

The field of organic electronics has seen a steady growth over the last 20 years. At the same time, our scientific understanding of how to achieve optimum device performance has grown, and this book gives an overview of our present-day knowledge of the physics behind organic semiconductor devices. Based on the very successful first edition, the editors have invited top scientists from the US, Asia, and Europe to include the developments from recent years, covering such fundamental issues as:

- growth and characterization of thin films of organic semiconductors,
- charge transport and photophysical properties of the materials as well as their electronic structure at interfaces, and
- analysis and modeling of devices like organic light-emitting diodes, photovoltaic cells or field-effect transistors.

The result is an overview of the field for both readers with basic knowledge and for an application-oriented audience. It thus bridges the gap between textbook knowledge largely based on crystalline molecular solids and those books focusing more on device applications.



**Wolfgang Brütting**, University of Augsburg, Germany. Professor Brütting received his PhD in Physics from the University of Bayreuth in 1995 with a work on charge-density wave systems. Thereafter he moved to the field of organic semiconductors where he could take part in the development of organic light-emitting devices for display applications, inter alia as a visiting scientist at Kyushu University and IBM Zurich Research Laboratory. In 2003 he became Professor for Experimental Physics at the University of Augsburg. His current research activities include thin film growth, photophysics and electrical transport in organic semiconductor devices.



**Chihaya Adachi**, received his PhD from Kyushu University in 1991. In 2005, he was appointed Full Professor at the Center for Future Chemistry in Kyushu Univ. and since 2010 he is director of the Center for Organic Photonics and Electronics Research (OPERA). He is serving on the editorial board of *Organic Electronics* (Elsevier). His current research interests are organic opto-electronics such as OLED, organic FET, organic solar cells, organic laser diode and fundamental photo-physical and electronic processes in organic solidstate thin films.

ISBN 978-3-527-41053-8



www.wiley-vch.de

9 783527 410538



# Contents

Foreword V

Preface VII

List of Contributors XIX

## Part One Film Growth, Electronic Structure, and Interfaces 1

### 1 Organic Molecular Beam Deposition 3

*Frank Schreiber*

#### 1.1 Introduction 3

#### 1.2 Organic Molecular Beam Deposition 5

##### 1.2.1 General Concepts of Thin Film Growth 5

##### 1.2.2 Issues Specific to Organic Thin Film Growth 6

##### 1.2.3 Overview of Popular OMBD Systems 8

###### 1.2.3.1 PTCDA 8

###### 1.2.3.2 DIP 8

###### 1.2.3.3 Phthalocyanines 9

###### 1.2.3.4 Oligoacenes (*Anthracene, Tetracene, and Pentacene*) 10

#### 1.3 Films on Oxidized Silicon 10

##### 1.3.1 PTCDA 10

##### 1.3.2 DIP 11

##### 1.3.3 Phthalocyanines 13

##### 1.3.4 Pentacene 14

#### 1.4 Films on Aluminum Oxide 14

##### 1.4.1 PTCDA 16

##### 1.4.2 DIP 16

##### 1.4.3 Phthalocyanines 16

##### 1.4.4 Pentacene 17

#### 1.5 Films on Metals 17

##### 1.5.1 PTCDA 18

###### 1.5.1.1 Structure and Epitaxy of PTCDA/Ag(111) 18

###### 1.5.1.2 Comparison with Other Substrates 18



1.5.1.3	Dewetting and Thermal Properties	19
1.5.1.4	Real-Time Growth	19
1.5.2	DIP	21
1.5.3	Phthalocyanines	21
1.5.4	Pentacene	22
1.6	Films on Other Substrates	22
1.7	More Complex Heterostructures and Technical Interfaces	23
1.7.1	Inorganic–Organic Heterostructures	23
1.7.2	Organic–Organic Heterostructures	24
1.8	Summary and Conclusions	28
	References	29
<b>2</b>	<b>Electronic Structure of Interfaces with Conjugated Organic Materials</b>	<b>35</b>
	<i>Norbert Koch</i>	
2.1	Introduction	35
2.2	Energy Levels of Organic Semiconductors	37
2.3	Interfaces between Organic Semiconductors and Electrodes	40
2.3.1	Atomically Clean Metal Electrodes	41
2.3.2	Application-Relevant Electrodes	45
2.3.2.1	Low Work Function Electrodes	47
2.3.2.2	Conducting Polymer Electrodes	49
2.3.2.3	Adjusting the Energy Level Alignment at Electrodes	51
2.4	Energy Levels at Organic Semiconductor Heterojunctions	54
2.4.1	Molecular Orientation Dependence	54
2.4.2	Interfacial Charge Transfer	56
2.4.3	Electrode-Induced Pinning of Energy Levels	56
2.4.4	Molecular Dipoles for Energy Level Tuning	57
2.5	Conclusions	59
	References	59
<b>3</b>	<b>Electronic Structure of Molecular Solids: Bridge to the Electrical Conduction</b>	<b>65</b>
	<i>Nobuo Ueno</i>	
3.1	Introduction	65
3.2	General View of Electronic States of Organic Solids	66
3.2.1	From Single Molecule to Molecular Solid	66
3.2.2	Polaron and Charge Transport	69
3.2.3	Requirement from Thermodynamic Equilibrium	69
3.3	Electronic Structure in Relation to Charge Transport	70
3.3.1	Ultraviolet Photoemission Spectroscopy	70
3.3.2	Energy Band Dispersion and Band Transport Mobility	73
3.3.3	Density-of-States Effects in Polycrystalline Film	77
3.4	Electron–Phonon Coupling, Hopping Mobility, and Polaron Binding	79
3.4.1	Basic Background	79



3.4.2	Experimental Reorganization Energy and Polaron Binding Energy	82
3.5	Summary	86
	References	87
<b>4</b>	<b>Interfacial Doping for Efficient Charge Injection in Organic Semiconductors</b>	<b>91</b>
	<i>Jae-Hyun Lee and Jang-Joo Kim</i>	
4.1	Introduction	91
4.2	Insertion of an Interfacial Layer in the Organic/Electrode Junction	92
4.2.1	Electron Injection	92
4.2.2	Hole Injection	95
4.3	Doped Organic/Electrode Junctions	99
4.3.1	"Doping" in Organic Semiconductors	99
4.3.2	Dopants in Organic Semiconductors	100
4.3.3	Charge Generation Efficiencies of Dopants	101
4.3.4	Hole Injection through the p-Doped Organic Layer/Anode Junction	104
4.3.5	Electron Injection through the n-Doped Organic Layer/Cathode Junction	108
4.4	Doped Organic/Undoped Organic Junction	109
4.5	Applications	112
4.5.1	OLEDs	112
4.5.2	OPVs	112
4.5.3	OFETs	114
4.6	Conclusions	115
	References	115
<b>5</b>	<b>Displacement Current Measurement for Exploring Charge Carrier Dynamics in Organic Semiconductor Devices</b>	<b>119</b>
	<i>Yutaka Noguchi, Yuya Tanaka, Yukimasa Miyazaki, Naoki Sato, Yasuo Nakayama, and Hisao Ishii</i>	
5.1	Introduction	119
5.2	Displacement Current Measurement	123
5.2.1	DCM for Quasi-Static States	124
5.2.1.1	Basic Concepts of DCM	124
5.2.1.2	Trapped Charges and Injection Voltage	125
5.2.1.3	Intermediate State between Depletion and Accumulation	127
5.2.2	DCM for Transient States	129
5.2.2.1	Sweep Rate Dependence in DCM Curves	130
5.3	Charge Accumulation at Organic Heterointerfaces	135
5.3.1	Elements of Charge Accumulation at Organic Heterointerfaces	135
5.3.2	Interface Charges and Orientation Polarization	137
5.3.3	Light-Induced Space Charges in Alq <sub>3</sub> Film	144
5.4	Conclusions	147
	References	149



<b>6</b>	<b>Effects of Gaussian Disorder on Charge-Carrier Transport and Recombination in Organic Semiconductors 157</b>
	<i>Reinder Coehoorn and Peter A. Bobbert</i>
6.1	Introduction 157
6.2	Mobility Models for Hopping in a Disordered Gaussian DOS 161
6.2.1	The Extended Gaussian Disorder Model 161
6.2.2	The Extended Correlated Disorder Model 165
6.2.3	Mobility in Host–Guest Systems 166
6.3	Modeling of the Recombination Rate 169
6.3.1	Recombination in Systems with a Gaussian DOS 169
6.3.2	Recombination in Host–Guest Systems with a Gaussian Host DOS 172
6.4	OLED Device Modeling 173
6.4.1	Single-Layer OLEDs: Analytical Drift-Only Theory 173
6.4.2	The Role of Charge-Carrier Diffusion 176
6.4.3	The Role of Gaussian Disorder: One-Dimensional Device Simulations 179
6.4.4	The Role of Gaussian Disorder: Three-Dimensional Device Simulations 182
6.5	Experimental Studies 186
6.5.1	Overview 186
6.5.2	PF–TAA-Based Polymer OLEDs 189
6.6	Conclusions and Outlook 194
	References 196
<b>7</b>	<b>Charge Transport Physics of High-Mobility Molecular Semiconductors 201</b>
	<i>Henning Sirringhaus, Tomo Sakanoue, and Jui-Fen Chang</i>
7.1	Introduction 201
7.2	Review of Recent High-Mobility Small-Molecule and Polymer Organic Semiconductors 202
7.3	General Discussion of Transport Physics/Transport Models of Organic Semiconductors 208
7.3.1	Static Disorder Parameters $\sigma$ and $\Sigma$ 219
7.4	Transport Physics of High-Mobility Molecular Semiconductors 221
7.5	Conclusions 234
	References 234
<b>8</b>	<b>Ambipolar Charge-Carrier Transport in Molecular Field-Effect Transistors 239</b>
	<i>Andreas Opitz and Wolfgang Brütting</i>
8.1	Introduction 239



- 8.2 Ambipolar Charge-Carrier Transport in Blends of Molecular Hole- and Electron-Conducting Materials 244
- 8.3 Ambipolar Charge-Carrier Transport in Molecular Semiconductors by Applying a Passivated Insulator Surface 246
- 8.4 Electrode Variation for Ambipolar and Bipolar Transport 252
- 8.5 Applications of Bipolar Transport for Ambipolar and Complementary Inverters 256
- 8.6 Realization of Light-Emitting Transistors with Combined Al and TTF-TCNQ Electrodes 260
- 8.7 Conclusion 261  
References 262

## 9 Organic Magnetoresistance and Spin Diffusion in Organic Semiconductor Thin-Film Devices 267

*Markus Wohlgenannt*

- 9.1 Introduction 267
- 9.1.1 Organization of This Chapter 268
- 9.2 Organic Magnetoresistance 270
- 9.2.1 Dependence of Organic Magnetoresistance on Hyperfine Coupling Strength 271
- 9.2.2 Organic Magnetoresistance in a Material with Strong Spin–Orbit Coupling 272
- 9.2.3 Organic Magnetoresistance in Doped Devices 275
- 9.2.4 Conclusions for Organic Spintronics 277
- 9.3 Theory of Spin–Orbit Coupling in Singly Charged Polymer Chains 277
- 9.4 Theory of Spin Diffusion in Disordered Organic Semiconductors 280
- 9.5 Distinguishing between Tunneling and Injection Regimes of Ferromagnet/Organic Semiconductor/Ferromagnet Junctions 284
- 9.6 Conclusion 289  
References 290

## Part Three Photophysics 295

### 10 Excitons at Polymer Interfaces 297

*Neil Greenham*

- 10.1 Introduction 297
- 10.2 Fabrication and Structural Characterization of Polymer Heterojunctions 298
- 10.3 Electronic Structure at Polymer/Polymer Interfaces 305
- 10.4 Excitons at Homointerfaces 307
- 10.5 Type-I Heterojunctions 312
- 10.6 Type-II Heterojunctions 314



10.7	CT State Recombination	319
10.8	Charge Separation and Photovoltaic Devices based on Polymer: Polymer Blends	322
10.9	Future Directions	327
	References	328
<b>11</b>	<b>Electronic Processes at Organic Semiconductor Heterojunctions: The Mechanism of Exciton Dissociation in Semicrystalline Solid-State Microstructures</b>	<b>333</b>
	<i>Francis Paquin, Gianluca Latini, Maciej Sakowicz, Paul-Ludovic Karsenti, Linjun Wang, David Beljonne, Natalie Stingelin, and Carlos Silva</i>	
11.1	Introduction	333
11.2	Experimental Methods	334
11.3	Results and Analysis	334
11.3.1	Photophysics of Charge Photogeneration and Recombination Probed by Time-Resolved PL Spectroscopy	334
11.3.1.1	Absorption and Steady-State PL	334
11.3.1.2	Time-Resolved PL Measurements	335
11.3.1.3	Quantum Chemical Calculations	341
11.3.2	Solid-State Microstructure Dependence	342
11.3.2.1	Polymer Microstructure	342
11.3.2.2	Dependence of Time-Resolved PL on Molecular Weight	344
11.4	Conclusions	345
	References	345
<b>12</b>	<b>Recent Progress in the Understanding of Exciton Dynamics within Phosphorescent OLEDs</b>	<b>349</b>
	<i>Sebastian Reineke and Marc A. Baldo</i>	
12.1	Introduction	349
12.2	Exciton Formation	349
12.2.1	Background	349
12.2.2	Spin Mixing for Higher Efficiency	351
12.2.2.1	Exciton Mixing and Phosphorescence	351
12.2.2.2	CT State Mixing and Enhanced Fluorescence	352
12.2.2.3	Thermally Activated Delayed Fluorescence	355
12.2.2.4	Summary: Comparison between Phosphorescence, Extrafluorescence, and TADF	357
12.3	Distributing Excitons in the Organic Layer(s)	357
12.3.1.1	Excitonic Confinement: Host-Guest Systems	357
12.3.1.2	Exciton Generation Zone	358
12.3.1.3	Exciton Migration	359
12.3.1.4	Triplet Harvesting	361
12.4	High Brightness Effects in Phosphorescent Devices	362
	References	367



<b>13</b>	<b>Organometallic Emitters for OLEDs: Triplet Harvesting, Singlet Harvesting, Case Structures, and Trends</b>	<b>371</b>
	<i>Hartmut Yersin, Andreas F. Rausch, and Rafał Czerwieniec</i>	
13.1	Introduction	371
13.2	Electroluminescence	372
13.2.1	Triplet Harvesting	372
13.2.2	Singlet Harvesting	374
13.3	Triplet Emitters: Basic Understanding and Trends	375
13.3.1	Energy States	376
13.3.2	The Triplet State and Spin–Orbit Coupling	378
13.3.3	Emission Decay Time and Zero-Field Splitting: A General Trend	382
13.4	Case Studies: Blue Light Emitting Pt(II) and Ir(III) Compounds	386
13.4.1	Pt(II) Compounds	388
13.4.1.1	Photophysical Properties at Ambient Temperature	388
13.4.1.2	High-Resolution Spectroscopy: Triplet Substates and Vibrational Satellite Structures	391
13.4.2	Ir(III) Compounds	400
13.4.2.1	Photophysical Properties at Ambient Temperature	400
13.4.2.2	Electronic 0–0 Transitions and Energy Level Diagrams of the Emitting Triplet States	402
13.4.2.3	Vibrational Satellite Structures Exemplified on Ir(4,6-dFppy) <sub>2</sub> (acac)	404
13.4.2.4	Effects of the Nonchromophoric Ligands	405
13.4.3	Comparison of Photophysical Properties of Pt(II) and Ir(III) Compounds	407
13.5	Case Studies: Singlet Harvesting and Blue Light Emitting Cu(I) Complexes	408
13.5.1	Photophysical Properties at Ambient Temperature	408
13.5.2	Triplet State Emission and Thermally Activated Fluorescence	411
13.5.3	Singlet Harvesting: Cu(I) Complexes as OLED-Emitters	415
13.6	Conclusion	417
	References	420

## **Part Four Device Physics** 425

<b>14</b>	<b>Doping of Organic Semiconductors</b>	<b>427</b>
	<i>Björn Lüssem, Moritz Riede, and Karl Leo</i>	
14.1	Introduction	427
14.2	Doping Fundamentals	430
14.2.1	p-Type Doping	433
14.2.1.1	Control of the Position of the Fermi Level by Doping	433
14.2.1.2	Doping Efficiency	436
14.2.2	n-Type Doping	438
14.2.2.1	n-Type Doping Using Alkali Metals	438



14.2.2.2	n-Type Doping Using Molecular Compounds with Very High HOMO Levels	440
14.2.2.3	n-Type Doping Using Precursors	442
14.2.3	Contacts with Doped Semiconductors	446
14.3	Organic p-n Junctions	447
14.3.1	p-n-Homojunctions	447
14.3.1.1	Experiments	448
14.3.2	Reverse Currents in p-n-Junctions	452
14.4	OLEDs with Doped Transport Layers	454
14.4.1	Efficiency of OLEDs	454
14.4.1.1	External Quantum Efficiency $\eta_q$	455
14.4.1.2	Power Efficiency or Luminous Efficacy	457
14.4.2	p-i-n OLEDs	457
14.4.2.1	Highly Efficient Monochrome Devices	459
14.4.2.2	p-i-n Devices: White OLEDs	463
14.4.2.3	Triplet Harvesting OLEDs	466
14.4.2.4	Conclusion	468
14.5	Organic Solar Cells with Doped Transport Layers	468
14.5.1	Solar Cell Characteristics	472
14.5.2	Organic p-i-n Solar Cells	474
14.5.2.1	Brief History of Vacuum-Deposited Organic Solar Cells	474
14.5.2.2	Advantages of Molecular Doping in OSC	476
14.5.2.3	Optical Optimization	478
14.5.2.4	Tandem Devices	479
14.6	Conclusion	486
14.7	Summary and Outlook	486
	References	488

## **15 Device Efficiency of Organic Light-Emitting Diodes 497**

*Wolfgang Brütting and Jörg Frischeisen*

15.1	Introduction	497
15.2	OLED Operation	498
15.2.1	OLED Architecture and Stack Layout	498
15.2.2	Working Principles of OLEDs	499
15.2.3	OLED Materials	500
15.2.4	White OLEDs	502
15.3	Electroluminescence Quantum Efficiency	503
15.3.1	Factors Determining the EQE	503
15.3.2	Luminous Efficacy	505
15.4	Fundamentals of Light Outcoupling in OLEDs	506
15.4.1	Optical Loss Channels	506
15.4.2	Optical Modeling of OLEDs	508
15.4.3	Simulation-Based Optimization of OLED Layer Stacks	513
15.4.4	Influence of the Emitter Quantum Efficiency	515
15.4.5	Comprehensive Efficiency Analysis of OLEDs	516



15.5	Approaches to Improved Light Outcoupling	520
15.5.1	Overview of Different Techniques	520
15.5.2	Reduction of Surface Plasmon Losses	522
15.5.2.1	Basic Properties of SPPs	522
15.5.2.2	Scattering Approaches	523
15.5.2.3	Index Coupling	524
15.5.2.4	Emitter Orientation	529
15.6	Conclusion	533
	References	534
<b>16</b>	<b>Light Outcoupling in Organic Light-Emitting Devices</b>	<b>541</b>
	<i>Chih-Hung Tsai and Chung-Chih Wu</i>	
16.1	Introduction	541
16.2	Theories and Properties of OLED Optics	542
16.3	A Few Techniques and Device Structures to Enhance Light Outcoupling of OLEDs	544
16.3.1	Second-Antinode OLED	544
16.3.2	Top-Emitting OLEDs Capped with Microlens or Scattering Layers	549
16.3.3	OLED with Internal Scattering	554
16.3.4	OLED Utilizing Surface Plasmon Polariton-Mediated Energy Transfer	561
16.4	Summary	571
	References	571
<b>17</b>	<b>Photogeneration and Recombination in Polymer Solar Cells</b>	<b>575</b>
	<i>Carsten Deibel, Andreas Baumann, and Vladimir Dyakonov</i>	
17.1	Introduction	575
17.2	Photogeneration of Charge Carriers	577
17.3	Charge Carrier Transport in Disordered Organic Semiconductors	583
17.4	Recombination of Photogenerated Charge Carriers	588
17.5	Open-Circuit Voltage	593
17.6	Summary	595
	References	595
<b>18</b>	<b>Light-Emitting Organic Crystal Field-Effect Transistors for Future Organic Injection Lasers</b>	<b>603</b>
	<i>Hajime Nakanotani and Chihaya Adachi</i>	
18.1	Introduction	603
18.2	Highly Photoluminescent Oligo( <i>p</i> -phenylenevinylene) Derivatives	608
18.3	Ambipolar Light-Emitting Field-Effect Transistors Based on Organic Single Crystals	610
18.3.1	Ambipolar Carrier Transport Characteristics of Single Crystals of OPV Derivatives	610



18.3.2	EL Characteristics of LE-OFETs Based on Organic Single Crystals	611
18.3.3	Tuning of Carrier Density by Interfacial Carrier Doping in Single Crystals of OPV Derivatives	613
18.3.3.1	Interfacial Carrier Doping Based on Electron Transfer from an Organic Single Crystal into a MoO <sub>x</sub> Layer	613
18.3.3.2	Application of Interfacial Carrier Doping for Ambipolar LE-OFETs	614
18.3.3.3	Estimation of Singlet Exciton Density in the Recombination Zone	616
18.4	Summary and the Outlook for Future Organic Injection Lasers	617
	References	619
	<b>Index</b>	<b>623</b>