

Contents

List of Contributors XIII

Part One Materials for Thin Film Organic Photovoltaics 1

1 Overview of Polymer and Copolymer Materials for Organic Photovoltaics 3 *Solon P. Economopoulos, Grigoris Itskos, Panayiotis A. Koutentis, and Stelios A. Choulis*

- 1.1 Introduction 3
- 1.2 Early Efforts 4
- 1.3 Toward Devices with 5% Efficiencies 5
- 1.4 Novel Thiophene-Containing Polymers 8
- 1.5 Fluorene-Containing Molecules 11
- 1.6 Carbazole-Based Copolymers 13
- 1.7 New Heterocyclic Polymers 15
- 1.8 Polymers Based on Other Types of Building Blocks 16
- 1.9 Conclusions 17
- References 18

2 Thiophene-Based High-Performance Donor Polymers for Organic Solar Cells 27 *Bob C. Schroeder, Raja Shahid Ashraf, and Iain McCulloch*

- 2.1 Introduction 27
- 2.2 Bandgap Engineering 28
- 2.3 Charge Generation in Bulk Heterojunction Organic Solar Cells 29
- 2.4 Polyalkylthiophenes 31
 - 2.4.1 Synthesis 31
 - 2.4.2 Optical and Solid-State Properties 33
- 2.5 Polyalkylthiophene/PCBM Blends 35
- 2.6 Polythiophene Copolymers 37
- 2.7 Side Chain Functionalized P3AT Derivatives 38
- 2.8 Third-Generation Polythiophenes 39

2.9	Thiophene-Based Push–Pull Copolymers	42
2.10	Benz[1,2- <i>b</i> :4,5- <i>b'</i>]dithiophene-Based Polymers	44
2.11	Cyclopenta[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene-Based Polymers	46
2.12	Indacenodithiophene-Based Polymers	50
2.13	Conclusion and Outlook	54
	References	55
3	Molecular Design of Conjugated Polymers for High-Efficiency Solar Cells	61
	<i>Liqiang Yang, Huaxing Zhou, Andrew C. Stuart, and Wei You</i>	
3.1	Introduction	61
3.2	Structural Features of Conjugated Polymers	63
3.3	“D–A” Approach	64
3.3.1	Rational Design of Conjugated Backbones: “Weak Donor–Strong Acceptor” Copolymer	64
3.3.1.1	“Weak Donor” Moieties to Improve V_{OC}	67
3.3.1.2	Balancing V_{OC} and J_{SC} : Interplay of Bandgap and Energy Levels	71
3.3.1.3	From BT to 4DTBT: Why is a “Soluble Acceptor” Better?	72
3.3.1.4	“Strong Acceptor” Moieties to Increase J_{SC}	73
3.3.2	Side Chains Are NOT Trivial	76
3.3.2.1	Chain Positions	76
3.3.2.2	Shape and Size	80
3.3.3	Substituents Do Matter: The Curious Case of Fluorine	83
3.4	Quinoid Approach	88
3.5	Summary and Outlook	91
	References	91
4	Solution-Processed Molecular Bulk Heterojunction Solar Cells	95
	<i>Jianhua Liu, Bright Walker, and Thuc-Quyen Nguyen</i>	
4.1	Introduction	95
4.2	Monochromophoric Molecules	96
4.2.1	Conjugated Macrocycles and Polycycles	96
4.2.2	Acenes and Heteroacenes	98
4.2.3	Oligothiophenes	103
4.3	Multichromophoric Molecules	105
4.3.1	Colorant Chromophore-Containing Derivatives	107
4.3.1.1	Diketopyrrolopyrrole and Isoindigo Derivatives	107
4.3.1.2	Squaraine Derivatives	111
4.3.1.3	Merocyanine and Borondipyrromethene Derivatives	116
4.3.2	Oligothiophene Derivatives	117
4.3.3	Benzothiadiazole Analogue Derivatives	121
4.3.4	Triphenylamine Derivatives	126
4.4	Summary and Future Directions	129
	References	133

5	Vacuum-Processed Donor Materials for Organic Photovoltaics	139
	<i>Amaresh Mishra and Peter Bäuerle</i>	
5.1	Introduction	139
5.1.1	Basic Characterization of Organic Solar Cells	140
5.2	Planar and Bulk Heterojunction Solar Cells	142
5.3	Summary and Future Prospects	166
	Acknowledgments	167
	References	168
6	Polymer–Nanocrystal Hybrid Solar Cells	171
	<i>Michael Eck and Michael Krueger</i>	
6.1	Introduction	171
6.2	Semiconductor Nanocrystals	172
6.3	Working Principles and Device Structure	177
6.3.1	Donor and Acceptor Materials	181
6.4	Evolution of Polymer–NC Hybrid Solar Cells	184
6.5	Recent Approaches for Overcoming Current Limitations	188
6.5.1	In Situ Synthesis of NCs in the Polymer Film	188
6.5.2	Nanostructured Polymer-Based Assemblies in Solution	189
6.5.3	Lower Bandgap NC Acceptors	191
6.6	Novel Concepts and Perspectives	192
6.6.1	Ternary NC Systems: Energy Level and Bandgap Tuning	192
6.6.2	NC Ligand Design	195
6.6.3	Functionalized Polymers	195
6.6.4	Inorganic Framework for Interdigitated D–A Layers	196
6.6.4.1	Porous Alumina Template-Assisted Approach	197
6.6.4.2	Nanostructured Inorganic Semiconductors as Acceptor Material	198
6.6.5	Nanostructured Polymer	199
6.6.6	Carbon-Based Acceptors and Nanocomposites	199
6.6.7	Less Toxic NC Acceptor Materials	200
6.7	Summary and Outlook	200
	Acknowledgments	201
	References	201
7	Fullerene-Based Acceptor Materials	209
	<i>Alexander B. Sieval and Jan C. Hummelen</i>	
7.1	Introduction and Overview	209
7.2	Fullerenes as n-Type Semiconductors	211
7.2.1	Electron-Accepting and Transporting Properties	211
7.2.2	Other Electronic Properties	213
7.3	Fullerene Derivatives	214
7.3.1	[60]PCBM	215
7.3.2	[60]PCBM Analogues	219
7.3.3	Substituents on the Phenyl Moiety of PCBM	221
7.3.3.1	Alkoxy Groups	221

7.3.3.2	Fluorination	222
7.3.3.3	Deuterium Labeling	222
7.3.4	Other C ₆₀ Derivatives in OPVs	223
7.4	Derivatives of C ₇₀ and C ₈₄	226
7.4.1	Derivatives of C ₇₀	226
7.4.2	Derivatives of C ₈₄	229
7.5	Fullerene Bisadducts	230
7.6	Endohedral Compounds	233
7.7	Commercialization of Fullerene Derivatives	233
	References	234
8	Polymeric Acceptor Semiconductors for Organic Solar Cells	239
	<i>Antonio Facchetti</i>	
8.1	Introduction	239
8.2	Basics Principles and Operation for Organic Solar Cells	241
8.3	Polymeric Acceptor Semiconductors	245
8.3.1	Cyanated Polyphenylenevinylenes	246
8.3.2	Perylene- and Naphthalenediimide-Based Polymers	257
8.3.3	Benzothiadiazole-Based and Other Electron-Poor Polymers	275
8.4	Conclusions and Perspective	293
	References	296
9	Water/Alcohol-Soluble Conjugated Polymer-Based Interlayers for Polymer Solar Cells	301
	<i>Fei Huang, Chengmei Zhong, Hongbin Wu, and Yong Cao</i>	
9.1	Introduction	301
9.2	The Development of Water/Alcohol-Soluble Conjugated Polymers as Interlayer Materials	302
9.3	Interface Engineering for Polymer Solar Cells	305
9.3.1	Interface Modification for Metal Electrodes	306
9.3.2	Interface Modification for Metal Oxide Electrodes	308
9.3.3	Interface Modification for Graphene and Carbon Nanotube Electrodes	311
9.4	Discussion of the Working Mechanism	311
9.5	Summary	315
	References	316
10	Metal Oxide Interlayers for Polymer Solar Cells	319
	<i>Kevin M. O'Malley, Hin-Lap Yip, and Alex K.-Y. Jen</i>	
10.1	Introduction	319
10.2	Conventional Structure	320
10.2.1	Hole-Selective Layer: Replacing PEDOT:PSS	320
10.2.1.1	Nickel Oxide	322
10.2.1.2	Vanadium, Molybdenum, and Tungsten Oxides	324
10.2.2	Electron-Selective Layer	326
10.2.2.1	Titanium and Zinc Oxides	326

10.3	Inverted Structure	329
10.3.1	Electron-Selective Layer: Reducing the Effects of Cathode Oxidation	329
10.3.1.1	Titanium, Zinc, and Cesium Oxides	331
10.3.1.2	Modification via Molecular Self-Assembly	332
10.4	Tandem Structure	333
10.5	Additional Oxides (Cr_2O_3 , CuO_x , PbO)	338
10.6	Conclusions	339
	References	339
Part Two	Device Physics of Thin Film Organic Photovoltaics	343
11	Bimolecular and Trap-Assisted Recombination in Organic Bulk Heterojunction Solar Cells	345
	<i>Gert-Jan A.H. Wetzelaer, L.Jan Anton Koster, and Paul W.M. Blom</i>	
11.1	Introduction	345
11.2	Recombination at Open Circuit	348
11.3	Trap-Assisted Recombination at Open Circuit	351
11.4	Investigation of the Nature Recombination by Electroluminescence Measurements	353
11.5	Bimolecular Recombination Strength in Organic BHJ Solar Cells	358
11.6	Bimolecular Recombination Losses Under Short-Circuit Conditions	366
11.7	Effect of Bimolecular Recombination on Fill Factor and Efficiency	372
11.8	Conclusions	373
	References	373
12	Organic Photovoltaic Morphology	377
	<i>Brian A. Collins, Felicia A. Bokel, and Dean M. DeLongchamp</i>	
12.1	Introduction	377
12.2	Order in Bulk Heterojunctions	378
12.2.1	Optical Measurements of Order	378
12.2.2	X-Ray Measurement of Crystallinity	381
12.3	Nanoscale Morphology in Bulk Heterojunctions	385
12.3.1	Electron Microscopy	385
12.3.2	Small-Angle Scattering Measurements	388
12.4	Phases in a Bulk Heterojunction	390
12.5	Structure of the Interface between Phases	392
12.5.1	Inferences from Bulk Measurements	395
12.5.2	Surface-Sensitive Measurements	395
12.5.3	Measuring Buried Bilayer Interfaces	396
12.5.4	Measuring Buried Bulk Interfaces	401
12.6	<i>In Situ</i> Measurements of Morphology Development	403
12.6.1	<i>In Situ</i> X-Ray Measurements	403
12.6.2	<i>In Situ</i> Microscopy	407

12.6.3	<i>In Situ</i> Optical and Vibrational Spectroscopies	408
12.6.4	<i>In Operando</i> Measurements	412
12.6.5	The Future of <i>In Situ</i> Measurement	413
	References	413
13	Intercalation in Polymer:Fullerene Blends	421
	<i>Nichole Cates Miller, Eric T. Hoke, and Michael D. McGehee</i>	
13.1	Introduction	421
13.2	Methods for Detecting Molecular Mixing	423
13.2.1	X-Ray Diffraction	423
13.2.2	Photoluminescence Measurements	424
13.2.3	Diffusion Measurements	425
13.2.4	Transmission Electron Microscopy Techniques	427
13.2.5	Small-Angle Scattering Techniques	427
13.3	Factors Affecting Molecular Mixing	428
13.3.1	Fullerene Size	428
13.3.2	Side-Chain Attachment Distance	430
13.3.3	Side-Chain Linearity	430
13.3.4	Thermal Treatments	432
13.4	The Effect of Molecular Mixing on Electronic Properties and Solar Cells	433
13.4.1	Exciton Harvesting	434
13.4.2	Geminate Pair Separation, Charge Extraction, and Optimal Blend Ratio	436
13.4.3	Additional Device Implications	439
13.5	Conclusions	440
	References	441
14	Organic Tandem Solar Cells	445
	<i>Konstantin Glaser, Andreas Pütz, Jan Mescher, Daniel Bahro, and Alexander Colsmann</i>	
14.1	Introduction and Working Principle	445
14.2	Measurement Techniques	448
14.3	Efficient Intermediate Charge Carrier Recombination	450
14.4	Light Management	452
14.5	Choice of Materials	457
14.6	Parallel Tandem Architectures	458
14.7	New Tandem Solar Cell Concepts	459
14.8	Conclusions	460
	Acknowledgments	460
	References	461
15	Solid-State Dye-Sensitized Solar Cells	465
	<i>Jonas Weickert and Lukas Schmidt-Mende</i>	
15.1	Introduction	465
15.2	Working Principles of Solid-State Dye-Sensitized Solar Cells	467

15.2.1	Solar Cell Geometries	467
15.2.2	Light Absorption and Charge Separation	471
15.2.3	Charge Transport	475
15.3	Loss Mechanisms in Solid-State Dye-Sensitized Solar Cells	478
15.4	Solid-State Dye-Sensitized Solar Cells with Spiro-OMeTAD as Hole Conductor	483
15.5	Hybrid Solar Cells with Absorbing Hole Conductors	484
15.6	Ordered Nanostructures for Solid-State Dye-Sensitized Solar Cells	486
15.6.1	TiO ₂ Nanowires	487
15.6.2	TiO ₂ Nanotubes	488
15.7	Summary and Outlook	489
	References	490

Part Three Technology for Thin Film Organic PV 495

16	Reel-to-Reel Processing of Highly Conductive Metal Oxides	497
	<i>Matthias Fahland</i>	
16.1	Introduction	497
16.2	Materials	499
16.3	Deposition Technology	501
16.4	Equipment	503
16.4.1	Vacuum System	504
16.4.2	Winding System	505
16.4.3	Inline Measurement System	506
16.5	Alternative Approaches	507
	References	510
17	Flexible Substrate Requirements for Organic Photovoltaics	513
	<i>William A. MacDonald and Julian M. Mace</i>	
17.1	Introduction	513
17.2	Polyester Substrates	514
17.3	Properties of Base Substrates	516
17.3.1	Optical Properties	516
17.3.2	Thermal Properties	517
17.3.3	Solvent Resistance	520
17.3.4	Surface Quality	523
17.3.5	Mechanical Properties	524
17.3.6	Hydrolysis Resistance	526
17.3.7	UV Stability	527
17.3.8	Barrier	531
17.3.9	Conductive Coated Film	535
17.3.10	Adhesion	535
17.4	Concluding Remarks	536
	Acknowledgments	537
	References	537

18	Adhesives for Organic Photovoltaic Packaging	539
	<i>Markus Rojahn, Marion Schmidt, and Kilian Kreul</i>	
18.1	Introduction	539
18.2	Encapsulation Process for Organic Photovoltaics	540
18.2.1	Basic Process Information	540
18.2.2	Lamination Process Examples	542
18.2.2.1	Radiation-only Curing Process	542
18.2.2.2	Dual Curing Process	544
18.3	Chemistry Aspects of Barrier Adhesives	545
18.3.1	Radically Light Curing Adhesives	545
18.3.2	Cationically Curing Adhesives	549
18.4	Barrier Performance of OPV Adhesives	554
18.4.1	The Intrinsic Barrier Performance of OPV Barrier Adhesives	554
18.4.2	Adhesion of the OPV Barrier Adhesives to the Interfaces	556
18.5	Conclusions	558
	References	558
19	Roll-to-Roll Processing of Polymer Solar Cells	561
	<i>Dechan Angmo, Markus Hösel, and Frederik C. Krebs</i>	
19.1	Introduction	561
19.2	The Roll-to-Roll Process	562
19.3	Structure of Modules	564
19.4	Coating and Printing Techniques for PSC Materials	565
19.4.1	Slot Die Coating	565
19.4.1.1	Novel Slot Die Techniques for Use in PSCs	568
19.4.2	Gravure Printing	568
19.4.3	Knife-Over-Edge	572
19.4.4	Flexographic Printing	573
19.4.5	Screen Printing	574
19.4.6	Inkjet Printing	576
19.4.7	Offset Lithography	578
19.5	Roll-to-Roll Printing of Electrodes	579
19.6	R2R Encapsulation	580
19.7	Roll-to-Roll Characterization	581
19.8	Future and Outlook	582
	References	584
20	Current and Future Directions in Organic Photovoltaics	587
	<i>Giovanni Nisato and Jens Hauch</i>	
20.1	Scientific and Technological Aspects	590
20.2	Commercial Applications	592
20.3	Challenges and Major Hurdles	595
	Acknowledgments	597
	References	597
	Index	599