9-9-2013

Synthesis and characterization of conductive and soluble side-chain blue fluorescent polymers

Jianli Wang
Hong Kong Baptist University

Follow this and additional works at: https://repository.hkbu.edu.hk/etd_oa

Recommended Citation
https://repository.hkbu.edu.hk/etd_oa/14

This Thesis is brought to you for free and open access by the Electronic Theses and Dissertations at HKBU Institutional Repository. It has been accepted for inclusion in Open Access Theses and Dissertations by an authorized administrator of HKBU Institutional Repository. For more information, please contact repository@hkbu.edu.hk.
Synthesis and Characterization of Conductive and Soluble Side-Chain Blue Fluorescent Polymers

Wang Jianli

A thesis submitted in partial fulfillment of the requirements for the degree of
Doctor of Philosophy

Principal Supervisor: Dr. Louis M. Leung

Hong Kong Baptist University

September 2013
Declaration

I hereby declare that this thesis represents my own work which has been done after registration for the degree of PhD at Hong Kong Baptist University, and has not been previously included in a thesis, dissertation submitted to this or other institution for a degree, diploma or other qualification.

Signature: ______________________

Date: September 2013
Abstract

Semiconducting polymers had been well studied and applied in many research areas. They are such as electroactive actuators, electrochromic materials, microwave-absorbent coatings, polymer solar cells, polymer light-emitting diodes, etc. Traditional semiconductors are metals/oxides and they are expensive, toxic and harmful to the environment. Compared to the traditional π-conjugated main-chain polymers, side-chain conductive polymers have a lower volume percentage of the charge transport moieties yet they possess advantages such as excellent mechanical strength, good rheological properties, solubility in common organic solvents and purer emission hue. Furthermore, the performances of the side-chain semiconducting polymers can be engineered easily by changing their composition or by choosing an appropriate additional polymerization method. As a result, several series of soluble, semiconducting and luminescent side-chain homopolymers and copolymers have been synthesized and characterized.

In this thesis, several series of vinyl conductive polymers have been prepared using the facile solution free radical, anionic and atom transfer radical polymerization methods. The novel polymers including the homopolymer P(ADN), two highly soluble homopolymers P(2ADN) and P(3ADQ), two series of ADN moieties containing copolymer P(ADN-co-S) and P(ADN-co-VK), a series of pyrene moieties containing copolymer P(PyPA-co-VPy) and two novel amphiphilic BAB-type block copolymers, ADN-PEG3400-ADN and Py-PEG3400-Py which contain blue and greenish-blue fluorescent moieties.

The chemistry and physical properties of the intermediates, the resulting polymers were characterized using nuclear magnetic resonance spectroscopy
(NMR), matrix-assisted laser desorption ionization time-of-flight mass spectrum (MALDI-TOF MS), fourier-transform infrared spectroscopy (FT-IR), elemental analysis (EA), gel permeation chromatography (GPC), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), UV-Visible spectroscopy (UV-Vis), photoluminescence spectroscopy (PL), cyclic voltammetry (CV), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and fabrication of polymer light-emitting diodes (PLED) and their measurements.

\[
P(ADN) \quad X = \text{CH} \quad P(2ADN) \quad N \quad P(3ADQ) \\
P(PyPA-co-VPy) \quad P(PyPA) \\
P(ADN-co-S) \quad P(ADN-co-VK)
\]
Acknowledgements

I would like to express my deepest appreciation to my supervisor Dr. Louis M. Leung. With his patient guidance, I really learn how to do research with reasonable thinking and enjoyed the whole work process.

I would also like to thank Professor S. K. So and his student Mr Cyrus Y. H. Chan for the OLED and OTFT device fabrication and studies.

Thanks are also given to Scientific Officers and technicians who taught me how to use NMR, GPC, FT-IR, EA, TGA, DSC, UV, PL and CV.

Financial support from the Research Grant Council is gratefully acknowledged.

Last but not least, my gratitude also extends to my family who has been assisting, supporting and caring for me during my course of study.
Table of Contents

Declaration ................................................................................................................................. i
Abstract ......................................................................................................................................... ii
Acknowledgements .................................................................................................................... v
Table of Contents ....................................................................................................................... vi
List of Tables ............................................................................................................................... xiii
List of Figures ............................................................................................................................. xv
List of Schemes .......................................................................................................................... xxii
List of Symbols and Units .......................................................................................................... xxiii
List of Abbreviations ................................................................................................................... xxiv

Chapter 1  Introduction ........................................................................................................... 1

1.1  Background ....................................................................................................................... 1

1.2  The classification of the conductive polymers ................................................................. 1
  1.2.1 Conductively filled polymers ....................................................................................... 2
  1.2.2 Charge transfer polymers ............................................................................................ 3
  1.2.3 Ionically conducting polymers ..................................................................................... 3
  1.2.4 Main-chain conducting polymers ............................................................................... 4
  1.2.5 Side-chain conducting polymers ............................................................................... 5

1.3  The applications and progresses of the intrinsic semiconducting polymers ..................... 7
  1.3.1 Electroactive actuators .................................................................................................. 7
  1.3.2 Electrochromic materials .............................................................................................. 9
  1.3.3 Microwave-absorbent coatings .................................................................................... 12
  1.3.4 Polymer solar cells ....................................................................................................... 13
1.3.5 Polymer light-emitting diodes ........................................... 17
  1.3.5.1 Electron transport materials ........................................... 17
  1.3.5.2 Hole transport materials ............................................. 20
  1.3.5.3 Electron/Hole injection materials ..................................... 22
  1.3.5.4 Light emitting materials ............................................. 23

1.4 The polymerization of the side-chain conductive polymers ............. 29
  1.4.1 Free radical polymerization ............................................. 29
  1.4.2 Cationic polymerization ................................................. 30
  1.4.3 Anionic polymerization .................................................. 31
  1.4.4 Atom transfer radical polymerization .................................... 31

1.5 Scope of the thesis ................................................................ 35
  1.5.1 Blue luminescent side-chain semiconducting polymers for potential application electroluminescence .................. 35
  1.5.2 Block copolymers with potential applications in biophysics and biochemistry ......................................................... 36

1.6 References ............................................................................ 36

Chapter 2 Synthesis and Characterization of High Bandgap Blue Light Emitting Poly(9,10-di(1-naphthalenyl)-2-vinyl anthracene) .................. 52

2.1 Introduction ............................................................................... 52

2.2 Experimental ........................................................................... 54
  2.2.1 Materials and instruments ................................................ 54
  2.2.2 Synthesis ............................................................................ 56
    2.2.2.1 2-Methyl-1,4,4a,9a-tetrahydroanthracene-9,10-dione (Nad) ......................................................... 56
    2.2.2.2 2-Methyl-9,10-anthracenequinone (MAq) ..................... 56
2.2.2.3 2-Methylanthracene (MA) ............................................................. 57
2.2.2.4 9,10-Dibromo-2-methylanthracene (MADBr) ...................... 57
2.2.2.5 2-Methyl-9,10-di(1-naphthalenyl)anthracene (MADN) .. 58
2.2.2.6 2-(Bromomethyl)-9,10-di(1-naphthalenyl)anthracene (ADN-CH$_2$Br) ................................................................. 58
2.2.2.7 9,10-Di(1-naphthalenyl)anthracene-2-carbaldehyde (ADN-CHO) ............................................................. 59
2.2.2.8 9,10-Di(1-naphthalenyl)-2-vinylanthracene (Vinyl-ADN) ................................................................. 59
2.2.2.9 Homopolymer synthesis .................................................... 60

2.3 Results and discussion ................................................................. 61
2.3.1 Synthesis of monomer and polymers ..................................... 61
  2.3.1.1 Solution free radical addition polymerization .................. 63
  2.3.1.2 Anionic polymerization ............................................... 64
2.3.2 Spectroscopic analysis of the monomer and polymers.......... 65
2.3.3 Thermal properties ............................................................. 68
2.3.4 Optical characteristics of the monomer and polymers ......... 69
2.3.5 Electrochemical properties .................................................. 74
2.4 Conclusions ............................................................................. 77
2.5 References ............................................................................. 77

Chapter 3  Synthesis and Characterization of Highly Soluble Blue Emitting
Poly(2-vinylanthracene) with 9,10-Di(2-naphthalenyl) and 9,10-Di(3-quinolinyl) Substituents ............................................................. 82
  3.1 Introduction ........................................................................... 82
  3.2 Experimental ......................................................................... 84
3.2.1 Materials and instruments ................................................................. 84

3.2.2 Synthesis ............................................................................................. 84
   3.2.2.1 2-Naphthalenyl boronic acid (2NB) ........................................ 84
   3.2.2.2 2-Methyl-9,10-di(2-naphthalenyl)anthracene (2MADN) 85
   3.2.2.3 2-(Bromomethyl)-9,10-di(2-naphthalenyl)anthracene
           (2ADN-CH₂Br) ................................................................................... 86
   3.2.2.4 9,10-Di(2-naphthalenyl)anthracene-2-carbaldehyde
           (2ADN-CHO) .................................................................................... 86
   3.2.2.5 9,10-Di(2-naphthalenyl)-2-vinylantracene
           (Vinyl-2ADN) .................................................................................... 87
   3.2.2.6 3-Quinolinyl boronic acid (3QB) ............................................. 87
   3.2.2.7 2-Methyl-9,10-di (3-quinolinyl) anthracene (3MADQ) .. 88
   3.2.2.8 2-(Bromomethyl)-9,10-di (3-quinolinyl) anthracene
           (3ADQ-CH₂Br) .................................................................................. 88
   3.2.2.9 9,10-Di(3-quinolinyl) anthracene-2-carbaldehyde
           (3ADQ-CHO) .................................................................................... 89
   3.2.2.10 9,10-Di(3-quinolinyl)-2-vinylantracene (Vinyl-3ADQ) 89
   3.2.2.11 Poly(9,10-di(2-naphthalenyl)-2-vinylantracene)
           (P(2ADN)) ......................................................................................... 90
   3.2.2.12 Poly(9,10-di(3-quinolinyl)-2-vinylantracene)
           (P(3ADQ)) ......................................................................................... 90

3.3 Results and discussion ........................................................................ 90
   3.3.1 Synthesis and characterization of the polymers .......................... 90
   3.3.2 Thermal properties ................................................................. 95
   3.3.3 Optical properties .................................................................. 96
   3.3.4 Electrochemical and electrical properties ................................. 103
Chapter 4  Blue Fluorescent Conductive Homopolymer Poly(9,10-di(1-naphthalenyl)-2-vinylanthracene) and Its Highly Soluble Copolymers with Styrene or 9-Vinyl Carbazole ................................................................. 111

4.1 Introduction ............................................................................................................. 111

4.2 Experimental .......................................................................................................... 113

4.2.1 Materials and instruments .................................................................................. 113

4.2.2 Synthesis .............................................................................................................. 114

4.3 Results and discussion .......................................................................................... 116

4.3.1 Structure characterization of the homopolymers and copolymers .......................... 116

4.3.2 Molecular weights of the polymers ..................................................................... 121

4.3.3 Composition of the copolymers ......................................................................... 124

4.3.4 Solubilities of the polymers ............................................................................... 124

4.3.5 Thermal properties of the copolymers ............................................................... 125

4.3.6 Optical characteristics of the copolymers ......................................................... 130

4.3.7 Electrochemical properties ............................................................................... 138

4.3.8 Electrical properties .......................................................................................... 140

4.4 Conclusions ............................................................................................................ 142

4.5 References ............................................................................................................. 142

Chapter 5  Synthesis and Characterization of Greenish-blue Emitting Vinyl Copolymer Containing Pyrene and Triarylamino Moieties .................................................... 147

5.1 Introduction ............................................................................................................. 147
5.2 Experimental ........................................................................................................... 148
  5.2.1 Materials and instruments................................................................................. 148
  5.2.2 Synthesis............................................................................................................ 148
    5.2.2.1 1-Nitropyrene (NPy) .................................................................................. 148
    5.2.2.2 Pyren-1-amine (APy) ................................................................................ 149
    5.2.2.3 N,N-Diphenylpyren-1-amine (PyPA) ....................................................... 149
    5.2.2.4 4-(Phenyl(pyren-1-yl)amino)benzaldehyde
             (PyPA-CHO) ................................................................................................. 150
    5.2.2.5 N-Phenyl-N-(4-vinylphenyl)pyren-1-amine
             (Vinyl-PyPA) ................................................................................................. 151
    5.2.2.6 1-Vinyl pyrene (VPy) ................................................................................. 151
    5.2.2.7 Free radical polymerization ................................................................. 152
5.3 Results and discussion ......................................................................................... 152
  5.3.1 Synthesis of monomers and polymers ............................................................ 152
  5.3.2 Composition of the copolymers .................................................................... 156
  5.3.3 Molecular weights of the copolymers ............................................................ 157
  5.3.4 Thermal properties of the copolymers ........................................................... 158
  5.3.5 Optical characteristics of the copolymers ..................................................... 160
  5.3.6 Electrochemical properties of the copolymers .............................................. 164
  5.3.7 Electroluminescence properties ................................................................. 166
5.4 Conclusions ........................................................................................................... 170
5.5 References ............................................................................................................. 171

Chapter 6 Self-Assembly and Aggregation of ATRP Prepared Amphiphilic
BAB Tri-block Copolymers Contained Nonionic ethylene glycol and
Fluorescent 9,10-Di(1-naphthalenyl)-2-vinyl-anthracene/1-Vinyl-pyrene
<table>
<thead>
<tr>
<th>Segment</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1 Introduction</td>
<td>175</td>
</tr>
<tr>
<td>6.2 Experimental</td>
<td>177</td>
</tr>
<tr>
<td>6.2.1 Materials and instruments</td>
<td>177</td>
</tr>
<tr>
<td>6.2.2 Synthesis</td>
<td>178</td>
</tr>
<tr>
<td>6.2.2.1 Synthesis of 9,10-di(1-naphthalenyl)-2-vinylanthracene monomer</td>
<td>178</td>
</tr>
<tr>
<td>6.2.2.1 Synthesis of block copolymers</td>
<td>180</td>
</tr>
<tr>
<td>6.2.2.2 Synthesis of homopolymers</td>
<td>181</td>
</tr>
<tr>
<td>6.2.3 Self-aggregation of the block copolymers</td>
<td>181</td>
</tr>
<tr>
<td>6.3 Results and discussion</td>
<td>182</td>
</tr>
<tr>
<td>6.3.1 Structure characterization of monomer and polymers</td>
<td>182</td>
</tr>
<tr>
<td>6.3.2 Thermal properties</td>
<td>185</td>
</tr>
<tr>
<td>6.3.3 Optical properties</td>
<td>188</td>
</tr>
<tr>
<td>6.3.4 Self-aggregation behavior</td>
<td>189</td>
</tr>
<tr>
<td>6.4 Conclusions</td>
<td>194</td>
</tr>
<tr>
<td>6.5 References</td>
<td>194</td>
</tr>
</tbody>
</table>

Chapter 7 Conclusions ........................................................................... 199

Future Work .............................................................................................. 204

Appendix ..................................................................................................... 205

Curriculum Vitae ......................................................................................... 231
List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Caption</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Some common main-chain semiconducting/conducting polymers</td>
<td>5</td>
</tr>
<tr>
<td>1.2</td>
<td>Some PPy based actuators in recent years</td>
<td>8</td>
</tr>
<tr>
<td>1.3</td>
<td>Some selected PEDOT/PSS based actuators in recent years</td>
<td>9</td>
</tr>
<tr>
<td>1.4</td>
<td>Some selected thin films and electrochromic layers of electrochromic devices in recent years</td>
<td>11</td>
</tr>
<tr>
<td>1.5</td>
<td>Some selected semiconducting polymer based polymer solar cells in recent years</td>
<td>15</td>
</tr>
<tr>
<td>1.6</td>
<td>Physical properties of selected semiconducting polymers based PLEDs in recent years</td>
<td>27</td>
</tr>
<tr>
<td>2.1</td>
<td>P(ADN) synthesized by solution free radical addition polymerization under various conditions</td>
<td>64</td>
</tr>
<tr>
<td>2.2</td>
<td>P(ADN) polymerized by anionic polymerization under various conditions</td>
<td>65</td>
</tr>
<tr>
<td>2.3</td>
<td>Thermal properties of the polymers P(ADN)-F1, F4, A1 and A3</td>
<td>69</td>
</tr>
<tr>
<td>2.4</td>
<td>Optical properties of MADN, Vinyl-ADN and P(ADN)s in THF</td>
<td>73</td>
</tr>
<tr>
<td>2.5</td>
<td>Optical properties of MADN and P(ADN)s in solid-state</td>
<td>74</td>
</tr>
<tr>
<td>2.6</td>
<td>Electrochemical properties of the polymers</td>
<td>76</td>
</tr>
<tr>
<td>3.1</td>
<td>Summary of molecular weight measurements</td>
<td>94</td>
</tr>
<tr>
<td>3.2</td>
<td>Summary of thermal properties</td>
<td>96</td>
</tr>
<tr>
<td>3.3</td>
<td>Optical properties of 2MADN, Vinyl-2ADN, P(2ADN), 3MADQ, Vinyl-3ADQ and P(3ADQ) in THF solutions and in solid thin films</td>
<td>100</td>
</tr>
<tr>
<td>3.4</td>
<td>Electrochemical and electrical properties of 2MADN, 3MADQ,</td>
<td></td>
</tr>
</tbody>
</table>
P(2ADN) and P(3ADQ) .................................................................................. 105

4.1 The yields, the molecular weights and the PDIs of the copolymers..... 123
4.2 Compositions of the copolymers ......................................................... 124
4.3 Solubilities of the polymers ............................................................... 125
4.4 Thermal properties of the copolymers ............................................. 126
4.5 Optical properties of the small molecule MADN, the monomers and
the polymers in THF ................................................................. 137
4.6 Electrochemical properties of the small molecule MADN and the
polymers ................................................................................. 140

5.1 The elemental analysis result of the copolymers P(PyPA-co-VPy)..... 157
5.2 Yields, molecular weights and PDIs of the copolymers
P(PyPA-co-VPy) .............................................................................. 158
5.3 Thermal properties of the copolymers P(PyPA-co-VPy) ............... 160
5.4 Optical properties of the copolymers P(PyPA-co-VPy) in THF ........ 164
5.5 Electrochemical properties of the copolymers P(PyPA-co-VPy) .... 166
5.6 Data summary of multi-layer device (C) .......................................... 170
6.1 Summary of molecular weight measurements ............................ 184
6.2 Summary of thermal properties ...................................................... 187
6.3 Summary of optical properties in THF ........................................... 189
## List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Caption</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Several kinds of side-chain poly(vinylcarbazole)s</td>
<td>6</td>
</tr>
<tr>
<td>1.2</td>
<td>Chemical structures of PPy, PEDOT/PSS and some selected chemicals</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>used in electroactive actuators</td>
<td></td>
</tr>
<tr>
<td>1.3</td>
<td>Chemical structures of polythiophene and some selected chemicals</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>as thin films and electrochromic layers of electrochromic devices</td>
<td></td>
</tr>
<tr>
<td>1.4</td>
<td>Chemical structures of some selected chemicals used in polymer solar</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>cells</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>Chemical structures of PBD, NSD and some selected semiconducting</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>polymers containing oxadiazole units used as electron transport materials.</td>
<td></td>
</tr>
<tr>
<td>1.6</td>
<td>Chemical structures of TAZ and some selected semiconducting polymers</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>containing triazole units used as electron transport materials</td>
<td></td>
</tr>
<tr>
<td>1.7</td>
<td>Chemical structures of some main-chain and side-chain semiconducting</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>polymers used as hole transport materials</td>
<td></td>
</tr>
<tr>
<td>1.8</td>
<td>Chemical structures of some selected electron injection semiconducting</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>polymers</td>
<td></td>
</tr>
<tr>
<td>1.9</td>
<td>Chemical structures of selected main-chain semiconducting polymers</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>used as light emitting materials</td>
<td></td>
</tr>
<tr>
<td>1.10</td>
<td>Chemical structures of selected side-chain semiconducting polymers used</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>as light emitting materials</td>
<td></td>
</tr>
<tr>
<td>1.11</td>
<td>Common ligands and initiators used in ATRP</td>
<td>33</td>
</tr>
<tr>
<td>1.12</td>
<td>Some selected semiconducting polymers synthesized by ATRP</td>
<td>34</td>
</tr>
<tr>
<td>2.1</td>
<td>$^1$H NMR (DMSO-d) of Vinyl-ADN</td>
<td>65</td>
</tr>
</tbody>
</table>
2.2 ¹H NMR (CDCl₃) of P(ADN) for F₄, A₁, A₃, F₇ and Vinyl-ADN........... 66
2.3 FT-IR spectra of P(ADN)-F₁, A₁, F₄, A₃, Vinyl-ADN and MADN. KBr pellets.................................................................................................................. 67
2.4 TGA thermograms for P(ADN)-F₁, F₄, A₁, A₃ and MADN under nitrogen purge at a heating rate of 20 °C/min....................... 68
2.5 DSC thermograms for P(ADN)-F₁, F₄, A₁, A₃ under nitrogen purge at a scanning rate of 40 °C/min......................................... 69
2.6 Extinction coefficient and PL spectra of MADN, Vinyl-ADN and P(ADN)-F₁, A₁, F₄, A₃ in THF..................................................... 72
2.7 Absorption and PL spectra of solid-state MADN and P(ADN)-F₁, A₁, F₄, A₃ on quartz.............................................................. 72
2.8 PL life time of MADN and P(ADN)-F₁, A₁, F₄, A₃............................. 73
2.9 30 Cycles CV of MADN in ACN............................................. 75
2.10 CV voltmmogram of P(ADN) solid films coated on the electrode........ 76
3.1 FT-IR spectra of 2MADN, Vinyl-2ADN & P(2ADN) and 3MADQ, Vinyl-3ADQ & P(3ADQ)........................................................ 93
3.2 GPC chromatogram of P(2ADN) and P(3ADQ).................................. 94
3.3 TGA thermogram for P(2ADN) and P(3ADQ) and their parent small molecules 2MADN and 3MADQ at heating rate of 20 °C/min under nitrogen purge.............................................................. 95
3.4 DSC thermogram for P(2ADN) and P(3ADQ) under heating rate of 40 °C/min under nitrogen purge................................................. 96
3.5 Extinction coefficient and PL spectra of 2MADN, Vinyl-2ADN and P(2ADN) in THF........................................................................... 100
3.6 Optical absorption and PL spectra of 2MADN in a PMMA solid solution
3.7 Extinction coefficient and PL spectra of 3MADQ, Vinyl-3ADQ and P(3ADQ) in THF.......................................................... 101
3.8 Optical absorption and PL spectra of 3MADQ in a PMMA solid solution and P(3ADQ) thin film cast on quartz.......................................................... 101
3.9 PL life time spectra of 2MADN, Vinyl-2ADN, P(2ADN), 3MADQ, Vinyl-3ADQ and P(3ADQ)........................................................................... 102
3.10 PL spectra of 3MADQ (a) and P(3ADQ) (b) in a mixed ethanol/water (v/v = 1/1) solution with pH values adjusted by HCl and NaOH. The concentrations of 3MADQ and P(3ADQ) were both 5 ppm. The spectra (c) and (d) were the PL intensity cross-section for 3MADQ at 442 nm and P(3ADQ) at 457 nm against pH........................................................................... 103
3.11 CV of 2MADN and 3MADQ in ACN, and P(2ADN) and P(3ADQ) thin film cast on the Pt working electrode.......................................................... 105
4.1 ¹H NMR spectrum (DMSO-d) of the monomer Vinyl-ADN......................... 117
4.2 ¹H NMR spectrum (CDCl₃-d) of the homopolymer PS................................ 118
4.3 ¹H NMR spectrum (CDCl₃-d) of the copolymer P(ADN-co-S 1:6)............. 118
4.4 ¹H NMR spectrum (CDCl₃-d) of the homopolymer PVK.......................... 119
4.5 ¹H NMR spectrum (CDCl₃-d) of the copolymer P(ADN-co-VK 1:6)......... 119
4.6 FT-IR spectra of the copolymers P(ADN-co-S)......................................... 121
4.7 FT-IR spectra of the copolymers P(ADN-co-VK)..................................... 121
4.8 GPC chromatogram of P(ADN-co-S), recorded at 254 nm with the flow rate of 1 mL/min................................................................................................. 122
4.9 GPC chromatogram of P(ADN-co-VK), recorded at 254 nm with the flow rate of 1 mL/min................................................................................................. 123
4.10 TGA thermograms of the copolymers P(ADN-co-VK) at different mole feed ratios under the heating rate of 20 °C/min............................................ 127
4.11 TGA thermograms of the copolymers P(ADN-co-S) at different mole feed ratios under the heating rate of 20 °C/min.................................................... 127
4.12 DSC thermograms of the copolymers P(ADN-co-S) at different mole feed ratios under the scanning rate of 40 °C/min.................................................. 128
4.13 Variation of $T_g$ with the compositions of the copolymers P(ADN-co-S). Experimental data are shown as the solid circles; Fox equation was shown as the dashed line........................................................................................................ 128
4.14 DSC thermograms of the copolymers P(ADN-co-VK) at different mole feed ratios under the scanning rate of 40 °C/min........................................ 129
4.15 Variation of $T_g$ with the compositions of the copolymers P(ADN-co-VK). Experimental data are shown as the solid circles; Fox equation was shown as the dashed line........................................................................................................ 129
4.16 Optical absorption and PL spectra of MADN, Vinyl-ADN and P(ADN)..... 132
4.17 Optical absorption and PL spectra of P(ADN-co-S)................................. 133
4.18 Optical absorption and PL spectra of P(ADN-co-VK)............................... 133
4.19 PL spectra of P(ADN)/PVK mixture and P(ADN-co-VK) of at corresponding ratio................................................................................................. 134
4.20 Life time spectra of the copolymers P(ADN-co-S)........................................ 134
4.21 Relationship of $\tau$ and $\Phi_{fl}$ with compositions of the copolymers P(ADN-co-S)................................................................................................. 135
4.22 Life time spectra of the copolymers P(ADN-co-VK)........................................ 135
4.23 Relationship of $\tau$ and $\Phi_{fl}$ with compositions of the copolymers P(ADN-co-VK)................................................................................................. 136

xviii
<table>
<thead>
<tr>
<th>Section</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.24</td>
<td>PL spectrum of the homopolymer P(ADN) in different solvent</td>
</tr>
<tr>
<td>4.25</td>
<td>PL spectrum of P(ADN-co- VK 1:6) with different excitation</td>
</tr>
<tr>
<td>4.26</td>
<td>50 cycles CV diagram of the small molecule MADN in DCM</td>
</tr>
<tr>
<td>4.27</td>
<td>CV diagrams of the copolymers P(ADN-co-S) in ACN</td>
</tr>
<tr>
<td>4.28</td>
<td>CV diagram of the copolymers P(ADN-co-VK) in ACN</td>
</tr>
<tr>
<td>4.29</td>
<td>The current density vs voltage of the PLED device</td>
</tr>
<tr>
<td>4.30</td>
<td>The structure of OTFT device used for the mobility measurement</td>
</tr>
<tr>
<td>5.1</td>
<td>$^1$H NMR spectrum (CDCl$_3$) of the monomer Vinyl-PyPA</td>
</tr>
<tr>
<td>5.2</td>
<td>$^1$H NMR spectrum (CDCl$_3$) of the monomer VPy</td>
</tr>
<tr>
<td>5.3</td>
<td>$^1$H NMR spectrum (CDCl$_3$) of the copolymer P(PyPA-co-VPy)</td>
</tr>
<tr>
<td>5.4</td>
<td>FT-IR spectra of the copolymers P(PyPA-co-VPy). KBr pellet</td>
</tr>
<tr>
<td>5.5</td>
<td>GPC chromatogram of the copolymers P(PyPA-co-VPy)</td>
</tr>
<tr>
<td>5.6</td>
<td>TGA thermograms of the copolymers P(PyPA-co-VPy) at different mole feed ratios under the heating rate of 20 °C/min</td>
</tr>
<tr>
<td>5.7</td>
<td>DSC thermograms of the copolymers P(PyPA-co-VPy) at different mole feed ratios under the scanning rate of 40 °C/min</td>
</tr>
<tr>
<td>5.8</td>
<td>Optical absorption and photoluminescence spectra of the copolymers P(PyPA-co-VPy) in THF at room temperature</td>
</tr>
<tr>
<td>5.9</td>
<td>Optical absorption of PyPA and photoluminescence spectrum of pyrene</td>
</tr>
<tr>
<td>5.10</td>
<td>Lifetime spectrum of the copolymers P(PyPA-co-VPy)</td>
</tr>
<tr>
<td>5.11</td>
<td>Relationship of τ and Φ$_{Fl}$ with the compositions of copolymers P(PyPA-co-VPy)</td>
</tr>
<tr>
<td>5.12</td>
<td>50 cycles CV diagram of PyPA in DCM</td>
</tr>
<tr>
<td>5.13</td>
<td>Cyclic voltammogram of the copolymers P(PyPA-co-VPy)</td>
</tr>
<tr>
<td>5.14</td>
<td>Three device structures for the PLED. (A) Single-layer device</td>
</tr>
</tbody>
</table>
configuration with different HTL materials. (B) Single-layer device configuration with different composition P(PyPA-co-VPy)s. (C) Multi-layer device configuration with different composition P(PyPA-co-VPy)s... .......................................................................................................................... 168

5.15 The performance of PLED (A) ITO/HIL/P(PyPA-co-VPy 50:50)/LiF/Al.... 168
5.16 EL spectra for devices (B) ITO/CFx/P(PyPA-co-VPy)/LiF/Al................. 169
5.17 The curves of current density vs voltage and the luminance vs voltage of devices(C) ITO/CFx/P(PyPA-co-VPy)/TPBi/LiF/Al................................. 169

6.1 $^1$H NMR spectra of PEG3400, Br-PEG3400-Br, ADN-PEG3400-ADN and Py-PEG3400-Py................................................................. 183
6.2 GPC chromatogram of ADN-PEG3400-ADN, Py-PEG3400-Py, P(ADN) and P(Py)....................................................................................... 185
6.3 TGA thermogram for PEG3400, Br-PEG3400-Br, ADN-PEG3400-ADN, Py-PEG3400-Py, P(ADN) and P(Py) at heating rate of 20 °C/min under nitrogen purge................................................................................................. 186
6.4 DSC thermogram for for PEG3400, Br-PEG3400-Br, ADN-PEG3400-ADN, Py-PEG3400-Py, P(ADN) and P(Py) at heating rate of 40 °C/min under nitrogen purge............................................................... 187
6.5 Extinction coefficient and PL spectra of ADN-PEG3400-ADN, Py-PEG3400-Py, P(ADN) and P(Py) in THF..................................................... 188
6.6 TEM microphotographs of spherical aggregates corona and core structures from amphiphilic tri-block copolymers (A) Py-PEG3400-Py and (B) ADN-PEG3400-ADN at concentration 10 ppm (magnified optical images of the spherical aggregates in the black boxes of Figure 7 (A) and (D), respectively)............................................................ 191
6.7 TEM microphotographs of spherical aggregates from amphiphilic tri-block copolymers Py-PEG3400-Py and ADN-PEG3400-ADN. (A) Py-PEG3400-Py concentration 10 ppm; (B) 50 ppm; (C) 200 ppm and (D) ADN-PEG3400-ADN concentration 10 ppm; (E) 50 ppm; (F) 200 ppm..... 192

6.8 Effect of amphiphilic tri-block copolymers Py-PEG3400-Py and ADN-PEG3400-ADN concentrations on the micelle diameters.......................... 192

6.9 TEM microphotographs of the linear and crosslinked pearl-necklace-like aggregates from amphiphilic tri-block copolymers (A) Py-PEG3400-Py and (B) ADN-PEG3400-ADN at concentration 1000 ppm............................... 193

6.10 Proposed molecular packing models for the self-assemblies of ADN-PEG3400-ADN and Py-PEG3400-Py in THF/H$_2$O (1/20, v/v)......... 193
## List of Schemes

<table>
<thead>
<tr>
<th>Scheme</th>
<th>Caption</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>TEM General mechanism for ATRP. Where, $k_a$ is activation rate constant; $k_d$ is deactivation rate constant; $k_p$ is propagation rate constant; $k_t$ is termination rate constant; M is monomer and R-X is alkyl halide.</td>
<td>32</td>
</tr>
<tr>
<td>2.1</td>
<td>Synthetic routes for the monomer Vinyl-ADN and its polymers.</td>
<td>63</td>
</tr>
<tr>
<td>3.1</td>
<td>Synthetic routes for the polymers P(2ADN) and P(3ADQ).</td>
<td>91</td>
</tr>
<tr>
<td>3.2</td>
<td>The equilibrium equations for 3MADQ and P(3ADQ) at different pH values.</td>
<td>99</td>
</tr>
<tr>
<td>4.1</td>
<td>Synthetic routes for the monomer of Vinyl-ADN and its copolymers P(ADN-co-S) and P(ADN-co-VK).</td>
<td>116</td>
</tr>
<tr>
<td>5.1</td>
<td>Synthetic routes for the monomers Vinyl-PyPA and VPy and their copolymer P(PyPA-co-VPy).</td>
<td>153</td>
</tr>
<tr>
<td>6.1</td>
<td>Synthetic routes for the block copolymers ADN-PEG3400-ADN &amp; Py-PEG3400-Py (A) and the homopolymers P(ADN) &amp; P(Py) synthesized by ATRP method (B).</td>
<td>179</td>
</tr>
</tbody>
</table>
# List of Symbols and Units

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>Degree Celsius</td>
</tr>
<tr>
<td>ν</td>
<td>Wavenumber in cm$^{-1}$</td>
</tr>
<tr>
<td>δ</td>
<td>Chemical shift</td>
</tr>
<tr>
<td>$\Phi_F$</td>
<td>Fluorescence quantum yield</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Molar absorptivity/molar extinction</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hz</td>
<td>Hertz</td>
</tr>
<tr>
<td>hrs</td>
<td>Hours</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer</td>
</tr>
<tr>
<td>eV</td>
<td>Electron volt</td>
</tr>
<tr>
<td>ppm</td>
<td>Part per million</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethylsulfoxide</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-Dimethylformamide</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>ACN</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>TCE</td>
<td>1,1,1,2,-Tetrachlorethane</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>FT-IR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</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 doublet</td>
</tr>
<tr>
<td>M+</td>
<td>Molecular ion</td>
</tr>
<tr>
<td>m/z</td>
<td>Mass to charge ratio</td>
</tr>
<tr>
<td>$E_g$</td>
<td>Energy gap</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel permeation chromatography</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultraviolet-visible</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>MALDI-TOF MS</td>
<td>Matrix-assisted laser desorption ionization time of flight mass spectrometry</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>Fc</td>
<td>Ferrocenyl</td>
</tr>
<tr>
<td>$T_g$</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>$T_m$</td>
<td>Melting temperature</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------------</td>
</tr>
<tr>
<td>$T_d$</td>
<td>Degradation temperature</td>
</tr>
<tr>
<td>a.u.</td>
<td>Arbitrary unit</td>
</tr>
<tr>
<td>$J$</td>
<td>Modulus of the coupling constant</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

1.1 Background

Semiconducting polymers have intrinsic volume conductivity lied between $10^{-8}$ S/cm to $10^{-2}$ S/cm with values similar to traditional inorganic semiconductors such as Si, Ge, Ga, etc. Structurally, semiconducting polymers are defined as 1-D long-chain molecules that can be spin-cast or coated into a large area flexible thin film.\(^1\)

The field of conducting polymers has its root in the 1977 discovery of the conducting properties of polyacetylene by Alan Heeger, Alan MacDiarmid and Hideki Shirakawa.\(^2\) The conductivity of the polyacetylene increased $10^9$ times after the polyacetylene was oxidized by chlorine, bromine or iodine vapor. This break-through earned these three researchers the 2000 Nobel Prize in Chemistry for the discovery and development of conductive polymers.\(^3\)-\(^5\) Since then, in the past several years, many research groups have devoted their efforts to the study of this new class of polymer material and great improvements had been achieved in the applications of antistatic materials,\(^6\)-\(^8\) printing electronic circuits,\(^9\)-\(^11\) electroactive actuators,\(^12\)-\(^14\) electrochromic materials,\(^15\)-\(^17\) supercapacitors,\(^18\)-\(^20\) chemical sensors,\(^21\)-\(^23\) biosensors,\(^24\)-\(^26\) electromagnetic shielding materials,\(^27\)-\(^29\) microwave-absorbent coatings,\(^30\)-\(^32\) polymer solar cells,\(^33\)-\(^35\) polymer light-emitting diodes (PLEDs).\(^36\)-\(^38\)

1.2 The classification of the conductive polymers

Typically, there are two kinds of conducting polymers since they have been
discovered so far. They include extrinsic conducting polymers and intrinsic conducting polymers. Extrinsic conducting polymers are insulating polymers that achieved high conductivity by the addition of conductive fillers. Intrinsic conducting polymers, on the other hands, could be classified into four major classes. They are charge transfer polymers,\cite{1,39} ionically conducting polymers,\cite{1,39} conjugated conducting polymers\cite{1,39} and non-conjugated conducting polymers.\cite{40,41} The traditional conjugated conducting polymers are main-chain conjugated polymers with the deficiency of poor solubility at high molecular weight. In contrast, the non-conjugated conducting polymers are usually side-chain polymers that remain soluble despite their high molecular weight. Before doping, most of the main-chain conducting polymers, side-chain conducting polymers and charge transfer polymers have conductivity in the range of $10^{-8}$ S/cm–$10^{2}$ S/cm which allow them to be fall in the category of electronically semiconducting materials.

1.2.1 Conductively filled polymers

Conductively filled polymers are usually fabricated by loading conductive fillers, such as carbon black, graphite, or metal oxide particles into an insulating polymer matrix. The first conductively filled polymers were invented in 1930 for purpose of preventing the corona discharge in electronic devices and have been used in advanced printed circuitries.\cite{39} Because of the ease of processing, good environmental stability and wide range of electrical properties, the potential uses of the conductively filled polymers have since been multiplied.\cite{1,39,42} As the conductively filled polymers are multiphase inhomogeneous materials, they have three phases, namely the polymer, the filler, and the interface. Therefore, such inhomogeneity results in problems such as heavily process-dependent, hard to
control reproducibility and weak dielectric strength.\textsuperscript{[1]} Therefore, it is critical significance in controlling the quality of dispersion in order to obtain homogeneous semiconducting polymer composites.

\textbf{1.2.2 Charge transfer polymers}

The conductivity of the charge transfer polymers are usually realized by transferring a fraction of electronic charge from the electron donor units to the accepter units. With the attached electron donor and/or acceptor moieties onto polymer backbones, the charge transfer semiconducting polymers exhibit good processability and stacking properties. In 1954, it was discovered resistivities in molecular charge transfer complexes were only 8 ohms·cm in combinations of perylene with iodine or bromine.\textsuperscript{[43,44]} These experimental progresses then promoted the developments of the semiconducting charge transfer polymers and finally led to the inventions of superconductivity the quasi-one dimensional organic conductor di-(tetramethyltetraselenafulvalene)-hexafluorophosphate in 1980 and with fullerene in 1986.\textsuperscript{[45,46]} In the past decade, due to their successful commercial application in xerographic photoreceptor field, charge transfer polymers (such as hole transport poly(phenylenevinylene) and electron transport diphenoquinones) have become the most established organic semiconducting system.\textsuperscript{[1,47]}

\textbf{1.2.3 Ionically conducting polymers}

With the ionic species attached to the polymer chains and the mobile counter ions, ionically conducting polymers have the advantages of high processibility and abundant availability. Since the ionic conductivity of the ionically conducting polymer poly(ethylene glycol) have been investigated systematically in 1975,\textsuperscript{[48]}

3
the applications in commerical area have been propelled by successful applications such as the block copolymer poly(ethylene glycol)-co-polystyrene in rechargeable batteries,[49] the block copolymer poly(dimethyl siloxane)-co-poly(benzimidazole) in fuel cells,[50-52] and the thin films of blends of poly(1,4-phenylenevinylene) and poly(ethylene oxide) complexed with lithium trifluoromethanesulfonate in polymer light-emitting devices.[53,54] Because the ionically semiconducting polymers require the dissociation of counter ions to realize the ionic conduction, water or other polar solvent is needed to provide the solvation of the counter ions. Therefore, the ionic conductivity of the ionically semiconducting polymer shows high sensitivity to humidity and ionically semiconducting polymers are highly insulating once dried.

1.2.4 Main-chain conducting polymers

“Main-chain conducting polymer” is so named due to the existence of alternating single and double bonds or conjugated segments along the polymer main chain. This main-chain semiconducting polymer could be transformed into a conducting form by the addition or extraction of electrons from the polymer main chain resulting in anions or cations by the addition of dopants, respectively. In this case, under the effect of the electrical field, radical anions or radical cations will act as the charge carriers jumping from one site to another, thus increasing conductivity. However, since no metal-like valence bands in the main chain, the non-doped main-chain conducting polymers usually show lower conductivities. Once doping happened, the loosely bound π-electron delocalized could hop round the polymer main chain by the attraction or repulsion of the dopant anion/cation.

Since Heeger, Shirakawa and MacDiarmid fabricated the first main-chain conducting polymer polyacetylene in 1977, extensive and systematic researches
have been focus on the polyconjugated polymer systems. The various main-chain semiconducting polymers that have been designed and synthesized \cite{55,56} are listed in Table 1.1 showing their repeating units and conductivities.\cite{57}

**Table 1.1 Some common main-chain semiconducting/conducting polymers.**

<table>
<thead>
<tr>
<th>No.</th>
<th>Polymer (date conductivity discovered)</th>
<th>Structure</th>
<th>d-d* gap (eV)</th>
<th>Conductivity (S/cm)</th>
</tr>
</thead>
</table>
| 1   | Polycetylene and analogues polyacetylene (1977) | \[
\begin{array}{c}
\text{C} \equiv \text{C} \equiv \text{C} \equiv \text{C} \\
\text{n}
\end{array}
\] | 1.5 | \(10^3\text{--}1.7\times10^5\) |
| 2   | Polypyrrrole (1979) | \[
\begin{array}{c}
\text{H} \\
\text{N}
\end{array}
\] | 3.1 | \(10^2\text{--}7.5\times10^3\) |
| 3   | Polythiophene (1981) | \[
\begin{array}{c}
\text{S} \\
\text{n}
\end{array}
\] | 2.0 | \(10^2\text{--}10^3\) |
| 4   | Polyphenylene and analogues poly(paraphenylene) (1979) | \[
\begin{array}{c}
\text{C} \equiv \text{C} \\
\text{n}
\end{array}
\] | 3.0 | \(10^2\text{--}10^3\) |
| 5   | Poly(p-phenylene vinylene) (1979) | \[
\begin{array}{c}
\text{C} \equiv \text{C} \\
\text{n}
\end{array}
\] | 2.5 | \(3\text{--}5\times10^3\) |
| 6   | Polyaniline (1980) | \[
\begin{array}{c}
\text{H} \equiv \text{N} \equiv \text{N} \equiv \text{N} \\
\text{H} \equiv \text{N} \equiv \text{N} \equiv \text{N} \\
\text{H} \equiv \text{N} \equiv \text{N} \equiv \text{N} \\
\text{N}
\end{array}
\] | 3.2 | \(30\text{--}200\) |

### 1.2.5 Side-chain conducting polymers

Side-chain conducting polymers have different forms of \(\pi\)-electron delocalization compared to the main-chain semiconducting polymers. Side-chain conducting polymers usually have extended \(\pi\)-electron delocalization on functional groups suspended to the backbone of the polymers. In this case, the
electrons in the side-chain semiconducting polymers could move in the pendant
groups but not in the main chains as in main-chain semiconducting polymers.
Compared with the traditional π-conjugated main-chain polymers, side-chain
conductive polymers have a lower volume percentage of the charge transport
moiety yet they possess advantages such as excellent mechanical strength, good
rheological properties, solubility in common organic solvents and purer emission
color (i.e. narrow emission peak width).[58,59] Furthermore, the performances of
the side-chain semiconducting polymers can be engineered easily by changing
their composition or choosing an appropriate additional polymerization method.
The most famous side-chain conducting polymer used in organic/polymer
light-emitting diode fields is poly(vinylcarbazole) (PVK) (Figure 1.1).[60] With
the easy polymerization process for the monomer N-vinylcarbazole, PVK exhibits
a high $T_g$ (around 227 °C) and good solubility in organic solvents (i.e. THF).
Attributed to its good conductivity, PVK is used as the hole transporting/limiting
component in multilayer PLED devices.[61-63]


Figure 1.1   Several kinds of side-chain poly(vinylcarbazole)s.
1.3 The applications and progresses of the intrinsic semiconducting polymers

Since the traditional semiconductors are metals/oxides and they are expensive, toxic and harmful to the environment, as a possible substitute, the intrinsic semiconducting polymers exhibit many potential applications. Below are some applications and progresses of the intrinsic semiconducting polymers in plastics electronics. They are such as electroactive actuators, electrochromic materials, microwave-absorbent coatings, polymer solar cells and PLEDs.

1.3.1 Electroactive actuators

Since the shape and/or dimension of the intrinsic semiconducting polymers could be changed under electrochemical stimulation, with the transportation of solvated ions between the internal polymer matrix and the external electrolyte solution, the electrostatic repulsion, and/or the structural distortion through oxidation of p-conjugated polymers, the intrinsic semiconducting polymers have shown prospect in the fabrication of the electroactive actuators.\(^{[64-67]}\)

Because of the unique properties of polypyrrole (PPy) including high stresses, moderate strains and low voltage operation, PPy has gained particular attention in the actuator fields (Figure 1.2). J. Foroughi et al.\(^ {\text{[12]}}\) reported a PPy-DEHS film of polypyrrole doped with di-(2-ethylhexyl) sulfosuccinate using electro-chemical oxidation of pyrrole. Their film showed a very large strain (about 30%) and also a high conductivity (75 S/cm). G. Alici et al.\(^ {\text{[13]}}\) had implanted Au ions on the surface of the PVDF substrates for the PPy-based polymer layers of the actuators to enhance their ionic-type conducting polymer actuator conductivity successfully. The actuator could be driven at very low operation voltage (0.1 V). Table 1.2 lists
the progress of PPy based actuator in recent years.

**Table 1.2 Some PPy based actuators in recent years.**

<table>
<thead>
<tr>
<th>No.</th>
<th>Actuator structures</th>
<th>Stress (MPa)</th>
<th>Strain (%)</th>
<th>Operation voltage (V)</th>
<th>Conductivity (S/cm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PPy/DEHS</td>
<td>35</td>
<td>33</td>
<td>--</td>
<td>--</td>
<td>[12]</td>
</tr>
<tr>
<td>2</td>
<td>PPy/Au/PVDF/Au/PPy</td>
<td>--</td>
<td>175</td>
<td>0.1–0.5</td>
<td>--</td>
<td>[13]</td>
</tr>
<tr>
<td>3</td>
<td>Au/PVDF/PPy</td>
<td>--</td>
<td>--</td>
<td>2</td>
<td>--</td>
<td>[68]</td>
</tr>
<tr>
<td>4</td>
<td>PPy(DBS)/Au/Kapton</td>
<td>80</td>
<td>2</td>
<td>--</td>
<td>--</td>
<td>[69]</td>
</tr>
<tr>
<td>5</td>
<td>PPy/PVDF/PPy</td>
<td>--</td>
<td>--</td>
<td>0.5</td>
<td>--</td>
<td>[70]</td>
</tr>
<tr>
<td>6</td>
<td>Au/PPy/(MWCNT/PPy)$_3$</td>
<td>--</td>
<td>--</td>
<td>1</td>
<td>--</td>
<td>[71]</td>
</tr>
<tr>
<td>7</td>
<td>PPy/NaPF$_6$</td>
<td>2.4</td>
<td>&gt; 6</td>
<td>0.4</td>
<td>--</td>
<td>[72]</td>
</tr>
<tr>
<td>8</td>
<td>DNA/PPy/CNT</td>
<td>--</td>
<td>4.41</td>
<td>1</td>
<td>--</td>
<td>[73]</td>
</tr>
<tr>
<td>9</td>
<td>Chitosan/PPy</td>
<td>--</td>
<td>0.54</td>
<td>--</td>
<td>3.1×10$^{-1}$</td>
<td>[74]</td>
</tr>
<tr>
<td>10</td>
<td>PPy(DBS)/PPy(ClO$_4$)/PPy(DBS)</td>
<td>10</td>
<td>0.02</td>
<td>4</td>
<td>2.2×10$^{-6}$</td>
<td>[75]</td>
</tr>
<tr>
<td>11</td>
<td>PPy:diPy-C$_1$/DBS(TBA)</td>
<td>--</td>
<td>5</td>
<td>--</td>
<td>17</td>
<td>[76]</td>
</tr>
</tbody>
</table>

Due to the availability as a colloidal particles in water, poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate) (PEDOT/PSS) has become a commercially successful conducting polymers (Figure 1.2). It exhibits superior mechanical properties, good thermal stability and high conductivity, which provides various potential applications to organic or plastic electronic devices. T. Dai $^{[77]}$ have synthesized a high strain (66%) conducting hydrogels composed of poly(acrylamide) (PAAm) and PEDOT-PSS through the construction of a special double-network structure. Their mechanically strong hydrogels showed a prospect in the electromechanical semiconducting polymer actuators. K. Ikushima $^{[78]}$ reported a micro autofocus lens actuators using semiconducting polymer with remarkable mechanical strength (about 21 MPa stress and 10% strain). Several selected actuators
fabricated based on PEDOT/PSS are listed in Table 1.3.

<table>
<thead>
<tr>
<th>No.</th>
<th>Actuator structures</th>
<th>Stress (MPa)</th>
<th>Strain (%)</th>
<th>Operation voltage (V)</th>
<th>Conductivity (S/cm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>PEDOT:PSS-MWCNT/PET/</td>
<td>--</td>
<td>1~4</td>
<td>0.8</td>
<td>36</td>
<td>[14]</td>
</tr>
<tr>
<td>13</td>
<td>PEDOT:PSS-MWCNT</td>
<td>--</td>
<td>0.6</td>
<td>10</td>
<td>29~164</td>
<td>[67]</td>
</tr>
<tr>
<td>14</td>
<td>PEDOT:PSS/PAAm</td>
<td>0.27</td>
<td>66</td>
<td>--</td>
<td>6.7×10⁻⁴~2.6×10⁻³</td>
<td>[77]</td>
</tr>
<tr>
<td>15</td>
<td>Non-porous PEDOT:PSS</td>
<td>--</td>
<td>2.46</td>
<td>10</td>
<td>150</td>
<td>[79]</td>
</tr>
<tr>
<td>16</td>
<td>PEDOT:PSS(PEO)/PVDF</td>
<td>~21</td>
<td>~10</td>
<td>1.4</td>
<td>6.2×10⁻²~3.2</td>
<td>[78]</td>
</tr>
</tbody>
</table>

**Table 1.3 Some selected PEDOT/PSS based actuators in recent years.**

---

**Figure 1.2** Chemical structures of PPy, PEDOT/PSS and some selected chemicals used in electroactive actuators.

1.3.2 Electrochromic materials

With an aromatic functional group or segment in the molecular structures, such as thiophene, pyrrole, aniline, furan, carbazole, azulene and indole etc.,
semiconducting/conducting polymers have been found to exhibit electrochromic ability and many have been systemically studied in recent years.\[80-88\] Among all these semiconducting polymers, polythiophenes, polypyrroles as well as their derivatives have received most attention as polymer electrochromic materials.

Polythiophenes have the advantages of ease of chemical/electrochemical synthesis, environmental stability and processability.\[88\] Thin polythiophene films are blue ($\lambda_{\text{max}} = 730$ nm) in the doped (oxidized) state and red ($\lambda_{\text{max}} = 470$ nm) in the un-doped state. Generally, there are two classic polythiophene with the difference in the 3-substituted and 3,4-disubstituted groups. Since many kinds of substituted thiophenes have been designed and prepared, tunable color could be obtained with different monomers. Besides of the electroactive actuators field, polypyrrole and its substituted derivatives also show a large prospect in electrochromic applications due to their relative ease of chemical/electrochemical synthesis. Generally, the parent polypyrrole thin films are yellow-green ($E_g \sim 2.7$ eV) in the un-doped insulating state and blue-violet in the doped conductive state. Unlike polythiophenes, polypyrroles could provide more substituted positions C-3, C-4 and N, and thus have many more derivatives. Several selected electrochromic devices based on the substituted polythiophenes and polypyrroles are summarized and listed in Table 1.4.
Table 1.4 Some selected thin films and electrochromic layers of electrochromic devices in recent years.

<table>
<thead>
<tr>
<th>No.</th>
<th>Electrochromic layer of the electrochromic devices and thin film</th>
<th>Optical contrast (%T)</th>
<th>Coloration efficiency (cm²/C)</th>
<th>Transmittance changing position (nm)</th>
<th>Operation voltage (V)</th>
<th>Switch time (s)</th>
<th>Color change (Neutral to oxidized states)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PANI-CNTs/PEDOT-CNTs</td>
<td>32.5</td>
<td>836</td>
<td>650</td>
<td>-0.2~1.5</td>
<td>--</td>
<td>Yellow to red</td>
<td>[89]</td>
</tr>
<tr>
<td>2</td>
<td>P(SNS-An-FC)/PEDOT</td>
<td>15.5</td>
<td>893</td>
<td>435, 610</td>
<td>-0.2~1.0</td>
<td>1.30</td>
<td>Yellow to blue</td>
<td>[90]</td>
</tr>
<tr>
<td>3</td>
<td>P(SNS-HE)/PEDOT</td>
<td>14.1</td>
<td>741</td>
<td>345, 570</td>
<td>0~1.5</td>
<td>0.92</td>
<td>No significant transition</td>
<td>[90]</td>
</tr>
<tr>
<td>4</td>
<td>P(SNS-An-Fc-co-EDOT)/PEDOT</td>
<td>22.2</td>
<td>484</td>
<td>512, 601</td>
<td>-1.0~1.3</td>
<td>0.38</td>
<td>Purple to blue</td>
<td>[90]</td>
</tr>
<tr>
<td>5</td>
<td>P(SNS-HE-co-EDOT)/PEDOT</td>
<td>26.6</td>
<td>708</td>
<td>461, 605</td>
<td>-0.2~1.0</td>
<td>0.46</td>
<td>No color to blue</td>
<td>[90]</td>
</tr>
<tr>
<td>6</td>
<td>PIn/PEDOT</td>
<td>15</td>
<td>510</td>
<td>600</td>
<td>-1.0~1.0</td>
<td>0.90</td>
<td>Green to blue-violet</td>
<td>[91]</td>
</tr>
<tr>
<td>7</td>
<td>P(EDOT-FE)/PEDOT</td>
<td>36</td>
<td>784</td>
<td>625</td>
<td>-1.0~1.0</td>
<td>0.50</td>
<td>Brown to blue</td>
<td>[92]</td>
</tr>
<tr>
<td>8</td>
<td>P(CNIn-co-EDOT)/PEDOT</td>
<td>48</td>
<td>680</td>
<td>630</td>
<td>-1.0~1.0</td>
<td>0.80</td>
<td>Brown to dark blue</td>
<td>[93]</td>
</tr>
<tr>
<td>9</td>
<td>PTTPA/PEDOT</td>
<td>38, 29, 53</td>
<td>--</td>
<td>430, 560, 710</td>
<td>0~1.0</td>
<td>2.57, 0.76, 2.10</td>
<td>Yellow- to cadet blue</td>
<td>[94]</td>
</tr>
</tbody>
</table>

Electrochromic thin films

<table>
<thead>
<tr>
<th>No.</th>
<th>Electrochromic thin films</th>
<th>Optical contrast (%T)</th>
<th>Coloration efficiency (cm²/C)</th>
<th>Transmittance changing position (nm)</th>
<th>Operation voltage (V)</th>
<th>Switch time (s)</th>
<th>Color change (Neutral to oxidized states)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>PDPTPA</td>
<td>52, 41</td>
<td>--</td>
<td>617, 852</td>
<td>0~1.2</td>
<td>0.60, 1.40</td>
<td>Brown-yellow to black</td>
<td>[95]</td>
</tr>
<tr>
<td>11</td>
<td>PBBTES</td>
<td>32</td>
<td>--</td>
<td>625</td>
<td>-0.5~0.8</td>
<td>--</td>
<td>Blue to light blue</td>
<td>[96]</td>
</tr>
<tr>
<td>12</td>
<td>PBBTEA</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0~1.2</td>
<td>--</td>
<td>Orange to gray</td>
<td>[96]</td>
</tr>
<tr>
<td>13</td>
<td>P(PE-co-EDOT)</td>
<td>25, 42</td>
<td>--</td>
<td>516, 1100</td>
<td>--</td>
<td>2.00</td>
<td>Red-brown to light-green</td>
<td>[97]</td>
</tr>
<tr>
<td>14</td>
<td>polyPTPy</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0~1.4</td>
<td>&lt; 1.00</td>
<td>Brown-yellow to dark blue</td>
<td>[98]</td>
</tr>
<tr>
<td>15</td>
<td>polyPhenTPy</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0~1.4</td>
<td>&lt; 1.00</td>
<td>Green-yellow to light blue</td>
<td>[98]</td>
</tr>
</tbody>
</table>
1.3.3 Microwave-absorbent coatings

For many military and civil applications such as in stealth technology, microwave absorbers are increasingly being used to enhance shielding performance at higher frequencies. With tunable nature of electrical properties, intrinsically semiconducting polymers have shown a great prospect in microwave absorption field.\cite{30-32} E. Håkansson et al. \cite{27} reported the up to 49.5% of the...
incident 30-35 W microwave radiation could be absorbed by either the anthraquinone-2-sulfonic acid or para-toluene-2-sulfonic acid doped polypyrrole. Rooted on the famous main-chain semiconducting polymer poly(\(p\)-phenylenevinylene), S.W. Phang et al.\(^{[99]}\) had prepared a new PPV-type polymer poly(4,4’-diphenylene diphenylvinylene). With thickness less than 5 mm, this non-magnetic semiconducting polymer was shown to be suitable for use as broadband absorber, whereas thicker samples with 10 mm thickness are useful as a narrow-band absorber.

### 1.3.4 Polymer solar cells

The photovoltaic effect required a material to be absorptive in the visible region and the ability to transport electricity, numerous semiconducting polymers have been designed and synthesized for the application of polymer solar cell in recent years.\(^{[33-35]}\) Semiconducting polymers show many unique advantages such as the low manufacturing costs in high volumes,\(^{[100]}\) good flexibility, solution processable,\(^{[33]}\) tunable energy gap and high optical absorption coefficient.\(^{[101,102]}\) However, in comparison to the traditional inorganic solar cell, the main disadvantages of the semiconducting polymer solar cells are low efficiency, low stability and low mechanical strength.

In recent years, polymer solar cells with PEDOT:PSS/P3HT:PCBM acted as the active layer have received increasing attentions. The solar cells showed moderate power conversion efficiencies (PCE) about 2%~5%, medium open circuit voltage (\(V_{\infty}\)) about 0.60~0.80 V and high short circuit current (\(J_{SC}\)) about 2.00~10.00 mA/cm\(^2\). Y. Jia et al.\(^{[35]}\) have fabricated an enhanced polymer solar cells based on P3HT:PC_{61}BM by using cesium acetate as the cathode buffer layer. The device showed a higher PCE (4.16%) and a high \(J_{SC}\) (10.20 mA/cm\(^2\)). There
are also researchers devoted their efforts on the ITO-free polymer solar cell due to the intrinsic drawbacks of ITO electrodes, such as the fragility, high thermal expansion coefficient and poor interfacial compatibility with organic materials. However, with low PCE, $V_{oc}$ and $J_{sc}$, this kind of solar cell still need further investigation. U. J. Lee reported a flexible solar cell by using surface-interpenetrated conducting polymer, PANI:CSA as an ITO-free organic electrode. Compared to similar polymer solar cell, their cell exhibited the highest PCE (3.51%), $V_{oc}$ (0.83 V) and $J_{sc}$ (8.70 mA/cm$^2$). Besides these two classic polymer solar cells, many other semiconducting polymers have been employed in the fabrication of OPV, such as PPV derivatives, PF, PFT and PCDTBT etc. A. Puetz et al. have demonstrated a PCDTBT based polymer solar cell which exhibited a high PCE (4.50%) and a very high open circuit voltage of about 1.6 V. An exciting result comes from Prof. Wu’s group that their PTB7 based polymer solar cell presented an extremely high PCE of more than 9.2%. Their prospective work opened up new opportunities to improve polymer solar cells with a view to achieving power conversion efficiency above 10%. Table 1.5 lists the progress of semiconducting polymer based polymer solar cell in recent years.
Table 1.5 Some selected semiconducting polymer based polymer solar cells in recent years.

<table>
<thead>
<tr>
<th>No.</th>
<th>Polymer solar cell configurations</th>
<th>Power conversion efficiency, PCE (%)</th>
<th>Short circuit current, ( J_{sc} ) (mA/cm(^2))</th>
<th>Open circuit voltage, ( V_{oc} ) (V)</th>
<th>Fill factor, FF (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT:PSS/P3HT:PCBM active layer polymer solar cells</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Glass/ITO/PEDOT:PSS/P3HT:PCBM/Ca/Al</td>
<td>3.54</td>
<td>9.00</td>
<td>0.59</td>
<td>66</td>
<td>[108]</td>
</tr>
<tr>
<td>2</td>
<td>Glass/ITO/PEDOT:PSS/P3HT:PCBM/Rb(_2)CO(<em>3)/IZO/CuPc/C(</em>{60})/BCP/Al</td>
<td>3.11</td>
<td>8.91</td>
<td>0.86</td>
<td>63</td>
<td>[109]</td>
</tr>
<tr>
<td>3</td>
<td>Glass/ITO/hydrogenated amorphous silicon/PEDOT:PSS/P3HT:PCBM/Al</td>
<td>2.22</td>
<td>7.70</td>
<td>0.78</td>
<td>37</td>
<td>[110]</td>
</tr>
<tr>
<td>4</td>
<td>Glass/ITO/PEDOT:PSS/P3HT:PCBM/CH(_3)COOCs/Al</td>
<td>4.16</td>
<td>10.20</td>
<td>0.64</td>
<td>64</td>
<td>[35]</td>
</tr>
<tr>
<td>5</td>
<td>Glass/ITO/PEDOT:PSS/P3HT:PCBM/C(_6)H(_4)COOLi/Al</td>
<td>3.41</td>
<td>10.40</td>
<td>0.66</td>
<td>50</td>
<td>[111]</td>
</tr>
<tr>
<td>ITO free polymer solar cells</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Quartz/carbon nanosheets/PEDOT:PSS/P3HT:PCBM/Ca/Al</td>
<td>1.73</td>
<td>5.43</td>
<td>0.58</td>
<td>55</td>
<td>[112]</td>
</tr>
<tr>
<td>7</td>
<td>Glass/FTO/B(_2)TiO(_3)/P3HT-COOH-TiO(_2)/P3HT/PEDOT:PSS/Au</td>
<td>0.79</td>
<td>4.50</td>
<td>0.47</td>
<td>37</td>
<td>[113]</td>
</tr>
<tr>
<td>8</td>
<td>Glass/PEDOT:S(_2)O(_5)/P3HT:PCBM/Al</td>
<td>1.05</td>
<td>4.89</td>
<td>0.54</td>
<td>40</td>
<td>[114]</td>
</tr>
<tr>
<td>9</td>
<td>PET/PANI:CSA/PEDOT:PSS/PCDTBT:PC(_{71})BM/Al</td>
<td>3.51</td>
<td>8.70</td>
<td>0.83</td>
<td>49</td>
<td>[105]</td>
</tr>
<tr>
<td>Other semiconducting polymers based polymer solar cells</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Glass/FTO/dense Nb-TiO(_2)/MEH-PPV/Ag</td>
<td>--</td>
<td>0.34</td>
<td>0.60</td>
<td>36</td>
<td>[115]</td>
</tr>
<tr>
<td>11</td>
<td>Glass/ITO/PEDOT:PSS/PF-PFT:PCBM/LiF/Al</td>
<td>--</td>
<td>2.00</td>
<td>0.60</td>
<td>35</td>
<td>[116]</td>
</tr>
<tr>
<td>12</td>
<td>Glass/ITO/PEDOT:PSS/MDMO-PPV:PCBM/LiF/Al</td>
<td>--</td>
<td>3.00</td>
<td>0.65</td>
<td>40</td>
<td>[116]</td>
</tr>
<tr>
<td>13</td>
<td>Glass/ITO/MoO(<em>3)/PCDTBT:PC(</em>{71})BM/ZnO/Au/MoO(<em>3)/PCDTBT:PC(</em>{71})BM/Ca/Al</td>
<td>4.50</td>
<td>5.30</td>
<td>1.59</td>
<td>54</td>
<td>[106]</td>
</tr>
<tr>
<td>14</td>
<td>Glass/ITO/PEDOT:PSS/POCbz:PC(_{70})BM/LiF/Al</td>
<td>3.22</td>
<td>10.60</td>
<td>0.73</td>
<td>41</td>
<td>[117]</td>
</tr>
<tr>
<td>15</td>
<td>Glass/ITO/PFN/PTB7:PC(_{71})BM/MoO(_3)/Al, Ag</td>
<td>9.21</td>
<td>17.46</td>
<td>0.75</td>
<td>70</td>
<td>[107]</td>
</tr>
</tbody>
</table>
Figure 1.4 Chemical structures of some selected chemicals used in polymer solar cells.
1.3.5 Polymer light-emitting diodes

In the past three decades, rapid progress had been drawn in the development of semiconducting polymer-based light emission devices.\textsuperscript{[118-122]} The shortcomings of the devices have been improved gradually, not only in the extensive research of the principle and degradation process of PLED,\textsuperscript{[123, 124]} but also on the enhancement of the properties of the devices such as luminance, color, lifetime, efficiency and stability, etc.\textsuperscript{[119-122,125-132]} Typically, based on their different functions in the application of PLEDs, semiconducting polymers could be classified into five major classes, electron transport materials, hole transport materials, electron injection materials, hole injection materials and light-emitting materials.

1.3.5.1 Electron transport materials

The imine nitrogen (C=N) is a well known electron deficient group which make it having the outstanding ability for transporting electrons. Oxadiazoles, pyridines, quinolines, quinoxazolines and triazines are some of the chemical moieties that known to process electron-transporting property.\textsuperscript{[133]} Oxadiazoles have been used in organic light-emitting diodes (OLEDs) for their electron transport and efficient hole blocking qualities due to its high electron affinity & mobility and large ionization potentials.\textsuperscript{[125, 126]} They could be fabricated into uniform thin films by vacuum sublimation. 2-Biphenyl-4-yl-5-(4-tert-butylphenyl)-3,4-oxadiazole (PBD) is the most famous small molecule oxadiazole compound. It was first developed by Tsutsui et al. in 1989.\textsuperscript{[134]} The emission efficiency of device with inserted PBD layer (ITO/NSD/PBD/MgA) tremendously increased $10^4$ times larger than that of the device without PBD (ITO/NSD/MgA). Because of its excellent properties, many modified oxadiazole moiety had been
introduced in the semiconducting polymer structures (Figure 1.5). Some of the semiconducting polymers containing oxadiazole for OLEDs are summarized in Table 1.6.

Figure 1.5 Chemical structures of PBD, NSD and some selected semiconducting polymers containing oxadiazole units used as electron transport materials.
Beside oxadiazole, another interesting electron deficient materials with similar thermal stable property is triazoles. Triazole derivatives have attracted considerable interest in OLEDs because of their electron transporting as well as hole blocking and exciton confining properties. Another typical electron transporting small molecule, 1-phenyl-3-(4-phenyl-[1,2,3]triazol-1-yl)-4-styryl-azetidin-2-one (TAZ), based on the 1,2,3-triazole had been designed by Aman Mahajan and coworker in 2010.[127] With the inter-band transition energies lie within 3.4-3.6 eV, the TAZ film has showed it could be employed as a hole blocking material in OLEDs due to its wide band-gaps (4.08-4.12 eV). Recently, many PLEDs based on semiconducting polymers containing the triazole moieties contained have been developed (Figure 1.6). The performances of the corresponding PLEDs are summarized and listed in Table 1.6.

![TAZ](image1.png)  ![TPAF](image2.png)  ![TPABTF](image3.png)

Figure 1.6 Chemical structures of TAZ and some selected semiconducting polymers containing triazole units used as electron transport materials.
1.3.5.2  Hole transport materials

In the PLED devices, charges are transported to the light emitting layer from the anodes by a hole transporting material which is either an electron-rich \(\pi\)-conjugated polymer or a triarylamine derivative due their relatively low ionization potentials. For the triarylamine derivatives, two famous hole transport dimers are \(\text{N,N'}\text{-bis(m-toly)}\text{-1,1'-biphenyl-4,4'-diamine (TPD)}\) and \(\text{N,N'}\text{-diphenyl-N,N'}\text{-bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine (NPB)}\).\(^{118,119,128,135}\) (Figure 1.3) Due to their reasonably high glass-transition temperatures (\(T_g\) of TPD = 65 °C and \(T_g\) of NPB = 95 °C), they have both been widely used in OLEDs as the hole transport materials.\(^{136}\) Besides the two small molecules, many main-chain \(^{135}\) and side-chain \(^{58,137-139}\) semiconducting polymers containing arylamine which exhibited high glass-transition temperatures have been designed and used in highly efficient multilayer devices with significant durability.\(^{136}\) (Figure 1.7) Table 1.6 lists the physical properties of the PLEDs with the usage of the main-chain and side-chain semiconducting polymer as the hole transport materials.
Main-chain semiconducting polymer

Side-chain semiconducting polymer

**Figure 1.7** Chemical structures of some main-chain and side-chain semiconducting polymers used as hole transport materials.
1.3.5.3 Electron/Hole injection materials

In the fabrication of PLEDs, the low hole injection efficiency could be attributed to the large energy level differences between the anode/hole-transport layer and/or the cathode/electron transport layer. Up until now, because of its great enhancement in terms of efficiency (from 16% to 22%),[103] brightness (from ~1000 cd/m² to ~2000 cd/m²),[103] lifetime (from 300 hrs to 2000 hrs) [130] and reduction of turn on voltage (from 22 V to 3 V),[103] PEDOT:PSS has been used as the most successful hole injection material for the PLED devices. The HOMO of PEDOT:PSS is -5.15 eV which is rather close to that of ITO anode (-4.8 eV), and therefore had been widely used to reduce the injection barrier problem on the anode side. Table 1.6 lists some PLED devices with PEDOT:PSS as the hole injection material. Besides PEDOT, some triarylamine contained polymers, such as PVK, also can be employed as the hole injection material.[131,132] With a triarylamine containing semiconducting polymer PMDA-DBABBD PI as the hole injection material, Y. Kim et al. [135] fabricated a very efficient PLED which exhibited a maximum performance of ~80,000 cd/m² and ~7 cd/A.

On the other end (cathode), in order to reduce the device turn-on voltage, low work function materials such as lithium fluoride (LiF),[129,140-142] cesium fluoride (CsF), calcium (Ca), are needed to be inserted between the metal cathode and the emissive layer for the purpose of improving the injection of electrons.[143-146] Besides of these small molecular electron injection materials, semiconducting polymers have also received interests in the development of polymer electron injection materials.[147,148] (see Figure 1.8) The related PLEDs based on polymer electron injection materials are listed in Table 1.6.
1.3.5.4 Light emitting materials

Besides the possibility of producing large area displays, semiconducting polymers offer several further unique advantages in comparison to their inorganic and small organic molecule counterparts.\textsuperscript{[118,119,121,122,149]} First of all, small molecules have the potential weaknesses such as low impact strength, stability, inter-diffusion of molecules, thermal induced re-crystallization and the requirement of vacuum evaporation for thin film formation.\textsuperscript{[123,135]} However, polymer thin films within the thickness range of 100 nm could be processed by using the low cost spin coating technique.\textsuperscript{[124]} Another advantage for polymer is its high dimensional strength which could be used to produced flexible displays or roll-up TV screens.\textsuperscript{[150]} At last, the emissive color can be tuned by simply adjusting the molecular structure of the monomers, modifying the functional
group on the monomers, or altering the ratio of the co-monomers, etc. Depending on the structures of the polymer chain, electroluminescent semiconducting polymers can be divided into two classes. They are the main-chain semiconducting polymers and the side-chain semiconducting polymers.

Since the first conductive polymer PPV used for PLED, many efforts have been devoted to the modification of the polymer and with great improvements. The most widely investigated π-conjugated light emitting polymers are poly(p-phenylenevinylene) (PPV), poly(p-phenylene) (PPP), polyfluorene (PF) derivatives and polythiophene (PT) derivatives. Though many attempts have been made to modify these main-chain semiconducting polymers, there are still several intrinsic disadvantages for the polymers. First of all, they are usually difficult to be synthesized and characterized because of their complex chemical structure which is the key for understanding and optimizing the PLED device performance. In many cases, the large scale application in PLEDs is restrained by the poor processability of the main-chain semiconducting polymers due to their poor solubility. The chemical structures of some selected main-chain semiconducting polymers are summarized below.
Figure 1.9 Chemical structures of selected main-chain semiconducting polymers used as light emitting materials.

Compared with the traditional π-conjugated main-chain polymers, side-chain semiconducting polymers have a lower volume percentage of the charge transport moieties yet they possess other advantages such as excellent mechanical strength, good rheological properties, solubility in common organic solvents and purer emission color (i.e. narrow emission peak width).\cite{58,59} Furthermore, the properties of vinyl polymers can be engineered easily by changing its composition or by choosing an appropriate addition polymerization method. In recent years, a large variety of fluorophores functional groups (e.g. pyrene\cite{139} and carbazole\cite{160}) have been attached as pendant groups in several side-chain semiconducting polymers (Figure 1.10). Furthermore, besides the light emitting moieties, some vinyl side-chain semiconducting copolymers also contains other functional groups, such as hole transporting triphenylamines\cite{138,160} and electron transporting/hole
blocking oxadiazoles. The performances of the corresponding PLEDs are summarized and listed in Table 1.6.

![Chemical structures of selected side-chain semiconducting polymers used as light emitting materials.](image)

**Figure 1.10** Chemical structures of selected side-chain semiconducting polymers used as light emitting materials.
Table 1.6 Physical properties of selected semiconducting polymers based PLEDs in recent years.

<table>
<thead>
<tr>
<th>No.</th>
<th>Cell configurations</th>
<th>Light intensity (cd/m²)</th>
<th>Turn on voltage (V)</th>
<th>Voltage at reported light intensity (V)</th>
<th>Current Density (mA/cm²)</th>
<th>External efficiency (% photon/e^-)</th>
<th>Current efficiency (cd/A)</th>
<th>Power efficiency (lm/W)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ITO/PEDOT:PSS/PTOA-PVK/Ca/Al</td>
<td>248</td>
<td>7</td>
<td>18</td>
<td>--</td>
<td>--</td>
<td>0.54</td>
<td>--</td>
<td>[161]</td>
</tr>
<tr>
<td>2</td>
<td>ITO/PEDOT:PSS/PDTOF/Al</td>
<td>--</td>
<td>5</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>[162]</td>
</tr>
<tr>
<td>3</td>
<td>ITO/PEDOT:PSS/SiHMOXD/Ca/Al</td>
<td>--</td>
<td>4.4</td>
<td>14</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>[163]</td>
</tr>
<tr>
<td>4</td>
<td>ITO/PEDOT:PSS/Ir(PPOHC)_3/TPBI/CsF/Al</td>
<td>6275</td>
<td>4.5</td>
<td>13</td>
<td>--</td>
<td>5.5</td>
<td>15.30</td>
<td>--</td>
<td>[164]</td>
</tr>
<tr>
<td>5</td>
<td>ITO/PEDOT:PSS/Cz-OXD-Ir/BCP/Alq₃/LiF/Al</td>
<td>394</td>
<td>9</td>
<td>21</td>
<td>--</td>
<td>--</td>
<td>1.00</td>
<td>--</td>
<td>[165]</td>
</tr>
<tr>
<td>6</td>
<td>ITO/PEDOT:PSS/TPABTF/Ca/Ag</td>
<td>172</td>
<td>8</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>2.60</td>
<td>--</td>
<td>[166]</td>
</tr>
</tbody>
</table>

PLED based on the electron transport (oxadiazole and triazole units contained) and hole injection (PEDOT:PSS) semiconducting polymers

<table>
<thead>
<tr>
<th>No.</th>
<th>Cell configurations</th>
<th>Light intensity (cd/m²)</th>
<th>Turn on voltage (V)</th>
<th>Voltage at reported light intensity (V)</th>
<th>Current Density (mA/cm²)</th>
<th>External efficiency (% photon/e^-)</th>
<th>Current efficiency (cd/A)</th>
<th>Power efficiency (lm/W)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>ITO/PMDA-DBABBD PI:NPB/Alq₃-QD-1/Alq₃/Li/Al</td>
<td>2000</td>
<td>3.6</td>
<td>20</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>[135]</td>
</tr>
<tr>
<td>8</td>
<td>ITO/P1/Alq₃/Mg</td>
<td>2300</td>
<td>--</td>
<td>10</td>
<td>53.4</td>
<td>0.61</td>
<td>--</td>
<td>--</td>
<td>[137]</td>
</tr>
<tr>
<td>9</td>
<td>ITO/P2/Alq₃/Mg</td>
<td>2900</td>
<td>--</td>
<td>10</td>
<td>39.7</td>
<td>1.09</td>
<td>--</td>
<td>--</td>
<td>[137]</td>
</tr>
<tr>
<td>10</td>
<td>ITO/P3/Alq₃/Mg</td>
<td>3700</td>
<td>--</td>
<td>10</td>
<td>28.7</td>
<td>1.25</td>
<td>--</td>
<td>--</td>
<td>[137]</td>
</tr>
<tr>
<td>11</td>
<td>ITO/P4/Alq₃/Mg</td>
<td>1800</td>
<td>--</td>
<td>10</td>
<td>27.4</td>
<td>1.22</td>
<td>--</td>
<td>--</td>
<td>[137]</td>
</tr>
<tr>
<td>12</td>
<td>ITO/P5/Alq₃/Mg</td>
<td>1000</td>
<td>--</td>
<td>10</td>
<td>15.4</td>
<td>1.00</td>
<td>--</td>
<td>--</td>
<td>[137]</td>
</tr>
<tr>
<td>13</td>
<td>ITO/P-HNPA/BCF/Alq₃/LiF/Al</td>
<td>170</td>
<td>4.8</td>
<td>--</td>
<td>90</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>[138]</td>
</tr>
<tr>
<td>14</td>
<td>ITO/P-MeONPA/BCF/Alq₃/LiF/Al</td>
<td>588</td>
<td>8.6</td>
<td>--</td>
<td>175</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>[138]</td>
</tr>
<tr>
<td>15</td>
<td>ITO/P-FNPA/BCF/Alq₃/LiF/Al</td>
<td>110</td>
<td>4.3</td>
<td>--</td>
<td>82</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>[138]</td>
</tr>
<tr>
<td>16</td>
<td>ITO/PEDOT:PSS/P(MeONPA)/Au</td>
<td>6608</td>
<td>8.5</td>
<td>20.8</td>
<td>474</td>
<td>--</td>
<td>3.52</td>
<td>--</td>
<td>[58]</td>
</tr>
<tr>
<td>17</td>
<td>ITO/PEDOT:PSS/P(MeONPA-co-OXA)/Au</td>
<td>23856</td>
<td>9.2</td>
<td>17.8</td>
<td>1075</td>
<td>--</td>
<td>4.2</td>
<td>--</td>
<td>[58]</td>
</tr>
<tr>
<td>18</td>
<td>ITO/PEDOT/poly(NPA-co-1py)/Ca/Al</td>
<td>1000</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.12</td>
<td>--</td>
<td>--</td>
<td>[139]</td>
</tr>
</tbody>
</table>

PLED based on the hole transport (triarylamine units contained) main-chain and side-chain semiconducting polymers
<table>
<thead>
<tr>
<th></th>
<th>ITO/PEDOT:PSS/MEH-PPV/WPXF/Ag</th>
<th>418</th>
<th>3.8</th>
<th>5.4</th>
<th>--</th>
<th>0.03</th>
<th>--</th>
<th>--</th>
<th>[147]</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>ITO/PEDOT:PSS/MEH-PPV/WPmXF/Ag</td>
<td>502</td>
<td>3.5</td>
<td>4.6</td>
<td>--</td>
<td>0.04</td>
<td>--</td>
<td>--</td>
<td>[147]</td>
</tr>
<tr>
<td>22</td>
<td>ITO/PEDOT:PSS/MEH-PPV/WPF-oxy-F/Ag</td>
<td>1768</td>
<td>3.1</td>
<td>5.8</td>
<td>--</td>
<td>0.4</td>
<td>--</td>
<td>--</td>
<td>[147]</td>
</tr>
<tr>
<td>23</td>
<td>ITO/PEDOT:PSS/MEH-PPV/PF-GOH/Al</td>
<td>8800</td>
<td>2.5</td>
<td>8.4</td>
<td>--</td>
<td>0.75</td>
<td>1.32</td>
<td>--</td>
<td>[148]</td>
</tr>
</tbody>
</table>

**PLED based on side-chain light emitting semiconducting polymers**

<table>
<thead>
<tr>
<th></th>
<th>ITO/PEDOT:PSS/SCzCz:Ir(ppy)3:t-PBD:TRZ/Mg/Ag</th>
<th>23400</th>
<th>7.6</th>
<th>--</th>
<th>--</th>
<th>12.3</th>
<th>2.6</th>
<th>[160]</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
<td>ITO/PEDOT:PSS/SCzCz:Ir(ppy)3:t-PBD/Mg/Ag</td>
<td>15800</td>
<td>7.2</td>
<td>--</td>
<td>--</td>
<td>17.5</td>
<td>3.8</td>
<td>[160]</td>
</tr>
<tr>
<td>30</td>
<td>ITO/PEDOT:PSS/SDBCz:Ir(ppy)3:t-PBD/Mg/Ag</td>
<td>16500</td>
<td>8.2</td>
<td>--</td>
<td>--</td>
<td>13.2</td>
<td>2.3</td>
<td>[160]</td>
</tr>
<tr>
<td>31</td>
<td>ITO/PEDOT:PSS/STPA:Ir(ppy)3:t-PBD/Mg/Ag</td>
<td>11000</td>
<td>6.3</td>
<td>--</td>
<td>--</td>
<td>10</td>
<td>2.7</td>
<td>[160]</td>
</tr>
<tr>
<td>33</td>
<td>ITO/PEDOT:PSS/PVK:t-PBD/Mg/Ag</td>
<td>6790</td>
<td>7.8</td>
<td>--</td>
<td>--</td>
<td>11.1</td>
<td>2.5</td>
<td>[160]</td>
</tr>
</tbody>
</table>
1.4 The polymerization of the side-chain conductive polymers

This thesis is focused on the synthesis of various small-molecule electroluminescence (EL) materials, EL vinyl monomers and their side-chain polymers. The usual polymerization methods for vinyl monomers are free radical polymerization, anionic/cationic polymerization, atom transfer radical polymerization (ATRP).

1.4.1 Free radical polymerization

Free radical polymerization has been used for the preparation of a wide variety of lab-size polymers, as well as a significant quantity for commercial applications. Free radical polymerization, until recently, has been the method of choice for the synthesis of many functional vinyl polymers because it tolerates many polar functional groups.[167-169] However, the disadvantages of free-radical polymerization are broad polydispersity, poor control over chain architecture, and end groups.[170] These problems are mainly due to the process is highly affected by termination or chain-transfer steps, which lead to deactivation or branching of the growing polymer. Therefore, to alleviate the effect of chain-transfer, toluene whose chain transfer constant is only 0.125 for styrene at 60 °C was used as the solvent for most of the vinyl polymer synthesis in this thesis.

In recent years, many series of polymers, such as P-HNPA, P-MeONPA, P-FNPA,[138] P(OXA),[58] P(PyPA),[171] PVPy,[171] PVK, P(ADN),[172] P(2ADN),[173] P(3ADQ),[173] etc., as well as their relevant copolymers, such as P(MeONPA-co-OXA-co-Pery), P(MeONPA-co-OXA),[58] poly(NPA-co-1py),[139] poly(4MeO1NPA-co-4VBSH), poly(4MeO1NPA-co-1py), poly(4MeOKPA-co-1py), poly(4MeO1NPA-co-AABE),[133] P(PyPA-co-VPy), P(ADN-co-VK),
P(ADN-co-S), etc., had been prepared via free radical polymerization in our group for application in PLEDs. The physical properties and chemical structures of these homopolymers and copolymers have been summarized and listed in Table 1.6 and Figure 1.10.

1.4.2 Cationic polymerization

Cationic polymerization is another chain growth polymerization in which a cationic initiator molecule transfers and binds to a monomeric unit. The activated units propagate with other monomeric units to form a polymer. The types of monomers necessary for cationic polymerization are quite limited including alkoxy-, phenyl-, vinyl-, and 1,1-dialkyl-substituted alkene vinyl monomers. Cationic polymerizations are sensitive to the types of solvents used. Specifically, a higher solvent polarity will give a higher cationic chain propagating velocity. The typical catalysts for cationic polymerization are usually strong $e^-$ acceptors, e.g. aprotic acids (Lewis acids & Friedel-Crafts halides), protonic (Brönsted) acids and carbenium-ions. Many of the catalysts, particularly the Lewis acids, required a co-catalyst such as a Lewis base or other proton donors.

In order to obtain high molecule weight homopolymer, cationic polymerization had been used for the preparations of P(PyPA), PVPy, PVK in works presented below. The general cationic polymerization of the vinyl monomers employed in this thesis was carried out in an evacuated dichloromethane solution containing the monomer, catalyst BF$_3$·Et$_2$O, and co-catalyst H$_2$O at 0 °C or 4 h. The polymer was further purified by re-dissolving in THF and re-precipitated in excess acetone to produce a yellow (P(PyPA)) or white (PVPy and PVK) solid.
1.4.3 Anionic polymerization

Anionic polymerization is also another chain-growth polymerization that involves the polymerization of vinyl monomers with strong electronegative groups.\textsuperscript{[176,177]} Anionic polymerizations have no formal termination pathways because protons transferred from solvent or other positive species does not occur. It therefore provides a chance to obtain polymer with very high molecular weight. Besides, when the monomers were exhausted in the reaction system, the carbanions at the end of the polymer chain would remain active and capable of adding another type of monomers. In this case, anionic polymerization could be used to prepare block or multi-block copolymers.

The solvent used in anionic addition polymerizations are determined by the reactivity of both the initiator and carbanion of the propagating chain end. The stability of the anionic propagating species is also dependent on the solvent as it is significantly reduced in polar solvents such as ethers due to the presence of the nucleophilic C-O bond of the ether. Less reactive chain ends, such as heterocyclic monomers, can use a wide range of solvents.\textsuperscript{[177]}

1.4.4 Atom transfer radical polymerization

Atom transfer radical polymerization (ATRP) is an example of living radical polymerization or a controlled radical polymerization. ATRP (or transition metal-mediated living radical polymerization) was independently discovered by Mitsuo Sawamoto\textsuperscript{[178]} and by Krzysztof Matyjaszewski and Jin-Shan Wang\textsuperscript{[179]} in 1995. A uniform polymer chain growth which leads to low polydispersity stems from the transition metal based catalyst. This catalyst allows an equilibrium exist between the active, and therefore propagating, polymer and an inactive form of
the polymer, known as the dormant form (Scheme 1.1). Since the dormant state of the propagating polymer is vastly preferred, side reactions are suppressed. This shift in the equilibrium also lowers the concentration of the propagating radicals and therefore suppressing unintentional termination with controlling molecular weight.

The polymerization system in ATRP contains monomer, initiator, catalyst and solvent. The classical initiators are alkyl halides, such as 1-(2-chloroethyl)benzene and 1-(chloromethyl)benzene. The catalysts are usually copper complexes produced from Cu(I)Br/Cu(I)Cl and ligand (e.g. 2,2’-bipyridine, N,N,N’,N”,N”-pentamethyl diethylenetriamine, etc.). An efficient ATRP catalyst consists of a transition metal species (Mt) which can expand its coordination sphere and increase its oxidation number, a complexing ligand, and a counterion which can form a covalent or ionic bond with the metal center. Figure 1.11 shows the typical ligands and initiators commonly used in ATRP.

The polymerization system in ATRP contains monomer, initiator, catalyst and solvent. The classical initiators are alkyl halides, such as 1-(2-chloroethyl)benzene and 1-(chloromethyl)benzene. The catalysts are usually copper complexes produced from Cu(I)Br/Cu(I)Cl and ligand (e.g. 2,2’-bipyridine, N,N,N’,N”,N”-pentamethyl diethylenetriamine, etc.). An efficient ATRP catalyst consists of a transition metal species (Mt) which can expand its coordination sphere and increase its oxidation number, a complexing ligand, and a counterion which can form a covalent or ionic bond with the metal center. Figure 1.11 shows the typical ligands and initiators commonly used in ATRP.
Ligands

- bipy
- PMDETA
- HMTETA
- Me₆-TREN
- PPh₃
- N-(alkyl)-2-pyridyl-methanimine

Initiators

- EBiB
- MBrP
- PEBr

Figure 1.11 Common ligands and initiators used in ATRP.

In recent years, ATRP had been used as a powerful tool to synthesize brush-like conducting polymers,[181-183] conducting segment end-caped polymers,[184] star-shaped conducting polymers[185] and block conducting polymers.[186,187] (Figure 1.12) By doping imidazole-H₃PO₄ complex to the brush-like copolymer P(VDF-co-CTFE)-g-PHEA, Y. W. Kim et al. [181] had prepared a comb-like conducting polymer. With the increase of the H₃PO₄ concentration, the conductivity of the copolymer P(VDF-co-CTFE)-g-PHEA/IDA/H₃PO₄ continuously increased and showed a maximum conductivity of 0.015 S/cm at 120 °C under anhydrous conditions. P.
Marcasuzaa et al.\textsuperscript{[184]} reported a tetra-aniline end-capped conducting polymers PS-TANI and its conductivity was in the range of 0.2~5 S/cm with 2\% to 7\% tetra-aniline contents. In 2009, Wen-Hsiang Chen and coworker\textsuperscript{[187]} reported an amphiphilic fluorescent CBABC- type pentablock copolymers containing pyrene group by a two-step ATRP. Fluorescence spectra of Py-PMMA-PEG4600-PMMA-Py exhibited strong excimer emission at 480 nm due to the aggregation of pyrene groups via interaction of the hydrophobic chains.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure1.12.png}
\caption{Some selected semiconducting polymers synthesized by ATRP.}
\end{figure}
1.5 Scope of the thesis

1.5.1 Blue luminescent side-chain semiconducting polymers for potential application electroluminescence

Since the first polymer-based PLED was introduced by Friends et al., PLED had attracted much attention to be the next-generation display. This is attributed to its low driving voltage, tuneable emission color, wide viewing angle, good film-forming capabilities. Additional advantage is the feasibility of using solution processing such as the roll-to-roll process, spin coating process, and inkjet printing process.

Deep blue color is defined as having an electroluminescent emission with a Commission Internationale d’Eclairage (CIE$_{x,y}$) coordinates at $x \sim 0.15$ and $y < 0.15$. For the realization of a full color displays, red, green and blue light-emitting polymers with high efficiency and good brightness are required. However, in comparison with red and green light-emitting polymers, only a limited blue light-emitting polymers shown a potential for the full color display application. It is therefore crucial to search for a stable and yet efficient blue light-emitting polymer.

In the present thesis, a series of bluish or greenish-blue side-chain homopolymers $P$(PyPA), $P$VPy, $PVK$, $P$(ADN), $P$(2ADN), $P$(3ADQ) as well as their random copolymers $P$(PyPA-co-VPy), $P$(ADN-co-VK), $P$(ADN-co-S) had been successfully prepared via free radical solution polymerization, cationic/anionic and ATRP process.
1.5.2 Block copolymers with potential applications in biophysics and biochemistry

Due to problems such as poor solubility, high potency, and low stability for many kinds of drugs, the process of drug loading and delivery has been a tremendous challenge.\textsuperscript{[203]} One of the efficient methods to deal with these problems is to fabricate the core/shell type micelle drug carriers. The carriers are usually formed by amphiphilic block copolymer. BAB block copolymers with the hydrophobic B segments and the hydrophilic A segment in the copolymer chain usually exhibit more complex micelle structures than those of the traditional ABA block copolymers in aqueous medium. At low concentration and in a good solvent for A, the B segments usually have a strong tendency to aggregate and generate the core of the micelle while the external corona will be covered by loops of A segments.\textsuperscript{[204-208]}

Therefore, in the present thesis, the preparation of two well-defined fluorescent block copolymers ADN-PEG3400-ADN and Py-PEG3400-Py using ATRP was presented. Due to the fluorescent properties of the segments ADN and Py segments, the copolymers may also be applied to the biophysics and biochemistry field as a fluorescent marker.

1.6 References


112.


[63] M. Bratcher, M. Declue, A. Grunnetjepsen, D. Wright, B. Smith, W.


14: 143.


[106] Andreas Puetz, Florian Steiner, Jan Mescher, Manuel Reinhard, Nico


[117] Ji-Hoon Kim, Hee Un Kim, Won Suk Shin, Sang-Jin Moon, Sung Cheol


Chapter 2

Synthesis and Characterization of High Bandgap Blue
Light Emitting Poly(9,10-di(1-naphthalenyl)-2-vinyl
anthracene)

2.1 Introduction

Since the first PLED was introduced by Friends et al.,[1] PLED had attracted much attention as the next-generation material for the display industry attributed to their low driving voltage, tune-able emission color, wide viewing angle, good film-forming capabilities.[1-5] Additional advantage is the feasibility of using solution processing such as the roll-to-roll process,[6] spin coating process,[7] and inkjet printing process.[8] For the realization of a full color displays, red, green and blue light-emitting polymers with high efficiency and good brightness are required.[9-11] However, in comparison with red [12,13] and green [14-16] light-emitting polymers, only a limited blue light-emitting polymers shown a potential for the full color display application.[17,18] It is therefore crucial to search for a stable and yet efficient blue light-emitting polymer.

Deep blue color is defined as having an electroluminescent emission with a Commission Internationale d’Eclairage (CIE_x,y) coordinates at x ~ 0.15 and y < 0.15.[19] In the past decade, considerable interests have been concentrated in developing a large bandgap blue light-emitting polymer mostly main-chain conjugated polymers such as poly(p-phenylene) (PPP),[20] poly(phenylenevinylene) (PPV),[21,22] polyfluorene (PF),[23,24] and poly(4H-cyclopenta[def]phenathrene)
(PCPP),\textsuperscript{[4]} etc. Compared with the traditional π-conjugated main-chain polymers, vinyl conductive polymers have a lower volume percentage of the charge transport moiety yet they possess advantages such as excellent mechanical strength, good rheological properties, solubility in common organic solvents and purer emission color (i.e. narrow emission peak width).\textsuperscript{[25,26]} Furthermore, the properties of vinyl polymers can be engineered easily by changing its composition or choosing an appropriate additional polymerization method.

There have been a large number of reports on the development of small molecule blue light-emitting materials.\textsuperscript{[27-30]} One of such blue emitters is a derivative of 9,10-anthracene, 9,10-di(2-naphthalenyl)anthracene (\(\beta,\beta\)-ADN) and have been studied extensively due to its excellent luminescence property and thermal stability either as the host\textsuperscript{[31-33]} or the dopant material.\textsuperscript{[34]} Moreover, the \(\beta,\beta\)-ADN shown almost the same hole and electron mobilities, which indicated that \(\beta,\beta\)-ADN is ambipolar.\textsuperscript{[35]} With \(\beta,\beta\)-ADN used as the host and 2, 5, 8, 11-tetra(t-butyl)-perylene as the dopant, the EL device produced a deep blue emission of CIE\textsubscript{x,y} (0.154, 0.232) and an EL efficiency around 3.5 cd/A with a half-life 4,000 hrs at an initial light output of 700 cd/m\textsuperscript{2}.\textsuperscript{[36]} However, when the \(\beta,\beta\)-ADN thin film was exposed under a prolonged electrical stress or high annealing temperature, it was morphologically unstable and tends to re-crystallize.\textsuperscript{[37]} This morphological change accelerated the decay and eventually reduced the lifetime of the device.\textsuperscript{[38]} Subsequently, additional methyl group was attached at the C-2 position of the anthracene moiety producing another derivative, 2-methyl-9,10-di(2-naphthalenyl)anthracene (\(\beta,\beta\)-MADN). The new \(\beta,\beta\)-MADN was shown to have improved morphological stability although with a lower luminance efficiency of 2.2 cd/A at 20 mA/cm\textsuperscript{2} and a saturated blue CIE\textsubscript{x,y} (0.15,
0.12) compared to that of β,β-ADN. As a wide bandgap host material for a doped deep blue OLED, 2-methyl-9,10-di(1-naphthalenyl)anthracene (MADN), was found to enhance the probability of carrier recombination near the interface of the hole transporting/emitting layers and maintaining charge balance in the emitting layer. The results were a much higher luminance efficiency of 3.3 cd/A and 1.3 lm/W with a deep blue CIEx,y (0.15, 0.13).[19]

However, the inherent mechanical weaknesses for small molecule materials, the problematic re-crystallization phenomenon under high thermal stress and the requirements of higher cost vacuum thin film deposition still persisted for the well designed β,β-MADN or MADN targeted for OLED applications.[40-45] Some of the inherent problems suggested above can be eliminated when the functional small molecules were covalently attached to a vinyl monomer and polymerizing into homopolymer or copolymer.

In the present chapter, a novel blue fluorescent monomer Vinyl-ADN based from the small molecule α,α-ADN was synthesized and its polymers P(ADN) were polymerized using solution free radical and anionic polymerization. The chemical structure and physical properties of the intermediates, the monomer Vinyl-ADN and the polymer P(ADN) were characterized using NMR, GPC, FT-IR, TGA, DSC, MALDI-TOF MS, UV-Vis, PL, CV and quantum yield measurements.

### 2.2 Experimental

#### 2.2.1 Materials and instruments

All solvents were analytical grade purified by distillation and stored under appropriate drying agents and/or inert nitrogen atmosphere prior to use. Unless
specified otherwise, all reagents were purchased from commercial sources and used without further purification. Benzoyl peroxide (BPO) and 2,2’-azobisisobutyronitrile (AIBN) were recrystallized in a chloroform/methanol mixed solvent before used.

The $^1$H and $^{13}$C NMR spectra were recorded on a Bruker-AF301 AT 400 MHz spectrometer using deuterated solvents (CDCl₃ or dimethyl sulfoxide-d (DMSO-d)) and with tetramethylsilane as the internal standard. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra measurements were carried out using an Autoflex Bruker MALDI-TOF mass spectrometer. Solid-state infrared spectra (KBr pellet) were recorded on a Nicolet Magna 550 Series II FTIR spectrometer. UV-Vis absorption spectra were obtained with a Varian Cary 200 spectrophotometer in a 10 ppm THF solution. Photoluminescence was measured on a Perkin Elmer LS55 Luminescence Spectrometer also in a 5 ppm THF solution. The fluorescence quantum efficiencies of the monomer and the polymers in THF were determined at room temperature against quinine sulfate (0.1 M H₂SO₄) standard ($\lambda = 313$ nm, $\Phi_F = 0.48$; $\lambda = 334$ nm, $\Phi_F = 0.56$). Cyclic voltammetry measurements were performed on a BAS CV-50W electrochemical analyzer at room temperature with a conventional three-electrode configuration (a platinum working electrode, an auxiliary electrode and an Ag/AgCl reference electrode). The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate ([Bu₄N]PF₆) dissolved in ACN. The measurement was calibrated with an internal standard, ferrocene/ferrocenium (Fc/Fc⁺) redox couple (taken HOMO of Fc/Fc⁺ = -4.8 eV). The molecular weight and polydispersity of the homopolymers were measured by gel permeation chromatography (GPC) on a HP 1050 series HPLC with a visible
wavelength and fluorescent detectors with THF as the mobile phase (HPLC column: Jordi Gel GBR Mixed Bed, 300 mm × 7.8 mm). The GPC results were calibrated against polystyrene standards with molecular weight at 1,350 (PDI = 1.03), 28,000 (PDI = 1.01), 87,000 (PDI = 1.02) and 410,000 (PDI = 1.03). Thermal analyses were performed under nitrogen purge on a Perkin-Elmer Pyris Diamond DSC and Perkin-Elmer TGA6 thermal analyzers at a heating rate of 40 °C/min (DSC) and 20 °C/min (TGA), respectively.

2.2.2 Synthesis

2.2.2.1 2-Methyl-1,4,4a,9a-tetrahydroanthracene-9,10-dione (Nad)

Nad was synthesized by the Diels-Alder reaction. 1,4-Naphthaquinone (10.00 g, 63.20 mmol) and isoprene (12.90 g, 189.60 mmol) were dissolved in 150 mL methanol. The reaction solution was heated to reflux and stirred overnight under open atmosphere. Most of the solvents were evaporated under reduced pressure and the residue was filtered to obtain a white solid (95% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) 8.06-8.02 (m, 2H), 7.77-7.73 (m, 2H), 5.44-5.41 (m, 1H), 3.44-3.32 (m, 2H), 2.54-2.42 (m, 2H), 2.26-2.15 (m, 2H), 1.69 (d, J = 0.56 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ (ppm) 193.26, 192.96, 129.02, 128.80, 128.75, 126.60, 121.61, 121.58, 113.30, 41.85, 41.19, 23.72, 19.59, 18.22. MS (MALDI-TOF) m/z = 222.1077 (M+H).

2.2.2.2 2-Methyl-9,10-anthracenequinone (MAq)

To a 250 mL two-mouth round bottom flask, the compound Nad (5.00 g, 22.10 mmol) and KOH (4.00 g, 100.00 mmol) were dissolved in 100 mL methanol. Compress air was introduced to oxidize the Nad. The solution was heated to 45 °C and stirred overnight. After filtration and washed by methanol to
obtained a yellowish solid (98% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 8.32-8.28 (m, 2H), 8.21 (d, $J = 7.92$ Hz, 1H), 8.11 (d, $J = 0.44$ Hz, 1H), 7.82-7.77 (m, 2H), 7.60 (dd, $J_1 = 1.04$ Hz, $J_2 = 7.96$ Hz, 1H), 2.54 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 183.37, 182.94, 145.27, 134.92, 134.03, 133.91, 133.54, 133.51, 133.33, 131.23, 127.47, 127.41, 127.13, 127.11, 21.91. MS (MALDI-TOF) $m/z$ = 222.0644 (M+).

2.2.2.3 2-Methylanthracene (MA)

To a 250 mL round bottom flask, MAq (4.00 g, 18.00 mmol), zinc powder (3.50 g, 72.00 mmol), cupric sulfate pentahydrate (0.10 g) and ammonia solution (200.00 g) were mixed. The mixture was heated to 85 °C. The mixture turned from red to colorless slowly. After filtration, the residue was washed by acetone. The acetone was then evaporated and methanol was added, a white solid was precipitated after addition of 1 mL conc. 37 wt% HCl (87% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 8.37 (s, 1H), 8.31 (s, 1H), 7.99-7.96 (m, 2H), 7.91 (d, $J = 8.68$ Hz, 1H), 7.75 (s, 1H), 7.45-7.40 (m, 2H), 7.31 (dd, $J_1 = 1.60$ Hz, $J_2 = 8.68$ Hz, 1H), 2.55 (d, $J = 0.40$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 134.88, 131.95, 131.80, 131.18, 130.29, 128.22, 128.15, 128.03, 127.93, 126.29, 125.91, 125.20, 125.13, 124.88, 21.98. MS (MALDI-TOF) $m/z$ = 193.1024 (M+).

2.2.2.4 9,10-Dibromo-2-methylanthracene (MADBr)

To a 250 mL round bottom flask, the compound MA (1.00 g, 5.20 mmol), n-bromosuccinimide (NBS) (2.23 g, 12.00 mmol) and 200 μL TFA was dissolved in 20 mL chloroform. The solution was stirred overnight at room temperature. Afterward, most of chloroform was evaporated, then methanol was added, yellowish needle-like crystals were obtained (90% yield). $^1$H NMR (400 MHz,
CDCl$_3$: $\delta$ (ppm) 8.58-8.54 (m, 2H), 8.48 (d, $J = 9.22$ Hz, 1H), 8.34 (s, 1H), 7.64-7.58 (m, 2H), 7.46 (dd, $J_1 = 1.52$ Hz, $J_2 = 8.96$ Hz, 1H), 2.63 (d, $J = 0.72$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 137.39, 131.04, 130.99, 130.40, 130.11, 129.61, 128.17, 128.07, 128.03, 127.22, 126.89, 126.34, 123.32, 122.34, 22.04. MS (MALDI-TOF) $m/z = 349.9127$ (M+).

2.2.2.5 2-Methyl-9,10-di(1-naphthalenyl)anthracene (MADN)

MADN was synthesized by the Suzuki Coupling reaction. A two-necked flask containing the compound MADBr (2.00 g, 5.69 mmol), 1-naphthaleneboronic acid (3.90 g, 22.70 mmol), tetrakis(triphenylphosphine) palladium(0) (325 mg, 28.50 mmol), and 2 M K$_2$CO$_3$ (3 mL) and THF (50 mL) equipped with a magnetic stirrer and a reflux condenser was heated to 70 °C overnight under N$_2$ purge. The reaction mixture was then poured into water and then extracted with DCM. The combined organic layer was dried with anhydrous Na$_2$SO$_4$ and evaporated to driness. The crude product was purified by silica-gel column chromatography using hexane as eluent affording the title compound as a pale yellow solid (80% yield). $^1$H NMR (400 MHz, DMSO-d): $\delta$ (ppm) 8.20 (d, $J = 8.20$ Hz, 2H), 8.14 (d, $J = 7.80$ Hz, 2H), 7.84-7.79 (m, 2H), 7.69-7.62 (m, 2H), 7.59-7.53 (m, 2H), 7.36-7.24 (m, 7H), 7.16-6.96 (m, 4H), 2.19 (s, 3H). MS (MALDI-TOF) $m/z = 445.1961$ (M+).

2.2.2.6 2-(Bromomethyl)-9,10-di(1-naphthalenyl)anthracene (ADN-CH$_2$Br)

To a 250 mL round bottom flask, MADN (1.10 g, 2.48 mmol) and NBS (0.48 g, 2.70 mmol), BPO (18 mg, 0.074 mmol) was dissolved in 50 mL benzene. The mixture was refluxed under N$_2$ purge overnight. Methanol was added, filtered, a pale yellow product was obtained (90% yield). $^1$H NMR (400 MHz, DMSO-d):
δ (ppm) 8.13-8.04 (m, 4H), 7.75-7.71 (m, 2H), 7.67-7.41 (m, 8H), 7.35-7.29 (m, 2H), 7.26-7.18 (m, 2H), 7.15-7.00 (m, 2H), 4.40 (s, 2H).

2.2.2.7 9,10-Di(1-naphthalenyl)anthracene-2-carbaldehyde (ADN-CHO)

To a 250 mL round bottom flask, 2-nitropropane (2.10 g, 23.60 mmol), KOH (1.32 g, 23.57 mmol), were added to methanol (20 mL). The mixture was stirred until it became a clear solution. ADN-CHO (1.00 g, 1.90 mmol) dissolved in 40 mL DMSO was added into the methanol solution above. The solution was stirred overnight at room temperature. Water was added to precipitate the crude product. The crude product was purified by silica-gel column chromatography using hexane\:chloroform (4:1) as eluent. A yellow solid product was obtained (80% yield). 1H NMR (400 MHz, DMSO-d): δ (ppm) 9.79 (s, 1H), 8.27-8.15 (m, 4H), 8.02 (s, 1H), 7.86-7.57 (m, 7H), 7.48-7.29 (m, 7H), 7.15-6.98 (m, 2H). MS (MALDI-TOF) m/z = 458.1695 (M+).

2.2.2.8 9,10-Di(1-naphthalenyl)-2-vinylanthracene (Vinyl-ADN)

Vinyl-ADN was synthesized by the Witting reaction. To a 250 mL round bottom flask, methyltriphénylphosphonium bromide (0.93 g, 2.60 mmol) was dissolved in 20 mL freshly distilled THF. Potassium t-butyl oxide (0.29 g, 2.60 mmol) was added and stirred for 30 mins in an ice bath. A yellowish solution was resulted. ADN-CHO (0.60 g, 1.30 mmol) dissolved in THF was added to the ylide/t-butyl oxide solution under continuous stirring. The mixture was stirred at room temperature until the reaction was completed as indicated by TLC. Hexane was then added and then filtered. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography using hexane as the eluent. A yellow solid was obtained with 90% yield. 1H NMR (400 MHz,
DMSO-d): δ (ppm) 8.21 (d, J = 8.20 Hz, 2H), 8.15 (d, J = 8.28 Hz, 2H), 7.83-7.81 (m, 2H), 7.72-7.64 (m, 2H), 7.58-7.56 (m, 3H), 7.37-7.27 (m, 7H), 7.20 (s, 1H), 7.13-6.99 (m, 2H), 6.58 (dd, J₁ = 17.44 Hz, J₂ = 10.96 Hz, 1H), 5.69 (d, J = 17.48 Hz, 1H), 5.17 (d, J = 10.84 Hz, 1H). MS (MALDI-TOF) m/z = 457.1954 (M+H).

2.2.2.9 Homopolymer synthesis

2.2.2.9.1 Free radical polymerization

To a single-mouth Schlenk reaction tube charged with a stirrer bar, 100 mg Vinyl-ADN and a free radical initiator (either AIBN or di-tert-butyl peroxide (DTBP)), was dissolved in pre-calculated dried toluene. The reaction mixture was degassed by freeze-pump-thaw cycles and then sealed off in nitrogen atmosphere. The reaction mixture was stirred at the reaction temperature for 10 h. Finally, a viscous yellowish polymer solution was resulted. The detailed compositions of initiator, solvent and reaction temperature were listed in Table 2.1. The polymer was further purified by re-dissolving in THF and re-precipitated in excess acetone to produce the resulting homopolymer F-P(ADN).

2.2.2.9.2 Anionic polymerization

400 mg Vinyl-ADN was added into a 25 mL two-mouth round bottom flask. Then, the flask was first purged by dried nitrogen. After that, 10 mL dried THF was injected into the flask with a stirrer bar. The reaction system was cooled to -78 °C (acetone/dry ice mixture). Then, 1 to 6 mol% (3.6 to 21.5 μL) n-butyl lithium (2.45 M, titrated by 2-butyralcohol with 2,2’-dipyridyl as the indicator in p-xylene) was injected into the system with the solution color turned deep red immediately. After 3 hrs reaction time, a small amount of purified methanol was injected to terminate the reaction and the solution turned light yellowish instantly.
The temperature of the reaction system was raised slowly to room temperature. Finally, a viscous yellowish polymer solution was resulted. The polymer was further purified by re-dissolving in THF and re-precipitated in excess acetone to produce the resulted homopolymer A-P(ADN).

2.3 Results and discussion

2.3.1 Synthesis of monomer and polymers

The synthesis pathway for the monomer Vinyl-ADN and its polymers is shown in Scheme 2.1. Details on the reaction procedures and their characterization have been given in the Synthesis section.
1,4-naphthaquinone (Nq)

2-methyl-1,4,4a,9a-tetrahydroanthracene-9,10-dione (Nad)

2-methyl-9,10-anthracenequinone (MAq)

2-methylanthracene (MA)

9,10-dibromo-2-methylanthracene (MADBr)

2-methyl-9,10-di(1-naphthalenyl)anthracene (MADN)

2-(bromomethyl)-9,10-di(1-naphthalenyl)anthracene (ADN-CH$_2$Br)

9,10-di(1-naphthalenyl)anthracene-2-carbaldehyde (ADN-CHO)

9,10-di(1-naphthalenyl)-2-vinylanthracene (Vinyl-ADN)
Scheme 2.1  Synthetic routes for the monomer Vinyl-ADN and its polymers.

2.3.1.1  Solution free radical addition polymerization

A series of P(ADN)) (F1-F7) were obtained by solution free radical addition polymerization under various reaction conditions for 10 hrs. The resulting yield and relative MW measurements under different reaction conditions are presented in Table 2.1. Polymers with MW as high as 17,600 (M_n) have been obtained. Two initiators were attempted and in general AIBN provided better yield and higher MW products. The reaction is also favored at lower reaction temperature (65 °C) and lower solvent contents (higher monomer concentrations). The solubility of the polymers, however, reduced at high MW. The solubility was compared by dissolving 1 mg of polymer in 10 mL of a solvent at room temperature in a supersonic bath for 20 mins. Highest molecular weight product F1 (M_n = 17,600) could only be dissolved completely in TCE, it is partially dissolved in solvents like THF, DCM, chloroform and toluene, and totally insoluble in methanol, ethanol and acetone. The degree of polymerization (or kinetic chain length) increased in proportion with the monomer concentrations (or low solvent contents) as predicted when the monomer involved in a chain transfer process.\textsuperscript{[47]} It is suggested delocalization at the homocyclic aromatic pendant ADN moieties can stabilized the radical species. As a result, the polydispersity index (PDI) is rather...
high (from 1.21 to 2.89) and increased with the monomer concentration.

### Table 2.1 P(ADN) synthesized by solution free radical addition polymerization under various conditions. a)

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Initiator  (mol %) b)</th>
<th>Temperature  (°C)</th>
<th>Toluene  (μL)</th>
<th>Yield  (%)</th>
<th>Soluble in THF  (wt%)</th>
<th>MW of dissolved homopolymer c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1 d)</td>
<td>AIBN, 2.0</td>
<td>65</td>
<td>400</td>
<td>98</td>
<td>30</td>
<td>17,600 50,900 2.89</td>
</tr>
<tr>
<td>F2</td>
<td>AIBN, 3.0</td>
<td>65</td>
<td>400</td>
<td>95</td>
<td>65</td>
<td>15,400 43,000 2.80</td>
</tr>
<tr>
<td>F3</td>
<td>AIBN, 3.0</td>
<td>65</td>
<td>600</td>
<td>93</td>
<td>94.5</td>
<td>13,400 36,800 2.75</td>
</tr>
<tr>
<td>F4</td>
<td>AIBN, 3.0</td>
<td>65</td>
<td>800</td>
<td>95</td>
<td>100</td>
<td>10,100 20,800 2.07</td>
</tr>
<tr>
<td>F5</td>
<td>AIBN, 3.0</td>
<td>65</td>
<td>1000</td>
<td>72</td>
<td>100</td>
<td>8,100 15,800 1.94</td>
</tr>
<tr>
<td>F6</td>
<td>AIBN, 3.0</td>
<td>85</td>
<td>800</td>
<td>70</td>
<td>100</td>
<td>6,000 9,600 1.60</td>
</tr>
<tr>
<td>F7</td>
<td>DTBP, 3.0</td>
<td>105</td>
<td>800</td>
<td>70</td>
<td>100</td>
<td>2,800 3,400 1.21</td>
</tr>
</tbody>
</table>

a) 100 mg of monomer was used for all reactions.
b) The initiator concentration unit “mol %” meant the mole ratio of the initiator to the monomer Vinyl-ADN was 2.0% (F1) or 3.0% (F2-F7).
c) The weight-averaged (M_w) and number-averaged (M_n) molecular weights were determined by GPC using poly(styrene) MW standards. Conditions: wavelength 254 nm (UV-Vis detector), flow rate 1 mL/min, mobile phase THF.
d) Only the THF soluble portion of the polymer F1 was used for the determination of the MW.

### 2.3.1.2 Anionic polymerization

Table 2.2 showed the results (A1-A4) of anionic polymerization for Vinyl-ADN at four different concentrations of the initiator n-butyl lithium. As expected, the MW of the polymers prepared by anionic polymerization decreased in proportion with an increase in the initiator concentration. The PDI (1.25 to 1.37) is also much lower than products obtained from free radical addition polymerization. The highest MW product A1 (M_n = 15,300) shown an improved
solubility compared to free radical polymerized products and is completely dissolved in THF probably due to its stereoregularity.

Table 2.2 P(ADN) polymerized by anionic polymerization under various conditions. a)

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Butyl lithium (mol%) b)</th>
<th>Temperature (°C)</th>
<th>THF (mL)</th>
<th>Yield (%)</th>
<th>Dissolved in THF (%)</th>
<th>M_n c)</th>
<th>M_w</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>1.0</td>
<td>-78</td>
<td>10</td>
<td>85</td>
<td>100</td>
<td>15,300</td>
<td>21,000</td>
<td>1.37</td>
</tr>
<tr>
<td>A2</td>
<td>2.0</td>
<td>-78</td>
<td>10</td>
<td>85</td>
<td>100</td>
<td>8,600</td>
<td>11,500</td>
<td>1.34</td>
</tr>
<tr>
<td>A3</td>
<td>4.0</td>
<td>-78</td>
<td>10</td>
<td>85</td>
<td>100</td>
<td>4,300</td>
<td>5,700</td>
<td>1.33</td>
</tr>
<tr>
<td>A4</td>
<td>6.0</td>
<td>-78</td>
<td>10</td>
<td>85</td>
<td>100</td>
<td>1,600</td>
<td>2,000</td>
<td>1.25</td>
</tr>
</tbody>
</table>

a) 400 mg of monomer was used for all reactions.

b) The initiator concentration unit “mol%” meant the mole ratios of the initiator to the monomer Vinyl-ADN were 1.0% (A1), 2.0% (A2), 4.0% (A3) and 6.0% (A4).

c) The weight-averaged (M_w) and number-averaged (M_n) molecular weights were determined by GPC using poly(styrene) MW standards. Conditions: wavelength 254 nm (UV-Vis detector), flow rate 1 mL/min, mobile phase THF.

2.3.2 Spectroscopic analysis of the monomer and polymers

![Figure 2.1 ¹H NMR (DMSO-d) of Vinyl-ADN.](image)
Figure 2.2  $^1$H NMR (CDCl$_3$) of P(ADN) for F4, A1, A3, F7 and Vinyl-ADN.

The $^1$H-NMR spectrum of Vinyl-ADN is given in Figure 2.1. After polymerization, the olefinic protons of Vinyl-ADN located at 5.17, 5.67 and 6.58 ppm disappeared and the mainchain aliphatic protons of P(ADN) were observed between 0.50-1.00 ppm (see Figure 2.2). The sharp peaks for the Vinyl-ADN aromatic protons between 7.00-8.00 ppm changed to a series of broad peaks between 6.00-8.50 ppm for the polymers. Furthermore, the broadness of the aromatic peaks increased with the MW of the polymers (see Figure 2.2) while there is no significant distinction between the NMR spectra for the anionic and free radical polymerized products.

Solid-state FT-IR measurements were also performed for the confirmation of the chemical structures. Their spectra were compared with the vinyl monomer
Vinyl-ADN and a model compound MADN and are shown in Figure 2.3. The FT-IR spectra for P(ADN)-F1, A1, F4 & A3, Vinyl-ADN and MADN have the following similar structural attributes: 3,055-3,057 cm\(^{-1}\) (\(\nu\), aromatic C-H stretching), 2,919-2,925 cm\(^{-1}\) (\(\nu\), sp\(^3\) C-H stretching), 1,625-1,254 cm\(^{-1}\) (\(\nu\), aromatic C=C stretching; \(\delta\), sp\(^3\) C-H deformation), 904 and 887 cm\(^{-1}\) (\(\delta\), =C-H out of plane deformation) and 798-757 cm\(^{-1}\) (\(\delta\), C-H out of plane deformation). As expected, the polymers also shown relative dominant absorption due to sp\(^3\) C-H stretching compared to sp\(^2\) aromatic C-H stretching due to the additional aliphatic backbone structures. The FT-IR spectra do not show any significant differences between the free radical and anionic polymerized products.

![Figure 2.3](image-url)
2.3.3 Thermal properties

The thermal properties for some of the polymers were investigated both by thermogravimetric analysis (TGA) under nitrogen purge at a heating rate: 20 °C/min, (see Figure 2.4), and differential scanning calorimetry (DSC), under nitrogen purge at a heating rate: 40 °C/min (see Figure 2.5) and the results are summarized in Table 2.3. All the polymers possessed similar $T_d$ around 396 °C irrespective of their MW and polymerization methods. The polymers, however, has higher $T_d$ than that of the small molecule MADN ($T_d = 363$ °C). The glass transition temperatures ($T_g$ mid-point) was found to between 228 to 237 °C and increased slightly with their MW. The broadness of the transition temperature range is also smaller for the anionic prepared products compared to free radical prepared products with high polydispersity. No melting or recrystallization for the polymers was observed upon repeated heating (up to 300 °C) and cooling indicated the polymers are completely amorphous.

![Figure 2.4 TGA thermograms for P(ADN)-F1, F4, A1, A3 and MADN under nitrogen purge at a heating rate of 20 °C/min.](image)

68
Figure 2.5  DSC thermograms for P(ADN)-F1, F4, A1, A3 under nitrogen purge at a scanning rate of 40 °C/min.

Table 2.3  Thermal properties of the polymers P(ADN)-F1, F4, A1 and A3.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Onset $T_d$ (°C) a)</th>
<th>Weight lost (%)</th>
<th>Midpoint $T_g$ (°C) b)</th>
<th>$\Delta C_p$ (J/g·°C) c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(ADN) F1</td>
<td>396</td>
<td>47.60</td>
<td>237</td>
<td>0.23</td>
</tr>
<tr>
<td>P(ADN) F4</td>
<td>396</td>
<td>66.97</td>
<td>235</td>
<td>0.22</td>
</tr>
<tr>
<td>P(ADN) A1</td>
<td>396</td>
<td>42.75</td>
<td>236</td>
<td>0.22</td>
</tr>
<tr>
<td>P(ADN) A3</td>
<td>395</td>
<td>67.69</td>
<td>228</td>
<td>0.22</td>
</tr>
</tbody>
</table>

a) About 5 mg samples were used for TGA under nitrogen purge at a heating rate: 20 °C/min.
b) About 20 mg samples were used for DSC under nitrogen purge at a heating rate: 40 °C/min.
c) The difference in specific heat capacity ($\Delta C_p$ J/g·°C) at the glass transition.

2.3.4  Optical characteristics of the monomer and polymers

The solution ultraviolet-visible (UV-Vis) absorption and photoluminescent (PL) spectra for the monomer Vinyl-ADN, polymers P(ADN)-F1, A1, F4, A4 and
the model compound MADN in THF are shown in Figure 2.6. Summary of the results are given in Table 2.4. Four prominent bands for MADN was observed at 340, 357, 376 and 396 nm, due to the $\pi \rightarrow \pi^*$ transition. A gradually red-shift of 4-9 nm for the absorption peaks same absorption bands were found for Vinyl-ADN and P(ADN)-F1, A1, F4, A3. The emission maxima of the small molecule MADN in solution were found at 409 and 429.5 nm, while Vinyl-ADN only showed a single broad emission at 428 nm with a slightly higher full-width-at-half-maximum (FWHM). All the polymer P(ADN)s showed similar emission characteristic maxima compared to MADN with 8-15 nm in red-shift. The red-shift is probably a result of short-range $\pi$-$\pi$ stacking interaction between adjacent ADN moieties.[48]

**Vinyl-ADN** have similar extinction coefficient compared to MADN. The extinction coefficient of the polymers P(ADN)-F1, A1, F4 and A3, however, decreased to only 63%, 53%, 50% and 33% to that of MADN, respectively. The trends could be attributed to excitons and dispersion-force interaction in the polymers with an orderly structure.[49-51] The dependence of the extinction coefficients with the MW of the polymers may be a result of easier in formation of the excimers for polymers with lower molecular weight polymers.[52] Both the UV-Vis and PL spectra for anionic and free radical prepared products do not show exceptional differences, while the anionic products showing a light decrease in FWHM. The PL spectra for P(ADN)-F1 were also investigated using different solvents (toluene, chloroform, TCE and THF), however, no obvious differences were observed indicating the non-polar nature of the ADN units.

The solid-state UV-Vis absorption and PL spectra of MADN and the polymer P(ADN)s were also examined and presented in Figure 2.7 and Table 2.5. The
solid thin film for the small molecule and monomer were prepared dispersing the small molecules in a commercial available poly(methyl methacrylate). The UV-Vis absorption spectra for the polymers in solid-state is similar to the results in THF solution, showing similar $\pi \rightarrow \pi^*$ transition and also suggesting a weak intermolecular interaction disrespected in solution or solid films. The emission maximum for MADN was in solid-state had a single sharp emission maximum at 434 nm and a narrow FWHM (43.5 nm). The polymers P(ADN)-F1, A1, F4 and A3 all have similar emission around 444 to 446 nm. A slightly larger red-shift of 10-12 nm was found for the solid-state samples compared to MADN. The single emission peak can be attributed to a close aggregating conformations for the small molecule MADN and polymer in the solid-states. The CIEs for the polymers in solid form are between $(x = 0.15, y = 0.06-0.08)$ (see Table 2.5) indicating they maintained the optical characteristics of MADN $(x = 0.15, y = 0.05)$ even after polymerization.

When the methyl group in MADN was replaced by an olefinic group, the PL lifetime ($\tau$) decreased from 6.15 ns (for MADN) to 7.83 to 9.05 ns (for polymers) (see Table 2.4). The lifetime of the polymers showed slight molecular weight dependent indicating weak intramolecular interaction between adjacent ADN moieties. The fluorescence decays of the polymers were found to be single-exponential (see Figure 2.8). The quantum efficiency of the polymers ranged from 0.40 to 0.42 is lower than that of the reference MADN (0.60).
Figure 2.6 Extinction coefficient and PL spectra of MADN, Vinyl-ADN and P(ADN)-F1, A1, F4, A3 in THF.

Figure 2.7 Absorption and PL spectra of solid-state MADN and P(ADN)-F1, A1, F4, A3 on quartz.
Figure 2.8   PL life time of MADN and P(ADN)-F1, A1, F4, A3.

Table 2.4   Optical properties of MADN, Vinyl-ADN and P(ADN)s in THF.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$\lambda_{\text{max}}$ absorption maximum (nm)</th>
<th>$\lambda_{\text{max}}$ emission maximum (nm)</th>
<th>FWHM (nm)</th>
<th>Life time (ns)</th>
<th>Quantum efficiencies</th>
<th>PL CIE (x, y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MADN</td>
<td>340, 357, 376, 396</td>
<td>409, 429.5</td>
<td>47.5</td>
<td>6.15</td>
<td>0.60</td>
<td>0.15, 0.03</td>
</tr>
<tr>
<td>Vinyl-ADN</td>
<td>342, 360, 379, 401</td>
<td>428</td>
<td>55</td>
<td>5.73</td>
<td>0.43</td>
<td>0.15, 0.04</td>
</tr>
<tr>
<td>P(ADN) F1</td>
<td>347, 361, 381, 402</td>
<td>423, 442.5</td>
<td>56</td>
<td>9.05</td>
<td>0.42</td>
<td>0.15, 0.04</td>
</tr>
<tr>
<td>P(ADN) F4</td>
<td>345, 360, 380, 401</td>
<td>422.5, 438.5</td>
<td>52.5</td>
<td>7.97</td>
<td>0.40</td>
<td>0.15, 0.05</td>
</tr>
<tr>
<td>P(ADN) A1</td>
<td>349, 360, 381, 402</td>
<td>423.5, 444</td>
<td>54</td>
<td>8.83</td>
<td>0.40</td>
<td>0.15, 0.04</td>
</tr>
<tr>
<td>P(ADN) A3</td>
<td>343, 360, 378, 400</td>
<td>417.5, 436</td>
<td>52</td>
<td>7.83</td>
<td>0.44</td>
<td>0.16, 0.04</td>
</tr>
</tbody>
</table>
Table 2.5  Optical properties of MADN and P(ADN)s in solid-state.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$\lambda_{\text{max}}$ absorption maximum (nm)</th>
<th>$\lambda_{\text{max}}$ emission maximum (nm)</th>
<th>FWHM (nm)</th>
<th>PL CIE (x, y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MADN a)</td>
<td>341, 357, 377, 398</td>
<td>434</td>
<td>43.5</td>
<td>0.15, 0.05</td>
</tr>
<tr>
<td>P(ADN) F1 b)</td>
<td>343, 362, 381, 403</td>
<td>446</td>
<td>52</td>
<td>0.15, 0.08</td>
</tr>
<tr>
<td>P(ADN) F4 b)</td>
<td>341, 357, 380, 401</td>
<td>444</td>
<td>49</td>
<td>0.15, 0.07</td>
</tr>
<tr>
<td>P(ADN) A1 b)</td>
<td>341, 362, 380, 402</td>
<td>444</td>
<td>51.5</td>
<td>0.15, 0.07</td>
</tr>
<tr>
<td>P(ADN) A3 b)</td>
<td>340, 359, 379, 401</td>
<td>443.5</td>
<td>49</td>
<td>0.15, 0.06</td>
</tr>
</tbody>
</table>

a) 5 wt% in PMMA.
b) Solvent cast thin films on quartz.

2.3.5  Electrochemical properties

The ionization potential and redox stability of MADN and the polymers P(ADN)-F1, A1, F4 and A3 were studied using cyclic voltammetry (CV). The CV of MADN was measured in ACN and the polymer measurements were effected by coating the polymers on the Pt working electrode. The results are summarized in Table 2.6. According to the voltammograms (see Figure 2.9 and 2.10), both MADN and P(ADN)s exhibited a quasi-reversible oxidation reaction in the positive sweep direction with the potential $E_{1/2}^{\text{ox}}$ 1.22 V (MADN), 1.31 V (P(ADN)-F1), 1.32 V (P(ADN)-A1), 1.33 V (P(ADN)-F4) and 1.32 V (P(ADN)-A3). The higher oxidation potential indicated that the polymers are more air-stable than MADN.

The first oxidation potential in the anodic sweep was used to calculate the Highest Occupied Molecular Orbital (HOMO) energy level with respect to the vacuum level using ferrocene as internal standard. The HOMO of the polymers was estimated using the equation $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.8) \text{ eV}$, where $E_{\text{ox}}$ is the onset potential for first oxidation relative to the Fc/Fc+ couple. The HOMO was
determined to be -5.56 eV (MADN) and -5.65 to -5.67 eV for the polymers. The Lowest Unoccupied Molecular Orbital (LUMO) energy level of MADN and the polymers was calculated by subtracting the bandgap energy (the bandgap energy was determined from the absorption edge of the UV-Vis absorption spectrum) from the HOMO. The LUMO were found to be -2.53 eV (MADN), and -2.66 to -2.70 eV for the polymers. A lower LUMO indicated better electron injection for the polymers than MADN (assuming LUMO of Ca = -2.9 eV). The polymers all showed to have similar HOMO/LUMO and energy bandgap, indicating the polymerization process and MW did not affecting the electrochemical properties significantly.

Figure 2.9 30 Cycles CV of MADN in ACN.
Figure 2.10 CV voltammogram of P(ADN) solid films coated on the electrode.

Table 2.6    Electrochemical properties of the polymers.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$E_{1/2}^{\text{ox}}$ (V, ferrocene) a)</th>
<th>$E_{\text{onset}}^{\text{ox}}$ (V, sample) a)</th>
<th>HOMO (eV) b)</th>
<th>LUMO (eV) c)</th>
<th>$E_g$ (eV)</th>
<th>UV-Vis absorption onset (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MADN</td>
<td>0.46</td>
<td>1.22</td>
<td>-5.56</td>
<td>-2.53</td>
<td>3.03</td>
<td>409</td>
</tr>
<tr>
<td>P(ADN) F1</td>
<td>0.46</td>
<td>1.31</td>
<td>-5.65</td>
<td>-2.68</td>
<td>2.97</td>
<td>417.5</td>
</tr>
<tr>
<td>P(ADN) F4</td>
<td>0.46</td>
<td>1.33</td>
<td>-5.67</td>
<td>-2.70</td>
<td>2.97</td>
<td>417</td>
</tr>
<tr>
<td>P(ADN) A1</td>
<td>0.46</td>
<td>1.32</td>
<td>-5.66</td>
<td>-2.69</td>
<td>2.97</td>
<td>417</td>
</tr>
<tr>
<td>P(ADN) A3</td>
<td>0.46</td>
<td>1.32</td>
<td>-5.66</td>
<td>-2.66</td>
<td>3.00</td>
<td>414</td>
</tr>
</tbody>
</table>

a) Oxidation potentials were measured in 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) ACN solution relative to Ag/AgCl electrode.

b) Assuming the HOMO of ferrocene is -4.8 eV.

c) Calculated from the bandgap energy deduced from the UV-Vis absorption onset.
2.4 Conclusions

A new series of true blue emitting fluorescent polymers, \( P(ADN) \)\(_s\), have been prepared successfully using solution free radical and anionic polymerization. Free radical process produced polymers with high polydispersity while anionic method produced polymers with better MW control and lower polydispersity. Polymerization has also attempted using cationic polymerization using BF\(_3\)/H\(_2\)O as the catalyst but with zero yields. The results could be the stabilization of the cation via delocalization in the pendant homocyclic ADN moiety. In comparison with the small molecule MADN, the polymers show better thermal stability, higher resistance to oxidation and a longer PL life time. The quantum efficiency of the polymers, however, is 30% smaller than MADN. The polymers have similar HOMO but a lower LUMO compared to MADN. A slight red-shift in the absorption and emission spectra was found compared to MADN due to \( \pi-\pi \) interaction between adjacent pendant ADN moieties, however, the CIE (\( x = 0.15, y = 0.06-0.08 \)) remains closed to the required values for a true blue hue.

2.5 References


14: 677.


Chapter 3

Synthesis and Characterization of Highly Soluble Blue Emitting Poly(2-vinylanthracene) with 9,10-Di(2-naphthalenyl) and 9,10-Di(3-quinolinyl) Substituents

3.1 Introduction

Over the past decade, the use of conductive polymers as light emitting materials has received increasing attention in polymer electroluminescent devices.[1-9] Although there have been significant progress in red [10,11] and green [12-14] light-emitting polymers, there are only limited blue light-emitting polymers reported that can fulfill the requirements for a full color display application.[15,16] Simultaneously, tremendous efforts have been concentrated in the development of blue-emitting small molecules.[17-29] The majority of the blue emitters are 9,10-anthracene derivatives.[30] For example, 2MADN, has been studied extensively due to its reasonable luminescence property, descent thermal stability and good ambipolar charge transporting ability.[31-35] For electroluminescent devices employing 2MADN as the host and 9-[4-(2-diphenylamino-9,9-diethylfluoren-7-yl)phenyl]-9-phenylfluorene as a dopant, a deep blue emission with CIE$_{x,y}$ (0.15, 0.13), a luminous efficiency of 5.3 cd/A, a power efficiency of 2.9 lm/W and an external quantum efficiency of 4.8% at 20 mA/cm$^2$ were achieved.[36] Another small molecule quinoline whose half-wave reduction potential at -2.13 eV and its derivatives (e.g. 3PQMPT [37]) have also been applied.
as the emitters and electron transporters. These compounds all have good thermal stability ($T_g > 200 \, ^\circ C$ and $T_d > 400 \, ^\circ C$), high solubility (completely soluble in formic acid), and excellent electron-accepting properties (EA 2.40-2.65 eV).

However, the inherent mechanical weaknesses, the problematic re-crystallization under thermal stress and the needs of the higher cost vacuum thin film deposition for small molecule materials demand further improvement for a successful full-color PLED application. Most of the inherent drawbacks for small molecules mentioned above can be eliminated by binding the functional moieties covalently into a polymer. As a result, polymers based on 2MADN and 3MADQ were prepared with the goals of disrupting the symmetry for recrystallization and eliminating the chance of phase separation of the dopant from the matrix and at the same time without significantly altering the overall electrical (LUMO/HOMO) and optical properties (CIE $x,y$).

In our previous work, a blue emitting vinyl polymer poly(9,10-di(1-naphthalenyl)-2-vinylanthracene) (P(ADN)) based on 2-methyl-9,10-di(1-naphthalenyl)anthracene (MADN) had shown to possess excellent thermal stability and retained most of the photoluminescent & electrochemical properties of the parent small molecule MADN. However, the solubility of P(ADN) diminished when its molecular weight (MW) became higher than 13,000. In this chapter, two novel blue fluorescent monomers Vinyl-2ADN and Vinyl-3ADQ rooted from the basic molecules 2MADN and 3MADQ were synthesized. Their polymers P(2ADN) and P(3ADQ) were prepared using free radical solution addition polymerization. Besides of the consideration of the steric effects, the replacement of the heteroatom N to CH at the C-3 position of the
2-naphthalenyl group also enhance the solubility for P(3ADQ). The chemistry and physical properties of the intermediates, the monomers and the resulting polymers were characterized using, NMR, GPC, FT-IR, TGA, DSC, MALDI-TOF MS, UV-Vis, PL, CV and quantum yield measurements.

3.2 Experimental

3.2.1 Materials and instruments

Unless specified otherwise, all reactions were carried out under the nitrogen atmosphere using standard Schlenk techniques. The glassware was dried in a 120 °C oven. The analytical grade solvents were purified by distillation with appropriate drying agents and blanketed with inert nitrogen atmosphere prior to use. Benzoyl peroxide (BPO) and 2, 2′-azobisisobutyronitrile (AIBN) were recrystallized in a chloroform methanol mixed solvent before use. All other chemicals (analytical grade) were purchased from commercial sources and were used as received. The operations of all the reactions and equipments were same to that mentioned in the Chapter 2.

3.2.2 Synthesis

Details on the reaction procedure of Nad, MAq, MA and MADBr have been given in the section Synthesis 2.2.2 (Chapter 2).

3.2.2.1 2-Naphthalenyl boronic acid (2NB)

To a two-neck 250 mL round bottom flask, triisopropyl borate (3.30 mL, 29.06 mmol) and 3-bromoquinoline (3.00 g, 14.49 mmol) was dissolved in dry THF (100 mL), then n-butyllithium (14.50 mL of a 2 M solution in hexane, 29.00 mmol) was added dropwise via a dropping funnel over 1 hr under N₂ at -78 °C.
After 2 hrs, the acetone dry ice bath was removed, and the reaction solution was allowed to warm to 0 °C. The reaction was then quenched with a 2 M HCl solution, and the pH value was adjusted to 7 with a solution of 2 M NaHCO₃. The resulting solution was extracted with ethyl acetate (EA) (3 × 100 mL). The combined organic layers were dried with MgSO₄ and evaporated to dryness. n-Hexane was then added to precipitated the product as a white solid (80% yield).

1H NMR (400 MHz, DMSO-d): δ (ppm) 8.38 (s, 1H), 8.22 (s, 2H), 7.93-7.86 (m, 4H), 7.54-7.51 (m, 2H). 13C NMR (100 MHz, DMSO-d): δ (ppm) 134.88, 133.96, 132.36, 130.56, 128.28, 127.42, 126.55, 126.33, 125.70. MS (MALDI-TOF) m/z = 195.0588 (M+Na).

3.2.2.2 2-Methyl-9,10-di(2-naphthalenyl)anthracene (2MADN)

2MADN was synthesized by the Suzuki cross-coupling reaction. A two-necked flask containing the compound MADBr (1.00 g, 2.85 mmol), 2NB (1.70 g, 9.99 mmol), tetrakis(triphenylphosphine)palladium(0) (300 mg, 2.60 mmol), and 2 M K₂CO₃ (3 mL) and THF (40 mL) was equipped with a magnetic stirrer and a reflux condenser was heated to reflux overnight under a N₂ purge. The mixture was then poured into water and extracted with 50 mL DCM. The combined organic layer was dried with anhydrous MgSO₄ and evaporated to dryness. The crude product was purified by silica-gel column chromatography using hexane as eluent affording the title compound as a pale yellow solid (80% yield). 1H NMR (400 MHz, CDCl₃): δ (ppm) 8.12-8.01 (m, 6H), 7.97-7.95 (m, 2H), 7.75-7.61 (m, 9H), 7.49 (s, 1H), 7.31-7.26 (m, 2H), 7.17 (d, J = 8.8 Hz, 1H), 2.36 (s, 3H). 13C NMR (100 MHz, CDCl₃): δ (ppm) 136.74, 136.01, 134.90, 133.50, 133.44, 132.78, 130.30, 130.24, 129.73, 129.63, 129.60, 128.74, 128.20, 128.14, 128.03, 127.97, 127.96, 127.94, 127.08, 126.99, 126.97, 126.45, 126.40,
126.23, 126.20, 125.16, 125.07, 124.76, 22.02. MS (MALDI-TOF) \( m/z = 444.1912 \) (M+).

### 3.2.2.3 2-(Bromomethyl)-9,10-di(2-naphthalenyl)anthracene (2ADN-CH$_2$Br)

To a 250 mL round bottom flask, 2MADN (0.85 g, 1.89 mmol) and NBS (0.37 g, 2.08 mmol), BPO (13 mg, 0.054 mmol) was dissolved in 35 mL benzene. The mixture was refluxed under N$_2$ purge overnight. Methanol was added, filtered, a pale yellow product was obtained. The product was used directly for the following reactions without further purification.

### 3.2.2.4 9,10-Di(2-naphthalenyl)anthracene-2-carbaldehyde (2ADN-CHO)

To a 250 mL round bottom flask, 2-nitropropane (0.80 g, 8.99 mmol), KOH (1.04 g, 22.61 mmol), were added to methanol (30 mL). The mixture was stirred until it became a clear solution. 2ADN-CH$_2$Br (0.90 g, 1.72 mmol) dissolved in 30 mL dimethyl sulfoxide (DMSO) was added into above methanol solution. The solution was stirred overnight at room temperature. Water was added to precipitate the crude product. The crude product was purified by silica-gel column chromatography using hexane/DCM (6:1) as the eluent. A yellow solid was obtained (92% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 9.89 (s, 1H), 8.25-5.26 (m, 1H), 8.16-8.04 (m, 5H), 8.01-7.96 (m, 3H), 7.84-7.73 (m, 4H), 7.67-7.60 (m, 6H), 7.44-7.37 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 191.20, 138.94, 136.54, 135.40, 134.67, 134.30, 132.43, 132.26, 132.21, 131.87, 131.76, 130.99, 130.53, 129.64, 129.21, 129.09, 128.07, 128.06, 127.95, 127.38, 127.24, 127.16, 127.06, 126.99, 126.90, 126.84, 126.43, 126.16, 125.69, 125.56, 125.55, 125.39, 124.89, 119.29. MS (MALDI-TOF) $m/z = 459.1820$ (M+H).
3.2.2.5 9,10-Di(2-naphthalenyl)-2-vinylanthracene (Vinyl-2ADN)

Vinyl-2ADN was synthesized by the Witting reaction. To a 250 mL round bottom flask, methyltriphenylphosphonium bromide (1.26 g, 3.53 mmol) was dissolved in 30 mL freshly distilled THF. Potassium t-butyl oxide (0.40 g, 3.57 mmol) was added and stirred for 30 mins in an ice bath. A yellow solution was resulted. 2ADN-CHO (0.65 g, 1.40 mmol) dissolved in THF was added to the ylide t-butyl oxide solution under continuous stirring. The mixture was stirred at room temperature until the reaction was completed as indicated by thin layer chromatography. Hexane was added. The mixture was then filtered. The solvent was then evaporated under reduced pressure and the residue was purified by column chromatography using hexane as the eluent. A yellow solid was obtained with 88% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 8.11 (d, J = 2.40 Hz, 1H), 8.09 (d, J = 2.40 Hz, 1H), 8.06-8.03 (m, 2H), 8.00 (s, 2H), 7.95-7.94 (m, 2H), 7.74-7.69 (m, 3H), 7.64-7.58 (m, 7H), 7.52 (dd, J$_1$ = 9.2 Hz, J$_2$ = 1.6 Hz, 1H), 7.33-7.29 (m, 2H), 6.70(ddd, J$_1$ = 17.6 Hz, J$_2$ = 10.8 Hz, 1H), 5.72 (d, J = 10.8 Hz, 1H), 5.21 (d, J = 17.6 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 135.33, 135.30, 132.99, 132.28, 132.27, 131.66, 131.63, 129.40, 129.11, 129.06, 129.02, 128.55, 128.46, 128.35, 127.01, 126.95, 126.90, 126.88, 126.77, 126.37, 125.97, 125.89, 125.32, 125.12, 124.94, 124.19, 124.12, 120.86, 113.13. MS (MALDI-TOF) m/z = 456.1894 (M+)

3.2.2.6 3-Quinolinyl boronic acid (3QB)

The procedures were the same as in 2NB, except that NaHCO$_3$ was replaced by NaOH. 3-Bromoquinoline (2.00 g, 9.62 mmol), 1.5 M n-butyllithium (12.50 mL, 18.75 mmol) and trisisoproborate (4.60 mL, 20.01 mmol) were used. White crystal of 3QB was obtained with 90% yield. $^1$H NMR (400 MHz, DMSO-d): $\delta$
(ppm) 9.16 (d, J = 1.6 Hz, 1H), 8.71 (s, 1H), 8.50 (s, 2H), 8.01-7.96 (m, 2H), 7.79-7.75 (m, 1H), 7.62-7.60 (m, 1H). $^{13}$C NMR (100 MHz, DMSO-d): $\delta$ (ppm) 154.77, 148.27, 142.91, 130.12, 128.58, 128.49, 127.21, 126.36.

3.2.2.7 2-Methyl-9,10-di (3-quinolinyl) anthracene (3MADQ)

MADQ was synthesized by the Suzuki cross-coupling reaction. The procedures were the same as in 2MADN, except that MADBr (0.65 g, 2.32 mmol), 3QB (1.60 g, 9.30 mmol), tetrakis (triphenylphosphine) palladium (0) (0.27 g, 0.23 mmol), 2 M K$_2$CO$_3$ (3 mL) and THF (40 mL) were used. The crude product was purified by silica-gel column chromatography using hexane/EA/chloroform (8:1:1) as the eluent affording the 3MADQ as a pale yellow solid (85% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 9.05 (t, J = 2.4 Hz, 2H), 8.35-8.31 (m, 4H), 7.99-7.95 (m, 2H), 7.91-7.86 (m, 2H), 7.73-7.61 (m, 5H), 7.44 (s, 1H), 7.39-7.35 (m, 2H), 7.25-7.22 (m, 1H), 2.38 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 152.98, 152.93, 152.86, 152.81, 147.62, 138.12, 138.08, 138.04, 138.00, 135.89, 133.63, 132.69, 132.16, 132.04, 130.72, 130.67, 129.96, 129.61, 129.58, 129.12, 128.84, 128.14, 128.08, 128.02, 127.92, 127.85, 127.31, 126.61, 126.49, 125.88, 125.56, 124.75, 22.04. MS (MALDI-TOF) $m/z$ = 447.1842 (M+H).

3.2.2.8 2-(Bromomethyl)-9,10-di (3-quinolinyl) anthracene (3ADQ-CH$_3$Br)

The procedures were the same as in 2MADN, except that 2MADQ (1.00 g, 2.24 mmol) and NBS (0.46 g, 2.58 mmol), BPO (27.00 mg, 0.11 mmol) and 35 mL benzene were used.
3.2.2.9 9,10-Di(3-quinolinyl) anthracene-2-carbaldehyde (3ADQ-CHO)

The procedures were the same as in 2ADN-CH₂Br, except that 2ADN-CH₂Br (1.00 g, 1.91 mmol), 2-nitropropane (2.18 g, 24.49 mmol), KOH (1.30 g, 23.21 mmol), methanol (30 mL) and DMSO (30 mL) were used. The crude product was purified by silica-gel column chromatography using hexane/EA/chloroform (4:1:0.5) as the eluent. A yellow solid was obtained (80% yield). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.49 (s, 1H), 9.09-9.04 (m, 2H), 8.40-8.33 (m, 4H), 8.21 (s, 1H), 8.00-7.91 (m, 4H), 7.82-7.73 (m, 6H), 7.50-7.49 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 191.92, 152.36, 152.31, 152.22, 152.16, 147.89, 147.75, 138.20, 138.12, 138.04, 136.71, 135.31, 134.43, 134.00, 132.38, 132.08, 131.19, 131.14, 130.87, 130.45, 130.28, 129.71, 129.67, 129.61, 129.51, 128.15, 128.08, 128.03, 127.70, 127.57, 127.08, 126.82, 121.41. MS (MALDI-TOF) m/z = 461.1653 (M+H).

3.2.2.10 9,10-Di(3-quinolinyl)-2-vinylanthracene (Vinyl-3ADQ)

Vinyl-3ADQ was synthesized by the Witting reaction. The procedures were the same as in Vinyl-3ADQ, except that 2ADN-CHO (0.50 g, 1.09 mmol) methyltriphenylphosphonium bromide (0.97g, 2.72 mmol), potassium t-butyl oxide (0.31 g, 2.76 mmol) and THF (20 mL) were used. The product was purified by silica-gel column chromatography using hexane/EA/chloroform (8:1:1) as the eluent. A yellow solid was obtained with 89.5% yield. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.07 (s, 2H), 8.36-8.32 (m, 4H), 7.96-7.85 (m, 4H), 7.70-7.67 (m, 5H), 7.58-7.54 (m, 2H), 7.38-7.35 (m, 2H), 6.67 (dd, J₁ = 17.6 Hz, J₂ = 11.2 Hz, 1H), 5.74 (d, J = 17.6 Hz, 1H), 5.24 (d, J = 11.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 151.70, 151.64, 151.57, 146.55, 146.52, 137.07, 136.99, 136.91,
135.44, 133.82, 132.77, 132.66, 130.70, 129.79, 129.50, 129.45, 128.95, 128.49, 128.47, 127.02, 126.96, 126.91, 126.76, 126.74, 126.72, 126.26, 125.91, 125.56, 125.46, 125.04, 124.94, 124.26, 121.77, 114.14. MS (MALDI-TOF) \( m/z = 459.1840 \) (M+H).

### 3.2.2.1 Poly(9,10-di(2-naphthalenyl)-2-vinylanthracene) (P(2ADN))

To a 10 mL one-mouth glass apparatus charged with a stirrer bar, Vinyl-2ADN (200.00 mg, 0.433 mmol) and free radical initiator AIBN (1.43 mg, 0.0087 mmol) was dissolved in 1 mL dried toluene. The reaction mixture was degassed by several freeze-pump-thaw cycles and then sealed off under nitrogen atmosphere. The reaction mixture was stirred at 75 °C for 10 hrs. Finally, a viscous yellowish polymer solution was resulted. The polymer was purified by re-dissolving in THF and re-precipitated in excess acetone. A yellow solid product was obtained (85% yield).

### 3.2.2.12 Poly(9,10-di(3-quinolinyl)-2-vinylanthracene) (P(3ADQ))

The procedures were the same as in P(2ADN). Vinyl-3ADQ (200.00 mg, 0.437 mmol), AIBN (1.43 mg, 0.0087 mmol) and dried toluene (0.5 mL) were used. A yellow solid product was obtained (72% yield).

### 3.3 Results and discussion

#### 3.3.1 Synthesis and characterization of the polymers

The synthetic pathway for the monomers Vinyl-2ADN & Vinyl-3ADQ and their polymers P(2ADN) & P(3ADQ) are shown in Scheme 3.1. Details on the reaction procedures and their characterizations have been given in above Synthesis section 3.2.2.
Scheme 3.1  Synthetic routes for the polymers P(2ADN) and P(3ADQ).
Solid-state FT-IR measurements were performed for the confirmation of the chemical structures. The spectrum for the polymer \textbf{P(2ADN)} in comparison with the vinyl monomer \textbf{Vinyl-2ADN} and a model compound \textbf{2MADN} was given in Figure 3.1. The FT-IR spectra of \textbf{2MADN, Vinyl-2ADN} and \textbf{P(2ADN)} have the following similar structural attributes: 3,052-3,054 cm\(^{-1}\) (v, aromatic C-H stretching), 1,629-1,336 cm\(^{-1}\) (v, aromatic C=C stretching; δ, sp\(^3\) C-H deformation) and 817-743 cm\(^{-1}\) (δ, C-H out of plane deformation). In Figure 3.1, \textbf{2MADN, Vinyl-2ADN} and \textbf{P(2ADN)} showed similar distinct peaks of aromatic C=C stretching vibration with little shift. \textbf{Vinyl-2ADN} showed a unique =C-H vibration at 987 and 912 cm\(^{-1}\) due to the vinyl group. An intense sp\(^3\) C-H stretching vibration at 2919 cm\(^{-1}\) for \textbf{P(2ADN)} was attributed to the polymer hydrocarbon main chain.

The FT-IR spectra of \textbf{3MADQ, Vinyl-3ADQ} and \textbf{P(3ADQ)} were also given in Figure 3.1. Common features of \textbf{3MADQ, Vinyl-3ADQ} and \textbf{P(3ADQ)} are attributed to the following structures moieties: 3,062-3,059 cm\(^{-1}\) (v, aromatic C-H stretching), 1,620-1,258 cm\(^{-1}\) (v, aromatic C=C stretching; δ, sp\(^3\) C-H deformation) and 788-751 cm\(^{-1}\) (δ, C-H out of plane deformation). Again, distinct peaks of =C-H vibration at 995 and 914 cm\(^{-1}\) was detected for \textbf{Vinyl-3ADQ} and a strong sp\(^3\) C-H stretching vibration due to the aliphatic main chain was observed for \textbf{P(3ADQ). 3MADQ, Vinyl-3ADQ} and \textbf{P(3ADQ)} all have similar distinct peaks for the aromatic C=C stretching vibration with slight shift.
The molecular weights of the polymers $P(2ADN)$ and $P(3ADQ)$ were determined using GPC with THF as the mobile phase and were calibrated against polystyrene MW standards (Figure 3.2). The resulting yield and relative MW measurements were presented in Table 3.1. The number-averaged molecular weights ($M_n$) of $P(2ADN)$ and $P(3ADQ)$ were found to be 21,500 and 15,400, with a relatively high PDI of 2.34 and 2.71, respectively. The high polydispersity could be a result of chain transfer to the aromatic moieties as well as stabilization of the radical species due to delocalization.

The solubility was compared by dissolving 1.00 mg of polymer in 10 mL of a solvent at room temperature in a supersonic bath for 20 mins. Both $P(2ADN)$ and $P(3ADQ)$ were found to be soluble in common organic solvents including THF.
CHCl₃, DCM, toluene, et al. **P(3ADQ)** showed improved solubility as it can also be dissolved in ethanol and an ethanol water (v/v = 1/1) mixture. In comparison with our previous work on **P(ADN)** based on 1-naphthalenyl, **P(2ADN)** have enhanced solubility which can be attributed to the lower steric hindrance for the 2-naphthalenyl substituted units.

### Table 3.1 Summary of molecular weight measurements.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Yield (%)</th>
<th>( M_n ) (^{a)} )</th>
<th>( M_w ) (^{a)} )</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>P(2ADN)</strong></td>
<td>85</td>
<td>21,500</td>
<td>50,300</td>
<td>2.34</td>
</tr>
<tr>
<td><strong>P(3ADQ)</strong></td>
<td>72</td>
<td>15,400</td>
<td>41,800</td>
<td>2.71</td>
</tr>
</tbody>
</table>

\(^{a)} \) The weight-averaged (Mₙ) and number-averaged (Mₘ) molecular weights were determined by GPC calibrated against poly(styrene) MW standards. GPC conditions: UV-Vis detector wavelength 254 nm, mobile phase THF at 1 mL/min.

![Figure 3.2 GPC chromatogram of P(2ADN) and P(3ADQ).]
3.3.2 Thermal properties

The thermal properties of the homopolymers were examined by TGA at a heating rate 20 °C/min and DSC at a heating rate 40 °C/min, all under nitrogen purge. The results were summarized in Figure 3.3, Figure 3.4 and Table 3.2, respectively. Both P(2ADN) and P(3ADQ) possessed excellent thermal stabilities with glass transition temperatures (T_g midpoint) at 343 °C and 298 °C, respectively. This is significantly higher than the T_g previously reported for P(ADN) (M_n = 17,600 and T_g = 237 °C). The T_d for P(2ADN) and P(3ADQ) at 424 °C and 414 °C are also higher than that of the model small molecule 2MADN (T_d = 380 °C) and 3MADQ (T_d = 376 °C). Neither of the polymers P(2ADN) or P(3ADQ) showed melting nor crystalline-related transitions upon repeated heating (up to 300 °C) and cooling indicating P(2ADN) and P(3ADQ) are completely amorphous.

Figure 3.3  TGA thermogram for P(2ADN) and P(3ADQ) and their parent small molecules 2MADN and 3MADQ at heating rate of 20 °C/min under nitrogen purge.
Table 3.2 Summary of thermal properties.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Onset $T_d$ (°C) a)</th>
<th>Weight lost (%)</th>
<th>Midpoint $T_g$ (°C) b)</th>
<th>$\Delta C_p$ (J/g·°C) c)</th>
<th>$T_m$ (°C) b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2MADN</td>
<td>380</td>
<td>95.73</td>
<td>127</td>
<td>0.45</td>
<td>261</td>
</tr>
<tr>
<td>P(2ADN)</td>
<td>424</td>
<td>20.77</td>
<td>343</td>
<td>0.21</td>
<td>/</td>
</tr>
<tr>
<td>3MADQ</td>
<td>376</td>
<td>84.46</td>
<td>127</td>
<td>0.41</td>
<td>255</td>
</tr>
<tr>
<td>P(3ADQ)</td>
<td>414</td>
<td>45.60</td>
<td>298</td>
<td>0.24</td>
<td>/</td>
</tr>
</tbody>
</table>

a) About 5mg samples were used for TGA under nitrogen purge at a heating rate 20 °C/min
b) About 20 mg samples were used for DSC under nitrogen purge at a heating rate 40 °C/min.
c) The change in specific heat capacity at $T_g$ ($\Delta C_p$ J/g·°C).

3.3.3 Optical properties

The UV-Vis absorption and PL emission spectra for 2MADN, Vinyl-2ADN and P(2ADN) in THF were given in Figure 3.5 with the results summarized in Table 3.3. Three prominent bands of 2MADN were observed at 359, 378 and 398 nm, which were all due to the $\pi\rightarrow\pi^*$ transition. A red-shift of about 5 nm for the same absorption peaks were found for P(2ADN). The small molecule 2MADN
has an emission maximum at 425.5 nm, while Vinyl-2ADN has a broader emission peak at 435.5 nm. A red-shift of 17 nm in PL spectrum for P(2ADN) was found in comparison to 2MADN. The red-shift is probably a result of short-range π-π stacking interaction between adjacent ADN moieties. The extinction coefficient of P(2ADN) decreased to only 62% to that of 2MADN, which could be attributed to the exciton and dispersion-force interaction in the polymer with an ordered structure.

The solid-state UV-Vis absorption and PL emission spectra of 2MADN (dispersed in a poly(methyl methacrylate) (PMMA) solid thin film) and a solvent cast P(2ADN) solid thin film were shown in Figure 3.6. The 2MADN/PMMA solid thin film was cast at room temperature from a 10 wt% PMMA chloroform solution with the concentration 2MADN/PMMA = 2 wt%. Both solid-state thin film and the THF solution have very similar π→π* transition absorption bands. A smaller red-shift in the absorption and emission spectra was found for the solid thin films than those in THF solutions. Similarly, P(2ADN) exhibited the same behavior in THF solution and in solid thin film. The UV-Vis absorption, PL emission spectra and CIE results indicated that the optical properties were preserved when Vinyl-2ADN was polymerized into P(2ADN).

Figure 3.7 and 3.8 showed the UV-Vis absorption and PL emission spectra for 3MADQ, Vinyl-3ADQ and P(3ADQ) in THF and in solid thin films. The results were also included in Table 3.3. The extinction coefficients of Vinyl-3ADQ and P(3ADQ) were only 65.5% and 51.6% of that of 3MADQ. The UV-Vis and PL spectra also showed a slight red-shifts for P(3ADQ) compared to 3MADQ. Compared to the UV-Vis absorption and PL emission spectra of 3MADQ and P(3ADQ) in THF solution, both solid film spectra of 3MADQ and
P(3ADQ) showed some red-shifts. This phenomenon can be attributed to the difference in dielectric constant of the environment.\textsuperscript{[30,53]}

The lifetimes of P(2ADN) and P(3ADQ) were 6.54 and 3.80 ns, respectively, which were both higher than those of the small molecules 2MADN (4.45 ns) and 3MADQ (3.51 ns) (see Figure 3.9). Vinyl-2ADN and P(2ADN) have similar fluorescence quantum efficiencies (\(\phi = 0.56\) and 0.43) and both were lowered than that of the small molecule 2MADN (\(\phi = 0.80\)). However, 3MADQ and Vinyl-3ADQ have similar fluorescence quantum efficiencies (\(\phi = 0.41\) and 0.39) and were both higher than that of the polymer P(3ADQ) (\(\phi = 0.24\)). Both the CIE of P(2ADN) and P(3ADQ) are in the range of CIE\(_{x,y}\) (0.14-0.15, 0.08-0.13) either in solid-state form or in solution, indicating both P(2ADN) and P(3ADQ) are within the requirements for a true blue display color.

The sensitivity of fluorescent on pH for a 5 ppm 3MADQ and P(3ADQ) in a mixed ethanol water (v/v = 1/1) solution were indicated in Figure 3.10 (a-b). The pH values were adjusted by adding different amounts of HCl and NaOH. This pH sensitive phenomenon could be attributed to the acid-base ionization equilibrium of ground state and or excited state quinoline groups suspended on the anthracene-core at low pH value environments (see Scheme 3.2).\textsuperscript{[54,55]}
Scheme 3.2 The equilibrium equations for 3MADQ and P(3ADQ) at different pH values.

The PL intensity of 3MADQ at 442 nm against pH is sigmoidal and was shown in Figure 3.10 (c). A similar sigmoidal relationship at 457 nm for P(3ADQ) was also given Figure 3.10 (d). According to the Henderson-Hasselbach equation (Eq. 3.1), the $pK_a$ of 3MADQ and P(3ADQ) was calculated to be 2.4 and 2.7, respectively, indicating they are weak alkalis. The equation is given as

$$pK_a = pH - \log \frac{I_{F,\text{max}} - I_F}{I_F - I_{F,\text{min}}}$$  \hspace{1cm} (Eq. 3.1)

where the fluorescence signal $I_{F,\text{max}}$ is the max fluorescence value, $I_{F,\text{min}}$ is the minimum fluorescence value, and $I_F$ is fluorescence value at a certain pH value.

At increasing pH, the PL intensity for 3MADQ increased faster than that of P(3ADQ) indicating P(3ADQ) was less sensitive to pH than 3MADQ. The observation could be related to the facts that the P(3ADQ) chains not being fully extended in the ethanol water ($v/v = 1/1$) mixed solution.
Table 3.3 Optical properties of 2MADN, Vinyl-2ADN, P(2ADN), 3MADQ, Vinyl-3ADQ and P(3ADQ) in THF solutions and in solid thin films.

<table>
<thead>
<tr>
<th>Materials</th>
<th>λ_{max} absorption maximum (nm)</th>
<th>λ_{max} emission maximum (nm)</th>
<th>FWHM (nm)</th>
<th>Life time (ns)</th>
<th>Quantum efficiencies (ϕ)</th>
<th>CIE</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOLUTION (in THF)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2MADN \textsuperscript{a)}</td>
<td>359, 378, 398</td>
<td>425.5</td>
<td>53.5</td>
<td>4.45</td>
<td>0.80</td>
<td>(0.15, 0.05)</td>
</tr>
<tr>
<td>Vinyl-2ADN \textsuperscript{a)}</td>
<td>360, 380, 400</td>
<td>435.5</td>
<td>56.5</td>
<td>3.95</td>
<td>0.56</td>
<td>(0.15, 0.06)</td>
</tr>
<tr>
<td>P(2ADN) \textsuperscript{a)}</td>
<td>364, 383, 403</td>
<td>442.5</td>
<td>59.5</td>
<td>6.54</td>
<td>0.43</td>
<td>(0.14, 0.08)</td>
</tr>
<tr>
<td>3MADQ \textsuperscript{a)}</td>
<td>362, 380, 400</td>
<td>436</td>
<td>55.5</td>
<td>3.51</td>
<td>0.41</td>
<td>(0.15, 0.06)</td>
</tr>
<tr>
<td>Vinyl-3ADQ \textsuperscript{a)}</td>
<td>366, 382, 404</td>
<td>440</td>
<td>56</td>
<td>3.51</td>
<td>0.39</td>
<td>(0.15, 0.07)</td>
</tr>
<tr>
<td>P(3ADQ) \textsuperscript{a)}</td>
<td>369, 384, 404</td>
<td>452</td>
<td>63.5</td>
<td>3.80</td>
<td>0.24</td>
<td>(0.14, 0.12)</td>
</tr>
<tr>
<td>SOLID-STATE</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2MADN \textsuperscript{b)}</td>
<td>362, 380, 401</td>
<td>434.5</td>
<td>45</td>
<td>/</td>
<td>/</td>
<td>(0.15, 0.06)</td>
</tr>
<tr>
<td>P(2ADN) \textsuperscript{c)}</td>
<td>367, 386, 404</td>
<td>447.5</td>
<td>56</td>
<td>/</td>
<td>/</td>
<td>(0.15, 0.10)</td>
</tr>
<tr>
<td>3MADQ \textsuperscript{b)}</td>
<td>386, 406</td>
<td>441.5</td>
<td>49</td>
<td>/</td>
<td>/</td>
<td>(0.15, 0.06)</td>
</tr>
<tr>
<td>P(3ADQ) \textsuperscript{c)}</td>
<td>388, 406</td>
<td>453</td>
<td>61.5</td>
<td>/</td>
<td>/</td>
<td>(0.15, 0.13)</td>
</tr>
</tbody>
</table>

a) THF solution (5 ppm).
b) Cast from 10 wt % PMMA in chloroform solution with dye/PMMA = 2 wt% on quartz.
c) Thin films solvent cast on quartz.

Figure 3.5 Extinction coefficient and PL spectra of 2MADN, Vinyl-2ADN and P(2ADN) in THF.
Figure 3.6 Optical absorption and PL spectra of 2MADN in a PMMA solid solution and P(2ADN) thin film cast on quartz.

Figure 3.7 Extinction coefficient and PL spectra of 3MADQ, Vinyl-3ADQ and P(3ADQ) in THF.

Figure 3.8 Optical absorption and PL spectra of 3MADQ in a PMMA solid solution and P(3ADQ) thin film cast on quartz.
Figure 3.9  PL life time spectra of 2MADN, Vinyl-2ADN, P(2ADN), 3MADQ, Vinyl-3ADQ and P(3ADQ).
Figure 3.10   PL spectra of 3MADQ (a) and P(3ADQ) (b) in a mixed ethanol water (v/v = 1/1) solution with pH values adjusted by HCl and NaOH. The concentrations of 3MADQ and P(3ADQ) were both 5 ppm. The spectra (c) and (d) were the PL intensity cross-section for 3MADQ at 442 nm and P(3ADQ) at 457 nm against pH.

3.3.4   Electrochemical and electrical properties

The ionization potential and redox stability of the model small molecules (2MADN and 3MADQ) and the polymers (P(2ADN) and P(3ADQ)) were investigated using CV. The CV of the small molecules 2MADN and 3MADQ were measured in ACN while the polymers P(2ADN) and P(3ADQ) measurements were effected by coating the polymers on the Pt working electrode. The first oxidation potential in the anodic sweep was used to determine the highest occupied molecular orbital (HOMO) energy level which was calculated by assuming the internal standard ferrocene was -4.8 eV with respect to the vacuum level. Hence, the HOMO of the polymers was estimated using the equations $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.8)$ eV, where $E_{\text{ox}}$ is the onset potential for first oxidation relative to the Fc/Fc$^+$ couple. As a result, the lowest unoccupied molecular orbital (LUMO) energy level of the polymers was found by subtracting the band-gap
energy (determined from the absorption edge of the UV-Vis absorption spectra) from the HOMO value.

The cyclic voltammograms for 2MADN, 3MADQ, P(2ADN) and P(3ADQ) were given in Figure 3.11 with the results summarized in Table 3.4. The first oxidation wave of 2MADN and P(2ADN) occurred at 1.15 and 1.18 V, respectively, which was lower than that of 3MADQ (1.24 V) and P(3ADQ) (1.21 V). Both the small molecules and the polymers have similar band-gap energy (E\textsubscript{g}) (2.95~2.98 eV for the small molecules and 2.88~2.91 eV for the polymers). The LUMO/HOMO for 3MADQ and P(3ADQ) were both shifted slightly downward (from -0.06 to -0.03 eV) compared to 2MADN and P(2ADN). The results indicated the LUMO, HOMO and energy gap were not altered significantly by converting the small molecules into polymers.

PLED devices based on the configuration ITO/MoO\textsubscript{3}/P(2ADN) or P(3ADQ)/LiF/Al have been prepared. The EL of the devices, however, were rather weak even under high biased voltage (> 20 V). The causes were further investigated by measuring the mobility of the polymers. The hole mobility (\(\mu\text{hole}\)) was measured using a top-contact OFET technique.\(^{[56]}\) The mobility of the polymers were found to be \(4.0\times10^{-7}\) and \(<10^{-8}\) cm\(^2\)/(V·s) for P(2ADN) and P(3ADQ), respectively (see Table 3.4). The low mobility indicated only minimum or partial \(\pi-\pi\) stacking between adjacent the 2ADN and 3ADQ moieties in their polymers. The results are in consistent with the PL observation that the polymers preserved similar PL characteristics in comparison with its small molecule. In addition, red-shift in PL max (and broadening of the full width at half maximum (FWHM)) between the small molecules and the polymers are even smaller in solid-state than in solution (see Table 3.3). The exception low mobility
for 3MADQ and P(3ADQ) could further be explained by the polar ADQ moieties can readily absorb moisture which are known traps for charges (especially for electrons).

Figure 3.11 CV of 2MADN and 3MADQ in ACN, and P(2ADN) and P(3ADQ) thin film cast on the Pt working electrode.

Table 3.4 Electrochemical and electrical properties of 2MADN, 3MADQ, P(2ADN) and P(3ADQ).

<table>
<thead>
<tr>
<th>Materials</th>
<th>$E_{1/2}^{ox}$ (V, ferrocene) $^a$</th>
<th>$E_{onset}^{ox}$ (V, sample) $^a$</th>
<th>HOMO (eV) $^b$</th>
<th>UV-Vis absorption onset (nm)</th>
<th>$E_g$ (eV)</th>
<th>LUMO (eV) $^c$</th>
<th>$\mu_{hole}$ (cm$^2$/V·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2MADN</td>
<td>0.46</td>
<td>1.15</td>
<td>-5.49</td>
<td>416.5</td>
<td>2.98</td>
<td>-2.51</td>
<td>6.5×10$^{-4}$</td>
</tr>
<tr>
<td>P(2ADN)</td>
<td>0.46</td>
<td>1.18</td>
<td>-5.52</td>
<td>426.5</td>
<td>2.91</td>
<td>-2.61</td>
<td>4.0×10$^{-7}$</td>
</tr>
<tr>
<td>3MADQ</td>
<td>0.46</td>
<td>1.24</td>
<td>-5.58</td>
<td>421.0</td>
<td>2.95</td>
<td>-2.63</td>
<td>10$^{-8}$</td>
</tr>
<tr>
<td>P(3ADQ)</td>
<td>0.46</td>
<td>1.21</td>
<td>-5.55</td>
<td>430.0</td>
<td>2.88</td>
<td>-2.67</td>
<td>&lt; 10$^{-8}$</td>
</tr>
</tbody>
</table>

$^a$ Oxidation potentials were measured in 0.1 M TBAPF$_6$ ACN solution relative to Ag/AgCl electrode.

$^b$ Assuming the HOMO of ferrocene is -4.8 eV.

$^c$ The LUMO was obtained by subtracting the HOMO from the band-gap energy which was deduced from the UV-Vis absorption onset.

d) The hole mobility was measured using a top-contact OFET method with MoO$_3$/Au as the contact electrodes. The small molecules were evaporated onto a PS dielectric layer and the polymers were spin coated on a SiO$_2$ layer.
3.4 Conclusions

Two blue fluorescent polymers $P(2\text{ADN})$ and $P(3\text{ADQ})$ were synthesized successfully using free radical solution addition polymerization. Both $P(2\text{ADN})$ and $P(3\text{ADQ})$ have excellent solubilities in common organic solvents compared to another blue emitting polymer poly(2-vinylanthracene) with 9,10-di(1-naphthalenyl) substituent. $P(3\text{ADQ})$ is also found to be dissolved in polar solvent including ethanol water (v/v = 1/1) mixture. $P(2\text{ADN})$ and $P(3\text{ADQ})$ are both amorphous and possess excellent thermal stabilities as well as a longer PL life time than that of their model molecules $2\text{MADN}$ and $3\text{MADQ}$. The quantum efficiencies of the polymers $P(2\text{ADN})$ and $P(3\text{ADQ})$, however, are 41% and 46% smaller than that of $2\text{MADN}$ and $3\text{MADQ}$, respectively. Both polymers have similar band-gap energy while their LUMO/HOMO is lightly lower for $P(3\text{ADQ})$ compared to $P(2\text{ADN})$. Only a slight red-shift in the absorption and emission spectra of both the polymers $P(2\text{ADN})$ and $P(3\text{ADQ})$ was found in comparison with their model compounds suggesting slight $\pi$-$\pi$ interaction between adjacent pendant ADN (or ADQ) moieties in the polymer chains. The CIE coordinates ($x = 0.15, y = 0.10$ for $P(2\text{ADN})$; $x = 0.15, y = 0.13$ for $P(3\text{ADQ})$) remained closed to the values required for a true blue display color.

The preliminary study on the electroluminescent of the polymers was rather weak as explained by their poor mobility. The wide band-gap polymers, however, can be used as a host for a range of dopants emitters that need further investigation. The $3\text{MADQ}$ and $P(3\text{ADQ})$ also shown to have remarkable pH sensitivity, suggesting their applications in pH and environmental monitoring.

3.5 References


[14] Jun Liu, Laju Bu, Jinpeng Dong, Quanguo Zhou, Yanhou Geng, Dongge


[34] Qin Xue, Shiming Zhang, Guohua Xie, Zhensong Zhang, Yang Luo, Li Zhao, Ping Chen, Yi Zhao, Shiyong Liu, Thin Solid Films, 2011. 519: 3816.


[38] Abhishek P. Kulkarni, Christopher J. Tonzola, Amit Babel, Samson A.


Chapter 4

Blue Fluorescent Conductive Homopolymer

Poly(9,10-di(1-naphthalenyl)-2-vinylanthracene) and Its Highly Soluble Copolymers with Styrene or 9-Vinyl Carbazole

4.1 Introduction

Over the past decade, as the light emitting materials, conductive polymers have received considerable interests in the polymer electroluminescent device field,\textsuperscript{[1-9]} especially the true blue light conductive polymer.\textsuperscript{[10-13]} Simultaneously, the tremendous research effort has been concentrated in the development of blue light small molecule materials.\textsuperscript{[14-17]} One of the majority blue emitters is 9,10-di(2-naphthalenyl)anthracene (ADN) which was firstly developed by Shi and coworkers at Kodak in 2002 by utilizing the ADN as the blue host and 2,5,8,11-tetra(t-butyl)-perylene (TBP) as the dopant to generate a deep blue emission of CIE\textsubscript{x,y} (0.154, 0.232).\textsuperscript{[18]} However, though ADN showed good luminescence property and thermal stability either as the host \textsuperscript{[19-21]} or the dopant material,\textsuperscript{[22]} when the ADN thin film was exposed under a high annealing temperature or a prolonged electrical stress, it was morphologically unstable and tended to re-crystallize.\textsuperscript{[23]} In 2004, based on the ADN molecule, Chen and co-workers designed a blue host material 2-methyl-9,10-di(2-naphthyl)anthracene, which bears a small additional methyl substituent at C-2 position of the anthracene core with the purpose of disrupting the symmetry of ADN and
enhancing the morphological stability and color purity.\textsuperscript{[24]} The 2-methyl-9,10-di(2-napthyl)anthracene thin-film was shown to have more robust morphological stability although with a lower luminance efficiency of 2.2 cd/A at 20 mA/cm\textsuperscript{2} and a saturated blue CIE\textsubscript{x,y} (0.15, 0.12) compared to that of ADN.\textsuperscript{[25]}

However, because of the inherent mechanical weaknesses for small molecule materials, the problematic re-crystallization phenomenon under high thermal stress still persisted for the well designed 2-methyl-9,10-di(2-napthyl)anthracene and the requirements of the higher cost vacuum thin film deposition method was also needed further improvement targeted in the light-emitting diode (OLED) applications.\textsuperscript{[26-31]} Recently, besides of the ADN derivatives, several other kinds of anthracene derivatives with high T\textsubscript{g} have already been reported.\textsuperscript{[32-34]} With tetraphenylsilane as the core, Lyu et al. \textsuperscript{[32]} have successfully developed a series of high T\textsubscript{g} silicon-cored anthracene derivatives as the blue host materials for OLEDs, such as bis(3-anthracen-9-yl-phenyl) diphenylsilane, bis[3-(10-phenylanthracen-9-yl) phenyl]diphenylsilane and bis[3-(10-naphthalen-2-yl-anthracen-9-yl)phenyl] diphenylsilane. With the addition of a spiro linkage into the structure, Shen et al. \textsuperscript{[33]} have reported another kind of anthracene derivative 2,2’-bis(10-phenylanthracen-9-yl)-9,9’-spi-robiﬂuorene (Spiro-FPA) to reduce the crystallization tendency and increase the T\textsubscript{g} to the monomeric units. When Spiro-FPA was used as the host, the devices exhibit a highly efficient blue electroluminescence with a high external quantum efficiency of more than 7\%.\textsuperscript{[34]} Besides introducing the special molecular structure into the anthracene derivatives, most of the inherent problems suggested above can also be eliminated when the functional moieties were covalently attached to a vinyl monomer and polymerized into homopolymer or copolymer. Beside this, in order to improve the solubility
and the photoluminescent property of the polymer, styrene and/or 9-vinyl carbazole were chosen as the second monomers in the copolymerization system.

In the present article, with the goals of disrupting the symmetry for recrystallization and eliminating the chance of phase separation of the dopant from the matrix and at the same time without significantly altering the electrical (LUMO/HOMO) and optical properties (CIE<sub>x,y</sub>), a new vinyl monomer of Vinyl-ADN and its homopolymer P(ADN) was synthesized. A series of soluble conductive vinyl copolymers containing ADN moiety, S and/or VK at different composition ratios were also prepared in good yields by free radical solution polymerization. Details of synthesis and the characterizations of the homopolymer and copolymers are described in this contribution.

### 4.2 Experimental

#### 4.2.1 Materials and instruments

All reactions were carried out under nitrogen atmosphere with the use of standard Schlenk techniques unless specified otherwise. Glass wares were oven-dried at ca 120 °C. Analytical grade solvents were purified by distillation over appropriate drying agents under an inert nitrogen atmosphere prior to use. All other reagents and chemicals were used as-received without further purification. The operations of all the reactions and equipments were same to that mentioned in the Chapter 2, except the CV measurement. The CV measurements of the small molecule was performed on a BAS CV-50W electrochemical analyzer at room temperature using a three-electrode cell configuration in 0.1 M TBAPF<sub>6</sub> DCM solution, while the polymers measurements were coated on electrode and carried out in ACN solution.
4.2.2 Synthesis

The synthesis pathway for the monomer and the copolymers $P(\text{ADN-co-S})$ and $P(\text{ADN-co-VK})$ are shown in **Scheme 4.1**, respectively. Details on the reaction procedure of the monomer Vinyl-ADN has been given in the section **Synthesis 2.2.2** (Chapter 2).
Scheme 4.1  Synthetic routes for the monomer of Vinyl-ADN and its copolymers P(ADN-co-S) and P(ADN-co-VK).

To a single-mouth Schlenk reaction tube charged with a stirrer bar, the respective vinyl-monomers with different feed ratio (total = 1.1 mmol) of Vinyl-ADN and VK or S, and azobisisobutyronitrile (3.6 mg, 0.02 mmol) was dissolved in 1.0 mL dried toluene. The reaction mixture was degassed by freeze-pump-thaw cycles and then sealed off. The reaction mixture was stirred at 80 °C for 10 h. Finally, a gel was resulted. The polymer was further purified by re-dissolving in THF and re-precipitated in excess acetone to produce a white solid in 60.1-70.8% yields.

4.3 Results and discussion

4.3.1  Structure characterization of the homopolymers and copolymers

All the new compounds and polymers were characterized by common
spectroscopic techniques including $^1$H NMR spectroscopy, $^{13}$C NMR spectroscopy and MS spectrometry. The $^1$H-NMR spectrum of Vinyl-ADN was shown in Figure 4.1. The signals of the olefinic protons were located at 5.17, 5.67 and 6.58 ppm. The homopolymer PS and the copolymer P(ADN-co-S 1:6) were shown in Figure 4.2 and 4.3, respectively. The chemical shifts around 6.00-8.00 ppm are attributed to the aromatic ring protons. The $^1$H NMR spectra of the homopolymer PVK and the copolymer of P (ADN-co-VK 1:6) show a distinct signal at 4.86 ppm corresponding to the aromatic ring of the carbazole unit proton 1 (Figure 4.4 and 4.5). [35-37]

![Figure 4.1 $^1$H NMR spectrum (DMSO-d) of the monomer Vinyl-ADN.](image)
Figure 4.2 $^1$H NMR spectrum (CDCl$_3$-d) of the homopolymer PS.

Figure 4.3 $^1$H NMR spectrum (CDCl$_3$-d) of the copolymer P(ADN-co-S 1:6).
Figure 4.4 $^1$H NMR spectrum (CDCl$_3$-d) of the homopolymer PVK.

Figure 4.5 $^1$H NMR spectrum (CDCl$_3$-d) of the copolymer P(ADN-co-VK 1:6).

Solid-state FT-IR measurements were also performed for the confirmation of
the chemical structures of P(ADN), PS & PVK and the copolymers P(ADN-co-S) & P(ADN-co-VK) (Figure 4.6 and 4.7).

The FT-IR spectra for P(ADN) has the following structural attributes: 3055 cm\(^{-1}\) (\(\nu\), aromatic C-H stretching), 2919 cm\(^{-1}\) (\(\nu\), sp\(^3\) C-H stretching), 1622-1254 cm\(^{-1}\) (\(\nu\), aromatic C=C stretching; \(\delta\), sp\(^3\) C-H deformation), 798, 776, 758 cm\(^{-1}\) (\(\delta\), C-H out of plane deformation) (Figure 4.6 and 4.7). The common features of PS are attributed to the following structures/moieties: 3026 cm\(^{-1}\) (\(\nu\), aromatic C-H stretching), 2922 cm\(^{-1}\) (\(\nu\), sp\(^3\) C-H stretching), 1602 cm\(^{-1}\), 1492 cm\(^{-1}\) (\(\nu\), aromatic C=C stretching), 1452 cm\(^{-1}\), 1372 cm\(^{-1}\) (\(\delta\), sp\(^3\) C-H deformation), 756 cm\(^{-1}\), 698 cm\(^{-1}\) (\(\delta\), C-H out of plane deformation) (Figure 4.6). The FT-IR spectra peaks belonged to the structures of PVK are listed as following: 3046 cm\(^{-1}\) (\(\nu\), aromatic C-H stretching), 2926 cm\(^{-1}\) (\(\nu\), sp\(^3\) C-H stretching), 1624 cm\(^{-1}\) (\(\nu\), aromatic C=C stretching), 1596 cm\(^{-1}\) (\(\nu\), sp\(^3\) C-H deformation), 1484 cm\(^{-1}\) (\(\delta\), sp\(^3\) C-H deformation), 1452 cm\(^{-1}\) (aromatic cycle of VK moiety), 1326 cm\(^{-1}\) (\(\delta\), deformation of vinylidene groups), 1220 cm\(^{-1}\) (\(\nu\), C-N stretching), 1156 cm\(^{-1}\) (\(\delta\), C-H deformation), 744 cm\(^{-1}\), 720 cm\(^{-1}\) (\(\delta\), C-H out of plane deformation) (Figure 4.7). As expected, the P(ADN-co-S) series copolymers showed all the distinct peaks of PS and P(ADN) while with a little shift. The transmittances of these peaks varied with the differences of the corresponding compositions. The similar phenomenon could also be found in the P(ADN-co-VK) series copolymers.
4.3.2 Molecular weights of the polymers

The molecular weights of the copolymers were determined by GPC against
polystyrene molecular weight (MW) standards (MW = 1,350 (PDI = 1.03), 28,000 (PDI = 1.01), 87,000 (PDI = 1.02) and 410,000 (PDI = 1.03)) for calibration. The results are shown in Figure 4.8 and Figure 4.9. The calculated results were listed in Table 4.1. The results revealed the P(ADN-co-S) copolymers have $M_n$ ranging from 9,700 to 18,900, and the P(ADN-co-VK) copolymers have $M_n$ ranging from 9,800 to 22,100. All of the copolymers have high polydispersity indexes (PDI), which could be due to the chain-transfer reaction in the polymerization process.

![Figure 4.8](image.png)

**Figure 4.8**  GPC chromatogram of P(ADN-co-S), recorded at 254 nm with the flow rate of 1 mL/min.
Figure 4.9  GPC chromatogram of P(ADN-co-VK), recorded at 254 nm with the flow rate of 1 mL/min.

Table 4.1 Yields, molecular weights and PDIs of the copolymers.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Yield (%)</th>
<th>$M_n$ a)</th>
<th>$M_w$ a)</th>
<th>PDI a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(ADN)</td>
<td>68</td>
<td>29,100</td>
<td>61,200</td>
<td>2.1</td>
</tr>
<tr>
<td>P(ADN-co-S 2:1)</td>
<td>58</td>
<td>18,900</td>
<td>49,300</td>
<td>2.6</td>
</tr>
<tr>
<td>P(ADN-co-S 1:1)</td>
<td>60</td>
<td>15,200</td>
<td>38,000</td>
<td>2.5</td>
</tr>
<tr>
<td>P(ADN-co-S 1:2)</td>
<td>63</td>
<td>9,700</td>
<td>21,500</td>
<td>2.2</td>
</tr>
<tr>
<td>P(ADN-co-S 1:6)</td>
<td>58</td>
<td>16,100</td>
<td>22,600</td>
<td>1.4</td>
</tr>
<tr>
<td>PS</td>
<td>69</td>
<td>11,800</td>
<td>21,200</td>
<td>1.8</td>
</tr>
<tr>
<td>P(ADN-co-VK 2:1)</td>
<td>51</td>
<td>11,600</td>
<td>26,800</td>
<td>2.3</td>
</tr>
<tr>
<td>P(ADN-co-VK 1:1)</td>
<td>43</td>
<td>9,800</td>
<td>23,500</td>
<td>2.4</td>
</tr>
<tr>
<td>P(ADN-co-VK 1:2)</td>
<td>59</td>
<td>11,800</td>
<td>24,800</td>
<td>2.1</td>
</tr>
<tr>
<td>P(ADN-co-VK 1:6)</td>
<td>63</td>
<td>22,100</td>
<td>57,500</td>
<td>2.6</td>
</tr>
<tr>
<td>PVK</td>
<td>67</td>
<td>42,700</td>
<td>89,600</td>
<td>2.1</td>
</tr>
</tbody>
</table>

a) The weight-averaged ($M_w$) and number-averaged ($M_n$) molecular weights were determined by GPC using PS MW standards. Conditions: wavelength 254 nm (UV-Vis detector), flow rate 1 mL/min, mobile phase THF.
4.3.3 Composition of the copolymers

The composition of the monomers incorporated in each copolymer was estimated from the absorbance associated with repeat unit herein. The content of ADN unit was calibrated with $P(\text{ADN})$ ($\lambda_{\text{max}} = 380 \text{ nm}$). The content of styrene or carbazole unit was calculated by subtracting the content of ADN unit from the total content. The composition result was list in Table 4.2.

### Table 4.2 Compositions of the copolymers.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>ADN (Feed, $f_1$)</th>
<th>S/VK (Feed, $f_2$)</th>
<th>ADN $^a$) $F_1$ (mole ratio)</th>
<th>S/VK $^a$) $F_2$ (mole ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P(\text{ADN})$</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>$P(\text{ADN-co-S 2:1})$</td>
<td>0.67</td>
<td>0.33</td>
<td>0.63</td>
<td>0.37</td>
</tr>
<tr>
<td>$P(\text{ADN-co-S 1:1})$</td>
<td>0.50</td>
<td>0.50</td>
<td>0.49</td>
<td>0.51</td>
</tr>
<tr>
<td>$P(\text{ADN-co-S 1:2})$</td>
<td>0.33</td>
<td>0.67</td>
<td>0.35</td>
<td>0.65</td>
</tr>
<tr>
<td>$P(\text{ADN-co-S 1:6})$</td>
<td>0.14</td>
<td>0.86</td>
<td>0.18</td>
<td>0.82</td>
</tr>
<tr>
<td>PS</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>$P(\text{ADN-co-VK 2:1})$</td>
<td>0.67</td>
<td>0.33</td>
<td>0.64</td>
<td>0.36</td>
</tr>
<tr>
<td>$P(\text{ADN-co-VK 1:1})$</td>
<td>0.50</td>
<td>0.50</td>
<td>0.45</td>
<td>0.55</td>
</tr>
<tr>
<td>$P(\text{ADN-co-VK 1:2})$</td>
<td>0.33</td>
<td>0.67</td>
<td>0.30</td>
<td>0.70</td>
</tr>
<tr>
<td>$P(\text{ADN-co-VK 1:6})$</td>
<td>0.14</td>
<td>0.86</td>
<td>0.12</td>
<td>0.88</td>
</tr>
<tr>
<td>PVK</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

$^a$ The composition of the copolymers was determined by UV-Vis spectroscopy. (Extinction coefficients (M$^{-1}$·cm$^{-1}$) of $P(\text{ADN})$ are 9547.2 (380 nm).

4.3.4 Solubilities of the polymers

The polymer solubility results were listed in Table 4.3. In comparison with the homopolymer $P(\text{ADN})$, both $P(\text{ADN-co-S})$ and $P(\text{ADN-co-VK})$ showed better solubilities and were found to be soluble in common organic solvents, such
as THF, CHCl₃, DCM, toluene, and so on. With the increase of the VK/S ratio, both of the P(ADN-co-S) and P(ADN-co-VK) copolymers became more soluble. Compared to the P(ADN-co-VK) copolymers, P(ADN-co-S) copolymers showed even better solubilities. This may be attributed to the addition of the high soluble S and/or VK moieties in the copolymer main chains than those of ADN units in P(ADN).

### Table 4.3 Solubilities of the polymers.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Completely dissolved</th>
<th>Incompletely dissolved</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(ADN)</td>
<td>1,1,1,2,-tetrachlorethane (TCE)</td>
<td>DCM, CHCl₃, THF, Toluene, ACN</td>
</tr>
<tr>
<td>P(ADN-co-S 2:1)</td>
<td>TCE, CHCl₃, THF, Toluene</td>
<td>DCM, ACN</td>
</tr>
<tr>
<td>P(ADN-co-S 1:1)</td>
<td>TCE, CHCl₃, THF, Toluene</td>
<td>DCM, ACN</td>
</tr>
<tr>
<td>P(ADN-co-S 1:2)</td>
<td>TCE, DCM, CHCl₃, THF, Toluene</td>
<td>ACN</td>
</tr>
<tr>
<td>P(ADN-co-S 1:6)</td>
<td>TCE, DCM, CHCl₃, THF, Toluene</td>
<td>ACN</td>
</tr>
<tr>
<td>PS</td>
<td>TCE, DCM, CHCl₃, THF, Toluene</td>
<td>ACN</td>
</tr>
<tr>
<td>P(ADN-co-VK 2:1)</td>
<td>TCE, THF, Toluene</td>
<td>DCM, CHCl₃, ACN</td>
</tr>
<tr>
<td>P(ADN-co-VK 1:1)</td>
<td>TCE, THF, Toluene</td>
<td>DCM, CHCl₃, ACN</td>
</tr>
<tr>
<td>P(ADN-co-VK 1:2)</td>
<td>TCE, THF, Toluene</td>
<td>DCM, CHCl₃, ACN</td>
</tr>
<tr>
<td>P(ADN-co-VK 1:6)</td>
<td>TCE, THF, Toluene, DCM, CHCl₃</td>
<td>ACN</td>
</tr>
<tr>
<td>PVK</td>
<td>TCE, DCM, CHCl₃, THF, Toluene</td>
<td>ACN</td>
</tr>
</tbody>
</table>

### 4.3.5 Thermal properties of the copolymers

The thermal properties of the homopolymers and copolymers were examined by TGA (Figure 4.10 and 4.11) and DSC (Figure 4.12 and 4.14). The onset degradation temperature (Tᵈ) and the glass transition mid-point temperature (Tᵣ) were determined respectively. The values of Tᵣ and Tᵈ for the copolymers are summarized in Table 4.4. The Tᵣ of PS was only 102 °C. The copolymers
$P(\text{ADN-co-S})$ exhibited high $T_d$ from 384 °C to 390 °C. The $T_g$ of the copolymers were from 203 °C to 223 °C. The $T_d$ of $P(\text{ADN-co-VK})$ were in the range of 388 °C to 474 °C, and $T_g$ 236 °C to 237 °C.

**Figure 4.13** and **4.15** showed the experimentally observed $T_g$ values compared with prediction from the Fox equation, shown substantial positive deviation. The positive deviations suggested the interactions of ADN & styrene and ADN & VK repeating units were both positive/attractive effects. The data revealed our copolymers had good thermal stability which is essential for OLED application.

**Table 4.4** Thermal properties of the copolymers.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Onset $T_d$ (°C)</th>
<th>Weight lost (%)</th>
<th>Midpoint $T_g$ (°C)</th>
<th>$\Delta C_p$ (J/g·°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P(\text{ADN})$</td>
<td>396</td>
<td>48</td>
<td>237</td>
<td>0.23</td>
</tr>
<tr>
<td>$P(\text{ADN-co-S 2:1})$</td>
<td>390</td>
<td>40</td>
<td>223</td>
<td>0.22</td>
</tr>
<tr>
<td>$P(\text{ADN-co-S 1:1})$</td>
<td>388</td>
<td>51</td>
<td>219</td>
<td>0.21</td>
</tr>
<tr>
<td>$P(\text{ADN-co-S 1:2})$</td>
<td>384</td>
<td>63</td>
<td>215</td>
<td>0.20</td>
</tr>
<tr>
<td>$P(\text{ADN-co-S 1:6})$</td>
<td>388</td>
<td>69</td>
<td>203</td>
<td>0.19</td>
</tr>
<tr>
<td>PS</td>
<td>364</td>
<td>100</td>
<td>102</td>
<td>0.15</td>
</tr>
<tr>
<td>$P(\text{ADN-co-VK 2:1})$</td>
<td>388</td>
<td>47</td>
<td>237</td>
<td>0.21</td>
</tr>
<tr>
<td>$P(\text{ADN-co-VK 1:1})$</td>
<td>399</td>
<td>48</td>
<td>237</td>
<td>0.19</td>
</tr>
<tr>
<td>$P(\text{ADN-co-VK 1:2})$</td>
<td>420</td>
<td>75</td>
<td>236</td>
<td>0.17</td>
</tr>
<tr>
<td>$P(\text{ADN-co-VK 1:6})$</td>
<td>438</td>
<td>86</td>
<td>236</td>
<td>0.15</td>
</tr>
<tr>
<td>PVK</td>
<td>464</td>
<td>94</td>
<td>229</td>
<td>0.12</td>
</tr>
</tbody>
</table>

a) About 5 mg samples were measured by TGA under nitrogen purge at a heating rate: 20 °C·min$^{-1}$.

b) About 20 mg samples were measured by DSC under nitrogen purge at a heating rate: 40 °C·min$^{-1}$.

c) The difference of specific heat capacity ($\Delta C_p$ J/g·°C).
Figure 4.10   TGA thermograms of the copolymers P(ADN-co-VK) at different mole feed ratios under the heating rate of 20 °C/min.

Figure 4.11   TGA thermograms of the copolymers P(ADN-co-S) at different mole feed ratios under the heating rate of 20 °C/min.
Figure 4.12  DSC thermograms of the copolymers P(ADN-co-S) at different mole feed ratios under the scanning rate of 40 °C/min.

Figure 4.13  Variation of $T_g$ with the compositions of the copolymers P(ADN-co-S). Experimental data are shown as the solid circles; Fox equation was shown as the dashed line.
Figure 4.14  DSC thermograms of the copolymers P(ADN-co-VK) at different mole feed ratios under the scanning rate of 40 °C/min.

Figure 4.15  Variation of T\text{g} with the compositions of the copolymers P(ADN-co-VK). Experimental data are shown as the solid circles; Fox equation was shown as the dashed line.
4.3.6 Optical characteristics of the copolymers

The absorption and emission spectra of the small molecule MADN, monomer Vinyl-ADN and homopolymer P(ADN) were displayed in Figure 4.16 and 4.17. Four prominent bands of MADN could be observed at 341, 357, 376 and 396 nm. However, similar four absorption bands of Vinyl-ADN and P(ADN) showed small red-shifts compared to the MADN. In addition, P(ADN) showed even higher red-shift than that of Vinyl-ADN. MADN has indigo emission maxima at 409 and 429.5 nm, while Vinyl-ADN showed a broad emission around 428 nm. The PL results showed there were a slight red-shift for P(ADN) (14 nm) compared to MADN. When the methyl group of MADN was substituted by the vinyl groups, the PL lifetime (τ) increased slightly. P(ADN) showed even higher lifetime than Vinyl-ADN (Figure 4.20). Vinyl-ADN and P(ADN) showed the similar fluorescence quantum yield and were both lower that of the small molecule MADN. In addition, no PL differences could be found when P(ADN) in different solvents (Figure 4.24).

The absorption and emission spectra of the P(ADN-co-S) copolymers were displayed in Figure 4.17. All the copolymers exhibited very similar absorption features with P(ADN), which displayed four prominent bands at 341, 358, 379 and 401 nm attributed to the \( \pi \rightarrow \pi^* \) transition arising from the ADN moiety. The PL results showed, with the increasing ratio of styrene moiety in copolymers, there were a slightly increasing blue-shift for P(ADN-co-S) (4-8 nm) compared to P(ADN). This can be attributed to the decrease of the \( \pi-\pi \) stacking caused by the addition of styrene moieties in the copolymers. The fluorescence decay of the P(ADN-co-S) copolymers was found to be a single-exponential, with the τ ranging from 6.8 to 7.9 ns (Figure 4.20). The lifetimes of the copolymers were all
slightly lower than that of homopolymer P(ADN) (8.4 ns). The fluorescence quantum yields of the P(ADN-co-S) copolymers were range from 0.32 to 0.57. When the styrene units increased in the copolymer, the copolymer lifetime didn’t increase notably, while the quantum efficiency showed an overall increasing tendency. This might be attributed to the increasing of styrene units in copolymers resulted in the decreasing concentration of the ADN moieties, which will decrease the fluorescence quenching effectively (Figure 4.21).

The absorption and PL spectra of VK and PVK were shown in Figure 4.18. The maximum absorptions of VK are 326 and 339 nm, which is originated from the \( \pi \rightarrow \pi^* \) electronic transitions. After the polymerization, the maximum absorptions of VK slightly increased to 328 and 343 nm, respectively. The VK has sharp emission maxima at 349 and 363.5 nm but PVK has a broad emission around 372.5 nm. This indicated that \( \pi-\pi \) stacking of VK moieties resulted in the formation of exciplexes. PVK exhibited a longer lifetime (11.1 ns) than that of VK (8.0 ns) (Figure 4.22). The fluorescence quantum yields of the homopolymer PVK was much lower than that of the monomer VK.

The prominent absorbance bands of all the P(ADN-co-VK) series copolymers could be observed at 328, 343, 361, 380, 401 nm (Figure 4.18). The bands centered at 328 and 343 nm were dominantly attributed to the \( \pi \rightarrow \pi^* \) transition of VK moieties in the copolymers, while the band at 361, 380 and 401 nm were belonged to the \( \pi \rightarrow \pi^* \) transition arising from the ADN moieties. When the ratio of VK increased in P(ADN-co-VK), a gradually shift of emission wavelengths was observed. The photoluminescence spectrum of VK overlapped significantly with the absorption spectrum of ADN indicating possibility of energy transfer from PVK to P(ADN). This can be proved by the much smaller emission of VK
moiety in P(ADN-co-VK) than that of in the mixtures of P(ADN) and PVK with the same ratio to the copolymer (Figure 4.19). This phenomenon indicated that most of the VK moiety emission in the copolymers had been absorbed by ADN units. The lifetime of the copolymers increased from 7.8 to 8.8 ns with the increase in VK contents (Figure 4.24). On the contrary, the quantum efficiencies of the copolymers decreased with the increase of VK fraction (Figure 4.23). Furthermore, with different excitations, the PL peaks of P(ADN-co-VK 1:6) have the same wavelength, only the intensity change with the intensity of absorbance at the excitation wavelength (Figure 4.25).

A summary of optical properties of the small molecule MADN, the monomers and the polymers was listed in Table 4.5.

Figure 4.16  Optical absorption and PL spectra of MADN, Vinyl-ADN and P(ADN).
Figure 4.17  Optical absorption and PL spectra of P(ADN-co-S).

Figure 4.18  Optical absorption and PL spectra of P(ADN-co-VK).
Figure 4.19  PL spectra of P(ADN)/PVK mixture and P(ADN-co-VK) of at corresponding ratio.

Figure 4.20  Life time spectra of the copolymers P(ADN-co-S).
Figure 4.21  Relationship of $\tau$ and $\Phi_{FL}$ with compositions of the copolymers P(ADN-co-S).

Figure 4.22  Life time spectra of the copolymers P(ADN-co-VK).
Figure 4.23  Relationship of $\tau$ and $\Phi_{FL}$ with compositions of the copolymers P(ADN-co-VK).

Figure 4.24  PL spectrum of the homopolymer P(ADN) in different solvent.
Figure 4.25 PL spectrum of P(ADN-co-VK 1:6) with different excitation.

Table 4.5 Optical properties of the small molecule MADN, the monomers and the polymers in THF.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>$\lambda_{\text{max}}$ absorption maximum (nm)</th>
<th>$\lambda_{\text{max}}$ emission maximum (nm)</th>
<th>FWHM (nm)</th>
<th>Life time (ns)</th>
<th>Quantum efficiencies</th>
<th>PL CIE (x, y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MADN</td>
<td>341, 357, 376, 396</td>
<td>409, 429.5</td>
<td>47.5</td>
<td>5.97</td>
<td>0.60</td>
<td>0.15, 0.03</td>
</tr>
<tr>
<td>Vinyl-ADN</td>
<td>341, 358, 379, 401</td>
<td>428</td>
<td>55</td>
<td>6.25</td>
<td>0.43</td>
<td>0.15, 0.04</td>
</tr>
<tr>
<td>P(ADN)</td>
<td>344, 361, 380, 401</td>
<td>423, 442</td>
<td>56</td>
<td>8.40</td>
<td>0.40</td>
<td>0.15, 0.04</td>
</tr>
<tr>
<td>P(ADN-co-S 2:1)</td>
<td>360, 380, 401</td>
<td>422.5, 438</td>
<td>57</td>
<td>6.93</td>
<td>0.42</td>
<td>0.15, 0.05</td>
</tr>
<tr>
<td>P(ADN-co-S 1:1)</td>
<td>360, 380, 400</td>
<td>412.5, 440</td>
<td>55</td>
<td>7.91</td>
<td>0.45</td>
<td>0.15, 0.04</td>
</tr>
<tr>
<td>P(ADN-co-S 1:2)</td>
<td>360, 378, 399</td>
<td>418.5, 436</td>
<td>56</td>
<td>6.82</td>
<td>0.52</td>
<td>0.15, 0.04</td>
</tr>
<tr>
<td>P(ADN-co-S 1:6)</td>
<td>342, 359, 378, 399</td>
<td>418.5, 434</td>
<td>54</td>
<td>7.34</td>
<td>0.58</td>
<td>0.15, 0.04</td>
</tr>
<tr>
<td>PS</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>P(ADN-co-VK 2:1)</td>
<td>362, 381, 402</td>
<td>424, 440</td>
<td>59</td>
<td>7.87</td>
<td>0.36</td>
<td>0.15, 0.05</td>
</tr>
<tr>
<td>P(ADN-co-VK 1:1)</td>
<td>328, 343, 361, 380, 401</td>
<td>421.5, 439.5</td>
<td>57.5</td>
<td>7.79</td>
<td>0.31</td>
<td>0.15, 0.04</td>
</tr>
<tr>
<td>P(ADN-co-VK 1:2)</td>
<td>329, 343, 360, 380, 401</td>
<td>420.5, 433</td>
<td>57</td>
<td>8.58</td>
<td>0.24</td>
<td>0.15, 0.04</td>
</tr>
<tr>
<td>P(ADN-co-VK 1:6)</td>
<td>330, 343, 360, 380, 401</td>
<td>421.5, 434.5</td>
<td>55.5</td>
<td>8.75</td>
<td>0.19</td>
<td>0.15, 0.04</td>
</tr>
<tr>
<td>PVK</td>
<td>328, 343</td>
<td>372.5</td>
<td>70.5</td>
<td>11.10</td>
<td>0.07</td>
<td>0.16, 0.01</td>
</tr>
<tr>
<td>VK</td>
<td>326, 339</td>
<td>349, 363.5</td>
<td>34</td>
<td>8.02</td>
<td>0.30</td>
<td>0.17, 0.01</td>
</tr>
</tbody>
</table>
4.3.7 Electrochemical properties

As the polymers are electroluminescent, the ionization potential and redox stability of MADN, P(ADN), PVK, P(ADN-co-S) and P(ADN-co-VK) copolymers were studied using CV. The redox reversibility of the MADN is excellent, which could be proved by the repeated anodic oxidation and reduction (50 cycles) without changing the peak shape in the cyclic voltammogram (Figure 4.26). All the P(ADN-co-S) series copolymers had similar the first oxidation wave to the homopolymer P(ADN), which should be owe to the copolymers are oxidized at ADN (Figure 4.27). In general, with the increasing styrene contents, the HOMO of P(ADN-co-S) copolymers increased from -5.73 eV to -5.58 eV. The first oxidation wave of the copolymer P(ADN-co-VK) occurred at potentials from +1.28 to +1.46 V and these oxidation potentials give HOMO values ranging from -5.61 to -5.73 eV for all copolymers. The band gaps of the copolymers were all about 2.96 eV, which were all smaller than that of MADN (3.04 eV) and PVK (3.54 eV) (Figure 4.28, Table 4.6).

![Figure 4.26 50 cycles CV diagram of the small molecule MADN in DCM.](image)
Figure 4.27  CV diagrams of the copolymers P(ADN-co-S) in ACN.

Figure 4.28  CV diagram of the copolymers P(ADN-co-VK) in ACN.
Table 4.6 Electrochemical properties of the small molecule MADN and the polymers.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$E_{1/2}^{ox}$ (V, ferrocene) $^a$</th>
<th>$E_{1/2}^{ox}$ (V, sample) $^b$</th>
<th>HOMO (eV) $^c$</th>
<th>LUMO (eV) $^d$</th>
<th>$E_g$ (eV)</th>
<th>UV-vis absorption onset (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MADN</td>
<td>0.57</td>
<td>1.32</td>
<td>-5.55</td>
<td>-2.51</td>
<td>3.04</td>
<td>408.5</td>
</tr>
<tr>
<td>P(ADN)</td>
<td>0.47</td>
<td>1.38</td>
<td>-5.71</td>
<td>-2.75</td>
<td>2.96</td>
<td>418.8</td>
</tr>
<tr>
<td>P(ADN-co-S 2:1)</td>
<td>0.47</td>
<td>1.40</td>
<td>-5.73</td>
<td>-2.76</td>
<td>2.97</td>
<td>417.3</td>
</tr>
<tr>
<td>P(ADN-co-S 1:1)</td>
<td>0.47</td>
<td>1.36</td>
<td>-5.69</td>
<td>-2.71</td>
<td>2.98</td>
<td>416.8</td>
</tr>
<tr>
<td>P(ADN-co-S 1:2)</td>
<td>0.54</td>
<td>1.36</td>
<td>-5.62</td>
<td>-2.64</td>
<td>2.98</td>
<td>416.2</td>
</tr>
<tr>
<td>P(ADN-co-S 1:6)</td>
<td>0.57</td>
<td>1.35</td>
<td>-5.58</td>
<td>-2.59</td>
<td>2.99</td>
<td>414.5</td>
</tr>
<tr>
<td>PS</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>P(ADN-co-VK 2:1)</td>
<td>0.47</td>
<td>1.39</td>
<td>-5.72</td>
<td>-2.76</td>
<td>2.97</td>
<td>418.1</td>
</tr>
<tr>
<td>P(ADN-co-VK 1:1)</td>
<td>0.47</td>
<td>1.40</td>
<td>-5.73</td>
<td>-2.76</td>
<td>2.97</td>
<td>417.6</td>
</tr>
<tr>
<td>P(ADN-co-VK 1:2)</td>
<td>0.47</td>
<td>1.28</td>
<td>-5.61</td>
<td>-2.64</td>
<td>2.97</td>
<td>417.4</td>
</tr>
<tr>
<td>P(ADN-co-VK 1:6)</td>
<td>0.47</td>
<td>1.39</td>
<td>-5.72</td>
<td>-2.74</td>
<td>2.97</td>
<td>417.0</td>
</tr>
<tr>
<td>PVK</td>
<td>0.47</td>
<td>1.28</td>
<td>-5.61</td>
<td>-2.08</td>
<td>3.53</td>
<td>351.6</td>
</tr>
</tbody>
</table>

$^a$ Oxidation potentials were measured in 0.1 M TBAPF$_6$ ACN solution with ferrocene as the internal standard.
$^b$ Versus Ag/AgCl electrode.
$^c$ Assuming the HOMO of ferrocene is -4.8 eV.
$^d$ Calculated from the band-gap which was deduced from the UV-vis absorption onset.

4.3.8 Electrical properties

Polymer light-emitting diode (PLED) devices based on the configurations ITO/MoO$_3$ (20 nm)/P(ADN)/LiF (1 nm)/Al (100 nm) has been fabricated. The J-V-L (current-voltage-luminescent) results for the devices are shown in Figure 4.29. The luminescence (cd/m$^2$) of the devices, however, was rather weak (ca 30-50 cd/m$^2$) even under a high biased voltage of 18 V. The deficiency was further investigated by measuring the mobility of the polymer.

The hole mobility ($\mu_{\text{hole}}$) was measured using a top-contact organic thin-film transistor (OTFT) technique.$^{[43]}$ The OTFT configuration is given in Figure 4.30.
The mobility of the polymer $\text{P(ADN)}$ was determined to be $4.7 \times 10^{-8} \text{ cm}^2/(\text{V} \cdot \text{s})$ compared to its model compound $\text{MADN}$ with $6.5 \times 10^{-4} \text{ cm}^2/(\text{V} \cdot \text{s})$. The low mobility indicated only minimum or partial $\pi-\pi$ stacking between the adjacent ADN moieties in the homopolymer. The result is also in consistent with the PL observation that $\text{P(ADN)}$ preserved similar PL characteristics in comparison with its small molecule ($\text{MADN}$). Further investigation is needed either to improve the mobility of the polymers or to employ the high band-gap polymers as a host layer for other conductive/emissive dopants.\cite{44-47}

![Graph](image)

**Figure 4.29** The current density vs voltage of the PLED device.

![Diagram](image)

**Figure 4.30** The structure of OTFT device used for the mobility measurement.
4.4 Conclusions

A new vinyl monomer Vinyl-ADN has been designed and synthesized in a high yield. A series of soluble true blue emitting fluorescent copolymers P(ADN-co-S) and P(ADN-co-VK) at different composition ratios have been prepared successfully by using free radical solution polymerization. In comparison with the small molecule MADN, the polymers were shown to have longer PL life times and narrower bandgaps. The quantum efficiencies of the copolymers P(ADN-co-S) are very similar to that of MADN and much higher than that of the homopolymer P(ADN). A slight red-shift in the absorption and emission spectra of the copolymer P(ADN-co-S) were found compared to MADN due to π-π interaction between adjacent pendant ADN moieties. However, notable energy transfer phenomena could be found in the copolymers P(ADN-co-VK). Both of the copolymers P(ADN-co-S) and P(ADN-co-VK) CIE coordinates (x = 0.15, y = 0.04~0.05) were closed to the required values for a true blue display hue. The preliminary study on the electroluminescent of P(ADN) was rather weak as explained by its poor mobility. The wide band-gap polymers, however, can be used as a host layer for a range of conductive dopants/emitters for EL applications.

4.5 References


[17] Jinhai Huang, BoXu, Mei-Ki Lam, Kok-Wai Cheah, Chin H. Chen,


[33] Wen-Jian Shen, Rajasekhar Dodda, Chang-Ching Wu, Fang-Iy Wu,


Chapter 5

Synthesis and Characterization of Greenish-blue Emitting Vinyl Copolymer Containing Pyrene and Triarylamine Moieties

5.1 Introduction

In recent years, considerable effort has been devoted in the design and synthesis of triarylamine derivatives for application in the highly efficient organic electroluminescent device field (OLED).\textsuperscript{[1-8]} Compared to their low molecular weight model compounds, triarylamine derivative bearing conductive polymers show good film forming capabilities,\textsuperscript{[9-11]} which may render them suitable for the fabrication of large area and flexible OLED by both spin coating and inkjet printing methods.\textsuperscript{[12-14]} Two types of triarylamine-based polymers have been reported: main-chain \textsuperscript{[5,15-24]} and side-chain triarylamine polymers.\textsuperscript{[25-35]} The side-chain polymers enjoy greater flexibility in tuning the physical, mechanical and rheological properties by simply varying the chemistry of the triarylamine moiety or by copolymerization with another kind of conducting/luminescent monomer at different compositions.

Pyrene and its derivatives had been widely used in the synthesis of emissive and charge transport materials for OLED applications because of their large π conjugated structures and coplanar aromatic groups.\textsuperscript{[36-41]} However, the major drawback of pyrene is the low fluorescence quantum yields (0.18). Since arylamine derivatives and their vinyl polymers generally possess relatively higher fluorescence quantum yields according to our previous results,\textsuperscript{[28,42-45]} copolymers
composed of arylamine-functionalized vinyl monomer and vinyl pyrene may be able to fulfill the desire for an improvement in the fluorescence quantum efficiency.

In the present article, a new vinyl triarylamine monomer was designed and synthesized with high yields. A series of soluble conductive vinyl copolymers containing triarylamine moieties and pyrene moieties at different composition ratios were prepared by free radical solution polymerization. Details of the synthesis and the characterization of the copolymers are described in this contribution.

5.2 Experimental

5.2.1 Materials and instruments

All reactions were carried out under nitrogen atmosphere with the use of standard Schlenk techniques unless specified otherwise. Glassware was oven-dried at ca 120 °C. Analytical grade solvents (e.g. toluene, THF, etc.) were purified by distillation over appropriate drying agents under an inert nitrogen atmosphere prior to use. All other reagents and chemicals (analytical grade) were used as-received without further purification. The operations of all the reactions and equipments were same to that mentioned in the Chapter 4. In addition, the actual compositions of the copolymers were determined on an Elementar Analysensysteme GmbH VarioEL V2.9 18.May 2001 CHNS Mode.

5.2.2 Synthesis

5.2.2.1 1-Nitropyrene (NPy)

In a 250 mL beaker, pyrene (5.00 g, 24.7 mmol) was added to 150 mL acetic
acid. The mixer was heated to 60°C with stirring until the pyrene was dissolved completely. Six mL nitric acid was added dropwise and reacted for an additional 30 mins. The mixture was then cooled to room temperature. The yellow precipitates were filtered and washed by acetic acid and water to obtain a yellow solid (95%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 8.91 (d, $J = 9.48$ Hz, 1H), 8.68 (d, $J = 8.48$ Hz, 1H), 8.35-8.31 (m, 3H), 8.25 (d, $J = 8.92$ Hz, 1H), 8.19-8.10 (m, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 142.67, 135.02, 131.49, 130.80, 130.77, 130.02, 127.66, 127.15, 127.07, 126.84, 124.76, 124.73, 124.12, 123.57, 122.67, 121.67.

5.2.2.2 Pyren-1-amine (APy)

NPY (1.00 g, 4.0 mmol) was added to 20 mL acetic acid. The mixture was heated to 80°C with stirring until the 1-nitropyrene has dissolved completely. Tin (II) chloride (4.00 g, 21.1 mmol) dissolved in 20 mL concentrated HCl was added dropwise in a dropping funnel and reacted for another 2 hrs. After cooling down to room temperature, the mixture was filtered and the residue washed 3 times by HCl. The solid was neutralized by 10% NaOH aqueous solution and extracted by DCM. The solution was removed under reduced pressure to obtain a brown solid (90% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 8.05-8.02 (m, 2H), 7.97-7.88 (m, 5H), 7.80 (d, $J = 8.88$ Hz, 1H), 7.34 (d, $J = 8.12$ Hz, 1H), 4.44 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 140.84, 132.14, 131.59, 127.57, 126.00, 125.99, 125.94, 125.43, 124.22, 124.06, 123.69, 123.50, 120.11, 116.80, 113.92.

5.2.2.3 N,N-Diphenylpyren-1-amine (PyPA)

APY (1.00 g, 4.6 mmol), iodobenzene (3.76 g, 18.4 mmol), Cu (0.29 g, 4.6 mmol), potassium carbonate (3.82 g, 27.6 mmol) were well-mixed in 10 mL
Nitrobenzene. The mixture was then heated to reflux with stirring overnight. Nitrobenzene was distilled by water vapor. The residue was purified by sol-gel column chromatography using hexane/ethyl acetate (EA) (10:1) as eluent. Yellow crystals were obtained (63% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 8.19-8.10 (m, 4H), 8.06 (s, 2H), 8.00-7.92 (m, 2H), 7.83 (d, $J = 8.12$ Hz, 1H), 7.22-7.18 (m, 4H), 7.08-7.06 (m, 4H), 6.97-6.93 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 148.62, 140.86, 131.20, 131.02, 129.51, 129.15, 128.16, 127.88, 127.66, 127.18, 127.08, 126.31, 126.18, 125.99, 125.17, 125.07, 124.79, 123.30, 122.03, 121.72.

5.2.2.4 4-(Phenyl(pyren-1-yl)amino)benzaldehyde (PyPA-CHO)

PyPA (2.00 g, 5.4 mmol) was allowed to dissolve completely in 3.32 mL N,N-dimethylformamide and 20 mL chlorobenzene. POCl$_3$ (2.00 mL, 21.5 mmol) was added dropwise to the mixture at room temperature. The mixture was heated to 75°C with stirring for 5 hrs. Upon cooling, the mixture was poured into an ice-bath and neutralized with sodium bicarbonate. The product was extracted with chloroform and purified by sol-gel column chromatography using hexane/EA (7/1) as eluent to afford a white solid (92.5 % yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 9.77 (s, 1H), 8.20 (dd, $J_1 = 1.92$ Hz, $J_2 = 7.44$ Hz, 2H), 8.15 (d, $J = 7.32$ Hz, 1H), 8.12-7.97 (m, 5H), 7.85 (d, $J = 8.12$ Hz, 1H), 7.64 (dd, $J_1 = 1.92$ Hz, $J_2 = 7.00$ Hz, 2H), 7.65-7.62 (m, 4H), 7.13-7.09 (m, 1H), 6.92 (d, $J = 8.80$ Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 154.04, 146.44, 138.91, 131.53, 131.15, 130.91, 130.41, 129.67, 128.73, 128.71, 128.27, 127.81, 127.53, 127.12, 126.47, 126.25, 126.15, 125.70, 125.53, 125.01, 124.69, 122.56, 118.01.
5.2.2.5 N-Phenyl-N-(4-vinylphenyl)pyren-1-amine (Vinyl-PyPA)

To a 250 mL round-bottom-flask, methyltriphenylphosphonium bromide (4.44 g, 12.4 mmol) was dissolved in 20 mL freshly distilled THF. Potassium t-butyloxide (1.39 g, 12.4 mmol) was added and stirred for 30 mins in an ice-bath. A yellow solution was resulted. **PyPA-CHO** (2.00 g, 5.0 mmol) dissolved in THF was added to the ylide/t-butyl oxide solution under continuous stirring. The mixture was stirred at room temperature until the reaction was completed as indicated by thin layer chromatography (TLC). Fifty mL hexane was added. The mixture was then filtered. Then the solvent was evaporated under reduced pressure and the residue was purified by column chromatography using hexane as the eluent. A yellow solid was obtained with 90 % yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 8.19-8.17 (m, 2H), 8.14 (d, J = 13.08 Hz, 2H), 8.11 (s, 2H), 8.07-7.92 (m, 2H), 7.83 (d, J = 8.16 Hz, 1H), 7.24-7.19 (m, 7H), 7.11-7.08 (m, 2H), 7.02-6.95 (m, 3H), 6.80 (dd, $J_1$ = 10.92 Hz, $J_2$ = 17.60 Hz, 1H), 6.64 (dd, $J_1$ = 0.80 Hz, $J_2$ = 17.56 Hz, 1H), 6.12 (dd, $J_1$ = 0.76 Hz, $J_2$ = 10.84 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 148.43, 148.38, 140.66, 136.29, 131.27, 131.08, 129.68, 129.28, 128.21, 128.03, 127.65, 127.24, 127.22, 127.14, 126.39, 126.28, 126.06, 125.29, 125.20, 124.86, 123.30, 122.50, 122.14, 121.63, 111.81.

5.2.2.6 1-Vinyl pyrene (VPy)

Methyltriphenylphosphonium bromide (4.68 g, 13.1 mmol) was first dissolved in 40 mL fleshly distillated THF. Potassium tert-butoxide (1.46 g, 13.1 mmol) was then added and stirred for 30 mins. 1-Pyrene-carboxaldehyde (2.00 g, 8.7 mmol) was added and the mixture was stirred at room temperature for 3 hrs. Finally, a yellow solution was obtained. The mixture was neutralized by HCl and then extracted by chloroform. The crude product was purified by silica column.
chromatography eluting with hexane. After the removal of solvent, a yellow solid was obtained and the yield was approx. 84%. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 8.38 (d, J = 9.28 Hz, 1H), 8.21-8.09 (m, 5H), 8.03-7.97 (m, 3H), 7.80 (dd, $J_1$ = 11.00 Hz, $J_2$ = 17.32 Hz, 1H), 5.98 (dd, $J_1$ = 1.20 Hz, $J_2$ = 17.28 Hz, 1H), 5.61 (dd, $J_1$ = 1.20 Hz, $J_2$ = 10.96 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 134.21, 132.36, 131.46, 130.97, 130.89, 128.10, 127.59, 127.46, 127.29, 125.96, 125.27, 125.05, 125.03, 124.92, 124.88, 123.69, 123.03, 117.25.

5.2.2.7 Free radical polymerization

To a 10 mL one-mouth glass apparatus charged with stirrer bar, the respective vinyl-compound(s) Vinyl-PyPA and VPy at different feed ratios (total=1.1 mmol) and 2,2’-azobis(2-methylpropionitrile) (3.60 mg, 0.02 mmol) was dissolved in 0.2 mL dried toluene. The reaction mixture was degassed by freeze-pump-thaw cycles and then sealed off. The reaction mixture was stirred at 80°C for 10 hrs. Finally, a pale orange gel was resulted. The polymer gel was dissolved in THF and then precipitated in excess methanol for several times to obtain a yellowish powder.

5.3 Results and discussion

5.3.1 Synthesis of monomers and polymers

The synthesis pathway for the monomers Vinyl-PyPA and VPy and their copolymer P(PyPA-co-VPy) are shown in Scheme 5.1. Details on the reaction procedures and their characterizations have been given in the Synthesis section 5.2.2. The copolymers could be dissolved in the common organic solvents such as THF, toluene, chloroform and DCM, however, exhibit poor solubilities in methanol, ethanol and ACN.
**Scheme 5.1** Synthetic routes for the monomers Vinyl-PyPA and VPy and their copolymer P(PyPA-co-VPy).
The $^1$H NMR spectra of Vinyl-PyPA, VPy and P(PyPA-co-VPy) were shown in Figures 5.1, 5.2 and 5.3, respectively. The copolymers were shown to have broad peaks for the methylene (2H) and methane (1H) protons on the main-chain around 1.2 and 2.0 ppm, while the olefinic protons for the monomer were found at 5-6 ppm. Broad signals around 6.2-7.9 ppm were assigned to the aromatic protons in the side-chain.

Figure 5.1 $^1$H NMR spectrum (CDCl$_3$) of the monomer Vinyl-PyPA.
Figure 5.2 $^1$H NMR spectrum (CDCl$_3$) of the monomer VPy.

Figure 5.3 $^1$H NMR spectrum (CDCl$_3$) of the copolymer P(PyPA-co-VPy).

The FT-IR spectrum of P(PyPA-co-VPy) was show in Figure 5.4, Peak a
located at 842 cm\(^{-1}\) was belong to C-H bond in aromatic ring in pyrene. Peak b located at 1266 cm\(^{-1}\) was belonged to C-N bond in aromatic amide. Peak c in 1491 cm\(^{-1}\) and peak d in 1593 cm\(^{-1}\) are belong to C=C bond in benzene ring. It was easily to observer that the content of PyPA in copolymer increased with the increasing of the PyPA ratio in the feed and the content of pyrene in copolymer increased with the increasing of the pyrene ratio in the feed.

![FT-IR spectra of the copolymers P(PyPA-co-VPy). KBr pellet.](image)

**Figure 5.4** FT-IR spectra of the copolymers P(PyPA-co-VPy). KBr pellet.

### 5.3.2 Composition of the copolymers

The actual composition of each copolymer was determined by EA and the result was listed in Table 5.1. The copolymers contained higher pyrene contents than their feed ratios which indicating VPy has higher reactivity than that of Vinyl-PyPA. This may be caused by the resonance stabilized VPy free radical compared to that of Vinyl-PyPA.
Table 5.1 Elemental analysis result of the copolymers P(PyPA-co-VPy).

<table>
<thead>
<tr>
<th>Mole feed ratio</th>
<th>PyPA $(f_1, \text{mole} %)$</th>
<th>Pyrene $(f_2, \text{mole} %)$</th>
<th>C (wt %)</th>
<th>N (wt %)</th>
<th>C/N</th>
<th>Molar composition in copolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PyPA $(F_1, \text{mole} %)$</td>
<td>Pyrene $(F_2, \text{mole} %)$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>0</td>
<td>89.78 $^a$</td>
<td>3.49 $^a$</td>
<td>25.71 $^a$</td>
<td>100</td>
</tr>
<tr>
<td>75</td>
<td>25</td>
<td>25</td>
<td>87.65</td>
<td>2.59</td>
<td>33.85</td>
<td>65.47</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>50</td>
<td>88.37</td>
<td>1.73</td>
<td>51.08</td>
<td>37.86</td>
</tr>
<tr>
<td>25</td>
<td>75</td>
<td>75</td>
<td>88.78</td>
<td>0.85</td>
<td>104.30</td>
<td>16.41</td>
</tr>
<tr>
<td>0</td>
<td>100</td>
<td>0</td>
<td>94.74 $^a$</td>
<td>0 $^a$</td>
<td>----</td>
<td>0</td>
</tr>
</tbody>
</table>

a) The data of homopolymers were calculated from molecular formulas.

5.3.3 Molecular weights of the copolymers

GPC is a method that separate polymers according to their hydrodynamic volume and therefore molecular weight. The GPC chromatograms of polystyrene standard and P(PyPA-co-VPy) was showed in Figure 5.5. The signals were recorded at 254 nm, which was used to detect aromatic rings present on all the monomers. The molecular weight results were listed in Table 5.2. In general, the present PDI for the copolymers were considerably high. This could be attributed to the chain transfer reaction to non-reactive small MW species (e.g. monomers and initiator) and to an extent contributed by the relatively high monomer concentration employed in the polymerization process. Usually, the high monomer concentration could result in a high conversion yield and high viscosity, which could lead to the auto acceleration and high PDI.
Figure 5.5  GPC chromatogram of the copolymers P(PyPA-co-VPy).

Table 5.2 Yields, molecular weights and PDIs of the copolymers P(PyPA-co-VPy).

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Yield (%)</th>
<th>$M_n$ a)</th>
<th>$M_w$ a)</th>
<th>PDI a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(PyPA-co-VPy 100:0)</td>
<td>86</td>
<td>7,700</td>
<td>16,900</td>
<td>2.2</td>
</tr>
<tr>
<td>P(PyPA-co-VPy 75:25)</td>
<td>93</td>
<td>22,300</td>
<td>42,400</td>
<td>1.9</td>
</tr>
<tr>
<td>P(PyPA-co-VPy 50:50)</td>
<td>89</td>
<td>15,300</td>
<td>30,700</td>
<td>2.0</td>
</tr>
<tr>
<td>P(PyPA-co-VPy 25:75)</td>
<td>84</td>
<td>12,700</td>
<td>25,400</td>
<td>2.0</td>
</tr>
<tr>
<td>P(PyPA-co-VPy 0:100)</td>
<td>85</td>
<td>10,600</td>
<td>25,400</td>
<td>2.4</td>
</tr>
</tbody>
</table>

a) The weight-averaged ($M_w$) and number-averaged ($M_n$) molecular weights were determined by SEC using polystyrene molecular weight (MW) standards. Conditions: wavelength 254 nm (UV-Vis detector), flow rate 1 mL/min, mobile phase THF.

5.3.4  Thermal properties of the copolymers

The thermal properties of the homopolymers and copolymers were examined
by the TGA (Figure 5.6) and DSC (Figure 5.7). The onset degradation temperature ($T_d$) and the glass transition mid-point temperature ($T_g$) were determined, respectively. The values of $T_g$ and $T_d$ for the copolymers are summarized in Table 5.3.

The results revealed that all of the copolymers exhibited high $T_d$ from 377 °C to 394 °C. The $T_g$ of the copolymers were recorded from 190 °C to 201 °C. The reason why PVPy had relatively higher $T_g$ than P(PyPA) could be due to the small rotational moment and rigid planar structure. Besides, the $T_g$ is also correlated with the MW of the copolymer. The data also revealed our polymers have good thermal stability which is essential for OLED applications.

![Figure 5.6](image_url)  
**Figure 5.6**  TGA thermograms of the copolymers P(PyPA-co-VPy) at different mole feed ratios under the heating rate of 20 °C/min.
Figure 5.7  DSC thermograms of the copolymers P(PyPA-co-VPy) at different mole feed ratios under the scanning rate of 40 °C/min.

Table 5.3  Thermal properties of the copolymers P(PyPA-co-VPy).

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Onset $T_d$ (°C) $^a$</th>
<th>Weight lost (%)</th>
<th>Midpoint $T_g$ (°C) $^b$</th>
<th>$\Delta C_p$ (J/g·°C) $^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(PyPA-co-VPy 100:0)</td>
<td>395</td>
<td>59</td>
<td>190</td>
<td>0.27</td>
</tr>
<tr>
<td>P(PyPA-co-VPy 75:25)</td>
<td>393</td>
<td>65</td>
<td>197</td>
<td>0.28</td>
</tr>
<tr>
<td>P(PyPA-co-VPy 50:50)</td>
<td>383</td>
<td>73</td>
<td>196</td>
<td>0.24</td>
</tr>
<tr>
<td>P(PyPA-co-VPy 25:75)</td>
<td>385</td>
<td>65</td>
<td>192</td>
<td>0.23</td>
</tr>
<tr>
<td>P(PyPA-co-VPy 0:100)</td>
<td>377</td>
<td>74</td>
<td>201</td>
<td>0.28</td>
</tr>
</tbody>
</table>

$^a$ About 20 mg samples were measured by DSC under nitrogen purge at a heating rate 40 °C·min$^{-1}$.
$^b$ About 5 mg samples were measured by TGA under nitrogen purge at a heating rate 20 °C·min$^{-1}$.
$^c$ The difference of specific heat capacity ($\Delta C_p$ J/g·°C).

5.3.5  Optical characteristics of the copolymers

The UV-vis absorption and PL emission spectra for P(PyPA-co-VPy) in THF are given in Figure 5.8 and the results summarized in Table 5.4. The small-molecule PyPA had prominent absorbance bands at 298 and 381 nm, while
the absorption of P(PyPA) was at 301 and 402 nm (Figure 5.8), which had a small red shift compared to PyPA. The absorption band of 298 nm in PyPA and 301 nm in P(PyPA) were due to the $\pi \rightarrow \pi^*$ transition. The band of 381 nm in PyPA and 402 nm attributed to the $n \rightarrow \pi^*$ transition. The P(PyPA) has a greenish-blue emission (max 475 nm), which exhibited a red shift compared to the emission of PyPA (max 459.5 nm). The small-molecule pyrene had prominent absorbance bands at 320 and 335 nm, and PVPy had absorption band at 330 and 347 nm, which were all due to the $\pi \rightarrow \pi^*$ transition. The pyrene monomer had sharp emission maxima at 372.5, 382 and 393 nm but PVPy had a broad emission around 490.5 nm (Figure 5.8). This indicated that $\pi-\pi$ stacking of pyrene moieties resulted in the formation of excimers: an excimer formed between the two parallel pyrene molecules in the polymer and red shifted the emission. The copolymers had prominent absorbance bands at 301, 329, 347, and 402 nm (Figure 5.8). The absorption band of 402 nm was attributed to the $n \rightarrow \pi^*$ transition arising from the PyPA moiety. The absorption band of 329 and 347 nm were due to the $\pi \rightarrow \pi^*$ transition of pyrene moiety in VPy monomer. The absorption band at 301 nm was attributed to the $\pi \rightarrow \pi^*$ transition of pyrene moiety in Vinyl-PyPA monomer. As shown in Figure 5.9, the photoluminescence spectrum of pyrene overlapped significantly with the absorption spectrum of PyPA indicating possibility of energy transfer from PVPy to P(PyPA). For copolymers, only a greenish-blue emission similar to that of PyPA was detected suggesting emission by pyrene has been transferred to PyPA units completely, which indicated the pyrene could be prevented to form the excimers by the non-planar PyPA.

In Table 5.4 revealed that the fluorescence quantum yield of the P(PyPA) homopolymer was 0.48, and the PVPy homopolymer was 0.13, respectively. An
exciting result was that the $\Phi_{F1}$ of the copolymers were all increased to about 0.51. The lifetime spectra of the polymers were shown in Figure 5.10. The results were calculated and collected in Table 5.4. The lifetime of the copolymers increased from 10.24 to 29.73 ns with the increase in pyrene content (Figure 5.11).

![Figure 5.8](image1.png)  
**Figure 5.8** Optical absorption and photoluminescence spectra of the copolymers P(PyPA-co-VPy) in THF at room temperature.

![Figure 5.9](image2.png)  
**Figure 5.9** Optical absorption of PyPA and photoluminescence spectrum of pyrene.
Figure 5.10  Lifetime spectrum of the copolymers P(PyPA-co-VPy).

Figure 5.11  Relationship of $\tau$ and $\Phi_{F1}$ with the compositions of copolymers P(PyPA-co-VPy).
Table 5.4  Optical properties of the copolymers P(PyPA-co-VPy) in THF.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$\lambda_{\text{max absorption}}$ maximum (nm)</th>
<th>$\lambda_{\text{max emission}}$ maximum (nm)</th>
<th>FWHM (nm)</th>
<th>$\tau$ (ns)</th>
<th>$\Phi_{F1}$</th>
<th>PL CIE (x, y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PyPA</td>
<td>298, 381</td>
<td>459.5</td>
<td>60</td>
<td>8.42</td>
<td>0.61</td>
<td>0.14, 0.13</td>
</tr>
<tr>
<td>P(PyPA-co-VPy 100:0)</td>
<td>301, 402</td>
<td>475</td>
<td>64</td>
<td>10.24</td>
<td>0.48</td>
<td>0.14, 0.23</td>
</tr>
<tr>
<td>P(PyPA-co-VPy 75:25)</td>
<td>329, 402</td>
<td>474.5</td>
<td>64</td>
<td>10.82</td>
<td>0.51</td>
<td>0.14, 0.25</td>
</tr>
<tr>
<td>P(PyPA-co-VPy 50:50)</td>
<td>329, 402</td>
<td>475.5</td>
<td>64</td>
<td>11.70</td>
<td>0.51</td>
<td>0.14, 0.25</td>
</tr>
<tr>
<td>P(PyPA-co-VPy 25:75)</td>
<td>330, 347, 402</td>
<td>478.5</td>
<td>64</td>
<td>15.27</td>
<td>0.51</td>
<td>0.14, 0.25</td>
</tr>
<tr>
<td>P(PyPA-co-VPy 0:100)</td>
<td>330, 347</td>
<td>490.5</td>
<td>82</td>
<td>29.73</td>
<td>0.13</td>
<td>0.17, 0.35</td>
</tr>
<tr>
<td>Pyrene</td>
<td>320, 335</td>
<td>372.5, 393</td>
<td>64</td>
<td>22.08</td>
<td>0.18</td>
<td>0.16, 0.06</td>
</tr>
</tbody>
</table>

5.3.6  Electrochemical properties of the copolymers

CV was employed to evaluate the ionization potential and the redox stability of the copolymers. The redox reversibility for the PyPA was excellent, as it can be concluded from the repeated anodic oxidation and reduction (50 cycles) without changing the peak shape in the cyclic voltammogram (Figure 5.12). The P(PyPA) had a pair of reversible anodic oxidation wave with the half-wave potential 0.99 V (vs. Ag/AgCl) (Figure 5.13). The HOMO of the copolymers were close to the value of P(PyPA) owing to the facts that oxidization occurred at PyPA (Table 5.5). The HOMO of the copolymers remained unchanged relatively to P(PyPA), while the LUMO varied from -2.41 eV to -2.51 eV with an increase of pyrene ratio in the copolymers. The bandgap energies of the copolymers (from 2.70 eV to 2.81 eV) were smaller than those of P(PyPA) (2.82 eV) and PVPy (3.47 eV). Compared to the bandgap of PyPA, the energy bandgaps of the copolymers P(PyPA-co-VPy) showed to have obvious linear variation, indicating the polymerization process and MW did not affect the electrochemical properties significantly.
Figure 5.12  50 cycles CV diagram of PyPA in DCM.

Figure 5.13  Cyclic voltammogram of the copolymers P(PyPA-co-VPy) in ACN.
Table 5.5  Electrochemical properties of the copolymers P(PyPA-co-VPy).

<table>
<thead>
<tr>
<th>Materials a)</th>
<th>$E_{1/2}^{ox}$ (V, ferrocene) b)</th>
<th>$E_{1/2}^{ox}$ (V, sample) b)</th>
<th>HOMO (eV) c)</th>
<th>LUMO (eV) d)</th>
<th>$E_g$ (eV)</th>
<th>UV-vis absorption onset (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PyPA</td>
<td>0.49</td>
<td>0.96</td>
<td>-5.27</td>
<td>-2.43</td>
<td>2.84</td>
<td>436</td>
</tr>
<tr>
<td>P(PyPA-co-VPy 100:0)</td>
<td>0.56</td>
<td>0.99</td>
<td>-5.24</td>
<td>-2.41</td>
<td>2.82</td>
<td>439</td>
</tr>
<tr>
<td>P(PyPA-co-VPy 75:25)</td>
<td>0.49</td>
<td>0.91</td>
<td>-5.22</td>
<td>-2.41</td>
<td>2.81</td>
<td>441</td>
</tr>
<tr>
<td>P(PyPA-co-VPy 50:50)</td>
<td>0.49</td>
<td>0.92</td>
<td>-5.23</td>
<td>-2.43</td>
<td>2.80</td>
<td>443</td>
</tr>
<tr>
<td>P(PyPA-co-VPy 25:75)</td>
<td>0.49</td>
<td>0.90</td>
<td>-5.21</td>
<td>-2.51</td>
<td>2.70</td>
<td>458</td>
</tr>
<tr>
<td>P(PyPA-co-VPy 0:100)</td>
<td>0.49</td>
<td>1.09</td>
<td>-5.40</td>
<td>-1.93</td>
<td>3.47</td>
<td>357</td>
</tr>
</tbody>
</table>

a) Oxidation potentials were measured in 0.1M TBAPF$_6$ solution with ferrocene as the internal standard.
b) Versus Ag/AgCl electrode.
c) Assuming the HOMO of ferrocene is -4.8eV.
d) Calculated from the band-gap which was deduced from the UV-vis absorption onset.

5.3.7  Electroluminescence properties

Several single-layer homojunction type PLED devices were fabricated to evaluated the EL properties of the copolymers P(PyPA-co-VPy). (see Figure 5.14) The homojunction devices referred to the facts that all holes, electrons transportation and excitons formation all occurred within the single copolymer layer. Four different methods for the enhancement of hole injection (HIL) were employed including CFx (CFx plasma treated ITO surface), MoO$_3$ (10 nm), MoO$_3$ (5 nm), and PEDOT:PSS (40 nm). Single-layer PLEDs (device A in Figure 5.14) based on P(PyPA-co-VPy 50:50) were used to evaluate the performance of the HIL material. The results as shown in Figure 5.15, indicated CFx plasma treatment provided the best hole injection properties from ITO anode. A series of PLED based on CFx with the device structure ITO(CFx treated)/P(PyPA-co-VPy)/LiF/Al (device B in Figure 5.14) were fabricated to
evaluated the EL properties of the copolymers at different compositions. The devices (B) achieved only a max luminance of 16-67 cd/m² and with the best current density at 0.012 cd/A. A second series of PLEDs was attempted by inserting an electron transporting layer (ETL) TPBi at the cathode. This is because all arylamine-based small molecules and polymers are known hole transporting materials and the poor performance of the single-layer PLED could be a result of lack of electron transport instead. The device (C) with the configuration ITO(CFx treated)/P(PyPA-co-VPy)/TPBi/LiF/Al (see device C in Figure 5.14) were fabricated with substantial improvement in the device performance detected. With the insertion of the electron transporting layer (ETL) TPBi, the EL of the PLEDs improved with luminance ranging from 665 to 1,143 cd/m² and current density from 0.67 to 1.07 cd/A both operated under 100 mA/cm² (Table 5.6 and Figure 5.17). The best performance PLED with an ETL inserted was obtained for the copolymer P(PyPA-co-VPy 100:0) indicating P(PyPA) is mostly hole transporting. While without the ETL layer, the homopolymer P(VPy) has the best EL properties indicating it has both hole and electron transporting properties. The EL spectra for the two homopolymers P(PyPA), P(VPy) and the copolymer P(PyPA-co-VPy 50:50) are given in Figure 5.16. The EL peaks ranged from 480 nm to 524 nm.
### Figure 5.14
Three device structures for the PLED. (A) Single-layer device configuration with different HTL materials. (B) Single-layer device configuration with different composition P(PyPA-co-VPy)s. (C) Multi-layer device configuration with different composition P(PyPA-co-VPy)s.

### Figure 5.15
The performance of PLED (A) ITO/HIL/P(PyPA-co-VPy 50:50)/LiF/Al.
Figure 5.16  EL spectra for devices (B) ITO/CFx/P(PyPA-co-VPy)/LiF/Al.

Figure 5.17  The curves of current density vs voltage and the luminance vs voltage of devices (C) ITO/CFx/P(PyPA-co-VPy)/TPBi/LiF/Al.
Table 5.6 Data summary of multi-layer device (C).

<table>
<thead>
<tr>
<th>Copolymers</th>
<th>Current density at 100 mA/cm²</th>
<th>Luminance at 100 mA/cm² (cd/m²)</th>
<th>Current density at 100 mA/cm² (cd/A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(PyPA-co-VPy 100:0)</td>
<td>106</td>
<td>1143</td>
<td>1.08</td>
</tr>
<tr>
<td>P(PyPA-co-VPy 50:50)</td>
<td>110</td>
<td>854.9</td>
<td>0.78</td>
</tr>
<tr>
<td>P(PyPA-co-VPy 25:75)</td>
<td>99</td>
<td>665.3</td>
<td>0.67</td>
</tr>
<tr>
<td>P(PyPA-co-VPy 0:100)</td>
<td>103</td>
<td>699.4</td>
<td>0.68</td>
</tr>
</tbody>
</table>

5.4 Conclusions

Two fluorescent monomers N-phenyl-N-(4-vinylphenyl)pyren-1-amine (Vinyl-PyPA) and 1-vinyl pyrene (VPy) were synthesized in good yields. A series of soluble conductive vinyl copolymers P(PyPA-co-VPy) containing Vinyl-PyPA and VPy moieties at different composition ratios were prepared in good yields by free radical solution polymerization. These copolymers showed high $T_g$ (190 °C to 201 °C) and good thermal stabilities. The photoluminescence (PL) emission maxima of these copolymers were all in the range of 474.5 nm to 478.5 nm, which were similar to the poly(N-phenyl-N-(4- vinylphenyl)pyren-1-amine) (P(PyPA)) (475 nm) but were blue shifted compared to poly(1-vinyl pyrene) (PVPy) (490.5 nm). The lifetime of the copolymers increased from 10.24 to 29.73 ns with an increase in pyrene contents. The copolymers had higher quantum yields (0.51) than those of the homopolymer of P(PyPA) (0.48) and PVPy (0.13). The HOMO of the copolymers remained relatively unchanged with P(PyPA), while the LUMO varied from -2.41 eV to -2.51 eV with an increase of pyrene ratio in the copolymers. The energy bandgaps of the copolymers (from 2.70 eV to 2.81 eV) were smaller than those of P(PyPA) (2.82 eV) and PVPy (3.47 eV). All the CIEs of copolymers P(PyPA-co-VPy) are very similar and closed to the greenish-blue
hue. The EL spectra have peaks located at 480-524 nm. Highest luminance was obtained from the PLED using \( \text{P(PyPA-co-VPy 100:0)} \) at 1,143 cd/m\(^2\) while a max current density was obtained from the device with \( \text{P(PyPA-co-VPy 50:50)} \) at 110 mA/cm\(^2\).

5.5 References


Chapter 6

Self-Assembly and Aggregation of ATRP Prepared Amphiphilic BAB Tri-block Copolymers Contained Nonionic ethylene glycol and Fluorescent 9,10-Di(1-naphthalenyl)-2-vinyl-anthracene/1-Vinyl-pyrene Segments

6.1 Introduction

The shortcomings of synthetic drugs such as poor aqueous solubility, high potency, and poor stability have been a major challenge for the process of loading and delivery drug in human patients.\textsuperscript{[1]} One efficient method that can circumvent the problem is to fabricate a bio-compatible core/shell type micelle drug carrier employing amphiphilic block copolymers. Based on the differences in occupied volumes, contour lengths and effective cross-sectional areas of the copolymer external and internal segments, the amphiphilic block copolymers could self-assemble into different specific supramolecular structures, such as spherical micelles, tubular micelles, vesicles and worm-like micelle, etc.\textsuperscript{[2-7]} These particular structures not only have the capacity of loading the hydrophobic drugs in their hydrophobic core, but they also shown to affect the drug controlled release mechanism. In addition, the amphiphilic block copolymers also found applications in nano-reactor, nano-materials, artificial tissue and biological soft materials, etc.\textsuperscript{[8-13]}

BAB block copolymers with the hydrophobic B segments and the hydrophilic A segment usually exhibit more complex micelle-like structures than those of the
traditional ABA block copolymers in aqueous medium. At low concentration and in a good solvent for A, the B segments usually have a strong tendency to aggregate and generate the core of the micelle while the external corona will be covered by loops of A segments.\cite{7,14-17} At higher polymer concentrations, the copolymers form bridges connecting the adjacent micelles into a cross-linked 3D necklace-like network.\cite{18-22} This type of morphological changes has rarely been reported and thus the aggregation behaviour is highly interesting from both the theoretical and practical perspectives.

Pyrene, an aromatic bluish-green fluorescent dye, is often used as a biological probe due to its attractive features such as high fluorescent efficiency and a long lifetime for the excited state.\cite{23-25} Monomers containing the pyrene moiety have already been applied in the fields of membrane, biophysics and biochemistry.\cite{25-30} Its vinyl polymers, such as poly(1-vinylpyrene), have restricted biological applications due to its poor solubility in aqueous media. In our previous work, a blue-light emitting vinyl polymer poly(9,10-di(1-naphthalenyl)-2-vinylanthracene) (P(ADN)) based on the 2-methyl-9,10-di(1-naphthalenyl)anthracene (MADN) had been synthesized using free radical and anionic polymerization techniques.\cite{31} This polymer had shown to possess excellent thermal stability and retained most of the photoluminescent properties of its parent small molecule MADN. Similarly, P(ADN) also has limited solubility especially when its MW > 13,000. As a result, a nonionic ethylene glycol (PEG) oligomer with excellent solubility in aqueous medium was chosen as the hydrophilic A segment for the formation of the amphiphilic BAB block copolymers. Beside excellent solubility, PEG is non-toxic and non-immunogenic, and therefore can be excreted from the body rapidly.\cite{28,30} PEG containing copolymers have been investigated extensively for both chemical
and bio-logical applications.\textsuperscript{[21-30,32-37]} In consideration of the construability of the micelle structure, a high MW crystalline PEG block could have promoted a strong bridging effect thus leading to a 3D framework easily while a low MW amorphous PEG would result in poor solubility for the block copolymer. As a balance, a medium MW PEG (\(M_n = 3,400\)), was selected as the hydrophilic segment for the two block copolymers prepared.

ATRP is commonly used to produce amphiphilic block copolymers with predetermined composition and narrow PDI.\textsuperscript{[9,38-42]} In the present work, two well-defined fluorescent and amphiphilic block copolymers \textbf{ADN-PEG3400-ADN} and \textbf{Py-PEG3400-Py} was successfully synthesized using ATRP and a brominated \textbf{PEG3400} as the macro-initiator. The chemistry and physical properties of the intermediates, the resulting block copolymers were carefully characterized using NMR, GPC, TGA, DSC, MALDI-TOF MS, XPS, UV-Vis, PL and TEM measurements.

6.2 Experimental

6.2.1 Materials and instruments

All solvents were analytical grade purified by distillation and stored under appropriate drying agents and/or inert nitrogen atmosphere prior to use. Benzoyl peroxide (BPO) was obtained from Aldrich and was recrystallized in a chloroform/methanol mixed solvent before use. Copper(I) bromide (CuBr, purchased from Aldrich) was purified by stirring in glacial acetic acid, washed by absolute ethanol and ethyl ether, and then dried under vacuum. \textbf{PEG3400} was purchased from Fisher Scientific (Fair Lawn, NJ, USA) and was dried by azeotropic distillation with toluene prior to use. All other reagents were analytical
grade and used without further purification. The operations of all the reactions and equipments were same to that mentioned in the Chapter 4. In addition, the XPS analysis was performed on a Physical Electronics 5600 multi-technique system using Al monochromatic X-ray at a power of 150W. The TEM images were obtained by using a high-resolution JEOL 2010F TEM system operating with a LaB6 filament at 200 kV.

6.2.2 Synthesis

6.2.2.1 Synthesis of 9,10-di(1-naphthalenyl)-2-vinylanthracene monomer

The synthetic pathway for the homopolymers P(ADN) & P(Py) and the block copolymers ADN-PEG3400-ADN & Py-PEG3400-Py synthesized by ATRP method were shown in Scheme 6.1, respectively. Details on the reaction procedures of the monomer Vinyl-ADN and Vinyl-Py have been given in the section Synthesis 2.2.2 (Chapter 2) and Synthesis 5.2.2 (Chapter 5), respectively. In the present chapter, unless specified otherwise, the homopolymer P(ADN) and P(Py) are both obtained by ATRP method.
Scheme 6.1  Synthetic routes for the block copolymers ADN-PEG3400-ADN & Py-PEG3400-Py (A) and the homopolymers P(ADN) & P(Py) synthesized by ATRP method (B).
6.2.2.1 Synthesis of block copolymers

6.2.2.1.1 Br-PEG3400-Br macro-initiator

To a 10 mL round bottom flask, PEG3400 (3.70 g, 1.09 mmol) and triethylamine (0.5 mL, 3.59 mmol) were dissolved in 20 mL dry DCM, then maintained in an ice bath. The bromoacetyl bromide (0.7 mL, 8.08 mmol) dissolved in 20 mL DCM was added dropwise to the system under dry N₂. Subsequently the temperature was allowed to rise to room temperature and stirred overnight under N₂ atmosphere. After completion reaction, the solution was filtered, then poured into water to wash multiple times and extracted with DCM. The DCM solution was washed by 1M HCl, 1M NaOH and 1% Na₂CO₃ solution and extracted by DCM, then dried by MgSO₄ overnight, and the solvent was removed under reduced pressure, the concentrated solution was precipitated from ether, dissolved in DCM and re-precipitated from ether severer times, then the macroinitiator was collected and dried under vacuum overnight at room temperature. The Br-PEG3400-Br was obtained with a 50% yield.

6.2.2.1.2 ADN-PEG3400-ADN and Py-PEG3400-Py

To a single-mouth Schlenk reaction tube charged with a stirrer bar, CuBr (1.89 mg, 0.0132 mmol), 1,1,4,7,7-Pentamethyldiethylenetriamine (PMDTEA) (7.3 μL, 0.0350 mmol), Br-PEG3400-Br (44.7 mg, 0.0132 mmol), and 200 mg Vinyl-ADN (200 mg, 0.438 mmol) or 1-Vinyl pyrene (100 mg, 0.438 mmol) were dissolved in 1 mL dry toluene. The reaction mixture was degassed by freeze-pump-thaw cycles and then sealed off in nitrogen atmosphere. The reaction mixture was stirred at 75 °C for 24 hrs. Finally, a viscous yellowish polymer solution was resulted. The polymers were passed through a short silica column.
(SiO₂) to remove the copper complex and further purified by dialysis to produce the resulted BAB-type block copolymers ADN-PEG3400-ADN (62% yield) and Py-PEG3400-Py (69% yield).

6.2.2.2 Synthesis of homopolymers

The homopolymers P(ADN) and P(Py) were prepared for the comparison of physical properties with their corresponding block copolymer. CuBr (1.89 mg, 0.0132 mmol), PMDTEA (7.3 μL, 0.0350 mmol), benzyl chloride (1.67 mg, 0.0132 mmol), and Vinyl-ADN (200 mg, 0.438 mmol) or 1-Vinyl pyrene (100 mg, 0.438 mmol) were added and dissolved in 1 mL dried toluene in a single-mouth Schlenk reaction tube charged with a stirrer bar. The reaction mixture was degassed by freeze-pump-thaw cycles and then sealed off in nitrogen atmosphere and stirred at 75 °C for 24 hrs. Finally, a viscous yellowish polymer solution was resulted. The polymer was passed through a short silica column (SiO₂) to remove the copper complex and further purified by dialysis to produce the resulted homopolymers P(ADN) (58% yield) and P(Py) (54% yield).

6.2.3 Self-aggregation of the block copolymers

The nano-size micelles were prepared by dissolved the block copolymer in THF completely, and then 1 mL of the copolymer-containing THF solution was added dropwise by syringe into 20 mL deionized H₂O under stirring. The micelle solution was agitated at least 12 hrs in a sealed conical flask for achieving of equilibrium micelle shape and size. The preparation processes were conducted under ambient conditions.
6.3 Results and discussion

6.3.1 Structure characterization of monomer and polymers

The $^1$H NMR spectra for ADN-PEG3400-ADN, Py-PEG3400-Py, Br-PEG3400-Br and PEG3400 are presented in Figure 6.1. Changes in the polarity of the environment can be monitored according to the positions of the residual H$_2$O signals. As the two –OH end groups in PEG3400 have been replaced by –CH$_2$Br in Br-PEG3400-Br, hydrogen bonding was reduced. As a result, the H$_2$O peak shifted to high field from 2.63 ppm in PEG3400 to 2.07 ppm in Br-PEG3400-Br and finally 1.60 ppm for the nonpolar block copolymers. Upon copolymerization, both ADN-PEG3400-ADN and Py-PEG3400-Py exhibited broad aromatic peaks in the range from 5.50 to 8.50 ppm. Since the absolute MW for the PEG segment has been determined by MALDI (see section below), the composition ratios for the A/B segments can be calculated by comparing the integral area at 3.49 ppm (for PEG3400 segment) to the integral area for the aromatic peak range. As a result, the number of repeating units and the overall MW of the two copolymers has been calculated and were listed in Table 6.1 for comparison with the GPC results.
The molecular weight of the PEG3400 has been reaffirmed by MALDI-TOF MS. The $M_n$, $M_w$, and polydispersity index (PDI) for PEG3400 were determined to be 3,371, 3,391 and 1.01, respectively, and thus its formula is $\text{HO-}(\text{CH}_2\text{CH}_2\text{O})_{76}\text{-H}$. The degree of conversion from PEG3400 to the macro-initiator Br-PEG3400-Br has been determined by measuring the Br mass fraction in Br-PEG3400-Br using a XPS. Under the present reaction conditions, the Br content was found to be 4.33 wt % which was closed to the theoretical value of 4.42 wt % for 100 % bromination. As a conclusion, the percentage conversion for PEG3400 into Br-PEG3400-Br was 97.96 mol %. The molecular weights of the block copolymers ADN-PEG3400-ADN and Py-PEG3400-Py have been measured using GPC using THF as the mobile phase and were...
calibrated against polystyrene MW standards (see Figure 6.2). Since a UV-Vis detector was employed in the GPC measurement, only the aromatic moieties but not the PEG could be detected. The absolute MWs of the two block copolymers have also been calculated using $^1$H NMR signals by comparing the integral area ratio of the aromatic peaks (5.50 to 8.50 ppm for the P(ADN) or P(Py) segments) to the aliphatic peak for the PEG3400 segment at 3.49 ppm. Both the relative MW from GPC and the absolute NMR results are presented in Table 6.1. The number-averaged molecular weights ($M_n$) of ADN-PEG3400-ADN and Py-PEG3400-Py from GPC were found to be 9,600 and 13,800, respectively. The PDI of ADN-PEG3400-ADN and Py-PEG3400-Py were 1.35 and 1.32, respectively, and were only slightly higher than their homopolymers P(ADN) and P(Py). This phenomenon may be attributed to the lower propagation efficiency of the macro-initiator used in the present copolymerization process. Similar results have been reported by Iddon et al. [43] and Ydens et al. [44] The NMR derived $M_n$, however, has higher value at 15,200 and 20,300 respectively, which give the formula ADN$_{13}$-PEG$_{76}$-ADN$_{13}$ and Py$_{37}$-PEG$_{76}$-Py$_{37}$ for the two BAB block copolymers.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Overall Yield (%)</th>
<th>$M_n$ (GPC) $^a$</th>
<th>$M_w$ (GPC) $^a$</th>
<th>PDI (GPC)</th>
<th>$M_n$ (NMR) $^b$</th>
<th>Repeating units</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADN-PEG3400-ADN</td>
<td>62</td>
<td>9,600</td>
<td>13,000</td>
<td>1.35</td>
<td>15,200</td>
<td>ADN$<em>{13}$-PEG$</em>{76}$-ADN$_{13}$</td>
</tr>
<tr>
<td>Py-PEG3400-Py</td>
<td>69</td>
<td>13,800</td>
<td>18,200</td>
<td>1.32</td>
<td>20,300</td>
<td>Py$<em>{37}$-PEG$</em>{76}$-Py$_{37}$</td>
</tr>
<tr>
<td>P(ADN)</td>
<td>58</td>
<td>8,800</td>
<td>11,300</td>
<td>1.28</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>P(Py)</td>
<td>54</td>
<td>4,100</td>
<td>5,100</td>
<td>1.25</td>
<td>/</td>
<td>/</td>
</tr>
</tbody>
</table>

$a$) The weight-averaged ($M_w$) and number-averaged ($M_n$) molecular weights were determined by GPC calibrated against poly(styrene) MW standards. GPC conditions: UV-Vis detector wavelength 254 nm, mobile phase THF at 1 mL/min.

$b$) The averaged molecular weight ($M_n$) of ADN or Pyrene was calculated by the areas of aromatic ring and PEG in the NMR spectra.
Figure 6.2  GPC chromatogram for ADN-PEG3400-ADN, Py-PEG3400-Py, P(ADN) and P(Py) in comparison with the PS MW standards.

6.3.2  Thermal properties

The thermal properties of the block and homopolymers were examined by TGA at a heating rate 20 °C/min and DSC at a heating rate 40 °C/min, all under nitrogen purge and the results are given in Figure 6.3 and Figure 6.4, respectively. As the onset degradation temperature (T_d) for the PEG was 352 °C, which is substantially lower than the T_d for the Py and ADN segments at 362 and 404 °C, it set the lower limit for the thermal stability for the block copolymers.

PEG3400 have a melting temperature (peak) at 63 °C, while the less polar macro-initiator Br-PEG3400-Br has an even lower T_m at 55 °C. The lowering in T_m may be attributed to weaker hydrogen bonding between the brominated molecules. The glass transition temperatures (T_g midpoint) for the ADN and Py segments in their corresponding copolymers were 230 °C and 193 °C, respectively, which are both very closed to the values of their homopolymers at 233 °C and 192 °C. The results indicated the polar and nonpolar segments in the block copolymers
were almost completely microphase separated in solid-state. The purity of the microdomain can also be compared by the change in heat capacity ($\Delta C_p$) at $T_g$ or heat of melting ($\Delta H_m$) at $T_m$ for the block copolymers. The $\Delta C_p$ for the homopolymer at $T_g$ (0.22-0.28 J/g·°C) is similar to the $\Delta C_p'$ (0.21-0.26 J/g·°C, $\Delta C_p$ corrected of the ADN and Py weight fraction) for the block copolymers, whereas the $\Delta H_m'$ (113-112 J/g, $\Delta H_m$ corrected for the PEG weight fraction) for the copolymers is also identical to $\Delta H_m$ of Br-PEG3400-Br (111 J/g).

![Figure 6.3](image-url) **Figure 6.3** TGA thermogram for PEG3400, Br-PEG3400-Br, ADN-PEG3400-ADN, Py-PEG3400-Py, P(ADN) and P(Py) at heating rate of 20 °C/min under nitrogen purge.
Figure 6.4  DSC thermogram for PEG3400, Br-PEG3400-Br, ADN-PEG3400-ADN, Py-PEG3400-Py, P(ADN) and P(Py) at heating rate of 40 °C/min under nitrogen purge.

Table 6.2 Summary of thermal properties.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Onset $T_d$ (°C)</th>
<th>Midpoint $T_g$ (°C)</th>
<th>$\Delta C_p$ (J/g·°C)</th>
<th>$\Delta C_p'$ (J/g·°C)</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$\Delta H_m'$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG3400</td>
<td>352</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>63</td>
<td>151</td>
<td>/</td>
</tr>
<tr>
<td>Br-PEG3400-Br</td>
<td>333</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>55</td>
<td>111</td>
<td>/</td>
</tr>
<tr>
<td>ADN-PEG3400-ADN</td>
<td>335, 402</td>
<td>230</td>
<td>0.16</td>
<td>0.21</td>
<td>65</td>
<td>25</td>
<td>113</td>
</tr>
<tr>
<td>Py-PEG3400-Py</td>
<td>334, 365</td>
<td>193</td>
<td>0.22</td>
<td>0.26</td>
<td>64</td>
<td>19</td>
<td>112</td>
</tr>
<tr>
<td>P(ADN)</td>
<td>404</td>
<td>233</td>
<td>0.22</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>P(Py)</td>
<td>362</td>
<td>192</td>
<td>0.28</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
</tbody>
</table>

a) About 5 mg samples were used for TGA under nitrogen purge at a heating rate 20 °C/min.
b) About 15 mg samples were used for DSC under nitrogen purge at a heating rate 40 °C/min.
c) The change in specific heat capacity at $T_g$ ($\Delta C_p$, J/g·°C).
d) The $\Delta C_p' = \Delta C_p/H$, where H is the weight percentage of ADN or Py segments in the copolymer ADN-PEG3400-ADN or Py-PEG3400-Py, respectively.
e) The melting enthalpy of the sample from the second DSC heating scans at $T_m$ ($\Delta H_m$, J/g).
f) The $\Delta H_m' = \Delta H_m/S$, where S is the weight percentage of PEG3400 segment in the copolymer ADN-PEG3400-ADN or Py-PEG3400-Py, respectively.
6.3.3 Optical properties

The UV-vis absorption and PL spectra for ADN-PEG3400-ADN, Py-PEG3400-Py, P(ADN) and P(Py) in THF are all given in Figure 6.5 with the results summarized in Table 6.3.

Three prominent absorption bands were observed at 359, 379 and 400 nm for ADN-PEG3400-ADN, which were all due to $\pi \rightarrow \pi^*$ transition. Its emission maxima were found at 423.5 and 441.5 nm. Both the absorption and emission bands are similar to its homopolymer P(ADN). The extinction coefficient of ADN-PEG3400-ADN, however, decreased to 38.37% to that of P(ADN) due to differences in ADN weight concentration. Py-PEG3400-Py also have similar absorption maxima at 329 and 346 nm and emission band at 490 nm compared to its homopolymer P(Py). Its extinction coefficient also decreased to 30.05% of its homopolymer. Both ADN-PEG3400-ADN and Py-PEG3400-Py have very similar fluorescent spectra compared to their homopolymers as shown in Figure 6.5 except a slightly broader (5-7 nm) FWHM which maybe due to energy dissipation/transfer at the copolymer interface. The quantum efficiency is similar for both the homopolymers and the block copolymers at 0.16-0.40.

![Graph showing extinction coefficient and PL spectra](image-url)
### Table 6.3 Summary of optical properties in THF

<table>
<thead>
<tr>
<th>Materials</th>
<th>$\lambda_{\text{max absorption}}$ maximum (nm)</th>
<th>$\lambda_{\text{max emission}}$ maximum (nm)</th>
<th>FWHM (nm)</th>
<th>Quantum efficiencies</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADN-PEG3400-ADN</td>
<td>345, 359, 379, 401</td>
<td>423.5, 441.5</td>
<td>58</td>
<td>0.39</td>
</tr>
<tr>
<td>Py-PEG3400-Py</td>
<td>329, 346</td>
<td>488.5</td>
<td>89</td>
<td>0.18</td>
</tr>
<tr>
<td>P(ADN)</td>
<td>345, 360, 380, 401</td>
<td>422.5, 438.5</td>
<td>52.5</td>
<td>0.40</td>
</tr>
<tr>
<td>P(Py)</td>
<td>327, 347</td>
<td>490.5</td>
<td>82</td>
<td>0.16</td>
</tr>
</tbody>
</table>

#### 6.3.4 Self-aggregation behavior

The morphology of the BAB-type amphiphilic block copolymers in solution depends on the solvent selected, temperature and concentration.\[^{45-49}\] Figure 6.6, 6.7 and 6.8 give typical TEM images of ADN-PEG3400-ADN and Py-PEG3400-Py self-aggregate behavior at different initial polymer concentrations. As shown in Figure 6.6, two regions with distinct optical intensity were clearly observed, highlighting the formation of a core-shell type micelle structure. In the presence of a polar aqueous environment, it is expected the hydrophobic (ADN or Py) blocks constituted the core of the micelle, whereas the hydrophilic PEG3400 segments along with the solvent formed the shell. (for details see Figure 6.10)

The average particle size for Py-PEG3400-Py increased from ca. 30 nm to 55 nm, as the polymer concentration increased from 10 ppm to 50 ppm (Figure 6.7). As the concentration continuous increased to 200 ppm, the average diameter of the spherical micelle increased to ca. 90 nm which was near the stability limit for the individually spherical micelles. The concentration dependence of spherical micelle diameter had also been reported by Lam et al.,\[^{50,51}\] Kabanov et al.\[^{52}\] and Nagarajan,\[^{53}\] respectively. The average micelle diameters for the copolymer ADN-PEG3400-ADN were all larger than those of the copolymer
**Py-PEG3400-Py** at the same concentration despite it has lower MW. It is therefore suggested the hydrodynamic volume occupied by the **ADN** units is substantial larger than that of **Py**. Similarly, **ADN-PEG3400-ADN** formed single spherical micelles with average diameters ca. 40 nm to 90 nm with concentration from 10 ppm to 50 ppm respectively. The average micelle sizes increased to ca. 160 nm eventually at 200 ppm. The dependence of the average particle diameter as a function of concentration below and above the stability transitional regions is shown in Figure 6.9.

At concentrations above 200 ppm, aggregation of individual micelles into a range of linear or even cross-linked pearl-necklace-like (or worm-like) aggregates is observed in Figure 6.8 (at 1000 ppm). These phenomena may be attributed to the bridging effect of the amphiphilic copolymer molecules in the aggregates.\[^{18-22}\]

As seen in Figure 6.10, the spherical micelles initially consist of an inner core containing the hydrophobic B blocks with an outer corona containing both the hydrophilic A blocks and aqueous solvent molecules. The continuous growth in diameter for the micelles is limited by the contour length of the BAB block copolymers. However, at medium to higher concentrations (200-1000 ppm), physical cross-linking between adjacent spherical micelles can be resulted by the relaxation in molecular dimension, by the **PEG3400** segments. As seen in Figure 6.10, further growth in dimension for the aggregates can be resulted by the bridging of the PEG segments at the corona between two adjacent micelles.\[^{19,54-56}\]
Figure 6.6 TEM microphotographs of spherical aggregates corona and core structures from amphiphilic tri-block copolymers (A) Py-PEG3400-Py and (B) ADN-PEG3400-ADN at concentration 10 ppcm (magnified optical images of the spherical aggregates in the black boxes of Figure 6.7 (A) and (D), respectively)
Figure 6.7 TEM microphotographs of spherical aggregates from amphiphilic tri-block copolymers Py-PEG3400-Py and ADN-PEG3400-ADN. (A) Py-PEG3400-Py concentration 10 ppm; (B) 50 ppm; (C) 200 ppm and (D) ADN-PEG3400-ADN concentration 10 ppm; (E) 50 ppm; (F) 200 ppm.

Figure 6.8 TEM microphotographs of the linear and crosslinked pearl-necklace-like aggregates from amphiphilic tri-block copolymers (A) Py-PEG3400-Py and (B) ADN-PEG3400-ADN at concentration 1000 ppm.
**Figure 6.9**  Effect of amphiphilic tri-block copolymers Py-PEG3400-Py and ADN-PEG3400-ADN concentrations on the micelle diameters.

**Figure 6.10**  Proposed molecular packing models for the self-assemblies of ADN-PEG3400-ADN and Py-PEG3400-Py in THF/H₂O (1/20, v/v).
6.4 Conclusions

Two fluorescent amphiphilic BAB-type tri-block copolymers were synthesized successfully using ATRP. The copolymers ADN\textsubscript{13}-PEG\textsubscript{76}-ADN\textsubscript{13} and Py\textsubscript{37}-PEG\textsubscript{76}-Py\textsubscript{37} with absolute MW determined from NMR have narrow polydispersity at 1.35 and 1.32, respectively. Similar absorption and emission spectra of both the copolymers ADN-PEG\textsubscript{3400}-ADN and Py-PEG\textsubscript{3400}-Py were also found to be comparable with their respective homopolymers. By comparing the transitional temperatures (like \(T_g\), \(\Delta C_p\), \(T_m\) and \(\Delta H_m\)) between the block and homopolymers, a well-defined and completely microphase segregated individual microdomain is expected for the block copolymer at solid-state. However, at the concentration range between 10-200 ppm in a (1/20, v/v) THF/water solution, the copolymers were found to self-assemble into individual core-shell like spherical aggregates. As the concentrations further increased to 1000 ppm, a linear or even three-dimensional cross-linked pearl-necklace-like aggregate was observed with the suggestion that the PEG segments bridging between adjacent micelles.

6.5 References

[6] Zhilian Zhou, Zhibo Li, Yu Ren, Marc A., Hillmyer, Timothy P. Lodge, J.


9: 481.


Chapter 7

Conclusions

Several series of blue fluorescent vinyl monomers and their side-chain vinyl polymers for potential opto-electronic applications have been designed, synthesized and polymerized with good yields. The novel homopolymers and copolymers included the homopolymers $P(\text{ADN})$ (Scheme 2.1), two highly soluble homopolymers $P(2\text{ADN})$ and $P(3\text{ADQ})$ (Scheme 3.1), two series of ADN moieties containing copolymer $P(\text{ADN-co-S})$ and $P(\text{ADN-co-VK})$ (Scheme 4.1), a series of pyrene moieties containing copolymer $P(\text{PyPA-co-VPy})$ (Scheme 5.1) and two novel amphiphilic BAB-type block copolymers, $\text{ADN-PEG3400-ADN}$ and $\text{Py-PEG3400-Py}$ which contained either the blue (ADN) and bluish-green (Py) fluorescent moieties (Scheme 6.1).

In chapter 2, a new blue-emitting conductive vinyl polymer poly(9,10-di(1-naphthalenyl)-2-vinylanthracene) ($P(\text{ADN})$) was polymerized using solution free radical and anionic addition polymerization. Anionic polymerization produced polymers with narrow polydisperisity index from 1.25 to 1.37 and better MW control than solution free radical method. The amorphous polymers possess high $T_g$ from 228 to 237 °C and $T_d$ ca 400 °C. $P(\text{ADN})$s exhibited four prominent absorption bands at around 343, 362, 381 and 403 nm due to the $\pi \to \pi^*$ transition and is similar to the reference materials $\text{MADN}$. The emission of $P(\text{ADN})$s ($\text{PL}_{\text{MAX}} = 444$ nm) in solid-state, however, was slightly red-shifted comparing to 2-methyl-9,10-di(1-naphthalenyl) anthracene ($\alpha,\alpha$-$\text{MADN}$) ($\text{PL}_{\text{MAX}} = 434$ nm) due to only partial $\pi-\pi$ stacking between adjacent pendant ADN moieties. The color coordinates (CIE = (0.15, 0.07)) of $P(\text{ADN})$s, however, is similar to that of the small molecule $\text{MADN}$ (CIE = (0.15, 0.05)) which are the requirements for a
true blue color display. The PL lifetime and quantum yield was determined to be 7.83-9.05 ns and 0.40 to 0.44, respectively. The HOMO, LUMO and the bandgap energy of P(ADN)s were found to be ca. -5.66 eV, -2.68 eV and 2.97 eV.

In chapter 3, two new blue fluorescent polymers, poly(9,10-di(2-naphthalenyl)-2-vinylanthracene) (P(2ADN)) and poly(9,10-di(3-quinolinyl)-2-vinylanthracene) (P(3ADQ)), were polymerized from free radical solution addition polymerization with $M_n = 21,500$ and 15,400, respectively. The polymers are highly soluble in common organic solvents while P(3ADQ) is also soluble in polar solvents including a 1/1 mixture of ethanol/water. Both polymers are amorphous with excellent thermal stability ($T_g$ (Midpoint) = 343 °C and 298 °C for P(2ADN) and P(3ADQ), respectively). P(2ADN) exhibited three prominent absorption bands in tetrahydrofuran (364, 383 and 403 nm) and is similar to that of P(3ADQ) (369, 384 and 404 nm). The solid-state Commission Internationale d’Eclairage (CIE$_{x,y}$) color coordinates for illumination were (0.15, 0.10) for P(2ADN) and (0.15, 0.13) for P(3ADQ) which lied within the requirements for a true blue display color. The PL of the polymers red-shifted 16-17 nm from their respective pendant chromophore 2-methyl-9,10-di(2-naphthalenyl)anthracene (2MADN) and 2-methyl-9,10-di(3-quinolinyl)anthracene (3MADQ) which can be attributed to partial π-π stacking between the adjacent aromatic pendant groups in the polymer chains. The luminescences of 3MADQ and P(3ADQ) are sensitive to pH and the $pK_a$ for the alkalescent 3MADQ and P(3ADQ) calculated was 2.4 and 2.7, respectively. Both polymers have similar bandgap energy between 2.88-2.91 eV, while the LUMO/HOMO for P(3ADQ) is shifted slightly downward -0.06 to -0.03 eV compared to P(2ADN). The mobility ($\mu_{\text{hole}}$) of the two polymers were measured to be $4.0 \times 10^{-7}$ and $10^{-8}$ cm$^2$/(V·s) for P(2ADN) and
P(3ADQ), respectively.

In chapter 4, two soluble conductive vinyl copolymers P(ADN-co-S) and P(ADN-co-VK) were polymerized from free radical solution polymerization. All the polymers showed high glass transition temperatures (Tg mid-point, 203 °C to 237 °C). The PL emission of these copolymers were all similar to P(ADN) (with two maxima at 423 and 442 nm). The lifetimes (6.82 to 7.91 ns) of P(ADN-co-S) were all slightly lower than that of P(ADN) (8.40 ns). The lifetime of P(ADN-co-VK) increased from 7.8 to 8.8 ns with an increase in VK contents. The fluorescence quantum yields of P(ADN-co-S) showed an overall increasing tendency from 0.42 to 0.58 with the increase of the ratio S to ADN. The quantum efficiencies of P(ADN-co-VK), however, decreased from 0.36 to 0.19 with an increase of VK fraction. With increasing in S/VK contents, the HOMO of P(ADN-co-S)/P(ADN-co-VK) were all ranging from -5.58 eV to -5.73 eV, which were similar to that of P(ADN) (-5.71 eV). The bandgaps of P(ADN-co-S) and P(ADN-co-VK) were all about 2.97 eV, which were equal to that of P(ADN), and smaller than that of 2-methyl-9,10-di(1-naphthalenyl)anthracene (MADN) (3.04 eV) and poly(9-vinyl carbazole) (PVK) (3.54 eV). Preliminary electroluminescent results for a homojunction device with the configuration ITO/MoO₃ (20 nm)/P(ADN)/LiF (1 nm)/Al (100 nm) achieved only 30-50 cd/m² which was due to P(ADN) has a low mobility 4.7×10⁻⁸ cm²/(V·s) which compared to its model compound MADN has 6.5×10⁻⁴ cm²/(V·s). The wide bandgap polymers, however, can be used as a host layer for a range of conductive dopants/emitters for EL applications.

In chapter 5, two greenish-blue fluorescent monomers N-phenyl-N-(4-vinylphenyl)pyren-1-amine (Vinyl-PyPA) and 1-vinyl pyrene (VPy) were
synthesized in good yields. A series of soluble conductive vinyl copolymers P(PyPA-co-VPy) containing Vinyl-PyPA and VPy moieties at different composition ratios were prepared by free radical solution polymerization. These copolymers showed high T$_g$ midpoint from 190 °C to 201 °C. The photoluminescence (PL) emission maxima of these copolymers were all in the range of 474.5 nm to 478.5 nm, which were similar to poly(N-phenyl-N-(4-vinylphenyl)pyren-1-amine) (P(PyPA)) (475 nm) but were blue shifted in comparison to poly(1-vinyl pyrene) (PVPy) (490.5 nm). The lifetime of the copolymers increased from 10.24 to 29.73 ns with an increase in pyrene contents. The copolymers had high quantum yields (0.51) than those of the homopolymer of P(PyPA) (0.48) and PVPy (0.13). The HOMO of the copolymers remained relatively unchanged with P(PyPA), while the LUMO varied from -2.41 eV to -2.51 eV with an increase of pyrene content in the copolymers. The energy bandgaps of the copolymers (from 2.70 eV to 2.81 eV) were smaller than those of P(PyPA) (2.82 eV) and PVPy (3.47 eV). The EL spectra have peaks located at 480-524 nm. Highest luminance was obtained from homojunction PLED employing P(PyPA-co-VPy 100:0) with 1,143 cd/m$^2$ (at 100 mA/cm$^2$) while a max current density was obtained from the device with P(PyPA-co-VPy 50:50) at 110 mA/cm$^2$.

In chapter 6, two novel amphiphilic BAB-type block copolymers, ADN-PEG3400-ADN and Py-PEG3400-Py containing deep blue and bluish-green fluorescent moieties were prepared using atom transfer radical polymerization (where, ADN = poly(9,10-di(1-naphthalenyl)-2-vinylanthracene), Py = poly(1-vinyl pyrene) and PEG3400 = poly(ethylene glycol) with M$_n$ = 3,400). The overall GPC number averaged MW of the block copolymers were M$_n$
= 9,600 and 13,800, respectively, based on polystyrene MW standards. The PEG3400 segment has a $T_m$ at 64-65 °C, whereas the $T_g$ midpoint of the ADN and Py segments were found to be 230 °C and 193 °C, respectively, and are similar to their respective homopolymers indicating complete microphase segregation. The PL emission of the copolymers ADN-PEG3400-ADN exhibited two maxima at 423.5 nm and 441.5 nm while Py-PEG3400-Py has a maximum at 488.5 nm. Both copolymers form individual spherical micelles with diameter from 30-90 nm for Py-PEG3400-Py and 40-160 nm for ADN-PEG3400-ADN. The micelles, however, transform into cross-linked pearl-necklace-like aggregates at polymer concentrations above 1000 ppm.

In conclusion, all the blue/greenish blue fluorescent homopolymers and copolymers showed relatively high glass transition temperatures. All the vinyl copolymers showed good solubilities in common organic solvents. In comparison with the small molecule model compounds, the polymers were shown to have better thermal stability and a longer PL life time. The polymers have similar HOMO and LUMO compared to their fluorescent moieties. Though, usually slight red-shifts in the absorption and emission spectra could be found compared to the small molecule model compounds, the CIEs remained closed to the required values for a true blue hue for display, with the exception of the greenish-blue copolymers P(PyPA-co-VPy). All the results may indicate these polymers may have a potential prospective in the opto-electronic applications.
Future Work

1. More $\pi$-stacking polymers should be designed and synthesized.

2. Choose an appropriate polymerization method to obtain higher MW and lower PDI polymers.

3. Some high mobility materials should be used as the dopant in the device fabrication.

4. More HOMO/LUMO matching HTL and ETL should be added in the device.
## Appendix

<table>
<thead>
<tr>
<th>Appendix</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. $^1$H NMR (CDCl$_3$) of NPy</td>
<td>207</td>
</tr>
<tr>
<td>2. $^{13}$C NMR (CDCl$_3$) of NPy</td>
<td>207</td>
</tr>
<tr>
<td>3. $^1$H NMR (CDCl$_3$) of APy</td>
<td>208</td>
</tr>
<tr>
<td>4. $^{13}$C NMR (CDCl$_3$) of APy</td>
<td>208</td>
</tr>
<tr>
<td>5. $^1$H NMR (CDCl$_3$) of PyPA</td>
<td>209</td>
</tr>
<tr>
<td>6. $^{13}$C NMR (CDCl$_3$) of PyPA</td>
<td>209</td>
</tr>
<tr>
<td>7. $^1$H NMR (CDCl$_3$) of PyPA-CHO</td>
<td>210</td>
</tr>
<tr>
<td>8. $^{13}$C NMR (CDCl$_3$) of PyPA-CHO</td>
<td>210</td>
</tr>
<tr>
<td>9. $^1$H NMR (CDCl$_3$) of Vinyl-PyPA</td>
<td>211</td>
</tr>
<tr>
<td>10. $^{13}$C NMR (CDCl$_3$) of Vinyl-PyPA</td>
<td>211</td>
</tr>
<tr>
<td>11. $^1$H NMR (CDCl$_3$) of VPy</td>
<td>212</td>
</tr>
<tr>
<td>12. $^{13}$C NMR (CDCl$_3$) of VPy</td>
<td>212</td>
</tr>
<tr>
<td>13. $^1$H NMR (CDCl$_3$) of Nad</td>
<td>213</td>
</tr>
<tr>
<td>14. $^{13}$C NMR (CDCl$_3$) of Nad</td>
<td>213</td>
</tr>
<tr>
<td>15. $^1$H NMR (CDCl$_3$) of MAq</td>
<td>214</td>
</tr>
<tr>
<td>16. $^{13}$C NMR (CDCl$_3$) of MAq</td>
<td>214</td>
</tr>
<tr>
<td>17. $^1$H NMR (CDCl$_3$) of MA</td>
<td>215</td>
</tr>
<tr>
<td>18. $^{13}$C NMR (CDCl$_3$) of MA</td>
<td>215</td>
</tr>
<tr>
<td>19. $^1$H NMR (CDCl$_3$) of MADBr</td>
<td>216</td>
</tr>
<tr>
<td>20. $^{13}$C NMR (CDCl$_3$) of MADBr</td>
<td>216</td>
</tr>
<tr>
<td>21. $^1$H NMR (DMSO-d) of MADN</td>
<td>217</td>
</tr>
<tr>
<td>22. MALDI-TOF MS of MADN</td>
<td>217</td>
</tr>
<tr>
<td>23. $^1$H NMR (CDCl$_3$) of ADN-CH$_2$Br</td>
<td>218</td>
</tr>
<tr>
<td>24.</td>
<td>$^1$H NMR (DMSO-d) of ADN-CHO</td>
</tr>
<tr>
<td>25.</td>
<td>MALDI-TOF MS of ADN-CHO</td>
</tr>
<tr>
<td>26.</td>
<td>$^1$H NMR (DMSO-d) of Vinyl-ADN</td>
</tr>
<tr>
<td>27.</td>
<td>MALDI-TOF MS of Vinyl-ADN</td>
</tr>
<tr>
<td>28.</td>
<td>$^1$H NMR (DMSO-d) of 2NB</td>
</tr>
<tr>
<td>29.</td>
<td>$^{13}$C NMR (DMSO-d) of 2NB</td>
</tr>
<tr>
<td>30.</td>
<td>$^1$H NMR (DMSO-d) of 2MADN</td>
</tr>
<tr>
<td>31.</td>
<td>$^{13}$C NMR (CDCl$_3$) of 2MADN</td>
</tr>
<tr>
<td>32.</td>
<td>$^1$H NMR (CDCl$_3$) of 2ADN-CHO</td>
</tr>
<tr>
<td>33.</td>
<td>$^{13}$C NMR (CDCl$_3$) of 2ADN-CHO</td>
</tr>
<tr>
<td>34.</td>
<td>$^1$H NMR (CDCl$_3$) of Vinyl-2ADN</td>
</tr>
<tr>
<td>35.</td>
<td>$^{13}$C NMR (CDCl$_3$) of Vinyl-2ADN</td>
</tr>
<tr>
<td>36.</td>
<td>$^1$H NMR (DMSO-d) of 3QB</td>
</tr>
<tr>
<td>37.</td>
<td>$^{13}$C NMR (DMSO-d) of 3QB</td>
</tr>
<tr>
<td>38.</td>
<td>$^1$H NMR (CDCl$_3$) of 3MADQ</td>
</tr>
<tr>
<td>39.</td>
<td>$^{13}$C NMR (CDCl$_3$) of 3MADQ</td>
</tr>
<tr>
<td>40.</td>
<td>$^1$H NMR (CDCl$_3$) of 3ADQ-CHO</td>
</tr>
<tr>
<td>41.</td>
<td>$^{13}$C NMR (CDCl$_3$) of 3ADQ-CHO</td>
</tr>
<tr>
<td>42.</td>
<td>$^1$H NMR (CDCl$_3$) of Vinyl-3ADQ</td>
</tr>
<tr>
<td>43.</td>
<td>$^{13}$C NMR (CDCl$_3$) of Vinyl-3ADQ</td>
</tr>
<tr>
<td>44.</td>
<td>MALDI-TOF MS of 3MADQ</td>
</tr>
<tr>
<td>45.</td>
<td>MALDI-TOF MS of 3ADQ-CHO</td>
</tr>
<tr>
<td>46.</td>
<td>MALDI-TOF MS of Vinyl-3ADQ</td>
</tr>
</tbody>
</table>
1. $^1$H NMR (CDCl$_3$) of NPy

2. $^{13}$C NMR (CDCl$_3$) of NPy
3. $^1$H NMR (CDCl$_3$) of APy

4. $^{13}$C NMR (CDCl$_3$) of APy
5. $^1$H NMR (CDCl$_3$) of PyPA

6. $^{13}$C NMR (CDCl$_3$) of PyPA
4-phenyl(pyren-1-yl)amino)benzaldehyde
(PyPA-CHO)

7. $^1$H NMR (CDCl$_3$) of PyPA-CHO

8. $^{13}$C NMR (CDCl$_3$) of PyPA-CHO
N-phenyl-N-(4-vinylphenyl)pyren-1-amine

(Vinyl-PyPA)

9. $^1$H NMR (CDCl$_3$) of Vinyl-PyPA

10. $^{13}$C NMR (CDCl$_3$) of Vinyl-PyPA
11. $^1$H NMR (CDCl$_3$) of VPy

12. $^{13}$C NMR (CDCl$_3$) of VPy
2-methyl-1,4,4a,9a-tetrahydroanthracene-9,10-dione (Nad)

13. $^1$H NMR (CDCl$_3$) of Nad

14. $^{13}$C NMR (CDCl$_3$) of Nad
2-methyl-9,10-anthracenequinone

(\text{MAq})

15. $^1\text{H NMR (CDCl}_3\text{)}$ of MAq

16. $^{13}\text{C NMR (CDCl}_3\text{)}$ of MAq
17. $^1$H NMR (CDCl$_3$) of MA

18. $^{13}$C NMR (CDCl$_3$) of MA
9,10-dibromo-2-methylanthracene

(MADBr)

19. $^1$H NMR (CDCl$_3$) of MADBr

20. $^{13}$C NMR (CDCl$_3$) of MADBr
21. $^1$H NMR (DMSO-d) of MADN

22. MALDI-TOF MS of MADN
23. $^1$H NMR (CDCl$_3$) of ADN-CH$_2$Br
24. $^1$H NMR (DMSO-d) of ADN-CHO

25. MALDI-TOF MS of ADN-CHO
26. $^1$H NMR (DMSO-d) of Vinyl-ADN

27. MALDI-TOF MS of Vinyl-ADN
28. $^1$H NMR (DMSO-d) of 2NB

29. $^{13}$C NMR (DMSO-d) of 2NB
2-Methyl-9,10-di(2-naphthalenyl)anthracene
(2MADN)

30. $^1$H NMR (DMSO-d) of 2MADN

31. $^{13}$C NMR (CDCl$_3$) of 2MADN
223

9,10-Di(2-naphthalenyl)anthracene-2-carbaldehyde (2ADN-CHO)

32. $^1$H NMR (CDCl$_3$) of 2ADN-CHO

33. $^{13}$C NMR (CDCl$_3$) of 2ADN-CHO
34. $^1$H NMR (CDCl$_3$) of Vinyl-2ADN

35. $^{13}$C NMR (CDCl$_3$) of Vinyl-2ADN
36. $^1$H NMR (DMSO-d) of 3QB

37. $^{13}$C NMR (DMSO-d) of 3QB
2-Methyl-9,10-di-(3-quinolinyl) anthracene

(3MADQ)

38. $^1$H NMR (CDCl$_3$) of 3MADQ

39. $^{13}$C NMR (CDCl$_3$) of 3MADQ
227

40. $^1$H NMR (CDCl$_3$) of 3ADQ-CHO

41. $^{13}$C NMR (CDCl$_3$) of 3ADQ-CHO
9,10-Di(3-quinolinyl)-2-vinylanthracene
(Vinly-3ADQ)

42. $^1$H NMR (CDCl$_3$) of Vinyl-3ADQ

43. $^{13}$C NMR (CDCl$_3$) of Vinyl-3ADQ
44. MALDI-TOF MS of 3MADQ

45. MALDI-TOF MS of 3ADQ-CHO
46. MALDI-TOF MS of Vinyl-3ADQ
Curriculum Vitae

Academic qualifications of the thesis author, Wang Jianli （王建利）

Born in Shanxi, China.

Education background

2003, Bachelor, School of Chemical & Environmental Engineering, China University of Mining & Technology (Beijing), China.

2006, Master, School of Chemical & Environmental Engineering, China University of Mining & Technology (Beijing), China.

Publications


highly soluble copolymers with styrene or 9-vinyl carbazole", *Polymer International*, **2013**, In Press, DOI: 10.1002/pi.4574.


September 2013