

	Acknowledgment	37
	References	38
	Part I	MOF Chemistry of Metallic Clusters and Other Nodes 41
3	Reticular Chemistry of Metal–Organic Frameworks Composed of Copper and Zinc Metal Oxide Secondary Building Units as Nodes	43
	<i>Alexander Schoedel and Omar M. Yaghi</i>	
3.1	Introduction	43
3.2	Secondary Building Units (SBUs): The Design Principles of MOFs	43
3.3	Points of Extension	44
3.3.1	Three Points of Extension	45
3.3.2	Four Points of Extension	46
3.3.3	The Discovery and Importance of Open Metal Sites	47
3.3.4	Six Points of Extension	51
3.3.5	Eight Points of Extension	55
3.3.6	Nine Points of Extension	56
3.3.7	Twelve Points of Extension	57
3.3.8	Twelve or Twenty-Four Points of Extension: Metal–Organic Polyhedra	61
3.3.9	Infinite Secondary Building Units	65
3.4	Concluding Remarks	69
	Acknowledgment	69
	References	69
4	Alkaline Earth Metal-Based Metal–Organic Frameworks: Synthesis, Properties, and Applications	73
	<i>Debasis Banerjee, Hao Wang, Benjamin J. Deibert, and Jing Li</i>	
4.1	Introduction	73
4.2	Synthesis	74
4.2.1	Types of Synthesis: Hydrothermal, Solvothermal, and Ionothermal Routes	74
4.2.2	Types of Linkers: Carboxylate, Phosphonate, and N-based Ligands	75
4.3	Structures	76
4.3.1	Beryllium-Based AE-MOFs	76
4.3.2	Magnesium-Based AE-MOFs	77
4.3.3	Calcium-Based AE-MOFs	80
4.3.4	Strontium-Based AE-MOFs	82
4.3.5	Barium-Based AE-MOFs	84
4.3.6	Structural Trends in AE-MOFs	85
4.4	Properties and Applications	86
4.4.1	Gas Storage and Separation	86

- 4.4.2 Catalysis 93
- 4.4.3 Luminescence-Based Chemical Sensing 94
- 4.4.4 Proton and Ionic Conductivity 96
- 4.5 Conclusions and Outlook 97
- Acknowledgments 98
- List of Abbreviations 98
- References 99

- 5 Synthesis, Structure, and Selected Properties of Aluminum-, Gallium-, and Indium-Based Metal–Organic Frameworks 105**
Lars-Hendrik Schilling, Helge Reinsch, and Norbert Stock
- 5.1 Introduction 105
- 5.2 Properties of Al³⁺, Ga³⁺, and In³⁺ ions 106
- 5.3 Synthesis and Characterization of G13-MOFs 109
- 5.4 Prevalent Framework Structures and Inorganic Building Units in G13-MOFs 110
- 5.5 Selected G13-MOFs 119
 - 5.5.1 Aluminum 119
 - 5.5.2 Gallium 121
 - 5.5.3 Indium 122
- 5.6 Selected Aspects of G13-MOFs 125
 - 5.6.1 Recent Developments in Synthesis 125
 - 5.6.2 Breathing 127
 - 5.6.3 Postsynthetic Modification 128
- References 130

- 6 Group 4 Metals as Secondary Building Units: Ti, Zr, and Hf-based MOFs 137**
Mathieu Bosch, Shuai Yuan, and Hong-Cai Zhou
- 6.1 Introduction 137
 - 6.1.1 Titanium-Based MOFs 139
 - 6.1.2 MIL-125 141
 - 6.1.2.1 MIL-125 Derivatives and Studies 142
 - 6.2 Zirconium-Based MOFs 144
 - 6.2.1 Introduction 144
 - 6.2.2 UiO-66 and Derivatives 145
 - 6.2.2.1 Stability of the UiO-66 Series 146
 - 6.2.2.2 UiO-66 Titanium Postsynthetic Exchange 147
 - 6.2.2.3 The UiO-66 Series and Modulated Synthesis 148
 - 6.2.2.4 UiO-66 Series Applications 151
 - 6.2.3 Zirconium Porphyrinic MOFs 156
 - 6.2.4 Toward Rationally Designed Zr-MOFs 163
 - 6.2.4.1 PIZOFs 163
 - 6.2.4.2 Zr(IV) Based Metal–Organic Frameworks with Intentionally Altered Topology 163

6.2.4.3	NU-1000	164
6.3	Summary and Conclusions	166
	References	168
7	Iron and Groups V- and VI-based MOFs	171
	<i>Christian Serre and Thomas Devic</i>	
7.1	Introduction: The Chemistry in Solution	171
7.2	MOFs Based on Iron, Chromium, or Vanadium	172
7.2.1	Metal Phosphonates	172
7.2.2	Metal Carboxylates	174
7.2.3	Other Ligands	178
7.3	MOFs Based on Nb, Ru, Mo, and W	179
7.4	Synthesis at the Nanoscale	181
7.5	Properties	182
7.5.1	Flexible MOFs	182
7.5.2	Mechanical Properties	183
7.5.3	Analysis of Their Acidic Behavior	184
7.5.4	Stability Issues	185
7.5.5	Bioapplications of MOFs	186
7.5.6	Redox Properties	188
7.5.7	Catalytic Properties	189
7.5.8	Inclusion	190
7.5.9	Adsorption/Separation	192
7.5.9.1	Gas Storage	192
7.5.9.2	Fluid Separation	192
7.6	Conclusion	194
	Acknowledgments	195
	References	195
8	Platinum Group Metal–Organic Frameworks	203
	<i>Elisa Barea, L. Marleny Rodríguez-Albelo, and Jorge A. R. Navarro</i>	
8.1	Introduction	203
8.2	Single Node Frameworks	204
8.3	Metalloligands for the Construction of Mixed Metal–Organic Frameworks (M'MOFs)	207
8.4	Hofmann-Type MOFs	214
8.5	Coordination Polymers with Paddle-Wheel Metal Clusters	221
8.5.1	One-Dimensional Paddle-Wheel Coordination Polymers	222
8.5.2	Two-Dimensional Paddle-Wheel Coordination Polymers	224
8.5.3	Three-Dimensional Paddle-Wheel Coordination Polymers	225
8.6	Summary and Conclusions	227
	References	227

- 9 Group 3 Elements and Lanthanide Metals 231**
Klaus Müller-Buschbaum
- 9.1 Introduction 231
- 9.2 Chemistry and Structures of Group 3 and Lanthanide-Based MOFs 232
- 9.2.1 Relevant Chemical Properties and Background of Group 3 and Lanthanide Elements 232
- 9.2.2 Synthesis and Design of Group 3 and Ln-MOFs 235
- 9.2.3 Carboxylate and Noncarboxylate Group 3 and Ln-MOFs 236
- 9.3 Electronic and Optical Properties of Group 3 and Lanthanide-Based MOFs 246
- 9.3.1 Electronic Properties of Group 3 and Lanthanide Ions 246
- 9.3.2 Luminescence of Group 3 and Ln-MOFs 249
- 9.3.3 Sensing by Luminescence of Group 3 and Ln-MOFs 257
- 9.4 Summary and Conclusions 263
- References 264

Part II Functional Linkers 271

- 10 Extended Linkers for Ultrahigh Surface Area Metal–Organic Frameworks 273**
Hiroyasu Furukawa and Xixi Sun
- 10.1 Introduction 273
- 10.2 Brief Introduction of the History of Porous MOFs 273
- 10.2.1 Design of Ultrahigh Porosity 273
- 10.2.2 Use of Highly Porous MOFs 279
- 10.3 General Synthetic Strategy for Extended Organic Linkers 280
- 10.3.1 Designing Linker Synthesis 280
- 10.3.2 Core Unit 283
- 10.3.3 Extending Units 283
- 10.3.4 Construction of Linker Backbones 283
- 10.3.5 Introduction of Binding Sites into Linkers 285
- 10.4 Case Studies of Extended Linkers 285
- 10.4.1 Ditopic Linkers 285
- 10.4.2 Tritopic Linkers 289
- 10.4.3 Tetratopic Linkers 293
- 10.4.4 A Pentatopic Linker 298
- 10.4.5 Hexatopic Linkers 298
- 10.4.6 Octatopic Linkers 301
- 10.4.7 Dodecatopic Linkers 302
- 10.5 Summary and Conclusions 303
- Acknowledgment 304
- References 304

11	Porous Metal Azolate Frameworks 309
	<i>Pei-Qin Liao, Chun-Ting He, Dong-Dong Zhou, Jie-Peng Zhang, and Xiao-Ming Chen</i>
11.1	Introduction 309
11.2	Imidazolate Coordination Modes 311
11.2.1	Zeolitic and Zeolite-Like Frameworks 311
11.2.2	Polyimidazolates 315
11.3	Pyrazolate Coordination Modes 317
11.3.1	Cluster-Based Networks 318
11.3.2	Chain-Based Pillared-Column Frameworks 324
11.4	Triazolate Coordination Modes 329
11.4.1	1,2,4-Triazolate Coordination Modes 329
11.4.2	1,2,3-Triazolate Coordination Modes 332
11.5	Tetrazolate and Other Coordination Modes 335
11.6	Summary and Conclusions 338
	Acknowledgments 338
	References 338
12	Functional Linkers for Catalysis 345
	<i>Alexandre Legrand, Jérôme Canivet, and David Farrusseng</i>
12.1	Introduction: MOF in Catalysis 345
12.2	Self-Assembled Frameworks 347
12.2.1	Organocatalyst Ligands 347
12.2.2	Metal-Functionalized Ligands 352
12.3	Postsynthetic Modification 361
12.3.1	Organocatalyst Grafting 361
12.3.2	Postsynthetic Metalation 366
12.4	Relevant and Accurate Characterizations as Key for the Design of MOF Catalyst 376
	List of Abbreviations 381
	References 383
13	Chiral Linker Systems 387
	<i>Christel Kutzscher, Philipp Müller, Silvia Raschke, and Stefan Kaskel</i>
13.1	Introduction 387
13.2	Section A: Classes of Chiral Linkers 388
13.2.1	Amino Acids and Related Linkers 388
13.2.1.1	Amino Acid Derivatives 389
13.2.1.2	Peptide-Related Linkers 392
13.2.2	Linkers from Natural Sources 396
13.2.3	Rigid Linkers with Chiral Substituents 397
13.2.4	Salen Linkers 399
13.2.5	Linkers with Axial Chirality 401
13.3	Section B: Enantioselective Separation and Chromatography with Chiral MOFs 408

- 13.3.1 Conceptual Remarks 408
- 13.3.2 Analytical Separations 410
 - 13.3.2.1 Liquid Chromatography: LC, HPLC, CEC 410
 - 13.3.2.2 GC 413
- 13.3.3 Preparative Separations 413
- 13.3.4 Simulation 414
- 13.4 Summary and Conclusions 415
- References 415

- 14 Functional Linkers for Electron-Conducting MOFs 421**
Gang Xu, Guo Cong Guo, Ming Shui Yao, Zhi Hua Fu, and Guan E. Wang
- 14.1 Introduction 421
- 14.2 Methods for Measuring Electrical Properties 422
- 14.3 Linkers 424
 - 14.3.1 Carboxylates 424
 - 14.3.2 Dtoa and Its Derivatives 431
 - 14.3.3 Halogens 436
 - 14.3.3.1 MX 436
 - 14.3.3.2 MMX 438
 - 14.3.4 Nitrogen-Containing Heterocyclic Compounds 440
 - 14.3.5 Catechol and Its Derivatives 442
 - 14.3.6 TCNQ and Its Derivatives 446
 - 14.3.7 Cyanide as Linkers 452
- 14.4 Conclusion and Perspective 456
- Acknowledgments 458
- References 459

- 15 Linkers with Optical Functionality 463**
Mark D. Allendorf, Kirsty Leong, and Ryan A. Zarkesh
- 15.1 Linker Electronic Structure 463
- 15.2 Design Principles 468
 - 15.2.1 Primary Structure 473
 - 15.2.2 Secondary Structure 473
 - 15.2.3 Tertiary Structure 473
 - 15.2.4 Quaternary Structure 474
- 15.3 Linkers for Light Harvesting 474
 - 15.3.1 Porphyrin Linkers 476
 - 15.3.2 Organometallic Complexes as Linkers 477
 - 15.3.3 Guest-Facilitated Energy Transfer 478
- 15.4 Bioimaging 479
 - 15.4.1 Magnetic Resonance Imaging (MRI) 480
 - 15.4.2 Optical Imaging 481
 - 15.4.3 X-Ray Computed Tomography (CT) 482
- 15.5 Linkers for Chemical Sensing 483

- 15.6 Radiation Detection 485
15.7 Conclusions 487
References 487

Contents to Volume 2

List of Contributors XIII

Part III Special MOF Classes and Morphology Design of MOFs 491

- 16 **Nanoparticles** 493
Michael Beetz, Andreas Zimpel, and Stefan Wuttke
- 17 **SURMOFs: Liquid-Phase Epitaxy of Metal–Organic Frameworks on Surfaces** 523
Lars Heinke, Hartmut Gliemann, Pierre Tremouilhac, and Christof Wöll
- 18 **Granulation and Shaping of Metal–Organic Frameworks** 551
U-Hwang Lee, Anil H. Valekar, Young Kyu Hwang, and Jong-San Chang

Part IV Progress in Advanced Characterization of MOFs 573

- 19 **Adsorption Methodology** 575
Irena Senkowska, Katie A. Cychosz, Philip Llewellyn, Matthias Thommes, and Stefan Kaskel
- 20 **Nuclear Magnetic Resonance of Metal–Organic Frameworks (MOFs)** 607
Stephan I. Brückner, Julia Pallmann, and Eike Brunner
- 21 **Electron Paramagnetic Resonance** 629
Matthias Mendt, Mantas Šimėnas, and Andreas Pöppl
- 22 **IR and Raman Spectroscopies Probing MOFs Structure, Defectivity, and Reactivity** 657
Francesca Bonino, Carlo Lamberti, and Silvia Bordiga
- 23 **In Situ X-ray Diffraction and XAS Methods** 691
Irena Senkowska and Volodymyr Bon
- 24 **In Situ Studies of the Crystallization of Metal–Organic Frameworks** 729
Richard I. Walton and Franck Millange

25 **Role of Molecular Simulations in the Field of MOFs** 765
Guillaume Maurin

26 **Defects and Disorder in MOFs** 795
Olesia Halbherr and Roland A. Fischer

A **Appendix A: MOF Suppliers** 823

B **Appendix B: Datasheets** 825

Index 833

Volodymyr Bon
 Technische Universität Dresden
 Department of Inorganic
 Chemistry
 Bergstr. 66
 01062 Dresden
 Germany

Francesca Bonito
 University of Torino
 Department of Chemistry
 NIS and IMSTM Reference
 Center
 Via Quarello 15
 10135 Torino
 Italy

Séverin Bonigo
 University of Torino
 Department of Chemistry
 NIS and IMSTM Reference
 Center
 Via Quarello 15
 10135 Torino
 Italy

Matthew Bosch
 Texas A&M University
 Department of Chemistry
 325 TAMU
 College Station
 TX 77843
 USA