ABSTRACT

The main objective of the present research is to investigate structure property of a series of carbazole-thiophene. Electronic properties were evaluated by UV-Vis, cyclic voltammogram and theoretical calculations. Particularly, the effects of conjugation connectivity on photophysical and electrochemical properties, as well as the correlation between carbazole-thiophene were linked at the N-9 position for different core groups via biphenyl, dimethylbiphenyl and phenyl were studied. Literature review on the carbazole-thiophene moieties and their derivatives and methods for the synthesis of carbazole-thiophene have been described. The literature search on the various potential application of carbazole-thiophene were also studied. A brief introduction on the background of this study was provided which gave an insight of the key step involved in the synthesis of carbazole-thiophenes via Suzuki Miyaura and Ullmann coupling reaction. Results of the physical properties on the electronic absorption spectroscopy via UV-visible and fluorescence were discussed. We noted a maximum absorption wavelength at a higher absorbance, indicating that the attachment of thiophene groups at the 3- and 6-positions of the carbazole significantly enhances the optical properties. The absorption bands of all of the compounds were gradually red shifted, when the thiophene group was connected to the carbazole at the 3- and 6-positions and the extent of π-conjugation in the compounds increased, as expected. After the functionalization of the carbazole groups, the fluorescence maxima ($\lambda_{em}$) gradually red shifted upon the addition of thiophene group, resulting a significant red shift in the emission spectrum. E_{pa} values for 2.38 (P1), 2.39 (P2), 2.40 (P3), 2.41 (P4), 2.42 (P5), 2.43 (P6), 2.44 (P7), 2.45 (P8), 2.46 (P9) and 2.47 (P10) are cathodically shifted compared to those for 1.4 (CBP), 2.36 (CDBP), 2.37 (BCP) by the subsequent addition of thiophene molecules, demonstrating that the connection with thiophene at
the 3- and 6-positions on carbazole of 1.4 (CBP), 2.36 (CDBP) and 2.37 (BCP) gives rise to high electrochemical stability and effectively enhances donor ability. Carbazole substituted with thiophene groups at the 3- and 6-positions leads to greater stabilization of HOMO and LUMO energy levels where the band gap (ΔE) of all the compounds is significantly reduced and such unit can be introduced into the backbone of 1.4 (CBP), 2.36 (CDBP) and 2.37 (BCP) π-conjugated small molecules to develop new materials with low band gap that may have potential application in optoelectronic fields. A brief introduction of theoretical calculation was provided. A brief theoretical calculation on the carbazole-thiophenes compounds by geometrical optimization and frontier molecular orbital calculations were also discussed. All computation were performed using GAUSSION 09W software package employing the Density Functional Theory (DFT) method with correlation functional B3LYP and 6-31G as functional basis set.
ABSTRAK

ACKNOWLEDGEMENTS

This thesis arose in part out of years of research that has been done and I would like to record my gratitude to my supervisor Professor Dr. Azhar Ariffin for his supervision, advice and guidance from the very early stage of this research as well as giving me extraordinary experiences throughout the work.

I gratefully acknowledge my co-supervisor, Associate Professor Dr. Khaulah Sulaiman for her advice, supervision and crucial contribution, which made her a backbone of this research and so to the thesis.

My special thanks to the Chemistry Department of University Malaya, for providing me the opportunities to fully utilize the lab facilities and the staff members of Chemistry Department for their cooperation.

Furthermore, thankful for the support of the Chemistry Department, Faculty of Science University Malaya, Kuala Lumpur, Malaysia, and for financial support from the Long term Research Grant Scheme (LRGS) (LR003-2011A), High Impact Research Grant (HIR) (UM.C/625/1/HIR/208) (J-21001-73865) and Postgraduate Research Grant (PPP) (PG021-2013A) for the financial support.

My parents Damit Haji Mojitar and Zaitun Mohd Zain deserve special mention for their inseparable support and prayers. Mohd Dzul Alfian, Ahmad Tharmizi and Deen Khairree, thanks for being supportive and caring siblings.

Words fail me to express my appreciation to my husband Azmi Ahmad whose dedication, love and persistent confidence in me. My beloved children Siti Aisyah and Afiq Haikal, who bring a smile to my face and joy to my heart.

Finally I would like to thank everybody who was important to the successful realization of thesis, as well as expressing my apology that I could not mention personally one by one.
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(Effect of Thiophenes)

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(Effect of Core Unit)

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<th>Symbol</th>
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<td>AcOH</td>
<td>glacial acetic acid</td>
</tr>
<tr>
<td>A&lt;sub&gt;calcd&lt;/sub&gt;</td>
<td>calculated absorbance</td>
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<td>abs</td>
<td>absorbance</td>
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<td>9-BBN</td>
<td>9-borabicyclo[3.3.1]nonane</td>
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<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CN</td>
<td>acetonitrile</td>
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<td>CuI</td>
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<td>CCl&lt;sub&gt;4&lt;/sub&gt;</td>
<td>carbon tetrachloride</td>
</tr>
<tr>
<td>CB</td>
<td>conduction band</td>
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<td>°C</td>
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<td>CBP</td>
<td>(4,4’-bis(9-carbazolyl)biphenyl)</td>
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<td>CDBP</td>
<td>(4,4’-bis(9-carbazolyl)-2,2’-dimethylbiphenyl)</td>
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<td>CV</td>
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<td>BCP</td>
<td>1,4-di(9H-carbazol-9-yl)benzene</td>
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<td>VB</td>
<td>valence band</td>
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<td>DFT</td>
<td>density functional theory</td>
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<td>dye-sensitized solar cell</td>
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<td>Eq.</td>
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<td>equivalent</td>
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<td>h</td>
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<td>MHz</td>
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<td>MS</td>
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<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
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<td>lowest unoccupied molecular orbital</td>
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<td>IR</td>
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<tr>
<td>ITO</td>
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<td>M</td>
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<td>organic solar cell</td>
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<tr>
<td>PCE</td>
<td>power conversion efficiency</td>
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<td>PPh$_3$</td>
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<td>SnMe₂Cl</td>
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Figure A24: $^1$H and $^{13}$C NMR of compound 2.48 (P11) in CDCl$_3$  
Figure A25: $^1$H and $^{13}$C NMR of compound 2.49 (P12) in CDCl$_3$  

APPENDIX B: THEORITICAL CALCULATION  

Table B1: Cartesian Coordinates (Å) of the Optimized Structure of compound 1.4 (CBP) at the B3LYP/6-31G Level  
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Table B8: Cartesian Coordinates (Å) of the Optimized Structure of compound 2.42 (P5) at the B3LYP/6-31G Level

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Table B10: Cartesian Coordinates (Å) of the Optimized Structure of compound 2.44 (P7) at the B3LYP/6-31G Level

Table B11: Cartesian Coordinates (Å) of the Optimized Structure of compound 2.45 (P8) at the B3LYP/6-31G Level

Table B12: Cartesian Coordinates (Å) of the Optimized Structure of compound 2.46 (P9) at the B3LYP/6-31G Level

Table B13: Cartesian Coordinates (Å) of the Optimized Structure of compound 2.47 (P10) at the B3LYP/6-31G Level

APPENDIX C: UV, FLUORESCENCE SPECTRA AND FERROCENE CV CURVE

Figure C1: Electronic absorption spectra of a) CBP, P1, P4, P7 and P9, b) CDBP, P2, P5, P8 and P10 and c) BCP, P3 and P6.

Figure C2: Emission spectra of a) CBP, P1, P4, P7 and P9, b) CDBP, P2, P5, P8 and P10 and c) BCP, P3 and P6.

Figure C3: Cyclic voltammogram of ferrocene in 0.1 M Bu$_4$NPF$_6$ THF.
CHAPTER 1: INTRODUCTION

1.1 Introduction

The most promising approaches to provide neat energy is by converting sunlight into electricity, which is an ample and renewable energy resource. Organic photovoltaic (OPV) can be fabricated by comparatively simpler and cost-effective processing system, such as screen printing, ink jet printing, dip coating and roll to roll processing for achieving low cost solar energy conversion devices. Additionally, lightweight and mechanically flexible is an extra advantages.

The greatest challenges of OPV are relatively low power conversion efficiency (PCE) compared to their single crystal silicon counterparts and the relative of electron accepting materials, which paired with hole conducting polymers to induce exciton dissociation at the interface.

In last four years, photovoltaic (PV) market showed average growth of 100 %. 87 % of the worldwide solar cell productions are primarily silicon based solar technologies. Further upstream, within the last couple of years to upgrade and maintain their respective in current market shares was by installation of new facilities in which polysilicon procedures kept up the PV market (European Photovoltaic Industry, 2010; Steeman et al., 2012).

Despite the growth in the PV industry, the particular PV market remains its dependency on beneficial government incentives. As a result, continuously lower costs along with improve cell efficiencies are the main challenge in manufactured silicon PV.
Simple processing techniques to make low-cost with lightweight products and fabricated on large-area represent organic solar cells (OSCs) as the potential candidate. Langmuir-Blodgett (LB) technique was used in the manufacture of high quality ultrathin, anisotropic organic film in sensorics, electrooptics and electronic devices and also biomimetic system (Brook & Narayanaswamy, 1998; Cabala et al., 1997; Iraqi & Wataru, 2004; Nguyen & Potje-Kamloth, 1999; Selampinar et al., 1995; Swager, 1998).

Throughout early April 2011, according to the Nikkei, a Japanese business daily, Mitsubishi Chemical reportedly 9.2 % conversion efficiency of organic solar cells. Three other firms – Konarka Technologies in Lowell, Massachusetts; SolarmerEnergy Inc. in El Monte, California; and Heliatek in Dresden, Germany reporting greater efficiency of 8 %. The figure could soon top up to 10 % and possibly reach 15 %. The technologies of organics efficiency is lower than others but they are catching up at fast pace. Another concern is lifetime of organic solar cells where sun can degrade many of organic solar cells (Service, 2011).

1.2 Organic Photovoltaic versus Polymer Photovoltaic

Organic photovoltaics (OPVs) were among the low cost alternatives to the silicon-based PV technology. Organic material based was utilized for the sensitive and specific chemical sensor of human exposure to chemical present in environment. A specific popular feature of organic cells in some applications where silicon technology is less capable has extremely developed. Under investigation of material science, band gap of PV polymer has successfully forced from near UV or visible towards near infrared region (NIR). Today, band gap of several PV polymers centered close to the
maximum of sun photon flux known as low band gap polymers (Blouin et al., 2008). Most research could not demonstrate schematic studies to improve OPV cell for optimal performance in most application of transparent PV cell over long time scale (Romero-Gáñ mez et al., 2015).

In recent years, most polymer solar cells makers focused on polymer designing which absorb all visible light down into the reds, the low-energy of the spectrum. The amount of light absorbed would improve the cells’ energy conversion. Polymer tandem makers try to make a barrier layer between two cells but the right barrier can be hard to make, because they must be not only conductive to collect electrical charges in the cells but also optically transparent. (Service, 2011)

1.3 Organic Photovoltaic Operation Principal

Mobility of charge carriers in molecular semiconductor critically determined the performance of organic cells. Charge transport properties in terms of material parameters is complicated due to the complex phenomena between range of length and scales control of charge transport in disordered organic semiconductors. Until now, trial and error efforts were done rather than schematic design in order to strengthen charge mobilities in molecular semiconductor. Nevertheless, recently the very first predictive simulation advancement reviews of charge transport in disordered organic semiconductors (Nelson et al., 2009).
Planar-layered framework of organic light-absorbing layer is sandwiched in two different electrodes in most organic solar cells. The two electrodes are (semi-)transparent, often Indium-tin-oxide (ITO) or a thin metal layer and aluminium (calcium, magnesium, gold and others are also used) is frequently used. The development of light emitting diodes (LEDs) and OPV are connected to each other, however the fundamental theory of light-harvesting organic PV cell is reverse of the particular principle in LEDs (Figure 1.1). Standard electrode materials are shown in the Figure 1.1. Within each instances, an organic material is sandwiched between two electrodes. In PVs electrons tend to be gathered at the metal electrode and holes are collected at the ITO electrode. The reverse happens in a LED: electrons are introduced at the metal electrode (cathode), that recombined with holes introduced at the ITO electrode (anode) (Spanggaard & Krebs, 2004).

![Diagram](image)

**Figure 1.1:** A PV device (right) is the reverse of LED (left).

In LEDs an electron is introduced at the low-workfunction electrode (cathode) and a hole at the high-workfunction (anode). Light was emitted upon recombination of electron and the hole (Burroughes *et al.*, 1990; Friend *et al.*, 1997; Greenham *et al.*, 1993). In contrast with a PV device, light is absorbed an
electron and then promoted from the highest occupied molecular orbital (HOMO) towards the lowest unoccupied molecular orbital (LUMO) creating an exciton (Figure 1.2). On irradiation an electron is promoted to the LUMO leaving a hole behind in the HOMO. Electrons are collected at the Al electrode and holes at the ITO electrode.

**Figure 1.2:** Energy levels and light harvesting. $\Phi$: workfunction, $\chi$: electron affinity, IP: ionisation potential, $E_g$: optical band gap.

Exciton dissociation in the PV device is where electron have to reach one electrode and the hole must reach the other electrode. Electrical field is necessary in order to attain charge separation that offered by the asymmetrical ionisation energy/workfunctions of the electrodes. Electron-flow is more favored from the low-workfunction electrode towards the high-workfunction electrode (forward bias) caused by the asymmetry, which this phenomenon referred to as rectification. Positioning levels of energy in light harvesting process is depicted in Figure 1.2.
Three-dimensional crystal lattice the individual LUMOs as well as HOMOs inside a crystalline inorganic semiconductor form a conduction band (CB) and valence band (VB). Weak intermolecular between LUMOs and HOMOs in three-dimensional crystal lattice could not form a CB and VB, which is fundamentally different from most organic dye semiconductor. For instance, charge carrier mobility within organic and polymeric semiconductor is generally low compared with inorganic semiconductors due to localize hoping charge transport, instead of transport within a band.

Low dielectric constant makes charge separation is more difficult within organic semiconductor. Photon absorption creates a totally free electron along with a hole (sometime called charge carriers) in several inorganic semiconductors, whereas the excited electron is bound to the hole (at room temperature) within organic semiconductors. Approximately, conjugated polymers lay between the inorganic semiconductor and organic dyes. Generally, excitons tend to be localized and in some cases they are delocalized on specific chain segments which known as palarons (Frankevich et al., 1992; Rauscher et al., 1990).

Depending on organic semiconductors in simple PV devices and diodes, the electrode interface site reach by main exciton (other sites consist defects in the crystal lattice, absorbed oxygen or even impurities) (Rothberg, Yan, Papadimitrakopoulos, et al., 1996; Rothberg, Yan, Son, et al., 1996). The effectiveness of light harvesting limit by the thickness of the device, if the layer is too thick, the exciton never reaches the electrode interface since excitons created in the center of the organic layer. Instead they recombine as describe above. Distances of standard exciton diffusion are on the order of 10 nm.
1.4 Thiophene-Based for Organic Solar Cells (OSCs)

Thiophene draws a substantial interest in advanced materials such as organic TFTs, light emitting devices, and dye-sensitized organic solar cells. Thiophene derivatives possess an interesting behavior in spectroscopic properties, electrochemical behaviors, as well as liquid crystalline characteristic (Facchetti et al., 2003; Funahashi et al., 2007; Koumura et al., 2006; McCullough, 1998; Murphy et al., 2005; Tour, 1996; Yamashiro et al., 1999; Yasuda et al., 2006). A wide variety of thiophene derivatives developed through artificial methods has been a significant issue in organic functionality (Briehn et al., 2001; Izumi et al., 2003; Kobayashi et al., 2006; Masui et al., 2004; Satoh & Miura, 2007; Sugie et al., 2006; Takahashi et al., 2006; Yokooji et al., 2004; F. Zhang & Bäuerle, 2007).

Design and synthesis of conjugated materials utilized thiophene as the importance building block because they have amazing optic, electronic and redox properties in addition to prominent supramolecular behavior on the solid surface or in the bulk. Thiophene is a heterocyclic rings which could be selectively modified at the α- and β-position as well as the sulfur atom to establish flexible structures. For example, solution processibility and self-assembly capability guarantees by affixing long alkyl side-chains at the α- or even β-position which incorporation from the α-linked thiophene units into oligomers makes a competent conjugation across the primary chain backbone. Higher polarizibility posses by the soft sulfur atoms in thiophene rings make the prominent contribution towards the electron-donating and charge-transport properties. Formerly, oligothiophenes as donor materials in OSCs have been widely investigated as the narrow absorption of sunlight spectra indicated low PCEs (Noma et al., 1995b).
1.5 Literature Review

Fascinating in new \( \pi \)-conjugated organic materials are caused by their potential applications in numerous electronic devices (Klauk, 2006; Sheats, 2004), such as organic photovoltaics (OPVs) (Klauk, 2006; Sheats, 2004), organic light emitting diodes (OLEDs) (Klauk, 2006; Sheats, 2004), organic field effect transistor (OFETs) (Anthony, 2008; Dimitrakopoulos & Malenfant, 2002; Mas-Torrent & Rovira, 2008; Murphy & Frechet, 2007; Newman et al., 2004; Yamashita, 2009) and sensors (J. Chen et al., 2003; Thomas et al., 2007). A remarkable electrochemical and optoelectrical properties posses by thiophene, a sulfur-containing aromatic heterocycle due to their various potential applications in a wide range of the organic electronic devices (Cheng et al., 2009; Guo et al., 2009; Haas et al., 2009; Okamoto et al., 2008; Shinamura et al., 2010; Sista et al., 2010; L. Zhang et al., 2009). Thiophene derivatives are now excellent applicants and crucial precursors for the design and synthesis variety of advanced novel material (Mishra et al., 2009; Perepichka & Perepichka, 2009). Carbazole moiety an excellent hole-transporting material has been widely used in organic light-emitting diodes (OLEDs) (Kato, Shimizu, et al., 2012).

Rigorous research in organic low band gap materials has been the subject owing to their light-harvesting capability for organic photovoltaics (OPVs) (Boudreault et al., 2010; Brabec et al., 2011; Bundgaard & Krebs, 2007; Cheng et al., 2009; Inganäs et al., 2009; Rasmussen et al., 2011; Thompson & Fréchet, 2008; Van Mullekom et al., 2001; Zhou et al., 2012). Factors that counteract the decrease in band gap are steric hindrance, which preventing a completely planar configuration in conjugated compounds (Havinga et al., 1992, 1993).
Synthesizing short-chain conjugated compounds have become interesting researches, as they are not amorphous and could be synthesized as well-defined structures (Y. Lei et al., 2013). The size and shape of molecules are as much a part of molecular structure as is the order in which the component atoms are bonded. Contrary to the impression from structural formulas, complex molecules are not flat and formless, but have well-defined spatial arrangements that are determined by the lengths and directional characters of their chemical bonds. This means that it is often possible to design ionic compounds having certain well-defined and desirable properties. Furthermore, the distinctive electronic properties, high photoluminescence quantum effectiveness and thermal stability have attracted much attention on shorter conjugated molecules models (Brownell et al., 2013; Morvillo & Bobeico, 2008).

Carbazole known as hole-transporting as well as electroluminescent unit. This unique properties permit numerous photonic application (photoconductivity, electroluminescence and photorefraction) for polymers that contains carbazole moieties in the primary or side chain (Mello et al., 2002; Sanda et al., 2004). A large number of 3,6-functionalized carbazole derivatives have been analyzed as carbazole easily functionalized through electrophilic aromatic substitution at its 3,6-positions (para position from the nitrogen atom) with high electron density (Gauthier & Frechet, 1987). Consequently, due to the extremely electron donating ability of mixed π-conjugated polymers and oligomers made of carbazoles and thiophenes are a brand new course of functional compounds (Melucci et al., 2007; Zhan et al., 2001; Zotti et al., 2002).

The 3,6-di(2-thienyl) substituent of compound 1.1 can be found at the para positions in accordance with the nitrogen atom of the carbazole moiety, while the 2,7-di(thienyl) substituent of compound 1.2 are at the meta positions. Therefore, the
electron-donating capability of the carbazole moiety in 1.1 is actually improved through the 3,6-di(2-thienyl) groups compared to 1.2 due to the cross-conjugation. The electronic effects of thienyl groups in the carbazole moiety 1.1 and 1.3 had been acquired at the B3LYP/6-311G**//B3LYP/6-31G* level of theory which provide considerably different value 4.09 and 3.47 eV respectively, where most of LUMO density on 1.3 resides on 2,2’-bithiophen-5-yl unit (Kato, Shimizu, et al., 2012).

Carbazole-based materials exhibit hole-transport properties even though numerous acceptor moieties such as 4,4’Bis(carbazol-9-yl)biphenyl (Matsusue et al., 2005) 1.4 (CBP) synthesized by Ullmann reaction have been popular as donors in a number of electronic devices (Koene et al., 1998).
Shin-ichiro Kato et al. (2014) prepared a number of systematically elongated alternating 2,7-linked and 3,6-linked carbazole-thiophene oligomers which has been synthesized by Suzuki-Miyaura coupling in Scheme 1.1 and Scheme 1.2, respectively. Higher degree of π-conjugation and high fluorescence quantum yields was observed in connection with thiophene at 2,7-position of carbazole \( (\textbf{1.5}) \) and donor ability improved at 3,6-positions \( (\textbf{1.12}) \). 2,7-linked oligomers successfully extend π-conjugation as the increase in the molecular length.

\[
\begin{align*}
\text{1.5}
\end{align*}
\]

The synthesis of \( \textbf{1.5} \) was outlined in Scheme 1.1. The lithium-bromine exchange between \( \textbf{1.6} \) and \( n\text{-BuLi} \) followed by the successive addition of trimethoxyborane and aqueous HCl gave boronic acid \( \textbf{1.7} \) which was converted to boronic acid pinacol ester \( \textbf{1.8} \) in 48% yield in two steps. Bromide \( \textbf{1.10} \) was prepared by the coupling reaction of \( \textbf{1.8} \) and 3 eq of 2,5-dibromothiophene \( \textbf{1.9} \) in 20% yield and then was subjected to the coupling reaction with \( \textbf{1.11} \) to furnish \( \textbf{1.5} \) in 63% yield.
The synthesis of compound 1.12 was outlined in Scheme 1.2. The synthesized following a two-step transformation from 1.1. Thus, the bromination of 1.1 with NBS was carried out and then the cross-coupling reaction of dibromide 1.13 with 1.14 afforded the desired 1.12 in 64% yield.
Scheme 1.2: Synthesis of 1.12. Reaction conditions: (i) NBS, DMF, rt (ii) [Pd(PPh)_3]_4, K_2CO_3, DME / water, reflux.

Shin-ichiro Kato et al. (2012) also report bicarbazoles in a large series of conjugated carbazole dimmers, which had been synthesized through Suzuki-Miyaura, Sonogashira, Hay and McMurry coupling reaction. Connection at the 1-,2-, or 3-position directly or via an acetylenic (1.15) (Scheme 1.3) or olefinic (1.16) (Scheme 1.4) spacer in both carbazole ensures high extent of \( \pi \)-conjugation at the 1-position of carbazole, while electron-donating ability improves at the 3-position and both acetylenic and olefinic spacers extend \( \pi \)-conjugation, which also leads to the increase of the donor ability.
The synthesis of compound 1.15 was outlined in Scheme 1.3. For the synthesis of 1.15, compound 1.17, was synthesized by the Sonogashira reaction of 1.6 and trimethylsilylactylene (TMSA) followed by the removal of TMS group with \( \text{K}_2\text{CO}_3 \). The Sonogashira reaction of 1.18 and 1.6, however, produced no desired 1.15. Therefore, bromide 1.6 was converted to iodide 1.19 with excess amounts of CuI/LiI in DMSO. The reaction of 1.18 and 1.19 with Pd(PPh\(_3\))\(_4\) catalyst and CuI cocatalyst was first examined, but 1.15 was again not isolated. Finally, when Pd(PPh\(_3\))\(_4\) was employed as the sole catalyst in the absence of CuI, the homocoupling reaction of 1.18 was suppressed to some extent and 1.15 was obtained.

Scheme 1.3: Synthesis of compound 1.15. Reaction conditions: (i) TMSA, PdCl\(_2\)(PPh\(_3\))\(_2\), CuI, PPh\(_3\), piperidine, 100 °C. (ii) K\(_2\)CO\(_3\), THF / MeOH, rt. (iii) Pd(PPh\(_3\))\(_4\), THF / Et\(_3\)N, reflux (based on 1.17).
The synthesis of compound 1.16 was outlined in Scheme 1.4. The preparation of 1.16 rely on McMurry coupling reactions (1989). Thus, lithium–bromine exchange between 1.6 and n-BuLi followed by the successive addition of piperidine-1-carbaldehyde and aqueous NH₄Cl gave aldehyde 1.20, which was allowed to react with TiCl₄ and zinc powder in THF to furnish 1.16 in 78% yield.

Scheme 1.4: Synthesis of compound 1.16. Reaction conditions: (i) a) n-BuLi, THF, -78 °C b) Piperidine-1-carbaldehyde, 78 °C to rt c) NH₄Cl aq. (ii) Zn, TiCl₄, THF / pyridine, reflux.

Hannah Ziehlke et al. (2011) documented a series of dicyanovinyl-terthiophenes (1.21) with various alkyl side chains. Absorption, energy levels, and thin film roughness were affected by the variance of side chain substitution patterns where the morphology of the evaporated thin film was depending on the length of the substances. The effectiveness of energy transfers is dependence on the type of side chain.
Synthesis of compound 1.21 was outlined in Scheme 1.5. Dis-tannylated dimethylthiophene 1.23 is prepared from 2,5-dibromo-3,4-dimethylthiophene 1.22 by lithiation with n-butyllithium and subsequent quenching with trimethylstannyl chloride. Two-fold Pd0-catalyzed Stille-type coupling reaction of central building block 1.23 and dicyanovinyl-substituted bromothiophene 1.24 gives 1.21 in 80% yield.

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{Me} \\
\text{Br} & \quad \text{Br} \\
\text{Me}_3\text{Sn} & \quad \text{SnMe}_3 \\
\text{Br} & \quad \text{Br}
\end{align*}
\]

(i) \[\text{Me}_3\text{SnCl} \]

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{Me} \\
\text{SnMe}_3 & \quad \text{SnMe}_3 \\
\text{Br} & \quad \text{Br}
\end{align*}
\]

(ii) \[\text{Pd(PPh}_3\text{)}_4\]

\[
\begin{align*}
\text{NC} & \quad \text{CN} \\
\text{NC} & \quad \text{CN} \\
\text{NC} & \quad \text{CN} \\
\text{NC} & \quad \text{CN}
\end{align*}
\]

\[
\begin{align*}
\text{NC} & \quad \text{CN} \\
\text{NC} & \quad \text{CN}
\end{align*}
\]

Scheme 1.5: Synthesis of compound 1.21. Reaction conditions: (i) a) n-BuLi b) SnMe₃Cl (ii) Pd(PPh₃)₄.

Naresh Duvva et al. (2015) have synthesized two push-pull substances employing carbazole alkyl thiophene (1.25) and carbazole triphenylamine (1.26) as donor moieties. They have use the cyanoacrylic group as the acceptor. The moderate photovoltaic efficiency of the sensitizers may be related to the poor light absorption of the sensitizers in the visible area. Density functional theory (DFT) calculations have shown a powerful intramolecular charge transfer character, with the HOMOs of both the sensitizers exclusively localized on the corresponding donor moieties and LUMOs on the cyanoacrylic acid acceptor. However, less extended and intense absorption spectra in the visible region caused by the calculated high dihedral angle between the carbazole donor and the phenyl bridge impedes the conjugation across the dyes backbone.
The synthetic approach to these single donor (1.25) and double donor (1.26) metal-free organic sensitizers involves Miyaura borylation, Suzuki and Knoevenagel reactions and the synthetic routes are outlined in Schemes 1.6 and 1.7.

Compound 1.25 was synthesized by Suzuki coupling reaction of compound 1.27. In a typical synthesis, compound 1.27 and 5-hexylthiophene-2-yl-2-boronic acid 1.28 were dissolved in DME and Na₂CO₃ solution. Pd(PPh₃)₄ were added and reaction mixture refluxed for 18 h gives 1.29. Compound 1.29, cyanoacetic acid and ammonium acetate were dissolved in acetic acid and refluxed for 14 h gives 1.25 in 76 % yield.
Scheme 1.6: Synthesis of compound 1.25. Reaction conditions: (i) Pd(PPh₃)₄, Na₂CO₃, DME, H₂O. (ii) AcOH, cyanoacetic acid, CH₃COO’NH₄⁺, reflux 14 h.

Compound 1.26 was synthesized similar to the procedure adopted for preparing compound 1.25. Compound 1.31 was synthesized by palladium catalyzed Suzuki coupling between compound 1.27 and compound 1.30. KOAc and Pd(PPh₃)₂Cl₂ were dissolved in DMF reflux for 6 h give 1.31. Compound 1.31, cyanoacetic acid and ammonium acetate were dissolved in acetic acid and refluxed for 14 h gives 1.26 in ~76 % yield.

Scheme 1.7: Synthesis of compound 1.26. Reaction conditions: (i) Pd(PPh₃)₂Cl₂, KOAc (ii) AcOH, cyanoacetic acid, CH₃COO’NH₄⁺, reflux 14 h.
Koumura and co-workers (Koumura et al., 2006; Z.-S. Wang et al., 2008) systematically investigated the effect of π-conjugated system series of n-hexyl-substituted oligothiophenes (1.32 and 1.33), which are carbazole sensitizers with regard to DSSCs overall performance.
The molecular structure of the dyes in DSSCs substantially depends on the number and position of thiophene moieties. The existence of n-hexyl chains linked to the thiophene groups cause retardation of charge recombination, which led to an increase in electron lifetime. The addition of n-hexyl chains to the thiophene groups has improved open-circuit photovoltage ($V_{oc}$) and the solar to electric power conversion efficiency ($\eta$) of DSSCs.

For the very first time, Miyasaka and co-workers used the carbazole based polymer (poly(N-vinyl-carbazole)) (PVK) (1.34) in dye-sensitized solar cell as a hole transporting layer and the cell demonstrated power efficiency of 2.4 and 2.0 % at 0.25 and 1 sun (AM 1.5) light irradiation, respectively (Ikeda & Miyasaka, 2005).

![Diagram](image-url)
Recently, Han and co-workers reported efficient carbazole based sensitizer showing versatile flexible circle chain embracing $\pi$-spacer (1.35), that has an efficiency of 9.2 %. In the majority of the carbazole sensitizers, cyanoacrylic group is often utilized as an anchoring group (J. Liu et al., 2013). Chemical substituents that can act as an anchor, enabling their adsorption onto a metal oxide substrate. This adsorption provides a means for electron injection, which the process that initiates the electrical circuit in a DSSCs.

![Image of compound 1.35]

1.35

Synthesis of compound 1.35 was outlined in Scheme 1.8. Bromination of 1.36 with NBS was carried out and then the cross-coupling reaction of dibromide 1.37 with 1.38 afforded compound 1.39. Compound 1.41 was synthesized by palladium catalyzed Suzuki coupling between compound 1.39 and compound 1.40. A solution of aldehyde 1.41, cyanoacetic acid, piperidine in CHCl$_3$ was reflux for 10 h to afford the desired dye 1.35 as a purple solid in 87 % yield.
Scheme 1.8: Synthesis of compound 1.35. Reaction conditions: (i) NBS (ii) K₂CO₃, Pd(PPh₃)₄, THF, H₂O, 50 °C (iii) K₂CO₃, Pd(PPh₃)₄, 1,4-dioxane, H₂O, 90 °C. (iv) piperidine, CHCl₃, reflux for 10 h.

Nevertheless, Harima and co-workers (2013) reported new carbazole based sensitizers bearing pyridine anchoring group along with a thiophene (1.42 and 1.43) unit as a π-bridge, accomplished the efficiency of 1.61 %. By substituting correct functional groups at C3, C6 and N9 positions of the carbazole scaffold, it is possible to tune the optoelectronic properties and therefore the device performance.
Xinliang Feng (2011) reported thiophene-based conjugated oligomer with molecular architectures from 1D to 3D in developing high-performance OSCs. This represent an enormous source of materials for OSCs and have taken aggressive benefits more polymeric materials. A well balanced device overall performance depending on their synthetic reproducibility and the ability to form long range crystalline ordering in the solid state which is beneficial for the charge carrier transport. Furthermore, low molecular weights, great thermal stabilities and device fabrication could be done by vacuum-deposited or solution-processable (or both) method. Currently, oligothiophene-based donor materials in organic solar cells have achieved excellent PCEs of over 8 % ("Heliatek GmbH Press Release," 2010).

High PCE over 7 % for OPVs had been achieved with 2,7-carbazole-containing polymer such as poly(2,7-carbazole-alt-dithienylbenzothiadiazole) (1.44) (T.-Y. Chu et al., 2011).
Over the past three years, a considerable investigation associated with new building blocks in developing high end polymer semiconductors has been an extensive research (He et al., 2014). For instance, the film morphology and molecular stacking could be control by the side chain in order to significantly enhance the charge carrier mobility (T. Lei et al., 2012). The energy levels might reduce while maintaining the band gaps almost unchanged by fluorinated building blocks (H.-Y. Chen et al., 2009; Liang et al., 2009). However, development of new building blocks still needs a lot of work.

1.6 Objective of the Study

One strategy to design new functional materials would be to imitate the actual framework from the well-known as well as well-studied substances, even though their synthesis may be a great challenge. Structurally, CBP can be viewed as a carbazole end–capped biphenyl. To design new semiconducting compound for OPV application, we investigate the behaviors associated with a series of thiophene-carbazole-based derivatives. The objective of this research are i) to synthesize a series of symmetric carbazole-thiophene based derivatives, ii) to investigate their electronic behavior by varying the conjugation connectivity as well as the number of thiophene units to study the actual structure-property relationships associated with carbazole-thiophene-based materials that have taken biphenyl, benzene and dimethylbiphenyl as core and iii) to provide theoretical calculation of the electron distribution for HOMO and LUMO of carbazole-thiophene derivatives. In this context, we report the synthesis and fundamental properties, such as the structure features as well as electronic, photophysical properties on the basis of UV-Vis, fluorescence emission, cyclic voltammetry, supported by quantum chemical calculation (DFT) had been utilized in characterization of these new compounds.
CHAPTER 2: SYNTHESIS OF CARBAZOLE-THIOPHENE BASED DERIVATIVES

2.1 Introduction

Organic electronic devices have drawn a lot of interest for their properties. They could be easily tuned by suitable molecular design and could be produced on a large scale at low prices.

Formations of new carbon-carbon bonds are important reactions in development of complex bio-active drugs, agrochemicals and also ingeniously-designed organic materials. These bio-active materials show novel electronic, optical or mechanical properties, which can play significant role in the development of nanotechnology.

During the past forty years, the most crucial carbon-carbon bond-forming methodologies included utilizing transition metals to mediate the reactions in a controlled and selective method. Probably the most favored of those chemistries is Suzuki coupling, that is cross-coupling reaction of numerous organoboron compounds with organic electrophiles catalyzed by a palladium complex. It is now the fundamental element of any synthetic route to construct organic complex. This reaction turned out to be extremely versatile.

Since it was discovered a century ago (Ullmann, 1903), products of Ullmann-type aryl are essential in the pharmaceutical and material world, which has been observed on industrial-scale applications. The range of this reaction, nevertheless, is
significantly restricted to its high reaction temperature (Ley & Thomas, 2003). Classic Ullmann methods have been recognized for a complete hundred years for C-N, C-S, C-O and plus other bond formation. The entire evidence acquired demonstrated that copper noticeably much similar to palladium in cross-coupling chemistry.

Main method for the synthesis of novel heterocyclic compounds have been developed by copper-catalyzed C-N, C-O, and C-S bond formations between aryl halides and NH, OH, SH-containing heterocyclic (Beletskaya & Cheprakov, 2004; Klapars et al., 2002; Kunz et al., 2003; Kwong & Buchwald, 2003; Ley & Thomas, 2003; Lindley, 1984; Okano et al., 2003). Wide range of compounds from simple to complex molecules were regularly prepared by utilized copper-mediated C(aryl)-O, C(aryl)-N, and C(aryl)-S bond formation.

2.2 Suzuki-Miyaura Coupling

Common strategy and effective way for the formation of carbon-carbon bonds are palladium-catalyzed cross-coupling reaction between organoboron compounds and organic halides. Recently, this particular reaction may be known as Suzuki coupling, Suzuki reaction, or Suzuki-Miyaura coupling (SM). The coupling reaction offers several extra benefits. For an example, it is unaffected by the existence of water and also tolerate an extensive selection of functional groups, and generally regio- and stereoselective. Furthermore, the inorganic by-product from the reaction mixture is non-toxic and can be removed easily, therefore making the Suzuki coupling appropriate for commercial procedures (Akira Suzuki, 1999).
Recently, SM cross coupling that produces biaryls was the most popular even though other methods are also available, for examples, Kharash coupling, Negishi coupling, Stille coupling, Himaya coupling, Liebeskind-Srogl coupling and Kumuda coupling. Moderate reaction conditions and the industrial accessibility of variety boronic acids which are environmentally safer compared to other organometallic reagents were the key benefit of SM coupling (Kotha et al., 2002). Additionally in large-scale synthesis, the elimination of boron-containing byproducts is easy to handle. The SM reaction has become dominance within the last couple of years, which responsive in industrial synthesis of pharmaceuticals and fine chemicals since the conditions have many desirable features for large-scale synthesis (Kotha et al., 2002).

Aryl bromides, aryl iodide and aryl triflate frequently utilized in the Suzuki reaction. Aryl chlorides only utilized along with electron-deficient groups (Miyaura & Suzuki, 1995). However triflates are thermally labile, susceptible hydrolysis and costly in preparation. Aryl sulphonates tend to be a better choice and inexpensive compared to triflates because there are readily available starting materials. They could be find easily through phenol and more stable.

The different in the SM cross coupling reaction between coupling rate of the iodo- versus bromo-function offers some advantages in organic synthesis. Stepwise functionalisation procedure could be used for multifunctional substrates. This specificity of the reaction only for the iodinated carbon if the coupling partner is not utilized in excess.
In SM cross-coupling reaction, Na$_2$CO$_3$ base was typically used but often inadequate with sterically challenging substrates. In many cases, Ba(OH)$_2$ or K$_3$PO$_4$ were used which produce better yields. Other bases such as K$_2$CO$_3$, CS$_2$CO$_3$, KF and NaOH are also have been utilized. Within the coordination sphere of the palladium and the formation of the Ar-Pd(II)-OH from Ar-Pd(II)-X, the active base may speed up the transmetallation step (Figure 2.1) (Kotha et al., 2002). Pd-mediated SM cross-coupling reaction has several disadvantages. Only aryl bromides and iodides may be utilized. Chlorides only react gradually. In many cases, coupling products of phosphine-bound aryls byproducts are often formed such as self-coupling products. Particular disadvantage has formed scrambled derivatives which most probably Pd(PPh$_3$)$_4$ catalyst and phenyl group of the PPh$_3$ becomes affected in the product. Homocoupling products can be prevented under oxygen free conditions by de-gas the solvents to remove dissolved oxygen.

*Figure 2.1:* Catalytic cycle for cross-coupling of organic halides and organoboranes.
In the past ten years, numerous options in Suzuki reaction continually to develop such as solid phase Suzuki coupling may be created by utilizing either resin-bound aryl halides with solution phase boronic acids (A. Suzuki & Brown, 2003) or vice versa (Carboni et al., 1999).

Industry is trying to make use of much more environmentally-friendly procedures in which Suzuki coupling well suited. The adjustment of reaction either in aqueous media or with trace amounts of catalyst was actively investigated.

2.2.1 Suzuki Miyaura Reaction

2.2.1.1 Biphenylene System

SM cross-coupling reaction has become a useful tool for assembling biphenyl (paraphenyl) systems. They are important structural element in most liquid crystal, fluorescent compounds and conducting polymer (Kotha et al., 2002).

The Pd(PPh₃)₄ – catalysed SM cross coupling reaction of 3,8-dibromo-1,10-phenanthroline 2.1 with the arylboronic acids 2.2 and 2.3 to give the coupling products 2.4 and 2.5 (Scheme 2.1) (Dietrich-Buchecker et al., 1999).

![Scheme 2.1: Synthesis of 2.4 and 2.5. Reaction conditions: (i) Pd(PPh₃)₄ (10%), Na₂CO₃, toluene, 80 °C, 12 h.](image)

Scheme 2.1: Synthesis of 2.4 and 2.5. Reaction conditions: (i) Pd(PPh₃)₄ (10%), Na₂CO₃, toluene, 80 °C, 12 h.
2.2.1.2 Binapthyl System

Chiral binaphthyl-based ligands are useful for enantio- and diastereo-selective synthesis of organic molecules. Recent example of the synthesis of binaphthyl ligands via the SM cross-coupling reaction.

Pu et. al. have used the Pd(PPh$_3$)$_4$-catalysed SM cross-coupling of a fluorine containing binapthyl ligand 2.8 by using the SM cross-coupling of the preformed binaphthyl-based bispinacolboronate 2.6 with the fluorine-substituted halobenzene 2.7 (Scheme 2.2) (Huang & Pu, 2000).

Scheme 2.2: Synthesis of 2.8. Reaction conditions: (i) a) Pd(PPh$_3$)$_4$ aq., KOH, THF, (ii) 6N HCl, THF, reflux.
2.2.1.3 Reaction Involving 9-BBN Derivatives

The SM cross-coupling reaction has played an important role in the synthesis of complex natural products like ciguatoxin, gambierol, epothilone, phomactin, and halichlorine. In this regard, hydroboration of alkenes followed by the SM cross-coupling reaction has been used as a key step.

Johnson and Johns have reported the synthesis of the glycosidase inhibitor bis-aza sugar 2.12 by using the double SM cross-coupling reaction. The required borane is prepared from the terminal diene 2.9 and is coupled with the vinyl bromide 2.10. Peperidine ring formation was initiated by cleavage of trisubstituted olefin 2.11 and cyclization was accomplished via an intramolecular reductive amination to yield aza sugar 2.12 (Scheme 2.3) (Johns & Johnson, 1998).
Scheme 2.3: Synthesis of \( \text{2.11} \) and \( \text{2.12} \). Reaction conditions: (i) a) 9-BBN-H, THF b) PdCl\(_2\)(dpdpf), K\(_3\)PO\(_4\), DMF. (ii) a) O\(_3\), CH\(_2\)Cl\(_2\)/CH\(_3\)OH, -78 °C, DMS b) NaBH\(_3\)CN, pH 4 buffer, THF c) Pd/C (Degussa type), H\(_2\), MeOH.

2.2.1.4 Formation of Carbon–Heteroatom (C–N, C–O and C–S) Bonds

Lam and co-workers reported the Cu(OAc)\(_2\)-catalysed N-arylation of different NH-containing functional groups including amines, anilines and phenols with aryl \( \text{2.13} \) and vinylboronic acids \( \text{2.14} \) by using N-methyl- morpholine oxide, pyridine N-oxide, 2,2,6,6-tetramethyl-1- piperidinyl oxide and etc. as additives which facilitates the oxidation of Cu(II) to Cu(III) and easy reductive elimination to form the C – N and C –
O cross-coupled products 2.15 (Scheme 2.4) (Lam et al., 2001). SM cross-coupling reaction is more user-friendly than other coupling reactions and is widely employed in the synthesis of various natural and non-natural products.

Scheme 2.4: Synthesis of 2.15. Reaction condition: (i) Cu(OAc)$_2$ additive (1:1 eq) base (2 eq) CH$_2$Cl$_2$.

2.3 Ullmann Coupling

Aryl-aryl bond formation has been known for more than a century and was one of the first reactions using a transition metal (copper in its higher oxidation states should be considered a transition metal). The evolution of this field is also a good illustration of the development of modern organic chemistry, particularly the increasing importance of transition-metal catalysis. Indeed, during the first 70 years of the 20th century, copper was almost the only metal usable for aryl-aryl bond formation, initially as copper metal in the reductive symmetrical coupling of aryl halides (the Ullmann reaction). Several modifications and improvements of this reaction still justify today the use of copper derivatives in several synthetic cases.
For hundred years copper-promoted arylation of aromatic amines, initially diarylamines recognized as the classical Ullmann reaction (Ullmann, 1903). Demands severe extended heating at 200 °C or higher, in the existence of Cu(I) and Cu(II) salts, oxides, or Cu bronze, etc. and polar high-boiling solvents in the presence of base. Until now, copper-catalyzed cross-coupling only limited to iodo and bromo derivatives, while chloro-derivatives have not likely focus on regarded as for this chemistry with only a few exception (Beletskaya & Cheprakov, 2004).

Two conceivable mechanism are those involving radical intermediates and oxidative addition/reductive elimination (Figure 2.2) which have been suggested in the literature (Lindley, 1984) for such Ullmann-type condensation.

![Figure 2.2: Two alternative oxidative addition/ reductive elimination mechanistic pathways for copper catalyzed nucleophilic aromatic substitutions with aryl halides.](image)
Scheme 2.5: Expected behavior of 1,4-diiodobenzene 2.16 in the event that mechanism might involve radical anion intermediates.

According to literature (Bowman et al., 1984; Paine, 1987; Rossi & de Rossi, 1983), unimolecular pathway considerably faster even at brief reaction times, result in quasi-exclusive disubstitution. The nucleophile with halo-aryl radical 2.17 produced radical anion 2.18. Compound 2.18 does not undergo bimolecular electron transfer (to copper (II) or 1,4-diiodobenzene) to provide monosubstitution product, but instead formed aryl radical 2.20 by losing the second iodide ion (Scheme 2.5).
2.3.1 Reductive Coupling of Aromatic Halides (The Ullmann Reaction)

2.3.1.1 Symmetrical Coupling

The Ullmann reaction, initially was first reported in 1901. It has long been employed by chemists to generate a C-C bond between two aromatic rings. Typically two molecular equivalents of aryl halide are reacted with one equivalent of finely divided copper at high temperature (above 200 °C) to form a biaryl and a copper halide.

Symmetrical coupling of substituted benzene rings and aromatic heterocycles using copper as the reducing and coupling agent can be performed in both inter- and intramolecular reactions.

Sessler et al. (1994) developed an efficient procedure for the preparation of alkyl-substituted 2,2''-bipyrroles 2.25. It involved first the protection of the nitrogen atom (with di-tert-butyl-dicarbonate) 2.24 as the key step, then an Ullmann-type coupling, followed by the deprotection of the resulting 2,2''-bipyrroles 2.25.

\[ R_1 R_2 \quad \text{CO}_2\text{Et} \quad (i) \quad R_1 R_2 \quad \text{CO}_2\text{Et} \]

\[ Z = \text{tert-butoxycarbonyl} \]

\[ \text{Scheme 2.6: Synthesis of 2.25. Reaction condition: (i) 4.7 eq Cu(0), DMF, 100 °C.} \]
In an effort to maximize the extended $\pi$-conjugation in polymers and to study their corresponding optical and electronic properties, Tour et al. (1994) performed the synthesis of a zwitterionic pyrrole-derived polymer 2.29 using the Ullmann reaction (Scheme 2.7).

Scheme 2.7: Synthesis of 2.29. Reaction conditions: (i) n-BuBr, PTC, NBS, THF (ii) HNO$_3$, H$_2$SO$_4$ (fuming) (iii) Cu bronze, DME, 200 °C.
2.3.1.2 Unsymmetrical Coupling

A new class of suspected mutagens in the atmospheric environment, Suzuki et al. (1997) reported an Ullmann cross coupling between nitro-substituted iodobenzoates 2.30 and iodonaphthalenes 2.31 to synthesize polynitrobenzanthrenes 2.32 (Scheme 2.8). To obtain those high yields of unsymmetrical coupling a large excess of 4 eq iodonaphthalene 2.31 has to be used.

![Scheme 2.8: Synthesis of 2.32. Reaction condition: 7 eq Cu(0), DMF, 140-150 °C, 4 h.](image)

General synthesis of polythiophenes 2.35 bearing a carbonyl group (or other strongly electron-withdrawing substituents) directly attached to the 3-position of the thiophene ring 2.33, Pomerantz et al. (1995) naturally thought about using the Ullmann reaction (Scheme 2.9). Furthermore, polymers obtained by this route had better properties (i.e., lower polydispersity and longer conjugation lengths) than polymers prepared by a Ni(0) coupling reaction.
Scheme 2.9: Synthesis of 2.35. Reaction conditions: (i) a) Br₂, AcOH b) SOCl₂ c) ROH, pyridine (ii) Cu, DMF, 140 – 150 °C, 7 days.

2.4 Results and Discussion

2.4.1 Targeted Compounds

The explorations of green, affordable and renewable energy have obtained substantial improvement in harvesting sunlight energy. Low-cost and lightweight product of organic solar cells (OSCs) signify the guaranteeing prospect for versatile substrate potential to be fabricated on large-area.

A variety of application for example solar cells, displays, sending or radio frequency identification tags (RFIDs) (Dennler et al., 2007) make frequently used of organic semiconductor host materials. Carbazole structures such as 1.4 (CBP) (4,4’-bis(9-carbazolyl)biphenyl), 2.36 (CDBP) (4,4’-bis(9-carbazolyl)-2,2’-dimethylbiphenyl) (Hoffmann et al., 2010; Tanaka et al., 2004) and 2.37 (BCP) 1,4-di(9H-carbazol-9-yl)benzene (Kaafarani et al., 2013; Koene et al., 1998) are current interest which
promising possibilities for solid-state lighting. The architectural of these carbazole derivatives gives the effective white organic light emitting devices (WOLEDs) (Kamtekar et al., 2010).

Wide range of donor materials of conjugated small molecules own powerful absorption of sunlight spectra and great charge mobility. The most promising materials for OSCs are thiophene-based π-conjugated oligomers (Mishra et al., 2009; Noma et al., 1995a). Thiophenes posses remarkable optic, electronic and redox properties which become promising foundation for the design and synthesis of conjugated materials. Additionally, they have a prominent supramolecular behavior on the solid surface or in the bulk. For instance, competent conjugation along the primary chain backbone through α-linked thiophene units into oligomers.

We present here in depth the synthesis of carbazole-thiophene derivatives and the spectroscopic and quantum mechanical study on the electronic structures of these compounds, focusing on the impact associated with electron donor thiophene group on the 1.4 (CBP), 2.36 (CDBP) and 2.37 (BCP) on the nature of the optical transitions and discuss the relationship between the molecular architectures and photovoltaic properties. The structural features and the electronic photophysical properties of 1.4 (CBP), 2.36 (CDBP), 2.37 (BCP), 2.38 (P1), 2.39 (P2), 2.40 (P3), 2.41 (P4), 2.42 (P5), 2.43 (P6), 2.44 (P7), 2.45 (P8), 2.46 (P9), 2.47 (P10), 2.48 (P11) and 2.49 (P12) (Figure 2.3) based on UV-vis, fluorescence spectroscopies, cyclic voltammetry and theoretical calculation were investigated by evaluating these compound with the documented compound of 1.4 (CBP), 2.36 (CDBP) and 2.37 (BCP).
Figure 2.3: Structure of compounds.
2.4.2 Synthesis of Compound 1.4 (CBP), 2.36 (CDBP) and 2.37 (BCP).

Scheme 2.10 outlined the synthesis of compounds 1.4 (CBP), 2.36 (CDBP) and 2.37 (BCP). The Ullmann coupling reaction were performed on carbazole (2.50) with either 4,4-diiodobiphenyl (2.51), 4,4-diiodo-2’2’-dimethyl-1,1-biphenyl (2.52) or 1,4-diodobenzene (2.53) to give 1.4 (CBP), 2.36 (CDBP) and 2.37 (BCP) in 50 %, 60 %, and 80 % yields, respectively. Compounds 1.4 (CBP) (Kaafarani et al., 2013; Koene et al., 1998), 2.36 (CDBP) (Schrögel et al., 2011) and 2.37 (BCP) (Kaafarani et al., 2013; Koene et al., 1998) are known compounds. The procedure that we use have been adopted from the literature procedure reported by Schrögel et al. (2011).

Scheme 2.10: Synthesis of 1.4 (CBP), 2.36 (CDBP) and 2.37 (BCP). Reaction condition: (i) K$_2$CO$_3$, Cu, 18-crown-6, o-dichlorobenzene (DCB), and reflux for 3 days.
2.4.3 Synthesis of Compound 2.38 (P1), 2.39 (P2) and 2.40 (P3).

The synthesis of compounds 2.38 – 2.49 (P1-P12) was described in Scheme 2.11– 2.14. The key steps in the synthesis of the compounds involved Suzuki Miyaura (Miyaura & Suzuki, 1995) and Ullmann coupling (Beletskaya & Cheprakov, 2004) reactions. The detailed procedures for the synthesis of the compound are described in the experimental section.

The syntheses of compounds 2.38 (P1), 2.39 (P2) and 2.40 (P3) were achieved in three steps starting from carbazole (2.50) as described in Scheme 2.11. The first step involved iodination of 2.50 using 0.5 eq of iodine to give 3-iodocarbazole (2.25). This was followed by Suzuki Miyaura cross coupling of 2.54 with thiophene-2-boronic acid pinacol ester (2.55) to produce monothienyl-substituted carbazole (2.56). Ullmann coupling of compound 2.56 with compounds 2.51, 2.52 and 2.53 afforded compounds 2.38 (P1), 2.39 (P2) and 2.40 (P3) in 26 %, 35 % and 48 % yields, respectively (Damit et al., 2016). Proposed mechanism of Suzuki Miyaura cross coupling reaction for compound 2.56 and Ullmann coupling reaction for compound 2.38 were showed in Figure 2.4 and 2.5, respectively. All other compounds were followed similar reaction mechanisms.

Many of drawbacks of the classical Ullmann reaction such as high reaction temperatures, long reaction times, high metal loadings and low conversion proved unsatisfactory yield (Evano et al., 2008; Mangione & Spinalevello, 2015; Wipf & Lynch, 2003). Certain functional groups such as free NH or OH are not adequate and may cause side reactions, Pd-based methods are sensitive to moisture and oxygen and large
scale applications of this type of chemistry is restrictive because of the cost of the metal catalysts and ligands (Mangione & Spanevello, 2015).

\[ 2.50 \xrightarrow{(i)} 2.54 \xrightarrow{(ii)} 2.56 \xrightarrow{(iii)} 2.38 \text{(P1)} \]
\[ 2.51 \]
\[ 2.52 \text{(P2)} \]
\[ 2.53 \text{(P3)} \]

**Scheme 2.11:** Synthesis of 2.38 (P1), 2.39 (P2) and 2.40 (P3). Reaction conditions: (i) I\(_2\) (0.5 eq), AcOH and reflux for 10 min (ii) K\(_2\)CO\(_3\), Pd(PPh\(_3\))\(_4\), EtOH, and reflux for 24 h (iii) K\(_2\)CO\(_3\), copper powder, 18-crown-6, o-DCB, and reflux for 3 days.

\[ 2.50 \xrightarrow{(i)} 2.54 \xrightarrow{(ii)} 2.56 \xrightarrow{(iii)} 2.38 \text{(P1)} \]
\[ 2.51 \]
\[ 2.52 \text{(P2)} \]
\[ 2.53 \text{(P3)} \]

**Figure 2.4:** Proposed mechanism of Suzuki Miyaura cross coupling reaction for compound 2.56. (s = solvent).
2.4.4 Synthesis of Compound 2.41 (P4), 2.42 (P5) and 2.43 (P6).

In a similar approach, compounds 2.41 (P4), 2.42 (P5) and 2.43 (P6) were synthesized in three steps from compound 2.50 as described in Scheme 2.12. Iodination of compound 2.50 using 1 eq of iodine gave 3,6-diiodocarbazole (2.57), which was then refluxed with compound 2.55 to give dithienyl-substituted carbazole (2.58). Ullmann
coupling of 2.58 with 2.51, 2.52 and 2.53, gave compounds 2.41 (P4), 2.42 (P5) and 2.43 (P6) in 75 %, 60 % and 50 % yields, respectively (Damit et al., 2016).

Scheme 2.12: Synthesis of 2.41 (P4), 2.42 (P5) and 2.43 (P6). Reaction conditions (i) I₂ (1 eq), AcOH and reflux for 10 min. (ii) K₂CO₃, Pd(PPh₃)₄, EtOH, and reflux for 24 h. (iii) K₂CO₃, Cu, 18-crown-6, o-DCB, and reflux for 4 days.

2.4.5 Synthesis of Compound 2.44 (P7), 2.45 (P8) and 2.48 (P11).

In a similar approach, compounds 2.44 (P7), 2.45 (P8) and 2.48 (P11) were synthesized in three steps from compound 2.50 as described in Scheme 2.13. Iodination of compound 2.50 using 1 eq of iodine gave 3,6-diiodocarbazole (2.57), which was then refluxed with compound 2.59 to give dithienyl-substituted carbazole (2.60). Ullmann coupling of 2.60 with 2.51, 2.52 and 2.53, gave compounds 2.44 (P7), 2.45 (P8) and 2.48 (P11) in 40 %, 38 % and 40 % yields, respectively. Compound 2.48 (P11) was synthesized under Ullmann coupling reaction between 2.60 with 1,4-diiodobenzene.
(2.53) undergoes selective single coupling reaction due to the steric hinderance. The presence of bulkier groups at the reaction centre, cause mechanical interference and resulted attacking reagent difficult to reach the reaction site and thus slow down the reaction.

**Scheme 2.13:** Synthesis of 2.17 (P7), 2.18 (P8) and 2.48 (P11). Reaction conditions (i) I$_2$ (1 eq), AcOH and reflux for 10 min. (ii) K$_2$CO$_3$, Pd(PPh$_3$)$_4$, EtOH, and reflux for 24 h. (iii) K$_2$CO$_3$, Cu, 18-crown-6, o-DCB, and reflux for 4 days.

**2.4.6 Synthesis of Compound 2.46 (P9), 2.47 (P10) and 2.49 (P12).**

In a similar approach, compounds 2.46 (P9), 2.47 (P10) and 2.49 (P12) were synthesized in three steps from compound 2.50 as described in Scheme 2.14. Iodination of compound 2.50 using 1 eq of iodine gave 3,6-diiodocarbazole (2.57), which was then refluxed with compound 2.61 to give dithienyl-substituted carbazole (2.62). Ullmann coupling of 2.62 with 2.51, 2.52 and 2.53 gave compounds 2.46 (P9),
2.47 (P10) and 2.49 (P12) in 40 %, 36 % and 40 % yields, respectively. Compound 2.49 (P12) was synthesized under Ullmann coupling reaction between 2.62 with 1,4-diiodobenzene (2.53) undergoes selective single coupling reaction due to the steric hinderance. Similar observation was found with compound 2.48 (P11) as described previously. All of the compounds were fully characterized by spectroscopic methods such as ¹H NMR, ¹³C NMR and mass spectroscopy. For compounds 2.48 (P11) and 2.49 (P12), their electronic studies were not further discussed because these compound undergoes selective single coupling reaction, where the trend of these compounds structures did not followed compounds P1 to P10 of carbazole-thiophene derivatives series.

Scheme 2.14: Synthesis of 2.46 (P9), 2.47 (P10) and 2.49 (P12). Reaction conditions (i) I₂ (1 eq), AcOH and reflux for 10 min. (ii) K₂CO₃, Pd(PPh₃)₄, EtOH, and reflux for 24 h. (iii) K₂CO₃, Cu, 18-crown-6, o-DCB, and reflux for 5 days.
2.5 Suzuki Coupling Reactions

Order of reactivity is usually I > Br >> Cl in palladium-catalyzed Suzuki (Miyaura et al., 1985; Watanabe, 1992) and Stille (1986) coupling of aryl halides. Great yield has been reported in aqueous condition for cross coupling of 4-iodoanisole with phenylboronic acid with water-soluble Pd-TPPTS (triphenylphosphinetrisuwonate sodium salt) catalyst (Gene’t et al., 1995). Furthermore, the displacement reaction (i.e. SN2) in the liquid-liquid phase-transfer catalysis system (LL-PTC) system, aryl iodide give incomplete transformation (Starks et al., 1978; Starks & Owens, 1973).

Mechanism of Pd-catalyzed Suzuki reaction of aryl halides with aryl boronic acids involve oxidative addition of Pd(0) to aryl halide, transmetallation of the Ar-Pd-X with Ar1B(OH)3M+ and reductive elimination to give Ar-Ar1 (Negishi et al., 1987). Under “classical” conditions, oxidative addition proved to be the slow step when utilizing aryl bromides (Smith et al., 1994), while the rate-determining is the transmetallation step. An extremely wide range of palladium (0) catalyst and precursor were utilized, however PdCl2(PPh3)2 and Pd(OAc) in addition PPh3 or other phosphine ligands employed for cross coupling are also effective which are stable to air and readily reduced to active Pd(0) complexes with organometallics or phosphines (Miyaura & Suzuki, 1995).

All experiments were refluxed for 24 hours. 1 eq of aryl iodide with boronic acid with 1eq (entry 1 to 3) or 2 eq (entry 4 to 15) of boronic acid. All ratio of mixed cosolvent of organic solvent : water was maintained at 5:1. The representative synthesis and reaction conditions are summarized in Table 2.1.
Recently, water was used as solvent for the Suzuki reaction obtained much interest (Arcadi et al., 2003; DeVasher et al., 2004; Dupuis et al., 2001; Leadbeater, 2005; L. Liu et al., 2006; Shaughnessy & Booth, 2001; Uozumi & Nakai, 2002). Considering its safety, cost, and importance to eco harmless procedures, water as solvent offers advantages in organic synthesis (C.-J. Li & Chan, 1997). As shown in Table 2.1, remarkably we discovered that good yields was obtained in most aryl iodide coupling with boronic acid where sodium hydroxide as base in benzene/H$_2$O cosolvent (benzene is non-polar solvent) (Deloux et al., 1994; Miyaura et al., 1986; Miyaura et al., 1979; Punji et al., 2006), however the reaction stop at about 75 % conversion (entries 3, 6, 9, 12 and 15). Furthermore, the addition of strong bases of NaOH in benzene exerts an amazing impact of acceleration of the coupling rate (Daku et al., 2003; Guillier et al., 1994; Kelly et al., 1994; Rocca et al., 1993). Other cosolvents EtOH/H$_2$O and Dioxane/H$_2$O with weak base K$_2$CO$_3$ had been very ineffective (entries 2, 5, 7, 10 and 13) where less than 20 % and none of products had been discovered. Polar protic solvents (EtOH/H$_2$O) with K$_2$CO$_3$ weak base give much better outcomes for less hindered mono-thiophene boronic acid (entries 1 and 4) which give more than 80 % yield of products.

Cross coupling reaction of organoboron yielding nontoxic byproduct, tolerate an extensive of functionality and unaffected by the existence of water offers diverse application in laboratories and within sectors.