Design, synthesis and characterizations of novel electrochromic polymers

Cho, Ching Mui

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NANYANG
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**DESIGN, SYNTHESIS AND CHARACTERIZATIONS OF
NOVEL ELECTROCHROMIC POLYMERS**

CHO CHING MUI

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2016

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CHO CHING MUI

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
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Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

...4th July 2016
Date

.... Cho Ching Mui.
Student Name

Abstract

Electrochromic (EC) materials and their devices have been extensively researched over the years especially those based on conjugated polymers. Although these materials are now able to meet the key performance indicators such as high optical contrast and fast switching, there are still challenging problems faced by current EC technologies, particularly the stability of EC devices. This thesis is structured into different sections, starting from the motivation of this work, which is to explore the structural design of conjugated polymers to improve their EC properties (Chapter 1), followed by a literature review on the different types of EC materials and devices (Chapter 2) and the different experimental methodologies used (Chapter 3). In the subsequent sections, three different approaches for the design of new electrochromic polymers are proposed, and their electronic and EC properties are discussed.

First, in chapter 4 and 5, a new synthetic methodology based on the inverse electron demand Diels-Alder (iEDDA) reaction has been created for the synthesis of new electron acceptors. Using this new synthetic methodology, novel electron acceptors such as pyrrolo[3,4-*d*]pyridazine-5,7-dione (PPD) and pyrrolo-acenaphtho-pyridazine-diones (PAPD) have been successfully synthesized and found to be highly electron deficient with very low lying lowest unoccupied molecular orbital (LUMO) energy levels. Their LUMO energy levels are lower than most of the commonly used electron acceptors. As such, this new synthetic methodology can be used to synthesize novel electron acceptors and contribute in increasing the existing library of electron acceptors available in the preparation of donor-acceptor polymers. These newly prepared electron acceptors moieties, PPD and PAPD, are then used in the synthesis of electrochromic polymers **PPD1 – PPD3** and **PAPD1 – PAPD5** respectively. All the polymers obtained exhibit very high solubility in common organic solvents. The PPD series of polymers displays purple to transmissive blue electrochromism while the PAPD series shows red to grey electrochromism. In particular, **PAPD3** possesses very high optical contrast of 81 % in the near infra-red (NIR)

region and attains high redox stability with only a 0.6 % drop in optical contrast after 800 cycles of redox cycling.

Secondly, in chapter 6, the approach of utilizing 4,9-dihydro-*s*-indaceno[1,2-*b*:5,6-*b'*]dithiophene (IDT) as a building block for EC conjugated polymers has been demonstrated. Due to its good performances, IDT is frequently used to prepare organic electronics, but they are rarely reported in EC materials. Herein, the IDT units are co-polymerized with dioxythiophene-based units to test its feasibility as electrochromic building block. The resultant polymers are found to exhibit a red to black electrochromism with high optical contrasts in both visible and NIR regions. As such, IDT units can be considered as potential building blocks in electrochromic materials.

In chapter 7, the use of triphenylamine (TPA) as a tool to improve the redox stability of the electrochromic polymers has been demonstrated. A series of EC polymers with varying amount of TPA incorporated has been synthesized. The polymers are obtained in medium yields and highly soluble in organic solvents. High molecular weights ranging from 59 to 81 KDa are achieved and the polymers display multi-colored electrochromism. These polymers are able to transit from purple/red at reduced state, to grey at intermediate state, and then to transmissive blue at oxidized state. Notably, polymer **TPA3** is able to achieve a six-fold improvement in redox stability with the incorporation of just 15 % of TPA into its polymer chains. With such significant improvement, this simple yet effective design strategy could be potentially used to modify EC polymers to enhance their redox stabilities.

Lastly, a summary of my thesis is presented in chapter 8, where the three proposed design strategies are proven to be effective in creating good performance electrochromic materials. Some significant contributions made in this thesis are also being highlighted with a discussion on the suggestions for future work.

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Abbreviations

AFM	Atomic force microscopy
CV	Cyclic voltammetry
D-A	Donor-acceptor
DSC	Differential scanning calorimeter
EA	Elemental analysis
ECDs	Electrochromic devices
EDOT	3,4-Ethylenedioxythiophene
GPC	Gel permeation chromatography
HOMO	Highest occupied molecular orbitals
IDT	4,9-dihydro- <i>s</i> -indaceno[1,2- <i>b</i> :5,6- <i>b'</i>]dithiophene
iEDDA	Inverse electron demand Diels-Alder
ITO	Indium tin oxide
LUMO	Lowest unoccupied molecular orbital
NIR	Near infra-red
NMR	Nuclear magnetic resonance
PAPD	Pyrrolo-acenaphtho-pyridazine-dione
PB	Prussian blue
PEDOT	Poly(3,4-ethylenedioxythiophene)
PMMA	Poly(methyl methacrylate)
PPD	Pyrrolo[3,4- <i>d</i>]pyridazine-5,7-dione
TD-DFT	Time-dependent density functional theory
TGA	Thermogravimetric Analysis
TPA	Triphenylamine
XRD	X-ray diffraction

Chapter 1

Introduction

In this chapter, some of the problems that conventional electrochromic materials possess will be presented. Such electrochromic materials usually suffer from poor solution processability and stability, and the objective of this project is to develop new structural design methods to mitigate them. Various synthetic approaches are proposed for high performance electrochromic polymers and these polymers will then be characterized by the various characterization tools to determine their performance parameters. Subsequently, an overview of this thesis and a brief discussion on our studies where we established a novel synthetic methodology for the preparation of ultra-high electron deficiency electron acceptors is presented.

1.1 Problem Statement

Electrochromism is defined as a phenomenon of reversible optical color change displayed by a material upon a redox process induced by an external bias.¹ Electrochromic materials can be broadly categorized into five distinct families; mainly the oxides of transition metals, such as tungsten trioxide (WO_3) and Iridium dioxide (IrO_2)², metal-coordinated complexes such as Prussian blue (PB)³, small organic molecules like bipyridiliums (viologens)⁴, organic conjugated polymers⁵ and arylamine-based polymers such as triphenylamine based polyamides⁶ and epoxy⁷. The use of organic electrochromic materials as active layers in electrochromic devices (ECDs) is gaining popularity in recent years as they exhibit outstanding coloration efficiency⁸, high optical contrasts⁹, fast switching times^{9,10}, multiple colors within the same material¹¹, and thin film flexibility¹² which can reduce the cost of manufacturing¹³ and expand the area of usage.

However, despite the advantages that organic electrochromic polymers have over inorganic electrochromes, many of the current organic electrochromic polymers face drawbacks such as poor solution processability and low stability that limit their applicability in commercial applications. In order to reduce the cost of manufacturing and acquire the ability for large area deposition, there is a demand for good solubility polymers for their high processability using industrial techniques such as spray-coating or screen-printing on substrates. Moreover, it is essential for the polymers to exhibit high ambient and redox stability so as to extend the working life of the commercial electrochromic devices. This results in an increasing demand for novel high performance electrochromic polymers with good stability and solubility. Consequently, it is of utmost importance to develop design strategies for creating new conjugated electrochromic polymers to meet with the growing demand.

1.2 Objective and Scope

The main objective of this thesis is to develop new structural design methods for solving existing problems associated with organic polymer based electrochromic technologies,

especially the solubility of the polymers and the stability issue of the electrochromic devices. Several different approaches have been attempted to address these problems and they are presented as follows:

- (i) To design and synthesize new electron-deficient acceptor building blocks for the construction of donor-acceptor (D-A) electrochromic polymers with good solubility and stability.

The use of D-A methodology has been demonstrated by Reynolds' group to be an efficient way to design low bandgap polymers by structural modification of the electron donor and acceptors^{14,15}. It has been reported that if both the polymer oxidation and reduction potentials are sufficiently low, the degradation effects of low bandgap polymers due to the redox switching will be greatly reduced¹⁶. Further enhancement of the electrochromic properties is partially restricted by the limited number of suitable electron acceptors available in the literatures which can be used to obtain electrochromic materials with outstanding performance. Examples of some commonly studied electron acceptors are benzotriazole, thieno[3,4-*c*]pyrrole-4,6-dione, diketopyrrolo-pyrrole, quinoxaline, benzo[*c*][1,2,5]thiadiazole, as seen in Figure 1.1. Therefore, the main point of this objective is the acceptor engineering by creating new acceptors for use in the synthesis of D-A polymers. Suitable side chains will be added to the molecules to ensure the polymers are solution processable.

Figure 1.1 A series of commonly used electron acceptors. From left to right: Benzotriazole, thieno[3,4-*c*]pyrrole-4,6-dione, diketopyrrolo-pyrrole, quinoxaline, and benzo[*c*][1,2,5]thiadiazole.

- (ii) To develop electrochromic polymers using unexplored building blocks with 3,4-Ethylenedioxythiophene (EDOT)-based derivatives.

Poly(3,4-ethylenedioxythiophene) (PEDOT) is a homopolymer that is synthesized by chemical oxidative polymerization of the monomer, 3,4-ethylenedioxythiophene (EDOT). It was first developed by scientist at the Bayer AG research laboratories in Germany¹⁷. Even though it is a homopolymer, it exhibits a combination of moderate bandgap and low oxidation potential that give rise to a highly stable and conductive polymer and show evidence of excellent optical transparency in the visible region¹⁸. Furthermore, it is also stable under ambient and elevated temperature conditions as compared with other polythiophenes¹⁹. However, PEDOT has poor solubility in organic solvents, which affects its solution processability. Therefore, the derivatives of EDOT with modified solubilizing alkyl chains can be combined with other new potential building units to create new types of solution processable polymers.

- (iii) To design and synthesize electrochromic polymers with triphenylamine (TPA) incorporated.

Triphenylamine, a high electron-rich building block is commonly used by Liou and his group to obtain high performance TPA based polymers for organic electronics applications²⁰⁻²⁴. His group has obtained anodically high performing electrochromic polymers with TPA or its analogue units built into the polymers' main chains or as pendants. Given the high performance of TPA based engineering polymer as electrochromic materials, it is a good opportunity to explore the idea of inserting a small composition of TPA into the main chains of the electrochromic polymers by random copolymerization to obtain highly stable electrochromic polymers. TPA could be utilized to tune the effective conjugation of the conjugated polymers, manipulating the physical properties and morphological properties of the polymer films, thereby opening a new way to enhance the stability of the polymers.

In this thesis, three different strategies are proposed for the synthesis of new electrochromic conjugated polymers. These polymers will be prepared using both new and existing monomers. Following the synthesis of the new materials, various characterization technologies and spectroscopic techniques have been adopted to un-ambiguously characterize the chemical nature of the materials as well as their associated physical properties. Nuclear Magnetic Resonance (NMR) and Elemental Analysis (EA) were used for determination of chemical structures and purity. Thermogravimetric Analysis (TGA) and Differential Scanning Calorimeter (DSC) were used to investigate their thermal stability and thermal transitions. UV-*vis*-NIR absorption spectroscopy and Cyclic Voltammetry (CV) were used to study the photophysical and electrochemical properties of the monomers and polymers. Time-dependent density functional theory (TD-DFT) computational modelling of the model compounds was used to compute the electronic structures, thus helping to understand and explain the experimental phenomenon observed. X-ray diffraction (XRD) was used for the morphology study of the polymer thin films and surface film morphology can be studied by Atomic Force Microscopy (AFM).

Standard window-type absorption/transmission device was fabricated and characterized. The configuration of the device (Figure 1.2) is a sandwich structure Glass/ITO|polymer|gel electrolyte|ITO/Glass. The gel electrolyte is poly(methyl methacrylate) (PMMA) with lithium perchlorate (LiClO_4). The only variation between devices is the electrochrome which is the polymer layer. The devices fabricated were characterized and their electrochromic properties were measured.

Figure 1.2 Cross-section of the electrochromic device.

1.3 Dissertation Overview

This thesis adopts different polymer design methodologies that can be used to overcome the existing limitations of current electrochromic polymers.

Chapter 1 provides the rationale of the research project and outlines the goals and scope.

Chapter 2 reviews the literature concerning organic electrochromic polymers, electrochromic devices and applications, and the performance parameters of electrochromic devices.

Chapter 3 discusses the principles underlying the synthesis, and the different characterization techniques employed for the work presented in this thesis.

Chapter 4 reports a new synthetic methodology devised for the synthesis of new electron acceptors with ultra-high electron deficiency. The mechanism of the new synthetic method will be presented and discussed. In addition, the synthesis and characterizations of the new electron acceptor (PPD) synthesized via the new method, and its polymers will also be explored.

Chapter 5 is an extension of the new synthetic methodology discovered in Chapter 4. An even higher electron deficiency monomer (PAPD) is synthesized successfully and its synthesis and characterizations are presented. The properties of its polymers are investigated and presented in the same chapter.

Chapter 6 describes the use of an uncommon building block 4,9-dihydro-*s*-indaceno[1,2-*b*:5,6-*b'*]dithiophene (IDT) together with the derivatives of EDOT to synthesize new series of solution processable electrochromic polymers with a rare transition color change. The synthesis, characterizations and electrochromic properties of the polymers will be discussed.

Chapter 7 presents the synthesis of a series of thiophene based polymers with varying quantity of TPA incorporated. The synthesis, characterization and electrochromic properties of the polymers will be examined.

Chapter 8 discusses the implications of the research work and suggests some direction for the future work.

1.4 Findings and Outcomes

This research project has led to the establishment and analysis of a novel synthesis methodology. This new synthesis method which relies on an inverse electron demand Diels-Alder (iEDDA) reaction, opens up a new pathway to prepare new electron acceptors with ultra-high electron deficiency, which are not only useful in electrochromic applications, but also in other organic electronics field. Through this new synthetic methodology, two new electron acceptors with ultra-low lowest unoccupied molecular orbital (LUMO) energy levels are obtained. Their LUMO energy levels which are amongst the lowest LUMO levels of common electron acceptors are -3.67 and -3.92 eV for PPD and PAPD units respectively. By using these newly synthesized electron acceptors, D-A type electrochromic polymers are then prepared, and the polymers are found to exhibit good electrochromic properties which give the possibility of using this new synthesis method for future preparation of new electron acceptors. Furthermore, we also explored the other alternatives besides the D-A approach to obtain highly stable electrochromic polymers. From our studies, a varying composition of TPA is incorporated into the polymer main chains during the synthesis to investigate the effect of TPA on both the optical and electrochromic properties of the polymers. The resultant polymers achieved good electrochromic properties with enhanced redox stability. Notably, only a small amount of about 15 % of TPA is required to increase the stability of the polymers significantly. With this approach, potential polymers with good electrochromic properties can be easily modified to further enhance their device stabilities. With these technical means at hand, the developed technologies and strategies would pave new ways for potential commercialization of organic electrochromic materials in the future.

References

1. Monk, P., Roger Mortimer, and David Rosseinsky, *Electrochromism and Electrochromic Devices*. Cambridge: Cambridge University Press. : 2007.
2. Dautremont-Smith, W. C. *Displays* **1982**, 3, (1), 3-22.
3. Huang, Y. *Solid state ionics* **2003**, 165, (1-4), 269-277.
4. Cao, L.-c.; Mou, M.; Wang, Y. *Journal of Materials Chemistry* **2009**, 19, (21), 3412-3418.
5. Mortimer, R. J.; Dyer, A. L.; Reynolds, J. R. *Displays* **2006**, 27, (1), 2-18.
6. Huang, L.-T.; Yen, H.-J.; Wu, J.-H.; Liou, G.-S. *Organic Electronics* 2012, 13, (5), 840-849.
7. Chuang, Y.-W.; Yen, H.-J.; Wu, J.-H.; Liou, G.-S. *ACS Applied Materials & Interfaces* **2014**, 6, (5), 3594-3599.
8. Sonmez, G.; Meng, H.; Wudl, F. *Chemistry of Materials* **2004**, 16, (4), 574-580.
9. Sapp, S. A.; Sotzing, G. A.; Reynolds, J. R. *Chemistry of Materials* **1998**, 10, (8), 2101-2108.
10. Kumar, A.; Welsh, D. M.; Morvant, M. C.; Piroux, F.; Abboud, K. A.; Reynolds, J. R. *Chemistry of Materials* **1998**, 10, (3), 896-902.
11. Balan, A.; Baran, D.; Gunbas, G.; Durmus, A.; Ozyurt, F.; Toppare, L. *Chemical Communications* **2009**, (44), 6768-70.
12. Beaujuge, P. M.; Reynolds, J. R. *Chemical Reviews* **2010**, 110, (1), 268-320.
13. Akbaşoğlu, N.; Balan, A.; Baran, D.; Cirpan, A.; Toppare, L. *Journal of Polymer Science Part A: Polymer Chemistry* **2010**, 48, (23), 5603-5610.
14. Beaujuge, P. M.; Amb, C. M.; Reynolds, J. R. *Accounts of Chemical Research* **2010**, 43, (11), 1396-407.
15. Thompson, B. C.; Kim, Y. G.; McCarley, T. D.; Reynolds, J. R. *Journal of the American Chemical Society* **2006**, 128, (39), 12714-25.
16. Sönmez, G.; Schwendeman, I.; Schottland, P.; Zong, K.; Reynolds, J. R. *Macromolecules* **2003**, 36, (3), 639-647.
17. A.G. Bayer *European Patent* 339,340, **1988**.

18. Roncali, J.; Blanchard, P.; Frère, P. *Journal of Materials Chemistry* **2005**, *15*, (16), 1589-1610.
19. Sankaran, B.; Reynolds, J. R. *Macromolecules* **1997**, *30*, (9), 2582-2588.
20. Liou, G.-S.; Hsiao, S.-H.; Chen, H.-W. *Journal of Materials Chemistry* **2006**, *16*, (19), 1831-1842.
21. Yen, H.-J.; Chen, C.-J.; Liou, G.-S. *Advanced Functional Materials* **2013**, *23*, (42), 5307-5316.
22. Yen, H.-J.; Liou, G.-S. *Journal of Materials Chemistry* **2010**, *20*, (44), 9886-9894.
23. Cheng, S.-H.; Hsiao, S.-H.; Su, T.-H.; Liou, G.-S. *Macromolecules* **2005**, *38*, (2), 307-316.
24. Yen, H.-J.; Lin, H.-Y.; Liou, G.-S. *Chemistry of Materials* **2011**, *23*, (7), 1874-1882.

Chapter 2

Literature Review

In this chapter, an introduction on electrochromism is presented, followed by a discussion on the three broad categories of current existing electrochromic materials: the inorganic compounds and complexes, small organic bipyridinium molecules (viologens) and conjugated polymers. The advantages of using conjugated polymers over their inorganic counterparts have spurred the interest of developing new high performance organic electrochromic materials via new design strategies, and these will be discussed. Then, the principles and materials needed for electrochromic device construction, and important electrochromic performance parameters for qualification of potential electrochromic materials are examined.

2.1 Electrochromism

Species which are electroactive are able to undergo redox reactions (oxidation and reduction) on an electrode surface. This leads to a change in the number of electrons in the frontier molecular orbitals. As the different redox states typically have different electronic configurations and associated electronic energy transitions, the compound will experience spectral changes upon redox reactions. However, if the electronic transitions do not occur within the visible range (400 – 700 nm) of the electromagnetic spectrum, the changes in color due to the spectral changes of the electroactive species cannot be observed by the human eyes.

Electrochromism is defined as a phenomenon of reversible optical color change displayed by material upon a redox process induced by an external bias.¹ The color change is between the colorless (bleached) state and the colored state, or between two colored states. The material is termed to be “electrochromic” if it exhibits such color changes and the compound undergoing such change is referred to as an electrochrome. Electrochromic materials that possess several colored states are known as polyelectrochromic and such electrochromism is termed as multicolor-electrochromism.²

2.2 Types of Electrochromic materials

Electrochromic materials can be broadly categorized into two types: inorganic and organic materials. The inorganic electrochromic materials include mainly the oxides of transition metals such as tungsten oxide and iridium oxides, as well as the Prussian blue system. On the other hand, organic electrochromic materials vary from the small organic molecules like bipyridyliums (viologens) to large macromolecules such as conjugated polymers.

2.2.1 Metal oxides

Inorganic electrochromic materials are mainly the oxides of transition metal, such as tungsten, iridium, manganese, nickel, cobalt and molybdenum.³⁻⁷ The first example of inorganic electrochromic device was revealed by Deb in the year 1969 using tungsten oxide.⁸ He created electrochromic color by applying electric field across a film of tungsten oxide that was vacuum-deposited on a quartz substrate. He termed that phenomenon “electrophotography”, which he derived from his molybdenum oxide experiments.

Among the different transition metal oxides, tungsten trioxide, WO_3 , is one of the metal oxides that exhibit the most intense electrochromic color changes. As a result, it has been intensively investigated in the past 30 years and became one of the most widely industrially used electrochromic materials today due to superior electrochromic properties over other inorganic oxides.^{7,9-11} In WO_3 , all the tungsten sites have the same oxidation state of W^{VI} and the film of tungsten trioxide appears very pale yellow or colorless. The injection and extraction of electrons and cations (e.g. Li^+ , Na^+ , H^+) is believed to play an important role in the electrochromism process and the reaction is depicted as Eq. 2.1. During an electrochemical reduction process, electrons are transferred to some sites of W^{VI} , reducing them to W^V , giving the film a deep blue color.

Researchers have also put in much effort on the study of the preparation methods of metal oxide films. For the construction of electrochromic devices, the metal oxides are deposited as a layer of thin film on a conducting substrate using some of the common methods such as sputtering under vacuum, chemical vapor deposition, electrodeposition, and sol-gel techniques. Comprehensive details on the preparation of such metal oxide films are described in the book by Granqvist³.

2.2.2 Prussian blue (PB)

Prussian blue (PB) with the formula $[\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6]^-$ is traditionally used extensively as a synthetic pigment¹² in the formulation of paints, printing inks and lacquer, but it was later found to possess strong coloration upon electrochromism. Upon application of a voltage across the PB film, oxidation occurs near the positive electrode producing $[\text{Fe}^{\text{III}}\text{Fe}^{\text{III}}(\text{CN})_6]^-$ which is yellow (Eq. 2.2), and reduction occurs at the negative electrode to yield $[\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}(\text{CN})_6]^{2-}$ which is transparent (Eq. 2.3). The electrochromic device is deemed to be net half-bleached. In other words, PB can be bleached both anodically and cathodically.

PB is an example of the many polynuclear transition-metal hexacyanometallates which belong to the major class of insoluble mixed-valance compounds.¹³ Ever since the first report¹⁴ on the electrochemistry of PB was published, it has attracted numerous studies on the electrochemistry of PB and its derivatives.^{2,13,15} In the area of PB, notable achievements were made where optically transparent electrodes for a seven segment display¹⁶ were achieved by modifying with PB. Additionally, an electrochromic device was built successfully with a film of PB without the use of conventional electrolyte.¹⁷

2.2.3 Viologens

Progress in the area of viologens has also been made significantly over the years^{1,18-20}. The prototype viologen, 1,1'-dimethyl-4,4'-bipyridilium, is commonly referred to as 'methyl viologen' while bipyridylium species other than the dimethyl is known as the 'substituent viologens'. As seen in Scheme 2.1¹⁸, there are mainly three common viologen redox states: a dication, a radical cation and a di-reduced neutral species. The dication which is commercially available is the most stable of the three. It is colorless when pure except when it undergoes optical charge transfer with the counter anion, or other electron donating

species. When the dication is being reduced, a radical cation which has an intense colour will be formed. This radical cation is one of the most stable organic radicals, as the radical electron is able to delocalise throughout the π -framework of the bipyridyl framework, with the nitrogen substituents bearing some of the charge. During electrochromism, radical cations have intense color due to the optical charge transfer between the positive and zero-charge nitrogens, and the type of substituents on the nitrogen will affect the colours of the radical cations.²¹ As for the di-reduced species, the intensity of the colour exhibited is low as no significant optical charge transfer is possible.

Scheme 2.1 Three common bipyridyl redox states

Although viologens exhibit very high redox stability, they are not commonly used for electrochromic applications as they usually operated in their solution forms, resulting in leakage issues.

2.2.4 Conjugated conducting polymers

There have been many conducting polymers developed over the years, and π -conjugated polymers with resonance-stabilized aromatic molecules have attracted the most attention. Conjugated polymers are organic macromolecules with a backbone chain of alternating double and single bonds. The overlapping of the p -orbitals forms the π -orbitals where the π -electrons are delocalized and act as charge carriers. These charge carriers move

throughout the system, resulting in the polymers being semiconductive or conductive upon doping. Some examples of common conjugated polymers are shown in Figure 2.1.

Figure 2.1 Structures of some common conjugated polymers

In general, all redox-active conjugated polymers are potentially electrochromic in their thin film state, where redox switching will give rise to new absorption bands.^{22,23} The conductivity of the conjugated polymers can be enhanced tremendously by doping. Upon oxidation, the conjugated polymers have positive charge carriers, or holes, and are balanced with counter anions (p-doping), forming a delocalized π -electron band structure. New electronic states are formed within the bandgap, resulting in new electronic transitions of lower energy gap, where they absorb light at a longer wavelength. Upon further oxidation, more polarons are formed which may condense to form bipolarons which have longer wavelength absorption.²⁴ New polaronic and bipolaronic bands that appear during oxidation of the polymers contribute to the new bands appearing in the far red and near-infrared region.²⁵ Coupled with a depletion of the absorption maximum in the visible region, the transmissivity of the polymer increases and the conjugated polymer changes from colored to transmissive. During the reduction process of the p-doped conjugated polymers, the electronic doping could be removed by both the concurrent counter anion and the electrolyte cation to afford the un-doped neutral state. In the un-doped polymer, the magnitude of optical bandgap between the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) determines the absorption of the neutral polymer and ultimately the color change between the doped and un-doped states of a polymer.

2.2.4.1 Polyaniline (PANI)

PANI is one of the most widely used anodically coloring electrochromic polymers. It is a polyelectrochromic material²⁶⁻²⁸ which is able to exhibit four different kinds of colors (yellow-green-blue-black) during a redox reaction. PANI is a unique electrochromic material where its electrical and electrochromic properties depends on both its oxidation and protonation state. Hence, its electrochromic properties could be modified by altering the pH value of the electrolyte.²⁹ The structures of PANI depicting the various color states are shown in Figure 2.2. The fully reduced PANI form is called leucoemeraldine, and is transmissive yellow. This form can be oxidized to the emeraldine state. Emeraldine can exist as emeraldine salt or base, both of which have a ratio of one quinoidal ring to three benzenoid rings which are electrically conductive. Further oxidation leads to the fully reduced deep blue form, called pernigraniline.

Figure 2.2 Four types of PANI at different redox states

There is a growing interest to use PANI-based materials for multicolor electrochromism. In 2005, Manisankar³⁰ reported the synthesis and electrochromic properties of the copolymer of aniline and 4,4'-diaminodiphenyl sulfide (DDS) which is able to display

multicolor electrochromism under different applied voltages. At the concentration of 0.1 M DDS and 0.3 M aniline, the color of the polymer can be changed progressively from yellow to green and then to blue. When the concentration of DDS is increased to 0.5 M, the color of the polymer changes from yellow to dark green and then to dark blue. Besides having multi colored electrochromism, PANI also possesses outstanding stability with cycle stabilities up to 10^6 for yellow to green transitions.²⁷ This leads to an increase in the use of PANI or its derivatives for electrochromic applications. Dual-layer electrochromic devices such as PANI/ WO_3 ,^{31,32} PANI/PEDOT^{33,34} and PANI/Prussian blue³⁵ have also been reported to exhibit good electrochromic performance. Huang and coworkers³⁶ reported the successful synthesis of poly(2,5-dimethoxy aniline) (PMDA) in year 2002. When the applied potential was switched, PDMA showed reversible color changes from yellow to green with a coloration time of only 9 s, which is much shorter than that of PANI (22 s).

2.2.4.2 Polythiophenes

Polythiophenes have attracted much interest and are widely studied as electrochromic materials due to their ease of properties manipulation through chemical structural modifications, facile preparation and processability. In terms of their electrochromic performance, polythiophenes display high color versatility, high optical contrasts, fast response times and low power consumption during operation. The thin films of polythiophene are blue ($\lambda_{\text{max}} = 730 \text{ nm}$) at the oxidized state and red ($\lambda_{\text{max}} = 470 \text{ nm}$) in the neutral state.³⁷ In addition, further functionalization of the parent monomer has proved to be achievable and a huge variety of substituted thiophenes have been successfully synthesized, with emphasis on poly(3-substituted thiophene)s and poly(3,4-disubstituted thiophene)s.³⁸ A major advantage of using polythiophene as electrochromic materials is the ability to tune the color states simply by choosing a suitable monomer. For example, poly(3-methylthiophene) is purple ($\lambda_{\text{max}} = 530 \text{ nm}$) at neutral state, and turns pale blue upon oxidation.³⁹ The color difference exhibited by polythiophene and poly(3-methylthiophene) shows the possibility of tuning the optical properties through functionalization on the 3- and 4- position of the monomer.

To further enhance the electronic richness of polythiophene backbones, electron donating alkoxy substituents are attached onto the polythiophenes. Such alkoxy-substituted poly(thiophene)s, especially poly(3,4-ethylenedioxythiophene) (PEDOT) are intensively investigated for their electrochromic properties.^{40,41}

PEDOT was first discovered by Bayer AG research laboratories⁴² and has a bandgap lower than those of polythiophene or alkyl substituted polythiophenes. It exhibits a deep-blue color with a strong absorption band at $\lambda_{\max} = 615$ nm in its neutral state and becomes transmissive light-blue color upon oxidation.⁴³ The absorption band at the visible region corresponds to the π - π^* interband transition. As seen in Figure 2.3⁴⁴, upon p-doping, the interband transition decreases, and two new absorption peaks emerge in the NIR region which corresponds to the formation of polaronic and bipolaronic bands, and the color of the polymer begins to bleach forming a transmissive light blue color. PEDOT not only has a smaller bandgap than the unsubstituted thiophene, but it is also easily oxidized and highly stable in the doped state. This is due to the presence of the electron-donating oxygens adjacent to the thiophene ring (Figure 2.4). Upon oxidation, PEDOT becomes highly electrically conductive and transmissive in the visible region. However, this polymer is limited by its insolubility. To overcome this limitation, the aqueous dispersion of the doped form of PEDOT with the polyelectrolyte, poly(styrenesulfonate) (PSS), was produced. Cast films of PEDOT:PSS have greater than 75% transmissivity in the visible region and greater than 120 S/cm film conductivity.⁴⁵

Figure 2.3⁴⁴ Spectroelectrochemical series for a film of PEDOT

Figure 2.4 Radical cation mesomeric stabilization with oxygen contribution

A variety of PEDOT derivatives with attached solubilizing chains were soon discovered along with the first examples of soluble PEDOTs (with longer chains, namely $-\text{C}_8\text{H}_{17}$ and $-\text{C}_{14}\text{H}_{29}$).⁴⁶⁻⁵⁰ These substituents proved that the modulation of PEDOT's bandgap is similar to polythiophenes. Furthermore, a significant enhancement of switching properties was obtained with a reduction of switching times (in the 12 s range), along with a more

effective depletion of the absorption of the neutral state on full-oxidation. This is attributed to the ability of the lateral chains to facilitate inward/outward migration of the dopant counterions.⁵¹ The solubilizing chains have also proven to have an important influence on cycling stability, with PEDOT-C14 withstanding 16000 cycles while retaining 60% of its electroactivity, compared to that of the parent PEDOT which retained 65 % after 6000 cycles.⁴⁹

PEDOT analogues with expanded alkylene bridges have also been synthesized and tested by Reynolds⁵² *et al.* (Figure 2.5). It was found that the size of the alkylene bridge has an important role in determining the redox and optical properties. Reynolds' group demonstrated that better properties such as higher optical contrast and shorter switching times were obtained for the butylenedioxy bridge (PBDOT), then followed by propylenedioxy (PProDOT), and lastly the ethylenedioxy bridge of PEDOT. This phenomenon can be attributed to the more open morphology induced by the larger bridges that facilitates the diffusion of counterions.⁵³ With such promising results, Reynolds' group have then developed a large library of different PProDOT derivatives for use as electrochromic materials.⁵⁴⁻⁵⁶

Figure 2.5 Structures of PEDOT, ProDOT and PBDOT

2.3 Electrochromic devices (ECDs)

ECDs operate like rechargeable electrochemical cells, where the structure consists of two or more electrodes separated by an electrolyte. The electrolyte is usually insert between the primary electrochromic electrode and a charge balancing secondary electrode. The

switching of color will occur when a suitable voltage is applied through the charge or discharge process. ECDs can be divided into two categories: transmissive electrochromic devices for the visible range and reflective electrochromic device for the IR range. In this thesis, as we are using the former, we will discuss only transmissive devices.

There are two types of transmissive electrochromic devices, the single-layer electrochromic device and the complementary electrochromic device as seen in Figure 2.6. The configuration of a single-layer electrochromic device is of a sandwich structure.^{57,58} In the device, four layers of materials are positioned between the two substrates in a laminate configuration. The substrates are normally made up of flexible polyethylene terephthalate (PET) or glass. Then, conducting electrode layers such as indium tin oxide (ITO) are coated on the substrates. The electrochromic materials to be tested will be spin-coated or spray-coated onto one of the conducting substrates. A layer of electrolyte is then spread onto the surface of the electrochromic layer. During the redox reaction, the electrolyte layer functions as both the ionic conductor and a source/sink for ions moving through the electrochromic and electrolyte interface.

Another type of transmission electrochromic device is the complementary electrochromic device.^{59,60} Comparing the complementary ECD with the single-layered ECD as described above, the complementary ECD has one more layer of ion storage film positioned onto the other electrode. This ion storage film is usually an electrochromic material. In a typical complementary electrochromic device, one electrochromic layer is cathodically colored and the other is anodically colored. With such a setup, the complementary ECD can achieve a higher contrast as compared to the single-layer electrochromic device. Furthermore, the stability of the complementary ECD is also better as the charge produced during the oxidation reaction on one electrode can be depleted by the reduction reaction on the other electrode without any loss of materials in the complementary electrochromic device.

Figure 2.6 (a) Single-layer electrochromic device with a sandwich structure (b) Complementary electrochromic device

2.3.1 Components of ECDs

2.3.1.1 Electrochromic layer

Electrochromic layer is one of the key components that directly affect the electrochromic performance of the ECD. It is usually formed with the electrochromic material using techniques such as spin-coating, spray coating, dip coating and blading. Details on the different types of electrochromic materials have been discussed in section 2.2.

2.3.1.2 Transparent electrodes

Typically, most ECDs would need no less than one optically transparent electrode. However, for absorption/transmissive mode devices, such as goggles, spectacles and smart windows, a second optically transparent electrode is used as the rear electrode. A widely employed transparent electrode in an ECD is the indium tin oxide which is usually sputtered onto the glass or flexible PET. Alternatively, fluorine-doped tin oxide (FTO) may be used to replace ITO.⁶¹⁻⁶³ These transparent conducting oxides are semiconducting, and are transparent to visible light.⁶⁴⁻⁶⁶ The working electrode of ECDs is usually the electrochromic material layer coated onto the substrate. For a single-layer ECD, the counter electrode plays the role of charge balancing. For a complementary ECD, the counter electrode is also coated with an electrochromic layer which complements the

electrochromic layer on the working electrode, thereby resulting in different absorption spectra.

2.3.1.3 Electrolytes

The electrolyte layer between the two electrodes in an ECD has to be ionically conductive but electronically insulating. Also, it has to have low volatility and be transparent in the wavelength range where the ECD will be used. The commonly used electrolytes are gel electrolytes, and they can be broadly categorized into two groups: polymer electrolytes and polyelectrolytes. Polymer electrolytes consist of neutral macromolecular species such as poly(ethylene oxide) (PEO), poly(ethylene glycol) (PEG), poly(vinyl alcohol) (PVA) and poly(methyl methacrylate) (PMMA). Inert salt such as lithium perchlorate (LiClO_4) is dissolved in the electrolyte solvent to supply the mobile ions. Polyelectrolytes, on the other hand, are also called polysalts, are polymers with ion-labile groups, where each repeating unit of the polymer bears an electrolyte group along its backbone and display similar properties to both electrolytes and polymers. One common example is the poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS).

Even though gel electrolytes are the most widely used electrolytes for electrochromic devices due to the relative ease of device fabrication, they have some limitations which are difficult to overcome, such as thermal instability, toxicity, and solvent evaporation which can lead to poor conductivity. Recently, ionic liquids⁶⁷⁻⁷⁰ which consist of nitrogen containing organic cations and inorganic anions, have been employed to fabricate electrochromic devices. Some examples of ionic liquids are 1-butyl-3-methylimidazolium hexafluorophosphate ($[\text{BMIM}][\text{PF}_6]$), 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{BMIM}][\text{BF}_4]$), 1-butyl-3-methylimidazolium bromide ($[\text{BMIM}][\text{Br}]$), 1-butyl-3-methylimidazolium bis(trifluoromethane) sulfonimide ($[\text{BMIM}][\text{Tf}_2\text{N}]$), and 1-butyl-1-methylpyrrolidinium bis(trifluoromethane)sulfonimide ($[\text{BMPY}][\text{Tf}_2\text{N}]$). As ionic liquids have many advantageous properties over gel electrolytes such as being non-volatile, non-flammable, having good thermal stability, good conductivity and being relatively inexpensive, they are now widely used in the fabrications of electrochromic devices⁷⁰,

lithium batteries⁷¹, solar cells⁷², fuel cells⁷³ and supercapacitors⁷⁴. Despite the many advantages ionic liquids have, they are prone to leakage problems. This limitation is mitigated by blending ionic liquids with polymeric ionic liquids⁷⁰ or using other polymers such as poly(vinylidene fluoride)-hexafluoropropylene (PVDF-HFP) copolymer⁷⁵ as the electrolyte layer instead.

2.3.2 Parameters for electrochromic materials characterization

In order to qualify as a promising electrochromic material, one or more of the following standard performance parameters have to be fulfilled depending on the intended application.

2.3.2.1 Optical contrast

Electrochromic optical contrast is an important parameter in evaluating an electrochromic material. It is often reported as the percentage change in transmittance (ΔT %) at a specific wavelength between the two redox states, where the polymer has the highest change in optical contrast. The transmittance values are recorded when square-wave potential steps are applied to the polymer film placed in a spectrophotometer.

2.3.2.2 Switching rate

The switching rate which is often reported as the response time is defined as the time required for the electrochrome to switch from the oxidized state to the reduced state, and *vice versa*, which are commonly known as the coloration or bleaching process. This is an important characteristic of an ECD, especially for applications such as dynamic displays that require a rapid color change. In this thesis, the response times of the ECDs were calculated based on the time required to achieve 95 % of the full switch. A value of 95 % is chosen as the human eye is not sensitive enough to discern the remaining 5 % change in optical contrast. The switching speed of the ECD is dependent on several factors⁷⁶ such as the conductivity of the electrolyte, the ease of ion diffusion in the thin film, the magnitude of the external voltage applied and the thickness and morphology of the polymer film.

2.3.2.3 Coloration efficiency

Coloration efficiency (η) is a practical and efficient method to measure the power requirements of the electrochromic layer and to compare the efficiency of different EC materials. It is defined as the optical absorbance change per charge density required to induce a full switch at a certain wavelength, and is calculated based on the equation below⁷⁷:

$$CE(\eta) = \frac{\log(T_{ox}/T_{red})}{Q_d} \quad \text{Eq. 2.4}$$

where T_{ox} refers to the percent transmittance of the bleached state, T_{red} the percent transmittance of the colored state, and Q_d is the injected/ejected charge per unit area (C/cm^2).

2.3.2.4 Cycle life

The cycle life is the number of the cycles an ECD can perform before any significant degradation in performance. It is usually used to measure the stability of an ECD. The measurement of cycle life is accomplished by switching the device repeatedly between its colored and bleached states. The stability of the electrochromic material is important as degradation of the material will affect the performance of the electrochromic device such as a reduction in the optical contrast. Other common degradation factors include the irreversible redox behaviors at extreme potentials, presence of water and oxygen which result in redox interference, photodegradation, and heating due to repeated switching⁷⁶ or NIR absorption.

2.3.3 Applications of ECDs

In recent years, there have been an increasing number of commercial applications of electrochromic devices such as anti-glare car mirrors, smart windows for use in cars, aircrafts, and buildings. The anti-glare electrochromic car rear-view mirror is able to adjust the brightness so that the strong light from the cars at the back will not blind the driver's

eyes. Also, the use of electrochromic smart windows either for cars or buildings promotes energy saving and results in huge savings from air-conditioner costs which is worth billions of dollars every year. There are also some potential applications which include protective eyewear, glare-reduction systems for offices and camouflage materials for military use.

2.4 Developments of organic electrochromic polymers

Conjugated polymers have been gaining attention due to their ease of structural modification for color tuning.⁷⁸ Their electrochromic properties can be simply achieved by monomer functionalization and copolymerization^{79,80}. Some of these properties of electrochromic polymers can even outperform their inorganic counterparts. A comparison table between inorganic electrochromic materials and conjugated electrochromic polymers is shown in Table 2.1. Given the relative ease of synthesis in general, organic electrochromic polymers are now a step closer for technological development. Several design strategies have been adopted to synthesize high performance electrochromic polymers are listed and discussed below.

Table 2.1 Comparison between inorganic materials and electrochromic polymers⁹⁹.

Properties	Inorganic materials	Electrochromic polymers
Method of preparation of thin film	Sophisticated techniques such as electrodeposition, sputtering under vacuum, chemical vapor deposition	Simple techniques such as spin-coating, spray-coating, dip-coating
Processability	Poor	Good
Cost	High	Low
Color	Limited	Large range
Contrast	Moderate	High
Switching speed	Slow	Fast
Lifetime	10^3 - 10^5 cycles	10^4 - 10^6 cycles

2.4.1 Donor-acceptor (D-A) polymers

The electrochromism phenomenon of most organic electrochromic polymers relies on oxidative doping, and thus the stability of the doped state is very important. The oxidized states of polymers are often unstable under high potentials, leading to poor electrochemical stabilities and degradation of polymer chains. This in turn results in short life cycles of the electrochromic devices. As such, recent research on conjugated polymers focuses on the engineering of the bandgaps to improve the long term stability of ECDs and the donor-acceptor approach.

A donor-acceptor polymer consists of both electron rich donor (D) and electron deficient acceptor (A) moieties on the backbone. D-A polymers have been extensively investigated with the aim of obtaining low bandgap polymers⁸¹. In comparison with homopolymers, D-A polymers may exhibit smaller bandgaps. Some D-A conjugated polymers with good stabilities are shown in Figure 2.7⁸²⁻⁸⁵.

Figure 2.7 Structures of reported D-A polymers with good stabilities

Besides the ability to improve the stability of organic electrochromic polymers, the D-A approach can be used for the spectral engineering of the polymers. A dual absorption band, which includes a short and long wavelength band in the visible region is often shown by D-A polymers⁸⁶, resulting in saturated green hue polymers. Wudl⁸⁵ *et al.* was the first to prepare a saturated green hue D-A polymer by electrochemically polymerizing 2,3-dithien-3-yl-5,7-dithien-2-yl-thieno[3,4-*b*]pyrazine (DDTP). The polymer switches from a green reduced state to a pale green upon oxidation. The cycling stability was also proven to be good, reporting a mere 1.5 % loss in redox activity after 10 000 cycles. However, the

drawback is that the observed optical contrast is quite low at 23 % at 370 nm and 12 % at 735 nm. Reynolds' team has demonstrated the possibility of tuning the intensity and color of D-A polymers by varying the contribution of donors and acceptors in the polymer backbone. They achieved a polymer with a broad absorption over the whole visible spectrum where it exhibited a black hue as seen in Figure 2.8⁸⁷. This polymer switched to a highly transmissive oxidized form upon oxidation with an optical contrast of 50 %.

Figure 2.8 Left: Structure of the D-A polymer developed by Reynolds *et al.* Right: Spectroelectrochemical spectrum of the polymer. Bottom: Colors obtained on electrochemical switching.

2.4.2 Triphenylamine functionalized aromatic polyamides and polyimides

Triphenylamine derivatives are commonly used as hole-transport donor organic materials with (N,N'-Bis(3-methylphenyl)-N,N'-diphenylbenzidine) (TPD) being a popular preference⁸⁸. The charged states of this material are highly stable delocalized radical cations with quinod character^{89,90}. In the past decade, Liou's group⁹¹⁻⁹⁷ have actively researched on non-conjugated polymeric triphenylamine based systems, where they synthesized a variety of polyimides and polyamides by combining N,N,N',N'-tetraphenyl-1,4-phenylenediamine moieties with different aromatic and non-aromatic spacers in the main chain as seen in Figure 2.9. The resultant polymers possess good solubility in most polar aprotic solvents. Hence, drop-casting technique was used to obtain the amorphous films. The films are multichromic, where they show a color transition from colorless to

green to blue when oxidized, and showed high contrast values ($> 60\%$ in the visible region) with high redox stabilities. It was shown that the methoxy groups on the triphenylamine unit (b. in Figure 2.9) in the *para*-position is able to lower the oxidation potential and more stable radical intermediates are obtained, which prevent dimerization reactions to occur at these positions⁹⁷. This has led to an improved material with optical contrast of around 75 % in the visible region and a redox stabilities up to 1000 cycles with a 5 % and 10 % drop in coloration efficiencies for the colorless to green transition, and colorless to blue respectively.

Figure 2.9 Examples of polyimides and polyamides incorporating triphenylamine moieties

2.5 Polymers in this thesis

Even though current research has shown that organic electrochromic polymers have good electrochromic properties, it still lacks of some features to qualify for use in commercial electrochromic applications. The insolubility and low stability of these materials have yet to achieve favorable limits for industrial applications. Scientists have discovered several design strategies to create high performance electrochromic polymers. Simply by using a variable monomer structure, or by adjusting the composition of copolymers, composites and blends, the colored states of the EC polymers can be easily tuned. Reynolds' group have also researched intensively on the donor-acceptor approach to obtain good performing EC polymers with low bandgap. For Liou's group, they have utilized triphenylamine to create high stability EC polymers.

In this thesis, we will be adapting some design strategies to create high performance EC polymers with the emphasis on the solubility and stability problems. Even though the use of donor-acceptor approach can obtain good performance electrochromic polymers, there is only a small pool of outstanding and promising electron acceptors such as benzotriazole, diketopyrrolopyrrole, benzothiadiazole, etc. There is a need to synthesize more new electron acceptors to increase the monomer pool. Here, we propose new synthetic methodologies for synthesizing new electron deficient monomers with solubilizing properties. This is necessary as this will open another pathway for synthesizing highly electron deficient building blocks for use in the donor-acceptor approach to yield solution processable polymers.

Also, we have discussed the high optical contrast and shorter switching times obtained by the derivatives of PEDOT. In this thesis, we will use ProDOT, a derivative of EDOT with expanded alkylene bridges as the electron donor during the polymerization. This type of monomer has been used to synthesize polymers with good performance. Furthermore, it is possible to functionalize ProDOT with long alkyl chains to enhance the solubility of the polymer chains. Here, we will explore the possibility of using 4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene (IDT) as a building block in the area of electrochromic polymers.

Though IDT is commonly used in organic thin film transistor and organic solar cells, it is rarely reported in electrochromic materials. ProDOT will be used to copolymerize IDT to determine the potential of such combination for use in electrochromic applications.

From the literature review done on the work by Liou's group on triphenylamine based polyimide or polyamide^{91,92,97,98}, it was found that the presence of triphenylamine in the polymer chains can give multi-colored electrochromism as well as good cycling stabilities. This motivates us to attempt to incorporate a varying amount of triphenylamine into the polymer chain to investigate the effect of triphenylamine on the stability of the polymer. This synthetic approach is simple and straight-forward, where small amount of triphenylamine is just added during the polymerization process. This has been demonstrated as a very useful method to enhance the stability of the polymers.

References

1. Monk, P., Roger Mortimer, and David Rosseinsky, *Electrochromism and Electrochromic Devices*. Cambridge: Cambridge University Press. : 2007.
2. Paul M. S. Monk, R. J. M., David R. Rosseinsky *Electrochromism: Fundamentals and Applications*. VCH, Weinheim, Germany: 1995.
3. Granqvist, C. G., In *Handbook of Inorganic Electrochromic Materials*, Elsevier Science B.V.: Amsterdam, 1995.
4. Deshpande, R.; Lee, S. H.; Mahan, A. H.; Parilla, P. A.; Jones, K. M.; Norman, A. G.; To, B.; Blackburn, J. L.; Mitra, S.; Dillon, A. C. *Solid State Ionics* **2007**, 178, (13–14), 895-900.
5. Song, Y.-Y.; Gao, Z.-D.; Wang, J.-H.; Xia, X.-H.; Lynch, R. *Advanced Functional Materials* **2011**, 21, (10), 1941-1946.
6. Lee, S. H.; Deshpande, R.; Parilla, P. A.; Jones, K. M.; To, B.; Mahan, A. H.; Dillon, A. C. *Advanced Materials* **2006**, 18, (6), 763-766.
7. Wang, J.; Khoo, E.; Lee, P. S.; Ma, J. *The Journal of Physical Chemistry C* **2009**, 113, (22), 9655-9658.

8. Deb, S. K. *Applied Optics* **1969**, 8, (S1), 192-195.
9. Granqvist, C. G. *Solar Energy Materials and Solar Cells* **2000**, 60, (3), 201-262.
10. Granqvist, C. G.; Avendaño, E.; Azens, A. *Thin Solid Films* **2003**, 442, (1-2), 201-211.
11. Wang, J.; Khoo, E.; Lee, P. S.; Ma, J. *The Journal of Physical Chemistry C* **2008**, 112, (37), 14306-14312.
12. Kraft, A. *Bulletin for the history of Chemistry* **2008**, 33, (2), 61-67.
13. de Tacconi, N. R.; Rajeshwar, K.; Lezna, R. O. *Chemistry of Materials* **2003**, 15, (16), 3046-3062.
14. Neff, V. D. *Journal of The Electrochemical Society* **1978**, 125, (6), 886-887.
15. Itaya, K.; Uchida, I.; Neff, V. D. *Accounts of Chemical Research* **1986**, 19, (6), 162-168.
16. Itaya, K.; Shibayama, K.; Akahoshi, H.; Toshima, S. *Journal of Applied Physics* **1982**, 53, (1), 804-805.
17. Carpenter, M. K.; Conell, R. S. *Journal of The Electrochemical Society* **1990**, 137, (8), 2464-2467.
18. Mortimer, R. J. *Electrochimica Acta* **1999**, 44, (18), 2971-2981.
19. Chen, P.-Y.; Chen, C.-S.; Yeh, T.-H. *Journal of Applied Polymer Science* **2014**, 131, (13), 40485
20. Bar, G.; Larina, N.; Grinis, L.; Lokshin, V.; Gvishi, R.; Kiryushev, I.; Zaban, A.; Khodorkovsky, V. *Solar Energy Materials and Solar Cells* **2012**, 99, 123-128.
21. Monk, P. M. S. *The Viologens: Physicochemical Properties, Synthesis and Applications of the Salts of 4,4'-Bipyridine*. Chichester: J. Wiley & Sons: November 1998.
22. Camurlu, P.; Gültekin, C. *Solar Energy Materials and Solar Cells* **2012**, 107, 142-147.
23. Kang, J.-H.; Oh, Y.-J.; Paek, S.-M.; Hwang, S.-J.; Choy, J.-H. *Solar Energy Materials and Solar Cells* **2009**, 93, (12), 2040-2044.
24. Iucci, G.; Xing, K.; Lögdlund, M.; Fahlman, M.; Salaneck, W. R. *Chemical Physics Letters* **1995**, 244, (1-2), 139-144.

25. Scrosati, B. *Applications of Electroactive Polymers*. Chapman & Halls: London, 1998.
26. Syed, A. A.; Dinesan, M. K. *Talanta* **1991**, 38, (8), 815-837.
27. Kobayashi, T.; Yoneyama, H.; Tamura, H. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1984**, 161, (2), 419-423.
28. Bernard, M. C.; Cordoba-Torresi, S.; Goff, A. H.-L. *Solar Energy Materials and Solar Cells* **1992**, 25, (3-4), 225-240.
29. Watanabe, A.; Mori, K.; Iwasaki, Y.; Nakamura, Y.; Niizuma, S. *Macromolecules* **1987**, 20, (8), 1793-1796.
30. Manisankar, P.; Vedhi, C.; Selvanathan, G.; Somasundaram, R. M. *Chemistry of Materials* **2005**, 17, (7), 1722-1727.
31. Panero, S.; Scrosati, B.; Baret, M.; Cecchini, B.; Masetti, E. *Solar Energy Materials and Solar Cells* **1995**, 39, (2-4), 239-246.
32. Zhang, L.; Xiong, S.; Ma, J.; Lu, X. *Solar Energy Materials and Solar Cells* **2009**, 93, (5), 625-629.
33. Lin, T.-H.; Ho, K.-C. *Solar Energy Materials and Solar Cells* **2006**, 90, (4), 506-520.
34. Huang, L.-M.; Chen, C.-H.; Wen, T.-C. *Electrochimica Acta* **2006**, 51, (26), 5858-5863.
35. Duek, E. A. R.; De Paoli, M.-A.; Mastragostino, M. *Advanced Materials* **1993**, 5, (9), 650-652.
36. Huang, L.-M.; Wen, T.-C.; Gopalan, A. *Synthetic Metals* **2002**, 130, (2), 155-163.
37. Garnier, F.; Tourillon, G.; Gazard, M.; Dubois, J. C. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1983**, 148, (2), 299-303.
38. Roncali, J. *Chemical Reviews* **1992**, 92, (4), 711-738.
39. Mastragostino, M.; Arbizzani, C.; Bongini, A.; Barbarella, G.; Zambianchi, M. *Electrochimica Acta* **1993**, 38, (1), 135-140.
40. Groenendaal, B. L.; Jonas, F.; Freitag, D.; Pielartzik, H.; Reynolds, J. R. *Advanced Materials* **2000**, 12, (7), 481-494.
41. Groenendaal, L.; Zotti, G.; Aubert, P. H.; Waybright, S. M.; Reynolds, J. R. *Advanced Materials* **2003**, 15, (11), 855-879.

42. A.G. Bayer European Patent 339,340, 1988.
43. Sonmez, G.; Sonmez, H. B. *Journal of Materials Chemistry* **2006**, 16, (25), 2473-2477.
44. Dyer, A. L. (2007) *Conjugated Polymer Electrochromic and Light-Emitting Devices* (Dissertation) University of Florida.
45. Argun, A. A.; Cirpan, A.; Reynolds, J. R. *Advanced Materials* **2003**, 15, (16), 1338-1341.
46. Havinga, E. E.; Mutsaers, C. M. J.; Jenneskens, L. W. *Chemistry of Materials* **1996**, 8, (3), 769-776.
47. Sapp, S. A.; Sotzing, G. A.; Reynolds, J. R. *Chemistry of Materials* **1998**, 10, (8), 2101-2108.
48. Kumar, A.; Reynolds, J. R. *Macromolecules* **1996**, 29, (23), 7629-7630.
49. Sankaran, B.; Reynolds, J. R. *Macromolecules* **1997**, 30, (9), 2582-2588.
50. Welsh, D. M.; Kumar, A.; Morvant, M. C.; Reynolds, J. R. *Synthetic Metals* **1999**, 102, (1-3), 967-968.
51. Schwendeman, I.; Gaupp, C. L.; Hancock, J. M.; Groenendaal, L.; Reynolds, J. R. *Advanced Functional Materials* **2003**, 13, (7), 541-547.
52. Kumar, A.; Welsh, D. M.; Morvant, M. C.; Piroux, F.; Abboud, K. A.; Reynolds, J. R. *Chemistry of Materials* **1998**, 10, (3), 896-902.
53. Welsh, D. M.; Kumar, A.; Meijer, E. W.; Reynolds, J. R. *Advanced Materials* **1999**, 11, (16), 1379-1382.
54. Reeves, B. D.; Grenier, C. R. G.; Argun, A. A.; Cirpan, A.; McCarley, T. D.; Reynolds, J. R. *Macromolecules* **2004**, 37, (20), 7559-7569.
55. Welsh, D. M.; Kloeppner, L. J.; Madrigal, L.; Pinto, M. R.; Thompson, B. C.; Schanze, K. S.; Abboud, K. A.; Powell, D.; Reynolds, J. R. *Macromolecules* **2002**, 35, (17), 6517-6525.
56. Gaupp, C. L.; Welsh, D. M.; Reynolds, J. R. *Macromolecular Rapid Communications* **2002**, 23, (15), 885-889.
57. Hu, C.-W.; Lee, K.-M.; Huang, J.-H.; Hsu, C.-Y.; Kuo, T.-H.; Yang, D.-J.; Ho, K.-C. *Solar Energy Materials and Solar Cells* **2009**, 93, (12), 2102-2107.

58. Hu, C.-W.; Lee, K.-M.; Vittal, R.; Yang, D.-J.; Ho, K.-C. *Journal of The Electrochemical Society* **2010**, 157, (7), P75-P78.
59. Camurlu, P.; Cirpan, A.; Toppare, L. *Journal of Electroanalytical Chemistry* **2004**, 572, (1), 61-65.
60. Ak, M.; Durmus, A.; Toppare, L. *Solid State Sciences* **2007**, 9, (9), 843-849.
61. Syrrakou, E.; Papaefthimiou, S.; Yianoulis, P. *Solar Energy Materials and Solar Cells* **2005**, 85, (2), 205-240.
62. Pennisi, A.; Simone, F.; Barletta, G.; Di Marco, G.; Lanza, M. *Electrochimica Acta* **1999**, 44, (18), 3237-3243.
63. Di Marco, G.; Lanza, M.; Pennisi, A.; Simone, F. *Solid State Ionics* **2000**, 127, (1–2), 23-29.
64. Chopra, K. L.; Major, S.; Pandya, D. K. *Thin Solid Films* **1983**, 102, (1), 1-46.
65. Granqvist, C. G. *Applied Physics A* 57, (1), 19-24.
66. Granqvist, C. G.; Hultåker, A. *Thin Solid Films* **2002**, 411, (1), 1-5.
67. Rogers, R. D.; Seddon, K. R. *Science* **2003**, 302, (5646), 792-793.
68. Ma, L.; Li, Y.; Yu, X.; Yang, Q.; Noh, C.-H. *Solar Energy Materials and Solar Cells* **2008**, 92, (10), 1253-1259.
69. Šurca Vuk, A.; Jovanovski, V.; Pollet-Villard, A.; Jerman, I.; Orel, B. *Solar Energy Materials and Solar Cells* **2008**, 92, (2), 126-135.
70. Marcilla, R.; Alcaide, F.; Sardon, H.; Pomposo, J. A.; Pozo-Gonzalo, C.; Mecerreyes, D. *Electrochemistry Communications* **2006**, 8, (3), 482-488.
71. Garcia, B.; Lavallée, S.; Perron, G.; Michot, C.; Armand, M. *Electrochimica Acta* **2004**, 49, (26), 4583-4588.
72. Wang, P.; Zakeeruddin, S. M.; Comte, P.; Exnar, I.; Grätzel, M. *Journal of the American Chemical Society* **2003**, 125, (5), 1166-1167.
73. Susan, M. A. B. H.; Noda, A.; Mitsushima, S.; Watanabe, M. *Chemical Communications* **2003**, (8), 938-939.
74. Stenger-Smith, J. D.; Webber, C. K.; Anderson, N.; Chafin, A. P.; Zong, K.; Reynolds, J. R. *Journal of The Electrochemical Society* **2002**, 149, (8), A973-A977.
75. Fuller, J.; Breda, A. C.; Carlin, R. T. *Journal of Electroanalytical Chemistry* **1998**, 459, (1), 29-34.

76. Argun, A. A.; Aubert, P.-H.; Thompson, B. C.; Schwendeman, I.; Gaupp, C. L.; Hwang, J.; Pinto, N. J.; Tanner, D. B.; MacDiarmid, A. G.; Reynolds, J. R. *Chemistry of Materials* **2004**, 16, (23), 4401-4412.
77. Sonmez, G.; Meng, H.; Wudl, F. *Chemistry of Materials* **2004**, 16, (4), 574-580.
78. Schwendeman, I.; Hickman, R.; Sönmez, G.; Schottland, P.; Zong, K.; Welsh, D. M.; Reynolds, J. R. *Chemistry of Materials* **2002**, 14, (7), 3118-3122.
79. Bulut, U.; Toppare, L.; Yılmaz, F.; Yağcı, Y. *European Polymer Journal* **2004**, 40, (11), 2421-2426.
80. Erden, A.; Sahin, E.; Güllü, M.; Toppare, L. *European Polymer Journal* **2006**, 42, (8), 1866-1874.
81. Havinga, E. E.; ten Hoeve, W.; Wynberg, H. *Synthetic Metals* **1993**, 55, (1), 299-306.
82. Gunbas, G. E.; Durmus, A.; Toppare, L. *Advanced Functional Materials* **2008**, 18, (14), 2026-2030.
83. Beaujuge, P. M.; Vasilyeva, S. V.; Ellinger, S.; McCarley, T. D.; Reynolds, J. R. *Macromolecules* **2009**, 42, (11), 3694-3706.
84. İçli, M.; Pamuk, M.; Algi, F.; Önal, A. M.; Cihaner, A. *Chemistry of Materials* **2010**, 22, (13), 4034-4044.
85. Sonmez, G.; Shen, C. K.; Rubin, Y.; Wudl, F. *Angewandte Chemie* **2004**, 43, (12), 1498-502.
86. Gunbas, G. E.; Durmus, A.; Toppare, L. *Advanced Materials* **2008**, 20, (4), 691-695.
87. Beaujuge, P. M.; Ellinger, S.; Reynolds, J. R. *Nature Materials* **2008**, 7, (10), 795-9.
88. Mitschke, U.; Bauerle, P. *Journal of Materials Chemistry* **2000**, 10, (7), 1471-1507.
89. Malagoli, M.; Brédas, J. L. *Chemical Physics Letters* **2000**, 327, (1-2), 13-17.
90. Low, P. J.; Paterson, M. A. J.; Puschmann, H.; Goeta, A. E.; Howard, J. A. K.; Lambert, C.; Cherryman, J. C.; Tackley, D. R.; Leeming, S.; Brown, B. *Chemistry – A European Journal* **2004**, 10, (1), 83-91.
91. Cheng, S.-H.; Hsiao, S.-H.; Su, T.-H.; Liou, G.-S. *Macromolecules* **2005**, 38, (2), 307-316.

92. Chang, C.-W.; Liou, G.-S.; Hsiao, S.-H. *Journal of Materials Chemistry* **2007**, 17, (10), 1007-1015.
93. Hsiao, S.-H.; Liou, G.-S.; Kung, Y.-C.; Yen, H.-J. *Macromolecules* **2008**, 41, (8), 2800-2808.
94. Yen, H.-J.; Liou, G.-S. *Journal of Materials Chemistry* **2010**, 20, (44), 9886-9894.
95. Yen, H.-J.; Lin, H.-Y.; Liou, G.-S. *Chemistry of Materials* **2011**, 23, (7), 1874-1882.
96. Yen, H.-J.; Liou, G.-S. *Chemistry of Materials* **2009**, 21, (17), 4062-4070.
97. Liou, G.-S.; Chang, C.-W. *Macromolecules* **2008**, 41, (5), 1667-1674.
98. Chang, C.-W.; Chung, C.-H.; Liou, G.-S. *Macromolecules* **2008**, 41, (22), 8441-8451.
99. Somani, P. R.; Radhakrishnan S. *Materials Chemistry and Physics* **2002**, 77, 117–133

Chapter 3

Experimental methodology

This chapter briefly describes the toolbox of characterization techniques employed for the work presented in this thesis. It is essential to verify the identity of the newly synthesized materials correctly as well as to characterize their properties accurately. Techniques such as the nuclear magnetic resonance (NMR) and elemental analysis (EA) were used for the identification of the synthesized materials as their compositions consist largely of hydrocarbons. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) are some of the widely used characterization techniques for evaluating the thermal properties of polymers. The electrochromic properties of the polymers are usually determined by the UV-vis-NIR spectroscopy, cyclic voltammetry (CV) and spectroelectrochemistry. These techniques work together for the evaluation of the electrochemical properties of the electrochromic polymers. Next, the experimental methods for the synthesis and purification of polymers are discussed. In this thesis, still cross coupling reaction which is one of the most efficient polymerization methodologies, was employed for the preparation of polymers.

3.1 Introduction

Chapter 2 described the importance of creating novel monomers and polymers for electrochromic applications, as well as the chemical and electrochromic properties that arise from them. Properties such as their structure, thermal characteristics, electrochemistry, and color are important aspects of electrochromic materials and the experimental techniques used to quantitatively characterize these properties have largely been the realm of scientists who are interested in describing such materials. Considering a large number of synthetic and characterization tools which have been developed by scientists for the investigation of the material performance, useful approaches have to be identified for the nature and accuracy of the information that they can provide. In this chapter, the polymer synthetic method and characterization techniques used during the course of this thesis will be described.

The identity and purity of a novel monomer has to be confirmed before it can be used for the synthesis of polymers. The identification process can be done by using Nuclear Magnetic Resonance (NMR) spectroscopy where chemists in most laboratories today use it to determine the structures of the compounds. As the organic compounds that we have synthesized consist of mainly hydrogen and carbon atoms, it is rationale to use NMR as the ^1H and ^{13}C isotopes are the most commonly detectable NMR signals. To further verify the structure of the new monomers, crystallization of the monomer to get a single crystal for testing in x-ray diffraction is essential.

The synthesis of our electrochromic polymers is by Stille cross coupling reaction. Stille cross coupling reactions are one of the most efficient polymerization methodologies for the chemical synthesis of conjugated polymers¹. Similarly, the structure of the new conjugated polymers that we have synthesized can be confirmed with NMR as well. The physical and electrochemical properties of the polymers will then be investigated before they are applied in the fabricated electrochromic device.

First, the polymers' molecular weights are determined by the gel permeation chromatography (GPC), and their purities further verified by using the elemental analysis (EA). GPC provides a fast and convenient method for determining the molecular weights of the polymers. Usually, the samples can be analyzed under an hour or less. From the gel permeation chromatogram, the molecular weight of the polymers can be determined. If the polymers contain much of the low molecular weight fraction, they have to undergo further purification, as small molecules may cause defects in the polymer film during electrochemical switching, thereby affecting the performances of the devices. Therefore, it is practical to use a quick and easy method for estimation of the molecular weights and distribution of polymer samples, so that any molecular weight related problem could be identified quickly before further characterizations are being done. Another commonly used methodology to access the molecular weight information for polymers is matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectroscopy. As MALDI-TOF MS sometimes has difficulty in ionizing high molecular weight polymers leading to inaccurate molecular weight obtained, hence, this technique is not applied in this thesis for polymer molecular weight determination².

Elemental analysis (EA) is a method that can provide quantitative results, where the mass fractions of the elements can be determined. As EA is usually used for the measurements of carbon, hydrogen, nitrogen and heteroatoms (e.g., sulphur) of a sample, we acquired the use of this method as our polymers contain such elements. Together with the NMR results, they help in the determination of the purity of the synthesized compounds.

The thermal properties of the synthesized polymers are investigated using the thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA is one of the most widely used experimental techniques for evaluating the thermal stability of the polymers. Since TGA uses a high precision scale to measure the mass loss of the sample, only a very small sample of a few milligrams is needed. Therefore, there is no need to synthesize large amount of polymers for thermal stability testing.

DSC is commonly used for examining the thermal transitions of polymers. Similar to TGA, small amounts of sample (a few milligrams) is needed for the analysis. From the DSC analysis, the melting points and glass transition temperatures can be determined.

The electrochromic properties of the polymers are determined by using the UV-*vis*-NIR spectroscopy, cyclic voltammetry and spectroelectrochemistry. These techniques work hand-in-hand to investigate the absorption and electrochemical properties of the polymers. Important electrochromic properties such as the optical contrast, the stability of the electrochromic devices have to be investigated using the UV-*vis*-NIR spectroscopy as it is able to provide the optical change when the polymers are oxidized or reduced.

Cyclic voltammetry is a powerful and fast tool to evaluate the electrochemical properties of conjugated polymers. Key information such as the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels can be obtained from the onsets of oxidation and reduction respectively. The redox properties can be easily examined in a simple setup, using the three-electrode electrochemical cell. It consists of an electrolyte solution, a working electrode with the test sample, a counter electrode and a reference electrode. To perform the analysis, only a minimal amount of test sample is needed to drop-cast onto the working electrode and the results can be obtained in a short time.

Spectroelectrochemistry is one of the most basic tools to evaluate the electrochromic behavior of electrochromic devices. It is used for the monitoring of formation of ionic states (polarons and bipolarons) upon progressive application of an electrical bias. As it is able to examine transmittance changes over a large range of wavelengths, which is from visible to near infra-red (NIR) region, optical transitions associated with charge-carrier formations can be evaluated. These optical transitions correspond to the electrochromism of a material which is one of the important properties of an electrochromic material.

A methodology has to be introduced to describe the different color states exhibited by electrochromic devices on electrochemical switching based on the CIE (Commission

Internationale de l'Eclairage) standards for color matching. Therefore, the colorimetry method based on CIE 1976 is used to determine the color of the electrochromic devices. In order for the electrochromic materials to be potentially used for commercial applications, there is a need to precisely define their color by a colorimeter as there could be discrepancy and variation among the eyes of different people.

The atomic force microscopy (AFM) is used to study the morphologies of the electrochromic polymer surfaces where a three-dimensional surface profile could be obtained. In addition, polymer samples can be analyzed by the AFM at ambient environment and do not require any special treatments such as metal or carbon coatings. These coatings could potentially change or damage the polymer samples. Thus, the AFM is chosen for the study of the morphology of the polymer thin films.

The above synthesis and characterization techniques are often referred to in the subsequent chapters in this thesis and the intent of this chapter is to provide a brief background of these techniques and the methods to perform these experiments.

3.2 Synthesis

3.2.1 Transition Metal Mediated Polymerization - Stille cross coupling reaction

In the past 40 years, the continuous development in the area of transition metal mediated cross coupling reactions has led to the massive growth of conjugated polymer research. These polymerization methods enable carbon-carbon bonds to form directly between sp/sp^2 carbons³, giving a platform to build an extended alternate single-double bond polymer backbone, which is the main structure of conjugated polymers. These transition metal mediated polymerization methodologies include mainly the Stille⁴, Suzuki-Miyaura⁵, Kumada-Corriu^{6, 7}, Sonogashira, Heck and Negishi⁸ couplings, which are coupling reactions of aromatic halides with aromatic organotin, organoboron, organomagnesium, triple bonds, double bonds and organozinc derivatives respectively. These coupling

reactions share a similar catalytic cycle which involves mainly three steps: oxidative addition, transmetallation and finally a reductive elimination.

The Stille coupling reaction is believed to be one of the most effective cross coupling reactions for the synthesis of conjugated polymers as it requires mild reaction conditions and possesses high resistance to the surrounding chemical environment. It is first introduced by Toshihiko Migita⁹ in 1976 and then further developed by John Stille¹⁰ in 1978. It has then become a well-known palladium catalyzed cross coupling reaction between organotin compounds and a range of organic electrophiles such as organic halides and triflates. As it is a versatile method for constructing carbon-carbon bonds between molecules containing sp^2 bonds, Stille coupling reaction has been widely used in synthesizing natural products¹¹, drug discovery¹² and materials chemistry¹³. And most recently, this Stille coupling reaction has been popular in synthesizing organic polymers for electrochromic applications, and in this dissertation, we used Stille coupling reaction as the dominant polymerization method.

The catalytic cycle for Stille coupling reaction consists of mainly three steps:

- (i) Oxidative addition
- (ii) Transmetallation
- (iii) Reductive elimination

The mechanism begins with the oxidative addition of the organohalide **2** to the palladium catalyst Pd(0) **1** to form the organopalladium complex Pd(II) **3**.

Then, transmetallation occurs where the R group of the organostanne replaces the halide anion on the palladium complex to form the complex **5**.

This is followed by a reductive elimination which gives the final product **7**, and restores the palladium catalyst, and the whole catalytic cycle can start again.

A typical schematic illustration of the catalytic cycle for Stille coupling reaction is shown in Figure 3.1.

Figure 3.1 General reaction scheme and mechanism of Stille coupling¹⁴

Typically, the monomers involved in a Stille coupling reaction are electron deficient halides and electron rich organotin compounds. It was reported that the oxidative addition of the Pd(0) step was favoured by a system with better electron affinity and a system which is strongly electron donating activates the C-Sn bond during the transmetallation step¹⁵. However, the synthesis of di-tin monomers possesses a few problems. Firstly, the purification process is a major issue. Even though purification of di-tin monomers can be achieved by vacuum distillation and recrystallization, most are oils with high boiling points. It is also challenging to purify using column chromatography even with triethylamine treated silica gel. Although this method can reduce the decomposition of the tin compounds, it could not eliminate the problem entirely. Secondly, organotin compounds are highly toxic and exposure will result in serious health and environmental problems. As such, extra precautions have to be implemented when handling tin compounds including disposal.

Stille coupling reactions are used for all the polymerizations presented in this thesis. The general setup is as follows. All polymerizations in general are run in a round bottom flask. The bis(trimethylstanne) and dibromide monomers are weighed accurately as the mass of the monomers will directly affect their relative ratio. These monomers are placed in the round bottom flask and anhydrous toluene solvent is added. A condenser is attached onto the flask and all ground glass joints are greased with high vacuum silicon grease from Dow Corning. The flask is purged with Argon for at least 30 mins before the catalyst is added. Then, the whole setup is purged with Argon for another 15 mins, and then heated to reflux with stirring for 48 hours.

3.2.2 Copolymerization

Copolymerization is a process when two or more different types of monomers combine together to form copolymer. On the other hand, if there is only one type of monomer being used, a homopolymer will be created instead. There are a few types of copolymers mainly the (i) alternating copolymers, (ii) random copolymers and (iii) block copolymers Figure 3.2.

Alternate copolymerization is a process where a copolymer comprising of two different types of monomers arranged in an alternate sequence is formed. Random copolymers which are also known as statistical copolymers have a sequence where the different types of monomers follow a statistical rule. They have irregular monomer sequences but the probability of finding a particular type of monomer at a particular point in the polymer chain is always equal to the molar ratio of the monomer in that polymer chain. Block copolymers are formed when two or more blocks of homopolymer are linked together.

Random polymerization is a powerful and useful method in the field of conjugated polymers where different types of monomers can be combined in varying ratios. Their relative ratios can be conveniently adjusted to achieve the desired bandgaps, energy levels and optical properties. In this thesis, we primarily use the alternate copolymerization (in Chapter 6) and random copolymerization (in Chapters 4, 5 and 7) constructions with Stille

cross coupling polymerization to synthesize our polymers. These copolymerization methods will be introduced and discussed here.

To reduce the complexity of the discussion, the positions of the functional groups are assumed not to affect their reactivity. As seen in Figure 3.2, the Stille polymerization of two different types of monomers, $\text{Me}_3\text{Sn}-\text{A}-\text{Br}$ and $\text{Me}_3\text{Sn}-\text{B}-\text{Br}$, each having two different functionalities will generate a totally random copolymer. The probability of finding an **A** or **B** unit in the polymer backbone is equal to the mole ratio of that particular monomer in the polymer.

If difunctional monomers with the same functionality are used in the polymerization, either the alternate or random copolymers will be created depending on the number of species used. In such reactions, it is important to ensure that the sum of the monomers having organotin functional groups must be equivalent to that with bromo groups, regardless of the number of species. A straight-forward polymerization of $\text{Me}_3\text{Sn}-\text{A}-\text{Me}_3\text{Sn}$ with $\text{Br}-\text{B}-\text{Br}$ gives an alternate copolymer with an alternate sequence of $-\text{A}-\text{B}-\text{A}-\text{B}-\text{A}-\text{B}-$. Upon adding a third monomer, $\text{Br}-\text{C}-\text{Br}$, a random copolymer is created where **A** can be bonded to **B** or **C**, but **B** cannot be adjacent to **C**. Such alternate and random polymers are what we have synthesized and presented in this thesis.

Monomers with different functionalities:

Monomers with the same functionalities:

Figure 3.2 Illustration of alternate and random copolymerization via Stille polymerization

3.2.3 Purification of polymeric materials

Purification is an important step in a synthesis process so as to achieve high performance materials. In this thesis where Stille coupling polymerization is the main process used in the synthesis of polymers, impurities may arise from the following sources: (i) tin halides formed during the transmetallation step of the polymerization process (ii) palladium catalyst (iii) low molecular weight oligomers and small molecules.

After the polymerization process, the polymer solution is cooled to room temperature, and excess solvent is removed. Then, the polymer is pipetted into methanol where the amount of methanol used is about the 20 times the polymer solution. In this process, tin halides and other small molecules will remain in the methanol solution and the polymer will precipitate out. The polymer will be separated from the impurities through a filtration step. However, this process cannot remove the impurities completely especially those being trapped in the polymer network. As such, Soxhlet extraction purification process is used.

Generally, a Soxhlet extraction process is a continuous solid-liquid extraction when the desired compound from the bulk material dissolved in the solvent, while the impurity remains insoluble in that solvent. This process is very efficient as it involves the recycling of solvent which resulted in only a small amount of solvent being used to dissolve a large amount of material. However for our case, this process is reversed. The desired compounds which are our pure polymers will remain insoluble, whereas the impurities will be dissolved as seen in Figure 3.3. Therefore, a careful selection for the extraction solvents has to be carefully made. In most cases for polymer purification, the first Soxhlet extraction will start with acetone as the solvent. Acetone is a poor solvent for most polymers but a good solvent for tin halides, catalysts and other small molecules. After which, hexane is used to remove impurities such as low molecular oligomers and polymers. Lastly, chloroform is used for the extraction to dissolve the pure polymer into the solution, and at the same time filtering the polymer through the extraction thimble.

Figure 3.3 General setup of Soxhlet extraction.

3.2.4 Monomer Crystallization

The crystal structure of monomer can provide important information such as the bond length, degree of planarity and the relative orientation of the rings within the monomer. The crystal structure could also confirm the identity of the monomer, which is useful during the synthesis of a novel monomer. There are several methods that could be used to obtain the single crystal needed for X-ray diffraction in this thesis. Typically, one of the more common ways is to leave the monomer solution in a capped NMR tube and let the solvent slowly evaporate over a period of time, usually several weeks. In most cases, the NMR solvent $CDCl_3$ is used. The high surface area to volume ratio of an NMR tube provides a suitable environment for crystallization to occur as compared to most other larger containers. The common solvents used for aromatic compounds are chloroform, dichloromethane, toluene, and benzene. In all cases, the monomer solution is at a nearly saturation point, filtered, and then added to a clean NMR tube to prevent any particulates that may result in non-productive nucleation.

Another method to obtain single crystal of the monomer is by vapor diffusion. In this method, a nearly saturated monomer solution in a good solvent is filtered and placed into a small open vial. This small vial is then placed into a larger vial which contains a solvent that is of high vapor pressure but a poor solvent for the monomer, such as hexane. This larger vial is then sealed to allow the contents of the two vials to reach equilibrium over a period of time. During the process, the poor solvent from the larger vial will diffuse into the small vial, further saturating the monomer solution, inducing crystallization to occur. It is important to ensure that the two solvents are miscible, and sufficient free volume is available in the small vial to allow diffusion to occur without overflowing the monomer solution.

3.3 Fabrication of Window-type Absorption/Transmission Device

Over the years, electrochromic research groups have come out with unique ways in constructing an electrochromic device suitable for their own electrochromic materials. For our group, the window-type absorption/transmission device was constructed using ITO coated glass slides with surface resistivity $15 \text{ } \Omega/\text{sq}$. The configuration of the device is a sandwich structure Glass/ITO|polymer||gel electrolyte||ITO/Glass. The polymer was deposited on the glass via spray casting or spin coating from chlorobenzene. Then, gel electrolyte was applied on the polymer. The gel electrolyte was prepared by dissolving lithium perchlorate (0.512 g) and poly(methyl methacrylate) (MW 120 000 g/mol, 2.8 g) in a solution of propylene carbonate (PC) (6.65 mL) and dry acetonitrile (ACN) (28 mL). To prevent electrical contact between the substrates in the device, parafilm was used as the spacer. Separate pieces of scotch tape were then used to hold the device together. A schematic of the construction of the electrochromic device and the cross-section are illustrated in Figure 3.4.

Figure 3.4 Schematic and cross-section of the electrochromic device.

3.4 Characterizations

3.4.1 Nuclear Magnetic Resonance (NMR)

NMR is an important analytical tool for scientists as they can obtain essential information on the molecular structure and purity of a sample. It is a physical phenomenon where nuclei absorb and re-emit electromagnetic radiation. These nuclei are placed in an external magnetic field and a specified frequency of electromagnetic radiation is applied. Then, a spectrum is obtained through the detection of the absorption signal peaks. By analyzing the positions, intensities and the fine structures of these peaks in the spectrum, we can obtain both qualitative and quantitative information about the chemical species, and hence able to determine the structures of the molecules or the purity of the sample. Some NMR spectrometers in use today are ^1H NMR, ^{13}C NMR, ^{15}N NMR, ^{19}F NMR, ^{31}P NMR and others. In this thesis, we only use ^1H NMR and ^{13}C NMR to analyze the new monomers and polymers synthesized. These NMR spectra are obtained by Avance 400 MHz Bruker NMR spectrometer in CDCl_3 . ^1H NMR allows the researcher to determine the number of different chemical environment the protons are present in, and together with the chemical shifts and the spin-spin coupling between protons, the structure of the chemical species can be determined. Moreover, the integration curve for each type of protons represents the abundance of those protons. Coupled with ^{13}C NMR, the unknown chemical species can be accurately identified.

3.4.2 Gel Permeation Chromatography (GPC)

Gel permeation chromatography also known as size exclusion chromatography works on the theory of separation of materials by size¹⁶. The GPC machine consists of a high performance pump and a column packed with porous cross linked polystyrene which acts as the stationary phase. In our work here, we use tetrahydrofuran (THF) as our mobile phase. The polystyrene beads aids in the separation of the polymer by hydrodynamic volume and not by chemical affinity. As the polymer analyte moves through the column, the larger size or higher molecular weight polymer chains which are unable to fit into the porous beads, will travel through the void spaces outside the beads, and elute out first. On the other hand, the smaller size or lower molecular weight polymer chains will be trapped in the porous beads, and take a longer time to elute out. The time taken to elute out will be compared against a calibration curve from a set of polymer standard. The polymer standards used in our projects are polystyrene. From the calibration curve, we can determine the molecular weight of the polymers from the elution time.

3.4.3 Elemental Analysis (EA)

Elemental analysis is a process where a material sample is analyzed for its elemental composition. It is generally used for the determination of carbon, hydrogen, nitrogen and heteroatoms. The material sample of known mass is combusted in air completely, producing carbon dioxide, water and nitric oxide. From the masses of these combustion products, the composition of the unknown sample can be calculated. Elemental analysis can be either qualitative or quantitative depending on the user needs. Typically, it can be used to determine what types of elements are present or the percentage weights of each type of elements present. In our work in this thesis, we used the elemental analysis to determine the percentage weights of carbon, hydrogen, nitrogen and sulphur in the polymers we synthesized. All the compound samples were dried in an oven for 24 hours prior to testing to remove any water content. Samples were tested using the Flash EA 1112 series.

3.4.4 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is an analytical equipment used to investigate a material's thermal stability and its composition of volatile components¹⁷. It is achieved by monitoring the changes in weight before and after the sample is heated. Typically, there are two methods in using the TGA. It can be used to measure the weight changes as a function of increasing temperature while maintaining constant heating rate; or weight changes as a function of time while maintaining constant temperature. There are typically two kinds of pans available for TGA measurement – aluminum and platinum pans. Aluminum has a melting point of 660 °C but its pans soften at around 550 °C. In order not to affect the TGA results, platinum pans are used for any test that requires heating above 550 °C. The measurements are usually carried out under air or inert (e.g. N₂) atmosphere. In this thesis, the TGA is used to determine the thermal stability of the newly synthesized polymers and we defined the decomposition temperatures of the polymers as the temperatures where the polymers experience a 5 % weight loss during the measurements. The polymers are assessed using a Perkin Elmer TGA-7 thermal analyzer under nitrogen condition. Polymer samples of about 6 – 10 mg were used and heated to 50 °C for equilibrium to a constant mass. Then, the samples were heated from 50 °C to 900 °C at a heating rate of 20 °C/min.

3.4.5 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry is a thermoanalytical tool where it measures the heat differences needed to increase the temperature of the specimen and reference as a function of temperature. These heat flows are usually associated with thermal transitions such as melting, crystallization, and glass transition. The results generated by the DSC can provide both qualitative and quantitative information about physical and chemical changes in the form of endotherms or exotherms, depending on the process or change. The basic principle underlying this DSC analysis is that during the measurement, both the specimen pan and the reference pan are to be maintained at approximately the same temperature. When a sample undergoes a phase transition, depending on whether the process is exothermic or

endothermic, more or less heat will be required to flow to the sample in order to maintain the same temperature as the reference. For example, when a solid sample melts into liquid, the solid sample absorbs heat as it undergoes an endothermic reaction, resulting in more heat needed to flow to the sample to increase the temperature. By observing this heat flow difference between the sample and reference, differential scanning calorimeter is able to measure the amount of heat absorbed or released during such transitions.

3.4.6 UV-vis spectroscopy

UV-vis spectroscopy measures the light absorption through a sample solution or the reflectance of the light off a sample's surface. It is used to determine the absorption, transmission and reflectivity of the sample materials, and for investigating the optical and electronic properties of the materials. Data such as the energy bandgap could be determined by the onset of absorption from the low energy side (Figure 3.5) using the following equation:

$$E_g^{\text{opt}} = 1240 / \lambda_{\text{onset}} \text{ (eV)} \quad \text{Equ 3.1}$$

Figure 3.5 Spectrum showing the onset value which is the intersection of the extrapolations of the linear parts

3.4.7 Cyclic Voltammetry

Cyclic voltammetry is a common electrochemical technique used for studying the electroactivity of conjugated polymers¹⁸. It is usually used to determine the chemical reversibility of an electrochemical reaction, to probe a redox reaction in both forward and reverse directions, and to study the potentials at which oxidation and reduction processes take place. Information such as the onsets of oxidation and reduction (HOMO and LUMO energy levels), half-wave potentials and electrochemical bandgap can be obtained. The oxidation process corresponds to an electron extraction from the HOMO level, and the reduction process corresponds to the electron affinity and is associated with the LUMO level. In a typical cyclic voltammetry setup, the current is measured while the voltage is continuously swept. During the experiment, the initial and final voltage as well as the scan rate will be input, and the results obtained are the current intensities and the voltages at which the current peaks occur. The onset potentials of oxidation and reduction are determined from the intersection of the tangents between the baseline and the signal current as seen in Figure 3.6. These oxidation and reduction onset potentials will provide the HOMO and LUMO energy levels, as well as the electrochemical bandgap of the analyzed sample according to the equations below:

$$E_{\text{HOMO}} = -(E_{\text{onset,ox}} \text{ vs ferrocene}) - 4.8 \quad \text{Equ 3.2}$$

$$E_{\text{LUMO}} = -(E_{\text{onset,red}} \text{ vs ferrocene}) - 4.8 \quad \text{Equ 3.3}$$

$$E_{\text{g}}^{\text{opt}} = E_{\text{LUMO}} - E_{\text{HOMO}} \quad \text{Equ 3.4}$$

Figure 3.6 Cyclic voltammogram showing the onsets of oxidation and reduction potential

In this project, we use the three point electrode method with the setup seen in Figure 3.7, with Ag/AgCl as the reference electrode, polymeric material coated glassy carbon electrode as the working electrode and platinum as the counter electrode. The tested sample solution was drop cast onto the glassy carbon electrode. During the cyclic voltammetry experiment, the potential is swept at a constant rate while the current is being monitored. The Ag/AgCl electrode is usually calibrated against a reversible redox species e.g. Fc (ferrocene)/Fc⁺ couple. A 0.1 M LiClO₄/ACN electrolyte/solvent couple was used and all measurements were recorded at 50 mV/s.

Figure 3.7 Setup of three point electrode cyclic voltammetry

3.4.8 Spectroelectrochemistry

Spectroelectrochemistry is a useful technique that combines both the electrochemical and spectroscopic techniques together. It is used to examine the optical changes that occurred during the oxidation or reduction of an electrochromic film. When progressive electrical bias was applied to the polymer film, the formation of polarons and bipolarons in the polymer chains will affect the changes observed in the film absorption spectra. As such, this technique can be used to probe structural changes and give information about the electronic band modifications during the redox processes. In this thesis, measurements were conducted using a UV-*vis*-NIR spectrophotometer and a potentiostat. The electrochromic device was placed into a UV-*vis*-NIR spectrophotometer and then connected to a potentiostat which controls the output potentials. The polymer was then switched over several potentials, and by monitoring and recording the absorption spectrum of the polymers, the point where the polymer is at its neutral state and the point where the polymer is fully oxidized was determined. With the potentials established, the polymers were scanned in potential steps of about 100 mV increments from the neutral to the fully oxidized state while the absorption was scanned from 1600 nm to 350 nm.

3.4.9 Colorimetry

As there is an increasing trend of using conjugated polymers for color related applications, there is a need to quantify the color of the light being absorbed or emitted from the polymers. Colorimetry is a spectroscopy tool that is able to quantify and describe the perception of the human eye.

It is essential to use a colorimeter to ensure consistency when studying the color changes in the electrochromic devices during electrochemical switching. Colorimetry is basically the measurement of the sensitivities of the three types of cones which overlap across the visible region. As it is not feasible to represent colors using the cone values, there are currently several systems created to identify colors in a more useful way. One of the more popular methods in determining the color is using the CIE $L^*a^*b^*$ 1976 color standards.

This standard is a convenient tool to assess the small color differences between sample materials. This is useful for use in electrochromic devices as the color may only differ slightly and goes undetected with the human eyes. The CIE Lab 1976 system contains three color coordinates, the ' L^* ', ' a^* ' and ' b^* ' values. The L^* coordinate which represents the lightness dimension has a scale from 0 to 100. At $L^* = 0$, it represents the pure black while it is the brightest white at $L^* = 100$. The a^* and b^* define the hue and saturation of the color respectively. The a^* axis represents the red and green colors, where a positive $a^* =$ red, and a negative $a^* =$ green. And for the b^* axis, it represents the yellow and blue axis, where a positive $b^* =$ yellow and a negative $b^* =$ blue (Figure 3.8). In this thesis, colorimetric measurements of the polymer films were done using a Hunterlab ColorQuest XE with a D65/10° illuminant.

Figure 3.8 CIE Lab color space¹⁹

3.4.10 Atomic Force Microscopy (AFM)

The atomic force microscopy was invented by Binnig, Quate and Gerber in 1986 and consisted of a diamond shard attached to a strip of gold foil for contacting the surface directly by utilizing the van der Waals force.²⁰ Since then, it has rapidly become the

imaging method of choice for the studying of nanoscale morphologies in polymer networks. The principles work in the way where a mechanical probe, which is a cantilever equipped with a nanometer-sized tip, is used to 'sense' the matter by detecting the various forces present on the surface of the materials, and a laser beam is reflected from the top of the probe into a photodiode array detector. The AFM can be operated using different modes including contact, non-contact and tapping.

The contact mode of AFM works in a way where the scanning is done with a sharp tip at close proximity with the sample surface. In this contact mode AFM, the magnitude of the deflection of the cantilever is compared with a desired value. Adjustments are made through a feedback signal by applying a voltage to the piezo to increase or decrease the displacement between the tip and the sample so as to keep the cantilever at a constant position. This applied voltage will relate to the measurement of the height features of the sample surface. However, there are problems with the contact mode. As the tip is "dragged" across the surface of the sample during measurement, the sample may be damaged and distorted image may be obtained instead.

For the non-contact mode of AFM, this method is useful in situations where the samples are vulnerable to the tip contact. In this mode, the tip hovers 50 – 150 Å above the sample surface. The topographical images are constructed by scanning the tip above the sample surface and detect the attractive van der Waals forces acting between the tip and the surface. However, these van der Waals forces are much weaker, and the cantilever tip has to be oscillated so that detection methods can be used to detect the small forces between the tip and the sample by measuring the change in amplitude, phase or frequency. When the sample is tested at ambient environment, there is a possibility that a few monolayers of adsorbed fluid may be lying on the surface of the sample. By using the non-contact mode, the oscillating probe could become trapped in the fluid layer and an inaccurate image of the surface morphology may be obtained.

Alternatively, the tapping mode of AFM could be used for the characterization of soft matter such as polymer networks. During the characterization of the surface morphology

of polymer samples under ambient conditions, there are usually two main problems. First is the possibility of damaging the surface when the tip is moved across the surface during the contact mode. Second, the presence of a liquid layer which may hinder the detection of weak forces pose a problem for non-contact mode when testing under ambient environment. As such, the tapping mode is used to bypass these problems. In the tapping mode, the cantilever is driven to oscillate up and down at or near its resonance frequency and this is achieved with a small piezo element in the cantilever holder. The frequency and amplitude of the driving signal are kept constant, leading to a constant amplitude of the cantilever oscillation as long as there is no interaction with the surface. When the cantilever tip is scanned across an increased height on the surface, there will be less room for the cantilever to oscillate and hence, the oscillation amplitude will decrease. Conversely, when the cantilever tip scanned across a depression, more room will be available for it to oscillate, thereby increasing the oscillation amplitude. The feedback signal will then adjust the tip-sample separation to ensure a constant amplitude and force being applied on the sample. The tip vibration causes the cantilever to tap the surface at small intervals creating a high resolution image. Unlike the contact mode, when the tip contacts the surface in the tapping mode, it has sufficient oscillation amplitude to overcome the tip-sample adhesion forces. Also, the surface material is not pulled sideways by shear forces since the applied force is always vertical and this creates minimal damage to the substrate sample. As such, the tapping mode is commonly used for the morphology study of polymer surface, and all the AFM images in this thesis were imaged by the tapping mode.

3.5 Overview of Methodologies

We have discussed the method used for the synthesis of the polymers in this thesis and the characterization tools for the polymers synthesized. These characterization tools are used for evaluation of the electrochromic polymers to determine if they meet the criteria for future potential electrochromic applications. Structural confirmation tools such as the NMR, GPC and EA ensure that the polymers being tested are of the right structures and of high purity. TGA and DSC enable us to study the thermal properties of the polymers. UV-vis spectroscopy, CV, spectroelectrochemistry and colorimetry enables us to investigate

the electrochromic properties of the polymers to determine if they are favorable for electrochromic applications. And lastly, AFM studies the morphology of the polymer film.

References

1. Carsten, B.; He, F.; Son, H. J.; Xu, T.; Yu, L. *Chemical Reviews* **2011**, 111, (3), 1493-1528.
2. Axelsson, J.; Scrivener, E.; Haddleton, D. M.; Derrick, P. J. *Macromolecules* **1996**, 29, (27), 8875-8882.
3. Espinet, P.; Echavarren, A. M. *Angewandte Chemie* **2004**, 43, (36), 4704-34.
4. Stille, J. K. *Angewandte Chemie International Edition in English* **1986**, 25, (6), 508-524.
5. Miyaura, N.; Yamada, K.; Suzuki, A. *Tetrahedron Letters* **1979**, 20, (36), 3437-3440.
6. Corriu, R. J. P.; Masse, J. P. *Journal of the Chemical Society, Chemical Communications* **1972**, (3), 144a.
7. Tamao, K.; Sumitani, K.; Kumada, M. *Journal of the American Chemical Society* **1972**, 94, (12), 4374-4376.
8. King, A. O.; Okukado, N.; Negishi, E.-i. *Journal of the Chemical Society, Chemical Communications* 1977, (19), 683.
9. Kosugi, M.; Shimizu, Y.; Migita, T. *Chemistry Letters* **1977**, 6, (12), 1423-1424.
10. Milstein, D.; Stille, J. K. *Journal of the American Chemical Society* **1978**, 100, (11), 3636-3638.
11. Sofiyev, V.; Navarro, G.; Trauner, D. *Organic Letters* **2008**, 10, (1), 149-52.
12. Amans, D.; Bellosta, V.; Cossy, J. *Organic Letters* **2007**, 9, (23), 4761-4.
13. Song, C.; Swager, T. M. *Macromolecules* 2009, 42, (5), 1472-1475.
14. Czako, L. K. B., *Strategic Applications of Named Reactions in Organic Synthesis, 1st Edition*. Academic Press: 2005.
15. Armin de Meijere, S. B., Martin Oestreich, *Metal-Catalyzed Cross-Coupling Reactions and More*. Wiley-VCH Verlag GmbH & Co. KGaA: 2013.

16. Lathe, G. H.; Ruthven, C. R. *The Biochemical journal* **1955**, 60, (4), xxxiv.
17. Coats, A. W.; Redfern, J. P. *Analyst* **1963**, 88, (1053), 906-924.
18. Heinze, J. *Angewandte Chemie International Edition in English* **1984**, 23, (11), 831-847.
19. Color Space Color Model. Retrieve from <https://www.colorcodehex.com/color-model.html>
20. Binnig, G.; Quate, C. F.; Gerber, C. *Physics Review Letters* **1986**, 56, (9), 930-933.

Chapter 4

Synthesis of ultrahigh electron deficient Pyrrolo[3,4-*d*]pyridazine-5,7-dione (PPD) and its application as electrochromic materials

*A novel pyrrolo[3,4-*d*]pyridazine-5,7-dione (PPD) acceptor was designed and synthesized via an inverse electron demand Diels–Alder reaction. This PPD building block was then incorporated into D-A type conjugated polymers through Stille coupling polymerization to obtain a series of polymers **PPD1** – **PPD3** of varying compositions. The polymers exhibited excellent solubility in common organic solvents and revealed electrochromism, switching between purple and transmissive sky blue states. All the polymers exhibited fast switching with coloration time of about 1 – 2 s and high coloration efficiencies of about 450 cm²C⁻¹ in the NIR region.*

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4.1 Introduction

Electron deficient π -conjugated materials are generally termed as electron acceptors, and are commonly used for the synthesis of functional dyes and organic electronics materials. It is important to include electron acceptors as they are able to fine-tune the energy levels of the frontier orbitals and the absorption of the materials¹. In many cases, the choice of the acceptor is the key to obtain high performance materials^{2,3}. One important attribute of an electron acceptor is its electron deficiency and high electron deficiency is of great importance for many applications, e.g., donor-acceptor dyes with near infrared absorption and emissions^{4,5}, n-type organic field effect transistors^{6,7} and light absorption materials in bulk heterojunction blend solar cells^{8,9}.

Currently, there are a few outstanding and promising electron acceptors which are commonly used in the area of organic electron materials, for example, benzotriazole, diketopyrrolopyrrole, benzothiadiazole. These electron-deficient building blocks are usually combined with electron-rich units to form a D-A type conjugated system which is able to achieve high performance materials. As such, this motivates us to create new ultra-highly electron deficient acceptors so as to achieve high performance polymers in the electrochromic field.

In this chapter, a newly found methodology to synthesize a novel electron acceptor with ultra-high electron deficiency was presented. The key synthesis relies on an inverse electron demand Diels-Alder (iEDDA) reaction on tetrazine. The iEDDA reaction has been studied intensively, in both theoretical^{10,11} and experimental^{12,13} on tetrazine, and works generally well for electron rich and strained dienophiles. The reaction has also been claimed to be a versatile “click” approach for bio-related applications. However, using the iEDDA reaction with electron deficient dienophiles has not been widely reported and such approach is believed to be very challenging. As such, we challenged the synthesis of 6-alkyl-pyrrolo[3,4-*d*]pyridazine-5,7-dione (PPD) *via* an iEDDA reaction of functionalized tetrazine with electron deficient 1-alkyl-*1H*-pyrrole-2,5-dione moiety. There are two great properties of the new acceptor which need to be highlighted. First, we are able to obtain an

ultra-high electron deficiency of the electron acceptor. We compared the lowest unoccupied molecular orbital (LUMO) energy level of the PPD unit with some of those widely reported acceptors (Figure 4.1) used in organic electronic materials. Out of the ten relevant acceptors examined, only bisbenzothiadiazole has a LUMO energy level lower than the PPD unit. Next, the structure of the PPD is designed to undergo convenient side-chain engineering and easy incorporation into polymeric materials. Besides these, we have also observed an interesting phenomenon where only the inverse electron demand Diels-Alder pathway was observed on thiophene and furan decorated tetrazine, making the reaction selective. Thus, time-dependent density functional theory (TD-DFT) calculation was carried out to better comprehend this selective process. Lastly, we test the feasibility of using the new PPD unit as an electron acceptor in electrochromic polymers. A new series of high performance electrochromic polymers using the newly developed PPD monomer and thiophene-based electron donors was synthesized and its properties investigated.

Figure 4.1 The LUMO energy levels (calculated) of a series of relevant acceptor monomers. From left to right: benzotriazole, 5-alkyl-thieno[3,4-c]pyrrole-4,6-dione, diketopyrrolo-pyrrole (DPP), 2-alkyl-isoindole-1,3-dione, benzo[1,2,5]thiadiazole (BT), iso-indigo, 5,6-difluoro-benzo[1,2,5]thiadiazole, [1,2,5]thiadiazolo[3,4-c]pyridine, tetrazine, 6-alkyl-pyrrolo[3,4-d]pyridazine-5,7-dione (PPD), bisbenzothiadiazole (BBT).

4.2 Experimental Methods

4.2.1 Synthesis

All reagents and starting materials were purchased from commercial sources and used without further purification.

Compounds **4** and **6** are prepared according to the reported literature¹⁴.

3,6-Di(furan-2-yl)-1,2,4,5-tetrazine (3): To a dry round bottom flask was added furan-2-acarbonitrile (3 g, 0.0323 mol), sulfur powder (0.72 g, 0.022 mol), hydrazine monohydrate (50-60%, 3.3 g) and ethanol (15 mL). The mixture was refluxed at 80 °C for 2 h and cooled to room temperature. The brown precipitate was collected via suction filtration and thoroughly dried under vacuum. It was used directly for the next step without further purification.

The brown precipitate was added into a round bottom flask followed by isoamyl nitrite (35 mL) and chloroform (150 mL). The mixture was stirred at room temperature overnight. The solvent was then removed by rotary evaporation and the collected residue was subject to silica gel column chromatography (Hex:CHCl₃=1:1 then CHCl₃ as eluent) to afford the target molecule as a red powder. (1.5g, yield = 43%). ¹H NMR (400 MHz, CDCl₃): δ ppm = 7.81 (m, 2H), 7.68-7.67 (m, 2H), 6.72-6.71 (m, 2H). ¹³C NMR (100MHz, CDCl₃): δ ppm = 157.99, 147.79, 147.64, 117.06, 113.43. HR-EI-MS: *m/z* = 214.0490, calculated 214.0491, error : -0.51 ppm.

3,6-Bis(5-bromofuran-2-yl)-1,2,4,5-tetrazine (5): To a dry round bottom flask was added 3,6-di(furan-2-yl)-1,2,4,5-tetrazine (2 g, 9.35mmol), NBS (3 equiv. 28.05 mmol, 5 g) and anhydrous DMF (20 mL). The mixture was heated to 90 °C overnight with light shield. After cooling to room temperature, a lot of insoluble precipitate was observed. The DMF solution was poured into methanol (100 mL). The purple precipitate was collected via suction filtration and washed thoroughly with methanol and hexane. The target molecule has very bad solubility in chloroform and hence the collected purple precipitate was used directly for the next step without further purification. ¹H NMR (400 MHz, CDCl₃): δ ppm

= 7.61-7.60 (d, 2H, $J = 3.6$ Hz), 6.66-6.65 (d, 2H, $J = 3.6$ Hz). ^{13}C NMR cannot be recorded due to poor solubility. HR-EI-MS: $m/z = 371.8677$, calculated exact mass: 371.8681, error: -1.05 ppm.

1,4-Bis(5-bromofuran-2-yl)-6-hexyl-5H-pyrrolo[3,4-*d*]pyridazine-5,7(6H)-dione (7):

To a dry round bottom flask was added 3,6-bis(5-bromofuran-2-yl)-1,2,4,5-tetrazine (300 mg, 0.81 mmol), 1-(2-hexyl)-1H-pyrrole-2,5-dione (146 mg, 0.81 mmol) and diphenyl ether (10 mL). The mixture was purged with argon for 15 min and then heated to 160 °C for 16 h. After cooling to room temperature, the mixture was directly subject to silica gel column chromatography. Hexane was used first to flush away the diphenyl ether. The target compound was then collected as yellow powder using mixture solvent (Hex:CHCl₃ = 1:1) then CHCl₃ as eluent (310 mg, 73%). ^1H NMR (400 MHz, CDCl₃): δ ppm = 8.03- 8.02 (d, $J = 3.6$ Hz, 2H), 6.62-6.61 (d, $J = 4$ Hz, 2H), 3.77-3.73 (t, $J = 7.6$ Hz, 2H), 1.70-1.65 (m, 2H), 1.32 (m, 6H), 0.89-0.86 (t, $J = 6.4$ Hz, 3H). ^{13}C NMR (100MHz, CDCl₃): δ ppm = 167.72, 148.30, 139.78, 134.38, 132.09, 122.47, 121.47, 43.81, 37.37, 32.31, 32.27, 31.85, 30.31, 30.02, 29.97, 29.93, 29.75, 29.68, 26.62, 23.08, 14.52. HR-EI-MS: $m/z = 520.9586$, calculated exact mass: 520.9580, error: 1.04 ppm.

1,4-Bis(5-bromothiophen-2-yl)-6-hexyl-5H-pyrrolo[3,4-*d*]pyridazine-5,7(6H)-dione

(8): To a dry round bottom flask was added 3,6-bis(5-bromothiophen-2-yl)-1,2,4,5-tetrazine (300 mg, 0.743 mmol), 1-(2-hexyl)-1H-pyrrole-2,5-dione (135 mg, 0.743 mmol) and diphenyl ether (10 mL). The mixture was purged with argon for 15 min and then heated to 160 °C for 16 h. After cooling to room temperature, the mixture was directly subject to silica gel column chromatography. Hexane was used first to flush away the diphenyl ether. The target compound was then collected as yellow powder using mixture solvent (Hex:CHCl₃ = 1:1) then CHCl₃ as eluent (230 mg, 56%). ^1H NMR (400 MHz, CDCl₃): δ ppm = 8.62-8.61 (d, $J = 4$ Hz, 2H), 7.20-7.18 (d, $J = 3.6$ Hz, 2H), 3.79-3.76 (t, $J = 7.6$ Hz, 2H), 1.72-1.67 (m, 2H), 1.33 (m, 6H), 0.91-0.87 (t, $J = 6.4$ Hz, 3H). ^{13}C NMR (100MHz, CDCl₃): δ ppm = 167.47, 148.32, 139.74, 134.33, 132.09, 122.57, 121.47, 39.64, 31.66, 28.58, 26.92, 22.87, 14.40. HR-EI-MS: $m/z = 552.9136$, calculated exact mass: 552.9123, error: 2.28 ppm.

1,4-Bis(5-bromofuran-2-yl)-6-(2-octyldodecyl)-5H-pyrrolo[3,4-d]pyridazine-5,7(6H)-dione (9): To a dry round bottom flask was added 3,6-bis(5-bromofuran-2-yl)-1,2,4,5-tetrazine (1.48 g, 4 mmol), 1-(2-octyldodecyl)-1H-pyrrole-2,5-dione (4 mmol, 1.51 g) and diphenyl ether (15 mL). The mixture was degassed by purging with argon and then heated to 160 °C for 16h. After cooling to room temperature, the mixture was directly subject to silica gel column chromatography. Hexane was used first to flush away the diphenyl ether. The target compound was then collected as yellow powder using mixture solvent (Hex:CHCl₃ =1:1) then CHCl₃ as eluent (1.86 g, 65%). ¹H NMR (400 MHz, CDCl₃): δ ppm = 8.06 (d, 2H, *J* = 3.6 Hz), 6.64-6.63 (d, 2H, *J* = 3.6 Hz), 3.66-3.64 (d, 2H, *J* = 7.6 Hz), 1.57 (m, 1H), 1.24 (m, 32H), 0.89-0.85 (m, 6H). ¹³C NMR (100MHz, CDCl₃): δ ppm = 166.89, 149.69, 143.31, 128.45, 122.25, 121.37, 115.17, 43.77, 37.29, 32.30, 31.81, 30.30, 30.01, 29.73, 29.67, 26.59, 23.07, 14.51. HR-EI-MS: *m/z* = 719.1476, calculated exact mass: 719.1756, error: -1.41 ppm.

1,4-Bis(5-bromothiophen-2-yl)-6-(2-octyldodecyl)-5H-pyrrolo[3,4-d]pyridazine-5,7(6H)-dione (10): To a dry round bottom flask was added 3,6-bis(5-bromothiophen-2-yl)-1,2,4,5-tetrazine (3 g, 7.43 mmol), 1-(2-octyldodecyl)-1H-pyrrole-2,5-dione (2.8 g, 7.43 mmol) and diphenyl ether (20 mL). The mixture was purged with argon for 15 min and then heated to 160 °C for 16h. After cooling to room temperature, the mixture was directly subject to silica gel column chromatography. Hexane was used first to flush away the diphenyl ether. The target compound was then collected as yellow powder using mixture solvent (Hex:CHCl₃ =1:1) then CHCl₃ as eluent (3.42g, 62%). ¹H NMR (400 MHz, CDCl₃): δ ppm = 8.63-8.62 (d, *J* = 4 Hz, 2H), 7.19-7.18 (d, *J* = 4 Hz, 2H), 3.67-3.65 (d, *J* = 7.2 Hz, 2H), 1.90 (m, 1H), 1.25-1.24 (m, 32H), 0.89-0.85 (m, 6H). ¹³C NMR (100MHz, CDCl₃): δ ppm = 167.72, 148.30, 139.78, 134.38, 132.09, 122.47, 121.47, 43.81, 37.37, 32.31, 32.27, 31.85, 30.31, 30.02, 29.97, 29.93, 29.75, 29.68, 26.62, 23.08, 14.52. HR-EI-MS: *m/z* = 750.1408, calculated exact mass: 750.1393, error: -2.1 ppm.

General procedure for Stille cross-coupling polymerization.

1,4-bis(5-bromothiophen-2-yl)-6-(2-octyldodecyl)-5H-pyrrolo[3,4-d]pyridazine-5,7(6H)-dione, 6,8-dibromo-3,3-bis((dodecyloxy)methyl)-3,4-dihydro-2H-thieno[3,4-

b][1,4]dioxepine (200 mg, 0.281 mmol), and 2,5-bis(trimethylstannyl)thiophene (128 mg, 0.312 mmol) were dissolved in 12 mL of toluene. The mixture was stirred and purged with Argon for about 15 min, and then Pd(PPh₃)₄ (18.1 mg, 0.016 mmol) was added. The flask was purged with Argon for another 15 min before the mixture was heated to 110 °C for 48 hrs. Excess solvent was removed under reduced pressure and the polymer was precipitated with methanol. The suspension was filtered to give the crude product, which was then purified by Soxhlet extraction with acetone and chloroform. The chloroform fraction was evaporated to dryness to afford purple-red solid.

Random polymer PPD1. Yield 68%. ¹H NMR (main signals) (CDCl₃): δ 7.16-7.07 (br, s), 4.22 (br, s), 3.63-3.43 (br, m), 1.25 (br, s), 0.87 (br, s). GPC: PMMA in THF as standard: M_n = 16.9 k, M_w = 21.8 k, PDI = 1.30.

Random polymer PPD2. Yield 70%. ¹H NMR (main signals) (CDCl₃): δ 7.06-7.00 (br, s), 4.16 (br, s), 3.62-3.42 (br, m), 1.25 (br, s), 0.88 (br, s). GPC: PMMA in THF as standard: M_n = 13.5 k, M_w = 17.2 k, PDI = 1.28.

Random polymer PPD3. Yield 50%. ¹H NMR (main signals) (CDCl₃): δ 7.17-7.07 (br, s), 4.22 (br, s), 3.62-3.45 (br, m), 1.25 (br, s), 0.88 (br, s). GPC: PMMA in THF as standard: M_n = 18.8 k, M_w = 28.2 k, PDI = 1.50.

4.2.2 Chemical Analysis

¹H and ¹³C NMR spectra were recorded using Advance 400 MHz Bruker spectrometer in CDCl₃. All chemical shifts are quoted in ppm, relative to tetramethylsilane, using the residual solvent peak as a reference standard. Column chromatography was performed on silica gel 60 (Merck 40-60 nm, 230-400 mesh). Polymer molecular weights were determined using an Alliance Waters model 2690 Gel Permeation Chromatography system calibrated with polystyrene as the standard and THF as the eluent. Polymer of 5mg/ml concentration was prepared and filtered prior to sample injection. HR-EI-MS was carried out on Finnigan TSQ 7000 triple stage quadrupole mass spectrometer. HR-APCI-MS was

carried out on AmaZon X with Dionex Ultimate 3000 RSLC system and Kd Science Syringe pump infusion system. All UV-vis/UV-vis-NIR absorption spectra were recorded using a Shimadzu UV-3600 UV-vis-NIR spectrophotometer. Cyclic voltammetry and chronoamperometry experiments were carried out using an Autolab PGSTAT128N potentiostat. Colorimetry data was acquired using Hunterlab ColorQuest XE and the color of each polymer was assessed by utilizing the CIE 1976 L*a*b* color space with a D65/10° illuminant.

4.2.3 Cyclic Voltammetry and Spectroelectrochemistry

For cyclic voltammetry, measurements were done in a MBraun LABmaster 130 glove box. The solutions of **PPD1** – **PPD3** in chlorobenzene (10 mg/mL) were drop cast onto glassy carbon electrode. A three-electrode cell configuration with polymer-coated glassy carbon, Pt wire and Ag wire as the working, counter and pseudo-reference electrodes respectively was employed. A 0.1 M LiClO₄/ACN electrolyte/solvent couple was used and all measurements were recorded at 50 mV/s. The pseudo-reference electrode was calibrated against the ferrocene/ferrocenium redox couple. For spectroelectrochemical studies, the polymers were analyzed in their device forms.

4.2.4 Device Fabrication

Electrochromic layers of **PPD1** – **PPD3** on ITO/glass were deposited by spin-coating. The gel electrolyte was prepared by mixing 0.512 g of lithium perchlorate and 2.8 g of poly(methyl methacrylate) of molecular weight 120 000 g/mol in 6.65 ml of propylene carbonate (PC) and 28 mL of dry acetonitrile (ACN). A window-type absorption/transmission electrochromic device (ECD) was constructed, with the sandwich structure glass/ITO|polymer||electrolyte||ITO/glass. Parafilm was used as the spacer to prevent electrical contact between the substrates.

4.3 Results for PPD monomers

4.3.1 Molecular design of PPD monomers

Scheme 4.1 Synthesis of imide-fused pyridazines **7-10**. Reaction conditions: i) hydrazine, sulfur, Ethanol; then isoamyl nitrite; ii) NBS, DMF, 100 °C; iii) 1-alkyl-1*H*-pyrrole-2,5-dione, diphenyl ether, 160 °C. The single crystal structures of compounds **7** and **8** are shown with hydrogen atoms omitted for clarity.

The synthesis of the new building blocks is shown in Scheme 4.1. Starting from the commercially available 2-cyano furan **1** and 2-cyano thiophene **2**, the tetrazine heterocycle was synthesized using literature methods¹⁵⁻¹⁷ and intermediates **3** and **4** were obtained in 43% and 52% yields, respectively. Then, bromination of **3** and **4** with NBS in hot DMF gave the dibrominated products **5** and **6** in good yields.

The approach to react the tetrazine derivative **6** with the alkylated imide via Diels-Alder reaction is deemed to be challenging. Generally, tetrazines with electron-donating substituents are much less reactive towards iEDDA reaction as compared with those having electron-withdrawing groups. Moreover, electron-deficient dienophiles are less likely to undergo Diels-Alder reaction with tetrazine^{12, 13, 18, 19}. As such, we have to test the Diels-Alder reaction between tetrazine derivative **6** and alkylated imide under various conditions.

To test the feasibility of our reaction, we tried reacting the tetrazine derivative **6** with 1-hexyl-1*H*-pyrrole-2,5-dione in refluxing chloroform (60 °C), dioxane (100 °C) and toluene (110 °C) for 16 h, but no Diels-Alder product was formed. Then, we further increased the reaction temperature to 160 °C in diphenyl ether, and iEDDA reaction took place successfully with 50 – 70% yield²⁰ after 16 h. This shows that the reaction temperature was the crucial parameter to pushing the reaction forward and a high reaction temperature of 160 °C was necessary to overcome the energy barrier for the reaction to proceed.

4.3.2 Molecular Characterizations

The chemical structures of the new building blocks are verified by NMR spectra, HR-EI-MS and single crystal XRD.

Figure 4.2 ^1H NMR spectrum of **8** in CDCl_3 .

Using the ^1H NMR of **8** as an example (Figure 4.2), the peaks at the two aromatic regions (7.2 – 8.6 ppm) belong to the H atoms on the thiophene moiety. The signal at around 3.7 ppm corresponds to the N-CH₂ of the imide and the signal at around 0.8 – 1.7 ppm corresponds to the hexyl chain on the imide. The protons integrated are corresponding well to the molecular structure of **8**.

Figure 4.3 ^{13}C NMR spectrum of **8** in CDCl_3 .

The ^{13}C NMR spectrum of **8** was collected in CDCl_3 . As seen from Figure 4.3, the carbon atoms located at the range of 121.5 – 167.5 ppm belongs to the six aromatic carbons. As the molecule is symmetrical, only six aromatic carbon peaks were observed. As for the peaks in the region of 14.4 to 39.6 ppm, these belong to the straight hexyl chain attached to the N atom.

Figure 4.4 HR-EI-MS of compound **8**.

The HR-EI-MS result shown in Figure 4.4 further confirmed the successful synthesis of the monomers. The chemical formula of **8** is C₂₀H₁₇Br₂N₃O₂S₂ and the calculated m/z value for **8** is 552.9123. The actual m/z value of that found in the spectrum is 552.9136, which is well consistent with the calculated result.

The structures of **7** and **8** were also determined via the single crystal XRD as seen in Scheme 4.1.

4.3.3 Mechanism Discussion

Interestingly, even though both the thiophene and furan are known to undergo Diels-Alder reaction, we did not observe the generation of D-A products on the furan and thiophene units when intermediates **5** and **6** were tested under various temperatures (25 – 160 °C). Thus, it is possible that this route of Diels-Alder reaction is region-selective on tetrazine rather than on thiophene and furan. To better elucidate the reactivity of D-A reaction, we

carried out time-dependent density functional theory calculations at the B3LYP/6-31G level. The inverse electron demand D-A reaction (pathway #1) involves the interaction between the $\text{HOMO}_{\text{dienophile}}$ and $\text{LUMO}_{\text{diene}}$ while the normal D-A reaction involves the interaction between the $\text{HOMO}_{\text{diene}}$ and $\text{LUMO}_{\text{dienophile}}$ (pathway #2)²¹. As the distribution and the energy level of the frontier orbitals are essential for the occurrence of Diels-Alder reaction, the HOMO/LUMO profiles and their energy levels of the reacting species are calculated and shown in Figure 4.5. For compounds **5** and **6**, the HOMO is evenly distributed over the π -system whereas the LUMO is located on the tetrazine unit. Compounds **5** and **6** had similar HOMO and LUMO energy levels. The active double bond of model compound **11** was involved in both the HOMO and LUMO. Given the calculated frontier orbitals, both pathways #1 and #2 are possible to occur due to the matching phases and similar energy differences of relevant frontier orbitals.

Energy level (eV)

Figure 4.5 HOMO/LUMO energy profiles and energies (in eV) for compounds **5**, **6** and **11**. HOMO/LUMO interaction is shown as dotted lines and the observed pathway is highlighted in red.

To have a better grasp on the D-A reaction, the activation energy ($\Delta G^\ddagger$) for both the reaction pathways was calculated and the results are summarized in Figure 4.6. For pathway #1 which is the iEDDA reaction between tetrazine moiety and dienophiles, it is believed to undergo a two-step mechanism, that is, first, the formation of the bicyclic intermediates (e.g. **12** and **14**) and then the formation of the final pyridazine product (**7** - **10**) after a loss of nitrogen gas molecule^{10, 11}. As recent theoretical investigations have shown that the second step proceeds with a very low or almost non-existent energy barrier²², therefore in our study, we will focus our attention on the first step. For compound **6**, the activation energy barrier ($\Delta G^\ddagger$) of iEDDA reaction on the tetrazine (pathway #1) is 28.14 kcal/mol whereas the activation energy barrier of the normal Diels-Alder reaction on thiophene (pathway #2) is 31.46 kcal/mol. The higher energy barrier ($\Delta G^\ddagger$) of pathway #2 may justify for the observed selectivity for pathway #1. However, for the furan-attached tetrazine monomer **5**, the activation energy barrier for pathway #1 on the tetrazine is 26.66 kcal/mol while that of pathway #2 on the furan unit is 24.25 kcal/mol. The activation energy of the normal Diels-Alder reaction on the furan unit of **5** is much higher than that of alkyl-substituted furan which has activation energy in the range of 9.6 - 10 kcal/mol^{23, 24} which could be due to the attachment of electron withdrawing moieties on the furan unit. From here, pathway #2 is clearly kinetically favored over pathway #1. However, during our experiments on the different reaction conditions, we did not observe any substantial amount of D-A products on the furan unit. One reason could be the reversibility of the D-A reaction between furan and imide²⁵, as the dynamic covalent nature of cyclo-adduct between furan and imide (**15**) could lead to dissociation to occur at temperature > 90 °C. We also postulate that the iEDDA reaction between furan and tetrazine took place concurrently at 160 °C. At this reaction temperature, the dissociation of cyclo-adduct **15** is concurrently happening with the association process and the inverse electron demand D-A route gradually consumes the starting material in an irreversible way, thereby resulting in a regioselective reaction. Hence, any formed **15** were gradually consumed with only the inverse electron demand D-A product obtained. This observed selectivity could be rationalized in the proposed mechanism shown in Figure 4.7.

Figure 4.6 Free energy profiles of normal Diels-Alder reaction and inverse electron demand Diels-Alder reaction pathways to attach **11** to compounds **5** and **6**. Gibbs free energies are shown in kcal/mol.

Figure 4.7 Proposed mechanism for the selective inverse electron demand Diels-Alder reaction.

4.3.4 Electrochemistry

The frontier orbital energy levels of monomers **9** and **10** were investigated by cyclic voltammetry. The observed LUMO energy levels for compounds **9** and **10** are -3.66 and -3.67 eV, respectively as seen in Figure 4.8, hence confirming the strong electron deficiency of the PPD unit. As the pyridazine imide monomers (**7** - **10**) are designed for convenient side chain engineering and easy integration into conjugated functional polymers, such monomers would be of great usefulness as versatile building blocks for polymeric organic electronics materials.

Figure 4.8 Cyclic voltammetry of compounds **9** and **10** and their LUMO energy levels.

4.4 Results for PPD-based Polymers

4.4.1 Polymers Design

In this chapter, we also demonstrated the preparation of high performance electrochromic (EC) materials with the pyridazine-imide unit embedded. The random polymers **PPD1** – **PPD3**²⁰ were prepared *via* Stille coupling polymerization in the presence of $\text{Pd}(\text{PPh}_3)_4$ catalyst according to Scheme 2. To investigate the effect of the newly synthesized acceptor **10** on both the optical and electrochromic properties, different ratios of acceptor **10** were incorporated into the polymer backbone during the synthesis of the polymers. The obtained crude copolymers were precipitated in cold methanol and filtered. Then, it was purified by Soxhlet extraction with acetone, followed by hexane, and then chloroform. The resultant polymers **PPD1** – **PPD3** were obtained in medium yields and highly soluble in common

organic solvents such as chloroform, toluene, dichloromethane and tetrahydrofuran due to the long alkyl chains on both the PPD and thiophene moiety.

Scheme 2. Synthetic route of polymers **PPD1 - PPD3**.

4.4.2 Polymers Characterizations

Figure 4.9 ^1H NMR spectrum of polymer **PPD1**.

The polymers **PPD1** – **PPD3** were structurally characterized by ^1H NMR. Using the ^1H NMR spectrum of the polymer **PPD1** as an example (Figure 4.9), a signal was observed at around 4.2 ppm which corresponded to the protons of N-CH₂ of the PPD unit and the pair of O-CH₂ from the two long alkoxy groups of the ProDOT moiety. As for the peak at about 3.4 – 3.6 ppm, it belongs to the protons from the other 2 pairs of O-CH₂ from the seven-membered ring ProDOT moiety. From the integration of these two characteristics peaks, the polymer compositions were estimated and the results were found to be consistent with the reaction feed compositions. This shows that the random polymerization has taken place successfully.

The molecular weights of **PPD1** – **PPD3** as determined by gel permeation chromatography (GPC) against poly(methylmethacrylate) as standards range from 13 500 to 18 800 g·mol⁻¹ with reasonable polydispersity indexes of 1.28 – 1.50 (Table 4.1). The polymers' decomposition temperature (T_d), which was taken as the temperature at 5 % weight loss, is in the range of 352 – 381 °C in nitrogen, indicating that the polymers possessed high thermal stability (Table 4.1).

Table 4.1 Compositions, synthetic yields, molecular weights, polydispersity indexes and thermal decomposition temperatures of polymers **PPD1** – **PPD3**.

Polymers	Feed ratio (x:y)	Actual ratio (x:y)	Yields (%)	M _n (g/mol)	M _w (g/mol)	PDI	T _d (°C)
PPD1	0.1:0.9	0.09:0.91	68	16 900	21 800	1.30	381
PPD2	0.3:0.7	0.31:0.69	70	13 500	17 200	1.28	377
PPD3	0.5:0.5	0.49:0.51	50	18 800	28 200	1.50	352

M_n: the number average molecular weight. M_w: the weight average molecular weight. PDI: polydispersity index.

4.4.3 UV-vis absorption spectroscopy

The UV-vis absorption characteristics of **PPD1** – **PPD3** were investigated in chlorobenzene solutions and in films (Figure 4.10). Related data are summarized in Table 4.2. All polymers absorbed strongly in the visible range with strong absorption band (λ_{max}) at around 530 nm and a purple color is exhibited at the neutral state. However, the absorption onset of the polymers' thin films displayed spectral broadening and bathochromic shifts as compared to those in solution states. This suggests the presence of aggregation of the polymer main chains in the solid state which reduces the energy difference between the LUMO and HOMO energy levels. As the amount of electron acceptors increased from **PPD1** to **PPD3**, the absorption onset of the polymer thin films increased from 699 to 732 nm. This red-shifting phenomenon could be attributed to the effect of the donor-acceptor interactions between the acceptor PPD and the neighboring thiophene donor units. The optical bandgap was calculated from the absorption onset of polymers' thin films, where it showed a gradual reduction from 1.77 eV for **PPD1** to 1.69 eV for **PPD3** with increasing percentage of the electron acceptor unit in the polymers (Table 4.2).

Figure 4.10 UV-visible absorption spectra of **PPD1**, **PPD2** and **PPD3** solutions (in chlorobenzene) and thin films.

4.4.4 Electrochemistry

Figure 4.11 shows the result of the cyclic voltammograms of polymers **PPD1** – **PPD3** and their CV data are summarized in Table 4.2. It was performed in a three-electrode cell configuration, with platinum wire as counter electrode, silver wire as reference electrode, glassy carbon coated with polymer as working electrode and 0.1 M LiClO₄/ACN as electrolyte. **PPD1** – **PPD3** showed quasi reversible oxidation upon p-doping. The energy levels of the HOMO and LUMO of the polymers **PPD1** – **PPD3** were estimated from the oxidation onset of the first peak. From Table 4.2, it was observed that as the molar ratio of electron acceptors in the polymer backbone increases, that is from **PPD1** – **PPD3**, a gradual deepening of the HOMO energy level from -4.92 to -5.00 eV was observed.

Figure 4.11 Cyclic voltammograms of **PPD1** – **PPD3**. Calibration was done vs. ferrocene/ferrocenium couple. The ferrocene/ferrocenium redox couple is taken to occur at -4.8 eV relative to the vacuum level.

Table 4.2 Optical and Electrochemical Properties of Polymers.

	$\lambda_{\text{max, solution}}$ (nm)	$\lambda_{\text{onset, solution}}$ (nm)	$\lambda_{\text{max, film}}$ (nm)	$\lambda_{\text{onset, film}}$ (nm)	Optical bandgap (eV)*	HOMO (eV)	LUMO (eV)*
PPD1	533	660	544	699	1.77	-4.92	-3.15
PPD2	528	690	530	724	1.71	-4.95	-3.24
PPD3	532	713	530	732	1.69	-5.00	-3.31

Optical bandgap is calculated based on the formula: $E_g(\text{Op}) = 1240 / \lambda_{\text{onset, film}}$. LUMO is calculated based on the formula: $\text{LUMO} = \text{HOMO} + E_g(\text{Op})$.

4.4.5 Spectroelectrochemistry

The spectro-electrochemical study was carried out on the sandwich devices of polymers **PPD1** – **PPD3** and the results are shown in Figure 4.12. When the applied potential was increased from 0.0 V to about 1.8 V, it was observed that there is a suppression of the absorption peak in the visible region. Simultaneously, new absorption bands were formed in the near infrared (NIR) region around 800 nm and 1400 nm, which suggests the formation of polarons and bipolarons. As a result, there is a color change from purple at the neutral state, to cyan hue in the oxidized state. For polymer **PPD1**, when 1.3 V or above is applied to it, the intensity of the bipolaron band increased but the polaron bands were suppressed, showing two clear isosbestic points at about 640 and 840 nm. This in turn established the presence of interconverting neutral, polaronic and bipolaronic species. However, for **PPD2** and **PPD3**, there is only one isosbestic point that was observed at about 640 nm despite the increased in bias. A possible reason for such phenomenon could be due to the saturation of the polarons, where they are unable to convert into bipolarons. In the fully oxidized state, it was also noted that there is an increasing residue absorption in the visible region with increasing electron acceptors in the polymer backbone, resulting in a decrease in optical contrast in **PPD2** and **PPD3**.

In their neutral states, **PPD1** – **PPD3** showed purple color as reflected by the positive a^* values. When oxidized, the L^* value increased while the a^* value dropped, giving the polymers transmissive blue color as seen in Figure 4.13.

Figure 4.12 UV-*vis*-NIR absorptions of (a) **PPD1**, (b) **PPD2**, (c) **PPD3** devices at various applied potentials from 0.0 V to 1.8 V.

Figure 4.13 Color states of **PPD1** – **PPD3** at neutral and oxidized states.

4.4.6 Electrochromic Performance

The electrochromic properties of polymers **PPD1** – **PPD3** were evaluated using the fabricated absorption/transmission type devices. The data for optical contrasts, switching times, and coloration efficiencies were summarized in Table 4.3. The optical contrast is the difference between the transmittance of the oxidized and reduced states in a full switch. The switching time is defined as the time needed to reach 95 % of the full switch, and the coloration efficiencies (CE) are calculated based on 95 % of the full switches. The switching properties of the polymers **PPD1** – **PPD3** were investigated by chronamperometry where the polymers were switched between 1.5 and -1.5 V and the results are illustrated in Figure 4.14 and summarized in Table 4.3. The optical contrast of **PPD1** is the highest among the three polymers, followed by **PPD2** and then **PPD3**. From our observation, an increase in electron acceptors in the polymer backbone increases the residual absorption in the visible region as seen from the spectroelectrochemical spectra above. This could be due to the increased amount of electron acceptors moiety reduces the polymers' susceptibility towards oxidation. All the three polymers exhibited fast switching with coloration time of about 1 – 2 s and bleaching time of about 7 – 8 s in the visible region. From here, we can see that the amount of electron acceptors in the polymer

backbone does not significantly affect the switching time of the polymers. **PPD1** showed the highest coloration efficiency of 436 cm²/C and 457 cm²/C in the visible and NIR region respectively.

Table 4.3 Performance of Electrochromic Devices.

	Visible				NIR			
	Contrast (%)	Bleaching Time (s)	Coloration Time (s)	CE (cm ² /C)	Contrast (%)	Bleaching Time (s)	Coloration Time (s)	CE (cm ² /C)
PPD1	34.1	7.62	2.38	436	54.2	2.24	7.12	457
PPD2	12.4	7.47	0.87	282	47.2	0.85	7.35	453
PPD3	10.9	8.30	0.92	331	36.2	0.66	8.06	454

Figure 4.14 Square-wave potential-step absorptiometry of (a) **PPD1**, (b) **PPD2**, (c) **PPD3** devices in the visible and NIR regions.

4.5 Conclusions

In conclusion, a novel ultrahigh electron deficient PPD building block has been successfully synthesized *via* a regio-selective inverse electron demand Diels-Alder reaction (iEDDA). Different types of side chains can be easily attached on the PPD monomer. Investigation was done on the region-selective Diels-Alder reaction by TD-DFT and it was strongly believed that it is the high activation energy of the thiophene-imide interaction and the dynamic covalent nature of the furan-imide cyclo-adduct that promotes the observed selectivity. A novel series of Donor-Acceptor polymers using the newly synthesized PPD monomers was prepared by palladium-catalyzed cross coupling reactions to be used as electrochromic materials. The polymers possess fast switching speed, high optical contrast and high coloration efficiency which are the important properties of high performance electrochromic materials.

References

1. Takimiya, K.; Osaka, I.; Nakano, M. *Chemistry of Materials* **2014**, 26, (1), 587-593.
2. Zhang, Y.; Zou, J.; Cheuh, C.-C.; Yip, H.-L.; Jen, A. K. Y. *Macromolecules* **2012**, 45, (13), 5427-5435.
3. Stuart, A. C.; Tumbleston, J. R.; Zhou, H.; Li, W.; Liu, S.; Ade, H.; You, W. *Journal of the American Chemical Society* **2013**, 135, (5), 1806-1815.
4. Qian, G.; Wang, Z. Y. *Chemistry – An Asian Journal* **2010**, 5, (5), 1006-1029.
5. Ellinger, S.; Graham, K. R.; Shi, P.; Farley, R. T.; Steckler, T. T.; Brookins, R. N.; Taraneekar, P.; Mei, J.; Padilha, L. A.; Ensley, T. R.; Hu, H.; Webster, S.; Hagan, D. J.; Van Stryland, E. W.; Schanze, K. S.; Reynolds, J. R. *Chemistry of Materials* **2011**, 23, (17), 3805-3817.
6. Zhan, X.; Facchetti, A.; Barlow, S.; Marks, T. J.; Ratner, M. A.; Wasielewski, M. R.; Marder, S. R. *Advanced Materials* **2011**, 23, (2), 268-284.

7. Zhao, Y.; Guo, Y.; Liu, Y. *Advanced Materials* **2013**, 25, (38), 5372-5391.
8. Duan, C. H.; Huang, F.; Cao, Y. *Journal of Materials Chemistry* **2012**, 22, (21), 10416-10434.
9. Pron, A.; Leclerc, M. *Progress in Polymer Science* **2013**, 38, (12), 1815-1831.
10. Gomez-Bengoa, E.; Helm, M. D.; Plant, A.; Harrity, J. P. A. *Journal of the American Chemical Society* **2007**, 129, (9), 2691-2699.
11. Hayden, A. E.; Houk, K. N. *Journal of the American Chemical Society* **2009**, 131, (11), 4084-4089.
12. Boger, D. L.; Sakya, S. M. *The Journal of Organic Chemistry* **1988**, 53, (7), 1415-1423.
13. Sauer, J.; Heldmann, D. K.; Hetzenegger, J.; Krauthan, J.; Sichert, H.; Schuster, J. *European Journal of Organic Chemistry* **1998**, 1998, (12), 2885-2896.
14. Kurach, E.; Djurado, D.; Rimarcik, J.; Kornet, A.; Wlostowski, M.; Lukes, V.; Pecaut, J.; Zagorska, M.; Pron, A. *Physical Chemistry Chemical Physics* **2011**, 13, (7), 2690-2700.
15. Li, Z.; Ding, J. *Macromolecular Chemistry and Physics* **2011**, 212, (20), 2260-2267.
16. Wen, S.; Dong, Q.; Cheng, W.; Li, P.; Xu, B.; Tian, W. *Solar Energy Materials and Solar Cells* **2012**, 100, 239-245.
17. Hwang, D. K.; Dasari, R. R.; Fenoll, M.; Alain-Rizzo, V.; Dindar, A.; Shim, J. W.; Deb, N.; Fuentes-Hernandez, C.; Barlow, S.; Bucknall, D. G.; Audebert, P.; Marder, S. R.; Kippelen, B. *Advanced Materials* **2012**, 24, (32), 4445-4450.
18. Sauer, J.; Heldmann, D. K. *Tetrahedron* **1998**, 54, (17), 4297-4312.
19. Miller, G. P.; Tetreau, M. C. *Organic Letters* **2000**, 2, (20), 3091-3094.
20. Ye, Q.; Neo, W. T.; Cho, C. M.; Yang, S. W.; Lin, T.; Zhou, H.; Yan, H.; Lu, X.; Chi, C.; Xu, J. *Organic Letters* **2014**, 16, (24), 6386-6389.
21. Fleming, I., *Molecular Orbitals and Organic Chemical Reactions*. John Wiley & Sons, Inc: 2009.
22. Sadasivam, D. V.; Prasad, E.; Flowers, R. A., 2nd; Birney, D. M. *The journal of physical chemistry. A* **2006**, 110, (4), 1288-94.

23. Gandini, A.; Coelho, D.; Silvestre, A. J. D. *European Polymer Journal* **2008**, 44, (12), 4029-4036.
24. Liu, X.; Du, P.; Liu, L.; Zheng, Z.; Wang, X.; Joncheray, T.; Zhang, Y. *Polymer Bulletin* **2013**, 70, (8), 2319-2335.
25. Bergman, S. D.; Wudl, F. *Journal of Materials Chemistry* **2008**, 18, (1), 41-62.

Chapter 5

Synthesis of electron deficient pyrrolo-acenaphtho-pyridazine-dione (PAPD) based donor-acceptor conjugated electrochromic polymers

A new series of novel electron acceptors 2-alkyl-6,9-di(thiophen-2-yl)-1H-pyridazino[4',5':2,3]indeno[6,7,1-def]isoquinoline-1,3(2H)-dione and 2-alkyl-6,9-di(furan-2-yl)-1H-pyridazino[4',5':2,3]indeno[6,7,1-def]isoquinoline-1,3(2H)-dione has been designed from pyrrolo-acenaphtho-pyridazine-dione (PAPD) via an inverse electron demand Diels-Alder (iEDDA) reaction. The resulting monomers possess very low LUMO levels and were used for the synthesis of a series of Donor-Acceptor type conjugated polymers with varying ratios of PAPD. All the synthesized polymers reveal electrochromism and their electrochromic properties were investigated where they exhibit outstanding performances.

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5.1 Introduction

Building off the successful synthesis of new electron deficient monomers,¹ there is a need to explore the feasibility of this methodology which uses the iEDDA reaction to combine aryl-substituted tetrazine and dienophiles together. To further explore the viability of this new methodology, new building blocks are envisaged to be applicable and achievable by varying the dienophile identities.

In this chapter, a new building block with strong electron-withdrawing imide group, a five-membered ring and a pyridazine moiety together was prepared using our previous established methodology. A new series of pyrrolo-acenaphtho-pyridazine-diones (PAPD) monomers were successfully obtained. These PAPD based species were tested to have ultrahigh levels of electron deficiency which is beneficial for the fine-tuning of physical properties, such as the bandgap, color and frontier orbital energy levels²⁻¹⁰ of D-A type conjugated polymers. Time-dependent density functional theory (TD-DFT) calculations were done for the LUMO energy levels of some of those commonly used electron acceptors and our newly synthesized PAPD unit was compared against them as shown in Figure 5.1. Among the electron acceptors examined, the LUMO energy level of PAPD unit is the lowest at -3.42 eV, which is lower than those units commonly used in D-A polymers such as benzotriazole and benzothiadiazole based electron acceptors. Remarkably, this new PAPD monomer has achieved an even larger electron deficiency than the pyrrolo[3,4-*d*]pyridazine-5,7-dione (PPD) monomer in Chapter 4.

Besides having ultrahigh electron deficiency, the monomer has to be designed in such a way that its devices can be fabricated through solution processing method. Therefore, the ease of side chain engineering is an important aspect of the monomer. For PAPD monomers, the attachment of side chains at the imide-N position occurs easily for ease of incorporation into the structures of polymers by the common palladium catalyzed cross-coupling polymerization reactions.

As such, the feasibility and effectiveness of this new PAPD building block as an electron acceptor was tested by incorporating into D-A electrochromic polymers. A new series of

high performance electrochromic D-A conjugated polymers with the new PAPD incorporated was synthesized, and their electrochromic properties were investigated and discussed in the later part of this chapter.

Figure 5.1 Calculated LUMO energy levels of a series of electron acceptors. The identities of the electron acceptor moiety from left to right: benzotriazole, benzothiadiazole, 5,6-difluorobenzo[1,2,5]thiadiazole, 6-alkylpyrrolo[3,4-*d*]pyridazine-5,7-dione and a PAPD monomer.

5.2 Experimental Methods

5.2.1 Synthesis

All reagents and starting materials were purchased from commercial sources and used without further purification.

2-(2-Octyldodecyl)-1*H*-indeno[6,7,1-*def*]isoquinoline-1,3(2*H*)-dione (6) 2-(2-octyldodecyl)-6,7-dihydro-1*H*-indeno[6,7,1-*def*]isoquinoline-1,3(2*H*)-dione (0.50 mmol), N-bromosuccinimide (0.55 mmol), benzoyl peroxide (0.05mmol) and dichloroethane (10 mL) were added to a round bottom flask. The mixture was purged with argon for 15 min and then refluxed overnight. The precipitate was directly removed by filtration and the resultant filtrate was rotary evaporated to dryness. The crude product was used without further purification. A solution of the above crude product (0.40 mmol), LiBr (1.2 mmol) and dry N,N-dimethylformamide (DMF) (10 mL) was heated at 115 °C for 2 hours. After cooling to room temperature, the solvent was removed by rotary evaporation and the

residue was directly subjected to silica gel column chromatography using eluent (hexane : chloroform = 3 : 1) to afford the target compound. Yield: 63%. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.33 – 8.31 (d, 2H, J = 6.8 Hz), 7.72 – 7.70 (d, 2H, J = 6.8 Hz), 7.07 (s, 2H), 4.08 – 4.06 (d, 2H, J = 7.2 Hz), 1.96 – 1.94 (m, 1H), 1.39 – 1.21 (m, 32H), 0.88 – 0.83 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 164.7, 144.7, 133.3, 132.1, 127.9, 125.4, 123.7, 123.3, 44.8, 37.3, 32.3, 32.1, 30.4, 30.0, 29.7, 26.9, 23.1, 14.5. HR-EI-MS: m/z = 501.36086, calculated exact mass: 501.36013, error: 1.44 ppm.

6,9-Bis(5-bromothiophen-2-yl)-2-(2-octyldodecyl)-1H-

pyridazino[4',5':2,3]indeno[6,7,1-*def*]isoquinoline-1,3(2H)-dione (10) To a dry round bottom flask was added 3,6-bis(5-bromothiophen-2-yl)-1,2,4,5-tetrazine (**8**) (0.50 mmol), 2-(2-octyldodecyl)-1H-indeno[6,7,1-*def*]isoquinoline-1,3(2H)-dione (**6**) (0.50 mmol) and diphenyl ether (10 mL). The mixture was purged with argon for 15 min and then heated to 160 °C overnight. After cooling to room temperature, the mixture was directly subjected to silica gel column chromatography. Hexane was used first to flush away the diphenyl ether and the target compound was then collected as red solid using eluent (hexane : chloroform = 1 : 2). Yield: 40%. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.49 – 8.44 (m, 4H), 7.62 – 7.61 (d, 2H, J = 4.0 Hz), 7.29 – 7.28 (d, 2H, J = 3.6 Hz), 4.05 – 4.03 (d, 2H, J = 7.2 Hz), 1.93 (m, 1H), 1.37 – 1.20 (m, 32H), 0.86 – 0.82 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 163.6, 150.2, 140.4, 137.7, 133.5, 132.3, 131.0, 129.7, 127.1, 125.7, 118.1, 45.1, 37.2, 32.3, 32.1, 30.4, 30.0, 29.72, 29.70, 26.9, 23.1, 14.5. HR-EI-MS: m/z = 873.16315, calculated exact mass: 873.16275, error: 0.46 ppm.

6,9-Bis(5-bromothiophen-2-yl)-2-hexyl-1H-pyridazino[4',5':2,3]indeno[6,7,1-

***def*]isoquinoline-1,3(2H)-dione (11)** To a dry round bottom flask was added 3,6-bis(5-bromothiophen-2-yl)-1,2,4,5-tetrazine (**8**) (0.50 mmol), 2-hexyl-1H-indeno[6,7,1-*def*]isoquinoline-1,3(2H)-dione (**7**) (0.50 mmol) and diphenyl ether (10 mL). The mixture was purged with argon for 15 min and then heated to 160 °C overnight. After cooling to room temperature, the mixture was directly subjected to silica gel column chromatography. Hexane was used first to flush away the diphenyl ether and the target compound was then collected as red solid using eluent (hexane : CHCl_3 = 1 : 2). Yield: 42%. ^1H NMR (400

MHz, CDCl₃): δ (ppm) 8.51 – 8.45 (m, 4H), 7.63 – 7.62 (d, 2H, J = 3.2 Hz), 7.30 – 7.29 (d, 2H, J = 2.8 Hz), 4.15 – 4.11 (t, 2H, J = 7.6 Hz), 1.89 (m, 2H), 1.74 – 1.67 (m, 2H), 1.42 – 1.32 (m, 4H), 0.90 – 0.87 (t, 3H, J = 6.8 Hz). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 163.2, 150.2, 140.4, 137.8, 133.5, 132.2, 131.0, 129.7, 127.1, 125.8, 125.6, 118.1, 41.1, 31.9, 28.7, 27.2, 22.9, 14.4. HR-EI-MS: m/z = 676.94481, calculated exact mass: 676.94364, error: 1.72 ppm.

6,9-Bis(5-bromofuran-2-yl)-2-hexyl-1H-pyridazino[4',5':2,3]indeno[6,7,1-

def]isoquinoline-1,3(2H)-dione (12) To a dry round bottom flask was added 3,6-bis(5-bromofuran-2-yl)-1,2,4,5-tetrazine (**9**) (0.50 mmol), 2-hexyl-1H-indeno[6,7,1-def]isoquinoline-1,3(2H)-dione (**7**) (0.50 mmol) and diphenyl ether (10 mL). The mixture was purged with argon for 15 min and then heated to 160 °C overnight. After cooling to room temperature, the mixture was directly subjected to silica gel column chromatography. Hexane was used first to flush away the diphenyl ether and the target compound was then collected as red solid using eluent (hexane : CHCl₃ = 1 : 2). Yield: 38%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.87 – 8.85 (d, 2H, J = 7.6 Hz), 8.58 – 8.56 (d, 2H, J = 7.6 Hz), 7.60 – 7.59 (d, 2H, J = 3.2 Hz), 6.73 – 6.72 (d, 2H, J = 3.6 Hz), 4.20 – 4.16 (t, 2H, J = 7.6 Hz), 1.79 – 1.68 (m, 2H), 1.46 – 1.25 (m, 6H), 0.93 – 0.89 (t, 3H, J = 6.8 Hz). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 163.2, 153.0, 144.7, 136.9, 132.0, 131.2, 130.8, 129.3, 125.1, 124.8, 116.4, 115.3, 41.1, 32.0, 28.7, 27.2, 23.0, 14.5. HR-EI-MS: m/z = 644.99016, calculated exact mass: 644.98933, error: 1.28 ppm.

General procedure for Stille cross-coupling polymerization

6,9-bis(5-bromothiophen-2-yl)-2-(2-octyldodecyl)-1H-pyridazino[4',5':2,3]indeno[6,7,1-def]isoquinoline-1,3(2H)-dione (**10**) (0.05 mmol), 6,8-dibromo-3,3-bis((dodecyloxy)methyl)-3,4-dihydro-2H-thieno[3,4-*b*][1,4]dioxepine (**13**) (0.45 mmol) and 2,5-bis(trimethylstannyl)thieno[3,2-*b*]thiophene (**14**) (0.50 mmol) were dissolved in 12 mL of toluene. The mixture was stirred and purged with argon for about 15 min, and then Pd(PPh₃)₄ (0.025 mmol) was added. The flask was purged with argon for another 15 min before the mixture was heated to 110 °C for 48 hrs. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was precipitated in

methanol. The suspension was filtered to give the crude product, which was then purified by Soxhlet extraction with acetone, hexane and chloroform. The chloroform fraction was evaporated to dryness to afford dark red solid.

PAPD1: Yield 55%. ^1H NMR (main signals) (400 MHz, CDCl_3): δ (ppm) 7.36 – 7.30 (br, m), 4.35 – 4.05 (br, m), 3.61 – 3.46 (br, m), 1.56 – 1.26 (br, m), 0.88 (br, s). Anal. Calcd for $\text{C}_{39}\text{H}_{60}\text{O}_4\text{S}_3$: C, 67.97; H, 8.78; S, 13.96. Found: C, 67.91; H, 8.79; S, 13.99. GPC using PS in THF as standard: Number-average molecular weight (M_n) = 50.5 k, Weight-average molecular (M_w) = 94.2 k, polydispersity index (PDI) = 1.86.

PAPD2: Yield 55%. ^1H NMR (main signals) (400 MHz, CDCl_3): δ (ppm) 8.44 – 6.87 (br, m), 4.22 – 4.06 (br, m), 3.60 – 3.45 (br, m), 2.04 (br, s), 1.67 – 1.58 (br, m), 0.87 – 0.71 (br, m). Anal. Calcd for $\text{C}_{40.1}\text{H}_{59.1}\text{N}_{0.3}\text{O}_{3.8}\text{S}_{3.1}$: C, 68.26; H, 8.44; N, 0.59; S, 14.09. Found: C, 68.07; H, 8.45; N, 0.54; S, 14.01. GPC using PS in THF as standard: (M_n = 42.1 k, M_w = 83.5 k, PDI = 1.98)

PAPD3: Yield 50%. ^1H NMR (main signals) (400 MHz, CDCl_3): δ (ppm) 8.48 – 6.87 (br, m), 4.21 – 4.04 (br, m), 3.60 – 3.44 (br, m), 2.04 (br, s), 1.68 – 1.59 (br, m), 0.87 (br, s). Anal. Calcd for $\text{C}_{41.2}\text{H}_{58.2}\text{N}_{0.6}\text{O}_{3.6}\text{S}_{3.2}$: C, 68.52; H, 8.12; N, 1.16; S, 14.21. Found: C, 67.97; H, 8.16; N, 0.99; S, 14.08. GPC using PS in THF as standard: (M_n = 48.3 k, M_w = 73.4 k, PDI = 1.52)

PAPD4: Yield 54%. ^1H NMR (main signals) (400 MHz, CDCl_3): δ (ppm) 8.60 – 6.72 (br, m), 4.22 – 4.04 (br, m), 3.60 – 3.44 (br, m), 2.02 – 2.00 (br, m), 1.58 (br, s), 0.87 (br, s). Anal. Calcd for $\text{C}_{42.3}\text{H}_{57.3}\text{N}_{0.9}\text{O}_{3.4}\text{S}_{3.3}$: C, 68.78; H, 7.82; N, 1.71; S, 14.33. Found: C, 68.60; H, 7.83; N, 1.65; S, 14.28. GPC using PS in THF as standard: (M_n = 54.5 k, M_w = 93.8 k, PDI = 1.72)

PAPD5: Yield 52%. ^1H NMR (main signals) (400 MHz, CDCl_3): δ (ppm) 8.52 – 6.88 (br, m), 4.22 – 4.07 (br, m), 3.59 – 3.44 (br, m), 2.13 – 2.01 (br, m), 1.57 – 0.86 (br, m). Anal. Calcd for $\text{C}_{46.7}\text{H}_{53.7}\text{N}_{2.1}\text{O}_{2.6}\text{S}_{3.7}$: C, 69.70; H, 6.73; N, 3.66; S, 14.74. Found: C, 69.29; H,

6.75; N, 3.52; S, 14.64. GPC using PS in THF as standard: ($M_n = 67.2$ k, $M_w = 114.7$ k, PDI = 1.71)

5.2.2 Chemical Analysis

^1H NMR and ^{13}C NMR spectra were obtained in CDCl_3 on Avance 400 MHz Bruker spectrometer. HR-ESI-MS was carried out on Finnigan TSQ 7000 triple stage quadrupole mass spectrometer. UV-vis/UV-vis-NIR absorption spectra were obtained with a Shimadzu UV 3600 UV-vis-NIR spectrophotometer. All chemical shifts are quoted in ppm, relative to tetramethylsilane, using the residual solvent peak as a reference standard. Polymer molecular weights were determined using an Alliance Waters model 2690 gel permeation chromatography (GPC) system calibrated with polystyrene (PS) as the standard and THF as the eluent. Polymer of 5 mg/mL concentration was prepared and filtered prior to sample injection. Elemental analysis data were acquired on a Flash EA 1112 series. The thermogravimetric analysis of the polymers was performed on a Perkin Elmer TGA-7 thermal analyzer under nitrogen at a heating rate of 20 $^\circ\text{C}/\text{min}$. Differential scanning calorimetry (DSC) measurements were carried out using a PDSC Q100 from TA instruments with a heat-cool profile from -40 $^\circ\text{C}$ to 200 $^\circ\text{C}$ at a rate of 10 $^\circ\text{C min}^{-1}$ for three cycles under a constant N_2 flow. Cyclic voltammetry and chronoamperometry experiments were carried out using an Autolab PGSTAT128N potentiostat. Colourimetry data was acquired using Hunterlab ColorQuest XE and the colour of each polymer film was assessed by utilizing the CIE 1976 $L^*a^*b^*$ colour space with a D65/10 $^\circ$ illuminant. X-ray diffraction (XRD) patterns of the thin films were recorded using a $\text{Cu-K}\alpha$ radiation source ($\lambda = 0.15406$ nm) on a Shimadzu XRD-6000. X-ray crystal structure determination was performed on a Bruker X8 Diffractometer. The structures were solved by direct methods with any remaining non-hydrogen atoms located from different Fourier maps. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions with fixed isotropic thermal parameters. Refinements were made by full-matrix least-squares methods and final refinements were made on F2 using a weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2) + 2(F_c^2)]/3$.

5.2.3 Cyclic Voltammetry and Spectroelectrochemistry

For cyclic voltammetry, measurements were done in a MBraunLABmaster 130 glove box. The solutions of **PAPD1** – **PAPD5** in chlorobenzene (10 mg/mL) were drop casted onto glassy carbon electrode. A three electrode cell configuration with polymer-coated glassy carbon, Pt wire and Ag wire as the working, counter, and pseudo-reference electrodes respectively was employed. A 0.1 M LiClO₄/ACN electrolyte/solvent couple was used and all measurements were recorded at 50 mV/s. The pseudo-reference electrode was calibrated against the ferrocene/ferrocenium redox couple. For spectroelectrochemical studies, the polymers were analyzed in their device forms.

5.2.4 Device Fabrication

Electrochromic layers of **PAPD1** – **PAPD5** on ITO/glass were deposited by a drop-and-spread method. The gel electrolyte was prepared by mixing 0.512 g of lithium perchlorate and 2.8 g of poly(methyl methacrylate) of molecular weight 120 kg/mol in 6.65 mL of propylene carbonate and 28 mL of dry acetonitrile (ACN). A window-type absorption/transmission electrochromic device (ECD) was constructed, with the sandwich structure Glass/ITO|polymer||electrolyte||ITO/Glass. Parafilm was used as the spacer to prevent electrical contact between the substrates.

5.3 Results for PAPD-based monomers

5.3.1 Molecular Synthesis

Scheme 5.1 Synthesis of PAPD-based monomers **10 – 12**

The synthesis of the new building blocks **10 – 12** is shown in Scheme 5.1. For this synthesis, we tried to fuse a strong electron-withdrawing imide group, five-membered ring and pyridazine moiety together so as to create a high electron deficient moiety. Starting from the commercially available acenaphthene **1**, intermediates **2 – 5** were synthesized using reported synthetic methods^{11,12}. Intermediates **4** and **5** were then brominated using NBS and the reaction was conducted in hot 1,2-dichloroethane. Subsequently, the dienophile intermediates 2-(2-alkyl)-1*H*-indeno[6,7,1-*def*]isoquinoline-1,3(2*H*)-diones **6 – 7**¹³ were obtained *via* an elimination process. Then by following the previous established methodology in Chapter 4, monomers **10 – 12**¹³ were successfully obtained by an iEDDA reaction between the dienophile moiety (**6** and **7**) and the diene units (**8** and **9**^{1, 14}) at 160 °C in diphenyl ether.

5.3.2 Molecular Characterizations

The chemical structures of the new PAPD building blocks are confirmed by ^1H NMR spectrum, ^{13}C NMR, HR-EI-MS and single crystals XRD.

Figure 5.2 ^1H NMR spectrum of compound **11** (CDCl_3 , room temperature).

Using the ^1H NMR of **11** as an example (Figure 5.2), the peaks around 8.45 – 8.51 ppm belongs to the H atoms on the thiophene moiety, and the peaks at 7.62 and 7.30 ppm belongs to the H atoms on the acenaphthylene group. The signal at around 4.11 – 4.15 ppm corresponds to the N-CH₂ of the imide and the signal around 0.87 – 1.89 ppm corresponds to the hexyl chain on the imide. The protons integrated correspond to the molecular structure of **11**.

Figure 5.3 ¹³C NMR spectrum of compound **11** (CDCl₃, room temperature).

The ¹³C NMR spectrum of **11** was collected in CDCl₃. As seen from Figure 5.3, the carbon atoms located at the region 118.1 – 163.2 ppm belong to the twelve aromatic carbons. As the molecule is symmetrical, only twelve aromatic carbon peaks were observed. The peaks in the region 14.4 – 41.1 ppm belong to the straight hexyl chain attached to the N atom.

Figure 5.4 HR-EI-MS spectrum of compound **11**.

The HR-EI-MS result shown in Figure 5.4 further confirmed the successful synthesis of the new building blocks. The chemical formula of **11** is C₃₀H₂₁Br₂N₃O₂S₂ and the calculated m/z value for **11** is 676.94364. The actual m/z value of that found in the spectrum is 676.94481, which is well consistent with the calculated result.

The structures of **11** and **12** were also determined *via* the single crystal XRD where the method of vapor diffusion of was used. The crystals were obtained from the slow diffusion of methanol into the toluene solutions. From Figure 5.5, the PAPD backbone structure was clearly verified by the refined crystal structures.

Figure 5.5 Single crystal structures of compounds (a) **11** and (b) **12**; Hydrogen atoms are omitted for clarity

5.3.3 Mechanism Discussion

In this new series of monomers, an identical phenomenon similar to what was observed in the previous chapter was seen. It was observed that the regio-selective Diels-Alder reaction does not occur on the thiophene or furan group, but on the central tetrazine unit instead. In order to comprehend the selectivity of Diels-Alder reaction, the activation energy ($\Delta G^\ddagger$) was calculated for the two probable reaction pathways, that is the reaction between intermediates **6** and **8**; and **6** and **9**. To simplify the computational process, the branched substituent on **6** was replaced to an ethyl group and the results are summarized in Figure 5.6.

The activation energy barrier of the iEDDA reaction of **8** with the central tetrazine moiety was lower, at about 41.02 kcal mol⁻¹, whereas that of normal Diels-Alder reaction at the thiophene position is about 51.78 kcal mol⁻¹. Similarly for the furan attached tetrazine monomer **9**, the activation energy barrier of the iEDDA reaction tetrazine (35.75 kcal mol⁻¹) is also lower than the normal Diels-Alder reaction at the furan position (47.37 kcal mol⁻¹). Through this calculation, it is believed that the iEDDA reaction on tetrazine was favored kinetically due to the lower $\Delta G^\ddagger$ barrier and this may contribute to the selectivity for such reaction pathway instead of the normal Diels-Alder reaction. Furthermore, as one nitrogen molecule was eliminated during the iEDDA reaction, this could contribute to the forward reaction. With all the above reasons, it is logical to observe only the iEDDA reaction.

Figure 5.6 Gibbs free energy profiles of normal Diels-Alder reaction and iEDDA reaction pathways to attach compound **6'** onto compounds **8** and **9**.

5.3.4 Electrochemistry

The frontier orbital energy level of compound **10** was investigated by cyclic voltammetry (Figure 5.7). The onset reduction potential versus ferrocene ($E_{\text{onset,red vs ferrocene}}$) is -0.876 V. The LUMO energy level of **10** was calculated using the following formula:

$$E_{\text{LUMO}} = -(E_{\text{onset,red vs ferrocene}}) - 4.8 \text{ (eV)}$$

The LUMO energy level estimated from the reduction onset of the first peak was -3.92 eV, and this proved that the PAPD monomer is highly electron deficient¹⁵. In fact, its LUMO level is 0.26 eV lower than the PPD monomer¹ reported in Chapter 4.

Figure 5.7 Cyclic voltammetry of compound **10** and its LUMO energy level.

From the above sections, we have successfully synthesized the new PAPD based monomers and further verified the feasibility of our new synthetic methodology for creating new monomers. The new monomers show promising results as strong electron acceptors. Moreover, the ease of side chain engineering allows us to attach branched alkyl chains on the monomers, thereby improving the solubility of the polymers. In the next section, we attempted to use the PAPD based monomer **10** in the synthesis of a new series of donor-acceptor polymers, and to investigate the performance and effects of the new electron acceptor in the polymers.

5.4 Results for PAPD-based Polymers

5.4.1 Polymers Design

In this section, we report a series of random copolymers using the PAPD based monomer. The polymers **PAPD1** – **PAPD5**¹³ were synthesized by Stille coupling polymerization of the electron acceptor **10**, 6,8-dibromo-3,3-bis((dodecyloxy)methyl)-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine **13** and 2,5-bis(trimethylstannyl)thieno[3,2-*b*]thiophene **14** as

seen in Scheme 5.2. A varying ratio of **10** was used in the designing and synthesis of the polymers. **PAPD1** was synthesized without the electron acceptor so as to see the effect of the electron acceptor. To investigate the effect of the newly synthesized electron acceptor **10** on both the optical and electrochromic properties, **PAPD2** – **PAPD5** were synthesized with different ratios (from low to high) of electron acceptor **10**.

Scheme 5.2 Synthetic route of polymers **PAPD1** – **PAPD5**

5.4.2 Polymers Characterizations

Figure 5.8 ^1H NMR spectrum of Polymer **PAPD3** (CDCl_3 , room temperature).

The polymers **PAPD1** – **PAPD5** were structurally characterized by ^1H NMR and elemental analysis. Using the ^1H NMR spectrum of the polymer **PAPD3** as an example (Figure 5.8), the peak at around 4.2 ppm corresponds to the N-CH₂ of the PAPD unit and a pair of O-CH₂ from the two long alkoxy groups of the ProDOT moiety. As for the signal observed at around 3.6 ppm, it belongs to the other 2 pairs of O-CH₂ from the seven membered ring of the ProDOT moiety. From the integration intensity of these two characteristic peaks, the polymer compositions were estimated and the results were found to be consistent with the reaction feed compositions.

To further verify the identity of the polymers, elemental analysis were performed. From the elemental analysis results, it was shown that the percentage of the elements C, H, N and S corresponds well to the theoretical value (Table 5.1), implying that the molecular structure of the polymers are as expected.

Table 5.1 Elemental analysis results of **PAPD1** – **PAPD5**.

	Theoretical	Experimental
	C : H : N : S	C : H : N : S
PAPD1	67.97 : 8.78 : 0.00 : 13.96	67.91 : 8.79 : 0.00 : 13.99
PAPD2	68.26 : 8.44 : 0.59 : 14.09	68.07 : 8.45 : 0.54 : 14.01
PAPD3	68.52 : 8.12 : 1.16 : 14.21	67.97 : 8.16 : 0.99 : 14.08
PAPD4	68.78 : 7.82 : 1.71 : 14.33	68.60 : 7.83 : 1.65 : 14.28
PAPD5	69.70 : 6.73 : 3.66 : 14.74	69.29 : 6.75 : 3.52 : 14.64

The polymers were produced in medium yield of about 50 - 55 %. Generally, crude yields above 85 % were obtained for these polymers. However, during the purification process, where the polymers were first precipitated, followed by Soxhlet extraction with acetone, hexane and chloroform, low and moderate molecular weights polymers were removed during the purification process. This is due to the polymers having long straight and branched alkyl chains which resulted in increased solubility in acetone and hexane. Therefore, the chloroform fraction which contains mainly the high molecular weight

polymers appeared to be of lower yield at about 50 %. The obtained polymers from the chloroform fraction have high average molecular weights (M_n) ranging from of 42 000 – 67 000 g mol⁻¹ with polydispersity indexes of 1.52 – 1.98 (Table 5.2).

Table 5.2 Synthetic yields, molecular weights, polydispersity indexes and thermal decomposition temperatures of polymers **PAPD1 – PAPD5**.

Polymers	Yields (%)	M_n (g/mol)	M_w (g/mol)	PDI	T_D (°C)
PAPD1	55	50,500	94,200	1.86	354
PAPD2	55	42,100	83,500	1.98	389
PAPD3	50	48,300	73,400	1.52	389
PAPD4	54	54,500	93,800	1.72	398
PAPD5	52	67,200	114,700	1.71	398

M_n : the number average molecular weight. M_w : the weight average molecular weight. PDI: polydispersity index. T_D : decomposition temperature at 5 % weight loss in N₂.

The thermal stability of the polymers was evaluated with thermogravimetric analysis (TGA) under N₂ environment. Generally, the polymers exhibited high thermal stability and their thermograms are depicted in Figure 5.9. The polymers' decomposition temperatures at 5% weight loss are about 390 °C for **PAPD2 – PAPD5**. But for **PAPD1** which does not contain any electron acceptor, it has a lower decomposition temperature of about 354 °C (Table 5.2).

Figure 5.9 TGA thermograms of **PAPD1 – PAPD5**.

From the differential scanning calorimetry studies (Figure 5.10), there was no melting or glass-transition temperature observed for temperature -40 °C to 200 °C.

Figure 5.10 DSC thermograms of **PAPD1 – PAPD5**

XRD measurements were done on the polymers and it was confirmed that they are amorphous (Figure 5.11). The amorphous nature of the polymers could be attributed due to the bulky and branched alkyl chains that are attached on the conjugated polymers along with the random structure of the polymers which could disturb the π - π packing¹⁶.

Figure 5.11 XRD diffractograms of **PAPD1 – PAPD5**.

5.4.3 UV-*vis* absorption spectroscopy

The normalized UV-*vis* absorption spectra of polymers **PAPD1 – PAPD5** in chlorobenzene solutions and as thin films are shown in Figure 5.12 and the data are summarized in Table 5.3. All the five polymers absorbed strongly in the visible region with strong absorption band (λ_{max}) in the region 400 – 600 nm. When compared to the solution state, the absorption of the polymers' thin films displayed spectral broadening and bathochromic shifts, suggesting the presence of aggregation in the solid state. When the amount of electron acceptors increased from **PAPD1 – PAPD5**, the polymers' absorption maxima in both the solution and film state reveal a systematic decrease from 535 to 500 nm and 550 to 505 nm respectively. The distortion of the planarity of the conjugated polymers could be accounted for the blue-shift phenomenon. Upon increasing the content of the PAPD unit in the polymer chains, it leads to an increase in steric hindrance caused by the branched side chain of the PAPD unit, and as a result, the backbone of the polymer chains could be twisted, interfering with the coplanarity. Such similar phenomenon was also observed by Reynolds's group¹⁷. Even though, the amount of electron acceptors in the polymer chain led to differences in the absorption maxima, there is negligible effect on the bandgap of the polymers. The optical bandgaps (E_g^{opt}) were calculated from the absorption

onset of the thin films and were approximated to be 1.90 – 1.99 eV for polymers **PAPD1** – **PAPD5**.

Figure 5.12 Normalized UV-*vis* absorption spectra of **PAPD1** – **PAPD5** in chlorobenzene and in thin film state.

5.4.4 Electrochemistry

Figure 5.13 shows the cyclic voltammograms of polymers **PAPD1** – **PAPD5**. All five polymers **PAPD1** – **PAPD5** showed quasi-reversible oxidation upon p-doping and no reduction peak was seen in the *n*-doping region. A gradual deepening of the HOMO energy level was observed as the molar ratio of electron acceptor **10** increases, from -5.03 eV for **PAPD1** to -5.32 eV for **PAPD5**. With such deep HOMO energy levels, the polymers are likely to have higher ambient stability.

Figure 5.13 Cyclic voltammograms of **PAPD1 – PAPD5** thin films in a 0.1M LiClO₄/ACN electrolyte/solvent couple at a scan rate of 50 mV·s⁻¹ calibrated against the ferrocene/ferrocenium couple.

Table 5.3 Summary of optical and electrochemical properties of polymers **PAPD1 – PAPD5** in solution and in film state.

	In solution		In film state		^a E _g ^{opt} (eV)	^b HOMO (eV)	^c LUMO (eV)
	λ _{max} (nm)	λ _{onset} (nm)	λ _{max} (nm)	λ _{onset} (nm)			
PAPD1	535	629	550	651	1.90	-5.03	-3.13
PAPD2	528	622	540	646	1.92	-5.07	-3.15
PAPD3	519	623	522	640	1.94	-5.11	-3.17
PAPD4	510	624	510	640	1.94	-5.21	-3.27
PAPD5	500	604	505	622	1.99	-5.32	-3.33

^aE_g^{opt} is calculated following the equation E_g^{opt} = 1240/ λ_{onset} (eV); ^bE_{HOMO} = -(E_{onset,ox} vs ferrocene) - 4.8; ^cE_{LUMO} = E_{HOMO} + E_g^{opt}

5.4.5 Spectroelectrochemistry

The UV-*vis*-NIR spectra from the spectroelectrochemical analysis and the color states of the sandwich devices of **PAPD1 – PAPD5** were shown in Figure 5.14 and 5.15 respectively. When the applied potential was increased from 0.0 V to 2.0 V, it was observed that there is a reduction in intensity of the absorption peak at the visible region. New

absorption peaks were seen arising at the near infrared (NIR) region at 750 nm and 1230 nm, where they demonstrate the formation of polaronic and bipolaronic bands. For polymers **PAPD1** and **PAPD2**, when the applied potential is 1.7 V or above, the bipolaronic bands increased in intensity while there is a suppression of the polaronic bands, and as a result, two clear isosbestic points were seen at 620 nm and 830 nm, validating the presence of the interconverting neutral, polaronic and bipolaronic species. In contrast, for **PAPD3 – PAPD5**, only one isosbestic point at about 600 nm was observed despite the increase in applied potential. This could be due to the saturation of the polarons where they are unable to convert into bipolarons. In particular for polymer **PAPD5**, there is a small decrease in the peak intensity at the visible region, which could translate to a reduction in electroactivity of the polymer (Figure 5.14e). Such observation was also seen in our previous work^{18,19}.

For **PAPD1** and **PAPD2**, at the fully oxidized state of 2.0 V, a residual tailing was observed in the visible region, but for **PAPD3 – PAPD5**, an additional distinct peak was seen instead. This peak at around 450 nm may be attributed to the intrinsic color of the electron acceptor unit. In their neutral state, polymers **PAPD1 – PAPD5** exhibited a range of color transiting from purple to red. In their reduced or neutral states, the polymers possess very positive a^* values (32 – 41), but different hues as described by the substantially different b^* values going from -18 to 24.²⁰ In their oxidized states, the a^* values significantly decreased to -2 to 20 with minimal changes in b^* values. Therefore, in general, the polymers transit from purple/red when reduced/neutral to grey/grey-blue when oxidized (Figure 5.15).

Figure 5.14 Spectroelectrochemistry of (a) **PAPD1**, (b) **PAPD2**, (c) **PAPD3**, (d) **PAPD4** and (e) **PAPD5** at various applied potentials.

Figure 5.15 Color states of **PAPD1 – PAPD5** at 0.0 V (purple/red) and 2.0 V (blue/grey) with L* a* b* values.

5.4.6 Electrochromic Performance

To study the electrochromic performance of polymers **PAPD1 – PAPD5**, the performance of these polymers was evaluated using the fabricated absorption/transmission type devices. The optical contrasts, switching times and coloration efficiencies in both visible and NIR regions are summarized in Table 5.4.

The switching properties of **PAPD1 – PAPD5** were carried out by chronamperometry where the polymers switched between +1.6 V and -1.6 V at 90 seconds interval and the plots are shown in Figure 5.16. From the spectroelectrochemical spectra shown above (Figure 5.14), the residual absorption in the visible region increased with increasing amount of electron acceptors in the polymer backbone. This could be ascribed to the increased concentration of highly electron-accepting groups, which decreases the polymer's tendency towards oxidation. Consequently, the optical contrast of the polymers at the visible region decreased with increasing mole ratio of the electron acceptors (Table 5.4). Notably, **PAPD1** attained the highest optical contrast of 43.0 % at 540 nm as it does not display any residual absorption when fully oxidized due to the absence of electron acceptor in the polymer chain. On the contrary, **PAPD5** which contain the highest

concentration of electron acceptor displayed the lowest optical contrast of 2.0 % at the visible region.

Figure 5.16 Square-wave potential step absorptiometry of polymer **PAPD1 – PAPD5** device in the visible and NIR regions.

The coloration efficiencies of **PAPD1 – PAPD5** were 361, 212, 328, 239 and 156 cm²/C at their λ_{max} respectively. These values are significantly higher than the commonly benchmarked electrochromic polymer PEDOT of 183 cm²/C²¹.

The stability studies of the polymer electrochromic devices (ECDs) were evaluated by monitoring the percentage transmittance changes as a function of the number of cycles at the infra-red region at 1500 nm. The ECDs were repeatedly switched between + 1.6 V and - 1.6 V with full switching cycle of 40 s. This redox reversibility of ECDs relates closely to the reactivity and stability of the polarons (radical cations) which were formed during an electrochemical oxidation. From Figure 5.17, it illustrated the optical contrasts of the first and last 60 redox cycles of **PAPD3** ECD. As seen, the ECD of **PAPD3** experienced a very small drop of only 0.6 % in percentage transmittance after 800 full redox cycles, indicating **PAPD3** is a highly redox stable polymer. However, the polymers **PAPD1**, **PAPD2**, **PAPD4** and **PAPD5** exhibited much poorer stability performance as compared to **PAPD3**. The rationale for **PAPD3** ECD to have such outstanding stability performance is unclear but we postulate that a preferable ratio of electron acceptor to electron donor is preferred in a donor-acceptor conjugated polymer structure. An optimal electron acceptor ratio between 10 – 30 % could facilitate electrochromic properties such as long term redox stability.

Figure 5.17 Stability testing of **PAPD3** ECD through square-wave potential step absorptiometry monitored at 1500 nm between 1.6 V and -1.6 V with a switch time of 40 s. The transmittance for graphs is offset for clarity and it does not reflect the actual transmittance values.

Table 5.4 Performance of electrochromic device of polymers **PAPD1 – PAPD5**.

	Visible (λ_{max})				NIR (1500 nm)			
	Contrast (%)	Bleaching (s)	Coloration (s)	CE (cm^2/C)	Contrast (%)	Bleaching (s)	Coloration (s)	CE (cm^2/C)
PAPD1	43.0	55.0	10.0	361	78.6	14.5	38.7	353
PAPD2	32.1	50.4	5.5	212	59.5	12.4	29.2	300
PAPD3	16.4	73.7	8.2	328	80.5	22.5	31.6	368
PAPD4	15.5	59.8	4.9	239	66.1	17.3	54.8	394
PAPD5	2.0	71.5	9.7	156	54.0	30.8	68.6	46.4

5.4.7 Thin Film Morphology

Atomic force microscopy (AFM) was used to probe the polymers' surface over a $5 \times 5 \mu\text{m}$ area and the images are shown in Figure 5.18. The polymers have a surface roughness of 9.78, 2.61, 5.38, 7.59 and 26.6 nm for **PAPD1 – PAPD5** respectively. An increase in roughness of the surface due to the clustering of the polymer and inhomogeneous distribution of the polymer mass over the film might hinder the movement of the counter ions as well as the complete doping of the polymers during redox switching as observed from **PAPD5** which has the lowest electroactivity but the highest surface roughness. Being in agreement with our previous observation, the homogeneity and surface roughness of the polymer film play an important role in determining the performance of the electrochromic devices.^{18,19,22}

Figure 5.18 AFM images of (a) **PAPD1**, (b) **PAPD2**, (c) **PAPD3**, (d) **PAPD4**, (e) **PAPD5** thin films. Scan size: $5 \times 5 \mu\text{m}$

5.5 Conclusions

A novel ultrahigh electron deficient PAPD building block has been successfully synthesized *via* a region-selective inverse electron demand Diels-Alder (iEDDA) reaction. A new series of Donor-Acceptor polymers with good solubility was prepared using the newly synthesized PAPD unit via palladium-catalyzed cross coupling reactions. The polymers exhibited electrochromism by switching between purple/red and blue/grey when voltage is applied. They possess high electrochromic performance such as good redox stability and high optical contrasts. Furthermore, the ultrahigh electron deficiency and the ease of side chain engineering to increase solubility overall makes these PAPD units exciting new potential candidates in the field of organic electronic materials.

References

1. Ye, Q.; Neo, W. T.; Cho, C. M.; Yang, S. W.; Lin, T.; Zhou, H.; Yan, H.; Lu, X.; Chi, C.; Xu, J. *Organic Letters* **2014**, 16, (24), 6386-6389.
2. Amb, C. M.; Beaujuge, P. M.; Reynolds, J. R. *Advanced Materials* **2010**, 22, (6), 724-728.

3. Balan, A.; Baran, D.; Gunbas, G.; Durmus, A.; Ozyurt, F.; Toppare, L. *Chemical Communications* **2009**, (44), 6768-70.
4. Beaujuge, P. M.; Ellinger, S.; Reynolds, J. R. *Nature Materials* **2008**, 7, (10), 795-799.
5. Beaujuge, P. M.; Ellinger, S.; Reynolds, J. R. *Advanced Materials* **2008**, 20, (14), 2772-6.
6. Beaujuge, P. M.; Vasilyeva, S. V.; Liu, D. Y.; Ellinger, S.; McCarley, T. D.; Reynolds, J. R. *Chemistry of Materials* **2012**, 24, (2), 255-268.
7. Cui, W.; Wudl, F. *Macromolecules* **2013**, 46, (18), 7232-7238.
8. Du, Q.; Wei, Y.; Zheng, J.; Xu, C. *Electrochimica Acta* **2014**, 132, (0), 258-264.
9. Hung, Y.-C.; Chao, C.-Y.; Dai, C.-A.; Su, W.-F.; Lin, S.-T. *The Journal of Physical Chemistry B* **2012**, 117, (2), 690-696.
10. İçli, M.; Pamuk, M.; Algi, F.; Önal, A. M.; Cihaner, A. *Chemistry of Materials* **2010**, 22, (13), 4034-4044.
11. Barattin, R.; Gourdon, A. *European Journal of Organic Chemistry* **2009**, 2009, (7), 1022-1026.
12. Herrera, H.; de Echegaray, P.; Urdanpilleta, M.; Mancheno, M. J.; Mena-Osteritz, E.; Bauerle, P.; Segura, J. L. *Chemical Communications* **2013**, 49, (7), 713-715.
13. Cho, C. M.; Ye, Q.; Neo, W. T.; Lin, T.; Lu, X.; Xu, J. *Polymer Chemistry* **2015**, 6, (43), 7570-7579.
14. Kurach, E.; Djurado, D.; Rimarcik, J.; Kornet, A.; Wlostowski, M.; Lukes, V.; Pecaut, J.; Zagorska, M.; Pron, A. *Physical Chemistry Chemical Physics* **2011**, 13, (7), 2690-2700.
15. Takimiya, K.; Osaka, I.; Nakano, M. *Chemistry of Materials* **2014**, 26, (1), 587-593.
16. Mondal, R.; Becerril, H. A.; Verploegen, E.; Kim, D.; Norton, J. E.; Ko, S.; Miyaki, N.; Lee, S.; Toney, M. F.; Bredas, J.-L.; McGehee, M. D.; Bao, Z. *Journal of Materials Chemistry* **2010**, 20, (28), 5823-5834.
17. Steckler, T. T.; Abboud, K. A.; Craps, M.; Rinzler, A. G.; Reynolds, J. R. *Chemical Communications* **2007**, (46), 4904-4906.

18. Ye, Q.; Neo, W. T.; Lin, T.; Song, J.; Yan, H.; Zhou, H.; Shah, K. W.; Chua, S. J.; Xu, J. *Polymer Chemistry* **2015**, 6, (9), 1487-1494.
19. Neo, W. T.; Ye, Q.; Lin, T. T.; Chua, S. J.; Xu, J. *Solar Energy Materials and Solar Cells* **2015**, 136, (0), 92-99.
20. *CIE Technical Report No. 15.2004, Colorimetry*; CIE Central Bureau: Vienna, Austria, 2004.
21. Gaupp, C. L.; Welsh, D. M.; Rauh, R. D.; Reynolds, J. R. *Chemistry of Materials* **2002**, 14, (9), 3964-3970.
22. Huang, J. H.; Hsu, C. Y.; Hu, C. W.; Chu, C. W.; Ho, K. C. *ACS Applied Materials & Interfaces* **2010**, 2, (2), 351-9.

Chapter 6

Red-to-black electrochromism of 4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene (IDT) based polymers

Currently, there are very few studies on electrochromic polymeric materials that possess red-to-black electrochromism. In most cases, such black electrochromism is achieved by using two or more different polymers together or via viologens, instead of just using a single polymeric material. In this chapter, we synthesized a new series of solution processable electrochromic polymers that are able to achieve the switching from red to black and with high optical switching contrast ratios.

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6.1 Introduction

As discussed in Chapter 4 and 5, a common strategy in obtaining highly stable and high performance electrochromic materials is through the donor-acceptor approach. Another approach that I propose here is the use of thiophene-based building blocks. From the literature review Chapter 2.2.4.2 and 2.2.4.3, I have discussed the use of thiophene-based polymers for electrochromism. Particularly, there has been extensive research done on poly(dioxythiophene) based electrochromic polymers ever since the highly stable poly(3,4-ethylenedioxythiophene) (PEDOT) was discovered to display blue to transmissive electrochromism with high optical contrast stability. In lieu of the potential of thiophene-based electrochromic polymer system, co-polymerization with thiophene-based units could result in the synthesis of high performance electrochromic materials.

Recently, there is an increasing trend in using 4,9-dihydro-*s*-indaceno[1,2-*b*:5,6-*b'*]dithiophene (IDT)^{1,2} as the monomer for the synthesis of conjugated electronic polymers in recent years. The rise in interest is due to the presence of sp³-hybridized carbon atoms on the IDT moiety where the solubility of the polymers can be altered by attaching different functional side chains on the IDT unit^{3,4}. Moreover, the structure of the IDT moiety resembles a “ladder” structure which enhances the extent of π electron delocalization, making it highly electron-rich and fulfils the role of a good electron donor. As a result, this IDT building block has been applied extensively in area of organic thin film transistor⁵⁻⁹ and organic solar cells¹⁰⁻¹³. This in turn motivated us to explore the possibility of using the IDT building block in solution processable electrochromic polymers, where they have been much less explored.

To determine the effectiveness of using IDT monomer as a building block in the field of electrochromic materials, a new series of electrochromic polymers was synthesized using the IDT and various thiophene analogues. Here, 3,4-bis(alkoxy)thiophene and its derivatives were specially selected as they were found to give great electrochromic performances¹⁴⁻¹⁶. The new polymers obtained exhibit red to black electrochromism, a property which usually requires more than one type of polymers or viologens¹⁷⁻¹⁹. Very

few materials were reported to achieve such color transition by using only one polymer, an example of which includes poly(thiophene-3-acetic acid)¹⁷.

6.2 Experimental Methods

6.2.1 Synthesis

Materials

All reagents and starting materials were purchased from commercial sources and used without further purification unless otherwise stated.

General procedure for Stille cross-coupling polymerization

Monomer (**M1**) (0.200 mmol) and (4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-s-indaceno[1,2-*b*:5,6-*b'*]dithiophene-2,7-diyl)bis(trimethylstannane) (**M4**) (0.200 mmol) were dissolved in 12 ml of toluene. The mixture was stirred and purged with argon for 15 min, and then Pd(PPh₃)₄ (16.2 mg, 0.014 mmol) was added. The flask was purged with argon for another 15 min before the mixture was heated to 110 °C for 72 hrs. After cooling to room temperature, excess solvent was removed under reduced pressure and the polymer was precipitated in methanol. The suspension was filtered to give the crude product, which was then purified by Soxhlet extraction with acetone, hexane and chloroform. The chloroform fraction was evaporated to dryness to afford dark red solid.

IDT-Th: Yield 60%. ¹H NMR (400MHz, CDCl₃, δ): 7.16 (m, 10H, Ar H), 7.14 – 7.07 (m, 10H, Ar H), 4.07 – 4.06 (b, 4H, OCH₂), 2.55 (m, 8H, CH₂), 1.82 – 1.81 (b, 4H, CH₂), 1.43 – 1.25 (m, 68H, CH₂), 0.87 – 0.86 (m, 18H, CH₃). GPC using polystyrene (PS) in THF as standard: (M_n = 14.9 k, M_w = 22.6 k, PDI = 1.52, Degree of polymerization, DP = 11)

IDT-Pro: Yield 65%. ¹H NMR (400MHz, CDCl₃, δ): 7.21 – 7.14 (m, 10H, Ar H), 7.06 – 7.00 (m, 10H, Ar H), 4.13 (b, 4H, OCH₂), 3.56 – 3.52 (m, 4H, OCH₂), 3.41 (m, 4H, OCH₂), 2.56 – 2.55 (m, 8H, CH₂), 1.29 – 1.23 (m, 72H, CH₂), 0.87 (m, 18H, CH₃). GPC using PS in THF as standard: (M_n = 19.8 k, M_w = 32.5 k, PDI = 1.64, DP = 14)

IDT-Edot: Yield 50%. ^1H NMR (main signals) (CDCl_3): δ (ppm) 7.17 – 7.15 (m, 10H, Ar H), 7.07 – 7.00 (m, 10H, Ar H), 4.36 (b, 4H, OCH_2), 2.55 (m, 8H, CH_2), 1.46 – 1.42 (m, 8H, CH_2), 1.14 – 1.11 (m, 24H, CH_2), 0.85 – 0.71 (m, 12H, CH_3). GPC using PS in THF as standard: ($M_n = 21.5$ k, $M_w = 39.2$ k, PDI = 1.82, DP = 21)

6.2.2 Chemical Analysis

^1H NMR (400 MHz) spectra were obtained in CDCl_3 and TMS was used as the internal reference on Avance 400 MHz Bruker spectrometer. Polymer molecular weights were determined using a Alliance Waters model 2690 gel permeation chromatography system calibrated with polystyrene as the standard and THF as the eluent. Solution of polymers with concentration 5 mg/mL were prepared and filtered prior to sample injection. All UV-vis/UV-vis-NIR absorption spectra were obtained with a Shimadzu UV 3600 UV-vis-NIR spectrophotometer. Cyclic voltammetry and chronoamperometry experiments were carried out using an Autolab PGSTAT128N potentiostat.

6.2.3 Cyclic Voltammetry and Spectroelectrochemistry

For cyclic voltammetry, measurements were done in a MBraun LABmaster 130 glove box. The solutions of **IDT-Th**, **IDT-Pro**, and **IDT-Edot** in chlorobenzene (10 mg/mL) were drop casted onto glassy carbon electrode. A three electrode cell configuration with polymer-coated glassy carbon, Pt wire and Ag wire as the working, counter, and pseudo-reference electrodes respectively was employed. A 0.1 M $\text{LiClO}_4/\text{ACN}$ electrolyte/solvent couple was used, and all measurements were recorded at 50 mV/s. The pseudo-reference electrode was calibrated against the ferrocene/ferrocenium redox couple. For spectroelectrochemical studies, the polymers were analysed in their device forms.

6.2.4 Device Fabrication

Electrochromic layers of **IDT-Th**, **IDT-Pro**, and **IDT-Edot** on ITO/glass were deposited by manual blading. The gel electrolyte was prepared by mixing 0.512 g of lithium perchlorate and 2.8 g of poly(methyl methacrylate) of molecular weight 120k g mol⁻¹ in 6.65 mL of propylene carbonate (PC) and 28 ml of dry acetonitrile (ACN). A window-type absorption/transmission electrochromic device (ECD) was constructed, with the sandwich structure glass/ITO|polymer||electrolyte||ITO/glass. Parafilm was used as the spacer to prevent electrical contact between the substrates.

6.3 Results for IDT-based polymers

6.3.1 Polymers Design

Scheme 6.1 Synthetic route of **IDT-Th**, **IDT-Pro**, and **IDT-Edot**

The synthesis of IDT based polymers with different thiophene analogues was shown in Scheme 1. Three different types of thiophene-based building blocks were used to investigate their influence on the electrochromic properties of the polymers. The monomers 2,5-dibromo-3,4-bis(dodecyloxy)thiophene (**M1**), 6,8-dibromo-3,3-bis((dodecyloxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (**M2**), 5,7-dibromo-2,3-dihydrothieno[3,4-b][1,4]dioxine (**M3**) and (4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-2,7-diyl)bis(trimethylstannane) (**M4**) were first prepared according to literature procedures²⁰⁻²³. Then **M1**, **M2** and **M3** were

copolymerized *via* Stille coupling polymerization with **M4** to obtain **IDT-Th**, **IDT-Pro**, and **IDT-Edot**²⁴ respectively.

6.3.2 Polymers Characterizations

Figure 6.1 ¹H NMR spectrum of polymer **IDT-Th**

The chemical structures of the newly synthesized polymers were confirmed by ¹H NMR and the spectrum of **IDT-Th** was illustrated in Figure 6.1. The peaks at 7.07 – 7.16 ppm corresponds to the aromatic protons of the polymer. The signal at 4.06 – 4.07 ppm corresponds to the $\text{--O--CH}_2\text{--}$ of the thiophene unit. The eight protons in the region 2.55 ppm are likely to belong to the benzylic protons. The protons in the region 0.86 – 1.82 ppm are the protons on the alkyl chains.

Figure 6.2 ¹H NMR spectrum of polymer **IDT-Pro**

The spectrum of **IDT-Pro** was shown in Figure 6.2. The peaks at 7.00 – 7.21 ppm corresponds to the aromatic protons of the polymer. The signal at 4.13 ppm corresponds to the pair of O-CH₂ (H_c) from the two long alkoxy groups of the ProDOT moiety. The peaks at 3.41 – 3.56 ppm corresponds to the other two pairs of O-CH₂ from the seven membered ring of the ProDOT moiety (H_a and H_b). The eight protons in the region 2.55 – 2.56 ppm belong to the benzylic protons. The protons in the region 0.87 – 1.29 ppm are the protons on the alkyl chains.

Figure 6.3 ¹H NMR spectrum of polymer **IDT-Edot**

The spectrum of **IDT-Edot** was shown in Figure 6.3. The peaks at 7.00 – 7.52 ppm corresponds to the aromatic protons of the polymer. The signal at 4.36 ppm corresponds to the pair of O-CH₂ from of the EDOT moiety. The eight protons in the region 2.55 ppm belong to the benzylic protons. The protons in the region 0.71 – 1.46 ppm are the protons on the alkyl chains.

The polymers were produced in moderate yields of 50 – 65 % and are highly soluble in common organic solvents. This is due to the polymers having the tetraphenyl-substituted IDT units embedded in them. The molecular weights of the obtained polymers were 14 000 – 21 500 g mol⁻¹ with polydispersity index of 1.52 – 1.82 (Table 6.1).

The thermal stability of the polymers was evaluated with thermogravimetric analysis under N₂ environment and the results are seen in Table 6.1. Their decomposition temperatures

are in the order **IDT-Edot** > **IDT-Pro** > **IDT-Th**. **IDT-Edot** has the highest decomposition temperature and this could be attributed to the lack of alkyl chains on the thiophene unit which may degrade faster under heat.

Table 6.1 Synthetic yields, molecular weights, polydispersity indexes, and thermal decomposition temperatures of polymers **IDT-Th**, **IDT-Pro**, and **IDT-Edot**

Polymers	Yields (%)	M _n (g/mol)	M _w (g/mol)	PDI	T _D (°C)
IDT-Th	60	14 900	22 600	1.52	359
IDT-Pro	65	19 800	32 500	1.64	401
IDT-Edot	50	21 500	39 100	1.82	443

M_n: the number average molecular weight. M_w: the weight average molecular weight. PDI: polydispersity index. T_D: decomposition temperature at 5 % weight loss in N₂.

6.3.3 UV-vis absorption spectroscopy

The UV-*vis* absorption characteristics of polymers **IDT-Th**, **IDT-Pro**, and **IDT-Edot** were investigated in chlorobenzene solutions and as thin film states (Figure 6.4). The related data are summarized in Table 6.2. All three polymers absorbed strongly in visible region and their absorption maxima are in the region of 400 – 600 nm. Well defined and distinctly separated absorption peaks at 520 – 532 nm and at 548 – 573 nm were also observed. Going from **IDT-Th** to **IDT-Pro** to **IDT-Edot** solution, the maximum absorption bands experienced red-shifting from $\lambda_{\text{max}} = 548$ nm to 560 nm to 573 nm. However, in the thin film state, no such bathochromic shifts was detected. Notably, there was no significant shift in absorption maxima for the film states when compared to the solution states. This could be due to the four alkyl phenyl chains on the *sp*³ carbons of the IDT units as they may inhibit the formation of inter-chain $\pi - \pi$ stacking effect in the film state. This phenomenon is similar to that of my group has observed previously²⁵.

The optical bandgaps (E_g^{opt}) of **IDT-Th**, **IDT-Pro**, and **IDT-Edot** were calculated from the onset of absorption of the thin films, and were approximated to be around 2.04 – 2.08 eV. Such bandgap values are comparable to those previously synthesized IDT-thiophene

polymers²⁵, implying that the identity of co-monomer has negligible effect on the polymers' bandgaps.

Figure 6.4 Normalized UV-vis absorption spectra of **IDT-Th**, **IDT-Pro**, and **IDT-Edot** (a) in chlorobenzene and (b) as drop cast films

6.3.4 Electrochemistry

Figure 6.5 shows the cyclic voltammograms of **IDT-Th**, **IDT-Pro**, and **IDT-Edot**. All three polymers showed quasi reversible oxidation upon p-doping. The onset oxidation potential versus ferrocene is 0.43, 0.34 and 0.22 V respectively for **IDT-Th**, **IDT-Pro**, and **IDT-Edot**. The highest occupied molecular orbital (HOMO) energy levels were calculated from this onset oxidation potentials and were found to be -5.23, -5.14 and -5.02 eV for **IDT-Th**, **IDT-Pro**, and **IDT-Edot** respectively (Table 6.2). The type of attachment on the thiophene based monomers could account for the differences in HOMO energy levels. As no distinct reduction peak was observed during n-doping at negative applied potentials, the lowest unoccupied molecular orbital (LUMO) energy levels were estimated based on the HOMO and the optical bandgaps (Table 6.2).

Figure 6.5 Cyclic voltammograms of **IDT-Th**, **IDT-Pro**, and **IDT-Edot**

Table 6.2 Summary of optical and electrochemical properties of polymers in solution and in film state

Polymers	λ_{max} solution (nm)	λ_{max} film (nm)	$E_{\text{g}}^{\text{opt}}$ (eV) ^a	HOMO (eV) ^b	LUMO (eV) ^c
IDT-Th	520, 548	518, 551	2.08	-5.23	-3.15
IDT-Pro	526, 560	525, 564	2.06	-5.14	-3.08
IDT-Edot	532, 573	529, 563	2.04	-5.02	-2.98

^a $E_{\text{g}}^{\text{opt}}$ is calculated following the equation $E_{\text{g}}^{\text{opt}} = 1240 / \pi_{\text{onset}}$ (eV); ^b $E_{\text{HOMO}} = -(E_{\text{onset, ox vs ferrocene}}) - 4.8$. ^c $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{g}}^{\text{opt}}$

6.3.5 Time-dependent density functional theory (TD-DFT) calculations

To better understand the electronic properties of this series of polymers, TD-DFT calculation study at B3LYP/6-31(d) theory level were carried out. Studies were made on the monomers **M1** – **M3** and shown in Figure 6.6. From the optimized structures of dialkoxythiophene and 3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine, the aliphatic carbon atoms that were attached on the oxygen deviated from the plane of the thiophene unit, causing steric effects, hence affecting the conjugation between the oxygen atoms and the thiophene. From the distribution of the HOMO and LUMO levels, the oxygen atoms attached on the thiophene rings were involved in both the frontier orbitals, implying that the functional groups (alkoxyl, 1,4-dioxepane, and 1,4-dioxane) of the thiophene units could affect and result in different frontier orbital energy for **M1** to **M3** and **IDT-Th** to

IDT-Edot. The calculated HOMO level for **M3** (-4.446 eV) is the highest which corresponds to the experimental data where **IDT-Edot** attained the highest HOMO energy level among the three polymers.

Figure 6.6 Optimized structures of model compounds **M1** – **M3** and HOMO /LUMO profiles. The calculated energy levels are shown in parenthesis below the profiles

6.3.6 Spectroelectrochemistry

The spectroelectrochemical properties of **IDT-Th**, **IDT-Pro**, and **IDT-Edot** were studied using fabricated electrochromic devices (ECDs) and the results are shown in Figure 6.7. By increasing the applied potential from 0.0 to 2.0 V, a reduction in the absorption peak intensity was observed at the visible region for all three polymers and new absorption peaks were formed at around 840 and 1500 nm which are the polaronic and bipolaronic bands. When the applied potential is 1.5 V or above, the bipolaronic bands increased in intensity while there is a suppression of the polaronic bands. As a result, two clear isobestic points

were seen at 604 nm and 930 nm, confirming the presence of interconverting neutral polaronic and bipolaronic moieties in the three polymers.

The color of the ECDs were measured quantitatively based on 1976 CIE lab ($L^*a^*b^*$). At their neutral state, the polymers' ECDs exhibited dark red color due to the absorption peak around 526 nm. Interestingly, the absorption spectrum of the polymer film for **IDT-Edot** cover the entire visible region at its fully oxidized state, and as a result, it appeared black (Figure 6.8). As for **IDT-Th** and **IDT-Pro**, they appeared dark brown due to the slight tailing of the absorption across the visible region. Other IDT polymers linked with thiophene, thieno[3,2-b]thiophene and bithiophene were reported to exhibit a greyish hue when fully oxidized²⁵. This suggests that the attachment on the thiophene could be used as a fine-tuning tool for the color changes.

Figure 6.7 Spectroelectrochemistry of (a) **IDT-Th** and (b) **IDT-Pro** and (c) **IDT-Edot** at various applied potentials.

Figure 6.8 Color states of **IDT-Th**, **IDT-Pro** and **IDT-Edot** with $L^*a^*b^*$ values

6.3.7 Electrochromic Performance

The electrochromic performance of **IDT-Th**, **IDT-Pro** and **IDT-Edot** were evaluated using in-situ square wave potential step absorptiometry. Table 6.3 summarized the data for the optical contrast, switching time and coloration efficiencies. The ECDs of the three polymers were switched between 1.8 V and -1.8 V at 100 s interval at $\lambda_{\max}$ and 1500 nm (Figure 6.9). Generally, similar switching behaviors were observed in both the visible and NIR regions, indicating that the types of linkage units have negligible influence on the overall electrochromic performance. All three polymers attained high optical contrasts in both the visible and NIR region. Particularly, **IDT-Edot** achieved an outstanding optical contrast of 91.1% in the NIR region and will be deemed useful for NIR applications. When compared to the thiophene based IDT polymers my group has previously published²⁵, this current series of IDT polymers exhibited much higher optical contrasts. This suggests that by using thiophene analogues with alkoxy groups, the optical contrasts of the ECDs could be improved.

Figure 6.9 Square-wave potential step absorptiometry of **IDT-Th**, **IDT-Pro** and **IDT-Edot** devices in the visible and NIR regions.

The stability studies for the polymers' ECDs were evaluated by monitoring the percent transmittance changes as a function of the number of cycles at 1500 nm. The ECDs were switched repeatedly between +1.6 V and -1.6 V with a switching cycle of 18 s (Figure 6.10). All three polymers experienced good stability performance where their percentage transmittance remained fairly constant during the 60 redox cycles.

Figure 6.10 Stability testing of **IDT-Th**, **IDT-Pro** and **IDT-Edot** electrochromic devices.

The colouration efficiencies of **IDT-Th**, **IDT-Pro** and **IDT-Edot** were 326, 302 and 349 cm² C⁻¹ respectively. Interestingly, the short optical memory phenomenon which my group has observed in the thiophene based IDT polymers²⁵ was not seen for this series of polymers

and this could be due to the surface morphology of the polymer films. AFM was used to study the polymers' surfaces and the images are shown in Figure 6.11. For the thiophene based IDT polymers, distinct porous features were observed and there may be a possibility that some quencher species could have penetrated into the polymer films, neutralizing the charged polymers and leads to the short term memory effect²⁵.

On the other hand for this series of polymers, a surface roughness about 1 nm was obtained and this affirms my hypothesis that surface morphology has an effect on the optical memory. A homogenous and smooth film could aid in preventing moisture and oxygen to diffuse into the interior of the film which could neutralize the polaron and bipolarons. Therefore, it is important to control the morphology of the thin film for optimization of the electrochromic performances²⁶.

Table 6.3 Performance of electrochromic devices

	Visible (λ_{max})				NIR (1500 nm)			
	Contrast (%)	Bleaching Time (s) ^a	Coloration Time (s) ^b	CE (cm ² /C)	Contrast (%)	Bleaching Time (s) ^a	Coloration Time (s) ^b	CE (cm ² /C)
IDT-Th	36.8	66.05	0.81	503	56.9	36.16	33.52	326
IDT-Pro	50.0	45.30	1.44	295	84.7	3.61	33.58	302
IDT-Edot	37.6	60.12	3.58	242	91.1	6.05	21.19	349

^aThe bleaching time is defined as the time required for an ECD to change from its colored to bleached state. In our studies the bleaching time is defined as the time required for increase of the transmittance to 95% of the transmittance difference between the coloured and bleached states.

^bThe coloration time is defined as the time required for an ECD to change from its bleached to coloured state. In our studies the coloration time is defined as the time required for reduction of the transmittance to 95% of the transmittance difference between the bleached and coloured states.

Figure 6.11 AFM images of (a) **IDT-Th**, (b) **IDT-Pro**, (c) **IDT-Edot** thin films ($2.5 \times 2.5 \mu\text{m}$) obtained using the drop – and – spread method

6.4 Conclusions

A new series of IDT based polymers with alkoxy-thiophene analogues were synthesized via Stille coupling reaction to obtain good solubility dark red polymers in moderate yields. These polymers exhibited electrochromism by switching between dark red and dark brown/black upon oxidation and achieved high optical contrast in both visible and NIR region. With the absence of the low optical memory phenomenon and the good electrochromic properties, this series of polymers could be potential candidates for electrochromic applications.

References

1. Yang, Y., Li, Gang, *Progress in High-Efficient Solution Process Organic Photovoltaic Devices*. Springer-Verlag Berlin Heidelberg: 2015.
2. Christoph Brabec, U. S., Vladimir Dyakonov, *Organic Photovoltaics: Materials, Device Physics, and Manufacturing Technologies*. Wiley-VCH, Hoboken: 2014; Vol. 2nd edition.
3. Liu, X.; Li, Q.; Li, Y.; Gong, X.; Su, S.-J.; Cao, Y. *Journal of Materials Chemistry A* **2014**, 2, (11), 4004-4013.

4. Dang, D.; Chen, W.; Himmelberger, S.; Tao, Q.; Lundin, A.; Yang, R.; Zhu, W.; Salleo, A.; Müller, C.; Wang, E. *Advanced Energy Materials* **2014**, 4, (15).
5. Sun, Y.; Chien, S.-C.; Yip, H.-L.; Chen, K.-S.; Zhang, Y.; Davies, J. A.; Chen, F.-C.; Lin, B.; Jen, A. K. Y. *Journal of Materials Chemistry* **2012**, 22, (12), 5587-5595.
6. Bronstein, H.; Frost, J. M.; Hadipour, A.; Kim, Y.; Nielsen, C. B.; Ashraf, R. S.; Rand, B. P.; Watkins, S.; McCulloch, I. *Chemistry of Materials* **2013**, 25, (3), 277-285.
7. Bronstein, H.; Leem, D. S.; Hamilton, R.; Woebkenberg, P.; King, S.; Zhang, W.; Ashraf, R. S.; Heeney, M.; Anthopoulos, T. D.; de Mello, J.; McCulloch, I. *Macromolecules* **2011**, 44, (17), 6649-6652.
8. Chan, S.-H.; Chen, C.-P.; Chao, T.-C.; Ting, C.; Lin, C.-S.; Ko, B.-T. *Macromolecules* **2008**, 41, (15), 5519-5526.
9. Zhang, W.; Smith, J.; Watkins, S. E.; Gysel, R.; McGehee, M.; Salleo, A.; Kirkpatrick, J.; Ashraf, S.; Anthopoulos, T.; Heeney, M.; McCulloch, I. *Journal of the American Chemical Society* **2010**, 132, (33), 11437-11439.
10. Chen, K. S.; Zhang, Y.; Yip, H. L.; Sun, Y.; Davies, J. A.; Ting, C.; Chen, C. P.; Jen, A. K. Y. *Organic Electronics* **2011**, 12, (5), 794-801.
11. Yong, W.; Zhang, M.; Xin, X.; Li, Z.; Wu, Y.; Guo, X.; Yang, Z.; Hou, J. *Journal of Materials Chemistry A* **2013**, 1, (45), 14214-14220.
12. Sun, Y.; Chien, S.-C.; Yip, H.-L.; Zhang, Y.; Chen, K.-S.; Zeigler, D. F.; Chen, F.-C.; Lin, B.; Jen, A. K. Y. *Chemistry of Materials* **2011**, 23, (22), 5006-5015.
13. Wang, M.; Hu, X.; Liu, L.; Duan, C.; Liu, P.; Ying, L.; Huang, F.; Cao, Y. *Macromolecules* **2013**, 46, (10), 3950-3958.
14. Gunbas, G.; Toppare, L. *Chemical Communications* **2012**, 48, (8), 1083-1101.
15. Gaupp, C. L.; Zong, K.; Schottland, P.; Thompson, B. C.; Thomas, C. A.; Reynolds, J. R. *Macromolecules* **2000**, 33, (4), 1132-1133.
16. Gaupp, C. L.; Welsh, D. M.; Reynolds, J. R. *Macromolecular Rapid Communications* **2002**, 23, (15), 885-889.
17. Giglioti, M.; Trivinho-Strixino, F.; Matsushima, J. T.; Bulhões, L. O. S.; Pereira, E. C. *Solar Energy Materials and Solar Cells* **2004**, 82, (3), 413-420.

18. Shin, H.; Kim, Y.; Bhuvana, T.; Lee, J.; Yang, X.; Park, C.; Kim, E. *ACS Applied Materials & Interfaces* **2012**, 4, (1), 185-191.
19. Ah, C. S.; Song, J.; Cho, S. M.; Kim, T.-Y.; Kim, H. N.; Oh, J. Y.; Chu, H. Y.; Ryu, H. *Bulletin of the Korean Chemical Society* **2015**, 36, (2), 548-552.
20. Neo, W. T.; Cho, C. M.; Song, J.; Chin, J. M.; Wang, X.; He, C.; Chan, H. S. O.; Xu, J. *European Polymer Journal* **2013**, 49, (9), 2446-2456.
21. Aubert, P.-H.; Knipper, M.; Groenendaal, L.; Lutsen, L.; Manca, J.; Vanderzande, D. *Macromolecules* **2004**, 37, (11), 4087-4098.
22. Sun, Y.; Chien, S.-C.; Yip, H.-L.; Zhang, Y.; Chen, K.-S.; Zeigler, D. F.; Chen, F.-C.; Lin, B.; Jen, A. K. Y. *Journal of Materials Chemistry* **2011**, 21, (35), 13247-13255.
23. Beaujuge, P. M.; Ellinger, S.; Reynolds, J. R. *Advanced Materials* **2008**, 20, (14), 2772-6.
24. Cho, C. M.; Ye, Q.; Neo, W. T.; Lin, T.; Song, J.; Lu, X.; Xu, J. *Journal of Materials Science* **2015**, 50, (17), 5856-5864.
25. Neo, W. T.; Ye, Q.; Lin, T. T.; Chua, S. J.; Xu, J. *Solar Energy Materials and Solar Cells* **2015**, 136, (0), 92-99.
26. Ye, Q.; Neo, W. T.; Lin, T.; Song, J.; Yan, H.; Zhou, H.; Shah, K. W.; Chua, S. J.; Xu, J. *Polym. Chem.* **2015**, 6, (9), 1487-1494.

Chapter 7

Synthesis of dithienothiophene-based triphenylamine containing polymers for electrochromic applications

In this chapter, a new series of multi-electrochromic Dithienothiophene (DTT) based conjugated polymers was prepared from 2,6-bis(trimethylstannyl)dithieno[3,2-b:2',3'-d]thiophene, 2,5-dibromo-3,4-bis(dodecyloxy)thiophene and tris(4-bromophenylamine) in medium yields. Varying amount of triphenylamine (TPA) was used during the synthesis to investigate its effect on the electrochromic performances. The obtained polymers are highly soluble and possess high molecular weights. Notably, the polymers have achieved outstanding redox stability with the addition of TPA, rendering it a potential strategy to produce electrochromic polymers with higher stabilities.

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7.1 Introduction

Organic conjugated polymers are gaining popularity as electrochromic (EC) materials due to their excellent solution processability, ease of tuning their colors and ability to exhibit high optical contrasts. To be potentially suitable for commercial applications, one of the main criteria for EC materials is to create long-lasting devices with high operational stability, leading to a constant search for the optimal EC conjugated polymers.

Currently, there are two common categories of highly stable organic conjugated electrochromic polymers: donor-acceptor type and thiophene-based pure donor polymers. I have discussed such donor-acceptor type polymers in Chapter 4 and 5, and the thiophene-based pure donor type in Chapter 6. In this chapter, we will explore the possibility of a new strategy by embedding triphenylamine (TPA) units into thiophene based conjugated polymers to improve the operational stability of ECDs.

Triphenylamine-based non-conjugated polymers, such as polyimides, and epoxy polymers have been extensively researched as high performance and high stability polymers by Liou¹⁻¹¹ and his group. The structure of triphenylamine is unique as its nitrogen center, which is the electroactive site of the whole molecule, is connected to three electron rich phenyl group in a propeller-shaped geometry³. This resulted in TPA-based derivatives being highly electron rich and exhibited outstanding thermal stability as well as good film-forming ability. Moreover, they have good solubility in common organic solvents and are commonly used as hole-transport materials, photoconductors and light emitters for optoelectronics application¹². Furthermore, it was observed that TPA based materials are easily oxidized with a change in color, and experienced high redox stability when undergoing reversible redox cycles¹³. All the above are good properties that are able to fulfill the requirements of a good electrochromic material.

In this chapter, I am interested in incorporating TPA units into 3,4-dialkoxy-substituted thiophenes and dithienothiophene (DTT) based conjugated polymers. DTT which has a fused ring system is an added advantage in polymeric systems as it is able to increase the rigidity and extend π -conjugation of the system. Therefore, it is commonly used in the

synthesis of a range of compounds with promising properties for electronic and optical applications¹⁴. Unfortunately, most work on DTT-based polymers are facing the low solubility issue which is critical for commercial applications.

In this chapter, a new series of solution processable copolymers using dithieno[3,2-*b*:2',3'-*d*]thiophene (DTT) and 3,4-dialkoxythiophene building blocks were designed and synthesized. Varying ratio of TPA units will be incorporated into the polymer chains to determine its effect on the photophysical, electrochemical and EC properties.

7.2 Experimental Methods

7.2.1 Synthesis

All reagents and starting materials were purchased from commercial sources and used without further purification.

Using the synthesis of **P2** as an example:

2,6-Bis(trimethylstannyl)dithieno[3,2-*b*:2',3'-*d*]thiophene (**1**) (261 mg, 0.50 mmol), 2,5-dibromo-3,4-bis(dodecyloxy)thiophene (**2**) (275 mg, 0.45 mmol) and tris(4-bromophenylamine) (**3**) (16.1 mg, 0.033 mmol) were dissolved in 12 mL of toluene. The mixture was stirred and purged with argon for about 15 min, and then Pd(PPh₃)₄ (5 mol%, 0.025 mmol) was added. The flask was purged with argon for another 15 min before the mixture was heated to 110 °C for 48 hrs. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was precipitated in methanol. The suspension was filtered to give the crude product, which was then purified by Soxhlet extraction with acetone, hexane and chloroform. The chloroform fraction was evaporated to dryness to afford purple-red solid.

TPA1: Yield (168 mg, 52 %). ¹H NMR (main signals) (400 MHz, CDCl₃, 25 °C, TMS): δ (ppm) = 7.52 (broad, s, Ar-H), 4.18 (broad, s, OCH₂), 1.91 – 1.27 (broad, m, CH₂), 0.88 (broad, s, CH₃). GPC using PS in THF as standard: Number-average molecular weight (M_n)

= 65.9 k, weight-average molecular weight (M_w) = 90.3 k, polydispersity index (PDI) = 1.37)

TPA2: Yield (169 mg, 55 %). ^1H NMR (main signals) (400 MHz, CDCl_3 , 25 °C, TMS): δ (ppm) = 7.31 (broad, s, Ar-H), 4.18 (broad, s, OCH_2), 1.64 – 1.26 (broad, m, CH_2), 0.88 (broad, s, CH_3). GPC using PS in THF as standard: (M_n = 60.8 k, M_w = 96.6 k, PDI = 1.59)

TPA3: Yield (140 mg, 50 %). ^1H NMR (main signals) (400 MHz, CDCl_3 , 25 °C, TMS): δ (ppm) = 7.39 (broad, s, Ar-H), 4.17 (broad, s, OCH_2), 1.60 – 1.26 (broad, m, CH_2), 0.88 (broad, s, CH_3). GPC using PS in THF as standard: (M_n = 59.2 k, M_w = 99.1 k, PDI = 1.67)

TPA4: Yield (133 mg, 53 %). ^1H NMR (main signals) (400 MHz, CDCl_3 , 25 °C, TMS): δ (ppm) = 7.53 – 6.98 (m, Ar-H), 4.18 – 4.00 (m, OCH_2), 1.90 – 1.18 (broad, m, CH_2), 0.88 – 0.87 (broad, m, CH_3). GPC using PS in THF as standard: (M_n = 81.3 k, M_w = 108.5 k, PDI = 1.34)

7.2.2 Chemical Analysis

^1H NMR spectra were obtained in CDCl_3 on Avance 400 MHz Bruker spectrometer. All chemical shifts are quoted in ppm, relative to tetramethylsilane, using the residual solvent peak as a reference standard. UV-*vis*/UV-*vis*-NIR absorption spectra were obtained with a Shimadzu UV 3600 UV-*vis*-NIR spectrophotometer. Polymer molecular weights were determined using an Alliance Waters model 2690 gel permeation chromatography (GPC) system calibrated with polystyrene (PS) as the standard and THF as the eluent. Polymer of 5 mg/mL concentration was prepared and filtered prior to sample injection. The thermogravimetric analysis of the polymers was performed on a Perkin Elmer TGA-7 thermal analyzer under nitrogen at a heating rate of 20 °C/min. Differential scanning calorimetry (DSC) measurements were carried out using a PDSC Q100 from TA instruments with a heat-cool profile from -40 °C to 200 °C at a rate of 10 °C min⁻¹ for three cycles under a constant N₂ flow. Cyclic voltammetry and chronoamperometry experiments were carried out using an Autolab PGSTAT128N potentiostat. Colorimetry data was

acquired using Hunterlab ColorQuest XE and the color of each polymer film was assessed by utilizing the CIE 1976 L*a*b* color space with a D65/10° illuminant.

7.2.3 Cyclic Voltammetry and Spectroelectrochemistry

For cyclic voltammetry, measurements were done in a MBraunLABmaster 130 glove box. The solutions of **TPA1** – **TPA4** in chlorobenzene (10 mg/mL) were drop casted onto glassy carbon electrode. A three electrode cell configuration with polymer-coated glassy carbon, Pt wire and Ag wire as the working, counter, and pseudo-reference electrodes respectively was employed. A 0.1 M LiClO₄/ACN electrolyte/solvent couple was used and all measurements were recorded at 50 mV/s. The pseudo-reference electrode was calibrated against the ferrocene/ferrocenium redox couple. For spectroelectrochemical studies, the polymers were analyzed in their device forms.

7.2.4 Device Fabrication

Electrochromic layers of **TPA1** – **TPA4** on ITO/glass were deposited by a manual blading method. The gel electrolyte was prepared by mixing 0.512 g of lithium perchlorate and 2.8 g of poly(methyl methacrylate) of molecular weight 120 kg/mol in 6.65 mL of propylene carbonate and 28 mL of dry acetonitrile (ACN). A window-type absorption/transmission electrochromic device (ECD) was constructed, with the sandwich structure Glass/ITO|polymer||electrolyte||ITO/Glass. Parafilm was used as the spacer to prevent electrical contact between the substrates.

7.3 Results for TPA-based polymers

7.3.1 Polymers Design

In this section, a series of dithienothiophene-based random copolymers **TPA1** – **TPA4**¹⁵ were prepared (Scheme 1). Monomers **1** and **2** were prepared according to literature procedures^{16,17}. **TPA1** was synthesized from 2,6-bis(trimethylstannyl)dithieno[3,2-*b*:2',3'-*d*]thiophene **1** and 2,5-dibromo-3,4-bis(dodecyloxy)thiophene **2** while **TPA2** – **TPA4** were prepared with different feed compositions of 2,6-bis(trimethylstannyl)dithieno[3,2-*b*:2',3'-

d]thiophene **1**, 2,5-dibromo-3,4-bis(dodecyloxy)thiophene **2** and tris(4-bromophenylamine) (TPA) **3** to examine the effect of TPA on both the optical and electrochromic properties.

Scheme 1. Synthetic route leading to polymers **TPA1 – TPA4**.

7.3.2 Polymers Characterizations

Figure 7.1 ^1H NMR spectrum of **TPA2**.

The polymers **TPA1 – TPA4** were structurally confirmed by ^1H NMR. Using the ^1H NMR spectrum of **TPA2** as an example (Figure 7.1), the peak at around 7.31 ppm belongs to the aromatic protons and the signal at 4.18 ppm belongs to the pair of O-CH₂ from the two alkoxy groups of the dialkoxythiophene monomer. The signal at the region 0.86 – 1.64 ppm corresponds to the alkyl chains of the dialkoxythiophene.

From the ^1H NMR spectrum, we were able to estimate the actual ratio of TPA units in the polymers by using comparing the integration intensity of the aromatic peaks and the alkoxy peaks. The calculations is shown below:

Aromatic protons : $-\text{OCH}_2$ protons

$$\frac{2}{3} (1 - x) \times (12 \text{ TPA protons}) + (2 \text{ thiophene protons}) : (4 - \text{OCH}_2 \text{ protons})x$$

$$10 - 8x : 4x = 0.885 : 1$$

$$0.885 (4x) = 10 - 8x$$

$$x = 0.87$$

Using the same calculation method, the actual composition of TPA units in the polymers is shown in Table 7.1 below. It was found that the polymer compositions consistent with the reaction feed compositions.

Table 7.1 Compositions of polymer **TPA1 – TPA4**.

Polymers	X (theoretical)	X (experimental)
TPA1	1	1
TPA2	0.9	0.87
TPA3	0.7	0.66
TPA4	0.5	0.47

The four polymers **TPA1 – TPA4** were obtained in reasonable yields of 50 – 55 % and showed good solubility in common organic solvents. The increased solubility could be accounted for by the TPA moiety in the polymer chains and the long dialkoxy chains present on the thiophene monomer as well as the TPA moiety. The obtained polymers have high number-average molecular weights (M_n) ranging from 59,200 – 81,300 g/mol with polydispersity indexes of 1.34 – 1.67. These polymers attained high thermal stability with decomposition temperatures at 5 % weight loss in the range of about 325 – 337 °C under nitrogen (Table 7.2).

Table 7.2 Synthetic yields, molecular weights, polydispersity indexes, and thermal decomposition temperatures of polymers **TPA1 – TPA4**

Polymers	Yields (%)	M _n (g/mol)	M _w (g/mol)	PDI	T _D (°C)
TPA1	52	65 900	90 300	1.37	325
TPA2	55	60 800	96 600	1.59	337
TPA3	50	59 200	99 100	1.67	335
TPA4	53	81 300	108 500	1.34	333

M_n: the number average molecular weight. M_w: the weight average molecular weight. PDI: polydispersity index. T_D: decomposition temperature at 5 % weight loss in N₂.

7.3.3 UV-*vis* absorption spectroscopy

The UV-*vis* absorption spectra of **TPA1 – TPA4** were studied in chlorobenzene solutions and film states (Figure 7.2) and the data are summarized in Table 7.3. All four polymers absorbed strongly with their absorption maxima (λ_{max}) in the region of 400 – 600 nm. Going from the solution to film states, all the polymers' thin films exhibited spectral broadening and bathochromic shifts in the absorption maxima, indicating the presence of aggregation in the solid state. Going from **TPA1 – TPA4** solution, a blue-shift in the absorption maxima was observed from 526 nm for **TPA1** to 469 nm for **TPA4**. This could be due to the increasing concentration of TPA units embedded in the polymer chains. When TPA is being introduced into the polymer chains, an extensive branched system may be formed which results in a break in conjugation. This is observed clearly in **TPA4** which has the highest content of TPA. **TPA4** experienced the largest blue-shift from **TPA1** which does not have any TPA content. Although there are differences in the polymers' absorption maxima due to the presence of TPA, there is minimal effect on the polymers' bandgaps. The optical bandgaps ($E_{\text{g}}^{\text{opt}}$) of **TPA1 – TPA3** were determined from the onset of absorption of the thin films and were around 1.81 – 1.88 eV. However, for **TPA4** where a significant blue-shifting was observed due to the higher content of TPA, the bandgap was significantly higher at 1.99 eV (Figure 7.3b).

Figure 7.2 Normalized UV-vis absorption spectra of **TPA1 – TPA4** (a) in chlorobenzene and (b) as drop cast films.

7.3.4 Electrochemistry

The cyclic voltammetry was carried out to analyze the electrochemical properties and Figure 7.3 shows the cyclic voltammograms of polymers **TPA1 – TPA4**. The polymers showed quasi-reversible peaks upon p-doping and the highest occupied molecular orbital (HOMO) energy levels were estimated from the oxidation onset of the first peak. Upon *n*-doping at negative applied potentials, no distinct peak was observed and hence the lowest unoccupied molecular orbital (LUMO) energy levels could only be approximated from the optical bandgaps. A gradual deepening of the HOMO levels was observed with an increasing content of TPA in the polymers, from -4.89 eV (**TPA1**) to -5.22 eV (**TPA4**) as seen in Table 7.3. With a deeper HOMO energy level, the polymers are deemed to have enhanced ambient stability.

Figure 7.3 Cyclic voltammograms of **TPA1** – **TPA4** thin films in a 0.1M LiClO₄/ACN electrolyte/solvent couple at a scan rate of 50 mV·s⁻¹ calibrated against the ferrocene/ferrocenium couple.

Table 7.3 Summary of optical and electrochemical properties of polymers **TPA1** – **TPA4** in solution and in film state.

Polymer	Solution		Film state		^a E _g ^{opt} (eV)	^b E _{HOMO} (eV)	^c E _{LUMO} (eV)
	λ _{max} (nm)	λ _{onset} (nm)	λ _{max} (nm)	λ _{onset} (nm)			
TPA1	526	648	532	658	1.88	-4.89	-3.01
TPA2	520	661	559	677	1.83	-4.92	-3.09
TPA3	509	657	546	686	1.81	-4.98	-3.17
TPA4	469	574	474	624	1.99	-5.22	-3.23

^aE_g^{opt} is calculated following the equation E_g^{opt} = 1240/ λ_{onset film} (eV); ^bE_{HOMO} = -(E_{onset,ox} vs ferrocene) – 4.8; ^cE_{LUMO} = E_{HOMO} + E_g^{opt}

7.3.5 Spectroelectrochemistry

The spectroelectrochemical properties of **TPA1** – **TPA4** were studied using fabricated electrochromic devices (ECDs) to simulate their real-life working functionalities. Figure 7.4 shows the spectroelectrochemical spectra of **TPA1** – **TPA4**. The wavelength at maximum absorption occurs at the region 470 – 560 nm which corresponds to the π–π* transition. **TPA1** – **TPA4** possess significantly different absorption maxima which resulted

in distinct color differences of the ECDs observed at the neutral states. The colors observed range from purple to red as seen in Figure 7.5. Generally, all four polymers revealed multi-colored electrochromism at different potentials. They were observed to switch from purple/red to grey then to blue at neutral state, at 1.5 V, and at 2.0 V respectively.

When the applied potential was increased from 0.0 to 2.0 V, a suppression of the absorption peak intensity at visible region was observed with two new charge carrier absorption bands arising at the near infrared region at 700 and 1300 nm. These new absorption bands are the polaronic and bipolaronic bands formed upon oxidation. At applied potential of 1.5 V, the absorption spectrum covers the entire visible region, resulting in a grey polymer film being formed. At applied potentials of 1.6 V and above, it was observed that the polaron bands' intensity decreased but that of bipolaron bands increased, suggesting the conversion of polarons into bipolarons. Two distinct isosbestic points at about 620 and 830 nm validated the occurrence of the interconverting neutral, polaronic and bipolaronic species. When the polymers are fully oxidized at 2.0 V, a residual tailing was observed in the visible region, resulting in the polymers to appear as light blue color.

In their neutral or reduced states, **TPA1 – TPA4** exhibited a purple or red color where they have similar a^* values, but significantly different in b^* values which define their hues. Their b^* values has a wide range from -14 to 42. At potential 1.5 V, both the a^* and b^* values were seen declining considerably, thereby resulting in grey color. At the fully oxidized states, a further drop in a^* and b^* values resulted in the light blue color observed (Figure 7.5).

Figure 7.4 Spectroelectrochemistry of (a) **TPA1**, (b) **TPA2**, (c) **TPA3**, and (d) **TPA4** at various applied potentials.

Figure 7.5 Color states of **TPA1** – **TPA4** at 0.0 V (purple/red), 1.5 V (grey) and 2.0 V (blue/grey) with L* a* b* values.

7.3.6 Electrochromic Performance

The switching properties of **TPA1** – **TPA4** were investigated by chronamperometry where the polymers were switched between +1.6 V and -1.6 V at 90 s at $\lambda_{\max}$ and 1500 nm. The results are illustrated in Figure 7.6 and summarized in Table 7.4. **TPA1** – **TPA4** showed similar switching behaviors in both the visible and NIR region (Figure 7.6). The optical contrast of **TPA2** which has a small amount of TPA incorporated into the polymer chains is about 30 and 70 % at visible and NIR region respectively. These results are similar to that of **TPA1** which does not contain any TPA. Likewise for the switching time and coloration efficiencies, **TPA2** showed no substantial difference compared to **TPA1**. **TPA2** attained a bleaching time of about 30 s (visible) and 10 s (NIR) with high coloration efficiencies of about 400 cm²/C in both the visible and NIR regions.

Figure 7.6 Square-wave potential step absorptiometry of the devices in visible ($\lambda_{\max}$) and NIR (1500 nm) regions

Table 7.4. Performance of ECDs of polymers **TPA1** – **TPA4**.

	Visible(λ_{max})				NIR (1500 nm)			
	Contrast (%)	Bleaching (s)	Coloration (s)	CE (cm ² /C)	Contrast (%)	Bleaching (s)	Coloration (s)	CE (cm ² /C)
TPA1	44.7	37.0	4.9	370	79.4	14.7	19.9	406
TPA2	29.3	29.0	5.8	353	69.9	9.0	24.5	446
TPA3	14.2	52.8	8.9	68	42.8	3.3	14.3	140
TPA4	19.1	50.9	5.2	199	59.2	35.0	28.3	320

The stability studies for the polymers' ECDs were evaluated by monitoring the percentage transmittance changes against the number of cycles at 1500 nm. The ECDs were switched repeatedly between +1.6 V and -1.6 V with full switching cycle of 18 s. The first 60 cycles of the stability tests are shown in Figure 7.7. From the graphs, for polymer **TPA1**, a drastic drop in optical contrast was observed during the initial cycles and continued to decline thereafter. On the other hand, a fairly constant optical contrast was maintained for **TPA3** throughout the first 60 cycles.

As seen from the degradation graph (Figure 7.8), generally, the redox stability increases in the presence of TPA in the polymeric system. This was also demonstrated by many reports where TPA-thiophene based polymer system possessed excellent redox stability¹⁸⁻²¹. **TPA1** which has no TPA, experienced a 50 % drop in optical contrast after the first 50 cycles. On the contrary, a 50 % reduction was only observed after 300 redox cycles for **TPA3**. This shows that the 15% of TPA in **TPA3** increased the polymer's redox stability by six-fold.

Figure 7.7 Stability testing of **TPA1 – TPA4** ECDs through square-wave potential step absorptiometry. (1st 60 cycles shown)

Figure 7.8 Degradation profile of **TPA1 – TPA4** ECDs.

The stabilization of TPA on the EC stability could be explained based on Figure 7.9. When TPA was incorporated into the polymer chains, the polaron or bipolaron generated during oxidation could be on the central nitrogen atom of the TPA units and could probably delocalize with the surrounding phenyl rings, thereby increasing the stability (Figure 7.9).

Furthermore, the phenyl rings of the TPA units contribute to increasing the redox stability by providing the steric hindrance for kinetic stability of the charges²²⁻²⁴.

However, if a large amount of TPA is incorporated into the polymer system in the case of **TPA4**, it was observed that the stability is much lower. As polytriphenylamine was reported as a relatively unstable EC material⁴, the high concentration of phenylene groups in **TPA4** could account for the low stability observed. Phenylene group is comparatively less efficient in stabilizing the charges as compared with thiophene based moieties in EC materials. Thus, it can be concluded that the introduction of an optimal amount of TPA is an efficient and straightforward method for improving the EC performance for pure donor type EC polymers. This strategy could be a very useful and practically important for the preparation of applicable EC materials.

Figure 7.9 A simplified diagram showing the location of radical cations formation in the polymers.

7.4 Conclusions

A new series of thiophene based branched copolymers containing TPA moiety were prepared *via* a Stille coupling reaction. The polymers displayed multi-colored electrochromism, switching from purple/red to grey and then to a transmissive blue color.

The introduction of a small amount of TPA into the polymer chains has proven beneficial for improving the redox stability. Excessive amount of TPA, however, has opposite effect. The optimal amount of TPA was discovered for obtaining highly stable polymers, thereby proving that this strategy is probable for the preparation of highly stable EC materials.

References

1. Liou, G.-S.; Chang, C.-W. *Macromolecules* **2008**, 41, (5), 1667-1674.
2. Liou, G.-S.; Hsiao, S.-H.; Chen, H.-W. *Journal of Materials Chemistry* **2006**, 16, (19), 1831-1842.
3. Liou, G.-S.; Lin, H.-Y. *Macromolecules* **2009**, 42, (1), 125-134.
4. Liou, G.-S.; Yang, Y.-L.; Chen, W.-C.; Su, Y. O. *Journal of Polymer Science Part A: Polymer Chemistry* **2007**, 45, (15), 3292-3302.
5. Chang, C.-W.; Chung, C.-H.; Liou, G.-S. *Macromolecules* **2008**, 41, (22), 8441-8451.
6. Chang, C.-W.; Liou, G.-S.; Hsiao, S.-H. *Journal of Materials Chemistry* **2007**, 17, (10), 1007-1015.
7. Cheng, S.-H.; Hsiao, S.-H.; Su, T.-H.; Liou, G.-S. *Macromolecules* **2005**, 38, (2), 307-316.
8. Chuang, Y.-W.; Yen, H.-J.; Wu, J.-H.; Liou, G.-S. *ACS Applied Materials & Interfaces* **2014**, 6, (5), 3594-3599.
9. Hsiao, S.-H.; Liou, G.-S.; Kung, Y.-C.; Yen, H.-J. *Macromolecules* **2008**, 41, (8), 2800-2808.
10. Hu, Y.-C.; Chen, C.-J.; Yen, H.-J.; Lin, K.-Y.; Yeh, J.-M.; Chen, W.-C.; Liou, G.-S. *Journal of Materials Chemistry* **2012**, 22, (38), 20394-20402.
11. Huang, L.-T.; Yen, H.-J.; Wu, J.-H.; Liou, G.-S. *Organic Electronics* **2012**, 13, (5), 840-849.
12. Iwan, A.; Sek, D. *Progress in Polymer Science* **2011**, 36, (10), 1277-1325.
13. Chen, W.-H.; Wang, K.-L.; Liaw, D.-J.; Lee, K.-R.; Lai, J.-Y. *Macromolecules* **2010**, 43, (5), 2236-2243.

14. Cinar, M. E.; Ozturk, T. *Chemical Reviews* **2015**, 115, (9), 3036-3140.
15. Cho, C. M.; Neo, W. T.; Ye, Q.; Lu, X.; Xu, J. *ChemPlusChem* **2015**, 80, (8), 1306-1311.
16. Neo, W. T.; Cho, C. M.; Song, J.; Chin, J. M.; Wang, X.; He, C.; Chan, H. S. O.; Xu, J. *European Polymer Journal* **2013**, 49, (9), 2446-2456.
17. Frey, J.; Bond, A. D.; Holmes, A. B. *Chemical Communications* **2002**, (20), 2424-2425.
18. Cheng, X.; Zhao, J.; Cui, C.; Fu, Y.; Zhang, X. *Journal of Electroanalytical Chemistry* **2012**, 677–680, (0), 24-30.
19. Xu, C.; Zhao, J.; Cui, C.; Wang, M.; Kong, Y.; Zhang, X. *Journal of Electroanalytical Chemistry* **2012**, 682, (0), 29-36.
20. Zhao, J.; Yang, X.; Wang, S.; Yu, J. *ECS Journal of Solid State Science and Technology* **2014**, 3, (7), R121-R130.
21. Chahma, M. h.; Gilroy, J. B.; Hicks, R. G. *Journal of Materials Chemistry* **2007**, 17, (45), 4768-4771.
22. Abe, M. *Chemical Reviews* **2013**, 113, (9), 7011-7088.
23. Nelsen, S. F.; Li, G.; Schultz, K. P.; Tran, H. Q.; Guzei, I. A.; Evans, D. H. *Journal of the American Chemical Society* **2008**, 130, (35), 11620-11622.
24. Nishinaga, T.; Wakamiya, A.; Yamazaki, D.; Komatsu, K. *Journal of the American Chemical Society* **2004**, 126, (10), 3163-3174.

Chapter 8

Summary and suggestions for future work

In this chapter, a summary of this thesis is presented and the significant contributions made in this thesis is highlighted. New structural design methodologies for high performance electrochromic polymers and devices have been successfully developed in this project. An entirely novel synthetic methodology based on the inverse electron demand Diels-Alder reaction has been successfully developed where ultra-low lying lowest occupied molecular orbitals (LUMO) energy levels electron acceptors have been successfully synthesized. This methodology contributes significantly in increasing the small library of electron acceptors for use in the preparation of donor-acceptor polymers. Next, the design approach of incorporating small composition of triphenylamine (TPA) into electrochromic polymers by random copolymerization to enhance their stability significantly has been successfully demonstrated. Such method is efficient and straightforward, and could be a very useful and easy technique to prepare high performance electrochromic polymers with enhanced stability. Lastly, some suggestions for the future work is discussed.

8.1 Summary

In recent development of electronic devices, the increased focus on flexible, or foldable devices, led to a change in the manufacturing strategies resulting in a constant search for high performance and cost effective functional materials. While the search of such materials is ongoing, several challenges are present namely: (i) How to design and integrate material for current operating systems without making major changes in the device structures? (ii) How will organic electronics achieve or outperform the performance of existing inorganic counterparts? (iii) How can the manufacturing of these materials remain cost effective?

In today applications such as portable devices, which require low weight, thickness and power consumption, organic electronics could offer a competitive alternative to their conventional inorganic counterparts. π -conjugated polymers which exhibit mechanical flexibility, ease in color tuning, ease of scalability and processing, are attracting much attention in this area. As mentioned in the introducing chapters of this thesis (Chapter 1 and 2), organic polymeric materials have found widespread applications in thin film transistors, sensors, light emitting diodes, photovoltaic cells and electrochromic devices.

Considering the growing interest in organic electrochromic devices, it is essential to develop organic materials as high performance electrochromic polymers for commercial applications. Therefore, it is of utmost importance to develop design strategies for creating such new conjugated electrochromic polymers to meet with this growing demand which is also the main focus of this thesis. A variety of methods was used to characterize the resulting conjugated polymers (Chapter 3) and three different synthetic design approaches have been attempted and are presented in Chapter 4 – 7.

Chapter 4 presented a new synthetic methodology, which was successfully developed for the synthesis of electron acceptors. Through this methodology, the synthesis of novel electron acceptors could potentially increase the library of synthetic targets for use in polymerization. A unique ultrahigh electron deficient Pyrrolo[3,4-*d*]pyridazine-5,7-dione

(PPD) based monomer was synthesized and its LUMO level was found to be -3.67 eV. In order to test its feasibility as a building block for electrochromic materials, it was used in the synthesis of a new series of D-A conjugated polymers. As the PPD moiety is able to undergo side chain engineering to increase processability, the obtained polymers showed good solubility in common organic solvents. The synthesized polymers have molecular weights ranging from 13.5 to 18.8 kDa and polydispersities ranging from 1.28 to 1.50. Using polymer **PPD1** as an example, a high optical contrast of 34 and 54 % were achieved in the visible and NIR regions respectively and its electrochromic device showed a transition of purple color to transmissive blue upon oxidation. This demonstrates that the new methodology is able to synthesize suitable building blocks for EC polymers.

In Chapter 5, we continued to test the viability of the new synthetic methodology presented in Chapter 4 by synthesizing more building blocks using the same methodology. Novel electron acceptors were derived from pyrrolo-acenaphtho-pyridazine-dione (PAPD) and the LUMO levels achieved were even lower than the monomers obtained in Chapter 4. Similarly, the feasibility of this building block for EC materials is tested by incorporating into a series of conjugated donor-acceptor polymers. The obtained polymer **PAPD3** showed a color change from red to grey upon oxidation and exhibit very high optical contrast of 81 % in the NIR region. Most remarkably, the switching stability of the EC devices only resulted in a 0.6 % drop in optical contrast after 800 cycles. All these evidences demonstrated that the new synthetic methodology that we created is capable of creating new potential building blocks. Future work can be directed towards applying this new synthetic methodology in the synthesis of electron acceptors for D-A polymers.

Chapter 6 demonstrated the utilization of unexplored building block 4,9-dihydro-*s*-indaceno[1,2-*b*:5,6-*b'*]dithiophene (IDT) for EC polymers. IDT has been a common building block with good performances for many of the organic electronics, but it has not been employed in the area of electrochromic polymers. Together with dioxythiophene-based monomers which have been considered as ideal electrochromic building blocks, three polymers were synthesized to determine the efficacy of the IDT units. The resultant polymers were found to possess a unique red-to-black electrochromism which is not

commonly reported. To achieve red to black electrochromism, a combination of two or more materials is usually needed, but in our case here, the use of only one EC material is sufficient to achieve such a rare color change. As such, the application of IDT moiety in the area of electrochromic polymers is feasible as well.

Chapter 7 revealed the success of using TPA to increase the redox stability of electrochromic polymers. Varying amounts of TPA was used in the synthesis of a series of thiophene-based polymers to investigate the effects of TPA on the properties of the polymers. The obtained polymers were highly soluble in common organic solvents and possess molecular weights from 59 to 81 kDa. Moreover, the polymers exhibited multi-color electrochromism, where they changed from purple/red at the reduced state, to grey at the intermediate states, and finally transmissive blue when fully oxidized. In particular for **TPA3**, its redox stability increased tremendously as compared to the polymer without TPA. A significant six-fold improvement in stability was observed with just 15 % of TPA being incorporated into the polymer chains. Therefore, the addition of small quantity of TPA during the synthesis of the polymers could be a potential strategy to enhance the performances, in particular the stability of the electrochromic devices.

8.2 Significant Contributions

In this thesis, two significant design approaches have been developed to obtain high performance electrochromic polymers and devices. The first approach which is discussed in Chapter 4 and 5 is the design of new electron acceptors for use in the synthesis of D-A electrochromic polymers through a new synthetic methodology which has been developed based on the inverse electron demand Diels-Alder (iEDDA) reaction. The reasons why this thesis is focusing on electron acceptors are as follows:

1. The D-A approach is a well-known methodology for tuning the bandgap of conjugated polymers. Since the energy levels (bandgaps) of the D-A polymers are determined by the mixing of E_{HOMO} of the donor units, and the E_{LUMO} of the acceptor units, the

bandgaps could be tuned by tuning the E_{HOMO} of donor units to be high and E_{LUMO} of acceptor units to be low as seen in Figure 8.1.

Figure 8.1 Energy band diagram for D-A conjugated polymers

2. Since thiophene based electron donors have been extensively investigated and well established to be good electron donors, and thiophene-(Acceptor unit)-thiophene moiety are highly regarded as the model compound of D-A polymers, the search for the optimal electron acceptors is carried out. While preserving the E_{HOMO} of the electron donors, the E_{LUMO} has to be lowered in order to get a low bandgap. Nonetheless, the number of electron acceptors is limited, resulting in a need for more electron acceptors to be synthesized.
3. There has been studies done on electron acceptors that contain either an amide or imide system such as naphthalene diimide⁹ and perylene diimide¹⁰ for use in electrochromic polymers. These electron acceptors are highly electron deficient and possess high stability and good charge transport properties. Inspired from these properties, new electron acceptors are created based on this similar system. In this thesis, two new electron acceptors are designed based on the imide system. The acceptor monomer PPD is designed to have a strong electron deficiency by the addition of a highly electron deficient pyridazine group to the electron withdrawing imide. Moreover, as the imide group is open to easy side chain engineering, the prepared polymers are thus predicted to have sufficient solubility to make solution-based processing techniques viable. In an

attempt to further lower the bandgap, an acenaphtho group is incorporated to form the PAPD electron acceptor. Through the new synthetic methodology, these two new ultra-low lying LUMO energy levels electron acceptors were successfully prepared and they were presented in Chapter 4 and 5. A comparison of the newly synthesized electron acceptors (PPD and PAPD) with a range of commonly used electron acceptors (Figure 8.2 and Table 8.1) revealed that our synthesized PAPD building block exhibited the lowest LUMO levels of -3.92 eV, and our PPD building block is also among one of the lowest LUMO energy levels of -3.67 eV. This shows that our new synthetic methodology is viable in preparing ultra-low lying LUMO electron acceptors which aids in meeting the demands of new types of electron acceptors.

While very low bandgap polymers were expected from the coupling of these electron acceptors with strong electron donors, they were not achieved. Instead, PAPD polymers possessed higher bandgap than the PPD polymers. This suggests that the electron density of the donors/acceptors units are not the only factors that control the photophysical properties of the polymers. There are many other factors such as the extent of π interaction, planarity and steric hindrance which could affect the bandgap of the polymers.

By changing the type of electron acceptor and the amount of acceptor moiety in D-A type polymers, the colors, saturation and hue of the polymers could be controlled. Besides the influence of colors, there are also observation that changing the amount of acceptor moiety in D-A type polymers has impact on the electrochromic contrasts and stabilities. In chapter 4, **PPD1** with a lower electron acceptor content exhibited the larger optical contrast among the polymers. On the other hand, in chapter 5, **PAPD3** with a moderate electron acceptor content experienced the highest optical contrast of 81 % in NIR and has the highest redox stability. This could be due to both the coplanarity of the polymer chains and the acenaphtho group present. These results show that not only the identity of the electron acceptor is important, but a compromise may need to exist, where an optimal ratio of donor to acceptor ratio is required.

Figure 8.2 Th-A-Th type monomers with the central electron-deficient building blocks as discussion subject

Table 8.1 E_{LUMO} of the Th-A-Th building blocks^{1, 2}

	$E_{\text{LUMO, experimental}} / \text{eV}$	$E_{\text{LUMO, calculated}} / \text{eV}$
DPP	-3.25	-2.51
BTz	-3.23	-2.61
TzTz	-2.66	-2.18
NTz	-3.44	-2.92
TPD	-2.91	-2.19
NDI	-3.82	-3.35
PPD	-3.67	-3.08
PAPD	-3.92	-3.42

The second design approach is to incorporate small quantity of TPA into the polymer chains to increase the polymers' redox stability (Chapter 7). The typical TPA-bearing electrochromic polymers usually have high percentage of TPA units built into the polymers' main chains or as pendants, resulting in large bandgaps. In this thesis, we incorporated a small percentage of 15 % of TPA into the polymer and the stability was able to achieve a six fold improvement, without significantly affecting the bandgap and electrochromism. This simple method has proved to be effective and could be used for other polymer systems.

8.3 Suggestions for future work

Though the use of the above mentioned approaches could generally enhance the performances of the electrochromic devices, none of these approaches could achieve outstanding performances in all aspects required of an electrochromic device. Thus, there is a need to prioritize the properties which are considered to be more essential for the devices' functionality. Take for example, if the device is used for displays, the switching rate will be of utmost importance. Consequently, one could also use a combination of two or more approaches in polymers design. For example, the addition of small amount of TPA in the polymer chains has negligible influence on the color and bandgap of the polymers, but significantly increases the redox stability of the devices. One could tap on the D-A approach to tune the color of the polymers, and incorporate small amounts of TPA into the polymer chains during the synthesis so as to enhance the stability of the electrochromic devices.

Another new chemical strategy was successfully developed to carry out post-polymerization modification on benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT). This electron-rich benzodithiophene moiety has a planar and symmetrical structure, and the presence of flexible alkyl chains on benzodithiophene improves the solubility and processability of the polymers. It has been reported in various electronic applications such as efficient field-effect transistors^{3,4} and high performance bulk heterojunction solar cell materials⁵⁻⁷ but has not yet been utilized for electrochromic materials.

Usual methods of preparing functionalized thiophene moiety involve the attachment of the side chains or functional groups at the monomer stage before polymerization takes place. However, such functional groups may not be suitable for all polymerization reaction conditions, where side reactions may be generated that could terminate or affect the polymerization. Therefore, the use of post-polymerization modifications strategy can avoid such incompatibility. Moreover, the polymer upon undergone post-polymerization modification also known as polymer-analogous modification⁸ may retain some of its parent polymer's property such as the degree of polymerization.

This new strategy is efficient and direct and works by attaching bromine atoms on the 3- and 7- positions of the BDT units in the conjugated backbone. It was simply achieved through electrophilic bromination with N-bromosuccinimide. Subsequently, this brominated polymer has demonstrated successful Stille coupling with a 2-dodecylthiophene moiety as seen in Scheme 8.1. Direct functionalization on the 3 and 7- positions of the BDT unit has never been reported and hence this newly developed chemical strategy would be of great usefulness in providing new ways to attempt further modification and extension of the BDT unit for organic electronics research.

Scheme 8.1 Synthetic procedures of polymers **P1** – **P3**.

As shown from the NMR spectrum in Figure 8.3, the aromatic peak present in **P1** was ascribed to the hydrogen atoms on the 3- and 7- positions of the BDT units in the polymer backbone. After bromination, the aromatic proton peak is absent, indicating a very efficient bromination process which converted all the aromatic hydrogens on BDT units to bromine atoms. As aromatic bromine is a versatile functional group for a series of potential chemical conversions such as cyanation and palladium-catalyzed cross coupling reactions, and direct functionalization on 3- and 7- position of the BDT unit has not been reported, this newly discovered chemical strategy would render more innovative approaches to prepare BDT based oligomeric and polymeric functional conjugated systems. I demonstrated the

feasibility of the cross-coupling reaction on the brominated 3- and 7- position of the BDT unit of **P2**, by cross-coupling the bromide atoms with alkylated-thiophene, and the reaction proceeds successfully under the usual Stille coupling reaction conditions. As seen from Figure 8.3, new aromatic peaks belonging to the newly coupled thiophene moiety in **P3** clearly confirmed the success of the reaction.

Figure 8.3. NMR spectra of **P1** – **P3** (CDCl_3 , room temperature).

Preliminary results have shown that all three polymers exhibit electrochromism. At the neutral state, the electrochromic devices showed purple, pink and orange color respectively for **P1** – **P3** as seen in Figure 8.4. Upon oxidation, all three devices turned transmissive grey.

Figure 8.4 Color states of **P1**, **P2** and **P3** in neutral and oxidized states.

More work has to be done on characterizing the different parameters of the electrochromic devices to determine their efficiencies. Also, in order to test the viability of this chemical strategy, more functional groups (eg. CN) should be attempted on the 3- and 7- positions of the BDT. If this newly developed chemical strategy is feasible, it would pave new approaches for the further development and frontier orbital energy level control of BDT based oligomers and polymers for organic electronics.

8.4 Outstanding Question

During the course of this research, there is a question that was always left unanswered. How much electron acceptors should one use in a D-A polymers? During the synthesis of the D-A polymers, the amount of electron acceptors was varied across the polymers to investigate the effects of varying amounts of acceptors on the performances of the polymers. It will be interesting if there is a donor to acceptor optimal ratio for high performances which could be applied for all D-A polymers, which may result in more effective research.

References

1. Takimiya, K.; Osaka, I.; Nakano, M. *Chemistry of Materials* **2014**, 26, (1), 587-593.
2. Köse, M. E. *The Journal of Physical Chemistry A* **2012**, 116, (51), 12503-12509.
3. Tang, M. L.; Bao, Z. *Chemistry of Materials* **2011**, 23, (3), 446-455.
4. Schmidt, R.; Oh, J. H.; Sun, Y.-S.; Deppisch, M.; Krause, A.-M.; Radacki, K.; Braunschweig, H.; Könemann, M.; Erk, P.; Bao, Z.; Würthner, F. *Journal of the American Chemical Society* **2009**, 131, (17), 6215-6228.
5. Bronstein, H.; Frost, J. M.; Hadipour, A.; Kim, Y.; Nielsen, C. B.; Ashraf, R. S.; Rand, B. P.; Watkins, S.; McCulloch, I. *Chemistry of Materials* **2013**, 25, (3), 277-285.
6. Stuart, A. C.; Tumbleston, J. R.; Zhou, H.; Li, W.; Liu, S.; Ade, H.; You, W. *Journal of the American Chemical Society* **2013**, 135, (5), 1806-1815.
7. Albrecht, S.; Janietz, S.; Schindler, W.; Frisch, J.; Kurpiers, J.; Kniepert, J.; Inal, S.; Pingel, P.; Fostiropoulos, K.; Koch, N.; Neher, D. *Journal of the American Chemical Society* **2012**, 134, (36), 14932-14944.
8. Gauthier, M. A.; Gibson, M. I.; Klok, H.-A. *Angewandte Chemie International Edition* **2009**, 48, (1), 48-58.
9. Koyuncu, F.B.; *Electrochimica Acta* **2012**, 68, 184-191.
10. Baysec, S.; Unlu N. A.; Hacıoglu, S. O.; Udum, Y. A.; Cirpan, A.; Toppare, L. *Journal of Macromolecular Science, Part A*, **2014**, 52, 1-9.

APPENDIX

List of Ph.D Related Publications:

1. Ye, Qun; **Cho, Ching Mui**; Neo, Wei Teng; Xu, Jianwei, "Donor-acceptor polymers for electrochromic applications", PCT Int. Appl. (2016), WO 2016010485 A1 20160121
2. **Cho, Ching Mui**; Ye, Qun; Neo, Wei Teng; Lin, Tingting; Lu, Xuehong; Xu, Jianwei, "Ultrahigh electron-deficient pyrrolo-acenaphtho-pyridazine-dione based donor-acceptor conjugated polymers for electrochromic applications", Polymer Chemistry (2015), 6(43), 7570-7579
3. **Cho, Ching Mui**; Ye, Qun; Neo, Wei Teng; Lin, Tingting; Song, Jing; Lu, Xuehong; Xu, Jianwei, "Red-to-black electrochromism of 4,9-dihydro-s-indaceno[1,2-b:5,6-b'] dithiophene-embedded conjugated polymers", Journal of Materials Science (2015), 50(17), 5856-5864
4. **Cho, Ching Mui**; Neo, Wei Teng; Ye, Qun; Lu, Xuehong; Xu, Jianwei, "Dithienothiophene-based triphenylamine-containing branched copolymers for electrochromic applications", ChemPlusChem (2015), 80(8), 1306-1311.
5. Ye, Qun; Neo, Wei Teng[#]; **Cho, Ching Mui**[#]; Yang, Shuo Wang; Lin, Tingting; Zhou, Hui; Yan, Hong; Lu, Xuehong; Chi, Chunyan; Xu, Jianwei, "Synthesis of Ultrahighly Electron-Deficient Pyrrolo[3,4-d]pyridazine-5,7-dione by Inverse Electron Demand Diels-Alder Reaction and Its Application as Electrochromic Materials", Organic Letters (2014), 16(24), 6386-6389. [#] These authors have contributed equally to this work.
6. Neo, Wei Teng; **Cho, Ching Mui**; Shi, Zugui; Chua, Soo-Jin; Xu, Jianwei, "Modulating high-energy visible light absorption to attain neutral-state black electrochromic polymers", Journal of Materials Chemistry C: Materials for Optical and Electronic Devices, 4 (1), 28-32

7. Neo, Wei Teng; Shi, Zugui; **Cho, Ching Mui**; Chua, Soo-Jin; Xu, Jianwei, "Effects of Chemical Composition, Film Thickness, and Morphology on the Electrochromic Properties of Donor-Acceptor Conjugated Copolymers Based on Diketopyrrolopyrrole", *ChemPlusChem* (2015), 80(8), 1298-1305
8. Ding, Guoqiang; **Cho, Ching Mui**; Chen, Chuanxiang; Zhou, Dan; Wang, Xiaobai; Tan, Angeline Yan Xuan; Xu, Jianwei; Lu, Xuehong, "Black-to-transmissive electrochromism of azulene-based donor-acceptor copolymers complemented by poly(4-styrene sulfonic acid)-doped poly(3,4-ethylenedioxythiophene)", *Organic Electronics* (2013), 14(11), 2748-2755
9. Lim, Shaun Zhi Hao; Neo, Wei Teng; **Cho, Ching Mui**; Wang, Xiaobai; Tan, Angeline Yan Xuan; Chan, Hardy Sze On; Xu, Jianwei, "Electrochromic π -Conjugated Copolymers Derived from Azulene, Fluorene, and Dialkyloxybenzothiadiazole", *Australian Journal of Chemistry* (2013), 66(9), 1048-1056
10. Neo, Wei Teng; Loo, Lee May; Song, Jing; Wang, Xiaobai; **Cho, Ching Mui**; Chan, Hardy Sze On; Zong, Yun; Xu, Jianwei, "Solution-processable blue-to-transmissive electrochromic benzotriazole-containing conjugated polymers", *Polymer Chemistry* (2013), 4(17), 4663-4675
11. Neo, Wei Teng; **Cho, Ching Mui**; Song, Jing; Chin, Jia Min; Wang, Xiaobai; He, Chaobin; Chan, Hardy Sze On; Xu, Jianwei, "Solution-processable multicolored dithienothiophene-based conjugated polymers for electrochromic applications", *European Polymer Journal* (2013), 49(9), 2446-2456