.0085	0.0000	4.0392	0.0000
8	4.3431	0.0106	4.2542	0.0010	4.1534	0.0000
9	4.4200	0.2376	4.3334	0.0101	4.2395	0.1170
10	4.4210	0.0000	4.3758	0.1718	4.3092	0.0000
11	4.4915	0.1257	4.4137	0.1928	4.3611	0.0106
12	4.5634	0.0000	4.4361	0.0001	4.4135	0.2288
13	4.7151	0.0000	4.7043	0.0352	4.5927	0.0000
14	4.7154	0.0392	4.7499	0.0037	4.6305	0.0002
15	4.7666	0.0000	4.7604	0.0000	4.6651	0.0000
16	5.0919	0.0130	4.9018	0.0120	4.7119	0.0000
17	5.3019	0.1207	5.1048	0.1365	4.7158	0.0000
18	5.4475	0.0010	5.2329	0.0004	4.7566	0.0331
19	5.5262	0.0010	5.2789	0.0001	4.7992	0.0000
20	5.5364	0.0382	5.4490	0.0075	4.9375	0.1385

^aTDDFT/B3LYP/6-311+G(d,p) level of theory on geometry optimized structures (where R = Me for all structures) where *k* = order of excitation energy and *f* = oscillator strength.

Table A.4 - TDDFT calculated optical transitions and oscillator strengths for DTTA derivatives **3.24**, **3.25** and **3.26** from Chapter 3.^a

<i>k</i>	3.24		3.25		3.26	
	E (eV)	<i>f</i>	E (eV)	<i>f</i>	E (eV)	<i>f</i>
1	2.4026	0.0382	2.0858	0.0175	1.9857	0.0139
2	2.8539	0.0011	2.3665	0.0041	2.2337	0.0047
3	3.1997	0.0000	2.9835	1.5882	2.9068	1.6323
4	3.2019	0.0037	3.2132	0.0006	3.2088	0.0013
5	3.2408	0.0026	3.4519	0.0199	3.3413	0.0606
6	3.5839	1.0581	3.4649	0.0852	3.4151	0.0664
7	4.0145	0.0000	3.4961	0.0403	3.4466	0.0767
8	4.2491	0.0137	3.5875	0.0751	3.4810	0.0130
9	4.3360	0.0102	3.6050	0.0802	3.5372	0.1052
10	4.4070	0.1824	3.6877	0.0034	3.6214	0.0067
11	4.4152	0.1217	3.6896	0.0009	3.6300	0.0000
12	4.4734	0.0246	3.9833	0.0003	3.8247	0.0002
13	4.5689	0.0901	3.9870	0.2722	3.8710	0.2592
14	4.6559	0.0075	4.0327	0.0000	4.0307	0.0000
15	4.7257	0.0000	4.2650	0.0059	4.1824	0.0284
16	5.0160	0.0142	4.3402	0.0025	4.2953	0.0013
17	5.1285	0.0472	4.3488	0.0114	4.3442	0.0104
18	5.3278	0.0000	4.4521	0.0057	4.4141	0.0015
19	5.3768	0.0000	4.4701	0.0823	4.4430	0.0607
20	5.4301	0.0681	4.5227	0.0001	4.4589	0.0048

^a TDDFT/B3LYP/6-311+G(d,p) level of theory on geometry optimized structures (where R = Me for all structures) where *k* = order of excitation energy and *f* = oscillator strength.

Table A.5 - TDDFT calculated optical transitions and oscillator strengths for thienoacene derivatives **4.49-4.52** from Chapter 4.^a

k	4.49		4.50		4.51		4.52	
	E(eV)	<i>f</i>	E(eV)	<i>f</i>	E(eV)	<i>f</i>	E(eV)	<i>f</i>
1	2.5844	0.0012	2.4994	0.0017	3.1585	1.0053	2.8814	1.3623
2	2.6659	0.3982	2.5040	0.6708	3.4377	0.0743	3.1553	0.1426
3	3.1367	0.0000	2.9087	0.0009	3.6433	0.0000	3.2788	0.0001
4	3.1743	2.1559	3.2268	0.0060	3.8099	0.0000	3.4304	0.0008
5	3.3815	0.0000	3.2753	1.7656	3.8990	0.0000	3.5655	0.0010
6	3.4001	0.1994	3.2810	0.0476	3.9419	0.3250	3.5955	0.5281
7	3.4545	0.4282	3.3836	0.5855	4.0167	0.0000	3.6169	0.0000
8	3.7375	0.0000	3.5249	0.0001	4.1382	0.0000	3.7884	0.0003
9	3.7980	0.0000	3.7396	0.0004	4.1892	0.0000	3.8317	0.0345
10	3.8838	0.0000	3.7695	0.1446	4.2390	0.5398	3.8567	0.9390
11	3.9209	0.0000	3.8069	0.0034	4.2592	0.0001	3.9167	0.0000
12	3.9908	0.1466	3.9171	0.0007	4.3202	0.0330	3.9582	0.1569
13	4.0053	0.0000	4.0087	0.0000	4.3842	0.0000	3.9836	0.0001
14	4.0136	0.0000	4.0321	0.0004	4.4579	0.0000	4.0215	0.0000
15	4.0512	0.0007	4.0353	0.0096	4.4880	0.3821	4.0804	0.0008
16	4.0577	0.0000	4.0593	0.0544	4.5483	0.0000	4.1464	0.2407
17	4.2035	0.0000	4.1781	0.0005	4.6176	0.0000	4.1523	0.0000
18	4.2250	0.0908	4.2027	0.0002	4.6455	0.0003	4.1794	0.0035
19	4.2906	0.0000	4.3358	0.0933	4.6704	0.0000	4.2188	0.0000
20	4.3049	0.0000	4.3566	0.0602	4.6999	0.0000	4.2545	0.0228

^aTDDFT/B3LYP/6-311+G(2d,p) level of theory on geometry optimized structures (where R = Me for all structures) where k = order of excitation energy and f = oscillator strength.

Table A.6 - TDDFT calculated optical transitions and oscillator strengths for HATN derivatives **5.31** & **5.32** from Chapter 5.^a

<i>k</i>	5.31		5.32	
	E (eV)	<i>f</i>	E (eV)	<i>f</i>
1	2.3728	0.5288	2.0792	0.0000
2	2.4229	0.4885	2.1348	0.1253
3	2.6077	0.0064	2.1349	0.1251
4	2.7005	0.0004	2.4719	0.2217
5	2.7640	0.2393	2.4720	0.2217
6	2.7697	0.0289	2.5423	0.0000
7	2.7792	0.0276	2.5989	0.0000
8	2.7871	0.0320	2.6350	0.2633
9	2.8412	0.4374	2.6351	0.2670
10	2.8547	0.4996	2.7108	1.1736
11	2.9931	0.0266	2.7109	1.1772
12	3.0008	0.0198	2.7857	0.0000
13	3.1100	0.1591	2.9638	0.0000
14	3.1172	0.1412	2.9642	0.0000
15	3.1251	0.0098	2.9844	0.1751
16	3.1308	0.1760	2.9846	0.1744
17	3.1919	0.0944	3.0304	0.0000
18	3.2022	0.0813	3.0355	0.0040
19	3.2064	0.1865	3.1410	0.0000
20	3.2161	0.0572	3.1525	0.0000

^a TDDFT/B3LYP/6-31G(d) level of theory on geometry optimized structures (where R = Me for all structures) where *k* = order of excitation energy and *f* = oscillator strength.

A.3

NMR Spectra

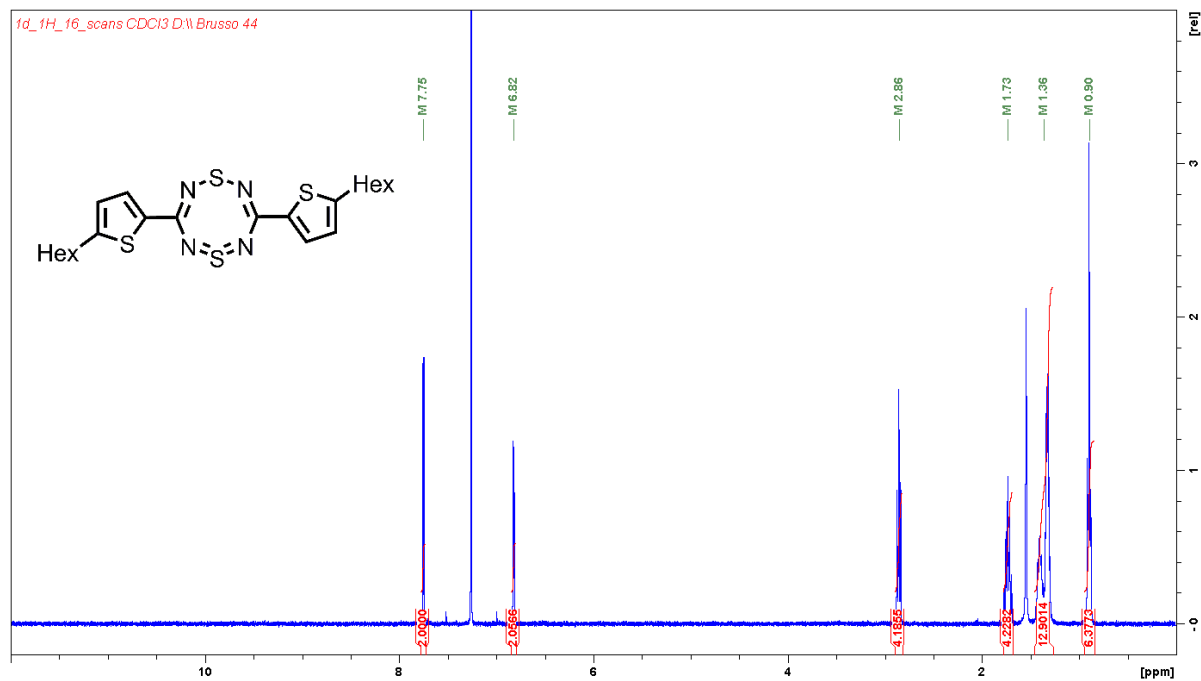


Figure A.1 - ^1H NMR spectrum of 3.22.

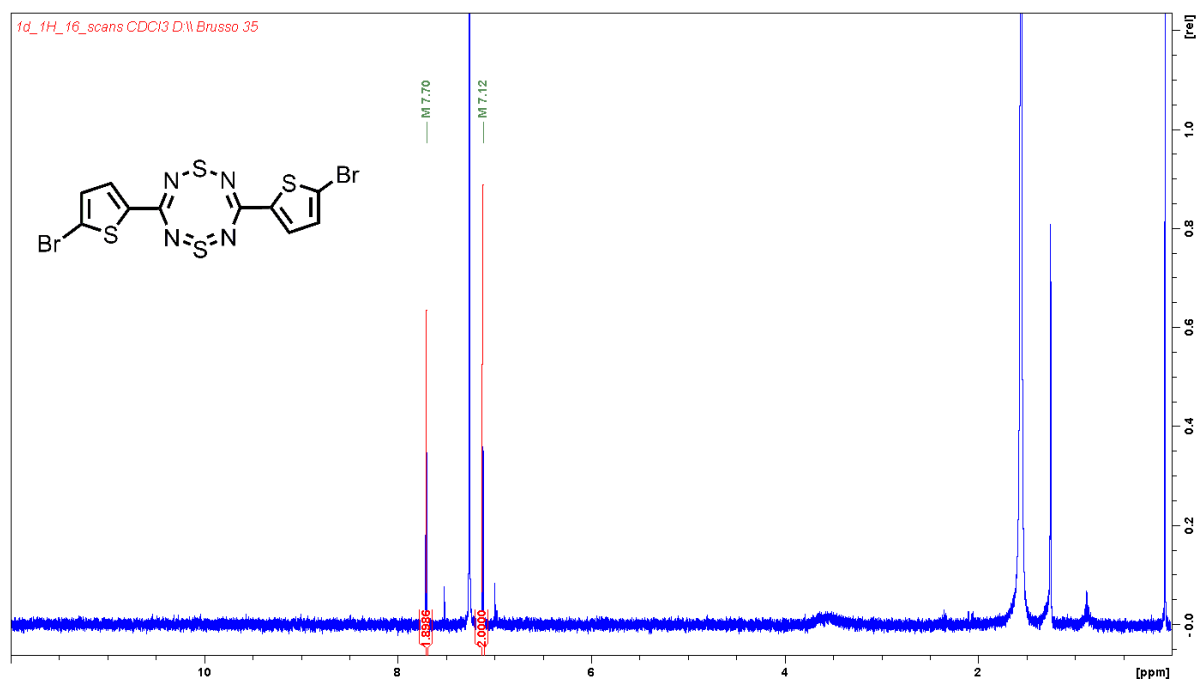


Figure A.2 - ^1H NMR spectrum of 3.23.

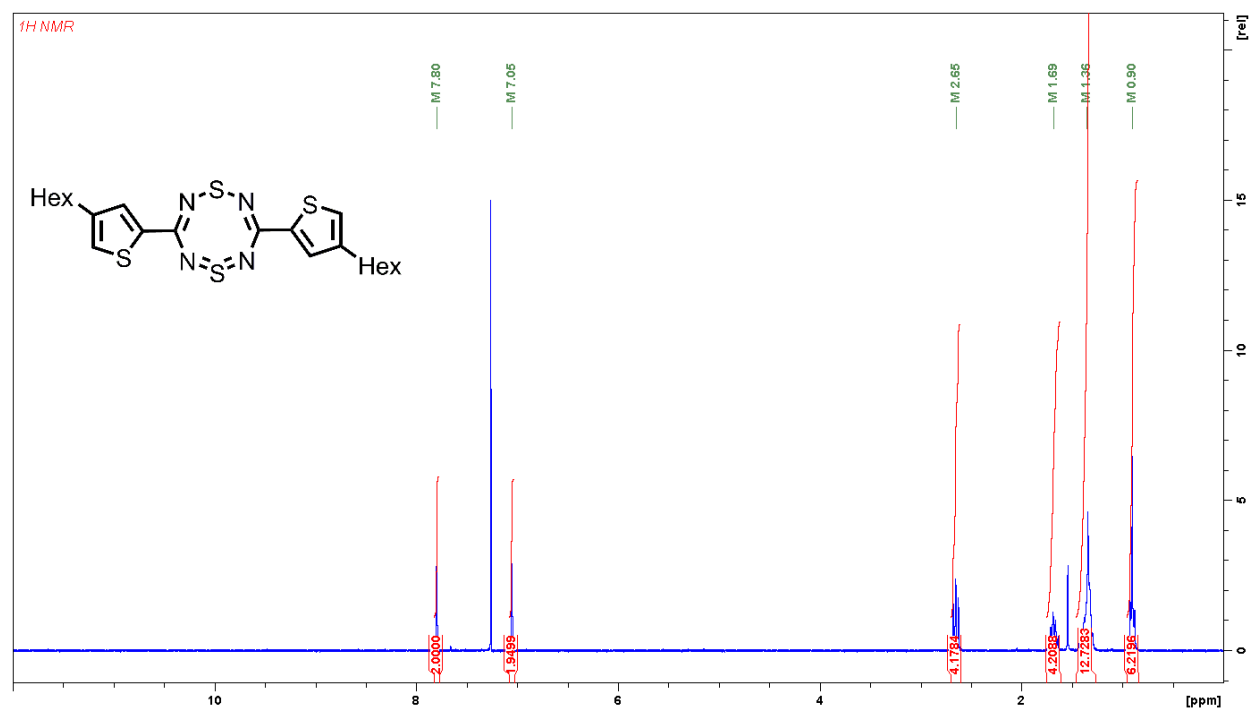


Figure A.3 - ¹H NMR spectrum of 3.24.

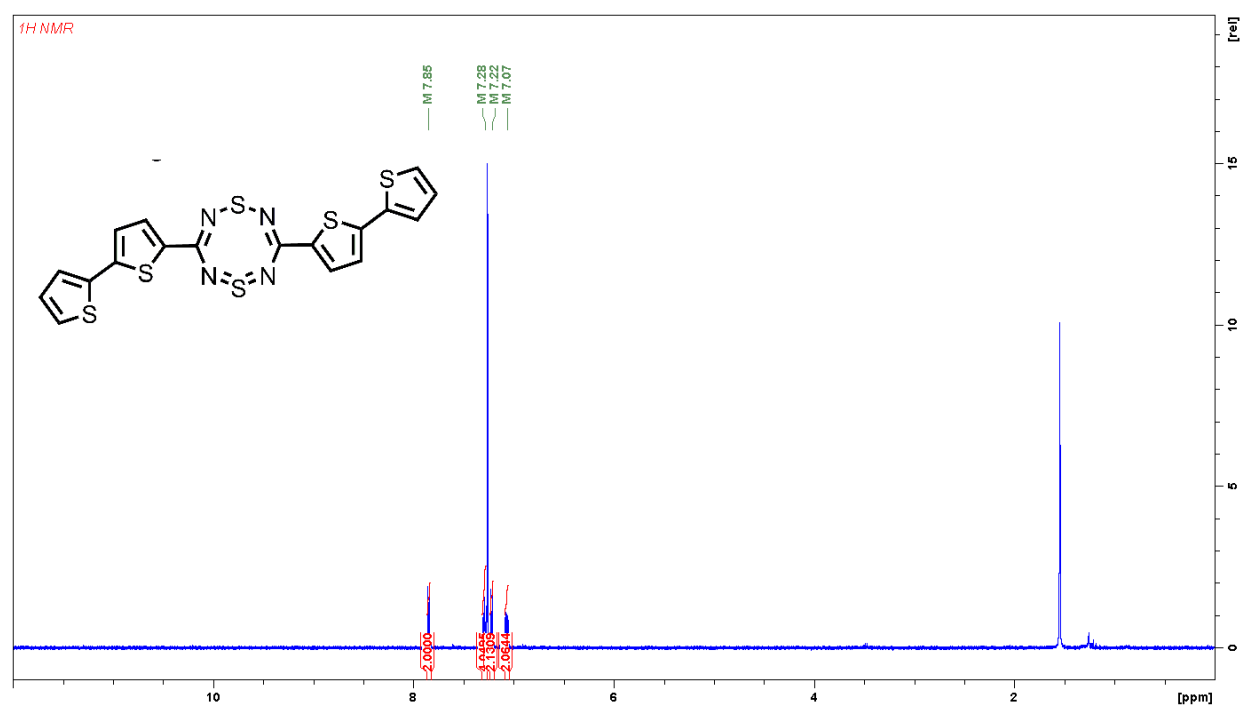


Figure A.4 - ¹H NMR spectrum of 3.25.

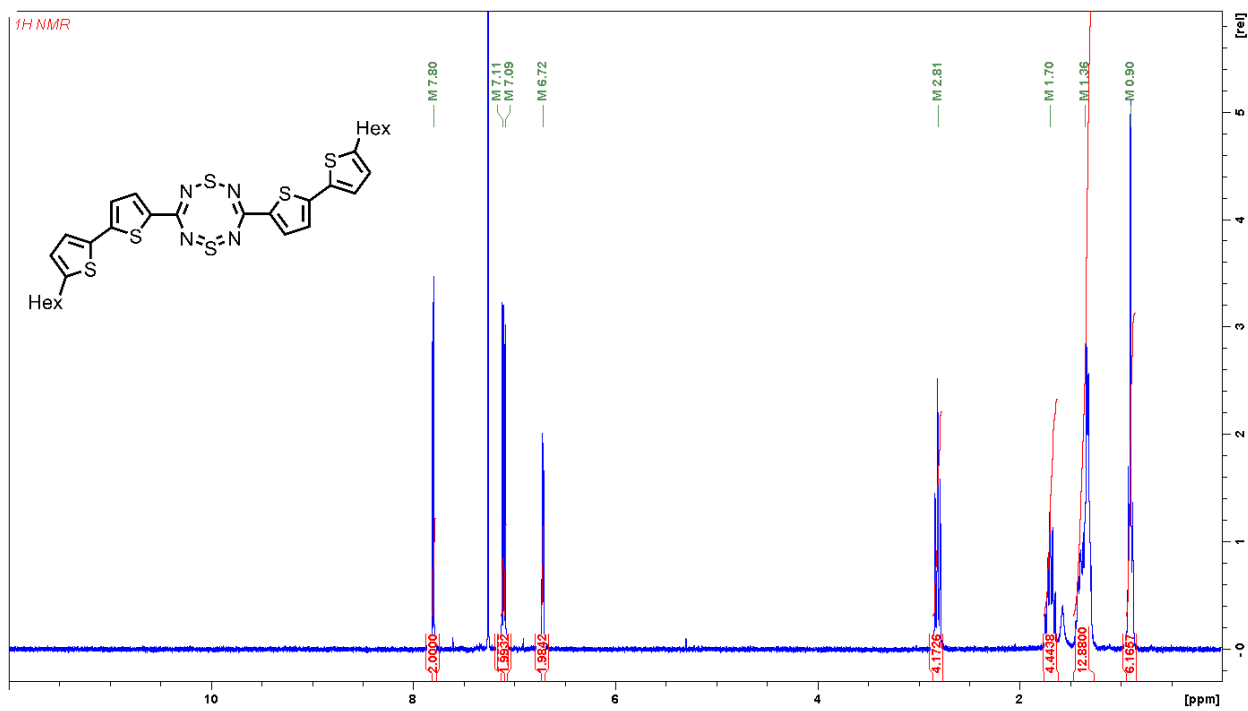


Figure A.5 - ¹H NMR spectrum of 3.26

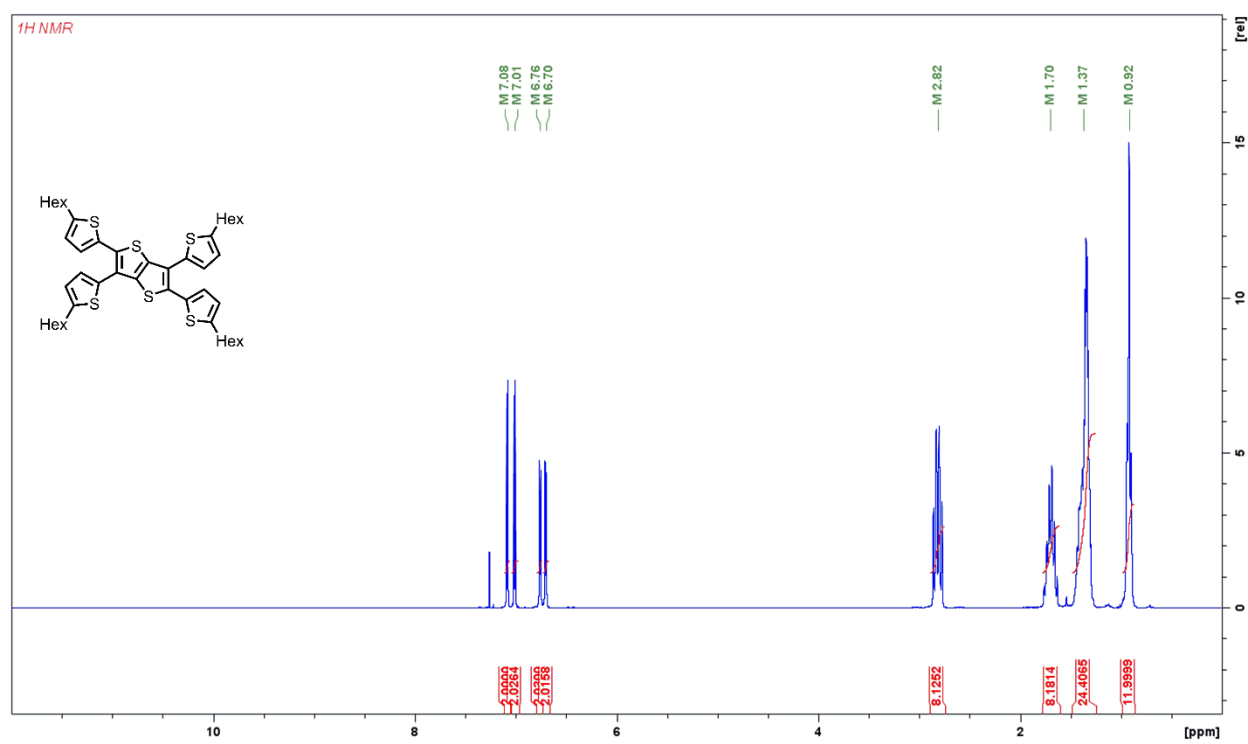


Figure A.6 - ¹H NMR spectrum of 4.36.

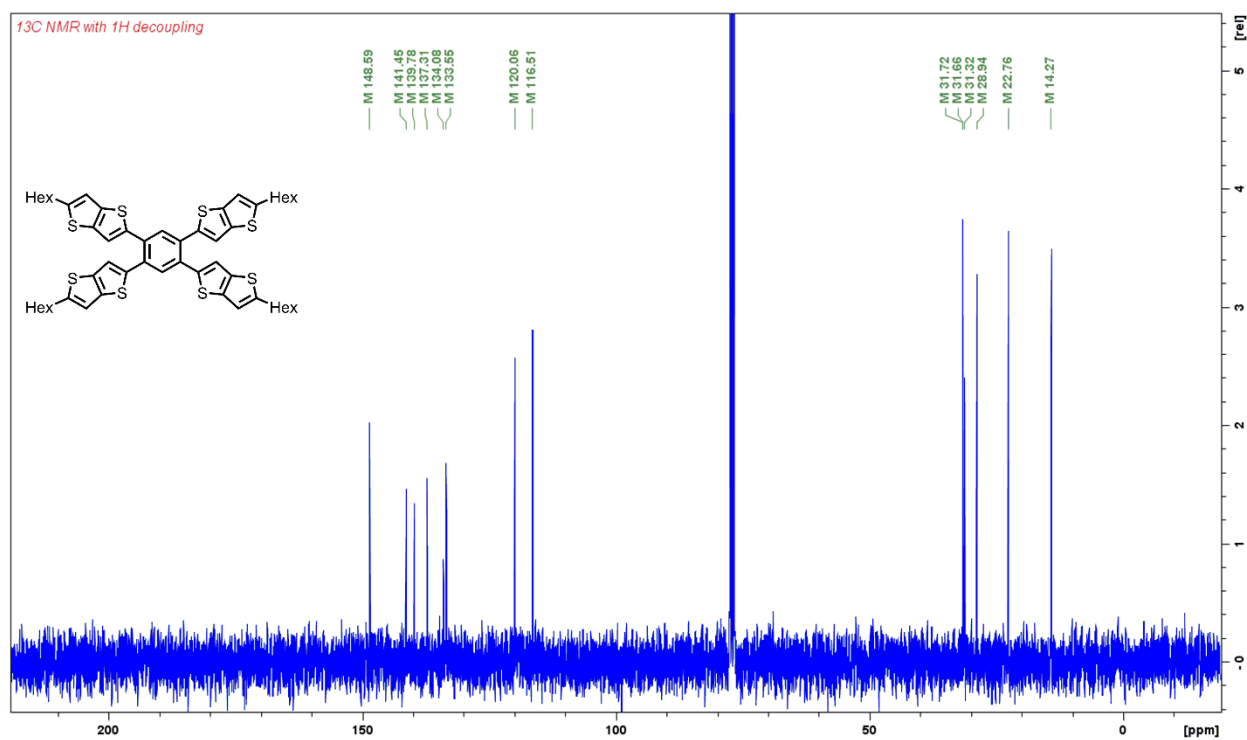


Figure A.9 - ¹³C NMR spectrum of 4.46.

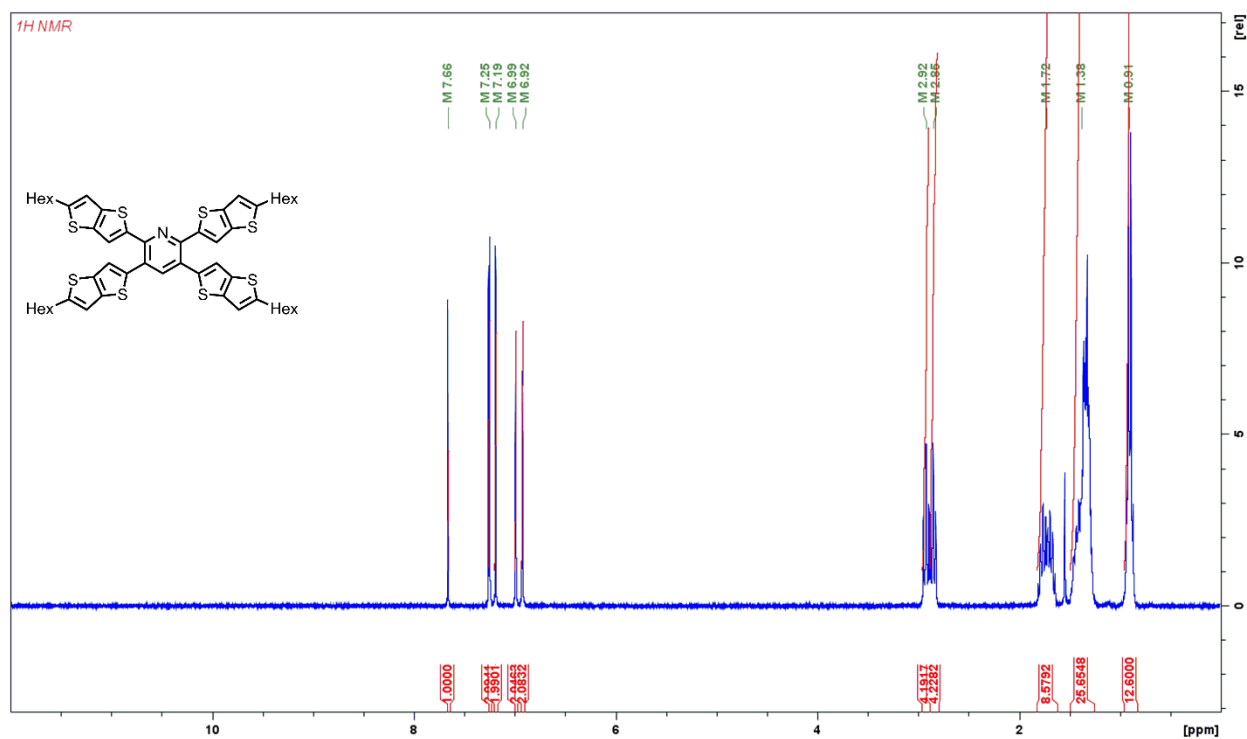


Figure A.10 - ¹H NMR spectrum of 4.47.

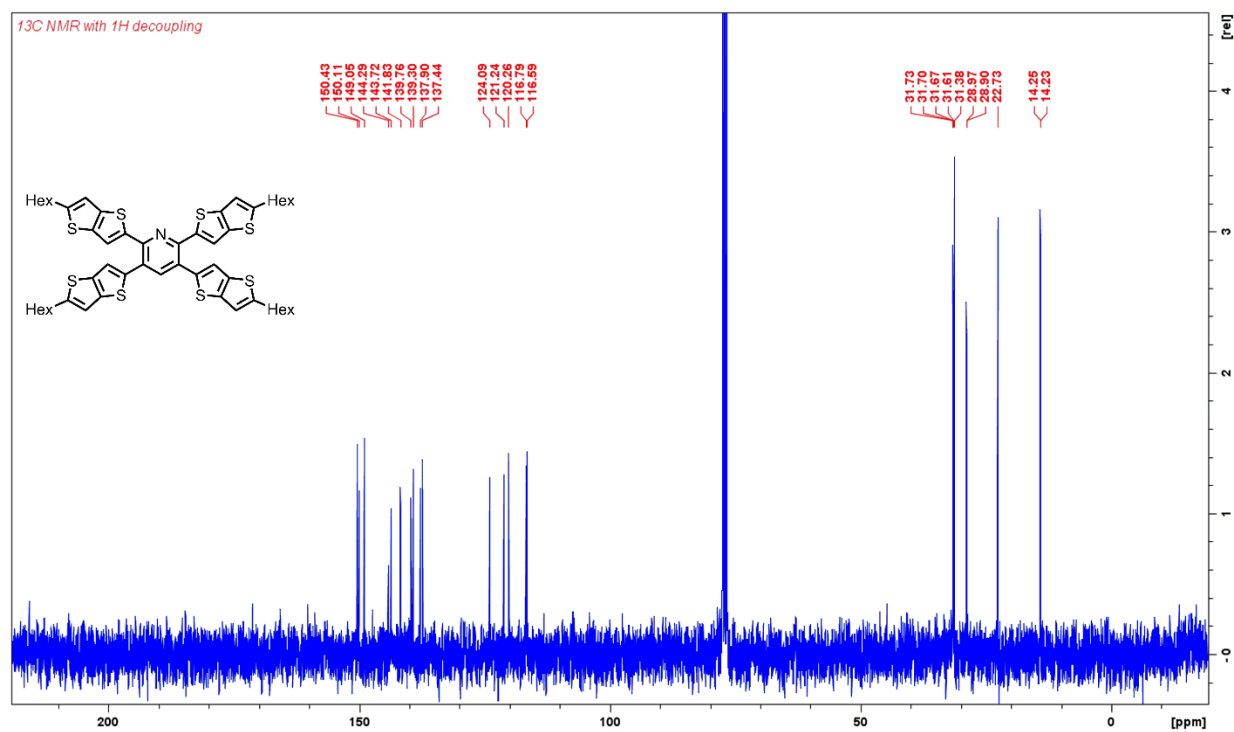


Figure A.11 - ¹³C NMR spectrum of 4.47.

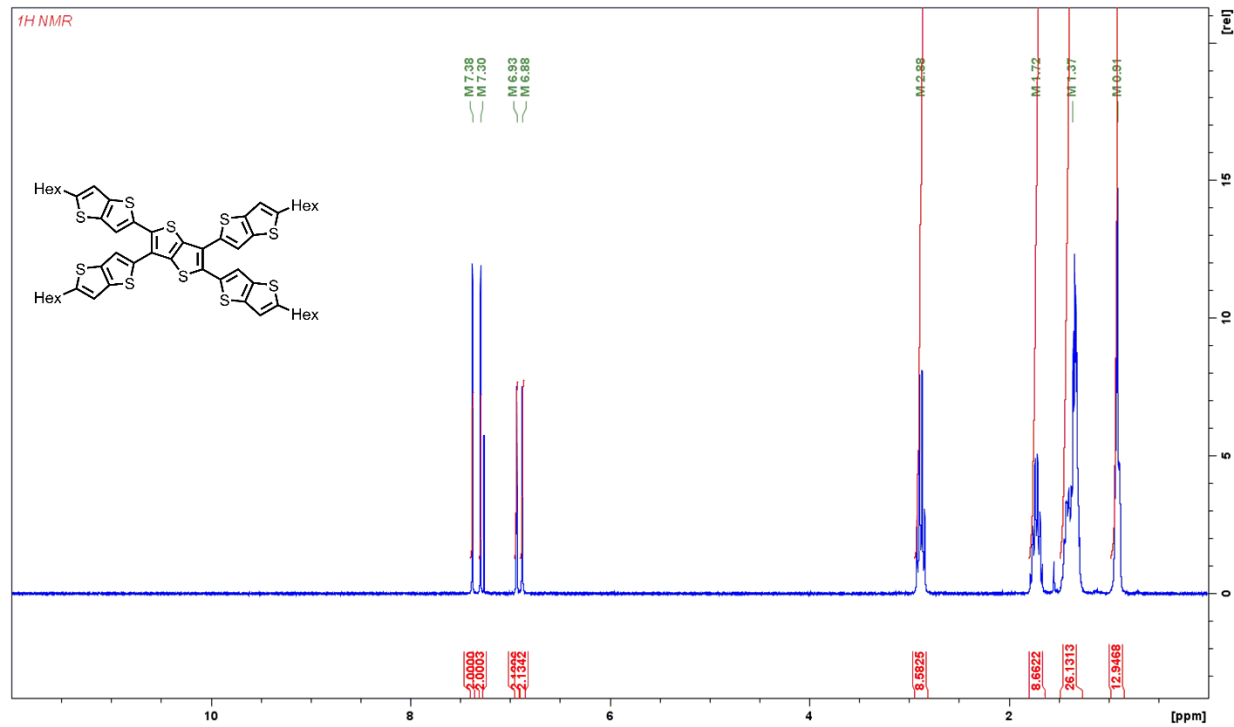


Figure A.12 - ¹H NMR spectrum of 4.48.

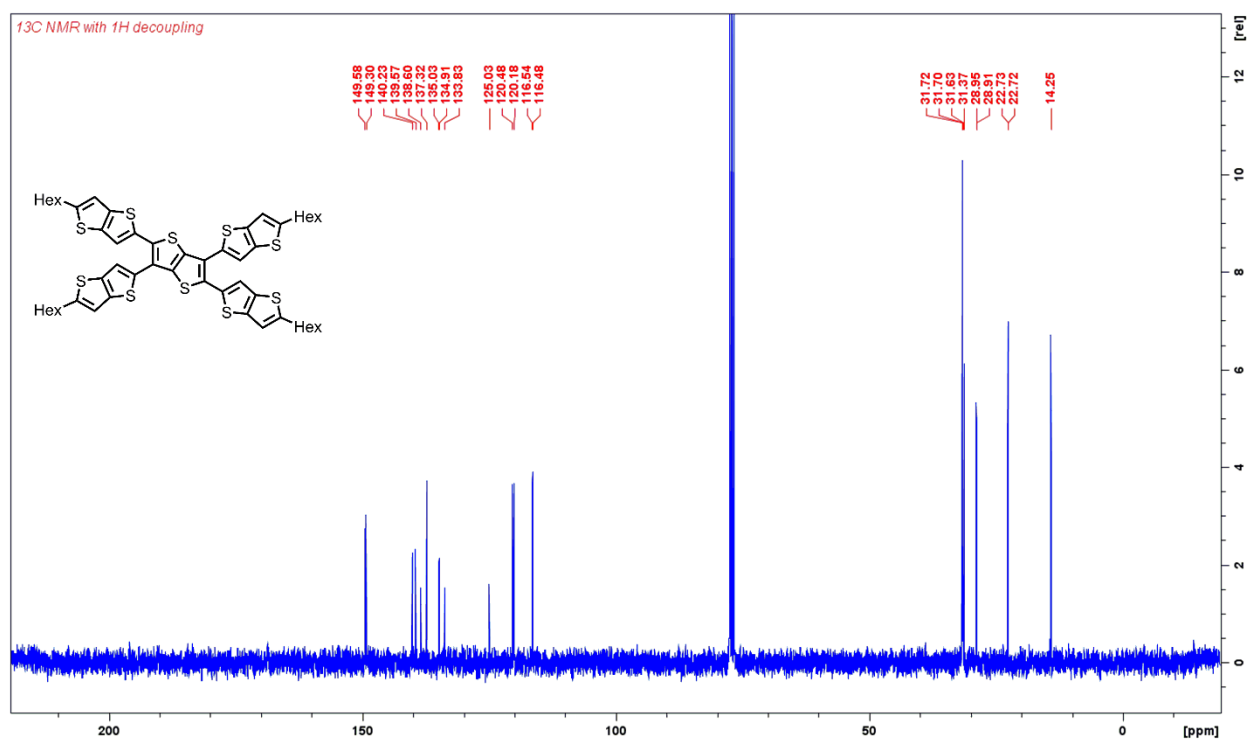


Figure A.13 - ¹³C NMR spectrum of 4.48.

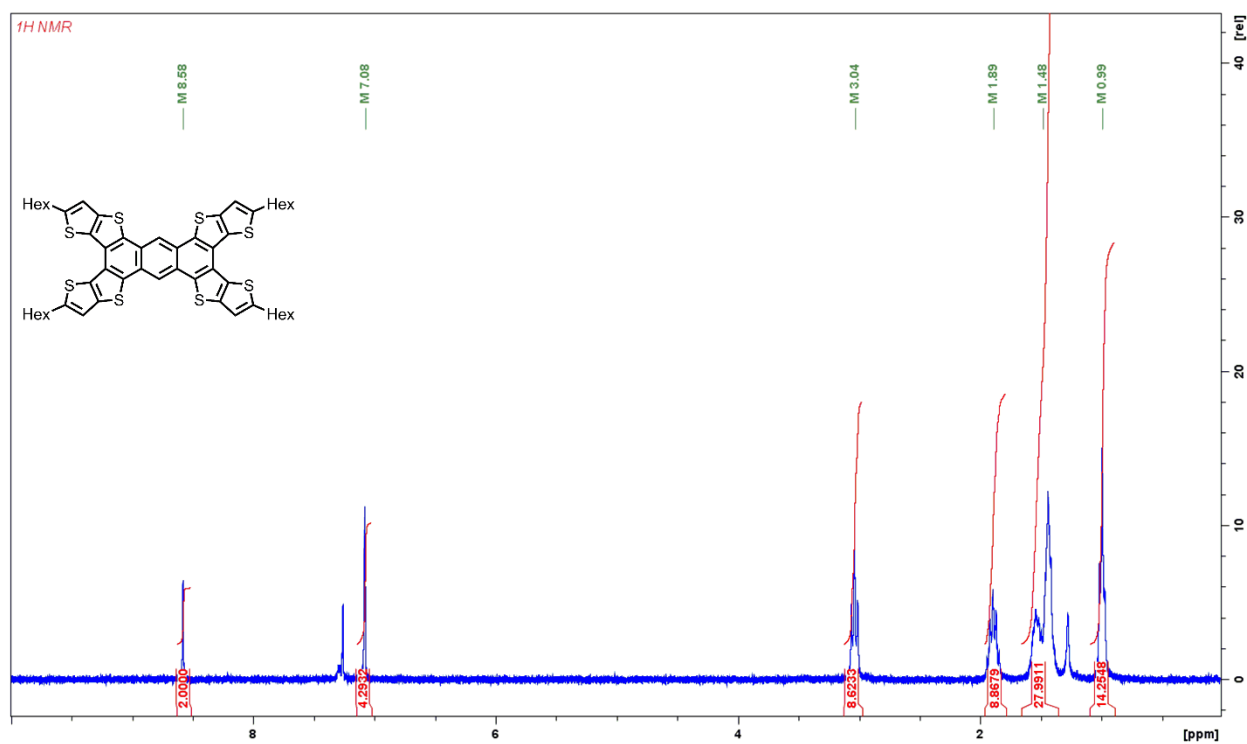


Figure A.14 - ¹H NMR spectrum of 4.49.

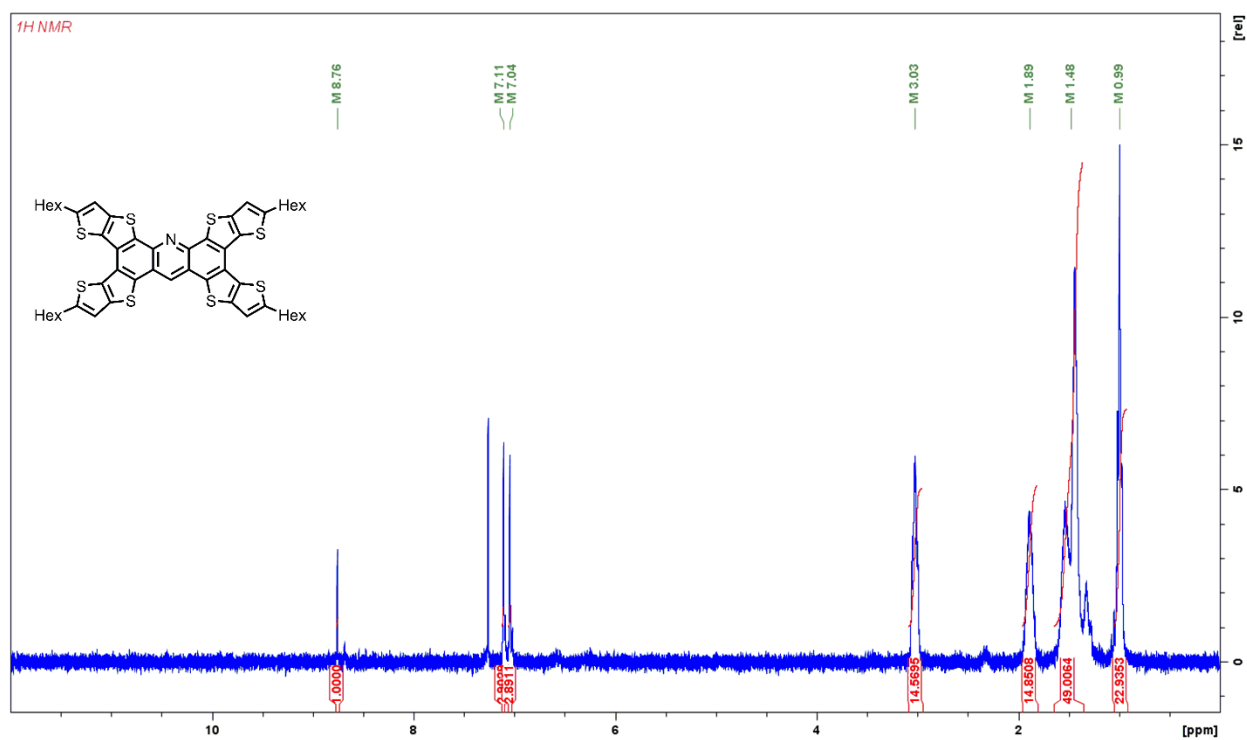


Figure A.15 - ¹H NMR spectrum of 4.50

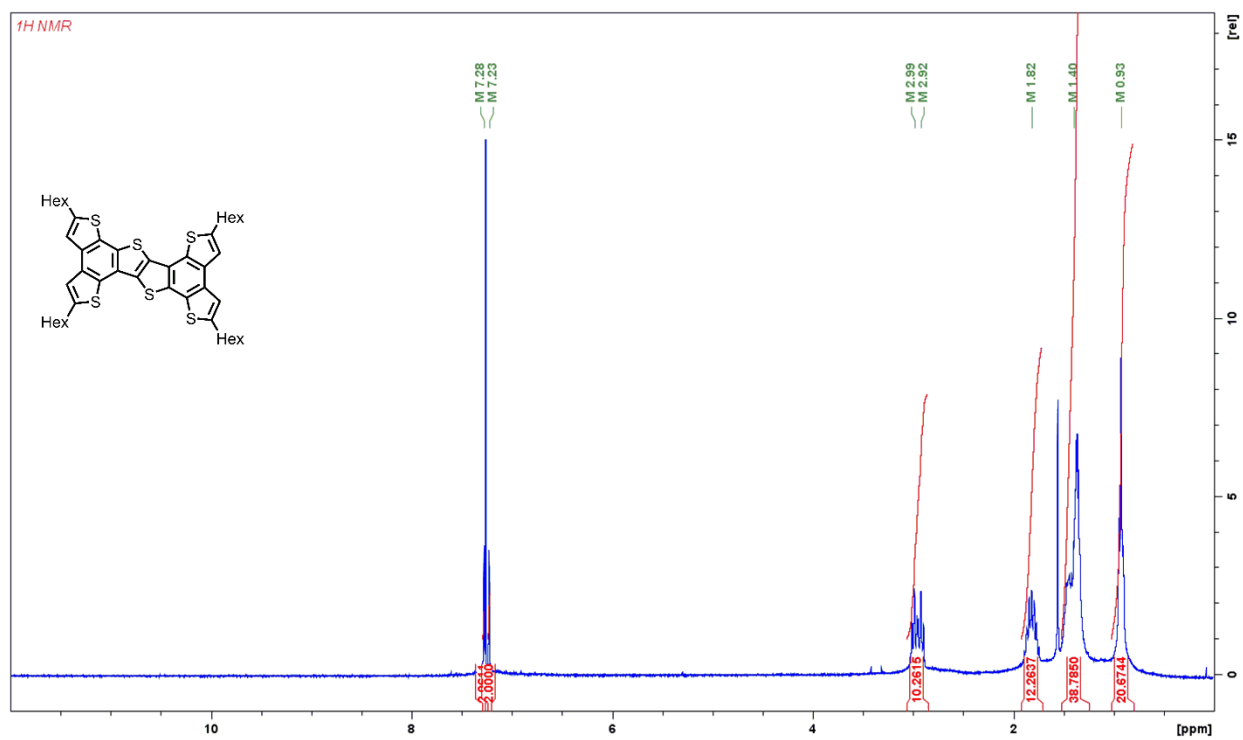


Figure A.16 - ¹H NMR spectrum of 4.51.

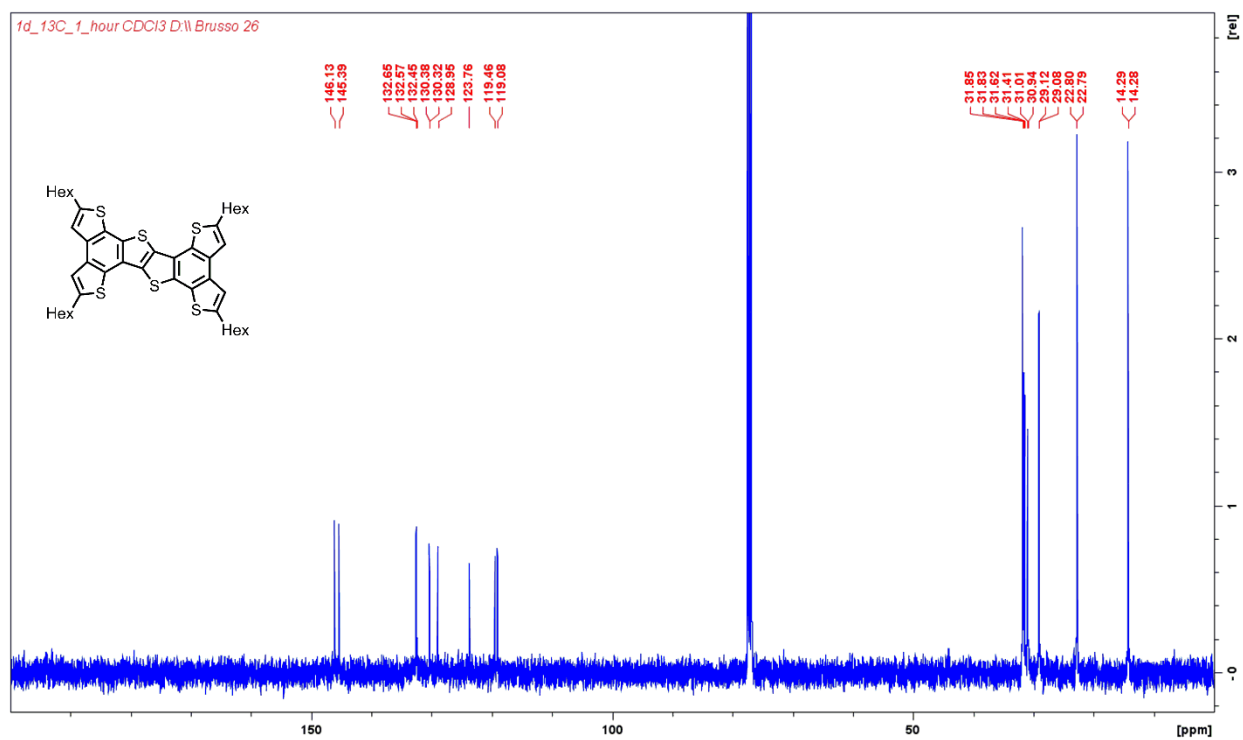


Figure A.17 - ^{13}C NMR spectrum of 4.51.

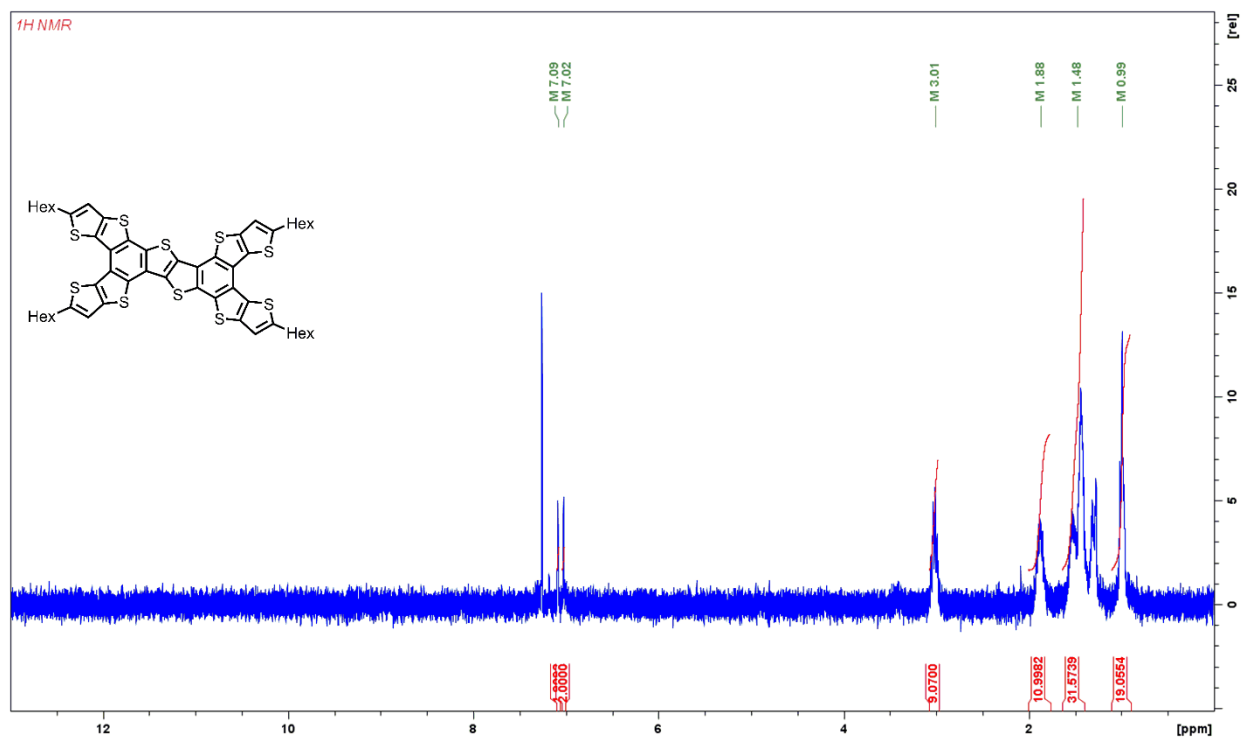


Figure A.18 - ^1H NMR spectrum of 4.52.

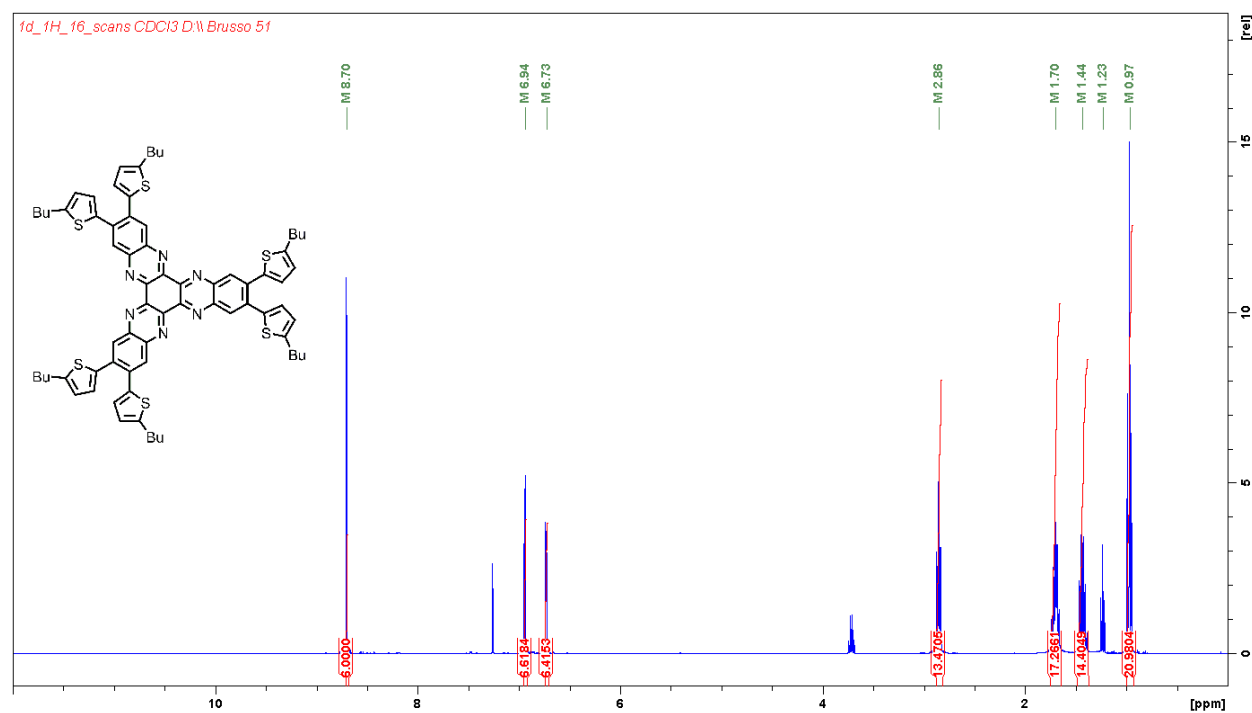


Figure A.19 - ^1H NMR spectrum of 5.31.

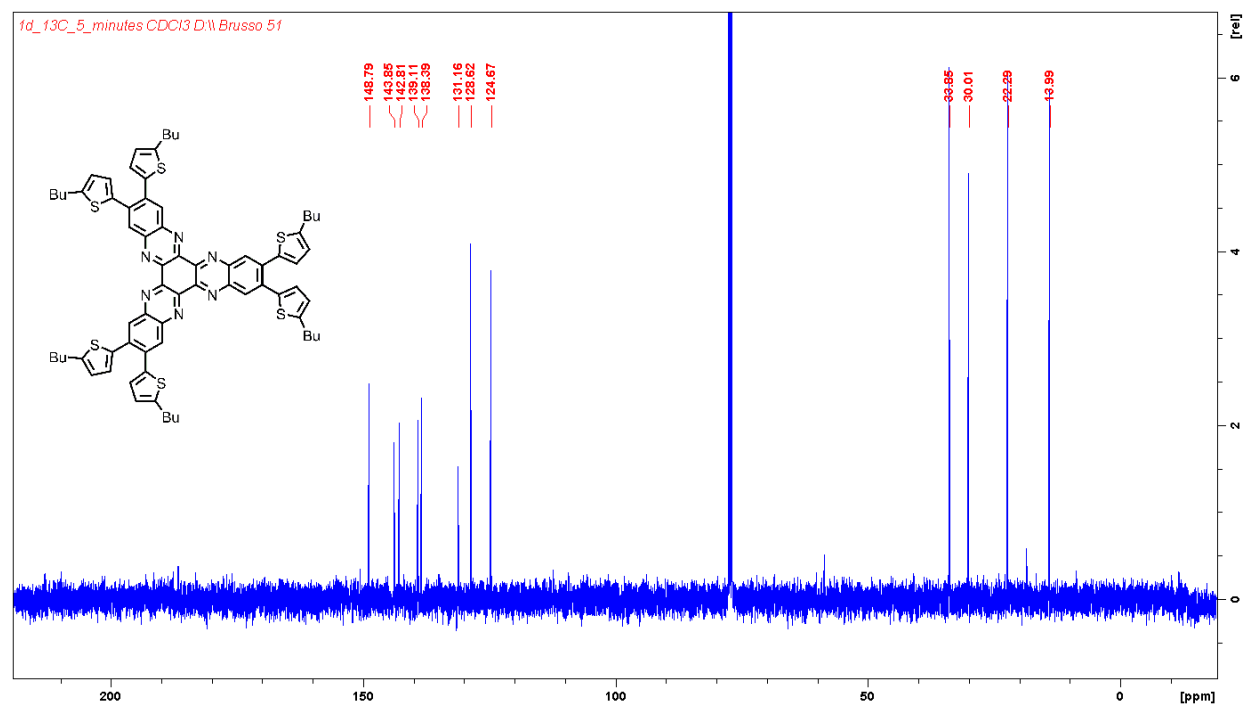


Figure A.20 - ^{13}C NMR spectrum of 5.31.

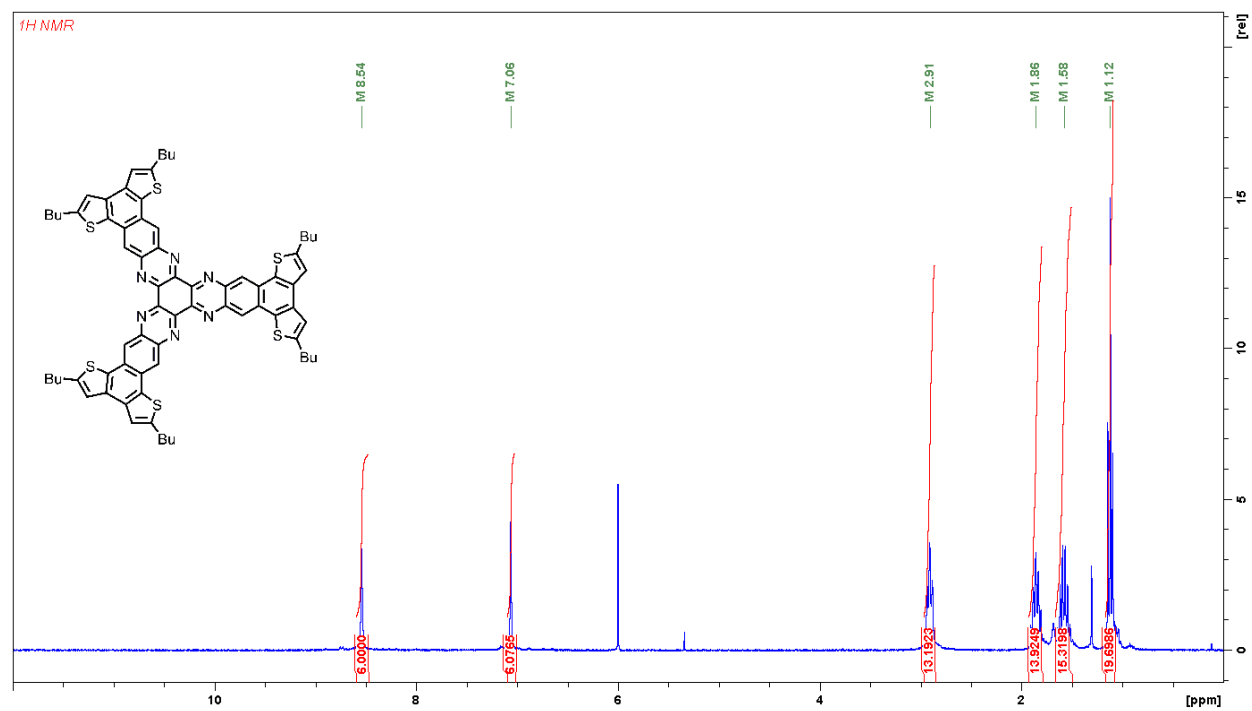


Figure A.21 - ¹H NMR spectrum of 5.32.

A.4

Archival Files

Archival file for the geometry optimization of 3.14

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#N B3LYP/6-311+G(d,p) OPT(EstFC)\8_member_ring_3\0,1\C,0.00734259
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\C,1.1698721576,-0.0000373238,2.2884278908\N,2.3534168391,0.0004096194
,1.6858410826\N,0.8692155175,-0.000514221,3.5831267621\S,1.5246497724,
-0.0007962432,5.0284804493\N,3.0802066836,-0.0005381143,5.3441743129\C
,4.2637513822,-0.0000897163,4.7415874499\N,4.5644080125,0.0003887109,3
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113023995,-0.0001718623,6.6202016019\C,6.7348591157,-0.000258391,7.578
6611863\C,5.4262815347,-0.0001713253,7.0248230978\H,4.5139937316,-0.00
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1350681,-0.5486464661\H,0.9196305844,0.0003325578,-0.5744971153\H,-1.5
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2776925
```

Archival file for the geometry optimization of 3.22 (where R = Me)

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#N B3LYP/6-311+G(d,p) OPT(EstFC)\8_member_ring_3_CH3_2_high_level
\0,1\C,0.0079190515,-0.0000912202,0.0132103742\C,0.0038543028,0.00000
67343,1.5114454857\S,1.4950186341,0.0000954382,2.41685111\C,0.63447500
64,0.0001140529,3.9390517602\C,1.3643233186,0.0001229501,5.2186772933\
N,0.5951624188,0.0001874756,6.3019932757\S,0.6782450356,0.0002576594,7
.8871251352\N,2.009813337,0.0002772285,8.7514818951\C,3.3355065759,0.0
002580035,8.6449622002\N,4.1044661636,0.0001973607,7.5615942037\S,4.02
13960463,0.0001303322,5.976188134\N,2.6896794585,0.0001073889,5.111861
8754\C,4.0644462034,0.000276911,9.9245295726\S,3.2080582206,0.00033926
16,11.4458355811\C,4.6945622723,0.0002599871,12.3511907581\C,5.7758086
007,0.000294907,11.5067922956\C,5.421475803,0.0002529522,10.1323111729
\H,6.1307339981,0.000225034,9.3163592326\H,6.7993199295,0.0002908284,1
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3.7328711598\C,-1.0749800958,0.0000566756,2.3563798118\H,-2.0976529998
,0.0000278011,1.9997809783\H,-1.4303731717,0.0002141101,4.5485653326\H
,-1.0188078346,-0.000173225,-0.3582389565\H,0.5121637141,0.8823853894,
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Archival file for the geometry optimization of 3.23

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40418,0.0001193478,1.6914281861\N,0.8565865995,-0.0001312665,3.5840599
785\S,1.5078998881,-0.0002151441,5.0317558003\N,3.0632081329,-0.000151
7564,5.3455788061\C,4.2474026303,-0.000047191,4.7458540879\N,4.5562156
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011,0.0001001891,3.4529469777\S,3.9049022891,0.0001831949,2.0052511391
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Archival file for the geometry optimization of **3.24** (where R = Me)

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0.,6.9229148413\N,4.3893744327,0.,7.1474337807\C,5.5419644649,0.,6.486
3399606\N,5.7766155424,0.,5.1782200627\S,5.036055932,0.,3.7750851857\N
,3.4657984886,0.,3.5440343624\C,6.7484420126,0.,7.3340785606\C,8.06165
14906,0.,6.9380198649\C,8.98937799,0.,8.0227489145\C,8.3431702724,0.,9
.2311869814\S,6.6184478274,0.,9.0737167466\H,8.7873584701,0.,10.215987
0576\C,10.4835063353,0.,7.8488206714\H,10.99354731,0.,8.8139122582\H,1
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88\H,0.2577595437,0.,-0.5959940488\H,-1.2316117791,-0.8823218117,-0.25
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Archival file for the geometry optimization of **3.25**

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3882617185\H,8.2764333111,0.0650371227,2.2668530919\H,6.2586125254,0.0
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.6359736401,-0.0037231759,-1.9679150854\C,-3.0290839879,-0.0232049196,
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519,-0.0034442597,0.3552125454\C,-5.2348371231,-0.0229643304,-0.957144
0372\C,-6.1396584069,0.524334603,-1.8385282494\C,-7.4941575567,0.33237
88018,-1.4522242709\C,-7.6190671725,-0.3525064651,-0.2762415975\S,-6.0
7607634,-0.7922262236,0.3740262838\H,-8.5203143178,-0.6265394792,0.250
261307\H,-8.3398561123,0.7000818662,-2.0181965283\H,-5.8360334582,1.07
22296687,-2.72061867\H,-3.4666844457,-0.0609997322,-3.200805911\H,-0.8
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Archival file for the geometry optimization of **3.26** (where R = Me)

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0.9475401288,-0.5088906054,1.9324954262\C,0.813850601,-0.6956877982,3.
336040934\C,-0.3155939211,-0.1157327521,3.8617340296\S,-1.2285171814,0
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0.0514933564,-0.1454013257,6.3723665436\C,-0.6824168213,-0.1374502328,
7.5812393227\C,-2.0418138391,-0.0715311293,7.3909212815\S,-2.436169047
5,-0.040171314,5.6908955984\C,-3.1038296175,-0.0271740239,8.4081299867
\N,-4.3415305008,0.0389394525,7.9276995251\S,-5.8614454229,0.111087737
6,8.3812535428\N,-6.3797031576,0.1219453807,9.8821064693\C,-5.95352648
85,0.0869040464,11.140783285\N,-4.7158146026,0.0203227012,11.623369810
5\S,-3.1997766169,-0.0499071588,11.1635386993\N,-2.6754356206,-0.06084
82979,9.6669360231\C,-7.0141508408,0.1300617127,12.1595050703\C,-6.882
9191633,0.1052898967,13.5272373594\C,-8.1217478614,0.1424806848,14.208
3994445\C,-9.2108769807,0.2065504535,13.364206333\S,-8.6933628058,0.22
32952911,11.6923370457\C,-10.6105161099,0.2843562887,13.7341745104\C,-
11.1534291543,0.8281242348,14.8734278424\C,-12.5699971702,0.7179857758
,14.936042261\C,-13.127098221,0.1001753342,13.8494307663\S,-11.8825791
279,-0.3786349134,12.7216902635\C,-14.5728526306,-0.1740107326,13.5698
113514\H,-15.1827089281,0.190003692,14.3991939465\H,-14.9129357951,0.3
260134713,12.6577651825\H,-14.7700458799,-1.2439139002,13.4523490491\H
,-13.1639297284,1.0981773274,15.7580665175\H,-10.5538764031,1.31786271
85,15.6294269339\H,-8.2183573263,0.0961678909,15.2849929334\H,-5.91927
95347,0.0454664097,14.0134686685\H,-0.2382294048,-0.1623714673,8.56646
70464\H,1.1322485155,-0.1593000219,6.3243598955\H,1.5119059813,-1.2637
337061,3.9367770807\H,1.7724424848,-0.9036658311,1.3522303766\H,0.5623
609921,0.198649493,-0.6643936387\H,-1.1945724903,0.1543097626,-0.47711
46697\H,-0.3166885714,1.6619379563,-0.2072440542
```

Archival file for the geometry optimization of **4.49** (where R = Me).

```
1\1\GINC-TITAN\FOpt\RB3LYP\6-311+G(2d,p)\C34H18S8\APACHE\01-Dec-2015\0
\#N B3LYP/6-311+G(2d,p) OPT Geom=Connectivity\T(HTT)A 2\0,1\C,-0.00
0344561,-0.0003590987,0.0235035976\C,-0.0008976305,-0.0002633501,1.518
9386311\C,1.0702392569,-0.0002049999,2.3617507685\C,0.6771612949,-0.00
01244851,3.72426153\S,1.5749177468,-0.0000003392,5.2108512253\C,0.0825
034821,0.0000556405,6.135567503\C,0.054160166,0.000189149,7.5635460519
\C,1.2032053877,0.000267518,8.3540241305\C,1.1501092545,0.0004110588,9
.7477031722\C,-0.1315882708,0.0004872812,10.390823274\C,-1.2806335209,
0.0004029219,9.6003451994\C,-1.2275374254,0.0002524794,8.2066661563\C,
-2.3892850404,0.0001488765,7.3758420807\S,-4.0226892693,0.0001803669,8
.019574303\C,-4.6778665614,-0.0000132099,6.4112652059\C,-3.6858803693,
-0.0000943292,5.4465739932\C,-2.3512133558,0.0000009905,5.9771128488\C
,-1.0616098909,-0.0000269565,5.3300258271\C,-0.6891695382,-0.000123341
2,3.9429081537\S,-1.5154238563,-0.0002115997,2.4027659724\S,-4.4267300
068,-0.0003531124,3.863578021\C,-6.0405710946,-0.0003327065,4.54947861
72\C,-6.0051423276,-0.0001453962,5.9119802076\H,-6.8949114469,-0.00011
02944,6.5269157046\C,-7.2397859848,-0.0004472589,3.6560527925\H,-8.148
8969334,-0.0009176854,4.2593211817\H,-7.2657739586,0.8815871848,3.0105
324305\H,-7.2652149891,-0.8820992137,3.0099944502\H,-2.2494221606,0.00
04562477,10.086456321\C,-0.1599316853,0.0006531932,11.8188018332\S,-1.
6523459391,0.0007820102,12.7435181622\C,-0.7545893267,0.000960175,14.2
```



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301077623\C,0.6117413422,0.0009186329,14.0114613012\C,0.9841817396,0.0
007372353,12.6243435074\C,2.2737851303,0.000630841,11.9772564876\C,2.3
118568671,0.0004819275,10.5785272493\S,3.9452610982,0.0003700851,9.934
7949552\C,4.6004383867,0.0005141188,11.5431041352\C,3.6084521868,0.000
6417767,12.5077953289\S,4.3493016346,0.000762442,14.0907912819\C,5.963
1427761,0.0006394859,13.4048908358\C,5.9277141191,0.0005155734,12.0423
89243\H,6.8174832241,0.0004261869,11.4274537219\C,7.1623572325,0.00066
87703,14.2983172371\H,7.1880707161,0.882537519,14.9440712387\H,7.18805
98446,-0.8811490887,14.9441419766\H,8.0714686428,0.0006387716,13.69504
93695\S,1.4379955554,0.0011591507,15.5516035331\C,-0.0765313211,0.0012
992047,16.4354309532\C,-1.1476677226,0.0011723865,15.5926186012\H,-2.1
725019959,0.0012308984,15.9383778565\C,-0.0770824174,0.0014941498,17.9
30865915\H,-1.1041244989,0.0018285208,18.299105135\H,0.4250306881,-0.8
804394124,18.3375971708\H,0.4255256049,0.8832470611,18.3373719573\H,2.
1719940155,0.0002154655,7.8679129827\H,2.0950732196,-0.0002201451,2.01
59906578\H,-0.502738159,0.8814388225,-0.3831722614\H,1.0266981938,-0.0
003436565,-0.3447337724\H,-0.5026709166,-0.8822476582,-0.3830595243\
version=EM64L-G09RevA.02\State=1-A\HF=-4492.6010348\RMSD=7.511e-09\RMSF
=6.246e-06\Dipole=-0.0000006,0.0000045,0.\Quadrupole=10.3913784,-33.50
00436,23.1086652,0.0007865,8.528435,0.0057239\PG=C01 [X(C34H18S8)]\@

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Archival file for the geometry optimization of 4.50 (where R = Me)

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1\1\GINC-TITAN\FOpt\RB3LYP\6-311+G(2d,p)\C33H17N1S8\APACHE\20-Dec-2015
\0\#N B3LYP/6-311+G(2d,p) OPT Geom=Connectivity\T(HTT)Ac 2\0,1\C,-0
.0118483014,0.0009497064,0.017285326\C,-0.0083790013,0.0007529785,1.51
26416915\C,1.0656045048,0.0007646539,2.3518505248\C,0.6810064412,0.000
5683287,3.7173015647\S,1.5914327734,0.0004699324,5.1980311672\C,0.1020
553706,0.0002087608,6.1126207459\C,0.0912981297,0.0000082127,7.5356361
532\N,1.2499792965,0.0000432144,8.1988184844\C,1.2396534367,-0.0001642
384,9.5338253963\C,0.0264235599,-0.0004495054,10.2988313104\C,-1.17393
52434,-0.0004664325,9.5918366205\C,-1.1804821058,-0.0002322194,8.19876
03752\C,-2.3548992546,-0.0002192085,7.3885907625\C,-2.3338481146,-0.00
00033749,5.9883563511\C,-3.6744645385,-0.0000295072,5.4757022841\C,-4.
6551605161,-0.0002658364,6.4519191402\S,-3.9808584825,-0.0004633977,8.
053124608\C,-5.9877171984,-0.0002783615,5.9668938966\C,-6.0373175017,-
0.0000382855,4.6045831292\S,-4.4308699023,0.0001797326,3.9010316477\C,
-7.2459346665,0.000085189,3.7239262345\H,-7.2778758743,-0.8813662447,3
.0779862167\H,-8.1486729921,-0.0004879233,4.3365853837\H,-7.2783654166
,0.8822056175,3.0789190801\H,-6.8710813203,-0.0004554984,6.5909987715\
C,-1.0531074699,0.0001998494,5.3228450368\C,-0.687905665,0.0004072682,
3.9364838328\S,-1.5214686062,0.0004925038,2.3998180642\H,-2.1141865395
,-0.0006681928,10.1321966487\C,0.1351764797,-0.0007374255,11.721435612
3\C,1.3556149105,-0.0007286198,12.4081893658\C,1.1236349551,-0.0011672
373,13.8246108961\C,-0.213570006,-0.0014349142,14.1804851319\S,-1.2575
80393,-0.0012223568,12.7917509061\C,-0.4653677382,-0.0020056057,15.576
0338081\C,0.6867319758,-0.0021562566,16.3047413477\S,2.1033819516,-0.0
017703679,15.2709286379\C,0.8391757997,-0.002603028,17.7923814508\H,-0
.1446556087,-0.0030868324,18.2639360617\H,1.3809721235,-0.8843266074,1
8.1448533748\H,1.3803875676,0.8792459412,18.1454447079\H,-1.4493385815
,-0.0022234974,16.0250774324\C,2.5754181052,-0.000291584,11.6366432071
\C,3.9571305766,-0.0000008056,12.0190569709\C,4.835683304,0.0003718984
,10.9466266894\S,4.0146433506,0.0004048389,9.4145269721\C,2.4745926526
,-0.00007946,10.2409427473\C,6.2090937655,0.0007322254,11.301754889\C,
6.3934997994,0.0006668003,12.6522016271\S,4.8651967425,0.0001404401,13
.5129055845\C,7.6837812319,0.0010171347,13.4080300702\H,8.5209949282,0

```

```
.0010242692,12.7084911833\H,7.779952178,0.8829467945,14.0469727601\H,7
.7802426082,-0.8806364863,14.0473055008\H,7.027233805,0.0010313679,10.
5941760305\H,2.088861015,0.0009026331,2.0011837854\H,1.0140637223,0.00
08940496,-0.3539099945\H,-0.5156569899,-0.8807347549,-0.3878090018\H,-
0.515474458,0.8828485801,-0.3875732574\\Version=EM64L-G09RevA.02\State
=1-A\HF=-4508.6512234\RMSD=9.206e-09\RMSF=2.821e-05\Dipole=-0.3488524,
-0.0000271,0.200485\Quadrupole=10.7171785,-33.658734,22.9415556,0.0056
077,10.489833,-0.0096091\PG=C01 [X(C33H17N1S8)]\\@
```

Archival file for the geometry optimization of **4.51** (where R = Me)

```
1\1\GINC-TITAN\FOpt\RB3LYP\6-311+G(2d,p)\C26H16S6\APACHE\28-Dec-2015\0
\\#N B3LYP/6-311+G(2d,p) OPT Geom=Connectivity\\T(HT)BTBT 2\\0,1\C,0.0
035184123,-0.0001596933,0.0190770651\C,0.0031858802,-0.0003507692,1.51
35331387\S,1.5227371643,-0.0002444721,2.3982267774\C,0.6831456826,-0.0
007176405,3.9322242047\C,1.2412085573,-0.000926294,5.2162454269\S,2.95
18930474,-0.0008508862,5.621847823\C,2.5646504304,-0.0013664291,7.3286
526523\C,1.2055800414,-0.0014954197,7.5458483021\C,0.4130555803,-0.001
2386109,6.3586791384\C,-0.9848814946,-0.0013386833,6.1655847734\C,-1.5
58040613,-0.001120844,4.8857657298\C,-2.9908514139,-0.0012824764,4.939
6089237\C,-3.4992657685,-0.0016280139,6.1976077074\S,-2.2211841527,-0.
001735909,7.4020553869\C,-4.9331721388,-0.0019007698,6.6201191337\H,-5
.1789334148,0.87928898,7.2188442172\H,-5.5786660124,-0.0018197085,5.74
05619517\H,-5.1786976301,-0.8833827302,7.2185109064\H,-3.6239042063,-0
.0011635211,4.0617985831\C,-0.7088175543,-0.0008004996,3.7462439774\C,
-1.0600416446,-0.0005687621,2.3563809347\H,-2.0807855136,-0.0005977849
,1.9968035388\S,0.8183354825,-0.0017263736,9.2526499632\C,2.5290187348
,-0.0016910643,9.6582557937\C,3.3571740561,-0.0014647748,8.5158201805\
C,4.7551088125,-0.0014581421,8.7089245191\S,5.991411603,-0.0012162965,
7.4724493664\C,7.2694899278,-0.0013459784,8.6768892782\C,6.7610796211,
-0.0016191521,9.9348930735\C,5.3282707397,-0.00165852,9.9887418118\C,4
.4790434071,-0.0018863496,11.1282605574\C,3.0870818103,-0.0019027028,1
0.9422767917\S,2.2474789041,-0.0021234888,12.4762671314\C,3.7670373465
,-0.0023942155,13.3609744893\C,4.830261201,-0.0021432975,12.5181242886
\H,5.8510044286,-0.002205565,12.8777061579\C,3.7666974137,-0.002790983
1,14.85542215\H,4.7925749415,-0.0027816679,15.2265888898\H,3.261469792
5,0.8783279009,15.2603285447\H,3.2616528244,-0.8842294078,15.259865030
9\H,7.3941393252,-0.0017594849,10.8126981729\C,8.7034101054,-0.0011819
004,8.2544208166\H,9.3488668358,-0.001424416,9.1340042978\H,8.94909933
05,-0.8823333699,7.6556103407\H,8.9490538228,0.8803360711,7.656129168\
H,-1.0223625883,-0.0001901593,-0.3520765857\H,0.5085925369,0.881204098
6,-0.3854826352\H,0.5087134475,-0.8813577317,-0.3856990845\\Version=EM
64L-G09RevA.02\State=1-A\HF=-3390.0408823\RMSD=4.310e-09\RMSF=1.113e-0
4\Dipole=-0.0000118,-0.0000932,-0.0000036\Quadrupole=12.9444297,-24.70
2446,11.7580162,-0.0001509,15.3968136,-0.006134\PG=C01 [X(C26H16S6)]\\@
```

Archival file for the geometry optimization of **4.52** (where R = Me)

```
1\1\GINC-TITAN\FOpt\RB3LYP\6-311+G(2d,p)\C34H16S10\APACHE\21-Dec-2015\
0\\#N B3LYP/6-311+G(2d,p) OPT Geom=Connectivity\\T(HT)BTBT 2\\0,1\C,0
.0018968013,0.,0.0257152285\C,0.001308994,0.,1.5244772912\S,1.51446423
18,0.,2.4001172334\C,0.7016505196,0.,3.9430494297\C,1.0896104879,0.,5.
327867371\C,-0.069508379,0.,6.1387869652\C,0.0094696049,0.,7.532032629
7\C,1.2591562167,0.,8.1797006936\C,1.0849275989,0.,9.597272457\S,2.196
3747785,0.,10.9500427133\C,0.8470793796,0.,12.0766341958\C,-0.40248224
```

69,0.,11.4287818571\C,-0.2280358436,0.,10.0112786798\S,-1.3396069074,0.
.,8.658659555\C,-1.5611657104,0.,12.2274865908\C,-1.5124024771,0.,13.6
396145827\C,-2.8510009317,0.,14.166754399\C,-3.8448034838,0.,13.203942
9044\S,-3.1967145854,0.,11.5878338024\C,-5.1705719604,0.,13.7028733937
\C,-5.2029347666,0.,15.0669074916\S,-3.5912159082,0.,15.7458306448\C,-
6.3976672584,0.,15.9721290978\H,-6.1045542185,0.,17.0226969669\H,-7.01
89304917,0.8831849643,15.8029500984\H,-7.0189304917,-0.8831849643,15.8
029500984\H,-6.0594667694,0.,13.0863839786\C,-0.2353237165,0.,14.27987
56042\C,0.1517433492,0.,15.6644907935\C,1.5178041053,0.,15.8779247423\
S,2.4221158018,0.,14.3877564476\C,0.9250194216,0.,13.4699496803\C,1.91
57671106,0.,17.2382287147\C,0.8474618448,0.,18.0857099028\S,-0.6687811
867,0.,17.2064089075\C,0.8532672858,0.,19.5811728576\H,1.8815107853,0.
,19.9459802031\H,0.352323187,0.8818456495,19.9894790155\H,0.352323187,
-0.8818456495,19.9894790155\H,2.9418449415,0.,17.5802101405\C,2.417220
6487,0.,7.380118791\S,4.0532970617,0.,8.0171961503\C,4.6985418089,0.,6
.4004399716\C,3.7048476056,0.,5.4399484884\C,2.3669643584,0.,5.9676110
49\S,4.4396575533,0.,3.8553446813\C,6.0560841537,0.,4.534604429\C,6.02
45632931,0.,5.8972348913\H,6.9160982377,0.,6.5095579273\C,7.2521009096
,0.,3.6366812807\H,8.1634888241,0.,4.2364556774\H,7.275417987,-0.88187
0007,2.990883819\H,7.275417987,0.881870007,2.990883819\S,-1.5683676943
,0.,5.2231000826\C,-0.666372879,0.,3.73100148\C,-1.0676242131,0.,2.373
5083404\H,-2.0954277978,0.,2.0361147867\H,1.0163628823,0.,-0.374802802
3\H,-0.5081344769,-0.8831645474,-0.367408419\H,-0.5081344769,0.8831645
474,-0.367408419\\Version=EM64L-G09RevA.02\State=1-A'\HF=-5287.8248087
\RMSD=3.813e-09\RMSF=6.134e-06\Dipole=-0.0158151,0.,-0.0115344\Quadrup
ole=5.6747217,-37.2430576,31.5683359,0.,-10.3389562,0.\PG=CS [SG(C34H8
S10),X(H8)]\@

Archival file for the geometry optimization of **5.31** (where R = Me)

1\1\GINC-TITAN\FOpt\RB3LYP\6-31G(d,p)\C54H36N6S6\APACHE\16-May-2017\0\
\#N B3LYP/6-31G(d,p) OPT Geom=Connectivity\\(BuT)6HATN 2\\0,1\C,-0.002
1903657,0.009825231,0.00206643\C,-0.0016323818,0.0056423281,1.50097637
69\S,1.4895793543,0.0079755403,2.4082843409\C,0.639731807,-0.014023736
1,3.9475354052\C,1.3822673893,0.0542035787,5.2153153482\C,2.4929702821
,0.8783166183,5.3019493017\C,3.2054909376,1.0503606012,6.5126323809\N,
4.2794912981,1.8715484617,6.551071231\C,4.8966754919,2.0070255688,7.71
59812095\C,4.4456920488,1.3157085257,8.8949954797\C,5.1601986509,1.493
9833416,10.1740260993\C,6.3123205073,2.3537093673,10.2421563438\C,6.77
78770365,3.0605993859,9.0314895567\C,6.0765514269,2.8920268516,7.78628
56411\N,6.4635244056,3.514862222,6.6816846952\C,7.5482571665,4.3149709
59,6.7721713766\C,8.2510842841,4.4754588696,8.006478177\N,7.8446931207
,3.8405177526,9.1293086448\C,9.374314563,5.3353460254,8.0510335595\C,9
.8211921983,6.0162817627,6.93000943\C,9.1369290545,5.8130466241,5.6655
432498\C,8.0255059617,4.9908217671,5.6215834254\H,7.5141910749,4.80946
60305,4.6828634143\C,9.5704001514,6.4270458323,4.3938049186\S,11.17587
17063,6.1937195884,3.7212557845\C,10.7666936737,7.0610480566,2.2601824
49\C,9.4682540308,7.4939336827,2.3091561949\C,8.7888922212,7.128316273
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A.4

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