

***Star Shaped Thieno- and Thienylaryls
as Multifunctional Materials***

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**Dedicated to
Elaine A. Campbell and Clive K. Robertson,
My Parents**

For their unwavering love and support,
and for all that they have done for me in my life.

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Abstract

The work in this thesis was undertaken to explore both the effect of heteroatoms on the semiconducting properties of star-shaped thienoacenes, and to expand the scope of these materials to fields outside of organic semiconductors. Overall, new star-shaped molecules were prepared with a view towards applications such as thin film transistors, as the organic linker component in metal-organic frameworks, and as ligands that could coordinate to transition metals through the sulfur atom.

The first chapter describes the properties of star-shaped molecules, the theory underlying their semiconducting behaviour, and the previous work that motivated the research contained herein. The second chapter of this thesis outlines the synthetic methodology that was utilized to achieve the molecular targets, as well as the characterization techniques that are used to reveal the properties of organic semiconductors.

The third chapter of this thesis describes the synthesis and optoelectronic properties of novel nitrogen-containing semiconductor molecules called thienoacridines, and their comparison to carbon-and-sulfur based analogues, thienoanthracenes.

The fourth and fifth chapters concern the synthesis of functionalized star shaped thienylbenzene molecules. In Chapter 4, these molecules are decorated with carboxylic acid groups so that they may act as tetrapodal MOF linkers. In Chapter 5, they are equipped with *N*-aryl(azomethine)thiophene moieties to explore sulfur coordination and act as ligands. The sixth chapter provides conclusion to this work, and possible future directions of the research conducted herein.

Contributions

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List of Abbreviations, Nomenclature and Symbols

1. Chemical

amth	(azomethine)thiophene
Ar	aromatic group
BrTTAc	2,5,9,12-Tetrabromotrithieno- [2'',3'':5,6:3'',2'':3,4:3'',2'':7,8]acridine[1,2-b]thiophene
BrTTAn	2,5,9,12-Tetrabromotrithieno- [2'',3'':5,6:3'',2'':3,4:3'',2'':7,8]anthracene[1,2-b]thiophene
BrTTPy	2-Bromo-5-[2,4,5-tris(5-bromo-2-thienyl)pyridyl]thiophene
D	deuterium
DMA	<i>N,N'</i> -dimethylacetamide
DMSO	dimethylsulfoxide
EtOAc	ethyl acetate
Fc	ferrocene
HTTPy	2-(2,4,5-Tris(5-hexyl-2-thienyl)pyridyl)-5-hexylthiophene
L	ligand
M	metal
Me	methyl group
MeOH	methanol
MeCN	acetonitrile
NBS	<i>N</i> -bromosuccinimide
<i>n</i> -BuLi	<i>n</i> -butyl lithium
NMP	<i>N</i> -methylpyrrolidinone
OAc	acetate
OTAc	2,5,9,12-Tetra(5-hexyl-2-thienyl)trithieno- [2'',3'':5,6:3'',2'':3,4:3'',2'':7,8]acridine[1,2-b]thiophene
OTAn	2,5,9,12-Tetra(5-hexyl-2-thienyl)trithieno- [2'',3'':5,6:3'',2'':3,4:3'',2'':7,8]anthracene[1,2-b]thiophene
PCy ₃ ·HBF ₄	tricyclohexylphosphine tetrafluoroborate
Ph	phenyl
phamth	2-(phenyl)-5-(azomethine)thiophene
phth	2-(phenyl)thiophene
PPh ₃	triphenylphosphine
<i>p</i> -TSA	<i>para</i> -toluene sulfonic acid
py	pyridine
R	alkyl or aryl group
TBP	2,3,5,6-tetrabromopyridine
<i>t</i> -Bu	<i>tert</i> -butyl
TES	(triethylsilyl)ethynyl
Th	thiophene
THF	tetrahydrofuran
thpy	2-(2'-thienyl)pyridine
TIPS	(triisopropylsilyl)ethynyl
TTAc	2,5,9,12-Tetrahexyltrithieno- [2'',3'':5,6:3'',2'':3,4:3'',2'':7,8]acridine[1,2-b]thiophene

TTAn	2,5,9,12-Tetrahexyltrithieno- [2'',3'':5,6:3'',2'':3,4:3'',2'':7,8]anthracene[1,2-b]thiophene
TTB	1,2,4,5-tetra(2-thienyl)benzene
TPPy	2-[2,4,5-Tris(2-thienyl)phenyl]thiophene
X	halogen

2. Miscellaneous

%	percent
°	degree
°C	degrees centigrade
*	anti-bonding
A	ampère
Å	Angstrom
Anal. Calcd.	Calculated elemental analysis
Aq.	aqueous
B3	Becke's 3-parameter exchange functional
calcd.	calculated
CB	conduction band
<i>cf.</i>	<i>confer</i>
cm	centimetre
CV	cyclic voltammetry
d	doublet (NMR)
da	dalton
dd	doublet of doublets (NMR)
ddd	doublet of doublet of doublets (NMR)
DFT	density functional theory
DHA	direct heteroarylation
E	potential
ϵ	molar extinction coefficient
e ⁻	electron
$E_{1/2}$	half potential (of a redox process)
E^{lox}	first oxidation potential
EAS	electrophilic aromatic substitution
E_{gap}^{opt}	optical energy gap
EI-MS	electron impact mass spectroscopy
eq.	equivalent
eV	electron volt
f	oscillator strength
g	gram
HOMO	highest occupied molecular orbital
hr	hour
Hz	Hertz
I	current
IR	infrared
J	coupling constant (NMR)
K	degrees Kelvin

K_{dispr}	disproportionation constant
λ	wavelength
LUMO	lowest occupied molecular orbital
LYP	Lee-Yang-Parr functional
m	multiplet (NMR)
M	molarity
μ	charge carrier mobility or transition dipole moment
mA	milliampere
MALDI-TOF	matrix-assisted laser desorption ionization time of flight
mg	milligram
min	minute
mL	millilitres
MO	molecular orbital
MOF	metal-organic framework
mol	mole
m.p.	melting point
MS	mass spectroscopy
nm	nanometre
NMR	nuclear magnetic resonance
OFET	organic field effect transistor
OLED	organic light emitting diode
OPV	organic photovoltaic
OSC	organic semiconductor
OTFT	organic thin film transistor
π	pi (orbital)
PL	photoluminescence
PCM	polarizable continuum model
ppm	parts per million
rt	room temperature
s	singlet
σ	sigma (orbital)
SCE	saturated calomel electrode
SMS	small molecule semiconductor
SNAr	nucleophilic aromatic substitution
T	temperature
t	triplet (NMR)
TD-DFT	time-dependent DFT
UV-vis	ultraviolet-visible
V	volt
VB	valence band

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Chapter 1 – Introduction and Theory of Organic Semiconductors

§ 1.1 Brief Overview of Organic Semiconductors

Since the discovery that doping polyacetylene leads to conductivity of up to 10^4 S cm^{-1} (*cf.* metallic copper: 10^9 S cm^{-1}),^{1,2} the past twenty-five years have witnessed great development in the field of organic electronics. As the scientific community first investigated and then applied the properties that enable organic molecules to exhibit semiconducting behaviour, conjugated polymers and small molecules have been used to, for example, act as transistors (organic field effect transistors, OFETs),³⁻⁶ emit light (organic light emitting diodes, OLEDs),⁷⁻¹⁰ or generate electricity from solar radiation (organic photovoltaics, OPVs).¹⁰⁻¹³ In organic molecules, semiconducting properties are attributed to large π -conjugated systems and the way their electrons behave.¹⁴ The most successful structural motifs in organic semiconductor (OSC) research, taking fused acene structures and thiophene oligomers and polymers as examples, became ubiquitous.¹⁵ The reasons for their success informed the design of the molecules in this work, and are discussed below.

While polymers are an important class of OSCs, the primary focus of this thesis is on small molecule semiconductors (SMSs) and their rational design in pursuit of electronic behaviour, with charge transfer targeted in particular. Small molecules have a number of advantages over their polymeric counterparts: their composition is uniform and well defined; they can often be purified in the bulk using standard techniques (such as recrystallization, sublimation, etc.); their synthesis is highly reproducible and their structures can be tuned by conventional organic chemistry.^{11,16}

Small molecule organic semiconductors, however, are not without their own shortcomings. Perhaps the greatest challenge associated with SMSs is the control of their solid-state morphology. Currently, the best-performing organic semiconductors are those that pack in the solid state such that intermolecular interactions are enhanced, thereby providing a pathway for charge transfer.¹⁷ These interactions are a necessity for implementation into molecular electronics (such as OFETs, OLEDs, OPVs, *vide infra*). One of the benefits of using organic based materials over their inorganic counterparts (for example, silicon) is their solution processibility; to enhance solubility, the planar π -conjugated cores are often functionalized with solubilizing groups (for example, linear or branched alkyl chains), which allows the deposition of active layer thin films by inkjet printing or solution casting. While these substituents are required for solubility, they also influence packing in the solid-state, which results in a variety of common packing motifs, which will be discussed in Section 1.2.

§ 1.2 Solid State Morphology of SMSs

The solid-state morphology of small molecule semiconductors is an important factor when considering charge transport, as it significantly affects their intermolecular interactions.^{15,17-21} By far the most common morphology of SMSs is the herringbone array, in which the dominating interactions are $C-H\cdots H-C$ and “edge-to-face” $C-H\cdots\pi$ contacts with neighbouring molecules.²² These interactions cause the molecules to arrange at steep angles to one another, as illustrated in Figure 1.1 a and b. Less common than herringbone arrangements are the 1-D and 2-D π -stacking motifs, where the molecules are aligned in vertical columns (Figure 1.1 c and d). In these packing arrangements, the most prominent interactions are between the π -orbitals of adjacent

molecules within a column, which provide a pathway for charge transport along the axis of the π -stack. In 1-D π -stacks, the conductivity is isolated within each of the individual stacks, as C–H $\cdots$ H–C interactions between the stacks provide ineffective orbital overlap for inter-stack charge transfer.²³ However, in 2-D π -stacked morphologies, the molecules are arranged such that there are $\pi\cdots\pi$ contacts between neighbouring stacks, which allow charge transport to occur in more than one direction. This is an ideal configuration, since controlling the direction of charge transport in OSC films is another challenge facing their implementation.

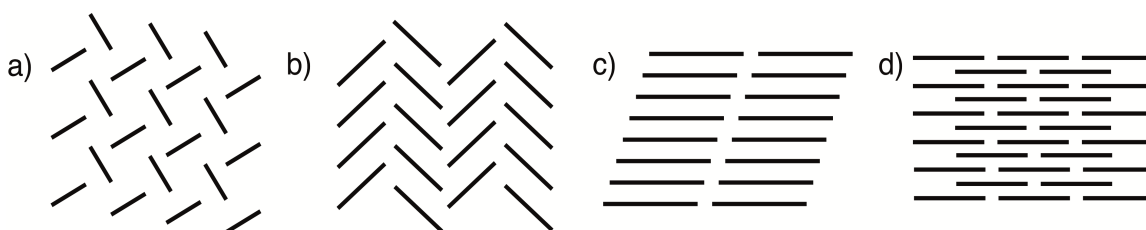


Figure 1.1 Cartoon representations of common crystalline packing motifs in SMSs: a) herringbone array without π - π interactions between molecules; b) herringbone arrays with intra-stack π - π interactions; c) 1-D π -stacks; and d) 2-D brickwork π -stacks (adapted from ref. 3 and 22, © Wiley-VCH Verlag GmbH & Co. KGaA 2008 and © American Chemical Society 2011).

Between herringbone and π -stacking morphologies, π -stacking is thought to be more favourable for conducting charge based on the intermolecular transfer integral,^{5,17,21} which is a parameter calculated from orbital overlap between molecules.²⁰ The evaluation of $\pi\cdots\pi$ interactions at various degrees of slippage in π -stacks indicated that the best-performing SMS-based devices should be those displaying 2-D π -stacking.²⁴ An experimental demonstration of this theoretical result was seen in the device performance of functionalized pentacenes (see Figure 1.2); the charge carrier mobility of thin film OFETs was shown to be greater by two orders of magnitude in two-dimensionally

stacked morphology of (triisopropylsilyl)ethynyl-functionalized pentacene (TIPS-pentacene, Compound **1.1**, $0.4 \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$), than in the one-dimensionally stacked morphology observed in (triethylsilyl)ethynyl-functionalized pentacene (TES-pentacene Compound **1.2**, $<0.001 \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$).³ Notably, TIPS-pentacene has been shown to arrange in a 2-D π -stacked configuration whether deposited from solution or from vacuum.²⁵

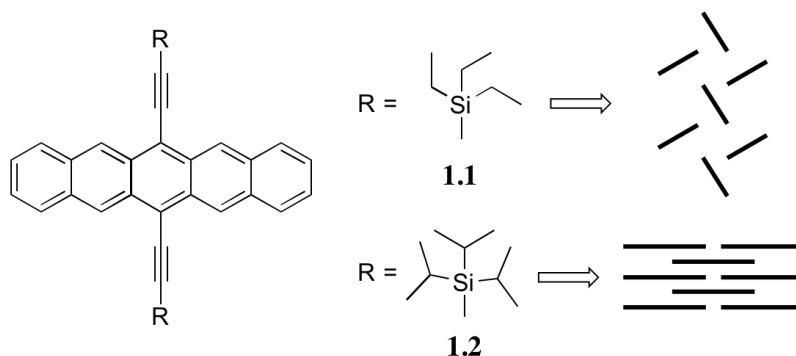


Figure 1.2 Depiction of functionalized pentacene, and the effect of the side chain on solid state morphology (adapted from ref. 3 © Wiley-VCH Verlag GmbH & Co. KGaA 2008).

Although $\pi \cdots \pi$ stacking is predicted to provide the best charge transport properties, it has been shown that edge-to-face $\text{C-H} \cdots \pi$ interactions, even at intermolecular distances exceeding the sum of van der Waals radii, can be suitable for conductivity in herringbone packing configurations.²⁶ Rubrene and pentacene (Compound **1.3** and **1.4**, respectively, shown in Figure 1.3), which are performance benchmarks for field-effect mobility (rubrene as a single crystal FET, pentacene as a thin film FET), have herringbone-packed structures.²⁷ However, these high mobilities are largely due to the highly effective $\text{C-H} \cdots \pi$ and $\pi \cdots \pi$ interactions that occur in their respective benchmark device configurations, instead of the $\text{C-H} \cdots \text{H-C}$ interaction that typically dominates the herringbone packing motif.

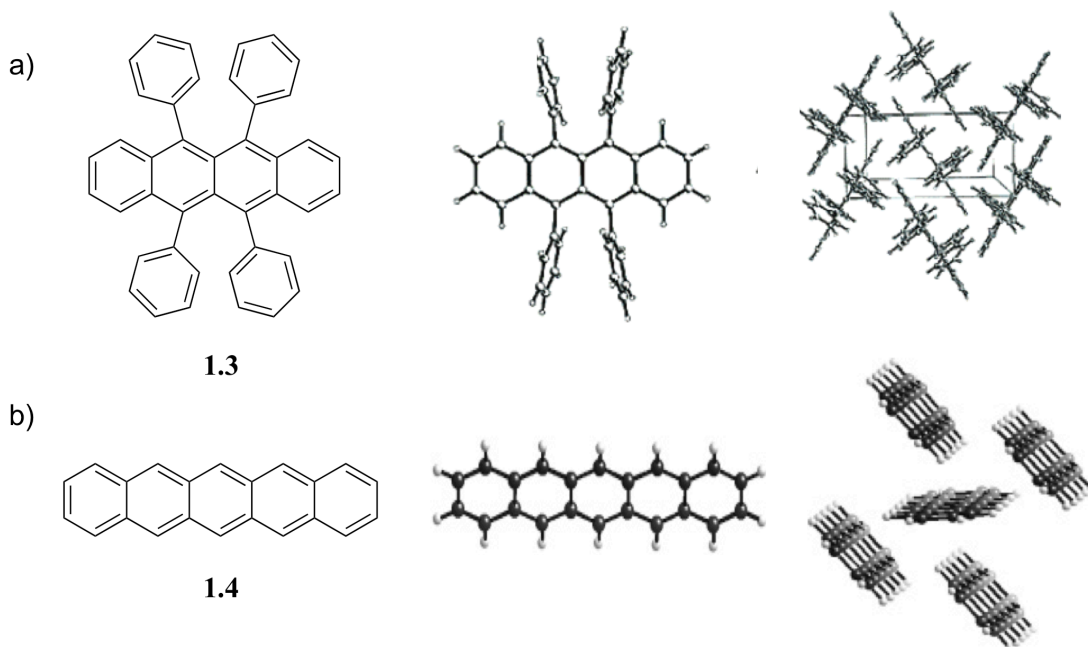


Figure 1.3 Schematics and crystallographically determined molecular structures and packing arrangements of a) Rubrene and b) Pentacene (adapted from ref. 3 and 22, © American Chemical Society 2007 and 2006).

Molecules that can self-associate into highly ordered morphologies (with numerous $\pi \cdots \pi$ interactions) when deposited as thin films, such as TIPS-pentacene, are highly desirable for device applications. The packing motifs of SMSs are determined by X-ray crystallography from single crystals; however, devices are often based on thin films that are prepared from either solution deposition or vacuum sublimation. As such, the resulting morphologies are often different than those observed in single crystals.²⁴ A great deal of research has focused on gaining control over the packing of SMSs by design of the chemical structure, by using strategies such as substituent variation and chalcogen $\cdots$ chalcogen interactions.²² The use of large and extended π -systems is also a common starting point in SMS design; these strategies will be discussed in Section 1.3.

§ 1.3 Tuning the Molecular Framework of Organic Semiconductors

In a conjugated molecule, the p- (or sp^2 -hybridized) orbitals of each atom are joined in an overlapping network of π -bonds, where the electrons of each π -bond are delocalized throughout the molecule. The fact that the electrons are shared across the π -conjugated core enables chemists to use a number of strategies to tune the energy levels of a molecule by modifying the molecular framework. For example, the use of electron donating groups (such as alkoxy chains) or electron withdrawing groups (such as fluorinated alkyl chains) increases the energy of the HOMO, or reduces the energy of the LUMO, respectively (Figure 1.4, Compound **1.5**, Compound **1.9**).²⁸ Furthermore, including pendant aryl rings (Figure 1.4, Compound **1.5**, Compound **1.6**) may increase the effective degree of π -conjugation; as the π -conjugation in an organic semiconductor increases, the energy gap between the HOMO and LUMO decreases because the LUMO energy is reduced simultaneously with the increasing of the HOMO energy.

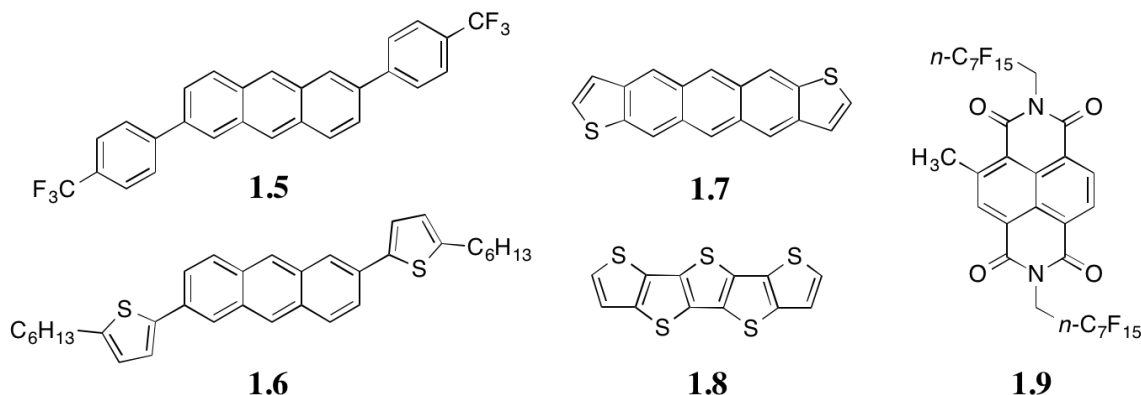


Figure 1.4 Small molecule semiconductors with functionalization highlighting commonly used chemical and morphological tuning strategies.

The energy levels of molecular orbitals have implications in both the optoelectronic behaviour of SMSs, and their stability towards air and moisture. The discussion thus far

has focused primarily on hydrocarbon-based SMSs such as linear acenes. However, chemists have increasingly turned to the inclusion of heterocycles such as pyrrole and thiophene (see Figure 1.5) into organic semiconductors to optimize their electronic properties, increase stability, and improve intermolecular communication.²⁹ With the inclusion of heterocycles into SMSs, a number of considerations come in to play: orbitals change in size and character; lone pairs may participate in conjugation (such as in thiophene); dipoles are introduced in heterocyclic analogues of aromatic hydrocarbons (e.g. pyridine vs. benzene); bond lengths may increase or contract, which along with different atomic radii (*vide infra*), can have effects on both the molecular geometry and solid state behaviour.³⁰

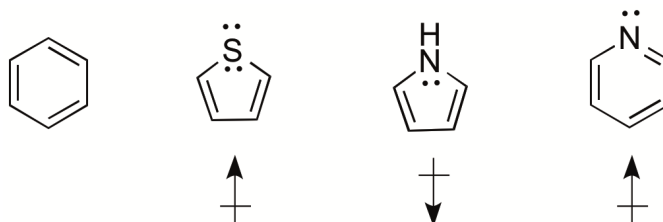


Figure 1.5 Benzene and aromatic heterocycles used to modify the orbital energetics and functionality of organic semiconductors, with associated molecular dipoles depicted.

The substitution of carbon with nitrogen in particular has been exploited to affect energy levels, as well as provide another functionalization point (see Figure 1.4, Compound **1.9**).³¹ The higher electron affinity of nitrogen reduces both the energy levels of the HOMO and LUMO, which can improve environmental stability, or even favour the injection of electrons over holes in devices.³¹ Substitution at nitrogen has also been used to add alkyl chains for solubility, attach phenyl rings to promote $\pi\cdots\pi$ interactions, and append fluorinated alkyl groups (such as $-\text{CF}_3$ or $-\text{CF}_2\text{CF}_3$) to further reduce orbital energies.³² Perylene dicarboximides functionalization with electron withdrawing groups

in this manner displayed electron mobilities of up to $0.64 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (Compound **1.11** as vapor-deposited top-contact OFETS, see Figure 1.6).³³ Furthermore, nitrogen can be protonated (e.g., pyrrole), which can lead to changes in molecular properties (prototropism) such as shifting absorbance and emission profiles.³⁴ Although nitrogen-containing heterocycles such as pyridine and pyrrole have been used in SMSs, perhaps the most commonly utilized across all classes of OSCs is thiophene.

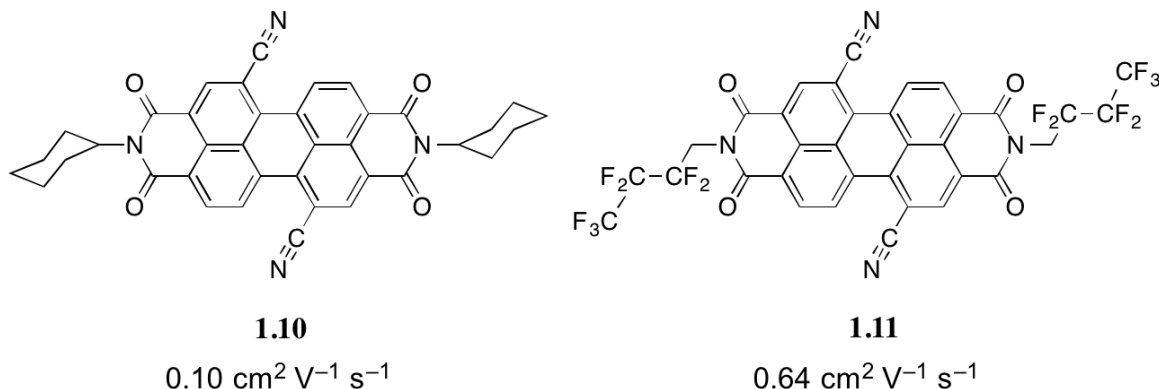


Figure 1.6 Air-stable perylene dicarboximides modified with additional electron withdrawing groups to enhance electron mobility.

§ 1.4 Thiophene in Organic Semiconductors

Among the reasons thiophene has become ubiquitous in the field of organic semiconductors is the larger size and greater polarizability of the sulfur orbitals compared to the second period elements that typically form organic molecules (e.g., C, N, O). Where a large, linear acene such as pentacene displays high conductivity, it is also susceptible to oxidation by atmospheric oxygen or water.¹⁵ This is partly due to the energy levels of the HOMO orbitals; however, acenes are also prone to Diels-Alder reactions to form dimers and trimers, which degrades their performance.²² While thiophene is isoelectronic with benzene, thiophenes do not undergo Diels-Alder reactions

in this manner.³⁵ Sulfur-containing analogues of linear acene systems can show conductivity comparable to or sometimes exceeding those of their parent systems, while displaying enhanced environmental stability.¹⁸ Incorporation of thiophene can also introduce additional intermolecular interactions, such as sulfur-sulfur and sulfur-hydrogen contacts, as well as interactions between sulfur and π -systems,²² which can act as additional paths for intermolecular charge transfer. The TES-functionalized anthradithiophene (Compound **1.12**, shown in Figure 1.7 b) displayed higher thin-film FET mobility ($1.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, drop-cast films),^{19,24} than either TIPS-pentacene ($0.4 \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$) or TES-pentacene. It is important to note, however, that due to the change in ring and atom size in these cases, the solid-state structures can vary from the parent compound to the heteroanalogue. For example, the anthradithiophene Compound **1.12** adopts a 2-D π -stacked morphology (like TIPS-pentacene, Compound **1.2**) instead of the parent 1-D arrangement.

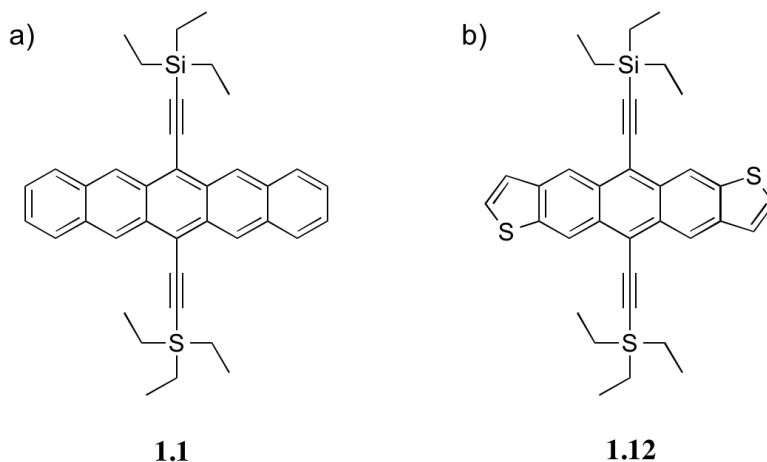


Figure 1.7 (a) TES-pentacene functionalized pentacene, and (b) air-stable TES-anthradithiophene analogue (adapted from ref. 3 © Wiley-VCH Verlag GmbH & Co. KGaA 2008).

§ 1.5 Fused-ring Systems in Organic Semiconductors

Another method often used to optimize molecular properties is to reduce or eliminate twisting of segments of the molecule out of the plane of its π -system.^{36,37} Pendant aryl rings, as in Compounds **1.5** and **1.6**, will often twist out of the conjugated plane due to steric C–H···H–C interactions, which segments the molecule into separately conjugated moieties.³⁸ On the other hand, systems with fused rings often exhibit greater effective conjugation length than their unfused counterparts, likely due to elimination of the rotational freedom of the aryl group. Computational studies have indicated that the energy lost due to structural rearrangement during excitation and relaxation processes (see Section 2.3) is also lower the larger the fused arene systems; an example of this effect is the decreasing reorganization energy through the progression from anthracene (137 meV) to tetracene (113 meV) to pentacene (97 meV).^{20,39}

Fused systems may also be advantageous in the solid state; increasing the carbon-to-hydrogen (C:H) ratio can result in a greater π ··· π interaction surface area, as well as make it more likely for molecules to adopt stacked solid state structures rather than herringbone ones.⁴⁰ To be effective semiconductors, the ability to transfer charge from one molecule to the next through orbital interactions is paramount, and these interactions must be optimized. The use of fused, rigid structures, and the extension of their π -conjugation, has been demonstrated to encourage these π ··· π interactions.⁴¹ Another strategy to encourage π ··· π interactions is to use star-shaped molecules, which are discussed in Section 1.6.

§ 1.6 Star-Shaped Molecules

The use of star-shaped molecules is a relatively recent strategy employed to achieve favourable solid-state morphologies such as π -stacks, which can maximize the close π ··· π

contacts that are required for charge transport in electronic devices.^{16,42} Star-shaped molecules are (ideally) planar molecules, designed using an aromatic “core” with “arm” moieties radiating from the core, which are often comprised of conjugated oligomers (such as Compound **1.13–1.16**, shown in Figure 1.8).¹⁶ Star-shaped molecules can also be tuned to display critical properties for OSC-based devices such as OLEDs and OPVs, namely high fluorescence efficiency and good charge separation, respectively.³⁸

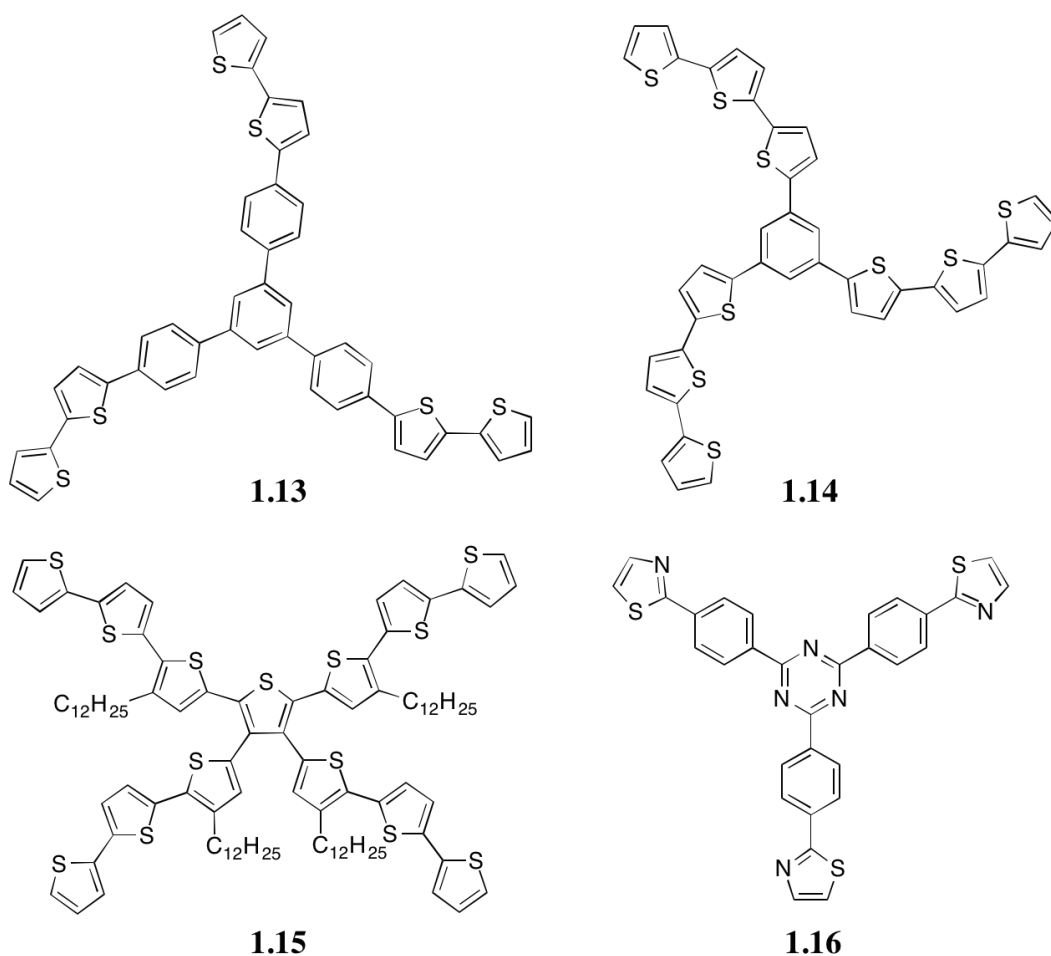


Figure 1.8 Star-shaped small molecule semiconductors based on small aromatic cores that are heavily functionalized with heterocyclic arms, such as oligothiophenes.

Star-shaped molecules have electronic properties that differ from their linear counterparts. One example of this is the nature of charge transport, specifically that

charge transport is more isotropic in star shaped molecules.⁴² In organic semiconductors, the magnitude of charge carrier mobility is often variable with crystallographic direction. More specifically, linear OSC molecules will generally display the highest charge carrier mobility along the axis of π -stacks. However, in star shaped molecules, the mobility is more regular (in other words, isotropic) than in linear structures constructed with the same building blocks.^{16,38} Isotropic charge transfer is favourable because, generally, device construction must ensure that the vector of greatest mobility is aligned to the path between the device electrodes; charge transport that is relatively isotropic is therefore an inherent advantage that star-shaped molecules have over linear SMSs. Additionally, the photophysical behaviour is markedly different in star-shaped molecules. These differences in electronic and optical behaviour are due to the geometry and symmetry of the molecular π -conjugated systems, which are both fundamentally different to those of their linear counterparts.

The molecular geometry, in other words the number of arms and overall shape of the core π -system, of star-shaped molecules can be used to control their electronic properties. Processes such as absorption and emission are polarized directionally along the arms, and are affected by the number of arms; in contrast, linear molecules have photophysical processes polarized along the longest molecular axis.⁴² Furthermore, the symmetry of the core can be varied to optimize energy levels, as demonstrated by Idzik and co-workers.^{43,44} They studied the effect of the number of thiophene arms substituted around a pyrene core and established that both the absorption and emission spectra bathochromically (red) shifted with increased arm substitution and the absorption coefficient was also increased.⁴⁵ The molecular geometry and number of arms can also be

used to increase arm-to-arm communication,⁴⁶ the latter of which could encourage multidirectional charge transport.¹⁶ Owing to the favourable properties and versatile chemistry of oligothiophenes, star-shaped molecules have recently moved towards incorporating these motifs as both arms and core components.¹⁶ Fused moieties such as a pyrenes and carbazoles (Compound **1.17** and Compound **1.18**, Figure 1.9) have also been used as cores and arm units of star-shaped molecules, due to their advantageous properties as outlined in Section 1.5.

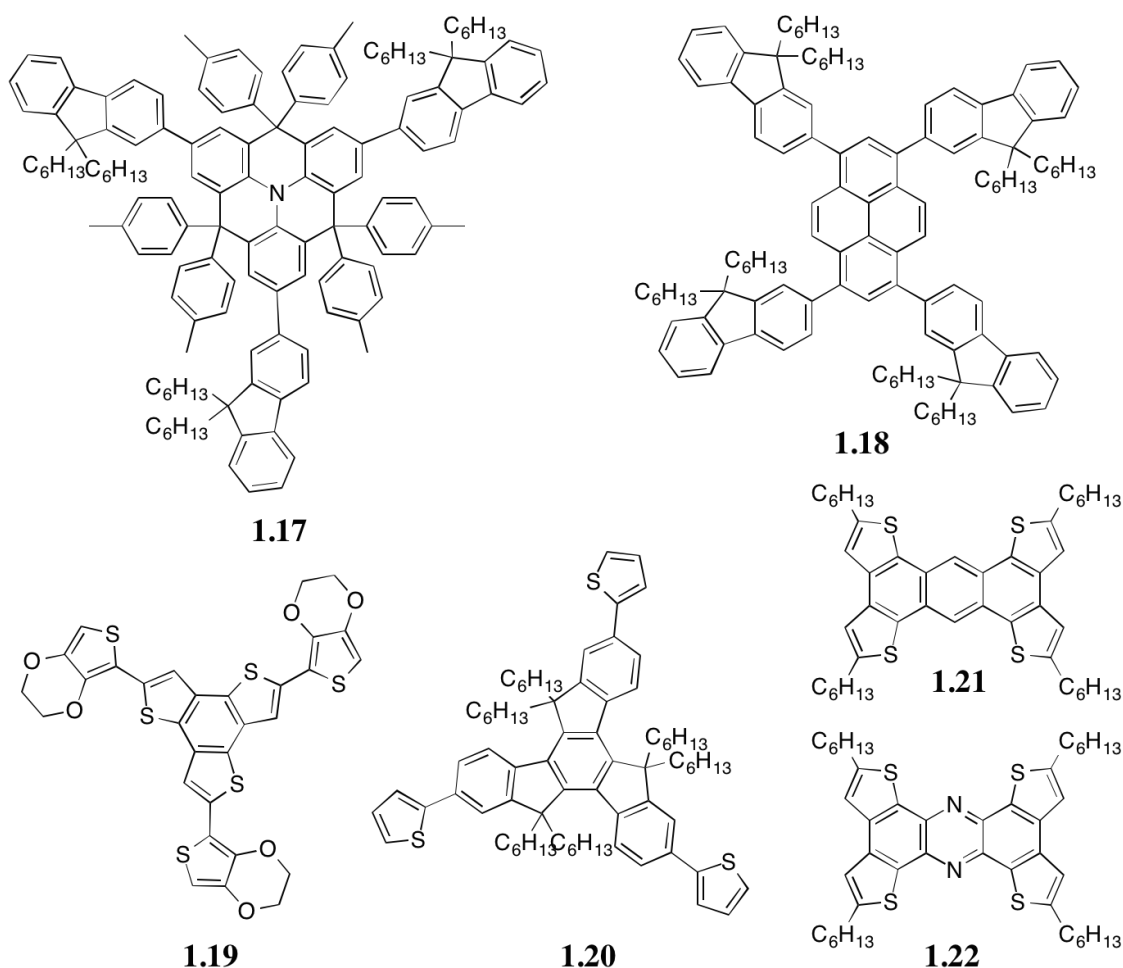


Figure 1.9 Star-shaped molecules with fused, rigid cores and arm moieties.

§ 1.7 From Individual Molecules to the Solid State

In order to contextualize the molecules discussed above, the tuning of their energies, and their photophysical properties and applications as semiconductors, attention must be briefly given to their electronic structures and the bonds they form, and how these bonds behave. Molecular orbital (MO) theory is used to describe the bonding within molecules. In basic MO theory, when atoms come together, their atomic orbitals form bonding, non-bonding and anti-bonding orbitals of varying energies, which are described by their wavefunctions.⁴⁷ As the number of atomic orbitals increases, so does the number of molecular orbitals formed, such that N atomic orbitals lead to N molecular orbitals. As more atomic orbitals mix, more molecular orbitals are formed and the energy differences between them decrease – i.e., the energy levels become very closely spaced.⁴⁸ As the number of molecular orbitals increases and these energy differences diminish, they begin to form a continuous band (see Figure 1.10).²⁴

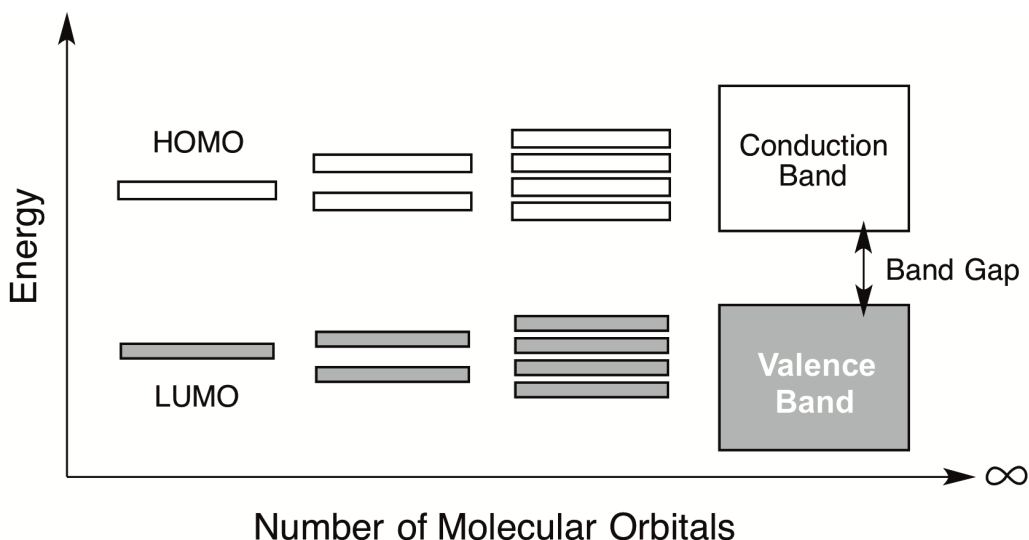


Figure 1.10 Cartoon representation of the formation of bands from molecular orbitals in semiconducting molecules (adapted from ref. 49, © Nature Publishing Group 2006).

The bands that are most relevant to electronic processes in semiconductors are the valence band (VB) and the conduction band (CB), which are comprised of the highest occupied molecular orbitals and lowest unoccupied molecular orbitals, respectively. The difference in energy between the VB and the CB constitutes the band gap. Materials, and their electrical and photophysical properties, can be categorized according to the size of their band gap, as depicted in Figure 1.11.

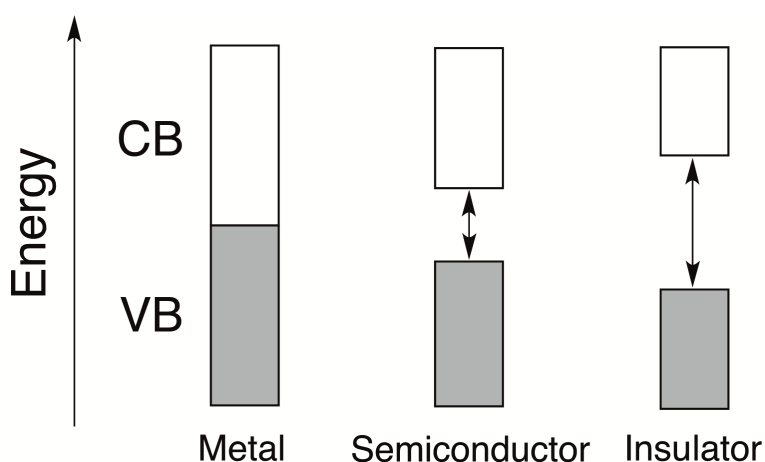


Figure 1.11 Diagram of simplified band structures for metals, semiconductors and insulators, with arrows depicting the relative size of the band gaps (adapted from ref. 10, © Wiley-VCH Verlag GmbH & Co. KGaA 2007).

In metals, there is no gap between the CB and VB, and electrons require no external stimuli to induce charge carriers. In other words, electrons in metals can move freely throughout the partially filled band. As such, metals are characterized by high electrical conductivity. Insulators, on the other hand, have large gaps between the VB and CB, such that it is very difficult to excite electrons into the CB. This leads to high electrical resistance in insulating materials. Semiconducting materials are a class of compounds that require external stimuli to induce charge carriers. They typically have band gaps that are on the order of energies of photons in the UV-visible spectrum (approximately 1.6 –

3.3 eV) or even the near infrared (<1.6 eV). Due to the fact that semiconductors possess band gaps in this energy range, their electrons can become excited through the application of a stimulus such as heat or light, enabling applications for which neither metals, nor insulators, are suited; for example, semiconductors that generate charge carriers by stimulation with light may be used for solar cells, and those that respond to an electric field can be applied to transistors.

§ 1.8 p-type and n-type Semiconductors

Semiconductors can be divided into p-type and n-type, based on the charge that they most stably bear and most effectively transfer. When an electron is removed from the valence band, it leaves behind a positively charged vacancy: in a conjugated molecule, this is a π -orbital with an unpaired electron. It is useful to treat this vacancy as a separate particle in its own right. These pseudo-particles are referred to as electron holes, or simply “holes”. Semiconductors that are p-type transport holes via cationic species, whereas n-type materials transport electrons via anionic species. Organic semiconductors are most commonly p-type; however, n-type semiconductors have begun to appear more frequently in literature as structural motifs that are particularly conducive to electron transport, such as perylene diimides, have become better understood.^{6,42,50} The energy levels of the HOMO and LUMO mainly determine the charge that can be injected (or removed) from a semiconducting molecule, hence whether that molecule is p-type or n-type. The energy levels of the HOMO and LUMO orbitals also determine whether a semiconductor molecule can be stable under atmospheric conditions (semiconductor stability is discussed in more detail in Section 1.12). There exist also ambipolar semiconductors, which are capable of transporting both charges with relatively equal

facility; these are less common in the field of organic semiconductors, and where they do occur, the electron mobilities are usually lower than the hole mobilities.^{18,31} As the operation of devices depends on the movement of charges through the active layer, charge transfer in organic semiconductors is discussed in Section 1.9.

§ 1.9 Charge Transfer in Organic Semiconductors

Regardless of the specific application (for example, OFET, OLED, or OPV) the active material in an OSC-based device must be able to transfer charge carriers from one molecule to the next. In non-crystalline organic semiconductors operating at ambient temperatures, the intermolecular transfer of charges is described by a thermally-enabled electron hopping mechanism.²¹ It is worth noting that the charges in these devices are not transported as associated excitons, but as cations and anions – in other words, vacancies (holes), or additional electrons. Furthermore, the semiconductor molecules must be able to stably bear these charges (see Section 1.11) in addition to being capable of charge transfer processes.

In semiconductors, the band gap determines how much energy must be applied to excite electrons from the valence band into the conduction band.⁵³ In p-type active materials with narrow band gaps, the electrons in the HOMO may be relatively easy to excite at ambient temperatures; in other words, the energy required to remove these electrons from the valence band (generating holes) will be lower than in wide band gap materials under the same conditions.⁵³ However, if the band gap is too narrow, electrons can become excited unintentionally, causing devices to function in a manner other than which they were designed to, which is undesirable. The most common devices based on organic semiconductors are briefly discussed in Section 1.10.

§ 1.10 Thin Film Devices

The three primary target applications of small molecule semiconductors are the transistor, which is in the most fundamental sense an on/off switch;²⁴ the light-emitting diode, which emits photons when charges are injected;⁸ and the photovoltaic cell, which absorbs light, creates excitons, and separates their charges to generate current.¹² Cartoons of OFET, OLED and OPV devices are presented in Figure 1.12.

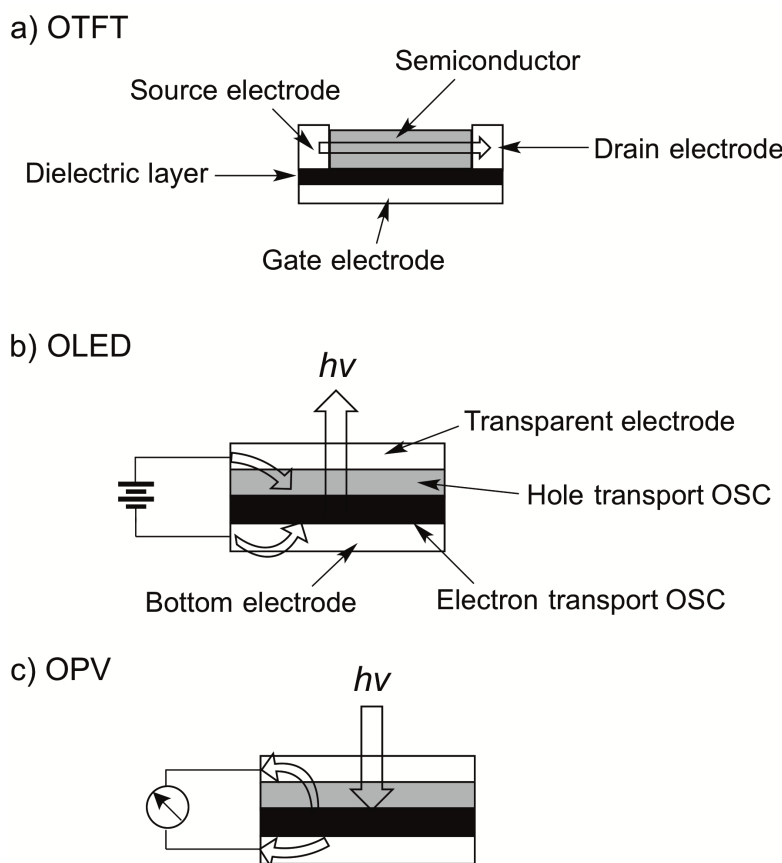


Figure 1.12 Cartoon depictions of devices based on organic semiconductor active layers: a) a thin-film field effect transistor, b) light emitting diode and c) photovoltaic cell; the components of devices b) and c) are the same. Vertical arrows represent the absorption or emission of light; curved and horizontal arrows represent the movement of charge (adapted from ref. 54, © Taylor & Francis, 2011).

Transistors are essential components to integrated circuits, which are the basis of modern electronics. In transistor devices, the most important figures of merit are the charge

carrier mobility μ (the speed at which charges move through the active layer between two electrodes), the current-on to current-off ($I_{\text{on}}/I_{\text{off}}$) ratio, and the threshold or turn-on voltage V_{th} .²⁴ The $I_{\text{on}}/I_{\text{off}}$ ratio is the maximum current (with an applied gate voltage) divided by the minimum current (without a gate voltage). $I_{\text{on}}/I_{\text{off}}$ is an indicator of the purity of the active layer, as impurities may trap charges, oxidize or reduce the semiconductor, and allow conduction in the absence of a bias.²² The threshold voltage is the minimum potential bias that must be applied to the gate electrode of the device in order to begin conducting charge. For high performance transistors, both the charge carrier mobility and the $I_{\text{on}}/I_{\text{off}}$ ratio should be as large as possible, while the threshold voltage should be minimized.

OLED devices operate on the principle of electroluminescence; that is, charges are injected at the electrodes, separately into a hole transporting layer and an electron transporting layer; the charges recombine, and the relaxation of the resulting exciton emits photons from the device. Like transistors, the charge mobility μ and threshold voltage (V_{th}) of OLEDs are important operating parameters, and are ideally as high and low as possible, respectively. Additionally, the efficiency and performance metrics of the devices are critical; these include maximum brightness L_{max} , peak external quantum efficiency η_{ext} and power efficiency η_{p} , which should all be maximized.⁵⁵ The band gap of the emitting OSC determines the energy of the photon that is emitted.

The operation of OPV devices is the opposite of the mechanism of OLEDs; photons from a light source are absorbed, which generates excitons in the active layer. The most common configuration of organic photovoltaics is the bulk heterojunction cell, where two different organic semiconductors are mixed and have many interfaces.⁵⁶ At these

interfaces, excitons become separated and their component electrons and holes are transported to opposite electrodes to generate a current; much research effort is directed towards ensuring high surface area between semiconductor materials, to maximize charge separation. Like OLEDs, the band gap of the absorbing semiconductors is a key feature for OPVs: only photons with energies above the band gap may, in principle, be absorbed and used to generate current. Furthermore, high absorptivity across a wide range of photonic energies greater than the band gap are favourable. Important device parameters include the power conversion efficiency (PCE), a measure of the overall performance of the cell, as well as the open-circuit voltage (V_{OC}), short-circuit current (J_{SC}), and fill factor (FF). The V_{OC} and J_{SC} are inter-related circuit parameters, and are determined by fixing the other parameter at zero (0 V or 0 mA cm⁻²). The PCE is maximized when the V_{OC} , J_{SC} , and FF are as large as possible.⁵⁷

§ 1.11 Charge Carrier Stability

Whether semiconductor molecules are excited by absorption of photons (e.g., OPVs), or charges are injected from electrodes (in OLEDs and OFETs), they must stably support the charges. In other words, they must be stable when oxidized or reduced to cations for p-type materials and anions for n-type materials, respectively. Additionally, reaction of charge carriers with the environment can lead to degradation of the active layer components. One of the difficulties associated with n-type semiconductors is the reactivity of anionic organic compounds.³³ This is due to the energy level of the LUMO, which commonly lies above the redox potentials of oxygen and water.⁵⁸ Since these are present in ambient conditions, this often necessitates encapsulation of n-type devices.

However, as the LUMO energy levels are lowered, these anions become less reducing, and this detrimental reactivity may be limited.³¹

On the other hand, the cationic species that act as charge carriers in p-type semiconductors are generally less prone to stability issues, as the HOMO energy is lower than the LUMO energy, and thus more likely to lie below the redox potentials for oxygen and water (see Figure 1.10). However, all-hydrocarbon p-type semiconductors can be prone to degradation at ambient conditions due to their high-lying HOMO levels. For example, pentacene has a band gap of 1.8 eV and a HOMO level of -5.0 eV vs. vacuum.^{59,60} While pentacene is capable of impressive hole mobilities ($5.0 \text{ cm}^2 \text{ V}^{-1} \text{ cm}^{-1}$), high $I_{\text{on}}/I_{\text{off}}$ ratios (10^8), and low turn-on voltages (0.0 V),²² the fact that its HOMO level is -5.0 eV means it has a low ionization potential,⁶¹ thus making it susceptible to oxidation in air.^{60,62} In order to become widespread, OSCs must exhibit high performance while maintaining stability in ambient conditions to facilitate processing and long operational lifetimes, regardless of the charge that is transported. The energy levels of the semiconductor, as well as the energy involved in molecular excitation and relaxation processes, therefore require careful consideration and optimization; in particular, the oxidation potentials should be kept below region (b) as shown in Figure 1.13.

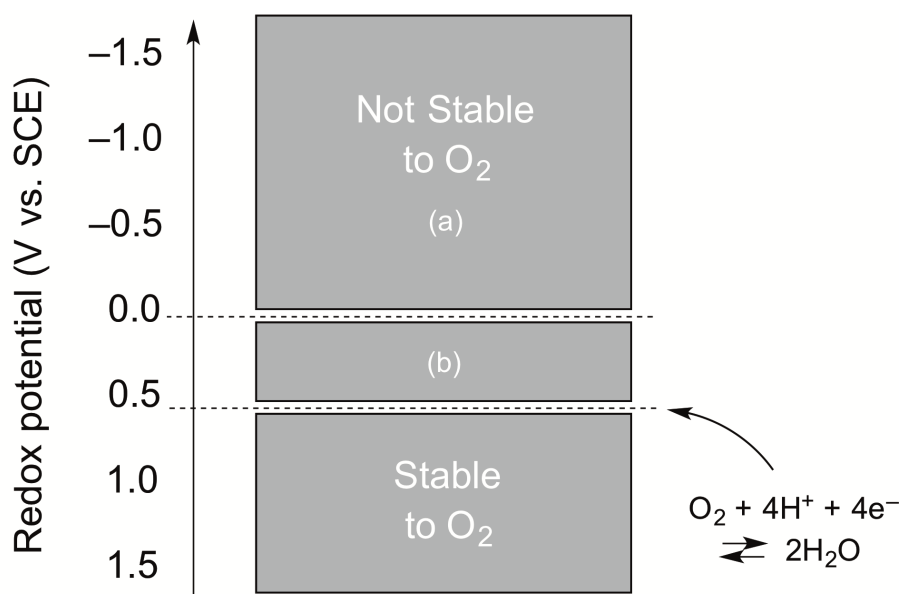


Figure 1.13 Regions of stability of organic semiconductors with respect to the potential of their redox processes. Region (a) assumes a free energy of activation (overpotential) for the electrode process of approximately 0.5 V. Region (b) assumes an overpotential of between 0.0 and 0.5 V. SCE is the redox potential of the saturated calomel electrode. *Note: a more positive redox potential reflects a more negative orbital energy vs. vacuum* (adapted from ref. 58, © Elsevier Science S.A. 1997).

§ 1.12 Tetrathienoanthracene

Tetrathienoanthracene (**TTAn**, shown in Figure 1.14) is a small molecule, which combines the tactics for optimizing OSCs described earlier in this thesis to prepare stable semiconductors with high charge transfer mobility. Namely, **TTAn** takes advantage of the properties of star shaped molecules, as well as the enhanced stability and strong intermolecular chalcogen-chalcogen contacts provided by thiophenes.⁶³ Additionally, the thiophene moieties of these molecules are fused to the anthracene core – in other words, bonded through both the α and β carbons of the thiophenes, which limits out-of-plane twisting and enhances molecular rigidity and conjugation length. These features translated to semiconductor molecules that were stable both to ambient conditions such as

oxygen and moisture, as well as elevated temperatures, which is promising for device fabrication.

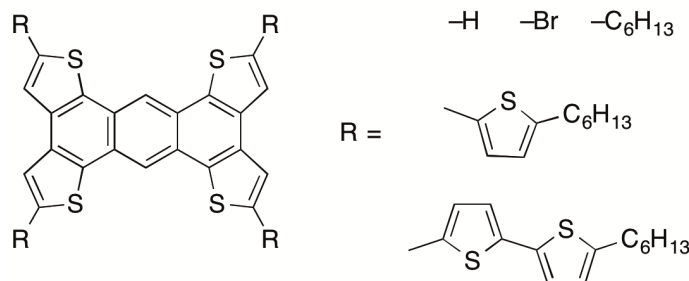


Figure 1.14 Tetrathienoanthracene (TTAn) framework with numerous arm functionalizations that had effects on their electronic, physical and photophysical properties.

Recently, Leitch *et al.* prepared a number of soluble **TTAn** derivatives for OFETs, including those with conjugation extended by thiophene and oligothiophene arms.⁶⁴ Furthermore, in the solid state, crystalline brominated **TTAn** derivatives were demonstrated to form 1-D π -stacks, which is a morphology that is favourable to charge transport, as discussed in Section 1.2. All of the **TTAn**-based molecules displayed π - π contacts that promote effective charge transport in OSCs, with more contacts found in molecules with longer oligothiophene arms.⁴¹ The advantageous properties and overall stability of **TTAn**-based molecules motivated the research described in this thesis, namely the optimization of **TTAn** properties through modification to the molecular structure of the core; this work is discussed in more detail in Chapter 3.

§ 1.13 Aims and Outline of the Thesis

In this thesis, molecules were designed and synthesized by incorporating the principles outlined in this introduction, specifically using star-shaped motifs that have been

substituted with heteroatoms. The overall intention of this work was to prepare these materials for a variety of applications such as thin film transistors, as the organic component in metal-organic frameworks, and as polydentate linear and star-shaped ligands that could coordinate through the sulfur of thiophene.

The second chapter of this thesis explains the methodology and instrumentation that was utilized for this work and outlines some of the general synthetic reactions that are relevant to all the compounds prepared. Furthermore, important characterization techniques that are used to reveal the properties of organic semiconductors, and were applied to the molecules described herein, are discussed in more detail in Chapter 2.

With regard to small molecule semiconductors, utilizing 2-dimensionally fused cores (such as **TTAn**) can be an effective way to encourage π - π interactions in the solid-state, especially when extending the conjugation with pendant thiophenes. The third chapter of this thesis describes the synthesis and optoelectronic properties of thienoacridines, which are nitrogenated analogues of **TTAn**-based molecules. The properties of thienoacridines are then compared with their thienoanthracene counterparts, to study the effects of nitrogenation of thiophene-containing star shaped molecules.

The fourth and fifth chapters concern the synthesis of star shaped thienylbenzene molecules with carboxylic acid groups at the periphery, and the synthesis of linear and star shaped (azomethine)thiophene molecules, respectively. These motifs were targeted for the implementation of star shaped semiconductor molecules into metal-organic frameworks and for use as ligands for applications such as catalysis and chemical sensing. The sixth chapter consists of the conclusions and future directions for this work.

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Chapter 2 – Methodology

This chapter focuses on the methodology used throughout the course of this thesis, initially focusing on common reactions utilized in the synthesis of target molecules. This section will be followed by an outline of the instrumental techniques required to characterize those compounds and study their optoelectronic and solid-state properties, which are relevant to the field of organic electronics. As well, how we interpret the data and extract important information regarding the optoelectronic properties of our molecules will be included. The final section will focus on the methodology of and data derived from *ab initio* calculations.

§ 2.1 Reactions

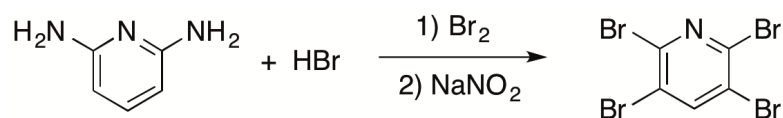
The design and synthetic methodology to prepare the star-shaped molecules herein depended on intermolecular and intramolecular carbon–carbon bond formation of aromatic heterocycles. To accomplish these transformations, metal-catalyzed cross couplings and oxidative coupling reactions were ideally suited. Oxidative couplings have proven useful for the formation of C–C bonds to construct complex discoid molecules,¹ such as the preparation of triphenylenes from functionalized phenyl rings,^{2,3} as well as in large hydrocarbon-based π -conjugated OSCs such as hexabenzocoronenes,⁴ and even graphitic disks (see Section 2.1.4).⁵ Importantly, especially in the context of this thesis, oxidative couplings have also been shown to be effective with thiophene-containing molecules;^{6,7} at reactive carbon positions (such as the α -position of thiophene) these reactions can be performed by irradiation with ultraviolet light as well as chemical oxidants such as FeCl_3 . The latter method was used for the oxidative couplings in this

work, and is discussed further in Section 2.1.4. The addition of bromine to aromatic heterocycles was also important to the synthetic strategy for preparing the OSC molecules studied in this thesis, and is discussed next.

§ 2.1.1 Bromination Reactions

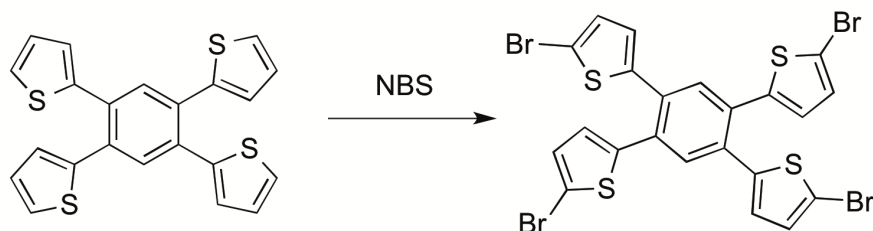
Many metal-catalyzed cross-coupling reactions require a halogen on one of the coupling species. In order to prepare the thienoacridines that are the focus of Chapter 3, tetrabrominated pyridine was required to complete the four-fold Stille coupling reaction, and further bromination was necessary to extend the conjugation of the star-shaped molecules. Bromination reactions can be carried out with reagents such as *N*-bromosuccinimide (NBS) and bromine (Br₂).

Elemental bromine can undergo diverse reactions, performing both electrophilic aromatic substitutions (EAS) and nucleophilic substitution reactions on aromatic rings (S_NAr).⁸ In this work, both EAS and S_NAr reactions were used sequentially in a one-pot fashion to obtain the tetrabromopyridine from 2,6-diaminopyridine.⁹ In the EAS reaction, the pyridyl 3- and 5-positions accept the substitution of bromine, and in the S_NAr reaction, sodium nitrite is used to diazotize the amino groups, whereupon they become effective leaving groups (as N₂) and bromine can substitute as a nucleophile (see Scheme 2.1).



Scheme 2.1 Synthesis of 2,3,5,6-tetrabromopyridine, the coupling precursor for the synthesis of tetrathienylpyridines, by sequential bromination/diazotization.

Bromination can also be performed using NBS. For example, as shown in Scheme 2.2, the halogenation of thiophenes proceeds with regioselectivity for the 2-position of thiophenes due to the higher spin density at the α -carbon.^{10,11} NBS is considered to be a more “gentle” brominating reagent than elemental bromine.

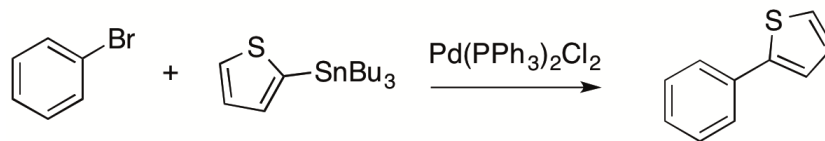


Scheme 2.2 Bromination of tetrathienylbenzene using *N*-bromosuccinimide.

§ 2.1.2 Palladium-catalyzed Cross Coupling: the Stille Reaction

Carbon-carbon bond forming reactions are critical to the preparation of organic molecules, especially large complex conjugated molecules.¹²⁻¹⁵ Numerous transition metal-catalyzed coupling reactions (such as Stille,^{16,17} Negishi,¹⁸ Suzuki-Miyaura,^{19,20} and Mizoroki-Heck²¹ reactions) have been investigated thoroughly, targeting different reactant pairs (such as aryl, carbonyl, aliphatic) and chemical environments.²² Organic semiconductors comprise extended conjugated systems, so Stille reactions to prepare OSCs will couple aromatic organohalides (or pseudohalides such as triflate) with aromatic organostannanes, such as 2-tributylstannylthiophene (see Scheme 2.3). Organostannanes tend to be very stable to air and moisture, which means they are conveniently purified and can be stored for long periods of time in ambient conditions, and the reaction itself is often insensitive to water and oxygen.^{16,17} Furthermore, the Stille

reaction can be employed to perform multiple simultaneous C–C couplings,^{12,23,24} which was utilized in Chapter 3.

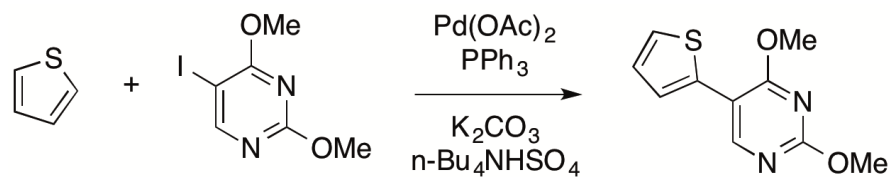


Scheme 2.3 Stille cross-coupling reaction between bromobenzene and 2-tributylstannylthiophene to form 2-phenylthiophene.

In the Stille reaction, the palladium⁰ catalyst inserts into the carbon-halogen bond and becomes oxidized.¹⁷ The organotin reagent transmetalates with the resulting complex, generating a tin halide and transferring the remaining organic group to the palladium centre. When a *cis*-conformation is achieved between the organic groups to be coupled, a reductive elimination both furnishes the desired product and restores the active Pd⁰ catalyst.¹⁶

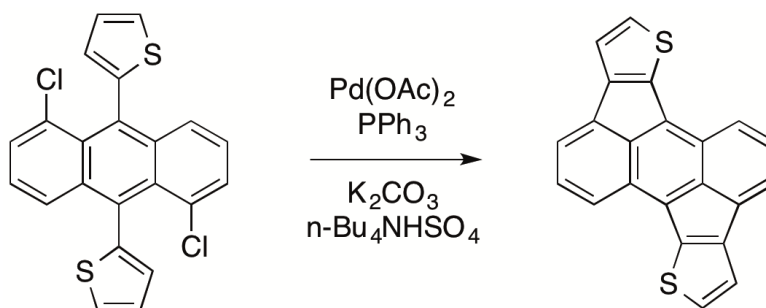
§ 2.1.3 Palladium-catalyzed Cross Coupling: Direct C–H Arylation

Methods of synthesizing organic molecules without the negative aspects of earlier transition metal coupling reactions (toxic organometals or stoichiometric amounts of waste) are very attractive as they may promote the mass industrialization of functional organic materials such as SMSs. Very recently, direct C–H activated (hetero)arylation (DHA) has emerged as such a tool (see Scheme 2.4). The reaction was developed targeting substrates such as functionalized phenyl groups, but regioselectivity was an early challenge.^{25,26}



Scheme 2.4 Direct C–H arylation of functionalized heterocycles with thiophenes (from ref. 26 © American Chemical Society 2007).

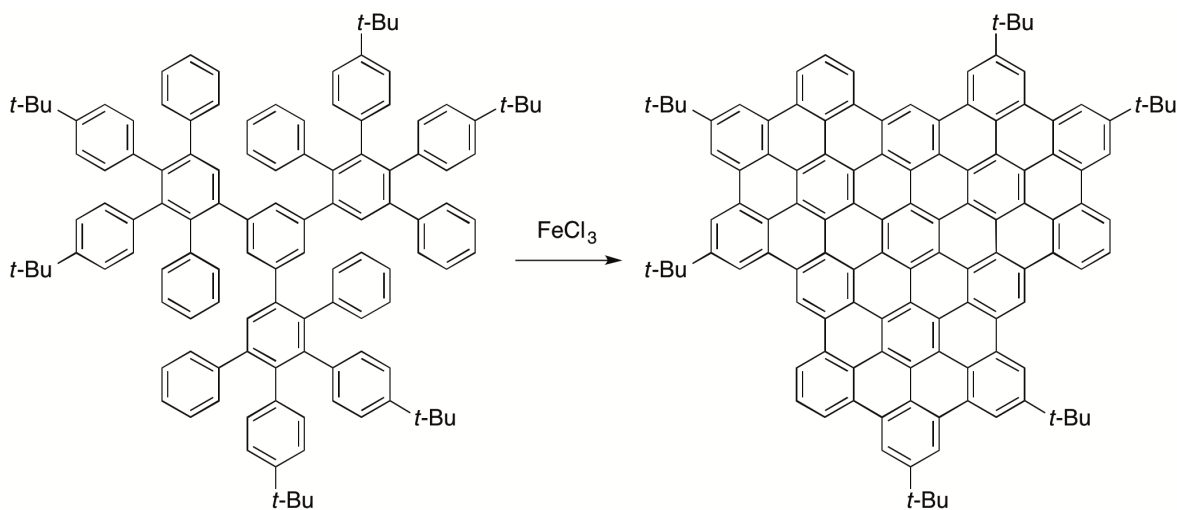
Fagnou and co-workers introduced direct heteroarylation with unfunctionalized thiophenes, where the regioselectivity for the alpha position is promoted by the higher acidity of those protons.²⁷ This has allowed the reaction to be used for the synthesis of functional materials, and its scope has expanded to encompass both discrete molecular synthesis and the synthesis of conjugated polymers.²⁸ Furthermore, C–H activated heteroarylation conditions have been used for the fusion of large, rigid molecules through intramolecular C–C bond formation, effective with heterocycles such as pyrrole, furan and thiophene (see Scheme 2.5).²⁶ The direct C–H activated heteroarylation reaction was used for the preparation of functionalized thienylbenzene and tetrathienylbenzene ligand scaffolds in this work.



Scheme 2.5 Direct C–H arylation with a variety of heterocycles to prepare diverse large conjugated molecules (from ref. 26 © American Chemical Society 2007).

§ 2.1.4 Dehydrogenative Oxidative Cyclization

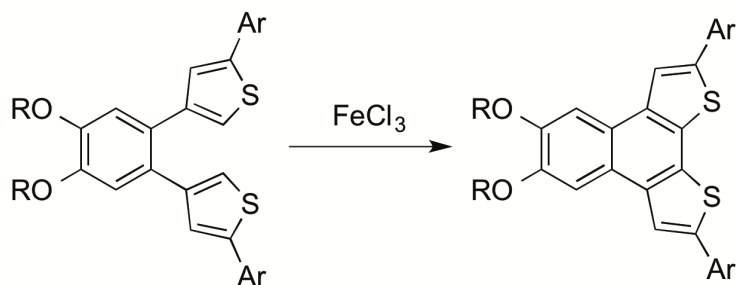
While direct C–H activated heteroarylation conditions can be used for the intramolecular formation of rings, both a halogen and a late transition metal catalyst are required. Chemical oxidation can accomplish similar ends, and is commonly used for a number of applications due to the availability of reagents such as FeCl_3 , which is largely due to the abundance of iron and its ease of synthesis.¹ While reaction with FeCl_3 can be used to construct polymers by oxidative coupling,^{29,30} it can also perform intramolecular cyclizations of large aromatic molecules (see Scheme 2.6),^{2-5,13,31} provided the appropriate geometry is ensured (for example, protonated carbons arranged to form a new 5- or 6- membered ring).⁶



Scheme 2.6 A graphitic disc prepared from an unfused, dendritic oligophenyl benzene precursor using FeCl_3 (from ref. 1 © Royal Society of Chemistry 2009).

Rather than undergo intramolecular cyclization in the same manner as phenyl rings, thiophene-based species such as tetrathienylbenzene will self-polymerize if the reactive α -carbons of the thiophenes are not blocked;¹² with bromine or alkyl chains at the α -position, polymerization can be prevented and intramolecular cyclization achieved

affording fused molecules as shown in Scheme 2.7. Oxidative cyclodehydrogenations were used to fuse tetrathienylpyridines to prepare the thienoacridines for this thesis.



Scheme 2.7 Oxidative cyclization of heterocyclic molecules (adapted from ref. 6, © American Chemical Society 2002).

§ 2.2 Characterization Techniques

Interest in new small molecule semiconductors is driven by their target applications. The operation of devices relies on molecular properties such as the energy difference between the HOMO and LUMO, and the absolute energies of those orbitals, which affect the way the molecules absorb light or behave in devices. For each of the following characterization techniques, the theory underlying the properties being investigated will be briefly outlined, and the molecular information that is important to semiconductor applications will be discussed. A description of how that information is derived from the raw data, as well as the instrumentation used to study these properties follows. Different instrumental configurations are available for potentiostats, spectrometers and fluorimeters. However, for the purposes of this thesis, only the set-ups of instruments utilized for data collection for this work will be discussed here.

§ 2.2.1 Molecules Interacting with Electromagnetic Radiation

One of the most important methods to understand the behaviour and properties of semiconductors is spectroscopy, the study of their interactions with light. Prior to discussing these interactions, the underlying processes between molecular and quantum states will be considered. A Jablonski diagram (see Figure 2.1) is useful for this purpose. The electronic states of small (diatomic) molecules are often idealized as harmonic oscillators that are modeled by nearly-parabolic potential energy wells, the energies of which vary with respect to a nuclear coordinate.³² However, spectroscopy is used to study whole molecules, which in the case of OSCs can be quite large. The wavefunctions of electrons in large molecules are better approximated by multidimensional potential energy surfaces,³³ but 1-D potential energy wells are sufficient for an initial discussion. In whole molecules, the potential energies vary with the configuration coordinate, which is a combination of their geometric and electronic conformations.³⁴

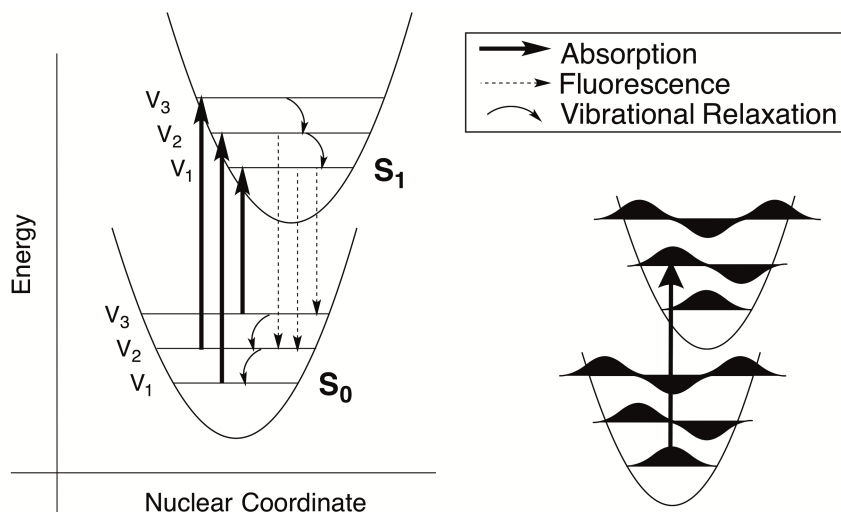


Figure 2.1 Jablonski diagram of a theoretical molecule, displaying singlet state excitation and relaxation processes; visualization of the first three vibronic wavefunctions within an energy level and the Franck-Condon factor are displayed in the lower right (adapted from ref. 16).

As shown in the Jablonski diagram, each electronic state (S_0 and S_1) can be described by a potential well consisting of a number of vibrational states (V_1, V_2, V_3 , etc.). According to the Franck-Condon principle, electronic transitions occur “vertically” (with respect to configuration coordinate) between vibronic states, with an intensity that is related to both vertical wavefunction overlap of the involved states (Franck-Condon factor, see lower right of Figure 2.1) and the magnitude of the transition dipole moment μ between the ground and the excited states.³² When a photon impinging on a molecule has an electromagnetic field coupled to μ , and energy that is matched to the energy difference between two vibronic states in that molecule, it may absorb the photon (see Section 2.2.2A).

§ 2.2.2 Optical Spectroscopy

For organic semiconductors, understanding a molecule’s behaviour includes the study of its electronic structure and properties, which can be probed using optical spectroscopy. For OSCs, the most important interactions with photons are those involving the excitation and relaxation of electrons between frontier molecular orbitals, which in OSCs are typically large conjugated systems comprised of π -orbitals. The gaps between the bonding and anti-bonding π -orbitals, as well as between non-bonding (n) orbitals and π^* -orbitals, are the smallest energy gaps in OSCs,³⁵ and therefore the most important transitions for investigation in this thesis.

The energy of the HOMO–LUMO transitions (and other more energetic transitions) of OSCs generally lie in the range of the UV-visible region (ultraviolet: 190 nm – 400 nm, visible: 400 nm – 700 nm) of the electromagnetic spectrum. Since the energies of absorbed and emitted electrons are directly related to the energy difference between the

orbitals involved in a transition,³² the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions are the most easily excited in OSCs. In molecules with extremely narrow HOMO–LUMO gaps, infrared photons are capable of exciting electrons, but for most molecules these absorptions can only excite vibrations and rotations of molecules and bonds (see Section 4.4).³⁶ Processes related to the absorption of other photonic energies are not considered in this work.

§ 2.2.2A Absorption Spectroscopy

Absorption spectroscopy is a component of optical spectroscopy that is used to study the absorptive behaviour of molecules. For OSCs, one important feature in an absorption spectrum is the onset of absorption, which indicates the least energetic photon that the molecule will absorb with simultaneous excitation of an electron. In an isolated, solvated molecule, this energy corresponds to the optical gap, or the energy difference between the HOMO and LUMO. In the solid state, the absorption onset corresponds to the energy gap, or the energy difference between the valence and conduction band.³⁵ For OSCs, the optical and energy gaps are important for applications such as photovoltaics, light emitting diodes and conductive materials. For example, in OPVs the energy gap is the minimum photonic energy to generate excitons in the active layer, which must then be separated to draw current from a device. In addition to the determination of the HOMO–LUMO gap, both the intensity of a molecule's absorbances, and the wavelengths at which it absorbs are also relevant to OSC applications. To use the example of OPVs again, materials must have strong absorbance across a wide range of the visible spectrum in order to harness as large a portion of the solar flux as possible.¹⁰

In solution, interactions with solvent molecules cause the broadening of discrete absorptions into distributions, forming peaks.³² This means the absorption onset can

appear at a slightly longer wavelength than that of the discrete transition energy. The wavelength used to calculate the optical gap is obtained by taking a tangent to the peak and the intersection of that tangent with the baseline. A cartoon of an absorption spectrum for a hypothetical small molecule semiconductor is presented in Figure 2.2.

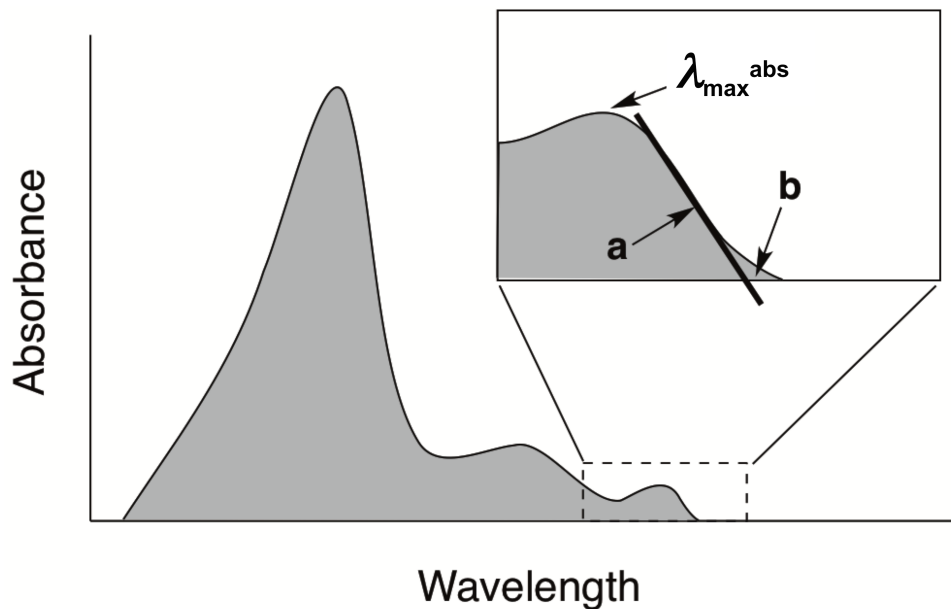


Figure 2.2 Absorption spectrum for a hypothetical OSC. $\lambda_{\max}^{\text{abs}}$ is the peak of the HOMO–LUMO transition, **a** indicates the tangent to the absorption, and **b** is the wavelength from which the optical gap is estimated.

The wavelength of an optical absorption or emission can be used to calculate the energy difference between the orbitals involved in that transition via Equations 2.1 and 2.2:³²

$$E = \frac{hc}{\lambda} \quad (2.1)$$

$$1 \text{ joule} = 6.242 \text{ eV} \times 10^{18} \text{ eV} \quad (2.2)$$

where E is energy in joules, which is commonly converted to electron volts (eV); c is the speed of light; h is Planck’s constant; and λ is the wavelength of light being absorbed.

The two general methods most relevant to the characterization of OSCs are solution state and solid-state absorption spectroscopy. Solution-state spectroscopy can be used to determine transitions resulting from the orbitals in isolated molecules, and was the method used in this thesis. Solid-state UV-visible spectroscopy can be performed on films of molecules (particularly insoluble molecules)⁵ to study their absorptive and emissive behaviour in the bulk, but this technique was not used and will not be discussed further. The setup of the solution-state absorbance spectrometer used in this thesis briefly outlined below.

A double-beam spectrometer was used to analyze dilute solutions of OSC molecules against a blank reference sample. Analyzers measured the difference between the absorbance of the sample solution and the reference solution. The absorbance was measured from 250 nm to 700 nm. Absorbance depends on Beer-Lambert Law, and is determined by the spectrometer using Equations 2.3 and 2.4:³²

$$A_{\lambda} = -\log_{10} \left(\frac{I_f}{I_i} \right) \quad (2.3)$$

$$A_{\lambda} = \epsilon c l \quad (2.4)$$

where A is the absorbance at a specific wavelength, which is a dimensionless value. I_f is the final intensity of an incident beam which has passed through a sample solution, I_i is the initial intensity of the incident beam; ϵ is the molar absorptivity of a compound in $\text{L mol}^{-1} \text{ cm}^{-1}$ at that wavelength, c is the concentration in solution (mol L^{-1}) and l is the path length of the sample cell in centimeters (traditionally 1.0 cm).

To determine the molar absorptivity ϵ of a certain transition – that is, a certain photonic energy – the absorption at that wavelength is measured in a number of solutions of varying analyte concentration. The concentration-dependent absorbances are then calculated using Equation 2.4. From these measurements, a linear relationship between concentration and absorptivity can be constructed, and the slope of that relationship is the molar absorptivity at that wavelength. Sample solutions must be adequately dilute, especially with π -conjugated organic molecules, as aggregation can occur in solution and may cause changes in the absorptive behaviour – such a deviations from the linearity of the concentration-absorbance relationship.³⁷ Quartz cuvettes must be used, as most glasses absorb in the ultraviolet region, which can contain parts of the molecular absorption spectrum.

§ 2.2.2B Emission Spectroscopy

While the absorption of photons will excite electrons in OSCs, the relaxation of excited electrons is, for singlet and triplet states respectively, fluorescence and phosphorescence. When the excited molecules that relax emissively were excited by the absorption of photons, it is photoluminescence (PL), which can be studied using emission spectroscopy. In conjunction with absorption spectroscopy, emission spectroscopy can reveal the photophysical properties of OSCs. The most important feature in a PL spectrum is the $\lambda_{\text{max}}^{\text{em}}$, which is the most energetic emission peak. Additionally, the use of absorption and emission spectroscopies in conjunction provides the Stokes shift of an OSC (*vide infra*).

When a molecule is photoexcited to a vibronic level of the first excited state, it will then undergo relaxation processes that can be either radiative or non-radiative. Non-radiative

relaxations – such as molecular vibrations (internal conversions) or collisions with solvent molecules – have shorter lifetimes than radiative ones (10^{-12} s *cf.* 10^{-8} s for fluorescence).^{32,38} Practically, this means that prior to radiative relaxation, an excited molecule will first lose energy to drop to the lowest vibronic level of the first excited state. Therefore, the energy of an emitted photon from a photoexcited molecule will be lower than energy of the photon that was absorbed.³² A cartoon of an emission spectrum is shown in Figure 2.3.

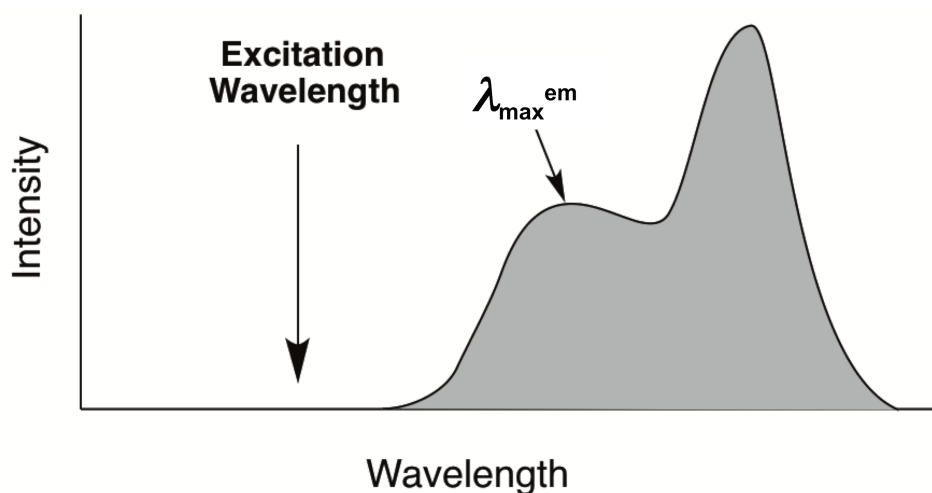


Figure 2.3 Cartoon of an emission spectrum for a hypothetical OSC molecule.

As in solution-state absorption spectroscopy, interactions with the solute cause a distribution of transition energies, leading to broadening of the emission peaks. Due to the “vertical” nature of electronic transitions (Figure 2.1), emission spectra often mirror their corresponding absorption spectra since the criteria for photoemission, as well as the energy levels involved, are the same as for photoexcitation.^{32,38} The emission spectrum provides information about the behaviour of excited semiconductor molecules, of which one of the most important for OSCs is the Stokes shift; this is the lowest peak-to-peak

difference between the absorption and emission spectra, measured from the maxima of the lowest energy absorption to the maxima of the highest energy emission (see Figure 2.4). The Stokes shift is significant to organic semiconductors, as it provides an approximate measure of how much energy is lost to molecular vibrations during the excitation and relaxation processes.³² The amount of energy lost is ideally as small as possible; in other words, the energy transmitted by excited molecules should be as close as possible to the initial energy input for effective active materials, which is especially important for OPVs and OLEDs. The setup of the fluorescence spectrometer used in this thesis is described below.

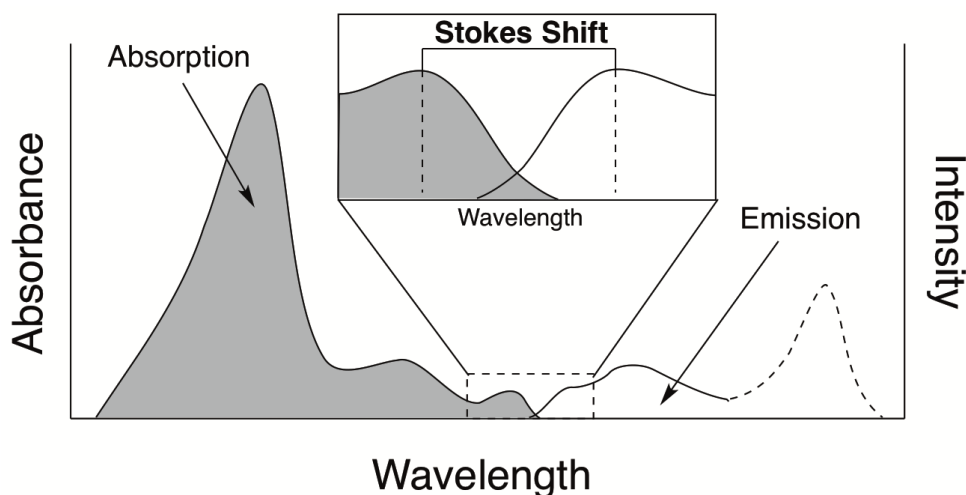


Figure 2.4 Absorption and emission spectra for a hypothetical OSC, with the inset indicating the Stokes' shift.

A monochromatic light source was used to photoexcite a very dilute solution of the sample. The path of the excitation beam and the path of the analyzer were oriented at a 90° angle to minimize the measurement of scattered light. Unlike absorbance spectroscopy, the wavelength of the excitation beam is held constant. The wavelength

and intensity of the emitted photons is scanned and used to construct the fluorescence spectrum.

§ 2.2.3 Electrochemistry

An electronic device utilizing a small molecule semiconductor as its charge transfer material must be able to extract charges from, or inject charges into, the conjugated systems of that semiconductor. The reduction and oxidation processes corresponding to the addition and removal of electrons from the semiconductor molecule, respectively, may be probed using electrochemistry. As mentioned in Section 1.12, in order to function as charge-transporting layers, not only must molecules interact in the solid state, but they must also be stable during the charge transfer processes. Electrochemistry is a useful technique for determining the formal redox potentials for these processes, as well as examining the stability of these molecules. From the formal redox potentials, the energy levels of the HOMO and LUMO can be calculated, which can reveal information about the electronic structure of an OSC molecule and be used to predict its stability to atmospheric conditions (*vide infra*).

One of the most useful electrochemical techniques for characterizing an OSC is Cyclic Voltammetry (CV). In this technique, the potential between two electrodes is increased and decreased cyclically at a constant rate (see Figure 2.5 a), and as the potential of the electrodes reaches the oxidation or reduction potentials of the chemical analyte, current (in other words, the flow of electrons to or from the electrodes) is measured as the response. A voltammogram is formed as the plot of current with respect to voltage (Figure 2.5 b, c). Cyclic voltammetry can be used to determine what the redox potentials of a species are, and the number of electrons involved in a redox process. Redox

potentials may be used to determine the energies of the orbitals, because when electrons are added to the molecules, they enter the LUMO, and when they are removed they are extracted from the HOMO. As discussed in Section 1.12, the stability of semiconductor to various detrimental oxidation and reduction processes can be predicted using the energy levels determined through electrochemistry. The stability of a charged species can also be observed from the reversibility of a redox wave.

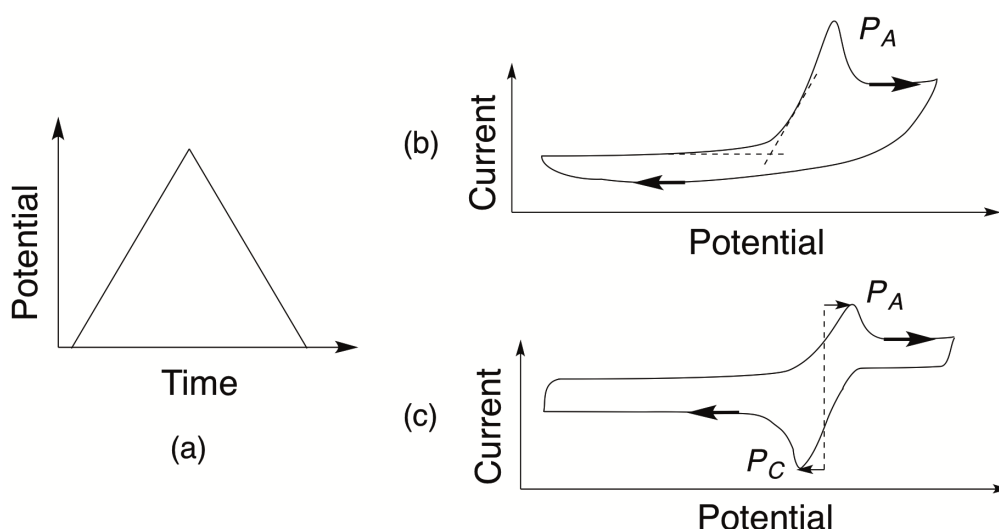


Figure 2.5 a) Triangle-wave scan of the potential between electrodes in a typical CV scan. Hypothetical b) irreversible, c) reversible oxidation processes with their corresponding redox potential determination.

A number of conditions must be satisfied for a redox process to be considered reversible: both oxidation and reduction waves must be observed; the difference in potentials of the anodic and cathodic peaks (the peak separation) is 59 mV for a one-electron process; the currents of the anodic and cathodic peaks are equivalent; the redox potential is independent of the scan rate. For a reversible reduction or oxidation process, the potential is extracted from the halfway point between the positive-sweeping (anodic) peak P_A and the negative-sweeping (cathodic) peak, P_C (Figure 2.5 c). For an irreversible process,

usually only an oxidation or a reduction peak is observed. In this case, the redox potential is taken from the onset of reduction or oxidation, in other words the intersection of the “zero-current” baseline and the tangent of the observed peak (Figure 2.5 b).

The electron affinity and the ionization potential of a material are properties that are directly related to the orbital energies of the LUMO and HOMO, respectively.³⁹ The ionization potential is the potential at which a material loses its highest-lying electron by separating into a radical cation and a free electron; the electron affinity is the potential at which a material gains a free electron. The ionization potential and electron affinity are gas-phase properties; however, they may be estimated from the electrochemically measured redox processes:⁴⁰

$$IP \approx E^{1ox} + E^{vac} + 4.8 \text{ eV} \quad (2.5)$$

$$EA \approx IP - E_g \quad (2.6)$$

Where E^{1ox} is the first oxidation potential, E^{vac} is an experimentally determined scaling correction for referencing solid state properties to the gas state (typically 1.5 eV), the additional 4.8 eV is a scaling factor relating the saturated calomel electrode (SCE) to the vacuum level, and E_g is the band gap of the material in question. Furthermore, the HOMO levels of molecules can be calculated from the first oxidation potential using the equation:⁴¹

$$E_{HOMO} = -e(E^{1ox} + E^{Fc/Fc^+} + 4.8) \text{ eV} \quad (2.7)$$

where E^{Fc/Fc^+} is the formal reduction potential of ferrocene/ferrocenium against the SCE. The LUMO level (and electron affinity) can be calculated in the same manner, should a reduction process be present.

Depending on the charge that a given semiconductor is designed to transport, knowledge of the HOMO and LUMO levels are important to the stability of reaction with O₂ and H₂O, and to their success as active layers in devices. However, the stability of a charged chemical species in the absence of environmental contaminants is also critical. For p-type semiconductors, the stability of their oxidized form can be understood using the disproportionation constant (K_{dispr}), which is related inversely to the separation of two oxidation processes. In a p-type disproportionation process, two identical charged species react to result in a neutral species and a doubly charged species.⁴² A small K_{dispr} may aid in suppression of polaron-bipolaron disproportionation, which would be favorable in transistors based on SMSs.¹² In semiconductors, polarons are interactions between atoms in crystal lattices and the electrons that are passing through them.⁴³ The K_{dispr} can be computed using the equation:

$$E_{1/2}^{1ox} - E_{1/2}^{2ox} = -0.059 \log K_{\text{dispr}} \quad (2.8)$$

A typical electrochemical cell consists of three electrodes: working, auxiliary and reference. The auxiliary and reference electrodes are ideally held at the same potential, while the potential of the working electrode changes with respect to the other two, with the experiment controlled by a potentiostat. For an electrochemical experiment studying organic semiconductor redox processes, a supporting electrolyte is used to provide a conductive solution, and to provide charge-balancing counter-ions to the oxidized or reduced species generated during the experiment. The solvent must be free of moisture and oxygen, which is accomplished by drying the solvent and purging with inert gas. Water and oxygen can both react with the radical and charged species generated during electrochemical experiments. After confirming the absence of air and moisture, the

analyte is introduced to the solution, and then the redox behaviour of the analyte may be probed with cyclic voltammetry experiments.

The potentials of the observed redox processes can depend on the conditions of the experiment. Oxidations and reductions must be referenced to well-defined redox couples, such as the Standard Hydrogen Electrode (SHE) or Saturated Calomel Electrode (SCE), although these are not regularly employed. Instead, reliable internal standards such as ferrocene (Fc/Fc^+) can be added to the working solution after experimentation to reference the observed redox processes to the SHE or SCE.

§ 2.3 Computational Chemistry

Computational chemistry is the use of number theory and the approximation of electronic behaviour in atoms and molecules to correlate, predict, and rationalize molecular properties. Computational chemistry has become increasingly important and widely used to calculate the properties of organic semiconductors as the cost of computing power has decreased, and as theories for treating electrons have improved.^{33,34,44-50} This section will introduce the fundamentals of the calculations used in this work, namely those involved with structure optimization and the prediction of optoelectronic behaviour of OSCs. Of the data that may be obtained from computational chemistry, the properties that are most central to OSCs will be highlighted, with a brief description of the calculation methods following.

The way electrons are treated (such as their properties, both inherent and relative to elemental nucleus they belong to) by computational levels of theory is critical to the accuracy of the predicted properties of molecules. Methods of treating electrons are split

into two general areas: calculations of full wavefunctions, which is computationally expensive (in other words, the calculation time is large) and difficult for all but the smallest molecules; and considering electrons as density functionals, which is relatively inexpensive, and can be used for calculations involving large and complex molecules.^{50,51} This second method is called Density Functional Theory (DFT). DFT works well for closed-shell systems,⁵¹ and as well as being the most widely utilized method, it was chosen for the computational chemistry in this thesis. Other methods will not be discussed further.

Many functionals and basis sets (in other words, the ways electrons are treated in calculations) exist and are chosen depending on the identity of the elements involved in the calculation and thus the electron orbitals that must be considered. One of the more widely used combinations of functionals these is the hybrid functional Becke 3 Lee-Yang-Parr (B3LYP) with the basis set 6-311+G(d,p). This combination was used for the computational work in this thesis, due to the consistency and accuracy of calculations involving the elements hydrogen through argon.^{33,47}

In order to simulate a property of a molecule, an optimized structure of that molecule must be calculated at the appropriate level of theory. A molecular geometry is either taken directly from a crystal structure, or optimized in the gas phase using an iterative process (outlined below) until a stable structure that is a minimum on the potential energy surface has been reached; this is referred to as convergence.³³ The infrared vibrations of the structure are then calculated, where the presence imaginary frequencies would indicate that the geometry had converged upon a saddle point in the potential energy surface, or a minimum in one dimension but not necessarily others. The converged

structure is then used as input for calculating properties such as electronic transition wavelengths.

Time-dependent DFT calculations (TD-DFT) can be used to simulate the electronic transitions in organic semiconductors, so that they may be correlated with experimentally observed optical transitions. Data obtained from these calculations include the orbitals involved in the transition, the energy gap between the orbitals, and the transition oscillator strengths.⁴⁷ With this information, it is possible to both predict and correlate how molecular structures determine aspects of their optoelectronic behaviour. However, that behaviour is most often investigated using solutions of the target semiconductor molecule. In order to mimic the environment of the dissolved molecules from which the UV-visible absorption and emission spectra are measured, a polarizable continuum (PC) must be used. The polarizable continuum is a uniform electric field, into which the gas phase structure is inserted in a cavity. The properties (such as dielectric constant) of the solvent used in spectroscopic optical studies are mimicked using the PC. In this environment, the initial gas phase structure is re-optimized, and the resulting “solution state” structure is then used as the input for TD-DFT calculations.

In addition to photonic excitation, it is possible to use computational chemistry to predict aspects of charge transport (CT). These include the two primary theoretical components of CT, the overlap integral between molecules and the internal reorganization energy. The former is computed based on the crystal packing or another representation of solid-state morphology, where the favorable sign-matched overlap of adjacent molecular orbitals is calculated. The latter is computed based on adiabatic potential energy surfaces, which are conceptually presented in Figure 2.6.

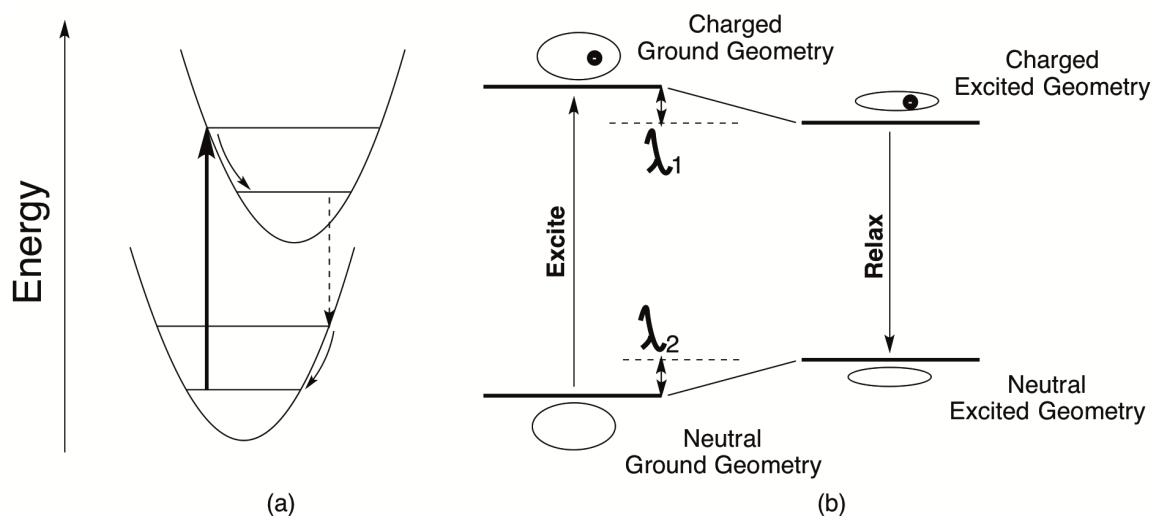


Figure 2.6 Calculation of the internal reorganization energy of hypothetical molecule represented by a) adiabatic potential surfaces, and b) the associated geometries as determined by computational methods, where $\lambda = \lambda_1 + \lambda_2$.

Performing calculations using DFT utilizes an iterative process of calculating the electron densities, and then determining single electron orbitals from the potentials of the initial calculation.⁵² The electron density is re-evaluated based on these single electron orbitals. This process is repeated until the self-consistent field has converged to within defined reasonable limits of interatomic forces in a molecule at final geometry.

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Chapter 3 – Functionalized Thienoacridines: Synthesis, Optoelectronic and Structural Properties

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§ 3.1.1 Introduction

Research interest in small molecule semiconductors for active layers in devices such as organic light emitting diodes (OLEDs) and thin film transistors (OTFTs) has been driven by the promise of materials that are solution processible and compatible with plastic substrates. Devices fabricated from these materials may therefore have the ability to be flexible and lightweight, leading to novel applications. Structures based on linear oligoacenes and fused thiophene oligomers with extended π -conjugation have been the best candidates for these devices. Incorporating heteroatoms into these molecules allows for the improvement of properties such as environmental stability; for example, sulfur-containing molecules have a stability advantage over their all-carbon counterparts, while their larger orbitals improve intermolecular communication.¹⁻³ Further use of heteroatoms such as nitrogen may allow favorable S–N and N–HC interactions.⁴ As described in detail in Chapter 1, “star shaped” SMSs,⁵⁻⁹ those in which conjugation has been extended in two-dimensions, have received increased interest for use as potential device active layers due to their relatively facile synthesis, enhanced thermal stability (compared with linear acenes), and good film-forming properties.¹⁰

§ 3.1.2 Tetrathienoanthracenes

A large family of fused thienoacenes has been reported, synthesized utilizing an iterative four-fold Stille coupling synthetic strategy to prepare star-shaped SMSs with oligothiophene arms of up to four monomers in length.⁵⁻⁷ These molecules were designed both with conjugation extended in two dimensions, and the inclusion of heteroatoms (namely sulfur), as key strategies to improve their semiconductor performance and stability relative to linear, all-carbon counterparts. Built around the tetrathienoanthracene (**TTAn**) core, which is presented in Figure 3.1, these molecules displayed the close π - π contacts that are necessary for charge transport; furthermore, they showed high thermal stability, which is favourable for device fabrication.⁹ Additionally, Brusso and co-workers extended the conjugation further by functionalizing the **TTAn** core with hexylated oligothiophene arms.^{6,7} It was shown that adding oligothiophenes is associated with an increase in the number of π -stacking interactions, in addition to an enhancing the effective conjugation length.^{7,11}

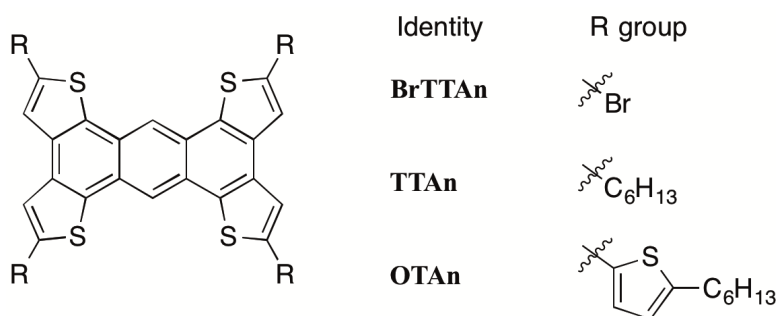


Figure 3.1 Fused thienoanthracenes as heteroatom-containing, star-shaped organic semiconductor molecules

As discussed in Section 1.10, one of the target applications of small molecule semiconductors is the transistor. Thin film transistors were prepared using functionalized thienoanthracenes to study their semiconductor performance. In spin-coated thin film

transistor (TFT) devices, **TTAn** showed a hole mobility (μ_h) of $2.5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ cm}^{-1}$. **OTAn**, a thienoanthracene with extended conjugation through four additional thiophenes, showed μ_h that was comparable ($5.2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ cm}^{-1}$) to what was observed in devices using their smaller counterpart.^{6,7} $I_{\text{on}}/I_{\text{off}}$ ratios for devices from both molecules were approximately 10^4 . Notably, the mobility of **TTAn** improved by two orders of magnitude when devices were prepared by vacuum sublimation.⁵

§ 3.1.3 Nitrogen-Substituted Thienoacenes

The work of this chapter was targeted towards optimizing and investigating the electronic character of thienoacenes with conjugation in two dimensions, while preserving their advantageous properties such as tolerance to elevated temperatures and ambient conditions (*vide supra*). One strategy for tuning the HOMO and LUMO levels of OSCs and making them more electron-deficient, may be accomplished by incorporating nitrogen atoms into the conjugated core, which should result in lowering of the both the HOMO and LUMO energy levels.¹²⁻¹⁴ Nitrogen substitution can therefore be used to enhance the stability of OSCs in ambient conditions, while simultaneously modulating their electronic properties. The tetrathienoacridine (**TTAc**) core, shown in Figure 3.2, represents the ideal target for the exploration of this strategy. **TTAc** is conceptualized by replacing benzene with the relatively electron-deficient pyridyl moiety in the tetrathienoacene core.

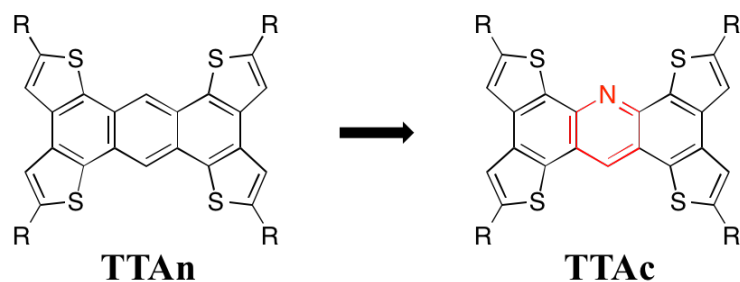


Figure 3.2 Conceptualization of the tetrathienoacridine (**TTAc**) core from tetrathienoanthracene (**TTAn**) by insertion of the pyridyl moiety.

The acridine chromophore (Compound **3.1**, Figure 3.8), has appeared recently in SMS research efforts – notably as potential sensitizers for dye-sensitized solar cells¹⁵ and dopants for C₆₀.¹⁶ A number of acridine salts with extended conjugation such as Compound **3.2** have been prepared and explored,¹⁵ but as of yet, the acridine moiety (Compound **3.8**) has been absent from star-shaped frameworks pursued as active materials for implementation into organic transistors. Like its analogue **TTAn**, **TTAc** features a planar, delocalized π -system and is expected to form highly organized 2-D thin film networks, as well as retain stability to atmospheric conditions and high temperatures.⁵⁻⁷ However, there is a dipole moment associated with the acridine moiety. Phenazine (Compound **3.9**) is the next nitrogenated heteroanalogue of anthracene; unlike acridine, however, there is no dipole moment associated with the phenazine moiety. Therefore, large fused molecules containing the phenazine moiety (such as Compound **3.14**) will not provide information as to the photophysical behaviour of the C-H/N dipole. During the course of this work, a report was published where the phenazine moiety was incorporated into structures related to **TTAn** for thin film transistors.¹⁷

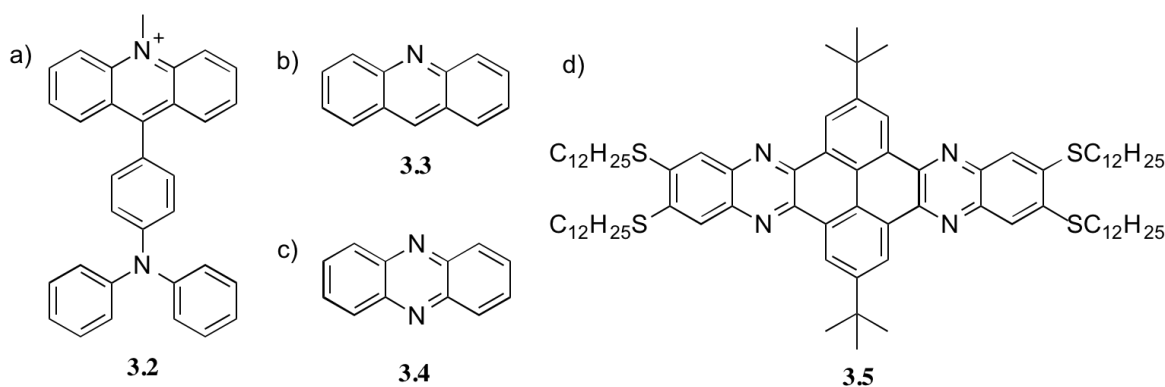


Figure 3.3 a) Acridine-based dye sensitizer for potential organic photovoltaics applications (ref. 21); chromophores b) acridine and c) phenazine; d) a fused pyrene structure incorporating phenazine (ref. 27).

§ 3.1.4 Goals and Outline

In this work, the aim was to construct thienoacridines by substituting a central CH of the anthracene core with nitrogen, in order to investigate the effects of the more electron-deficient core and associated dipole moment on the properties of star-shaped thienoacenes; this chapter will consist of a detailed description of the changes to the photophysical and electronic characteristics of these molecules as a result of nitrogen substitution. In the first section of this chapter, the synthetic routes followed in the preparation of the desired targets are discussed. After the preparation of tetrathienoacridine derivatives and octathienoacridine, the optical spectroscopy and electrochemistry of these molecules were then examined in the context of SMSs, and compared to their thienoanthracene analogs. Computational studies were then used to correlate the observed properties using DFT and time-dependent DFT calculations. Finally, the X-ray studies and thermochromism of brominated tetrathienoacridine were considered. Overall, this chapter embodies a fundamental study of the results of

modifying the cores of 2-D conjugated, star shaped molecules, in pursuit of improved semiconductor properties.

§ 3.2 Results and Discussion

§ 3.2.1 General Synthetic Plan

Following a similar synthetic route as the one discussed in Section 3.1.2,⁵⁻⁷ 2,3,5,6-tetrabromopyridine (**TBP**, Compound **3.6**) was needed for four-fold Stille coupling reactions with stannylated thiophenes to prepare tetrathienylpyridines. This reaction could be followed by oxidative cyclodehydrogenation to fuse the 3-positions of the thiophenes,¹⁸ thereby realizing the **TTAc** core. One of the primary advantages of the four-fold Stille reaction was that, in the case of unfunctionalized thiophenes, the product of the initial coupling - 2-[2,4,5-tris(2-thienyl)phenyl]thiophene (**TTPy**, Compound **3.6**) - could be brominated at the thiophene 5-positions. This would enable an additional four-fold Stille coupling to extend the π -conjugation after fusing, to provide the acridine analogue (**OTAc**, Compound **3.13**) of octathienoanthracene (**OTAn**, Compound **3.14**). The compounds discussed in this chapter are presented in Figure 3.4.

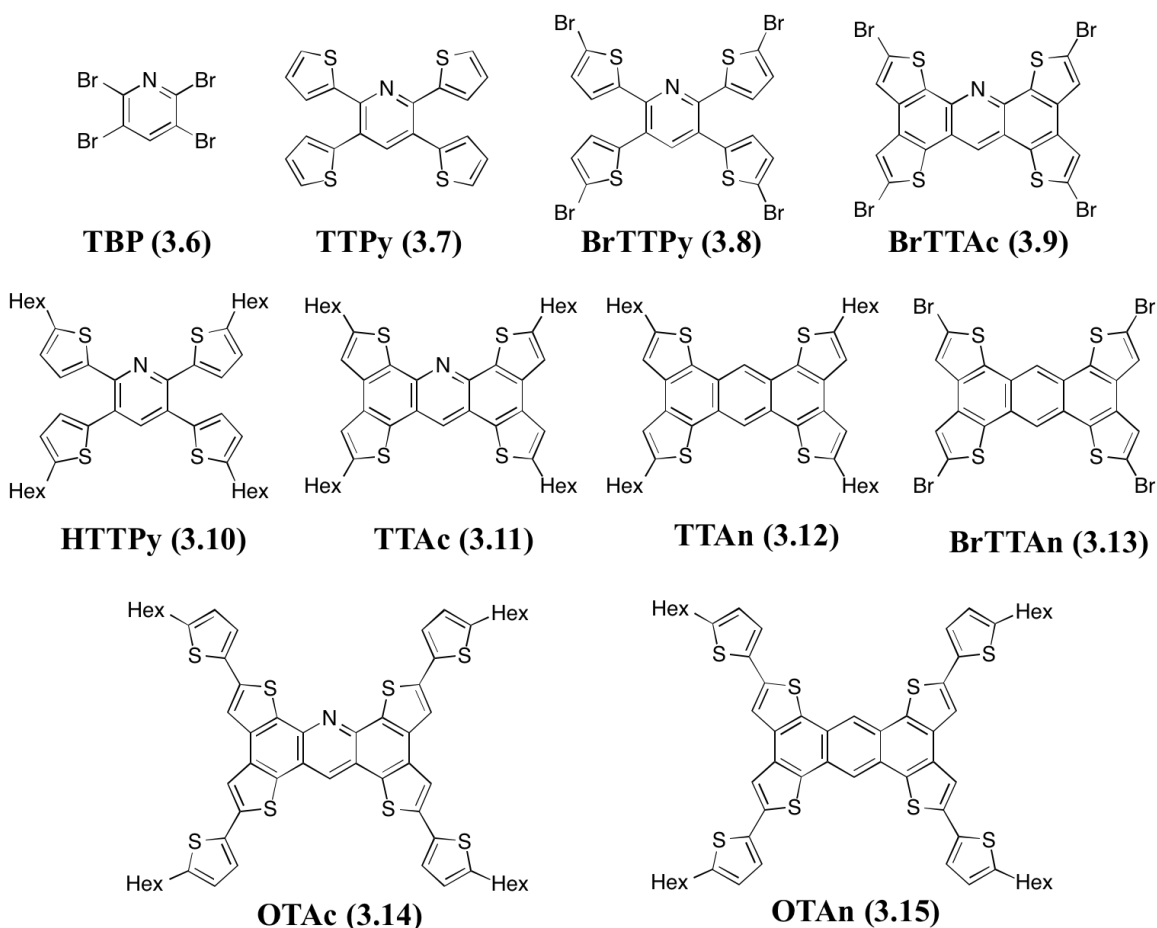
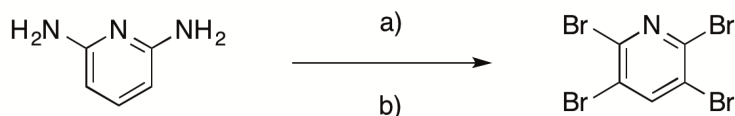


Figure 3.4 Precursors and derivatives of the thienoacridine and thienoanthracene molecules considered in this chapter.

§ 3.2.2 Synthetic Work

TBP was synthesized from 2,6-diaminopyridine utilizing a one-pot sequential electrophilic aromatic substitution (EAS) and diazotization, as outlined in Scheme 3.1.¹⁹ More specifically, a solution of 2,6-diaminopyridine was stirred at 0 °C in 48% HBr, providing a white suspension. Bromine was added dropwise, turning the suspension bright orange as the EAS reaction took place. After 60 minutes, a saturated aqueous solution of sodium nitrite was slowly added, resulting in a vigorous reaction as nitrogen was produced from the diazotization. The addition took place over approximately five

hours; the reaction generated a thick foam, through which it was difficult to maintain stirring. Neutralization of the reaction mixture followed by extraction with ether afforded a crude orange product, which was recrystallized from hexanes to afford orange needles.

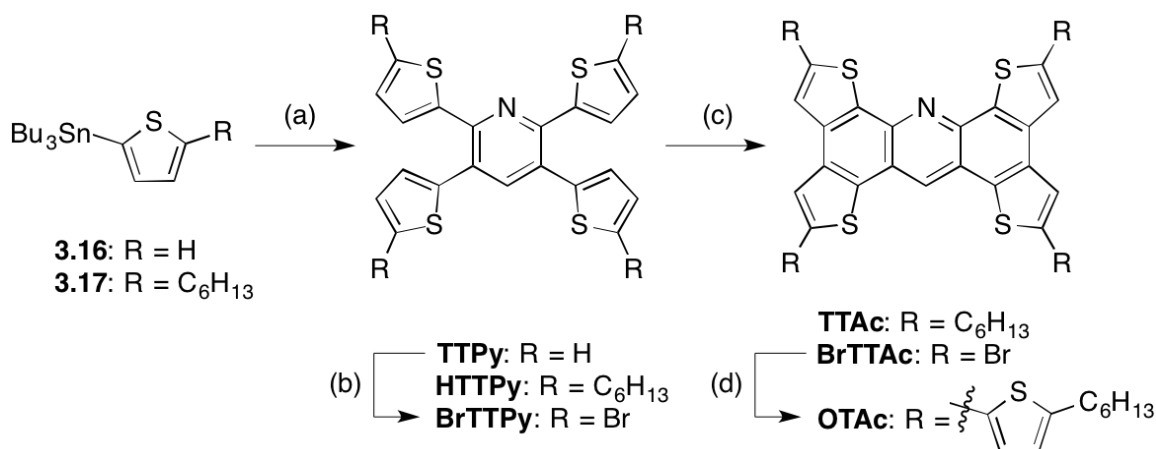


Scheme 3.1 Synthesis of **TBP**. *Reagents and conditions:* (a) 48% HBr, Br₂, 0 °C. (b) saturated NaNO₂ (aqueous) 0 °C.

To prepare the precursor to the **TTAc** core, the four-fold Stille reaction was performed to couple **TBP** with 2-tributylstannylthiophene (see Scheme 3.2 a). The reaction mixture was a brown suspension, which turned black after the reaction had initiated at high temperature, affording **TTPy**. A 6:1 ratio of stannylated thiophene to tetrabromopyridine was necessary to ensure the complete substitution (to avoid 2- and 3- substituted products). The reaction mixture was cooled to room temperature and diluted with hexanes. A silica plug (9:1 hexanes/ethyl acetate) was employed both to remove the palladium catalyst and to separate the excess 2-tributylstannylthiophene, which eluted from the plug with the solvent front. **TTPy** was obtained by continued elution (the eluent was concentrated as a yellow solid), which was recrystallized from ethyl acetate.

The preparation of hexylated tetrathienylpyridine (**HTTPy**, Compound **3.10**) followed the same route as **TTPy** (namely, the four-fold Stille reaction), except the tin reagent was 2-hexyl-5-tributylstannylthiophene. Unlike **TTPy**, the use of a silica plug or silica gel chromatography could not separate **HTTPy** from its precursor tin reagent, possibly because of the enhanced solubility provided by the hexyl chains (*cf.* **TTPy**). However,

the excess 2-hexyl-5-tributylstannylthiophene was successfully removed by vacuum distillation at 200 °C and 0.7 torr using a Kugelrohr apparatus. Unlike its benzene analogue, which is a green solid when crude, **HTTPy** is a highly viscous yellow oil even below 0 °C.



Scheme 3.2 Synthesis of fused thienoacridines. *Reagents and conditions:* (a) **TBP**, [Pd(PPh₃)₂Cl₂], DMF, 130 °C. (b) NBS, THF, 0 °C. (c) FeCl₃, CH₂Cl₂, MeNO₂. (d) 5-(hexyl)-2-(tributylstannyl)thiophene, [Pd(PPh₃)₂Cl₂], DMF, 130 °C.

The next step in the preparation of fused thienoacridines was oxidative cyclodehydrogenation. It had previously been shown that attempts to oxidatively cyclodehydrogenate unsubstituted tetrathienylbenzene using FeCl₃ resulted in polymerization by coupling the reactive α -positions of the peripheral thiophenes.⁵ **HTTPy** was not expected to polymerize when undergoing cyclodehydrogenation, as the hexyl substituents block the reactive α -positions on the thienyl groups. However, **TTPy** has four open α -positions that required blocking. This was accomplished with bromination (Scheme 3.2 b), by combining a 6:1 ratio of *N*-bromosuccinimide (NBS) with a cold solution of **TTPy** in THF, which was protected from ambient light using foil. The reaction afforded an orange solution, from which **BrTTPy** (Compound **3.8**) was

isolated as a yellow powder after washing with water and methanol to remove NBS. Importantly, bromination also enabled the extension of the conjugation length using a further four-fold Stille reaction to provide the octathienoacridine (Scheme 3.2 d, *vide infra*). **BrTTPy** was recrystallized from dichloromethane.

Compared to the benzene derivatives, oxidative cyclodehydrogenation of the tetrathienylpyridines required larger excesses of FeCl_3 . The anthracene-based compounds could be prepared by reacting with six equivalents of FeCl_3 – in other words, three equivalents per coupling.⁵ Initially, cyclization of **HTTPy** was attempted with these conditions. ^1H NMR of the product showed both peaks that corresponded to the product (two singlets for the two magnetically unique thieno protons, see Figure 3.5 h), as well as a side product with proton signatures corresponding to both the 3- and 4-position of thiophenes (two singlets and two doublets from six unique protons, see Figure 3.5 b and e). This indicated that the reaction did not go to completion. Furthermore, the broad NMR peaks suggest the presence of a paramagnetic species, which would occur if the pyridyl nitrogen coordinated to an iron centre.

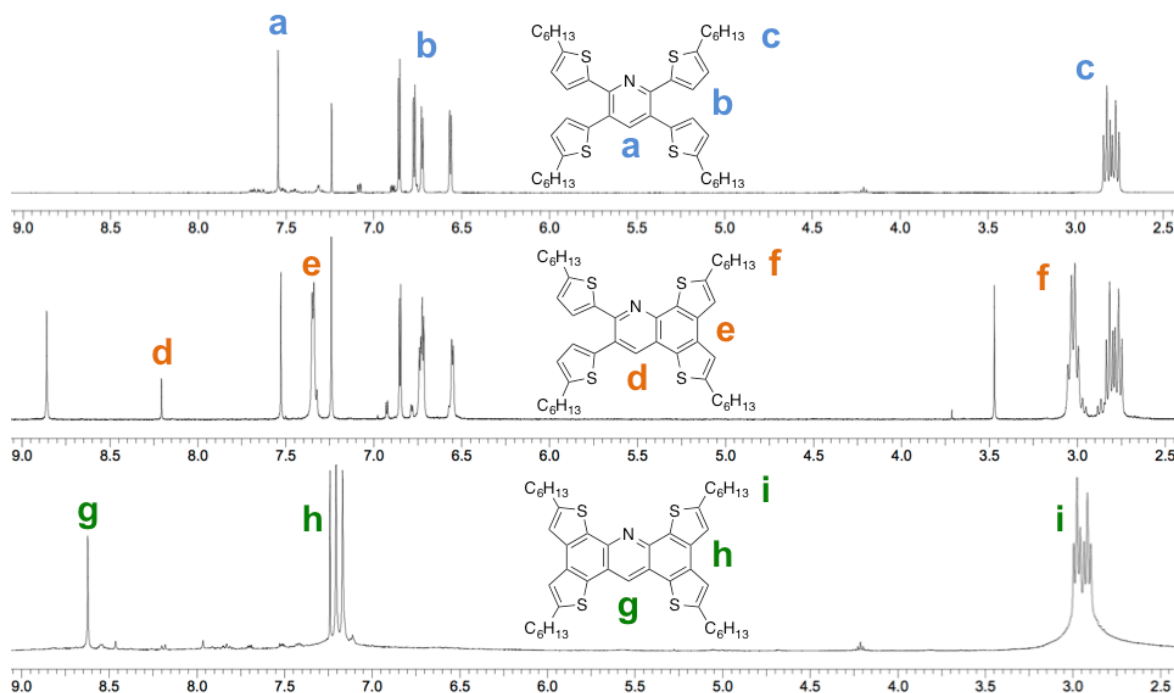


Figure 3.5 ^1H NMR spectra of **HTPy** (top), and the reactions to prepare **TTAc** utilizing six equivalents of FeCl_3 (middle), and fourteen equivalents of FeCl_3 (bottom); the spectra are zoomed to highlight the aromatic and downfield alkyl regions.

To overcome this challenge, a solution of **HTPy** in dry CH_2Cl_2 was treated with fourteen equivalents of FeCl_3 (seven equivalents per coupling), resulting in the isolation of a dark red solid product. The ^1H NMR of this product indicated the acridine species, manifested as two singlets with broad peaks. An orange-yellow solid was isolated by subjecting the dark red product to silica gel chromatography with 10% CH_2Cl_2 in hexanes. The ^1H NMR signatures of this product were sharp peaks rather than the characteristically broad paramagnetic peaks, indicating free **TTAc** (Compound **3.11**). This isolated solid was recrystallized by slowly cooling a saturated ethyl acetate solution, and its identity was confirmed to be **TTAc** by elemental analysis. Attempts to grow single crystals suitable for X-ray diffraction by slow evaporation, slow cooling, and solvent-antisolvent mixtures were unsuccessful. Instead, microcrystalline clusters were

obtained, the largest of which were obtained from slow-cooled saturated solutions.

The oxidative cyclodehydrogenation to prepare **BrTTAc** (Compound **3.9**) was performed by dissolving Compound **3.8** in warm, dry chlorobenzene, which provided a yellow solution. FeCl₃ in MeNO₂, a dark red mixture, was added in 15:1 excess to the solution of Compound **3.8**, causing a deep brown precipitate to form. The reaction was stirred for one hour and then diluted with methanol. The crude product, a waxy red solid, was filtered off and washed copiously with methanol, before being suspended in 10% HCl. Acidification turned the crude product into a yellow-brown powder. This crude **BrTTAc** was purified by vacuum sublimation using a three-zone tube furnace, with the zone temperatures at 350–280–240 °C at a pressure of 10⁻⁴ torr, which afforded yellow needles that were suitable for single crystal X-ray studies (see Section 3.3). It is noteworthy that the temperatures required to sublime **BrTTAc** were approximately 80 °C lower than those necessary for **BrTTAn** at 10⁻⁴ Torr.⁵ During vacuum sublimation, it was discovered that **BrTTAc** exhibits reversible thermochromism, which will be discussed in more detail in Section 3.4.

To compare the acridine-based thienoacenes with extended conjugation to octathienoanthracene, **OTAc** (Compound **3.14**) was prepared from sublimed **BrTTAc** using the four-fold Stille reaction. **BrTTAc** is insoluble in organics; however, the reaction slowly initiated, even as a thick orange suspension, at the high temperatures used for the reaction (130 °C). With each coupling, the solubility of the product increases as the hexylthiophene groups are added to the periphery.⁶ The reaction became dark red over time. A small amount of yellow crystalline **BrTTAc** remained unreacted; this could be removed by filtration during the recrystallization due to its insolubility. **OTAc** was

recrystallized using dichloroethane ($\text{C}_2\text{H}_4\text{Cl}_2$), which afforded small red flakes. Attempts to grow single crystals suitable for X-ray crystallography, using the same methods as for **TTAc**, resulted in iridescent red microcrystalline clusters that were unsuitable for diffraction. The difficulties with obtaining high-quality single crystals may have been due to the dipole moment in acridine-based thienoacenes, which introduces a requirement for dipole ordering to minimize the lattice energy of the crystals (see Section 3.4).

§ 3.2.3 Spectroscopic, Electrochemical, and Computational Studies

Electrochemical and optical spectroscopy studies were carried out on solutions of **TTAc** and **OTAc** in dichloromethane. Computational studies using DFT and TD-DFT were performed using the functional and basis set combination B3LYP and 6-311+G(d,p). The resulting data for thienoacridines were compared with those of their thienoanthracene analogs in order to investigate the influence of substituting a core carbon with nitrogen. The results of these studies are presented in Table 3.1.

Table 3.1 Theoretical,^a Electrochemical,^b and Photophysical Properties^c for **TTAn**,^d **TTAc**, **OTAn**,^e **OTAc**.

	TTAn	TTAc	OTAn	OTAc
$E_{\text{HOMO}}^{\text{calcd}}$ (eV)	−5.21	−5.50	−5.12	−5.28
$E_{\text{gap}}^{\text{calcd}}$ (eV)	3.35	3.32	2.95	2.83
E^{ox1} (V)	1.15	1.33 ^f	0.94	0.98 ^f
E^{ox2} (V)	1.43	1.86 ^f	–	1.61 ^f
$E_{\text{HOMO}}^{\text{expt}}$ (eV) ^g	−5.33	−5.50	−5.11	−5.16
$\lambda_{\text{max}}^{\text{abs}}$ (nm)	431	450	475	500
$\lambda_{\text{edge}}^{\text{abs}}$ (nm)	440	483	493	530
$E_{\text{gap}}^{\text{opt}}$ (eV) ^h	2.83	2.57	2.52	2.34
Calcd. $\lambda_{\text{max}}^{\text{abs}}$ (nm) ⁱ	416	436	501	528
Calcd. $\lambda_{\text{edge}}^{\text{abs}}$ (nm) ⁱ	430	452	527	550
Calcd. $E_{\text{gap}}^{\text{opt}}$ (nm) ⁱ	3.303	3.300	2.833	2.796
$\lambda_{\text{max}}^{\text{PL}}$ (nm) ^j	435	482	490	490
Stokes shift (eV)	0.03	0.06	0.08	0.08

^aDFT/B3LYP/6-311+G(d,p) level of theory where R = Me. ^bIn CH₂Cl₂, 0.1 M *n*Bu₄NPF₆ as supporting electrolyte, referenced to the Fc/Fc⁺ couple of ferrocene at +0.48 V vs. SCE.²⁰ ^cMeasurements performed in CH₂Cl₂. ^dData taken from ref. 5 and provided here for comparison. ^eData taken from ref. 6 and provided here for comparison. ^fMeasured from the anodic peak. ^gDerived using the following expression: $E_{\text{HOMO}} = -e(E^{\text{ox}} - E^{\text{Fc/Fc}^+} + 4.8)$,²¹ calculated from oxidation onset. ^hCalculated from λ_{edge} . ⁱDetermined from TD-DFT calculations. ^jIn CH₂Cl₂, upon excitation at 370 nm for **TTAn**, 340 nm for **TTAc**, 320 nm for **OTAn**, 400 nm for **OTAc**.

§ 3.2.3.1 Electrochemistry

Cyclic voltammetry (CV) was used to determine the redox behaviour and HOMO levels of fused thienoacenes. The voltammograms obtained for thienoacridines are presented in Figure 3.6. Experiments were carried out in CH₂Cl₂ solutions with tetrabutylammonium hexafluorophosphate (NBu₄PF₆) as the supporting electrolyte. The electrolyte

concentration for measurements was 0.1 M. Platinum wires were used for all three electrodes and the potentials were referenced internally to the Fc/Fc^+ redox couple.

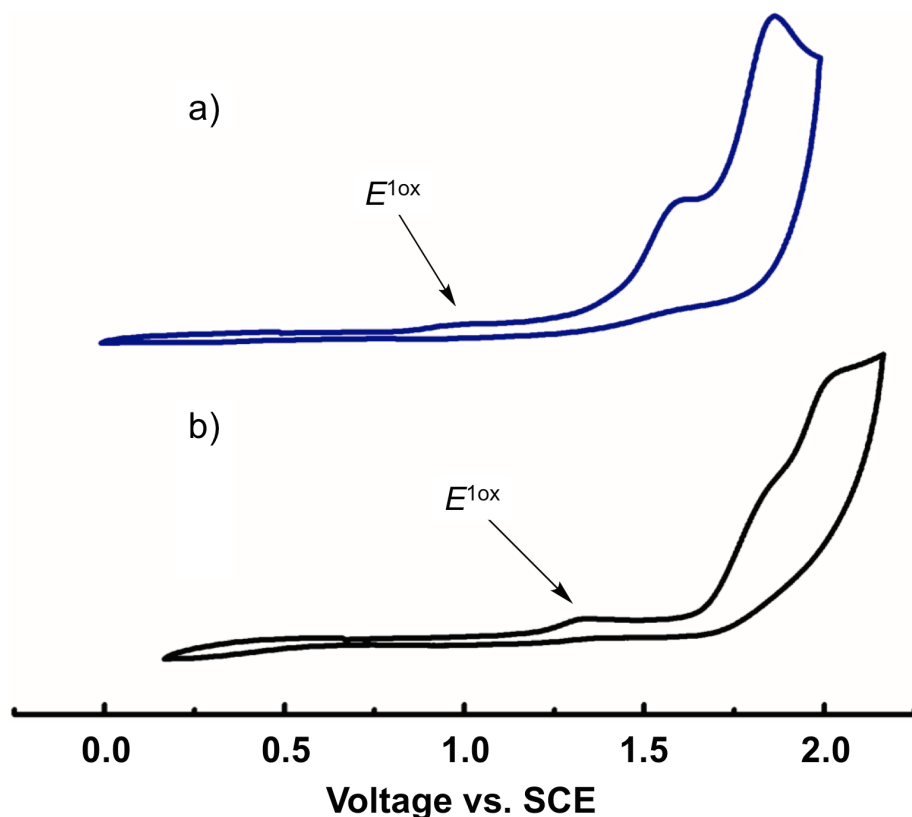


Figure 3.6 Cyclic voltammograms of a) **OTAc** and b) **TTAc** at 100 mV s^{-1} , in CH_2Cl_2 with 0.1 M TBAPF_6 as supporting electrolyte.

Acridines typically show both oxidations and reductions, which tend to be irreversible.^{16,22} Three irreversible oxidations were observed for both **TTAc** and **OTAc**. No reductions were observed. For thienoacridines, the first two oxidations were spaced widely apart: 1.33 and 1.86 V vs. SCE for **TTAc**, and 0.98 and 1.61 V vs. SCE for **OTAc**. The first oxidations corresponded to the generation of the radical cationic species. The cation generated through the second oxidation of **TTAc** was observed as a precipitate being deposited at the working electrode surface on the first scan. This caused a rapid decrease of the response signal, manifested as a drop in current; furthermore, this

deposition prevented the collection of a cyclically stable voltammogram. The same precipitation and deposition was observed for the first oxidation of **OTAc**.

As discussed in Section 2.2.2, the HOMO levels of molecules can be calculated from the first oxidation potential using the expression $E_{\text{HOMO}} = -e(E^{\text{1ox}} - E^{\text{Fc/Fc}^+} + 4.8)$. The HOMO levels of **TTAc** and **OTAc** were thus calculated to be -5.50 eV and -5.16 eV vs. vacuum, respectively. An increase in conjugation length is expected to raise the energy of the HOMO as well as lower the energy of the LUMO.²³ The HOMO of **OTAc** was significantly (0.34 eV) higher than that of **TTAc** as a result of extending the conjugation length with additional thiophenes.

The energies of the HOMO levels for both tetrathieno- and octathienoacenes are expected to be reduced when molecules become more electron-deficient.¹² **TTAn** was reported to have two closely spaced one-electron oxidations (1.15 and 1.43 V),⁵ the former of which corresponds to a HOMO level of -5.33 eV vs. vacuum. **OTAn** displayed a quasi-reversible one-electron oxidation (0.94 V),⁶ which corresponded to a HOMO level of -5.11 eV vs. vacuum. Comparing the thienoacridines to their anthracene-based analogues, the HOMO levels were lowered by 0.17 eV (**TTAn**→**TTAc**) and 0.05 eV (**OTAn**→**OTAc**), which demonstrates the effect of the pyridyl ring on the π -conjugated cores. Furthermore, in thienoacridines, the lifting of the energy of the HOMO by extending conjugation (**TTAc**→**OTAc** *cf.* **TTAn**→**OTAn**) was more pronounced than in the thienoanthracene series (0.34 eV vs. 0.22 eV).

§ 3.2.3.1A Stability of Charged Species

The stability of excited charge carriers is important to the function of organic

semiconductors. Charge carriers such as radical cations can disproportionate, in other words one species oxidizes the other and *vice versa*,^{24,25} as shown in Equation 3.1.



The propensity of this disproportionation occurring is related to the potential difference of two redox processes (both oxidations or both reductions). A small disproportionation constant is ideal for organic semiconductors (see Section 2.2.6), as two radicals with a large disproportionation constant might react to form a neutral and a closed-shell cation or anion.²⁶ If the anion or cation were unstable under the device operating conditions, reduced performance may occur.

The acridine derivatives **TTAc** and **OTAc** displayed wide separations of $E^{1ox}-E^{2ox}$, with each being greater than 0.5 V. Using Eq. 2.8,¹ the disproportionation constants for **TTAc** and **OTAc** were calculated to be 7.0×10^{-10} and 2.1×10^{-11} , respectively. **TTAn** was shown to have a thermodynamically stable radical cation, which was embodied by a redox peak separation of approximately 0.3 V, providing a calculated $K_{dispr} = 3 \times 10^{-5}$.⁵ The K_{dispr} of both **TTAc** and **OTAc** are five and six orders of magnitude smaller than that derived for **TTAn**, which indicates that the acridine core is more capable of stabilizing a radical cation than the anthracene core.

§ 3.2.3.2 Optical Studies

§ 3.2.3.2A UV-visible Spectroscopy

Optical studies were performed on the soluble hexylated thienoacridines to determine the effect of including the acridine chromophore in thienoacenes on their interactions with

¹ $E_{1/2}^{1ox}-E_{1/2}^{2ox} = -0.059 \log K_{dispr}$

photons. UV-visible spectroscopy was utilized to study the absorptive behaviour of thienoacridines. The UV-visible absorption profiles of **OTAc** and **TTAc** were investigated and compared with their anthracene analogues, the results of which are presented in Figure 3.7 and Table 3.1.

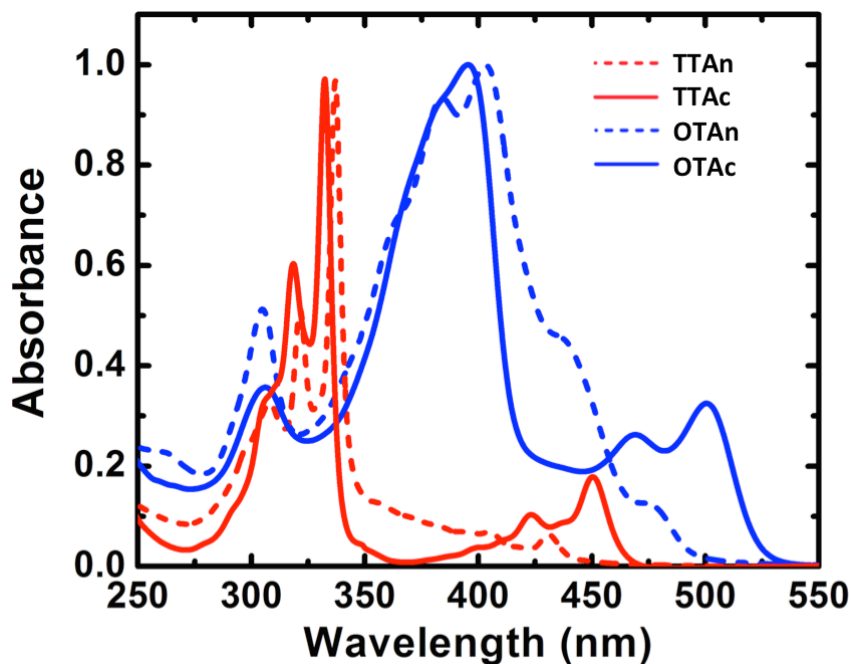


Figure 3.7 Normalized experimental absorption spectra of thienoacenes in CH_2Cl_2 .

The absorption profile of **TTAc** was composed of two regions, consisting of weak absorptions in the low-energy region and strong absorptions in the high-energy region. There were two pronounced peaks at 422 and 450 nm, of which the latter (the HOMO→LUMO transition) was more intense. The high-energy region showed two closely spaced transitions at 322 and 318 nm. The absorption onset of **TTAc** was at 483 nm, which corresponds to an optical gap of 2.57 eV. The overall absorption profile of **OTAc** resembled that of **TTAc** – in other words, there were strong transitions at shorter wavelengths, and weak transitions at longer wavelengths. The long-wavelength region

was composed of two transitions at 465 and 500 nm, the latter of which being the HOMO→LUMO transition. The absorption edge was located at 530 nm, which corresponds to an optical gap of 2.34 eV; comparison of the optical gaps of **TTAc** and **OTAc** provides insight into the effect of extending the conjugation of the thienoacridine framework: the absorption edge was red-shifted by 47 nm, corresponding to a reduction of the optical gap by 0.23 eV.

Brusso *et al.* investigated the photophysical behaviour of **TTAn**.⁵ Like **TTAc**, the absorption profile of **TTAn** had strong transitions in the region between 300 and 350 nm, and much weaker transitions between 350 and 440 nm. The absorption onset of **TTAn** was located at 440 nm, from which the optical gap was determined to be 2.83 eV. The absorption profile of **TTAc** and **TTAn** displayed close resemblance; however, the long-wavelength region of **TTAc** was much more intense. Furthermore, the high-energy absorptions of **TTAc** showed a slight hypsochromic shift with respect to **TTAn**, in other words appearing at a shorter wavelength, whereas the HOMO→LUMO transition was red-shifted by 19 nm. The optical gap of **OTAn** was 2.52 eV.⁶ The general absorption profile of **OTAn** closely resembles that of **OTAc**, with more sharply resolved transitions. Relative to **OTAn**, the absorption onset of **OTAc** was red-shifted by 26 nm, corresponding to diminishing of the optical gap by 0.18 eV.

According to the optical data, the effect of including the electron-deficient pyridyl ring into the aromatic core of thienoacenes resulted in more narrow optical gaps for thienoacridines than thienoanthracenes, as well as stronger HOMO→LUMO transitions. Furthermore, the effect of extending conjugation, as manifested by shrinking of the optical gap, was less pronounced in thienoacridines than in thienoanthracenes

(**TTAc**→**OTAc** 0.23 eV *cf.* **TTAn**→**OTAn** 0.31 eV). In conjunction with the conclusions of the electrochemistry experiments – specifically, that conjugation extension causes a greater lifting of HOMO levels in thienoacridines than their thienoanthracene counterparts – the smaller optical gap decrease from **TTAc** to **OTAc** may indicate that the LUMO levels in thienoacridines do not experience the same energy reduction as the HOMO levels when the conjugated system is extended.

§ 3.2.3.2B Molar Absorptivity

The molar extinction coefficients (ϵ) of the tetrathieno– and octathienoanthracenes and acridines transitions were studied to identify the effect of the electron deficient pyridyl ring on specific transitions, such as the HOMO→LUMO transition. Solutions were prepared in CH₂Cl₂; the results are summarized in Table 3.2. The intensity of a transition is related to the electric dipole along the direction of that transition. With chromophores such as anthracene and acridine, the short axis of the molecule is the vector of the least energetic transition,²⁷ and the electric dipole of acridine is greater than that of anthracene,²⁸ so it would be expected that the intensity of transitions in that direction are greater for compounds with the acridine chromophore. In addition to the red shifts mentioned above, the extinction coefficients for the long-wavelength transitions (such as the HOMO→LUMO transition) for both the tetrathieno- and octathienoacridine increased by more than three-fold relative to anthracene analogues. The extinction coefficients of the short wavelength absorptions (HOMO–1→LUMO transitions) increased slightly upon the introduction of nitrogen, with a larger effect from **OTAn**→**OTAc** (15% increase) than that **TTAn**→**TTAc** (8% increase).

Table 3.2 Wavelength-dependent molar extinction coefficients^a for fused thienoacenes **TTAn**, **TTAc**, **OTAn** and **OTAc**.

TTAn		TTAc		OTAn		OTAc	
λ (nm)	ε (L mol ⁻¹ cm ⁻¹)	λ (nm)	ε (L mol ⁻¹ cm ⁻¹)	λ (nm)	ε (L mol ⁻¹ cm ⁻¹)	λ (nm)	ε (L mol ⁻¹ cm ⁻¹)
431	8200	450	25800	476	10800	501	35300
337	121100	425	16400	438	41300	469	28900
322	61300	322	128200	404	95800	395	112900
308	38500	318	82800	384	87500	306	39500
–	–	–	–	305	49600	–	–

^a Measurements performed in CH₂Cl₂.

§ 3.2.3.2C Photoluminescence Spectroscopy

Photoluminescence spectroscopy was used to study the emissive behaviour of thienoacridines. In the photoluminescence (PL) spectra, **TTAc** and **OTAc** were observed to emit blue ($\lambda_{\text{max}} = 462$ nm) and green ($\lambda_{\text{max}} = 521$ nm), respectively, whereas **TTAn** and **OTAn** emit indigo and blue-green, with $\lambda_{\text{max}} = 435$ nm and 490 nm, respectively.^{5,6} The PL profile of **TTAc** was observed to have less fine structure than that of **TTAn**, but the PL profiles of the octathieno- compounds were very similar. Like the absorption spectra, the extension of conjugation from **TTAc** to **OTAc** resulted in some degree of fine structure loss in the PL spectra. Since this also occurred due to conjugation extension from **TTAn** to **OTAn**, this may indicate that a reduction of the overall rigidity of the π -system occurred as the electron density was spread over the unfused peripheral thiophenes. The photoluminescence spectra of thienoacenes in CH₂Cl₂ are presented in Figure 3.8.

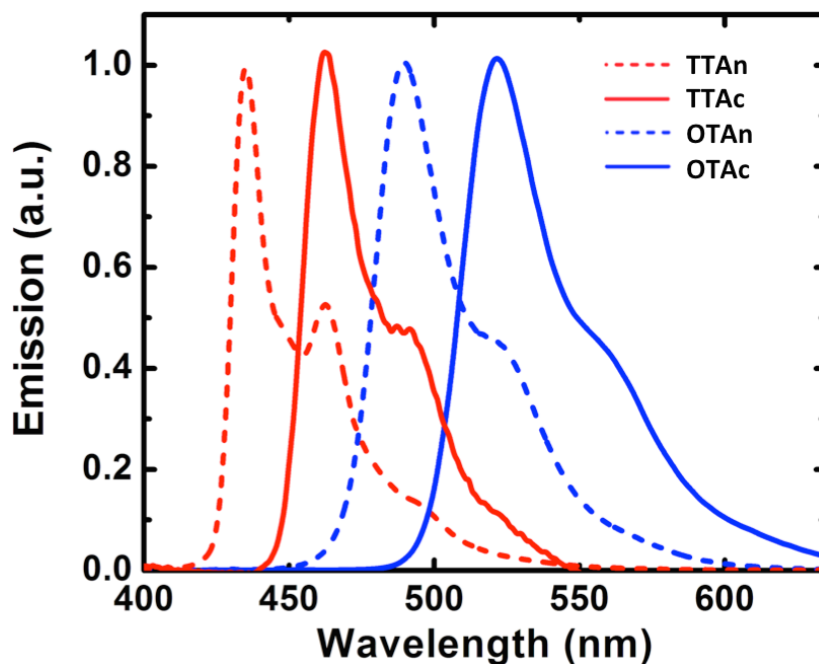


Figure 3.8 Normalized experimental photoluminescence spectra of thienoacenes in CH_2Cl_2 .

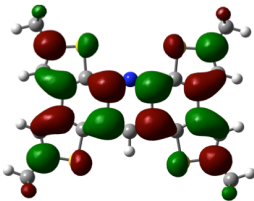
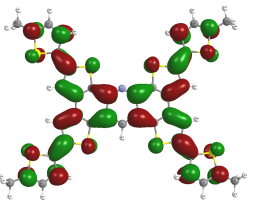
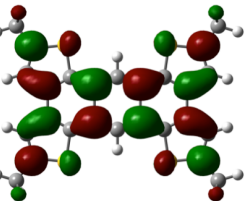
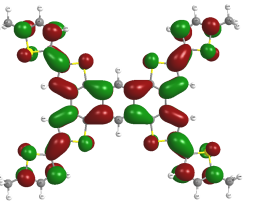
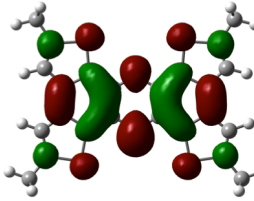
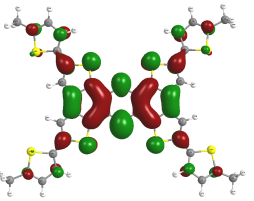
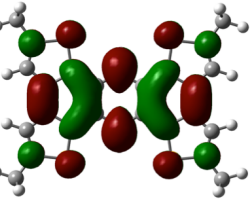
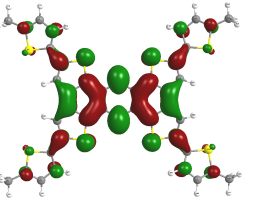
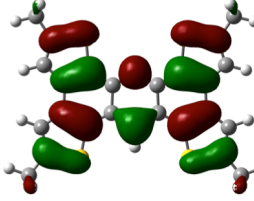
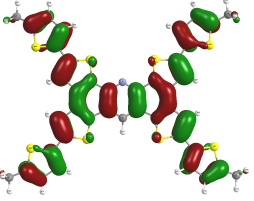
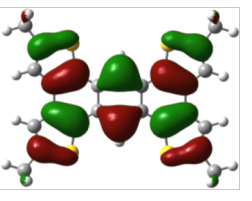
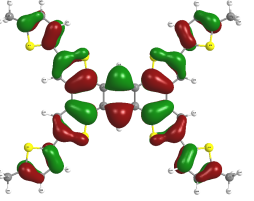
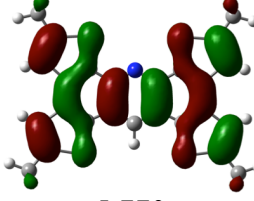
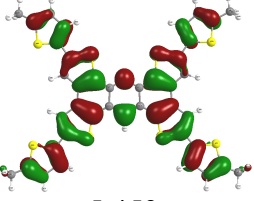
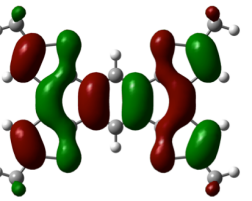
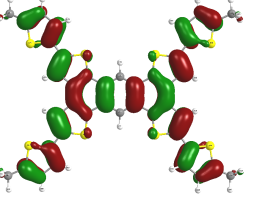
The Stokes' shift, or the separation of the lowest energy absorption peak and highest energy emission peak, can be used as an indicator of the amount of energy lost during structural relaxation associated with the excitation and emission processes.²⁹ It is a manifestation of the difference in molecular geometry between the ground and excited states. As such, a small Stokes' shift indicates that the energy losses associated with excitation and relaxation are small. **TTAc** and **OTAc** exhibited Stokes' shifts of 0.06 eV and 0.08 eV, respectively. These compare well with Stokes' shifts of 0.03 eV⁵ and 0.07 eV⁶ for **TTAn** and **OTAn**, respectively; however, these slight increases suggest a greater amount of energy lost during excitation and emission in thienoacridines than in thienoanthracenes. This correlates well with the loss of fine structure that was observed in both the absorption and emission spectra of **TTAc** compared to **TTAn**. The absorption profile of **OTAc** appeared slightly less structured than that of **OTAn**, however, the

emission profiles appeared identical when considering apparent fine structure. The Stokes' shifts of the octathienoacenes are also similar, which indicates that they lose comparable amounts of energy during excitation and relaxation processes. The Stokes' shift of the **TTAn** core more than doubled when the conjugation was extended to **OTAn**; therefore, the similarity of the Stokes' shifts of **OTAc** and **OTAn** may indicate that the inclusion of unfused thiophene moieties, rather than the acridine chromophore, was responsible for the majority of the energy loss in thienoacenes with π -systems that were extended by additional thiophenes. Overall, substituting the central CH with nitrogen resulted in red shifts to the emission patterns due to smaller energy gaps; furthermore, thienoacridines had larger Stokes' shifts than their anthracene counterparts.

§ 3.2.3.3 Computational Studies

Density functional theory (DFT) calculations were performed on **TTAc**, **TTAn**, **OTAc**, and **OTAn** to correlate the experimental data observed with nitrogen substitution in the fused thienoacene core. The optimized gas phase molecules with their molecular orbitals and associated energies are presented in Table 3.3. Time Dependent DFT was used to assign the solution-state optical transitions for **TTAn**, **TTAc**, **OTAn**, and **OTAc**; the TD-DFT data was used to assign the optical transitions and generate simulated absorbance spectra (see Section 3.3.3.2). For full computational details, see Appendix A.1.

Table 3.3 Molecular orbitals and corresponding energies^a for **TTAc**, **OTAc**, **TTAn**, and **OTAn**; -CH₃ groups were used in place of -C₆H₁₃.

	TTAc	OTAc	TTAn	OTAn
L+1	 -1.499	 -2.219	 -1.419	 -2.177
L	 -2.397	 -2.654	 -2.138	 -2.452
H	 -5.697	 -5.450	 -5.441	 -5.285
H-1	 -5.770	 -5.453	 -5.718	 -5.425

^a Energies are in eV vs. vacuum. **H** and **L** refer to HOMO and LUMO, respectively.

§ 3.2.3.3A Molecular Orbitals and their Energy Levels

The orbitals in Table 3.3 demonstrate that the molecular orbital symmetries of the thienoacene cores are consistent for both anthracene and acridine-based molecules.

Typically, more “electron deficient” systems are lower in energy while more “electron

rich” systems are higher in energy.¹² It was observed from the calculated orbitals that nitrogen-containing compounds have less electron density in the cores, and that the orbitals in thienoacridines are lower in energy, than the same orbitals in thienoanthracenes. More specifically, the orbitals that have electron density over the central atoms had their energies reduced when nitrogen atoms were placed in the core, while orbitals with nodes over central atoms (e.g., LUMO+1 and HOMO–1) were closer in energy relative to the orbitals with identical symmetry in their thienoanthracene analogues. This was demonstrated most clearly by the switch of the orbital symmetries corresponding to the HOMO and HOMO–1 of **OTAc** compared to **OTAn**.

In the gas phase, the energy gaps for compounds **TTAc** and **TTAn** were calculated to be almost identical – 3.300 eV and 3.303 eV, respectively. However, experimentally, the optical gap of **TTAn** was 0.25 eV larger than that of **TTAc** (see Table 3.1). Despite the discrepancy in the energy gaps, the computed HOMO energies were in excellent agreement with the experimental HOMO values derived from cyclic voltammetry studies. The gas phase HOMO–LUMO gaps for octathieno- compounds were 2.796 eV and 2.833 eV for **OTAc** and **OTAn**, respectively. These energy gaps, as well as the computed HOMO levels of the octathienoacenes, reproduced the trends determined from the experimental results.

§ 3.2.3.3B Solution-State Calculations and Time-Dependent DFT Studies (TD-DFT)

TD-DFT has successfully been used to correlate the theoretical and experimental properties of organic semiconductors in the literature.³⁰⁻³² To simulate solution-state optical behaviour such as absorption spectra, the optimized gas phase geometry is re-optimized in a polarizable continuum representing the experimental solvent.³³ Electronic

excitations are then modeled within the same continuum. Solution-state TD-DFT calculations in CH₂Cl₂ for **TTAc**, **TTAn**, **OTAc** and **OTAn** were performed, and their results were used to simulate the absorption spectra of each compound. The spectra are presented in Figure 3.9; the calculated transitions in nanometers and the involved orbitals are presented in Table 3.4.

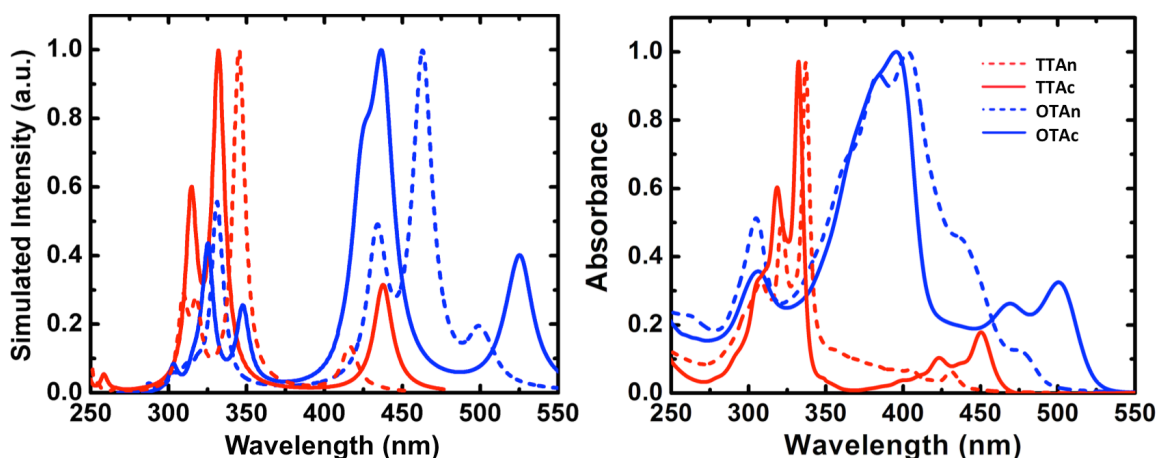


Figure 3.9 Simulated absorption spectra calculated by TD-DFT (B3LYP/6-311G(d,p)) and experimental absorption spectra of thienoacenes in CH₂Cl₂. All spectra are normalized.

Table 3.4 Selected TD-DFT calculated transitions with their theoretical assignments and corresponding experimental absorptions for **TTAc**, **OTAc**, **TTAn**, and **OTAn**.

	Observed absorption band (λ_{max})	Calculated by TD-DFT	Assigned transition(s)	Oscillator strength (f)
TTAc	318 nm	317 nm	HOMO -1 $\rightarrow$ LUMO +1 HOMO -4 $\rightarrow$ LUMO	0.695
	322 nm	333 nm	HOMO $\rightarrow$ LUMO +1 HOMO -1 $\rightarrow$ LUMO	1.241
	450 nm	436 nm	HOMO -1 $\rightarrow$ LUMO HOMO $\rightarrow$ LUMO +1	0.401
TTAn	308 nm	308 nm	HOMO -4 $\rightarrow$ LUMO HOMO -1 $\rightarrow$ LUMO +1	0.366
	322 nm	317 nm	HOMO -1 $\rightarrow$ LUMO +1 HOMO -4 $\rightarrow$ LUMO	0.330

OTAc	337 nm	345 nm	HOMO → LUMO +1 HOMO -1 → LUMO	1.522
	431 nm	416 nm	HOMO -1 → LUMO HOMO → LUMO +1	0.200
	306 nm	327 nm	HOMO -1 → LUMO +4 HOMO -2 → LUMO +2 HOMO -3 → LUMO +3	0.730
	306 nm	349 nm	HOMO -4 → LUMO	0.431
	383 nm ^a	423 nm	HOMO → LUMO +1 HOMO -2 → LUMO	0.786
	395 nm	436 nm	HOMO -1 → LUMO +1 HOMO → LUMO	1.568
	469 nm	515 nm	HOMO -1 → LUMO	0.093
	500 nm	523 nm	HOMO → LUMO HOMO -1 → LUMO +1	0.673
OTAn	305 nm	333 nm	HOMO -4 → LUMO HOMO -2 → LUMO +2 HOMO → LUMO +4 HOMO -3 → LUMO +3	1.096
	384 nm	428 nm	HOMO -1 → LUMO +1	0.910
	404 nm	459 nm	HOMO → LUMO +1 HOMO -1 → LUMO	2.053
	438 nm ^a	501 nm	HOMO -1 → LUMO HOMO → LUMO +1	0.241
	476 nm	509 nm	HOMO → LUMO	0.111

^a shoulder peak.

The TD-DFT calculations revealed that the symmetry of the molecular orbitals responsible for optical transitions are the same in both **TTAc** and **TTAn**, which is expected as the large conjugated frameworks are nearly identical. However, as in the experimental spectra, the oscillator strengths of the calculated spectra indicated that the HOMO→LUMO transitions were not only red shifted in thienoacridines relative to their thienoanthracene analogues, but that their intensities were also greater; furthermore, the HOMO→LUMO transitions of octathienoacenes were red shifted and more intense than those of their tetrathienoacene counterparts. The Franck-Condon principle states that increased transition intensities can result from either greater transition dipole moments or

greater wavefunction overlaps between the states involved.²⁹ However, the HOMO→LUMO transition of the anthracene chromophore (along the short axis of the anthracene moiety) is dipole-forbidden,²⁸ and only becomes enabled by interactions with the solvent. Conversely, the same transitions are dipole-allowed in thienoacridines as a result of the presence of the pyridyl ring, which corroborates the stronger oscillators.

For higher-energy absorptions of tetrathienoacenes (e.g., in the 300–350 nm region), the calculated transition energies and intensities agreed with the experimental optical spectra, and were assigned to the HOMO–4→LUMO, and HOMO–1→LUMO+1 transitions. For **TTAc**, the oscillator of the calculated HOMO→LUMO transition was weak ($f = 0.007$), while the HOMO–1→LUMO transition was relatively strong ($f = 0.401$), which is opposite to the experimental trend for those two transitions. The calculated oscillator intensities of the HOMO→LUMO and HOMO–1→LUMO transitions of **TTAn** were similar to what was observed for **TTAc** ($f = 0.006$ and $f = 0.200$, respectively). The calculated solution-state energies of the HOMO orbitals in tetrathienoacenes were slightly higher than their experimentally determined energies, as can be seen in Table 3.1. The intensity mismatch of the HOMO→LUMO and HOMO–1→LUMO transitions may have been due to the HOMO orbitals having overestimated energies in the solution state; in other words, the calculated orbital energies may have caused a switch of orbital symmetry, and therefore the transition intensities, from what was observed in the absorbance spectra.

In the octathienoacenes, the calculated transition energies were bathochromically shifted compared to the corresponding transitions in the experimental spectra, however, the absorption profiles and the relative oscillator strengths of the calculated transitions

correlated well with what was observed in the optical studies. The solution state HOMO→LUMO transition of **OTAc** was lower in energy than that of **OTAn**, which agreed with the experimentally observed red shift to that transition. The energy of the HOMO orbital of **OTAc** was lower in the TD-DFT calculations than those of the gas phase, such that it was nearly degenerate with the HOMO–1 (–5.427 eV for HOMO *cf.* – 5.431 eV for HOMO–1); furthermore, the HOMO levels in the TD-DFT calculations agreed with the CV-determined HOMO levels. As with **TTAn**, the HOMO→LUMO and HOMO–1→LUMO oscillators of **OTAn** corresponded to dipole-forbidden transitions,²⁸ and were therefore weak (f = 0.04 and 0.05, respectively).

The theoretical data revealed that substitution of carbon with nitrogen in the cores of these molecules strengthens the transitions to the LUMO, likely as a result of the dipole of the pyridyl moiety. The TD-DFT calculations indicated that the symmetry of the orbitals from which these transitions originated were consistent between tetrathienoacenes and octathienoacenes. Smaller energy gaps between the orbitals associated with HOMO→LUMO and HOMO–1→LUMO transitions caused red shifts to the longer wavelength transitions in thienoacridines *cf.* thienoanthracenes. However, the transitions in the shorter wavelength region – those from HOMO and HOMO–1 to the LUMO+1 – were blue shifted, which resulted from energy gaps that were increased relative to those in the thienoanthracenes. Overall, the TD-DFT calculated transitions agreed with the trends in the experimental absorption spectra.

§ 3.2.3.3C Reorganization Energies *via* Adiabatic Potential Surfaces

To further study the effects of nitrogen substitution on the properties of thienoacenes, the internal reorganization energies of **TTAc** and **TTAn** were calculated. The two theoretical components of charge transport in a thermally activated hopping mechanism (such as in a non-crystalline molecular film)³⁴ are the intermolecular transfer integral t and the reorganization energy, λ .^{35,36} As discussed in Section 2.4, the latter can be calculated using adiabatic potential energy surfaces. λ_{total} is the sum of the energies associated with the processes of relaxing the geometry of a charged molecule from the ground configuration (λ_1) and relaxing the geometry of a neutral molecule from the charged configuration (λ_2). DFT studies using B3LYP have been used to calculate and quantify the energies associated with geometry modifications during the charging of molecules.³⁷

λ_{total} for hole transport (in other words, where the charged species are cationic) in **TTAc** and **TTAn** were calculated to be 0.132 eV and 0.122 eV, respectively. For both **TTAc** and **TTAn**, λ_1 and λ_2 – which are the energy difference between the charged molecule in the ground geometry [G^+] and the neutral ground [G^0], and the energy difference between the neutral molecule in the excited geometry [E^0] and the charged excited molecule [E^+], respectively – were found to be within 1% of each other, as is expected for very rigid molecules.³⁷ In Section 3.2.3.2B, the Stokes' shifts (0.03 eV and 0.06 eV for **TTAn** and **TTAc**, respectively) and fine structure indicated that the amount of energy lost during photoexcitation and relaxation processes increased when the pyridyl moiety was introduced into the core of thienoacenes. However, the computed λ_{total} for charging processes suggest that the hole transport capabilities of **TTAc** would be comparable with

those of **TTAn**, assuming a similar level of electronic coupling (t) and isostructural packing arrangements in these isoelectronic thienoacenes.

§ 3.3 X-Ray Crystallography

X-ray crystallography can reveal information about solid-state morphology that is important to the applications of organic semiconductors. Particularly relevant to understanding the charge transfer of molecules such as thienoacenes are the packing mode and the distances between molecules in the crystalline state, which may be used to identify π - π close contacts. Purification and crystal growth of **BrTTAc** was performed by vacuum sublimation. Single crystals suitable for X-ray diffraction analysis were obtained using a three-zone tube furnace, as described in Section 3.2. The crystal structures were collected by X-ray diffraction at temperatures of 200 K and the d -spacing was determined by powder X-ray diffraction at 100 K and 300 K.

BrTTAc was found to be isostructural with **BrTTAn** and belongs to the monoclinic space group $P2_1/n$. The unit cell and the packing arrangement are presented in Figure 3.10. As is common with many SMSs, **BrTTAc** formed herringbone arrays (Figure 3.10 b). 50% disordering of the directionality of the acridine moiety was necessary to model the diffraction data. Intra-stack π - π close contacts were observed between carbon and sulfur (3.564 Å and 3.580 Å at 200 K). Inter-stack contacts were observed (bromine-bromine 3.528 Å, bromine-sulfur 3.592 Å and 3.529 Å at 200 K).

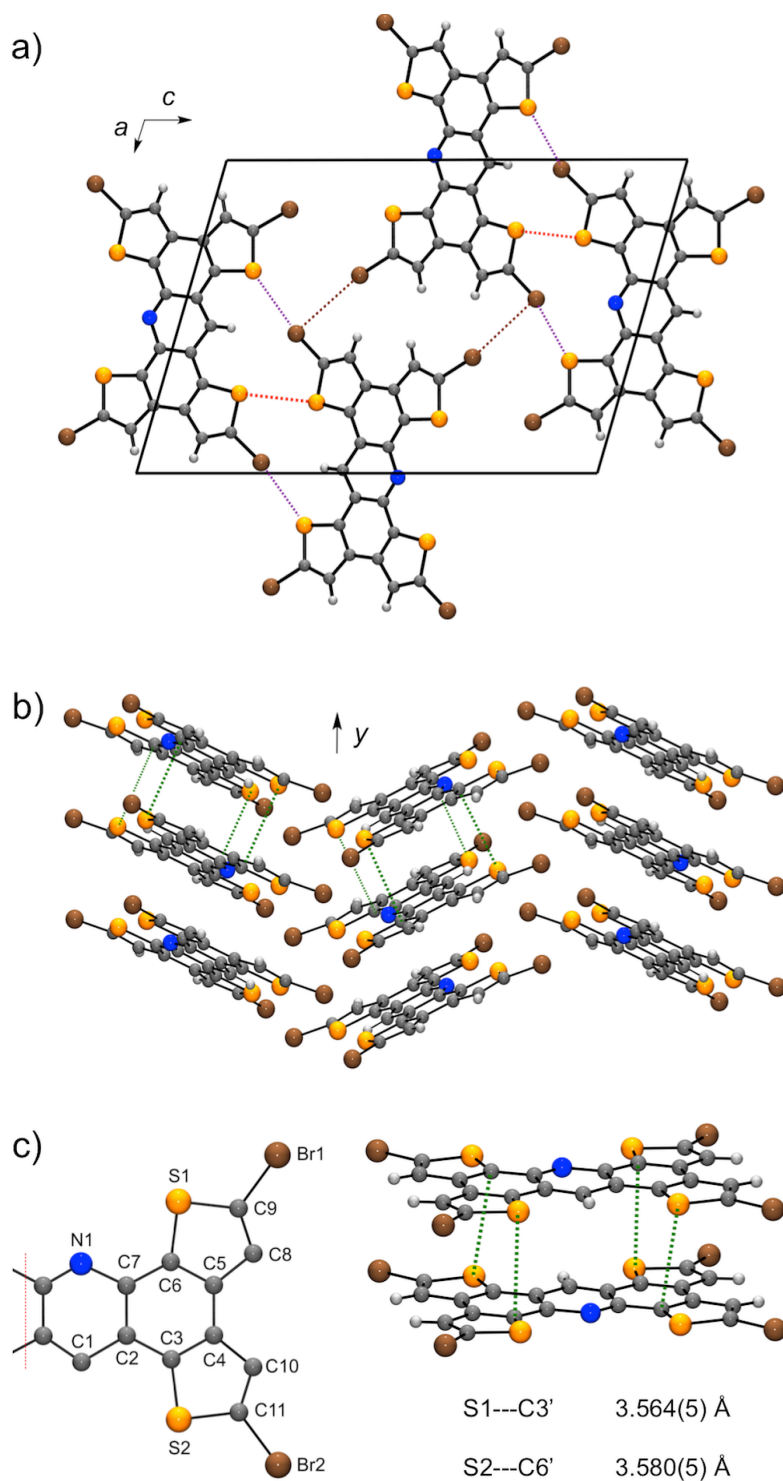


Figure 3.10 X-ray crystal structure of **BrTTAc** at 200 K depicting a) the unit cell and inter-stack close contacts, b) the herringbone stacking arrangement, and c) the asymmetric unit with atom labeling and dimer unit. Close contact are indicated in red for S $\cdots$ S interactions, purple for S $\cdots$ Br interactions, and brown for Br $\cdots$ Br interactions. Intra-stack S $\cdots$ C close contacts indicated in green.

§ 3.4 Thermochromic Behaviour of Thienoacridine Crystals

The crystals of **BrTTAc**, which were yellow at room temperature, were observed to undergo a gradual colour transition that began at approximately 100 °C and continued through yellow-orange to orange; the colour ceased to change at approximately 300 °C. Upon cooling, the original yellow colour was restored. There was no observable degradation or cracking of the crystals. When the golden-yellow **BrTTAn** crystals were subjected to the same heating, a very slight deepening of the yellow colour occurred. A side-by-side comparison on heating is presented in Figure 3.11. Both compounds are thermally stable above 400 °C, and high thermal stability has been a notable feature of the thienoanthracenes family, which is favourable with a view to the fabrication of SMS-based devices.⁴

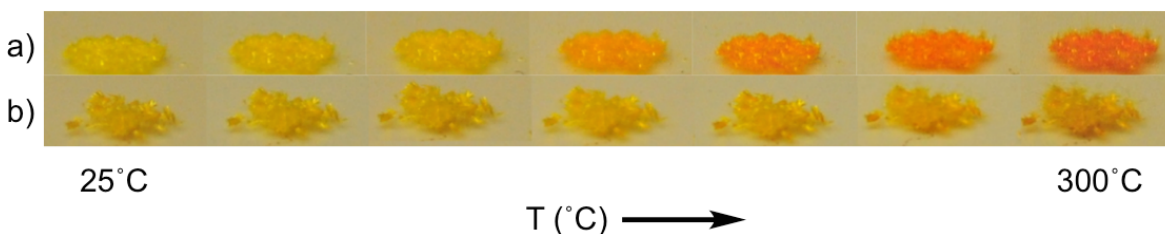


Figure 3.11 Photographic comparison of crystalline samples of a) **BrTTAc** and b) **BrTTAn**, upon heating from r.t. → 300 °C. Heating was staged in approximately 50 °C increments, and held at each temperature to equilibrate.

As **BrTTAn** and **BrTTAc** are isostructural in the crystalline form, and otherwise chemically identical, and the thermochromic behaviour is likely due to the pyridyl moiety of **BrTTAc**. Differential Scanning Calorimetry (DSC) was used (see Figure 3.12) to probe both **BrTTAn** and **BrTTAc** from room temperature to 400 °C. Both **BrTTAc** and **BrTTAn** displayed small endothermic peak during the heating cycle at 103 °C, as well as exothermic peaks during the cooling cycle at 74 °C. However, the energy magnitudes of

these peaks were too small to be attributed to the chemical processes typically associated with thermochromism, as discussed below.

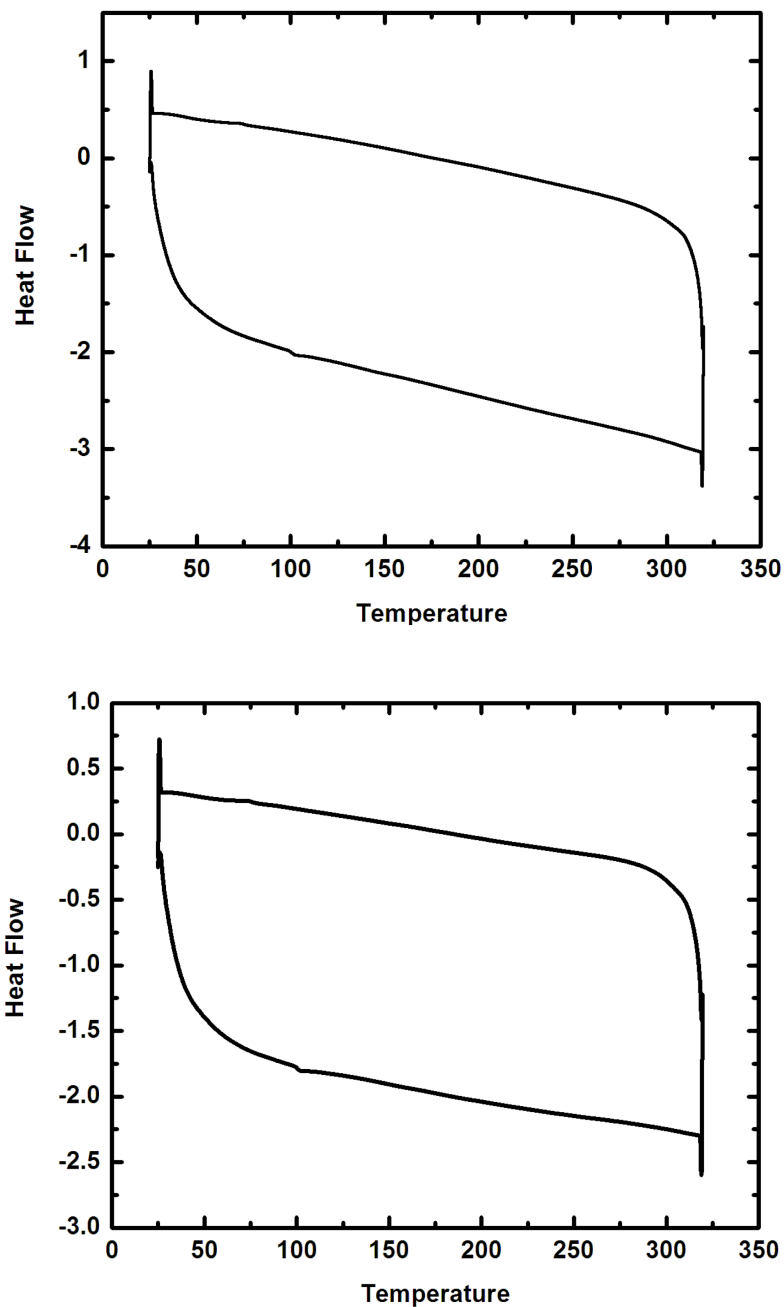


Figure 3.12 Differential Scanning Calorimetry traces of **TTAc** (top) and **TTAn** (bottom). The inset shows the region of the 70–110 °C to emphasize the observed features.

Thermochromism is commonly observed in molecules capable of proton exchange

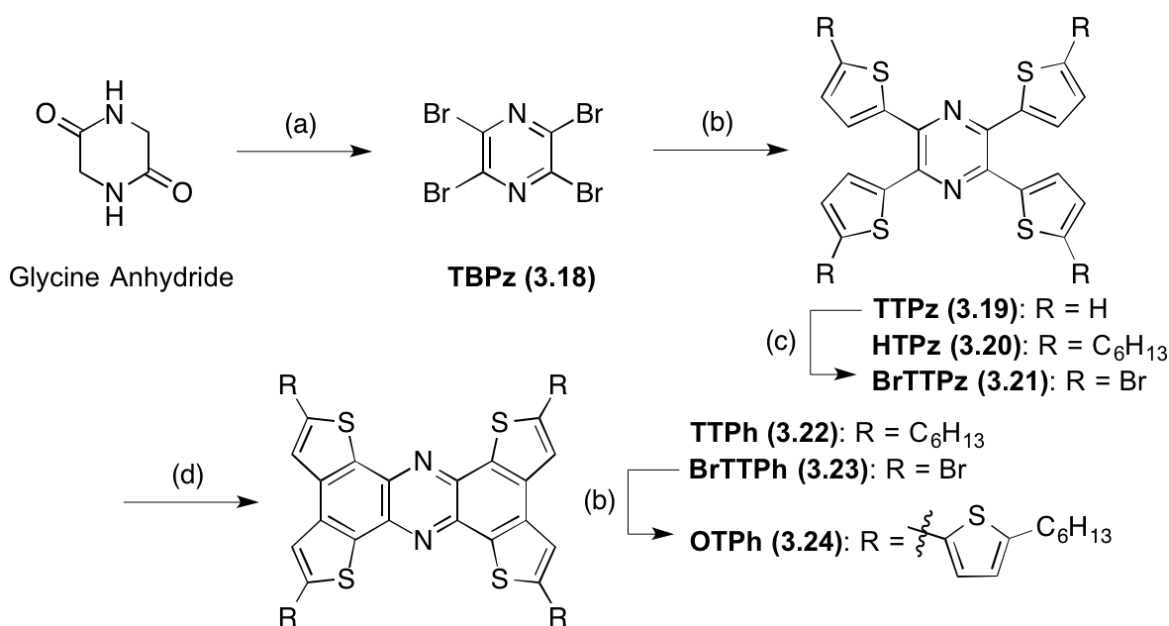
(desmotropy) or conjugated structures in which the rings can be easily rearranged;³⁸ these processes are typically accompanied by large peaks in DSC measurements.^{39,40} Beyond the initial minor feature in the DSC, the colour shift from yellow to orange was not accompanied by pronounced thermal events, which eliminates proton transfer/desmotrophy-based thermochromism. Furthermore, BrTTAn and BrTTAc are both chemically incapable of those processes. As the thermochromism could not be ascribed to an event observable by DSC, the crystals were studied by powder X-ray Diffraction at temperatures of 100 K, 200 K and 300 K. The inter-planar distance δ of **BrTTAc** increased with temperature, from 3.515 Å (100 K) to 3.535 Å (200 K) and 3.558 Å (300 K). For comparison, at 200 K **BrTTAn** displayed $\delta = 3.558$ Å.

As mentioned above, close π - π contacts were observed at 200 K; an increase in the energy of the π -systems is expected due to π - π interactions. The degree of interaction would have decreased as the inter-planar distance grew with increasing temperature; this lowered interaction would have reduced the energy of the π -system, corresponding to a red shift in the absorption profile and a red shift in the transmitted colour. However, the effects of these π -system interactions should be observed in both **BrTTAc** and **BrTTAn**. **BrTTAc** has a dipole moment, whereas the anthracene analogue does not. It is expected that, while the X-ray crystal structure was modeled with 50% occupancy for the central N/C-H position (N and C-H are isoelectronic and difficult to distinguish by XRD), the actual crystals will arrange in stacks with their dipoles arranged in opposite directions between adjacent molecules to minimize the lattice energy.⁴¹ Previous work revealed that the singlet n - π^* transition of pyridine reverses the direction of its dipole moment.⁴²⁻⁴⁴ The dipole-dipole ordering in the crystal would thus be disrupted by excitation in

BrTTAc, leading to an increase in molecular energy, and thereby the energy gap. However, as the interplanar distance δ was shown to increase with elevating temperatures, the increased energy from the dipole disordering could have been relieved to the extent that colour changes were discernable. In other words, the HOMO–LUMO absorption band shifting to red (hence, the yellow–orange thermochromism) was likely due to weaker dipole–dipole interactions in the solid state at elevated temperatures. This effect would be seen only in **BrTTAc**, as **BrTTAn** does not have a molecular dipole.

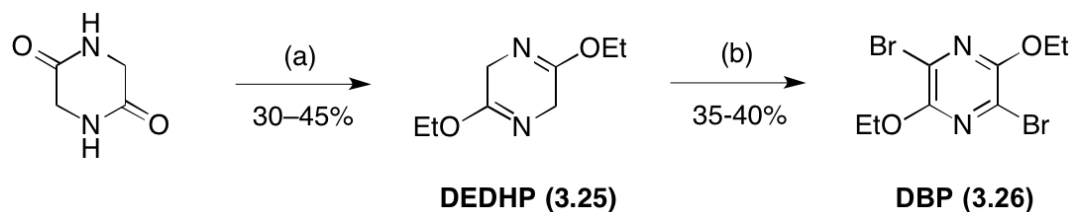
§ 3.5 Synthetic Efforts Towards Tetrathienophenazine

At the outset of this work, a complete study of the incremental nitrogen substitution of thienoacenes, namely of thienoacridines and thienophenazines, was envisioned. As in previous work and earlier in this chapter, the four-fold Stille reaction was chosen as the synthetic strategy to prepare tetrathienophenazine (**TTPh**, Compound **3.16**) from thiophenes and a nitrogen-laden small molecule. This strategy required 2,3,5,6-tetrabromopyrazine (**TBPz**, Compound **3.18**) as the precursor for the **TTPh** core, as presented in Scheme 3.8. Yudin and co-workers reported a synthetic route to a variety of pyrazine derivatives,⁴⁵ including tetrahalopyrazines such as **TBPz**. However, the reported sequential halogenation/aromatization reaction in both acetonitrile and DMSO resulted in an insoluble solid that could not be characterized.



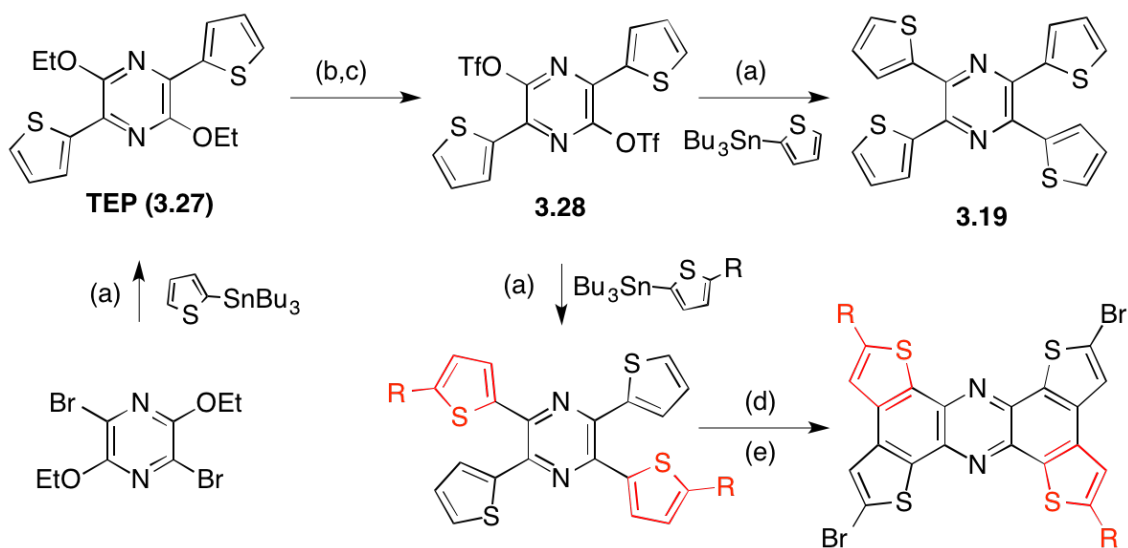
Scheme 3.3 Proposed synthetic route to tetrathienylpyrazine through 2,3,5,6-tetrabromopyrazine. *Reagents and conditions:* (a) Br₂, PBr₅, DMSO, 80 °C. (b) 2-(tributylstannyl)thiophene, [Pd(PPh₃)₂Cl₂], DMF, 130 °C. (c) NBS, THF, 0 °C. (d) FeCl₃, CH₂Cl₂, MeNO₂.

An alternate route was to alkylate the carbonyl oxygen of glycine anhydride while tautomerizing to the cyclic diimine, 2,5-diethoxy-3,6-dihydropyrazine (**DEDHP**, Compound 3.25).^{46,47} This would be followed by sequential proton abstraction with bromine, which would provide the aromatic pyrazine, and electrophilic aromatic substitution (see Scheme 3.4).⁴⁵ The ethoxy groups would be cleaved to the alcohols with NaSEt, followed by transformation to a pseudohalide such as triflate.^{48,49} One foreseen advantage of this route was the possibility of choosing different substituted thiophenes for two separate coupling steps leading to an asymmetrically substituted thienophenazine.



Scheme 3.4 Synthetic route to the modified pyrazine Stille reagent. *Reagents and conditions:* (a) BF_4OEt_3 , K_2CO_3 , CH_2Cl_2 , reflux. (b) Br_2 , MeCN , reflux.

The initial coupling would be performed on the 2,5-dibromo-3,6-diethoxypyrazine (**DBP**, Compound **3.26**) to provide the 2,5-bis(2-thienyl)-3,6-diethoxypyrazine (**TEP**, Compound **3.27**). Following the isolation of **3.27**, conversion to the triflate (**3.28**) and Stille coupling could be used to prepare either symmetric or asymmetric tetrathienylpyrazines (see Scheme 3.5), as well as Compound **3.19**. These would be cyclodehydrogenated to afford symmetric or asymmetric tetrathienophenazines, which would allow for a number of unique fused structures for various SMS applications.



Scheme 3.5 Proposed synthetic route to multifunctional tetrathienylphenazines. *Reagents and conditions:* (a) $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$, DMF , $130\text{ }^\circ\text{C}$. (b) NaSEt , DMF , $90\text{ }^\circ\text{C}$ (c) TiF_2O , Et_3N , CH_2Cl_2 , r.t. (d) NBS , THF , $0\text{ }^\circ\text{C}$ –r.t. (e) FeCl_3 , CH_2Cl_2 , MeNO_2 , r.t.

Reacting glycine anhydride with BF_4OEt_3 (a strong alkylating reagent) with base in anhydrous CH_2Cl_2 afforded mixtures of monoalkylated imine and dialkylated diimine (Compound **3.25**), with crude yields of 30-35% after over 48 hours at reflux. When a large excess of BF_4OEt_3 was used, greater crude yields of were obtained, but conversion was not improved. It was determined that the use of base *in situ* was preventing one of the ethoxylations from occurring. Neat reaction of BF_4OEt_3 with glycine anhydride, followed by basification during workup, did not improve yields, but increased the proportion of the desired product to 75% based on ^1H NMR. The use of chlorobenzene, which enabled higher reaction temperatures, furnished improved yields (57%) and complete conversion (Figure 3.13). Removal of the solvent yielded long needle-like crystals of the crude product, the NMR characterization of which was consistent with literature data.⁵⁰

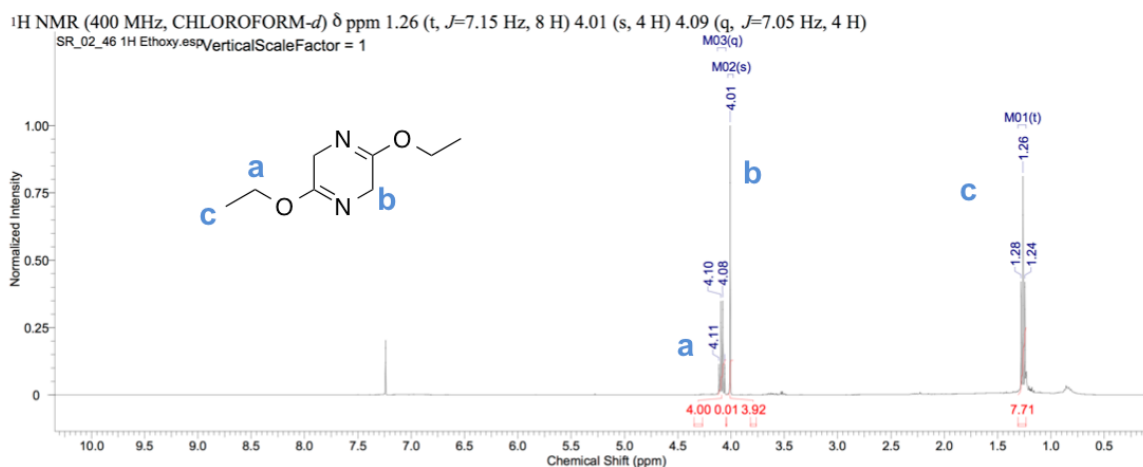


Figure 3.13 ^1H NMR spectrum of Compound **3.15** synthesized in refluxing chlorobenzene.

The aromatization/bromination conditions outlined in Scheme 3.4 were attempted with Compound **3.25**. Bromination using *N*-bromosuccinimide (NBS) in acetonitrile resulted in a loss of the ethoxyl groups. Reaction with NBS in chloroform at room temperature

produced a product with aromatic proton signatures and ethoxyl group protons, indicating that the aromatization had occurred but the desired bromination had not. Refluxing in chloroform with NBS provided a mixture of products.

Bromination using Br₂ in refluxing dry acetonitrile initially gave a red-orange reaction mixture, which turned brown and collected white solid in the condenser. Upon workup, this reaction produced a solid brown product, the ¹H and ¹³C NMR spectra of which showed a mixture containing the desired compound (Compound **3.26**). To encourage the radical splitting of Br₂, irradiation with long-wavelength UV light was used under similar conditions;⁵¹ this provided a brown solid with TLC and NMR characterization (see Figure 3.14) indicating the sole desired product in 40% yield, consistent with the results of Yudin *et al.*⁴⁵ From Compound **3.26**, asymmetrically functionalized tetrathienophenazines are accessible, according to the route in Scheme 3.5. However, in the course of this work, Xie *et al.* published a report on the synthesis of hexylated tetrathienophenazine via an alternate synthetic pathway;¹⁷ Xie and co-workers' preparation method excludes the possibility of studying the effect of conjugation through preparation of octathienophenazines, which is possible through the route in Scheme 3.5.

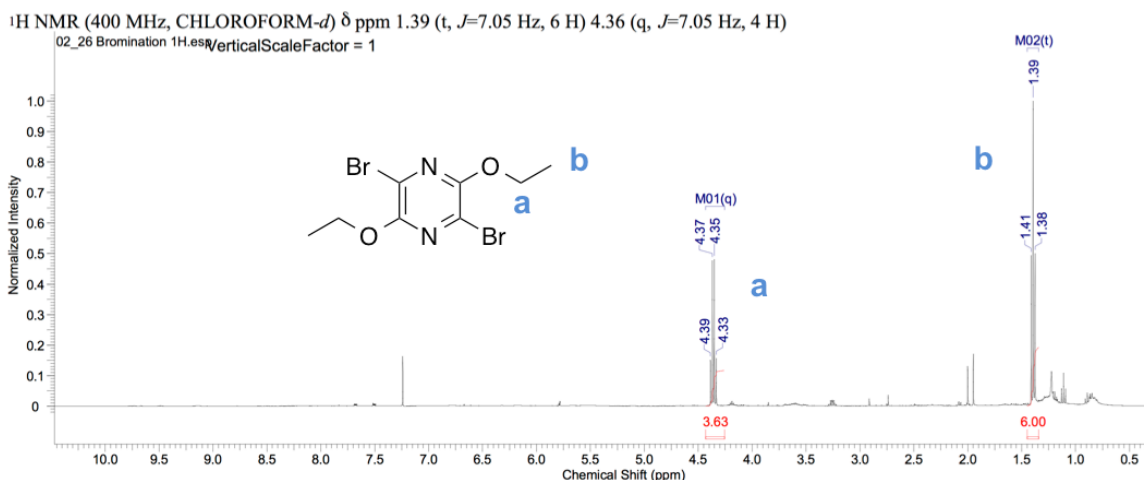


Figure 3.14 ¹H NMR spectrum of Compound **3.25** synthesized by reaction with Br₂ in refluxing acetonitrile under UV irradiation.

§ 3.6 Conclusions

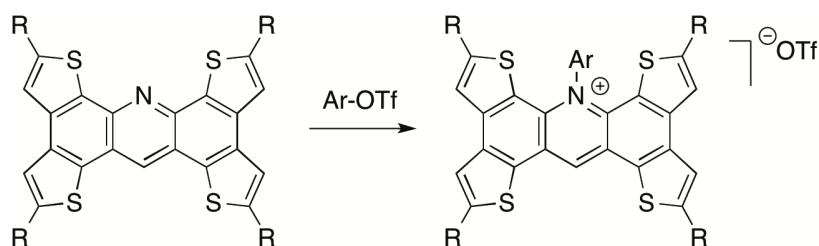
Minute structural changes such as heteroatom substitution can modify the optoelectronic properties of π -conjugated molecules and, as demonstrated, even large fused polyheteroarenes. Hexylated and brominated tetrathienoacridines and hexylated octathienoacridine, nitrogenated analogues of thienoanthracenes, were synthesized. Electrochemistry was used to characterize the redox behaviour of the acridine compounds. Unlike the anthracene derivatives, which exhibit quasi-reversible oxidations, the acridine systems oxidize irreversibly; however, they appear to have lower disproportionation constants than their anthracene analogues. It was found through experimental and computed optoelectronic properties that the presence of nitrogen decreases the frontier molecular orbital energy levels and optical transition energies of the tetrathienoacene skeleton. Simultaneously, the molar absorptivities of the acridine compounds are increased, and the HOMO→LUMO transition is strengthened. Investigation of the theoretical components of charge transfer revealed that the reorganization energies of **TTAn** and **TTAc** were nearly identical. **BrTTAc** was

synthesized and shown to be isostructural with its thienoanthracene counterpart. Crystals of **BrTTAc** displayed a gradual yellow-to-orange thermochromism, which may be attributed to additional dipole-dipole interactions that resulted from the replacement of a CH group in the core with nitrogen. Further structural analysis and temperature-dependent UV-visible spectroscopic studies may provide a more complete understanding of this behaviour.

§ 3.7 Future Work

Preparing FET devices from **TTAc** and **OTAc** would determine what the effects of lowering the energy levels of, and introducing a dipole moment to, these thienoacenes would have on their charge transport capabilities. Given the similar Stokes' shifts of **OTAn** and **OTAc**, which suggest comparable reorganization energies, and the dissimilar values between **TTAc** and **TTAn**, this may provide valuable information about the effects of including a core/framework with slightly less rigidity on large, planar organic semiconducting molecules applied to transistors.

The thermal and redox stability that is characteristic of thienoacenes, and the increased molar absorptivities of thienoacridines, are favorable for their applications as sensitizers for dye-sensitized solar cells as discussed in Section 3.1. Acridines may be functionalized through nitrogen to extend their conjugation as *N*-arylated salts,⁵² and incorporate different donor and acceptor moieties to tune the electronic properties and solid-state structures of tetrathienoacenes and octathienoacenes; this opens the path to a wealth of new thienoacridine-based molecules (see Scheme 3.6).



Scheme 3.6 Proposed synthetic route to *N*-aryl functionalized tetrathienoacridine-triflate salts.

The ability to tune the cores of star-shaped SMSs, and thus their electronics and properties, is one of the key advantages of using these molecules for semiconductor applications. The synthetic route to multifunctional pyrazines and thienophenazines proposed in Section 3.6 should be pursued further, as a number of interesting asymmetric SMSs may be prepared. Furthermore, it may be possible to prepare bis(2-thienyl)pyrazine and thienophenazine polymers by oxidative coupling and/or cyclization.

§ 3.8 Experimental Details

General Procedures and Starting Materials. The reagents 2,5-diaminopyridine, bromine, sodium nitrite, hydrobromic acid, palladium chloride and triphenylphosphine were obtained commercially and used as received. Compounds 5-(hexyl)-2-(tributylstannyl)-thiophene⁵³ and 2-(tributylstannyl)-thiophene⁵⁴ were prepared as outlined in the literature. All solvents were of at least reagent grade; tetrahydrofuran (THF) was dried by distillation from sodium and dimethylformamide (DMF) was dried over 4Å molecular sieves. All reactions were performed under an atmosphere of dry nitrogen. Melting points are uncorrected. ¹H and ¹³C NMR spectra were run in CDCl₃ solutions at r.t. on a Bruker Avance 400 MHz spectrometer. Infrared spectra were recorded on a Cary 630 FTIR spectrometer using Attenuated Total Reflection. UV-

visible spectra were measured with a Varian Cary Series UV-Vis-NIR spectrophotometer and the fluorescence spectra were obtained using a Varian Cary Eclipse fluorescence spectrometer. UV-visible and fluorescence spectra were measured on dichloromethane solutions with 1 cm precision quartz cuvettes. Elemental analyses were performed by MWH Laboratories, Phoenix, AZ. High resolution mass spectrometry was performed by the John L. Holmes Facility using a Concept 1S Electron Impact mass spectrometer, calibrated to 815.95 da with resolution +10,000.

Preparation of 2,3,5,6-tetrabromopyridine (TBP, Compound 3.6): Bromine (20.6 mL, 401 mmol) was added dropwise over 2 hr to a vigorously stirring suspension of 2,6-diaminopyridine (10.96 g, 100.4 mmol) in 48% hydrobromic acid (100 mL) at 0 °C; to the resulting orange precipitate, a solution of sodium nitrite (46 g, 660 mmol) in H₂O was added dropwise over 6 hr at 0 °C. The mixture was neutralized with saturated sodium carbonate, and then transferred to a separatory funnel, where it was extracted six times with diethyl ether (100 mL). The combined extracts were washed three times with saturated sodium carbonate, twice with distilled water and twice with brine (100 mL each) then dried over MgSO₄. The solvent was removed under reduced pressure to afford the crude product, an orange solid (24.73 g, 62.6 mmol, 62%) which was recrystallized from hexanes to afford orange needles (15.52 g, 39.32 mmol, 39%); Characterization data were consistent with that reported in the literature.⁵⁵ ¹H NMR (δ, CDCl₃, RT, 400 MHz): 8.08 (1H, s) ppm. ¹³C NMR (δ, CDCl₃, RT, 400 MHz): 145.4, 140.6, 123.0 ppm.

Preparation of 2-[2,4,5-Tris(2-thienyl)phenyl]thiophene (TTPy, Compound 3.7): 2,3,5,6-tetrabromopyridine (2.04 g, 5.15 mmol), PdCl₂ (65 mg, 0.37 mmol), PPh₃ (210 mg, 0.801 mmol) and 2-tributylstannylthiophene (9.9 mL, 32 mmol) were stirred in

dry, degassed DMF (0.25 mL) at 130 °C for 18 hours. After cooling to r.t., hexanes were added and the crude product (1.73 g, 4.24 mmol, 82 %) was filtered and washed with hexanes. The crude product was dissolved in dichloromethane and passed through a silica plug (eluent: 9:1 hexanes-dichloromethane) to afford an orange solid. Recrystallization from ethyl acetate afforded yellow needles (1.23 g, 3.02 mmol, 58%). Characterization data were consistent with that reported in the literature.⁴⁹ m.p.: 223 °C. ¹H NMR (δ, CDCl₃, RT, 400 MHz): 7.65 (1H, s), 7.43 (2H, dd, 4 Hz, 4 Hz), 7.35 (2H, dd, 4 Hz, 4 Hz), 7.10 (4H, d, 4 Hz) 6.90 (4H, d, 4 Hz) ppm. Anal. Calcd for C₂₁H₁₃NS₄: C 61.88, H 3.22, N 3.44; found C 61.96, H 3.25, N: 3.50.

Preparation of 2-Bromo-5-[2,4,5-tris(5-bromo-2-thienyl)pyridyl]thiophene (BrTTPy, Compound 3.8): *N*-bromosuccinimide (5.18 g, 29.1 mmol) was added to a stirring solution of Tetrathienylpyridine (1.58 mg, 3.87 mmol) in THF at 0 °C. The reaction was stirred for 16 hours at room temperature. The THF was removed under reduced pressure and the resulting yellow precipitate was washed with water, then methanol. The crude product (2.61 g, 3.60 mmol, 93 %) was collected by filtration and washed with methanol, then dried. The crude product was recrystallized from dichloromethane to afford a yellow microcrystalline solid (1.63 g, 2.25 mmol, 70 %). m.p. 208 °C. ¹H NMR (δ, CDCl₃, RT, 400 MHz): 7.50 (1H, s), 7.06 (2H, d, 7 Hz), 6.87 (2H, d, 7 Hz), 6.85 (4H, d, 7 Hz) 6.69 (2H, d, 7 Hz) ppm. ¹³C NMR (δ, CDCl₃, RT, 400 MHz): 149.3, 144.4, 143.8, 140.3, 130.9, 130.5, 128.8, 128.4, 123.2, 117.3, 113.7 ppm. IR: ν_{max} = 1443 (m), 1427 (m), 1405 (m), 1200 (w), 975 (m), 953 (m), 924 (w), 790 (s), 770 (s) cm⁻¹. The identity and purity of this product was based on ¹H and ¹³C NMR.

Preparation of 2,5,9,12-Tetrabromotrithieno-[2'',3'':5,6:3'',2'':3,4:3'',2'':7,8]acridine [1,2-b]thiophene (BrTTAc, Compound 3.9): A solution of FeCl₃ (8.50 g, 52.4 mmol) in nitromethane (30 mL) was added dropwise to a solution of **BrTTPy** (3.19 g, 4.42 mmol) in warm chlorobenzene (50 mL). After 60 min, methanol (150 mL) was added and the reaction was stirred for 60 min. The resulting red solid was collected by filtration and rinsed with hot methanol, then stirred in 100 mL of 10 % HCl. This yellow-brown solid was collected by filtration, washed with 10 % HCl and methanol, and dried (2.98 g, 4.14 mmol, 94%). The crude solid was sublimed using a three-zone tube furnace (340–280–240 °C) to afford yellow crystals. Single crystals suitable for X-ray work were obtained by repeating the sublimation. m.p. > 450 °C (dec.) IR: ν_{max} = 1486 (s), 1458 (vs, br), 1377 (s), 1306 (m), 974 (m), 915 (m), 888 (m), 819 (m), 804 (s), 784 (w), 722 (w), 502 (s) cm⁻¹. Anal. Calcd for C₂₁H₅Br₄NS₄: C 35.07, H 0.70, N 1.95; found C 35.17, H 0.90, N 1.98. Given the low solubility of this compound, ¹H and ¹³C NMR spectroscopic analysis were not possible. The identity of this compound was confirmed by X-ray crystallography and elemental analysis.

Preparation of 2-(2,4,5-Tris(5-hexyl-2-thienyl)pyridyl)-5-hexylthiophene (HTTPy, Compound 3.10): Tetrabromopyridine (1.91 g, 4.85 mmol), PdCl₂ (64 mg, 0.364 mmol), PPh₃ (194 mg, 0.740 mmol) and 2-tributyltin-5-hexylthiophene (13.35 g, 29.19 mmol) were stirred in 0.24 mL dry, degassed DMF at 130 °C for 18 h. After cooling to r.t., hexanes were added to the mixture, which was then passed through a silica plug (hexanes). From the resulting yellow oil, 5-(hexyl)-2-(tributylstannyl)-thiophene was removed by distillation using a K $\ddot{u}$ gelrohr apparatus. The isolated, viscous yellow oil was used without further purification (2.96 g, mmol, 82 %). ¹H NMR (δ , CDCl₃, RT, 400

MHz): 7.55 (1H, s), 6.86 (2H, d, 3.5 Hz), 6.77 (2H, d, 3.7 Hz), 6.73 (2H, d, 3.4 Hz) 6.56 (2H, d, 3.9 Hz) ppm. ^{13}C NMR (δ , CDCl_3 , RT, 400 MHz): 149.6, 149.3, 147.4, 143.4, 140.9, 137.3, 128.2, 127.2, 124.8, 124.4, 123.9, 31.7, 31.6, 31.6, 31.5, 30.3, 30.2, 29.2, 28.9, 28.7, 28.0, 27.9, 27.8, 27.4, 27.2, 26.9, 26.5, 22.6, 17.5, 14.1, 13.8, 13.6, 8.8 ppm. IR: ν_{max} = 2955 (s), 2922 (vs), 2852 (s), 1464 (s), 1458 (s), 1376 (w), 1073 (w), 876 (w), 800 (m), 778 (m), 689 (m), 669 (m) cm^{-1} . MS (EI): m/z : $\text{C}_{45}\text{H}_{61}\text{NS}_4$: 743.3687 Found: 743.3691 (100%, M^+). The identity and purity of this product was based on MS, ^1H and ^{13}C NMR.

Preparation of 2,5,9,12-Tetrahexyltrithieno[2'',3'':5,6:3'',2'':3,4:3'',2'':7,8]acridine

[1,2-b]thiophene (TTAc, Compound 3.11): A solution of FeCl_3 (0.87 g, 5.39 mmol) in nitromethane (15 mL) was added dropwise to a solution of **HTTPy** (267 mg, 0.359 mmol) in CH_2Cl_2 (15 mL). The reaction was stirred for 60 minutes, then diluted with NH_4Cl , washed with saturated aqueous NH_4Cl , aqueous NH_4OH and brine, then dried over MgSO_4 . The solvent was removed to afford yellow solid (186 mg, 0.252 mmol, 70 %), which was recrystallized from ethyl acetate to provide a microcrystalline yellow solid (111 mg, 0.151 mmol, 60%). m.p.: 232 °C. ^1H NMR (δ , CDCl_3 , RT, 400 MHz): 8.75 (1H, s), 7.29 (2H, s), 7.27 (2H, s), 3.01 (4H, t) 2.97 (4H, t), 1.80–1.84 (8H, m), 1.40–1.50 (8H, m), 1.30–1.40 (24H, m), 0.85–0.95 (12H, m) ppm. ^{13}C NMR (δ , CDCl_3 , RT, 400 MHz): 150.03, 147.04, 142.06, 135.78, 134.44, 133.77, 132.31, 125.35, 119.98, 119.94, 119.91, 31.69, 31.67, 31.62, 31.53, 31.13, 30.92, 28.90, 28.89, 22.63, 22.63, 14.14, 14.13 ppm. IR: ν_{max} = 2954 (m), 2918 (s), 2850 (s), 1541 (m), 1523 (m), 1458 (m), 1405 (s), 1376 (m), 962 (m), 881 (m), 820 (vs), 786 (m), 722 (m) cm^{-1} . Anal. Calcd for $\text{C}_{45}\text{H}_{57}\text{NS}_4$ C 73.02, H 7.76, N 1.89; found C 72.85, H 7.59, N 1.79.

Preparation of 2,5,9,12-Tetra(5-hexyl-2-thienyl)trithieno[2'',3'':5,6:3'',2'':3,4:3'',2'':

7,8]acridine[1,2-b]thiophene (OTAc, Compound 3.14): BrTTAc (372 mg, 0.518 mmol), PdCl₂ (10 mg, 0.06 mmol) PPh₃ (40 mg, 0.15 mmol) and 2-tributylstannyl-5-hexylthiophene (1.89 g, 4.1 mmol) were stirred in dry, degassed DMF (0.1 mL) at 130 °C for 18 hours. After cooling to r.t., the mixture was diluted in hexanes and the product was collected by filtration, and washed with hexanes and hot ethyl acetate to provide an orange powder (500 mg, 0.468 mmol, 90%). The crude product was recrystallized from dichloroethane, affording a microcrystalline red-orange solid (431 mg, 0.403 mmol, 91%). m.p. 176 °C. ¹H NMR (δ, CDCl₃, RT, 400 MHz): 7.93 (1H, s) 7.06 (2H, s) 7.04 (2H, s) 7.03 (2H, d, 3.3 Hz) 6.88 (2H, d, 3.3 Hz) 6.62 (2H, d, 3.3 Hz) 6.55 (2H, d, 3.3 Hz) 2.79 (4H, t, 7.5 Hz) 2.75 (4H, t, 7.8 Hz) 1.77–1.64 (8H, m) 1.50–1.40 (8H, m) 1.40–1.32 (16H, m) 0.95 (6H, t, 6.8 Hz) 0.94 (6H, t, 6.8 Hz) ppm. ¹³C NMR (δ, CDCl₃, RT, 400 MHz): 146.01, 145.88, 141.33, 140.63, 137.87, 135.45, 135.30, 134.77, 132.96, 132.18, 124.83, 124.73, 124.52, 124.51, 124.14, 119.42, 117.46, 117.40, 31.72, 31.71, 31.52, 31.44, 30.35, 30.29, 22.71, 14.23 ppm. IR: ν_{max} = 2920 (s), 2846 (s), 1702 (w), 1655 (w), 1536 (w), 1508 (m), 1458 (m), 1405 (s), 1375 (w), 1217 (w), 1037 (w), 974 (w), 877 (m), 849 (w), 811 (s), 792 (vs), 780 (vs), 723 (m) cm⁻¹. Anal. Calcd for C₆₁H₆₅NS₈ C 68.56, H 6.13, N 1.31; found: C 68.76, H 6.09, N 1.22.

Preparation of 2,5-diethoxy-3,6-dihydropyrazine (DEDHP, Compound 3.25): 1M BF₄OEt₃ in CH₂Cl₂ (12.5 mL, 12.5 mmol) was added a suspension of glycine anhydride (394 mg, 3.45 mmol) in dry chlorobenzene (10 mL). The resulting mixture was refluxed for 48 hours. The mixture was neutralized with 2M NaOH and then transferred to a separatory funnel, where it was extracted two times with dichloromethane (20 mL). The

combined extracts were washed twice with water and once with brine (20 mL each) then dried over MgSO_4 . The solvent was removed under reduced pressure to afford the crude product, yellow-brown needles (334 mg, 1.96 mmol, 57%). Characterization data were consistent with that reported in the literature.⁵⁰ ^1H NMR (δ , CDCl_3 , RT, 400 MHz): 4.08 (4H, q, 7.1 Hz) 4.01 (4H, s) 1.26 (6H, t, 7.1 Hz) ppm. ^{13}C NMR (δ , CDCl_3 , RT, 400 MHz): 162.3, 61.0, 121.1, 46.5, 14.3 ppm. IR: ν_{max} = 2981 (s), 2905 (m), 1699 (m), 1480 (s), 1363 (m), 1351 (m), 1242 (m), 1131 (m), 1027 (m).

Preparation of 2,5-diethoxy-3,6-dibromopyrazine (Compound 3.26): Bromine (0.15 mL, 2.92 mmol) was added to solution of 2,5-diethoxy-3,6-dihydropyrazine (125 mg, 0.73 mmol) in dry acetonitrile (10 mL) at 30 °C. The resulting mixture was refluxed for 48 hours. The mixture was neutralized with 2M NaOH and then transferred to a separatory funnel, where it was extracted two times with dichloromethane (20 mL). The combined extracts were washed twice with water and once with brine (20 mL each) then dried over MgSO_4 . The solvent was removed under reduced pressure to afford the crude product, a brown solid (92 mg, 0.28 mmol, 40%). Characterization data were consistent with that reported in the literature.⁴⁵ ^1H NMR (δ , CDCl_3 , RT, 400 MHz): 4.37 (4H, q) 1.40 (6H, t) ppm. ^{13}C NMR (δ , CDCl_3 , RT, 400 MHz): 151.0, 121.1, 64.6, 14.6 ppm. IR: ν_{max} = 2923 (s), 2855 (s), 1654 (m), 1432 (s), 1382 (s), 1331 (m), 1178 (m), 1023 (m).

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) 2013 BASi) employing a glass cell and platinum wires for working, counter

and pseudo-reference electrodes. The measurements were carried out on dichloromethane solutions (dried by Innovative Technology PureSolv solvent system and stored over 4Å molecular sieves) containing 0.5 M tetrabutylammonium hexafluorophosphate (Aldrich) as supporting electrolyte with a scan rate of 100 mV/s. The experiments were referenced to the Fc/Fc⁺ redox couple of ferrocene at +0.48 V vs. SCE.²⁰

Molar Absorptivity. To obtain the molar extinction coefficients a series of dichloromethane solutions were obtained by preparation of stock solutions and serial dilutions (concentrations in molarity; **TTAc**: 0.0130/0.0065/0.0052/0.0026; **OTAc**: 0.0234/0.0117/0.0094/0.0023; **TTAn**: 0.0162/0.0081/0.0065/0.0032; **OTAn**: 0.0524/0.0105/0.0052/0.0021) followed by analysis using UV-visible spectroscopy.

Crystal Growth. Crystals of **BrTTAc** suitable for X-ray analysis were grown using a three-zone tube furnace with zone temperatures of 350–280–240 °C at a pressure of 10⁻⁴ Torr.

X-Ray Diffraction. Data collection results for compound **BrTTAc** represent the best data set obtained in several trials. The crystals were mounted on thin glass fibers using paraffin oil. Prior to data collection crystals were cooled to 200 °K. Data were collected on a Bruker AXS KAPPA single crystal diffractometer equipped with a sealed Mo tube source (wavelength 0.71073 Å) and APEX II CCD detector. Raw data collection and processing were performed with APEX II software package from BRUKER AXS.⁷ Diffraction data for **8c** were collected with a sequence of 0.3° ω scans at 0, 120, and 240° in φ . Initial unit cell parameters were determined from 60 data frames with 0.3° ω scan each, collected at different sections of the Ewald sphere. Semi-empirical absorption

corrections based on equivalent reflections were applied.⁸ Systematic absences in the diffraction data-set and unit-cell parameters were consistent with monoclinic space group $P2_1/n$ (alternative setting for №14, $P2_1/c$). Solutions in the centrosymmetric space group yielded chemically reasonable and computationally stable refinement results. The structure was solved by direct methods, completed with difference Fourier synthesis, and refined with full-matrix least-squares procedures based on F^2 .

Diffraction data for the crystal of **BrTTAc** were collected to 0.75 Å resolution. However, due to small crystal size and weak diffraction it was discovered that both R(int) and R(sigma) exceed 35% for the data below 0.95 Å resolution. Based on R(sigma) value data were truncated to 0.90 Å resolution for refinement. The structural model of **BrTTAc** displays one molecule of the target compound located on the inversion centre symmetry element of the space group. Due to the location in this special position, it was necessary to model the disorder for atoms N(1) and C(7) in order to match the molecular structure. Disorder was modeled as a 50:50 split between two possible orientations of compound molecule in the lattice. All the atoms in the structural model were refined with full set of anisotropic displacement parameters.

For the compound all hydrogen atom positions were calculated based on the geometry of the 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.6.12.⁹

Table 3.5 Crystal structure and X-ray analysis details for **BrTTAc**

Empirical Formula	C ₂₁ H ₅ Br ₄ NS ₄
fw	719.14
<i>a</i> (Å)	13.9071(8)
<i>b</i> (Å)	3.9226(3)
<i>c</i> (Å)	20.0698(12)
β (deg°)	107.672(3)
<i>V</i> (Å ³)	1043.18(12)
ρ_{calcd} (g cm ⁻³)	2.289
Crystal System	monoclinic
Space Group	<i>P</i> 2 ₁ / <i>n</i>
<i>Z</i>	2
Temp (K)	200(2)
Wavelength (Å)	0.71073
Absorption coefficient (mm ⁻¹)	8.127
F(000)	684
θ range for data collection (°)	2.119 to 24.777
Limiting indices	<i>h</i> = ± 15 , <i>k</i> = ± 4 , <i>l</i> = ± 22
Reflections collected/unique	12355/ 1762
R(int)	0.0460
Completeness to θ (%)	98.1
Data/restraints/parameters	1762/33/145
Goodness-of-fit on F ²	1.06
Final R indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0397, <i>wR</i> ₂ = 0.0965
R indices (all data)	<i>R</i> ₁ = 0.0508, <i>wR</i> ₂ = 0.1022
Largest diff. peak/hole (e Å ⁻³)	1.562 / -0.947
τ (deg°) ^a	64.56(5)
δ (Å) ^b	3.542(3)

^a τ is the tilt angle between the mean molecular plane and the stacking axis. ^b δ is the mean interplanar separation between molecules along the π -stack.

Differential Scanning Calorimetry: DSC was run using a TA Instruments Q2000 with a heating rate of 1 °C min⁻¹ on samples of 6.36 mg for **BrTTAc** and 6.55 mg for **BrTTAn** in Tzero aluminum pans.

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Chapter 4 – Star Shaped Molecules as Metal–Organic Framework Linkers

§ 4.1 Introduction

Coordination compounds form the basis of many branches of chemical research and industry. Their formation and function are based on the bonding and interactions between positively charged metals or metalloids, and ligands, which are typically organic moieties containing donor atoms that are either anionic or have lone pair electrons to coordinate datively (for example, nitrogen). Some complexes are designed to exploit or promote the activity of multiple metal oxidation states, catalysts being a prominent example.¹⁻³ Others are designed to harness the electronic properties of a single oxidation state of an element, as their electronic configurations can be inherently useful (for example, high magnetic moment of dysprosium for single molecule magnets).⁴

In addition to discrete (“single molecule”) coordination compounds, many industrially useful complexes form porous, repeating networks. These are prepared using ligands that have more than one donor atom or coordination site similar to polydentate ligands; however, what differentiates these ligands is their ability to bind to more than one metal nucleus, more specifically, one or more through each coordination site. Of the repeating structures these ligands can form, the simplest are one-dimensional coordination polymers. Mesoporous zeolites are more complex, with multi-dimensional lattice structures. Porous networks are interesting due to their potential applications, such as separations, ion exchange, catalysis, gas storage and pharmaceutical agent delivery.⁵⁻¹¹ Zeolites, for example, are well-established catalysts and separating materials in industrial

settings.⁷ Recently, metal-organic frameworks have appeared as promising candidates for selective gas adsorption and storage due to high surfaces areas,^{7,9,12,13} and they could be important heterogeneous catalysts in the future due to post-synthetic chemical modifications.^{2,14}

§ 4.2 Metal-Organic Frameworks

§ 4.2.1 General Properties of MOFs

Metal-organic frameworks (MOFs) are microporous, infinitely repeating networks built from coordination compounds.^{13,15} They can be conceptualized from organic “linkers” (ligands) and metallic “nodes” (see Figure 4.1). Factors that determine the overall configuration and dimensionality of a MOF include the coordination geometry of the nodes (metal centres), the dimensions of the linker(s) and their number of coordination sites, as well the solvent they are synthesized in.

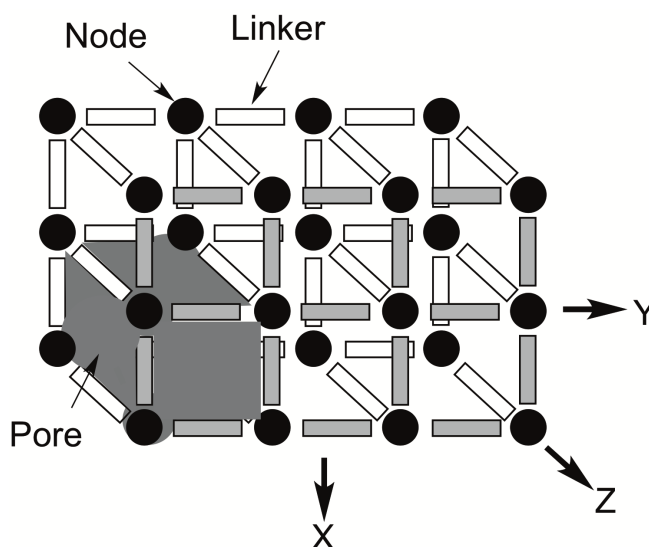


Figure 4.1 Cartoon representation of a metal-organic framework and its constituents.

The linkers used to prepare MOFs are usually aromatic molecules with their coordination sites geometrically arranged around a carbon-based skeleton. As with ligands in other coordination complexes and porous networks, electronegative donor atoms (such as oxygen and nitrogen) are used to coordinate to the nodes; a selection of linkers with the most common donor groups is presented in Figure 4.2.

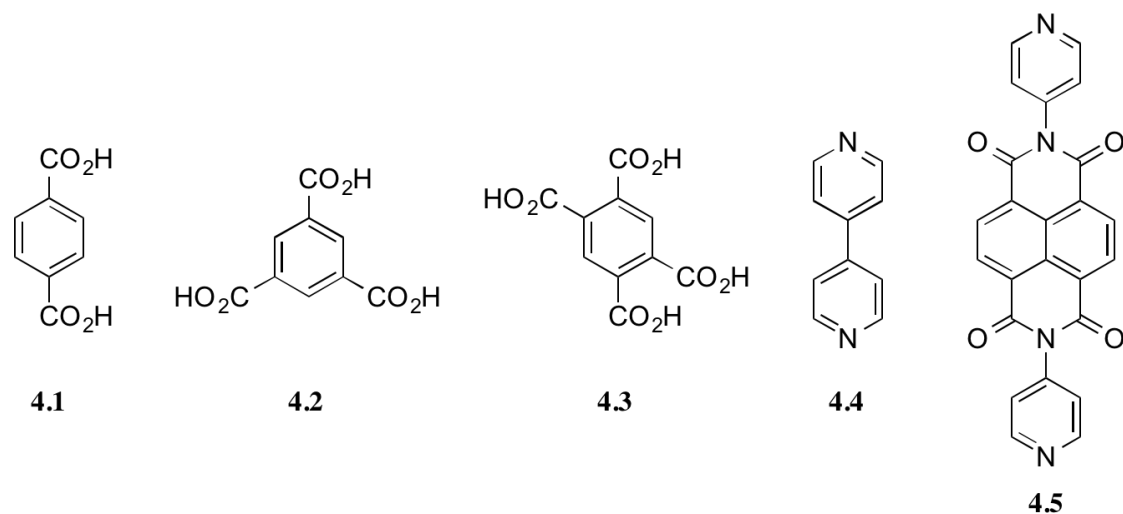


Figure 4.2 MOF linkers based on aromatic molecules with either pyridyl or carboxylic acid donor moieties.

The properties that enable MOFs to be used for the applications previously mentioned are their large pore sizes and high surface area.^{6,16,17} The size of the pores within a given MOF is determined in part by the dimensions of the linkers.⁹ In an isorecticular set of MOFs, the coordination modes and linker coordination geometry are preserved, while the specific linkers are varied by, for example, inserting additional phenyl rings between donor-containing fragments. Using an isorecticular design, Yaghi and co-workers were able to vary the pore size of MOFs from 3.8 – 28.8 Å in diameter.¹¹ This methodology can also be used to introduce functionality to a system by using linkers that contain, for example, catalytic moieties. Combining functional groups with other linker which vary

the size of the pores could therefore facilitate selective catalysis as reagents may be excluded or allowed depending on their size relative to the pores of the MOF.¹⁴

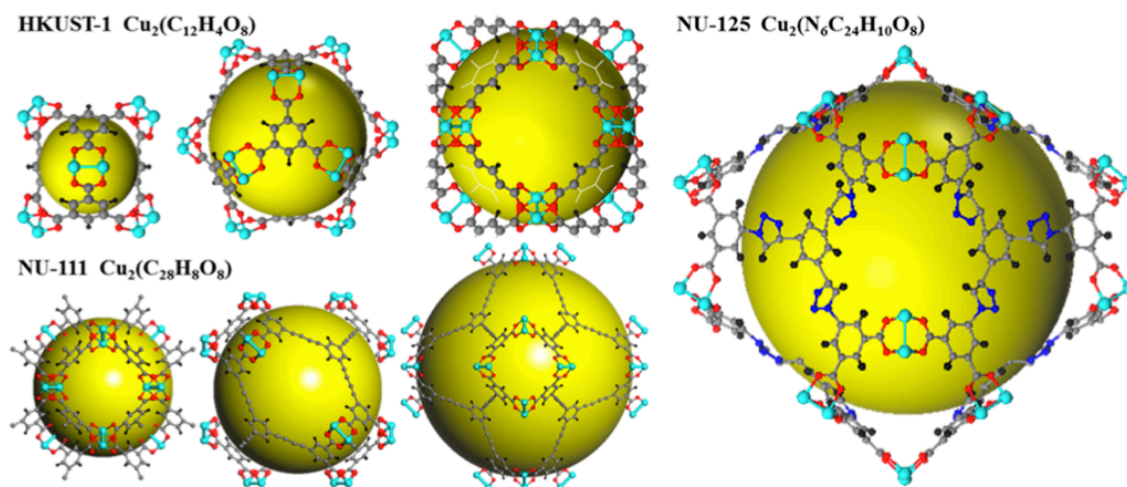


Figure 4.3 The varying pores of three isorecticular MOFs (**HKUST-1**, **NU-111**, and **NU-125**) (from ref. 13, © American Chemical Society, 2013).

In addition to the metal centres and the donor shape (or number of coordination sites), solvent plays an important role in regards to the growth of metal-organic frameworks. Solvent molecules that can datively coordinate to the metal centres are thought to act as a template as the network expands.¹⁶ In some cases, the solvent can have considerable effects on the final morphology of the network. Research efforts by Bureekaew and co-workers with the metal-linker system $\text{Zn}(\text{NO}_3)_2$, 2,2'-bithiophene-5,5'-dicarboxylic acid (**bt dc**) and 4,4'-bipyridine (**bpy**) explored how MOFs obtained using different solvent systems were formed.¹⁸ Using *N,N*-dimethylformamide (DMF) as the solvent, dense three-fold interpenetrated, or “catenated” (*vide infra*) MOFs were obtained. These MOFs showed a large number of π – π interactions between the thiophene-based linkers of each interpenetrated network, which held the overall structure rigid. However, MOFs prepared

in a mixture of benzene and DMF or in a mixture of toluene and cyclohexane had two-fold interpenetration, which allowed more flexibility in the overall structure. The authors attributed these less tightly interpenetrated formations to the disruption of linker-linker π - π interactions by solvent-linker interactions.¹⁸

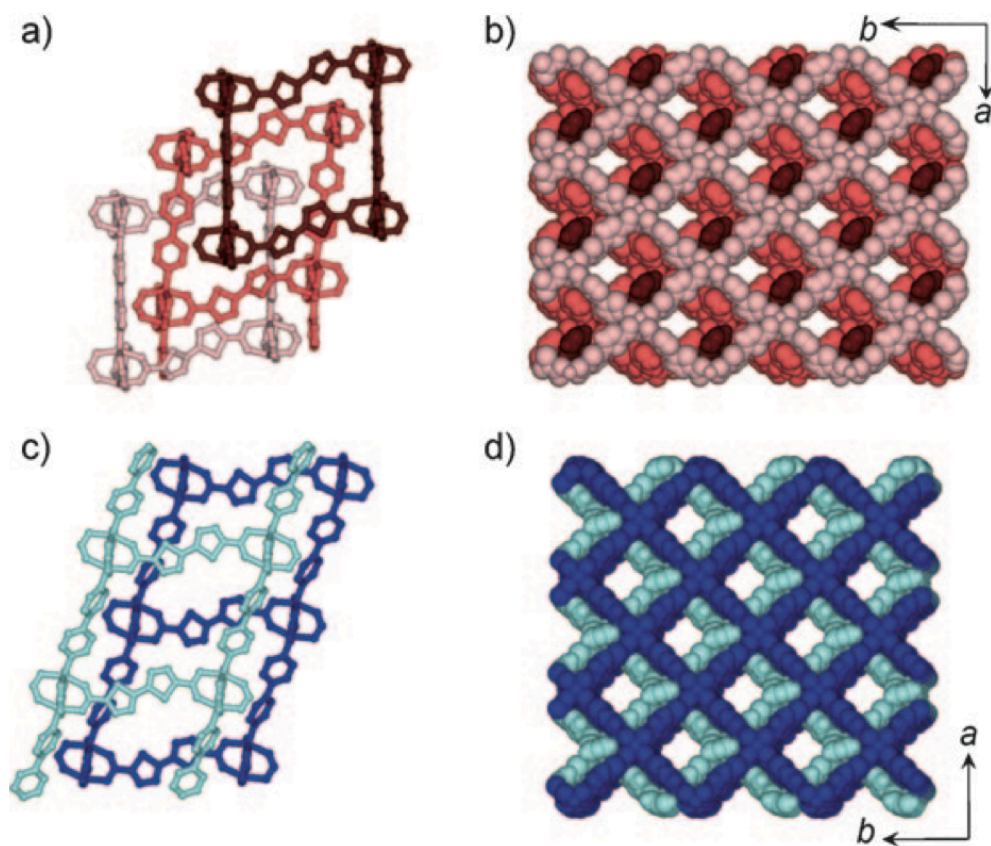


Figure 4.4 Crystal structures of MOFs prepared from $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, **btde** and **bpy**. (a,b) Structures from DMF, (c,d) structures from mixtures of DMF with benzene, cyclohexane or toluene. (a,c) views illustrate network interpenetration, (b,d) are views down the *c* axes. (from ref. 18 © Wiley-VCH Verlag GmbH & Co., 2010).

The interpenetration of networks can influence the accessible surface area of MOFs. Industrially useful porous materials such as zeolites typically have high surface areas, often in excess of $2,000 \text{ m}^2\text{g}^{-1}$.^{7,19} MOFs are capable of comparably high surface areas; for example, MOF-5 (Figure 4.5 a) displayed surface areas of up to $2,900 \text{ m}^2\text{g}^{-1}$,

determined by gas-adsorption isotherm.^{7,19,20} Yaghi's group also prepared MOF-177 (Figure 4.5 b), which had a calculated surface area of $4,500 \text{ m}^2 \text{ g}^{-1}$.⁷ Both of these MOFs are based around benzene-based linkers with carboxylate donor moieties. Heterogeneous catalysis in particular is dependent on high surface area, and possibly the size of the pores of MOFs. Hupp's group recently investigated manganese-based MOFs that catalyzed enantioselective olefin epoxidation with greater turn-over numbers than its catalytic motif, Mn-*salen*, did as a discrete molecule.² MOFs may be especially suitable for catalysis because their insolubility and robust structure would simplify their removal from the reaction mixture and re-use, as found by Cho *et al.*, where a MOF catalyst showed consistent performance after recycling.¹⁷ However, interpenetration, or catenation, is a challenge MOFs face when the desired property (such as catalytic activity) relies on the size of the pores.

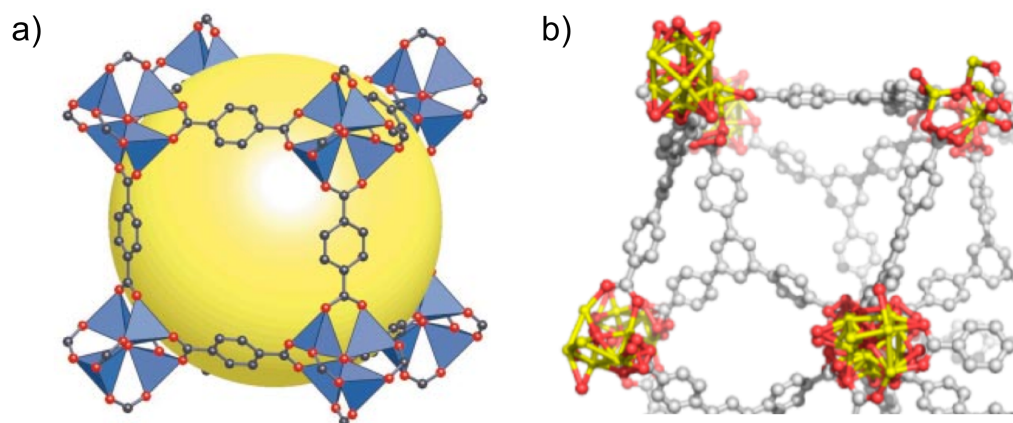


Figure 4.5 Structures of high surface area metal-organic frameworks: (a) Crystal structure of MOF-5 with internal pore depicted (from ref. 11 © Nature Publishing Group 2003) and (b) Crystal structure of MOF-177 (from ref. 15 © American Chemical Society 2012).

Catenation is the formation of multiple interlinked MOF networks, rather than one network with open pores.^{13,21-23} Two- and threefold catenation are the most common forms encountered, but fourfold and higher degrees that more severely limit pore size have been observed.²⁴ Catenation can greatly limit the pore size and accessible surface area of MOFs, which can determine the species that may access the inner cavities of the framework.^{8,21,22} On the other hand, Chen and co-workers found that *tris*(4-benzene)-1,3,5-triyl-tribenzoic acid (**H₃BTB**) (see Figure 4.6) formed interwoven networks where the networks were closely associated due to strong π - π and C-H- π interactions between aryl groups.⁸ This led to pore sizes 16.4 Å in diameter, which were the highest to date for catenated MOFs. While this pore size was exceptional, it also indicated that there is promise for MOFs using linkers that display strong π - π contacts. It is worth noting that catenation is not as detrimental to the adsorption of gases such as H₂ as it is for catalysis.¹⁹

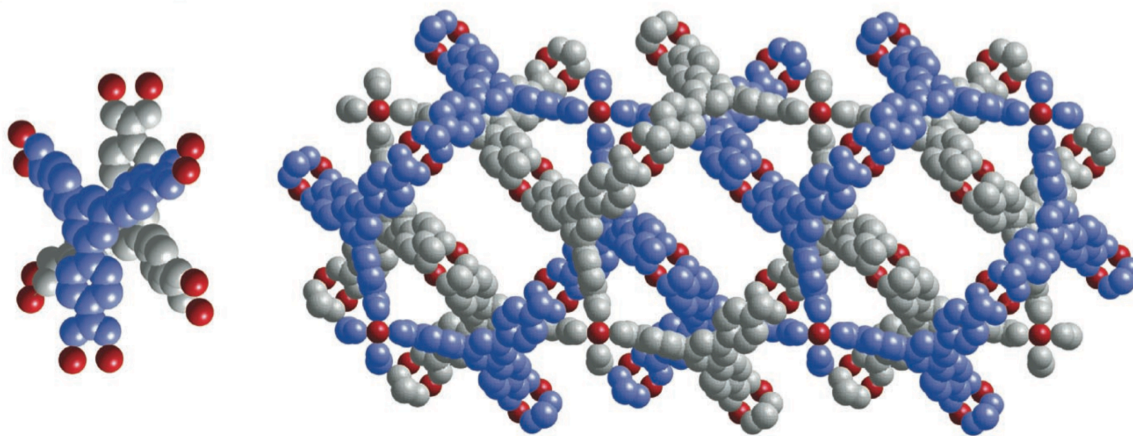


Figure 4.6 **H₃BTB**-based MOFs exhibiting tight π - π interactions that lead to closely associated, interwoven frameworks (from ref. 8, © American Association for the Advancement of Science, 2001).

Whether catenated or non-catenated, the reaction solvent and excess reagents become trapped in the pores of a MOF during synthesis. Regardless of the intended application for a MOF, these molecules must be removed from the pores, which is called “activation”. Activation is necessary in order to harness the high internal surface area, such that substrates can be incorporated into the framework, or molecules may be stored.²⁵ Standard procedure for activation is guest exchange with volatile solvents, followed by exposure to high vacuum.¹⁴ This activation can often lead to the MOF collapsing, and research efforts have been directed at designing robust structures that can withstand this treatment.¹² One strategy for preparing MOFs with high structural integrity is the use of tetrapodal linkers, or those with four coordinating groups.²³ Farha *et al.* explored this strategy with 1,2,4,5-tetraphenylbenzene linkers with *para*-carboxylate donor groups (Compound **4.8**), which formed 2-dimensional “sheets”; 4,4'-bipyridine linkers were used to connect the sheets, acting as “struts” in the third dimension. However, this method formed 2-fold catenated networks. To avoid catenation, the linkers were modified at the 3,6-positions of the central benzene, where bromine was placed as steric bulk (Compound **4.9**, Figure 4.7). The result was non-catenated MOFs for a number of linker combinations.²² Farha and co-workers’ two-linker work also enabled solvent-assisted linker exchange, where a MOF could be prepared and then modified to contain catalytic moieties.² The work of Farha *et al.* informed the research efforts in this chapter, specifically in the use of tetrapodal linkers with carboxylate donor moieties.

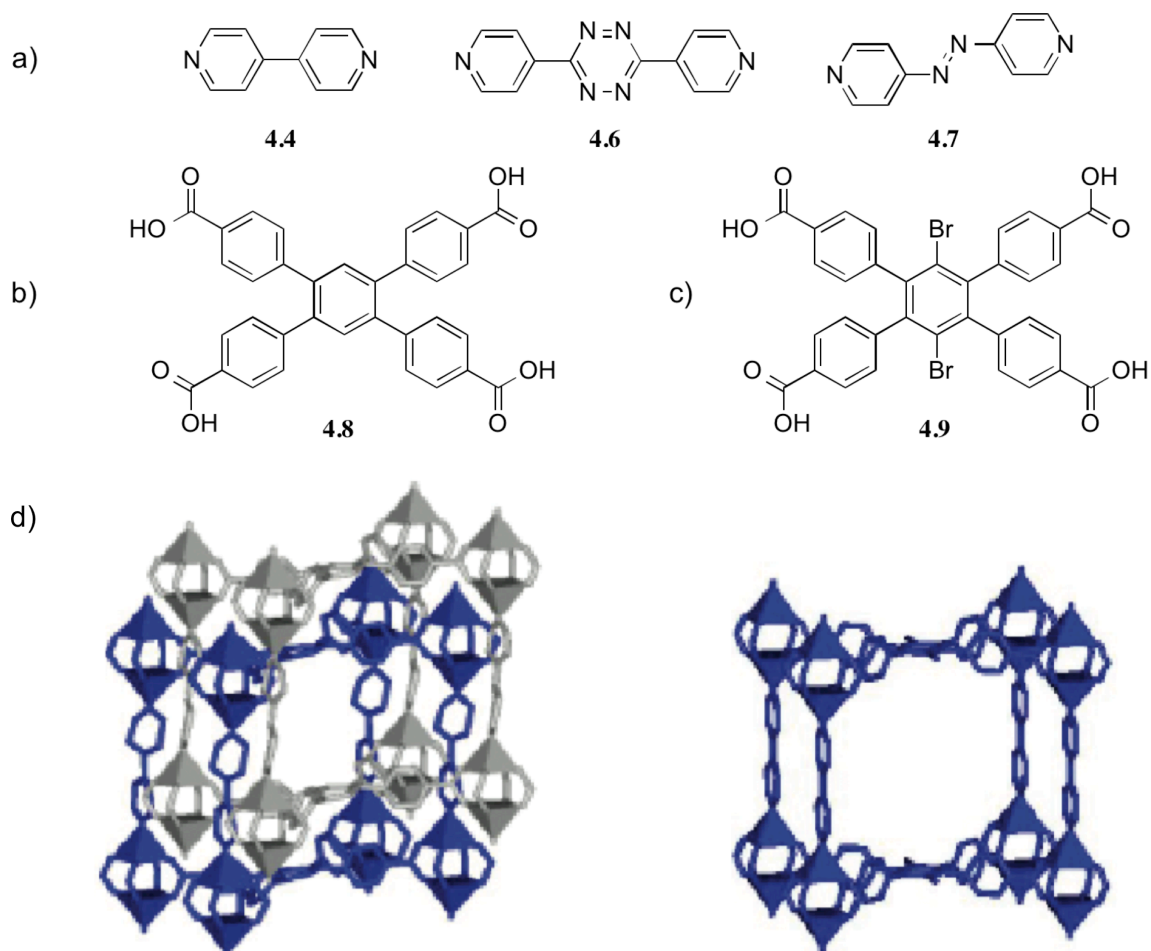


Figure 4.7 (a–c) Linker molecules used by Farha *et al.* to study MOF catenation effects. Linkers from *a* were combined with either *b* or *c*. MOFs prepared from *b* were catenated; MOFs prepared from *c* were non-catenated. (d) Left: catenated MOF from 4,4'-bipyridine and *b*, Right: noncatenated MOF from 4,4'-bipyridine and *c*. (from ref. 22, © American Chemical Society, 2010).

§ 4.2.2 Synthesis of Metal-Organic Frameworks

The synthesis of MOFs is generally considered to be a continuous self-assembly process towards the most thermodynamically favored network possible with a given set of reactants or building blocks.¹⁵ Although the mechanism is not precisely understood, it is thought to be a transition of the coordination sphere of the nodes from solvent molecules and initial donors to the desired linker and structural solvent molecules. As this transition

progresses, the repeating network forms to near-infinity.²⁶ A large number of possible kinetic products (those with various coordination modes or structural geometries) may occur during self-assembly *en route* to the final product. Ideally, these kinetic products remain soluble so that their constituent linkers and metal centres may exchange to contribute to the growth of the most thermodynamic network. In practice, insoluble precipitates can form, which removes reagents or partially equilibrated fragments of the final structure from the reaction mixture.¹⁵

In order to directly study the structure of MOFs, high quality crystalline products must be obtained for X-ray diffraction studies. This means that the thermodynamically favored crystalline structure must be obtained directly from the reaction mixture. However, the need for robust networks that can withstand pore activation treatments,¹² especially for gas adsorption and catalysis applications,¹³ necessitates strong metal-linker bonds. This can introduce a particular challenge to MOF synthesis, as the insoluble kinetic products will also contain these strong bonds, which may hinder equilibration to the thermodynamic structure. This may result in either low yields or crystals that are unsuitable for diffraction studies.

While MOFs can be prepared by room temperature layer-diffusion techniques, the most common method of preparation is the solvothermal (high-temperature solution) reaction.^{8,21-23,27-29} The principle behind this method is encouraging the equilibrium between the solvated kinetic products and the infinitely repeating framework in the direction of the latter. However, for many metal-linker systems (not including the isorecticular families) the most thermodynamic structure that will arise is unpredictable.⁹ Therefore, a systematic variation of reaction conditions (such as solvents, temperature,

and reactants ratio) must be explored to find those that are ideal for crystal growth and minimizing kinetic product formation.

§ 4.2.3 Aromatic Heterocycles as Metal-Organic Linkers

A large segment of the MOFs that have been studied were built using pyridyl groups or phenyl and oligophenyl chains as linkers.^{13,17} However, there has recently been exploration into MOFs built around other heterocyclic linkers, or heterocycles used in conjunction with phenyl rings.^{27,28,30} Yaghi's group prepared and studied MOF-75 using a simple thiophene-based MOF linker, 2,5-thiophenedicarboxylate, which provided a “twisted ladder” configuration (Figure 4.8).

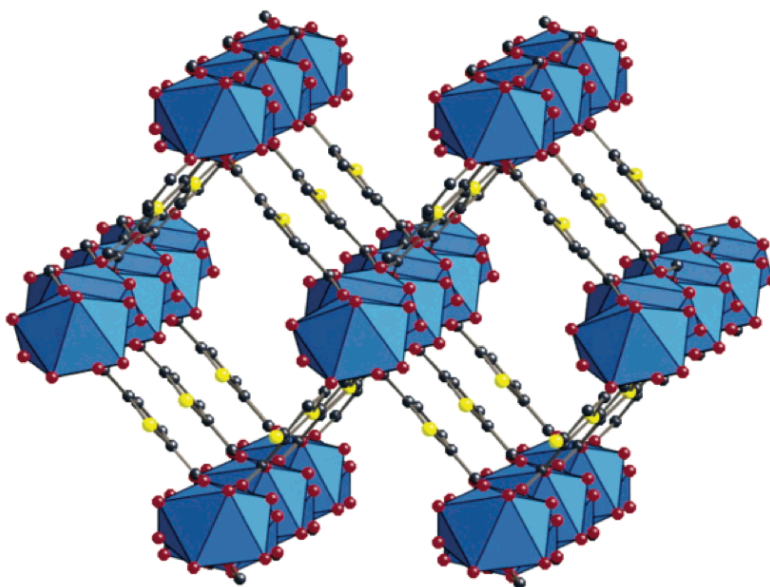


Figure 4.8 Structure of 2,5-thiophenedicarboxylate-based MOF-75 as prepared by Rosi *et al*, showing the TbO₈ bisdisphenoid nodes as blue polygons (from ref. 31 © American Chemical Society, 2005).

Fujita's group recently prepared a series of 2,5-(4-bipyridyl)[**cycle**] linkers, where [**cycle**] is one of furan, pyrrole, thiophene or 3,4-ethylenedioxythiophene (EDOT).^{32,33} These aromatic linkers were planar with a bend imposed by the 5-membered

heterocycles ($\theta = 127\text{--}149^\circ$). The bend angle in the linkers caused the formation of polyhedral structures instead of extended frameworks. The angles imposed by the heterocycle (see Figure. 4.9) caused polyhedra formed with $M = \text{Pt}^{2+}$ to be either $M_{12}L_{24}$ (furan) or $M_{24}L_{48}$ (thiophene, EDOT).

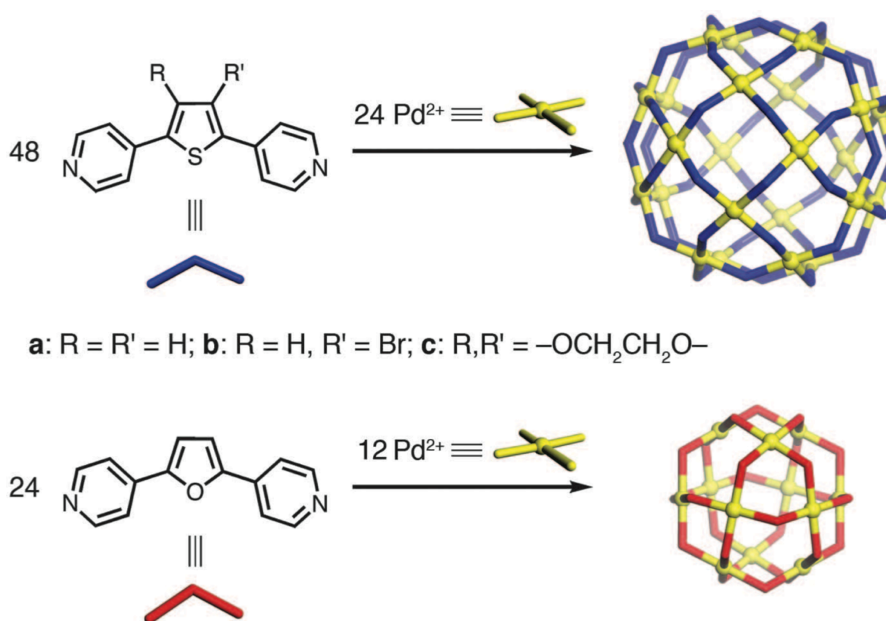


Figure 4.9 Metal organic polyhedra (MOPs) formed from bipyridyl[**cycle**] linkers and $\text{Pd}(\text{NO}_3)_2$. $\theta = 127^\circ$ for furan and 149° for thiophene derivatives (from ref. 32, © American Association for the Advancement of Science, 2010).

In addition to thiophene and thiophene-containing mixed aryl linkers, oligothiophenes have been explored for the preparation of MOFs. Earl and co-workers utilized bithiophenes and terthiophenes with carboxylic acids as the donor moieties for a number of frameworks.^{27,28} Due to the applicability of oligothiophenes to organic semiconductors, MOF-based semiconductor devices have recently been explored in the literature; these are generally prepared by growing thin films of MOFs on functionalized surfaces (Figure 4.10).¹⁷ Some applications of these MOF thin films are luminescent

coatings, quartz crystal microbalances and gas sensors, and porous membrane coatings.^{17,34}

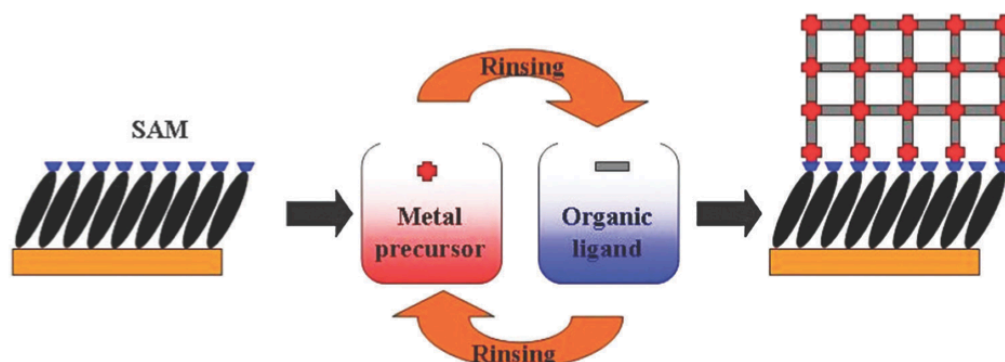


Figure 4.10 Cartoon schematic of stepwise growth for thin-films of MOFs on self-assembled monolayer surfaces (from ref. 17 © The Royal Society of Chemistry 2011).

§ 4.3 Chapter Goals and Outline

There have been efforts towards using oligothiophene-based MOFs for applications, notably in the form of thin films. MOFs designed using star-shaped thienylarenes are anticipated to combine the robust features of a tetrapodal design with the potential for semiconducting behaviour. The aims of this chapter were to prepare a tetrapodal linker based on star-shaped thiophene-containing molecules, followed by the use of that linker to the preparation of metal-organic frameworks. To that end, this chapter describes the synthesis of 1,2,5,6,-tetra(2-thienyl-5-carboxylic acid)benzene (Compound **4.10**) as well as the reactions undertaken to coordinate Compound **4.10** to metal salts, namely acetates of Manganese^{II}, Cobalt^{II} and Copper^{II}. Compound **4.10** was expected to form crystalline, repeating networks with these metal salts.

§ 4.4 Results and Discussion

The most common donor motifs used for MOF linkers are pyridyl rings (nitrogen) and carboxylic acids (oxygen).^{16,17,22,35} While the former can only coordinate to a single

metal ion in a head-on fashion, carboxylic acids can display a variety of binding modes (see Figure 4.11): (i) symmetric chelating, (ii) asymmetric chelating, (iii) bridging, and (iv) monodentate.^{15,27,28,36} In the context of MOFs, the variable binding modes of carboxylates provide a wealth of structural possibilities for a single linker. The versatility of the carboxylate donor moiety, as well as the previous success of thiophenecarboxylate linkers in the MOF literature, motivated the linker design within this work.

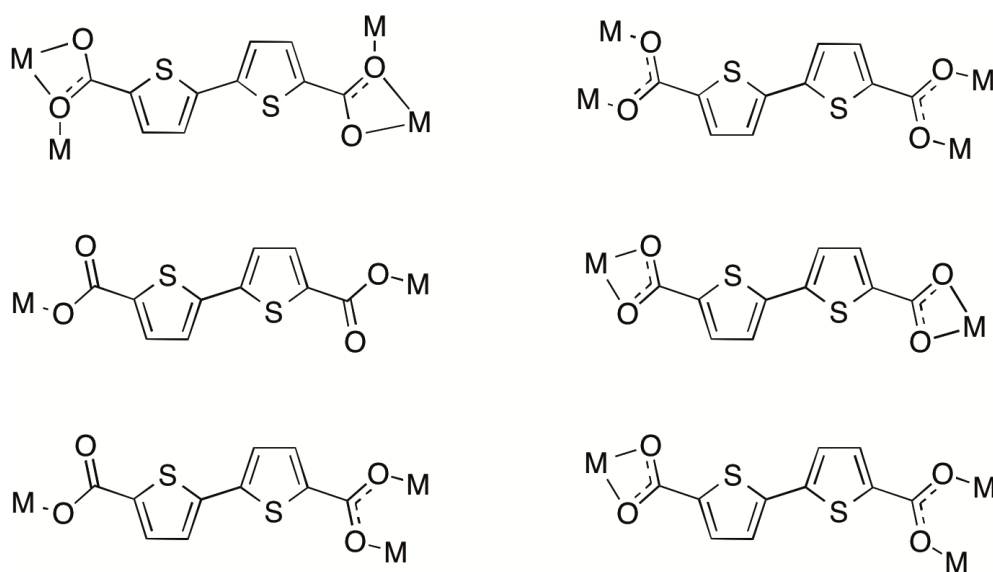
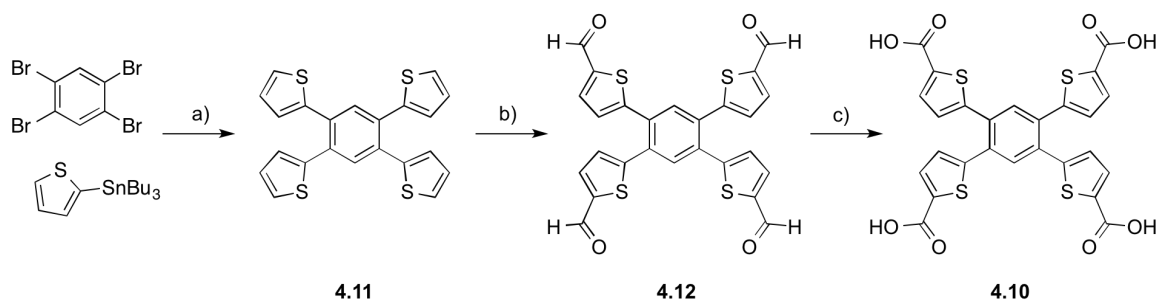


Figure 4.11 Binding modes observed in oligothiophene-based MOF linkers with carboxylic acid donors (adapted from refs. 27, 34, and 37).

§ 4.4.1 Synthesis of Tetracarboxyl Tetrathienylbenzene

The first objective was to obtain the tetrathienylbenzene tetracarboxylic acid linker, Compound **4.10**. Unfunctionalized tetrathienylbenzene (Compound **4.2**) could be prepared in the same manner as tetrathienylpyridine (Compound **3.2**). The four-fold Stille reaction (see Section 3.2) would then be employed with 1,2,4,5-tetrabromobenzene and 2-tributylstannylthiophene, as outlined in Scheme 4.1.³⁸ The carboxylic acid donor groups required to coordinate to the metal centres could be installed at the thienyl 5-

positions using a formylation-oxidation sequence. Due to the higher electron density of the thiophene α -carbon,^{30,38} deprotonation could be performed with a base such as *n*-butyl lithium (*n*-BuLi). The addition of *N,N*-dimethylformamide (DMF) would afford 5,5',5'', 5'''-(benzene-1,2,4,5-tetrayl)tetrakis(thiophene-2-formate) (Compound **4.12**), and oxidation of the aldehydes could be carried out using Oxone would produce the carboxylate product.³⁹



Scheme 4.1 Initial synthetic route to Compound **4.10** via aldehyde oxidation. *Reagents and Conditions:* a) $\text{PdCl}_2(\text{PPh}_3)_2$, DMF, 130°C b) i. *n*-BuLi, -78°C , THF. ii. DMF, -78° to r.t. b) Oxone, DMF.

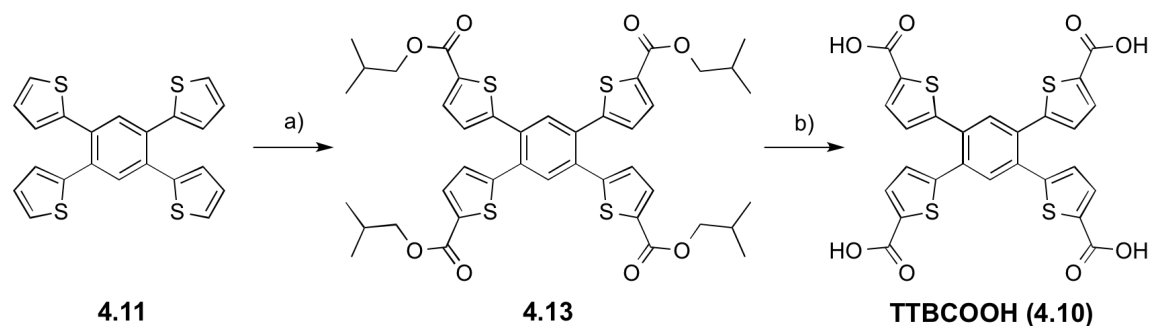
Compound **4.11** was dissolved in THF to provide gray solutions, which were cooled to -78°C ; *n*-BuLi was then added dropwise in single aliquots to these solutions. Due to the four thienyl α -carbon sites on Compound **4.11**, a mixture of products was expected from the lithiation reaction. Initially, four equivalents of *n*-BuLi were added. Intensely coloured precipitates appeared, presumably corresponding to the charges being introduced to the conjugated system: one equivalent caused a green precipitate, two equivalents orange, and four equivalents yellow. With prolonged stirring, the coloured precipitates eventually dissolved back into solution. Following the addition of *n*-BuLi, the reactions were allowed to warm gradually to room temperature. Dry DMF (four equivalents) was then added in one aliquot. This caused the reactions to turn bright

orange. The reactions were stirred at room temperature for one hour, before being quenched with aqueous NH_4Cl to provide solid, orange products. NMR, TLC and MALDI indicated a mixture of products. To circumvent this issue, eight equivalents of *n*-BuLi were reacted with Compound **4.11**; the additional four equivalents of *n*-BuLi caused the mixture to become milky white, however the solution did not clear as previous precipitates had. Eight equivalents of DMF were added, and the orange product was worked up as above. Compound **4.12** was identified in the MALDI at $m/z = 518$, but the threefold formylated species was a major side product, in addition to the twofold product in trace amounts ($m/z = 490$ and 462 , respectively). These challenges were finally overcome by using isobutyl chloroformate, to form an ester group.

To investigate what proportion of *n*-BuLi was required to deprotonate each thienyl 5-position, or in other words whether one equivalent of base would remove one proton, reactions were performed with one and two equivalents of *n*-BuLi. These both afforded mixtures of the desired product with either starting material (one equivalent) or under-functionalized side-product (two equivalents). The difficulties with formylation, namely under-functionalized derivatives, may have been due to the inadequacy of the dimethylamide ion as a leaving group, as $\text{N}(\text{CH}_3)_2^-$ is a strong base;⁴⁰ alternatively, it is possible that the lithiation step was the source of the mixture of products.

To overcome these synthetic challenges, the synthetic route was modified. As shown in Scheme 4.2, the preparation of Compound **4.10** could be achieved by using a different pathway to introduce the carboxylic acids, first investigated by Fu *et al.*³⁰ As in the route above, it rested on the use of excess *n*-butyl lithium to deprotonate all four α -carbon sites at once. However, instead of introducing a formyl group, Fu and coworkers utilized

isobutyl chloroformate; chloroformates are widely used to as electrophiles due to their high reactivity, as well as the chloride ion being an excellent leaving group.⁴¹ Compound **4.11** was dissolved and cooled as before, then lithiated with eight equivalents of *n*-butyl lithium; after reaching room temperature, the reaction was cooled back to $-78\text{ }^{\circ}\text{C}$ and eight equivalents of isobutyl chloroformate were added. This reaction was allowed to come to room temperature slowly, and provided a clear yellow solution. Workup with NH_4Cl extraction with ethyl acetate afforded the tetra isobutyl ester of tetrathienylbenzene (Compound **4.13**) as a yellow powder in crude yields of 90-95%. Compound **4.13** was recrystallized from ethyl acetate as small yellow crystals in yields of 60%. The isolated product had a strong, sweet smell.



Scheme 4.2 Synthetic route to TTBCOOH (Compound **4.10**) *via* ester saponification. *Reagents and Conditions:* a) i. *n*-BuLi, $-78\text{ }^{\circ}\text{C}$, THF. ii. Isobutyl chloroformate, -78 ° to r.t. b) excess KOH, EtOH/H₂O, reflux.

To prepare the carboxylate product Compound **4.10** following this route, the isobutyl esters were treated with strong base (60 equivalents of KOH in ethanol/H₂O)⁴¹ and the reaction mixture was refluxed for 48 hr, but became a deep red solution after XX hours. After 24 hours, the deep red solution became orange and a white precipitate of tetracarboxylate potassium formed. This salt was filtered from the basic reaction mixture as a light yellow solid and subsequently dissolved in water, affording a yellow solution.

The carboxylic acid form of Compound **4.10** was then prepared via acidification (pH < 1) with HCl, whereupon a bright blue precipitate formed. The precipitate was collected and dried, affording yields of approximately 75%. ^1H and ^{13}C NMR in DMSO- d_6 (presented in Figure 4.12) indicated benzene protons as a singlet at 7.79 ppm, and thiophene protons as doublets at 7.67 and 7.22 ppm, confirming that the 5-position of the thiophenes were functionalized. By comparison, in Compound **4.11** the aromatic region shows a doublet of doublets and a complex multiplet due to the presence of the thiophene α -proton. Carbon NMR displayed aromatic protons between 163 and 129 ppm. However, the expected carbonyl carbons and acidic protons were not observed; these usually appear above 200 ppm and 10 ppm, respectively.

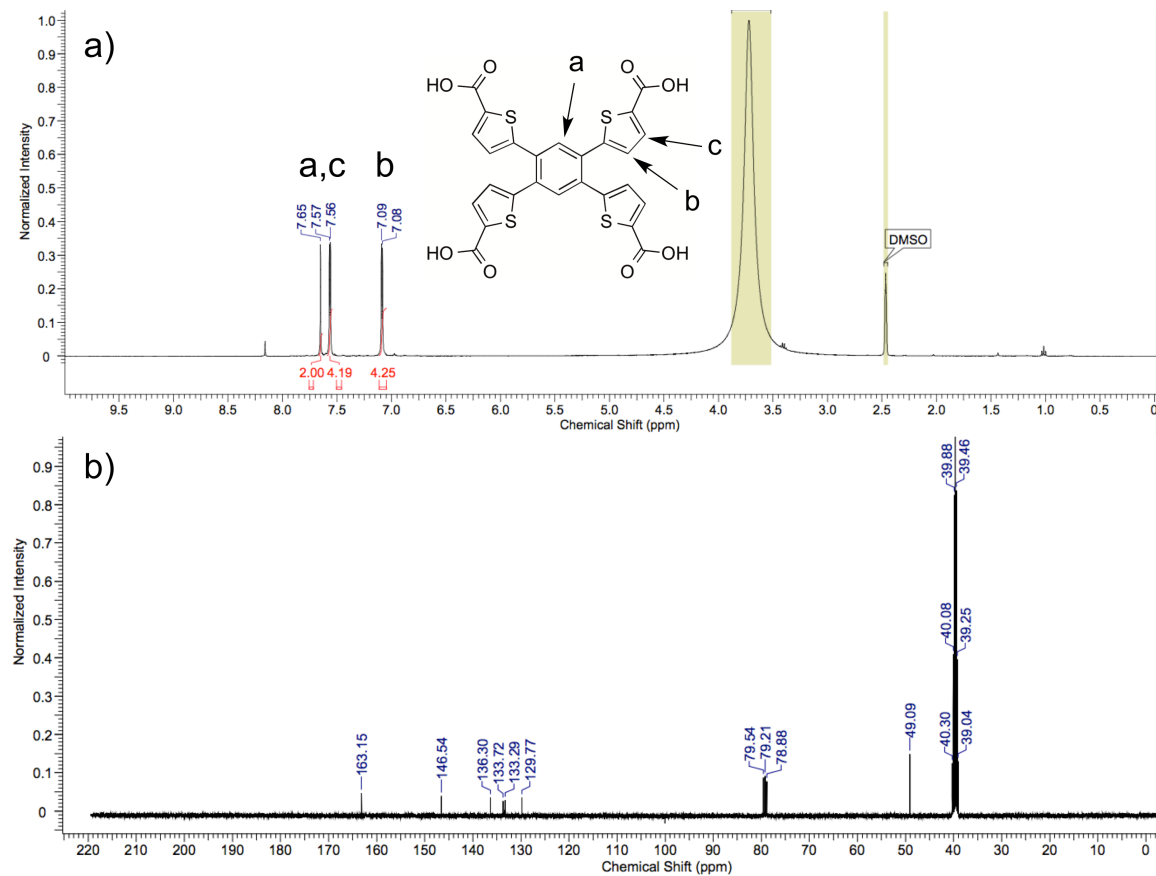


Figure 4.12 a) ^1H NMR spectrum (at 400 MHz) and b) ^{13}C NMR spectrum (at 100 MHz) of Compound **4.10** in a mixture of DMSO- d_6 and CDCl_3 .

Quaternary carbon signatures, such as the carbonyl carbon of Compound **4.10**, are frequently weak and sometimes do not appear due to slower nuclear relaxation times. Acidic protons are capable of exchange with trace amounts of H₂O in the sample or NMR solvent; the DMSO used for the NMR likely contained enough water for this to occur. Compound **4.10** was refluxed in benzene using a Dean Stark apparatus to remove water azeotropically; even after over 24 hours, a broad peak attributed to water was observed in the ¹H NMR spectrum, and the missing carbonyl and acidic proton peaks were absent.

The infrared spectrum is also informative as to the character of the carboxyl groups. Furthermore, the IR signature is important to the identification of metal-oxygen bonds. In the ligand that was obtained from azeotropic water removal from benzene (Figure 4.13, red line) the $\nu(\text{C=O})$ carboxyl stretch is clear at 1677 cm⁻¹. Absorptions at 1620 and 1540 cm⁻¹ correlated well with $\nu(\text{COO})_{\text{asym}}$ stretches, and absorptions at 1470 and 1440 cm⁻¹ corresponded to $\nu(\text{COO})_{\text{sym}}$ stretches. A very strong peak was observed at 1060 cm⁻¹, which is most likely attributed to the C–O vibration;⁴² however, it is also possible that these are C–C skeletal vibrations from benzene or the thiophenes, or C–H stretches from the same groups.

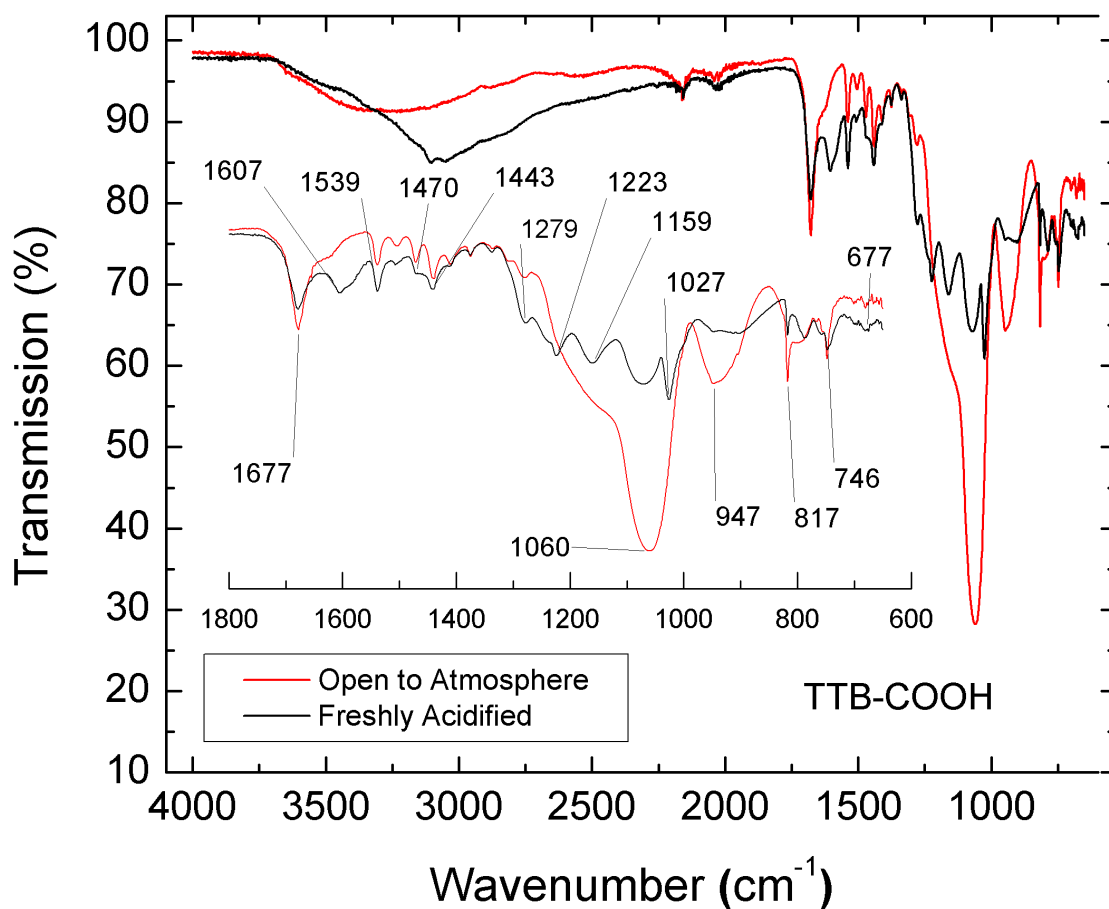


Figure 4.13 Infrared spectra of Compound **4.10**: as isolated from reaction (red) and after boiling in H_2SO_4 (black). The inset is a magnification of the carbonyl and fingerprint regions.

Compound **4.10** was observed to lose its blue colour over time, becoming light yellow with extended exposure to the atmosphere, as well as after rinsing with acetone or methanol following the initial acidification. One possible explanation is the lability of the carboxylic acid protons; it is possible that they slowly dissociate with the collection of atmospheric water, or can be removed by solvents. To test this possibility Compound **4.10** was boiled in 1M H_2SO_4 to regenerate the carboxylic acids. The NMR characterization remained unchanged, but upon this latter acidification, changes were observed in the IR spectrum: the $\nu(\text{C}=\text{O})$ carbonyl stretch at 1677 cm^{-1} lost intensity, and

the broad absorption in the O–H stretch region shifted and intensified. Furthermore, absorptions between 1280–900 cm⁻¹ resolved from the strong 1060 cm⁻¹ absorption, which suggests that it is the C–O vibration of Compound **4.10** rather than skeletal C–C modes. The sharp absorptions at 817 and 746 cm⁻¹ in the initially isolated Compound **4.10**, which corresponded to O–H bending modes, also weakened and resolved into a larger number of bands within the same range of wavenumbers in the IR spectrum of the newly acidified Compound **4.10**.

Compound **4.10** was marginally soluble in organic solvents. Fu *et al.* prepared the **TTA** tetracarboxylic acid analogue, which also showed low solubility, however that compound was fused to have an anthracene core. The acid groups could be deprotonated with alkali bases, whereupon Compound **4.10** became yellow. Heat and sonication was required to break up the granules of solid Compound **4.10** for dissolution. In this manner it could be partially dissolved in water and mixtures of water with miscible organics, however it was only fully dissolved by boiling in polar solvents such as DMF, DMSO, and *N*-methyl pyrrolidinone (NMP). Due to their high boiling points and polarity, these are also the most common solvents used for the solvothermal synthesis of MOFs.⁴³ The strategies for the formation of MOFs based on Compound **4.10**, and the synthetic work towards their preparation, are discussed in Section 4.4.2.

§ 4.4.2 Tetrapodal Pillared Paddlewheel MOF Synthetic Precedent

Two strategies were chosen to prepare MOFs from Compound **4.10**. First, following the route as outlined by Farha *et al.* for the pillared paddlewheel structures prepared from tetracarboxyl tetraphenylbenzenes,²² four equivalents of a given metal salt could be used for reactions. Secondly, as described by both Zhao *et al.*^{34,44} and Earl *et al.*,^{27,28} for

MOFs and coordination polymers synthesized from dicarboxyl oligothiophenes, equimolar amounts of metal salts could react with the ligand prepared herein. Both solvothermal and layer diffusion syntheses have been shown to be effective, the latter having been particularly effective for thiophene-based linkers. Before further discussion of experimental results, a brief outline of the characterization of MOFs via infrared spectroscopy will be presented.

§ 4.4.3 Infrared Spectroscopy of Metal-Organic Frameworks

The most common methods studying the structures of MOFs are single crystal X-ray crystallography and powder X-ray diffraction. On the other hand, information such as the binding modes of the linkers, and presence or structural role (if any) of the reaction solvent, can be determined from the infrared spectra of MOFs. Bonds between atoms, whether covalent, ionic or dative, have characteristic stretching, rotating and bending modes with consistent vibrational frequencies.⁴⁵ Infrared spectroscopy probes chemical bonds and functional groups by scanning with radiation of energy corresponding to these frequencies, such that a dipole moment has changed. The frequencies of these modes can be an indicator of bond order, bond strength, or chemical environment around a bond.⁴⁶ Characteristic absorptions that are especially pertinent to the study of MOFs that use carboxylates as the donor moiety are those associated with carbonyls – from approximately 1800 to 1500 cm^{-1} – and O–H stretches, which are found from approximately 3700 to 3200 cm^{-1} .

In the context of the MOFs synthesized in this chapter, infrared spectroscopy can be used to approximate the degree to which the coordination of carboxylic acids has occurred, as well as shed light on the binding mode or combination of bonding modes the carboxyl

groups adopt. Carbonyl $\nu(\text{C}=\text{O})$ stretches are typically strong, from $1800\text{--}1600\text{ cm}^{-1}$. In the absence of an O–H stretching absorption, the $\nu(\text{C}=\text{O})$ stretch can indicate the (O=C–O···M) binding mode. However, changes in the dipole moment of single bonds between metal centres and oxygen are usually found in the lower limits of the fingerprint region ($<700\text{ cm}^{-1}$). When one or both carboxyl oxygens are coordinated to metals, a number of characteristic vibrations appear. Multiple stretches where the electronic character of the double bond is partly delocalized, including both asymmetric and symmetric stretches, can be observed. The former, $\nu(\text{COO})_{\text{asym}}$, appear in the region of $1650\text{--}1500\text{ cm}^{-1}$; the symmetric $\nu(\text{COO})_{\text{sym}}$ stretches, where the electronic character of the oxygens are equivalent, are observed from $1500\text{--}1350\text{ cm}^{-1}$.^{42,47,48} The carbon-oxygen stretches associated with carboxyl groups were the primary indicator of structure for the MOF synthesis in this work.

Hydrogen-bonding IR absorptions such as the O–H stretch can also be a useful indicator of the morphology of MOFs, particularly if hydrated metal salts were used for node precursors or the solvent contains water. Large O–H absorptions will typically indicate physisorbed or structurally incorporated water molecules, though the well-defined absorptions that confirm a structural role for water are usually observed after MOF activation; O–H stretches for water molecules appear near 1620 cm^{-1} , and O–H bending frequencies from sources other than water can be observed in the region between $900\text{--}600\text{ cm}^{-1}$.⁴⁹

§ 4.4.4 Preliminary MOF Synthesis Work

Usually, the formation of MOFs occurs between room temperature and solvothermal conditions in a time range of hours.⁴³ Initial studies were undertaken to prepare MOFs with Compound **4.10** to screen combinations of conditions. Infrared spectroscopy was used to probe the results of these experiments. A combination of heating, stirring and sonication was applied to dissolve the granules of Compound **4.10** and prepare ligand solutions of concentration = 0.25 mM. Both solutions carried out without the use of base, and those including a stoichiometric amount of sodium hydroxide (NaOH) relative to the number of protons on the ligand were tested. Solutions containing four equivalents of metal salts (acetates of Manganese^{II}, Cobalt^{II} and Copper^{II}, concentration = 1.00 mM) were combined with the Compound **4.10** solutions to form a reaction mixture. The solutions were combined while they were hot (approximately 80 °C) as well as after they had cooled to room temperature.

It was noted that precipitates formed immediately for any combination (hot/cold, base/no base) of reagents. The precipitates of reactions using deprotonated Compound **4.10** appeared to be more dense and solid, while those from neat ligand solutions were more thin and cloudy. These precipitates were most likely kinetic rather than thermodynamic products of the ligand and metal centres, and due to their non-crystalline nature, were expected to show inconsistent bonding modes for the carboxylate donor moieties. Precipitates were suction filtered and rinsed copiously with acetone to remove reaction solvent, and dried under suction for 30 minutes. Following drying, they were studied using infrared spectroscopy to probe the bonding modes of the carboxylate groups, and to enable the identification of kinetic products should they arise from the solvothermal or

layer diffusion reactions. Manganese precipitates ranged from yellow to golden brown; Cobalt precipitates were pink and red; Copper precipitates were green-blue.

Mn^{II} and Co^{II} kinetic products formed from stirred reactions at room temperature and at 80 °C in dimethyl sulfoxide (DMSO), and displayed nearly identical features. The strong $\nu(\text{C}=\text{O})$ carbonyl stretch (1677 cm^{-1} in the free acid) disappeared from precipitates formed from Mn^{II} and Co^{II}, indicating that both oxygens were involved in binding (chelating or bridging modes), while it shifted to 1620 cm^{-1} for Cu^{II}, which suggested a monodentate binding mode for oxygen in the Cu^{II} product. The strongest carboxyl absorptions were in the region of $1560\text{--}1545\text{ cm}^{-1}$ for Mn^{II} and Co^{II}, which corresponded to $\nu(\text{COO})_{\text{asym}}$ stretches. For all metals, two bands appeared at 1435 and $1393\text{--}1373\text{ cm}^{-1}$, which corresponded to $\nu(\text{COO})_{\text{sym}}$ stretches. The intense C–O vibration at 1060 cm^{-1} remained intact for Mn^{II} and Co^{II}, while for Cu^{II} it shifted to 1012 cm^{-1} , which was consistent with a different carboxyl peaks in Cu^{II} from the other metal products. All three metals showed a sharp peak at 770 cm^{-1} , which was most intense in the copper species. This may be attributed to the O–H bending mode. Notably, only the copper species displayed a strong O–H stretch above 3000 cm^{-1} , which may indicate that hydrates were coordinated to copper in the kinetic species, or that some carboxylic acid groups did not coordinate to a node and remained free, or a combination of the two. An infrared spectrum of the stirred reaction between Compound **4.10** and Co(OAc)₂·4H₂O in DMF is presented in Figure 4.14.

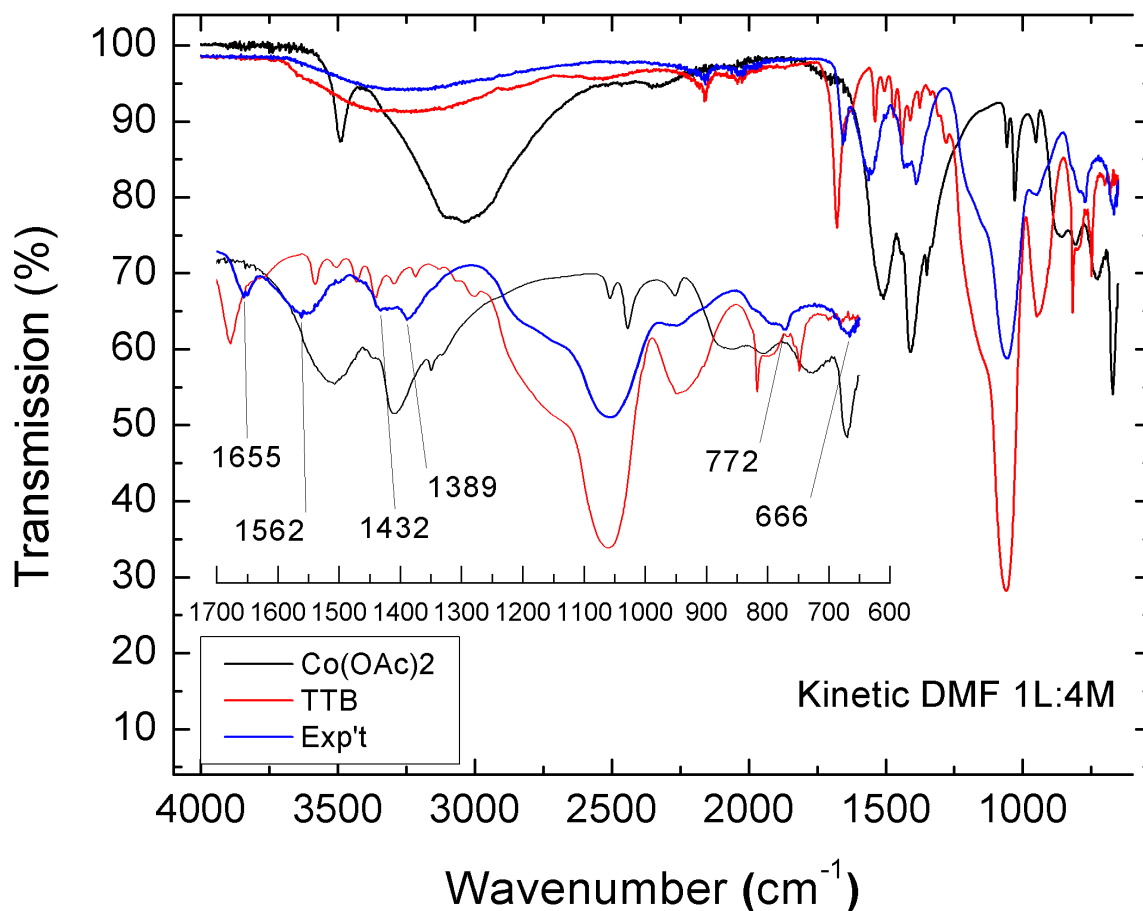


Figure 4.14 Representative infrared spectrum of kinetic products formed from the reaction between deprotonated Compound **4.10** and $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$. The inset is a magnification of the carbonyl and fingerprint regions.

Polar organic solvents such as amides *N,N*-dimethylformamide (DMF) and *N*-methylpyrrolidinone (NMP) are very common solvents for the preparation of MOFs, especially under solvothermal conditions. The infrared signatures of the precipitates from stirred reactions with all three metals in DMF and NMP showed close agreement, with $\nu(\text{C}=\text{O})$ stretches at 1655–1640 indicating intact carboxyl oxygens. In the spectrum in Figure 4.14, a broad $\nu(\text{COO})_{\text{asym}}$ stretch which may have been two unresolved absorptions appeared at 1562 cm^{-1} , and $\nu(\text{COO})_{\text{sym}}$ stretches appeared at 1432 and 1389 cm^{-1} . The C–O vibration at 1060 cm^{-1} remained unchanged in form, but lost intensity,

and again small peaks arose at 770 cm^{-1} . These peaks suggest that a number of coordination modes were present, including monodentate and chelating/bridging. No O–H stretches were observed, which indicated that no charge balancing hydroxyls, physisorbed water, or intact COOH groups were present. With kinetic products of reactions between metal salts and Compound **4.10** studied, reactions to prepare crystalline MOFs were undertaken; this work is described next.

§ 4.4.5 Layer Diffusion Reactions

In a layer diffusion (LD) reaction, the reagents are dissolved in separate solutions, which are subsequently layered such that those reagents can slowly diffuse together promoting a relatively slow reaction. This method was chosen as a strategy to prepare MOFs due to the fast precipitation exhibited during reactions described above. Additionally, a layer diffusion method was used successfully to prepare single-crystalline MOFs for oligothiophene linkers with carboxylic acid donors.³⁴ For Compound **4.10**, both single-solvent and multi-solvent systems were used. In the case of multi-solvent systems, the deprotonated ligand was solubilized in an organic solution, while the metal salts were dissolved in water. In each case, the solutions were layered according to density. For single-solvent systems, the metal salt solutions were slowly added on top of the solutions of Compound **4.10**; the precipitates that formed immediately acted as barriers to the complete mixing of the “layers”. These reactions were allowed to stand for at least 72 hours, and then the solids were isolated in the same manner as the kinetic products and analyzed by infrared spectroscopy.

LD reactions from DMSO/H₂O gave similar results for all three metals. Broad O–H peaks were observed, indicating either structural or physisorbed water, but these may

also indicate the presence of charge balancing hydroxyl groups. In the carbonyl region, $\nu(\text{C=O})$ stretches at $1655\text{--}1647\text{ cm}^{-1}$ were observed, which is indicative of uncoordinated carboxyl oxygen atoms. Stretches corresponding to $\nu(\text{COO})_{\text{asym}}$ were observed at 1560 cm^{-1} , similar to the kinetic products. These two signatures suggest that monodentate binding was present for all three metals in DMSO/H₂O LD conditions. However, for Mn^{II} and Cu^{II} four peaks between 1438 and 1317 cm^{-1} were present. These may be due to a range of $\nu(\text{COO})_{\text{sym}}$ stretches, potentially indicative of a degree of chelating or bridged bonding modes in products from reactions with Mn^{II} and Cu^{II}. The C–O vibrations in the Co^{II} reaction were at 984 and 882 cm^{-1} . In Mn^{II} and Cu^{II}, these were observed at 1010 and 950 cm^{-1} . All metals showed increased absorption below 700 cm^{-1} , possibly O–H bends from apically coordinated OH[−].

In NMP/H₂O LD reactions, precipitates from Co^{II} and Cu^{II} showed $\nu(\text{C=O})$ stretches at 1645 cm^{-1} , indicating uncoordinated carboxyl oxygens. All metals showed $\nu(\text{COO})_{\text{asym}}$ stretches at 1560 cm^{-1} , which for Co^{II} and Cu^{II} suggested monodentate coordination. IR signatures of Co^{II} and Mn^{II} products had clustered absorptions between 1430 and 1360 cm^{-1} corresponding to $\nu(\text{COO})_{\text{sym}}$ stretches, which suggested that either chelating or bridged binding was present. The copper product showed a broad stretch at 1407 cm^{-1} , which suggests the presence of symmetric COO stretches that overlapped. The C–O absorption of copper intensified relative to the bare ligand, and moved to 965 cm^{-1} . These absorptions were shifted to 993 cm^{-1} for Mn^{II} and 972 cm^{-1} for Co^{II}, suggesting a weakening of the C–O bond resulting from strong O[−]⋯M monodentate binding, consistent with the presence of carboxyl C=O stretches above. Co^{II} and Mn^{II} precipitates both showed peaks at 901 and 777 cm^{-1} . The region from 900 to 650 cm^{-1} showed strong

absorptions, which may have indicated O–H bends from water or hydroxyl groups. The copper LD product also displayed a strong O–H stretch, which may have been coordinated hydroxyls or physisorbed water.

In layered solutions of H₂O/H₂O, all three metals showed $\nu(\text{C}=\text{O})$ stretches at 1635, and $\nu(\text{COO})_{\text{asym}}$ at 1560–1550 cm⁻¹. Broad $\nu(\text{COO})_{\text{sym}}$ stretches appeared at 1380 cm⁻¹, while Cu^{II} had an additional peak at 1339 cm⁻¹. These results indicated that there were both monodentate and chelating/bridging carbonyl groups for all three metals. The C–O vibrations were shifted to 994–970 cm⁻¹, suggesting strong O···M monodentate bonds. Absorptions weaker than 700 cm⁻¹ were relatively intense for all species. The lack of O–H stretches suggested that there were no physisorbed or structurally incorporated water molecules, nor charge balancing hydroxyl groups.

LD reactions in acetonitrile and water provided results unlike the other solvent combinations. In each case, a precipitate was observed at the interface of the two solutions. However, over a period of several days, microcrystalline products were observed in reactions with Mn^{II} and Co^{II}. These were not of sufficient quality for X-ray work. From cobalt, the block-like pink crystals appeared to grow in many directions from each site of nucleation. For manganese, there were very small yellow needles. These products were collected in the same manner as those above, and analyzed using infrared spectroscopy.

The infrared signatures of both manganese- and cobalt-derived microcrystals showed O–H stretches, which may have been physisorbed or structurally incorporated water. This is consistent with occluded reaction molecules in MOFs before activation to evacuate the

pores. For these species, no $\nu(\text{C}=\text{O})$ stretches were present, therefore it was concluded that no monodentate binding had occurred. Co^{II} displayed a pair of $\nu(\text{COO})_{\text{asym}}$ stretches at 1560 and 1540 cm^{-1} , while that of Mn^{II} was a broad peak at 1532 cm^{-1} . $\nu(\text{COO})_{\text{sym}}$ stretches were observed at 1389 and 1375 cm^{-1} for Co^{II} and Mn^{II} , respectively.

The combination of the above carbonyl signatures suggested that the crystals were composed of structures with chelating or bridging acid groups. The presence of water indicated that molecules may have been trapped in the pores of MOF-like segments of product, or that they played a structural role in the complexes. The manganese product in MeCN/H₂O was the only product from a layered reaction where the intense C–O absorption was not the strongest absorption of the compound (see Figure 4.15). It had been shifted to 1020 cm^{-1} , indicating a weakened C–O bond relative to the free ligand, but not as weak as some instances of the same stretch above that had correlated with monodentate binding.

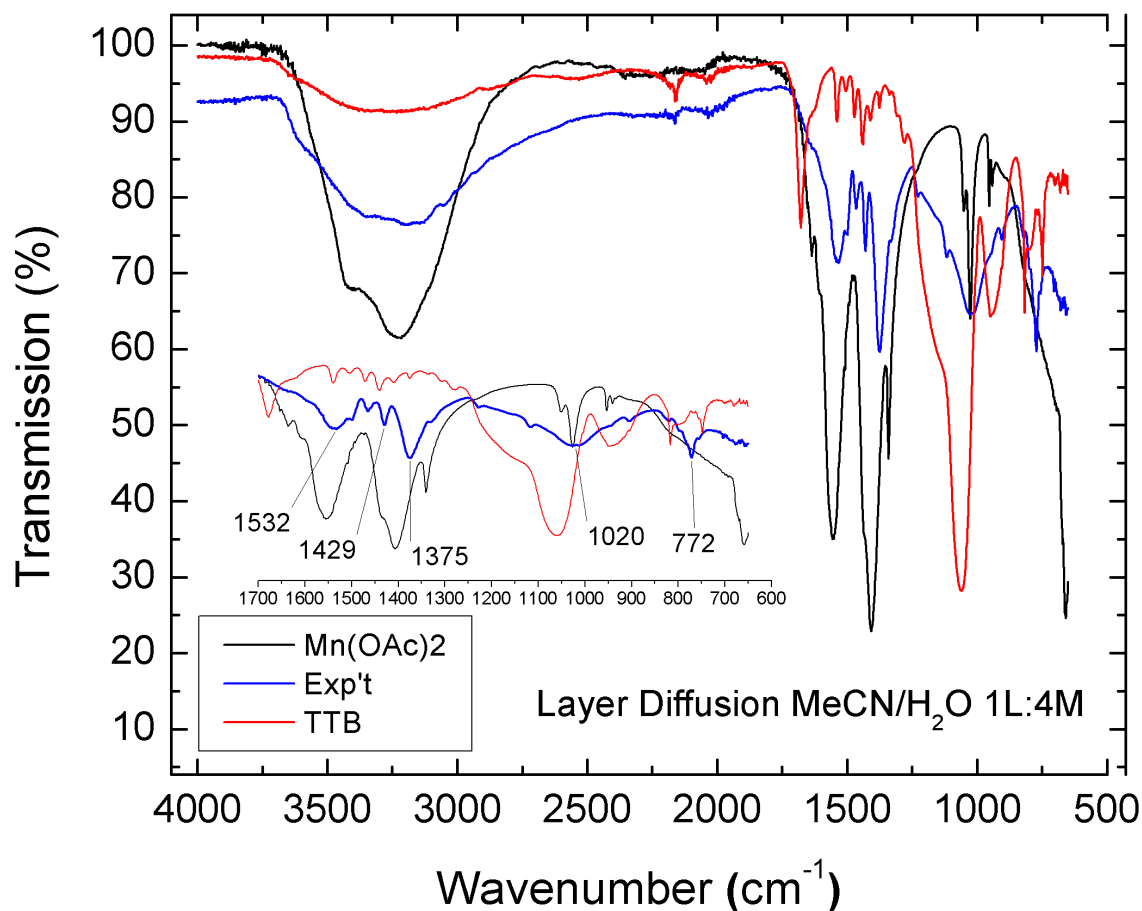


Figure 4.15 Representative infrared spectrum of products formed from layer diffusion reaction between deprotonated Compound **4.10** and $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ in MeCN/ H_2O . The inset is a magnification of the carbonyl and fingerprint regions.

In the crystals obtained from reactions with both cobalt and manganese, there were O–H bending absorptions at 773 cm^{-1} . In manganese-derived crystals, both this absorption and the $\nu(\text{COO})_{\text{sym}}$ peak at 1375 cm^{-1} were stronger than the broad peak at 1020 cm^{-1} . This is significant, as this reaction also yielded the largest crystals, which may suggest that symmetric chelating or bridging bonds are critical to the most crystalline structures. Non-crystalline precipitates largely contained uncoordinated oxygens (*vide supra*). Paddlewheel motifs in MOFs from carboxyl-based linkers are composed of metal-oxygen bonds in the bridging coordination mode.²¹⁻²³

The acquisition of microcrystalline clusters prompted the optimization of reaction conditions. Both layered and mixed reactions were pursued: rather than layering pure acetonitrile and H₂O, solutions of varying compositions were prepared, from 25–75% acetonitrile in H₂O and then layered in the same manner as above. The same solvent ratios were for room temperature reactions; solutions of the metal salts and deprotonated Compound **4.10** were mixed together manually. The immediate precipitate was removed by filtration, and subsequent precipitation was removed until the solutions remained clear. The reactions were then allowed to incubate in the reaction vessel for at least 48 hours.

Over a period of days, further kinetic products were observed to precipitate in the solution. In many cases, this was accompanied by the growth of microcrystalline clusters, similar to those obtained from the layered solvent diffusion reaction. These were unsuitable for X-ray work, but displayed consistent infrared data to those obtained from the other layered reactions. Because of the formation of microcrystals, the same solvent mixtures and techniques were used for further solvothermal work, as an attempt to encourage equilibration towards the thermodynamic, crystalline products (*vide infra*). Microcrystalline products were obtained from manganese and cobalt acetates, with the same morphology as those obtained from layered reactions. As with previous microcrystalline products, these were not of suitable quality for X-ray work.

Overall, the combination of Compound **4.10** and the acetates of metal salts resulted in immediate precipitation. ATR-FTIR analysis of these products indicated wide variety of metal-oxygen bond configurations, ranging from single monodentate bonds with intact carbonyls, to delocalized chelating and bridging oxygen bonds. Under layer diffusion

conditions, similar kinetic results were observed. In mixtures of water and acetonitrile under layer-diffusion conditions, microcrystalline clusters were obtained from reactions with Cobalt^{II} and Manganese^{II}. These displayed intense symmetrical carboxyl stretches and weakened carbon-oxygen bonds, which indicated bridging bonds consistent with the paddlewheel motif commonly observed in MOFs prepared from carboxyl-coordinating linkers. However, none of the products could be confirmed as crystalline MOF structures as they were not of sufficient quality for X-ray study.

§ 4.4.6 Solvothermal Reactions

The drawback of the reaction methods discussed above was that there was a lack of thermal equilibrium promoting the kinetic products to exchange components continuously, such that the most thermodynamically stable structures were formed. However, solvothermal synthesis occurs at high temperature and elevated pressures, encouraging this equilibration. Crystalline products may be obtained at the reaction temperature, or upon slowly cooling the solutions once a certain time period had elapsed.^{8,21-23,27-29} Solvothermal reactions in this work were prepared by combining solutions of deprotonated Compound **4.10** and metal salt solutions. Prior to subjecting them to solvothermal conditions, the precipitates that formed immediately were filtered off until the solutions remained clear. They were then placed in pressure vessels, which were elevated to 90 °C in an oil bath for 48 hours. Solutions were then cooled at a rate of approximately 1 °C min⁻¹ until reaching ambient conditions. Products were isolated by filtration and washing with acetone.

In DMF, the infrared signatures were similar for products from copper and cobalt reactions. The strong C–O absorption of Compound **4.10** remained dominant in these

spectra. The carbonyl regions were characterized by four broad absorptions, including $\nu(\text{C=O})$ stretches from 1655–1637 cm^{-1} , $\nu(\text{COO})_{\text{asym}}$ stretches at 1580–1560 cm^{-1} , and $\nu(\text{COO})_{\text{sym}}$ at 1384–1371 cm^{-1} . These infrared signatures were consistent with the kinetic products obtained from room temperature studies above, with uncoordinated carbonyl groups and carbon-oxygen bond strengths unchanged relative to the free ligand.

In DMSO, copper was characterized by broad IR absorptions in a pattern similar to those in DMF, both in intensity and wavenumber; however, none of the products displayed $\nu(\text{C=O})$ stretches, which suggests that there was no monodentate binding present (see Figure 4.16). For cobalt and manganese, broad O–H absorptions were observed in the region above 3100 cm^{-1} , suggesting some level of porosity or structural incorporation of water for both of these structures. However, as the reaction solutions did not contain water, the source of water molecules would have been the initial metal salt hydrate. This suggests that the water played a structural role in the ensuing paddlewheel structure.

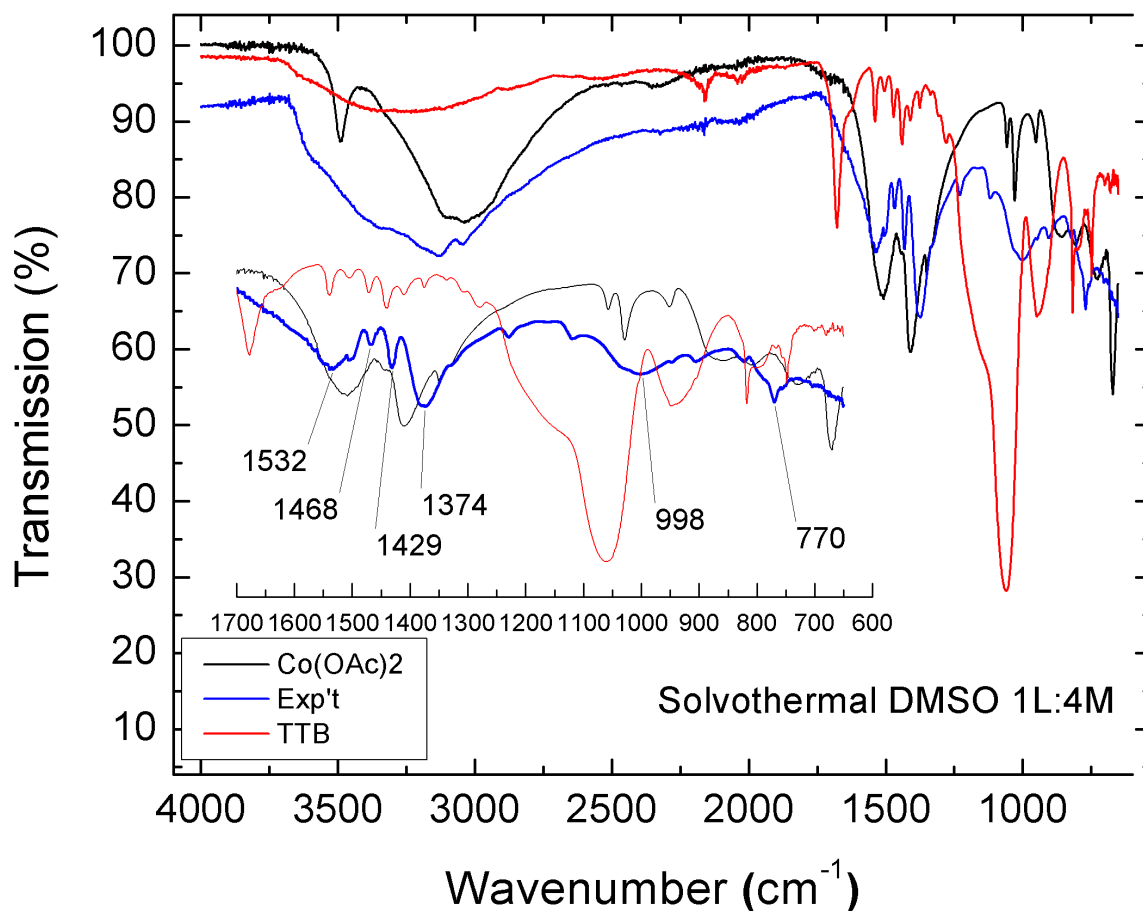


Figure 4.16 Representative infrared spectrum of products formed from solvothormal reaction between deprotonated Compound **4.10** and $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ in DMSO. The inset is a magnification of the carbonyl and fingerprint regions.

In the solvothermally synthesized manganese-derived product, the carboxyl absorptions were more intense and sharply defined, with $\nu(\text{COO})_{\text{asym}}$ at 1579 and $\nu(\text{COO})_{\text{sym}}$ at 1384 cm^{-1} ; interestingly, the C–O absorption at 1050 was broadened and split into two peaks at 1047 and 1017 cm^{-1} , indicating two modes that were weaker than the free ligand C–O vibrations. There were also strong, sharp peaks at 940, 792 and 770 cm^{-1} , the latter two of which were likely O–H bending frequencies from water in the paddlewheel structure. For the cobalt product, the C–O absorption shifted to 998 cm^{-1} and was much weaker than the other absorptions, similar to the microcrystalline manganese product from the

MeCN/H₂O LD reaction. These characteristics suggest that the manganese and cobalt products from solvothermal reactions in DMSO had a paddlewheel clusters.

In solvothermal reactions with mixtures of water and acetonitrile, precipitates were observed to occur during the initial 48 hours. However, over the course of the reactions, microcrystalline formations were observed from solutions of cobalt and manganese (pink and yellow needles, respectively). These crystals were not suitable for X-ray work. The infrared signatures and morphologies of both the kinetic and microcrystalline products were consistent with those obtained from MeCN/H₂O LD reactions.

4.5 Conclusions

The novel tetrapodal linker molecule, tetrathienylbenzene tetracarboxylic acid (Compound **4.10**), was synthesized. With the goal of incorporating star-shaped thiophene-based structures into MOFs, solvothermal and layered solvent diffusion reactions using this ligand and the metal salts Co(OAc)₂·4H₂O, Cu(OAc)₂·H₂O, and Mn(OAc)₂·4H₂O were pursued. This compound was shown to react quickly with metal salts, demonstrated by the immediate formation of precipitates upon mixture with metal salts. The majority of these experiments afforded non-crystalline insoluble products likely due to the low solubility of Compound **4.10**. Most of these products contained a range of carboxylate binding modes, evidenced by carbon-oxygen bond signatures using infrared absorption spectroscopy.

Products that were obtained from mixtures of acetonitrile and water were microcrystalline, and their infrared spectra displayed features which were indicative of network formation: namely, the disappearance of $\nu(\text{C}=\text{O})$ stretches, the appearance of

strong $\nu(\text{COO})$ absorptions indicating bridging or chelating carboxyl groups, and weaker C–O vibrations. These signatures point to paddlewheel structures, similar to those derived from other tetrapodal carboxylate linkers. However, the crystals that were obtained were unsuitable for X-ray work, and the formation of MOFs or MOF-like clusters could not be confirmed.

§ 4.6 Future Work

The first step that must be taken is the preparation of crystalline forms of Compound **4.10** metal complexes to study their structure, namely to confirm the nature of the complexes and whether or not it forms metal-organic frameworks. One of the greatest hindrances to the preparation of MOFs in this work was the insolubility of the kinetic products. As an effort to prepare more soluble tetrathienylbenzene MOF linkers, Compound **4.10** analogues with solubilizing alkyl groups could be prepared. Rather than 2-tributylstannylthiophene, stannylated thiophenes with alkyl chains at the 3- or 4-position (see Figure 4.17) could be used in the initial Stille reaction. These products could then be functionalized with acids using the same route as discussed above. Furthermore, semi- or micro-crystalline products obtained through the work in this chapter should be studied using powder X-ray diffraction (PXRD). PXRD can elucidate information about crystalline products such as lattice parameters, different phases, as well as a unit cell and possible determination of crystal structure with adequate data.

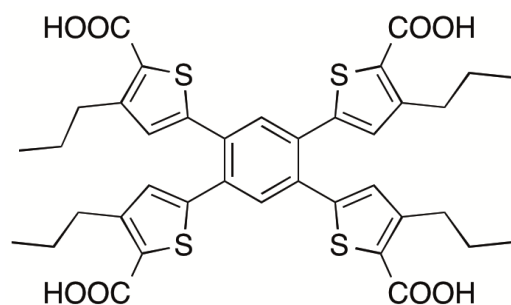


Figure 4.17 Proposed Compound **4.10** analogue, Compound **4.14** with additional solubility provided by alkyl chains at the 3-position.

Among the promising applications of MOFs are those of functional frameworks for catalysis or selective gas adsorption and purifications. In Chapter 3, tetrathienylpyridines were prepared in the same manner as tetrathienylbenzenes. Unlike the benzene-based linker, a tetrathienylpyridine linker (Compound **4.15**) would also contain a central coordination site (Figure 4.18). Aside from the carboxylate group, pyridine is the most common MOF donor moiety. The addition of a coordination pocket at this central position may also give rise to new topologies, although these are difficult to predict. Additionally, thienylpyridine has been shown to behave as a bidentate ligand towards copper.⁵⁰ While sulfur in thiophene is a weak donor, inclusion of this binding pocket in a MOF could prove valuable to applications in heavy metal separations using porous networks.

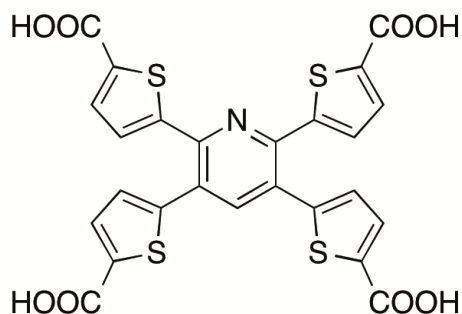


Figure 4.18 Proposed tetrapodal MOF linker, Compound **4.15**.

Carboxyl-functionalized tetrathienylpyridines may be prepared using the same pathway as the work explored in this chapter, the four-fold Stille coupling. Additionally, it is expected that tetracarboxyl-tetrathienylpyridine (**TTP-COOH**) would provide enhanced solubility of the pure ligand relative to its benzene counterpart. This prediction is based on the presence of a dipole moment in thienylpyridines, which would introduce the necessity for dipole ordering to minimize the lattice energy in the solid state. Increasing the solubility the ligand may combat its removal from the reaction through nucleation by the kinetic products, ensuring they are able to equilibrate and exchange pieces of complexes to contribute to the formation of crystalline products.

Among of the most widely cited and perhaps industrially important applications of MOFs are the high uptake and storage of hydrogen and methane, and the selective sequestration carbon dioxide, respectively.^{9,13} Following the successful preparation of Compound **4.10** and **TTP-COOH** MOFs, these should be evaluated for these applications. The pores of the frameworks must be evacuated, with the mass loss by solvent desorption monitored by thermogravimetric analysis. As these MOFs would be based on tetrapodal linkers, they should display robust structures that resist collapse.²² However, it must be determined whether the solvents used for their preparation, such as H₂O, play a structural role. MOFs based on bridging carboxylates are often supported by structural water molecules in axial positions.^{22,23} Non-essential solvents must be removed to the furthest extent possible using either supercritical CO₂ or solvent exchange and high vacuum at elevated temperature to activate their internal surface area.¹² Gas adsorption may then be evaluated.

MOFs based on Compound **4.10** and **TTP-COOH** could display interesting luminescent and electronic properties when prepared as thin films due to their incorporation of thiophene, which is widely used in organic semiconductors applications.¹⁷ The preparation of MOF thin films would involve incubating a substrate in an “aged” solvothermal MOF synthesis solution (in other words, the mother liquor from the reaction), provided the substrate has a suitably functionalized surface, such as carboxylic acid-terminated self-assembled monolayers as in Hermes *et al.*⁵¹

§ 4.7 Experimental Details

General Procedures and Starting Materials. The reagents 2,3,4,5-tetrabromobenzene, isobutyl chloroformate, *n*-butyl lithium (10 M), potassium hydroxide, ammonium chloride, palladium chloride and triphenylphosphine were obtained commercially and used as received. 2-tributylstannylthiophene was prepared as outlined in the literature.^{52,53} All solvents were of at least reagent grade; tetrahydrofuran (THF) was dried by distillation from sodium and dimethylformamide (DMF) was dried over 4Å molecular sieves. Lithiation and Stille reactions were performed under an atmosphere of dry nitrogen. Melting points are uncorrected. ¹H and ¹³C NMR spectra were run in CDCl₃ or DMSO-d₆ solutions at r.t. on a Bruker Avance 400 MHz spectrometer. Infrared spectra were recorded on a Cary 630 FTIR spectrometer using Attenuated Total Reflection.

Preparation of 2-[2,4,5-Tris(2-thienyl)phenyl]thiophene (Compound 4.11): Synthesized according to procedure of Brusso *et al.*³⁸ Compound **4.11** was characterized by ¹H NMR spectroscopy, which was consistent with literature data. ¹H NMR (CDCl₃, r.t., 400 MHz) δ = 7.65 (2H, s), 7.29 (4H, dd, 5 Hz, 1.3 Hz), 6.96 (8H, m) ppm.

Preparation of Tetraisobutyl-5,5',5'',5'''-(Benzene-1,2,4,5-tetrayl)tetrakis(thiophene-2-carboxylate) (Compound 4.13): Synthesized according to procedure of Fu *et al.*³⁰ Compound **4.13** was characterized by ¹H NMR and ¹³C spectroscopy, which was consistent with literature data. ¹H NMR (CDCl₃, r.t., 400 MHz) δ = 7.93 (1H, s) 7.06 (2H, s) 7.04 (2H, s) 7.03 (2H, d, 3.3 Hz) 6.88 (2H, d, 3.3 Hz) 6.62 (2H, d, 3.3 Hz) 6.55 (2H, d, 3.3 Hz) 2.79 (4H, t, 7.5 Hz) 2.75 (4H, t, 7.8 Hz) 1.77–1.64 (8H, m) 1.50–1.40 (8H, m) 1.40–1.32 (16H, m) 0.95 (6H, t, 6.8 Hz) 0.94 (6H, t, 6.8 Hz) ppm. ¹³C NMR (CDCl₃, r.t., 100 MHz) δ = 146.0, 145.9, 141.3, 140.6, 137.9, 135.5, 135.3, 134.8, 133.0, 132.2, 124.8, 124.7, 124.5, 124.5, 124.1, 119.4, 117.5, 117.4, 31.7, 31.7, 31.5, 31.4, 30.4, 30.3, 22.7, 14.2 ppm.

Preparation of 5,5',5'',5'''-(Benzene-1,2,4,5-tetrayl)tetrakis(thiophene-2-carboxylic acid) (Compound 4.10): Compound **4.13** (1.18 g, 1.46 mmol), and KOH (4.88 g, 87.0 mmol), were refluxed in 10% H₂O in ethanol for 24 hours. The off-white precipitate was filtered off and dissolved in 30 mL H₂O. 1M H₂SO₄ was added until the mixture reached pH < 1. The solid blue-green product was collected by suction filtration and washed with ice-cold methanol (0.626 g, 1.08 mmol, 74%). ¹H NMR (DMSO d₆, r.t., 400 MHz) δ = 7.79 (2H, s) 7.67 (4H, d, 3.7 Hz) 7.22 (4H, d, 3.7 Hz). ¹³C NMR (DMSO d₆, r.t., 100 MHz) δ = 163.2, 146.5, 136.3, 133.7, 133.3, 129.8. IR: ν_{max} = 3350 w (br), 1677 m, 1539 w, 1472 w, 1440 w, 1408 w, 1279 w, 1162 m (sh), 1058 vs (br), 942 m (br), 817 (m) cm⁻¹.

General Procedure for Layer Diffusion Reactions: A 1.00 mM solution of a metal acetate salt (5 mL) was layered carefully on top of a 0.25 mM solution of Compound **4.10** (5 mL, 52.8 mg). The reaction was allowed to stand for 48 hours, and the solid

products were collected by suction filtration and washed with acetone.

General Procedure for Solvothermal Reactions: A 1.00 mM solution of a metal acetate salt (5 mL) was mixed with a 0.25 mM solution of Compound **4.10** (5 mL, 52.8 mg). The combined solutions were filtered to remove precipitate until they remained clear. Solutions were transferred to a 50 mL glass pressure vessel heated to 90 °C for 48 hours, Reactions were then cooled at a rate of approximately 1 °C min⁻¹. Products were isolated by filtration and washing with acetone.

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Chapter 5 – Design of Novel Thiophene-Based Ligands through Schiff Base Formation

§ 5.1 Introduction

Interest in new complexes whose redox reactions can be harnessed for applications such as catalysis, photochemistry and dye sensitized solar cells has sparked recent studies of thiophene-containing ligands.¹⁻⁴ Oligothiophenes and polythiophenes are used widely in organic semiconductors due to their charge transfer capabilities, their stability, and their larger, more polarizable p-orbitals (with respect to carbon, nitrogen and oxygen), which promote intermolecular interactions such as S $\cdots$ S and S $\cdots$ π contacts. Thiophenes in metal complexes are usually pendant groups that do not interact directly with metal centres;^{2,3} however, combined in chelating systems with strong donors (such as nitrogen and oxygen), ligands with sulfur-coordinated thiophene can complex in a stable manner with metals. The interactions between metals and thienyl sulfurs are examined in Section 5.2, and ligands containing thiophenes chelating with supporting donors are presented in Section 5.3. The goals of this Chapter are outlined in Section 5.4. Finally, the exploratory work involving the preparation of novel mixed donor thiophene-based ligands, and the design and tuning strategies for expansion of the scope of the ligands herein, are discussed in Section 5.5.

§ 5.2 Thiophene Sulfur as a Donor

Some of the earliest examples of metal coordination by thiophene were in the petroleum refining industry: sulfur-containing compounds (including thiols, thiophenes, sulfides and disulfides) poison the noble metal catalysts used in octane upgrade reactions, and thus are removed using hydrodesulfurization (HDS) catalysts.⁵ The most common of these

sulfurous compounds are thiophenes, benzothiophenes and dibenzothiophenes.⁶ In HDS catalysts, metal disulfides (traditionally molybdenum and nickel disulfides) with coordinatively unsaturated sites bind compounds with thiophene moieties, which then undergo both C–S bond cleavage (to form thiametallacycles such as the complexes shown in Figure 5.1) and C=C bond hydrogenation.⁷ Other relatively electron-rich metals also tend to insert into the C–S bond during reaction with thiophenes (*vide infra*).⁸ Despite its ability to coordinate to noble metal catalysts, thiophene is likely the least-used heterocyclic ligand moiety; this can be attributed to the instability of bonds between the thiophene sulfur (henceforth referred to as S_{Th}) and metal centres, compared to heterocycles with harder donors such as the nitrogen in pyridine. In other words, direct η^1 -bonds through S_{Th} are too weak for the isolation and study of coordination complexes in the absence of cooperative binding. However, thiophenes can coordinate in η^2 -, η^4 - and η^5 -modes.⁸

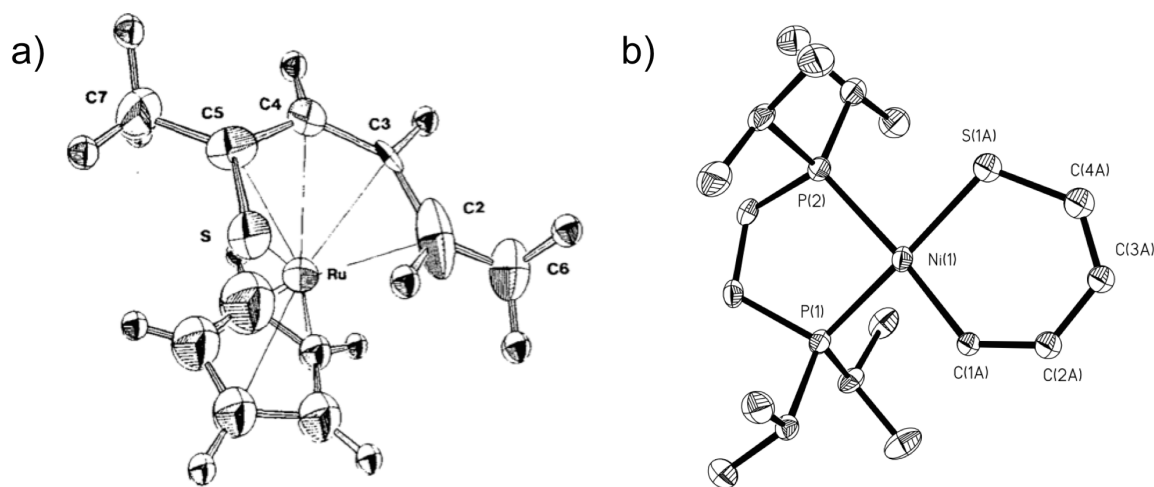


Figure 5.1 ORTEP drawings of a) Ru^{II}(Cp)-bound 2,5-dimethylthiophene cleaved by hydride (from ref. 9, © Elsevier-Sequoia, 1993), and b) a Ni^{II}(dippe) thiametallacycle (from ref. 10, © Elsevier B.V., 2005).

In the thiophene heterocycle, the sulfur is sp^2 -hybridized with two lone pairs, one of which is involved in the π -network of the aromatic sextet.¹¹ When thiophene $\eta^1(S_{Th})$ -coordination is observed, the bonding geometry at S_{Th} is pyramidal,¹²⁻¹⁴ so the vector of $M \cdots S_{Th}$ bonds lies at an angle (approximately 60°) to the plane of the heterocycle, as shown in Figure 5.2 b. This suggests that the sulfur has transitioned from sp^2 - to sp^3 -hybridization, while disrupting the participation of the sulfur lone pair in the aromaticity of the ring.⁸

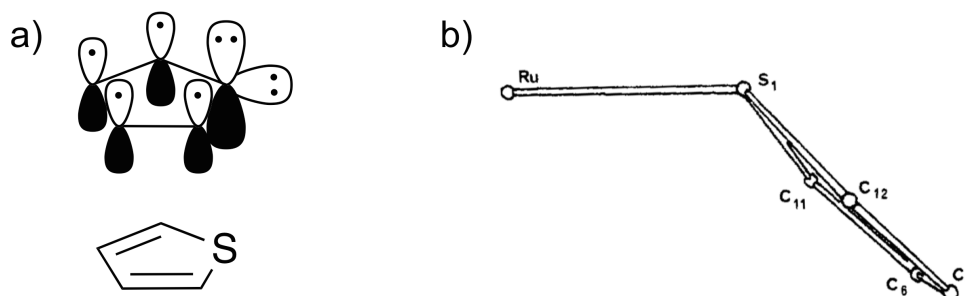


Figure 5.2 a) Cartoon depiction of the electronic structure of thiophene (adapted from ref. 11, © Taylor and Francis Group, LLC 2013). b) Crystallographic view of a $\eta^1(S_{Th})$ Ru $\cdots$ thiophene bond (from ref. 5, © American Chemical Society 1984).

§ 5.3 Thiophene-based Chelating Ligands

From the results of both experimental work¹⁰ and computational studies,^{15,16} metals such as platinum, ruthenium and nickel were as likely to cleave isolated thiophene as they were to coordinate in $\eta^1(S)$ fashion. However, a number of compounds with stable $\eta^1(S_{Th})$ coordination have been isolated by using a chelating strategy with other donors (such as nitrogen) to stabilize the metal $\cdots S_{Th}$ interaction;¹⁷ three instances of such bidentate ligands are shown in Figure 5.3. The 2-(2'-thienyl)pyridine (**thpy**) motif, for example, has been used to synthesize transition metals complexes with the ligand displaying (S,N)-coordination with Cu^{II} ,¹⁷ as well as Ir^I (Compound **5.1** and Compound

5.2, Figure 5.3).¹⁸ In these complexes, pyridine (a π -accepting donor moiety) relieves electron density from metal centres,¹⁹ thereby disfavoring insertion into the C–S bond.⁸ Due to the tetrahedral nature of the η^1 -bonded S_{Th}, these **thpy** ligands become twisted when complexed with metals, adopting dihedral angles from 25–35°. Bucknor and co-workers prepared dibenzothiophene (**DBT**) functionalized with diphenylphosphine, which is also a π -acceptor, and prepared a Ru^{II} complex that is η^1 (S_{DBT})-bonded (Compound **5.3**, Figure 5.3).⁵ Rather than Lewis basicity, the important characteristic for η^1 (S)-supporting donors seems to be their π -accepting capacity, especially in the case of Compound **5.3** where the triphenylphosphine ligands are good π -acceptors.

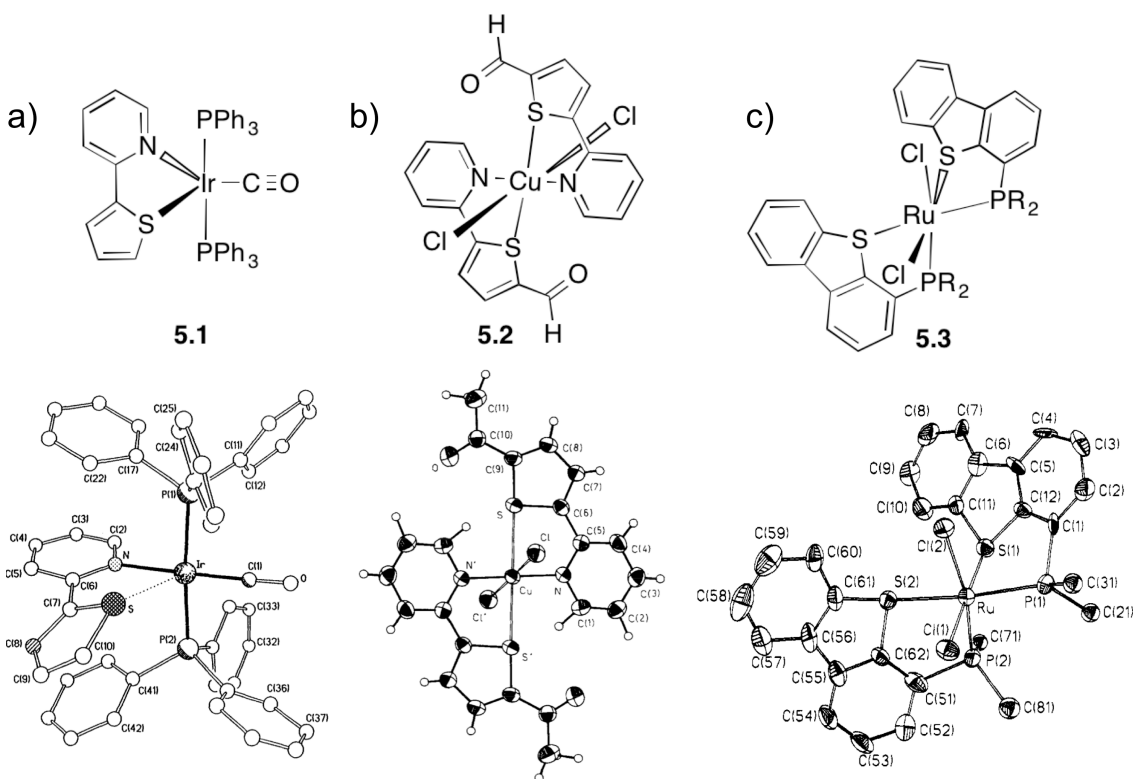


Figure 5.3 Crystal structures of coordination complexes containing bidentate η^1 (S_{Th})-supporting ligands: a) 2-(2'-thienyl)pyridine complexed with Ir^I(CO)(PPh₃)₂ (from ref. ¹⁸, © Elsevier-Sequoia, 1994); b) (5-pyridyl)-2-thiophenecarboxaldehyde complexed with Cu^{II}Cl₂ (from ref. ³⁷, © Elsevier-Sequoia, 1993); c) (4-diphenylphosphine)dibenzothiophene complexed with Ru^{II}Cl₂ (from ref. ⁵, © American Chemical Society, 1984).

Unlike the complexes in Figure 5.3, when thiophene-containing ligands are complexed with heavier or more highly charged transition metals (such as Ir^{III}), the thiophene ring has a propensity to cyclometalate – in other words, to become deprotonated and coordinate η^1 through C₃ rather than sulfur. This flips the thiophene ring, as demonstrated by Compound **5.4** and Compound **5.5** in Figure 5.4. Cyclometalated compounds with Ru^{II} find applications in dye-sensitized solar cells,^{3,20,21} and cyclometalated Ir^{III} complexes have been explored extensively for phosphorescent OLED emitters.²²

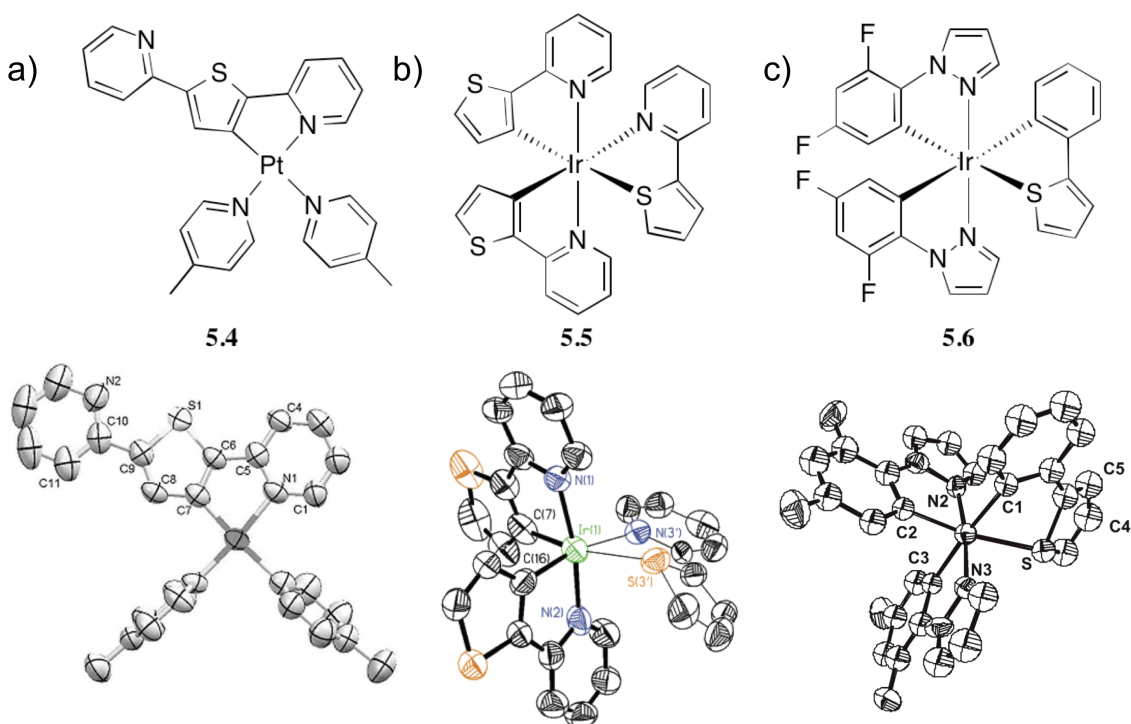


Figure 5.4 Crystal structures of thiophene-containing heavy metal complexes: a) 2,5-bis(2-pyridyl)thiophene complexed with Pt^{II}(4-methylpyridine)₂ (from ref. 18, © Elsevier-Sequoia, 1994). b) 2-(2-pyridyl)thiophene complexed with Ir^{III} (from ref. 37, © Elsevier-Sequoia, 1993). c) 2-(phenyl)thiophene complexed with Ir^{III}(dppz)₂ (from ref. 5, © American Chemical Society, 1984).

Levine and coworkers synthesized 2,5-bis(2-pyridyl)thiophene (**bpth**), and prepared coordination complexes with Pt^{II}(4-methylpyridine)₂.⁴ Where the thiophene-pyridine ligands shown earlier were (S,N)-coordinated, complexing **bpth** with Pt^{II} resulted in

cyclometalated compounds (Compound **5.4**, Figure 5.4). McGee and Mann prepared $\text{Ir}^{\text{III}}(\text{thpy})_3$ and found that, while two of the **thpy** ligands were (C,N)-cyclometalated, the third was (S,N)-coordinated (Compound **5.5**, Figure 5.4);²³ however, coordinating solvents displaced the $\eta^1(\text{S})$ -bonded thiophene, indicating that the $\text{S}_{\text{Th}} \cdots \text{M}$ bond was still relatively weak. Ren and coworkers prepared Ir^{III} complexes with either two 2-(phenyl)pyridine ligands or two 1-(2,4-difluorophenyl)pyrazole (**dppz**) ligands (Compound **5.6**, Figure 5.4), which were both (C,N)-cyclometalated, supporting a third bidentate ligand, 2-(phenyl)thiophene (**phth**); unlike the **thpy** complexes, these were stably $\eta^1(\text{S})$ -coordinated.²⁴ Cyclometalated carbon is a strong σ -donor, while also being a good π -acceptor and exerting a strong ligand field; π -accepting character in particular seems to be critical for stable $\eta^1(\text{S}_{\text{Th}})$ -coordination.²⁴ Conversely, pyridine does not appear to provide sufficient stabilization for $\eta^1(\text{S}_{\text{Th}})$ -coordination with highly charged heavy transition metals.

§ 5.4 Tridentate Ligands based on 2-(azomethine)thiophene

While a number of bidentate ligands containing cyclometalated and S-bound thiophenes have been studied, tridentate ligands have greater binding cooperativity than bidentates,¹⁹ which could promote the stability of compounds. One example of such a tridentate thiophene-containing ligand is (O,S,O)-coordinating 2,5-bis(2-bis(4,6-*tert*-butyl)phenol)thiophene (**bpt**) shown in Figure 5.5; catalytic activity for the polymerization of propylene was found for Zr^{II} and Ti^{II} **bpt** complexes.²⁵ Interestingly, the tetrahedral sulfur environment of the thiophene in this complex is consistent with the $\text{S}_{\text{Th}} \cdots \text{metal}$ interactions seen in previously discussed compounds.

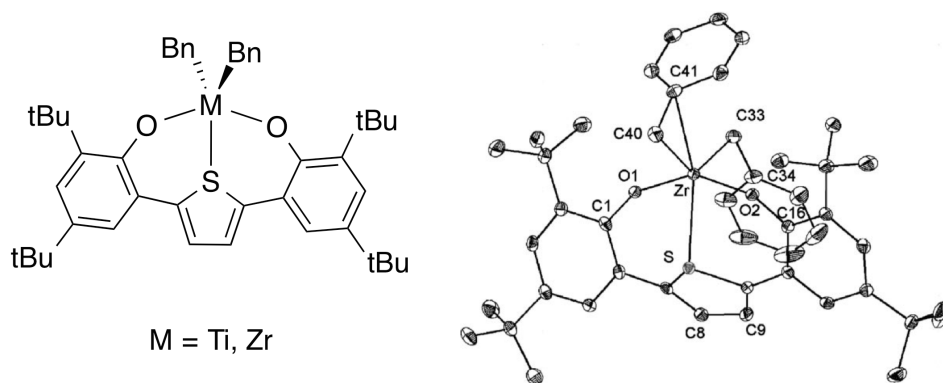


Figure 5.5 Chemdraw and crystal structure of bis(2,5-bis(2,4-*tert*-butyl)phenolate)thiophene coordination complex with $\text{Zr}^{\text{II}}(\text{Bn})_2$ (Bn = benzyl) (ref. 26, © American Chemical Society, 2008).

Beginning from the bidentate ligands **phth** and **thpy**, tridentate ligands could be prepared by the inclusion of an additional aromatic donor such as pyridine; on the other hand, an imine could be introduced to the system, acting as a hard nitrogen donor. Unlike pyridines, imines lack the steric bulk and rigidity of an aromatic ring. However, the imine carbon is sp^2 hybridized, and therefore may remain planar with delocalized π -systems. Imines are formed by the reaction of a primary amine and an aldehyde. *N*-alkylated or *N*-arylated imines are referred to as Schiff bases or azomethines. Important to the coordination of thiophenes, imines act as π -acceptors, and may be able to stabilize $\eta^1(\text{S})$ metal coordination like other π -accepting supporting donors.^{27,28}

A handful of 2-(azomethine)thiophene (**amth**) ligands have been investigated for coordinative behaviour with transition metals, including Ni^{II} ,^{1,29-31} Co^{II} ,²⁹⁻³² Mn^{II} ,^{29,32} Fe^{II} ,³⁰ Zn^{II} ,^{30,33} Cd^{II} ,³⁰ Ag^{I} ,³⁴ Cu^{I} ,³⁵ Cu^{II} ,²⁹⁻³² Pd^{II} ,³⁶ Pt^{II} ,³¹ Pt^{IV} ,³⁶ and Au^{III} .³⁶ Thus far, complexes based on **amth** have commonly been tested for antibacterial activity; however, the bis(2,5-azomethine)thiophene prepared by Pedras and coworkers, which is presented in Figure 5.6, was functionalized with pendant pyrene and naphthalene chromophores.

These compounds displayed enhanced fluorescence when complexed (in an N,S,N-fashion) with nickel and palladium, relative to the uncoordinated ligand, which could be harnessed for metal sensing applications.^{1,2}

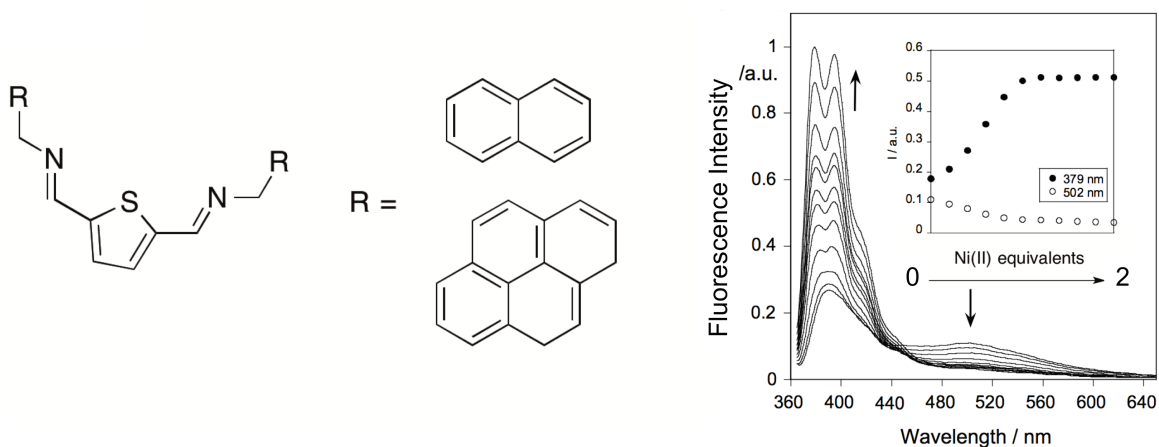


Figure 5.6 bis(2,5-azomethine)thiophenes *N*-functionalized with chromophores, with fluorescence spectra of pyrene-containing ligand complexing with Ni^{II} shown at right; the inset shows that fluorescence at 379 and 502 nm stabilized at one equivalent of metal (adapted from ref. 1, © Elsevier B.V., 2007).

Da Silva *et al.*,³³ and Patra and Goldberg,³⁵ prepared coordination compounds with *N,N'*-bis(thiophen-2-ylmethylene)ethane-1,2-diamine (**enth**), which contains two (azomethine)thiophene moieties (Compound **5.7**, Figure 5.7). When complexed with d¹⁰ transition metals (Cu^I, Zn^{II} and Ag^I), **enth** formed both 1-D coordination polymers as well as discrete M(L)₂ and M(L)X₂ complexes. From these structures, it is apparent that the imine groups each remain planar with their respective thiophenes, but a twist exists in the ethylene bridge. Notably, these complexes were found to be stable to atmospheric conditions as both a solid and in solution.

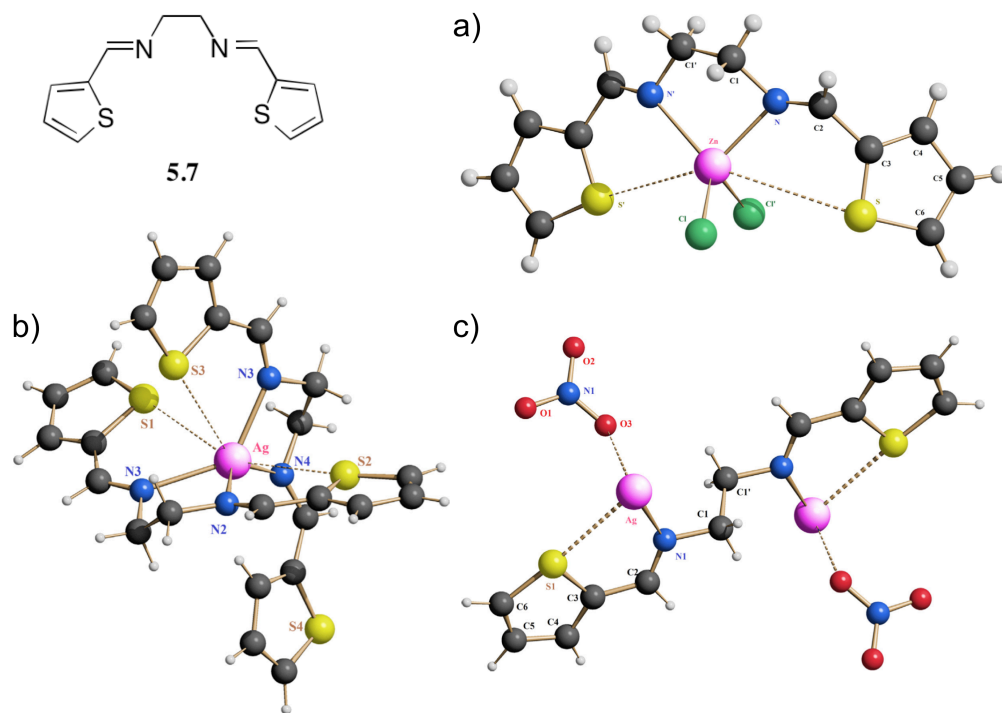
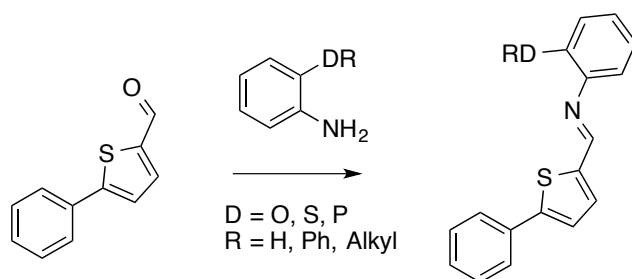


Figure 5.7 a) Chemdraw and b–d) crystal structures of *N,N'*-bis(thiophen-2-ylmethylene)ethane-1,2-diamine complexes: b) a monomeric complex with Zn^{II}Cl₂ b) a monomeric complex with Ag^I, and c) a 1D coordination polymer with Ag^I (from ref. 33, © Elsevier-Sequoia, 2014).

Considering the versatile donor behaviour of $\eta^1(\text{S})$ -coordinated thiophene in complexes, novel thiophene-based ligands have a number of potential applications, from antibacterial agents to optically functional materials (such as photosensitizers) to catalysts.^{1,2,26,33} For example, 2-(aryl)thiophenes such as **thpy** and **phth** have been explored, as have 2-(azomethine)thiophenes (**amth**), but these moieties have heretofore not been used in conjunction to prepare molecules such as 2-(phenyl)-5-(azomethine)thiophene, (henceforth referred to as **phamth**, shown in Scheme 5.1). Due to their π -accepting nature, both the azomethine group and the phenyl group are expected to favor $\eta^1(\text{S})$ -coordination of the thiophene ring, particularly where the phenyl ring is cyclometalated with heavy metals such as iridium and platinum.



Scheme 5.1 Synthetic strategy to access functionalized **phamth** ligands *via* Schiff base formation.

On the other hand, cyclometalation of the **phamth** may be difficult, as it tends to require strong initial coordination through another donor,³⁷ in this case the S_{Th}. Should cyclometalation prove troublesome, a third donor could be conveniently introduced during the formation of the azomethine group (see Scheme 5.1) to afford the desired tridentate stability. Notable examples in the literature informed the choice of the third donor for proof-of-concept molecules in the synthetic work of this chapter: Bercaw's group used bis(2,5-bis(2,4-*tert*-butyl)phenolate)thiophene in early transition metal complexes (*vide supra*);²⁶ Tang *et al* prepared 8-hydroxyquinoline aluminum (Alq₃), which is a benchmark electroluminescent emitter molecule for OLEDs (Compound **5.8**, Figure 5.8);³⁸ *N,N'*-bis(salicylidene)-1,2-phenylene-diamine (**salphen**) is a diimine diphenolate ligand,³⁹ and Kui and co-workers prepared a tetradentate, cyclometalating ligand with a phenolate donor, both of which have been applied as Pt^{II}-based OLED emitters (Compound **5.9** and Compound **5.10** in Figure 5.8, respectively) and showed high temperature stability (>400 °C).^{40,41} Therefore, the phenolate group is expected to promote stable, versatile coordination behaviour for both early and late transition metal complexes when combined with the **amth** moiety of the molecules herein.

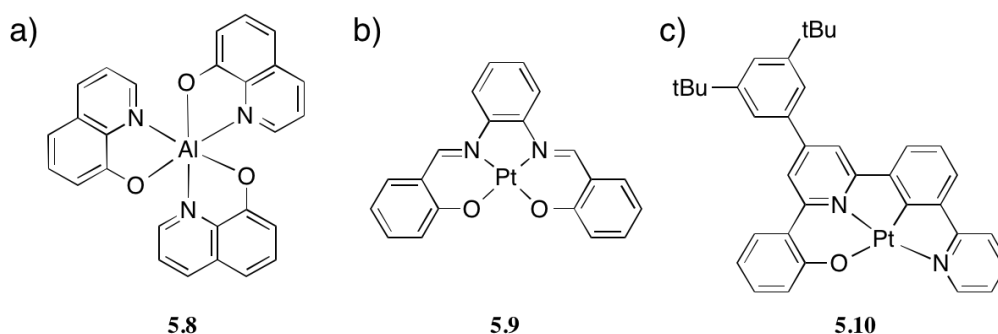


Figure 5.8 Phenol-containing electroluminescent emitters a) Alq₃, b) Pt(salphen), and c) [Pt(2-(4-(3,5-di-tert-butylphenyl)-6-(3-(pyridin-2-yl)phenyl)-pyridin-2-yl)phenolate)].

The **phamth** moiety may be used to prepare novel coordination complexes that could shed light on the behaviour of azomethine-supported, $\eta^1(\text{S})$ -coordinated thiophenes with cyclometalated aryl rings, as well as find applications such as OLED emitters, similar to the literature examples outlined above. However, the central theme of this thesis is star-shaped molecules, which display distinct electronic properties compared to linear organic semiconductor molecules. Incorporating the **amth** motif in star-shaped molecules could enable the binding of multiple transition metal nuclei, and therefore the study of metal-metal interactions (such as magnetic super-exchange) through the arms of the system;⁴² they may also promote the formation of metal-organic structures that self-assemble through $\pi \cdots \pi$ interactions and have different properties than related linear ligands.⁴³ 1,2,4,5-tetra(2-thienyl)benzene (**TTB**, Compound **5.11**, see Figure 5.9) is a star shaped core based on thiophene that is already well characterized; furthermore, functionalized **TTB** would be a four-fold scale-up of the tridentate ligand moiety described above, making it an ideal starting point for the investigation into star-shaped systems once the coordinative abilities of the **phamth** moiety are determined.

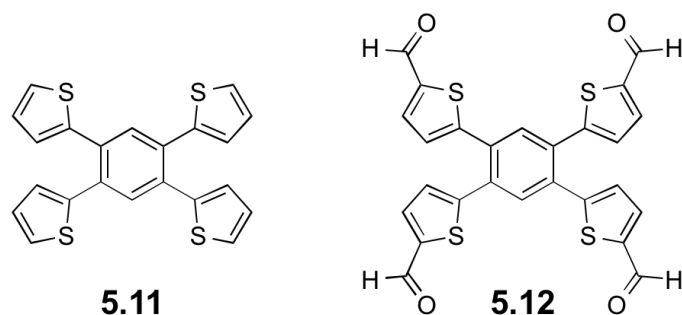
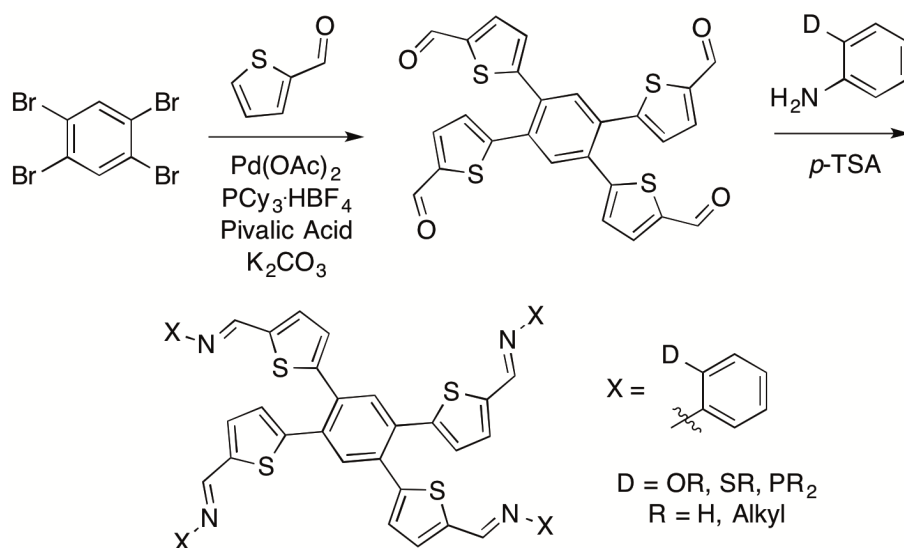


Figure 5.9 Star-shaped molecules **TTB** (Compound **5.11**), and its tetra-(5-formyl)2-thiophene)-functionalized analogue, **TFTTB** (Compound **5.12**).

To achieve a star-shaped ligand with four (azomethine)thiophene groups, an aldehyde precursor is required. In Chapter 4, the formyl-functionalized **TTB** derivative, Compound **5.12**, was prepared using the four-fold Stille reaction to generate **TTB**, followed by four-fold lithiation of the free α -positions and formylation using DMF. However, the formylation proved to be difficult to complete with all four arms in adequate yields. Instead, both Compound **5.12** and smaller, linear molecules containing the **phamth** moiety can be prepared by using the direct C–H activated (hetero)arylation (DHA) reaction between 2-thiophenecarboxaldehyde and 1,2,4,5-tetrabromobenzene, or bromobenzene, respectively. As shown in Schemes 5.1 and 5.2, the azomethine may then be generated by condensation with a chosen amine reagent.



Scheme 5.2 Synthetic strategy to prepare functionalized **TTB**-based star-shaped ligands.

§ 5.5 Chapter Goals and Outline

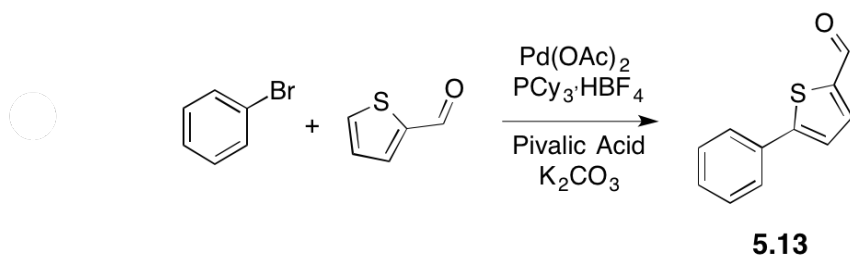
The first goal of this chapter was to prepare tridentate ligands utilizing $\eta^1(\text{S})$ -coordinated thiophene, a Schiff base, and a third donor atom (introduced either before or during Schiff base formation). The second goal of this chapter was preparation of functionalized tetrathienylbenzene compounds, in order to afford star-shaped molecules with the **amth** moiety, as shown in Scheme 5.2. It was expected that these molecules could be accessed *via* the Schiff base synthetic strategy; overall, this chapter comprises a discussion of the design strategy and synthetic work towards the preparation of these compounds.

§ 5.6 Results and Discussion

§ 5.6.1 Preparing the phamth Precursors Using the DHA Reaction

2-(phenyl)-5-thiophenecarboxaldehyde (henceforth referred to as Compound **5.13**) was the precursor that would allow access to the **phamth** moiety. In Chapters 3 and 4, C–C bond formation was accomplished with the Stille reaction; however, the DHA reaction (see Section 2.1.3) was chosen for this chapter. Direct heteroarylation has been used to

couple electron-deficient thiophene reagents with halogenated aryl rings, and can also perform multiple couplings, as indicated in Scheme 5.2. Furthermore, this route has the advantage of avoiding the preparation and use of the organotin reagents that are necessary for the Stille reaction. The synthesis of Compound **5.13** is presented in Scheme 5.3.



Scheme 5.3 Direct C-H activated heteroarylation to form 2-phenyl-5-thiophenecarboxaldehyde (**5.13**) from bromobenzene and 2-thiophenecarboxaldehyde.

High-boiling, polar solvents were needed as the reactions were to be stirred at 110 °C for 24 hours under N₂. Liegault *et al* showed that conversion results for DHA varied by the reaction solvent, depending on the reagents being coupled.⁴⁴ Reactions were performed in *N,N'*-dimethylacetamide (DMA), toluene, and *N*-methylpyrrolidinone (NMP). Neat bromobenzene and an excess (1.5 equivalents) of 2-thiophenecarboxaldehyde were measured into vials and sparged with an N₂ stream for 15 minutes. Pivalic acid, K₂CO₃, palladium (II) acetate and PCy₃·HBF₄ (30%, 1.5 equivalents, 5% and 10% respectively, as per literature procedure) were evacuated and back-filled with N₂, and then the oil reagents and degassed solvent were added by syringe. The reactions were then heated.

The reaction mixtures were initially translucent yellow-orange, but turned opaque within an hour of reaching reaction temperature. The reactions were allowed to proceed for 24 hours, whence they had become brown; they were then cooled and diluted water, which

separated the layers into dark brown on top and opaque white below. CH_2Cl_2 was then added, which pulled the brown-coloured products to the bottom of the solution. In a separatory funnel, the aqueous phase was extracted with CH_2Cl_2 ; the organic extracts were washed with water, then brine and finally dried with MgSO_4 before filtration and concentration *in vacuo*. The crude products were obtained as brown oil. Excess 2-thiophenecarboxaldehyde, palladium catalyst and unreacted bromobenzene were detected by TLC and ^1H NMR; attempts were made to remove these from the concentrated products by Kugelrohr apparatus at $110\text{ }^\circ\text{C}$ and 0.7 torr. Analysis of the remaining residue still indicated catalyst and bromobenzene, but the 2-thiophenecarboxaldehyde had been completely removed. A short silica plug eluted with 4:1 hexanes-ethyl acetate retained the dark brown material, and the filtrate was concentrated to afford an orange solid. The appearance and NMR signatures for the orange solid matched those in the literature for Compound **5.13** (shown in Figure 5.10),⁴⁵ however the highest isolated yield was significantly lower (28%) than what was reported in the literature (58%).⁴⁴ Of the three reaction solvents, DMA furnished the highest crude yields (54%) by a factor of two; therefore optimization attempts used only DMA.

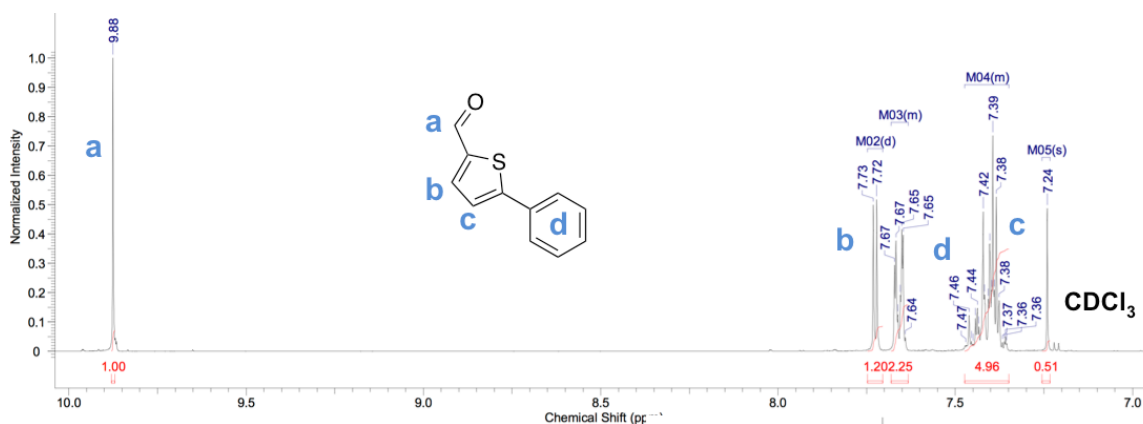


Figure 5.10 ^1H NMR spectrum of Compound **5.13** prepared from bromobenzene and 2-thiophenecarboxaldehyde using direct C-H activated heteroarylation.

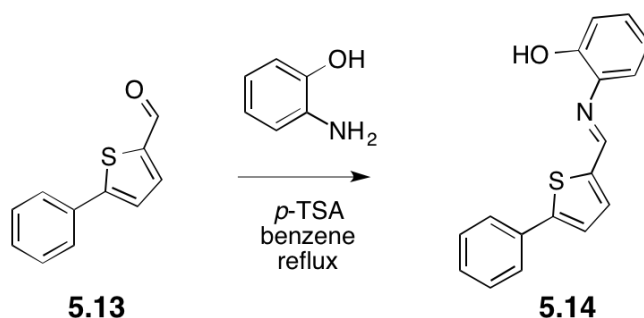
The excess of 2-thiophenecarboxaldehyde was increased to 2.5 equivalents, which improved crude yields to approximately 85% and resolved the incomplete conversion of bromobenzene. However, the purified yields appeared to be reduced by the distillation of 2-thiophenecarboxaldehyde; crystalline solid of Compound **5.13** was observed in the Kugelrohr collection bulbs, therefore an alternate purification procedure was devised.

Compound **5.13** was found to have very low solubility in hexanes at room temperature, while the thiophene reagent was miscible. The crude reaction mixture was therefore extracted with hexanes instead of CH_2Cl_2 . The extracts were concentrated to orange oil, which was similar in appearance to the crude products of the earlier procedure; to recover any incidentally extracted portion of Compound **5.13**, this was distilled. After removing 2-thiophenecarboxaldehyde (at 100 °C *cf.* 110 °C previously used), a brown residue remained. As Compound **5.13** was shown to sublime in previous trials, this residue was heated at 118 °C, which afforded a small amount of crystalline product – 16% of the theoretical yield. Lastly, the aqueous phase and solids filtered from the initial hexanes workup were combined and extracted with CH_2Cl_2 . The extracts were concentrated to a light brown-gray solid, which was passed through a silica plug with 4:1 hexanes-ethyl acetate to afford a gray solid; this material was identified by ^1H NMR to be Compound **5.13**, in 54% of the theoretical yield. The combined yield for this procedure was therefore 70%.

§ 5.6.2 Preparation of 2-(phenyl)-5-(azomethine)thiophene Schiff Bases

With the aldehyde reagent in hand, the formation of the Schiff base ligand could be pursued. A primary amine would act as a nucleophile on the carbonyl carbon. The removal of the carbonyl oxygen (as H_2O) can be facilitated by a catalytic source of H^+

such as *p*-toluene sulfonic acid (*p*-TSA). Furthermore, removing water from the reaction equilibrium will drive it towards the products, which can be accomplished by azeotropic distillation of water from the refluxing solvent with a Dean-Stark apparatus. 5-(phenyl)-2((*N*-(2-phenol)azomethinyl)thiophene (henceforth referred to as Compound **5.14**), a compound with both the **phamth** moiety and a phenol oxygen as the third donor, was thus prepared as shown in Scheme 5.4.



Scheme 5.4 Imine condensation synthesis of 5-(phenyl)-2((*N*-(2-phenol)azomethinyl)thiophene (Compound **5.14**).

Compound **5.13**, an excess of 2-aminophenol (1.2 equivalents) and a catalytic amount of *p*-TSA were placed in a flask and benzene was added. The solid reagents dissolved immediately, affording a yellow solution; the flask was equipped with a Dean-Stark apparatus and the reaction was heated to reflux, where the solution turned cloudy. As the reaction progressed, the mixture became opaque orange. After 24 hours, the solvent was removed under reduced pressure, leaving an orange solid with a small amount of oily residue remaining. This was passed through a plug of silica eluted with CH₂Cl₂, which retained the excess 2-aminophenol, whereupon Compound **5.14** was obtained as an orange-yellow solid. The ¹H NMR spectrum of this product is presented in Figure 5.11.

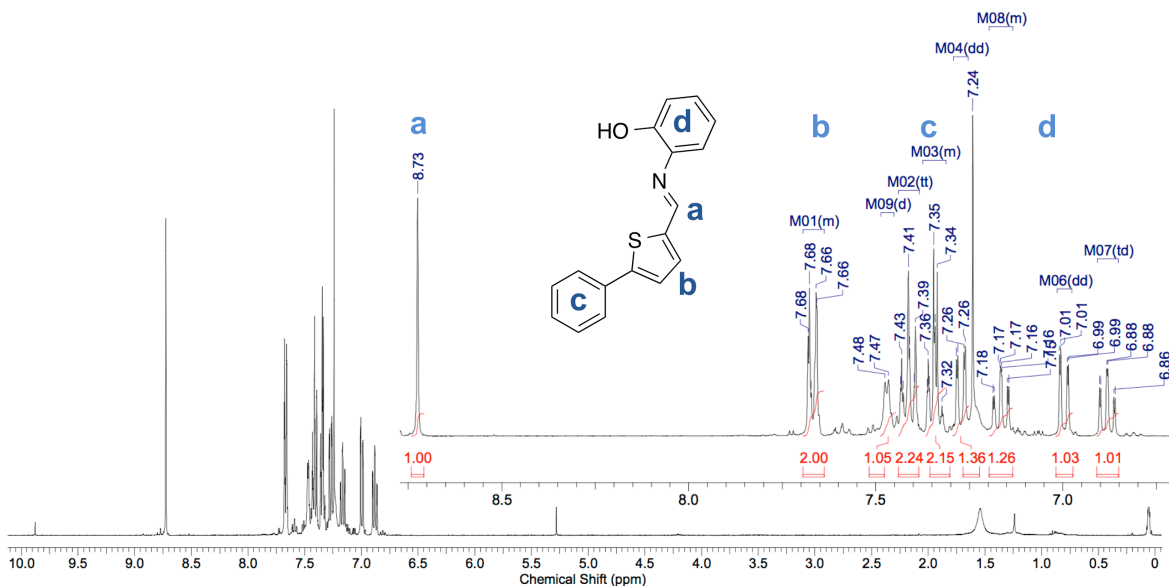


Figure 5.11 ^1H NMR spectrum of Compound **5.14**, with the expanded aromatic region in the inset.

§ 5.6.3 Preparation of tetra-1,2,4,5-(2-(5-(*N*-(2-phenol))azomethinyl)thienyl)benzene

A four-fold DHA reaction between 1,2,4,5-tetrabromobenzene and 2-thiophenecarboxaldehyde could be used to prepare **TFTTB** (Compound **5.12**); condensation with 2-aminophenol would form the Schiff bases at the 5-position of each thiophene arm, providing Compound **5.15** as shown in Scheme 5.2. The initial preparation of Compound **5.12** was tested with three different solvents: DMA, toluene, and NMP. With respect to 1,2,4,5-tetrabromobenzene, the initial catalyst ratio was 7% Pd(PCy₃)₂, with 1.5 equivalents of K₂CO₃ and 30% pivalic acid as per established DHA conditions. TLC analysis indicated that these reactions produced a mixture of compounds; Compound **5.12** was observed in each, as confirmed by comparison with that obtained from the lithiation route of Chapter 4, however no reaction completely consumed the starting material. At the conclusion of each reaction, the mixtures were

cooled to room temperature and diluted with methanol to precipitate a bright yellow-orange solid, which was collected by filtration. **TFTTB** was yellow when dry.

Possible optimization strategies included increasing the number of equivalents of base reagent, increasing the ratio of the 2-thiophenecarboxaldehyde, and increasing catalyst loading.⁴⁴ When the catalyst loading was increased to 9%, the conversion of the reaction in DMA improved (in other words, there were smaller amounts of partially-coupled side products), while reactions in toluene and NMP showed little change. For this reason, further reactions and optimizations were performed only in DMA. The ratio of K_2CO_3 with respect to 1,2,4,5-tetrabromobenzene was increased from 1.5 to 3.0 equivalents, which resulted in the complete consumption of the starting material. The number of equivalents of 2-thiophenecarboxaldehyde was increased from eight to twelve, which improved the ratio of fully coupled product. These optimized reaction conditions yielded Compound **5.12** in crude yields of 75–84%, which showed minor amounts of under-functionalized side products according to TLC. To separate **TFTTB** from these impurities, products were washed copiously with methanol and ethanol, which resulted in yields of 70–75%; the 1H NMR spectrum for **TFTTB** is presented in Figure 5.12.

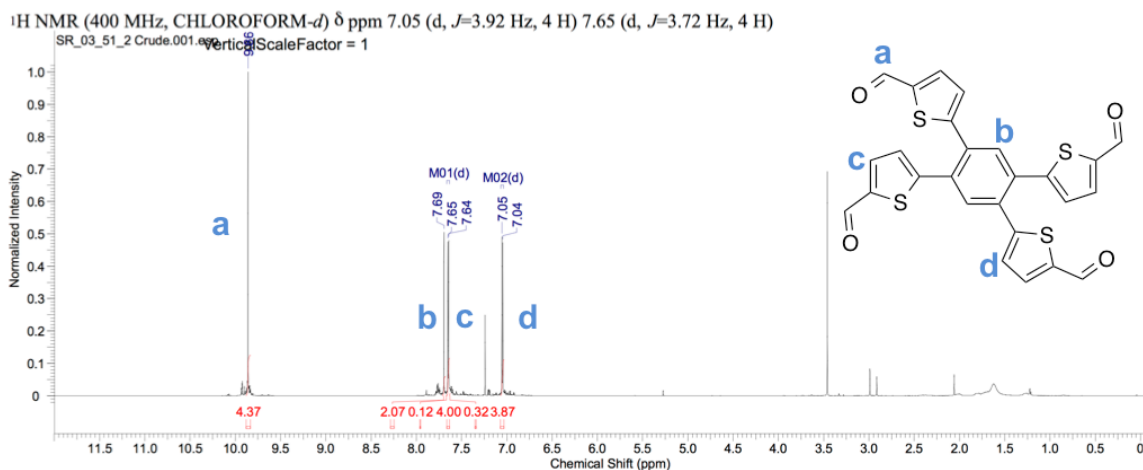
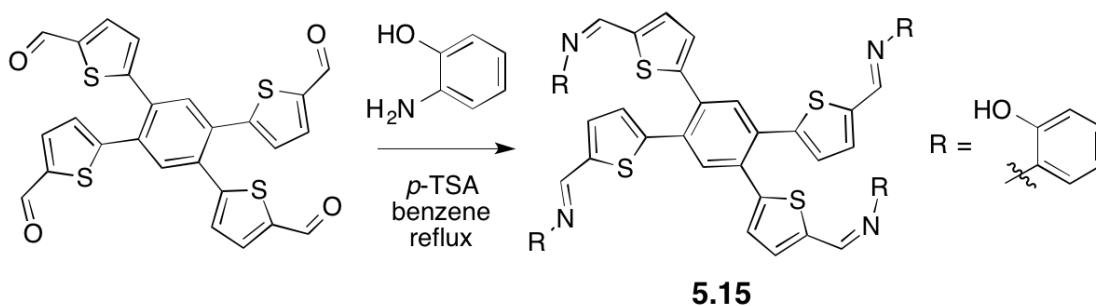


Figure 5.12 ¹H NMR spectrum of **TFTTB** (Compound **5.12**) prepared using four-fold direct C-H activated heteroarylation with 1,2,4,5-tetrabromobenzene and 2-thiophenecarboxaldehyde.

With the four-fold functionalized aldehyde reagent in hand, Schiff base formation would be performed with 2-aminophenol as above, to furnish tetra-1,2,4,5-(2-(5-(*N*-(2-phenol))azomethinyl)thienyl)benzene (Compound **5.15**, see Scheme 5.5); Compound **5.15** is not expected to be able to cyclometalate through crowded central benzene, so the third donors for tridentate metal coordination likely must be introduced during the imine formation.



Scheme 5.5 Imine condensation synthesis of tetra-1,2,4,5-(2-(5-(*N*-(2-phenol)azomethinyl))thienyl)benzene (Compound **5.15**).

Compound **5.12** and a six-fold excess of 2-aminophenol were placed in a flask with catalytic *p*-TSA, and then benzene was added to give an orange suspension. The flask was fitted with a Dean-Stark apparatus and the reaction was heated to reflux, where it became a clear orange solution. After a brief period at reflux, it became cloudy orange. The solution was refluxed for 24 hours, during which time the solution colour transitioned to dark red. TLC analysis after 24 hours revealed that the reaction was complete. To avoid the reversal of the imine formation by acidification, saturated NaHCO₃ was added; the resulting mixture was then extracted with ethyl acetate and concentrated to an orange powder. This was washed with methanol and ethanol to remove excess 2-aminophenol, affording a 62% crude yield. ¹H NMR analysis (Figure 5.13) showed that the peaks of the aldehyde (at 9.86 ppm) had been replaced by those corresponding to the imine (at 8.77 ppm).

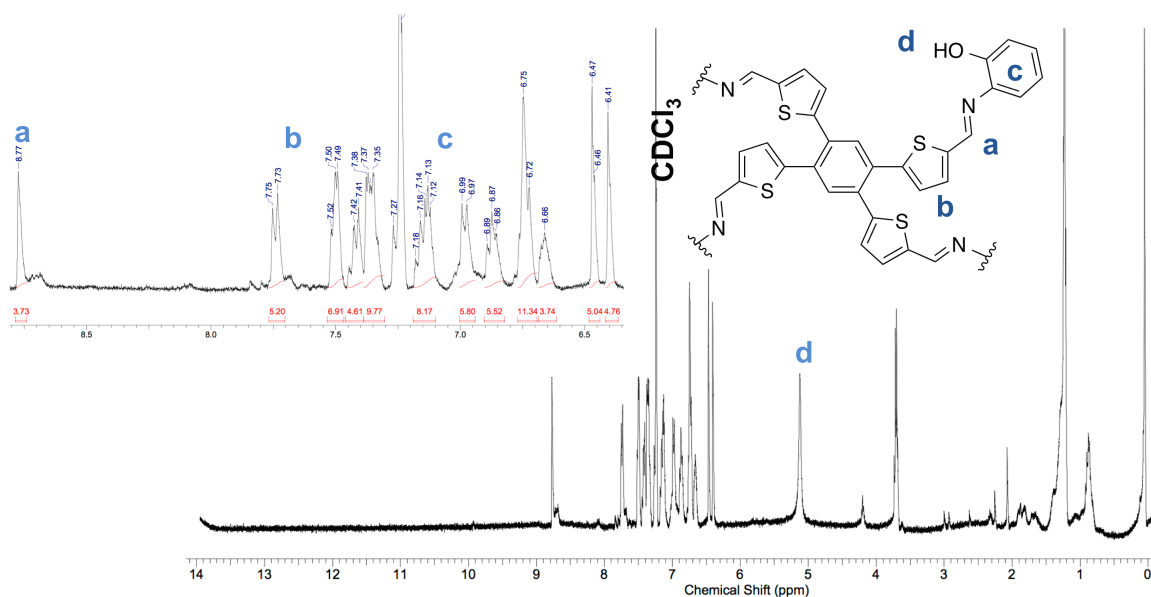


Figure 5.13 ¹H NMR spectrum of Compound **5.15**, prepared by condensation between Compound **5.12** and 2-aminophenol.

Using MALDI-MS analysis, the parent signature $[M+H]^+$ for Compound **5.15** was observed at 883 m/z ; the signature for a doubly-charged, three-armed side product were observed at 341 m/z , which may have been the result of the fragmentation at the thiophene-benzene bond. Parent signatures for under-functionalized side products were not observed. The MALDI-MS spectrum is shown in Figure 5.14.

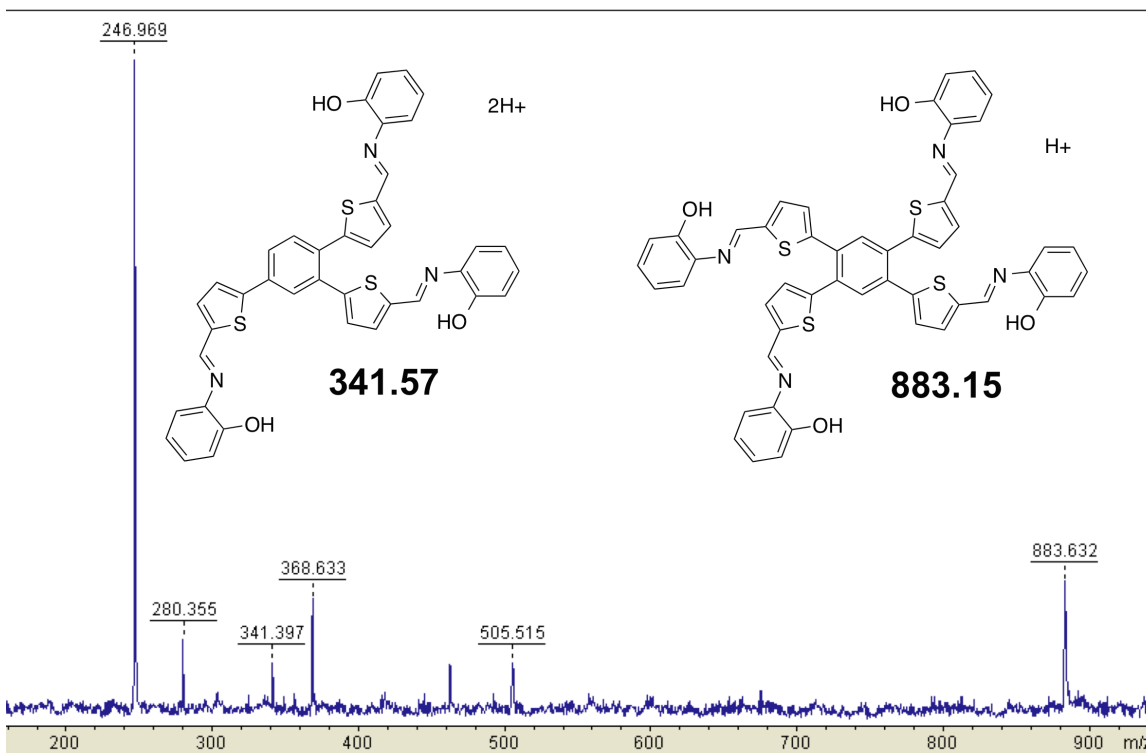


Figure 5.14 MALDI-MS spectrum of Compound **5.15**.

§ 5.7 Conclusions

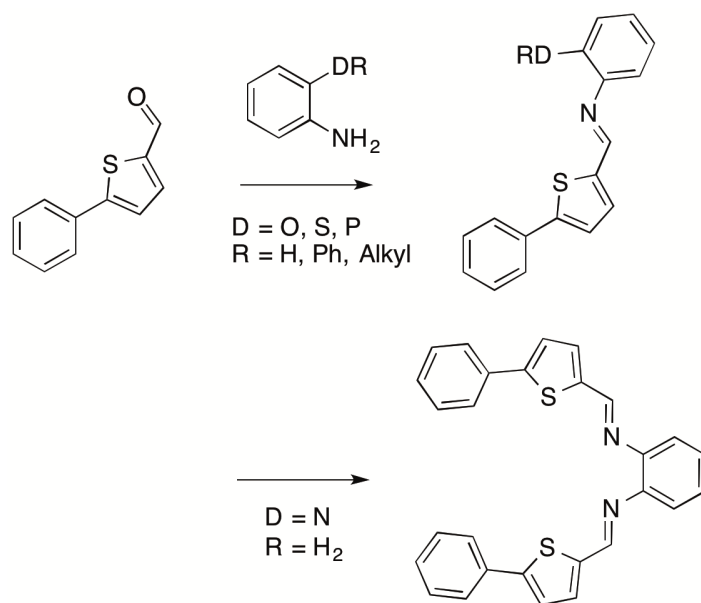
Direct C–H activated heteroarylation was used to synthesize 2-phenyl-5-thiophenecarboxaldehyde (Compound **5.13**) and tetra-1,2,4,5(2-thiophen-5-yl)benzene (Compound **5.12**). These products were prepared as the synthetic platforms to investigate mononuclear tridentate ligands, and multi-nuclear star-shaped coordination complexes, respectively, with thiophene and azomethine donors (**amth**). 5-(*N*-(2-

phenol)azomethine)-2-phenylthiophene (Compound **5.14**) and tetra-1,2,4,5-(2-(5-(*N*-(2-phenol)azomethine)thienyl)benzene (Compound **5.15**), respectively, were synthesized by condensation with 2-aminophenol, which afforded proof-of-concept Schiff base products containing the targeted **amth** moiety and phenol donors.

§ 5.8 Future Work

Full characterization of the **amth**-containing molecules Compound **5.14** and **5.15** should be completed. These molecules contain a versatile donor set, and are predicted to coordinate to both early and late d-block transition metals for various applications, such as OLED emitters. Metal coordination should be carried out with both the star-shaped and linear tridentate compounds. Cyclometalated C,S,N-ligands are expected with derivatives of Compound **5.14**, as bidentate C,S and S,N donor moieties have been shown to coordinate through thiophene. Star-shaped conjugated molecules with tridentate donor sites could provide interesting new materials, such as polynuclear organometallic complexes that could self-assemble into networks, or be utilized for optical materials such as dye-sensitizers.

Compounds **5.12** and **5.13** are platforms that allow tuning of the donor that is introduced during Schiff base formation. Following the investigation of the coordinative behaviour of Compounds **5.14** and **5.15**, modification of the amine reagents during Schiff base formation would produce new ligands, such as those in Scheme 5.6; dithienyl diimine molecules have already been shown to coordinate to metals with a d^{10} electron configuration (see Figure 5.8). Further judicious amine choice would be used to modulate the electronics and sterics of the complexes.



Scheme 5.6 Imine condensation synthesis plan to tune the donor group (5-phenyl)-2-imino(*N*-phenyl)thiophenes and the preparation of a symmetric cage ligand.

§ 5.9 Experimental Details

General Procedures and Starting Materials. All reagents were obtained commercially and used as received. All solvents were of at least reagent grade; dimethylacetamide (DMA) was dried over 4Å molecular sieves. All reactions were performed under an atmosphere of dry nitrogen. Melting points are uncorrected. ^1H and ^{13}C NMR spectra were run in CDCl_3 solutions at r.t. on a Bruker Avance 400 MHz spectrometer. Matrix-assisted laser desorption ionization mass spectrometry was performed using a Bruker microFlex MALDI-TOF mass spectrometer, calibrated to 815.95 da with resolution +10,000.

Preparation of tetra-1,2,4,5(2-thiophen-5-yl)benzene (TFTTB, Compound 5.12):

1,2,4,5-tetrabromobenzene (1.00 g, 2.54 mmol) and 2-thiophenecarboxaldehyde (3.0 mL, 32 mmol), $\text{Pd}(\text{OAc})_2$ (52 mg, 0.23 mmol) PCy_3HBF_4 (173 mg, 0.47 mmol) Pivalic acid

(96 mg, 0.94 mmol) and K_2CO_3 (0.53 g, 3.82 mmol) were stirred in 2.0 mL of degassed DMA at 110 °C for 48 h. After cooling to r.t., methanol was added to the mixture, precipitating a yellow solid, which was collected by filtration and washed with 100 mL each of cold methanol and cold ethanol (990 mg, 1.91 mmol, 75 %). m.p.: 220 °C (decomp.). 1H NMR (δ , $CDCl_3$, RT, 400 MHz): 9.86 (4H, s), 7.70 (2H, s), 7.65 (4H, d, 4 Hz) 7.05 (4H, d, 4 Hz) ppm. ^{13}C NMR (δ , $CDCl_3$, RT, 400 MHz): 182.8, 194.5, 144.9, 136.4, 133.7, 129.3 ppm.

Preparation of 2-phenyl-5-thiophenecarboxaldehyde (Compound 5.13):

Bromobenzene (808 mg, 5.15 mmol) and 2-thiophenecarboxaldehyde (1.52 g, 13.5 mmol) were measured into a vial and sparged with an N_2 stream for 15 minutes. Palladium (II) acetate (22.7 mg, 0.101 mmol), $PCy_3 \cdot HBF_4$ (77.3 mg, 0.209 mmol), pivalic acid (189 mg, 1.85 mmol) and K_2CO_3 (1.07 g, 7.71 mmol) were evacuated and back-filled with N_2 , and then the oil reagents and 5 mL DMA were added by syringe. The reaction was heated at 110 °C for 24 hr, then cooled and diluted with hexanes. The mixture was poured into 10 mL water and extracted with hexanes. The organics were dried and filtered, and the filtrate was concentrated to orange oil, which was fractionally distilled to recover 157 mg of Compound **5.13**. The aqueous phase and solids filtered from the initial hexanes workup were combined and extracted with CH_2Cl_2 . The extracts were concentrated to a light brown-gray solid, which was passed through a silica plug with 4:1 hexanes-ethyl acetate to afford 525 mg of gray solid (682 mg, 3.62 mmol, 70%); Characterization data were consistent with that reported in the literature.⁴⁵ 1H NMR (δ , $CDCl_3$, RT, 400 MHz): 9.88 (1H, s), 7.73 (1H, d, 4 Hz,) 7.68–7.63 (2H, m) 7.47–7.35

(4H, m) ppm. ^{13}C NMR (δ , CDCl_3 , RT, 400 MHz): 182.3, 154.3, 142.5, 137.5, 133.1, 129.5, 129.2, 126.5, 124.2 ppm.

Preparation of 5-(phenyl)-2-((*N*-(2-phenol)azomethinyl)thiophene (Compound 5.14):

Compound **5.13** (83 mg, 0.44 mmol), an excess of 2-aminophenol ((g, mmol) (1.2 equivalents) and a catalytic amount of *p*-TSA were placed in a flask equipped with a Dean-Stark apparatus and benzene was added. The reaction was refluxed for 24 hr, whence the solvent was removed under reduced pressure to afford an orange solid. This was passed through a plug of silica eluted with CH_2Cl_2 , whereupon Compound **5.4** was obtained as a fluorescent yellow solid. (100.4 mg, 0.36 mmol, 82%). m.p.: 108–110 °C. ^1H NMR (δ , CDCl_3 , RT, 400 MHz): 8.73 (1H, s), 7.67 (2H, d, 6 Hz), 7.47 (1H, d, 2Hz), 7.44–7.38 (2H, m), 7.37–7.31 (2H, m) 7.27 (1H, dd, 8 Hz, 1 Hz), 7.17 (1H, td, 8 Hz, 1 Hz), 7.00 (1H, dd, 8 Hz, 1 Hz), 6.88 (1H, td, 8 Hz, 1 Hz) ppm. ^{13}C NMR (δ , CDCl_3 , RT, 400 MHz): 152.3, 149.5, 133.7, 133.6, 129.1, 128.8, 128.7, 126.2, 123.9, 120.1, 115.7, 115.1 ppm.

Preparation of tetra-1,2,4,5-(2-(5-(*N*-(2-phenol))azomethinyl)thienyl)benzene

(Compound 5.15): Compound **5.12** (273 mg, 0.526 mmol) and 2-aminophenol (342 mg, 3.13 mmol) were added to a flask with catalytic *p*-toluene sulfonic acid, and then 20 mL benzene was added to give an orange suspension. The flask was fitted with a Dean-Stark apparatus and the reaction was refluxed for 24 hours. The dark red solution was cooled, and 10 mL saturated NaHCO_3 was added. The mixture was extracted with ethyl acetate, and the combined organics were washed with saturated NaHCO_3 , dried and concentrated to an orange solid (290 mg, 0.328 mmol, 62%). The product was identified by NMR spectroscopy and MALDI-MS. ^1H NMR (δ , CDCl_3 , RT, 400 MHz): 8.77 (4H, s),

7.74 (4H, d, 8 Hz), 7.53–7.47 (4H, m), 7.46–7.40 (4H, m), 7.39–7.34 (4H, m) 7.20–7.09 (4H, m), 6.98 (4H, d, 8 Hz), 6.47 (4H, d, 4 Hz), 6.41 (4H, d, 4 Hz) ppm. MS (MALDI): $C_{50}H_{34}N_4O_4S_4$ m/z : 882.15 Found: 883.63 (25%, $[M+H]^+$).

§ 5.10 References

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Chapter 6 – Conclusions and Future Directions

§ 6.1 Conclusions

The work described by this thesis explored the effect of nitrogen on the properties of star-shaped thienoacenes, and pursued new star-shaped molecules that could be used in the preparation of metal-organic frameworks and organometallic complexes.

In the third chapter, **TTAc**, **BrTTAc** and **OTAc**, novel molecules built around the novel tetrathienoacridine core, were synthesized. Their optoelectronic properties were investigated and compared to their carbon-and-sulfur based analogues, the thienoanthracenes. The replacement of a CH group in the core with nitrogen was demonstrated through experimental and computational studies to reduce the frontier orbital energy levels – which was correlated by electron deficiency in the core – and reduce the optical transition energies of thienoacridines *cf.* thienoanthracenes. Acridines also displayed greater molar absorptivities. Unlike the anthracene derivatives, which exhibit quasi-reversible oxidations, the acridine systems oxidize irreversibly; however, they exhibited lower disproportionation constants than their anthracene analogues. Furthermore, crystals of **BrTTAc** displayed yellow-to-orange thermochromism, which the anthracene analogue did not – this was attributed to the presence of nitrogen-induced dipoles.

The fourth chapter described efforts to incorporate star-shaped thiophene-based structures into metal-organic frameworks. Tetrathienylbenzene molecules were functionalized with carboxylate groups, such that they may act as tetrapodal linkers. MOF preparation reactions were undertaken with metal salts $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, and

Mn(OAc)₂·4H₂O. The linker, Compound **4.10**, was found to react quickly with metal salts; despite this hurdle, microcrystalline products were obtained from acetonitrile/water mixtures, and their infrared signatures displayed features pointed to possible paddlewheel structures, similar to those derived from other tetrapodal carboxylate linkers. These reactions require further optimization, but were indicative of promise for the synthesis of tetrathienylbenzene-based MOFs.

In Chapter 5, the *N*-aryl(azomethine)thiophene moiety was prepared in both mono- and multi-pocketed forms (2-phenyl-5-thiophenecarboxaldehyde and tetra-1,2,4,5-(2-thiophen-5-yl)benzene, respectively), using Direct C–H activated heteroarylation. To explore sulfur coordination in thiophenes with Schiff bases, proof-of-concept molecules 5-(*N*-(2-phenyl)azomethine)-2-phenylthiophene and tetra-1,2,4,5-(2-(5-(*N*-(2-phenyl)azomethine)thienyl)benzene were synthesized by condensation with 2-aminophenol.

§ 6.2 Future Directions

The molecules in this thesis represent a family of multifunctional materials that merit further characterization and investigation. The family of soluble thienoacridine molecules should be used for OTFT devices, owing to their favorable energetics and low disproportionation constant. Furthermore, *N*-functionalization can be performed with acridines to create conjugated salts; the thienoacridines herein are prime candidates for exploration in this vein.

The star-shaped metal-coordinating materials also demand further research attention. Metal-organic frameworks are materials with potential for catalysis, separations and

storage of guest molecules, and the unique thiophene-based tetrapod linker Compound **4.10** may be modified to increase solubility such that thermodynamic framework formation is enhanced. Furthermore, the synthetic tools utilized in this thesis can be applied to prepare tetrathienylpyridines for MOFs.

The **amth** moiety described in Chapter 5 has a number of possible applications. Thiophene-containing ligands are increasingly used for coordination compounds such as Ruthenium- and Iridium-based dye-sensitizers in organic solar cells. The tridentate coordinating sites are anticipated to provide an avenue for the study of sulfur coordination to transition metals, which would enhance the growing field of thiophene-based active materials. The aldehyde-functionalized star-shaped thienylaryl, tetra-1,2,4,5(2-thiophen-5-yl)benzene, could be used to construct covalent organic frameworks (COFs). Furthermore, the use of the Schiff base functional group means that a library of ligands can be constructed by variation of the chosen amine, providing access to expansive tuning of these ligands.

Appendix

A-1. DFT Calculations and Archival files

Molecular calculations were performed using the Gaussian 09 software suite,¹ utilizing the hybrid functional B3LYP with the basis set 6-311+G(d,p). Optimized structures (with R = Me) were used to examine the orbital energies and HOMO-LUMO gaps. The calculated UV-vis spectra and excitation energies were determined using TD DFT which employed the optimized B3LYP ground states. The solvent model and solvent were PCM and dichloromethane respectively, and twenty excited states were considered.

Table A.1 Energies of calculated TD-DFT optical transitions for **TTAc**, **OTAc**, **TTAn**, and **OTAn**, with associated transition oscillator strengths.

<i>k</i>	TTAc		OTAc		TTAn		OTAn	
	E (eV)	<i>f</i>	E (eV)	<i>f</i>	E (eV)	<i>f</i>	E (eV)	<i>f</i>
1	2.8033	0.0067	2.3437	0.6700	2.8471	0.0058	2.4378	0.1109
2	2.8446	0.4009	2.3826	0.0987	2.9824	0.2023	2.4785	0.2419
3	3.3724	0.0002	2.8061	1.5786	3.6001	0.0000	2.7040	2.0493
4	3.7253	1.2371	2.8797	0.8916	3.6022	1.5149	2.8977	0.9106
5	3.7778	0.0064	2.8844	0.0009	3.9171	0.3288	3.0282	0.0000
6	3.8518	0.0016	2.9017	0.0508	3.9229	0.0000	3.0740	0.0000
7	3.9125	0.6954	3.2320	0.0020	4.0253	0.3694	3.2196	0.0000
8	4.1091	0.0005	3.3263	0.0032	4.3048	0.0000	3.2388	0.0000
9	4.1307	0.0001	3.3590	0.0014	4.3459	0.0000	3.2954	0.0000
10	4.3163	0.0009	3.4100	0.0004	4.3829	0.0000	3.3643	0.0000
11	4.5387	0.0011	3.4544	0.0024	4.4088	0.0000	3.4148	0.0000
12	4.5674	0.0032	3.5326	0.0008	4.5928	0.0000	3.5748	0.0000
13	4.6297	0.0003	3.5419	0.4111	4.6634	0.0000	3.6765	0.1370
14	4.6588	0.0031	3.5807	0.0126	4.6949	0.0234	3.7169	0.0000
15	4.7112	0.0590	3.7564	0.7635	4.7033	0.0000	3.7282	1.0943
16	4.7256	0.0001	3.8147	0.0020	4.7186	0.0000	3.8182	0.0085
17	4.9539	0.0003	3.8231	0.0141	4.799	0.0000	3.8485	0.0201
18	4.9564	0.0956	3.8416	0.1214	4.8853	0.0000	3.8856	0.0837
19	4.9891	0.0022	3.8773	0.0351	4.9481	0.0003	3.9792	0.0877
20	5.0206	0.0000	4.0140	0.0191	5.0041	0.0000	4.0172	0.0002

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

Archival file for the Geometry Optimization of **TTAn**:

```
1\1\GINC-TITAN\FOpt\RB3LYP\6-311+G(d,p)\C26H18S4\APACHE\14-May-2014\0\
\#N B3LYP/6-311+G(d,p) OPT(EstMFC)\TTA\0,1\C,0.0013670447,-0.0000480
721,-0.0017819628\C,-0.0002504776,-0.0000093723,1.4955422491\S,1.51253
2124,-0.0000008717,2.3871734928\C,0.6701287546,0.0000478619,3.92436969
49\C,1.2843908062,0.0000413941,5.2202127731\C,2.6675684768,0.000003744
4,5.4167200294\C,3.2431357582,0.0000247304,6.6897158436\C,2.3780052625
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Archival file for the Geometry Optimization of **OTAn**:

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Archival file for the Geometry Optimization of **TTAc**:

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Archival file for the Geometry Optimization of **OTAc**:

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(1) M. J. Frisch, G. W. T., H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox; Revision A.02 ed.; Gaussian, Inc.: Wallingford, CT, 2009.