Contents

Preface XIII
Contributors XV

1 Triplet Emitters for Organic Light-Emitting Diodes: Basic Properties 1
Hartmut Yersin and Walter J. Finkenzeller
1.1 Introduction 1
1.2 Electro-Luminescence and the Population of Excited States 3
1.2.1 Multilayer Design of an OLED 3
1.2.2 Electron–Hole Recombination, Relaxation Paths, and Light Emission 7
1.3 Electronic Excitations and Excited States 11
1.3.1 Ligand-Centered (LC) Transitions: States and Splittings 11
1.3.2 Metal-Centered Transitions and States 15
1.3.3 Metal-to-Ligand Charge Transfer/Ligand-Centered Transitions: States in Organo-Transition Metal Triplet Emitters 18
1.3.3.1 Introductory MO Model and Energy States 18
1.3.3.2 Extended MO Model and Energy States 20
1.3.3.3 Spin–Orbit Coupling, Triplet Substates, Zero-Field Splitting, and Radiative Decay Rates 24
1.4 Zero-Field Splitting (ZFS) of the Emitting Triplet, Photophysical Trends, and Ordering Scheme for Organo-Transition Metal Compounds 29
1.4.1 Ordering Scheme 31
1.4.2 Photophysical Properties and ZFS 34
1.4.2.1 Singlet–Triplet Splitting 36
1.4.2.2 Intersystem Crossing Rates 37
1.4.2.3 Emission Decay Time and Photoluminescence Quantum Yield 38
1.4.2.4 Zero-Field Splitting – Summarizing Remarks 38
1.4.2.5 Emission Band Structures and Vibrational Satellites 39
1.4.2.6 Localization/Delocalization and Geometry Changes in the Excited Triplet State 39

1.5 Characterization of the Lowest Triplet State Based on High-Resolution Spectroscopy: Application to Pt(thpy)$_2$ 40

1.5.1 Highly Resolved Electronic Transitions 42

1.5.2 Symmetry and Grouptheoretical Considerations 43

1.6 Characterization of the Lowest Triplet State Based on Decay Time Measurements: Application to Ir(ppy)$_3$ 45

1.7 Phosphorescence Dynamics and Spin–Lattice Relaxation: Background and Case Study Applied to Pt(thpy)$_2$ 49

1.7.1 Processes of Spin–Lattice Relaxation 49

1.7.1.1 The Direct Process 49

1.7.1.2 The Orbach Process 50

1.7.1.3 The Raman Process 51

1.7.2 Population and Decay Dynamics of the Triplet Substates of Pt(thpy)$_2$ 51

1.8 The Triplet State Under Application of High Magnetic Fields: Properties of Ir(btp)$_2$(acac) 56

1.9 Vibrational Satellite Structures: Case Studies Applied to Pt(thpy)$_2$ and Ir(btp)$_2$(acac) 63

1.9.1 Vibrational Satellites: Background 63

1.9.1.1 Franck–Condon Activity 64

1.9.1.2 Herzberg–Teller Activity 67

1.9.2 Pt(thpy)$_2$ Emission: Temperature- and Time-Dependence of the Vibrational Satellite Structure 68

1.9.2.1 Herzberg–Teller-Induced Emission from Substate I: The 1.3 K Spectrum 69

1.9.2.2 Franck–Condon Activity in the Emissions from Substates II and III: The 20 K Spectrum 70

1.9.2.3 Time-Resolved Emission and Franck–Condon/Herzberg–Teller Activities 72

1.9.3 Ir(btp)$_2$(acac) Emission: Low-Temperature Vibrational Satellite Structure 75

1.10 Environmental Effects on Triplet State Properties: Case Studies Applied to Ir(btp)$_2$(acac) 76

1.10.1 Energy Distribution of Sites 77

1.10.2 Zero-Field Splittings at Different Sites 78

1.10.3 Emission Decay and Spin–Lattice Relaxation Times 80

1.11 Emission Linewidths and Spectral Broadening Effects 81

1.11.1 Inhomogeneous Linewidths 81

1.11.2 Homogeneous Linewidths 82

1.11.3 Line Broadening Effects on the Example of Pt(thpy)$_3$ 85

1.11.4 Phenomenological Simulation of Spectral Broadening 86

1.12 Conclusions 89
2 Spin Correlations in Organic Light-Emitting Diodes  
*Manfred J. Walter and John M. Lupton*

2.1 Introduction 99
2.2 Spin-Dependent Recombination of Charge Carriers and Spin-Lattice Relaxation 103
2.3 Studying Spin States using Electric Field Modulated Fluorescence and Phosphorescence 107
2.3.1 Electric Field Modulation of Fluorescence and Phosphorescence: Experimental Method 107
2.3.2 Estimating the Triplet Formation Rate from Transient Electroluminescence 113
2.3.3 Spin Persistence in Charge Carrier Pairs Generated by an Electric Field 114
2.3.4 Spin Persistence in Charge Carrier Pairs Generated Spontaneously 119
2.4 Summary and Outlook 125

3 Cyclometallated Organoiridium Complexes as Emitters in Electrophosphorescent Devices  
*Peter I. Djurovich and Mark E. Thompson*

3.1 Organic Light-Emitting Devices 131
3.2 Phosphorescent Materials as Emitters in OLEDs 132
3.3 Organometallic Complexes as Phosphorescent Emitters in OLEDs 134
3.4 Confining Triplet Excitons and Carriers in Phosphor-Doped OLEDs 136
3.5 Cyclometallated Complexes for OLEDs 139
3.5.1 Synthesis of Cyclometallated Ir Complexes 139
3.5.2 Excited States in Cyclometallated Complexes 140
3.5.3 MO Analysis of Ir Cyclometallates 142
3.5.4 Using Ancillary Ligands to Modify the Excited State Properties 143
3.5.5 Facial and Meridional Isomers of Tris-Cyclometallates 145
3.5.6 Ancillary Ligands with Low Triplet Energies 146
3.5.7 Ligand Tuning to Achieve Green to Near-Infrared Emission 148
3.5.8 Near-UV Luminescent Cyclometallated Complexes 150
3.6 Conclusion 154

4 Highly Efficient Red-Phosphorescent Iridium Complexes  
*Akira Tsuboyama, Shinjiro Okada, and Kazunori Ueno*

4.1 Introduction 164
4.2 Issues of Red-Emissive Materials 165
4.3 Red-Phosphorescent Iridium Complexes 165
4.3.1 Lowest Excited State of Iridium Complexes 165
4.3.2 Molecular Design and Structure 167
4.3.3 Phosphorescence Spectra 169
4.3.4 Phosphorescence Yield 171
4.3.5 Substituent Effects of Ir(piq)$_3$ (6) 173

4.4 OLED Device 177
4.4.1 Thermal Stability 177
4.4.2 Red OLED using Ir(4F5mpiq)$_3$ (10) 179

4.5 Summary 179

5 Pyridyl Azolate Based Luminescent Complexes: Strategic Design, Photophysics, and Applications 185
Yun Chi and Pi-Tai Chou
5.1 Introduction 185
5.2 Ligand Synthesis 186
5.2.1 Ligand Modifications 188
5.2.2 Fluorescent Behavior and Color Tuning 190
5.3 Phosphorescent OLED Applications 193
5.3.1 Osmium-Based Emitters 193
5.3.1.1 Blue-Emitting Materials 193
5.3.1.2 Red-Emitting Materials 198
5.3.2 Ruthenium-Based Emitters 203
5.3.3 Iridium-Based Emitters 207
5.3.3.1 Tuning the Color to Red 207
5.3.3.2 Blue-Emitting Materials 209
5.3.4 Platinum-Based Emitters 212
5.4 Concluding Remarks 216

6 Physical Processes in Polymer-Based Electrophosphorescent Devices 221
Xiao-Hui Yang, Frank Jaiser, and Dieter Neher
6.1 Introduction 221
6.2 Phosphorescent Devices Based on PVK 223
6.2.1 Charge Trapping in Devices with Ir(ppy)$_3$ 224
6.2.2 Competition Between Free Carrier Recombination and Trapping 227
6.2.3 Competition between Förster Transfer and Trapping 230
6.2.3.1 Exciplex Emission 235
6.2.4 Confinement of Singlet and Triplet Excitons on the PVK: PBD Matrix 239
6.3 Devices with PtOEP Doped into Conjugated Polymer Matrices 243
6.3.1 PtOEP in MeLPPP 245
6.3.1.1 Förster Transfer 245
6.3.1.2 Dexter Transfer 247
6.3.1.3 Electrophosphorescence 250
6.3.2 PtOEP in Polyfluorene 250
6.4 Conclusion and Outlook 251
7 Phosphorescent Platinum(II) Materials for OLED Applications 259
Hai-Feng Xiang, Siu-Wai Lai, P. T. Lai, and Chi-Ming Che
7.1 Introduction 259
7.1.1 Phosphorescent Materials for OLED Applications 259
7.1.2 Criteria for Complexes as OLED Emitters 260
7.2 Device Fabrication and Electroluminescence Measurements 260
7.3 Platinum(II) α-Diimine Arylacetylide Complexes 262
7.4 Tridentate Pt(II) Complexes 265
7.4.1 Cyclometalated 6-Aryl-2,2′-bipyridine Arylacetylide Pt(II) Complexes 265
7.4.2 Pt(II) Complexes bearing 6-(2-Hydroxyphenyl)-2,2′-bipyridine Ligands 268
7.5 Tetradentate Pt(II) Complexes 270
7.5.1 Pt(II) Schiff Base Complexes 270
7.5.2 Pt(II) Bis(phenox)diimine Complexes 273
7.5.3 Pt(II) Bis(pyrrole)diimine Complexes 276
7.5.4 Pt(II) Porphyrin Complexes 277
7.6 Concluding Remarks 279

8 Energy-Transfer Processes between Phosphorescent Guest and Fluorescent Host Molecules in Phosphorescent OLEDs 283
Isao Tanaka and Shizuo Tokito
8.1 Introduction 283
8.2 Electronic Structure and Energy Transfer in Guest–Host Systems 284
8.3 Luminescence Properties of Phosphorescent and Fluorescent Materials 286
8.4 Energy Transfer of Blue Phosphorescent Molecules in Guest–Host Systems 288
8.5 Energy Transfer Between Ir(ppy)3 and Alq3: Enhancement of Phosphorescence from Alq3 294
8.6 Energy Transfer Between Ir(ppy)3 and BAlq: Observation of Thermal Equilibrium of Triplet Excited States 301
8.7 Conclusion 306

9 High-Efficiency Phosphorescent Polymer LEDs 311
Addy van Dijken, Klemens Brunner, Herbert Börner, and Bea M.W. Langeveld
9.1 Introduction 311
9.2 The Route Toward High-Efficiency OLEDs 312
9.3 Singlet and Triplet Excited States 312
9.4 Phosphorescent Emitters 313
9.5 Host Materials for Phosphorescent Emitters 314
9.5.1 General Requirements 314
9.5.2 Carbazole-Based Host Materials 316
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.5.3</td>
<td>Tuning the Properties of Carbazole Derivatives</td>
<td>318</td>
</tr>
<tr>
<td>9.5.4</td>
<td>Carbazole-Based Polymers for High-Efficiency Phosphorescent pLEDs</td>
<td>322</td>
</tr>
<tr>
<td>9.6</td>
<td>Outlook</td>
<td>325</td>
</tr>
<tr>
<td>10</td>
<td>Electroluminescence from Metal-Containing Polymers and Metal Complexes with Functional Ligands</td>
<td>329</td>
</tr>
<tr>
<td>10.1</td>
<td>Introduction</td>
<td>329</td>
</tr>
<tr>
<td>10.2</td>
<td>Traditional Materials Used in OLEDs</td>
<td>330</td>
</tr>
<tr>
<td>10.2.1</td>
<td>Molecular Materials</td>
<td>330</td>
</tr>
<tr>
<td>10.2.2</td>
<td>Polymeric Materials</td>
<td>330</td>
</tr>
<tr>
<td>10.3</td>
<td>Development of Phosphorescent Materials for OLEDs</td>
<td>332</td>
</tr>
<tr>
<td>10.3.1</td>
<td>Small Molecules – Pure Organic Dyes and Organometallic Complexes</td>
<td>333</td>
</tr>
<tr>
<td>10.3.2</td>
<td>Polymeric Materials</td>
<td>334</td>
</tr>
<tr>
<td>10.4</td>
<td>Ruthenium Containing Polymers</td>
<td>335</td>
</tr>
<tr>
<td>10.4.1</td>
<td>Photophysics of Ruthenium Complexes</td>
<td>335</td>
</tr>
<tr>
<td>10.4.2</td>
<td>Examples of Ruthenium Complex Containing Polymers</td>
<td>337</td>
</tr>
<tr>
<td>10.4.3</td>
<td>Ruthenium Complexes for Light-Emitting Devices</td>
<td>339</td>
</tr>
<tr>
<td>10.4.4</td>
<td>Complexes Based on Multifunctional Ligands</td>
<td>343</td>
</tr>
<tr>
<td>10.4.5</td>
<td>Ruthenium Containing Polymers for Light-Emitting Devices</td>
<td>346</td>
</tr>
<tr>
<td>10.4.5.1</td>
<td>EL Devices Based on Ruthenium Complex Containing Nonconjugated Polymers</td>
<td>346</td>
</tr>
<tr>
<td>10.4.5.2</td>
<td>Multifunctional Ruthenium Complex Containing Conjugated Polymers</td>
<td>347</td>
</tr>
<tr>
<td>10.4.5.3</td>
<td>Conjugated Polymers with Pendant Metal Complexes</td>
<td>356</td>
</tr>
<tr>
<td>10.5</td>
<td>Summary</td>
<td>358</td>
</tr>
<tr>
<td>11</td>
<td>Molecular Engineering of Iridium Complexes and their Application in Organic Light Emitting Devices</td>
<td>363</td>
</tr>
<tr>
<td>11.1</td>
<td>Introduction</td>
<td>363</td>
</tr>
<tr>
<td>11.1.1</td>
<td>Ligand Field Splitting</td>
<td>364</td>
</tr>
<tr>
<td>11.1.2</td>
<td>Photophysical Properties</td>
<td>365</td>
</tr>
<tr>
<td>11.2</td>
<td>Phosphorescent Iridium Complexes</td>
<td>366</td>
</tr>
<tr>
<td>11.2.1</td>
<td>Tuning of Phosphorescence Colors in Neutral Iridium Complexes</td>
<td>366</td>
</tr>
<tr>
<td>11.2.2</td>
<td>Tuning of Phosphorescence Colors in Cationic Iridium Complexes</td>
<td>369</td>
</tr>
<tr>
<td>11.2.3</td>
<td>Tuning of Phosphorescence Colors in Anionic Iridium Complexes</td>
<td>372</td>
</tr>
<tr>
<td>11.2.3.1</td>
<td>Phosphorescent Color Shift in Anionic Iridium Complexes by Tuning of HOMO Levels</td>
<td>375</td>
</tr>
</tbody>
</table>
11.2.4 Controlling Quantum Yields in Iridium Complexes  377
11.3 Application of Iridium Complexes in Organic Light-Emitting Devices (OLEDs)  378
11.3.1 Standard OLED Device Architecture  379
11.3.2 Light-Emitting Electrochemical Cell (LEC) Device Architecture  387

12 Progress in Electroluminescence Based on Lanthanide Complexes  391
Zu-Qiang Bian and Chun-Hui Huang
12.1 Introduction  391
12.2 The Device Construction and Operating Principles  393
12.3 The Red Electroluminescence Based on Europium Complexes  396
12.4 The Green Electroluminescence Based on Terbium Complexes  404
12.5 The Near Infrared Electroluminescence Based on Neodymium, Erbium, or Ytterbium Complexes  411
12.6 The Ligand Emission Electroluminescence Based on Yttrium, Lanthanum, Gadolinium, or Lutetium Complexes  415
12.7 Conclusion  417

Index  421