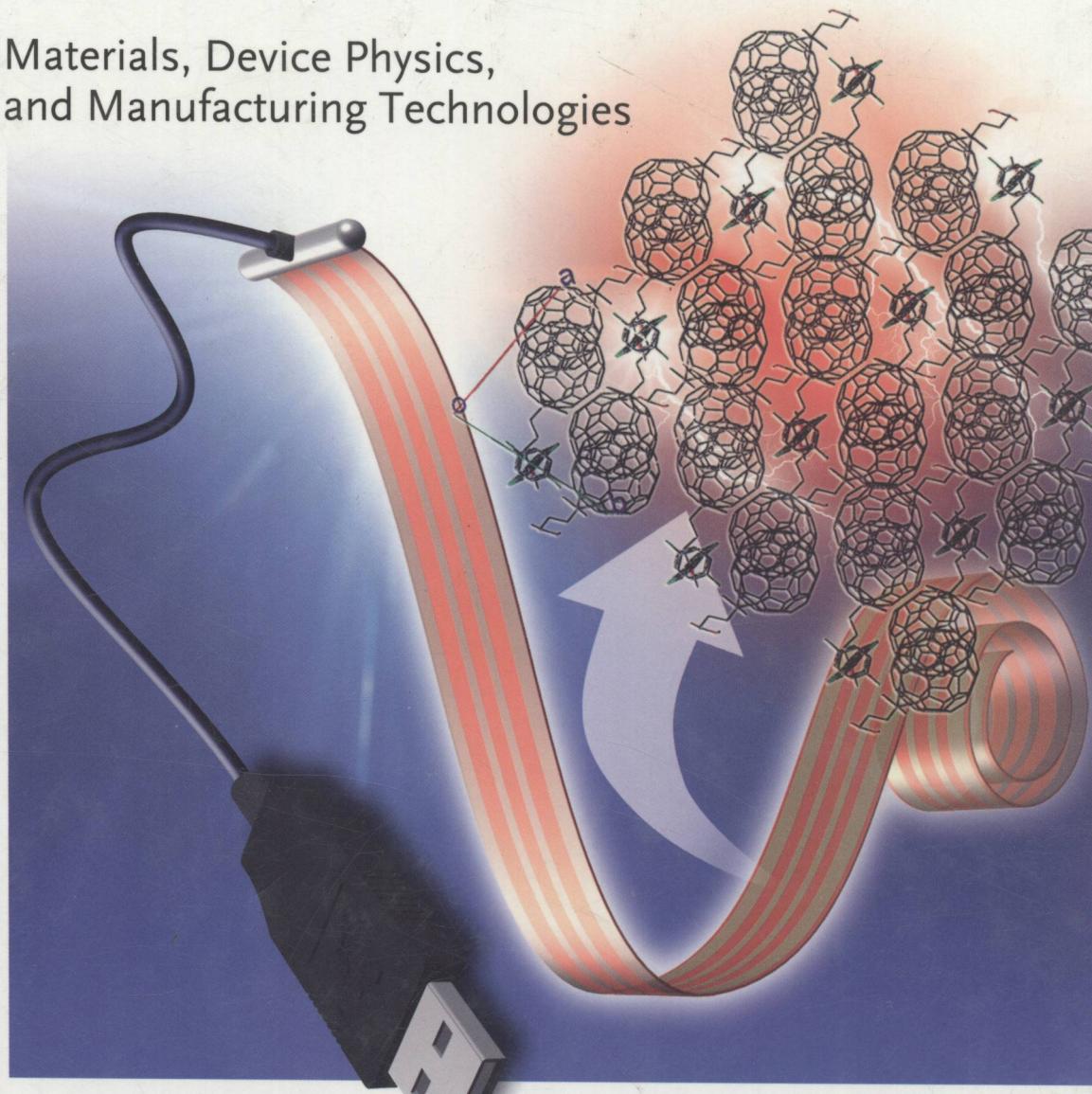


Edited by Christoph Brabec,  
Vladimir Dyakonov, Ullrich Scherf

WILEY-VCH

# Organic Photovoltaics

Materials, Device Physics,  
and Manufacturing Technologies



TM615  
068

# Organic Photovoltaics

Materials, Device Physics, and  
Manufacturing Technologies

*Edited by*

*Christoph Brabec, Vladimir Dyakonov, and  
Ullrich Scherf*



WILEY-  
VCH



E2008001605

WILEY-VCH Verlag GmbH & Co. KGaA

### **The Editors**

#### **Dr. Christoph Brabec**

Konarka Austria  
Altenbergerstr. 69  
4040 Linz  
Austria

#### **Prof. Dr. Vladimir Dyakonov**

Universität Würzburg  
Experimentalphysik VI  
Fakultät für Physik + Astronomie  
Am Hubland  
97074 Würzburg  
Germany

#### **Prof. Dr. Ullrich Scherf**

Institut für Makromolekulare Chemie  
Bergische Universität Wuppertal  
Gauss-Straße 20  
42097 Wuppertal  
Germany

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**

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

© 2008 WILEY-VCH Verlag GmbH & Co. KGaA,  
Weinheim

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photostriking, 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.

**Composition** Thomson Digital, Noida, India

**Printing** betz-druck GmbH, Darmstadt

**Bookbinding** Litges & Dopf GmbH, Heppenheim

**Cover Design** Schulz Grafik Design, Fußgönheim

Printed in the Federal Republic of Germany  
Printed on acid-free paper

**ISBN:** 978-3-527-31675-5

## **Organic Photovoltaics**

*Edited by*

*Christoph Brabec, Vladimir Dyakonov,  
and Ullrich Scherf*

## **Related Titles**

Scheer, R., Schock, H.-W.

### **Chalcogenide Photovoltaics Physics, Technologies, and Thin Film Devices**

2009

ISBN: 978-3-527-31459-1

Ronda, C. (ed.).

### **Luminescence From Theory to Applications**

2007

ISBN: 978-3-527-31402-7

Hadzioannou, G., Malliaras, G. G. (eds.)

### **Semiconducting Polymers Chemistry, Physics and Engineering**

2007

ISBN: 978-3-527-31271-9

Klauk, H. (ed.)

### **Organic Electronics Materials, Manufacturing and Applications**

2006

ISBN: 978-3-527-31264-1

Müllen, K., Scherf, U. (eds.)

### **Organic Light Emitting Devices Synthesis, Properties and Applications**

2006

ISBN: 978-3-527-31218-4

Brüttig, W. (ed.)

### **Physics of Organic Semiconductors**

2005

ISBN: 978-3-527-40550-3

Würfel, P.

### **Physics of Solar Cells From Principles to New Concepts**

2005

ISBN: 978-3-527-40428-5

Roth, S., Carroll, D.

### **One-Dimensional Metals Conjugated Polymers, Organic Crystals, Carbon Nanotubes**

2004

ISBN: 978-3-527-30749-4

Castaner, L., Silvestre, S.

### **Modelling Photovoltaic Systems Using PSpice**

2003

ISBN: 978-0-470-84527-1

## Preface

In 2007 the Norwegian Nobel prize committee gave for the first time the Nobel Prize for Peace to a large scientific consortium, which aims at investigating and proving the rapid environmental and economical change in the earth's climate, also called global warming. Stabilizing the global climate requires an in depth modification of mankind's energy supply habits, and, this will require again a lot of energy. Solar radiation is the renewable energy source with practically unlimited access, attracting equal interest from both politicians and scientists. Today, large expectations are set in photovoltaics to become a major energy supplying technology before 2030.

The main attraction of organic solar cells is their compatibility to conventional printing and coating technologies. Among all photovoltaic technologies, organic solar cells are unique as they will be fabricated by printing or coating processes resulting in a true low cost technology.

World wide research in organic solar cells just started 10 years ago, and since then the number of publications is growing exponentially. Over the last 8 years, the number of papers on all aspects of organic solar cells has increased by about 65% per annum and in 2006, already 10% of the scientific publications in the field of photovoltaics reported on organic solar cells. The performance of organic solar cells was evolving constantly over the last few years, from approx. 1% in 2000 to >5% in 2007. Mastering the next big challenge, organic solar cells with up to 10% efficiency, requires the intensified exchange of knowledge and experiences between all the different scientific subdisciplines in a truly interdisciplinary approach involving materials chemistry, materials characterization, device physics, as well as device, process and production technology.

This book aims to contribute to this very important interdisciplinary information exchange and reviews latest developments in organic photovoltaics in the fields of materials, device physics/technology and production aspects. Despite this book mainly reports on materials and components suitable for solution (wet) processing,

there is, of course, a clear commitment from the editors to the undoubtedly high importance of dye sensitized and vacuum processed organic photovoltaic devices. The presentation and discussion of these and further promising concepts will be covered in a future edition of this book.

April 2008

*Christoph J. Brabec  
Vladimir Dyakonov  
Ullrich Scherf*

## List of Contributors

**Martin Baumgarten**

Max Planck Institute for Polymer Research  
Ackermannweg 10  
55128 Mainz  
Germany

**Waldo J. E. Beek**

Eindhoven University of Technology  
Molecular Materials and Nanosystems  
P.O. Box 513  
5600 MB Eindhoven  
The Netherlands

**Paul W. M. Blom**

University of Groningen  
Zernike Institute for Advanced Materials  
Nijenborgh 4  
9747 AG Groningen  
The Netherlands

**Christoph J. Brabec**

Konarka Austria  
Altenbergerstrasse 69  
4040 Linz  
Austria

**Svetlana van Bavel**

Eindhoven University of Technology  
Department of Chemical Engineering and Chemistry  
Laboratory of Materials and Interface Chemistry  
P.O. Box 513  
5600 MB Eindhoven  
The Netherlands

**Gilles Dennler**

Konarka Austria  
Altenbergerstrasse 69  
4040 Linz  
Austria

**Andreas Elschner**

H.C. Starck GmbH  
Central Research & Development  
Chempark, Building B202  
51368 Leverkusen  
Germany

**Paul C. Ewbank**

Carnegie Mellon University  
Mellon College of Sciences  
Department of Chemistry  
4400 Fifth Avenue  
Pittsburgh, PA 15213  
USA

***Matthias Fahland***

Fraunhofer Institute for Electron Beam  
and Plasma Technology  
Winterbergstr. 28  
01277 Dresden  
Germany

***Andreas Gombert***

Fraunhofer Institute for  
Solar Energy Systems  
Heidenhofstr. 2  
79110 Freiburg  
Germany

***Vignesh Gowrishankar***

Stanford University  
Department of Materials Science and  
Engineering  
215 McCullough  
416 Escondido Mall, Bldg. 550  
Stanford, CA 94305-2205  
USA

***Neil C. Greenham***

University of Cambridge  
Department of Physics  
Optoelectronics Group  
Cavendish Laboratory  
J. J. Thomson Avenue  
Cambridge CB3 0HE  
UK

***Cecilia Guillén***

Complutense University  
Departamento de Energía (CIEMAT)  
Avda. Complutense 22  
Madrid 28040  
Spain

***Brian E. Hardin***

Stanford University  
Department of Materials Science and  
Engineering  
215 McCullough  
416 Escondido Mall, Bldg. 550  
Stanford, CA 94305-2205  
USA

***Alan J. Heeger***

University of California, Santa Barbara  
Center for Polymers and Organic Solids  
Santa Barbara, CA 93106-5090  
USA

Gwangju Institute of Science and  
Technology  
Heeger Center for Advanced Materials  
Gwangju 500-712  
Korea

***José Herrero***

Complutense University  
Departamento de Energía (CIEMAT)  
Avda. Complutense 22  
Madrid 28040  
Spain

***A. C. Hübler***

Chemnitz University of Technology  
Institute for Print and Media  
Technology  
Reichenhainer Str. 70  
09126 Chemnitz  
Germany

***Jan C. Hummelen***

University of Groningen  
Zernike Institute for Advanced  
Materials and Stratingh Institute of  
Chemistry  
Molecular Electronics  
Nijenborgh 4  
9747 AG Groningen  
The Netherlands

***René A. J. Janssen***

Eindhoven University of Technology  
 Molecular Materials and Nanosystems  
 P.O. Box 513  
 5600 MB Eindhoven  
 The Netherlands

***David Jones***

University of Melbourne  
 Bio21 Institute, School of Chemistry  
 Building 102 (Level 4)  
 30 Flemington Road, Parkville  
 Melbourne, Victoria 3010  
 Australia

***H. Kempa***

Chemnitz University of Technology  
 Institute for Print and Media  
 Technology  
 Reichenhainer Str. 70  
 09126 Chemnitz  
 Germany

***Jin Young Kim***

Gwangju Institute of Science and  
 Technology  
 Department of Materials Science  
 and Engineering  
 Gwangju 500-712  
 Korea

***Stephan Kirchmeyer***

H.C. Starck GmbH  
 Central Research & Development  
 Chempark, Building B202  
 51368 Leverkusen  
 Germany

***L. Jan Anton Koster***

University of Cambridge  
 Optoelectronics Group  
 Department of Physics  
 J.J. Thompson Avenue  
 Cambridge CB3 OHE  
 UK

***David F. Kronholm***

Solenne BV  
 Zernikepark 12  
 9747 AN Groningen  
 The Netherlands

***Darin Laird***

Plextronics, Inc.  
 Pittsburgh, PA  
 USA

***Kwanghee Lee***

Gwangju Institute of Science and  
 Technology  
 Department of Materials  
 Science and Engineering  
 Gwangju 500-712  
 Korea

***Martijn Lenes***

University of Groningen  
 Zernike Institute for Advanced  
 Materials  
 Nijenborgh  
 9747 AG Groningen  
 The Netherlands

***Jiaoli Li***

Max Planck Institute for  
 Polymer Research  
 Ackermannweg 10  
 55128 Mainz  
 Germany

***Joachim Loos***

Eindhoven University of Technology  
 Department of Chemical Engineering  
 and Chemistry  
 P.O. Box 513  
 5600 MB Eindhoven  
 The Netherlands

**William A. MacDonald**

DuPont Teijin Films (UK) Limited  
P.O. Box 2002  
Wilton, Middlesbrough TS90 8JF  
UK

**Richard D. McCullough**

Carnegie Mellon University  
Mellon College of Sciences  
Department of Chemistry  
4400 Fifth Avenue  
Pittsburgh, PA 15213  
USA

**Michael D. McGehee**

Stanford University  
Department of Materials Science and  
Engineering  
215 McCullough  
416 Escondido Mall, Bldg. 550  
Stanford, CA 94305-2205  
USA

**Valentin D. Mihailescu**

ECN Solar Energy  
P.O. Box 1  
1755 ZG Petten  
The Netherlands

**Ashok K. Mishra**

Max Planck Institute for  
Polymer Research  
Ackermannweg 10  
55128 Mainz  
Germany

**Lorenza Moro**

SRI International  
Material Research Laboratory  
333 Ravenswood Avenue  
Menlo Park, CA 94025  
USA

**Klaus Müllen**

Max Planck Institute for  
Polymer Research  
Ackermannweg 10  
55128 Mainz  
Germany

**Michael Niggemann**

Fraunhofer Institute for  
Solar Energy Systems (ISE)  
Department Materials Research and  
Applied Optics  
Heidenhofstraße 2  
79110 Freiburg  
Germany

**Wojciech Pisula**

Evonik Degussa GmbH  
Process Technology & Engineering  
Process Technology – New Processes  
Rodenhacher Chaussee 4  
63457 Hanau-Wolfgang  
Germany

Max Planck Institute for  
Polymer Research  
Ackermannweg 10  
Mainz 55128  
Germany

**Nicolas Schiller**

Fraunhofer Institut für  
Elektronenstrahl- und Plasmatechnik  
(FEP)  
Winterbergstrasse 28  
01277 Dresden  
Germany

**Robert Jan Visser**

Vitex Systems, Inc.  
2184 Bering Drive  
San Jose, CA 95131  
USA

**David Waller**

Konarka Technologies Inc.  
Boott Mill South  
3rd Floor, 116 John Street, Suite 12  
Lowell, MA 01852  
USA

**Bernhard Weßling**

Ormecon GmbH  
Ferdinand-Harten-Strasse 7  
22949 Ammersbek  
Germany

**Martijn M. Wienk**

Eindhoven University of Technology  
Molecular Materials and Nanosystems  
P.O. Box 513  
5600 MB Eindhoven  
The Netherlands

**Xiaoniu Yang**

Chinese Academy of Sciences  
Changchun Institute of  
Applied Chemistry  
State Key Laboratory of  
Polymer Physics and Chemistry  
Renmin Street No. 5625  
Changchun 130022  
P.R. China

**Bjoern Zeysing**

Ormecon GmbH  
Ferdinand-Harten-Strasse 7  
22949 Ammersbek  
Germany

**Zhengguo Zhu**

Konarka Technologies Inc.  
Boott Mill South  
3rd Floor, 116 John Street, Suite 12  
Lowell, MA 01852  
USA

## Contents

Preface XV

List of Contributors XVII

I	Materials 1
A	Donors 1
1	<b>Regioregular Polythiophene Solar Cells: Material Properties and Performance 3</b> <i>Paul C. Ewbank, Darin Laird, and Richard D. McCullough</i>
1.1	Introduction 3
1.1.1	Overview of Nomenclature and Synthesis 3
1.1.2	Advantages of the HT Architecture 5
1.2	Assembly and Morphology 6
1.2.1	Conformation 7
1.2.2	Aggregation 7
1.2.3	Solid Deposition 8
1.2.4	Solid-State Crystalline Order 9
1.2.5	Solid-State Phase Behavior and Thermal Analysis 10
1.2.6	Anisotropy 12
1.3	Characterization of Impurities 14
1.3.1	Fractionation and Effects of $M_w$ 14
1.3.2	Inorganic Impurities 15
1.4	Optical and Electronic Properties of PAT 16
1.4.1	Optical Properties: Intermolecular Excitons 16
1.4.2	HT-PT Electron Transport: Conductivity and Mobility 17
1.5	Benefits of HT-Regioregular Polythiophenes in Solar Cells 17
1.6	Bulk Heterojunctions: Focus on HT-PAT/PCBM Blends 18
1.6.1	Homogeneous PCBM Assembly 18
1.6.2	HT-PAT/PCBM Blends: Component Ratio 19
1.6.3	HT-PAT/PCBM Blends: Annealing 20

1.6.3.1	PCBM Phase Separation and Assembly	20
1.6.3.2	Polymer Phase Separation and Assembly	21
1.6.3.3	Evolution of Open-Circuit Voltage	21
1.6.3.4	Evolution of Short-Circuit Current	23
1.6.3.5	Evolution of Fill Factor, Power Conversion Efficiency ( $\eta$ )	23
1.6.4	HT-PAT/PCBM Blend: Layer Thickness	24
1.6.5	Summary	24
1.7	HT-PT in Other Blends	25
1.7.1	C <sub>60</sub> and Non-PCBM Fulleroids	25
1.7.2	Carbon Nanotubes and Other Organics	25
1.7.3	Hybrid Organic/Inorganic Nanocomposites	26
1.8	Surface Analysis of HTPT Films	26
1.8.1	AFM and STM	26
1.8.2	XPS/ESCA and Auger Spectroscopy	27
1.8.3	Rutherford Backscattering Spectrometry	28
1.8.4	X-Ray	29
1.8.5	Other Techniques (SIMS, UPS)	29
1.9	Summary and Future Directions	30
	Appendix 1.A. Survey of Photovoltaic Cells Incorporating Regioregular Polythiophenes (2001–2006)	30
	References	41
<b>2</b>	<b>Fluorene-Containing Polymers for Solar Cell Applications</b>	<b>57</b>
	<i>David Jones</i>	
2.1	Introduction	57
2.1.1	Bulk Heterojunctions	59
2.2	Fluorene-Containing Materials	61
2.2.1	Polyfluorene-Containing Photovoltaics	61
2.2.2	Polyfluorene Copolymers	63
2.2.2.1	Electron Transport Materials	63
2.2.2.2	Hole Transport Materials	64
2.2.3	Devices	65
2.2.3.1	Bulk Heterojunctions	65
2.2.3.2	Dye-Sensitized Solar Cells	66
2.3	Bulk Heterojunction Device Performance	68
2.3.1	Morphology	68
2.3.1.1	Techniques for Probing Thin-Film Morphology	69
2.3.1.2	Relating Film Morphology to Device Performance	71
2.3.1.3	Inkjet Printing	75
2.3.1.4	Microemulsions of Blends	76
2.4	Low-Bandgap Materials	76
2.4.1	New Low-Bandgap Materials	76
2.4.2	Alternative Structures	82
2.4.2.1	Carbazoles	82
2.4.2.2	Fluorenones	84

2.5	Future Directions	84
2.5.1	Controlled Morphology	84
2.6	Conclusions	86
	References	86
<b>3</b>	<b>Carbazole-Based Conjugated Polymers as Donor Material for Photovoltaic Devices</b>	<b>93</b>
	<i>Wojciech Pisula, Ashok K. Mishra, Jiaoli Li, Martin Baumgarten, and Klaus Müllen</i>	
3.1	Introduction	93
3.2	Synthesis of Carbazole-Based Polymers	96
3.3	Supramolecular Order of Carbazole-Based Polymers	111
3.4	Photovoltaic Devices	116
3.4.1	Polycarbazole	116
3.4.2	Ladder-Type Polymers Based on 2,7-Carbazole	121
3.5	Conclusions	125
	References	126
<b>4</b>	<b>New Construction of Low-Bandgap Conducting Polymers</b>	<b>129</b>
	<i>Zhengguo Zhu, David Waller, and Christoph J. Brabec</i>	
4.1	Introduction	129
4.2	Low-Bandgap Polymers Containing 4,7-Di-2-Thienyl-2,1,3-Benzothiadiazole Moieties	130
4.3	Low-Bandgap Polymers Containing 4,8-Di-2-Thienyl-Benzo[1,2- <i>c</i> :4,5- <i>c'</i> ]bis[1,2,5]thiadiazole Segments	136
4.4	Low-Bandgap Polymers Containing 4,9-Di-2-Thienyl[1,2,5]thiadiazolo[3,4- <i>g</i> ]quinoxalines	137
4.5	Low-Bandgap Polymers Containing Thieno[3,4- <i>b</i> ]pyrazines	138
4.6	Arylene Vinylene Based Low-Bandgap Polymers	140
4.7	Low-Bandgap Polymers Containing 4 <i>H</i> -Cyclopenta[2,1- <i>b</i> ;3,4- <i>b'</i> ]dithiophene or Its Analogues	142
4.8	Low-Bandgap Polymers Based on Other Types of Building Blocks	146
	References	148
<b>B</b>	<b>Acceptors</b>	<b>153</b>
<b>5</b>	<b>Fullerene-Based Acceptor Materials</b>	<b>155</b>
	<i>David F. Kronholm and Jan C. Hummelen</i>	
5.1	Introduction and Overview	155
5.2	Fullerenes as n-Type Semiconductors	158
5.2.1	Electron Accepting and Transport	158
5.2.2	Other Electronic Properties	159
5.3	[60]PCBM	162
5.4	Variations in Fullerene Derivative and Effect on OPV Device	165

5.4.1	Morphology Considerations – Solubility and Miscibility of the Fullerene Derivative	165
5.4.2	Solubility and Supersaturation in the Donor/Acceptor Blend	166
5.4.3	Miscibility	168
5.4.4	Morphology Fixation and Insoluble Fullerene Layers	169
5.4.5	Optical Absorption of the Fullerene Derivative	169
5.4.6	More Strongly Absorbing Fullerene Derivatives: [70]PCBM and [84]PCBM	170
5.4.7	LUMO Variation	170
5.4.8	Deuterated PCBM	172
5.5	Practical Considerations and Potential in Commercial Devices	172
5.5.1	Powder Morphology and Dissolution	172
5.5.2	Stability of the Fullerene Derivative and the Device Film	173
5.5.3	Impurities	174
5.5.4	Commercial-Scale Application	174
	References	175
<b>6</b>	<b>Hybrid Polymer/Nanocrystal Photovoltaic Devices</b>	179
	<i>Neil C. Greenham</i>	
6.1	Introduction	179
6.2	Classes of Polymer/Nanocrystal Device	181
6.2.1	Devices Based on CdSe Nanoparticles	181
6.2.1.1	Synthesis of CdSe Nanoparticles	181
6.2.1.2	Devices Using CdSe Nanoparticles	186
6.2.2	Devices Based on Metal Oxide Nanoparticles	189
6.2.2.1	Synthesis of ZnO Nanoparticles	190
6.2.2.2	Devices Based on ZnO Nanoparticles	190
6.2.3	Devices Based on Low-Bandgap Nanoparticles	192
6.2.4	Polymer Brush Devices	195
6.2.5	All-Nanoparticle Devices	195
6.3	Physical Processes in Polymer/Nanoparticle Devices	196
6.3.1	Absorption and Exciton Transport	197
6.3.2	Charge Transfer	198
6.3.3	Charge Separation and Recombination	202
6.3.4	Charge Transport	204
6.3.5	Electrical Characteristics and Morphology	206
6.4	Conclusions	207
	References	208
<b>C</b>	<b>Transport Layers</b>	211
<b>7</b>	<b>PEDOT-Type Materials in Organic Solar Cells</b>	213
	<i>Andreas Elschner and Stephan Kirchmeyer</i>	
7.1	Introduction	213
7.2	Chemical Structure and Impact on Electronic Properties	214

7.2.1	Chemical Structure of PEDOT-Type Materials	214
7.2.2	Polymerization	215
7.2.3	Morphology: $\pi$ - $\pi$ Stacking and Crystallization	216
7.2.4	Redox States of PEDOT	217
7.3	PEDOT-Type Materials in Organic Solar Cells	218
7.3.1	Preparation of PEDOT Layers	218
7.4	High-Conductive PEDOT:PSS as TCO-Substitution in OSCs	220
7.4.1	Conductivity of PEDOT:PSS	221
7.4.2	Morphology Impact on Conductivity	222
7.4.3	Optical Properties of PEDOT:PSS	226
7.4.4	Long-Term Stability	228
7.5	PEDOT-Type Materials as Hole-extracting Layers in OSCs	229
7.5.1	PEDOT:PSS as Buffer Layer in Solar Cells	229
7.5.2	Electronic Effects at the PEDOT:PSS–Semiconductor Interface	231
7.6	Conclusions	233
	References	234
<b>8</b>	<b>The Dispersion Approach for Buffer Layers and for the Active Light Absorption Layer</b>	<b>243</b>
	<i>Bjoern Zeysing and Bernhard Weßling</i>	
8.1	Introduction	243
8.2	Photovoltaic Devices	243
8.3	Conductive Polymers	245
8.3.1	Polyaniline	247
8.4	Polymers in Photovoltaic Devices	250
8.4.1	ITO Replacement	251
8.4.2	Polymer Photovoltaic Devices	252
8.5	The Dispersion Approach as a Productive Tool for Photoactive Layer Deposition	255
8.6	Discussion of the Influence of Polymer Morphology on Device Performance	257
8.7	Summary	257
	References	258
<b>II</b>	<b>Device Physics</b>	<b>261</b>
<b>A</b>	<b>Overview of the State-of-the-Art</b>	<b>261</b>
<b>9</b>	<b>Titanium Oxide Films as Multifunctional Components in Bulk Heterojunction “Plastic” Solar Cells</b>	<b>263</b>
	<i>Kwanghee Lee, Jin Young Kim, and Alan J. Heeger</i>	
9.1	Introduction	263
9.2	Sol–Gel Processed Titanium Oxide as an Optical Spacer in Polymer Solar Cells	263
9.3	Air-Stable Bulk Heterojunction Polymer Solar Cells	269
9.4	Efficient Polymer Solar Cells in the Tandem Architecture	272