2005

Electrochemical and photovoltaic properties of poly(thiophene)s

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ELECTROCHEMICAL AND PHOTOVOLTAIC PROPERTIES OF POLY(THIOPHENE)S

A thesis submitted in fulfilment of the

requirements for the award of the degree

DOCTOR OF PHILOSOPHY

from

UNIVERSITY OF WOLLONGONG

by

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DEPARTMENT OF CHEMISTRY

October 2005

DECLARATION

This is to certify that the work described in this thesis is my own unless otherwise indicated and has not been submitted for qualifications at any other academic institution.

George Tsekouras

October 2005

ACKNOWLEDGEMENTS

I would like to thank my supervisors, Prof Gordon Wallace and Dr Chee Too, for providing both general and technical advice, direction and support throughout the course of my study.

I greatly appreciate the help and support offered by all of my colleagues and friends at the Intelligent Polymer Research Institute (IPRI) at the University of Wollongong. In particular, I would like to acknowledge the technical assistance provided to me by Dr Jun Chen and Dr Peter Innis, and the administrative assistance given to me by Mr Elvis (Phil) Smugreski.

The efforts of Prof David Officer and his research group at the Nanomaterials Research Centre at Massey University, New Zealand, in the provision of polymer precursors and enlightening discussions, are greatly appreciated.

The financial support provided to me by the Australian Research Council (ARC) and by Prof Gordon Wallace for my PhD scholarship is greatly acknowledged.

Finally I dedicate this thesis to the memory of my late friend and colleague Dr Jeffrey (Gao) Jin, a man of great kindness and enthusiasm for life. The example you set is an inspiration to us all. I will remember you forever.

PUBLICATIONS

Tsekouras, G., Too, C.O. and Wallace, G.G., Effect of growth conditions on the photovoltaic efficiency of poly(terthiophene)-based photoelectrochemical cells, *Electrochimica Acta*, 50(16-17) (2005) 3224-3230.

CONFERENCE PRESENTATIONS

Tsekouras, G., Too, C.O. and Wallace, G.G., Conducting polymer solar cells (oral presentation), *26th Australasian Polymer Symposium (APS)*, Noosa, Australia, 2003.

Tsekouras, G., Too, C.O., Officer, D.L. and Wallace, G.G., Solar cells based on dye-doped poly(terthiophene) and a terthiophene derivative (oral presentation), *International Conference of Synthetic Metals (ICSM) Satellite Symposium*, Queenstown, New Zealand, 2004.

Tsekouras, G., Too, C.O. and Wallace, G.G., Morphology and photovoltaic characteristics of poly(terthiophene) (oral presentation), *International Conference of Synthetic Metals (ICSM)*, Wollongong, Australia, 2004.

Tsekouras, G., Too, C.O., Officer, D.L. and Wallace, G.G., Electrochemistry and photovoltaic characteristics of terthiophene and derivatives (oral presentation), *Interact*, Gold Coast, 2004.

Tsekouras, G., Too, C.O., Officer, D.L. and Wallace, G.G., Photovoltaic and electrochromic properties of poly(3-alkylthiophene)s and poly(4,4”-didecyloxyterthiophene)s (poster presentation), *2nd International Conference on Advanced Materials and Nanotechnology (AMN-2)*, Queenstown, New Zealand, 2005.

ABSTRACT

The utilisation of conducting polymers for photovoltaic applications represents the possibility of low-cost production of solar electricity. The chemical modification of the precursors used to prepare conducting polymers provides an avenue to the tuning of the photovoltaic, rheological and solubility properties of conducting polymers to suit photovoltaic applications.

Poly(thiophene)s have been widely utilised by researchers in the field of conducting polymer photovoltaics. The present study in part considered the utilisation of a range of thiophene precursors, in particular terthiophene derivatives, for the preparation of polymeric photoactive layers within photoelectrochemical cells. These precursors included a C_{60}-substituted terthiophene derivative, 3-alkylthiophenes and ether-substituted terthiophenes. Polymers synthesised from 3-alkylthiophene derivatives were also blended with a soluble C_{60} derivative to give composite films. Terthiophene itself was used to prepare photoelectrochemical cells based on poly(terthiophene). The effects of the conditions used to electrochemically grow poly(terthiophene), such as solvent, electropolymerisation technique and electropolymerisation temperature, were investigated. In addition, the incorporation of commercially available anionic dyes and cationic dyes into poly(terthiophene) during electropolymerisation and post-growth electrochemical reduction, respectively, was considered.

The investigations made in this study may be classified according to one of the following strategies for improving the photovoltaic efficiency of photoelectrochemical cells based on poly(thiophene)s: controlling polymer morphology, enhancing light

absorption, improving exciton dissociation or increasing the efficiency of electron transfer at the interface between the photoactive layer and liquid electrolyte. In this way the investigations in this study were all targeted at improving a particular aspect of the photovoltaic effect in photoelectrochemical cells.

In addition to the characterisation of the photovoltaic properties of the photoactive materials prepared, such materials were also characterised using techniques that included post-growth cyclic voltammetry, UV-Vis spectroscopy, photocurrent action spectroscopy, scanning electron microscopy and *in situ* spectroelectrochemistry. The results obtained from such characterisations gave an insight into the photovoltaic properties observed, in addition to general information on the properties of the photoactive materials investigated.

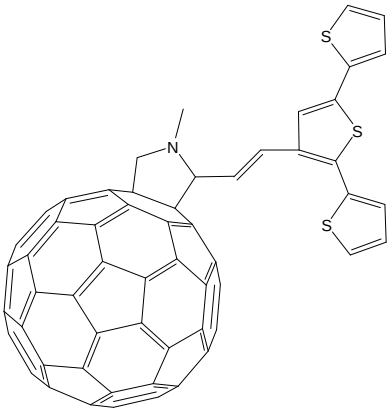
ABBREVIATIONS

A	Area
A^-	Anion
ACN	Acetonitrile
AFM	Atomic Force Microscopy
C^+	Cation
CE	Constant Potential
CI	Constant Current
CN-PPV	Cyano-substituted poly(*p*-phenylene vinylene)
CP	Conducting Polymer
CV	Cyclic Voltammetry
CrV	Crystal Violet
DCM	Dichloromethane
EC	Ethylene Carbonate
$E_{onset.ox}$	Potential at the Onset of Oxidation
EtOH	Ethanol
EV	Ethyl Violet
FF	Fill Factor
HH	Head-to-Head
^{1}H NMR	Proton Nuclear Magnetic Resonance
HT	Head-to-Tail
I_l	Illumination Intensity
I_{pp}	Current-at-Peak-Power
I_{sc}	Short-Circuit-Current

ITO	Indium Tin Oxide
I-V	Current-Voltage
LESR	Light-induced Electron Spin Resonance
LSV	Linear Sweep Voltammetry
MDMO-PPV	Poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-*p*-phenylene vinylene]
MEH-PPV	Poly(2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylene vinylene)
MeOH	Methanol
M_n	Number-averaged Molecular Weight
M_w	Weight-averaged Molecular Weight
NBB	Naphthol Blue Black
PA	Poly(acetylene)
PAn	Poly(aniline)
P(3AT)	Poly(3-alkylthiophene)
P(BTh)	Poly(2,2'-bithiophene)
PB-VF	Patent Blue VF
PC	Propylene Carbonate
PCBM	[6,6]-phenyl C_{61}-butyric acid methyl ester
PCE	Power Conversion Efficiency
P(3DDT)	Poly(3-dodecylthiophene)
PDI	Polydispersity Index
PEC	Photoelectrochemical Cell
PEO	Polyethylene Oxide
PET	Poly(ethylene teraphthalate)
P(3HT)	Poly(3-hexylthiophene)
PL	Photoluminescence

P(3MT)	Poly(3-methylthiophene)
P(3OT)	Poly(3-octylthiophene)
PPV	Poly(*p*-phenylene vinylene)
PPy	Poly(pyrrole)
PS	Polystyrene
PTh	Poly(thiophene)
P(TTh)	Poly(2,2':5',2"-terthiophene)
Q	Charge
S-B	Sulforhodamine B
SEC	Size Exclusion Chromatography
SEM	Scanning Electron Microscopy
TBAP	Tetrabutylammonium Perchlorate
TEM	Tunnelling Electron Microscopy
THF	Tetrahydrofuran
TPAI	Tetrapropylammonium Iodide
TPP-Th	3-tetraphenylporphyrinthiophene
TPP-TTh	3'-tetraphenylporphyrin-2,2':5',2"-terthiophene
UV-Vis	Ultra Violet-Visible
VB-R	Victoria Blue R
V_{oc}	Open-Circuit-Voltage
VPB-BO	Victoria Pure Blue BO
V_{pp}	Voltage-at-Peak-Power
XC-FF	Xylene Cyanole FF
λ_{max}	Wavelength of Maximum Absorption

MONOMER SYMBOLS



I

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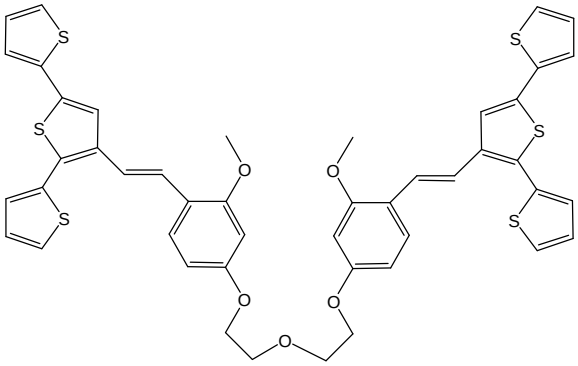
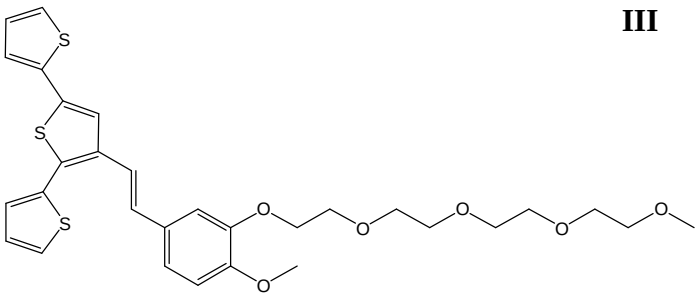


II

1,7-bis[3-methoxy-4-(2-[2,2’:5’,2”-terthiophen-3’-yl]ethenyl)phenyl]-1,4,7-trioxaheptane

III



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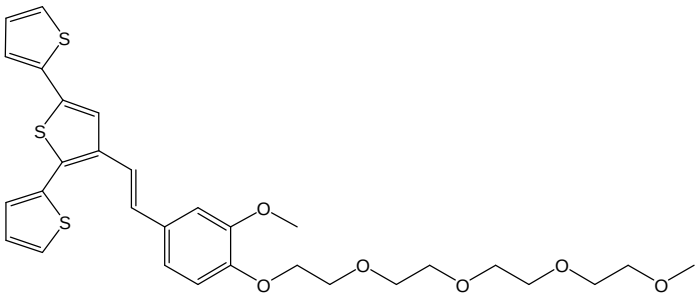
IV



3’-(2-[3-methoxy-4-(3,6,9,12-tetraoxatridec-1-yloxy)phenyl]ethenyl)-2,2’:5’,2”-terthiophene

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