

Boron

Sensing, Synthesis and Supramolecular Self-Assembly

Edited By

Meng Li

University of Bath, Bath, UK

Email: M.Li@bath.ac.uk

John S. Fossey

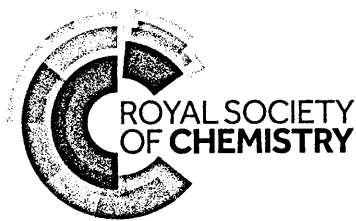
University of Birmingham, Edgbaston, UK

Email: j.s.fossey@bham.ac.uk

Tony D. James

University of Bath, Bath, UK

Email: t.d.james@bath.ac.uk



Contents

About the Editors	xxi
Acknowledgements	xxiii
Chapter 1 Supramolecular Chemistry of Boronic Acids	1
<i>Yasumasa Kanekiyo and Seiji Shinkai</i>	
1.1 Boronic Acid-Based Organogels	1
1.1.1 Low Molecular Weight Gelators	1
1.1.2 Polymeric Hydrogels	4
1.2 Boronic Acid-Appended Porphyrins	7
1.2.1 Monomeric Porphyrins	7
1.2.2 Dimeric Porphyrins	14
1.3 Interfacial Molecular Recognition by Boronic Acid-Appended Amphiphiles	16
1.4 Boronic Acid-Functionalized Metal Nanoparticles	20
1.4.1 Gold Nanoparticles	21
1.4.2 Other Metal Nanoparticles	24
1.5 Structure and Molecular Recognition of Boronic Acid-Containing Polymers	27
1.5.1 Polymers Containing Boronic Acid in the Main-Chain	27
1.5.2 Boronic Acid-Appended Polymers	29
1.5.3 Self-Assembly of Boronic Acids onto Polymers	35
1.6 Boronic Acid-Based Thin Films for Colorimetric Saccharide Sensing	37
References	41

Chapter 2	^{11}B NMR and Its Uses in Structural Characterization of Boronic Acids and Boronate Esters	44
	<i>Pedro Metola, Brette M. Chapin, and Eric V. Anslyn</i>	
2.1	Introduction	44
2.2	NMR Technique	45
2.3	^{11}B NMR Chemical Shifts	46
2.4	Tricoordinate Boranes and Trialkylboranes	47
2.5	Unsaturation and Heteroatoms in Alkylboranes	48
2.6	Boron Compounds with Oxygen Ligands	49
2.7	Borohydrides, Alkylborohydrides and Tetraalkylborates	49
2.8	^{11}B NMR in Boronic Acid Systems	50
2.9	Conclusions	57
	References	58
Chapter 3	Preparations and Applications of Hexyleneglycol Organoboronic Esters	61
	<i>Veronique Blandin and Pierre Y. Chavant</i>	
3.1	Introduction	61
3.1.1	Abbreviations	62
3.1.2	Early Work	62
3.1.3	Differences in Stability Among Cyclic Boronic Esters	63
3.2	Reagents for the Preparation of Organoboronic Esters	64
3.2.1	Trialkoxyboranes	64
3.2.2	Cyclic Dialkoxymboranes	64
3.2.3	Diboron Reagents	66
3.3	Alkylboronic Esters	67
3.3.1	Preparations of Hexyleneglycol Alkylboronic Esters	67
3.3.2	Applications of Hexyleneglycol Alkylboronic Esters	71
3.4	Alkenylboronic Esters	72
3.4.1	Preparations of Hexyleneglycol Alkenylboronic Esters	72
3.4.2	Applications of Hexyleneglycol Alkenylboronic Esters	75
3.5	Arylboronic Esters	83
3.5.1	Preparations of Hexyleneglycol Arylboronic Esters	83
3.5.2	Applications of Hexyleneglycol Arylboronic Esters	90
3.6	Conclusion	93
	References	94

Chapter 4	Fluorescent Chemosensors Based on Boronic Acid Derivatives	101
	<i>Zhiqian Guo and Juyoung Yoon</i>	
4.1	Introduction	101
4.2	Sensing Fluoride Ions	102
4.3	Sensing Carbohydrates	104
4.4	Sensing Dopamine and Related Substances	113
4.5	Sensing Metal Ions	115
4.6	Sensing Reactive Oxygen Species (ROS) and Reactive Nitrogen Species (RNS)	117
4.7	Conclusion	124
	References	124
Chapter 5	Boronic Acid Functionalized Viologens as Saccharide Sensors	128
	<i>Angel Resendez, Ritchie A. Wessling, and Bakthan Singaram</i>	
5.1	Introduction	128
5.2	Background and Illustration of Two-Component Glucose Sensing—Pyranine (HPTS) and a Boronic Acid-Substituted Viologen (BBV ²⁺)	132
5.3	Variations in the Viologen Quencher – Bipyridinium Quenchers	138
5.3.1	Glucose Binding Studies with <i>o</i> -BBV ²⁺ , <i>m</i> -BBV ²⁺ , and <i>p</i> -BBV ²⁺	139
5.3.2	Variations of Boronic Acid-Modified Viologens	140
5.3.3	Effects of Quencher Charge	142
5.4	Variations in Fluorescent Reporters-Sulfonamide Derivatives of HPTS	145
5.4.1	Glucose Sensing Across the Visible Spectrum with <i>m</i> -BBVBP ⁴⁺ and Anionic Fluorescent Dyes	147
5.4.2	Simultaneous Use of Multiple Fluorescent Dyes for Glucose Sensing	149
5.4.3	Using Quantum Dots as the Fluorophore Component	152
5.5	Solution-Phase Sensor Arrays with Boronic Acid-Appended Bipyridinium Salts	154
5.5.1	Recognition of Neutral Saccharides	155
5.5.2	Recognition of Phospho Sugars and Nucleotides	156
5.5.3	Enzyme Assays	159
5.6	Sensor Studies: Immobilizing Dye and Quencher in a Hydrogel	163
5.6.1	Hydrogel Preparation	164
5.6.2	Hydrogel in a Multiwell Plate	166

5.7 Use of the Two-Component Sensing System in a Glucose Monitor	169
5.8 Summary and Future Directions	173
Acknowledgements	174
References	175
Chapter 6 Chiral Recognition Using Fluorescent Boronic Acids Chemosensors	182
<i>Poulomi Majumdar, Caishun Zhang, and Jianzhang Zhao</i>	
6.1 General Introduction	182
6.2 BINOL-Derived Chiral Boronic Acid Chemosensors	184
6.3 Anthracene-Derived Chiral Boronic Acid Chemosensors	186
6.4 Enantioselective Monoboronic Acid Chemosensors	191
6.5 d-PET Fluorescent Boronic Acid Chemosensors	193
6.6 Boronic Acid–Chiral Amine Assemblies for ^1H NMR Determination of the e.e. Values of Chiral Diols	196
6.7 Conclusion and Outlook	198
Acknowledgements	200
References	200
Chapter 7 Boron-Containing BODIPY Chromophore for Fluorescent Sensing	202
<i>Chunchang Zhao and Weihong Zhu</i>	
7.1 Introduction	202
7.2 Synthetic Approach	203
7.2.1 Synthesis of the BODIPY Core	203
7.2.2 Modification of the <i>Meso</i> -Substituents	204
7.2.3 Functionalization of the BODIPY Scaffold	204
7.2.4 Modification at the Boron Center	206
7.3 Photophysical Properties	206
7.3.1 Photoinduced Electron Transfer (PET)	207
7.3.2 Intramolecular Charge Transfer (ICT)	207
7.3.3 Energy Transfer	207
7.4 Molecular Sensors	209
7.4.1 pH Sensors	209
7.4.2 Sensors for Metal Cations	211
7.4.3 Sensors for Anions	218
7.4.4 Sensors for Biomolecules	220
7.4.5 Labeling Biomolecules	229
7.5 Conclusion and Perspective	231
References	232

Chapter 8	Boron in Electroanalysis	236
	<i>Frank Marken</i>	
8.1	Introduction to Boron in Electrochemistry	236
8.2	Boron in Electrode Materials	240
8.3	Boron on Surface, in Films, and in Composites	241
8.4	Boron in Electroanalytical Processes	246
8.5	Summary and Outlook	250
	References	251
Chapter 9	Polymer Self-Assembly Mediated by Boronic Acid	256
	<i>Munenori Numata</i>	
9.1	Introduction	256
9.2	Self-Assembly of Polymers Aided by Boron–Diol Reaction	257
9.3	Polymer (Boronic Acid)–Polymer (Polyhydroxylated) Interaction	258
9.4	Polymer (Boronic Acid)–Saccharide Interaction	260
9.5	Polymer (Boronic Acid)–Saccharide Interaction	263
	References	266
Chapter 10	Boronic Acid-Containing Hydrogels: Synthesis and Their Applications	268
	<i>Ying Guan and Yongjun Zhang</i>	
10.1	Introduction	268
10.2	Synthesis and Properties of Boronic Acid-Containing Hydrogels	269
10.2.1	Boronic Acid-Containing Macroscopic Hydrogels	269
10.2.2	Boronic Acid-Containing Microgels	275
10.2.3	Boronic Acid-Containing Layer-by-Layer Assembled Hydrogel Films	278
10.3	Applications of Boronic Acid-Containing Hydrogels	279
10.3.1	Glucose and Sugar Sensing	280
10.3.2	Controlled Drug Release	289
10.3.3	Other Applications	292
10.4	Conclusion and Outlook	295
	Acknowledgements	295
	References	296

Chapter 11	Boronate Affinity Materials for the Selective Capture of <i>cis</i>-Diol-Containing Biomolecules	302
	<i>Daojin Li and Zhen Liu</i>	
11.1	Boronate Affinity	302
11.2	Interactions and Selectivity Manipulation	303
11.3	Binding pH and Binding Strength	306
11.3.1	Binding pH	306
11.3.2	Binding Strength	307
11.4	Strategies for Reducing the Binding pH	307
11.5	Strategies for Enhancing the Binding Strength	310
11.6	Boronate Affinity Materials	312
11.6.1	Materials with Boronate Affinity	312
11.6.2	Materials with Teamed Boronate Affinity	330
11.6.3	Materials with Boronate Avidity	333
11.6.4	Boronate Affinity-Based Molecularly Imprinted Polymers	334
11.7	Applications	341
11.7.1	Selective Enrichment of Nucleosides	342
11.7.2	Selective Enrichment of Intact Proteins	343
11.7.3	Specific Detection of Glycoprotein Disease Biomarkers	344
11.7.4	Selective Enrichment of Digested Glycopeptides	345
11.8	Conclusion	347
	References	348
Chapter 12	Boronate Microparticles: Preparation, Characterisation, and Functionalisation	361
	<i>Yuji Kubo and Ryuhei Nishiyabu</i>	
12.1	Introduction	361
12.2	Pyridine-Assisted Sequential Boronate Esterification: Development of Chemical-Stimulus Submicrospheres	362
12.2.1	Preparation of Boronate Submicroparticles	362
12.2.2	Chemical Stimulus-Triggered Transformation of Particles	366
12.3	Boronate Microparticle-Supported Nanogold and Nanopalladium Catalysts	368
12.3.1	Reduction of Nitroaromatic Compounds	368
12.3.2	Chemoselective Hydrogenation of Cinnamaldehyde	374
12.4	White-Light Emitting Boronate Microparticles	377

<i>Contents</i>		xix
12.5	Aggregation-Induced Emission-Active Boronate Particles	380
12.6	Conclusion and Future Prospects	384
	References	384
Chapter 13	Recent Advances/Contributions in the Suzuki–Miyaura Reaction	389
	<i>Benjamin R. Buckley</i>	
13.1	Introduction	389
13.2	Recent Methodology	391
13.3	Alternative Metal Catalysts	398
	13.3.1 Nickel	398
	13.3.2 Rhodium	400
	13.3.3 Other Metal Systems	402
13.4	Recent Applications	402
	13.4.1 In Natural Product Synthesis	402
	13.4.2 In Materials Chemistry	403
13.5	Conclusion	403
	References	407
	Subject Index	410