## 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  
1.5 Basic Photophysical Parameters: Lifetimes and Quantum Yields  62  
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 Electomers 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 $\pi$-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 Length 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

Index  399