# THIOPHENE-CONTAINING PHOTOFUNCTIONAL MOLECULES: PACMAN COMPLEXES, METALLACYCLES AND FLEXIBLE LEWIS PAIRS

by

Yang Cao

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## Abstract

Three types of photofunctional molecules based on thiophene-containing conjugated backbones have been designed, synthesized and characterized. It is shown that their light absorption and emission properties can be manipulated and applied for applications such as fluorescent imaging.

Binuclear Pt(II) terpyridine Pacman complexes with flexible thiophene-containing bisacetylide ligands are shown to exhibit structural folding/unfolding controllable by temperature change and different solvent environments. The structural folding and unfolding give rise to structural changes of the thiophene-containing backbone and different interactions between two metal-containing moieties, which are analyzed by DFT calculations and evidenced by UV-Vis and NMR spectroscopy.

Metallacycles with a *cis*-diphosphino Pt(II) metal center and different thiophenecontaining bisacetylides are designed to show room-temperature fluorescence and phosphorescence dual emission with different intensity ratios. Their absorption and emission properties are explained by DFT and TD-DFT analysis of ground state and singlet and triplet state energies and geometries.

An intramolecular Lewis pair system between a Lewis acidic -BMes<sub>2</sub> group and a Lewis basic phosphine oxide group based on a flexible bithiophene backbone is reported. Evidenced by NMR and IR spectra, the system is found to exhibit fast equilibrium between an open structure with unbound Lewis acid and a closed structure with Lewis adduct. The equilibrium is manipulated by lowering the temperature to favor the closed structures, or adding strong hydrogen bond donors that favor the open forms. The difference in coordination state of the boron center in these two states gives rise to an interesting single-component-two-state system with drastically different emission colors between states. The scope of such system was explored and different emission colors of the open and closed forms of the Lewis pairs are achieved by changing the backbone conjugation or strength of electron-donating groups. Furthermore, this system has been used as a two-color fluorescent dye system for fluorescence imaging of hydrophobic/hydrophilic environments in biological or medical applications.

## Preface

In all chapters, Prof. Michael Wolf acted as the supervisor. I am the principal author of the work reported in this thesis, and I carried out all the experiments except the ones noted otherwise. All X-ray crystallography structures were collected by Dr. Brian O. Patrick. DFT and TD-DFT calculations were performed by Dr. Jeffery Nagle at Bowdoin University in **Chapter 4** and by myself in other chapters.

Portions of **Chapter 2** have been previously published<sup>1</sup> except the synthesis and photophysical properties of compound **3** and all the computational results. A version of **Chapter 4** has been previously published.<sup>2</sup> I am the principal author of both works.

All the fluorescence imaging experiments in **Chapter 5** were performed by Xiaozhu (Hunter) Wang in the laboratory of Prof. Chris Orvig at UBC. The specimens of human-brain slices were provided by the laboratory of Prof. Emeritus Patrick L. McGeer at Faculty of Medicine, UBC.

A list of publications arising from work presented in the thesis:

- (1) Cao, Y.; Wolf, M. O.; Patrick, B. O. Inorg. Chem. 2013, 52, 5636.
- (2) Cao, Y.; Nagle, J. K.; Wolf, M. O.; Patrick, B. O. J. Am. Chem. Soc. 2015, 137, 4888.

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# List of Symbols and Abbreviations

ACN	acetonitrile
ATR	attenuated total reflectance
BMes <sub>2</sub>	bis(2,4,6-trimethylphenyl)boryl group, or dimesitylboryl group
bpy	2,2'-bipyridine
br	broad
calcd.	calculated
cat.	catalyst or catalytical amount
CB	conduction band
СТ	charge transfer
Су	cyclohexyl group
δ	chemical shift (ppm)
Δ	difference
$\Delta E_{g}$	band gap
D-A	donor-acceptor
dbbpy	4,4'-di-tert-butyl-2,2'-bipyridine
DCM	dichloromethane
DFT	density functional theory
dppp	1,3-bis(diphenylphosphino)propane
DSCs	dye-sensitised solar cells
DTE	dithienylethylene
$E_{00}$	0-0 transition energy
EM	emission
ESI	electrospray ionization
ET	electron transfer
eV	electronvolt
$E_{v}$	vertical transition energy
EX	excitation

f	oscillator strength		
$\Phi_{em}$	emission quantum yield		
FL	fluorescence		
FLP	frustrated Lewis pair		
FTIR	Fourier transform infrared spectroscopy		
GGA	generalized gradient approximation		
GS	ground state		
HB	hydrogen bond		
HBA	hydrogen bond acceptor		
НОМО	highest occupied molecular orbital		
HRMS	high resolution mass spectrometry		
Hz	hertz		
IC	internal conversion		
IR	infrared		
ISC	intersystem crossing		
Κ	kelvin		
$k_{ m FL}$	rate of fluorescence		
kisc	rate of intersystem crossing		
<i>k</i> <sub>NR</sub>	rate of nonradiative decay		
$k_{\rm PH}$	rate of phosphorescence		
LANL2DZ	Los Alamos National Laboratory effective core and valence basis		
	set of double-zeta quality		
LASER	light amplification by stimulated emission of radiation		
LC	ligand-centered or liquid chromatography		
LDA	local density approximation		
LEDs	light emitting diodes		
$\lambda_{em}$	emission wavelength		
$\lambda_{ex}$	excitation wavelength		
LLCT	ligand-to-ligand charge transfer		

LMCT	ligand-to-metal charge transfer
LUMO	lowest unoccupied molecular orbital
μ	micro
m/Z	mass-to-charge ratio
MC	metal-centered
<i>m</i> -CBPA	meta-chloroperoxybenzoic acid
MeOH	methanol
Mes	mesityl group
MHz	megahertz
mL	milliliter
MLCT	metal-to-ligand charge transfer
MMLCT	metal-metal-to-ligand charge transfer
mmol	millimole
$M_n$	number average molecular weight
MO	molecular orbital
mol	mole
MS	mass spectrometry
$MV^{2+}$	methyl viologen cation
<i>n</i> -BuLi	<i>n</i> -butyllithium
NIR	near infrared
NMR	nuclear magnetic resonance
NOESY	nuclear overhauser effect spectroscopy
NR	nonradiative decay
OFET	organic field effect transistors
OLEDs	organic light emitting diodes
ORTEP	Oak Ridge Thermal Ellipsoid Plot
OTf	trifluoromethylsulfonate
РЗНТ	poly-3-hexylthiophene
PBE0	Perdew-Burke-Ernzerhof exchange-correlation functional

PBS buffer	phosphate-buffered saline
РСМ	polarizable continuum model
PDI	perylene diimide
PEDOT	poly-3,4-ethylenedioxythiophene
PH	phosphorescence
ppm	parts per million
PVs	photovoltaics
Ref	reference
RISC	reversed intersystem crossing
RNA	ribonucleic acid
SEM	scanning electron microscope
SOC	spin-orbit coupling
τ	lifetime
TADF	thermal-activated delayed fluorescence
tbtpy	4,4',4"-tri-tert-butyl-2,2':6',2"-terpyridine
<sup>t</sup> Bu	<i>tert</i> -butyl group
TD-DFT	time-dependent density functional theory
$ au_{em}$	emission lifetime
TEM	transmission electron microscopy
THF	tetrahydrofuran
TIP	2,4,6-tri( <i>i</i> -propyl)phenyl group
TMS	trimethylsilyl group
tpy	2,2':6',2"-terpyridine
υ	frequency
UV	ultraviolet
VB	valence band
Vis	visible
٤	spin-orbit coupling constant for atoms
Ζ	charge or atomic numbers of the element

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### **Chapter 1 Introduction**

#### 1.1 Overview

Light is deeply involved in many important theories of modern physics including relativity, quantum theory and the theory of gravity and electromagnetism. Many applications of light such as laser technology, X-ray and optical materials not only contribute greatly to advances in modern sciences but also improve the quality of human lives in many different ways. To acknowledge and promote of the achievements of light science and its applications, 2015 was proclaimed by the UN General Assembly as the International Year of Light and Light-based Technologies (IYL).<sup>3</sup>

Light has become an important workhorse for human society with the coming of the Information Age. Other than widely applied uses in illumination, light is also widely used in modern electronics to generate graphical signals, such as on television screens and the displays of almost all digital devices. Far beneath the oceans, light is used to carry heavy intercontinental Internet traffic through optical fibers in communication cables.<sup>4</sup> Solar energy in the form of light is considered to be a sustainable alternative to fossil fuels, the combustion of which causes global environmental issues such as air pollution and climate change. Moreover, the generation, manipulation, and detection of light are also believed to be the key to possible future technologies<sup>5</sup> such as quantum computing<sup>6</sup> and quantum communication.<sup>7</sup> The development of materials with a variety of different photofunctionalities is therefore highly important.

Photovoltaics (PVs) and light emitting diodes (LEDs) are two types of devices employing photofunctional materials. Both types of devices have been successfully commercialized with

multi-billion global markets. In PVs charge separation occurs after which absorbed light energy is converted to electricity, whereas in LEDs charges are combined using electric power to emit light. Both applications are moving towards using more flexible, light-weight materials with high efficiency and lower economic and environmental costs. Organic semiconductors are becoming more and more advantageous compared to conventional inorganic counterparts for these applications. Organic photofunctional materials can be easily applied to flexible substrates using low-cost and high-throughput processing techniques such as roll-coating<sup>8</sup> and inkjet printing<sup>9</sup>, etc. For example, SolarWindow Technologies, Inc. in Maryland has developed an organic photovoltaic (OPV) material that can be coated on any window surface to generate on-site electricity for buildings.<sup>10</sup> Samsung, LG, and Apple have recently released wearable devices such as smartwatches integrated with highly energy-efficient organic LED (OLED) displays.

Conjugated materials with delocalized  $\pi$ -electrons have been promising photofunctional materials since their discovery, due to the unique optical and electrical properties of organic semiconductors.<sup>11</sup> Moreover, they can be synthetically tailored to have desired properties such as strong light absorption or high charge carrier mobility for certain applications such as in OPVs, OLEDs and organic field effect transistors (OFETs). It has also been shown that conjugated materials can also incorporate other photofunctionalities such as metal-containing moieties, or donor-acceptor pairs. In this thesis, three different thiophene-containing photofunctional conjugated materials that show environment-dependent light absorption and emission properties are demonstrated.

### **1.2 Conjugated Materials**

#### **1.2.1** Structures and Molecular Orbitals

The metal-like conductivity of polyacetylene doped with halogen vapour was first observed in the late 1970s by Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa,<sup>12</sup> who in 2000, shared the Nobel prize in Chemistry "for the discovery and development of conductive polymers".<sup>11</sup> This finding challenged the commonly held perception of organic materials as being poor conductors and started decades of extensive scientific research on different types of conjugated materials.



**Figure 1-1.** Simplified diagram showing the narrowed HOMO-LUMO energy gap and the formation of band structure with increasing  $\pi$ -conjugation from ethylene to polyacetylene.

The properties of polyacetylene can be explained by its molecular orbital (MO) diagram. As shown in **Figure 1-1**, with additional conjugation length from ethylene to 1,3-butadiene and 1,3,5-

hexatriene, the highest occupied molecular orbital (HOMO) increases in energy while the energy of the lowest unoccupied molecular orbital (LUMO) decreases. The HOMO-LUMO energy difference reduces as a result. In polyacetylene where the conjugation is extended enough, the occupied and unoccupied MOs merge into continuous band-like structures with a valence band (VB) which is filled with paired electrons, and an empty conduction band (CB). The band gap  $\Delta E_g$ in polyacetylene is small enough for the material to be semiconducting. In pristine polyacetylene no MO is present between the VB and CB, however, additional interband states can be introduced by doping the material with iodine, resulting in metal-like electric conductivity.

Scheme 1-1. Examples of conjugated polymers.



Over the years, many variants of different conjugated materials have been developed such as polythiophene, polypyrrole, poly(*p*-phenyleneacetylene) and polyfluorene, etc (**Scheme 1-1**). A common feature of these systems is alternating double and single carbon-carbon bonds with overlapped  $\pi$ -bonding orbitals along the length of the structures. Different building blocks with different steric and electronic properties can be used alone or combined to engineer the conformation and electronics of the resulting conjugated material. Side-groups such as alkyl chains can also be added to improve the solubility and processability of conjugated materials which were not available in the original synthesis of polyacetylene.

Conjugated materials with atoms other than carbon in the backbone can also be made

(Figure 1-2). For instance, the filled p orbital of  $sp^2$  hybridized nitrogen atoms or the empty p orbital of  $sp^2$  hybridized boron atoms can also overlap effectively with the carbon p orbitals of the conjugated  $\pi$  system to form either electron-rich or electron-deficient materials, respectively. Similarly, the *d*-orbitals of some transition metals with suitable symmetry and energy level (such as the  $d_{xz}$  orbital of Pt(II) in Figure 1-2) can also result in a less degree of conjugation of the conjugated  $\pi$  system. These materials can potentially exhibit the photophysical properties of both the heteroatoms and the carbon-containing counterparts, and in some cases, new properties such as light-induced charge transfer (CT) can also arise between them.



**Figure 1-2.** Examples of hybrid conjugated polymers (top) and schematics of the orbital overlap of corresponding conjugated systems.

### **1.2.2** Photophysical Properties

Conjugated materials with different band structures or frontier molecular orbitals show

different photophysical properties when interacting with light. They may absorb light at different wavelengths and give rise to different emission.

For instance, in **Figure 1-3**, a photon is absorbed by a ground state (GS) molecule which is in the lowest singlet state (total electron spin, S = 0) and promotes an electron from the HOMO to LUMO (**Figure 1-3**, left) on a femtosecond (10<sup>-15</sup> s) time scale. This process of light-induced electron excitation is extremely fast and can be approximated without changing the position of nucleus in the molecule, as known as the vertical excitation. Immediately after excitation, molecules are usually at higher vibronic states of the resulting excited state, and always undergo rapidly relaxation to the lowest vibronic states prior to emission (**Figure 1-3**, right).



**Figure 1-3.** HOMO and LUMO of different electronic states (left) and a Jablonski diagram showing the vibronic states of each electronic states (right, bold lines indicate the lowest vibronic states).

The excited molecule will be in a singlet state (e.g.  $S_1$  state) if the total spin of electrons is conserved, or can be converted into a triplet state (e.g.  $T_1$  state) in a dark process called intersystem

crossing (ISC) in which one of the electrons undergoes a spin flips without interacting with additional photons. Conversion between states with different electron spin multiplicity is forbidden by selection rules. Therefore, ISC in organic molecules is usually very slow unless facilitated by spin-orbit coupling (SOC) of heavy atoms.<sup>13</sup> Another dark process is internal conversion (IC), which is the fast conversion ( $\tau \sim 10^{-12}$  s) of excited states to lower energy states with the same multiplicity, such as S<sub>2</sub> $\rightarrow$ S<sub>1</sub>, T<sub>2</sub> $\rightarrow$ T<sub>1</sub> or S<sub>1</sub> $\rightarrow$ S<sub>0</sub>.

An excited state molecule can go back to GS via radiationless decay, or by emitting a photon. Emission from the singlet and triplet excited states are called fluorescence and phosphorescence, respectively (**Figure 1-3**, right). Again due to selection rules, the former is usually many orders of magnitude faster than the latter ( $k_{FL} >> k_{PH}$ ). Phosphorescent triplet excited states are sensitive to O<sub>2</sub>, whereas fluorescence is usually not. The O<sub>2</sub> sensitivity of phosphorescent materials has been widely used in applications such as O<sub>2</sub> sensors and hypoxia imaging in tumor tissues.

The fluorescence and phosphorescence intensity and emission lifetimes ( $\tau$ ) of  $\pi$ -conjugated materials can be attenuated by the presence of heavy atoms and engineering the energies and MOs of corresponding singlet and triplet excited states. This has become especially important for OLED applications in that phosphorescent materials are considered to have much higher theoretical electroluminescence quantum efficiencies than fluorescent ones.<sup>14</sup>

#### **1.1.1 Charge Transfer Processes**

Light absorption by pristine  $\pi$ -conjugated materials usually does not result in excited state electron density that is significantly shifted from the GS. Such excitation processes are called  $\pi - \pi^*$ 

excitations which are typically highly probable due to good overlap of MOs. By contrast, processes that involve large displacement of electron density are called charge transfer (CT) transitions, these are less probable compared to  $\pi$ - $\pi$ \* transitions due to reduced orbital overlap. Charge transfer transitions with absolutely no overlap between frontier MOs of the corresponding states are forbidden. However, most frontier MOs of CT excited states share some degree of overlap with the GS and can be populated with low probability..



**Figure 1-4.** Schematics of HOMO of  $\pi^*$  and CT excited states of thiophene (left) and thiophene with an  $sp^2$  boron CT acceptor at the  $\beta$ -position (right). Red solid and hollow circles are representative of the contributions of atomic *p* orbitals to the HOMO.

In general, in a given molecule the CT absorption bands are often weaker than the  $\pi$ - $\pi$ \* bands in the UV-Vis spectra. Unfortunately, radiationless decay (or nonradiative decay, NR) of an excited state with  $\pi$ \* character can also be very rapid for similar reasons. This is one of the major limitations to high emission quantum efficiency of  $\pi$ -conjugated materials. However, NR can be minimized by enabling lower energy CT excited states so that NR from the  $\pi$ \* excited state can be suppressed (**Figure 1-4**).

Some molecules with charge transfer  $S_1$  and  $T_1$  excited state have very small  $S_1$ - $T_1$  energy gaps due to weak interaction between unpaired electrons, which is beneficial for reversed intersystem crossing (RISC) from  $T_{1\rightarrow}S_1$ . This principle has been used in thermally-activated delayed fluorescence (TADF) applications to harness triplet excited states without the presence of transition metals, achieving high emission efficiency in fluorescent materials. Some compounds with CT excited state can also undergo photo-induced electron transfer (ET) with neighboring molecules inducing charge separation between molecules, this is an important process in both dye-sensitized solar cells (DSSCs) and photo-redox catalysts.





Negative Solvatochromism

Figure 1-5. Schematics of solvatochromism of CT transitions.

Light absorption and emission of CT transitions usually shows some degree of a spectroscopic solvent effect depending on the polarities of the states involved, called solvatochromism (illustrated in **Figure 1-5**). If the excited CT state is more polar than the ground state, it will be stabilized more in more polar solvents (**Figure 1-5**, left). As a result, the absorption and emission colors are red-shifted with a higher solvent polarity, known as positive

solvatochromism. By contrast, a molecule with a more polar ground state will give rise to negative solvatochromism, thus showing blue-shifted features in more polar solvents (**Figure 1-5**, right). In rare cases, the polarities of the initial and final states in a CT process are very similar. Therefore, solvatochromism can be used to identify a CT transition, however, a lack of solvent effect cannot be used to exclude CT processes.

In the context of photofunctional conjugated materials, charge transfer transitions can be achieved by adding  $\pi$ -donating groups (e.g. aniline derivatives) and/or  $\pi$ -accepting groups (e.g. nitro- and cyanide groups) to the conjugated backbone. The combination of these two types of groups results in materials containing donor-acceptor (D-A) pairs. In the following sections of this chapter,  $\pi$ -accepting Lewis acidic groups with unquenched reactivity (e.g. 3-coordinated boranes) and transition metals (e.g. Pt(II) containing moieties), which can be both  $\pi$ -donating and  $\pi$ -accepting, will be further discussed in the context of thiophene-containing conjugated materials.

### **1.3 Thiophene-Containing Conjugated Materials**

Conjugated oligomers and polymers can be constructed using thiophene-containing building blocks via palladium-catalyzed Suzuki, Negishi, and Stille coupling reactions (**Scheme 1-2**). In recent years, direct C-H activation methods<sup>15</sup> that avoid usage of organometallic reagents have become increasingly popular as more step-economic alternatives. It is also common practice to add side-chains such as hexyl groups to enhance the solubility of the final product so that higher molecular weight can be achieved when making polymers.
**Scheme 1-2.** Nomenclature of the thiophene ring and general synthetic routes to oligothiophenes and polythiophenes.



**Scheme 1-3.** Examples of thiophene-containing groups (left) and thiophene-containing polymers (right) with red color indicating electron deficient groups.



As one of the common building blocks for conjugated materials, thiophene is more electronrich than benzene.<sup>16</sup> As shown in **Scheme 1-3**, materials with only thiophene rings on the conjugated backbone, such as poly-3-hexylthiophene (P3HT, **68**) and poly-3,4ethylenedioxythiophene (PEDOT, **69**), are electron-rich and can be P-doped with oxidants. Thiophene derivatives with electron-donating groups (e.g. **65** and **66**) are incorporated in donoracceptor (D-A) materials (polymer **70**)<sup>17</sup>, serving as electron donors to electron-deficient groups such as perylene diimide (PDI). Some thiophene derivatives such as compound **67** in **Scheme 1-3** with strong electron-withdrawing groups can also become electron acceptors.<sup>17</sup>



**Figure 1-6.** Thiophene-thiophene s-*trans* and s-*cis* coplanar conformations (left) and conformation changes as the result of weak interactions.

Pairs of adjacent non-substituted thiophene rings have two energy minima: the s-*trans* and s-*cis* conformations (**Figure 1-6**, left). In 2,2'-bithiophene, the former is slightly more stable, about 0.8 kcal/mol lower in energy compared to the latter with a energy barrier between the two of 20±8 kcal/mol.<sup>18</sup> Substitutions on thiophene rings may affect the planarity of the backbone (**Figure 1-6**, right) which can be important for the performance of the material. Torsion between thiophene rings usually results in less effective conjugation of the backbone and consequently weaker light absorption.

Regioregular head-to-tail poly-3-hexylthiophene (HT-P3HT, **71** in **Figure 1-6**) shows better conductivity and a lower bandgap compared to isomers with head-to-head (HH, **72**) coupling patterns, due to a higher degree of coplanity between thiophene rings.<sup>19</sup> In solar cell applications, on the other hand, the torsion between thiophene rings by repulsion of alkyl groups has been used to increase the open-circuit voltage.<sup>20</sup> Recently, it was shown that the weak attractions between thiophene donors and imide acceptors can also contribute to the planarity of the D-A conjugated backbone.<sup>17,21</sup> These weak interactions are an important factor to be considered when engineering the molecular conformation and intermolecular interaction in thiophene-containing conjugated materials, especially for applications that require reversible tuning of backbone conjugation.

## 1.4 Photofunctional Conjugated Materials with Pt(II) Moieties



**Figure 1-7.** Transition metal-containing conjugated materials (blue circles represent metal complexes while grey tiles indicate the conjugated backbone).<sup>22</sup>

Additional photophysical properties can be introduced to thiophene-containing conjugated

materials by incorporating transition metals. There are three basic types of transition metalcontaining conjugated materials as summarized in **Figure 1-7**.<sup>22</sup> In Type I systems, the metalcontaining moieties are tethered to the backbone by non-conjugated linkers such as alkyl chains. Such systems show relatively separate behavior of the metal and the  $\pi$ -system. Type II and III systems involve the electronic coupling of the metal to the  $\pi$ -system, where in the latter case the metal becomes part of the main-chain  $\pi$ -conjugation.



**Figure 1-8.** Two scenarios for light absorption in transition metal-containing  $\pi$ -systems.

As shown in **Figure 1-8**, ligand-centered (LC) processes are typically  $\pi - \pi *$  transitions with little or no participation of the metal. Forbidden by selection rules, metal centered (MC) *d-d* transitions are usually very weak and give rise to NR decay which can be minimized by increasing the *d-d* energy gap with strong  $\sigma$ -donating ligands.<sup>23</sup>

Photo-induced electronic transitions between metal and  $\pi$ -system will result in CT processes. Ligand-to-metal charge transfer (LMCT) indicate CT from the  $\pi$ -system to the metal (**Figure 1-8**, left), which is common between metal centers with low-energy empty *d*-orbitals and ligands with high-lying HOMO levels. CT in the opposite direction, namely metal-to-ligand charge transfer (MLCT) (**Figure 1-8**, right), is common between late transition metals with high-energy filled *d*orbitals and ligands with low-lying  $\pi$ \* orbitals. Ligand-to-ligand charge transfer (LLCT) between multiple ligands on the same metal center is also possible and sometimes can become predominant. Charge transfer transitions with mixed origins in large and complex  $\pi$ -systems can be described with their major components such as MLCT/LLCT, or simply CT in general for convenience.





Square planar Pt(II) metal centers with  $d^8$  electronic configurations are important photofunctional entities that can be incorporated into conjugated materials. In most Pt(II) photofunctional materials, strong  $\sigma$ -donating conjugated ligands such as acetylides are used to avoid NR decay through *d*-*d* excited states and increase conjugation and electronic coupling between the metal and its ligand(s). Two major types of photofunctional Pt(II) acetylides include complexes with phosphine ancillary ligands, and complexes containing polypyridyl ligands (**Scheme 1-4**). Pt(II) acetylides with phosphine ligands generally do not show a strong tendency for CT unless the acetylide ligands are highly electron rich or deficient.<sup>24</sup> By contrast, Pt(II) acetylides with electron-deficient polypyridyl ligands feature planar structures and strong CT

transitions.

#### 1.4.1 Photofunctional Pt(II) Acetylides with Phosphine Ligands

Pt(II) acetylides with phosphine ancillary ligands have two possible geometries: the *cis*isomer with two acetylides adjacent to one another, and the *trans*- isomer with acetylides on opposite sides of the metal. Due to the trans effect,<sup>25</sup> in the process of installing the two acetylides, they prefer to be *trans* to each other on the Pt(II) center unless the *cis*- geometry is enforced by chelating ligands such as 1,3-diphenylphosphinopropane (*dppp*). The *trans*-substituted complexes can also be converted to the *cis*-isomers by simply reacting with diphosphine chelating ligands (**Figure 1-9**, right).<sup>26</sup>



**Figure 1-9.** *Cis*- and *trans*-substituted Pt(II) bisacetylides with phosphine ancillary ligands, and an example of a *trans*-substituted Pt(II) bisacetylide transforming to its *cis*-isomer.<sup>26</sup>

The *cis*-substituted Pt(II) centers have been used in supramolecular assembly and synthesis of metal-containing macrocycles as templates for 90° geometries.<sup>27</sup> It is also known that *cis*-substituted Pt(II) acetylides with phosphine ancillary ligands can undergo oxidation (by I<sub>2</sub>) inducing reductive elimination to form coupled alkynes while the trans-substituted isomers cannot (**Figure 1-9**).<sup>28</sup> This reaction is useful in making conjugated C-C bonds between alkynes that are otherwise difficult to obtain due to structural tension or steric repulsion,<sup>29</sup> when the corresponding *cis*-substituted Pt (II) bisacetylides precursor is easier to synthesize.



**Figure 1-10.** Schematics of  $S_1$  and  $T_1$  states of polymer **15** and origin of its fluorescence and phosphorescence.

The photophysical properties of Pt(II) bisacetylides with phosphine ancillary ligands relies heavily on the properties of the conjugated ligand. For instance, absorption and emission properties of *trans*-substituted Pt(II) bisacetylide polymers indicates that  $S_1$  singlet excited states are delocalized between a few repeating units while the  $T_1$  excited states are only localized on one of the conjugated ligands (**Figure 1-10**). As a result, conjugated polymers of *trans*-Pt(II) bisacetylides with phosphine ancillary ligands shows phosphorescence that is not dependent on the conjugation length. In rare cases fluorescence from the  $S_1$  state is also observed, result in dual fluorescence and phosphorescence. This phenomenon can be enabled by low-lying triplet excited states of thiophene-containing conjugated ligands, which will be further discussed and explored in **Chapter 3**.

To sum up, in Pt (II) acetylides with phosphine ligands, the role of the metal atom is to facilitate ISC to triplet excited states, to provide communication between acetylide ligands in the singlet manifolds and to segregate ligand based triplet states.

#### 1.4.2 Photofunctional Pt(II) Acetylides with Polypyridyl Ligands

Pt (II) acetylides with polypyridyl ligands exhibit extensive electron delocalization over the entire  $\pi$ -system giving rise to intense charge transfer absorption and emission. The orbitals on the metal and the electron poor polypyridyl ligand are highly mixed, resulting in more complicated photophysics.

Scheme 1-5. Examples of common polypyridyl ligands.



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The first syntheses of Pt(II) acetylide photofunctional materials with bipyridine and terpyridine ligands (**Scheme 1-5**) were first reported by Yam<sup>30</sup> and Eisenberg,<sup>31</sup> respectively. Their light absorption and emission properties have been further investigated by Schanze<sup>32</sup> and Castellano<sup>33</sup> using nanosecond spectroscopy and ultrafast transient absorption spectroscopy. In general, with light excitation, these compounds undergo CT to the electron deficient polypyridyl ligand from Pt(II) (MLCT) or from the acetylide ligands (LLCT) (**Figure 1-11**). In cases where aromatic acetylides are used, MLCT/LLCT mixture is observed and LLCT contributes more when the acetylides are more electron-rich. The initial excited state after light absorption is the singlet state (e.g. <sup>1</sup>MLCT) which rapidly undergoes ISC to a triplet state (<sup>3</sup>MLCT) slightly lower in energy.



**Figure 1-11.** MLCT and LLCT using a terpyridyl Pt(II) acetylide complex as an example (left) and energetics of singlet and triplet MLCT excited states and LC excited states. The terpyridine ligand is highlighted in blue while the acetylide ligand is in red.

In some cases, the triplet CT state can further relax by transferring its energy to a low-lying <sup>3</sup>LC excited state localized on the acetylide ligand. In these cases, <sup>3</sup>LC of the acetylide is

"sensitized" with relatively low energy photon compared to direct excitation to its singlet  $\pi^*$  excited state <sup>1</sup>LC. Such processes can be very useful to encourage ligand based phosphorescence from <sup>3</sup>LC without undesired fluorescence from the <sup>1</sup>LC state, <sup>34</sup> and has also been used to encourage up-conversion using triplet-triplet annihilation.<sup>35</sup> The <sup>3</sup>LC state may also encourage fast NR from <sup>3</sup>LC state depending on the nature of the acetylide ligand.

Scheme 1-6. Terpyridyl Pt(II) acetylides for water reduction<sup>36</sup> and DSC applications.<sup>37</sup>



The charge transfer excited state of complex **86** was found to reduce water and generate  $H_2$  under visible light with the assistance of the methyl viologen cation  $MV^{2+}$  and Pt colloidal catalyst.<sup>36</sup> Yam *et al.* also developed a series of terpyridyl Pt(II) acetylide dyes including **87** and **88** with thiophene based ligands for DSC applications.<sup>37</sup>

Another outstanding feature of polypyridyl Pt(II) acetylides is their tendency to form aggregates.<sup>38</sup> The large planar conjugated system in polypyridyl Pt(II) acetylides allows tight stacking between molecules driven by  $\pi$ - $\pi$  dispersion attractions and metallophilic Pt-Pt interactions (**Figure 1-12**). The aggregation of Pt(II) polypyridyl complexes can be tuned by changing the substituents on the bipyridine and terpyridine ligand (R<sup>1</sup> in Figure 1-12). The ligands **83** and **85** in (**Scheme 1-5**) with bulky *t*-Bu groups can effectively prevent intermolecular

aggregation in both solution and solid state whereas non-substituted ligands 82 and 84 can give rise to significant  $\pi$ - $\pi$  stacking and Pt-Pt interactions with the addition of poor solvents.



Figure 1-12. Schematics of MLCT and MMLCT transitions.

Aggregation of a terpyridyl Pt(II) acetylides can give rise to a new type of electronic transition called metal-metal-to-ligand charge transfer (MMLCT). In **Figure 1-12**, the formation of aggregated dimer leads to interaction and splitting of the MOs of each individual molecule. The two Pt  $d_z^2$  orbitals can interact strongly and produce one "bonding" and one "antibonding" orbital with a larger energy gap than the  $\pi$ -orbitals. The "antibonding" orbital can be elevated to become

the HOMO which requires less energy to be promoted to the LUMO compared to monomeric complexes.

Therefore, the aggregation of terpyridyl Pt(II) acetylides can be identified in UV-Vis spectra with red-shifted, low energy MMLCT absorption bands. Similarly, MMLCT phosphorescence that is redshifted from monomeric MLCT emission is expected, arising from the corresponding <sup>3</sup>MMLCT triplet state relaxed from the initial <sup>1</sup>MMLCT state. Additionally, in <sup>1</sup>H NMR spectra, aggregation may also lead to peak broadening due to restricted rotation of substitutions, as well as up-field shifts of pyridyl proton signals due to the shielding effect of the folded aromatic rings.

Scheme 1-7. Terpyridyl Pt(II) acetylide 89 that is able to form emissive metallogels.<sup>39</sup>



Positively charged terpyridyl Pt(II) acetylides are stable as monomers in good solvents due to the static repulsion between cations. The intermolecular aggregation of these compounds can be encouraged by the addition of a poor solvent (a solvent that the compounds have very low solubility in) such as diethyl ether<sup>40</sup> to the solution of the compound, or using static attraction of negatively charged macromolecules such as RNA to overcome the static repulsion.<sup>41</sup> The

aggregation can also be used in metallophilic gelation of molecules containing these "sticky ends" and multiple long alkyl chains, such as **89**.<sup>39</sup> The metallogel formed by **89** in DMSO has a coillike superstructures under SEM, and give rise to strong MMLCT emission in the NIR region. A wide variety of applications in sensing have also been reported, using MMLCT absorption or emission feature as spectroscopic handles for negatively charged analytes.

Scheme 1-8. Binuclear Pt(II) containing foldamer by Che<sup>42</sup> (left) and Yam<sup>43</sup> (right).



*n* = 1(90), 2(91), 3(92), 4(93), 5(94), 6 (95) and 7(96)



Such Pt-Pt and  $\pi$ - $\pi$  interaction between Pt(II) "sticky ends" can also be used to encourage conformation changes of the conjugated backbone. Che<sup>42</sup> *et al.* reported foldable dimers **90-06** with an *ortho*-phenylene ethynylene backbone with 60° angles (**Scheme 1-8**, left). By adding water into an acetonitrile (CH<sub>3</sub>CN) solution of these compounds, the emission is red-shifted which is attributed to inter- and/or intramolecular aggregation of terpyridyl Pt(II) moieties. A TEM image of **94** shows that the aggregate forms nanoparticles in a H<sub>2</sub>O/CH<sub>3</sub>CN mixture.

A similar system of binuclear complexes **91- 101** is reported by Yam<sup>43</sup> *et al.* featuring a meta-phenylene ethynylene backbone with 120° angles (**Scheme 1-8**, right). Only **101** can offer a full 360° turn to form effective intramolecular Pt-Pt interactions, evidenced by red-shifted

MMLCT features in UV-Vis and phosphorescence spectra, upon changing the solvent from CH<sub>3</sub>CN to dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>). This work was followed by the preparation of chiral binuclear Pt(II) helical structures enabled by enantiomeric pure binaphthalene containing bisacetylide ligands.<sup>44</sup> The aggregation results in changed circular dichroism. These systems are considered to be a synthetic mimic of the chiral helical structure in biological systems and foldamers.<sup>44</sup>

## 1.5 Photofunctional Conjugated Materials Containing Lewis Acidic Boron Groups

A Lewis acid is a molecule with empty orbitals that can accept a pair of electrons from a donor while a Lewis base is a molecule that can provide such a pair of electrons. Lewis acids tend to bind with Lewis bases to form Lewis adducts.

Three-coordinated boron is especially suitable for photofunctional materials when integrated with conjugated materials due to the good orbital overlap of the empty p orbital with the  $\pi$ -system.<sup>45</sup> The electron-demanding nature can give rise to CT excited states with suppressed NR decay.<sup>46</sup> These conjugated materials containing Lewis acidic boron centers are usually highly fluorescent in contrast to their transition metal-containing counterparts, which are usually phosphorescent due to fast ISC. Additionally, the Lewis acid has unquenched chemical reactivity towards binding Lewis bases, which can be applied in sensing<sup>47</sup> applications or anionic supermolecular recognition.<sup>48</sup>

#### **1.5.1 Small Conjugated Molecules**

In 2000, Yamaguchi *et al.* reported an anthracene-based molecule **102** which allows the conjugation of three conjugated aromatic groups to delocalize through the empty *p* orbital of boron (**Scheme 1-10**, left).<sup>49</sup> It also gives rise to a CT excited state that localizes on the boron atom. Compound **102** is found to react with fluoride ion in a 1:1 molar ratio to give **103**, accompanied by reduced conjugation and disappearance of CT absorption in the UV-Vis spectrum. This group also reported **104** with boron "side-on" (**Scheme 1-10**, right),<sup>50</sup> which allows change of the LUMO from boron-based in **104** to  $\pi$ \* based in **105**, giving rise to either CT emission or  $\pi$ - $\pi$ \* emission.

Scheme 1-10. Lewis acidic compounds 102<sup>49</sup> and 104<sup>50</sup> binding with fluoride anion.



Scheme 1-11. Boron containing heterocycles.<sup>51</sup>



Conjugated systems with Lewis acidic boron can be built based on two important type of boron containing heterocycles shown in **Scheme 1-11**. Type I is an anti-aromatic five-membered

borole ring which is isoelectronic to the 1,3-cyclopentadiene cation as described by Yamaguchi<sup>51a</sup> *et al.*, while Type II is the aromatic seven-membered borole compounds isoelectronic to tropylium cation as described by Piers *et al.*<sup>51b</sup> Both types can be synthesized from the corresponding organotin precursor. For instance, the synthesis of the seven-membered borole **108** involves the transformation of **106** to **107** followed by installation of a bulky R group such as the mesityl group (Mes, 2,4,6-trimethylphenyl) to protect the empty *p*-orbital of boron.<sup>51b</sup> It is shown that the aromatic Type II heterocycles can undergo similar reaction as the benzene analogs, such as bromination by electrophilic aromatic substitution and palladium-catalyzed coupling reactions, which allows construction of larger conjugated systems.<sup>52</sup>



Figure 1-14. Synthesis and emission colors of boron-containing bithiophene derivatives.<sup>46</sup>

A bithiophene-based conjugated system with a 3-coordinate boron group in the 3-position of one of the thiophene rings has also been developed by the Yamaguchi group (**Figure 1-14**).<sup>46</sup> Lithiation of **109** with *n*-BuLi followed by installation of the boron group using-BMes<sub>2</sub> gives **110** 

which can be brominated under mild condition to afford **111**. Molecules **112-116** with various substitutions can be synthesized by reacting **111** with corresponding aryl boronic acids under Suzuki coupling conditions. All these compounds are stable in coordinating solvents and stable to oxidation in air in that the empty p orbital of the boron is "blocked" by the *ortho*- methyl groups of the mesityl groups on boron.

Compounds **110** and **112-116** are highly emissive compounds in both solution and the solid state. The photophysical process can be described as shown in **Figure 1-4**: Upon excitation, the electron-rich bithiophene backbone undergoes CT to the -BMes<sub>2</sub> group resulting in an excited state that is heavily localized on the boron atom. Such CT excited states give rise to very efficient fluorescence due to weak NR decay. The emission color can be red-shifted with added conjugation and the presence of more electron-donating groups on the bithiophene backbone as they elevate the energy of the  $\pi$ -bonding HOMO without notably changing the LUMO energy. Additionally, the bithiophene backbone is significantly twisted out of the plane (e.g. 56.0° torsion angle in **110**) resulting in poor intermolecular  $\pi$ - $\pi$  interaction and high emission quantum yield in the solid state. An interesting feature of this system is that the synthetic method can be easily adapted to make larger conjugated systems, either oligomeric or polymeric.

#### 1.5.2 Conjugated Oligomers and Polymers

Polymeric conjugated materials containing multiple Lewis acidic boron groups can be made by either coupling the monomers via boron atoms using boration reactions, or via carbon atoms using Pd catalyzed coupling reactions. Scheme 1-12. Preparation of main-chain boron-containing polymers via hydroboration<sup>53</sup> and halo-phenylboration.<sup>54</sup>



The first well-characterized polymers were obtained by hydroboration of bisacetylides using arylboranes MesBH<sub>2</sub> (**Scheme 1-12**, left), reported by the Chujo group.<sup>53</sup> The resulting polymers are oxygen stable and strongly blue-emissive. The molecular weight of polymer **119** are as high as 16000 ( $M_n$ ). Boron-containing polymers can also be obtained using halo-phenylboration reactions between bisacetylides and Ph<sub>2</sub>BBr, also reported by the same group (**Scheme 1-12**, right)<sup>54</sup> with a lower degree of polymerization.



Scheme 1-13. Preparation of main-chain boron-containing polymers via tin-boron exchange.<sup>55</sup>

Scheme 1-14. Preparation of main-chain boron-containing polymers via coupling reactions.<sup>56</sup>



The Jäkle group has explored another approach via highly selective tin-boron exchange reactions (**Scheme 1-13**, right).<sup>55</sup> Compound **124** can be made from **123**, which then reacts in a 1:1 molar ratio with **123** to give polymer **125** containing reactive B-Br bonds. Compound **125** can then react with aryl Cu(I) reagents to allow installation of a bulky aryl group such as a mesityl or 2,4,6-tri(*i*-propyl)phenyl (TIP) group, and obtain polymers **126** and **127**, respectively.

Recently, the Jäkle group reported the synthesis of thiophene containing conjugated polymers analogs to **126** and **127**, using a C-C coupling approach.<sup>56</sup> Both the monomer **129** and monomer **130** can be prepared from a non-substituted precursor **128** via either deprotonation-stannylation or iodination reactions at the  $\alpha$  position of the thiophene rings.

#### **1.5.3 Reactions with External Lewis Bases**



**Figure 1-15.** Reaction of a  $\pi$ -conjugated Lewis acid with external Lewis bases.

Reactions with Lewis bases will give rise to major photophysical changes to a conjugated system with Lewis acidic boron centers installed (**Figure 1-15**). The empty *p* orbital on boron can be filled and transformed into a  $\sigma$  bonding orbital with the Lewis base. This results in quenched Lewis acidity of the material and disappearance of corresponding CT absorption and emission bands. Additionally, the conjugation between the aromatic groups on the boron center will decrease, resulting in more localized  $\pi$ - $\pi$ \* transitions. Structure-wise, the geometry of the boron atom changes from trigonal planar to tetrahedral with the C-B-C bond angles going from ~ 120 ° to ~108 °. The C-B bonds will also lengthen due to decreased bond orders.

Most photofunctional materials with Lewis acidic boron centers have bulky aromatic groups on the boron atom to increase their stability. Therefore, many such materials can only react with a limited scope of small Lewis bases such as fluoride anions, cyanide anions and pyridine.

For instance, in sensory applications for fluoride anions, reactions with the analyte results in CT fluorescence turn-off. This process can be reversed to recover the unbound free Lewis base

with addition of water which strongly hydrogen bonds to fluoride anion with much higher affinity. However, for the same reason, most boron-based fluoride-sensing molecules do not work in aqueous medium unless their affinity towards fluoride anions are enhanced by a second interaction. A few fluoride binding molecules are shown in **Scheme 1-15**. Compound **132** has strong affinity for fluoride because the resulting Lewis adduct is stabilized by cooperative binding with the adjacent boron center.<sup>57</sup> Compound **135** binds to fluoride anion stronger than **133** and **134** due to the favourable Coulombic attraction of the positively charged phosphonium cation as well as "chelation" effect of the interaction between the fluoride and the P atom in the adduct **136**.<sup>58</sup> Many boron-based fluorescent sensor molecules with different colors have been developed based on these principles.





Yam *et al* showed that reaction of the Lewis acidic center can be used to modulate photoisomerization of the  $\pi$ -conjugated system (Scheme 1-16).<sup>59</sup> The photo-induced ring closing of the dithienylethene (DTE) moiety involves the  $6\pi$  conrotatory cyclization of the  $\pi^*$  orbitals. Molecule 72 with a Lewis acidic center has a boron-centered CT excited state that is lower in energy than the  $\pi^*$  orbital, thus the latter cannot be effectively populated. Therefore, **72** can't undergo light induced ring-closing while **73**, with a favorable  $\pi - \pi^*$  transition, can.



Scheme 1-16. Molecular switches 138 and 139.<sup>59</sup>

Scheme 1-17. Photochemistry of Lewis adduct 141<sup>60</sup> and 143.<sup>61</sup>



In some cases, the Lewis base can only bind weakly to the boron center and is, therefore, "hemilabile". These systems can exhibit interesting photo-induced changes. For example, the 2,6-lutidine moiety in Lewis adduct **141** can migrate to the 2-position of the four-membered borole ring under irradiation at low temperature. The resulting isomer **142** can revert to **141** at elevated temperatures.<sup>60</sup> Strained Lewis adduct **143** can undergo photo-induced dissociation of the Lewis base, releasing the free Lewis acid **144** that emits at higher wavelengths.<sup>61</sup>

#### **1.5.4** Interactions with Internal Lewis Bases

The 3-coordinate boron center can also interact with internal Lewis bases to either form Lewis adducts or remain unreacted pairs. The latter case is often due to steric hindrance or low reactivity of the Lewis base.

The Wang group has studied 4-coordinate N,C-chelated borates which are intramolecular adducts between the Lewis basic pyridine-ring and the Lewis acidic -BMes<sub>2</sub> group.<sup>62</sup> While similar N,N-chelates such as **145** based on the bipyridine backbone are stable OLED materials,<sup>63</sup> these molecules exhibit interesting photo-reactivity (**Scheme 1-18**). Under UV-light, **146** is transformed to another adduct **147** with a boron containing 3-membered ring. The mechanism involves photo-reactive triplet excited states as the isomerization can be inhibited by triplet acceptors.<sup>64</sup>

Scheme 1-18. Lewis adducts 145,<sup>62</sup> 146<sup>63</sup> and 147.<sup>63</sup>



Scheme 1-19. Compounds 31<sup>65</sup> and 32.<sup>66</sup>





Lewis adduct, 31

Frustrated Lewis Pair, 32

The Wang group has investigated a Lewis acid-base containing naphthalene-based system **31** with a phosphine-borane interaction (**Scheme 1-19**, left).<sup>65</sup> The P-B interaction is evidenced by chemical shifts in the <sup>31</sup>P NMR spectra as well as <sup>11</sup>B NMR spectra. Mebs *et al.* showed that such interaction can be interrupted or "frustrated" by using a rigid acenaphthene bridge which enforces a longer P-B distance.<sup>66</sup> The resulting molecule **32** shows <sup>31</sup>P NMR and <sup>11</sup>B NMR chemical shifts typical for free phosphine and boranes.

Scheme 1-20. Reaction of intramolecular Lewis pair 148.<sup>67</sup>



Frustrated Lewis pairs (FLPs) are interesting systems where free Lewis acid and base coexist without forming adduct due to steric reasons. They often exhibit special cooperative reactivity of the Lewis acid and base. An interesting example of a FLP was reported in the context of conjugated materials by Yamaguchi *et al.* (Scheme 1-20).<sup>67</sup> The frustration of the Lewis acid and Lewis base in 148 can add to the acetylene bridge in a *5-endo-dig* fashion to form ladder-like structure 149.

## 1.6 Goals and Scope

The goal of this thesis is to synthesize and characterize photo-functional molecules based on thiophene-containing conjugated molecules. Specifically, I've focused my research on tunable absorption and emission properties of conjugated molecules with two types of functionalities: square planar Pt(II) acetylides (Chapters 2 and Chapter 3), and 3-coordinated Lewis acidic boron groups (Chapter 4 and Chapter 5).

Chapter 2 explores thiophene-containing complexes with two identical square planar terpyridyl Pt(II) metal centers. Flexible thiophene-containing conjugated ligands are designed to facilitate Pt-Pt and  $\pi$ - $\pi$  interaction between metal centers, which give rise to MMLCT-based absorption and emission. Inspired by the work by Che and Yam, modulation of the folding/unfolding of the structure by changing the solvent environment, monitored by UV-Vis and photoluminescence spectra is explored in Chapter 2.

Chapter 3 examines the emission properties of three Pt(II) bisacetylide metallacycles with thiophene-containing ligands. The ligands are modified systematically to change the S<sub>1</sub> and T<sub>1</sub> excited state energies of the corresponding metallacycles, resulting in room-temperature dual emissive materials with tunable fluorescence/phosphorescence (FL/PH) ratios.

Scheme 1-21. Bithiophene based interacting Lewis acid-base pair.



Chapter 4 sets out to explore intramolecular interactions between a boron-containing Lewis acid and a phosphine oxide Lewis base, based on a flexible bithiophene skeleton (**Scheme 1-21**). The bound/unbound states of the Lewis acid-base pair exhibit different emission properties, and

are shown to be in equilibrium with each other as evidenced by UV-Vis, fluorescence, infrared (IR) and <sup>31</sup>P NMR spectra. Chapter 4 also contains an exploration of the impact of solvent and temperature on this equilibrium.

More intramolecular Lewis bases are explored based on the findings in Chapter 5. Additionally, the effect of the conjugation lengths and electron densities on the backbone are systematically explored using a series of molecules with different emission colors in two states. The use of such a binary equilibrium as a fluorescent probe to indicate hydrophilic/hydrophobic environments in biological samples is also attempted.

# Chapter 2 Platinum(II) Terpyridine Pacman Complexes with Thiophene-Containing Alkynyl Ligands

#### 2.1 Introduction

Functional oligothiophenes have attracted attention for their application in organic light emitting devices (OLEDs), organic photovoltaic cells (OPVs) and in chemical/biological sensors.<sup>68</sup> Conformational control of the conjugated backbone is critical to the functionality of these molecules since the effective  $\pi$ -conjugation length is determined by torsion along the backbone.<sup>69</sup> Stimuli responsive torsion of oligothiophene backbones is interesting as it allows access to variable conjugation lengths in the backbone, thus providing control over electronic and photophysical properties. Photoisomerizable moieties,<sup>70</sup> cation binding sites,<sup>71</sup> and switchable transition metal centers<sup>72</sup> have all been introduced to oligothiophene backbones to alter conformation in different physical or chemical environments. Approaches that utilize supramolecular interactions to achieve this, however, have scarcely been explored, with only a few reported cases to date.<sup>73</sup> Differing molecular packing modes as a result of altered oligothiophene backbone conformation have rarely been studied, even though packing can have a profound impact on the performance of bulk optoelectronic molecular materials.<sup>74</sup>

Recently, square planar alkynylplatinum terpyridine complexes have been explored as tools to encourage reversible aggregation via their  $\pi$ - $\pi$  stacking propensities. The aggregate-dependent spectroscopic (NMR, UV-Vis and luminescence) properties of these complexes can be used to

report aggregation.<sup>75</sup> Attaching alkynylplatinum terpyridine end groups to flexible organic ligands such as meta-/ortho-phenyleneethynylene oligomers, Yam<sup>43</sup> and Che<sup>42</sup> were able to obtain solvent-dependent and temperature-responsive materials which form folded/helical structures under certain conditions (**Scheme 1-8**). Other metal groups have been previously used to template the folding of oligoamides<sup>76</sup> and other systems.<sup>77</sup>

Scheme 2-1. Pt(II) terpyridine complexes synthesized in this chapter.



Foldable structure of  $Pt_2a_2T_3$ -OTf (2)



In this Chapter, two foldable Pt(II) terpyridine complexes 2 and 3 using thiophenecontaining ligands that tethers two alkynylplatinum terpyridine moieties are reported. Solid state crystal structures of 2 with the coplanar alkynylplatinum terpyridine moieties folded and unfolded, leading to torsion of the flexible terthiophene linker, are obtained. The "Pacman-like" behavior of these complexes is studied in solution by <sup>1</sup>H NMR, NOESY NMR, and UV-Vis absorption spectroscopy.

## 2.2 Results and Discussion

### 2.2.1 Synthesis and Solid-state Structures

Scheme 2-2. Synthesis of complexes PtHa<sub>2</sub>T<sub>3</sub>-OTf (1) and Pt<sub>2</sub>a<sub>2</sub>T<sub>3</sub>-OTf (2).



Scheme 2-3. Synthesis of complexes Pt<sub>2</sub>a<sub>2</sub>TCCT-OTf (3).



The bimetallic and monometallic complexes shown in Scheme 2-2 and Scheme 2-3 were

synthesized in good yields from precursor [( ${}^{t}Bu_{3}tpy$ )PtCl](OTf) (**4**) and terthiophene-based ligand H<sub>2</sub>a<sub>2</sub>T<sub>3</sub> (**5**) or H<sub>2</sub>a<sub>2</sub>TCCT (**6**). All reactions were carried out under a N<sub>2</sub> atmosphere using standard Schlenk techniques. The synthesis of the ligand **5**<sup>78</sup>, **6**<sup>79</sup> and precursor **4**<sup>80</sup> has been previously reported. Mono-metalation of **5** by **4** gave PtHa<sub>2</sub>T<sub>3</sub>-OTf (**1**), and bimetalation of **5** and **6** gave complexes Pt<sub>2</sub>a<sub>2</sub>T<sub>3</sub>-OTf (**2**) and Pt<sub>2</sub>a<sub>2</sub>TCCT-OTf (**3**). Complexes with perchlorate counter ions were also prepared and showed similar photophysical properties to the complexes with PF<sub>6</sub><sup>-</sup> counter ions.



**Figure 2-1.** (a) Structure of one of the "folded" **2** molecules in the crystal obtained from  $CH_3CN$ . (b) Structure of "unfolded" **2** obtained from  $CHCl_3$  (hydrogen atoms, *tert*-butyl groups and solvent molecules have been omitted for clarity in both cases, thermal ellipsoids drawn at 50% probability).

Two crystal structures of the bimetallic complex **2** were obtained: one "folded" structure from CH<sub>3</sub>CN ( $2 \cdot 3$ CH<sub>3</sub>CN, **Figure 2-2**), and an "open" structure from a chloroform (CHCl<sub>3</sub>) solution ( $2 \cdot 5$ CHCl<sub>3</sub>, **Figure 2-3**). In the structure of the folded complex crystallized from CH<sub>3</sub>CN, the thiophene rings adopt S-C-C-S torsion angles of 172.35° and 153.70°, slightly twisted from an all-trans conformation of terthiophene. The spatial proximity of the two terminal alkynes allows the two alkynylplatinum terpyridine moieties to be almost parallel to each other with a small dihedral angle of only 1.89° between planes (**Figure 2-1a**). The bulkiness of the peripheral *tert*butyl groups on the pyridine rings keeps the two intramolecular terpyridine planes at interplane distances of 3.62 to 4.06 Å from one another, while the pyridine rings interact more strongly with the closest alkynyl groups (distance = 3.34 and 3.52 Å). The side view of this structure resembles a closed Pacman figure (**Figure 2-1a**). By contrast, the structure obtained from CHCl<sub>3</sub> is similar to an open Pacman (**Figure 2-1b**). The thiophene rings in the unfolded **2**·5CHCl<sub>3</sub> structure are further twisted from the all-trans conformation with S-C-C-S torsion angles of 144.82° and 143.76°. The two terpyridine planes in the molecule open up in the unfolded structure, resulting in a dihedral angle of 58.98°. As a result, no intramolecular  $\pi$ - $\pi$  interaction is observed in this case, and an open cavity is created between the terpyridine planes (**Figure 2-1b**).



**Figure 2-2.** ORTEP structure of  $2 \cdot 3$ CH<sub>3</sub>CN. Anions, hydrogen atoms, CH<sub>3</sub>CN molecules and minor disordered fragments have been removed for clarity.



**Figure 2-3.** ORTEP structure of **2**·5CHCl<sub>3</sub>. Anions, hydrogen atoms, CHCl<sub>3</sub> molecules have been omitted for clarity.



**Figure 2-4.** ORTEP structure showing (a) C-H···O and C-H···Cl hydrogen bonds in the crystal structure of 2.5CHCl<sub>3</sub>, and (b) Cl- $\pi$  interactions in the same structure.

Interestingly, one of the CHCl<sub>3</sub> molecules in the 2.5CHCl<sub>3</sub> structure is captured in the open cavity of the Pacman structure and anchored to the cation by the triflate counter ion with C-H···O hydrogen bonds (**Figure 2-4a**). The remaining four solvent molecules form a network of weak C-H···Cl hydrogen bonds,<sup>81</sup> with two of them connected to the triflate counter-ion by C-H···O

hydrogen bonds.<sup>82</sup> Two different modes of Cl- $\pi$  interactions are present in the structure,<sup>83</sup> an edgeon mode with Cl···C contacts and a face-on mode with a short Cl to centroid distance (**Figure 2-4b**).<sup>84</sup> Some disorder is found in the **2**·3CH<sub>3</sub>CN structure in both solvent molecules and the *tert*butyl groups. By contrast, in the **2**·5CHCl<sub>3</sub> structure, there are five CHCl<sub>3</sub> molecules surrounding each bimetallic cation, and all the solvent molecules, cations and anions are highly ordered (**Figure 2-4a**). The open Pacman structure appears to be stabilized by these weak intermolecular C-H···O hydrogen bonds, C-H···Cl hydrogen bonds and Cl- $\pi$  interactions. Together, these weak interactions are sufficient to overwhelm the tendency of the conjugated backbone to maintain coplanarity between thiophene rings and the  $\pi$ - $\pi$  interactions that keep the structure closed in the **2**·3CH<sub>3</sub>CN crystals. Recently, Cl- $\pi$  interactions have been recognized as important in biology,<sup>83,85</sup> however here a case is presented where this interaction is shown to be involved in the conformation of a synthetic foldable structure.

The two different conformations of the Pacman molecules also result in changes in molecular packing. In the 2·3CH<sub>3</sub>CN structure (**Figure 2-5a**, **b**), identical molecules form chiral helical columns, in which each molecule is rotated 120° about the *c*-axis with respect to the one above it. Moreover, columns with the same chirality organize into a hexagonal packing arrangement, in which only one of the stereoisomers of the bimetallic complex is found. In the 2·5CHCl<sub>3</sub> structure, however, the bimetallic complex forms infinite zigzag chains with racemic molecules (**Figure 2-5c**, **d**). This may be driven by intermolecular  $\pi$ - $\pi$  interactions between head-to-tail stacked alkynylplatinum pyridine moieties (shortest interplane distance ~3.35 Å), which are weaker in the helical structure.



Figure 2-5. (a) Helixes in the structure of  $2 \cdot 3 \text{CH}_3 \text{CN}$ . (b) Top view of chiral columns formed by a single stereoisomer of the binuclear complex. (c) Zigzag chains in the structure of  $2 \cdot 5 \text{CHCl}_3$ . (d) Top view of the chains in  $2 \cdot 5 \text{CHCl}_3$ . Hydrogen atoms, *tert*-butyl groups, solvent molecules and counter-ions have been omitted for clarity in all cases.

#### 2.2.2 Electronic Absorption and Emission Spectra



**Figure 2-6.** UV-vis absorption spectra of **1** in CHCl<sub>3</sub> with increasing percentage of CH<sub>3</sub>CN added (from 0 % to 100 %,  $5 \times 10^{-5}$  M). The inset shows the shift in the low energy MLCT/LLCT absorbance band.

The monometallic complex **1** is bright orange in CH<sub>3</sub>CN solution. The UV-vis absorption spectra in CHCl<sub>3</sub> to which an increasing amount of CH<sub>3</sub>CN is added (**Figure 2-6**), show an intense absorption feature at 300-350 nm assigned to intraligand (IL)  $\pi \rightarrow \pi^*$  transitions of the terpyridyl and alkynyl moieties. Features between 350 nm and 450 nm are attributed to  $\pi \rightarrow \pi^*$  transitions of terthiophene. The low-energy band between 450-600 nm is assigned as a MLCT/LLCT (mixed metal-to-ligand charge-transfer and alkynyl-to-terpyridine ligand-to-ligand charge transfer) transition. This band blue-shifts as increasing amounts of CH<sub>3</sub>CN are added to the CHCl<sub>3</sub> solution.

This negative solvatochromism is typically observed in alkynylplatinum (II) terpyridine complexes since the excited state is less polar than the ground state (**Figure 1-5**).<sup>42-43,86</sup>



**Figure 2-7.** UV-vis absorption spectra of **2** in CHCl<sub>3</sub> with increasing percentage of CH<sub>3</sub>CN added (from 0 % to 100 %,  $2.0 \times 10^{-5}$  M). The inset shows the change in the low energy absorbance band with an isosbestic point at ~550 nm.

The absorption spectra of the bimetallic complex 2 show significantly different behavior as a function of solvent composition. With increasing amounts of  $CH_3CN$  added to  $CHCl_3$ , the MLCT/LLCT absorption at 510 nm decreases while a new feature grows in at 530 nm, showing a clear isosbestic point (inset, **Figure 2-7**). Interestingly, this feature still shows subtle negative solvatochromism when the percentage of  $CH_3CN$  present is greater than 50% (**Figure 2-8**), indicating that this new feature still maintains its MLCT/LLCT character. Intermolecular aggregation can be ruled out as an explanation for this behavior since the extinction coefficient of
this absorbance remains constant from 1.14 to 100  $\mu$ M (**Figure 2-9**). Similar phenomena have also been reported in other di-platinum complexes with flexible linkages,<sup>42-43</sup> and this behavior is consistent with the formation of a folded structure in solution. The absorbance of the  $\pi \rightarrow \pi^*$ (alkynyl) shoulder at 340 nm, and the  $\pi \rightarrow \pi^*$  (terthiophene) transition at 380 nm, decreases with the addition of increasing amounts of CH<sub>3</sub>CN to CHCl<sub>3</sub>. Both of these changes are not observed in the monometallic complex, and are consistent with conformational changes of the ligand resulting from the formation of the closed Pacman structure in solution.



Figure 2-8. Subtle negative solvatochromism of 2 when CH<sub>3</sub>CN is greater than 50 vol %  $(2.0 \times 10^{-5} \text{ M})$ .



**Figure 2-9.** UV-Vis absorbance spectra of **2** in CH<sub>3</sub>CN, from 1.14 to 100  $\mu$ M. Inset: Plot of the absorbance at 530 nm as a function of concentration.

A similar bidentate ligand **6** was employed to make complex **3**. UV-vis spectra of **3** in CHCl<sub>3</sub> solution with increasing amount of CH<sub>3</sub>CN content are shown in **Figure 2-10**. In CHCl<sub>3</sub>, the MLCT/LLCT low energy absorption of **3** shows a maximum at 470 nm higher in energy than that of **2** (510 nm). Similar to **2**, with higher CH<sub>3</sub>CN content, the ligand based  $\pi \rightarrow \pi^*$  absorption of **3** between 350-390 nm increases, and a low energy tail grows in while MLCT/LLCT band at 470 nm decreases in intensity with a isosbestic point at 510 nm. These features show that excited states involved in the MLCT absorption processes are higher in energy in **3** compared to **2**, and that **3** is also capable of folding/unfolding conformational changes in similar conditions. No emission was observed in solution from **1**, **2** or **3**, possibly due to energy transfer quenching from low-lying, ligand-based triplet states on the terthiophene containing ligand moiety. Yet **3** is emissive in the solid state where hindered molecular motions lead to less favorable thermal non-radiative

processes (spectra shown in **Figure 2-11**). The two broad emission features observed at 610 nm and 700 nm are unassigned.



**Figure 2-10.** UV-vis absorption spectra of **3** in CHCl<sub>3</sub> with increasing percentage of CH<sub>3</sub>CN added (from 0 % to 100 %,  $1.5 \times 10^{-5}$  M).



Figure 2-11. Solid state emission spectra of 3 on glass slides (background subtracted).

### 2.2.3 NMR Spectra

<sup>1</sup>H NMR experiments were carried out to further investigate the molecular behavior in solution. The pyridine protons on the bimetallic complex appear at a lower chemical shift compared to those of the monometallic complex. They are also shifted upfield in CD<sub>3</sub>CN relative to the signals in CDCl<sub>3</sub> (**Figure 2-12**). This is typically observed in systems with  $\pi$ - $\pi$  interactions.<sup>43,87</sup> Furthermore, variable temperature NMR experiments with the bimetallic complex showed no significant shift or broadening in CDCl<sub>3</sub> (**Figure 2-13**). In CD<sub>3</sub>CN, however, the pyridine protons are broadened and shifted upfield at lower temperatures, while the thiophene proton signals are only slightly altered (**Figure 2-14**). These changes are consistent with restricted rotation of the alkynylplatinum terpyridine moieties and stronger  $\pi$ - $\pi$  stacking.



**Figure 2-12.** Partial <sup>1</sup>H-NMR spectra (aromatic region) of **1** in (a) CDCl<sub>3</sub> and (b) CD<sub>3</sub>CN, **2** in (c) CDCl<sub>3</sub> and (d) CD<sub>3</sub>CN. Pyridine protons are labeled.



Figure 2-13. Variable temperature <sup>1</sup>H NMR spectra of complex 2 in CDCl<sub>3</sub>.



Figure 2-14. Variable temperature <sup>1</sup>H NMR spectra of complex 2 in CD<sub>3</sub>CN.

NOESY experiments of **2** (mixing time =  $0.8 \ \mu s$ ) show cross peaks between the *tert*-butyl protons and the thiophene protons in CD<sub>3</sub>CN (**Figure 2-15**), indicating spatial proximity of these protons, that is absent in CDCl<sub>3</sub> (**Figure 2-16**). An intermolecular origin of these cross peaks can be excluded since they are absent in **1** (**Figure 2-17**). These results are consistent with the unfolding of the molecule in CDCl<sub>3</sub> and folding in CD<sub>3</sub>CN, analogous to the conformations observed in the solid state structures obtained from the respective solvents.



Figure 2-15. Partial NOESY spectrum of 2 in CD<sub>3</sub>CN.



Figure 2-16. Partial NOESY spectrum of 2 in CDCl<sub>3</sub>.



Figure 2-17. Partial NOESY spectrum of 1 in CD<sub>3</sub>CN.

# 2.2.4 Density Functional Theory (DFT) Simulations

Density functional theory (DFT) calculations were carried out to find the optimized geometry of folded and unfolded cations of molecule 2 and 3 in solutions with PCM<sup>88</sup> solvation model without interaction with their triflate anions.



Figure 2-18. Optimized structure of folded and unfolded 2 in CH<sub>3</sub>CN and CHCl<sub>3</sub>.



Figure 2-19. Optimized structure of folded and unfolded 3 in CH<sub>3</sub>CN and CHCl<sub>3</sub>.

The geometry optimized structures of **2** (**Figure 2-18**) show angles of  $9.6^{\circ}$  and  $57.1^{\circ}$  between two platinum terpyridine moieties in CH<sub>3</sub>CN and CHCl<sub>3</sub> respectively, in line with  $1.9^{\circ}$  for the folded structure and  $59.0^{\circ}$  for the unfolded structure in the solid state. Similarly, by DFT calculation, **3** (**Figure 2-19**) shows angles of  $7.5^{\circ}$  and  $86.5^{\circ}$  between two platinum terpyridine moieties in CH<sub>3</sub>CN and CHCl<sub>3</sub> respectively. It is intriguing that with only difference in dielectric constant, we are already seeing folding and unfolding of the cationic structure.

Even though the Pt-Pt distance in folded structures of **2** and **3** are too long (4.32 Å and 3.97 Å, respectively) for effective Pt-Pt bonds, the two Pt atoms still interact with each other through  $dz^2$ (Pt) orbitals. As depicted in **Figure 2-20** and detailed in **Table 2-1** and **Table 2-2**, the two  $dz^2$ (Pt) orbitals still interact in folded **2** and **3** structures to give a bonding MO and antibonding MO. By contrast in unfolded **2** and **3**, the MOs resulting from two  $dz^2$ (Pt) orbitals are mostly degenerate (with very small energy differences of 0.008 and 0.005 eV, respectively) with no effect on Pt-Pt bonding.

The intramolecular interaction between two  $dz^2(Pt)$  orbitals can be evaluated by the splitting (energy difference) of the resulting bonding and antibonding MOs (**Figure 2-20**), which is smaller in folded **2** (0.373 eV) than that in folded **3** (0.601 eV). However, both bonding and antibonding orbitals are lower in energy than HOMO thus populated with a pair of electrons, so the overall effect is still non-bonding. MMLCT absorption is not the lowest energy transition as in Che's and Yam's systems (**Scheme 1-8**, page 23) and depicted in **Figure 1-12** (page 21) since the Pt-Pt antibonding MO is still lower in energy compared to Pt +  $\pi$  MOs.



Figure 2-20. Interactions of  $dz^2(Pt)$  orbitals in 2 (up) and 3 (down).



Figure 2-21. Frontier MOs of geometry optimized 3 in CHCl<sub>3</sub> and CH<sub>3</sub>CN.

The frontier MOs of **3** are shown in **Figure 2-21**, and detailed in **Table 2-3** and **Table 2-4**. The lowest energy absorptions of **3** are attributed to MLCT/LLCT transitions, since HOMO and HOMO-1 orbitals are localized mostly on the conjugated bisacetylide ligands and partially on the metal centers while the LUMO and LUMO-1 orbitals are mostly on the Pt(II) polypyridyl moieties. The MLCT/LLCT absorption is lower in energy in the folded structures of **3** due to different degrees of energy splitting in HOMO and LUMO.

## 2.3 Experimental

#### 2.3.1 General

<sup>1</sup>H NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectrometer. All syntheses were carried out under a dry N<sub>2</sub> atmosphere using standard Schlenk techniques. Dry toluene and tetrahydrofuran (THF) were obtained after treatment with solvent purification system. All other chemicals were purchased from commercial sources, and used without further purification. <sup>1</sup>H NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectrometer, and chemical shifts are referenced to the residual protio-solvent signals. MALDI-TOF mass spectra were measured using a Bruker Autoflex MALDI-TOF mass spectrometer. UV-Vis absorption spectra were obtained on a Varian Cary 5000 UV-Vis-NIR spectrophotometer. Excitation and emission spectra were obtained on a Photon Technology International (PTI) QuantaMaster Fluorimeter and were uncorrected for lamp intensity.

#### 2.3.2 Synthesis

Copper(I) iodide (purum,  $\geq$  99.5%), diisopropylamine ( $\geq$  99.5%), 4,4',4''-tri-tert-butyl-2,2':6',2''-terpyridine (tbtpy, 95%) and lithium trifluoromethanesulfonate (96%) were purchased from Sigma-Aldrich and potassium tetrachloroplatinate(II) (K<sub>2</sub>PtCl<sub>4</sub>, 99.9%) were purchased from Strem Chemicals, Inc. All chemicals were used without purification. [('Bu<sub>3</sub>tpy)PtCl](OTf) (4)<sup>42</sup> and ligand 5<sup>89</sup> and 6 were synthesized according to literature. Pt<sub>2</sub>a<sub>2</sub>T<sub>3</sub>-OTf (**2**): A mixture of CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and diisopropylamine (15 mL) was sparged with nitrogen gas for 15 minutes, then added to a N<sub>2</sub> filled reaction vessel containing H<sub>2</sub>a<sub>2</sub>T<sub>3</sub> (**5**) (60 mg, 0.20 mmol) and **4** (312 mg, 0.40 mmol). The vessel was quickly sealed after introduction of CuI (1 mg), and the reaction mixture was stirred overnight at room temperature. The solvent was then removed under vacuum and the crude product purified by column chromatography on silica gel using a CH<sub>2</sub>Cl<sub>2</sub>-acetone mixture (5:1 v/v) as eluent, giving a dark red powder (231 mg, 65 %). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$  9.00 (d with Pt satellites, <sup>3</sup>*J* = 6.0 Hz, 4H, terpyridyl C*H*), 7.93 (d, <sup>4</sup>*J* = 2.0 Hz, 4H, terpyridyl C*H*), 7.88 (s, 4H, terpyridyl C*H*), 7.50 (dd, <sup>3</sup>*J* = 6.0 Hz, <sup>4</sup>*J* = 2.0 Hz, 4H, terpyridyl C*H*), 7.35 (s, 2H, thienyl C*H*), 7.31 (d, <sup>3</sup>*J* = 6.0 Hz, 2H, thienyl C*H*), 7.06 (d, <sup>3</sup>*J* = 6.0 Hz, 2H, thienyl C*H*), 1.44 (s, 18H, CH<sub>3</sub>), 1.41 (s, 36H, CH<sub>3</sub>). Positive MALDI-TOF: m/z = 743.7 [M-2OTf]<sup>2+</sup>, 1487.4 [M-2OTf]<sup>+</sup> and 1636.4 [M-OTf]<sup>+</sup>. For experimental and calculated isotopic pattern analysis of [M-2OTf]<sup>2+</sup> see **Figure A-1** and **Figure A-2**. Elemental analysis calc. for C<sub>72</sub>H<sub>76</sub>F<sub>6</sub>N<sub>6</sub>O<sub>6</sub>Pt<sub>2</sub>S<sub>5</sub>: C, 48.42; H, 4.29; N, 4.71. found: C, 48.02; H, 4.61; N, 4.36.

PtHa<sub>2</sub>T<sub>3</sub>-OTf (1): The same procedure used for **2** was followed except **5** (148 mg, 0.50 mmol) and **4** (196 mg, 0.25 mmol) were used. The crude product was purified by silica chromatography using a CH<sub>2</sub>Cl<sub>2</sub>-acetone mixture (10:1 v/v) as eluent, giving a red powder (130 mg, 51 %). <sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$  9.10 (d with Pt satellites, <sup>3</sup>*J* = 6.0 Hz, 2H, terpyridyl C*H*), 8.34 (s, 2H, terpyridyl C*H*), 8.26 (d, <sup>3</sup>*J* = 2.0 Hz, 2H, terpyridyl C*H*), 7.57 (dd, <sup>3</sup>*J* = 6.0 Hz, 1H, thienyl C*H*), 7.27 (d, <sup>3</sup>*J* = 6.0 Hz, 1H, thienyl C*H*), 7.18 (d, <sup>3</sup>*J* = 6.0 Hz, 1H, thienyl C*H*), 7.08 (s, 1H, thienyl C*H*), 6.96 (d, <sup>3</sup>*J* = 6.0 Hz, 1H, thienyl C*H*), 3.59 (s, 1H, alkynyl C*H*), 1.56 (s, 9H,

C*H*<sub>3</sub>), 1.40 (s, 18H, C*H*<sub>3</sub>). Positive MALDI-TOF: *m*/*z* = 445.6 [M-OTf]<sup>+</sup>. Elemental analysis calc. for C<sub>44</sub>H<sub>42</sub>F<sub>3</sub>N<sub>3</sub>O<sub>3</sub>PtS<sub>4</sub>: C, 50.76; H, 4.07; N, 4.04. found: C, 51.06; H, 4.24; N, 3.87.

Pt<sub>2</sub>a<sub>2</sub>TCCT-OTf (**3**): The same procedure used for **2** was followed except that ligand H<sub>2</sub>a<sub>2</sub>TCCT (**6**) (48 mg, 0.20 mmol) and **4** (312 mg, 0.40 mmol) were used. The crude product was purified by column chromatography on silica gel using a CH<sub>2</sub>Cl<sub>2</sub>-acetone mixture (5:1 v/v) as eluent, giving a red powder (207 mg, 60 %). <sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$  9.00 (d with Pt satellites, <sup>3</sup>*J* = 5.9 Hz, 4H, terpyridyl C*H*), 7.93 (d, <sup>4</sup>*J* = 1.6 Hz, 4H, terpyridyl C*H*), 7.88 (s, 4H, terpyridyl C*H*), 7.46 (d, <sup>3</sup>*J* = 5.2 Hz, 2H, thienyl C*H*), 7.50 (d, <sup>3</sup>*J* = 4.7 Hz, 4H, terpyridyl C*H*), 6.99 (d, <sup>3</sup>*J* = 5.2 Hz, 2H, thienyl C*H*), 1.42 (s, 18H, CH<sub>3</sub>), 1.41 (s, 36H, CH<sub>3</sub>). Positive MALDI-TOF [M-OTf]<sup>+</sup>: *m*/*z* = 1575.4190 calc. for C<sub>68</sub>H<sub>74</sub>N<sub>6</sub>O<sub>3</sub>F<sub>3</sub>S<sub>3</sub><sup>194</sup>Pt<sub>2</sub>, found: 1575.4213.

#### **2.3.3 DFT Simulations**

Calculations were carried out using the Gaussian 09 Rev.D01 suite of Programs.<sup>90</sup> The PBE0 hybrid functional<sup>91</sup> with 6-31G\* basis set (for C, H, S and P atoms) and the LANL2DZ effectivecore pseudopotential<sup>92</sup> (for Pt) was employed to simulate ground state S<sub>0</sub> structure of **2** and **3**. Structural coordinates from X-ray crystallography have been used as starting points of geometry optimizations for **2**. Optimized structures were confirmed to be the minimum on the potential energy surface by vibrational frequency calculations. Vertical absorptions are simulated using time-dependent density functional theory (TD-DFT) by looking at the first 20 low-energy electronic transitions. For all simulations, solvation effect of CHCl<sub>3</sub> ( $\varepsilon$  = 4.7113) or CH<sub>3</sub>CN ( $\varepsilon$  = 35.688) was implemented using the polarizable continuum model<sup>88</sup> (PCM) on Gaussian 09.



# **Table 2-1.** Molecular orbitals and relative energies of complex 2 involving $dz^2(\text{Pt})$ orbitals.

\* Energies are referenced to the MO with the lowest energy in the table.



**Table 2-2.** Molecular orbitals and relative energies of complex **3** involving  $dz^2(Pt)$  orbitals.

\* Energies are referenced to the MO with the lowest energy in the table.

MOs	eV	Top-view	Side-view
LUMO+1 (297)	-3.58		A CONTRACTOR OF A CONTRACTOR
LUMO (296)	-3.59		or a state of the
HOMO (295)	-6.60		and the second s
HOMO-1 (294)	-6.62		

Table 2-3. Molecular orbitals and energies of complex 3 orbitals in CHCl<sub>3</sub>.

### **TD-DFT simulated absorptions:**

Band A: 2.38 eV, 521 nm, oscillator strength f=0.2176.

HOMO-1  $\rightarrow$  LUMO (45 %) HOMO  $\rightarrow$  LUMO+1 (51 %)

Band B: 2.41 eV, 514 nm, oscillator strength f=0.1407.

HOMO-1  $\rightarrow$  LUMO+1 (33 %) HOMO  $\rightarrow$  LUMO (63 %)

MOs	eV	Top-view	Side-view
LUMO+1 (297)	-2.90		
LUMO (296)	-3.00		
HOMO (295)	-5.65		<b>Sources</b> Sources
HOMO-1 (294)	-6.32		Contraction of the second seco

Table 2-4. Molecular orbitals and energies of complex 3 orbitals in CH<sub>3</sub>CN.

### **TD-DFT simulated absorptions:**

Band A: 2.05 eV, 606 nm, oscillator strength f=0.0183.

 $\mathrm{HOMO} \to \mathrm{LUMO}$ 

Band B: 2.19 eV, 565 nm, oscillator strength f=0.0801.

 $HOMO \rightarrow LUMO+1$ 

# 2.4 Conclusions

In conclusion, a novel terthiophene based alkynylplatinum terpyridine Pacman complex 2 has been made, which exhibits reversible folding in both solution and solid state. Analogue 3 was synthesized from ligand 6 showing higher MLCT absorption energies, and also shows reversible folding in solution. In the cases of both 2 and 3, reversible torsion of the flexible thiophene-containing backbone in response to changes in the solvent environment have been successfully achieved via introduction of alkynylplatinum terpyridine moieties.

It is also revealed by DFT simulations that the two Pt atoms in folded 2 and 3 are able to interact even though there is no net bonding between them. Finally, as revealed by solid state structures in 2, Cl- $\pi$  interactions, along with weak C-H hydrogen bonding play a role in the folding/unfolding behavior of this synthetic foldable structure, one of the first observations of this behavior in a non-protein structure.

# **Chapter 3 Dual Emissive Platinum(II) Metallacycles**

# 3.1 Introduction

Heavy atom-induced spin-orbit coupling (SOC) has been widely used to encourage intersystem crossing (ISC) in organic molecules from singlet exited-states to triplet manifolds (**Figure 3-1**). For instance, iridium containing dyes allows highly efficient ISC and emission from both the triplet and singlet excited states, resulting in up to 100% internal efficiency in organic light emitting devices (OLEDs) using these materials. This is significantly higher than the 25% efficiency limit of most fluorescent compounds that only emit from their singlet excited states.<sup>93</sup>



**Figure 3-1.** Energy diagrams of electronic transitions involving GS and excited states ( $k_{ISC}$ ,  $k_{NR}$ ,  $k_{FL}$  and  $k_{PH}$  are rates of ISC, NR decay, fluorescence and phosphorescence, respectively).

According to the selection rules, any electronic transitions that change the total spin quantum number are "spin forbidden" due to conservation of the spin angular momentum of electrons (with

operator  $\hat{S}$ ). This is why ISC is very slow compared to "spin-allowed" transitions in systems containing only atoms in the first two rows on the periodic table. In heavy atoms, the interaction between the magnetic moment of the electron spin and orbiting nuclei (in the reference frame of the electron) is no longer negligible, the spin will couple with the orbital angular momentum of the electron (with operator  $\hat{L}$ ). The coupling strength can be defined using Hamiltonian  $\hat{H}_{SO}$  in **Equation 3-1**, where  $\zeta$  represent the SOC constant for atoms. The value  $\xi$  is found to rapidly increase with higher atomic numbers of the element ( $\xi \propto Z^4$ ).<sup>94</sup>

$$\hat{H}_{SO} = hc\xi\hat{L}\cdot\hat{S}$$
 ..... (Equation 3.1)

For instance, while  $\zeta$  for Na is only 0.1 kcal/mol (0.004 eV),  $\zeta_{5d}$  of Pt(II) in the 5d<sup>10</sup> configuration is 4129 cm<sup>-1</sup> (0.51 eV),<sup>95</sup> comparable with the energy gaps between electronic states. As the result of stronger SOC, the "spin flip" of the electron on heavier atoms becomes more favourable in heavy atoms.

In molecules, SOC leads to the mixing of singlet and triplet wave functions and the coupling coefficient  $\lambda$  is proportional to the spin-orbit coupling energy  $E_{so}$  in Equation 3.2.

$$\lambda = E_{so}/(E_s - E_T)$$
 ..... (Equation 3.2)

It is reported that ISC is much faster when corresponding frontier MOs of singlet and triplet states have a stronger contribution from heavy atoms since there is more involvement of atomic orbitals with higher angular momentum.<sup>24,96</sup> Therefore, in molecules with heavy metal centers such as platinum(II), it is possible to attenuate ISC by variating the relative contribution of the metal atom in related MOs, or by tuning the singlet-triplet ( $E_S - E_T$ ) energy gap (**Equation 3.2**), so that S<sub>1</sub> and T<sub>1</sub> states can both be populated upon excitation of the molecules. This also allows control

over fluorescence/phosphorescence (FL/PH) ratios which is potentially useful for various important applications such as white-emitting OLEDs<sup>97</sup>, ratiometric oxygen sensors<sup>98</sup> and hypoxia imaging in biological systems.<sup>99</sup> It is worth mentioning that limiting the non-radiative decay rates ( $k_{NR}$ ) in **Figure 3-1** is also crucial for these applications since such decay usually result in degraded performance and device overheating.

Scheme 3-1. Pt(II) bisacetylides 11,<sup>99</sup> 12,<sup>100</sup> 13<sup>101</sup>, 14<sup>102</sup> and 15.<sup>102</sup>

 $\begin{array}{c} & & & & & \\ PEt_3 & & & & \\ PEt_3 & & & \\ PEt_3 & & & \\ \end{array}$ 

Cis-substituted Pt(II) Bisacetylide Metallacycles

Trans-substituted Pt(II) Bisacetylides



Oligomers and polymers containing trans-substituted Pt(II) bisacetylide complexes (**Scheme 3-1**) have broad applications in non-linear optics materials, OLEDs, polymer solar cells and other molecular electronics applications,<sup>100</sup> and have been extensively studied. They typically exhibit high triplet yields and long-lived ligand-localized triplet excited states.<sup>24,103</sup> The strong

 $\sigma$ -donating ligands of trans-substituted Pt(II) bisacetylides reduces the non-radiative decay from excited metal *5d* states by elevating their energy. However, they still suffer from insufficient photo-stability and relatively low emission quantum efficiency for many applications due to relatively weak Pt-C bonds and thermal deactivation through rotations and vibrations in the molecule. Metallacycles containing *cis*-Pt bisacetylide metal centers were first reported almost two decades ago,<sup>101-102</sup> and were also found to give rise to very efficient ISC, thus have been considered good candidates as triplet sensitizers, and for non-linear optical applications.<sup>104</sup> Castellano *et al.* showed that metallacycles show enhanced light absorption compared to their non-cyclic analogues.<sup>104b,104c</sup> Additionally, the more rigid cyclic structure gives rise to suppressed thermal deactivation and thus higher emission quantum efficiency. Therefore, *cis*-Pt bisacetylide metallacycles with higher stability and room temperature tunable florescence and phosphorescence dual emission would be interesting for the applications discussed above, and remain unknown to date.





It is reported in molecules containing [*trans*-Pt(PR<sub>3</sub>)<sub>2</sub>(–C=C–Ar–C=C–)] units (**Scheme** 3-2, left), replacing the phenylene aryl groups in 11 with a thiophene rings results in lower T<sub>1</sub> states in molecule 16 with relatively unchanged energy gap between S<sub>1</sub> and T<sub>1</sub> states (term  $E_S - E_T$  in **Equation 3-2**). A similar effect was observed both in monomeric and polymeric 11 and 16, except the  $E_S - E_T$  gap is smaller in polymers.<sup>24</sup> Furthermore, when polymeric 11 was randomly blended with small percentage of repeating unit of 16, the resulting polymer shows preferential formation of triplet excited states on the thiophene containing segments due to localized lower T<sub>1</sub> states, known as "triplet traps".<sup>105</sup> In polymer 17, 18 and 19, the T<sub>1</sub> excited state is lowered even more when the ligand is extended in length from thiophene, bithiophene to terthiophene (**Scheme 3-2**, right), while the energy gap between S<sub>1</sub> and T<sub>1</sub> (term  $E_S - E_T$  in **Equation 3-2**) remains relatively constant.<sup>106</sup>

From **17** to **19**, the increasing number of thiophene rings reduces the influence of the heavy metal center which is mainly responsible for the intersystem crossing, making the  $T_1$  state less accessible. Additionally, a larger conjugated system gives rise to a lower energy  $T_1$  state which makes ISC less efficient from higher singlet excited states ( $S_n$ ). Therefore,  $S_1$  states are relatively more efficiently populated than  $T_1$  via fast IC processes resulting in stronger florescence.<sup>106</sup> These observations provide guidance to use similar strategies in phosphorescent platinum metallacycles to encourage stronger fluorescence, allowing room temperature dual fluorescence (FL) and phosphorescence (P) to be simultaneously observed with various FL/PH ratios.

In this chapter, three new cis-Pt(II) bisacetylides metallacycles **4**, **5** and **6** are discussed, and compared with complex **7**<sup>104c</sup> previously reported by Castellano *et al* (**Scheme 3-3**). Complex **7** provides a good starting point for these studies since it only shows green ligand-based phosphorescence at 497 nm in deaerated solutions. The effect of introducing thiophene rings at different positions in the ligand system while maintaining the cyclic structure is systematically explored, first by replacing the two phenyl rings in **7** with thiophene rings to give complex **4**. Similarly, by introducing one additional thiophene ring to **4** metallacycle **5** is formed. Finally, by changing the bridging acetylene in **7** to a thiophene ring **6** is obtained. Complex **5** is found to fluoresce while **6** and **7** show dual emission with different FL/PH ratios.

Scheme 3-3. Pt(II) bisacetylide metallacycles.



### 3.2 Result and Discussion

### 3.2.1 Synthesis

Metallacycles **4**, **5** and **6** were synthesized using a modification of Hagihara's method<sup>107</sup> using TMS-protected bidentate pro-ligands **8**, **9** and **10** respectively, as shown in **Scheme 3-4**. Alkynes were deprotected *in situ* and reacted with  $Pt(dppp)Cl_2$  to incorporate the metal center with phosphine ancillary ligands. Pro-ligand **9** was previously reported by our group,<sup>89</sup> and **8** and **10** 

were conveniently synthesized via Sonogashira reactions between trimethylsilylacetylene and the corresponding dibromo precursors in reasonable yields (see **Scheme 3-5**, Page 87 for details).



Scheme 3-4. Synthesis of metallacycles 8-10.

## 3.2.2 Solid-State Structures



**Figure 3-2.** ORTEP presentations of metallacycle (a) **4** and (b) **5** showing CH<sub>2</sub>Cl<sub>2</sub> solvent molecules hydrogen-bonding with each metallacycle in different ways. Ellipsoids at the 50% probability level, hydrogens on metallacycles omitted for clarity.



**Figure 3-3.** (a) ORTEP presentations two different crystallographic structures of **6** connected by hydrogen bonding interactions. (b) Top-view of one of the structures. Ellipsoids at the 50% probability level, hydrogens on metallacycles omitted for clarity.

Crystal structures of **4**, **5** and **6** (**Figure 3-2** and **Figure 3-3**) were obtained. Important bond lengths and angles are summarized in **Table 3-9** and **Table 3-10** on page 92. Complex **6** has two crystallographically distinct structures (A and B) in the unit cell with different ligand conformations as shown in **Figure 3-3**, with multiple hydrogen bonds between them. The metal centers in both structures A and B have almost identical C-Pt-C bond angles, unaffected by conformational differences in the relatively remote bisacetylide ligands. All the metallacycles have square-planar geometries at the platinum centers, in line with other similar *cis*-platinum bisacetylides in the literature.<sup>101-102,108</sup> Compared with **5** and **6**, **4** has a smaller C-Pt-C bond angle of 84.8°, which indicates some degree of ring strain in this structure. While the bisacetylide ligands in **4** and **5** are only slightly twisted (S1-C4-C7-S2 torsion angle of 14.8° in **4**, dihedral angles between adjacent rings of 9.9° and 4.9° in **5**), the central thiophene ring in **6** is significantly out of the plane (dihedral angles between adjacent rings of 35.2° and 30.6° in structure A; 26.0° and 25.5° in structure B). Interestingly, crystals of **4**, **5** and **6** all have CH<sub>2</sub>Cl<sub>2</sub> solvent molecules in the crystal lattice. The CH<sub>2</sub>Cl<sub>2</sub> molecules form hydrogen bonds with only one side of the ligand in **4**,

while in **5** they bound to both sides of the ligand as well as with the sulfur atom on the central thiophene ring (with H44A). The  $CH_2Cl_2$  molecules interact with **6** in a similar fashion to how they do with **5**, however, two protons are involved (**Figure 3-2**).





**Figure 3-4.** (a) UV-Vis spectra of ligands **8**, **9** and **10** in CH<sub>2</sub>Cl<sub>2</sub> ( $1.0 \times 10^{-5}$  M) and excitation and emission spectra of **8** (b), **9** (c) and **10** (d) in CH<sub>2</sub>Cl<sub>2</sub> ( $1.0 \times 10^{-5}$  M).

The absorption spectra of **8**, **9** and **10** are shown in **Figure 3-4** (a). The lowest energy absorption maxima of **8** and **10** are at 380 nm and 343 nm, respectively, in CH<sub>2</sub>Cl<sub>2</sub>. **9** absorbs at

higher wavelength into the visible region showing a maximum at 405 nm and a shoulder at ~430 nm. The resulting yellow color is attributed to the relatively smaller HOMO-LUMO gap of the  $\pi$ - $\pi$ \* transition on the more conjugated terthiophene moiety. The excitation spectra of **8**, **9** and **10** are shown in **Figure 3-4** (b, c, and d). All the emission spectra show some vibrational fine structure. Emission maxima are at 392 nm, 475 nm and 412 nm for **8**, **9** and **10**, respectively. Complex **8** has the smallest Stokes shift indicating a smaller degree of geometrical relaxation in the excited state.



Figure 3-5. UV-Vis spectra of 4 (a), 5 (b) and 6 (c)  $(1.0 \times 10^{-5} \text{ M in CH}_2\text{Cl}_2)$ .

The absorption spectra of metallacycles **4**, **5** and **6** in CH<sub>2</sub>Cl<sub>2</sub> are shown in **Figure 3-5**. All the complexes absorb strongly below wavelength of 350 nm, attributed to high energy localized  $\pi$ - $\pi$ \* transitions of the acetylene moieties. Complex **4** shows a lowest-energy peak at 398 nm, similar to the absorption features of **8**, however red shifted approximately 20 nm. The low-energy absorption shoulder of **5** is shifted to 500 nm, from 430 nm in **9**, and **6** shows only a very weak feature tailing to 460 nm without a clear maximum indicating a low oscillator strength between S<sub>0</sub> and S<sub>1</sub> states. In all cases, the metallacycle absorption is somewhat red-shifted from the absorption of the proligands. This can be rationalized by restricted rotation and planarization of the structure upon formation of a bidentate chelate, and the resulting more extended  $\pi$ -conjugation narrowing the HOMO-LUMO gap.



Figure 3-6. Excitation spectrum of 4 and its emission spectra under different conditions.

The excitation and emission spectra of metallacycle **4** in  $CH_2Cl_2$  are shown in **Figure 3-6**. Compared with the purely phosphorescent analogue **7** in the literature, which emits at 497 nm, metallacycle **4** with two thiophene rings in the ligand instead of two *o*-phenylene groups shows significantly red-shifted phosphorescence at 610 nm and additionally a broad weak band between 400 nm and 550 nm. This relatively higher energy emission is considered to be fluorescence as assessed by its sensitivity to oxygen. According to **Figure 3-1**, this is suggestive of  $k_{ISC}$  to T<sub>1</sub> being on the same time-scale as  $k_{FL}$ , slow enough so that both S<sub>1</sub> and T<sub>1</sub> states are effectively populated and emitting.



Figure 3-7. (a) Variable temperature fluorescence spectra of 5 in a MeOH/EtOH medium, and (b) excitation and emission spectra of metallacycle 5 in air-equilibrated solution. No phosphorescence was observed under argon  $(1.0 \times 10^{-5} \text{ M in CH}_2\text{Cl}_2)$ .

By contrast, metallacycle **5** with three thiophene rings shows no phosphorescence up to 800 nm (even at lower temperatures, **Figure 3-7a**) but instead bright yellow fluorescence is observed in solution (**Figure 3-7b**). Some terthiophene-containing structures are known to have low-lying non-emissive triplet states. The non-radiative decay rate of triplet excited states is known to increase exponentially as the triplet energy ( $T_1$ - $S_0$  gap) decreases while non-radiative decay of  $S_1$  is relatively energetically insensitive.<sup>1,103a,109</sup> Therefore, the absence of phosphorescence of **5** in the visible region may be explained by a terthiophene-centered  $T_1$  excited state that is very low in

energy and decays rapidly through non-radiative pathways or near-IR emissions.

Metallacycle **6** was designed by introducing only one thiophene ring by replacing the central acetylene bridge in complex **7**, with anticipation to lower the ligand based triplet state and allow both phosphorescence and fluorescence. Complex **6** can also be considered as an analogue of **5**, but with two thiophene rings replacing the phenyl rings. This change indeed gives rise to dual emission with a higher FL/PH ratio close to 1 (**Figure 3-8**). Interestingly, phosphorescence of **6** is stronger with shorter excitation wavelengths compared to fluorescence. After ruling out the possibility of contamination by trace amounts of emissive residue ligand, it is considered possible that higher singlet excited states (S<sub>n</sub> states in **Figure 3-1**) of **6** may have stronger coupling with the T<sub>1</sub> state. Therefore, when excited with higher-energy photons, these states are populated giving rise to faster ISC to T<sub>1</sub> thus stronger phosphorescence. Similar effects are known in some intrachain platinum conjugated polymers<sup>110</sup>.



**Figure 3-8.** (a) Emission spectra of **6** under argon show two bands (500 nm and 620 nm) while excitation spectra of the two bands diverge at higher energy. (b) Emission of **6** in air, and dual emission under argon.

Emission of both **4** and **6** are sensitive to oxygen to some extent, yet still remain slightly phosphorescent in air-equilibrated solutions (**Figure 3-6** and **Figure 3-8b**). The phosphorescence can only be completely quenched under 100% O<sub>2</sub>, which is beneficial for high concentration ratiometric O<sub>2</sub> sensing using unaffected fluorescent intensity as a reference. Moreover, **4** and **6** have similar  $T_1$ -S<sub>0</sub> energy gaps in that they phosphoresce at similar wavelengths. However, **6** fluoresces at a higher wavelength than **4** at 490 nm indicating a lower-lying first single excited state (S<sub>1</sub>) state in **6**. This is consistent with the computed energy diagrams in **Figure 3-9**, showing that the higher FL/PH ratio in **6** than **4** can be achieved without a significant change in  $T_1$  energies relative to S<sub>0</sub>.

	Absorption	Fluorescence			Phosphorescence		
Complex	$\lambda_{abs}$ (nm)	$\lambda_{em}$ (nm)	$\Phi_{ m em}$	$\tau_{em}(ns)$	$\lambda_{em}$ (nm)	$\Phi_{ m em}$	$\tau_{em}(\mu s)$
	( )	( )					
4	398	405	0.011	0.70	610	0.053	2.23
5	500	536	0.15	0.45	-	-	-
6	385	490	0.0062	0.61	620	0.0054	1.97

Table 3-1. Electronic absorption and emission of metallacycles in CH<sub>2</sub>Cl<sub>2</sub> solution.

Electronic absorption and emission data including emission lifetimes ( $\tau_{em}$ ) and quantum yields ( $\Phi_{em}$ ) of the three metallacycles are summarized in **Table 3-1**. All complexes show short fluorescence life time of less than 1 ns, while **4** and **6** show relatively long phosphorescent lifetimes ~ 2 µs, indicating that  $k_{PH}$  is 3 orders of magnitude slower than  $k_{FL}$ . The fluorescence quantum efficiency of **5** is moderate while **4** shows much weaker dual emission with a FL/PH ratio around 0.2. The FL/PH ratio of **6** is approximately 0.9 higher than that of **4**, however, the overall emission

quantum efficiency is barely 1 percent.

By comparing **4** with **7**, and **5** with **6** (Scheme 3-3), it is noticeable that replacing phenyl groups with thiophene rings in metallacycles can induce or enhance fluorescence without adding extra conjugation. The difference between **4** and **5** demonstrates that adding conjugation length to the ligand leads to drastically increased fluorescence, however, the phosphorescence is diminished in the visible region. It should be pointed out that although complex **4** and **6** show many similarities, they are not directly comparable in an empirical way in which only one type of group (C-C triple bond, benzene or thiophene ring) is replaced with another.

#### **3.2.4 DFT and TD-DFT Simulations**

DFT and TD-DFT calculations were carried out to help understand the photophysics of the metallacycles and simulate their ground and excited state properties. Optimized ground-state ( $S_0$ ) geometries of **4**, **5** and **6** are shown in **Table 3-2** (left column). All structures show no symmetry ( $C_1$ ) despite their symmetric bisacetylide ligands. Complexes **4** and **5** show almost completely planar ligand geometries, however, the central thiophene ring on **6** still lies out of the plane by 44.5 °.

DFT calculated geometry optimization of the lowest triplet state ( $T_1$ ) of the metallacycles in  $CH_2Cl_2$  solutions are shown in **Table 3-2** (right column). TD-DFT calculated optimized geometries of the first singlet excited state ( $S_1$ ) of metallacycles in  $CH_2Cl_2$  solutions are presented in **Table 3-2** (central column). All three metallacycles exhibit highly planar  $T_1$  and  $S_1$  excited states structures.

Compound	$S_0$	$\mathbf{S}_1$	$T_1$
4	A A A A A A A A A A A A A A A A A A A		A A A A A A A A A A A A A A A A A A A
5	A CONTRACTOR	A CONTRACT	A.
6	A Contraction of the second se	A	A

Table 3-2. Calculated geometry of 4, 5 and 6 at S<sub>0</sub>, S<sub>1</sub> and T<sub>1</sub> electronic states.

Frontier orbitals of the ground-state metallacycles are presented in **Tables 3-3**. All three complexes have  $\pi$  character localized on the ligand in the HOMO and  $\pi$ \* character in the LUMOs. The HOMO and LUMO of **4** are uniformly distributed with some contributions from  $5d_{xz}$  and  $5d_{yz}$  orbitals on platinum, yet mostly comprised of  $\pi$  or  $\pi$ \* orbitals from the bisacetylide ligand. In metallacycles **5** and **6**, however, the LUMOs are strongly metal-centered with contributions from empty  $6p_z$  orbitals on platinum while the HOMOs are delocalized. This is indicative of metal-to-ligand charge transfer (MLCT) states in **5** and **6**, which have previously been observed in conjugated Pt polymers with electron-rich ligands.<sup>110-111</sup>

Compound	MOs	E (eV)	Top-down	Side View
4	HOMO (178)	-5.29		
	LUMO (179)	-1.53		
5	HOMO (193)	-4.93		
	LUMO (194)	-1.68		
6	HOMO (191)	-5.61		
	LUMO (192)	-1.55		

Table 3-3. Frontier orbitals and their energies of ground state metallacycles.

\* According to TD-DFT calculations, only the HOMO and LUMO are involved in the lowest energy  $S_0 \rightarrow S_1$  electronic transitions for all three complexes



Table 3-4. Bond lengths (Å) of 4, 5 and 6 in the ligand at different electronic states.

Selected bond lengths in the optimized geometries of **4**, **5** and **6** in different electronic states are presented in **Table 3-4**. In the ground state, all metallacycles show bond averaging between single and double bonds on the innermost ring. In **4** and **5**, the thiophene double bond is notably longer (1.40 Å) on the inside circle compared to the ones outside (1.36 Å). These observations along with a down field shift of the proton signal on the central thiophene ring of **5** ( $\delta = 6.72$  ppm, while  $\delta = 7.06$  ppm in the proligand **9**, both in CDCl<sub>3</sub>), indicate the presence of "ring currents" on the metallacycle.
At the  $S_1$  and  $T_1$  excited states, however, all metallacycles have almost perfectly planar ligand structures. This indicates that **6** undergoes significant planarization going from GS to  $S_1$  or  $T_1$  excited states, resulting in a poor overlap between GS and excited state MOs. It's also consistent with its very weak low energy absorption features, and may also lead to very low fluorescence and phosphorescence quantum efficiencies of **6** since NR processes with low energy barrier becomes more favorable. Additionally, in **Table 3-4**, all metallacycles in the excited state specially in  $T_1$ , show "quinoid-like" structure with reversed bond length of single and double bonds in the GS geometry. It's also clear that the geometry of metallacycles have much more in common between the excited states  $S_1$  and  $T_1$  than between GS and  $T_1/S_1$ .

Relative energies of metallacycles **4**, **5** and **6** in  $T_1$  and  $S_0$  electronic states with  $T_1/S_0$  geometries are summarized in **Table 3-5**. Their relative energies in  $S_1$  and  $S_0$  electronic states with  $S_1/S_0$  geometries are summarized in **Table 3-6**. These energies are used to construct energy diagrams of electronic states of metallacycles **4**, **5** and **6** in **Figure 3-9**.

Complex	Electronic State	S <sub>0</sub> Geometry	T <sub>1</sub> Geometry	
		Relative Energy (eV)	Relative Energy (eV)	
4	$S_0$	0.00	0.34	
	$T_1$	2.25	1.89	
5	$\mathbf{S}_0$	0.00	0.37	
	$T_1$	1.92	1.54	
6	$\mathbf{S}_0$	0.00	0.45	
	$T_1$	2.80	2.06	

Table 3-5. Relative energies of optimized S<sub>0</sub> and T<sub>1</sub> states.

Complex	Electronic State ——	S <sub>0</sub> Geometry	S <sub>1</sub> Geometry	
		Relative Energy (eV)	Relative Energy (eV)	
4	$S_0$	0.00	0.20	
	$\mathbf{S}_1$	3.10	2.90	
5	$S_0$	0.00	0.29	
	$S_1$	2.44	2.23	
6	$S_0$	0.00	0.35	
	$S_1$	3.22	2.63	

Table 3-6. Relative energies of optimized S<sub>0</sub> and S<sub>1</sub> states.

 $S_1$  $S_1$ 0.20 0.59  $T_1$ S<sub>1</sub> E<sub>v</sub> E<sub>00</sub> 2.70 2.90  $T_1$ 0.31 0.74 T<sub>1</sub> ' 0.36 0.38 E,  $E_{00}$ 2.28 2.63 E<sub>v</sub> E<sub>v</sub> 3.10 2.25 E<sub>v</sub> E<sub>00</sub> 1.55 1.89 E, E<sub>00</sub> Ε<sub>ν</sub> 3.22 Е<sub>v</sub> 2.80 1.94 2.23 E'  $E_{00}$ 1.61 2.06 E′  $E_{00}$ 1.17 1.54 E<sub>v</sub> E<sub>v</sub> 2.44 1.92 ູS₀ S<sub>0</sub> S₀

Figure 3-9. Summarized energy diagrams and electronic transitions of metallacycles 4, 5 and 6. Energies shown in the above diagrams are in eV ( $E_v$  = vertical transition energy,  $E_{00}$  = 0-0 transition energy).

Metallacycle 5 has the lowest calculated  $T_1$  state. The  $T_1$ -S<sub>0</sub> transition energies of 1.54 eV

(0-0) and 1.17 eV (vertical) corresponds to phosphorescence in the near-IR region (808 nm and 1060 nm), where fast thermal-deactivation may render the  $T_1$  state non-emissive at room temperature. Similarly, metallacycle **4** and **6** are calculated to exhibit phosphorescence with 0-0 transition energies of 1.89 eV and 2.06 eV (**Table 3-5**), respectively, close to the experimental values at maximum intensity (2.02 eV and 1.99 eV).

Metallacycle	Electronic State	Major transition	Vertical Transition	oscillator
wieddiaddycie		wingor transition	Energy (eV)	strength
4	$\mathbf{S}_1$	HOMO-LUMO	3.10	0.169
	$T_1$	HOMO-LUMO	2.25	-
5	$\mathbf{S}_1$	HOMO-LUMO	2.44	0.100
	$T_1$	HOMO-LUMO	1.92	-
6	$\mathbf{S}_1$	HOMO-LUMO	3.22	0.001
	$T_1$	HOMO-LUMO	2.80	-

 Table 3-7. Vertical excitation energies of lowest singlet and triplet excited states.

Table 3-8. Calculated absorption and emission properties.

	Absorption wavelength (nm)	Emission wavelength (nm)		
Metallacycles	Vertical $S_0 \rightarrow S_1$	Vertical $S_1 \rightarrow S_0$	0-0 $S_1 \rightarrow S_0$	$0\text{-}0  T_1 \rightarrow S_0$
4	400 (398) <sup>a</sup>	459	428 (410)	655 (610)
5	508 (500)	639	557 (536)	-
6	385 (no maxima)	544	471(485)	602 (620)
<b>7</b> <sup>b</sup>	329 (355)	-	-	497 (497)

<sup>a</sup> Experimental values given in parentheses. <sup>b</sup> Data of 7 adopted from literature.<sup>104c</sup>

Vertical transition energies and oscillator strengths have also been calculated and are summarized in Table 3-7. From 4 to 6, the decreasing oscillator strength of the vertical  $S_0$ - $S_1$ excitation is in line with the incrementally weaker molar extinction coefficients of the lowest energy absorption bands (Figure 3-5). The  $T_1$  state in 6 has a much higher vertical excitation energy, but suffers more energy loss during relaxation to its lowest vibronic state: 0.74 eV is lost vs. 0.35 eV in 4 and 0.39 eV in 5 (Figure 3-9). This may be related to the rotation of the thiophene ring between the ground state and excited states. Calculated absorption and emission wavelengths are summarized in Table 3-8. Calculated absorption and triplet emission (phosphorescence) energies are in good agreement with the experimental values. Singlet emission energies were calculated using non-equilibrium solvation of the excited states, assuming vertical emission from relaxed  $S_1$  states decaying with frozen geometry (i.e. vertical relaxation), yet large discrepancies with experimental data were observed. Interestingly calculated emission by assuming decay from relaxed S<sub>1</sub> state to relaxed GS (i.e. 0-0 relaxation) agrees very well with the experimental values. Indeed, the vibronic fine structure in the fluorescence spectra of 5 at both room temperature and lower temperatures (Figure 3-7b) shows that first peak is always strongest in intensity. Therefore, 0-0 relaxation is the more reasonable assumption to predict fluorescence of 4, 5 and 6.

## 3.3 Experimental

### 3.3.1 General

<sup>1</sup>H NMR, <sup>13</sup>C{<sup>1</sup>H} NMR, and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectrometer. <sup>31</sup>P NMR chemical shifts are referenced to external 85% H<sub>3</sub>PO<sub>4</sub>, and other chemical shifts are referenced to the residual solvent signals. ESI mass spectra were

measured in-house using a Waters LC-MS ESI mass spectrometer. Infrared spectroscopy (IR) was performed on an attenuated total reflection (ATR) crystal using a Perkin-Elmer Frontier FTIR spectrometer. Absorption spectra were obtained on a Varian Cary 5000 UV-Vis-NIR spectrophotometer, and emission measurements were performed on a PTI QuantaMaster 50 fluorimeter. Quantum yields were measured using a Labsphere general purpose integrating sphere.

All syntheses were carried out under a dry  $N_2$  atmosphere using standard Schlenk techniques. Dry toluene and tetrahydrofuran (THF) were obtained after treatment with solvent purification system. All other chemicals were purchased from commercial sources and used without further purification. All syntheses involving air sensitive compounds were carried out using standard Schlenk-type procedures under an atmosphere of  $N_2$ .

### 3.3.2 Synthesis

Scheme 3-5. Synthesis of ligands.



- (a) CaC<sub>2</sub>, *cat.* Pd(PPh<sub>3</sub>)<sub>4</sub>, *cat.* CuI, CH<sub>3</sub>CN/NEt<sub>3</sub>, room temperature.
- (b) 2,5-diiodothiophene, *cat.* Pd(PPh<sub>3</sub>)<sub>4</sub>, THF/H<sub>2</sub>O, 70 °C.
- (c) Trimethylsilylacetylene, *cat.* Pd(PPh<sub>3</sub>)<sub>4</sub>, (*i*-Pr)<sub>2</sub>NH/toluene, reflux.

Proligand TMS<sub>2</sub>T<sub>3</sub> (9)<sup>89</sup> and Pt(dppp)Cl<sub>2</sub><sup>107</sup> were synthesized using reported methods. Br<sub>2</sub>TCCT (20)<sup>79</sup> and Br<sub>2</sub>BTB (21)<sup>112</sup> were synthesized using different methods from literature.

Br<sub>2</sub>TCCT (**20**). CaC<sub>2</sub> (3.85 g, 60 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (1.16 g, 1.0 mmol) and CuI (380 mg, 2.0 mmol) were added to a round-bottom flask with a side-arm under N<sub>2</sub>. N<sub>2</sub>-sparged CH<sub>3</sub>CN (60 mL) was then added to the flask, followed by triethylamine (8.4 mL, 60 mmol) and 3-bromo-2-iodothiophene (3.70 g, 12.8 mmol). H<sub>2</sub>O (1.1 mL, 60 mmol) was added slowly with stirring over 30 minutes while the reaction temperature was maintained below 50 °C. The mixture was then kept at 50 °C using an oil bath and stirred overnight. Black insoluble solids were filtered off and the solvent removed from the filtrate under vacuum to obtain a brown-yellowish crude product. The pure product was obtained using flash column chromatography on silica (hexanes) as a white solid. Yield 1.70 g, 76 %. The <sup>1</sup>H NMR and mass spectra matched with literature values.

Br<sub>2</sub>BTB (**21**). 2-bromo-phenylboronic acid (1.69 g, 8.4 mmol), 2,5-diiodothiophene (1.34 g, 4.0 mmol), K<sub>2</sub>CO<sub>3</sub> (2.32 g, 16.8 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (462 mg, 0.4 mmol) were added to a roundbottom flask with a stir-bar under N<sub>2</sub>. N<sub>2</sub>-sparged mixed solvent consisting of 20 mL THF and 20 mL de-ionized water was added to the flask with stirring. The mixture was slowly warmed to 70 °C and stirred for 18 hours. The mixture was concentrated *in vacuo* to remove THF and extracted with diethyl ether (3×20 mL). The organic phases were combined, washed with water and brine, and dried over magnesium sulfate. The crude product was obtained after filtration and removal of the solvent under vacuum. The pure product was obtained using flash column chromatography on silica (hexanes) as an off-white solid. Yield 1.08 mg, 68 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.20 (td, *J*<sub>1</sub> = 10.4 Hz, *J*<sub>2</sub> = 2.2 Hz, 2H, 2 CH), 7.33-7.39 (m, 4H, 4 CH), 7.59 (dd, *J*<sub>1</sub> = 10.3 Hz, *J*<sub>2</sub> = 2.2 Hz, 2H, 2 CH), 7.72 (dd, *J*<sub>1</sub> = 10.6 Hz, *J*<sub>2</sub> = 1.3 Hz, 2H, CH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz): δ 122.6 (C4, C-Br), 127.6 (CH, thienyl), 127.8 (CH, phenyl), 129.1 (CH, phenyl), 131.9 (CH, phenyl), 133.9 (CH, phenyl), 135.0 (CH, phenyl), 142.4 (CH, thienyl). Positive HRMS (APCI/ESI): *m*/Z = 392.8944, [M+H]<sup>+</sup>.

TMS<sub>2</sub>TCCT (8). 20 (696 mg, 2.0 mmol), CuI (80 mg, 0.4 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (280 mg, 0.4 mmol) were added to a round-bottom flask with a stir-bar under N<sub>2</sub>. N<sub>2</sub>-sparged mixed solvent of 15 mL diisopropylamine and 30 mL toluene was added to the flask with stirring, followed by trimethylsilylacetylene (471.5 mg, 4.8 mmol). The mixture was slowly warmed to 75 °C and stirred for 12 hours. The reaction mixture was added to 30 mL saturated NH<sub>4</sub>Cl solution and extracted with ethyl acetate (4×20 mL). The organic phases were combined, washed with water and brine, and dried over magnesium sulfate. The brown crude product was obtained after filtration and removal of the solvent under vacuum. The pure product was obtained using flash column chromatography on silica (hexanes) as a light-yellow solid. Yield 580 mg, 76 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  0.28 (s, 18H, 6 CH<sub>3</sub>), 7.03 (d, *J* = 5.3 Hz, 2H, CH), 7.19 (d, *J* = 5.2 Hz, 2H, CH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  0.1 (CH<sub>3</sub>), 89.8 (C4, C=C), 98.8(C4, C=C), 99.7 (C4, C=C), 126.7 (CH, thienyl), 127.0 (C4, thienyl), 127.1 (C4, thienyl), 129.8 (CH, thienyl). Positive HRMS (APCl/ESI): *m*/Z = 383.0774, [M+H]<sup>+</sup>. FTIR (ATR) = 2152 cm<sup>-1</sup> (*v*<sub>C=C</sub>).

TMS<sub>2</sub>BTB (10). The same reaction conditions, work-up procedure and purification method were used for **8** except that **21** was used as the starting material. A pale-yellow solid was obtained after column purification in 52 % yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  0.29 (s, 18H, 6 CH<sub>3</sub>), 7.23 (td,  $J_1 = 7.6$  Hz,  $J_2 = 1.2$  Hz, 2H, CH), 7.35 (td,  $J_1 = 7.6$  Hz,  $J_2 = 1.4$  Hz, 2H, CH), 7.59-7.64 (m, 4H, 2 CH), 7.79 (s, 2H, CH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  -0.1 (CH<sub>3</sub>), 99.7 (C4, C=C),

105.2 (C4, C=C), 120.2 (C4, phenyl), 127.0 (CH, phenyl), 127.4 (CH, phenyl), 128.6 (CH, phenyl), 129.0 (CH, phenyl), 134.6 (CH, thienyl), 135.9 (C4, phenyl), 142.2 (C4, thienyl). Positive HRMS (APCI/ESI): m/Z = 429.1522,  $[M+H]^+$ . FTIR (ATR) = 2150 cm<sup>-1</sup> ( $v_{C=C}$ ).

Pt(dppp)TCCT (4). Proligand **8** (193 mg, 0.505 mmol), Pt(dppp)Cl<sub>2</sub> (339 mg, 0.500 mmol) and CuI (10 mg, 0.05 mmol) were added a round-bottom flask with a stir-bar under N<sub>2</sub>. Then 20 mL N<sub>2</sub> -sparged mixed solvent of 15 mL diisopropylamine and 15 mL CH<sub>2</sub>Cl<sub>2</sub> was added to the flask with stirring. A THF solution of 1.0 M tetrabutylammonium fluoride (TBAF, 2.1 mL, 2.1 mmol) was slowly added to the mixture over 30 minutes, and the resulting solution is stirred for 18 hours. Solvents were removed under vacuum to give the crude mixture, which was then purified using flash column chromatography on silica (20% CHCl<sub>3</sub> in hexanes, v/v) to give the pure product as a yellow powder. Yield 282 mg, 67 %. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz):  $\delta$  2.00-2.11 (m, 2H, CH<sub>2</sub>), 2.62 (br, 4H, 2CH<sub>2</sub>), 6.51 (d, *J* = 5.2 Hz, 2H, 2 CH), 7.10 (d, *J* = 5.2 Hz, 2H, 2 CH), 7.39-7.44 (m, 12H, 12 CH), 7.77-7.82 (m, 8H, 8 CH). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 162 MHz):  $\delta$  -6.92 (*J*<sub>Pt-P</sub> = 2215 Hz). Positive ESI-TOF: *m*/*Z* = 843.0982, [C<sub>41</sub>H<sub>31</sub>S<sub>2</sub>P<sub>2</sub><sup>194</sup>Pt+H]<sup>+</sup>. FTIR (ATR) = 2095 cm<sup>-1</sup> (*v*<sub>C=C</sub>).

Pt(dppp)T<sub>3</sub> (**5**). The same procedure used for **4** was used employed except proligand **9** was used instead. An orange powder was obtained as the pure product. Yield 288 mg, 64 %. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz): δ 1.93-2.06 (m, 2H, CH<sub>2</sub>), 2.56-2.60 (m, 4H, 2CH<sub>2</sub>), 5.95 (d, *J* = 5.2 Hz, 2H, 2 CH), 6.72 (s, 2H, 2 CH), 6.74 (d, *J* = 5.2 Hz, 2H, 2 CH), 7.41-7.44 (m, 12H, 12 CH), 7.67-7.72 (m, 8H, 8 CH). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 162 MHz): δ -5.99 (*J*<sub>Pt-P</sub> = 2177 Hz). Positive ESI-TOF: m/Z = 923.0652, [C<sub>43</sub>H<sub>32</sub>S<sub>3</sub>P<sub>2</sub><sup>194</sup>Pt+Na]<sup>+</sup>. FTIR (ATR) = 2098 cm<sup>-1</sup> ( $\nu$  c=c).

Pt(dppp)BTB (6). The same procedure used for 4 was used employed except proligand 10

was used instead. A yellow powder was obtained as the pure product. Yield 249 mg, 56 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  2.02-2.17 (m, 2H, CH<sub>2</sub>), 2.52 (br, 4H, 2CH<sub>2</sub>), 6.23 (dd, *J*<sub>1</sub>= 7.7 Hz, *J*<sub>2</sub>= 0.9 Hz, 2H, 2 CH), 6.78 (td, *J*<sub>1</sub>= 7.6 Hz, *J*<sub>2</sub>= 1.2 Hz, 2H, 2 CH), 6.98-7.02 (m, 4H, 4 CH), 7.35-7.42 (m, 12H, 12 CH), 7.70-7.72 (m, 8H, 8 CH). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 162 MHz):  $\delta$  -5.58 (*J*<sub>Pt-P</sub> = 2183 Hz). Positive ESI-TOF: *m*/*Z* = 889.1721, [C<sub>47</sub>H<sub>37</sub>SP<sub>2</sub><sup>194</sup>Pt+H]<sup>+</sup>. FTIR (ATR) = 2105 cm<sup>-1</sup> (*v*<sub>C=C</sub>).

## **3.3.3 X-ray Crystallography**

Crystals of **4**, **5** and **6** suitable for single crystal X-ray diffraction were obtained by diffusion of pentane into solutions of the complexes in CH<sub>2</sub>Cl<sub>2</sub> or CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN mixed solvent. X-ray diffraction data were collected with a Bruker X8 APEX II diffractometer with graphite monochromated Mo-K $\alpha$  radiation. Data were collected and integrated using the Bruker SAINT<sup>70</sup> software package. Data were corrected for absorption effects using the multi-scan technique (SADABS).<sup>113</sup> The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods.<sup>114</sup> All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions.

Selected bond lengths and bond angles for **4** and **5** (**Table 3-9**) and two crystallographically independent structures of **6** (**Table 3-9**) are summarized.

$4 \cdot CH_2Cl_2$		5•1.2[CH <sub>2</sub> Cl <sub>2</sub> ]•0.8CH <sub>3</sub> CN		
Pt(1)–C(12)	2.0061(16)	Pt(1)–C(14)	2.026(2)	
Pt(1)–C(14)	1.9927(16)	Pt(1)–C(16)	2.012(2)	
Pt(1)–P(1)	2.2916(5)	Pt(1)–P(1)	2.3019(6)	
Pt(1)–P(2)	2.2843(4)	Pt(1)–P(2)	2.2928(5)	
C(11)–C(12)	1.214(2)	C(13)–C(14)	1.217(3)	
C(13)–C(14)	1.215(2)	C(15)–C(16)	1.216(3)	
C(12)-Pt(1)-C(14)	84.80(6)	C(14)–Pt(1)–C(16)	88.95(8)	
P(1)-Pt(1)-P(2)	94.875(16)	P(1)-Pt(1)-P(2)	92.91(2)	
Pt(1)-C(12)-C(11)	170.61(14)	Pt(1)-C(14)-C(13)	172.85(19)	
Pt(1)-C(14)-C(13)	175.30(14)	Pt(1)-C(16)-C(15)	174.52(19)	

Table 3-9. Selected bond lengths (Å) and angles (°) for crystal structures of 4 and 5.

**Table 3-10.** Selected bond lengths (Å) and angles (°) for the two crystallographic independent structures in  $6 \cdot CH_2Cl_2$  crystals.

Structure A		Structure B		
Pt(1)–C(1)	2.016(2)	Pt(2)–C(48)	2.007(2)	
Pt(1)–C(20)	2.010(2)	Pt(2)–C(67)	2.008(2)	
Pt(1)–P(1)	2.2846(6)	Pt(2)–P(3)	2.2927(6)	
Pt(1)–P(2)	2.2834(6)	Pt(2)–P(4)	2.2827(6)	
C(1)–C(2)	1.206(3)	C(48)–C(49)	1.209(3)	
C(19)–C(20)	1.204(3)	C(66)–C(67)	1.206(3)	
C(1)-Pt(1)-C(20)	88.95(8)	C(48)–Pt(1)–C(67)	88.94(9)	
P(1)-Pt(1)-P(2)	96.99(2)	P(3)-Pt(2)-P(4)	93.79(2)	
Pt(1)-C(1)-C(2)	172.5(2)	Pt(2)-C(48)-C(49)	175.0(2)	
Pt(1)-C(20)-C(19)	177.3(2)	Pt(2)-C(67)-C(66)	177.1(2)	

**4**•CH<sub>2</sub>Cl<sub>2</sub> crystallizes with one disordered CH<sub>2</sub>Cl<sub>2</sub> solvent molecule in the asymmetric unit. The structure is in *P* 2<sub>1</sub>/*n* space group, with a primitive monoclinic unit cell containing four **4** molecules. **5**•1.2[CH<sub>2</sub>Cl<sub>2</sub>]•0.8CH<sub>3</sub>CN crystallizes with one complete CH<sub>2</sub>Cl<sub>2</sub> molecule as well as one site that is partially occupied by CH<sub>2</sub>Cl<sub>2</sub> and also by CH<sub>3</sub>CN (~1:4) in the asymmetric unit. The structure is in *P* -1 space group, with a primitive triclinic unit cell containing two **5** molecules. **6**•CH<sub>2</sub>Cl<sub>2</sub> crystallizes with two crystallographically independent molecules in the asymmetric unit. Additionally, there are two molecules of CH<sub>2</sub>Cl<sub>2</sub> in the asymmetric unit. The structure is in *P* 2<sub>1</sub>/*n* space group with a primitive monoclinic unit cell containing eight **6** molecules.

#### **3.3.4 DFT Simulations**

Density functional theory (DFT) calculations were carried out using the Gaussian 09 Rev.D01 suite of Programs.<sup>90</sup> The PBE0 hybrid functional<sup>91</sup> with 6-31G\* basis set (for C, H, S and P atoms) and the LANL2DZ effective-core pseudopotential<sup>92</sup> (for Pt) was employed to simulate ground state ( $S_0$ ) and  $T_1$  structure of all three metallacycles. Triplet states are treated using unrestricted formalism. Structural coordinates from X-ray crystallography were used as starting points of geometry optimizations. Optimized structures were confirmed to be the minimum on the potential energy surface by vibrational frequency calculations.

Time-dependent DFT (TD-DFT) calculations were also performed to understand S<sub>1</sub> excited state electronics and absorption and emission behaviors of these complexes. For all simulations, solvation effect of CH<sub>2</sub>Cl<sub>2</sub> ( $\epsilon = 8.93$ ) was implemented using the polarizable continuum model<sup>88</sup> (PCM) on Gaussian 09. TD-DFT method is also employed to calculate optimized structures of the metallacycles in their  $S_1$  excited states which are confirmed to be the minimum on the potential energy surface by excited state vibrational frequency calculations.

Complex –	Calculate	Experimental	
	Symmetric Mode (strong)	Antisymmetric Mode (weak)	
4	2067 cm <sup>-1</sup>	2014 cm <sup>-1</sup>	2095 cm <sup>-1</sup>
5	2112 cm <sup>-1</sup>	2096 cm <sup>-1</sup>	2098 cm <sup>-1</sup>
6	2125 cm <sup>-1</sup>	2116 cm <sup>-1</sup>	2105 cm <sup>-1</sup>

**Table 3-11.** Calculated and experimental vibrational frequencies of  $C \equiv C$  bonds.

Frequency calculations on 4, 5 and 6 in their optimized geometry confirmed that they are on the global minimum on the potential energy surface. Frequency calculations also give us some insight into their IR absorptions. They are predicted to show symmetric and antisymmetric stretching modes where vibrations of the two C=C bonds are in phase or out of phase respectively. The antisymmetric mode is calculated to have much weaker IR absorption than the symmetric mode. Experimentally, only one peak is observed in 4, 5 and 6. The same goes for compound 7 in literature.<sup>104c</sup> This may be due to constrained geometry in cyclic structures as similar acyclic cis-Pt(II) bisacetylides show two peaks.<sup>115</sup> After applying an empirical scaling factor of 0.95 (for PBE0 hybrid functional and 6-31G\* basis set),<sup>116</sup> the predicted IR frequencies are reasonably close to experimental values (**Table 3-11**). Small discrepancies may be attributed to the PCM solvation assumptions used in DFT calculations while IR spectra were actually recorded in the solid state using powder samples.

## 3.4 Conclusions

In summary, we have prepared and characterized three different thiophene-containing Pt metallacycles **4**, **5** and **6** with dppp ancillary ligands. Crystal structures show that they all possess square planar metal centers with similar metallacycle ring size. In solution, both phosphorescence and fluorescence are attributed to ligand-based excited states. It is confirmed that replacing phenyl groups with thiophene rings in metallacycles can induce or enhance fluorescence without adding extra conjugation to the ligand, thus obtaining room temperature fluorescence and phosphorescent dual emission from with different FL/PH ratios. It is also learned that adding thiophene rings to extend conjugation length in metallacycles (from **4** to **5**) will likely shut down phosphorescence in the visible region due to ligand-based low lying  $T_1$  states. Excited state transient absorption spectroscopy could be used in the future to gain more detailed experimental understanding of the photophysics of these metallacycles.

DFT and TD-DFT calculations show that upon excitation from  $S_0$  to  $S_1$ , **5** and **6** undergo charge transfer from the ligand to the empty  $6p_z$  orbital of Pt atom while **4** shows only  $\pi$ - $\pi$ \* transitions. It is also revealed that all three metallacycles show very planar quinoid-like structure in the  $S_1$  and  $T_1$  excited state with contracted single bonds and lengthened double/triple bonds in the ligand. Complex **6** undergoes significant planarization going from the GS to the  $S_1$  or  $T_1$  excited states, resulting in weaker absorbance and much larger energy loss in IC processes compared to **4** and **5**. Both fluorescence and phosphorescence maxima of these metallacycles are attributed to 0-0 relaxation from corresponding relaxed  $S_1$  and  $T_1$  excited states, and match up with calculated values. We anticipate the above findings may be useful in future applications in single-component white-emitting OLEDs, self-referencing oxygen sensors, and hypoxia contrast agents.

# **Chapter 4 Bithiophene-Based Flexible Lewis Pairs**

# 4.1 Introduction

Lewis acids and bases are important reactive species with applications in catalytic transformations,<sup>117</sup> molecular recognition and chemical sensing.<sup>47,50,118</sup> Molecules containing both Lewis acid and base functionalities (Lewis pairs) are intriguing systems where either Lewis adducts, or sterically hindered, unbound species with unusual reactivity, such as frustrated Lewis pairs (FLPs), can form (**Scheme 4-1**).<sup>119</sup>

Scheme 4-1. FLP activation of dihydrogen and catalyzed hydrogenation of imines.



Although most Lewis pairs exist either as unreactive adducts, or reactive unbound pairs, the development of systems where these forms exist in equilibrium with each other is intriguing (**Scheme 4-2**).<sup>120</sup> Such "flexible" systems may allow control of chemical behavior by tuning of the solvent, temperature or other environmental factors to favor either the unbound form or Lewis

adduct.

The ability to use absorption or emission color to instantaneously assess the state of such flexible systems would be useful, yet the photophysical properties of unbound Lewis pairs have rarely been explored to date.<sup>121</sup> It is known that the presence of charge-accepting Lewis acidic boron centers gives rise to intense light absorbance or photoluminescence,<sup>46,52,122</sup> which is absent when 4-coordinate boron is formed upon reaction with fluoride or cyanide anions.<sup>47,118b</sup> Carefully designed flexible Lewis pairs may, therefore, enable reversible tuning of photophysical behavior, based on whether the boron is free or engaged in a Lewis adduct. Absorption or emission changes can then be used to conveniently assess catalytic activity *in situ*, and may allow applications in sensors.





There are ways to reduce or even prohibit the interaction between Lewis acids and base, such as introducing strong steric hindrance to make them inaccessible to one another, lowering Lewis acidity/basicity so that the adduct is less thermodynamically favored, or in rare cases by using rigid acenaphthene bridges between the Lewis acid and base moieties to make the adduct geometrically unfavored (**Scheme 4-3**).<sup>66</sup> However, it is still difficult to design a robust system with a tunable and reversible equilibrium between the Lewis adduct and unbound Lewis pairs.

Scheme 4-3. A naphthalene-based Lewis adduct 31<sup>65</sup> and an acenaphthene-based FLP 32.<sup>66</sup>



Scheme 4-4. Bithiophene-based Lewis pair between -BMes<sub>2</sub> and -P(O)R<sub>2</sub> groups.



In this chapter, a flexible boron-phosphine oxide Lewis pair system will be disclosed in which manipulation of the equilibrium between unbound pair and Lewis adducts results in a fundamental alteration in the photophysical properties of the system. A key feature of this system is the flexibility of the bithiophene backbone which allows rotation about the interannular C-C bond to form the closed structure as a Lewis adduct or the open structure as an unbound Lewis pair (**Scheme 4-4**). The phosphine oxide functionality as the Lewis basic component of the system has special advantages in that it is air stable, easy to synthesize, and has dual functionality as both

Lewis base<sup>123</sup> and strong hydrogen bond acceptor (HBA) capable of forming hydrogen bonds (HBs) with amines,<sup>124</sup> alcohols,<sup>125</sup> H<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub>,<sup>126</sup> and even weak hydrogen donors such as CHCl<sub>3</sub>.<sup>127</sup> Other intramolecular borane-phosphine oxide pairs are known however none of them are able to switch between three- and four-coordinated boron centers.<sup>120i,128</sup>

## 4.2 **Result and Discussion**

### 4.2.1 Synthesis and Solid-State Structures

Scheme 4-5. Synthesis of 24a-c and 25.



The boron-phosphine oxide (B-PO) Lewis acid-base pairs **24a-24c** were synthesized from 3,3'-dibromo-5,5'-dibutylbithiophene (**22**) by sequentially introducing the phosphine and Lewis acidic boron centers (**Scheme 4-5**). Oxidation gave air-stable **24a-24c** as light yellow solids. Compound **25** was synthesized in a similar fashion for comparison except that a proton was introduced instead of the dimesitylboryl group.

The solid-state structure of **24a** (**Figure 4-1**) obtained by recrystallizing the compound from acetone shows that the phosphine oxide moiety forms a Lewis adduct with the boron center (**24a**<sub>closed</sub>), despite the presence of the bulky mesityl groups. The B-O bond length in **24a**<sub>closed</sub> is comparable to that in a related Lewis adduct supported on a 1,8-naphthalene linker;<sup>65</sup> however in that case the structure is highly congested and rigid whereas in **24a**<sub>closed</sub> there is sufficient flexibility for repulsions to be minimized. In **24a**<sub>closed</sub> the two thiophene rings are slightly twisted relative to each other with a small S(1)-C(4)-C(5)-S(2) dihedral angle of 20.94(15)°. The P-O bond length of 1.5194(10) Å in **24a**<sub>closed</sub> is longer than that in a similar, but free, phosphine oxide<sup>123</sup> due to weakened oxygen-to-phosphorus bonding. By contrast, **24c** crystallizes as an unbound Lewis pair **24c**<sub>open</sub> (**Figure 4-2**) due to substantial steric hindrance in this compound. In **24c**<sub>open</sub> the S-C-C-S dihedral angle is large (130.10(7)°), and the P=O bond length (1.4846(8) Å).



**Figure 4-1.** Solid-state molecular structure of **24a**. The thermal ellipsoids are drawn at 50% probability and H atoms are omitted for clarity.



**Figure 4-2.** Solid-state molecular structure of **24c**. The thermal ellipsoids are drawn at 50% probability and H atoms are omitted for clarity.

## 4.2.2 Infrared and NMR Spectroscopic Studies

In the solid state, the infrared (IR) spectrum of **24a** shows a stretching band ( $v_{P=O}$ ) at 1116 cm<sup>-1</sup>, close to values obtained for similar Lewis acid-base adducts containing -P(O)Ph<sub>2</sub> group,<sup>129</sup> and consistent with the bonding found in the crystal structure. However, the IR stretching band of **24c** in the solid state ( $v_{P=O} = 1185$  cm<sup>-1</sup>) is typical of free phosphine oxides.

The solution structure of compound **24a** was found to vary in different solvents, as evidenced by both IR and NMR spectra. In hexanes, a non-HB donating solvent, the P=O stretching band is at 1120 cm<sup>-1</sup>, similar to v<sub>P=O</sub> in the solid state and consistent with a Lewis adduct (**24a**<sub>closed</sub>) also being present in this solvent. In addition, the <sup>31</sup>P NMR spectrum in hexanes shows a single peak at  $\delta = 34.5$  ppm, significantly downfield from the peak in MeOH-*d*<sub>4</sub> or CDCl<sub>3</sub> (**Figure 4-3**) and broadened (peak width 28.5 Hz) relative to the narrower peak in MeOH-*d*<sub>4</sub> (peak width = 3.5 Hz). These spectral features are consistent with the Lewis adduct  $24a_{closed}$  being present in hexanes, with the broadening attributed to the presence of the quadrupolar <sup>10</sup>B and <sup>11</sup>B centers bonded to the oxygen center.



**Figure 4-3.** Stacked <sup>31</sup>P{<sup>1</sup>H} NMR spectra of **24a** in various solvents.



**Figure 4-4.** Stacked <sup>31</sup>P{<sup>1</sup>H} NMR spectra of **25** in various solvents.

In the strong HB solvent MeOH,  $v_{P=O}$  of **24a** is at 1187 cm<sup>-1</sup>, similar to the value typically observed for free P=O bonds.<sup>130</sup> The sharp upfield resonance in the <sup>31</sup>P NMR spectrum in MeOH*d*<sub>4</sub> is consistent with the presence of mostly **24a**<sub>0</sub>pen in this solvent. In contrast to **24a**, the <sup>31</sup>P NMR resonance in boron-free **25** shifts downfield with progressively more HB donating solvents<sup>131</sup> (**Figure 4-4**) due to the increasingly deshielded <sup>31</sup>P nucleus. <sup>11</sup>B NMR spectra of **24a** also show a downfield shift in stronger HB donor solvents, consistent with the presence of 3-coordinate boron.



**Figure 4-5.** FTIR spectra of **24a** in CD<sub>2</sub>Cl<sub>2</sub> solution (CD<sub>2</sub>Cl<sub>2</sub> was used instead of CH<sub>2</sub>Cl<sub>2</sub> to avoid overlapping C-H bending absorptions).

Interestingly, in CD<sub>2</sub>Cl<sub>2</sub> the IR spectrum of **24a** shows two P=O stretching peaks at 1196 cm<sup>-1</sup> and 1120 cm<sup>-1</sup> (**Figure 4-5**). The former is close to  $v_{P=O}$  of **25** at 1187 cm<sup>-1</sup>, corresponding to the presence of a free P=O group in **24a**<sub>open</sub>, while the latter is due to the presence of **24a**<sub>closed</sub>. This is indicative of the coexistence of both structures in this weak HB donating solvent. In CDCl<sub>3</sub>, another weak HB donating solvent, only a single broadened <sup>31</sup>P peak ( $\delta = 26.2$  ppm) is observed (**Figure 4-3**) and the peak width of 12.6 Hz lies between the 28.5 Hz observed for **24a**<sub>closed</sub> in hexanes and the 3.5 Hz of **24a**<sub>open</sub> in methanol, due to rapid equilibration in CDCl<sub>3</sub>. The interconverting two forms of **24a** cannot be distinguished due to a much faster exchange rate than the chemical shift difference in <sup>31</sup>P NMR ( $k_{ex} >> \Delta v$ ).<sup>132</sup>

The equilibrium responds to the addition of an external Lewis base such as fluoride anion. Reaction of **24a** in either CDCl<sub>3</sub> or acetone- $d_6$  solution with tetrabutylammonium fluoride (TBAF) results in an upfield shift, and sharpening, of the <sup>31</sup>P resonance (from  $\delta = 26.1$  to 21.7 ppm in CDCl<sub>3</sub> and from  $\delta = 33.4$  to 19.6 ppm in acetone-*d*<sub>6</sub>). This is attributed to cleavage of the B-O bond and formation of a fluoride adduct at boron (**Figure 4-6**).



Figure 4-6. Stacked  ${}^{31}P{}^{1}H$  NMR of 24a and 24a+F<sup>-</sup> in various NMR solvents.



**Figure 4-7.** Stacked <sup>31</sup>P{<sup>1</sup>H} NMR of **24b** in various NMR solvents (very broad peak in hexanes due to restricted rotation induced by bulky isopropyl groups).

Compound **24b** behaves similarly to **24a** in different solvents (**Figure 4-7**). The <sup>31</sup>P NMR peak of **24b**<sub>closed</sub> is very broad in hexanes due to restricted rotations of both mesityl groups on boron and isopropyl groups on phosphine in a steric crowded environment. The broadening is less

evident in CDCl<sub>3</sub> or MeOH- $d_4$  in that rotation of isopropyl groups in **24b**<sub>open</sub> is faster. This can be evidenced by <sup>1</sup>H NMR spectra: all peaks are well resolved at 25 °C in methanol (**Figure 4-8**), however in non-HB solvent benzene- $d_6$  the isopropyl CH signals and one of the mesityl CH<sub>3</sub> signals are very broad at 25 °C (**Figure 4-10**) and much sharper at 50 °C (**Figure 4-11**).

Moreover, the phosphine oxide moiety on **24b** has alkyl <sup>1</sup>H NMR signals due to the isopropyl substituents, well separated from aromatic peaks, allowing the intramolecular through-space interaction between the Lewis acid and base groups to be probed with 2D-NOESY experiments. In methanol- $d_4$ , a NOE was not detected between the CH and CH<sub>3</sub> groups on the isopropyl moiety and the methyl groups on the Mes<sub>2</sub>B unit (**Figure 4-8** and **Figure 4-9**), consistent with the spatial separation of these groups in **24b**<sub>open</sub>. In contrast, in the non-HB solvent benzene- $d_6$ , NOE interactions were observed (**Figure 4-11** and **Figure 4-12**), indicating proximity of these groups in agreement with the closed structure **24b**<sub>closed</sub>.



Figure 4-8. Assignment of the <sup>1</sup>H NMR spectrum of  $24b_{open}$  in methanol- $d_4$  (25 °C).

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**Figure 4-9.** <sup>1</sup>H NOESY spectrum of **24b**<sub>open</sub> in methanol- $d_4$  (25 °C, mixing time = 800 ms). No NOE is observed between H(6)/H(7) and H(13).



**Figure 4-10.** Assignment of the <sup>1</sup>H-NMR spectrum of **24b**<sub>closed</sub> in benzene- $d_6$  (25 °C) Signals from H(6) and H(13) are very broad, which leads to low sensitivity for NOESY experiments at this temperature.



**Figure 4-11.** Assignment of <sup>1</sup>H-NMR spectrum of **24b**<sub>closed</sub> in benzene- $d_6$  (50 °C, mixing time = 800 ms). Peak ~ 0.6 ppm arises from residue H<sub>2</sub>O.



**Figure 4-12.** <sup>1</sup>H NOESY spectrum of **24b**<sub>closed</sub> in benzene- $d_6$  (50 °C, mixing time = 800 ms). NOE interactions between H(6)/H(7) and H(13) are indicated with red dashed boxes. Even though H(4) and H(13) overlapped in the <sup>1</sup>H NMR spectrum, the labeled NOE signal should

only be attributed to H(13) since intramolecular through space interactions between H(4) and H(6)/H(7) are not geometrically allowed.



**Figure 4-13.** Stacked <sup>31</sup>P{<sup>1</sup>H} NMR spectra of **24c** in different NMR solvents (the spectrum of **24c** in MeOH- $d_4$  is not shown due to poor solubility).

The similarities between the behavior of **24a** and **24b** shows that bithiophene-based Lewis pair systems with either aryl or alkyl phosphine oxide substituents show flexible switching between Lewis adducts and unbound Lewis pairs in response to HB donating solvents. By introducing excessively bulky mesityl groups on both Lewis acid and base centers (**24c**) the Lewis adduct can be prevented from forming. Similarly to B-free phosphine oxide **25**, the <sup>31</sup>P NMR resonance of **24c** shifts downfield with more HB donating solvents (22.07 ppm in MeOH-*d*<sub>4</sub>, 20.52 ppm in CDCl<sub>3</sub> and 19.50 ppm in hexanes), with no indication of Lewis adduct formation in any solvent (**Figure 4-13**). Attempts have been made to determine the equilibrium constant between **24a**<sub>open</sub> and **24a**<sub>closed</sub> from <sup>31</sup>P NMR chemical shifts in different solvents. However, this is not practical since the inherent chemical shifts of **24a**<sub>open</sub> and **24a**<sub>closed</sub> unrelated to the equilibrium may also be solvent dependent and are unknown.



#### 4.2.3 Electronic Absorption and Emission Spectra

Figure 4-14. Left: UV-Vis spectra of 24a in various solvents; right: UV-Vis spectra of 24b in various solvents.

The absorption spectrum of **24a** depends on the HB donor ability of the solvent (**Figure 4-14a**). In very weak or non-HB donor solvents such as hexanes, the spectra show a dominant band at ~370 nm, however, with increasing HB donor strength ( $CH_2Cl_2 < CHCl_3 < MeOH$ ),<sup>14</sup> this absorption band becomes weaker, and the bands between 260-350 nm strengthen. In MeOH, the absorption spectrum is similar to that observed previously for a boryl-substituted bithiophene,<sup>46</sup> where the absorption is assigned as a charge-transfer band involving the 3-coordinate Lewis acidic boron center. Although the low energy absorptions of **24a**<sub>closed</sub> and **24a**<sub>open</sub> are very close in wavelength, they have quite different origins (see **Table 4-2** in the DFT calculation section below). The same trend is observed in the absorption spectra of **24b** (**Figure 4-14b**), while those of **24c** shows no significant solvent dependence due to its persistent unbound nature.



**Figure 4-15.** Emission from **24a**,  $\lambda_{ex} = 366$  nm using an 18.4 W UV lamp for excitation.



Figure 4-16. (a) Normalized emission and excitation spectra of  $24a_{closed}$  in hexanes (black trace) and  $24a_{open}$  in methanol (red trace). (b) Excitation energy dependent mixed emission from  $24a_{open}$  and  $24a_{closed}$  in CHCl<sub>3</sub>.

The emission of **24a** is also solvent dependent (**Figure 4-15**). In MeOH, **24a** shows strong emission at 540 nm (**Figure 4-16a**) with a quantum yield of 0.60. The relatively large Stokes shift (13400 cm<sup>-1</sup>) is consistent with a CT excited state in **24a**<sub>0pen</sub> as the source of the emission. In hexanes, **24a** shows bright blue emission with a smaller Stokes shift (5050 cm<sup>-1</sup>) assigned to decay of a bithiophene-localized excited state. In weak HB donating solvents such as CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub>,

compound **24a** luminesces with mixed color. Emission spectra of **24a** in CHCl<sub>3</sub> show excitationdependent luminescence (**Figure 4-16b**) with higher energy excitation resulting in lower energy emission. This unusual behavior is the result of simultaneous emission from both **24a**<sub>closed</sub> and **24a**<sub>open</sub>; at different excitation wavelengths the two compounds contribute differently to the total output. In contrast, dissolving **24c** in any of the solvents used here results only in intense CT emission coincident with that of **24a**<sub>open</sub>, since the Lewis adduct is not able to form in this case.



**Figure 4-17.** (a) Emission and excitation spectra of **24a** in methanol, *n*-BuOH, *s*-BuOH and *t*-BuOH. (b) Emission from **24a** irradiated at 366 nm using an 18.4 W UV lamp.

The emission spectra of **24a** in *n*-butanol, *s*-butanol and *t*-butanol show an increase in the blue region near 440 nm concomitant with increased steric bulk of the solvent molecule and higher electron density on the -OH groups (**Figure 4-17**). This is due to a decrease in the strength of the HB donating ability of the solvent<sup>131</sup> resulting in weaker interaction with the phosphine oxide thus more of the closed structure **24a**<sub>closed</sub> being present.



**Figure 4-18.** (a) Emission spectra of **24a** at decreasing temperatures in a MeOH/EtOH (v/v =1:4) solution excited at 330 nm. (b) Variable temperature <sup>31</sup>P NMR spectra of **24a** and **25** in CD<sub>3</sub>OD (-65 °C to 25 °C at 10 °C intervals).

The emission of **24a** is highly temperature-dependent in alcohol solvent. At room temperature, where **24a<sub>open</sub>** is the major species present in strong HB donor solvents, the dominant emission from **24a** is at ~540 nm. However, with cooling, the emission band at 440 nm (assigned to **24a<sub>closed</sub>**) increases in intensity with a concomitant decrease in the band at 540 nm (**Figure 4-18**). The variable temperature <sup>31</sup>P NMR spectra of **24a** in methanol- $d_4$ , show significant downfield shifts and broadening as more **24a<sub>closed</sub>** forms at lower temperatures while the <sup>31</sup>P NMR spectrum of boron-free compound **25** shows only slight broadening and upfield shifts over the same temperature range (**Figure 4-18b**). The observed temperature dependence of the **24a<sub>closed</sub>/24a<sub>open</sub>** equilibrium is possibly due to the decrease in entropy resulting from the increased rigidity of **24a<sub>closed</sub>** relative to **24a<sub>open</sub>**.

## 4.2.4 DFT and TD-DFT Simulations



**Figure 4-19.** Optimized ground state geometries of (a) **24a**<sub>closed</sub> and (b) **24a**<sub>open</sub> rendered by PyMol software.

Table 4-1. Calculated molecular orbitals of 24aclosed and 24aopen in different solvents.



DFT computational (all-electron TZ2P basis sets at the BP86 level using ADF2013 software suite) studies by Prof. Jeffery Nagle confirmed that **24a**<sub>open</sub> and **24a**<sub>closed</sub> both correspond to minima on the ground state potential energy surface (**Figure 4-19**). The calculated B-O distance increases

from 1.64 Å in **24a**<sub>closed</sub> to 3.67 Å in **24a**<sub>open</sub>, and the S-C-C-S dihedral angle also significantly increases from 23.4° in **24a**<sub>closed</sub> to 65.0° in **24a**<sub>open</sub>. Single-point calculations of the ground-state structures confirmed that the LUMO of **24a**<sub>closed</sub> is mostly bithiophene-localized, while the LUMO of **24a**<sub>open</sub> is strongly boron-centered (**Table 4-1**).

Structur	re State	Transition	Туре	Energy	Oscillator Strength
24a <sub>closed</sub>	1 A	71.5% HOMO – LUMO	ππ*	269	0.291
	d IA	23.7 % HOMO-1 - LUMO	CT	308 mm	0.201
24a <sub>open</sub>	1A	HOMO - LUMO	CT	366 nm	0.075
	2A	HOMO-1 - LUMO	CT	340 nm	0.345

 Table 4-2. TD-DFT simulated vertical excitation energy and oscillator strengths of 24 in different solvents.

TD-DFT calculations (using BPE0 hybrid functional and all-electron TZ2P basis sets) were used to calculate absorption transitions for both  $24a_{closed}$  and  $24a_{open}$  by simulating vertical electronic excitation with frozen nuclear coordinates. The results are presented in **Table 4-2**, absorption wavelengths and oscillator strengths (indicative of relative absorption intensity) are in good agreement with experimental values in **Figure 4-14** (page 109). These show that the lowest energy absorption of  $24a_{closed}$  involves a bithiophene-localized  $\pi$ - $\pi$ \* transition mixed with a charge transfer transition from a mesityl  $\pi$ -orbital to the LUMO. The lowest energy absorption in  $24a_{open}$ arises from charge transfer (CT) processes from a mesityl-localized  $\pi$ -orbital and a bithiophenelocalized  $\pi$ -orbital to the boron-centered LUMO. This again confirmed the predominant existence of  $24a_{open}$  and  $24a_{closed}$  in MeOH and THF respectively.

## 4.3 Experimental

### 4.3.1 General

<sup>1</sup>H NMR, <sup>13</sup>C{<sup>1</sup>H} NMR, and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectrometer at 25 °C. <sup>11</sup>B NMR spectroscopic data were recorded at 25 °C on a 600 MHz Varian INOVA spectrometer equipped with a B-free 5 mm dual broadband gradient probe (Nalorac, Varian Inc., Martinez, CA) using boron-free quartz NMR tubes. Residual protio-solvent peaks were used in the calibration of <sup>1</sup>H NMR spectra. Peaks of the deuterated solvents were used to calibrate <sup>13</sup>C{<sup>1</sup>H} NMR spectra. All <sup>31</sup>P{<sup>1</sup>H} NMR spectra are referenced to 85% H<sub>3</sub>PO<sub>4</sub> as an external standard. Absorption spectra were obtained on a Varian Cary 5000 UV-Vis-NIR spectrophotometer, and emission measurements were performed on a PTI QuantaMaster 50 fluorimeter. Infrared spectroscopy (IR) was performed on an attenuated total reflection (ATR) crystal using a Perkin-Elmer Frontier FTIR spectrometer. X-Ray crystallography data were collected on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-Ka radiation. CHN elemental analyses were performed using an EA1108 elemental analyzer, using a suitable certified organic standard (OAS) of a known elemental composition for calibration.

All syntheses involving air sensitive compounds were carried out using standard Schlenktype procedures under an atmosphere of N<sub>2</sub>. Tetrahydrofuran (THF) was distilled from Na and stored under a N<sub>2</sub> atmosphere. Chlorodiphenylphosphine (ClPPh<sub>2</sub>, 98%), bis(2,4,6trimethylphenyl)phosphorus chloride (Mes<sub>2</sub>PCl, 95%), chlorodiisopropylphosphine (*i*-Pr<sub>2</sub>PCl, 96%), dimesitylboron fluoride (Mes<sub>2</sub>BF, 90%), di and hydrogen peroxide solution (H<sub>2</sub>O<sub>2</sub>, 30 wt. % in H<sub>2</sub>O) were purchased from Sigma-Aldrich and used without further purification. 3,3'- Dibromo-5,5'-dibutyl-2,2'-bithiophene (22) was synthesized according to literature procedure.<sup>133</sup>

### 4.3.2 Synthesis

3-Bromo-3'-diphenylphosphino-5,5'-dibutyl-2,2'-bithiophene, (23a): Compound 22 (1.4 g, 3.2 mmol) was placed in a dry round bottom flask with a side-arm under N<sub>2</sub>, and anhydrous THF (40 mL) was added to the flask. The solution was cooled to -78 °C and *n*-BuLi (1.6 M in hexanes, 2.1 mL, 3.4 mmol) was added drop-wise, after which the solution was stirred for another 1 hour at -78 °C. Ph<sub>2</sub>PCl (0.77 g, 3.5 mmol) was then added and the mixture was slowly warmed up to room temperature and stirred overnight. The reaction was then quenched with 1 mL deionized water, and THF was removed using a rotary evaporator. The mixture was extracted with diethyl ether  $(4 \times 10 \text{ mL})$  and the organic phase washed with first water and then brine before drying the organic layer over anhydrous MgSO<sub>4</sub>. The mixture was filtered and the solvent removed under vacuum. Purification by flash column chromatography (hexanes:  $CHCl_3 = 3:1$ ) gave a pale yellow viscous liquid. Yield: 1.25 g, 72%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 0.95-1.01 (m, 6H, 2CH<sub>3</sub>), 1.37-1.48 (m, 4H, CH<sub>2</sub>), 1.64-1.72 (m, 4H, CH<sub>2</sub>), 2.76-2.80 (m, 4H, 2CH<sub>2</sub>), 6.49 (s, 1H, thienyl CH), 6.76 (s, 1H, thienyl CH), 7.35-7.44 (m, 10H, phenyl CH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz): δ 13.8 (CH<sub>3</sub>), 13.8 (CH<sub>3</sub>), 22.2 (CH<sub>2</sub>), 22.3 (CH<sub>2</sub>), 30.0 (overlapping 2CH<sub>2</sub>), 33.1 (CH<sub>2</sub>), 33.6 (CH<sub>2</sub>), 111.1 (thienyl quaternary C-Br), 127.5 (thienyl CH), 127.9 (d,  ${}^{3}J_{PC} = 3.6$  Hz, thienyl C4), 128.3 (d,  ${}^{3}J_{PC} = 6.5$  Hz, phenyl CH), 128.4 (phenyl CH), 128.9 (d,  ${}^{2}J_{PC} = 1.5$  Hz, thienyl C4), 133.2 (d,  $^{2}J_{PC} = 19.2$  Hz, phenyl CH), 136.7 (d,  $^{2}J_{PC} = 16.5$  Hz, thienyl C4), 137.7 (d,  $^{1}J_{PC} = 37.1$  Hz, thienyl C4), 138.3 (d,  ${}^{1}J_{PC} = 11.0$  Hz, phenyl C4), 147.2 (d,  ${}^{5}J_{PC} = 1.7$  Hz, thienyl C4), 147.5 (d,  ${}^{3}J_{PC} =$ 2.3 Hz, thienyl C4).  ${}^{31}P{}^{1}H{}$  NMR (CDCl<sub>3</sub>, 162 MHz):  $\delta$  -23.62. Elemental Analysis calc. 62.10 116

% C, 5.58 % H. found. 62.28 % C, 5.58 % H.

3-dimesitylboryl-3'-diphenylphosphoryl-5,5'-dibutyl-2,2'-bithiophene, (24a): Compound **23a** (1.5 g, 2.7 mmol) was placed in a dry round bottom flask with a side-arm under  $N_2$ , and anhydrous THF (40 mL) was added to the flask. The solution was cooled to -78 °C and n-BuLi (1.6 M in hexanes, 1.8 mL, 2.9 mmol) was added drop-wise and stirred for 1 hour at -78 °C. Mes<sub>2</sub>BF (90 %, 912 mg, 3.4 mmol) was added at -78 °C and the solution was slowly warmed up to room temperature and stirred overnight. The reaction was then quenched by addition of  $H_2O$ and an excess amount of  $H_2O_2$  (10 mL, 30 wt. % in  $H_2O$ ) was added. The THF was removed from the resulting mixture on a rotary evaporator, and the mixture was then extracted with diethyl ether (4×10 mL) and the organic phase washed with first water and then brine, before drying over anhydrous MgSO<sub>4</sub>. The mixture was filtered and the solvent was removed from the filtrate under vacuum. Purification by flash column chromatography (hexanes: acetone=10:1) gave a yellow solid. Yield: 1.0 g, 52%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 0.88-0.92 (m, 6H, 2CH<sub>3</sub>), 1.22-1.25 (m, 2H, CH<sub>2</sub>), 1.29-1.34 (m, 2H, CH<sub>2</sub>), 1.42-1.47 (m, 2H, CH<sub>2</sub>), 1.52-1.57 (m, 2H, CH<sub>2</sub>), 2.05 (s, 12H, 4CH<sub>3</sub>), 2.23 (s, 6H, 2CH<sub>3</sub>) 2.56 (t, J = 7.4 Hz, 2H, CH<sub>2</sub>), 2.67 (t, J = 7.6 Hz, 2H, CH<sub>2</sub>), 6.10 (d,  ${}^{3}J_{PH} = 4.1$  Hz, 1H, thienyl CH), 6.49 (s, 1H, thienyl CH), 6.61 (s, 4H, mesityl phenyl CH), 7.39-7.44 (m, 4H, phenyl CH), 7.49-7.55 (m, 6H, phenyl CH).  ${}^{13}C{}^{1}H{}$  NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$ 13.9 (CH<sub>3</sub>), 13.9 (CH<sub>3</sub>), 21.2 (CH<sub>3</sub>), 22.0 (CH<sub>2</sub>), 22.2 (CH<sub>2</sub>), 23.9 (CH<sub>3</sub>), 29.4 (CH<sub>2</sub>), 29.6 (CH<sub>2</sub>), 33.6 (CH<sub>2</sub>), 33.9 (CH<sub>2</sub>), 123.8 (d,  ${}^{2}J_{PC} = 9.9$  Hz, thienyl C4), 128.3 (d,  ${}^{3}J_{PC} = 12.2$  Hz, phenyl CH), 128.3 (mesityl CH), 128.8 (d,  ${}^{2}J_{PC} = 17.5$  Hz, thienyl C4), 131.8 (d,  ${}^{4}J_{PC} = 2.3$  Hz, phenyl CH), 132.2 (d,  ${}^{2}J_{PC} = 9.9$  Hz, phenyl CH), 132.5 (thienyl CH), 133.3 (d,  ${}^{1}J_{PC} = 107.4$  Hz, phenyl C4), 136.9 (mesityl C4), 138.3 (d,  ${}^{3}J_{PC} = 2.3$  Hz, thienyl C4), 141.4 (mesityl C4), 144.5 (br, mesityl

C4), 145.1 (d,  ${}^{3}J_{PC} = 16.0$  Hz, thienyl C4), 147.1 (thienyl C4), 147.9 (d,  ${}^{1}J_{PC} = 9.9$  Hz, thienyl C4), 154.7 (br, thienyl C4).  ${}^{31}P{}^{1}H{}$  NMR (CDCl<sub>3</sub>, 162 MHz):  $\delta$  26.3.  ${}^{11}B$  NMR (CDCl<sub>3</sub>, 193 MHz):  $\delta$  55.8. Elemental Analysis calc. 76.02 % C, 7.21 % H. found. 76.24 % C, 7.23 % H.

3-Dimesitylboryl-3'-diisopropylphosphoryl-5,5'-dibutyl-2,2'-bithiophene, (24b): compound 24b was synthesized from 1 without isolation of intermediate 23b. Compound 1 (1.09 g, 2.5 mmol) was placed in a dry round bottom flask with a side-arm under N<sub>2</sub>, and anhydrous THF (40 mL) was added to the flask. The solution was cooled to -78 °C and *n*-BuLi (1.6 M in hexanes, 1.6 mL, 2.5 mmol) was added drop-wise, after which the solution was stirred for another 1 hour at -78 °C. *i*-Pr<sub>2</sub>PCl (0.40 g, 2.6 mmol) was then added and the mixture was slowly warmed up to room temperature and stirred overnight. After the formation of 23b, the solvent and unreacted *i*Pr<sub>2</sub>PCl was removed under vacuum, and the resulting residue dissolved using 40 mL fresh anhydrous THF. The solution was cooled to -78 °C and n-BuLi (1.6 M in hexanes, 1.7 mL, 2.7 mmol) was added. The mixture was stirred at -78 °C for 2 hours and reacted with Mes<sub>2</sub>BF (90 %, 834 mg, 2.8 mmol) followed by the same work-up procedure as used in the preparation of 3. Compound 24b was obtained as a yellow solid. Yield: 542 mg, 33%. <sup>1</sup>H NMR (CD<sub>3</sub>OD, 400 MHz): δ 0.88-0.94 (m, 6H, 2CH<sub>3</sub>), 1.01 (q,  ${}^{3}J_{PH} = 16$  Hz,  ${}^{3}J_{HH} = 7.2$  Hz, 6H, 2CH<sub>3</sub>), 1.20-1.26 (q,  ${}^{3}J_{PH} = 16$  Hz,  ${}^{3}J_{HH}$ = 7.1 Hz, 6H, 2CH<sub>3</sub>), 1.31-1.40 (m, 2H, CH<sub>2</sub>), 1.43-1.51 (m, 2H, CH<sub>2</sub>), 1.56-1.64 (m, 2H, CH<sub>2</sub>), 2.04 (s, 12H, 4CH<sub>3</sub>), 2.16 (s, 6H, 2CH<sub>3</sub>), 2.23-2.33 (m, 2H, 2CH), 2.65 (t, <sup>3</sup>*J*<sub>HH</sub> = 7.3 Hz, 2H, CH<sub>2</sub>), 2.72 (t,  ${}^{3}J_{HH} = 7.3$  Hz, 2H, CH<sub>2</sub>), 6.44 (s, 1H, thienyl CH), 6.55 (d,  ${}^{3}J_{PH} = 2.7$  Hz, 1H, thienyl CH), 6.61 (s, 4H, phenyl CHs).  ${}^{13}C{}^{1}H$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz):  $\delta$  14.1 (overlapped 2CH<sub>3</sub>), 15.8 (d,  ${}^{2}J_{PC} = 62.9$  Hz, CH<sub>3</sub>), 20.0 (2CH<sub>3</sub>), 22.5 (CH<sub>2</sub>), 22.5 (CH<sub>2</sub>), 24.5 (4CH<sub>3</sub>), 27.1 (d,  ${}^{1}J_{PC} = 70.0$  Hz, 2CH), 29.8 (CH<sub>2</sub>), 30.0 (CH<sub>2</sub>), 33.9 (CH<sub>2</sub>), 34.5 (CH<sub>2</sub>), 118.8 (d, <sup>1</sup>J<sub>PC</sub> =85.9 Hz, thienyl C4), 126.2

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(d,  ${}^{2}J_{PC}$  =15.5 Hz, thienyl CH), 129.2 (phenyl CHs), 135.1 (phenyl C4),135.1 (thienyl CH), 136.0 (thienyl C4), 141.5 (br, phenyl C4), 145.7 (d,  ${}^{1}J_{PC}$  =13.5 Hz, thienyl C4), 146.4 (thienyl C4), 147.9 (phenyl C4), 151.5 (thienyl C4), 157.9 (thienyl C4).  ${}^{31}P{}^{1}H{}$  NMR (CD<sub>3</sub>OD, 162 MHz):  $\delta$  53.3 Hz. Elemental Analysis calc. 72.93 % C, 8.57 % H. found. 72.95 % C, 8.57 % H.

3-dimesitylboryl-3'-dimesitylphosphoryl-5,5'-dibutyl-2,2'-bithiophene, (24c): Compound 24c was synthesized from 22 without isolation of intermediate 23c, following a similar synthetic procedure to that used for 24b, except that Mes<sub>2</sub>PCl (0.80 g, 2.6 mmol) was used instead of *i*-Pr<sub>2</sub>PCl. Compound **24c** was obtained as a yellow solid. Yield: 1.0 g, 50%. <sup>1</sup>H NMR (CD<sub>3</sub>OD, 400 MHz):  $\delta$  0.83-0.87 (m, 6H, 2CH<sub>3</sub>), 1.08-1.17 (m, 2H, CH<sub>2</sub>), 1.23-1.37 (m, 4H, 2CH<sub>2</sub>), 1.43-1.51 (m, 2H, CH<sub>2</sub>), 2.14 (br, 12H, 4CH<sub>3</sub>), 2.19 (s, 12H, 4CH<sub>3</sub>), 2.23 (br, 6H, 2CH<sub>3</sub>), 2.31 (s, 6H, 2CH<sub>3</sub>), 2.47 (t,  ${}^{3}J_{HH} = 7.2$  Hz, 2H, CH<sub>2</sub>), 2.61 (t,  ${}^{3}J_{HH} = 7.5$  Hz, 2H, CH<sub>2</sub>), 6.09 (d,  ${}^{3}J_{PH} = 5.2$  Hz, 1H, thienyl CH), 6.47 (s, 1H, thienyl CH), 6.66 (br, 4H, phenyl CH), 6.86 (d,  ${}^{3}J_{PH} = 3.3$  Hz, 4H, phenyl CHs). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz): δ 13.8 (CH<sub>3</sub>), 13.9 (CH<sub>3</sub>), 21.1 (d, <sup>5</sup>*J*<sub>PC</sub> =1.1 Hz, CH<sub>3</sub>), 21.3 (CH<sub>3</sub>), 21.8 (CH<sub>2</sub>), 22.2 (CH<sub>2</sub>), 23.5 (d, <sup>3</sup>J<sub>PC</sub> =8.3 Hz, CH<sub>3</sub>), 23.9 (br, CH<sub>3</sub>), 29.31 (CH<sub>2</sub>), 29.4 (CH<sub>2</sub>), 33.4 (CH<sub>2</sub>), 33.8 (CH<sub>2</sub>), 128.2 (br, phenyl CHs), 130.0 (d,  ${}^{2}J_{PC}$  =18.5 Hz, thienyl CH), 130.8 (d, <sup>1</sup>*J*<sub>PC</sub>=98.9 Hz, thienyl C4), 131.0 (thienyl CH), 131.0 (d, <sup>3</sup>*J*<sub>PC</sub> =11.0 Hz, phenyl CH), 138.0 (phenyl C4), 140.6 (d,  ${}^{2}J_{PC}=2.7$  Hz, phenyl C4), 141.1 (br, phenyl C4), 142.1 (d,  ${}^{4}J_{PC}=2.2$  Hz, phenyl C4), 142.5 (d,  ${}^{1}J_{PC}$ =10.1 Hz, phenyl C4), 144.3 (d,  ${}^{2}J_{PC}$ =9.4 Hz, thienyl C4), 145.5 (d,  ${}^{3}J_{PC}$ =15.4 Hz, thienyl C4), 147.4 (thienyl C4), 151.3 (thienyl C4), signals from the two carbons linked to boron were not observed. <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>3</sub>OD, 162 MHz): δ 20.52 Hz; Elemental Analysis calc. 77.01 % C, 7.95 % H. found. 77.37 % C, 7.87 % H.

3'-Diphenylphosphoryl-5,5'-diphenyl-2,2'-bithiophene, (25): Compound 23a (1.08 g, 2.0

mmol) was added to a dry round bottom flask under N<sub>2</sub>, and anhydrous THF (40 mL) added to the flask. The solution was cooled to -78 °C and *n*-BuLi (1.6 M in hexanes, 1.3 mL, 2.1 mmol) was added drop-wise. The cold solution was then stirred for 1 hour while maintaining the temperature at -78 °C. The reaction was first quenched with H<sub>2</sub>O, and H<sub>2</sub>O<sub>2</sub> (10 mL, 30 wt. % in H<sub>2</sub>O) was then added to oxidize the phosphine. The THF was removed from the resulting mixture on a rotary evaporator. The mixture was then extracted with diethyl ether  $(4 \times 10 \text{ mL})$  and the organic phase washed with water and brine and then dried over anhydrous MgSO<sub>4</sub>. The mixture was filtered after which the solvent was removed under vacuum. Recrystallization from methanol gave white needle-like crystals of pure 25. Yield: 840 mg, 88%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 0.85-0.89 (m, 6H, 2 CH<sub>3</sub> triplets), 1.19-1.37 (m, 4H, 2 CH<sub>2</sub>), 1.45-1.59 (m, 4H, 2 CH<sub>2</sub>), 2.43-2.67 (m, 4H, 2 CH<sub>2</sub>), 6.36 (s, 1H, thienyl CH), 6.37 (s, 1H, thienyl CH), 7.17 (d,  ${}^{3}J_{PC} = 3.6$  Hz, thienyl CH), 7.31-7.42 (m, 10H, phenyl CH), 7.63-7.68 (m, 4H, phenyl CH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz): δ 13.8 (CH<sub>3</sub>), 13.8 (CH<sub>3</sub>), 21.9 (CH<sub>2</sub>), 22.1 (CH<sub>2</sub>), 29.5 (CH<sub>2</sub>), 29.6 (CH<sub>2</sub>), 33.6 (CH<sub>2</sub>), 33.6 (CH<sub>2</sub>), 124.9 (thienyl CH), 128.2 (d,  ${}^{3}J_{PC} = 12.2$  Hz, phenyl CH), 128.5 (d,  ${}^{1}J_{PC} = 105$  Hz, phenyl C4), 129.7 (thienyl CH), 130.0 (d,  ${}^{2}J_{PC} = 16.0$  Hz, thienyl CH), 131.4 (d,  ${}^{4}J_{PC} = 2.7$  Hz, phenyl CH), 131.5 (thienyl C4), 131.6 (d,  ${}^{2}J_{PC} = 9.9$  Hz, phenyl CH), 133.4 (d,  ${}^{1}J_{PC} = 106$  Hz, phenyl C4), 144.4  $(d, {}^{2}J_{PC} = 10.8 \text{ Hz}, \text{ thienyl C4}), 144.9 (d, {}^{3}J_{PC} = 15.3 \text{ Hz}, \text{ thienyl C4}), 147.8 (thienyl C4). {}^{31}P{}^{1}H{}$ NMR (CDCl<sub>3</sub>, 162 MHz): δ 21.37. Elemental Analysis calc. 70.26 % C, 6.53 % H. found. 70.45 % C, 6.43 % H.

#### 4.3.3 DFT Simulations

The 2013.01 version of the Amsterdam Density Functional (ADF) program was used for all

calculations.<sup>134</sup> All electrons were included in the variational treatment (i.e., no frozen-core approximation was applied).  $C_1$  (NOSYM) symmetry-unrestricted ground state geometry optimizations were performed with experimental X-ray crystallographic geometries, where available, as starting points. The ground state optimized geometries were used as starting points for the TD-DFT excited state geometry optimizations.

Energies, geometries, and the orbital electronic structure were calculated using the generalized gradient approximation (GGA) of density functional theory (DFT) at the BP86 level. The GGA proceeds from the local density approximation (LDA), where exchange is described by Slater's  $X\alpha$  potential<sup>135</sup> and correlation is treated in the VWN parameterization,<sup>136</sup> and is augmented with nonlocal corrections to exchange due to Becke<sup>137</sup> and correlation due to Perdew added self-consistently.<sup>138</sup> Relativistic effects were taken into account in all cases using the zeroth-order relativistic approximation (ZORA)<sup>139</sup> and all-electron TZ2P basis sets from the ADF ZORA basis sets library were used for all atoms.<sup>140</sup> The BPE0 hybrid functional<sup>141</sup> was used for TD-DFT<sup>142</sup> calculations of excitation energies.<sup>143</sup> All other parameters were the same as for the BP86 ground state geometry optimizations.

# 4.4 Conclusions

This chapter reports the design and synthesis of flexible Lewis pairs **24a** and **24b** that undergo a temperature or solvent dependent structural change. <sup>31</sup>P and <sup>11</sup>B NMR shifts, NOESY effects and P=O stretching frequencies are used to track the structural changes. An unusual reversible system where various interactions between Lewis acidic and basic moieties on a  $\pi$ - conjugated bithiophene backbone give rise to different light absorbing and luminescence properties is demonstrated. The formation of the open structure is driven by hydrogen bond formation with the solvent, which stabilizes the free P=O bond.

# Chapter 5 Bithiophene-Based Flexible Lewis Pairs: Scope and Applications

# 5.1 Introduction

In **Chapter 4**, a bithiophene-based system with tunable interaction between pendant dimesitylboryl group (-BMes<sub>2</sub>) Lewis acid and phosphoryl group (-P(O)R<sub>2</sub>, where R = phenyl or isopropyl) Lewis base moieties was described. This system exhibits a dynamic equilibrium of competitive binding of the Lewis base, to either the internal Lewis acid or external HB donors. Such equilibrium is found to be temperature dependent and can be shifted by changing the solvent's HB donating strength.

Scheme 5-1. Work in Chapter 4 and Chapter 5.



In this Chapter, the bithiophene based Lewis acid-base pair system is further explored with

different Lewis bases, as well as variations on the bithiophene backbone. Some preliminary results of fluorescence microscopy imaging of these flexible Lewis pairs in hydrophobic/hydrophilic biological environments will also be discussed.

# 5.1.1 Fluorescence Microscopy and Fluorescent Dyes



Figure 5-1. Schematics of an inverted optical fluorescence microscope.

Fluorescence microscope allows scientists to detect microscopic fluorescent entities which may not be visible under a regular light microscope (**Figure 5-1**). Since its invention in 1910, fluorescence microscopy has become one of the most important and frequently used imaging methods in biology and medicinal applications.<sup>144</sup> For instance, in 2008, the Nobel Prize in Chemistry was awarded jointly to Osamu Shimomura, Martin Chalfie and Roger Y. Tsien *"for the discovery and development of the green fluorescent protein, GFP"*.<sup>145</sup> And in 2014, the Nobel

Prize in Chemistry was given to Erik Betzig, Stefan W. Hell and W. E. Moerner "*for the development of super-resolution fluorescence microscopy*",<sup>146</sup> solving the long standing resolution issue known as the Abbe diffraction limit<sup>147</sup> for a microscope, making subwavelength resolution possible. Modern fluorescence microscopy has truly entered the era of single molecule detection and imaging in the nanometer regime.<sup>148</sup>

Scheme 5-2. Examples of fluorescent dyes.



Intrinsic fluorescence of biological samples is usually weak and non-specific. Therefore, it is necessary to introduce fluorescent entities which can be used to selectively label targets of interest. Chemists can contribute greatly to this area by developing a wide variety of fluorescent dyes that are available for routine imaging using optical fluorescence microscopes, as well as more detailed measurements using advanced methods such as confocal laser fluorescence microscopy. Even though most fluorescent dyes suffer from photo-bleaching with long irradiation time, they are still preferred in many applications due to advantages such as ease of use, relatively small size compared to fluorescent proteins and the ability to be synthetically tailored for specific purposes.

There are many commercialized fluorescent dyes such as the members of the fluorescein, rhodamine and BODIPY families (Scheme 5-2). Functionalities can be added such as the

isothiocyanate group in **61** for bio-conjugation and aromatic groups for tuning of HOMO-LOMO energy levels for a desired emission color. A common feature of these dyes is that the core structure of the molecule (**Scheme 5-2**, highlighted with blue color) only exhibits one type of emission in different chemical environments. However, fluorescent dyes with reversible and stimuli responsive emission changes are scarce. A rare example was reported recently<sup>149</sup> where a flexible thiophenebased push-pull "fluorescent flippers" system (**Scheme 5-3**, left) exhibits shifted charge-transfer fluorescence under stress. The mechanosensitive emission of **64** is due to planarization of the backbone under pressure which gives rise to increased conjugation and decreased HOMO-LUMO energy gap. These molecules are able to indicate tension on membranes.<sup>73b,150</sup>





The bithiophene-based flexible Lewis acid-base pair system reported in the last chapter is found to exhibit two emission modes with different photophysical origins in different environments: strong HB donating solvents and non HB-donating solvents give rise to bright yellow and blue emissions of compound **24a**, respectively (**Scheme 5-3**, right). These chemical environments coincide with the hydrophilic (such as in lipid droplets and between lipid bilayers, etc.) and hydrophobic environments (in aqueous medium and ionic channels, etc.) in biological systems. Therefore, it would be interesting to use this type of flexible Lewis pair molecule as a two-color-channel fluorescent indicator for hydrophobic/hydrophilic environments., This would be potentially applicable to important research topics such as lipid metabolism, membrane crossing processes and even the study of diseases such as multiple sclerosis (MS) etc. Other benefits of this system include generally high emission quantum efficiency, high stability (long shelf-life) and generally low cytotoxicity of boron-containing compounds. Other fluorescent dyes that that can provide fluorescence contrast for hydrophobic and hydrophilic environments are not known to date.

## 5.1.2 Targets

The compounds shown in **Scheme 5-4** were synthesized. Compound **33** and **34** were made by arranging the Lewis acid and base differently on the bithiophene backbone. Variations of the Lewis base moiety give rise to compounds **24a-d** and **35a-c**. The color tunability in terms of conjugation length was also systematically explored by comparing **33**, **36**, **37**, **42** and **43**, and the electron density on the backbone by comparing compound **37-41**. Bi-cationic Lewis pair **46** was made through intermediates **44** and **45**, for better water solubility. Preliminary fluorescence imaging was carried out by Xiaozhu (Hunter) Wang using compounds **24a**, **41** and **46** on pig adipocytes (fat cells) and human brain slices (provided by Dr. Pat McGeer) as a proof of concept.



Scheme 5-4. Lewis pairs discussed in this chapter.

# 5.2 Results and Discussion

## 5.2.1 Scope of the Lewis Pair System

#### 5.2.1.1 Synthesis

Lewis pair **33** was prepared from **47**, and **34** was synthesized from **48** (**Scheme 5-5**). The synthetic strategy is the same as described in **Chapter 4**, however diethyl ether was used as the solvent for the synthesis of **33** to avoid deprotonation at the 5 and 5' positions of bithiophene.

During purification by flash column chromatography, **34** showed much higher polarity than **33** in the hexanes-THF eluent, indicative of the presence of free phosphine oxide instead of the less polar Lewis adduct.

Scheme 5-5. The 3,3'- and 5,5'-substituted Lewis pairs 33 and 34.



Scheme 5-6. Lewis pairs containing different Lewis bases.



Lewis pairs **24a-c** were reported in **Chapter 4**, and compound **24d** was made using a similar approach except that chlorodicyclohexylphosphine (Cy<sub>2</sub>PCl) was used instead of Ph<sub>2</sub>PCl. Compound **24d** has a similar electronic structure to **24c**, but is expected to be more congested

between the Lewis acid and base centers. Compound **35a** was made by introduction of -SMe and -BMes<sub>2</sub> groups in a stepwise fashion. Selective oxidation of **35a** with one or two equivalent of *m*-CPBA (3-chloroperbenzoic acid) at 0 °C gave **35b** and **35c** (**Scheme 5-6**). Please refer to **Section 5.3.2.2** for synthetic details.

#### 5.2.1.2 IR and Photophysics

IR resonances of polar X=O groups (X = C, N, S and P, *etc.*) are considered to be good spectroscopic handles in that they usually give rise to strong absorptions and are less strongly coupled with other IR transitions. Combined with UV-Vis and fluorescence spectra of these compounds, solid state IR spectra of compounds **24a-d**, **33**, **34**, **35a-c** were measured to provide insight into the chemical environment of the S=O or P=O groups. A red-shift in IR absorption of the X=O group is expected in the closed structure due to decreased bond strength when the group is bond to a Lewis acid center, while the open structure with 3-coordinated boron should give rise to charge transfer emission with larger Stokes shifts.

For bithiophene-based Lewis pairs with phosphine oxides as the Lewis base component, adducts can only be effectively formed intramolecularly: **33** and **34** show IR absorption at 1199 cm<sup>-1</sup> and 1117 cm<sup>-1</sup> in the solid state, respectively, indicative of Lewis adduct and free phosphine oxide. As discussed in **Chapter 4**, compound **24a** also shows a strong resonance at 1116 cm<sup>-1</sup> consistent with a Lewis adduct. Similarly, **24c** and **24d** do not show IR absorption expected of free alkyl phosphine oxides consistent with the presence of a Lewis adduct in the solid state. However, **24b** shows strong absorption at 1185 cm<sup>-1</sup> indicative of free phosphine oxide. The closed structure of **24b** containing a Lewis adduct cannot be formed due to bulky mesityl groups on both Lewis 130

acid and base centers. Concentration dependent  $(0.5 \times 10^{-5} \text{ M to } 1 \times 10^{-4} \text{ M})$  UV-Vis spectra of **33** are shown in **Figure 5-2**, in both methanol and THF solution, with no indication of intermolecular Lewis adduct formation. This confirms that the Lewis adduct cannot be effectively formed intermolecularly in solution at these concentrations.



Figure 5-2. UV-Vis spectra of 33 at various concentrations in (a) MeOH and (b) THF.



**Figure 5-3.** (a) Normalized excitation ( $\lambda_{em} = 520 \text{ nm}$ ) and emission ( $\lambda_{ex} = 320 \text{ nm}$ ) spectra of **33** in MeOH. (b) Normalized excitation (( $\lambda_{em} = 420 \text{ nm}$ ) and emission ( $\lambda_{ex} = 350 \text{ nm}$ ) spectra of **33** THF.



**Figure 5-4.** (a) Normalized excitation ( $\lambda_{em} = 520 \text{ nm}$ ) and emission ( $\lambda_{ex} = 320 \text{ nm}$ ) spectra of **24a-d** in MeOH. (b) Normalized excitation ( $\lambda_{em} = \text{individual maxima}$ ) and emission ( $\lambda_{ex} = 350 \text{ nm}$ ) spectra of **24a-d** in THF.

Excitation and emission spectra of **33** in THF and MeOH are shown in **Figure 5-3**. Similar to compound **24a** discussed in **Chapter 4**, **33** shows a much larger Stokes shift in MeOH than in THF consistent with a mostly open structure with 3-coordinated boron.

Excitation and emission spectra of Lewis pairs **24a-d** with different phosphine oxide Lewis bases are shown in **Figure 5-4**. Only **24b** remained open regardless of the solvent with CT emission maxima at 530 nm due to steric hindrance. By comparison, in methanol, **24c** and **24d** with dialkyl phosphine oxide moieties show significant amount of emission from the closed structure near 425 nm due to incomplete opening of Lewis adducts. Compound **24a** shows only a very small amount of emission from the closed form (emits at 450 nm in THF) in MeOH. This can be attributed to more polarized P=O bonds in the dialkyl phosphine oxide group compared to in the diaryl ones, resulting in stronger B-O bonds that are harder for methanol molecules to disrupt. Even though HB between solvent and P=O bonds may also be stronger in these cases, the overall effect still favors the closed structure. Compared to **24c** with the  $(i-Pr)_2P(O)$ - group, **24d** with  $Cy_2P(O)$ - group shows slightly less emission from the closed form in methanol. It is suggestive of a less favorable closed form of **24d** due to greater steric bulk of the Lewis base, considering they have similar emission quantum yields in both solvents (**Table 5-1**).



**Figure 5-5.** UV-Vis spectra of **35b** and **35c** in methanol and THF (left). Excitation and emission spectra of **35b** and **35c** in methanol and THF (right).

With Lewis pairs containing S=O groups as the Lewis base, **35b** shows a typical strong S=O stretching resonance of a free sulfoxide group at 1048 cm<sup>-1</sup>, and **35c** shows both symmetric and asymmetric stretching peaks of free S=O bonds at 1138 cm<sup>-1</sup> and 1311 cm<sup>-1</sup>, respectively. These findings indicate no significant binding of sulfoxide or sulfone groups to the Lewis acidic dimesitylboryl group in the solid state. UV-Vis spectra of **35b** and **35c** (**Figure 5-5**, left) are almost identical in both solvents, showing only slightly weaker low energy absorbance near 370 nm in MeOH. Even though **35c** emits at slightly higher wavelength than **35b** (**Figure 5-5**, right), these compounds show similar excitation and emission features in different solvents, with large Stokes shifts typical for open structures. Therefore, it can be concluded that S=O bonds in sulfoxides or

sulfones do not form closed Lewis adducts with the dimesitylboryl Lewis acid center. This may be attributed to a weaker polarization of the S=O bond compared to the P=O bond, making the partially negatively charged oxygen atom a less potent Lewis base to form a Lewis adduct with the -BMes<sub>2</sub> group.

## 5.2.2 Emission Color Tunability

#### 5.2.2.1 Synthesis

Two series of Lewis pairs were synthesized (a) **Series A** with different backbone conjugation lengths as shown in **Scheme 5-7** and (b) **Series B** with different electron donating or electron withdrawing groups as shown in **Scheme 5-8**. The purpose of introducing various substitutions was to access more emission colors of the Lewis pair in both open and closed structures, so that the system has wider scope in applications such as fluorescence imaging.





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Scheme 5-8. Electron-donating and withdrawing groups on the backbone (Series B).



Scheme 5-9. General synthesis of flexible phosphine oxide-borane Lewis pairs.



Scheme 5-10. Preparation of water-soluble flexible Lewis pair 20.



Synthesis of Lewis pairs **36-44** was successfully carried out following a general one-pot method as shown in **Scheme 5-9**, from corresponding dibromo-starting materials (please refer to

Section 5.6.2.2 for details). Compound 45 with reactive alkyiodide groups was synthesized by heating 44 to reflux with excess sodium iodide in acetone for two days (Scheme 4-10). Compound 46 was conveniently obtained by treating 45 with trimethylamine. 46 have the same fluorophore as 33, 44 and 45, however, it is specifically designed for higher water solubility while 33, 44 and 45 is only soluble in organic solvents.



#### 5.2.2.2 Electronic Absorption and Emission Spectra

**Figure 5-6.** UV-Vis spectra of  $1.0 \times 10^{-5}$  M solutions of **Series A** compounds (a) in MeOH with open structures and (b) in THF with closed structures.

UV-Vis spectra of the **Series A** compounds (**33**, **36**, **37**, **42** and **43**) in MeOH are shown in **Figure 5-6a**. All compounds show weaker CT absorption at higher wavelengths relative to their high energy absorptions. This shoulder-like feature which is typical for oligothiophene derivatives with pendant 3-coordinate -BMes<sub>2</sub> groups,<sup>46</sup> red-shifts from **33** (~350 nm) to **36** (~370 nm), **37** (~390 nm) to **43** (~420 nm). This is consistent with increasing backbone conjugation since **36** with

the mesityl group out of the plane is less conjugated than **37**, and the absorbance of **43** is redshifted relative to **37** because thiophene rings offer more effective conjugation than phenyl rings in this context.<sup>151</sup> The CT absorption of **42** is only slightly lower in energy than that of **37**, indicating that alkynyl groups do not contribute significantly to the increase in effective conjugation length. However, the molar absorption coefficient of **42** is much higher than **37** as a result of the presence of two more bridging alkynyl groups. UV-Vis spectra of **Series A** in THF are shown in **Figure 5-6b**. The lowest energy bands of the **Series A** molecules in THF show much stronger absorption and red-shifted compared to corresponding open structures observed in MeOH. This feature is attributed to predominantly  $\pi$ – $\pi$ \* absorptions of the more planar conjugated backbone in the closed Lewis adduct in THF. The same trend is seen here, molecules with longer conjugation length shows more red-shifted absorptions.



Figure 5-7. Normalized excitation ( $\lambda_{em}$  = individual emission maxima) and emission spectra ( $\lambda_{ex}$  = individual excitation maxima) of  $1.0 \times 10^{-5}$  M solutions of the Series A compounds (a) in MeOH with open structures and (b) in THF with closed structures.

Electronic excitation and emission spectra of the **Series A** compounds in MeOH and THF are shown in **Figure 5-7a** and **Figure 5-7b**, respectively. They all show large Stokes shifts in MeOH which is in line with energy loss in CT processes of the open structures. However, in THF where the closed structure is dominant, a much smaller Stokes shift is observed due to less energy loss between absorption and emission in the  $\pi$ - $\pi$ \* transitions. The emission colors of the **Series A** compounds range from blue to orange in the open structures and violet to green in the closed ones.



**Figure 5-8.** UV-Vis spectra of  $1.0 \times 10^{-5}$  M solutions of **Series B** compounds (a) in MeOH with open structures and (b) in THF with closed structures.

The UV-Vis spectra of the **Series B** compounds (**37-41**) are shown in **Figure 5-8**. In MeOH, all these compounds show a low energy weak CT absorption shoulder typical for open structures. This feature red-shifts from **37** to **41** with relatively consistent intensity. This is consistent with increasing electron density in the  $\pi$ -conjugated backbone resulting in a lower energy requirement for charge transfer to the electron deficient boron center. The absorptions of the closed forms of **Series B** in THF (**Figure 5-8**, right) show a similar trend where the more electron-rich substitution on the backbone gives rise to a lower energy absorption, except in **38** with -CF<sub>3</sub> groups. In both

solvents, the absorption energy differences between the **Series B** compounds are much smaller compared to that of the **Series A** compounds. The only exception is compound **41** with a strongly electron donating -NMe<sub>2</sub> group which behaves very differently from **37-40**. In fact, **41** also shows a strong effect of added conjugation as seen in **Series A** in that the -NMe<sub>2</sub> group is coplanar with the backbone with a notable contribution to its conjugation length, consistent with DFT calculated frontier molecular orbitals (entry 41, **Table 5-2** and **Table 5-3**).



**Figure 5-9.** Normalized excitation and emission spectra of  $1.0 \times 10^{-5}$  M solutions of the **Series B** compounds (a) in MeOH with open structures and (b) in THF with closed structures.

Electronic excitation and emission spectra of the **Series B** compounds in MeOH and THF are shown in **Figure 5-9**. Again, compound **41** shows a significant red-shift from **37-40**, due to the reasons discussed above. The emission colors of **Series B** range from green to red in the open structures and cyan to yellow in the closed ones. Emission of **41** in methanol shows a shoulder feature at around 540 nm possibly due to a small amount of closed structures which is much more

emissive than the open ones (**41** shows a much higher emission quantum efficiency in THF than in MeOH, see **Table 5-1**). It is also possible that the electron-rich compound gets oxidized by oxygen under excitation and forms highly emissive impurities.

**Table 5-1.** Summary of low energy absorption maxima ( $\lambda_{abs}$ ), emission maxima ( $\lambda_{em}$ ) and emission quantum yields ( $\Phi_{em}$ ) of **33** and **36-43** in MeOH and THF.

Compound	Open Structure (in MeOH)			Closed Structure (in THF)		
	$\lambda_{abs}$ (nm)	$\lambda_{em} (nm)$	$\Phi_{\text{em}}$	$\lambda_{abs}$ (nm)	$\lambda_{em} \left( nm \right)$	$\Phi_{\rm em}$
33	350*	512	0.52	345	429	0.23
36	370*	536	0.84	366	472	0.55
37	392	558	0.75	402	488	0.58
38	389	548	0.41	405	468	0.089
39	396	572	0.54	409	498	0.16
40	402	586	0.55	415	513	0.52
41	435	645	0.18	445	552	0.49
42	400	560	0.61	417	498	0.063
43	418	605	0.17	431	536	0.060

\* Maxima wavelength of some shoulder-like features are estimated.

The electronic properties of flexible Lewis pairs in **Series A** and **Series B** are summarized in **Table 5-1**. Interestingly for the open and closed structures of the same compound, there is almost no overlap between the absorption of one structure and the emission spectra of the other structure. This effectively prevents energy transfer between adjacent closed and open structures in the case of an equilibrium, so that the existence of one structure does not decrease/quench the emission of the other. This can be important for imaging applications where both forms are present and may allow quantification of the open/closed ratio via measurement of emission intensities.

## 5.2.3 Fluorescence Imaging

Initial trials of staining pig adipocytes (fat cells) with culture medium were performed by Hunter (Xiaozhu) Wang in the Orvig research group at UBC. Pig adipocytes were selected because their large size (~100  $\mu$ m) and the hydrophobic environment in their large internal lipid droplets (**Figure 5-10a**). Three molecules (**Scheme 5-10**) were used as dyes, compounds **24a** and **46** have the same fluorophore and were measured to show the same emission pattern of yellow/blue colors in hydrophilic/hydrophobic environments. By contrast, compound **41** with a longer conjugation length and electron donating groups show red-shifted emission in hydrophilic/hydrophobic media (orange/green). These experiments were carried out as proof-of-concept of the application of the reversible two-color fluorescent dye for hydrophobic/hydrophilic environments.





The sample slides were immersed in the dye-containing PBS buffer (phosphate-buffered saline) with 1 vol % DMSO and 10  $\mu$ g/mL dyes for one hour, and was then washed extensively

with fresh buffer to remove any dye that wasn't absorbed by the sample. The sample was then placed under UV (385 nm) excitation and observed using an inverted fluorescence microscope (**Figure 5-1**). The emission was filtered by long pass or band-pass lenses to cut off undesired light.



**Figure 5-10.** (a) Schematic of adipocytes and (b) blue emission of molecule **24a** inside the lipid droplets of adipocytes (scale bar =  $100 \mu m$ , 485 nm long pass filter was used).



**Figure 5-11.** (a) Yellow-greenish emission of molecule **46** in the membrane of adipocytes (scale bar 100  $\mu$ m, 520 nm long pass filter was used) and (b) blue emission on the cell membrane (scale bar 100  $\mu$ m, 410-460 band-pass filter was used).

Preliminary results showed that 24a preferentially stayed in the lipid droplets (Figure 5-10)

due to its low water solubility while **46** was only attracted to the peripheral of the cells (**Figure 5-11**) showing both blue and yellow emission. This can be explained by part of the **46** molecules inserting into the hydrophobic lipid bilayer in a similar fashion to some membrane probes,<sup>152</sup> while the rest of the molecule dissolved in the very thin layer of water medium around the lipid droplet (the cytoplasm). It is also possible that part of the molecules of **46** are attracted to either/both sides of the cell membrane by the slightly negatively charged membrane surface.



**Figure 5-12.** (a) Yellow emission of molecule **46** in the periphery and blue emission of **24a** in the lipid droplet of adipocytes (scale bar = 100  $\mu$ m). (b) Yellow emission of molecule **46** in the periphery and yellow emission of **41** in the lipid droplet of adipocytes (scale bar = 100  $\mu$ m). A 485 nm long pass filter was used in both cases.

The different distribution of **24a** and **46** in adipocytes allows us to use a mixture of the two molecules to simultaneously light up both environments (**Figure 5-12a**). Similarly, **41** can also be used in combination with **46** (**Figure 5-11**, right) in that **41** is also much more soluble in lipid than in water. The green emission color inside the adipocytes comes from closed **41** while the peripheral green color is attributed mostly to the open **46** structures. An advantage of these dyes is that the

distribution and color can be tuned separately by changing the side chain and fluorophore, respectively. Moreover, many more functionalities such as targeting vectors can be easily introduced by nucleophilic substitution of the  $S_N 2$  reactive iodine atoms on **45** (Scheme 5-10).



**Figure 5-13.** (a) Schematics of neurons and their structures.<sup>153</sup> (b) Parallel nerve fibers can be seen in dashed box with stronger emission from dye **46** (scale bar 100  $\mu$ m).

These results suggested it would be useful to look for other important biological structures with rich lipid content or membranes. Neural system samples such as those from the brain are of interest since they contain numerus neurons with rich lipid contents and complicated intra-cellular and inter-cellular membrane structures. For instance, the insulating myelin sheath of axons contains many layers of membranes that help with the fast propagation of out-going neural signals. Some diseases such as multiple sclerosis (MS) and Guillain-Barré syndrome are related to malfunctioning or degrading myelin sheath structures. It may be interesting to apply the dyes investigated here for fluorescence imaging membrane structures in brain samples such as myelin sheath, since myelin sheathes is conventionally imaged under TEM spectroscope using heavy metal stained samples.<sup>154</sup>

Staining of human brain slices was performed by Xiaozhu (Hunter) Wang using bi-cationic dye **46** and dye **41** following similar protocols to those described above. The fluorescence image of nerve fibers parallel to axons (**Figure 5-13**, right) shows moderate contrast in that only emission from the outside membrane is detected. By comparison, fluorescence images of cross sections of axons are much more illustrative. The images obtained using dye **46** (**Figure 5-14**) shows myelin sheath structures as bright circles since this dye is attracted to the negative charges on membranes. There is more blue emission from the background compared to areas inside the circular myelin sheath structures where emission is visibly more yellow. This is due to richer lipid content outside axons and thus more emission is observed from the closed Lewis pair structure. However, inside axons is a more aqueous environment which give rise to the open structure that emits yellow.



**Figure 5-14.** Fluorescent images of brain slices showing cross-section of axons using **46**. Scale bars are (a)100  $\mu$ m and (b) 20  $\mu$ m.

The images obtained using dye **41** (**Figure 5-15**) show stronger green emission from the lipid-rich matter surrounding the axons due to the much higher emission quantum yield of the closed form compared to the open form (**Table 5-1**). The open structure emission inside the axons

is much weaker by comparison. However, **41** does clearly outline the multiple layer of membranes in the myelin sheath (**Figure 5-15b**).



**Figure 5-15.** Fluorescent images of brain slices showing cross-section of axons using **41**. Scale bars are (a)100  $\mu$ m and (b) 20  $\mu$ m.

## 5.2.4 DFT Simulations

The purposes of DFT calculations are to have insight into the different emission colors of the flexible Lewis pairs with different substitutions and to understand the unusual photophysical trends of the **Series B** compounds. These include red-shifted excitation and emission features of compound **41** in THF and MeOH, as well as slightly red-shifted low-energy absorption of **38** in THF compared to **37**.

DFT calculations were carried out to simulate GS structure of Lewis pairs **37-41** in **Series B**. For all simulations, the solvation effect of either methanol or THF was implemented using the polarizable continuum model (PCM) solvation method. DFT calculated frontier orbitals of the optimized GS structures of **37-41** are summarized in **Table 5-2** (open structure in MeOH) and **Table 5-3** (closed structure in THF). The HOMO and LUMO energy levels of the compounds in **Series B** are summarized in **Table 5-4** for qualitative comparisons. TD-DFT simulated low-energy absorption transitions of the closed and open structures of **Series B** are presented in **Table 5-5**.



Table 5-2. HOMO-1, HOMO and LUMO of the open structure of the compounds in Series B.

\* The colors for atoms are C (grey), O (red), S (yellow), P (orange), B (pink) and N(blue).



Table 5-3. HOMO and LUMO of the closed structure of the compounds in Series B.

\* In the ball-and-stick models the colors for atoms are C (grey), O (red), S (yellow), P (orange), B (pink) and N(blue). Hydrogens are omitted.

As for the open structures modeled with MeOH solvation, the LUMOs of **37**, **39-41** are heavily boron-centered, while the LUMO of **38** also receives a strong contribution from the  $\pi^*$ orbital of the relatively electron poor backbone (**Table 5-2**, LUMO entry 38) due to the presence of the electron withdrawing -CF<sub>3</sub> groups. This leads to a relatively consistent LUMO energy levels 148 of **37**, **39** to **40** and **41**, while the LUMO of **38** is slightly higher in energy (**Table 5-4**, left). The HOMO energies of the compounds in **Series B** consistently increases with more electron density on the backbone in the order of 38 < 37 < 39 < 40 < 41. Therefore, the HOMO-LUMO energy gap ( $\Delta E_{OPEN}$ ) in methanol gets larger in the same order as the result of more electron donating groups.

Frontier orbitals of the closed structures the compounds in **Series B** modeled with THF solvation show very consistent  $\pi$ - $\pi$ \* character. Their HOMO-LUMO energy gaps also do not show significant differences from one another except for compound **41** (**Table 5-4**, right), indicating that the electron donating and withdrawing groups of the closed structure have similar effects on the  $\pi$  orbitals (HOMO) and  $\pi$ \* orbitals (LUMO). Compound **41** shows different behavior since there are some degree of charge transfer from HOMO to LUMO, and the  $sp^2$  nitrogen atoms also contribute significantly to extended conjugation of the backbone.

**Table 5-4.** HOMO and LUMO energies and HOMO-LUMO gaps ( $E_{HOMO}$ ,  $E_{LUMO}$  and  $\Delta E$ , respectively, in eV) of the closed and open structures of the compounds in **Series B**.

Compound –	Open Structure (in MeOH)			Closed Structure (in THF)			
	E <sub>HOMO</sub>	E <sub>LUMO</sub>	$\Delta E_{OPEN}$	Еномо	E <sub>LUMO</sub>	$\Delta E_{\text{CLOSED}}$	
37	-6.05	-1.87	4.17	-5.75	-2.13	3.62	
38	-6.20	-2.01	4.19	-5.55	-1.87	3.67	
39	-5.94	-1.86	4.08	-5.46	-1.83	3.63	
40	-5.71	-1.84	3.87	-5.30	-1.75	3.55	
41	-5.15	-1.76	3.39	-4.86	-1.61	3.25	

	OĮ	oen Structure (in MeOI	H)	Closed Structure (in THF)			
Compound	Wavelength	Major Transitions	Oscillator Strength	Wavelength	Transitions	Oscillator Strength	
37	372 nm	HOMO-LUMO	0.089	410	HOMO-LUMO	0.89	
	345 nm	HOMO-1-LUMO	0.32	410 nm			
38	372 nm	HOMO-LUMO	0.072	415	HOMO-LUMO	0.93	
	347 nm	HOMO-1-LUMO	0.36	415 nm			
39	379 nm	HOMO-LUMO	0.16	416	HOMO-LUMO	1.05	
	348 nm	HOMO-1-LUMO	0.32	410 nm			
40	396 nm	HOMO-LUMO	0.26	125 mm	HOMO-LUMO	1.00	
	354 nm	HOMO-1-LUMO	0.15	423 mm			
41	446 nm	HOMO-LUMO	0.28	466 nm	HOMO-LUMO	1.17	
	347 nm	HOMO-1-LUMO	0.22				

**Table 5-5.** TD-DFT calculated low-energy absorption transitions of the closed and open structures of the compounds in **Series B**.

# 5.3 Experimental Section

#### 5.3.1 General

<sup>1</sup>H NMR, <sup>13</sup>C{<sup>1</sup>H} NMR, and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectromete. Residual protio-solvent peaks were used in the calibration of the <sup>1</sup>H NMR spectra. Peaks of the deuterated solvents were used to calibrate the <sup>13</sup>C{<sup>1</sup>H} NMR spectra. All <sup>31</sup>P{<sup>1</sup>H} NMR spectra were referenced to 85% H<sub>3</sub>PO<sub>4</sub> as an external standard. Absorption spectra were obtained on a Varian Cary 5000 UV-Vis-NIR spectrophotometer, and emission

measurements were performed on a PTI QuantaMaster 50 fluorimeter. Infrared spectroscopy (IR) was performed on an attenuated total reflection (ATR) crystal using a Perkin-Elmer Frontier FTIR spectrometer.

All syntheses involving air sensitive compounds were carried out using standard Schlenktype procedures under an atmosphere of N<sub>2</sub>. Anhydrous tetrahydrofuran (THF) and diethyl ether (Et<sub>2</sub>O) was obtained using solvent purification system (SPS). Chlorodiphenylphosphine (ClPPh<sub>2</sub>, 98 %), chlorodicyclohexylphosphine (Cy<sub>2</sub>PCl, 97 %), dimethyl disulfide (CH<sub>3</sub>SSCH<sub>3</sub>, 99 %), 5bromo-2-hexylthiophene (97 %), 3-chloroperbenzoic acid (*m*-CPBA,  $\leq$  77 %), hydrogen peroxide solution (H<sub>2</sub>O<sub>2</sub>, 30 wt. % in H<sub>2</sub>O), NMe<sub>3</sub> solution (~45 wt.% in H<sub>2</sub>O), phenylboronic acid (95 %), 4-trifluoromethyl-phenylboronic acid (95 %), 4-*tert*-butylphenylboronic acid (95 %), 4methoxyphenylboronic acid (95 %), 4-(dimethylamino)phenylboronic acid (95 %) were purchased from Sigma-Aldrich. Dimesitylfluoroborane (Mes<sub>2</sub>BF, 98%) was ordered from TCI America. All purchased chemicals were used without further purification.

## 5.3.2 Synthesis

The phosphine oxide-borane Lewis pairs were synthesized using a general method described in Scheme 5-9 from corresponding substituted dibromo precursors (Scheme 5-12 in parentheses) which were made from either 3,3',5,5'-tetrabromo-2,2'-bithiophene (33)<sup>155</sup> or 3,3'-dibromo-5,5'-diiodo-2,2'-bithiophene (34)<sup>156</sup> via Suzuki, Sonogashira or Negishi cross-coupling reactions (Scheme 5-13 and Scheme 5-14).  $22^{133}$ ,  $47^{157}$ ,  $48^{158}$ ,  $54^{159}$  are known in literature. The sulfur-borane Lewis pair 35a-c were synthesized according method described in Scheme 5-6, from

an intermediate 49 which was made from 22.



Scheme 5-12. Phosphine oxide-borane Lewis pairs and their precursors in parentheses.

#### 5.3.2.1 Synthesis of Lewis Pairs

*3'-Dimesitylboryl-3-diphenylphosphinyl-2,2'-bithiophene* (**33**): **47** (745 mg, 2.30 mmol) was dissolved in 40 mL of dry diethyl ether and cooled to -78 °C. *n*-BuLi (1.6M in hexanes, 1.58 mL, 2.53 mmol) was added and the mixture was stirred for 1 hour at the same temperature. Ph<sub>2</sub>PCl (560 mg, 2.53 mmol) was then added and the mixture was slowly warmed up to room temperature and stirred for another 1 hour. The mixture was cooled to -78 °C again and *n*-BuLi (1.6M in

hexanes, 1.73 mL, 2.76 mmol) was added followed by one hour of stirring. Solid Mes<sub>2</sub>BF (800 mg, 3.04 mmol) was directly added under a high N2 flow, and the reaction was stirred for 1 hour before it was warmed up to room temperature and stirred for an additional 18 hours. The reaction was then guenched by 5 mL H<sub>2</sub>O and an excess amount of H<sub>2</sub>O<sub>2</sub> (1 mL, 30 wt. % in H<sub>2</sub>O) was added. The mixture was stirred for 4 more hours and then extracted with diethyl ether (4×10 mL). The organic phases were combined and washed with water and brine, before drying over anhydrous MgSO<sub>4</sub>. The mixture was filtered and the solvent was removed from the filtrate under vacuum. Purification by flash column chromatography (hexanes: THF = 5:1) gave a white solid. Yield: 1.06 g, 76 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  2.04 (s, 12H, CH<sub>3</sub>), 2.23 (s, 6H, CH<sub>3</sub>), 6.49 (dd,  ${}^{3}J_{HH} = 5.3$  Hz,  ${}^{3}J_{PH} = 3.7$  Hz, 1H, thienyl CH), 6.61 (s, 4H, phenyl CH), 6.82 (d,  ${}^{3}J_{HH} = 5.0$ Hz, 1H, thienyl CH), 7.05 (dd,  ${}^{3}J_{HH} = 5.4$  Hz,  ${}^{4}J_{PH} = 2.4$  Hz, 1H, thienyl CH), 7.18 (d,  ${}^{3}J_{HH} = 5.0$ Hz, 1H, thienyl CH), 7.39-7.55 (m, 10H, phenyl CH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz): δ 21.1 (CH<sub>3</sub>), 24.0 (CH<sub>3</sub>), 123.9 (d,  ${}^{1}J_{PC} = 105.5$  Hz, thienyl C4), 125.1 (d,  ${}^{2}J_{PC} = 16.4$  Hz, thienyl CH), 126.4 (thienyl CH), 128.4 (d,  ${}^{3}J_{PC} = 13.6$  Hz, phenyl CH), 128.5 (phenyl CH), 131.9 (d,  ${}^{3}J_{PC} =$ 17.8 Hz, thienyl CH), 132.0 (d,  ${}^{4}J_{PC} = 2.8$  Hz, phenyl CH), 132.0 (d,  ${}^{1}J_{PC} = 109.3$  Hz, thienyl C4), 132.2 (d,  ${}^{2}J_{PC} = 10.5$  Hz, phenyl CH), 136.0 (thienyl CH), 136.5 (phenyl C4), 138.5 (d,  ${}^{3}J_{PC} = 2.2$ Hz, thienyl C4), 141.3 (phenyl C4), 144.7 (phenyl C4), 150.5 (d,  ${}^{3}J_{PC} = 10.4$  Hz, thienyl C4), 156.1 (thienyl C4). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 162 MHz): δ 29.1. ESI-TOF: *m*/Z [M+H]<sup>+</sup> 614.2153 calc. for C<sub>38</sub>H<sub>37</sub>OPS<sub>2</sub><sup>10</sup>B, found: 614.2143.

5'-Dimesitylboryl-5-diphenylphosphinyl-2,2'-bithiophene (**34**): A similar procedure as for **1** was followed using **48** (650 mg, 2.00 mmol) as starting material and THF as the solvent. Purification by flash column chromatography (hexanes: THF=2:1) gave an off-white solid. Yield: 882 mg, 72 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 2.14 (s, 12H, CH<sub>3</sub>), 2.31 (s, 6H, CH<sub>3</sub>), 6.84 (s, 4H, phenyl CH), 7.31 (dd,  ${}^{3}J_{HH} = 3.7$  Hz,  ${}^{4}J_{PH} = 1.8$  Hz, 1H, thienyl CH), 7.35 (m, 2H, thienyl CH), 7.40 (dd,  ${}^{3}J_{HH} = 3.8$  Hz,  ${}^{3}J_{PH} = 7.5$  Hz, 1H, thienyl CH), 7.47-7.51 (m, 4H, phenyl CH), 7.55-7.57 (m, 2H, phenyl CH), 7.73-7.79 (m, 4H, phenyl CH).  ${}^{13}C{}^{1}H{}$  NMR (CDCl<sub>3</sub>, 100 MHz): δ 21.4 (CH<sub>3</sub>), 23.1 (CH<sub>3</sub>), 125.8 (d,  ${}^{3}J_{PC} = 12.7$  Hz, thienyl CH), 127.3 (thienyl CH), 128.4 (thienyl CH), 128.8 (d,  ${}^{3}J_{PC} = 12.6$  Hz, thienyl CH), 132.0 (d,  ${}^{2}J_{PC} = 10.3$  Hz, thienyl CH), 132.5 (d,  ${}^{4}J_{PC} = 2.7$  Hz, thienyl CH), 132.7 (d,  ${}^{1}J_{PC} = 109.4$  Hz, thienyl C4), 133.6 (d,  ${}^{1}J_{PC} = 109.6$  Hz, thienyl C4), 137.9 (d,  ${}^{2}J_{PC} = 8.7$  Hz, thienyl C4), 139.0 (phenyl C4), 141.0 (phenyl C4), 141.0 (br, phenyl C4), 141.4 (thienyl CH), 145.9 (d,  ${}^{3}J_{PC} = 5.3$  Hz, thienyl C4), 147.9 (thienyl C4), 150.8 (thienyl C4).  ${}^{3}P{}^{1}P{}^{1}H{}$  NMR (CDCl<sub>3</sub>, 162 MHz): δ 21.74. ESI-TOF: m/Z [M+H]<sup>+</sup> 615.2117 calcd. for C<sub>38</sub>H<sub>37</sub>OPS<sub>2</sub><sup>11</sup>B, found: 615.2127.

*5,5'-Dimesityl-3'-dimesitylboryl-3-diphenylphosphinyl-2,2'-bithiophene* (**36**): A similar as method for **33** was followed except **50** (1.12 g, 2.00 mmol) was used as starting material and THF as the solvent. Purification by flash column chromatography (hexanes: THF=5:1) gave a light-yellow solid. Yield 1.14 g, 67 %. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz):  $\delta$  2.05 (s, 6H, 2CH<sub>3</sub>), 2.09 (s, 12H, 4CH<sub>3</sub>), 2.17 (s, 6H, 2CH<sub>3</sub>), 2.24 (s, 6H, 2CH<sub>3</sub>), 2.29 (s, 6H, 2 overlapped CH<sub>3</sub>), 6.27 (d, <sup>3</sup>*J*<sub>PH</sub> = 4.0 Hz, 1H, thienyl CH), 6.44 (s, 1H, thienyl CH), 6.64 (s, 4H, phenyl CH), 6.90 (2H, phenyl CH), 6.91 (2H, phenyl CH), 7.43-7.45 (m, 4H, phenyl CH), 7.52-7.56 (m, 6H, phenyl CH). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz):  $\delta$  20.9 (CH<sub>3</sub>), 21.0 (CH<sub>3</sub>), 21.2 (2 overlapped CH<sub>3</sub>), 21.2 (CH<sub>3</sub>), 24.2 (CH<sub>3</sub>), 124.3 (d, <sup>1</sup>*J*<sub>PC</sub> = 103.3 Hz, thienyl C4), 128.3 (phenyl CH), 128.5 (phenyl CH), 128.7 (d, <sup>3</sup>*J*<sub>PC</sub> = 12.6 Hz, phenyl CH), 132.4 (d, <sup>4</sup>*J*<sub>PC</sub> = 2.5 Hz, phenyl CH), 132.5 (d, <sup>2</sup>*J*<sub>PC</sub> = 10.6 Hz, phenyl
CH), 132.5 (d,  ${}^{1}J_{PC} = 109.2$  Hz, phenyl C4), 136.4 (thienyl CH), 136.8 (phenyl C4), 138.1 (phenyl C4), 138.2 (phenyl C4), 138.4 (phenyl C4), 138.9 (phenyl C4), 138.9 (thienyl C4), 141.7 (d,  ${}^{3}J_{PC} = 16.1$  Hz, thienyl C4), 141.8 (phenyl C4), 142.8 (thienyl C4), 145.4 (phenyl C4), 150.1 (d,  ${}^{2}J_{PC} = 9.7$  Hz, thienyl C4), 157.4 (thienyl C4).  ${}^{31}P{}^{1}H{}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 162 MHz):  $\delta$  30.2. ESI-TOF: *m*/Z [M+H]<sup>+</sup> 850.3718 calcd. for C<sub>56</sub>H<sub>57</sub>OPS<sub>2</sub><sup>10</sup>B, found: 850.3723.

5,5'-Dibutyl-3-dicyclohexylphosphinyl-3'-dimesitylboryl-2,2'-bithiophene (24d): A similar method as for 33 was followed except 22 (870 mg, 2.00 mmol) was used as starting material. Also THF was used as the solvent and chlorodicyclohexylphosphine was used instead of chlorodiphenylphosphine. Purification by flash column chromatography (hexanes: THF=4:1) gave a yellow powder. Yield 1.20 g, 81 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 0.88-0.95 (m, 6H, 2CH<sub>3</sub>), 1.21-1.76 (m, 30H, 14CH<sub>2</sub> and 2CH), 2.05 (s, 12H, 4CH<sub>3</sub>), 2.20 (s, 6H, 2CH<sub>3</sub>), 2.66-2.72 (m, 4H,  $2CH_2$ ), 6.30 (d,  ${}^{3}J_{PH} = 2.4$  Hz, 1H, thienyl CH), 6.44 (s, 1H, thienyl CH), 6.62 (s, 4H, phenyl CH). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz): δ 13.9 (CH<sub>3</sub>), 13.9 (CH<sub>3</sub>), 21.1 (CH<sub>3</sub>), 21.9 (CH<sub>2</sub>), 22.2 (CH<sub>2</sub>), 24.1 (CH<sub>3</sub>), 25.6 (d,  ${}^{3}J_{PC} = 3.1$  Hz, CH<sub>2</sub>), 25.6 (CH<sub>2</sub>), 25.9 (CH<sub>2</sub>), 26.5 (d,  ${}^{2}J_{PC} = 12.8$  Hz, CH<sub>2</sub>), 26.7  $(d, {}^{2}J_{PC} = 13.5 \text{ Hz}, \text{CH}_{2}), 29.4 (\text{CH}_{2}), 29.6 (\text{CH}_{2}), 33.5 (\text{CH}_{2}), 34.0 (\text{CH}_{2}), 37.3 (d, {}^{1}J_{PC} = 68.8 \text{ Hz},$ CH<sub>2</sub>), 121.4 (d,  ${}^{1}J_{PC} = 111.3$  Hz, thienyl C4), 125.7 (d,  ${}^{2}J_{PC} = 13.5$  Hz, thienyl CH), 128.5 (phenyl CHs), 132.9 (thienyl CH), 136.2 (phenyl C4), 136.2 (thienyl C4), 141.1 (mesityl C4), 145.3 (d, <sup>2</sup>J<sub>PC</sub> =17.6 Hz, thienyl C4), 145.5 (phenyl C4), 146.5 (thienyl C4), 148.7 (phenyl C4), 154.8 (thienyl C4). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 162 MHz): δ 49.1. ESI-TOF: *m*/Z [M+H]<sup>+</sup> 739.4308 calcd. for C<sub>46</sub>H<sub>65</sub>OPS<sub>2</sub><sup>11</sup>B, found: 739.4323.

*3'-Dimesitylboryl-3-diphenylphosphinyl-5,5'-diphenyl-2,2'-bithiophene* (**37**): A similar method as for **33** was followed except **51** (943 mg, 2.00 mmol) was used as starting material and

THF as the solvent. Purification by flash column chromatography (hexanes: THF=4:1) gave a yellow solid. Yield 859 mg, 56 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  2.10 (s, 12H, CH<sub>3</sub>), 2.27 (s, 6H, CH<sub>3</sub>), 6.63 (s, 4H, phenyl CH), 6.74 (d, <sup>3</sup>*J*<sub>PH</sub> = 4.4 Hz, 1H, thienyl CH), 7.10 (s, 1H, thienyl CH), 7.25-7.58 (m, 20H, phenyl CH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  21.1 (CH<sub>3</sub>), 24.4 (CH<sub>3</sub>), 123.7 (d, <sup>1</sup>*J*<sub>PC</sub> = 104.6 Hz, thienyl C4), 125.9 (phenyl CH), 126.2 (phenyl CH), 127.0 (d, <sup>2</sup>*J*<sub>PC</sub> = 17.8 Hz, thienyl CH), 127.5 (phenyl CH), 128.3 (phenyl CH), 128.5 (d, <sup>3</sup>*J*<sub>PC</sub> = 12.8 Hz, phenyl CH), 128.7 (phenyl CH), 128.8 (phenyl CH), 129.1 (phenyl CH), 131.1 (d, <sup>1</sup>*J*<sub>PC</sub> = 110.6 Hz, phenyl C4), 132.3 (d, <sup>4</sup>*J*<sub>PC</sub> = 2.5 Hz, phenyl CH), 132.5 (d, <sup>2</sup>*J*<sub>PC</sub> = 10.6 Hz, phenyl CH), 132.7 (thienyl C4), 134.2 (phenyl C4), 136.1 (phenyl C4), 137.0 (thienyl C4), 141.6 (phenyl C4), 143.1 (d, <sup>3</sup>*J*<sub>PC</sub> = 16.0 Hz, thienyl C4), 144.9 (thienyl C4), 145.4 (phenyl C4), 150.4 (d, <sup>2</sup>*J*<sub>PC</sub> = 10.0 Hz, thienyl C4), 159.7 (thienyl C4). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 162 MHz):  $\delta$  30.2. ESI-TOF: *m*/Z [M+Na]<sup>+</sup> 789.2562 calcd. for C<sub>50</sub>H<sub>44</sub>OPS<sub>2</sub><sup>11</sup>BNa, found: 789.2573.

*3'-Dimesitylboryl-3-diphenylphosphinyl-5,5'-bis(4-trifluoromethylphenyl)-2,2'-bithiophene* (**38**): A similar method as for **33** was followed except **52** (1.22 g, 2.00 mmol) was used as starting material and THF as the solvent. Purification by flash column chromatography (hexanes: THF=5:1) gave a light-yellow solid. Yield 1.04 g, 58 %.<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  2.02 (s, 12H, CH<sub>3</sub>), 2.19 (s, 6H, CH<sub>3</sub>), 6.57 (s, 4H, phenyl CH), 6.74 (d, <sup>3</sup>*J*<sub>PH</sub> = 4.4 Hz, 1H, thienyl CH), 7.10 (s, 1H, thienyl CH), 7.44-7.60 (m, 18H, phenyl CH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  21.1 (CH<sub>3</sub>), 24.4 (CH<sub>3</sub>), 124.0 (q, <sup>1</sup>*J*<sub>FC</sub> = 270.3 Hz, C4 on -CF<sub>3</sub>), 125.0 (d, <sup>1</sup>*J*<sub>PC</sub> = 104.7 Hz, thienyl C4), 125.0 (q, <sup>3</sup>*J*<sub>FC</sub> = 3.9 Hz, phenyl CH), 125.7 (q, <sup>3</sup>*J*<sub>FC</sub> = 3.7 Hz, phenyl CH), 126.0 (phenyl CH), 126.3 (phenyl CH), 128.4 (d, <sup>2</sup>*J*<sub>PC</sub> = 17.6 Hz, thienyl CH), 128.7 (d, <sup>3</sup>*J*<sub>PC</sub> = 12.7 Hz, phenyl CH), 128.9 (phenyl CH), 129.2 (q, <sup>2</sup>*J*<sub>FC</sub> = 32.5 Hz, phenyl CH), 130.1 (q,  ${}^{2}J_{FC}$  = 32.6 Hz, phenyl CH), 130.8 (d,  ${}^{1}J_{PC}$  = 110.6 Hz, phenyl C4), 132.4 (d,  ${}^{2}J_{PC}$  = 10.8 Hz, phenyl CH), 132.6 (d,  ${}^{4}J_{PC}$  = 2.7 Hz, phenyl CH), 134.1 (thienyl CH), 136.2 (phenyl C4), 136.5 (phenyl C4), 137.4 (phenyl C4), 138.0 (d,  ${}^{3}J_{PC}$  = 2.3 Hz, thienyl C4), 141.6 (phenyl C4), 147.6 (phenyl C4), 147.6 (d,  ${}^{3}J_{PC}$  = 15.7 Hz, thienyl C4), 143.3 (thienyl C4), 145.0 (phenyl C4), 150.8 (d,  ${}^{2}J_{PC}$  = 9.5 Hz, thienyl C4), 160.1 (thienyl C4).  ${}^{31}P{}^{1}H{}$  NMR (CDCl<sub>3</sub>, 162 MHz):  $\delta$  30.5.  ${}^{19}F{}^{1}H{}$  NMR (CDCl<sub>3</sub>, 376 MHz):  $\delta$  -62.2, -62.3. ESI-TOF: m/Z [M+Na]<sup>+</sup> 924.2346 calcd. for C<sub>52</sub>H<sub>42</sub>OF<sub>6</sub>PS<sub>2</sub><sup>10</sup>BNa, found: 924.2341.

3'-Dimesitylboryl-3-diphenylphosphinyl-5,5'-bis(4-tert-butylphenyl)-2,2'-bithiophene (**39**): A similar method as for 33 was followed except 53 (950 mg, 2.00 mmol) was used as starting material and THF as the solvent. Purification by flash column chromatography (hexanes: THF=5:1) gave a light-yellow solid. Yield 894 mg, 51 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  1.32 (s, 9H, CH<sub>3</sub>), 1.34 (s, 9H, CH<sub>3</sub>), 2.03(s, 12H, CH<sub>3</sub>), 2.22 (s, 6H, CH<sub>3</sub>), 6.57 (s, 4H, phenyl CH), 6.65 (d,  ${}^{3}J_{PH} = 4.4$  Hz, 1H, thienyl CH), 7.00 (s, 1H, thienyl CH), 7.26-7.45 (m, 12H, phenyl CH), 7.50-7.56 (m, 6H, phenyl CH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz): δ 21.1 (CH<sub>3</sub>), 24.4 (CH<sub>3</sub>), 31.3 (*t*butyl CH<sub>3</sub>), 31.4 (*t*-butyl CH<sub>3</sub>), 34.7 (*t*-butyl C4), 34.8 (*t*-butyl C4), 123.1 (d,  ${}^{1}J_{PC} = 105.4$  Hz, thienyl C4), 125.6 (phenyl CH), 125.7 (phenyl CH), 125.9 (phenyl CH), 126.0 (phenyl CH), 126.7 (d,  ${}^{2}J_{PC} = 17.8$  Hz, thienyl CH), 128.5 (d,  ${}^{3}J_{PC} = 12.7$  Hz, phenyl CH), 128.8 (phenyl CH), 130.2 (phenyl C4), 131.0 (d,  ${}^{1}J_{PC} = 110.5$  Hz, phenyl C4), 131.5 (phenyl C4), 132.3 (d,  ${}^{4}J_{PC} = 2.7$  Hz, phenyl CH), 132.5 (d,  ${}^{2}J_{PC} = 10.6$  Hz, phenyl CH), 132.6 (thienyl CH), 135.9 (phenyl C4), 136.4 (thienyl C4), 141.6 (phenyl C4), 143.0 (d,  ${}^{3}J_{PC} = 15.8$  Hz, thienyl C4), 144.7 (thienyl C4), 145.6 (phenyl C4), 150.4 (d,  ${}^{2}J_{PC} = 9.6$  Hz, thienyl C4), 150.6 (phenyl C4), 151.6 (phenyl C4), 159.9 (thienyl C4). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 162 MHz): δ 31.2. ESI-TOF: *m*/Z [M+Na]<sup>+</sup> 900.3850 calcd. for  $C_{58}H_{60}OPS_2^{10}BNa$ , found: 900.3850.

3'-Dimesitylboryl-5,5'-bis(4-methoxyphenyl)-3-diphenylphosphinyl-2,2'-bithiophene (40): A similar method as for 33 was followed except 54 (803 mg, 1.50 mmol) was used as starting material and THF as the solvent. Purification by flash column chromatography (hexanes: THF=2:1) gave an orange-colored solid. Yield 533 mg, 43 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  2.06 (s, 12H, CH<sub>3</sub>), 2.22 (s, 6H, CH<sub>3</sub>), 3.80 (s, 6H, CH<sub>3</sub>), 3.82 (s, 6H, CH<sub>3</sub>), 6.57 (d,  ${}^{3}J_{PH} = 4.4$  Hz, 1H, thienyl CH), 6.59 (s, 4H, phenyl CH), 6.84 (d,  ${}^{3}J_{HH} = 8.8$  Hz, 2H, phenyl CH), 6.89 (d,  ${}^{3}J_{HH} = 8.8$ Hz, 2H, phenyl CH), 6.95 (s, 1H, thienyl CH), 7.33 (d,  ${}^{3}J_{HH} = 8.8$  Hz, 2H, phenyl CH), 7.43 (d,  ${}^{3}J_{\text{HH}} = 8.8 \text{ Hz}, 2\text{H}, \text{ phenyl CH}), 7.41-7.45 (m, 4\text{H}, \text{ phenyl CH}), 7.52-7.57 (m, 6\text{H}, \text{ phenyl CH}).$ <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz): δ 21.1 (CH<sub>3</sub>), 24.4 (CH<sub>3</sub>), 55.4 (s, -OCH<sub>3</sub>), 55.5 (s, -OCH<sub>3</sub>), 114.1 (phenyl CH), 114.5 (phenyl CH), 122.9 (d,  ${}^{1}J_{PC} = 105.7$  Hz, thienyl C4), 125.7 (thienyl C4),  $125.8 (d, {}^{2}J_{PC} = 18.0 Hz$ , thienyl CH), 127.10 (thienyl C4), 127.2 (phenyl CH), 127.4 (phenyl CH), 128.5 (d,  ${}^{3}J_{PC} = 12.6$  Hz, phenyl CH),128.7 (phenyl CH), 131.0 (d,  ${}^{1}J_{PC} = 110.5$  Hz, phenyl C4),131.8 (thienyl CH), 132.2 (d,  ${}^{4}J_{PC} = 2.7$  Hz, phenyl CH), 132.5 (d,  ${}^{2}J_{PC} = 10.7$  Hz, phenyl CH), 135.8 (phenyl C4), 136.0 (d,  ${}^{3}J_{PC} = 2.4$  Hz, phenyl C4), 141.6 (phenyl C4), 142.8 (d,  ${}^{3}J_{PC} =$ 16.1 Hz, thienyl C4), 144.5 (thienyl C4), 145.6 (phenyl C4), 149.8(d,  ${}^{2}J_{PC} = 9.8$  Hz, thienyl C4), 159.2 (phenyl C4), 159.7 (thienyl C4), 159.7 (phenyl C4). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 162 MHz):  $\delta$  31.0. ESI-TOF: m/Z [M+H]<sup>+</sup> 827.2954 calcd. for C<sub>52</sub>H<sub>49</sub>O<sub>3</sub>PS<sub>2</sub><sup>10</sup>B, found: 827.2955.

*3'-Dimesitylboryl-5,5'-bis*(*4-dimethylaminophenyl*)-*3-diphenylphosphinyl-2,2'-bithiophene* (**15**): A similar method as for **33** was followed except **55** (840 mg, 1.50 mmol) was used as starting material and THF as the solvent. Purification by flash column chromatography (hexanes: THF=2:1) gave an orange-red solid. Yield 410 mg, 33 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 2.27 (s, 12H, CH<sub>3</sub>), 2.45 (s, 6H, CH<sub>3</sub>), 3.19 (s, 6H, CH<sub>3</sub>), 3.22 (s, 6H, CH<sub>3</sub>), 6.75 (d,  ${}^{3}J_{PH} = 4.3$  Hz, 1H, thienyl CH), 6.79 (s, 4H, phenyl CH), 6.89 (d,  ${}^{3}J_{HH} = 8.7$  Hz, 2H, phenyl CH), 6.91 (d,  ${}^{3}J_{HH} = 8.7$  Hz, 2H, phenyl CH), 7.10 (s, 1H, thienyl CH), 7.52 (d,  ${}^{3}J_{HH} = 9.0$  Hz, 2H, phenyl CH), 7.61 (d,  ${}^{3}J_{HH} = 8.8$  Hz, 2H, phenyl CH), 7.64-7.66 (m, 4H, phenyl CH), 7.73-7.78 (m, 6H, phenyl CH). 1<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  21.1 (CH<sub>3</sub>), 24.4 (CH<sub>3</sub>), 40.5 (s, -N(CH<sub>3</sub>)<sub>2</sub>), 40.6 (s, -N(CH<sub>3</sub>)<sub>2</sub>), 112.4 (phenyl CH), 112.5 (phenyl CH), 121.2 (phenyl C4), 121.8 (d,  ${}^{1}J_{PC} = 107.3$  Hz, thienyl C4), 122.9 (phenyl C4), 124.6 (d,  ${}^{2}J_{PC} = 18.2$  Hz, thienyl CH), 126.8 (s, phenyl CH), 127.1 (s, phenyl CH), 128.4 (d,  ${}^{3}J_{PC} = 12.6$  Hz, phenyl CH), 128.7 (s, phenyl CH), 130.5 (s, thienyl CH), 131.0 (d,  ${}^{1}J_{PC} = 111.2$  Hz, phenyl C4), 132.1 (d,  ${}^{4}J_{PC} = 2.5$  Hz, phenyl CH), 132.6 (d,  ${}^{2}J_{PC} = 10.7$  Hz, phenyl CH), 135.0 (d,  ${}^{3}J_{PC} = 2.3$  Hz, thienyl C4), 135.5 (phenyl C4), 141.7 (phenyl C4), 143.4 (d,  ${}^{3}J_{PC} = 16.2$  Hz, thienyl C4), 150.3 (phenyl C4), 159.8 (thienyl C4),  ${}^{3}P_{1}H$  NMR (CDCl<sub>3</sub>, 162 MHz):  $\delta$  31.7. ESI-TOF: m/Z [M+Na]<sup>+</sup> 852.3623 calcd. for C<sub>54</sub>H<sub>55</sub>OPS<sub>2</sub><sup>10</sup>B, found: 852.3646.

*3'-Dimesitylboryl-5,5'-bis*(2-*phenylethynyl*)-*3-diphenylphosphinyl-2,2'-bithiophene* (**42**): A similar method as for **33** was followed except **56** (1.12 g, 2.0 mmol) was used as starting material and THF as the solvent. Purification by flash column chromatography (hexanes: THF=4:1) gave a yellow powder. Yield 944 mg, 58 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  1.98 (s, 12H, CH<sub>3</sub>), 2.25 (s, 6H, CH<sub>3</sub>), 6.58 (s, 4H, phenyl CH), 6.74 (d, <sup>3</sup>*J*<sub>PH</sub>= 8.7 Hz, 1H, thienyl CH), 7.02 (s, thienyl CH), 7.32-7.59 (m, 20H, phenyl CH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  20.9 (CH<sub>3</sub>), 24.4 (CH<sub>3</sub>), 80.9 (alkynyl C4), 83.2 (alkynyl C4), 94.8 (alkynyl C4), 95.6 (alkynyl C4), 121.7 (d, <sup>1</sup>*J*<sub>PC</sub> = 105.8 Hz, phenyl C4), 122.1 (phenyl C4), 122.6 (d, <sup>3</sup>*J*<sub>PC</sub> = 18.9 Hz, thienyl C4), 122.9 (phenyl C4), 124.0 (thienyl C4), 128.3 (phenyl CH), 128.3 (phenyl CH), 128.5 (d, <sup>3</sup>*J*<sub>PC</sub> = 13.0 Hz, phenyl CH), 128.5

(phenyl CH), 128.9 (phenyl CH), 129.0 (phenyl CH), 129.1 (d,  ${}^{1}J_{PC} = 112.7$  Hz, thienyl C4), 131.3 (phenyl CH), 131.4 (phenyl CH), 132.5 (d,  ${}^{2}J_{PC} = 10.1$  Hz, phenyl CH), 136.4 (d,  ${}^{4}J_{PC} = 2.8$  Hz, phenyl CH), 135.3 (phenyl C4), 135.5 (d,  ${}^{2}J_{PC} = 18.8$  Hz, thienyl CH), 136.4 (d,  ${}^{3}J_{PC} = 2.2$  Hz, thienyl C4), 141.6 (phenyl C4), 142.5 (thienyl CH), 145.8 (phenyl C4), 152.1 (d,  ${}^{2}J_{PC} = 9.2$  Hz, thienyl C4), 161.3 (thienyl C4).  ${}^{31}P{}^{1}H{}$  NMR (CDCl<sub>3</sub>, 162 MHz):  $\delta$  33.7. ESI-TOF: *m*/*Z* [M+Na]<sup>+</sup> 836.2598 calcd. for C<sub>54</sub>H<sub>44</sub>OPS<sub>2</sub><sup>10</sup>BNa, found: 836.2593.

3'-Dimesitylboryl-5,5'-bis(5-hexylthienyl)-3-diphenylphosphinyl-2,2'-bithiophene (43): A similar method as for 33 was followed except 57 (1.12 g, 2.0 mmol) was used as starting material and THF as the solvent. Purification by flash column chromatography (hexanes: THF=5:1) gave a red powder. Yield 572 mg, 31 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 0.89-0.93 (m, 6H, CH<sub>3</sub>), 1.33-1.39 (m, 12H, CH<sub>2</sub>), 1.62-1.69 (m, 4H, CH<sub>2</sub>), 1.96 (s, 12H, CH<sub>3</sub>), 2.20 (s, 6H, CH<sub>3</sub>), 2.75-2.80 (m, CH<sub>2</sub>), 6.51 (d,  ${}^{3}J_{PH} = 4.2$  Hz, 1H, thienyl CH), 6.53 (s, 4H, phenyl CH), 6.65 (d,  ${}^{3}J_{HH} = 3.6$  Hz, 1H, thienyl CH), 6.69 (d,  ${}^{3}J_{HH} = 3.6$  Hz, 1H, thienyl CH), 6.71 (s, thienyl CH), 6.90 (d,  ${}^{3}J_{HH} = 3.6$ Hz, 1H, thienyl CH), 6.92 (d,  ${}^{3}J_{HH} = 3.6$  Hz, 1H, thienyl CH), 7.40-.61 (m, 10H, phenyl CH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz): δ 14.3 (CH<sub>3</sub>), 14.3 (CH<sub>3</sub>), 21.0 (CH<sub>3</sub>), 23.0 (CH<sub>2</sub>), 23.0 (CH<sub>2</sub>), 24.6 (CH<sub>3</sub>), 29.1 (CH<sub>2</sub>), 29.1 (CH<sub>2</sub>), 30.5 (CH<sub>2</sub>), 30.5 (CH<sub>2</sub>), 32.0 (CH<sub>2</sub>), 32.0 (overlapped 2CH<sub>2</sub>), 32.0 (CH<sub>2</sub>), 122.0 (d,  ${}^{1}J_{PC} = 106.3$  Hz, thienyl C4), 124.1 (thienyl CH), 124.9 (thienyl CH), 125.3 (thienyl CH), 125.5 (thienyl CH), 126.4 (d,  ${}^{2}J_{PC} = 18.2$  Hz, thienyl CH), 129.0 (d,  ${}^{3}J_{PC} = 13.0$  Hz, phenyl CH), 129.3 (phenyl CH), 129.8 (d,  ${}^{1}J_{PC} = 110.7$  Hz, phenyl C4), 132.9 (thienyl C4), 132.9 (d,  ${}^{4}J_{PC} = 2.9$  Hz, phenyl CH), 133.0 (d,  ${}^{2}J_{PC} = 10.7$  Hz, phenyl CH), 133.4 (thienyl CH), 134.4 (d,  ${}^{3}J_{PC} = 2.0$  Hz, thienyl C4), 134.8 (thienyl C4), 135.6 (phenyl C4), 137.0 (d,  ${}^{3}J_{PC} = 17.0$  Hz, phenyl C4), 138.3 (thienyl C4), 141.9 (phenyl C4), 146.3 (thienyl C4), 146.5 (phenyl C4), 147.3 (thienyl

C4), 150.3 (d,  ${}^{2}J_{PC} = 9.8$  Hz, phenyl C4), 161.9 (thienyl C4).  ${}^{31}P{}^{1}H{}$  NMR (CDCl<sub>3</sub>, 162 MHz):  $\delta$  33.6. ESI-TOF: m/Z [M+Na]<sup>+</sup> 947.3749 calcd. for C<sub>58</sub>H<sub>65</sub>OPS<sub>4</sub><sup>11</sup>B, found: 947.3755.

5,5'-Bis(6-chlorohexyl)-3'-dimesitylboryl-3-diphenylphosphinyl-2,2'-bithiophene (44): A similar method as for 33 was followed except 58 (1.62 g, 2.5 mmol) was used as starting material and THF as the solvent. Purification by flash column chromatography (hexanes: THF=5:1) gave a pale-yellow powder. Yield 1.54 g, 73 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 1.22-1.60 (m, 12H, CH<sub>2</sub>), 1.72-1.76 (m, 4H, CH<sub>2</sub>), 2.04 (s, 12H, CH<sub>3</sub>), 2.23 (s, 6H, CH<sub>3</sub>), 2.57 (t, *J* = 7.4 Hz, 2H, CH<sub>2</sub>), 2.68  $(t, J = 7.4 \text{ Hz}, 2H, CH_2), 3.48-3.53 (m, 4H, CH_2), 6.10 (d, J_{PH} = 4.1 \text{ Hz}, 1H, thienyl CH), 6.48 (s, the second sec$ thienyl CH), 6.60 (s, 4H, phenyl CH), 7.40-7.55 (m, 10H, phenyl CH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  21.2 (CH<sub>3</sub>), 23.9 (CH<sub>3</sub>), 26.4 (CH<sub>2</sub>), 26.5 (CH<sub>2</sub>), 28.0 (CH<sub>2</sub>), 28.0 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 29.5 (CH<sub>2</sub>), 31.1 (CH<sub>2</sub>), 31.3 (CH<sub>2</sub>), 32.5 (CH<sub>2</sub>), 32.6 (CH<sub>2</sub>), 45.0 (CH<sub>2</sub>), 45.1 (CH<sub>2</sub>), 123.4 (d,  ${}^{1}J_{PC} = 105.7$  Hz, thienyl C4), 128.3 (phenyl CH), 128.3 (d,  ${}^{3}J_{PC} = 12.3$  Hz, phenyl CH), 128.8 (d,  $^{2}J_{PC} = 17.6$  Hz, thienyl CH), 131.8 (d,  $^{4}J_{PC} = 2.6$  Hz, phenyl CH), 132.1 (d,  $^{2}J_{PC} = 10.3$  Hz, phenyl CH), 132.9 (thienyl CH), 132.9 (d,  ${}^{1}J_{PC} = 108.0$  Hz, phenyl C4), 136.7 (phenyl C4), 137.9 (d,  ${}^{3}J_{PC}$ = 2.5 Hz, thienyl C4), 141.3 (phenyl C4), 144.5 (thienyl C4), 144.7 (d,  ${}^{3}J_{PC} = 15.6$  Hz, phenyl C4), 146.5 (thienyl C4), 148.2 (d,  ${}^{2}J_{PC} = 9.8$  Hz, phenyl C4), 155.2 (thienyl C4).  ${}^{31}P{}^{1}H{}$  NMR (CDCl<sub>3</sub>, 162 MHz): δ 27.1. ESI-TOF: *m*/Z [M+H]<sup>+</sup> 851.3215 calcd. for C<sub>50</sub>H<sub>59</sub>OPS<sub>2</sub>Cl<sub>2</sub><sup>11</sup>B, found: 851.3239.

5,5'-Bis(6-iodohexyl)-3'-dimesitylboryl-3-diphenylphosphinyl-2,2'-bithiophene (45): 44 (850 mg, 1.0 mmol) was heated to reflux with stirring in 20 mL of acetone with excess amount of NaI (3.0g, 20 mmol) in dark for 2 days. Then 100 mL deionized water was added and the aqueous phase was extracted with diethyl ether (4×5 mL). Organic phases were combined and dried over

anhydrous MgSO<sub>4</sub>. The mixture was filtered and the solvent was removed under vacuum. The resulting crude product was then purified by flash column chromatography (hexanes: THF = 5:1) giving a yellow powder. Yield 960 mg, 93 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 1.22-1.59 (m, 12H, CH<sub>2</sub>), 1.75-1.81 (m, 4H, CH<sub>2</sub>), 2.04 (s, 12H, CH<sub>3</sub>), 2.23 (s, 6H, CH<sub>3</sub>), 2.57 (t, <sup>3</sup>*J*<sub>HH</sub> = 7.4 Hz, 2H, CH<sub>2</sub>), 2.68 (t, J = 7.3 Hz, 2H, CH<sub>2</sub>), 3.14-3.18 (m, 4H, CH<sub>2</sub>), 6.11 (d,  ${}^{3}J_{PH} = 4.0$  Hz, 1H, thienyl CH), 6.48 (s, 1H, thienyl CH), 6.60 (s, 4H, phenyl CH), 7.40-7.55 (m, 10H, phenyl CH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz): δ 7.0 (I-CH<sub>2</sub>), 7.3(I-CH<sub>2</sub>), 21.2 (CH<sub>3</sub>), 23.9 (CH<sub>3</sub>), 27.6 (CH<sub>2</sub>), 27.7 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 29.5 (CH<sub>2</sub>), 30.0 (CH<sub>2</sub>), 30.2 (CH<sub>2</sub>), 31.1 (CH<sub>2</sub>), 30.3 (CH<sub>2</sub>), 33.4 (CH<sub>2</sub>), 33.5 (CH<sub>2</sub>), 123.4 (d,  ${}^{1}J_{PC} = 105.7$  Hz, thienvl C4), 128.3 (phenvl CH), 128.3 (d,  ${}^{3}J_{PC} = 12.4$  Hz, phenvl CH), 128.7 (d,  ${}^{2}J_{PC} = 17.4$  Hz, thienyl CH), 131.8 (d,  ${}^{4}J_{PC} = 2.7$  Hz, phenyl CH), 132.1 (d,  ${}^{2}J_{PC} = 2.7$  Hz, phenyl CH), 132.1 (d,  ${}^{2}$ 10.3 Hz, phenyl CH), 132.8 (thienyl CH), 132.8 (d,  ${}^{1}J_{PC} = 108.0$  Hz, phenyl C4), 136.7 (phenyl C4), 137.8 (d,  ${}^{3}J_{PC} = 2.6$  Hz, thienyl C4), 141.3 (phenyl C4), 144.6 (thienyl C4), 144.6 (d,  ${}^{3}J_{PC} =$ 15.7 Hz, phenyl C4), 146.4 (thienyl C4), 148.2 (d,  ${}^{2}J_{PC} = 9.8$  Hz, phenyl C4), 155.2 (thienyl C4). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 162 MHz):  $\delta$  27.2. ESI-TOF: m/Z [M+Na]<sup>+</sup> 1057.1747 calcd. for C<sub>50</sub>H<sub>58</sub>OPS<sub>2</sub>I<sub>2</sub><sup>11</sup>BNa, found: 1057.1744.

6,6'-(3'-Dimesitylboryl-3-diphenylphosphinyl-2,2'-bithienyl-5,5'-diyl)-bis(N,N,N-trimethyl-1-hexylammonium) diiodide. (46): 45 (516 mg, 0.50 mmol) was dissolved in 5.0 mL acetone andadded to excess amount of aqueous solution of trimethylamine (~45 wt. %, 1.0 mL) with stirringat room temperature in dark. The mixture was stirred for 12 hours and solvent was evaporated $under vacuum. Yield 575 mg, 99 %. <sup>1</sup>H NMR (methanol-<math>d_4$ , 400 MHz):  $\delta$  1.36-1.62 (m, 12H, CH<sub>2</sub>), 1.74-1.78 (m, 4H, CH<sub>2</sub>), 2.07 (s, 12H, CH<sub>3</sub>), 2.22 (s, 6H, CH<sub>3</sub>), 2.59 (t, *J* = 7.4 Hz, 2H, CH<sub>2</sub>), 2.72 (t, *J* = 7.4 Hz, 2H, CH<sub>2</sub>), 3.13 (s, 9H, CH<sub>3</sub>), 3.15 (s, 9H, CH<sub>3</sub>), 3.32-3.40 (m, 4H, CH<sub>2</sub>), 6.21 (d,  $J_{PH} = 4.3$  Hz, 1H, thienyl CH), 6.50 (s, thienyl CH), 6.65 (s, 4H, phenyl CH), 7.53-7.64 (m, 10H, phenyl CH). <sup>13</sup>C{<sup>1</sup>H} NMR (methanol- $d_4$ , 100 MHz):  $\delta$  21.4 (CH<sub>3</sub>), 23.8 (CH<sub>2</sub>), 23.8 (CH<sub>2</sub>), 24.1 (CH<sub>3</sub>), 26.9 (overlapped 2CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 29.4 (CH<sub>2</sub>), 30.1 (CH<sub>2</sub>), 30.3 (CH<sub>2</sub>), 32.3 (CH<sub>2</sub>), 32.5 (CH<sub>2</sub>), 53.6-53.7 (m, 2CH<sub>3</sub> on -NMe<sub>3</sub>), 67.8 (CH<sub>2</sub>), 67.8 (CH<sub>2</sub>), 126.9 (d, <sup>1</sup> $J_{PC} = 106.9$  Hz, thienyl C4), 129.3 (phenyl CH), 129.8 (d, <sup>3</sup> $J_{PC} = 12.3$  Hz, phenyl CH), 130.3 (d, <sup>2</sup> $J_{PC} = 17.9$  Hz, thienyl CH), 132.6 (thienyl CH), 132.9 (d, <sup>2</sup> $J_{PC} = 9.3$  Hz, phenyl CH), 133.4 (d, <sup>4</sup> $J_{PC} = 2.6$  Hz, phenyl CH), 134.7 (d, <sup>1</sup> $J_{PC} = 106.8$  Hz, phenyl C4), 147.1 (d, <sup>2</sup> $J_{PC} = 9.5$  Hz, phenyl C4), 147.6 (d, <sup>3</sup> $J_{PC} = 15.8$  Hz, phenyl C4), 148.3 (thienyl C4) 153.8 (thienyl C4). <sup>31</sup>P{<sup>1</sup>H} NMR (methanol- $d_4$ , 162 MHz):  $\delta$  26.0. ESI-TOF: m/Z [M-I]<sup>+</sup> 1025.4275 calcd. for C<sub>56</sub>H<sub>76</sub>N<sub>2</sub>OPS<sub>2</sub><sup>11</sup>BI, found: 1025.4264.

5,5'-Dibutyl-3'-dimesitylboryl-3-thiomethoxy-2,2'-bithiophene (**35a**): **49** (1.30 g, 2.21 mmol) was dissolved in 30 mL of dry diethyl ether and cooled to -78 °C. *n*-BuLi (1.6M in hexanes, 1.52 mL, 2.43 mmol) was added and the mixture was stirred for 1 hour at the same temperature. Solid Mes<sub>2</sub>BF (710 mg, 2.65 mmol) was then added under a high N<sub>2</sub> flow and the reaction was stirred for 1 hour before it was warmed up to room temperature and stirred for an additional 18 hours. The reaction was then quenched by H<sub>2</sub>O. The organic phases were combined and washed with water and brine, before drying over anhydrous MgSO<sub>4</sub>. The mixture was filtered and the solvent was removed from the filtrate under vacuum. Purification by flash column chromatography in hexanes gave a yellow solid. Yield: 920 mg, 73 %. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz):  $\delta$  0.94-1.00 (m, 6H, CH<sub>3</sub>), 1.29-1.30 (m, 2H, CH<sub>2</sub>), 1.33-1.49 (m, 2H, CH<sub>2</sub>), 1.51-1.54 (m, 2H, CH<sub>2</sub>), 1.64-1.71 (m, 2H, CH<sub>2</sub>), 2.11 (s, 12H, CH<sub>3</sub>), 2.24 (s, 6H, CH<sub>3</sub>), 2.61 (t, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 2H, CH<sub>2</sub>), 2.81

(t,  ${}^{3}J_{HH} = 7.4$  Hz, 2H, CH<sub>2</sub>), 6.47 (s, 1H, thienyl CH), 6.62 (s, 1H, thienyl CH), 6.70 (s, 4H, phenyl CH).  ${}^{13}C{}^{1}H{}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz):  $\delta$  14.1 (CH<sub>3</sub>), 14.2 (CH<sub>3</sub>), 19.1 (CH<sub>3</sub>), 21.4 (CH<sub>3</sub>), 22.5 (CH<sub>2</sub>), 22.7 (CH<sub>2</sub>), 23.6 (CH<sub>3</sub>), 30.0 (CH<sub>2</sub>), 30.2 (CH<sub>2</sub>), 34.1 (CH<sub>2</sub>), 34.5 (CH<sub>2</sub>), 126.4 (thienyl CH), 128.4 (phenyl CH), 130.8 (thienyl C4), 131.5 (thienyl C4), 131.7 (thienyl CH), 138.7 (phenyl C4), 141.1 (phenyl C4), 142.9 (thienyl C4), 143.0 (phenyl C4), 146.4 (thienyl C4), 146.8 (thienyl C4), 150.5 (thienyl C4). ESI-TOF: m/Z [M+Na]<sup>+</sup> 595.2674 calcd. for C<sub>35</sub>H<sub>45</sub>S<sub>3</sub><sup>11</sup>BNa, found: 595.2678.

5,5'-Dibutyl-3'-dimesitylboryl-2,2'-bithiophene-3-methylsulfoxide (35b): 35a (570 mg, 1.00 mmol) was dissolved in 10 mL CH<sub>2</sub>Cl<sub>2</sub> and solid *m*-CPBA (<77%, 224 mg, 1.30 mmol) was slowly added with stirring at 0 °C. The mixture was stirred for 8 hours and then washed with 5 mL 10 wt% aqueous solution of NaHCO3 and 5 mL brine. The organic phases were then dried over MgSO<sub>4</sub> and filtered. The mixture was filtered and the solvent was removed from the filtrate under vacuum. Purification by flash column chromatography (hexanes:THF = 5:1) gave a yellow solid. Yield: 522 mg, 89 %. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz):  $\delta$  0.93 (t, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, 2H, CH<sub>2</sub>), 0.96 (t, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, 2H, CH<sub>2</sub>), 1.26-1.33 (m, 2H, CH<sub>2</sub>), 1.35-1.43 (m, 2H, CH<sub>2</sub>), 1.47-1.54 (m, 2H, CH<sub>2</sub>), 1.62-1.69 (m, 2H, CH<sub>2</sub>), 2.08 (s, 12H, CH<sub>3</sub>), 2.23 (s, 6H, CH<sub>3</sub>), 2.61 (t, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, 2H, CH<sub>2</sub>), 2.80 (t,  ${}^{3}J_{HH} = 7.5$  Hz, 2H, CH<sub>2</sub>), 3.01 (s, 3H, CH<sub>3</sub>), 6.64 (s, 1H, thienyl CH), 6.70 (s, 1H, thienyl CH), 6.80 (s, 4H, phenyl CH). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz): δ 14.0 (CH<sub>3</sub>), 14.0 (CH<sub>3</sub>), 21.3 (CH<sub>3</sub>), 22.4 (CH<sub>2</sub>), 22.6 (CH<sub>2</sub>), 23.6 (CH<sub>3</sub>), 29.7 (CH<sub>2</sub>), 29.8 (CH<sub>2</sub>), 33.7 (CH<sub>2</sub>), 34.2 (CH<sub>2</sub>), 45.7 (CH<sub>3</sub>), 125.1 (thienyl CH), 128.5 (phenyl CH), 131.8 (thienyl CH), 134.8 (thienyl C4), 137.8 (thienyl C4), 139.2 (phenyl C4), 139.8 (thienyl C4), 141.1 (phenyl C4), 143.0 (phenyl C4), 147.3 (thienyl C4), 148.8 (thienyl C4), 153.2 (thienyl C4). ESI-TOF: m/Z [M+Na]<sup>+</sup> 610.2679 calcd. for C<sub>35</sub>H<sub>45</sub>OS<sub>3</sub><sup>11</sup>BNa, found: 610.2660.

5,5'-Dibutyl-3'-dimesitylboryl-2,2'-bithiophene-3-methylsulfone (35c): Similar to 35b, 35c was prepared by oxidation of **35a** with two equivalents of *m*-CPBA. **35a** (320 mg, 0.56 mmol) was dissolved in 10 mL CH<sub>2</sub>Cl<sub>2</sub> and solid *m*-CPBA (<77%, 250 mg, 1.45 mmol) was slowly added with stirring at 0 °C. The mixture was stirred for 8 hours and then washed with 5 mL 10 wt% aqueous solution of NaHCO<sub>3</sub> and 5 mL brine. The organic phases were then dried over MgSO<sub>4</sub> and filtered. The mixture was filtered and the solvent was removed from the filtrate under vacuum. Purification by flash column chromatography (hexanes:THF = 10:1) gave a yellow solid. Yield: 287 mg, 85 %. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz):  $\delta$  0.92 (t, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, 2H, CH<sub>2</sub>), 0.95 (t, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, 2H, CH<sub>2</sub>), 1.25-1.32 (m, 2H, CH<sub>2</sub>), 1.35-1.42 (m, 2H, CH<sub>2</sub>), 1.46-1.54 (m, 2H, CH<sub>2</sub>), 1.60-1.68 (m, 2H, CH<sub>2</sub>), 2.04 (s, 12H, CH<sub>3</sub>), 2.21 (s, 6H, CH<sub>3</sub>), 2.64 (t, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, 2H, CH<sub>2</sub>), 2.69 (s, 3H, CH<sub>3</sub>), 2.80 (t, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 2H, CH<sub>2</sub>), 6.63 (s, 1H, thienyl CH), 6.68 (s, 1H, thienyl CH), 6.90 (s, 4H, phenyl CH). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz): δ 14.0 (CH<sub>3</sub>), 14.0 (CH<sub>3</sub>), 21.3 (CH<sub>3</sub>), 22.4 (CH<sub>2</sub>), 22.5 (CH<sub>2</sub>), 23.4 (CH<sub>3</sub>), 29.8 (CH<sub>2</sub>), 30.1 (CH<sub>2</sub>), 33.9 (CH<sub>2</sub>), 34.3 (CH<sub>2</sub>), 42.6 (CH<sub>3</sub>), 120.2 (thienvl CH), 128.6 (phenvl CH), 132.2 (thienvl CH), 135.8 (thienvl C4), 138.6 (thienvl C4), 139.1 (phenyl C4), 141.0 (phenyl C4), 141.3 (thienyl C4), 142.7 (phenyl C4), 148.3 (thienyl C4), 149.1 (thienyl C4), 151.7 (thienyl C4). ESI-TOF: m/Z [M+Na]<sup>+</sup> 626.2625 calcd. for C<sub>35</sub>H<sub>45</sub>O<sub>2</sub>S<sub>3</sub><sup>11</sup>BNa, found: 626.2609.

#### 5.3.2.2 Synthesis of Precursors

Scheme 5-13. Synthesis of dibromo-bithiophene precursors 50-55.



*3,3'-Dibromo-5,5'-dimesityl-2,2'-bithiophene* (**50**): With stirring, 50 mL of deaerated H<sub>2</sub>O-THF (vol/vol=1:1) mixed solvent was added under N<sub>2</sub> into a three-necked round-bottom flask equipped with a condenser containing **59** (964 mg, 2.00 mmol), K<sub>2</sub>CO<sub>3</sub> (2.21 g, 16.0 mmol) and 2,4,6-trimethylphenylboronic acid (688 mg, 4.20 mmol). Then Pd(PPh<sub>3</sub>)<sub>4</sub> (230 mg, 0.20 mmol) was added against high N<sub>2</sub> flow. The mixture was slowly warmed to 70 °C, and stirred at the same temperature for 24 hours. THF was removed under reduced pressure and remaining mixture was extracted with diethyl ether (4×20 mL). The organic phases were combined and dried over anhydrous MgSO<sub>4</sub>. The mixture was then filtered and the solvent was removed from the filtrate under reduced pressure. Purification by flash column chromatography (hexanes) gave a white solid. Yield 680 mg, 61 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  2.24 (s, 12H, CH<sub>3</sub>), 2.35 (s, 6H, CH<sub>3</sub>), 6.82 (s, 2H, thienyl CH), 6.98 (s, 4H, phenyl CH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  20.9 (CH<sub>3</sub>), 21.3 (CH<sub>3</sub>), 111.5 (thienyl C4, C-Br), 128.4 (phenyl CH), 129.2 (thienyl C4), 129.5 (phenyl C4), 130.0 (thienyl CH), 138.3 (phenyl C4), 138.7 (phenyl C4), 143.5 (thienyl C4). EI-MS: *m*/Z [M]<sup>+</sup> 557.96862 calcd. for C<sub>26</sub>H<sub>24</sub>Br<sub>2</sub>S<sub>2</sub>, found: 557.96842. *3,3'-Dibromo-5,5'-diphenyl-2,2'-bithiophene* (**51**): A similar method to **50** was followed except phenylboronic acid (513 mg, 4.20 mmol) was used. The crude product can be recrystallized in hot ethanol to give pure product as yellow needles (626 mg, 66 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.30 (s, 2H, thienyl CH), 7.36-7.62 (m, phenyl CH).<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  112.7 (thienyl C4, C-Br), 125.7 (phenyl CH), 126.6 (thienyl CH), 128.0 (thienyl C4), 128.6 (phenyl CH), 129.1 (phenyl CH), 132.8 (phenyl C4), 145.5 (thienyl C4). EI-MS: *m*/*Z* [M]<sup>+</sup> 473.87472 calcd. for C<sub>20</sub>H<sub>12</sub><sup>79</sup>Br<sub>2</sub>S<sub>2</sub>, found: 473.87449.

*3,3'-Dibromo-5,5'-bis*(4-trifluoromethylphenyl)-2,2'-bithiophene (**52**): A similar method was followed except 4-trifluoromethyl-phenylboronic acid (797 mg, 4.2 mmol) was used. Purification by flash column chromatography (hexanes) gave an off-white solid. Yield 707 mg, 58 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.38 (s, 2H, thienyl CH), 7.66-7.71 (m, 8H, phenyl CH).  $^{13}C{^1H}$  NMR (CDCl<sub>3</sub>, 100 MHz): δ 113.3 (C-Br, C4), 124.1 (q,  $^{1}J_{FC}$  = 270.3 Hz, phenyl C4), 126.0 (phenyl CH), 126.3 (q,  $^{3}J_{FC}$  = 3.8 Hz, phenyl CH), 128.1 (thienyl CH), 129.2 (phenyl C4), 130.5 (q,  $^{2}J_{FC}$  = 32.5 Hz, phenyl C4), 136.1 (thienyl C4), 143.9 (thienyl C4).  $^{19}F{^1H}$  NMR (CDCl<sub>3</sub>, 376 MHz): δ -62.4. EI-MS: *m*/*Z* [M]<sup>+</sup> 609.84949 calcd. for C<sub>22</sub>H<sub>10</sub><sup>79</sup>Br<sub>2</sub>F<sub>6</sub>S<sub>2</sub>, found: 609.84913.

3,3'-*Dibromo-5,5'-bis*(4-tert-butylphenyl)-2,2'-bithiophene (**53**): A similar method was followed except 4-tert-butylphenylboronic acid (748 mg, 4.20 mmol) was used. Purification by flash column chromatography (hexanes) gave a yellow solid. Yield 762 mg, 65 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  1.36 (s, 18H, CH<sub>3</sub>), 7.25 (s, 2H, thienyl CH), 7.45 (d, *J* = 8.4 Hz, 4H, phenyl CH), 7.53 (d, *J* = 8.4 Hz, 4H, phenyl CH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  31.4 (CH<sub>3</sub>), 34.9 (*tert*-butyl, C4), 112.6 (thienyl C4, C-Br), 125.6 (phenyl CH), 126.2 (phenyl CH), 126.3 (thienyl 167 CH), 127.8 (thienyl C4), 130.2 (phenyl C4), 145.7 (thienyl C4), 152.0 (phenyl C4). EI-MS: *m*/Z [M]<sup>+</sup> 473.87472 calcd. for C<sub>20</sub>H<sub>28</sub><sup>79</sup>Br<sub>2</sub>S<sub>2</sub>, found: 585.99981.

*3,3'-Dibromo-5,5'-bis*(*4-methoxyphenyl*)-*2,2'-bithiophene* (**54**): A similar method was followed except 4-methoxyphenylboronic acid (638 mg, 4.20 mmol) was used. Purification by column chromatography (hexanes) gave a yellow solid. Yield 588 mg, 55 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  3.85 (s, 6H, CH<sub>3</sub>), 6.94 (d, *J* = 8.8 Hz, 4H, phenyl CH), 7.17 (s, 2H, thienyl CH), 7.52 (d, *J* = 8.8 Hz, 4H, phenyl CH). EI-MS: *m*/*Z* [M]<sup>+</sup> 533.89585 calcd. for C<sub>22</sub>H<sub>16</sub>O<sub>2</sub><sup>79</sup>Br<sub>2</sub>S<sub>2</sub>, found: 533.89540. This compound is known in literature.<sup>159</sup>

*3,3'-Dibromo-5,5'-bis*(*4-dimethylaminophenyl*)-*2,2'-bithiophene* (**55**): A similar method was followed except 4-(dimethylamino)phenylboronic acid (693 mg, 4.20 mmol) was used and **60** (1.15 g, 2.00 mmol) was added instead of **59**. Purification by column chromatography (hexanes:THF=5:1) gave an orange powder. Yield 559 mg, 49 %. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz):  $\delta$  3.00 (s, 12H, CH<sub>3</sub>), 6.73 (d, *J* = 8.9 Hz, 4H, phenyl CH), 7.13 (s, 2H, thienyl CH), 7.47 (d, *J* = 8.9 Hz, 4H, phenyl CH). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz):  $\delta$  40.5 (s, -N(CH<sub>3</sub>)<sub>2</sub>), 112.6 (phenyl CH), 112.7 (thienyl C4), 121.0 (phenyl C4), 124.2 (thienyl CH), 126.1 (thienyl C4), 126.9 (phenyl CH), 147.0 (thienyl C4), 151.2 (phenyl C4). EI-MS: *m*/Z [M]<sup>+</sup> 559.95911 calcd. for C<sub>24</sub>H<sub>22</sub><sup>79</sup>Br<sub>2</sub>N<sub>2</sub>S<sub>2</sub>, found: 559.95942.





*3,3'-Dibromo-5,5'-bis*(2-*phenylethynyl*)-2,2'-*bithiophene* (**56**): With stirring, 60 mL of deaerated diisopropylamine-THF (vol/vol=1:3) mixed solvent was added under N<sub>2</sub> into a three-necked round-bottom flask containing **60** (1.15 g, 2.00 mmol), CuI (34.4 mg, 0.18 mmol) and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (112 mg, 0.16 mmol). Phenylacetylene (430 mg, 4.2 mmol) was added through syringe, and the mixture was stirred at room temperature for 24 hours. THF was removed under reduced pressure and remaining mixture was extracted with diethyl ether (4×20 mL). The organic phases were combined and dried over anhydrous MgSO<sub>4</sub>. The mixture was then filtered and the solvent was removed from the filtrate under reduced pressure. Purification by column chromatography (hexanes:CH<sub>2</sub>Cl<sub>2</sub>=10:1) gave a yellow powder solid. Yield 960 mg, 92 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.23 (s, 2H, thienyl CH), 7.36-7.38 (m, 6H, phenyl CH), 7.51-7.54 (m, 4H, phenyl CH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  81.0 (C4, alkynyl), 96.2 (C4, alkynyl), 111.9 (thienyl C4, C-Br), 122.3 (phenyl C4), 125.6 (thienyl C4), 128.6 (phenyl CH), 129.2 (thienyl CH), 129.6 (thienyl C4), 131.7 (phenyl CH), 134.9 (phenyl CH). EI-MS: *m/Z* [M]<sup>+</sup> 521.87472

calcd. for  $C_{24}H_{12}^{79}Br_2S_2$ , found: 521.87506.

3,3'-Dibromo-5,5'-bis(5-hexylthienyl)-2,2'-bithiophene (57): An oven-dried 100 mL roundbottom flask under N<sub>2</sub> was added 5-bromo-2-hexylthiophene (1.04 g, 4.2 mmol) and 40 mL dry THF. The solution was cooled to -78 °C, and *n*-BuLi (1.6 M in hexanes, 2.90 mL, 4.6 mmol) was added slowly. The mixture was stirred at -78 °C for an hour after which ZnBr<sub>2</sub> (1.14 g, 4.6 mmol) was added against high N<sub>2</sub> flow. The mixture was warmed up to room temperature and stirred for another one hour. Pd(PPh<sub>3</sub>)<sub>4</sub> (230 mg, 0.20 mmol) and **59** (964 mg, 2.00 mmol) was added against high N2 flow. The mixture was slowly warmed up to 50 °C and stirred for 24 hours. Solvent was removed under reduced pressure and remaining mixture was added 50 mL H<sub>2</sub>O and 5 mL 1M HCl solution and extracted with diethyl ether (4×20 mL). The organic phases were combined and dried over anhydrous MgSO<sub>4</sub>. The mixture was then filtered and the solvent was removed from the filtrate under reduced pressure. Purification by column chromatography (hexanes) gave a yellow waxy solid. Yield 1.03 mg, 79 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  0.91 (t, *J* = 6.0 Hz, 6H, CH<sub>3</sub>), 1.32-1.41 (m, 12H, CH<sub>2</sub>), 1.65-1.73 (m, 4H, CH<sub>2</sub>), 2.81(t, J = 7.5 Hz, 4H, CH<sub>2</sub>), 6.70 (d, J = 3.4 Hz, 2H, thienyl CH), 7.02 (d, J = 3.4 Hz, 2H, thienyl CH), 7.05 (s, 2H, thienyl CH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz): δ 14.2 (CH<sub>3</sub>), 22.7 (CH<sub>2</sub>), 28.9 (CH<sub>2</sub>), 30.3 (CH<sub>2</sub>), 31.6 (CH<sub>2</sub>), 31.7 (CH<sub>2</sub>), 112.3 (thienyl C4, C-Br), 124.5 (thienyl CH), 125.2 (thienyl CH), 126.1 (thienyl CH), 126.6 (thienyl C4), 133.0 (thienyl C4), 139.4 (thienyl C4), 147.1 (thienyl C4). EI-MS: m/Z [M]<sup>+</sup> 653.97536 calcd. for C<sub>28</sub>H<sub>32</sub><sup>79</sup>Br<sub>2</sub>S<sub>4</sub> found: 653.97500.





3,3'-Dibromo-5,5'-bis(6-chlorohexyl)-2,2'-bithiophene (58): Under N<sub>2</sub>, 59 (1.93 g, 4.00 mmol) was dissolved in 100 mL dry THF and cooled to -78 °C. With stirring, n-BuLi (1.6 M in hexanes, 5.25 mL, 8.40 mmol) was added to the solution dropwise, and the mixture was stirred at the same temperature for 1 hour. 6-Chloro-1-iodohexane (2.20 g, 8.8 mmol) was added via syringe, and the mixture was slowly warmed up to room temperature and stirred for 12 hours. The reaction was quenched with 1 mL deionized water and solvent was removed under reduced pressure. Remaining mixture was added 20 mL H<sub>2</sub>O and 5 mL 1M HCl solution and extracted with hexanes  $(4 \times 10 \text{ mL})$ . The organic phases were combined and dried over anhydrous MgSO<sub>4</sub>. The mixture was then filtered and the solvent was removed from the filtrate under reduced pressure. Purification by column chromatography (hexanes) gave white waxy solid. Yield 1.90 g, 74 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 1.40-1.51 (m, 8H, CH<sub>2</sub>), 1.69-1.73 (m, 4H, CH<sub>2</sub>), 1.76-1.81 (m, 4H, CH<sub>2</sub>), 2.79 (t, J = 7.5 Hz, 4H, CH<sub>2</sub>), 3.55 (t, J = 6.7 Hz, 4H, CH<sub>2</sub>), 6.75 (s, 2H, thienyl CH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  26.6 (CH<sub>2</sub>), 28.4 (CH<sub>2</sub>), 30.2 (CH<sub>2</sub>), 31.0 (CH<sub>2</sub>), 32.5 (CH<sub>2</sub>), 45.1 (CH<sub>2</sub>), 111.1 (thienyl C4, C-Br), 126.7 (thienyl C4), 127.8 (thienyl CH), 147.2 (thienyl C4). EI-MS:  $m/Z [M]^+ 653.97536$  calcd. for C<sub>28</sub>H<sub>32</sub><sup>79</sup>Br<sub>2</sub>S<sub>4</sub>, found: 653.97500.

Scheme 5-16. Synthesis of 49.



3-Bromo-5,5'-dibutyl-3-thiomethoxy-2,2'-bithiophene (49): Under N<sub>2</sub>, 22 (2.10 g, 4.80 mmol) was dissolved in 100 mL dry THF and cooled to -78 °C. With stirring, n-BuLi (1.6 M in hexanes, 3.30 mL, 5.28 mmol) was added to the solution dropwise, and the mixture was stirred at the same temperature for 1 hour. Dimethyl disulfide (543 mg, 5.76 mmol) was added via syringe, and the mixture was slowly warmed up to room temperature and stirred for 12 hours. The reaction was quenched with water and solvent was removed under reduced pressure. Remaining mixture was added 20 mL H<sub>2</sub>O and extracted with hexanes (4×15 mL). The organic phases were combined and dried over anhydrous MgSO<sub>4</sub>. The mixture was then filtered and the solvent was removed from the filtrate under reduced pressure. Purification by column chromatography in hexanes gave a colorless oil. Yield 1.74 g, 90 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 0.94-0.99 (m, 6H, CH<sub>3</sub>), 1.40-1.47 (m, 4H, CH<sub>2</sub>), 1.64-1.73 (m, 4H, CH<sub>2</sub>), 2.40 (s, 3H, CH<sub>3</sub>), 2.77-2.82 (m, 4H, CH<sub>2</sub>), 6.74 (s, 1H, thienyl CH), 6.77 (s, 1H, thienyl CH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz): δ 13.8 (CH<sub>3</sub>), 13.9 (CH<sub>3</sub>), 18.6(CH<sub>3</sub>), 22.2 (CH<sub>2</sub>), 22.3 (CH<sub>2</sub>), 29.9 (CH<sub>2</sub>), 30.0 (CH<sub>2</sub>), 33.2 (CH<sub>2</sub>), 33.4 (CH<sub>2</sub>), 110.4 (thienyl C4, C-Br), 126.1 (thienyl CH), 127.0 (thienyl C4), 127.5 (thienyl CH), 127.6 (thienyl C4), 133.0 (thienyl C4), 146.6 (thienyl C4), 147.0 (thienyl C4). ESI-TOF: m/Z [M+H]<sup>+</sup> 403.0224 calcd. for C<sub>17</sub>H<sub>24</sub><sup>79</sup>BrS<sub>3</sub>, found: 403.0228.

## **5.3.3 Fluorescence Imaging**

Preliminary fluorescent images were obtained by Hunter (Xiaozhu) Wang in the Orvig research group at UBC, using facilities at the Biological Services Laboratory in the Chemistry Department, UBC. Olympus IX70 Inverted Fluorescence Microscope with a DC-330 3CCD MTI color camera and Image-Pro Plus analysis software were used to obtain the fluorescence images. A 11000v3 - UV filter cube purchased from Chroma was used with its emission filter changed for specific emission colors.

### **5.3.4 DFT Simulations**

DFT calculations were carried out using the Gaussian 09 Rev.D01 suite of Programs.<sup>90</sup> The PBE0 hybrid functional<sup>91</sup> with 6-31G\* basis set was employed to simulate GS structure of Lewis pairs **37-41**. Optimized structures were confirmed to be the minimum on the potential energy surface by vibrational frequency calculations. Vertical absorptions are simulated using TD-DFT methods by looking at the first 20 low-energy electronic transitions. For all simulations, the solvation effect of either methanol ( $\varepsilon = 32.613$ , for the open structures) or THF ( $\varepsilon = 7.4257$ , for the closed structures) was implemented using the polarizable continuum model<sup>88</sup> (PCM) on Gaussian 09.

## 5.4 Conclusions

In this chapter, the bithiophene-based Lewis pair system was systematically studied by changing the relative position of the Lewis acid and base on the backbone, and altering the Lewis base from different alkyl and aryl phosphine oxide to sulfoxide and sulfone groups. The Lewis adduct can only be formed intramolecularly with the 3,3'- substitution of Lewis acid and base centers on bithiophene. Only phosphine oxides can effectively form the B-O bond with -BMes<sub>2</sub> moiety, and the equilibrium of the open and closed structure is more favorable to the closed structures when the R<sub>2</sub>P(O)- group is more polarized on oxygen atom and less sterically hindered. It is also demonstrated that the emission colors of open and closed forms of the Lewis pairs can be red-shifted by increasing the backbone conjugation or adding electron-donating groups.

Additionally, preliminary bio-imaging experiments were carried out using pig adipocytes and human brain slices as proof-of-concept of a two-color fluorescent dye system for fluorescence imaging of hydrophobic/hydrophilic environments in biological or medical applications. It is also shown that the hydrophobic/hydrophilic distribution and emission colors can be modified separately, and other functionalities can be conveniently introduced by substituting the reactive iodine atoms in one of the precursors.

## **Chapter 6 Conclusions and Future Work**

This thesis sets out to explore photo-functional molecules by incorporating either Pt(II)containing functionalities or 3-coordinated Lewis acidic boron groups with thiophene-containing conjugated backbones. Molecules and materials that can give rise to controllable/tunable light absorption and emission properties are obtained, and attempts have been made to utilize these properties in corresponding applications.

In **Chapter 2**, two binuclear Pt(II) terpyridyl Pacman complexes **2** and **3** with flexible conjugated bisacetylide ligands are shown to exhibit structural folding/unfolding controllable by temperature changes and different solvent environments. For the first time, crystal structures of both the folded and unfolded structures of a foldable molecule containing Pt(II) terpyridyl groups are obtained. It is revealed that intramolecular  $\pi$ - $\pi$  interactions between pedant Pt(II) terpyridyl moieties can be used to encourage structural folding and planarization of the conjugated backbone while weak interactions such as Cl- $\pi$  interactions, and weak C-H hydrogen bonds can be used to stabilize unfolded structures with reduced conjugation on the backbone. This strategy can be used for designing stimuli responsive materials with different light absorption or electrical conductivity in different states.

It is also shown by DFT simulations that the two metal centers in unfolded structures of 2 and 3 are weakly or non-interacting, which give rise to almost degenerate MOs. By contrast, in folded structures, these MOs are coupled and split in energy. Such energy splitting can be used to modulate redox potentials and optical properties of the metal centers which may be useful in

electrochemistry and photochemistry applications. Additionally, the results indicate that the flexible thiophene-containing ligands are good foldable platforms to encourage and investigate tunable chromophore-chromophore interactions and allow convenient assessment by changes in light absorption and emission properties.

In **Chapter 3**, three Pt(II) metallacycles **4**, **5** and **6** with thiophene-containing bisacetylide ligands were synthesized and their fluorescence and phosphorescence properties examined. These complexes can be fluorescent when emitting from their S<sub>1</sub> states and phosphorescent when emitting from their T<sub>1</sub> states after intersystem crossing. These results show that by replacing the phenylene or ethynylene groups with thiophene rings on the bisacetylide ligand of *cis*-diphosphine Pt(II) metallacycles, the S<sub>1</sub> and T<sub>1</sub> states can be modulated to show relatively stronger fluorescence and weaker phosphorescence. It is also shown that more rigid and planar metallacycles suffer less from energy loss due to smaller degrees of structure reorganization and thermal deactivation. These are important factors to consider when designing similar single component fluorescence and phosphorescence dual emissive materials for applications such as white-emitting OLEDs, selfreferencing oxygen sensors, and hypoxia contrast agents.

**Chapter 4** discussed an intramolecular Lewis pair system between a Lewis acidic -BMes<sub>2</sub> group and a Lewis basic phosphine oxide group based on a flexible bithiophene backbone. The system is able to establish a fast equilibrium between open structures with unbound Lewis acids and bases and closed structures of Lewis adducts. Such equilibrium can be manipulated by changing the temperature or HB donating strength of the solvent, and conveniently probed according to the different emission feature of these two structures. This gives rise to an interesting single-component-two-state system with stimuli responsive emission colors. It is also shown that

the flexible bithiophene backbone can serve as a good platform for tunable and easily detectable interactions between Lewis acids and bases.

The scope of such system was further explored in **Chapter 5** showing that a flexible Lewis pair with a -BMes<sub>2</sub> Lewis acidic group can only be achieved by using Lewis basic groups of phosphine oxides. The equilibrium between the open and closed structure can be affected by the steric and electronic properties of the phosphine oxide groups. A wide variety of emission colors of the open and closed forms of the Lewis pairs can also be achieved by changing the backbone conjugation or electron density of the  $\pi$ -system on the backbone, as shown in **Series A** and **Series B** (page 134 to 135), respectively. Such flexible Lewis pair molecules can be used as two-color fluorescent dyes for fluorescence imaging of hydrophobic/hydrophilic environments in the context of biological or medical applications, with benefits of high-emission quantum yield, many choices of emission colors and potentially low toxicity. The hydrophobic/hydrophilic distribution of the molecules and their emission colors can be modified separately, and more functionalities can be conveniently installed by substituting the reactive iodine atoms in precursor **45**.



**Figure 6-1.** Modulating the fluoride anion affinity at the boron center by deriving the phosphine groups.

One future direction is to compare the fluoride anion affinity of the phosphine oxide-borane system with the corresponding phosphine-borane and phosphonium-borane systems (**Figure 6-1**). It is expected that molecule **145** with a phosphine-oxide group has the lowest affinity due to competitive binding of the Lewis base while molecule **147** with a phosphonium group has the highest affinity due to a more stabilized adduct with fluoride anion. By deriving the phosphine groups in **146**, the fluoride anion affinity at the boron center can be easily modified for fluoride sensors that requires different sensitivities.

In summary, three types of thiophene-containing photofunctional molecules with (a) two interacting terpyridyl Pt(II) acetylide groups and (b) a cyclometalated *cis*-diphosphino Pt(II) center and (c) a pair of flexible Lewis acid-base pair have been designed, synthesized and characterized. It is shown that flexible thiophene containing conjugated backbones are useful platforms to integrate interacting photo functionalities, and the resulting molecules can be designed to show tunable light absorption and emission properties for various applications.

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## Appendix



Figure A-1. Predicted isotopic distribution of the [M-2OTf]<sup>2+</sup> ion of 2 using ISO PRO3.1.<sup>6</sup>



Figure A-2. Measured isotopic distribution of [M-2OTf]<sup>2+</sup> of 2 using MALDI-TOF MS.