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Synthesis and Characterization of Novel Low Band Gap Semiconducting Polymers for Organic Photovoltaic and Organic Field Effect Transistor Applications

A Thesis Submitted For the Degree of Doctor of Philosophy
July 2012

By

Dickson Aleroh MSc(Hons) MPhil AMRSC

School of Engineering and Material Science (SEMS)
Queen Mary University of London
Mile End Road
London E1 4NS
Declaration

I hereby affirm that the content of this thesis, including the work and results presented, was performed principally by the author. However, as acknowledged, some of the works were administered by or with the aid of other co-workers and collaborators.

Dickson Aleroh MSc MPhil AMRSC
Abstract

This thesis describes the synthesis, characterization and device properties of a range of conjugated polymers incorporating 3,6-dilakylthieno[3,2-b]thiophene. We report a new and facile synthesis for the preparation of 3,6-dialkylthieno[3,2-b]thiophene, which is readily scaled up to the multi-gram scale. With this synthesis in hand, we initially investigated the properties of poly(thienothiophene-alt-vinylene) polymers incorporating both straight and branched side-chains. Two different polymerization methods were investigated to synthesise the conjugated polymers, namely Stille and Gilch polymerization. The Gilch route was found to lead to high molecular-weight polymers with less cis-defects in the backbone. The polymers were found to be largely amorphous by X-ray diffraction measurements, although there were clear signs of aggregation by optical investigations. Field-effect transistors fabricated with these polymers exhibited charge carrier mobilities up to 0.02 cm² V⁻¹ s⁻¹ for the straight chain analogue, with the branched polymer displaying lower mobilities. Blends with PC71BM were found to exhibit solar cell device efficiencies up to 2.5 %, with significant differences observed for polymers containing two different side-chains.

In the third chapter we investigated the properties of ethynylene-linked 3,6-dialkylthieno[3,2-b]thiophene polymers. The simple homo-polymers were found to exhibit much worse device performance than the analogous vinylene-containing polymers in transistor devices. Copolymers with a range of electron accepting monomers were also synthesized. These displayed low optical energy gaps and signs of aggregation in the solid state. Transistors were fabricated and their performance examined.

In the final part of this thesis, co-polymers bearing 3,6-dialkylthieno[3,2-b]thiophene donor and squaraine acceptor units were synthesized. These zwitterionic conjugated polymers displayed band gaps as low as 1.0 eV. The influence of the nature of the side-chains and co-monomer was investigated with regard to their optoelectronic properties.
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4.5 Reference.

Chapter 5

5.0 General Thesis Conclusions.
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## List of Polymers Synthesized

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</tr>
<tr>
<td><img src="image14.png" alt="Polymer" /></td>
<td>P6’-M</td>
<td>3 (218)</td>
</tr>
<tr>
<td><img src="image15.png" alt="Polymer" /></td>
<td>PBEHTTE-OTPD-M</td>
<td>3 (218)</td>
</tr>
<tr>
<td><img src="image16.png" alt="Polymer" /></td>
<td>P6”-M</td>
<td>3 (218)</td>
</tr>
</tbody>
</table>
$\text{PDC}_{16}\text{NEHPCBDDNE}$

$\text{-HPVTT}$

$\text{PDC}_{16}\text{BNEHPVSQTT}$

$\text{PSQ7}$

$\text{PBEHNEHPCBDENNE}$

$\text{-HPVTT}$

$\text{PBEHBNEHPVSQTT}$

$\text{PSQ8}$

4 (277)

4 (278)
## Abbreviations and Nomenclatures

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>A</td>
<td>Acceptor</td>
</tr>
<tr>
<td>ATR-FTIR</td>
<td>Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>BBMT</td>
<td>2,5-Bis(bromomethyl)thiophene.</td>
</tr>
<tr>
<td>BHJ</td>
<td>Bulk-heterojunction</td>
</tr>
<tr>
<td>BLA</td>
<td>Bond length alternation</td>
</tr>
<tr>
<td>BT</td>
<td>Benzo[2,1,3]thiadazole</td>
</tr>
<tr>
<td>13C NMR</td>
<td>Carbon-13 nuclear magnetic resonance spectroscopy</td>
</tr>
<tr>
<td>C&lt;br&gt;&lt;br&gt;</td>
<td>Capacitance</td>
</tr>
<tr>
<td>CS or CSS</td>
<td>Charge separated state</td>
</tr>
<tr>
<td>CT</td>
<td>Charge transfer state</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>C16</td>
<td>Hexadecyl</td>
</tr>
<tr>
<td>D</td>
<td>Donor</td>
</tr>
<tr>
<td>D-A-D</td>
<td>Donor-acceptor-donor</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>e or Z or q</td>
<td>Elementary charge</td>
</tr>
<tr>
<td>E</td>
<td>Electric field</td>
</tr>
<tr>
<td>F</td>
<td>Internal electric field</td>
</tr>
<tr>
<td>EH</td>
<td>2-ethylhexyl</td>
</tr>
<tr>
<td>EQE</td>
<td>Equilibrium quantum efficiency</td>
</tr>
<tr>
<td>FF</td>
<td>Fill factor</td>
</tr>
<tr>
<td>FL</td>
<td>Fluorescence</td>
</tr>
<tr>
<td>GC-MS</td>
<td>Gas chromatography mass spectroscopy</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel permeation chromatography</td>
</tr>
<tr>
<td>H-H, H-T, T-T</td>
<td>Head-to-Head, Head-to-Tail and Tail-to-Tail couplings</td>
</tr>
<tr>
<td>1H NMR</td>
<td>Proton nuclear magnetic resonance spectroscopy</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>ISD,lin</td>
<td>Drain-source current in the linear regime</td>
</tr>
<tr>
<td>ISD,sat</td>
<td>Drain-source current in the saturation regime</td>
</tr>
<tr>
<td>ION/I OFF</td>
<td>Current on-and-off ratio</td>
</tr>
</tbody>
</table>
IPCE  
Incident photon-to-current conversion efficiency

\( J_{\text{max}} \)  
Maximum short-circuit current density

\( J_{\text{SC}} \)  
Short-circuit current density

\( J_{\text{SC}} \)  
Charge Injection current

\( kT \)  
Thermal energy

\( I_{\text{in}} \)  
Light intensity

LUMO  
Lowest unoccupied molecular orbital

M  
Monomer

\( M \)  
Number average molecular weight

MDMO-PPV  
Poly(2 methoxy-5-(3’,7’-dimethyloctyloxy)-1,4-phenylene Vinylene)

MEH-PPV  
Poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene)

\( M_{\text{w}} \)  
Weight average molecular weight

NPAC  
N-alkylpyrrole carboxaldehyde

\( N_{\circ} \)  
Incident photon flux density

OTPD  
N-Octylpyrrolo[3,4-c]pyrrole-4,6-dione.

ODPP  
2,5-Octyldithienopyrrolo[3,4-c]pyrrole-1,4(2H, 5H)-dione

OPV  
Organic photovoltaic

OFET  
Organic field effect transistor

OSC  
Organic solar cell

\( ^{32}\text{P NMR} \)  
Phosphorous nuclear magnetic resonance spectroscopy

\( P_{\text{in}} \)  
Power input

\( P_{\text{out}} \)  
Power output

PL  
Photoluminescence

Pr  
Precursor

PAE  
Poly(arylene ethynylene)

pBTTT-C16  
poly(2,5-bis(3-hexadecylthiophene-2-yl)thieno[3,2-b]thiophene)

PC_{61}BM  
[6,6]-phenyl-C61-butyric acid methyl ester

PC_{71}BM  
[6,6]-phenyl-C71-butyric acid methyl ester

PCE  
Power conversion efficiency

PEDOT:PSS  
Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)

PDC_{10}TTV-M  

PDC_{12}TTV-M  
Poly[3,6-didodecylthieno[3,2-b]thiophen-2-yl vinylene]
Microwave

PDC\textsubscript{16}TTV-M
Poly(3,6-dihexadecylthieno[3,2-b]thiophen-2-yl vinylene)

Microwave

PBEHTTV-M
Poly(3,6-bis(2-ethylhexyl)thieno[3,2-b]thiophen-2-yl vinylene)

Microwave

PDC\textsubscript{16}TTV-S
Poly(3,6-dihexadecylthieno[3,2-b]thiophen-2-yl vinylene) Stille

PDC\textsubscript{16}TTV-G
Poly(3,6-hexadecylthieno[3,2-b]thiophen-2-yl vinylene) Gilch

PDC\textsubscript{16}TTE-M
Poly(3,6-dihexadecylthieno[3,2-b]thiophene-2-yl ethynylene)

Microwave

PBEHTTE-M
Poly(3,6-bis(2-ethylhexyl)thieno[3,2-b]thiophen-2-yl ethynylene)

Microwave

PDC\textsubscript{16}TTE-OTPD-M
Poly(3,6-hexadecylthieno[3,2-b]thiophene-2,5-yl ethynyl-alt-2,8-(N-octyl)thieno[3,4-c]pyrrole-4,6-dione) Microwave

PBEHTTE-OTPD-M
Poly(3,6-bis(2-ethylhexyl)thieno[3,2-b]thiophene-2,5-yl ethynyl-alt-2,8-(N-octyl)thieno[3,4-c]pyrrole-4,6-dione)

PDC\textsubscript{16}TTE-ODPP-M
Poly(3,6-hexadecylthieno[3,2-b]thiophene-2,5-yl ethynyl-alt-3,6-dithien-2-yl-2,5-diocetylpyrrolo[3,4-c]pyrrole-1,4-dione-5′,5″-diyl) Microwave

PBEHTTE-ODPP-M
Poly(3,6-bis(2-ethylhexyl)thieno[3,2-b]thiophene-2,5-diyl ethynyl-alt-3,6-bis(thien-2-yl)-2,5-diocetylpyrrolo[3,4-c]pyrrole-1,4-dione-5′,5″-diyl) Microwave

PDC\textsubscript{16}TTE-BT-M
Poly(3,6-dihexadecylthieno[3,2-b]thiophene-2,5-diyl ethynyl-alt-benzo[1,2,5]thiadiazole-4,7-diyl) Microwave

PDC\textsubscript{16}BNC\textsubscript{16}PVSQTT
Poly(3,6-dihexadecyl-2-(N-hexadecylpyrrol-2-yl)-5-(5-cyclobutadienediylium-1,3-diolate-N-hexadecylpyrrol-2-yl-5-vinyl)thieno[3,2-b]thiophene)

PDC\textsubscript{16}BNEHPVSQTT
Synthesis of Poly(3,6-dihexadecyl-2-N-2-ethylhexylpyrrol-2-yl)-5-(5-cyclobutadienediylium-1,3-diolate-N-2-ethylhexylpyrrol-2-yl-5-vinyl)thieno[3,2-b]thiophene)

PBEHBNEHPVSQTT
Synthesis of Poly(3,6-bis(N-2-ethylhexyl-2-N-2-ethylhexylpyrrol-2-yl)-5-(5-cyclobutadienediylium-1,3-diolate-N-2-ethylhexylpyrrol-2-yl-5-vinyl)thieno[3,2-b]thiophene)

PDC\textsubscript{16}BNC\textsubscript{8}PSQTT
Poly(3,6-dihexadecyl-2,5-bis(N-octylpyrrol-2-yl)thieno[3,2-
PDC$_{16}$BNC$_8$PCBDNC$_8$PTT Poly(3,6-dihexyldecyl-2-N-octylpyrrol-2-yl-5-(5-cyclobutenediylium-1,3-diolate-N-octylpyrrol-2-yl)thieno[3.2-b]thiophene)

PDI Polydispersity index

PESA Photoelectron spectroscopy in the air

Psq and PSQ Polysquaraine derivative with and without vinylene bridges

$R_s$ Series resistance

$R_{SH}$ Shunt resistance

SM Starting Material

$S_1$ Singlet state

SQ or Sq Squaric acid

$T_1$ Triplet state

TGA Thermogravimetric Analysis

T23bT Thieno[2,3-b]thiophene

T32bT Thieno[3,2-b]thiophene

T34bT Thieno[3,4-b]thiophene

T34cT Thieno[3,4-c]thiophene

TTA Thieno[3,2-b]thiophene acetylene

TTE Thieno[3,2-b]thiophene ethynylene

TTV Thieno[3,2b]thiophene vinylene

UPS Ultraviolet photoelectron spectroscopy

UV-vis Ultraviolet-visible spectroscopy

UV-vis-NIR Ultraviolet-visible-near-infrared

$V_{\text{max}}$ Maximum open-circuit voltage

$V_{DS}$ Drain-Source voltage

$V_{GS}$ Gate-Source voltage

$V_{th}$ Threshold voltage

$V_{OC}$ Open-circuit voltage

XRD X-ray diffraction

$\Lambda$ Incident photon wavelength

M Charge carrier or field effect mobility

$\tau$ Charge carrier lifetime