

Edited by
G. Hadzioannou and G.G. Malliaras

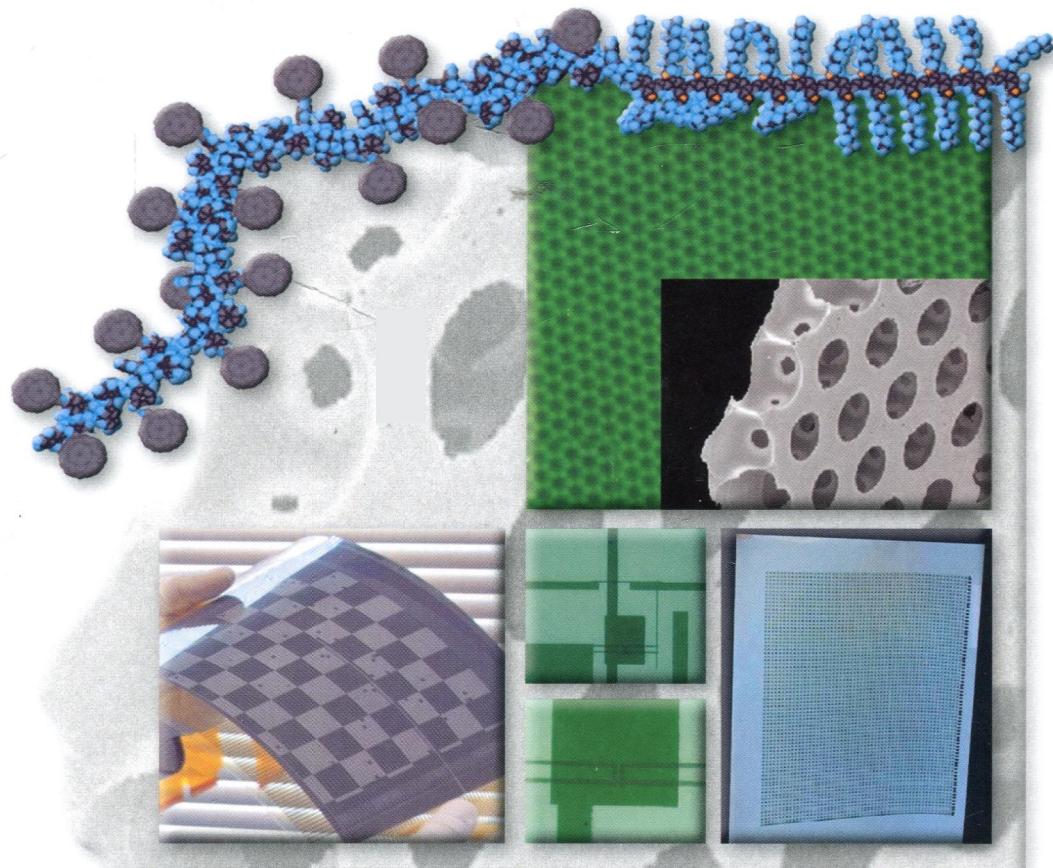
WILEY-VCH

Semiconducting Polymers

Chemistry, Physics and Engineering

Volume 2

Second, Completely Revised and Enlarged Edition



Semiconducting Polymers

Chemistry, Physics and Engineering

Volume 2

Edited by

Georges Hadzioannou and George G. Malliaras

Second, Completely Revised and Enlarged Edition



WILEY-VCH Verlag GmbH & Co. KGaA

The Editors

Prof. Dr. Georges Hadzioannou

Ecole Européenne Chimie
Polymères Matériaux (ECPM)
Université Louis Pasteur
and
CNRS

Laboratoire d'Ingenierie des Polymères
pour les Hautes Technologies
Université Louis Pasteur
25, rue Becquerel
67087 Strasbourg cedex 2
France
hadzii@ecpm.u-strasbg.fr

Prof. Dr. George G. Malliaras

Department of Materials Science
and Engineering
Cornell University
327 Bard Hall
Ithaca, NY 14853
USA
ggm1@cornell.edu

All books published by Wiley-VCH are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

**Bibliographic information published by
the Deutsche Nationalbibliothek**

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available in the Internet at <http://dnb.d-nb.de>.

© 2007 WILEY-VCH Verlag GmbH & Co. KGaA,
Weinheim, Germany

All rights reserved (including those of translation
into other languages). No part of this book may
be reproduced in any form – by photostripping,
microfilm, or any other means – nor transmitted
or translated into a machine language without
written permission from the publishers.

Registered names, trademarks, etc. used in this
book, even when not specifically marked as such,
are not to be considered unprotected by law.

Typesetting K+V Fotosatz GmbH, Beerfelden

Printing betz-druck GmbH, Darmstadt

Bookbinding Litges & Dopf Buchbinderei
GmbH, Heppenheim

Printed in the Federal Republic of Germany

Printed on acid-free paper

ISBN: 978-3-527-31271-9

Contents

Foreword V

Preface VII

List of Contributors XXI

VOLUME 1

Synthetic Methods

1	Synthetic Methods for Semiconducting Polymers	1
	<i>Alberto Bolognesi and Maria Cecilia Pasini</i>	
1.1	Introduction and Overview	1
1.2	Synthetic Pathways for PA	3
1.2.1	Classical Synthesis for PA	3
1.2.2	The Precursor Route	4
1.2.3	The Grafting Approach	5
1.3	Conjugated Polymers by Step-Growth Polymerizations	6
1.3.1	Poly(3-Alkylthiophenes)	7
1.3.2	Polyparaphenylenes	13
1.3.3	Polyfluorenes	18
1.3.4	Copolymers with Phenylenes and Other Aromatics	21
1.3.5	The PPV Family	25
1.3.6	Poly(phenyleneethynylenes)	31
1.3.7	Copolymers for Triplet Emitters	32
1.3.8	Polyazines and Polyazomethines	33
1.4	Block Copolymers	35
1.4.1	Anionic Polymerization Processes	36
1.4.2	BCs from Tetramethylpiperidinoxyl-mediated Polymerization	37
1.4.3	BCs from Atom Transfer Radical Polymerization	41
1.4.4	BCs from Polyfluorenes	42

1.4.5	<i>p–n</i> Diblock Polymers	46
1.4.6	Conjugated–Conjugated BCs	46
1.4.7	The Oligomeric Approach	50
1.5	Towards Autoorganized Devices	51
	References	62
2	Processable Semiconducting Polymers Containing Oligoconjugated Blocks	69
	<i>Ioannis K. Kallitsis, Panagiotis K. Tsolakis, and Aikaterini K. Andreopoulou</i>	
2.1	Introduction	69
2.2	Rod–Coil Block Copolymers	70
2.2.1	Poly(<i>p</i> -Phenylene)-Type Rod–Coil Copolymers	70
2.2.2	Poly(<i>p</i> -Phenylene-vinylene)-Type Rod–Coil Copolymers	73
2.2.3	Polyfluorene-Type Rod–Coil Copolymers	79
2.2.4	Poly(<i>p</i> -Phenyleneethynylene)-Type Rod–Coil Copolymers	83
2.2.5	Polythiophene-Type Rod–Coil Copolymers	87
2.2.6	Other Luminescent Rod–Coil Copolymers	89
2.3	Alternating Conjugated–Nonconjugated Polymers	92
2.3.1	Oligo(Phenylene-vinylenes)	92
2.3.2	Oligophenylenes	99
2.3.3	Oligothiophenes	102
2.3.4	Anthracenes	106
2.3.5	Other Aromatic Structures	109
2.3.6	Heteroatom-containing Structures	111
	References	113
Structure/Morphology		
3	Interfacial Aspects of Semiconducting Polymer Devices	121
	<i>Richard A. L. Jones</i>	
3.1	Introduction	121
3.2	Some Basics of Polymer Blend Thermodynamics and Dynamics	122
3.3	Surface Segregation, Surface-driven Phase Separation, Wetting and Self-Stratification	126
3.4	Morphology in Thin Films of Semiconducting Polymer Blends	129
3.5	Surface Segregation in Polymer-doped Conducting Polymers	131
3.6	Interface Structure	134
3.7	Conclusions	136
	References	137

Electronic Structure of Interfaces

4	Electronic Structure of Surfaces and Interfaces in Conjugated Polymers	141
	<i>Michael Lögdlund, Mats Fahlman, Stina K. M. Jönsson, and William R. Salaneck</i>	
4.1	Introduction	141
4.2	Photoelectron Spectroscopy	142
4.2.1	X-Ray Photoelectron Spectroscopy	145
4.2.2	Ultraviolet Photoelectron Spectroscopy	146
4.3	Theoretical Approaches	148
4.4	Materials	149
4.4.1	<i>Trans</i> -Polyacetylene	149
4.4.2	Poly(<i>p</i> -phenylenevinylene)	152
4.4.3	Poly(3,4-ethylenedioxythiophene)	154
4.4.4	Solvent Effect on Conductivity in PEDOT-PSS Films	156
4.5	Charge Storage States in Conjugated Polymers	158
4.6	Interface Formations in Conjugated Systems	161
4.7	Summary	172
	References	172

Photophysics

5	Photophysics of Conjugated Polymers	179
	<i>Lewis Rothberg</i>	
5.1	Introduction and Overview	179
5.2	Definitions and Terminology	180
5.3	Spectroscopy	182
5.3.1	Spectroscopy of the Conjugated Polymers in Solution	182
5.3.2	Spectroscopy of Conjugated Polymer Films	183
5.3.2.1	Mixed Solvent Studies of PL and Absorption	183
5.3.2.2	Further Experimental Evidence for the Two-Species Model	186
5.4	Photophysics	188
5.4.1	Photophysics and Excited-State Decay Dynamics in Solution	188
5.4.2	Photophysics in Neat Conjugated Polymer Films	189
5.4.2.1	Role of Interchain Polaron Pair Formation	190
5.4.2.2	Fate of Polaron Pairs	192
5.4.2.3	Formation of Excimers and Exciplexes	194
5.4.2.4	Spectral Dynamics in the Decay of PL	194
5.5	Summary	196
5.5.1	Spectroscopy	196
5.5.2	Exciton Binding Energy	197
5.5.3	Luminescence Quantum Yield	198

5.5.4	PL Decay Dynamics	199
5.6	Conclusion	200
	References	201
6	Photophysics in Semiconducting Polymers: The Case of Polyfluorenes	205
	<i>Christoph Gadermaier, Larry Luer, Alessio Gambetta, Tersilla Virgili, Margherita Zavelani-Rossi, and Guglielmo Lanzani</i>	
6.1	Introduction	205
6.2	Experimental	206
6.2.1	The Pump–Probe Technique	206
6.2.2	The Pump–Push–Probe Experiment	210
6.2.3	The Field-Assisted Pump–Probe Experiment	210
6.2.4	Excitation Cross-Correlation Photoconductivity	211
6.2.5	Quasi-Steady-State Photoinduced Absorption	211
6.3	Low-Dimensional Physics in Conjugated Chains	212
6.4	Ground-State Absorption and cw Photoluminescence	213
6.5	Long-Lived Photoexcitation in Polyfluorenes (PFs)	214
6.6	Singlet Exciton Dynamics	215
6.7	On-Chain Emissive Defects	218
6.8	Charged Excitations and Their Photogeneration Mechanism	221
6.9	Intrachain Dynamics	224
6.10	Three-Pulse Time-Resolved Experiments	226
6.11	Light-Emitting-Diode-Related Dynamics in the Ultrafast Timescale	229
	References	232
7	Spectroscopy of Photoexcitations in Conjugated Polymers	235
	<i>Z. Valy Vardeny and Markus Wohlgemann</i>	
7.1	Introduction	235
7.1.1	Basic Properties of π -Conjugated Polymers	235
7.1.2	Optical Transitions of Photoexcitations in Conducting Polymers	238
7.1.3	Optical Transitions of Charged Excitations in NDGS Polymers	238
7.1.3.1	Polaron Recombination and Quantum Efficiency of OLEDs	239
7.1.4	Optical Transitions of Neutral Excitations in NDGS Polymers	240
7.1.4.1	Singlet Excitons	240
7.1.4.2	Triplet Excitons	241
7.2	Experimental Methods	241
7.2.1	Photomodulation Spectroscopy of Long-Lived Photoexcitations	242
7.2.2	Picosecond Pump and Probe Spectroscopy	243
7.2.3	Optically Detected Magnetic Resonance Techniques	243
7.3	Experimental Results: cw PA Spectroscopy	245
7.3.1	Photophysics of Red-Emitting Polythiophenes: Regioregular, Regiorandom	245

7.3.1.1	Photomodulation Studies of RRa-P3HT	247
7.3.1.2	Photomodulation Studies in RR-P3HT	248
7.3.1.3	The Polaron Relaxation Energy	251
7.3.2	Photophysics of a Blue-Emitting Polyfluorene	251
7.3.2.1	Electronic Structure of PFO Phases	251
7.4	Transient Pump-and-Probe Spectroscopy	254
7.4.1	Ground and Excited State Absorption in PPV	254
7.5	Multiple-Pulse Transient Spectroscopy	257
7.5.1	mA_g Relaxation Dynamics	258
7.5.2	kA_g Relaxation Dynamics	260
7.6	ODMR Spectroscopy: Measurement of Spin-Dependent Polaron Recombination Rates	262
7.6.1	Spin-Dependent Exciton Formation Probed by PADMR Spectroscopy	262
7.6.2	Material Dependence of Spin-Dependent Exciton Formation Rates	264
7.7	Summary	265
	References	267

Transport/Injection

8	Charge Transport in Neat and Doped Random Organic Semiconductors	275
	<i>Vladimir I. Arkhipov†, Igor I. Fishchuk, Andriy Kadashchuk, and Heinz Bässler</i>	
8.1	Introduction	275
8.2	Charge Generation	276
8.3	Charge-Carrier Hopping in Noncrystalline Organic Materials	279
8.3.1	Outline of Conceptual Approaches	279
8.3.1.1	The Continuous Time Random Walk Formalism	279
8.3.1.2	The Gill Equation	280
8.3.1.3	The Hopping Approach	281
8.3.1.4	Monte Carlo Simulation	282
8.3.1.5	The Effective Medium Approach	284
8.3.1.6	Effect of Site Correlation	284
8.3.1.7	Polaron Transport	286
8.3.2	Stochastic Hopping Theory	287
8.3.2.1	Carrier Equilibration via Downward Hopping	290
8.3.2.2	Thermally Activated Variable-Range Hopping: Effective Transport Energy	292
8.3.2.3	Dispersive Hopping Transport	296
8.3.2.4	Equilibrium Hopping Transport	298
8.3.2.5	The Effect of Backward Carrier Jumps	300
8.3.2.6	Hopping Conductivity at High Carrier Density	301

8.3.2.7	Coulomb Effects on Hopping in a Doped Organic Material	304
8.3.3	Effective-Medium Approximation Theory of Hopping Charge-Carrier Transport	310
8.3.3.1	The EMA Theory Formulations	312
8.3.3.2	Miller-Abrahams Formalism	313
8.3.3.3	Temperature Dependence of the Drift Mobility	314
8.3.3.4	Electric-Field Dependence of the Drift Mobility	318
8.3.3.5	Hopping Transport in Organic Solids with Superimposed Disorder and Polaron Effects	321
8.3.3.6	Low-Field Hopping Transport in Energetically and Positionally Disordered Organic Solids	323
8.3.3.7	Charge-Carrier Transport in Disordered Organic Materials in the Presence of Traps	329
8.4	Experimental Techniques	333
8.4.1	Charge-Carrier Generation	333
8.4.1.1	Generation Versus Transport-Limited Photocurrents	333
8.4.1.2	Delayed Charge-Carrier Generation	335
8.4.1.3	Optically Detected Charge-Carrier Generation	335
8.4.2	Experimental Techniques to Measure Charge Transport	336
8.4.2.1	The Time-of-Flight Technique	336
8.4.2.2	Space-Charge-Limited Current Flow	337
8.4.2.3	Determination of the Charge-Carrier Mobility Based Upon Carrier Extraction by Linearly Increasing Voltage	339
8.4.2.4	Charge-Carrier Motion in a Field-Effect Transistor	340
8.4.2.5	The Microwave Technique	341
8.4.2.6	Charge-Carrier Motion Probed by Terahertz Pulse Pulses	342
8.5	Experimental Results	342
8.5.1	Analysis of Charge Transport in a Random Organic Solid with Energetic Disorder	342
8.5.2	The Effect of Positional Disorder	353
8.5.3	Trapping Effects	356
8.5.4	Polaron Effects	361
8.5.5	Chemical and Morphological Aspects of Charge Transport	365
8.5.6	On-Chain Transport Probed by Microwave Conductivity	371
8.6	Conclusions	373
	References	375
9	Charge Transport and Injection in Conjugated Polymers	385
	<i>Paul W. M. Blom, Cristina Tanase, and Teunis van Woudenberg</i>	
9.1	Introduction	385
9.2	Charge Transport	388
9.2.1	Disorder-Induced Localized States	388
9.2.2	Charge Transport in Polymer LEDs and FETs	391
9.2.2.1	Polymer LEDs	391

9.2.2.2	Charge Transport in Polymer FETs	393
9.2.3	Unification of the Charge Transport in Disordered Polymer LEDs and FETs	396
9.2.4	Origin of the Enhanced SCLC in PPV-Based Diodes	401
9.2.5	Thickness-Dependence of SCLC in PPV-Based LEDs	405
9.2.6	Summary	407
9.3	Charge Injection	407
9.3.1	Introduction	407
9.3.2	Classical Injection Models	408
9.3.3	Hopping-Based Injection	409
9.3.4	Temperature-Dependence of the Charge Injection	411
9.3.5	Application of the Hopping Injection Model	414
9.3.6	Conclusion	416
	References	417

VOLUME 2

Applications

10	Physics of Organic Light-Emitting Diodes	421
	<i>Ian H. Campbell, Brian K. Crone, and Darryl L. Smith</i>	
10.1	Introduction	421
10.2	Thin Films of Organic Semiconductors	423
10.2.1	Electronic Energy Structure	424
10.2.2	Optical Properties	425
10.2.3	Electrical Transport Properties	426
10.3	Device Electronic Structure	427
10.3.1	Internal Photoemission Measurements of Schottky Energy Barriers	427
10.3.2	Built-in Potentials in Device Structures	430
10.4	Single-Layer Devices	434
10.4.1	Single-Carrier Structures	435
10.4.2	Two-Carrier Structures	440
10.5	Multilayer Devices	444
10.5.1	Blocking Layers	445
10.5.2	Transport Layers	447
10.5.3	Two-Carrier Multilayer Devices	449
10.6	Conclusions	451
	References	452
11	Conjugated Polymer-Based Organic Solar Cells	455
	<i>Gilles Dennler, Niyazi Serdar Sariciftci, and Christoph J. Brabec</i>	
11.1	Introduction	455
11.1.1	Photovoltaics	455

11.1.2	Technology Overview and Forecasts	456
11.1.3	Motivation for OPV	459
11.2	Conjugated Polymers as Photoexcited Donors	460
11.2.1	Optical Properties	461
11.2.1.1	Linear Optical Properties	461
11.2.1.2	Photoinduced Absorption	462
11.2.1.3	Time-Resolved Photoinduced Studies	465
11.2.1.4	Photoinduced Infrared-Activated Modes Studies	466
11.2.2	Sensitization of Conductivity	467
11.2.3	Magnetic Properties	468
11.3	Bulk-Heterojunction Solar Cells	469
11.3.1	Basics of Organic Solar Cells	469
11.3.2	Pure Conjugated-Polymer Photovoltaic Devices	472
11.3.3	Conjugated Polymer-Based Bilayer Devices	474
11.3.4	Conjugated Polymer-Based Bulk-Heterojunction Devices	478
11.4	Determining Parameters of Bulk-Heterojunction Solar Cells	481
11.4.1	Voltage at Open Circuit	481
11.4.2	Light Harvesting	485
11.4.3	Morphology of the Photoactive Donor-Acceptor Blends	489
11.4.4	Charge-Carrier Transport in Bulk-Heterojunction Blends	493
11.4.4.1	Charge-Carrier Mobility	494
11.4.4.2	Recombination of Charge Carriers	496
11.4.5	Modeling Bulk-Heterojunction-Device Operation	502
11.4.5.1	Simple One-Diode Equivalent Circuit	502
11.4.5.2	The Extended One-Diode Model	504
11.4.5.3	Electric-Field-Assisted Dissociation of Electron–Hole Pairs	505
11.5	From Basics to Applications	507
11.5.1	Production Scheme	507
11.5.2	Encapsulation of Flexible Solar Cells	511
11.5.3	Routes for Improvements	516
11.5.3.1	Hybrid Solar Cells	516
11.5.3.2	Metal Nanoparticles	518
11.5.3.3	Carbon Nanotubes	518
11.6	Conclusions	519
	References	520
12	Organic Thin-Film Transistors	531
	<i>Gilles Horowitz</i>	
12.1	Introduction	531
12.2	The MISFET – A Reminder	532
12.2.1	The Metal–Insulator–Semiconductor (MIS) Junction	532
12.2.1.1	Work Function, Electron Affinity, Ionization Potential	532
12.2.1.2	Energy Diagram of the MIS Junction	533
12.2.1.3	Charge and Potential in the Ideal MIS Diode	536

12.2.2	The Metal–Insulator–Semiconductor Field-Effect Transistor (MISFET) 539
12.2.2.1	Structure and Operating Mode 539
12.2.2.2	Calculation of the Drain Current 541
12.3	The Organic Transistor – What's Different? 544
12.3.1	Threshold Voltage 545
12.3.2	Depletion Regime 546
12.3.3	Contact Resistance 546
12.3.3.1	Contact Resistance Extraction 546
12.3.3.2	Origin of Contact Resistance 550
12.3.4	Charge Distribution Across the Conducting Channel 551
12.4	Charge-Transport Mechanisms 555
12.4.1	Band-Like Transport 556
12.4.2	Polaron Transport 556
12.4.3	Hopping Models 558
12.4.4	Trap-Limited Transport 559
12.4.5	Gate-Voltage-Dependent Mobility 560
12.4.6	Role of the Insulator 562
12.5	Concluding Remarks 563
	<i>References</i> 564
13	n-Channel Organic Transistor Semiconductors for Plastic Electronics Technologies 567
	<i>Howard E. Katz</i>
13.1	Plastic Electronics Technology and Organic Semiconductors 567
13.2	n-Channel OFET Semiconductors 571
13.3	Conclusion 575
	<i>References</i> 575
14	Photochromic Diodes 579
	<i>Xavier Crispin, Peter Andersson, Nathaniel D. Robinson, Yoann Olivier, Jérôme Cornil, and Magnus Berggren</i>
14.1	Introduction 579
14.2	Photochromic Molecules 580
14.3	Organic Diodes 585
14.4	Electronic Switches – Device Concepts 586
14.4.1	Electronic Write Mode 587
14.4.1.1	Control of the Charge-Injection Barrier 587
14.4.1.2	Electronic Write and Readout Memory 591
14.4.2	Optical Write Mode 593
14.4.2.1	Optical Read Mode Based on Photocurrent Detection 593
14.4.2.2	Electronic Read Mode 600
14.5	Conclusions 609
	<i>References</i> 610

15	Organic/Polymeric Thin-Film Memory Devices	613
	<i>Yang Yang, Jianyong Ouyang, Liping Ma, Jia-Hung Tseng, and Chih-Wei Chu</i>	
15.1	Introduction	613
15.2	Review of Polymer and Organic Memory	614
15.2.1	Electric-Field-Induced Charge-Transfer Effect	614
15.2.2	Ionic Diffusion Effect	615
15.2.3	Nanoparticle Layered Structures	615
15.2.4	Crossbar Molecular Switch	616
15.3	OMO Nanoparticle Layered Memory Devices	616
15.3.1	Device Fabrication	617
15.3.2	Electrical Characteristics	619
15.3.3	Conduction and Switching Mechanisms	621
15.4	Polymer-Blend Composite System	621
15.4.1	Device Fabrication	622
15.4.2	Electrical Characteristics	623
15.4.3	Conduction and Switching Mechanisms	625
15.5	Advanced Memory Device Architecture	629
15.5.1	WORM Memory Devices	630
15.5.2	All-Organic Donor-Acceptor System	632
15.5.3	Polymer with Built-In Nanoparticle System	634
15.6	Conclusion	637
	References	639

16	Biosensors Based on Conjugated Polymers	643
	<i>Hoang-Anh Ho and Mario Leclerc</i>	
16.1	Introduction	643
16.2	Different Types of CPs	644
16.3	Colorimetric Methods	644
16.4	Fluorometric Methods	651
16.5	Electrochemical Methods	658
16.6	Conclusions and Perspectives	661
	References	662

Processing

17	Manufacturing of Organic Transistor Circuits by Solution-Based Printing	667
	<i>Henning Sirringhaus, Christoph W. Sele, Timothy von Werne, and Catherine Ramsdale</i>	
17.1	Introduction to Printed Organic Thin-Film Transistors	667
17.2	Overview of Printing-Based Manufacturing Approaches for OTFTs	670

17.2.1	Screen Printing	671
17.2.2	Offset Printing	671
17.2.3	Gravure Printing	673
17.2.4	Flexography	673
17.2.5	Inkjet Printing	674
17.2.6	Laser-Based Dry Printing Techniques	675
17.2.7	Other Nonlithographic Manufacturing Approaches	676
17.3	High-Resolution, Self-Aligned Inkjet Printing	677
17.3.1	Self-Aligned Printing by Selective Surface Treatment	680
17.3.2	Self-Aligned Printing by Surface Segregation	680
17.3.3	Self-Aligned Printing by Autophobicity	682
17.4	Performance and Reliability of Solution-Processed OTFTs for Applications in Flexible Displays	688
17.5	Conclusions	693
	References	694
18	High-Resolution Composite Materials for Organic Electronics	699
	<i>Graciela Blanchet</i>	
18.1	Introduction	699
18.2	Building Blocks	699
18.3	Large-Area Printing Process and Devices	701
18.3.1	Process: Thermal Imaging	701
18.3.2	Printed Devices: From TFTs to Large-Area Backplanes	702
18.3.2.1	Contact Resistance	704
18.3.2.2	Printed Backplane	708
18.4	Printable Materials	710
18.4.1	Polyaniline-Nanotube Composites: A High-Resolution Printable Conductor	710
18.4.2	Conducting Composites in an Insulating Matrix	715
18.4.3	Semiconducting Composites	720
18.4.3.1	The Pick-Up Stick Transistor	720
18.4.3.2	Single-Layer Composites	721
18.4.3.3	Bilayer Assemblies	723
18.5	Conclusion	728
	References	729
	Subject Index	731