SYNTHESIS AND CHARACTERIZATION OF CARBAZOLE DERIVATIVES FOR ORGANIC LIGHT-EMITTING DIODE AND INDOLE DERIVATIVES FOR DYE-SENSITIZED SOLAR CELL

THITIMA SIRIROEM

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE MAJOR IN CHEMISTRY

FACULTY OF SCIENCE
UBON RATCHATHANI UNIVERSITY
ACADEMIC YEAR 2015
COPYRIGHT OF UBON RATCHATHANI UNIVERSITY
UBON RATCHATHANI UNIVERSITY

THESIS APPROVAL

MASTER OF SCIENCE

MAJOR IN CHEMISTRY FACULTY OF SCIENCE

TITLE SYNTHESIS AND CHARACTERIZATION OF CARBAZOLE
DERIVATIVES FOR ORGANIC LIGHT-EMITTING DIODE AND
INDOLE DERIVATIVES FOR DYE-SENSITIZED SOLAR CELL

AUTHOR MISS THITIMA SIRIROEM

EXAMINATION COMMITTEE

ASST. PROF. DR. JARAY JARATJAROONPHONG CHAIRPERSON
ASST. PROF. DR. TINNAGON KEAWIN MEMBER
ASSOC. PROF. DR. SIRIPORN JUNGSUTTIWONG MEMBER

ADVISOR

(ASST. PROF. DR. TINNAGON KEAWIN)

(ASSOC. PROF. DR. UTITH INPRASIT) (ASSOC. PROF. DR. ARIYAPORN PONGRAT)
DEAN, FACULTY OF SCIENCE VICE PRESIDENT
FOR ACADEMIC AFFAIRS

COPYRIGHT OF UBON RATCHATHANI UNIVERSITY

ACADEMIC YEAR 2015
ACKNOWLEDGEMENTS

In this thesis was carried out at Center for Organic Electronics and Alternative Energy (COEA). Firstly I would like to thank Asst. Prof. Dr. Tinnagon Keawin my advisor for excellent suggestion, NMR experiments, supervision and understanding throughout my research work.

I wish to express appreciation and thank to Prof. Dr. Vinich Promarak for allowing me to undertake this project, advice and guiding me in this thesis. I would also like to thank everyone in the electronics group who advice and instrumentation to my project at Ubon Ratchathani University. In particular, I would like to thank Assoc. Prof. Dr. Siriporn Jungsuttiwong for constructive comments and suggestion. Thanks so much to the many people who contributed their time and advice to me for sharing knowledge of chemistry. In particular, Ms. A-monrat Thangthong for synthesis of newly developed organic materials used in this work, Dr. Narid Prachumrak for fabrication of all OLEDs present in my work and guidance on the OLED knowledge and Miss Rattanawalee Rattanawan for molecular orbital calculation.

I want to acknowledge the Center of Excellence for Innovation in Chemistry (PERCH-CIC) for providing financial support for this work. I would like to thank Ubon Ratchathani University for instrumentation and place of research. Finally, I am heartfelt thanks to my family for their love, support, and encouragement during my study.

Titima Siriroem

Titima Siriroem
Researcher
บทคัดย่อ

เรื่อง : การสังเคราะห์และพิสูจน์เอกลักษณ์อนุพันธ์คาร์บไซคล์ไบออกซ์สำหรับอุปกรณ์ไอโอติค
เรื่องแสง สารอินทรีย์และอนุพันธ์อินโคสสารสำหรับอุปกรณ์เซลล์และสาคัญคิด
สิ่งอ้อมใสแสง

ผู้จัด : วิธีมา ศรีเริ่ม
ชื่อวิทยานิพนธ์ : วิทยาศาสตรมหาบัณฑิต
สาขาวิชา : เคมี
อาจารย์ที่ปรึกษา : ผู้ช่วยศาสตราจารย์ ดร. ทิสกร แก้วอินทร์
ค่าสัมพันธ์ : โดไอเรียงแสงอินทรีย์, สารส่งผ่านประตู, สารเรืองแสง
ปฏิบัติการ : สรุป-คัดบัลลัง, อินโด, เชลส์แสงอาทิตย์ชนิดสิ่งอ้อมใสแสง

ในงานวิจัยนี้ได้ทำการสังเคราะห์อนุพันธ์คาร์บไซคล์ไบออกซ์ที่มีนูฟิททยาตัวใหม่ในกลุ่มของโพคิรน (CP2)
และแอนทร้าซี (CA2) โดยใช้ปฏิบัติการสังเคราะห์นูฟิททยา Suzuki cross-coupling และ
พิสูจน์เอกลักษณ์ด้วยเทคนิค 1H NMR, 13C-NMR, FT-IR, UV-Vis, fluorescence และ mass
spectroscopy และ cyclic voltammetry โดย 9-dodecyl-3,6-di(pyren-1-yl)carbazole
(CP2) และ 9-dodecyl-3,6-di(anthracen-1-yl)carbazole (CA2) ให้สังเกตรรการหาแสง
ในช่วงสัมภัณฑ์ที่ 430 nm และ 442 nm และนิยมแย่งแสงทางไฟฟ้าที่สูง สารเหล่านั้นจึงย่อมจะเป็น
อีกทางเลือกหนึ่งสำหรับใช้เป็นสารเรืองแสงสั่นบ้านเงินในโดไอเรียงแสงอินทรีย์

นอกจากนี้ยังได้ทำการสังเคราะห์อนุพันธ์อินโคสชนิดใหม่ In1-In5 ที่ไม่แตกต่างกับตัว
อนุพันธ์อินโคสเป็นใหญ่ให้อีทีคละรูป พืชระดุยหรืออนุพันธ์เป็นสายเชื่อมต่อและมุขครัวรังสีเป็น
หมู่รูปอีทีคละรูปและยีดั้งที่ได้เป็นในกลุ่มสั่นบ้านเงินในเซลล์แสงอาทิตย์ชนิดสิ่งอ้อมใสแสง
ไม่แตกต่างจากสังเคราะห์ที่ได้จากปฏิบัติการ Ullman coupling, ปฏิบัติการใดไอโอติค, ปฏิบัติการ
Knoevenagal condensation และ ปฏิบัติการ Vilsmeier–Haack โดยคาดหวังว่าในกลุ่มเป็นหมาย
In1-In5 จะถูกนำไปใช้เป็นสิ่งอ้อมในเซลล์แสงอาทิตย์ชนิดสิ่งอ้อมใสแสงได้อย่างมีประสิทธิภาพ
Sufficiently new and unique compounds In1-In5 were identified by techniques $^1$H-NMR, $^{13}$C-NMR, FT-IR and mass spectroscopy.
ABSTRACT

TITLE : SYNTHESIS AND CHARACTERIZATION OF CARBAZOLE DERIVATIVES FOR ORGANIC LIGHT-EMITTING DIODE AND INDOLE DERIVATIVES FOR DYE-SENSITIZED SOLAR CELL

AUTHOR : THITIMA SIRIROEM
DEGREE : MASTER OF SCIENCE
MAJOR : CHEMISTRY
ADVISOR : ASST.PROF.TINNAGON KEAWIN, Ph.D.
KEYWORDS : CARBAZOLE, ORGANIC LIGHT-EMITTING DIODES, SUZUKI CROSS-COUPLING REACTION, INDOLE, DYE-SENSITIZED SOLAR CELL

In this research, carbazole derivatives end-capped with pyrene (CP2) and anthracene (CA2) have been synthesized using bromination and Suzuki cross-coupling reaction and characterized by $^1$H NMR, $^{13}$C-NMR, FT-IR, UV-Vis, fluorescence and mass spectroscopy and cyclic voltammetry. Compound 9-dodecyl-3,6-di(pyren-1-yl)carbazole (CP2) and 9-dodecyl-3,6-di(anthracen-1-yl)carbazole (CA2) showed the PL spectra in deep blue region at 430 nm and 442 nm and exhibited high electrochemical stability. These compounds could be alternative materials for using as blue light-emitters in organic light emitting diodes.

Moreover, a new series of indole derivatives In1-In5, containing indole derivatives as electron donating, double bond or phenyl group as π-spacer and carboxyl group as electron acceptor and anchor, for using as dye molecules in DSSCs were successfully synthesized. The target molecules were synthesized by using Ullman coupling, hydrolysis reaction, Knoevenagal condensation and Vilsmeier-
Haack reaction. The target compound **In1-In5** could be promising candidates for improvement of the performance dye of the DSSCs.

Finally, target molecules, **In1-In5** were characterized by using $^1$H-NMR, $^{13}$C-NMR, FT-IR and mass spectroscopy.
## CONTENTS

<table>
<thead>
<tr>
<th>ACKNOWLEDGMENTS</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>THAI ABSTRACT</td>
<td>II</td>
</tr>
<tr>
<td>ENGLISH ABSTRACT</td>
<td>IV</td>
</tr>
<tr>
<td>CONTENTS</td>
<td>VI</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>VII</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>VIII</td>
</tr>
<tr>
<td>LIST OF ABBREVIATIONS</td>
<td>XIII</td>
</tr>
</tbody>
</table>

**CHAPTER 1** SYNTHESIS AND CHARACTERIZATION OF CARBAZOLE DERIVATIVES FOR ORGANIC LIGHT-EMITTING DIODE

1.1 INTRODUCTION 1
1.2 RESULTS AND DISCUSSION 8
1.3 CONCLUSION 19
1.4 EXPERIMENTAL 19

**CHAPTER 2** SYNTHESIS AND CHARACTERIZATION OF INDOLE DERIVATIVES FOR DYE-SENSITIZED SOLAR CELL

2.1 INTRODUCTION 24
2.2 RESULTS AND DISCUSSION 33
2.3 CONCLUSION 44
2.4 EXPERIMENTAL 47

REFERENCES 57
APPENDICES 63

A $^1$H NMR, $^{13}$C NMR and UV-Vis absorption spectrum of compounds 64

B Publication 82

VITAE 90
CONTENTS

<table>
<thead>
<tr>
<th>CONTENTS</th>
<th>PAGES</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>I</td>
</tr>
<tr>
<td>THAI ABSTRACT</td>
<td>II</td>
</tr>
<tr>
<td>ENGLISH ABSTRACT</td>
<td>IV</td>
</tr>
<tr>
<td>CONTENTS</td>
<td>VI</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>VII</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>VIII</td>
</tr>
<tr>
<td>LIST OF ABBREVIATIONS</td>
<td>XIII</td>
</tr>
<tr>
<td>CHAPTER 1 SYNTHESIS AND CHARACTERIZATION OF</td>
<td></td>
</tr>
<tr>
<td>CARBAZOLE DERIVATIVES FOR ORGANIC</td>
<td></td>
</tr>
<tr>
<td>LIGHT-EMITTING DIODE</td>
<td></td>
</tr>
<tr>
<td>1.1 INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.2 RESULTS AND DISCUSSION</td>
<td>8</td>
</tr>
<tr>
<td>1.3 CONCLUSION</td>
<td>19</td>
</tr>
<tr>
<td>1.4 EXPERIMENTAL</td>
<td>19</td>
</tr>
<tr>
<td>CHAPTER 2 SYNTHESIS AND CHARACTERIZATION OF</td>
<td></td>
</tr>
<tr>
<td>INDOLE DERIVATIVES FOR DYE-SENSITIZED</td>
<td></td>
</tr>
<tr>
<td>SOLAR CELL</td>
<td></td>
</tr>
<tr>
<td>2.1 INTRODUCTION</td>
<td>24</td>
</tr>
<tr>
<td>2.2 RESULTS AND DISCUSSION</td>
<td>33</td>
</tr>
<tr>
<td>2.3 CONCLUSION</td>
<td>44</td>
</tr>
<tr>
<td>2.4 EXPERIMENTAL</td>
<td>47</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>57</td>
</tr>
<tr>
<td>APPENDICES</td>
<td>63</td>
</tr>
<tr>
<td>A (^1)H NMR, (^13)C NMR and UV-Vis absorption spectrum of</td>
<td>64</td>
</tr>
<tr>
<td>compounds</td>
<td></td>
</tr>
<tr>
<td>B Publication</td>
<td>82</td>
</tr>
<tr>
<td>VITAE</td>
<td>90</td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE</th>
<th>DESCRIPTION</th>
<th>PAGES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Physical data of CP2 and CA2</td>
<td>15</td>
</tr>
<tr>
<td>1.2</td>
<td>Physical data of CP2 and CA2</td>
<td>18</td>
</tr>
<tr>
<td>FIGURE</td>
<td>Description</td>
<td>PAGES</td>
</tr>
<tr>
<td>----------</td>
<td>-----------------------------------------------------------------------------</td>
<td>-------</td>
</tr>
<tr>
<td>1.1</td>
<td>Organic light emitting diodes (OLEDs) display applications</td>
<td>2</td>
</tr>
<tr>
<td>1.2</td>
<td>Organic light emitting diodes (OLEDs) structure</td>
<td>2</td>
</tr>
<tr>
<td>1.3</td>
<td>Working principle of OLEDs</td>
<td>3</td>
</tr>
<tr>
<td>1.4</td>
<td>Chemical structure of TCF</td>
<td>4</td>
</tr>
<tr>
<td>1.5</td>
<td>Structure of benzo[b]thien-2-yl derivatives</td>
<td>5</td>
</tr>
<tr>
<td>1.6</td>
<td>Structure of bis-(4-benzenesulfonyl-phenyl)-9-phenyl-9H-carbazoles</td>
<td>6</td>
</tr>
<tr>
<td>1.7</td>
<td>Structure of DPACz1, DPACz2 and DPACz3</td>
<td>6</td>
</tr>
<tr>
<td>1.8</td>
<td>Structure of DETPCZ and DECZDEP</td>
<td>7</td>
</tr>
<tr>
<td>1.9</td>
<td>The target molecules CP2 and CA2</td>
<td>8</td>
</tr>
<tr>
<td>1.10</td>
<td>Structure of CP2 and CA2</td>
<td>9</td>
</tr>
<tr>
<td>1.11</td>
<td>Retrosynthesis of carbazole CP2 and CA2</td>
<td>9</td>
</tr>
<tr>
<td>1.12</td>
<td>Synthesis of 9-dodecylcarbazole</td>
<td>10</td>
</tr>
<tr>
<td>1.13</td>
<td>Mechanisms of alkylation reaction of carbazole</td>
<td>10</td>
</tr>
<tr>
<td>1.14</td>
<td>Bromination of 9-dodecylcarbazole</td>
<td>11</td>
</tr>
<tr>
<td>1.15</td>
<td>Mechanisms of bromination of 9-dodecylcarbazole</td>
<td>11</td>
</tr>
<tr>
<td>1.16</td>
<td>Synthetic of target molecules CP2</td>
<td>12</td>
</tr>
<tr>
<td>1.17</td>
<td>The proposed mechanism of Suzuki coupling reaction</td>
<td>13</td>
</tr>
<tr>
<td>1.18</td>
<td>Synthetic of target molecules CA2</td>
<td>13</td>
</tr>
<tr>
<td>1.19</td>
<td>Normalized absorption spectra (left) and normalized emission spectra (right)</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>in CH₂Cl₂ of CP2 and CA2</td>
<td></td>
</tr>
<tr>
<td>1.20</td>
<td>Cyclic voltammograms of CP2 (left) and CA2 (right) in dry</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>CH₂Cl₂ with scan rate of 0.05 V/s and 0.1 M n-Bu₄NPF₆ as electrolyte, muti</td>
<td></td>
</tr>
<tr>
<td></td>
<td>scan.</td>
<td></td>
</tr>
<tr>
<td>1.21</td>
<td>Oxidation process of pyrene</td>
<td>17</td>
</tr>
<tr>
<td>1.22</td>
<td>The HOMO (bottom) and LUMO (top) orbitals of CP2 and CA2</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>calculated by DFT/B3LYP/6-31G(d,p) method</td>
<td></td>
</tr>
<tr>
<td>FIGURE</td>
<td>PAGES</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>-------</td>
<td></td>
</tr>
<tr>
<td>2.1</td>
<td>Dye-sensitized solar cells structure (DSSCs) structure</td>
<td>25</td>
</tr>
<tr>
<td>2.2</td>
<td>Working principle of DSSCs</td>
<td>26</td>
</tr>
<tr>
<td>2.3</td>
<td>Chemical structures of JK-24, JK-25 and JK-28 dyes</td>
<td>27</td>
</tr>
<tr>
<td>2.4</td>
<td>Chemical structures of 1P-PSP and 1N-PSP dyes</td>
<td>27</td>
</tr>
<tr>
<td>2.5</td>
<td>Chemical structures of CBZ, WD-5, and DTA dyes</td>
<td>28</td>
</tr>
<tr>
<td>2.6</td>
<td>Dye-organic synthesis included of benzo[cd]indole group</td>
<td>28</td>
</tr>
<tr>
<td>2.7</td>
<td>The structure of dyed molecules included of carbazole (MK75, MK79, MK80), indole (MK81-83) and indoline (MK84-86)</td>
<td>29</td>
</tr>
<tr>
<td>2.8</td>
<td>The structure of ID1-ID3 dye-sensitized molecules</td>
<td>30</td>
</tr>
<tr>
<td>2.9</td>
<td>Dye-organic synthesis</td>
<td>30</td>
</tr>
<tr>
<td>2.10</td>
<td>The synthesis of organic dyes included of thiophene and N-methyl pyrrole as the connectors</td>
<td>31</td>
</tr>
<tr>
<td>2.11</td>
<td>structure of SD1 and SD2</td>
<td>32</td>
</tr>
<tr>
<td>2.12</td>
<td>structure of D1, D2 and D3</td>
<td>32</td>
</tr>
<tr>
<td>2.13</td>
<td>The target molecules In1-In5</td>
<td>33</td>
</tr>
<tr>
<td>2.14</td>
<td>Structure of In1-In5</td>
<td>34</td>
</tr>
<tr>
<td>2.15</td>
<td>Retrosynthesis of carbazole In1-In5</td>
<td>35</td>
</tr>
<tr>
<td>2.16</td>
<td>Synthesis of methyl 4-(indol-1-yl) benzoate 4</td>
<td>35</td>
</tr>
<tr>
<td>2.17</td>
<td>The proposed mechanism of Ullmann coupling reaction</td>
<td>36</td>
</tr>
<tr>
<td>2.18</td>
<td>Hydrolysis reaction of methyl 4-(indol-1-yl) benzoate 4</td>
<td>37</td>
</tr>
<tr>
<td>2.19</td>
<td>The proposed mechanism of hydrolysis reaction</td>
<td>37</td>
</tr>
<tr>
<td>2.20</td>
<td>Synthesis of methyl 4-(3-(4-bromophenyl)-4,6-dimethoxyindol-1-yl) benzoate 6</td>
<td>38</td>
</tr>
<tr>
<td>2.21</td>
<td>Hydrolysis reaction of methyl 4-(3-(4-bromophenyl)-4,6-dimethoxy indol-1-yl) benzoate 6</td>
<td>39</td>
</tr>
<tr>
<td>2.22</td>
<td>Knoevenagal reaction of indole-3-carbaldehyde 7</td>
<td>40</td>
</tr>
</tbody>
</table>
### LIST OF FIGURES (CONTINUED)

<table>
<thead>
<tr>
<th>FIGURE</th>
<th>Description</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.23</td>
<td>The proposed mechanism of Knoevenagal reaction</td>
<td>40</td>
</tr>
<tr>
<td>2.24</td>
<td>Vilsmeier-Haack reaction of 4,6-dimethoxyindole</td>
<td>41</td>
</tr>
<tr>
<td>2.25</td>
<td>The proposed mechanism of Vilsmeier-Haack reaction</td>
<td>42</td>
</tr>
<tr>
<td>2.26</td>
<td>Knoevenagal reaction of 3-formyl -4,6-dimethoxyindole</td>
<td>42</td>
</tr>
<tr>
<td>2.27</td>
<td>Methylation of 3-formyl -4,6-dimethoxyindole</td>
<td>43</td>
</tr>
<tr>
<td>2.28</td>
<td>Knoevenagal reaction of 3-formyl-4,6-dimethoxy-N-methylindol</td>
<td>44</td>
</tr>
<tr>
<td>FIGURE</td>
<td>PAGES</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>-------</td>
<td></td>
</tr>
<tr>
<td>A.1</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>A.2</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>A.3</td>
<td>66</td>
<td></td>
</tr>
<tr>
<td>A.4</td>
<td>66</td>
<td></td>
</tr>
<tr>
<td>A.5</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>A.6</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>A.7</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td>A.8</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td>A.9</td>
<td>69</td>
<td></td>
</tr>
<tr>
<td>A.10</td>
<td>69</td>
<td></td>
</tr>
<tr>
<td>A.11</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>A.12</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>A.13</td>
<td>71</td>
<td></td>
</tr>
<tr>
<td>A.14</td>
<td>71</td>
<td></td>
</tr>
<tr>
<td>A.15</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td>A.16</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td>A.17</td>
<td>73</td>
<td></td>
</tr>
<tr>
<td>A.18</td>
<td>73</td>
<td></td>
</tr>
<tr>
<td>A.19</td>
<td>74</td>
<td></td>
</tr>
</tbody>
</table>
**LIST OF FIGURES (CONTINUED)**

<table>
<thead>
<tr>
<th>FIGURE</th>
<th>PAGES</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.20</td>
<td>The $^{13}$C NMR spectra of 3-formyl-4,6-dimethoxyindole</td>
</tr>
<tr>
<td>A.21</td>
<td>The $^1$H NMR (in CDCl$_3$) spectrum of In4</td>
</tr>
<tr>
<td>A.22</td>
<td>The $^{13}$C NMR spectra of In4</td>
</tr>
<tr>
<td>A.23</td>
<td>The $^1$H NMR (in CDCl$_3$) spectrum of 3-formyl-4,6-dimethoxy-$N$-methylindol</td>
</tr>
<tr>
<td>A.24</td>
<td>The $^{13}$C NMR spectra of 3-formyl-4,6-dimethoxy-$N$-methylindol</td>
</tr>
<tr>
<td>A.25</td>
<td>The $^1$H NMR (in CDCl$_3$) spectrum of In5</td>
</tr>
<tr>
<td>A.26</td>
<td>The $^{13}$C NMR spectra of In5</td>
</tr>
<tr>
<td>A.27</td>
<td>UV-Vis absorption spectra of In1-In5 in DCM at 5x10$^{-6}$ M.</td>
</tr>
<tr>
<td>A.28</td>
<td>UV-Vis absorption spectra of In1 in DCM at 5x10$^{-6}$ M</td>
</tr>
<tr>
<td>A.29</td>
<td>UV-Vis absorption spectra of In2 in DCM at 5x10$^{-6}$ M.</td>
</tr>
<tr>
<td>A.30</td>
<td>UV-Vis absorption spectra of In3 in DCM at 1x10$^{-5}$ M.</td>
</tr>
<tr>
<td>A.31</td>
<td>UV-Vis absorption spectra of In4 in DCM at 5x10$^{-6}$ M.</td>
</tr>
<tr>
<td>A.32</td>
<td>UV-Vis absorption spectra of In5 in DCM at 5x10$^{-6}$ M</td>
</tr>
</tbody>
</table>
### LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>ABBREVIATION</th>
<th>FULL WORD</th>
</tr>
</thead>
<tbody>
<tr>
<td>OLED</td>
<td>Organic light-emitting diode</td>
</tr>
<tr>
<td>LCD</td>
<td>Liquid crystal display</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>HIL</td>
<td>Hole-injection layer</td>
</tr>
<tr>
<td>HIM</td>
<td>Hole-injection material</td>
</tr>
<tr>
<td>HTL</td>
<td>Hole-transporting layer</td>
</tr>
<tr>
<td>HTM</td>
<td>Hole-transporting material</td>
</tr>
<tr>
<td>EML</td>
<td>Emissive layer or emitting layer</td>
</tr>
<tr>
<td>ETL</td>
<td>Electron-transporting layer</td>
</tr>
<tr>
<td>ETM</td>
<td>Electron-transporting material</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>EL</td>
<td>Electroluminescence</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>TLC</td>
<td>Thin-layer chromatography</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>$^1$H-NMR</td>
<td>Proton nuclear magnetic resonance</td>
</tr>
<tr>
<td>$^{13}$C-NMR</td>
<td>Carbon nuclear magnetic resonance</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier transform Infrared</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra-violet</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Chemical shift in ppm relative to tetramethylsilane</td>
</tr>
<tr>
<td>s</td>
<td>Singlet</td>
</tr>
<tr>
<td>d</td>
<td>Doublet</td>
</tr>
<tr>
<td>dd</td>
<td>Doublet of doublets</td>
</tr>
</tbody>
</table>
### LIST OF ABBREVIATIONS (CONTINUED)

<table>
<thead>
<tr>
<th>ABBREVIATION</th>
<th>FULL WORD</th>
</tr>
</thead>
<tbody>
<tr>
<td>t</td>
<td>Triplet</td>
</tr>
<tr>
<td>ε</td>
<td>Molar absorption coefficient</td>
</tr>
<tr>
<td>eV</td>
<td>Electron volt</td>
</tr>
<tr>
<td>h</td>
<td>Hour/hours</td>
</tr>
<tr>
<td>rt</td>
<td>Room temperature</td>
</tr>
<tr>
<td>J</td>
<td>Coupling constant</td>
</tr>
<tr>
<td>MHz</td>
<td>Megahertz</td>
</tr>
<tr>
<td>V</td>
<td>Voltage</td>
</tr>
<tr>
<td>M</td>
<td>Molar concentration</td>
</tr>
<tr>
<td>µA</td>
<td>Microamperes</td>
</tr>
<tr>
<td>µm</td>
<td>Micrometer</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometers</td>
</tr>
<tr>
<td>mmol</td>
<td>Milimoles</td>
</tr>
<tr>
<td>mol</td>
<td>Moles</td>
</tr>
<tr>
<td>ppm</td>
<td>Part per million</td>
</tr>
<tr>
<td>min</td>
<td>minutes</td>
</tr>
<tr>
<td>Ω</td>
<td>Ohm</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>n-Bu4NPF₆</td>
<td>Tetrabutylammonium hexafluorophosphate</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>ΔEₜ</td>
<td>Hole energy barriers</td>
</tr>
<tr>
<td>ΔEₑ</td>
<td>Electron energy barriers</td>
</tr>
<tr>
<td>EA</td>
<td>Electron affinity</td>
</tr>
<tr>
<td>Eₙ</td>
<td>Energy gap</td>
</tr>
<tr>
<td>Eₒnset</td>
<td>Energy onset</td>
</tr>
</tbody>
</table>
**LIST OF ABBREVIATIONS (CONTINUED)**

<table>
<thead>
<tr>
<th>ABBREVIATION</th>
<th>FULL WORD</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Phi_F$</td>
<td>Fluorescent quantum yield</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength</td>
</tr>
<tr>
<td>$\lambda_{abs}$</td>
<td>Wavelength absorption</td>
</tr>
<tr>
<td>$\lambda_{em}$</td>
<td>Wavelength emission</td>
</tr>
<tr>
<td>$\lambda_{max}$</td>
<td>Wavelength maximum</td>
</tr>
<tr>
<td>$\lambda_{onset}$</td>
<td>Wavelength onset</td>
</tr>
<tr>
<td>$\lambda_{el}$</td>
<td>Wavelength electroluminescent</td>
</tr>
<tr>
<td>$T_g$</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>$T_c$</td>
<td>Crystallization temperature</td>
</tr>
<tr>
<td>$T_d$</td>
<td>Decomposition temperature</td>
</tr>
<tr>
<td>$T_m$</td>
<td>Melting temperature</td>
</tr>
</tbody>
</table>
CHAPTER 1
SYNTHESIS AND CHARACTERIZATION OF CARBAZOLE DERIVATIVES FOR ORGANIC LIGHT-EMITTING DIODE

1.1 INTRODUCTION

1.1.1 Organic light emitting diodes (OLEDs)

In the former time, many exhibited technologies, for example, cathode ray tube (CRT), liquid crystal displays (LCDs), light emitting diodes (LEDs) were inducing to show in the market. However, there are lots of limitations of the displays such as bulkiness, low viewing angle, color purity, etc [1]. Furthermore, the current demand generation displays are the brightness reproduction, pure color, high resolution, light weight, thin screen, and decreasing of cost and low power consumption, which was set in these OLED devices.

Organic light-emitting diodes (OLEDs) are relatively technology for light sources in which the emissive electroluminescent layer is a film of organic compound that emits light in response to an electric current [2]. First proposed by Ching W. Tang in 1987 [3], OLEDs have attracted significant attention from the scientific community due to their optical potential properties for future flat-panel displays and lighting applications [2]. OLEDs have high potential electronic and optical properties, for example, low voltage driving, high brightness, ability of multicolor emission selected by emitting materials, easy large-area fabrication, and thin-film devices which they have no added backlight required for brightness of the screen [4]. According to the varieties of report on improving OLEDs properties, there are witness that is significant advancement related to brightness, multi- or full-color emission, and OLEDs endurance and thermal stability.

In addition, organic light emitting diodes are more attended recently because they have a wide range of display applications. The application of OLED technology is thin solid films of organic molecules that use electricity to generate light. There are various devices found consist of mobile phones, computer monitors, car radios, digital cameras and large TV screen, and etc [5]. The movable applications
help OLEDs high light output to read easily in sunlight, and it helps create brighter, especially wavy images in the devices. OLEDs using accompany with various prominent advantage included lower and better power used since it lacks of backlight effects and a faster reaction in view of its high speed. Also, the diodes are really lightweight and flexible. The OLEDs is the basis technology in the present time, but it tends to be the most needed in the future because of effective devices.

Figure 1.1 Organic light emitting diodes (OLEDs) display applications [6]

1.1.2 Organic light emitting diodes structure

The OLEDs structure consist of four part including substrate, anode, organic layers and cathode [7] as shown in Figure 1.2.

Figure 1.2 Organic light emitting diodes (OLEDs) structure [8]
1.1.2.1 Substrate layer—It supports OLED and is made up of transparent plastic or glass film.

1.1.2.2 Anode layer—It is a transparent layer that removes electrons. Indium tin oxide is commonly used as the anode material.

1.1.2.3 Organic layer—Layer formed of organic molecules or polymers

1) Conductive layer—Transports holes from anode made up of organic plastic. Polymer light-emitting diodes: PLED, also light-emitting polymers: LEP, are used in electroluminescent conductive polymer. Typical polymers used in PLED displays include derivatives of poly (p-phenylene vinylene) and polyfluorene.

2) Emissive layer—Transports electrons from the cathode layer. It is made up of organic plastic.

1.1.2.4 Cathode layer—Injects electrons. It may be transparent or not. Metals such as aluminium and calcium are often used in the cathode

1.1.3 Working principle of organic light emitting diodes

The working principle of OLEDs was shown in Figure 1.3. When electrical current is applied to the electrodes anode and cathode the charges and electron start moving in the device under the influence of the electric field. Electrons leave the cathode, giving electrons to emissive layer and electrons remove form conducting layer to anode, giving holes (h⁺) at conducting layer. The holes jump to the emissive layer and recombine with the electrons. The recombination of this charges leads to the creation of a photon with a frequency given by the energy gap \((E = h\nu)\) between the LUMO and HOMO levels of the emitting molecules. Therefore, the electrical power applied to the electrodes is transformed into light [2].

![OLED device operation diagram](image)

**Figure 1.3 Working principle of OLEDs [9]**
1.1.4 Literature reviews of OLEDs

In this part, the publications of synthesis and study optical properties of organic light emitting diodes would be described. For example:

In 2012, a highly fluorescent bis (4-diphenylaminophenyl) carbazole end-capped fluorine, TCF, was synthesized and characterized by D. Meunmart and co-workers. This material showed greater ability as a solution processed blue emitter and hole-transporter for OLEDs than commonly used NPB. High-efficiency deep-blue and Alq3-based green devices with luminance efficiencies and CIE coordinates of 0.93 cd/A, (0.16, 0.09), and 3.78 cd/A and (0.29, 0.45) were achieved, respectively. The use of the triphenylamine-carbazole substituent might be an effective method to prepare amorphous molecules with excellent electrochemical, thermal, and morphological stabilities for OLEDs by forming dendritic structures with other fluorescent or non-fluorescent core units [10].

![Chemical structure of TCF](image)

### Figure 1.4 Chemical structure of TCF

In 2012, Sukrawee Pansay et al. [11] designed and synthesized four benzo[b]thien-2-yl derivatives 4a-4d (Figure 1.5). The properties of 4a -4d as a blue emissive layer (EML) in OLED were investigated. Under an applied voltage, the devices (4b–d) emitted a bright deep-blue light with maximum peaks (λ_{EL}) centered at 416, 428, and 436 nm, respectively. The electroluminescence (EL) spectra of all diodes matched their corresponding PL spectra indicating that the EL emission originates from the singlet-excited states of the EML materials. However, 4a did not show any EL property in the device. This may be due to its very small, planar structure
leading to fluorescence quenching in the solid state. Carbazole 4d bearing four benzo[b]thiophene substituents had the best EML properties among these four materials. The 4d-based device exhibited a high maximum brightness of 582 cd m$^{-2}$ for blue OLED at 8.6 V, a turn-on voltage of 4.1 V.

![Figure 1.5 Structure of benzo[b]thien-2-yl derivatives.](image)

In 2016, bis-(4-benzenesulfonyl-phenyl)-9-phenyl-9H-carbazoles were designed and synthesized by Bin Huang and co-workers [12]. The nondoped devices using 3,6-bis-(4-benzenesulfonyl-phenyl)-9-phenyl-9H-carbazoles 2a and 2,7-bis-(4-benzenesulfonyl-phenyl)-9-phenyl-9H-carbazoles 2b as the emitters show deep blue emission color with EL spectra peaks at 424 and 444 nm and the Commission Internationale de l'Eclairage (CIE) coordinates of (0.177, 0.117) and (0.160, 0.117), respectively. Furthermore, these materials based devices have high color-purity with small width at half-maximum (FWHM) of 65 and 73 nm, respectively. The results provide a novel approach for the design of deep blue emitter for high-color-purity nondoped OLEDs.
Figure 1.6 Structure of bis-(4-benzenesulfonyl-phenyl)-9-phenyl-9H-carbazoles.

In 2016, DPACz1, DPACz2 and DPACz3 were synthesized and characterized by Shahid Ameen et al [13]. Diphenylamine substituents at 1- or 1,8-positions of carbazoles show increasing of the band-gap compared with the previously reported 3,6- or 2,7-substituted ones. In addition, all materials indicated high triplet energy levels of 2.68, 2.60 and 2.45 eV, respectively. Based on suitable HOMO levels and high triplet energies, they were investigated for their potential as host materials for green phosphorescent OLEDs with the device configuration, [ITO/PEDOT:PSS/Emitting layer/TPBi/CsF/Al]. Moreover, the devices of all materials shown emitted typical green light with high luminance and had low turn-on voltages along with good luminous efficiencies. These results indicated the usefulness of new materials and kind of 1-/1,8-substitution of carbazole would open a new way of materials design.

Figure 1.7 Structure of DPACz1, DPACz2 and DPACz3
In 2016, Shi H. et al [14] presented two novel phenylethene-carbazole derivatives containing dimesitylboron groups, 3-(dimesitylboryl)-9-ethyl-6-(1,2,2-triphenylvinyl)-9H-carbazole DETPCZ and 1,2-bis(6-(dimesitylboryl)-9-ethyl-9H-carbazol-3-yl)-1,2-diphenylethene DECZDEP. The electrochemical, thermal and photophysical properties were reported. Both compounds show excellent thermal stability (Td up to 254 °C) and high electrochemical stability. Moreover, the multi-layer EL devices illustrated the sky blue-green emitting EL with high maximum luminance and maximum luminance efficiency of 15,780 cd m⁻² and 6.90 cd A⁻¹ at CIE of (0.20, 0.28) and (0.23, 0.41), respectively. The results provide a novel way for the design and application of novel AIE-luminophores.

Figure 1.8 Structure of DETPCZ and DECZDEP

Due to a variety of organic materials of OLED have been reported. We are particularly interested in synthesize organic compounds for OLEDs.

1.1.5 Aim of the thesis

Initially proposed by Ching W. Tang in 1987 [3], organic light-emitting diodes (OLEDs) have attracted significant attention from the scientific community due to their potential for future flat-panel displays and lighting applications [15]. Today, the developments of OLED technologies mainly focus on the optimization of device structures and on developing new emitting materials. Clearly, new materials emitting pure colors of red, green, and blue (RGB) with excellent emission efficiency and high stability, are the key point of OLED development for full-color flat displays. The performance of blue OLEDs is usually inferior to that of green and red OLEDs due to poor carrier injection into the emitters [16] and electroluminescent (EL)
properties of the blue OLEDs need to be improved. Therefore, one area of continuing research in this field is the pursuit of a stable-blue emitting material [17]. Although many fluorescent blue emitters have been reported such as pyrene derivatives [18], carbazole derivatives [19], anthracene derivatives [20], fluorene derivatives and aromatic hydrocarbons [21], there is still a clear need for further developments in terms of efficiency and color purity compared to red and green emitters.

In this research, we synthesize and characterize of a series of emissive materials based on carbazole derivatives. In addition, we synthesize the following a carbazole derivatives containing two pyrenyl and two anthracene endgroup of carbazole unit as core, whose chemical structure of target molecules, CP2 and CA2 are shown in Figure 1.9. They are used as light-emitting materials in OLEDs.

![Figure 1.9 The target molecules CP2 and CA2](image)

Objectives of this research

(1) To synthesize pyrene and anthracene-substituted carbazole derivatives as both emitting and hole-transporting materials for OLEDs.

(2) To characterize and identify the target product during the synthesis steps

(3) To study optical property and potential of the target molecules

1.2 RESULTS AND DISCUSSION

In this research, organic compounds, carbazole derivatives, were designed for studied OLEDs properties. The target molecules CP2 and CA2, pyrene and anthracene-substituted carbazole derivatives, were designed synthesized, characterized and studied optical property. Structure of CP2 and CP1 are shown in Figure 1.10.
1.2.1 Synthesis and characterization of CP2 and CA2

The target carbazole CP2 and CA2 were successfully synthesized by bromination and Suzuki cross coupling. The target carbazole were synthesized from Suzuki cross coupling of dibromocarbazole 3 with pyrene-1-boronic acid and 10-phenyl-9-anthraceneboronic acid. The dibromocarbazole 3 was synthesized alkylation of carbazole 1 with 1-bromododecane and following by bromination with N-bromosuccinimine (NBS) as shows in Figure 1.11.

First step, 9-dodecylcarbazole 2 was synthesized by alkylation reaction at the N-position of carbazole 1 with 1-bromododecane. The treatment of carbazole with
sodium hydride (NaH) and 1-bromododecane in DMF at 0 °C to room temperature overnight gave 9-dodecylcarbazole 2 in 97% yield as shows in Figure 1.12.

\[
\begin{array}{c}
\text{Figure 1.12 Synthesis of 9-dodecylcarbazole 2} \\
\text{The 9-dodecylcarbazole 2 was confirmed by } ^1\text{H-NMR and } ^1\text{C-NMR [11]. } ^1\text{H-NMR spectra of 9-dodecylcarbazole 2 still show eight aryl proton in the same region of carbazole and shows new triplet peak of N-CH}_2\text{-proton at } \delta = 4.36 (2H) \text{ and peak of alkyl protons at } \delta = 1.96 (2H), 1.41-1.37 (18H) \text{ and } \delta = 1.05 (3H) \text{ ppm. Remarkable, the NH proton of carbazole was absented. Moreover, } ^1\text{C-NMR spectrum} \\
\text{shows new signal of N-CH}_2\text{- at } \delta = 43.2 \text{ ppm and new ten peaks of 11 alkyl carbons. These results confirmed that product was compound 2.} \\
\text{The mechanism of alkylation reaction was purposed via nucleophilic substitution reaction as shows in Figure 1.13. Nitrogen anion intermediate [A] were generated by reaction of carbazole with hydride of NaH. Then, nitrogen anion attacked at C-1 position of 1-bromododecane to give 9-dodecylcarbazole 2.} \\
\end{array}
\]

Next step, selective bromination of 9-dodecylcarbazole 2 at C-3 and C-6 position were investigated. The treatment of compound 2 with NBS in THF at room temperature for 3h afforded 3,6-dibromo-9-dodecylcarbazole 3 in 91% yields as shows in Figure 1.14.
The compound 3 was confirmed by $^1$H-NMR and $^{13}$C-NMR [11]. $^1$H-NMR spectra of 3,6-dibromo-9-dodecylcarbazole 3 shows six aromatic protons at $\delta = 8.15$ (2H), 7.55 (2H) and 7.29 (2H) and shows twenty five alkyl protons in the same region of dodecyl group. The absented of two protons of carbazole was believe that bromination on carbazole 2 was appeared. Moreover, $^{13}$C-NMR spectrum shows CH aromatic carbon of carbazole only three signals at $\delta = 129.0$ (2 x CH), 123.5 (2 x CH), 123.3 (2 x CH). Therefore, NMR results confirm that two protons of carbazole were substituted by two bromine atoms. These results confirmed that product was compound 3.

The mechanism of bromination was purposed via electrophilic aromatic substitution as shows in Figure 1.15. Firstly, carbon C-3 position of carbazole as a nucleophile attacked at bromine atom of N-bromosuccinimide to give carbazole intermediate [B]. The aromatization of intermediate [B] via deprotonation gave intermediate compound [C]. Then, bromination at C-6 position of carbazole [C] in the same mechanisms gave intermediate [D] and 3,6-dibromo-9-dodecylcarbazole 3, respectively.

![Figure 1.14 Bromination of 9-dodecylcarbazole 2](image)

![Figure 1.15 Mechanisms of bromination of 9-dodecylcarbazole (2)](image)
Then, target molecules CP2 were synthesized by Suzuki cross coupling reaction. The treatment of compound 3, pyrene-1-boronic acid, Pd(PPh3)4 as the catalyst and aqueous Na2CO3 as the base in THF at reflux afforded target molecules CP2 in 53% yields as shown in Figure 1.16.

![Figure 1.16 Synthetic of target molecules CP2](image)

The target compound CP2 was confirmed by 1H-NMR and 13C-NMR. 1H-NMR spectra of compound CP2 show 24 aromatic protons (new more 18 aromatic protons from compound 3) and show twenty five alkyl protons in the same region of dodecyl group. The increasing of new 18 aromatic protons were believe that bromine atom were substituted by pyrenyl group. In addition, 13C-NMR spectra shows new 18 CH aromatic carbons and new 14 Cq aromatic carbons of pyrenyl group. Therefore, NMR results confirm that two bromine atoms were substituted by two pyrenyl groups. Moreover, the high resolution mass spectrometry (MALDI-TOF) of compound CP2 found 735.2981 (calcd for C56H49N: m/z 735.3865). These results confirmed that product was compound CP2.

The mechanism of Suzuki coupling reaction follows a three-step mechanism cycle, oxidative addition, transmetallation and reductive elimination as described in Figure 1.16. The oxidative addition at C-Br bond of compound 3 with Pd(0) gave organopaladium complex [E]. The reaction of complex [E] with Na2CO3 gave complex [F]. Transmetallation of complex [F] with organoboron species [G], preparing from reaction of boronic acid and Na2CO3, gave complex [H]. Finally, reductive elimination of complex [D] gave molecules [I]. Then, Suzuki coupling reaction at C-6 position of carbazole [I] in the same mechanisms gave target compound CP2.
Finally, the target molecules CA2 was synthesized by Suzuki cross coupling reaction. The treatment of compound 3, 10-phenyl-9-anthracene boronic acid, Pd(PPh3)4 as the catalyst and K'OBu as the base in THF at reflux afforded target molecules CA2 in 68% yields as shows in Figure 1.18.

The target compound CA2 was confirmed by 1H-NMR and 13C-NMR. 1H-NMR spectra of compound CA2 shows 32 aromatic protons (new more 26 aromatic protons from compound 3) and shows twenty five alkyl protons in the same region of
dodecyl group. The increasing of new 26 aromatic protons were believe that bromine atom were substituted by 10-phenyl-9-anthracenyl group. In addition, $^{13}$C-NMR spectrum shows new 26 CH aromatic carbon and new 14 Cq aromatic carbon of 10-phenyl-9-anthracenyl group. Therefore, NMR results confirm that two bromine atoms were substituted by 10-phenyl-9-anthracenyl group. Moreover, the high resolution mass spectrometry (MALDI-TOF) of compound CA2 found 839.3175 (calcld for C$_{64}$H$_{77}$N: m/z 839.4491). These results confirmed that product was compound CA2.

The mechanism of Suzuki coupling of compound CA2 similar to mechanism of Suzuki coupling reaction as described in Figure 1.17.

1.2.2 Optical properties of CP2 and CA2

The optical properties of the organic materials were investigated by UV-Vis and fluorescence spectrophotometer in dry dichloromethane (DCM). The UV-Vis absorption and photoluminescence spectra of the target molecules CP2 and CA2 were measured as shown in Figure 1.19 and the corresponding data summarized in Table 1.1. In solution absorption spectra, the UV-Vis spectra of the target molecules CP2 and CA2 exhibited two major absorption bands. The first absorption band of compounds CP2 and CA2 were assigned in terms of the strong absorption band in the region of 200-275 nm corresponding to the $\pi-\pi^*$ local electron transition of the carbazole moieties and the second absorption bands at longer wavelength around 350-400 nm corresponding to intermolecular charge transfer (ICT) transition between the carbazole and conjugated substituted dipyrene and dianthracene. However, the substitution dipyrene CP2 to substituted anthracene CA2 of carbazole increased the conjugation length of compounds resulting a red-shift and broad in absorption spectra. Therefore, the ICT of CA2 was stronger than ICT of CP2.

These compounds in solution show fluorescence in the blue region (430-442 nm) with featureless photoluminescence (PL) spectra. The emission spectra display maxima at 430 and 442 nm, for CP2 and CA2, respectively. From the substitution dipyrene CP2 to substituted anthracene CA2, the PL spectra also show a gradual red-shife, concomitant with the increasing conjugation length (Figure 1.19).
Figure 1.19 Normalized absorption spectra (left) and normalized emission spectra (right) in CH₂Cl₂ of CP2 and CA2

Table 1.1 Physical data of CP2 and CA2

<table>
<thead>
<tr>
<th>Compound</th>
<th>λ_{abs}(log ε)^a (nm M⁻¹ cm⁻¹)</th>
<th>λ_{em}^a (nm)</th>
<th>Eg^b (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP2</td>
<td>279 (5.37), 348 (2.35)</td>
<td>430</td>
<td>3.10</td>
</tr>
<tr>
<td>CA2</td>
<td>305 (3.93), 359 (4.09), 377 (4.24), 397 (4.23)</td>
<td>442</td>
<td>2.95</td>
</tr>
</tbody>
</table>

^a Measured in dilute CH₂Cl₂ solution.

^b Calculated from the absorption edge, Eg = 1240 per onset

The energy gaps (E_g) of the target molecules from the absorption edge were nearly identical (2.95-3.10 eV), despite the somewhat different molecular sizes and substance groups.

Conclusion of optical properties, compound CA2 has longer conjugate and stronger intermolecular charge transfer than CP2 from result of UV absorption spectra. Moreover, emission spectra conclude that compound CP2 and CA2 emit in the blue region but CA2 spectra showed peak shift of up to 12 nm from compound CP2.

1.2.3 Electrochemical properties of CP2 and CA2

The electrochemical properties of materials were performed using the cyclic voltameter (CV). All measurements were made at room temperature on sample dissolved in freshly distilled dichloromethane and 0.1 M tetra-n-
butylammonium hexafluorophosphate (n-Bu₄NPF₆) as electrolyte. The solutions were degassed by bubbling with argon. A typical electrochemical cell consists of three electrodes; a glassy carbon working electrode, platinum wire counter electrode, and Ag/AgCl/NaCl (Sat.) reference electrode, controlled by a potentiostat. The potential difference was applied between the working and counter. The third electrode was the reference electrode, through which no current flows, and from which the potentials of the other electrodes were measured. A part from the solutions, the solute in this work contained an electrolyte to decreases the resistivity.

The electrochemical stability of materials was performed by multiple-scan CV curves. The HOMO energy levels of materials were calculated from the oxidation onset potentials (E_{onset}) with empirical equation of HOMO = - (4.44 + E_{onset}) while LUMO energy levels were calculated by subtracting the E_g from HOMO levels.

Electrochemical behaviors of CP2 and CA2 investigated by cyclic voltammetry (CV), and resulting data are shown in Figure 1.20.

![Cyclic voltammograms of CP2 (left) and CA2 (right) in dry CH₂Cl₂ with scan rate of 0.05 V/s and 0.1 M n-Bu₄NPF₆ as electrolyte, muti scan.](image)

**Figure 1.20** Cyclic voltammograms of CP2 (left) and CA2 (right) in dry CH₂Cl₂ with scan rate of 0.05 V/s and 0.1 M n-Bu₄NPF₆ as electrolyte, muti scan.

Multiple CV scans of CA2 revealed identical CV curves with no additional peak at lower potentials on the cathodic scan (Epc) being observed. This suggests no electrochemical coupling at either the carbazole or anthracene peripheries, indicating electrochemically stable molecules. However, the target molecule CA2 more stable than target molecule CP2. The CV curve of CP2 shows three irreversible oxidation processes. The first oxidation is assigned to the removal of electrons from the
carbazole moiety resulting in carbazole radical cations (CBZ⁺). In all cases, during the cathodic scan additional peaks at lower potentials are observed, indicating electrochemical coupling reactions of the radical cations formed were taking place. As proposed in Figure 1.21, the generated CBZ⁺ is stabilized by electron delocalization through 1,8-substituted electron rich pyrene rings to form a pyrene radical cation (Py⁺) which is relatively less stable compared with the CBZ⁺. The Py⁺ readily undergoes a radical–radical dimerization coupling to form a stable neutral pyrene dimer as indicated by the presence of the cathodic peaks (Epc) around 0.61-0.94 V in their first CV scan and an increasing change in the CV curves under the repeated CV scans 10 Figure 1.20.

![Figure 1.21 Oxidation process of pyrene](image)

Moreover, they also showed similar wave in different scans, no distinct a slight shift of the CV curves. During in order oxidation cycle of all compounds, the oxidation progressively shifted to higher energy with increasing the aromatic unit. This might be the first example of pyrene and anthracene derivatives that undertake an electrochemical oxidation coupling reaction.

The HOMO energy levels of pyrene and anthracene derivatives were estimated to be -5.41 and -5.45 eV respectively. The LUMO energy levels of pyrene and anthracene derivatives were estimated to be -2.31 and -2.50 eV respectively (Table 1.2).
Table 1.2 Physical data of CP2 and CA2

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_g^b$ (eV)</th>
<th>HOMO$^c$ (eV)</th>
<th>LUMO$^d$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP2</td>
<td>3.10</td>
<td>-5.41</td>
<td>-2.31</td>
</tr>
<tr>
<td>CA2</td>
<td>2.95</td>
<td>-5.45</td>
<td>-2.50</td>
</tr>
</tbody>
</table>

$^b$ Calculated from the absorption edge, $E_g = 1240$ per onset

$^c$ Estimated from HOMO = -(4.44 + $E_{\text{onset}}^\text{ox}$)

$^d$ Estimated from LUMO = HOMO + $E_g$

1.2.4 HOMO and LUMO frontier orbitals of CP2 and CA2

To gain insights into the geometrical and electronic properties of these multiple substituted carbazoles, quantum chemistry calculations were performed using the DFT/B3LYP/6-31G(d,p) method. The optimized structures of CP2 reveal that the attached pyrene units twist out of the plane of the carbazole forming bulky substituents around the carbazole. This would facilitate the formation of amorphous materials. In all cases CP2 and CA2, π-electrons in the HOMO orbitals delocalize only over the carbazole and two substituents at the 3,6-positions substituted carbazole backbone, whereas after light irradiation (LUMO), the excited electrons are delocalized largely over the pyrene and anthracene plane.

![LUMO Orbitals](image1)
![HOMO Orbitals](image2)

Figure 1.22 The HOMO (bottom) and LUMO (top) orbitals of CP2 and CA2 calculated by DFT/B3LYP/6-31G(d,p) method.
1.3 CONCLUSION

In conclusion, we have successfully synthesized pyrene and anthracene-substituted carbazole (CP2, CA2) by the Suzuki-cross coupling reaction of dibromo intermediates with pyrene-1-boronic acid and 10-phenyl-9-anthraceneboronic acid, respectively. The target molecules were characterized by using melting points, $^1$H-NMR and $^{13}$C-NMR spectroscopy, FT-IR spectroscopy and mass spectrometer.

![Reaction Scheme]

The optical and electrochemical properties of both compounds can be tuned by varying the substituted on carbazole ring. The substitution dipyrene CP2 to substituted anthracene CA2 of carbazole increased the conjugation length of compounds resulting a red-shift and broad in absorption spectra. These compounds were emissive of blue light with high thermal stability which is potentially useful for applications in electroluminescent devices. Optimize structure and electron density of HOMO and LUMO have been performed by DFT/B3LYP/6-31G(d,p) method.

1.4 EXPERIMENTAL

1.4.1 GENERAL EXPERIMENT

All solvents and reagents were purchased from Aldrich, Acros and Fluka received unless otherwise stated. Analytical thin-layer chromatography (TLC) was performed with Merck aluminium plates coated with silica gel 60 F$_{254}$. Column chromatography was carried out using gravity feed chromatography with Merck silica gel mesh, 60 A. Where solvent mixtures are used, the portions are given by volume.
Melting points was measured by BUCHI 530 model in open capillary method and are uncorrected and reported in degree Celsius.

$^1$H-NMR and $^{13}$C-NMR spectra were recorded on a Bruker AVANCE 300 MHz spectrometer. Chemical shifts (δ) are reported relative to the residual solvent peak in part per million (ppm). Coupling constants (J) are given in Hertz (Hz). Multiplicities are quoted as singlet (s), broad (br), doublet (d), triplet (t), quartet (q), and multiplet (m).

The IR spectra were recorded on Perkin-Elmer FT-IR spectrum RXI spectrometer. The absorption peaks are quoted in wavenumber (cm$^{-1}$). MALDI-TOF mass spectra were recorded on Bruker Daltonics (Bremen, Germany) Autoflex II Matrix-Assisted Laser Desoprtion/Ionization-Time of Flight Mass Spectrometer (BIFEX) using α-cyano-4-hydroxycinnamic acid as matrix. UV–Vis spectra were recorded on a Perkin–Elmer UV Lambda 25 spectrometer.

The electrochemistry was performed using a AUTOLAB spectrometer. All measurements were made at room temperature on sample dissolved in freshly distilled dichloromethane, 0.1 M tetra-n-butylammonium hexafluorophosphate as electrolyte. The solutions were degassed by bubbling with argon. Dichloromethane was distilled from calcium hydride. A glassy carbon working electrode, platinum wire counter electrode, and a Ag/AgCl/NaCl (Sat.) reference electrode were used.

1.4.2 Synthesis of 9-Dodecylcarbazole (2)

![Chemical Structure]

To a solution of carbazole (10.1021 g, 59.80 mmol) in DMF (93 mL) was added NaH (2.3540g, 89.58 mmol) and then 1-bromododecane (15.9000 g, 89.70 mmol). The reaction mixture was stirred at 0 °C to rt for 20 h. Water (100 mL) was added and the mixture was extracted with ethyl acetate (50 mL x 3). The combined organic phases were washed with a dilute HCl solution (50 mL x 2), water (100 mL), and brine solution (50 mL), dried over anhydrous Na$_2$SO$_4$, evaporated and purified by column chromatography to give a pale yellow viscous oil (19.7825 g, yield 97%) [11].
C_{24}H_{33}N;

$^1$H-NMR (300 Hz, CDCl$_3$):
\[ \delta = 8.24 (2H, d, J = 7.8 \text{ Hz}), 7.79-7.49 (4H, m), 7.36 (2H, d, J = 14.4 \text{ Hz}), 4.36 (2H, t, J = 6.9 \text{ Hz}), 1.96 (2H, t, J = 6.6 \text{ Hz}), 1.41-1.37 (18H, m) \text{ and } 1.05 (3H, t, J = 5.4 \text{ Hz}) \text{ ppm.} \]

$^{13}$C-NMR (75 Hz, CDCl$_3$):
\[ \delta = 140.6 (2 \times Cq), 125.7 (2 \times CH), 123.0 (2 \times Cq), 120.5 (2 \times CH), 118.8 (2 \times CH), 108.8 (2 \times CH), 43.2 (N-CH$_2$), 32.1 (CH$_2$), 29.8 (2 \times CH$_2$), 29.75 (CH$_2$), 29.7 (CH$_2$), 29.6 (CH$_2$), 29.5 (CH$_2$), 29.1 (CH$_2$), 27.4 (CH$_2$), 22.9 (CH$_2$), 14.3 (CH$_3$) \text{ ppm.} \]

IR (KBr):
\[ \nu_{\text{max}} = 3052, 2922, 2851, 1597, 1484, 1451, 1324, 1152, 746, 720 \text{ cm}^{-1}. \]

1.4.3 Synthesis of 3,6-Dibromo-9-dodecylcarbazole (3)

\[
\begin{align*}
\text{C}_{12}H_{25}^N & \quad \text{2.1 eq NBS,} \quad \text{THF, rt, 3h.} \\
& \quad \text{Br} \\
\text{C}_{12}H_{25}^N & \quad \text{Br}
\end{align*}
\]

In the flask, covered with aluminum foil, to a solution of 3-monobromo-9-dodecylcarbazole 2 (0.5184 g, 1.54 mmol) in THF (15 mL) was added NBS (0.5772 g, 3.24 mmol) in small portions at 0°C. After stirred 0°C to rt for 3 h, the reaction mixture was poured into water. The mixture was extracted with methylene chloride (20 mL x 3), washed with water (20 mL x 3), dried over anhydrous Na$_2$SO$_4$, evaporated and purified by column chromatography to give a white pearl solid (0.6951 g, yield 91%). [11]

C$_{24}$H$_{31}$Br$_2$N; m.p. = 50-52°C

$^1$H-NMR (300 Hz, CDCl$_3$):
\[ \delta = 8.15 (2H, s), 7.55 (2H, d, J = 8.7 \text{ Hz}), 7.29 (2H, d, J = 8.7 \text{ Hz}), 4.25 (2H, t, J = 7.0 \text{ Hz}), 1.85 (2H, s), 1.30-1.21 (18H, m), 0.88 (3H, t, J = 6.3 \text{ Hz}) \]

$^{13}$C-NMR (75 Hz, CDCl$_3$):
\[ \delta = 139.4 \text{ (2 x Cq)}, 129.0 \text{ (2 x CH)}, 123.5 \text{ (2 x CH)}, 123.3 \text{ (2 x CH)}, 111.9 \text{ (2 x Cq)}, 110.4 \text{ (2 x CH)}, 43.4 \text{ (N-CH}_2\text{)}, 31.8 \text{ (CH)}, 29.6 \text{ (2 x CH)}, 29.5 \text{ (CH)}, 29.4 \text{ (CH)}, 29.3 \text{ (2 x CH)}, 28.8 \text{ (CH)}, 27.2 \text{ (CH)}, 22.7 \text{ (CH)}, 14.1 \text{ (CH}_3\text{)} \text{ ppm.} \]

IR (KBr):

\[ \nu_{\text{max}} = 2950, 2918, 2848, 1592, 1469, 1289, 1224, 1057, 802, 720 \text{ cm}^{-1}. \]

1.4.4 Synthesis of 9-Dodecyl-3,6-di(pyren-1-yl)carbazole (CP2)

To a stirred solution of 3,6-dibromo-9-dodecyl carbazole 3 (0.2000 g, 0.34 mmol) and Pd(PPh\(_3\))\(_4\) (0.0303 g, 0.02 mmol) in tetrahydrofuran (20 mL) were added pyrene-1-boronic acid (0.1759 g, 0.71 mmol) and an aqueous Na\(_2\)CO\(_3\) solution (0.5576 g, 5.26 mmol). The mixture was refluxed for 48 h. After cooling, the mixture was extracted with dichloromethane (30 mL x 3), washed with water (30 mL x 3), dried over anhydrous, evaporated and purified by column chromatography to give a white pearl solids (0.2506 g, yield 53%).

C\(_{56}\)H\(_{49}\)N; m.p. = 170-173 °C

\(^1\)H-NMR (300 Hz, CDCl\(_3\)):

\[ \delta = 8.40 \text{ (2H, s)}, 8.34 \text{ (2H, d, } J = 9.30 \text{ Hz)}, 8.25 \text{ (2H, d, } J = 7.80 \text{ Hz)}, 8.20-8.10 \text{ (10H, m)}, 8.06-7.97 \text{ (4H, m)}, 7.80 \text{ (2H, d, } J = 8.40 \text{ Hz)}, 7.65 \text{ (2H, d, } J = 7.64\text{), 4.47 (2H, t, } J = 7.20 \text{ Hz)}, 2.10 \text{ (2H, t, } J = 6.90 \text{ Hz)}, 1.57-1.30 \text{ (18H, m) and 0.91 (3H, t, } J = 6.90 \text{ Hz)} \]

\(^13\)C-NMR (75 Hz, CDCl\(_3\)):

\[ \delta = 140.3 \text{ (2 x Cq)}, 138.7 \text{ (2 x Cq)}, 132.1 \text{ (2 x Cq)}, 131.6 \text{ (2 x Cq)}, 131.1 \text{ (2 x Cq)}, 130.3 \text{ (2 x Cq)}, 128.9 \text{ (2 x Cq)}, 128.7 \text{ (2 x CH)}, 128.2 \text{ (2 x CH)}, 127.5 \text{ (2 x CH)}, 127.3 \text{ (2 x CH)}, 127.1 \text{ (2 x CH)}, 125.9 \text{ (2 x CH)}, 125.7 \text{ (2 x CH)}, 125.1 \text{ (2 x Cq)}, 125.0 \text{ (2 x Cq)}, 124.9 \text{ (2 x CH)}, 124.6 \text{ (4 x CH)}, 123.1 \text{ (2 x Cq)}, 122.5 \text{ (2 x CH)}, 108.7 \text{ (2 x CH)}, 43.6 \text{ (N-CH}_2\text{)}, 31.9 \text{ (CH}_2\text{)}, 29.7 \text{ (3 x CH}_2\text{)}, 29.6 \text{ (CH}_2\text{)}, 29.5 \text{ (CH}_2\text{)}, 29.4 \text{ (CH}_2\text{)}, 29.2 \text{ (CH}_2\text{)}, 27.5 \text{ (CH}_2\text{)}, 22.7 \text{ (CH}_2\text{)}, 14.1 \text{ (CH}_3\text{)} \text{ ppm.} \]
IR (KBr):

\[ \nu_{\text{max}} = 3038, 2919, 2849, 1600, 1480, 1279, 1153, 849, 817 \text{ cm}^{-1} \]

MALDI-TOF (m/z) calcd for $C_{56}H_{49}N$: 735.3865; found 735.2981 (M⁺).

1.4.5 Synthesis of 9-Dodecyl-3,6-di(anthracen-1-yl)carbazole (CA2)

![Chemical structure diagram]

To a stirred solution of 3,6-dibromo-9-dodecyl carbazole 3 (0.2507 g, 0.42 mmol) and Pd(PPH3)₄ (0.0246 g, 0.02 mmol) in tetrahydrofuran (25 mL) were added 10-phenyl-9 anthraceneboronic acid (0.2672 g, 0.89 mmol) and an aqueous t-BuOK solution (0.4789, 4.26 mmol). The mixture was refluxed for 48 h. After cooling, the mixture was extracted with dichloromethane (30 mL x 3), washed with water (30 mL x 3), dried over anhydrous, evaporated and purified by column chromatography to give a white pearl solids (0.3986 g, yield 68%).

$C_{64}H_{57}N$; m.p. >200 °C

$^1$H-NMR (300 Hz, CDCl₃):

\[ \delta = 8.19 (2H, s), 7.84-7.80 (4H, m), 7.74-7.68 (6H, m), 7.63-7.48 (12H, m), 7.33-7.26 (8H, m), 4.57 (2H, t, J = 6.9 Hz), 2.15 (2H, t, J = 7.5 Hz), 1.50-1.20 (18H, m) \text{ and } 0.86 (3H, t, J = 6.3 Hz) \]

$^{13}$C-NMR (75 Hz, CDCl₃):

\[ \delta = 140.4 (2 \times Cq), 139.2 (2 \times Cq), 137.9 (2 \times Cq), 136.8 (2 \times Cq), 131.42 (4 \times CH), 131.36 (2 \times CH), 130.6 (4 \times Cq), 129.9 (4 \times Cq), 129.5 (2 \times Cq), 129.4 (2 \times CH), 128.4 (4 \times CH), 127.4 (4 \times CH), 126.9 (4 \times CH), 124.9 (4 \times CH), 124.8 (4 \times CH), 123.3(2 \times CH), 122.8 (2 \times Cq), 108.8 (2 \times CH), 43.7 (N-CH₂), 31.9 (CH₂), 29.69 (3 \times CH₂), 29.66 (CH₂), 29.57 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 27.6 (CH₂), 22.7 (CH₂), 14.1 (CH₃) \text{ ppm.} \]

IR (KBr):

\[ \nu_{\text{max}} = 2921, 2851, 1599, 1492, 1440, 1388, 1281, 1232, 1025, 767, 700 \text{ cm}^{-1} \]

MALDI-TOF (m/z) calcd for $C_{64}H_{57}N$: 839.4491; found 839.3175 (M⁺).
CHAPTER 2
SYNTHESIS AND CHARACTERIZATION OF
INDOLE DERIVATIVES FOR DYE-SENSITIZED SOLAR CELL

2.1 INTRODUCTION

2.1.1 Dye-sensitized solar cells (DSSCs)

Actually, the capability of human is to extent dependently on the available energy sources. In the developing countries, energy consumption has reached a level of over $4 \times 10^{18}$ J already in the present annual worldwide and it is foresighted to multiply swiftly accompany with the increasing of world population and demand of energy [22]. As to the rising energy demand and more reduced fossil fuel reserves, the damaged environment and the improved greenhouse effect, affected by the combustion of fossil fuels, can out of control [23]. In other words, if the demands of energy have a chance to use renewable energy sources, the cost of environment could be decreased. Yearly, the sun could provide energy $3 \times 10^{24}$ J to the earth [24]. This is about 750000 times greater than the present consumption of global population. The expectation to absorb the sunlight and turn it into electric power or to generate chemical fuels, for example, hydrogen, is become reality in the last two decades. Colloids and nanocrystalline films of various semiconductor systems have been manipulated in form of transform the solar energy directly to be the chemical or electrical energy. The traditional photovoltaic which is based on the solid-state connection devices, such as crystalline or amorphous silicon, has exception of changing solar energy approximately 20% to become electricity efficiencies. To invent the photovoltaic, however, is extravagant because it has to use intensive high temperature energy and high vacuum processes.

In 1991, O'Regan and Gratzel distributed a progress of an option solar harvesting device, dye-sensitized solar cell (DSSCs), [25]. The device supplies 7% of altering a solar energy to electricity, based on a mesoscopic inorganic semiconductor. Then 2.5% of energy proficiency had been reached in this research field. Moreover, the some semiconductor surfaces such as TiO$_2$ or ZnO is stimulated by an optical
absorbing chromophore with properties of charge disunion that can absorb the solar light and its excited state inject electrons into the semiconductor [26].

2.1.2 Dye-sensitized solar cells structure

The dye-sensitized solar cell is a low-cost solar cell belonging to the group of thin film solar cells. It is based on a semiconductor formed between a photosensitized anode and an electrolyte, a photoelectrochemical system. Therefore, the DSSCs structure consist of 4 part including organic sensitizer coating, electrolyte solution, counter electrode and dye sensitizer [27] as shown in Figure 2.1.

![Figure 2.1 Dye-sensitized solar cells structure (DSSCs) structure [28]](image)

2.1.2.1 Organic sensitizer coating with wide band gap semiconductor which is placed in contact with a redox electrolyte, the material of choice has been TiO2 (anatase).

2.1.2.2 An electrolyte solution containing redox couple such as I-/I3, the regeneration of the sensitizer by iodide intercepts the recapture of the conduction band electron by the oxidized dye.

2.1.2.3 A counter electrode which is a platinized conductive glass substrate such as fluorine-doped tin oxide glass (FTO).

2.1.2.4 Dye sensitizer serve as the solar energy absorber in DSSC, whose proprieties will have much effect on the light harvesting efficiency and the overall photoelectric conversion efficiency. The ideal sensitizer for dye-sensitized solar cells should absorb all light below a threshold wavelength of about 920 nm. In addition, it
should be firmly grafted to the semiconductor oxide surface and inject electrons to the conduction band with a quantum yield of unity. Its redox potential should be sufficiently high that it can be regenerated rapidly via electron donation from the electrolyte or a hole conductor. Finally, it should be stable enough to sustain at least 108 redox turnovers under illumination corresponding to about 20 years of exposure to natural light.

2.1.3 Principle of Dye-sensitized solar cells

The working principle of DSSCs was shown in Figure 2.2. Dye in dye-sensitized solar cells discharges electrons when hit by sunlight. Discharged electrons move toward a transparent anode (negative electrode) through titanium dioxide (titania particles). Electrons that have reached the transparent anode (negative electrode) move toward counter electrode (positive electrode) through an external circuit. Iodide electrolyte receives electrons from the positive electrode. Electrolyte provides received electrons to dye, thanks to the working of iodide ions. Dye received electrons returns to their original condition. Dye-sensitized solar cells generate power by repeating the cycle [29].

![Figure 2.2 Working principle of DSSCs](image)

*Figure 2.2 Working principle of DSSCs [30]*
2.1.4 Literature reviews

In this part, the publications of synthesis and study optical properties of dye-sensitizer for DSSCs application would be described. For example:

In 2007, Kim, D et al. [31] investigated that the organic dyes (JK-24, JK-25 and JK-28) containing N-(9,9-dimethylfluoren-2-yl)carbazole or N-(4-(2,2-diphenylvinyl)phenyl)carbazole as electron donor and cyanoacrylic acid as electron acceptor bridged by thiophene units, gave an overall conversion efficiency (\(\eta\)) of 3.87-5.15%. Although many structure frameworks such as coumarin, aniline and indoline have been employed as good electron donor unit, the small molecular organic dyes containing the N-substituted carbazole structural have been little explored for DSSCs.

![Figure 2.3 Chemical structures of JK-24, JK-25 and JK-28 dyes](image)

In 2009, Chang, Y J. et al. [32] reported that the highly efficient and stable organic dyes (1P-PSP and 1N-PSP) composed of triphenylamine or \(N,N\)-diphenylnapthalen-1-amine moiety as the electron donor and cyanoacrylic acid moiety as the electron acceptor with an overall conversion efficiency of 5.25-7.08%.

![Figure 2.4 Chemical structures of 1P-PSP and 1N-PSP dyes](image)
In 2012, Wan, Z. et al. [33] investigated that the organic dyes (CBZ, WD-5, and DTA) containing carbazole, phenothiazine or diphenylamine as electron donor and cyanoacrylic acid as electron acceptor bridged by phenyl units, gave an overall conversion efficiency of 1.77-2.03%.

![Chemical structures of CBZ, WD-5, and DTA dyes](image)

**Figure 2.5** Chemical structures of CBZ, WD-5, and DTA dyes

In 2009, Jaejung, K. et al. [34] designed and synthesize organic dye benzo[cd]indole JK51. Firstly, benzoindole aldehyde 10JK were synthesized from 2, 6, 7, 8-tetrahydro-1-phenylbenzo[cd]indole 1JK via four steps reactions. Then aldehyde 10JK were reacted with cyanoacetic acid and piperidine to gain the substance JK51 as shown in **Figure 2.6**. The benzo[cd]indole JK51 show conversion conversion efficiency at 8.42%, short circuit at 17.43 mA/cm², open circuit voltage at 0.680 V, and fill factor at 0.71.

![Dye-organic synthesis included of benzo[cd]indole group](image)

**Figure 2.6** Dye-organic synthesis included of benzo[cd]indole group
In 2012, Shingo, K. et al. [35] synthesized new type of organic dying included of carbazole (MK75, MK79, MK80), indole (MK81-83), and indoline (MK84-86) as electron donors. These substances had cyanoacrylic acid which was electron acceptors and they were joined together with bi-3-n-hexylthiophene as shown in Figure 2.7. As for bringing this to study about conversion efficiency, carbazole MK75, MK79 and MK80 was valued from 5.1 to 5.4%, indole MK81-83 was valued between 3.5 to 3.9%, and indoline MK84-86 was valued from 3.0 to 3.7%.

![Figure 2.7 The structure of dye molecules included of carbazole (MK75, MK79, MK80), indole (MK81-83) and indoline (MK84-86)](image)

In 2014, Gang, W. et al. [36] studied about the property of electricity and dye-sensitized which had a system of D-π-A in form of isoindigo group. The study was done by synthesizing ID1, ID2, and ID3 as shown in Figure 2.8. The finding indicated that ID1 had extended range of absorption and energy conversion efficiency (\(\eta\)). Moreover, ID1 was the utmost value at 3.33% under 100 mW/cm² simulated AM 1.5 G solar irradiation.
In 2008, the efficiency and stability of organic dye JK79, improving working’s quality of dye-sensitized solar cells, were studied by Kim, D. et al [37]. The improvement could be done by combining of bis-dimethylfluorenyl amino and indole group to target dye-sensitized molecule for increasing pi bond conjugation. The target molecule JK79 was synthesized from indole substance 10JK. The four reaction steps of compound 10JK gave aldehyde 13JK, and then it was reacted with cyanoacetic acid and piperidine to be Knoevenagel consideration to gain the target compound JK79 as shown in Figure 2.9. The result of photo properties show that compound JK79 gave short circuit at 13.62 mA/cm², open circuit voltage at 0.705 V, fill factor at 0.74 and conversion efficiency at 7.18%
In 2013, Kim, B. H. et al. [38] synthesized organic dying (DP-T) and (DP-P) which included thiophene and N-methyl pyrrole as the connective between electron donors and electron acceptors respectively. The targets molecules were synthesized by Knoevenagel condensation of aldehyde (1c) and (2d) with cyanoacetic acid as shown in Figure 2.10. For bringing this to study about conversion efficiency, the result revealed that a thiophene derivative DP-T had the highest value as 3.53% and a methyl pyrrole derivative DP-P had the utmost value as 3.03%. It was clear that a thiophene derivative DP-T was more efficient than a methyl pyrrole derivative DP-P. This affected from thiophene captured and absorbed solar energy better than N-methyl pyrrole, so it was more conversion efficiency than N-methyl pyrrole.

![Figure 2.10 The synthesis of organic dying included of thiophene and N-methyl pyrrole as the connectors](image)

In 2014, dye-sensitized type D-D-π-A, indole SD1 and SD2 (Figure 2.11), were synthesized and studied by Liu, X. et al [39]. The synthesis compounds included triphenylamine and indole as electron donors. The results of conversion efficiency indicated that the conversion efficiency (η) of dye-sensitized type SD2 at 6.74% higher than the conversion efficiency (η) at 5.53% of SD1. It was believe that donated effective of SCN group of SD2 stronger than H aton of SD1.
In 2015, new D-π-A type indole dye-sensitized D1, D2 and D3 (Figure 2.12), were synthesized and studied by BaBu, D. D. et al [40]. The target dyes included indole as electron donor and cyanoacetic acid, rhodanine-3-acetic acid and 4-aminobenzoic acid as electron acceptor, respectively. The dye D1, D2 and D3 gave conversion efficiency at 1.04, 0.35 and 1.18%. Interestingly, the absorption maximum red shifted in the order D3 < D2 < D1 but the device sensitized by D3 displayed the highest efficiency.

**Figure 2.11 structure of SD1 and SD2**

![Structure of SD1 and SD2]

**Figure 2.12 structure of D1, D2 and D3**

![Structure of D1, D2 and D3]

### 2.1.5 Aim of the thesis

According to literature reviews, dye-sensitized molecule consist of major three parts [41]. The first part is electron donating group (D) which is electron rich function such as hetroaromatic group; carbazole, coumarins, triphenylamines and indolines. The second part is electron acceptor (A) which is electron withdrawing and polar group such as carboxyl group and sulfonyl group. The final part of dye is π-
spacer (π) which is conjugation linker between electron donating and electron acceptor group such as double bond and phenyl group.

In this research, we synthesized and characterized a new series of indole derivatives for dye-sensitized solar cells (DSSCs). The indole derivatives as electron donating group, containing double bond and phenyl group as π-spacer and benzoic and cyanoacetic acid group as electron acceptor, were designed, synthesized and characterized. The chemical structure of In1-In5 are shown in Figure 2.13.

![Chemical structures of target molecules In1-In5](image)

**Figure 2.13 The target molecules In1-In5**

2.1.5.1 Objectives of this research

To synthesize a series of aromatic or double bond and carboxyl-substituted indole derivatives as dye sensitizer for dye-sensitized solar cells.

To characterize and identify the target product during the synthesis steps.

2.2 RESULTS AND DISCUSSION

In this research, we synthesize and characterize a new series of dye-sensitized molecule for dye-sensitized solar cells (DSSCs) based on indole derivatives as electron donating group. Moreover, we designed and synthesized the following a indole containing double bond and phenyl group as π-spacer and benzoic and
cyanoacetic acid group as electron acceptor. The chemical structure of target molecules, In1-In5, are shown in Figure 2.14.

The target carbazole In1-In5 were successfully synthesized by Ullman coupling, hydrolysis reaction and Knoevenagal condensation. The targets In1 and In2 were synthesized from Ullman coupling of indole with iodoarylester following by hydrolysis reaction. In addition, The indoles In3-In5 was synthesized via Knoevenagal condensation of indolealdehyde with cyanoacetic acid as shows in Figure 2.15.
2.2.1 Synthesis and characterization of 4-(indol-1-yl)benzoic acid (In1)

The target dye In1, containing indole as electron donating group, phenyl as π-spacer at N-position of indole and carboxyl group as electron acceptor was designed. The 4-(indol-1-yl)benzoic acid (In1) was successfully synthesized by Ullman coupling and hydrolysis reaction. First step, compound 4 was synthesized by Ullman coupling reaction of indole with methyl 4-iodobenzoate. The treatment of indoie and methyl 4-iodobenzoate in the presence of copper iodide and trans-1,2-diaminocyclohexane as catalyst and K3PO4 as a base in toluene at reflux for 48 h led to compound 4 in 94% as show in Figure 2.16.
The compound 4 was confirmed by $^1$H-NMR and $^{13}$C-NMR. $^1$H-NMR spectra of compound 4 shows new peak of four protons of aryl group and the singlet peak of O-CH$_3$ protons at $\delta = 3.98$ (3H) ppm. Remarkable, the NH proton of indole was absented. Moreover, $^{13}$C-NMR spectrum shows peck of C = O carbons at $\delta = 166.4$ ppm, new peak of six carbons of aryl carbon and new signal of O-CH$_3$- at $\delta = 52.2$ ppm. These results confirmed that product was methyl 4-(indol-1-yl) benzoate 4.

The mechanism of Ullman coupling reaction follows a three-step mechanism cycle as described in Figure 2.17. The reaction of Cul, indole and K$_3$PO$_4$ afforded intermediate [M]. The oxidative addition at C-I bond of methyl 4-iodobenzoate with intermediate [M] gave organocopper complex [N]. Then, reductive elimination of complex [N] releases the coupling product 4 and the active Cul catalyst is regenerated.[42]

![Figure 2.17](image)

**Figure 2.17 The proposed mechanism of Ullmann coupling reaction**

Finally, the target molecule In1 was synthesized by hydrolysis reaction. The treatment of methyl 4-(indol-1-yl)benzoate 4 and KOH as the base in THF and IPA at reflux for 2 h afforded target molecules In1 in 64% yields as shows in Figure 2.18
The compound **In1** was confirmed by $^1$H-NMR and $^{13}$C-NMR. $^1$H-NMR spectra of compound **In1** still show ten proton of aryl group but peak of O-CH$_3$ disappeared. Remarkable, $^{13}$C-NMR spectrum of **In1** disappeared carbon peak of O-CH$_3$ group. Moreover, the high resolution mass spectrometry (MALDI-TOF) of compound **In1** found 237.1056 (calcd for C$_{15}$H$_{11}$NO$_2$: m/z 237.0790). These results confirmed that product was 4-(indol-1-yl) benzoic acid **In1**.

The mechanism of hydrolysis reaction was proposed via three-step as show in **Figure 2.19**[22]. First step, the hydroxide nucleophiles attacks at the electrophilic C=O of ester breaking the π bond and creating the intermediate [O]. The intermediate [O] collapses, reforming the C=O results in the loss of the leaving group the alkoxide, MeO$,^-$, leading to the carboxylic acid. Finally, A very rapid equilibrium where the alkoxide, MeO$^-$ functions as a base deprotonating the carboxylic acid, RCO$_2$H, (an acidic work up would allow the carboxylic acid **In1** to be obtained from the reaction).

**Figure 2.18 Hydrolysis reaction of methyl 4-(indol-1-yl)benzoate 4**

**Figure 2.19 The proposed mechanism of hydrolysis reaction**
2.2.2 Synthesis and characterization 4-(3-(4-bromophenyl)-4,6-dimethoxyindol-1-yl)benzoic acid (In2)

The target dye In2, containing 4,6-dimethoxyindole as electron donating group, phenyl as \( \pi \)-spacer at \( N \)-position of indole and carboxyl group as electron acceptor was designed. The 4-(3-(4-bromophenyl)-4,6-dimethoxyindol-1-yl) benzoic acid (In2) was synthesized via Ullman coupling and hydrolysis reaction similar to In1 synthetic partway. First step, methyl 4-(3-(4-bromophenyl)-4,6-dimethoxyindol-1-yl) benzoic acid (In2) was synthesized via Ullman coupling reaction of indole 5 with methyl 4-iodobenzoate. The treatment of indole 5 and methyl 4-iodobenzoate in the presence of copper iodide and trans-1,2-diaminocyclohexane as catalyst and \( K_3PO_4 \) as a base in toluene at reflux for 48 h led to ester 6 in 41% as show in Figure 2.20.

![Figure 2.20 Synthesis of methyl 4-(3-(4-bromophenyl)-4,6-dimethoxyindol-1-yl) benzoate 6](image)

The compound 6 was confirmed by \(^1\)H-NMR and \(^{13}\)C-NMR. \(^1\)H-NMR spectra of compound 6 show new peak of four protons of aryl group and new peak of three protons of O-CH\(_3\) group. Remarkable, the N-H proton of indole 5 was absented. Moreover, \(^{13}\)C-NMR spectrum shows peak of O=\( C \) carbons at \( \delta = 166.3 \) ppm, new peak of six carbons of aryl carbon and new peak of one carbon of O-CH\(_3\) group. These results confirmed that product was of methyl 4-(3-(4-bromophenyl)-4,6-dimethoxyindol-1-yl)benzoate 6.

The mechanism of Ullmann coupling of compound 6 similar to mechanism of Ullmann coupling of compound 4 as shown in Figure 2.17.

Finally, the target molecules In2 was synthesized by hydrolysis reaction. The treatment of methyl 4-(3-(4-bromophenyl)-4,6-dimethoxyindol-1-yl)benzoate 6
and KOH as the base in THF and IPA at reflux for 2 h afforded target molecules In2 in 46% yields as shown in Figure 2.21.

![Figure 2.21](image)

**Figure 2.21 Hydrolysis reaction of methyl 4-(3-(4-bromophenyl)-4,6-dimethoxy indol-1-yl)benzoate 6**

The compound In2 was confirmed by $^1$H-NMR and $^{13}$C-NMR. $^1$H-NMR spectra of compound In2 still show eleven protons of aryl group but proton of O-CH$_3$ reduced to six protons. Remarkable, $^{13}$C-NMR spectrum of In2 shown two carbon peak of O-CH$_3$ group. Moreover, the high resolution mass spectrometry (MALDI-TOF) of compound In2 found 451.0924 (calcd for C$_{23}$H$_{18}$BrNO$_4$: m/z 451.0419). These results confirmed that product was 4-(3-(4-bromophenyl)-4,6-dimethoxyindol-1-yl) benzoic acid (In2).

The mechanism of hydrolysis of compound 6 similar to mechanism of hydrolysis of compound 4 as shown in Figure 2.19.

### 2.2.3 Synthesis and characterization of 2-cyano-3-(indol-3-yl)acrylic acid (In3)

The target dye In3, containing indole as electron donating group, double bond as $\pi$-spacer at C3-position of indole and cyanoacetic acid as electron acceptor was designed. The 2-cyano-3-(indol-3-yl)acrylic acid (In3) was easy synthesized by Knoevenagal condensation. The commercial indole-3-carbaldehyde 7 was reacted with cyanoacetic acid and piperidine in chloroform at reflux for 48 h led to 2-cyano-3-(indol-3-yl)acrylic acid In3 in 24% as show in Figure 2.22.
The 2-cyano-3-(indol-3-yl)acrylic acid In3 was confirmed by $^1$H-NMR and $^{13}$C-NMR. $^1$H-NMR spectra of compound In3 still show five protons of aryl and one protons of N-H group and new one proton peak of C=C-H group. Remarkable, the formyl proton (–CHO) of indole-3-carbaldehyde 7 was absented. In addition, $^{13}$C-NMR spectrum shows new peck of carboxyl carbons (COOH) at $\delta = 165.9$ ppm, new peak of CN carbons at $\delta = 110.6$ ppm and new two carbon peak of alkene group. Moreover, the high resolution mass spectrometry (MALDI-TOF) of compound In3 found 212.0361 (calcd for C$_{12}$H$_8$N$_2$O$_2$: m/z 212.0586). These results confirmed that product was 2-cyano-3-(indol-3-yl)acrylic acid (In3).

The mechanism of Knoevenagal reaction follows a step mechanism as described in Figure 2.23.[44]. In the first step, deprotonation of the cyanoacetic acid by piperidine afforded carbanion intermediate [R]. On the other hand, aldehyde 7 reacted with piperidine to give intermediate [S] and then release OH$^-$ to give intermediate [T]. Next step, carbanion [R] attack at C=N of intermediate [T] gave intermediate [U]. Finally, elimination of piperidine afford target molecule In3.
2.2.4 Synthesis and characterization of 2-cyano-3-(4,6-dimethoxyindol-3-yl)acrylic acid (In4)

The target dye In4, containing 4,6-dimethoxyindole as electron donating group, double bond as π-spacer at C3-position of indole and cyanoacetic acid as electron acceptor was designed. The 2-cyano-3-(4,6-dimethoxyindol-3-yl)acrylic acid (In4) was successfully synthesized by Vilsmeier–Haack reaction and Knoevenagel condensation. First step, aldehyde 9 was synthesized by Vilsmeier–Haack reaction of 4,6-dimethoxyindole 8 [45]. The treatment of compound 8 with phosphoryl chloride in N,N-dimethylformamide stirred at 0 °C to room temperature for 1 h led to compound 9 in 58% as show in Figure 2.24.

![Figure 2.24 Vilsmeier–Haack reaction of 4,6-dimethoxyindole 8](image)

The compound 9 was confirmed by 1H-NMR and 13C-NMR. 1H-NMR spectra of compound 9 show new one peak proton of CHO group at 10.36 ppm, still show six protons of O-CH3 and one peak of N-H proton but protons of aryl group reduced to three proton. Moreover, 13C-NMR spectrum shows new peck carbon of CHO group at $\delta = 188.3$ ppm and one C-H carbon peak was absented compare to 13C-NMR of starting material. These results confirmed that product was 3-formyl-4,6-dimethoxyindole 9.

The mechanism of Vilsmeier–Haack reaction follows a step mechanism as described in Figure 2.25. In the first step, reaction of DMF and POCI3 gave intermediate [V] and then then release PCh2O2− afforded intermediate [W]. Next step, reaction C3 of indole 8 attack at C=N of intermediate [W] gave intermediate [X] and Cl−. Deprotonation of intermediate [X] gave intermediate [Y]. Finally, iminium hydrolysis of intermediate [Y] afford indole aldehyde [46] 9.
Finally, the target molecule In4 was synthesized by Knoevenagal reaction. The 3-formyl-4,6-dimethoxyindole 9 reacted with cyanoacetic acid and piperidine in chloroform at reflux for 48 h led to 2-cyano-3-(4,6-dimethoxyindol-3-yl) acrylic acid In4 in 27% as show in Figure 2.26.

The 2-cyano-3-(4,6-dimethoxyindol-3-yl) acrylic acid In4 was confirmed by $^1$H-NMR and mass spectrometry. $^1$H-NMR spectra of compound In4 still show three protons of aryl, one protons of N-H group and new one proton peak of C=C-H group. Remarkable, the formyl proton (–CHO) of 3-formyl -4,6-dimethoxyindole 9 was not appeared. Moreover, the high resolution mass spectrometry (MALDI-TOF) of compound In4 found 272.0978 (calcd for C$_{14}$H$_{12}$N$_2$O$_4$; m/z 272.0797). These results confirmed that product was 2-cyano-3-(4,6-dimethoxyindol-3-yl) acrylic acid In4.
The mechanism of Knoevenagal reaction of compound In4 similar to mechanism of Knoevenagal reaction of compound In3 as shown in Figure 2.23.

2.2.5 Synthesis and characterization of 2-cyano-3-(4,6-dimethoxy-N-methylindol-3-yl) acrylic acid (In5)

The target dye In5, containing 4,6dimethoxy-N-methylindole as electron donating group, double bond as π-spacer at C3-position of indole and cyanoacetic acid as electron acceptor was designed. The 2-cyano-3-(4,6-dimethoxy-N-methylindol-3-yl)acrylic acid (In5) was successfully synthesized by methylation and Knoevenagal reaction. First step, 3-formyl-4,6-dimethoxyindole 9 was synthesized by methylation reaction at the N-position. Treatment of 3-formyl-4,6-dimethoxyindole 9 with sodium hydride (NaH) and methyl iodide in DMF for 1.5 h under N₂ gas gave 3-formyl-4,6-dimethoxy-N-methylindol 10 in 97% as show in Figure 2.27.

![Figure 2.27 Methylation of 3-formyl-4,6-dimethoxyindole 9](image)

The 3-formyl-4,6-dimethoxy-N-methylindol 10 was confirmed by ¹H-NMR and ¹³C-NMR [25]. ¹H-NMR spectra of 9-dodecylcarbazole 2 still show proton of -CHO, aryl and OCH₃ group and shows new singlet peak of N-CH₃- proton at δ = 3.96 ppm. Remarkable, NH proton of 3-formyl-4,6-dimethoxyindole 9 was absented. Moreover, ¹³C-NMR spectrum shows new signal of N-CH₃- at δ = 39.2 ppm. These results confirmed that product was compound 10.

The mechanism of methylation reaction of compound 10 similar to mechanism of alkylation reaction of carbazole 1 as shown in chapter 1 Figure 1.13.

Finally, the target molecules In5 was synthesized by Knoevenagal reaction. The 3-formyl-4,6-dimethoxy-N-methylindol 10 reacted with cyanoacetic acid and piperidine in chloroform at reflux for 24 h led to 2-cyano-3-(4,6-dimethoxy-N-methylindol-3-yl)acrylic acid In5 in 79% as show in Figure 2.28.
Figure 2.28 Knoevenagal reaction of 3-formyl-4,6-dimethoxy-\(N\)-methylindol 10

The 2-cyano-3-(4,6-dimethoxy-\(N\)-methylindol-3-yl) acrylic acid \textbf{In5} was confirmed by \(^1\)H-NMR and \(^{13}\)C-NMR. \(^1\)H-NMR spectra of compound \textbf{In5} still show three protons of aryl, three protons of N-CH\(_3\) group, six protons of O-CH\(_3\) and new one proton peak of C=C-H group. Remarkable, the formyl proton (–CHO) of 3-formyl-4,6-dimethoxy-\(N\)-methylindol 10 was not appeared. \(^{13}\)C-NMR spectrum shows new peak of carboxyl carbons (COOH) at \(\delta = 165.4\) ppm, new peak of CN carbons at \(\delta = 114.5\) ppm and new two carbon peak of alkene group. Moreover, the high resolution mass spectrometry (MALDI-TOF) of compound \textbf{In5} found 286.1352 (calcd for C\(_{15}\)H\(_{14}\)N\(_2\)O\(_4\); \(m/z\) 286.0954). These results confirmed that product was 2-cyano-3-(4,6-dimethoxy-\(N\)-methylindol-3-yl) acrylic acid \textbf{In5}.

The mechanism of Knoevenagal reaction of compound \textbf{In5} similar to mechanism of Knoevenagal reaction of compound \textbf{In3} as shown in Figure 2.23.

2.3 CONCLUSION

In this research, a new series of indole derivatives \textbf{In1-In5}, containing varies electron donating, \(\pi\)-spacer and electron acceptor, for using as dye molecules in DSSCs were successfully synthesized. The target molecules were synthesized by using Ullman coupling, hydrolysis reaction, Knoevenagal condensation and Vilsmeier-Haack reaction.
In the first, the target molecule In1 was synthesized by Ullman coupling reaction of indole with methyl 4-iodobenzoate led to ester 4 in 94% and then hydrolysis of ester 4 with KOH afforded 2-cyano-3-(indol-3-yl)acrylic acid In1 in 64% yields.

In the same way, the target molecule In2 was synthesized by Ullman coupling reaction of 3-(4-bromophenyl)-4,6-dimethoxyindole 5 with methyl 4-iodobenzoate led to ester 6 in 41% and following by hydrolysis reaction of ester 6 with KOH afforded 4-(3-(4-bromophenyl)-4,6-dimethoxyindol-1-yl)benzoic acid In2 in 46%.
The target molecule In3 was easy synthesized by Knoevenagal condensation. The commercial indole-3-carbaldehyde 7 was reacted with cyanoacetic acid led to 2-cyano-3-(indol-3-yl)acrylic acid In3 in 24%.

\[
\begin{align*}
\text{In3} & \quad \text{Knoevenagal condensation} \\
\text{In3} & \quad \text{NC} - \text{COOH, piperidine, CHCl}_3, \text{reflux 31 h.}
\end{align*}
\]

The target molecule In4 was successfully synthesized by Vilsmeier–Haack reaction and Knoevenagal condensation. First step, Vilsmeier–Haack reaction of 4,6-dimethoxyindole 8 led to aldehyde 9 in 58%. Next, Knoevenagal reaction of aldehyde 9 with cyanoacetic acid led to 2-cyano-3-(4,6-dimethoxyindol-3-yl)acrylic acid In4 in 27%.

\[
\begin{align*}
\text{In4} & \quad \text{3 eq. POCl}_3, \text{DMF, } 0 \degree \text{C} \rightarrow \text{rt, 1 h.} \\
\text{In4} & \quad \text{NC} - \text{COOH, piperidine, CHCl}_3, \text{reflux, 48 h.}
\end{align*}
\]

The final target molecule In5 was successfully synthesized by methylation and Knoevenagal reaction. First step, methylation of aldehyde indole 9 gave 3-formyl-4,6-dimethoxy-N-methylindol 10 in 97%. Finally, Knoevenagal reaction of aldehyde 10 with cyanoacetic acid led to 2-cyano-3-(4,6-dimethoxy-N-methylindol-3-yl)acrylic acid In5 in 79%.

\[
\begin{align*}
\text{In5} & \quad \text{1.2 eq. NaH, 1.2 eq. CH}_3I, \text{DMF} \\
\text{In5} & \quad \text{NC} - \text{COOH, piperidine, CHCl}_3, \text{reflux, 48 h.}
\end{align*}
\]

All target molecules were characterized by using melting points, $^1$H-NMR and $^{13}$C-NMR spectroscopy, FT-IR spectroscopy and mass spectrometer. Unfortunately we have no time for fabrication of solar cell all of them but we will complete it in the
future. Moreover, we believe that the target compound In1-In5 are promising candidates for improvement of the performance of the DSSCs.

2.4 EXPERIMENTAL

2.4.1 General experiment

All solvents and reagents were purchased from Aldrich, Acros and Fluka received unless otherwise stated. Analytical thin-layer chromatography (TLC) was performed with Merck aluminium plates coated with silica gel 60 F254. Column chromatography was carried out using gravity feed chromatography with Merck silica gel mesh, 60 Å. Where solvent mixtures are used, the portions are given by volume.

Melting points was measured by BUCHI 530 model in open capillary method and are uncorrected and reported in degree Celsius.

1H and 13C NMR spectra were recorded on a Bruker AVANCE 300 MHz spectrometer. Chemical shifts (δ) are reported relative to the residual solvent peak in part per million (ppm). Coupling constants (J) are given in Hertz (Hz). Multiplicities are quoted as singlet (s), broad (br), doublet (d), triplet (t), quartet (q), and multiplet (m).

The IR spectra were recorded on Perkin-Elmer FT-IR spectrum RXI spectrometer. The absorption peaks are quoted in wavenumber (cm⁻¹). UV–Vis spectra were recorded on a Perkin–Elmer UV Lambda 25 spectrometer. MALDI-TOF mass spectra were recorded on Bruker Daltonics (Bremen, Germany) Autoflex II Matrix-Assisted Laser Desorption/Ionization-Time of Flight Mass Spectrometer (BIFEX) using α-cyano-4-hydroxycinnamic acid as matrix.
2.4.2 Synthesis of methyl 4-(indol-1-yl)benzoate

General Procedure of Ullman coupling:

A mixture of indole (0.1023 g, 0.8737 mmol), methyl 4-iodobenzoate (0.1908 g, 0.7281 mmol), Cul (0.0693 g, 0.3640 mmol), and K₃PO₄ (0.4636 g, 2.1843 mmol) in round bottom flask were added toluene (20 mL) and trans-1,2-diaminocyclohexane (0.0414 g, 0.3640 mmol). The mixture was degassed and stirred at reflux under N₂ for 48 h. After being cooled to room temperature, water (50 mL) was added and extracted with CH₂Cl₂ (50 mL x 3). The combined organic phases were washed with water (50 mL) and brine solution (70 mL), dried over MgSO₄ and evaporated under reduce pressure. Purification of crude reaction by column chromatography eluting with 1:3 v/v ethyl acetate/hexane gave methyl 4-(indol-1-yl)benzoate 4 (0.1719 g, 94%).

C₁₆H₁₃NO₂; m.p. = 50-52 °C

¹H-NMR (300 Hz, CDCl₃):
δ = 8.21 (d, 2H, ArH, J = 7.8 Hz), 7.72-7.55 (m, 4H, ArH), 7.39 (d, 1H, ArH, J = 2.4 Hz), 7.30-7.13 (m, 2H, ArH), 6.74 (d, 1H, ArH, J = 1.8 Hz), 3.98 (s, 3H, OCH₃) ppm.

¹³C-NMR (75 Hz, CDCl₃):
δ = 166.4 (C=O), 143.8 (Cq), 135.5 (Cq), 131.3 (2 x CH), 129.8 (Cq), 127.6 (Cq), 127.4 (CH), 123.3 (2 x CH), 122.9 (CH), 121.4 (CH), 121.0 (CH), 110.6 (CH), 104.9 (CH), 52.2 (OCH₃) ppm.

IR (KBr):
νmax = 3050, 2948, 1706, 1602, 1453, 1431, 1279, 1210, 1095, 745 cm⁻¹.
2.4.3 Synthesis of methyl 4-(3-(4-bromophenyl)-4,6-dimethoxyindol-1-yl)benzoate

According to general procedure of Ullman coupling, treatment of 3-(4-bromophenyl)-4,6-dimethoxyindole 5 (0.4000 g, 1.20 mmol), methyl 4-iodobenzoate (0.2629 g, 1.00 mmol), Cul (0.0094 g, 0.04 mmol), trans-1,2-diaminocyclohexane (0.0570 g, 0.50 mmol), K$_3$PO$_4$ (0.4473 g, 2.10 mmol) and toluene (40 mL) gave yellow oil methyl 4-(3-(4-bromophenyl)-4,6-dimethoxyindol-1-yl)benzoate 6 (0.1918 g, 41%).

C$_{24}$H$_{20}$BrN$_2$O$_4$;
H-NMR (300 Hz, CDCl$_3$):

$\delta$ = 8.21 (d, 2H, $J = 8.1$ Hz), 7.71-7.50 (m, 6H), 7.14 (s, 1H), 6.69 (s, 1H), 6.33 (s, 1H), 3.97 (s, 3H), 3.82 (s, 6H) ppm.

C-NMR (75 Hz, CDCl$_3$):

$\delta$ = 166.3 (O=C), 158.4 (Cq), 155.0 (Cq), 143.5 (Cq), 138.0 (Cq), 136.7 (Cq), 134.3 (Cq), 131.3 (2 x CH), 131.1 (2 x CH), 130.7 (2 x CH), 128.1 (Cq), 123.8 (CH), 123.7 (2 x CH), 120. 2 (Cq), 119.8 (Cq), 93.27 (CH), 86.6 (CH), 55.7 (OCH$_3$), 55.2 (OCH$_3$), 52.3 (OCH$_3$) ppm.

IR (KBr):

$\nu_{max}$ = 2996, 2946, 2843, 1718, 1602, 1433, 1274, 1206, 1174, 1085, 730 cm$^{-1}$. 
2.4.4 Synthesis of 4-(indol-1-yl)benzoic acid

![Chemical Structure]

General Procedure of Hydrolysis reaction:

Methyl 4-(indol-1-yl)benzoate 4 (0.1500 g, 0.5969 mmol) and KOH (0.0610 g, 1.1938 mmol) were dissolved in THF (10 mL) and IPA (10 mL). The reaction mixture was stirred at reflux for 2 h and monitored by TLC until it was complete. Acid H₃PO₄ 2M (50 mL) was added, and the reaction was extracted with DCM (20 mL x 2), washed with water (20 mL x 2) and bine solution (20 mL x 2), and then dried over Na₂SO₄ anhydrous, followed by recrystallization by hexane/EtOH to give 4-(indol-1-yl)benzoic acid In1 (0.0905 g, 64%).

C₁₅H₁₁N0₂; m.p. > 200 °C

¹H-NMR (300 Hz, CDCl₃):

δ = 8.29 (d, 2H, J = 8.1 Hz), 7.72–7.64 (m, 4H), 7.41 (d, 1H, J = 3.0 Hz), 7.31-7.19 (m, 2H), 6.75 (d, 1H, J = 2.4 Hz) ppm.

¹³C-NMR (75 Hz, CDCl₃):

δ = 169.9 (O=C), 144.5 (Cq), 135.4 (Cq), 132.0 (2 x CH), 129.9 (Cq), 127.3 (CH), 126.5 (Cq), 123.3 (2 x CH), 123.0 (CH), 121.4 (CH), 121.1 (CH), 110.6 (CH), 105.2 (CH) ppm.

IR (KBr):

ν_max = 1666, 1599, 1452, 1426, 1315, 1291, 933, 822, 775, 721 cm⁻¹.

UV-vis spectroscopy (in CH₂Cl₂ at 5x10⁻⁶ M):

λ_max = 320 nm (ε = 1.11 x 10⁵ cm⁻¹ M⁻¹), 273 nm (ε = 9.20 x 10⁴ cm⁻¹ M⁻¹), 228 nm (ε = 1.27 x 10⁵ cm⁻¹ M⁻¹)

MALDI-TOF (m/z) calcd for C₁₅H₁₁N0₂: 237.0790; found 237.1056(M⁺).
2.4.5 Synthesis of 4-(3-(4-bromophenyl)-4,6-dimethoxyindol-1-yl)benzoic acid

According to general procedure of hydrolysis reaction, treatment of methyl 4-(3-(4-bromophenyl)-4,6-dimethoxyindol-1-yl) benzoate 6 (0.1227 g, 0.26 mmol), KOH (0.0268 g, 0.52 mmol), THF (10 mL) and IPA (10 mL) at reflux for 2 h gave 4-(3-(4-bromophenyl)-4,6-dimethoxyindol-1-yl) benzoic acid \textbf{In2} (0.0549 g, 46%).

C\textsubscript{23}H\textsubscript{18}BrNO\textsubscript{4}; m.p. > 200°C

\textsuperscript{1}H-NMR (300 Hz, CDCl\textsubscript{3}):

δ = 8.29 (d, 2H, J = 8.4 Hz), 7.66 (d, 2H, J = 8.4 Hz), 7.51 (s, 4H), 7.16 (s, 1H), 6.72 (s, 1H), 6.35 (s, 1H), 3.84 (s, 3H), 3.83 (s, 3H) ppm.

\textsuperscript{13}C-NMR (75 Hz, CDCl\textsubscript{3}):

δ = 170.0 (O=C), 158.5 (Cq), 155.1 (Cq), 144.3 (Cq), 138.0 (Cq), 134.2 (Cq), 132.0 (2 x CH), 131.1 (2 x CH), 130.7 (2 x CH), 126.9 (Cq), 123.7 (2 x CH), 123.7 (Cq), 120.2 (Cq), 120.0 (Cq), 111.7 (Cq), 93.4 (CH), 86.7 (CH), 55.7 (OCH\textsubscript{3}), 55.2 (OCH\textsubscript{3}) ppm.

IR (KBr):

ν\textsubscript{max} = 1689, 1594, 1429, 1318, 1293, 1240, 1208, 1174, 1083, 815, 769 cm\textsuperscript{-1}.

UV-vis spectroscopy (in CH\textsubscript{2}Cl\textsubscript{2} at 5x10\textsuperscript{-6} M):

λ\textsubscript{max} = 339 nm (ε = 3.50 x 10\textsuperscript{4} cm\textsuperscript{-1} M\textsuperscript{-1}), 281 nm (ε = 7.28 x 10\textsuperscript{4} cm\textsuperscript{-1} M\textsuperscript{-1}), 231 nm (ε = 1.07 x 10\textsuperscript{5} cm\textsuperscript{-1} M\textsuperscript{-1})

MALDI-TOF (m/z) calcd for C\textsubscript{23}H\textsubscript{18}BrNO\textsubscript{4}: 451.0419; found 451.0924 (M\textsuperscript{+}).

2.4.6 Synthesis of 2-cyano-3-(indol-3-yl)acrylic acid
General Procedure of Knoevenagal condensation:

To solution of indole-3-carbaldehyde 7 (0.200 g, 1.38 mmol) and cyanoacetic acid (0.386 g, 4.54 mmol) in chloroform 20 mL was added piperidine (1 mL) and stirred at reflux for 48 h under N₂ gas. The mixture was extracted with ethyl acetate, washed with water, dried over MgSO₄ and evaporated under reduce pressure. The crude product was separated by column chromatography eluting with 1:9 v/v methanol/ethyl acetate to give 2-cyano-3-(indol-3-yl)acrylic acid In3 (0.0696 g, 24%).

C₁₂H₈N₂O₂; m.p. > 200°C

¹H-NMR (300 Hz, CDCl₃):
δ = 8.61 (s, 1H), 8.55 (s, 1H), 7.81–7.78 (m, 1H), 7.54 (s, 1H), 7.48–7.46 (m, 1H), 7.29–7.22 (m, 2H) ppm.

¹³C-NMR (75 Hz, CDCl₃):
δ = 165.9 (O=C), 147.0 (CH), 136.3 (Cq), 131.5 (CH), 127.6 (Cq), 123.6 (CH), 122.1 (CH), 118.4 (Cq), 117.8 (CH), 112.4 (CH), 110.6 (CN), 93.3 (Cq) ppm.

IR (KBr):
ν max = 3296, 3063, 2925, 2208, 1606, 1398, 1113, 956, 742, 608 cm⁻¹.

UV-vis spectroscopy (in CH₂Cl₂ at 1x10⁻⁵ M):
λ max = 389 nm (ε = 2.83 x 10⁴ cm⁻¹ M⁻¹), 276 nm (ε = 1.40 x 10⁴ cm⁻¹ M⁻¹), 229 nm (ε = 2.28 x 10⁴ cm⁻¹ M⁻¹)

MALDI-TOF (m/z) calcd for C₁₂H₈N₂O₂: 212.0586; found 212.0361 (M⁺).
**2.4.7 Synthesis of 3-formyl -4,6-dimethoxyindole (9)**

To a stirred and ice cooled solution of 4,6-dimethoxyindole 8 (0.5059 g, 2.86 mmol) in N,N-dimethylformamide (5 mL) was added dropwise an ice cooled solution of phosphoryl chloride (1.3159 g, 8.58 mmol) in N,N-dimethylformamide (5 mL). After stirred at 0 °C for 1 h, solution was allowed to come to room temperature and then was made strongly basic with 6 M sodium hydroxide solution (5 ml). The mixture was extracted with dichloromethane, washed with water, dried over MgSO4 and evaporated under reduce pressure. The crude product was separated by column chromatography eluting with 3:2 v/v ethyl acetate/hexane to give 3-formyl -4,6-dimethoxyindole 9 (0.3391 g, 58%).

C_{11}H_{11}NO_3; m.p. = 148-153 °C

^1H-NMR (300 Hz, CDCl₃):

δ = 10.36 (s, 1H, CHO), 10.31 (brs, 1H, NH) 7.07 (t, 1H, ArH, J = 2.6 Hz), 6.56 (t, 1H, ArH, J = 2.6 Hz), 6.17 (s, 1H, ArH), 4.05 (s, 3H, OCH₃), 3.99 (s, 3H, OCH₃) ppm.

^13C-NMR (75 Hz, CDCl₃):

δ = 188.3 (CHO), 163.1 (Cq), 160.2 (Cq), 136.7 (Cq), 122.7 (CH), 105.0 (Cq), 99.7 (Cq+CH), 86.8 (CH), 56.5 and 55.7 (2xOCH₃) ppm.

IR (KBr):

\nu_{\text{max}} = 3368, 2850, 1630, 1500, 1218 \text{ cm}^{-1}.
2.4.8 Synthesis of 2-cyano-3-(4,6-dimethoxyindol-3-yl)acrylic acid

![Chemical structures]

According to general procedure of Knoevenagal condensation, treatment of 3-formyl-4,6-dimethoxyindole (9) (0.0819 g, 0.40 mmol), cyanoacetic acid (0.0683 g, 0.80 mmol) and piperidine (0.10 mL) in chloroform 20 mL gave 2-cyano-3-(4,6-dimethoxyindol-3-yl)acrylic acid In4 (0.0290 g, 27%).

C_{14}H_{12}N_{2}O_{4}; m.p. = 171-174 °C

$^1$H-NMR (300 Hz, CD$_3$OD + CDCl$_3$):

$\delta$ = 8.49 (s, 1H, NH), 7.80 (d, 1H, ArH, $J$ = 3.6 Hz), 6.96 (d, 1H, ArH, $J$ = 3.6 Hz), 6.37 (s, 1H, CH), 5.30 (s, 1H, CH), 4.16 (s, 3H, OCH$_3$), 4.05 (s, 3H, OCH$_3$) ppm.

IR (KBr):

$\nu_{\text{max}}$ = 3100, 2921, 1633, 1603, 1264, 1070, 1050, 1032, 968, 719 cm$^{-1}$.

UV-vis spectroscopy (in CH$_2$Cl$_2$ at 5x10$^{-6}$ M):

$\lambda_{\text{max}}$ = 394 nm ($\varepsilon$ = 4.90 x 10$^4$ cm$^{-1}$ M$^{-1}$), 269 nm ($\varepsilon$ = 2.24 x 10$^4$ cm$^{-1}$ M$^{-1}$), 235 nm ($\varepsilon$ = 2.08 x 10$^4$ cm$^{-1}$ M$^{-1}$)

MALDI-TOF (m/z) calcd for C$_{14}$H$_{12}$N$_2$O$_4$: 272.0797; found 272.0978 (M$^+$).
2.4.9 Synthesis of 3-formyl-4,6-dimethoxy-N-methylindol

\[
\begin{array}{c}
\text{H}_3\text{CO} & \text{H}_3\text{CO} \\
\text{H}_2\text{N} & \text{H}_2\text{N} \\
(9) & (10)
\end{array}
\]

To a suspension of sodium hydride (NaH) (0.0145 g, 0.60 mmol) in N,N-dimethylformamide (DMF) 5 mL was added dropwise of 3-formyl-4,6-dimethoxyindole 9 (0.1022 g, 0.50 mmol) in DMF 5 mL. After stirred for 1 h, methyl iodide (0.0869 g, 0.60 mmol) was added into the reaction mixture and stirred for 1.5 h under N\textsubscript{2} gas. The mixture was neutralized with 6 M HCl, extracted with dichloromethane, washed with water, dried over MgSO\textsubscript{4} and evaporated under reduce pressure. The crude product was separated by column chromatography eluting with 1:4 v/v dichloromethane/hexane to give 3-formyl-4,6-dimethoxy-N-methylindol 10 (0.1055 g, 97%)

C\textsubscript{12}H\textsubscript{13}N\textsubscript{2}O\textsubscript{3}; m.p. = 100-106 °C

\textsuperscript{1}H-NMR (300 Hz, CDCl\textsubscript{3})

\[ \delta = 10.47 (s, 1H, CHO), 6.83 (d, 1H, H2, J = 3.0 Hz), 6.53 (d, 1H, H7, J = 3.0 Hz), 6.22 (s, 1H, H5), 4.05 (s, 3H, OCH\textsubscript{3}), 4.01 (s, 3H, OCH\textsubscript{3}), 3.96 (s, 3H, N-CH\textsubscript{3}) \text{ ppm} \]

\textsuperscript{13}C-NMR (75 Hz, CDCl\textsubscript{3})

\[ \delta = 188.0 (CHO), 165.0 (Cq), 159.2 (Cq3), 130.3 (CH), 115.8 (Cq), 107.2 (Cq), 99.1 (CH), 87.9 (CH), 57.2 (OCH\textsubscript{3}), 39.2 (NCH\textsubscript{3}) \]

IR (KBr):

\[ \nu_{\text{max}} = 2944, 2921, 2848, 1653, 1561, 1514, 1459, 1362, 1246, 1207, 727 \text{ cm}^{-1}. \]
2.4.10 Synthesis of 2-cyano-3-(4,6-dimethoxy-N-methylindol-3-yl)acrylic acid

According to general procedure of Knoevenagel condensation, treatment of 3-formyl-4,6-dimethoxy-N-methylindol (10) (0.7500 g, 3.43 mmol), cyanoacetic acid (0.582 g, 6.85 mmol) and piperidine (2.0 mL) in chloroform 20 mL gave 2-cyano-3-(4,6-dimethoxy-N-methylindol-3-yl)acrylic acid In5 (0.770 g, 79%).

C_{13}H_{14}N_{2}O_{4}; m.p. = 170-174 °C

$^1$H-NMR (300 Hz, CDCl$_3$)

$\delta$ = 8.55 (s, 1H, COOH), 6.61 (d, 1H, H-alkene, $J$ = 3Hz), 6.27 (d, 1H, H2, $J$ = 3Hz), 6.10(s, H, H5), 3.78 (s, 3H, OCH$_3$), 3.76 (s, 3H, OCH$_3$), 3.65 (s, 3H, N-CH$_3$) ppm

$^{13}$C-NMR (75 Hz, CDCl$_3$)

$\delta$ = 165.4 (C=O),157.8 (Cq),157.7 (Cq), 149.0 (CH), 135.9 (Cq), 129.0 (Cq), 116.2(Cq), 114.5 (CN), 103.7 (Cq), 100.2 (Cq), 98.8 (Cq), 87.1 (Cq), 55.2 (OCH$_3$), 55.1 (OCH$_3$), 36.8 (NCH$_3$).

IR (KBr)

$\nu_{\text{max}}$ = 2923, 2848, 1667, 1573, 1557, 1393, 1159, 1061, 1011, 708 cm$^{-1}$.

UV-vis spectroscopy (in CH$_2$Cl$_2$ at 5x10$^{-6}$ M):

$\lambda_{\text{max}}$ = 426 nm ($\varepsilon$ = 5.30 x 10$^4$ cm$^{-1}$ M$^{-1}$), 277 nm ($\varepsilon$ = 7.90 x 10$^4$ cm$^{-1}$ M$^{-1}$), 229 nm ($\varepsilon$ = 1.36 x 10$^5$ cm$^{-1}$ M$^{-1}$)

MALDI-TOF (m/z) calcd for C$_{13}$H$_{14}$N$_2$O$_4$: 286.0954; found 286.1352 (M$^+$).
REFERENCES
REFERENCES


REFERENCES (CONTINUED)


REFERENCES (CONTINUED)


REFERENCES (CONTINUED)


REFERENCES (CONTINUED)


APPENDICES
APPENDICES A

$^1$H NMR, $^{13}$C NMR and UV-Vis absorption spectrum of compounds
Figure A.1 The $^1$H NMR (in CDCl$_3$) spectrum of 9-dodecylcarbazole 2

Figure A.2 The $^{13}$C NMR spectra of 9-dodecylcarbazole 2
Figure A.3 The $^1$H NMR (in CDCl$_3$) spectrum of 3,6-Dibromo-9-dodecylcarbazole

Figure A.4 The $^{13}$C NMR spectra of 3,6-Dibromo-9-dodecylcarbazole
Figure A.5 The $^1$H NMR (in CDCl$_3$) spectrum of CP2

Figure A.6 The $^{13}$C NMR spectra of CP2
Figure A.7 The $^1$H NMR (in CDCl$_3$) spectrum of CA2

Figure A.8 The $^{13}$C NMR spectra of CA2
Figure A.9 The $^1$H NMR (in CDCl$_3$) spectrum of methyl 4-(indol-1-yl) benzoate 4

Figure A.10 The $^{13}$C NMR spectra of methyl 4-(indol-1-yl) benzoate 4
Figure A.11 The $^1$H NMR (in CDCl₃) spectrum of methyl 4-(3-(4-bromophenyl)-4,6-dimethoxyindol-1-yl)benzoate 6

Figure A.12 The $^{13}$C NMR spectra of methyl 4-(3-(4-bromophenyl)-4,6-dimethoxyindol-1-yl)benzoate 6
Figure A.13 The $^1$H NMR (in CDCl$_3$) spectrum of In1

Figure A.14 The $^{13}$C NMR spectra of In1
Figure A.15 The $^1$H NMR (in CDCl$_3$) spectrum of In2

Figure A.16 The $^{13}$C NMR spectra of In2
Figure A.17 The $^1$H NMR (in CDCl$_3$) spectrum of In3

Figure A.18 The $^{13}$C NMR spectra of In3
Figure A.19 The $^1$H NMR (in CDCl$_3$) spectrum of 3-formyl-4,6-dimethoxyindole 9

Figure A.20 The $^{13}$C NMR spectra of 3-formyl-4,6-dimethoxyindole 9
Figure A.21 The $^1$H NMR (in CDCl$_3$) spectrum of In4

Figure A.22 The $^{13}$C NMR spectra of In4
Figure A.23 The $^1$H NMR (in CDCl$_3$) spectrum of 3-formyl-4,6-dimethoxy-N-methylindol 10

Figure A.24 The $^{13}$C NMR spectra of 3-formyl-4,6-dimethoxy-N-methylindol 10
Figure A.25 The $^1$H NMR (in CDCl$_3$) spectrum of In5

Figure A.26 The $^{13}$C NMR spectra of In5
Figure A.27 UV-Vis absorption spectra of In1-In5 in DCM at 5x10^{-6} M.

Figure A.28 UV-Vis absorption spectra of In1 in DCM at 5x10^{-6} M.
Figure A.29 UV-Vis absorption spectra of In2 in DCM at $5\times10^{-6}$ M.

Figure A.30 UV-Vis absorption spectra of In3 in DCM at $1\times10^{-5}$ M.
Figure A.31  UV-Vis absorption spectra of In4 in DCM at $5 \times 10^{-6}$ M.

Figure A.32  UV-Vis absorption spectra of In5 in DCM at $5 \times 10^{-6}$ M.
APPENDICES B

Publication
ประชุมวิชาการ มหา. วิจัย ครั้งที่ 8

17 – 18 กรกฎาคม 2557

อาคารพระรัตนดริปภาค มหาวิทยาลัยอุบลราชธานี
Abstract

Carbazole derivatives containing pyrene and anthracene substituents were synthesized using bromination and Suzuki cross-coupling reactions, and their chemical structure were characterized by $^1$H NMR, UV-Vis, fluorescence spectroscopy and cyclic voltammetry. Compound 9-dodecyl-3,6-di(pyren-1-yl)carbazole (CP2) and 9-dodecyl-3,6-di(anthracen-1-yl)carbazole (CA2) showed the PL spectra in deep blue region at 430 and 442 nm and exhibited high electrochemical stability. These compounds could be alternative materials as blue light-emitters in organic light emitting diodes.

Keywords: Carbazole, Organic light-emitting diodes, Suzuki cross-coupling reaction

Introduction

Initially proposed by Ching W. Tang in 1987, organic light-emitting diodes (OLEDs) have attracted significant attention from the scientific community due to their potential for future flat-panel displays and lighting applications. Today, the developments of OLED technologies mainly focus on the optimization of device structures and on developing new emitting materials. Clearly, new materials emitting pure colors.
Methodology

Objective

The profitability in the production of platforms for OLEDs is significantly influenced by the performance of blue OLEDs, which is usually inferior to that of green and red OLEDs due to poor carrier injection into the emitters and electroluminescent (EL) properties of the blue OLEDs need to be improved. Therefore, one area of continuing research in this field is the pursuit of a stable-blue emitting material. Although many fluorescent blue emitters have been reported such as pyrene derivatives, carbazole derivatives, anthracene derivatives, fluorene derivatives, and aromatic hydrocarbons, there is still a clear need for further developments in terms of efficiency and color purity compared to red and green emitters.

Therefore, in this work, we reported the synthetic route and properties of 9-dodecyl-3,6-di(pyren-1-yl)carbazole (CP2) and 9-dodecyl-3,6-dianthracen-1-yl)carbazole (CA2) (end-capped carboxole with pyrene and anthracene groups, respectively as solution processed blue emitters for OLEDs.

Methodology and Experimental

1. General procedures

$^1$H NMR spectra were recorded on Bruker AVANCE (300 MHz) spectrometer. Chemical shifts (δ) are reported relative to the residual solvent peak in part per million (ppm). Coupling constants (J) are given in Hertz (Hz). UV-Visible spectra were recorded in CH$_2$CL$_2$ on a Perkin-Elmer UV Lambda 25 spectrometer. Fluorescence spectra were recorded in CH$_2$CL$_2$ on a Perkin-Elmer LS 50B Luminescence spectrometer. Analytical thin-layer chromatography (TLC) was performed with Merck aluminium plates coated with silica gel 60 F$_{254}$. Column chromatography was carried out using gravity feed chromatography Merck silica gel mesh, 60 Å. Solvent mixture was used and the portions are given by volume.

2. Synthetic procedures

2.1 Synthesis of 9-dodecylcarbazole (2)

To a solution of carbazole (10.0000 g, 59.80 mmol) in DMF (93 mL) was added NaH (2.1500 g, 89.58 mmol). Then, 1-Bromododecane (15.0000 g, 89.70 mmol) was added. The reaction mixture was stirred at 0°C–rt for 20 h. Water (100 mL) was added and the mixture was extracted with ethyl acetate (50 mL x 3). The combined organic phases were washed with a diluted HCl solution (50mL x 2), water (100 mL), and brine (50 mL), dried over anhydrous Na$_2$SO$_4$, evaporated and purified by column chromatography to give a pale yellow viscous oil (23.3776 8.9796); $^1$H NMR (300 MHz, CDC$_3$); δ 8.09 (2H, d, J = 2.4 Hz), 7.44 (4H, m), 7.25 (2H, d, J = 2.4 Hz), 4.3 (2H, t, J = 2.1 Hz), 1.88 (2H, t, J = 2.1 Hz), 1.33 (18H, m) and 0.89 (3H, t, J = 2.1 Hz)
2.2 Synthesis of 3,6-dibromo-9-dodecylcarbazole(3)

In the round bottom flask, covered with aluminum foil, a stirred solution of 9-
dodecylcarbazole (2) (0.0700 g, 0.16 mmol) in THF (15 mL) was added NBS (0.0400 g, 0.19 mmol) in small portions. The reaction mixture was poured into ice-cold water. The mixture was allowed to warm to room temperature overnight. The mixture was extracted with methylene chloride (20 ml x 3), washed with water (20 ml x 3), dried over anhydrous Na₂SO₄, evaporated and purified by column chromatography to give a white pearl solid (0.0719 g, 91%); 1H NMR (300 MHz, CDCl₃) δ 8.15 (2H, d, J = 1.5 Hz), 7.56 (2H, dd, J₁ = 0.9 Hz, J₂ = 0.6 Hz), 7.26 (2H, d, J = 0.9 Hz), 4.24 (2H, t, J = 0.9 Hz), 1.82 (2H, t, J = 0.9 Hz), 1.43 (18H, m), 0.87 (3H, t, J = 2.1 Hz)

2.3 Synthesis of 9-dodecyl-3,6-dipyrenylcarbazole (CP2)

To a stirred solution of 3,6-dibromo-9-dodecylcarbazole (3) (0.0400 g, 0.81 mmol) and Pd(PPh₃)₄ (0.0400 g, 0.04 mmol) in tetrahydrofuran (30 mL) was added pyrene-1-boronic acid (0.41g, 1.79mmol), and an aqueous Na₂CO₃ solution (0.8500 g, 8.10 mmol). The mixture was refluxed for 48 h. After cooling, the mixture was extracted with dichloromethane (30 mL x 3), washed with water(30mL x 3); dried over anhydrous, evaporated and purified by column chromatography to give a white pearl solid (0.3195 g, 53%); 1H NMR (300 MHz, CDCl₃) δ 8.41 (2H, s), 8.34 (2H, d, J = 9.30 Hz), 8.25 (2H, d, J = 7.80 Hz), 8.20-8.10 (10H, m), 8.06-7.97 (4H, m), 7.80 (2H, d, J = 8.4 Hz), 7.64 (2H, d, J = 7.64 Hz), 4.47 (2H, t, J = 7.2 Hz), 1.10 (2H, t, J = 6.9 Hz), 1.57-1.30 (18H, m) and 0.91 (3H, t, J = 6.9 Hz)

2.4 Synthesis of 9-dodecyl-3,6-dianthracenylcarbazole (CA2)

To a stirred solution of 3,6-dibromo-9-dodecylcarbazole (3) (0.2500g, 0.42 mmol) and Pd(PPh₃)₄ (0.020g, 0.05 mmol) in tetrahydrofuran (25 mL) were added 10-phenyl-9-anthraceneboronic acid (0.26g, 0.89 mmol), and an aqueous BuOK solution (0.47 g, 4.26 mmol). The mixture was refluxed for 48 h. After cooling, the mixture was extracted with dichloromethane (30 mL x 3), washed with water (30mL x 3), dried over anhydrous, evaporated and purified by column chromatography to give a white pearl solid (0.240 g, 68%); 1H NMR (300 MHz, CDCl₃) δ 8.18 (2H, s), 7.83-7.80 (5H, m), 7.74-7.68 (7H, m), 7.63-7.50 (12H, m), 7.32-7.26 (12H, m), 4.56 (2H, t, J = 6.9 Hz), 2.15 (2H, t, J = 7.5 Hz), 1.57-1.28 (18H, m) and 0.86 (3H, t, J = 6.3 Hz)

Results and Discussion

1. Synthesis of CP2 and CA2

The target molecules CP2 and CA2 were successfully synthesized as shown in scheme 1. The 9-dodecylcarbazole was first synthesized by nucleophilic substitution reaction at the 9-position of carbazole (1) with 1-bromododecane. Then, selective bromination of compound 2 at 3 at the 6-position with NBS in THF afforded compound 3 in 91% yields. The target molecule CP2, dipyrène substituted carbazole, was synthesized by Suzuki cross coupling of 3 with pyrene-1-boronic acid using Pd(PPh₃)₄ as catalyst and Na₂CO₃ as base in THF at reflux for 48 h. Dianthracene substituted carbazole (CA2) was
synthesized by Suzuki cross coupling reaction of 3 and 10-phenyl-9-anthraceneboronic acid with Pd(PPh₃)₄ as a catalyst and 'BuOK as a base in THF at reflux for 48 h. (Scheme 1.) All compounds were characterized by ¹H NMR analysis. The data are presented in the experimental section.

2. Optical properties

The spectroscopic properties of CP2 and CA2 were measured in dichloromethane (CH₂Cl₂) as shown in Figure 1. The solution absorption spectra exhibited two major absorption bands. The first absorption bands at around 200-275 nm could be attributed to the π-π* transition of the carbazole moieties and the second absorption bands at longer wavelength around 350-400 nm corresponded to the π-π* transition of the carbazole-pyrene and carbazole-anthracene cores. These compounds in solution fluoresced in the blue region (430-442 nm) with featureless photoluminescence (PL) spectra. The emission spectra displayed maxima at 430 and 442 nm, for CP2 and CA2, respectively. From the substituted dipyrone CP2 to substituted anthracene CA2, the PL spectra also showed red-shifted absorption and in PL spectra, concomitant with the increasing conjugation length (Figure 1).

Figure 1. Normalized absorption spectra (left) and normalized emission spectra (right) of CP2 and CA2 in CH₂Cl₂
3. Electrochemical properties

Electrochemical behaviors of CP2 and CA2 were investigated by cyclic voltammetry (CV), and the results were shown in Figure 2. Multiple cyclic voltammetry (CV) scans of CA2 revealed identical cyclic voltammograms with no additional peak at lower potentials on the cathodic scan (Epc). This suggested no electrochemical coupling at either the carbazole or anthracene peripheries, indicating electrochemically stable molecules.

The CV curve of CP2 showed three irreversible oxidation processes. The first oxidation is assigned to the removal of electrons from the carbazole moiety resulting in carbazole radical cations (CBZ+). In the case of CP2, during additional peaks at lower potentials were observed during the cathodic scan indicating electrochemical coupling reactions of the radical cations. The generated CBZ+ is stabilized by electron delocalization through 1,8-substituted electron rich pyrene rings to form a pyrene radical cation (Py+) which is relatively less stable compared with the CBZ+. The Py+ readily undergoes a radical-radical dimerization coupling to form a stable neutral pyrene dimer as indicated by the presence of the cathodic peaks (Epc) around 0.61–0.94 V in their first CV scan and an increasing change in the CV curves under the repeated CV scans (Figure 2). This might be the first example of pyrene derivatives that undertook an electrochemical oxidation coupling reaction. The HOMO energy levels were estimated to be -5.61 and -5.45 eV, respectively (Table 1).

![Graph](image)

Figure 2. Cyclic voltammograms of CP2 (left) and CA2 (right) in dry CH2Cl2 with scan rate of 0.05 V/s and 0.1 M n-Bu4NPF6 as electrolyte

<table>
<thead>
<tr>
<th>Table 1 Physical data of CP2 and CA2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Compound</strong></td>
</tr>
<tr>
<td>-------------</td>
</tr>
<tr>
<td>CP2</td>
</tr>
<tr>
<td>CA2</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

*Measured in dilute CH2Cl2

* Calculated from the absorption edge, \( E_g = 1240 / \lambda_{max} \)

*Estimated from HOMO = -4.44 + E(max)

*Estimated from LUMO = HOMO + \( E_g^0 \)
3. HOMO and LUMO frontier orbitals

To gain insights into the geometrical and electronic properties of these multiple substituted carbazoles, quantum chemical calculations were performed using the DFT/B3LYP/6-31G(d,p) method. The optimized structures of CP2 and CA2 revealed that the attached pyrene and anthracene units twisted out of the plane of the carbazole forming bulky substituents around the carbazole. This would facilitate the formation of amorphous morphology. In all cases for CP2 and CA2, \( \pi \)-electrons in the HOMO orbitals delocalized only over the carbazole and two substituents at the 3,6-positions substituted carbazole backbone, whereas after light irradiation (LUMO), the excited electrons were delocalized largely over the pyrene and anthracene plane.

![HOMO and LUMO orbitals](image)

**Figure 3.** The HOMO (bottom) and LUMO (top) orbitals of CP2 and CA2 calculated by DFT/B3LYP/6-31G(d,p) method.

Conclusion

In conclusion, we have successfully synthesized pyrene and anthracene-substituted carbazole (CP2, CA2) by the Suzuki-cross coupling reaction of dibromo intermediates with pyrene-1-boronic acid and 10-phenyl-9-anthraceneboronic acid, respectively. The electronic and electrochemical properties of both compounds could be tuned by varying the substituents on carbazole ring. The substitution of dipyrene CP2 by substituted anthracene in CA2 increased the conjugation length of compounds resulting in a red-shift and broad in absorption spectra. These compounds emitted blue light with high thermal stability, which is potentially useful for applications in electroluminescent devices. Optimize structures and electron density of HOMO and LUMO have been performed by DFT/B3LYP/6-31G(d,p) method.

Acknowledgement

This work was supported by Center of Excellence for Innovation in Chemistry (PERCH-CIC), and Faculty of Science, Ubon Ratchathani University.

References:


<table>
<thead>
<tr>
<th>NAME</th>
<th>Miss. Thitima Siriroem</th>
</tr>
</thead>
<tbody>
<tr>
<td>BORN</td>
<td>16 January 1989, Ubon Ratchathani, Thailand</td>
</tr>
<tr>
<td>EDUCATION</td>
<td>B. Sc. (Chemistry) Department of Chemistry, Faculty of Science, Ubon Ratchathani University, Ubon Ratchathani, Thailand, 2007-2010. M. Sc. (Chemistry), Department of Chemistry, Faculty of Science, Ubon Ratchathani University, Ubon Ratchathani, Thailand, 2011-2015.</td>
</tr>
</tbody>
</table>