

Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.

**THE SYNTHESIS AND
PROPERTIES OF POLYETHER
SUBSTITUTED
OLIGOTHIOPHENES**

**A thesis presented in partial fulfillment of the requirements
for the degree of**

**Doctor of Philosophy
in
Chemistry**

at Massey University, Palmerston North, New Zealand.

Daina Kim Grant

July 2003

Abstract

A number of novel dialkoxystyryl-substituted terthiophenes were synthesised as precursors to form conducting polymers. These compounds contained either crown ethers or polyether chains designed to complex metal cations, and polymerisable terthiophene moieties. Two isomeric cross-linked bis(terthiophene) crown ethers were also synthesised as monomers for conducting polymer synthesis, but could not be investigated further due to their insolubility. The solubility issue was circumvented by the formation of hemicrown compounds, containing two styryl-terthiophene units linked by a polyether chain. Thiophene analogues of the crown ether, open-chain ether, bis(terthiophene) crown ether and hemicrown compounds were also successfully synthesised and characterised.

The response of the terthiophene crown compounds, open-chain compounds and hemicrowns to a large range of metal cations was investigated by UV and fluorescence spectroscopy. The results obtained from this work were consistent with complexation based on size-fit and charge density of ions, and with hard-soft-acid-base theory.

Chemical polymerisation of the terthiophene crown monomers and open-chain ether terthiophene compounds was carried out using FeCl_3 . This led to the isolation of dimeric sexithiophene compounds in high yield. Characterisation of the pure sexithiophene derivatives showed that they were the product of regioselective dimerisation, caused by the asymmetric reactivity of the terthiophene-based monomers. This is believed to be due to uneven electron spin-density distribution, and theoretical calculations on the radical cation support this view. Producing dialkoxystyryl-substituted sexithiophenes by this synthetic route gave excellent yields of isomerically-pure product.

Chemical oxidation of terthiophene compounds using $\text{Cu}(\text{ClO}_4)_2$ was observed with UV/VIS/NIR spectroscopy. This allowed the observation and identification of absorption bands due to oxidised species. Reduction of these species led to sexithiophene dimers, as seen for chemical polymerisation using FeCl_3 .

Electrochemical polymerisations of the terthiophene, thiophene and sexithiophene compounds were carried out by cyclic voltammetry. Those that formed adherent films were analysed by UV/VIS/NIR spectroscopy in both the neutral and oxidised form. The electrochemical and spectroscopic evidence again pointed to the formation of dimers as the primary product of oxidation from terthiophene-based monomers. The surface morphology of the films was investigated by scanning electron microscopy, and showed a variety of morphologies.

CANDIDATE'S DECLARATION

This is to certify that the research carried out for my Doctoral thesis entitled "The Synthesis and Properties of Polyether Substituted Oligothiophenes" in the Institute of Fundamental Sciences, Massey University, Turitea, New Zealand is my own work and that the thesis material has not been used in part or in whole for any other qualification.

Candidate's Name: DAINA K. GRANT

Signature: 

Date: 5/12/03

CERTIFICATE OF REGULATORY COMPLIANCE

This is to certify that the research carried out in the Doctoral Thesis entitled “The Synthesis and Properties of Polyether Substituted Oligothiophenes” in the Institute of Fundamental Sciences at Massey University, New Zealand:

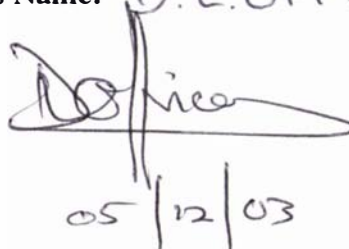
- (a) is the original work of the candidate, except as indicated by appropriate attribution in the text and/or in the acknowledgements;
- (b) that the text, excluding appendices/annexes, does not exceed 100,000 words;
- (c) all the ethical requirements applicable to this study have been complied with as required by Massey University, other organisations and/or committees which had a particular association with this study, and relevant legislation.

Candidate's Name: D.K. GRANT

Supervisor's Name: D.L. OFFICER

Signature: 

Signature:



Date: 5/12/03

Date:

05/12/03

Publications

Grant, D. K. (2002). "Synthesis and polymerisation of fully conjugated polyether-substituted terthiophenes." Synthetic Metals **135-136C**: 101-102.

Burrell, A. K., D. L. Officer and D. K. Grant (2002). "Functionalised poly(terthiophenes)." Synthetic Metals **135-136C**: 95-96.

Acknowledgements

Thank-you the management of Crop & Food Research for giving me the opportunity and the resources to undertake a PhD. In particular I would like to thank Dr Chris Downs for his unfailing support, for asking me how I was and genuinely caring about the reply.

To my chief supervisor Dr David Officer: this project wouldn't have gone ahead without your generous provision of financial support, equipment and space.

Thank-you to the staff and students of the Nanomaterials Research Centre and the Institute of Fundamental Sciences for long discussions that occasionally involved chemistry. In particular I would like to acknowledge Dr Wayne Campbell, who has made his friendship and chemical expertise freely available to me over many years. Thank-you also to Dr Gavin Collis and Dr Paul Plieger for teaching me the intricacies of pinball.

Thank-you to the support staff at both Massey University and Crop & Food Research (stores, workshop, electronics and administration) for doing what you could to help.

A special thank-you to Dr Simon Hall and Dr Keith Gordon for helpful discussions on electrochemistry and spectroscopy.

Thank-you to the staff of the Intelligent Polymer Research Institute in Wollongong and Industrial Research Ltd in Wellington for the opportunity to undertake research using your facilities and expertise.

Finally to my family and friends, especially my mother Lorraine, Koryn & Helga, Andy & Rachel, Jobee and Blake: thank-you for graciously accepting my unavailability at times during the course of this research and loving me anyway, and also for distracting me when I needed a break!

Table of Contents

Abbreviations	xix
Index of Figures	xxi
Index of Synthetic Schemes	xxix
Index of Tables	xxxix
Index of Compounds	xxxiii

1 INTRODUCTION AND LITERATURE REVIEW	1
1.1 Research Objectives	2
1.2 Crown Ethers	3
1.3 Conducting Polymers	6
1.3.1 Polymer growth	7
1.3.2 Charge transport in conducting polymers	8
1.3.3 Functionalised polymers based on thiophene	10
1.4 Past Work on Ether Functionalised Thiophenes	15
1.4.1 Open-chain ethers	15
1.4.2 Psuedo crown ethers	21
1.4.3 Alkyl spaced crown ethers	24
1.4.4 Directly bonded crown ethers	27
1.5 Past Work on Vinyl-Substituted Polythiophenes	32
1.6 Vinyl Linked Terthiophene Crown Ether Target Molecules	34
2 SYNTHESIS OF ETHER FUNCTIONALISED (TER)THIOPHENES	35
2.1 Literature Synthetic Methods	37
2.1.1 The synthesis of vinyl-substituted benzo-crown ethers	37
2.1.2 The synthesis of 3'-vinyl-substituted terthiophenes	44
2.1.3 The synthesis of vinyl-substituted thiophenes	45
2.2 Synthetic Studies Toward Monostyryl (Ter)thiophene Crowns	47
2.2.1 Synthesis of crown phosphonium salts	47
2.2.2 Wittig reactions using crown phosphonium salts	50
2.2.3 Synthesis of crown phosphonates	53
2.2.4 Horner-Emmons reactions using phosphonates	55
2.2.5 Synthesis of crown-functionalised thiophenes	58
2.3 Synthesis of Open-Chain Ether Functionalised (Ter)thiophenes	62
2.3.1 Open-chain terthiophenes	62
2.3.2 Open-chain thiophenes	68

3 SYNTHESIS OF ETHER FUNCTIONALISED BIS(TER)THIOPHENES__ 73

3.1	Literature Synthetic Methods	76
3.2	Synthesis of Bis(styryl (Ter)thiophene) Crowns	77
3.2.1	Synthesis of crown bis(phosphonium salt) and bis(phosphonate)	77
3.2.2	Wittig/Horner-Emmons reactions using mixed bis(phosphonium salt)s and bis(phosphonate)s	81
3.2.3	Synthesis of <i>syn</i> -bis(formylbenzo)-18-crown-6 XLV	83
3.2.4	Horner-Emmons reaction using <i>syn</i> -bis(formylbenzo)-18-crown-6	88
3.2.5	Synthesis of <i>anti</i> -bis(formylbenzo)-18-crown-6 XLVI	90
3.2.6	Horner-Emmons reaction using <i>anti</i> -bis(formylbenzo)-18-crown-6	94
3.2.7	Formation of bis(styryl thiophene) crowns	96
3.3	Synthesis of (Ter)thiophene Hemicrowns	98
3.3.1	Synthesis of terthiophene hemicrowns	98
3.3.2	Synthesis of thiophene hemicrowns LXIV - LXVI	103
3.4	Synthetic Summary	105

4 SPECTROSCOPIC ION BINDING STUDIES _____ 107

4.1	UV/VIS Spectroscopy	108
4.1.1	Literature review	108
4.1.1.1	Absorbance of substituted terthiophenes	108
4.1.1.2	Effect of cation complexation on absorbance of functionalised crown ethers	110
4.1.1.3	Effect of cation complexation on polyether-substituted polythiophenes	114
4.1.2	UV/VIS spectra of polyether-substituted oligothiophenes	118
4.1.2.1	Absorbance of terthiophene monomers	118
4.1.2.2	Absorbance of thiophene monomers	121
4.1.2.3	Absorbance of terthiophene dimers	122
4.1.3	Effect of cation complexation on terthiophene monomer UV/VIS spectra	124
4.1.3.1	Experimental procedure	125
4.1.3.2	Discussion	127
4.2	Fluorescence Spectroscopy	131
4.2.1	Literature review	131
4.2.1.1	Fluorescence of substituted crown ethers	131
4.2.1.2	Fluorescence of substituted terthiophenes	133
4.2.1.3	Fluorescence of crown ether-substituted thiophenes	135
4.2.2	Fluorescence of polyether-substituted oligothiophenes	137
4.2.3	Effect of cation complexation on terthiophene monomer fluorescence spectra	139
4.2.3.1	Experimental procedure	139
4.2.3.2	Discussion	142
4.3	Summary	145

5	CHEMICAL AND ELECTROCHEMICAL POLYMERISATION	147
5.1	Chemical Polymerisation	148
5.1.1	Literature review	148
5.1.2	FeCl ₃ polymerisation of terthiophene monomers	150
5.1.3	Cu(ClO ₄) ₂ polymerisation of terthiophene monomers	160
5.2	Electropolymerisation	168
5.2.1	Cyclic voltammetry in a three-electrode cell	168
5.2.2	Experimental procedures	172
5.2.3	Electropolymerisation of reference compounds	175
5.2.3.1	Terthiophene	177
5.2.3.2	Styryl terthiophene LXXVI	179
5.2.3.3	Methoxystyryl terthiophene LXXVII	182
5.2.4	Electropolymerisation of dialkoxystyryl-substituted terthiophene compounds	188
5.2.4.1	Dimethoxystyryl terthiophene XXIX	188
5.2.4.2	Styryl-15-crown-5 terthiophene I	192
5.2.4.3	Styryl-18-crown-6 terthiophene II	200
5.2.4.4	Open-chain substituted terthiophenes XXIII - XXVIII	201
5.2.4.5	Terthiophene hemicrowns LXI - LXIII	210
5.2.4.6	Styryl-15-crown-5 terthiophene copolymer formation	218
5.2.5	Electropolymerisation of thiophene monomers	229
5.2.5.1	Electropolymerisation of dialkoxystyryl-substituted thiophene compounds	229
5.2.5.2	Electropolymerisation of thiophene hemicrown compounds	230
5.2.5.3	Styryl-15-crown-5 thiophene copolymer formation	232
5.2.6	Electropolymerisation of sexithiophene compounds	236
5.2.7	Summary	239
6	CONCLUSIONS	241
7	EXPERIMENTAL DETAILS	245
	References	343

Abbreviations

AFM	atomic force microscopy
Anal.	analysis
aq.	aqueous
ArC	aromatic carbon atom
ArH	aromatic proton
AU	absorbance units
c.	concentrated
<i>ca.</i>	circa
calc	calculated
CV	cyclic voltammetry or cyclic voltammogram
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DMF	dimethylformamide
<i>E</i>	potential
Em	emission
ESR	electron spin resonance
Et	ethyl
EtOH	ethanol
eq.	equivalents
Ex	excitation
FAB-MS	fast atom bombardment mass spectrometry
Fig.	Figure
GPC	gel permeation chromatography
HOMO	highest occupied molecular orbital
HRMS	high-resolution mass spectrometry
h	hours
IR	infrared
ITO	indium tin oxide
<i>J</i>	coupling constant
L	litre
LDI-MS	laser desorption of ions mass spectrometry

LUMO	lowest unoccupied molecular orbital
μL	microlitre
mA	milliampere
MALDI-MS	matrix assisted laser desorption of ions mass spectrometry
max	maximum
Me	methyl
MeCN	acetonitrile
MeOH	methanol
min	minutes
mL	millilitre
mM	millimole/litre
mmol	millimole
mol	mole
NIR	near infrared
NMR	nuclear magnetic resonance
Ph	phenyl
SEM	scanning electron microscopy or scanning electron micrograph
TBAP	tetrabutylammonium perchlorate
ThC	thienyl carbon atom
ThH	thienyl proton
THF	tetrahydrofuran
r.t.	room temperature
sat.	saturated
TLC	thin layer chromatography
UV	ultraviolet
ν	scanning speed
V	volt
VIS	visible

Index of Figures

Figure	Page
1.1 Examples of crown ethers	3
1.2 Crown ether – metal ion complexation	4
1.3 Schematic representation of 2:1 and 3:2 ‘sandwich’ complexes	4
1.4 Examples of conjugated polymers	6
1.5 Redox activity of polythiophene	7
1.6 Polymer growth mechanism including oxidation, radical cation coupling and deprotonation	7
1.7 Degeneracy of poly(<i>trans</i> -acetylene) and non-degeneracy of polythiophene ground states	8
1.8 Thiophene	10
1.9 Coupling orientations of 3-substituted thiophenes	11
1.10 Regioregular polymers from disubstituted bithiophenes and terthiophenes	12
1.11 Regioselective chemical polymerisations by Gallazzi and McCullough, and Chen and Lere-Porte	13
1.12 Functionalisation space of polythiophene	14
1.13 Alkoxy substituted polythiophenes	16
1.14 3-Alkoxy substituted thiophenes synthesised by Roncali <i>et al.</i>	17
1.15 Cyclic voltammograms of poly[3-(3,6-dioxaheptyl)thiophene] in LiClO ₄ and TBAP	18
1.16 Heteroatom substituted polythiophenes synthesised by McCullough <i>et al.</i>	18
1.17 3-Alkoxy and 3-alkoxy-4-methylthiophenes synthesised by Feldhues <i>et al</i>	19
1.18 Poly(3-alkoxythiophenes) studied by Chen and Tsai	20
1.19 Alkoxy chain substituted polythiophenes (Scheib & Bauerle)	20
1.20 Formation of psuedo crown ether cavities during polymerisation	21
1.21 Oxyethylene linked bis(bithiophene) monomers of Roncali and Scheib	22

1.22	Oligo(oxyethylene) bridged EDOT monomers	22
1.23	Metal ion induced twisting of bithiophene monomer	23
1.24	Macrocyclic psuedo-crown ether cavities synthesised by Fabre <i>et al.</i>	24
1.25	Alkoxy spaced crowns synthesised by Bauerle and Scheib	25
1.26	Poly(3-alkoxy-4-methylthiophene)s	26
1.27	Planar and perpendicular bithiophene monomers designed by Sannicolo <i>et al.</i>	26
1.28	Crown ether functionalised thiophenes synthesised by Bicknell <i>et al.</i>	27
1.29	Directly π -conjugated monomers of Bauerle and Scheib	28
1.30	Crown ether functionalised thiophenes studied by Berlin <i>et al.</i>	29
1.31	Polymers synthesised by Yamamoto <i>et al.</i>	30
1.32	Crown containing copolymers by Bouachrine <i>et al.</i>	31
1.33	2- and 3-substituted styrylthiophenes	32
1.34	Nitrostyryl terthiophene synthesised by Cutler <i>et al.</i>	33
1.35	Vinyl linked terthiophene crown ether target molecules	34
2.1	Target compounds styryl-15-crown-5 and styryl-18-crown-6 terthiophene	36
2.2	Heck arylation of olefins	37
2.3	Synthesis of vinyl-substituted crown ethers <i>via</i> alcohol dehydration	38
2.4	Formation of vinyl-substituted dibenzo-18-crown-6	38
2.5	Vinylation of benzo-15-crown-5 <i>via</i> Knoevenagel condensation	39
2.6	Extension of Knoevenagel condensation method	39
2.7	Claisen-Schmidt condensation of crown derivatives	40
2.8	Formation of mono- and bis-crown ether styryl dyes according to the method of Gromov <i>et al.</i>	41
2.9	Formation of stilbene bis-crown ethers	42
2.10	Wittig reaction between ferrocene phosphonium salt and formylbenzo-15-crown-5	43

2.11	Formation of vinyl substituted crown <i>via</i> Wittig (or Horner Emmons) reaction	44
2.12	Synthesis of 3'-vinyl-2,2':5',2''-terthiophene <i>via</i> Grignard chemistry	44
2.13	Wittig/Horner-Emmons reactions used to synthesise vinyl-substituted terthiophenes	45
2.14	The use of Wittig reactions to synthesise vinyl thiophenes	46
2.15	¹ H NMR spectrum of styryl-15-crown-5 terthiophene I	52
2.16	¹ H NMR spectrum for benzo-15-crown-5 phosphonate XIII	55
2.17	Fully assigned ¹ H NMR spectrum of styryl-15-crown-5 thiophene XV	60
2.18	Open-chain polyether styryl-substituted terthiophenes targeted	62
2.19	Formation of open-chain ether functionalised terthiophenes	63
2.20	¹ H NMR spectra of open-chain terthiophenes XXIII-XXV (ether region)	66
2.21	Comparison of aromatic regions in ¹ H NMR spectra of compounds XXIII and XXVI	67
2.22	Styryl terthiophene reference compounds	68
2.23	¹ H NMR assignment for open-chain thiophene XXX	70
3.1	Potential for actuation effect caused by metal complexation	74
3.2	The two isomeric forms of bis(styryl terthiophene)-18-crown-6	75
3.3	MALDI-MS of <i>syn</i> -bis(styryl terthiophene)-18-crown-6 XVI after acid wash	89
3.4	Isomeric terthiophene hemicrowns targeted	98
3.5	Assigned ¹ H NMR spectrum of isovanillin-derived terthiophene hemicrown LXI	101
3.6	Comparison of ¹ H NMR spectra for terthiophene hemicrowns LXI, LXII and LXIII	102
4.1	The structure of terthiophene	108
4.2	Crown ether styryl dyes	111
4.3	Aza crown ether styryl dyes investigated by UV/VIS spectroscopy	112

4.4	Polyether substituted polythiophenes investigated by UV/VIS spectroscopy	115
4.5	Ionochromic polythiophenes synthesised by Marsella <i>et al.</i>	116
4.6	Crown ether functionalised (ter)thiophenes	117
4.7	Absorbance spectra of terthiophene monomers in MeCN	118
4.8	Solution and thin film UV/VIS spectra of 18-crown-6 terthiophene dimer LXVII	123
4.9	Change in absorbance maxima caused by addition of metal cations to terthiophene monomers	126
4.10	Styryl-15-crown-5 terthiophene I before and after addition of Mg^{2+}	128
4.11	Crown ether styryl dyes of Barzykin and Shin	132
4.12	Styryl-substituted aza crown ethers	133
4.13	Benzo-crown ether fluorophore synthesised by Cielen <i>et al.</i>	135
4.14	Pyridino crown ethers containing thiophene-based fluorophore(s)	136
4.15	Absorbance and fluorescence spectra for polyether-substituted terthiophene XXVII and polyether-substituted sexithiophene LXIX in CH_2Cl_2	138
4.16	Absorption and fluorescence spectra of styryl-15-crown-5 terthiophene I before and after addition of Mn^{2+}	140
4.17	Fluorescence quenching caused by addition of metal cations to terthiophene monomers	141
5.1	Chemical polymerisation of 15-crown-5 terthiophene to form head-to-tail, head-to-head or tail-to-tail linked dimers	151
5.2	1H NMR spectra (aromatic region) of styryl-15-crown-5 terthiophene I and 15-crown-5 terthiophene dimer LXVII	152
5.3	Fully assigned 1H NMR spectrum for terthiophene dimer LXXIII	155
5.4	Potential oligomers formed from chemical polymerisation of terthiophene hemicrown LXI	159
5.5	Oxidation and reduction of methoxystyryl terthiophene LXXVII as observed by UV/VIS spectroscopy	162
5.6	Schematic representation of a three electrode cell	169

5.7	Applied voltage, measured current and final cyclic voltammogram for ferrocene	170
5.8	Cyclic voltammetry for terthiophene	175
5.9	Post-polymerisation CVs of terthiophene in 0.1 M TBAP and 0.1 M LiClO ₄	176
5.10	Growth CV and surface morphology of terthiophene film on ITO-coated mylar	177
5.11	UV/VIS/NIR spectra of poly(terthiophene) in the neutral and oxidised forms	178
5.12	Cyclic voltammetry for styryl terthiophene LXXVI	179
5.13	Post-polymerisation CVs for styryl terthiophene LXXVI in 0.1 M TBAP and 0.1 M LiClO ₄	180
5.14	Growth CV and surface morphology of styryl terthiophene LXXVI film on ITO-coated mylar	181
5.15	UV/VIS/NIR spectra of poly(styryl terthiophene) in the oxidised form	182
5.16	Cyclic voltammetry for methoxystyryl terthiophene LXXVII	183
5.17	Post-polymerisation CVs of methoxystyryl terthiophene LXXVII in 0.1 M TBAP and 0.1 M LiClO ₄	184
5.18	Growth CV and SEM for methoxystyryl terthiophene LXXVII film	186
5.19	UV/VIS/NIR spectra of poly(methoxystyryl terthiophene) in the neutral and oxidised forms	187
5.20	Cyclic voltammetry for dimethoxystyryl terthiophene XXIX	188
5.21	Post-polymerisation CVs of dimethoxystyryl terthiophene XXIX in 0.1 M TBAP and 0.1 M LiClO ₄	190
5.22	Growth CV and SEM of dimethoxystyryl terthiophene XXIX film on ITO-coated mylar	191
5.23	UV/VIS/NIR spectra of poly(dimethoxystyryl terthiophene) in the neutral and oxidised forms	192
5.24	Cyclic voltammetry for styryl-15-crown-5 terthiophene I	193

5.25	Post-polymerisation CVs of styryl-15-crown-5 terthiophene I in 0.1 M TBAP and 0.1 M LiClO ₄	195
5.26	Growth CV for styryl-15-crown-5 terthiophene I	196
5.27	Post-polymerisation CVs of styryl-15-crown-5 terthiophene I in 0.1 M TBAP and 0.1 M LiClO ₄	197
5.28	Growth CV and SEM of styryl-15-crown-5 terthiophene I film	198
5.29	UV/VIS/NIR spectra of styryl-15-crown-5 terthiophene I in the neutral and oxidised forms	199
5.30	Overoxidation of styryl-15-crown-5 terthiophene I	200
5.31	Cyclic voltammetry for styryl-18-crown-6 terthiophene II	200
5.32	Cyclic voltammetry for open-chain terthiophene XXIII	202
5.33	Post-polymerisation CVs of open-chain terthiophene XXIII in 0.1 M TBAP and 0.1 M LiClO ₄	203
5.34	UV/VIS/NIR spectra of open-chain terthiophene XXIII in the neutral and oxidised forms	204
5.35	Growth CV and SEM image of XXVI film on ITO-coated mylar	205
5.36	Cyclic voltammetry for open-chain terthiophene XXVI	206
5.37	Post-polymerisation CVs of open-chain terthiophene XXVI in 0.1 M TBAP and 0.1 M LiClO ₄	207
5.38	Growth CV and SEM image of open-chain terthiophene XXVI film on ITO-coated mylar	208
5.39	UV/VIS/NIR spectrum of poly(XXVI) in the oxidised form	209
5.40	Cyclic voltammetry for open-chain terthiophene XXVII	209
5.41	Cyclic voltammetry for isovanillin hemicrown LXI	211
5.42	Post-polymerisation CVs of hemicrown LXI in 0.1 M TBAP and 0.1 M LiClO ₄	213
5.43	Growth CV and surface morphology of isovanillin hemicrown LXI film from 1:1 MeCN:CH ₂ Cl ₂	215
5.44	Growth CV and scanning electron micrograph of isovanillin hemicrown LXI film grown from CH ₂ Cl ₂	216
5.45	Schematic diagram of terthiophene hemicrown surface deposition	217
5.46	UV/VIS/NIR spectra of hemicrown LXI in the neutral and oxidised forms	218

5.47	Cyclic voltammetry for styryl-15-crown-5 terthiophene: terthiophene copolymer	219
5.48	Post-polymerisation CVs of 15-crown-5:terthiophene copolymer in 0.1 M TBAP and 0.1 M LiClO ₄	220
5.49	Growth CV and surface morphology of 15-crown-5 terthiophene: terthiophene copolymer film on ITO-coated mylar	221
5.50	UV/VIS/NIR spectra of styryl-15-crown-5 terthiophene: terthiophene copolymer in the neutral and oxidised forms	222
5.51	Cyclic voltammetry for 15-crown-5 terthiophene:terthiophene hemicrown copolymer	223
5.52	Post-polymerisation CVs of 15-crown-5 terthiophene: hemicrown copolymer in 0.1 M TBAP and 0.1 M LiClO ₄	224
5.53	Growth CV and surface morphology of 15-crown-5 terthiophene: hemicrown copolymer film on ITO-coated mylar	225
5.54	UV/VIS/NIR spectra of styryl-15-crown-5 terthiophene: hemicrown:copolymer in the neutral and oxidised forms	226
5.55	Cyclic voltammetry for styryl-15-crown-5 thiophene XV	227
5.56	Cyclic voltammetry for thiophene hemicrown LXV	231
5.57	Cyclic voltammetry for styryl-15-crown-5 thiophene: terthiophene copolymer	232
5.58	Post-polymerisation CVs of terthiophene:thiophene crown copolymer in 0.1 M TBAP and 0.1 M LiClO ₄	233
5.59	Growth CV and SEM of thiophene crown:terthiophene copolymer on ITO-coated mylar	234
5.60	UV/VIS/NIR spectra of thiophene crown:terthiophene copolymer in the neutral and oxidised forms	235
5.61	Cyclic voltammetry for open-chain sexithiophene LXXIII	237
5.62	Cyclic voltammetry for open-chain sexithiophene LXXII	237
5.63	Cyclic voltammetry for open-chain sexithiophene LXX	238

Index of Synthetic Schemes

Scheme		Page
1	Alternative routes toward target compounds I and II	48
2	Formation of benzo-crown phosphonium salts III and IV	49
3	Wittig reactions between phosphonium salts III-IV and nitrobenzaldehyde	51
4	Wittig reactions between phosphonium salts III-IV and terthiophene aldehyde	53
5	Formation of benzo-crown phosphonates XIII and XIV	54
6	Horner-Emmons reactions between phosphonates XIII-XIV and terthiophene aldehyde	57
7	Formation of styryl terthiophene crowns I and II from terthiophene phosphonate	58
8	Formation of styryl-15-crown-5 thiophene XV	59
9	Synthesis of styryl-18-crown-6 thiophene XVI	61
10	Formation of tosylated glycols according to Lauter <i>et al.</i>	63
11	Formation of polyether-substituted benzaldehydes XVII-XXII	64
12	Horner-Emmons reaction to form open-chain terthiophenes	65
13	Synthesis of dimethoxystyryl terthiophene	68
14	Open-chain ether functionalised thiophenes XXX-XXXV	69
15	Synthesis of dimethoxystyryl thiophene	71
16	Alternative routes toward target crown linked bis(terthiophene)s XXXVII and XXXVIII	78
17	Formation of <i>syn/anti</i> isomeric mixture of crown bis(phosphonium salt)s XXXIX and bis(phosphonate)s XL	79
18	Wittig-type reactions between disubstituted crowns XXXIX-XL and 4-nitrobenzaldehyde	83
19	Alternative routes toward <i>syn</i> -bis(formylbenzo)-18-crown-6 XLV	84
20	Products formed from attempted demethylation of 1,5-bis(2'-methoxy-4'-formylphenoxy)-3-oxapentane XLIX	85

21	S_N2 and S_NAr reactions between the thioethoxide ion and a substituted benzaldehyde	86
22	Horner-Emmons reaction between dialdehyde XLV and terthiophene phosphonate	88
23	Formation of <i>anti</i> -bis(formylbenzo)-18-crown-6 XLVI	92
24	Products formed from demethylation of 1-(2'-methoxy-4'-formylphenoxy)-5-(2''-methoxy-5''-formylphenoxy)-3-oxapentane LIV	94
25	Horner-Emmons reaction between dialdehyde XLVI and terthiophene phosphonate	95
26	Formation of <i>syn</i> -bis(styryl thiophene)-18-crown-6 LIX	96
27	Synthesis of <i>anti</i> -bis(styryl thiophene)-18-crown-6 LX	97
28	Formation of bis(terthiophene) hemicrowns LXI-LXIII	99
29	Synthesis of bis(thiophene) hemicrowns LXIV-LXVI	104

Index of Tables

Table	Page
4.1 Crown ether cavity sizes	111
4.2 Metal cation ionic diameters	112
4.3 Solution absorbance maxima of terthiophene monomers	120
4.4 Solution absorbance maxima of thiophene monomers	121
4.5 Solution and solid-state absorbance maxima of terthiophene dimers	122
4.6 Misono softness values for metal cations	129
4.7 Fluorescence data for terthiophene and sexithiophene monomers obtained in CH ₂ Cl ₂	137
5.1 Calculated spin density values for styryl-substituted terthiophenes	157
5.2 Oxidation and reduction absorbance data for terthiophene monomers treated with Cu(ClO ₄) ₂ and hydrazine	161
5.3 Absorption maxima for electrochemically produced films and chemically produced dimer films	227
5.4 Peak oxidation and reduction potentials obtained on electro-polymerisation by cyclic voltammetry over the range ± 1.0 V	228

Index of Compounds

For structures and systematic names of all compounds, refer to Chapter 7. A fold-out reference guide to the structures of terthiophene- and sexithiophene-based compounds is provided inside the back cover.

I	styryl-15-crown-5 terthiophene
II	styryl-18-crown-6 terthiophene
III	benzo-15-crown-5 phosphonium salt
IV	benzo-18-crown-6 phosphonium salt
V	formylbenzo-15-crown
VI	formylbenzo-18-crown-6
VII	hydroxymethylbenzo-15-crown-5
VIII	hydroxymethylbenzo-18-crown-6
IX	chloromethylbenzo-15-crown-5
X	chloromethylbenzo-18-crown-6
XI	nitrostyryl-15-crown-5
XII	nitrostyryl-18-crown-6
XIII	benzo-15-crown-5 phosphonate
XIV	benzo-18-crown-6 phosphonate
XV	styryl-15-crown-5 thiophene
XVI	styryl-18-crown-6 thiophene
XVII	isovanillin short-chain benzaldehyde
XVIII	isovanillin medium-chain benzaldehyde
XIX	isovanillin long-chain benzaldehyde
XX	vanillin short-chain benzaldehyde
XXI	vanillin medium-chain benzaldehyde
XXII	vanillin long-chain benzaldehyde
XXIII	isovanillin short-chain terthiophene
XXIV	isovanillin medium-chain terthiophene
XXV	isovanillin long-chain terthiophene
XXVI	vanillin short-chain terthiophene

XXVII	vanillin medium-chain terthiophene
XXVIII	vanillin long-chain terthiophene
XXIX	dimethoxystyryl terthiophene
XXX	isovanillin short-chain thiophene
XXXI	isovanillin medium-chain thiophene
XXXII	isovanillin long-chain thiophene
XXXIII	vanillin short-chain thiophene
XXXIV	vanillin medium-chain thiophene
XXXV	vanillin long-chain thiophene
XXXVI	dimethoxystyryl thiophene
XXXVII	<i>syn</i> -bis(styryl terthiophene)-18-crown-6
XXXVIII	<i>anti</i> -bis(styryl terthiophene)-18-crown-6
XXXIX	18-crown-6 bisphosphonium salt (isomeric mixture)
XL	18-crown-6 bisphosphonate (isomeric mixture)
XLI	bis(formylbenzo)-18-crown-6 (isomeric mixture)
XLII	bis(hydroxymethylbenzo)-18-crown-6 (isomeric mixture)
XLIII	bis(chloromethylbenzo)-18-crown-6 (isomeric mixture)
XLIV	bis(nitrostyryl)-18-crown-6 (isomeric mixture)
XLV	<i>syn</i> -bis(formylbenzo)-18-crown-6
XLVI	<i>anti</i> -bis(formylbenzo)-18-crown-6
XLVII	isovanillin methoxy hemicrown
XLVIII	isovanillin hydroxy hemicrown
XLIX	vanillin methoxy hemicrown
L	vanillin hydroxy hemicrown
LI	4-ethylsulfanyl-3-hydroxy-benzaldehyde
LII	3-hydroxy-4-[2-(2-hydroxy-ethoxy)-ethoxy]-benzaldehyde
LIII	3-[2-(2-chloro-ethoxy)-ethoxy]-4-methoxy-benzaldehyde
LIV	mixed methoxy hemicrown
LV	mixed hydroxy hemicrown
LVI	4-[2-(2-chloro-ethoxy)-ethoxy]-3-methoxy-benzaldehyde
LVII	4-ethylsulfanyl-3-methoxy-benzaldehyde
LVIII	4-hydroxy-3-[2-(2-hydroxy-ethoxy)-ethoxy]-benzaldehyde
LIX	<i>syn</i> -bis(styryl thiophene)-18-crown-6

LX	<i>anti</i> -bis(styryl thiophene)-18-crown-6
LXI	isovanillin terthiophene hemicrown
LXII	vanillin terthiophene hemicrown
LXIII	mixed terthiophene hemicrown
LXIV	isovanillin thiophene hemicrown
LXV	vanillin thiophene hemicrown
LXVI	mixed thiophene hemicrown
LXVII	15-crown-5 terthiophene dimer
LXVIII	18-crown-6-terthiophene dimer
LXIX	isovanillin short-chain terthiophene dimer
LXX	isovanillin medium-chain terthiophene dimer
LXXI	isovanillin long-chain terthiophene dimer
LXXII	vanillin short-chain terthiophene dimer
LXXIII	vanillin medium-chain terthiophene dimer
LXXIV	vanillin long-chain terthiophene dimer
LXXV	dimethoxystyryl terthiophene dimer
LXXVI	styryl terthiophene
LXXVII	methoxystyryl terthiophene
LXXVIII	styryl terthiophene dimer
LXXIX	methoxystyryl terthiophene dimer