

Contents

Preface *IX*

Table of Boxes *XI*

1	The Electronic Structure of Organic Semiconductors	1
1.1	Introduction	1
1.1.1	What Are “Organic Semiconductors”?	1
1.1.2	Historical Context	3
1.2	Different Organic Semiconductor Materials	5
1.2.1	Molecular Crystals	5
1.2.2	Amorphous Molecular Films	7
1.2.3	Polymer Films	9
1.2.4	Further Related Compounds	14
1.2.5	A Comment on Synthetic Approaches	15
1.3	Electronic States of a Molecule	17
1.3.1	Atomic Orbitals in Carbon	17
1.3.2	From Atomic Orbitals to Molecular Orbitals	19
1.3.3	From Orbitals to States	25
1.3.4	Singlet and Triplet States	28
1.4	Transitions between Molecular States	31
1.4.1	The Potential Energy Curve	31
1.4.2	Radiative Transitions: Absorption and Emission	37
1.4.3	A Classical Picture of Light Absorption	48
1.4.4	Non-Radiative Transitions: Internal Conversion and Intersystem Crossing	56
1.4.5	Basic Photophysical Parameters: Lifetimes and Quantum Yields	62
1.5	Spectroscopic Methods	64
1.5.1	Photoluminescence Spectra, Lifetimes, and Quantum Yields	67
1.5.2	Excited State Absorption Spectra	75
1.5.3	Fluorescence Excitation Spectroscopy	79
1.6	Further Reading	80
	References	81
2	Charges and Excited States in Organic Semiconductors	87
2.1	Excited Molecules from the Gas Phase to the Amorphous Film	87
2.1.1	Effects due to Polarization	87
2.1.2	Effects due to Statistical Averaging	91
2.1.3	Effects due to Environmental Dynamics	94
2.1.4	Effects due to Electronic Coupling between Identical Molecules – Dimers and Excimers	99

2.1.5	Effects due to Electronic Coupling between Dissimilar Molecules – Complexes and Exciplexes	111
2.1.6	Electromers and Electroplexes	113
2.2	Excited Molecules in Crystalline Phases – The Frenkel Exciton	114
2.2.1	The Frenkel Exciton Concept for One Molecule per Unit Cell	114
2.2.2	The Frenkel Exciton Concept for Two Molecules per Unit Cell	117
2.2.3	Coherent and Incoherent Motion of Frenkel Excitons	118
2.2.4	Förster and Dexter Type Energy Transfer	119
2.2.5	Experimental Examples for Frenkel Excitons in Ordered Molecular Arrays	123
2.3	Excited States in π -Conjugated Polymers	133
2.3.1	Crystalline Polymers: Poly(diacetylene)s (PDAs)	133
2.3.2	Concepts for Noncrystalline Polymers	136
2.3.3	Brief Overview Over Different Classes of Conjugated Polymers	144
2.4	Charged Molecules	155
2.4.1	The Creation of Charged Molecules by Injection, Absorption and Doping	157
2.4.2	Charged Molecules in Disordered Films	161
2.4.3	Charged Molecules in Crystals	164
2.4.4	Determining the Energy Levels of Charged Molecules by Cyclovoltammetry and Photoemission Spectroscopy	167
2.5	A Comparison between Inorganic and Organic Semiconductors	171
2.5.1	Crystals	171
2.5.2	Amorphous Solids	174
2.5.3	The Su–Schrieffer–Heeger (SSH) Model for Conjugated Polymers	175
2.6	Further Reading	181
	References	182
3	Electronic and Optical Processes of Organic Semiconductors	193
3.1	Basic Aspects of Electrical Current in a Device	194
3.1.1	Injection Limited Currents	195
3.1.2	Unipolar Space Charge Limited (SCL) Current	196
3.1.3	Bipolar Space Charge Limited Current	200
3.2	Charge Injection Mechanisms	201
3.2.1	Fowler–Nordheim Tunneling Injection	202
3.2.2	Richardson–Schottky Thermionic Injection	203
3.2.3	Thermally Activated Injection into a Disordered Organic Semiconductor	204
3.3	Charge Carrier Transport	208
3.3.1	Experimental Techniques to Measure Charge Carrier Mobility	208
3.3.2	Carrier Transport in the Band Regime and in the Hopping Regime	213
3.3.3	Trapping Effects	235
3.3.4	Transport at Higher Charge Carrier Densities	237
3.3.5	The Impact of Morphology on Transport	239
3.3.6	Charge Transport on Short Lengths Scales and Time Scales	244
3.4	Non-Geminate Charge Carrier Recombination	246
3.4.1	Recombination without Traps (Langevin-Type Recombination)	246
3.4.2	Recombination with Traps (Shockley–Read–Hall-Like Recombination)	247
3.5	Generation of Excitations	249
3.5.1	Optical Generation	249
3.5.2	Electrical Generation	251
3.5.3	Secondary Processes	252
3.6	Dissociation of Excitations	254
3.6.1	Geminate Pair Creation	254

3.6.2	The Dissociation of the Geminate Pair	263
3.7	Diffusion of Excitations	274
3.7.1	Exciton Diffusion in a Molecular Crystal	274
3.7.2	Diffusion of Excitations in Amorphous Condensed Phases	276
3.7.3	Experimental Techniques to Measure Exciton Diffusion	276
3.8	Decay of Excitations	283
3.8.1	Monomolecular Decay	283
3.8.2	Bimolecular Processes	287
3.9	Further Reading	292
	References	292
4	Fundamentals of Organic Semiconductor Devices	307
4.1	Basic Solar Cells and Light-Emitting Diode Structures	311
4.1.1	Basic Fabrication Steps	311
4.1.2	Electrode Geometries	315
4.1.3	The Basic Operation of a Single-Layer OLED	317
4.1.4	Multi-Layer OLED Architectures	322
4.1.5	The Current–Voltage–Luminance Characteristics of an OLED	324
4.1.6	The Basic Operation of an OSC	326
4.1.7	The Current–Voltage Characteristics of an OSC	327
4.2	Solar Cell Performance	331
4.2.1	Determining Solar Cell Efficiencies	331
4.2.2	Strategies to Increase the Photocurrent	334
4.2.3	Strategies to Increasing the Open-Circuit Voltage	345
4.2.4	Strategies to Improve the Fill-Factor	347
4.2.5	The Thermodynamic Efficiency Limit	349
4.3	Light-Emitting Diode Performance	353
4.3.1	Determining OLED Efficiencies and Color	353
4.3.2	Strategies to Improve the OLED Efficiencies	362
4.3.3	Strategies to Improving the Emission Color of OLEDs	366
4.4	Transistors	368
4.4.1	The Operational Principle of an OFET	369
4.4.2	Evaluating OFET Performance	373
4.4.3	Improving OFET Performance	374
4.4.4	Modifying the Polarity of OFETs	378
4.5	Further Reading	382
	References	382
	Appendices	389
	Chemical Structures	389
A.1	Selected Polymers	390
A.1.1	π -Conjugated Homopolymers	390
A.1.2	π -Conjugated Copolymers	391
A.1.3	Other Polymers of Interest	392
A.2	Selected π -Conjugated Low-Molecular Weight Compounds	393
A.3	Selected Phosphorescent Compounds	397
A.4	Non-Conjugated Low-Molecular Weight Compounds	397

