## **Contents**

| 1       | A Journey from Molecular Phthalocyanines to Polymeric            |  |  |
|---------|--|--|--|
|         | Materials 1  |  |  |
| 1.1     | Introduction 1   |  |  |
| 1.2     | Monophthalocyanines 4  |  |  |
| 1.2.1   | Tetra-Substituted Monophthalocyanines 6                          |  |  |
| 1.2.2   | Octa-Substituted Monophthalocyanines 7                           |  |  |
| 1.3     | Phthalocyanine-Based Oligomers 9                                 |  |  |
| 1.3.1   | Sandwich-Type Phthalocyanine-Based Complexes 9                   |  |  |
| 1.3.2   | μ-Oxo-Linked Phthalocyanine-Based Oligomers 12                   |  |  |
| 1.3.3   | Phthalocyanine-Based Supramolecular Oligomers 13                 |  |  |
| 1.3.4   | Phthalocyanine-Based Covalent-Bonded Oligomers 16                |  |  |
| 1.3.4.1 | Phthalocyanine-Based Fused Oligomers 16                          |  |  |
| 1.3.4.2 | Phthalocyanine-Based Covalent-Linked Oligomers 19                |  |  |
| 1.3.5   | Cofacial and Cage-Like Phthalocyanine-Based Compounds 20         |  |  |
| 1.4     | Phthalocyanine-Based Polymeric Materials 23                      |  |  |
| 1.4.1   | Phthalocyanine-Based Porous Molecular Crystals 23                |  |  |
| 1.4.2   | Phthalocyanine-Based Coordination Polymers 25                    |  |  |
| 1.4.3   | Phthalocyanine-Based Organic Polymers 29                         |  |  |
| 1.4.3.1 | Amorphous Phthalocyanine-Based Organic Polymers 29               |  |  |
| 1.4.3.2 | Phthalocyanine-Based COFs 33                                     |  |  |
| 1.5     | Porous Polymeric Materials for Functional Applications 36        |  |  |
| 1.5.1   | Phthalocyanine-Based Polymeric Materials for Chemical Sensors 36 |  |  |
| 1.5.2   | Phthalocyanine-Based Polymeric Materials for Electrocatalysis 37 |  |  |
| 1.5.3   | Phthalocyanine-Based Polymeric Materials for Photocatalysts 40   |  |  |
| 1.5.4   | Phthalocyanine-Based Polymeric Materials for Energy Storage 42   |  |  |
| 1.6     | Conclusion 43  |  |  |
|         | Abbreviations 43   |  |  |
|         | References 44  |  |  |
| 2       | Phthalocyanine-Based Cages 55                                    |  |  |
| 2.1     | Introduction 55  |  |  |
| 2.1.1   | Metal-Organic Cages 55   |  |  |



| vi | Contents |  |
|----|----------|--|
|    | 2.1.2    | Porous Organic Cages 56  |
|    | 2.2      | Phthalocyanine-Based Cages 57                                      |
|    | 2.2.1    | Pc-Based MOCs 57   |
|    | 2.2.2    | Pc-Based POCs 58   |
|    | 2.2.3    | Subphthalocyanine-Based Cages 64                                   |
|    | 2.2.4    | Other Phthalocyanine-Based Molecule Cages 65                       |
|    | 2.3      | Electrochemical Properties of Pc-Based Cages 73                    |
|    | 2.4      | Photophysical Properties of Pc-Based Cage 77                       |
|    | 2.5      | Gas-Sensing Properties of Pc-Based Cage 80                         |
|    | 2.6      | Host-Guest Properties of Pc-Based Molecular Cages 80               |
|    | 2.7      | Conclusion 82  |
|    |          | Abbreviations 84   |
|    |          | References 84  |
|    | 3        | Phthalocyanine-Based Coordination Polymers 89                      |
|    | 3.1      | Introduction 89  |
|    | 3.2      | Synthesis of Pc-Based MOFs 90                                      |
|    | 3.2.1    | The First Pc-Based Porous Coordination Polymers 91                 |
|    | 3.2.2    | MOFs Based on Octahydroxy-Pcs 92                                   |
|    | 3.2.3    | MOFs Based on Amino-Pcs 98   |
|    | 3.2.4    | MOFs Based on Carboxyl-Substituted Pcs 103                         |
|    | 3.3      | Electrochemical Properties of Pc-Based MOFs 106                    |
|    | 3.4      | The Nanocomposite of Pcs with Different MOFs Systems 113           |
|    | 3.5      | The Axial Polymer of Pcs 125                                       |
|    | 3.6      | The Polymers Based on the Co-Assembly of Pcs with Cyclodextrin 128 |
|    | 3.7      | The Nanocomposite of Pcs with MOFs and COFs 130                    |
|    | 3.8      | Conclusion 132   |
|    |          | Abbreviations 132  |
|    |          | References 133   |
|    | 4        | Porous Phthalocyanine-Based Organic Polymers 137                   |
|    | 4.1      | Introduction 137   |
|    | 4.2      | Pc-Based CMPs 139  |
|    | 4.2.1    | Imine-Linked Pc-Based CMPs 140                                     |
|    | 4.2.2    | Ethynyl-Linked Pc-Based CMPs 144                                   |
|    | 4.2.3    | Other Mode-Linked Pc-Based CMPs 146                                |
|    | 4.3      | Pc-Based COFs 148  |
|    | 4.3.1    | Octahydroxyphthalocyanine-Derived COFs 150                         |
|    | 4.3.2    | Octaaminophthalocyanine-Derived COFs 157                           |
|    | 4.3.3    | Octacarboxyphthalocyanine-Derived COFs 164                         |
|    | 4.3.4    | Hexadecafluorophthalocyanine-Derived COFs 169                      |
|    | 4.4      | Polyphthalocyanines 172  |
|    | 4.4.1    | Amorphous Polyphthalocyanines 173                                  |
|    | 4.4.2    | Crystalline Polyphthalocyanines 180                                |
|    | 4.5      | Conclusion 184   |

Abbreviations 185 References 188

| 5    | Sensors Based on Phthalocyanine Polymers and Covalent                               |
|------|---|
|      | Organic Frameworks 193  |
| 5.1  | Introduction 193  |
| 5.2  | Basic Parameters for Sensors 194  |
| 5.3  | Pc-Based NO <sub>2</sub> /NH <sub>3</sub> /NO <sub>2</sub> <sup>-</sup> Sensors 195 |
| 5.4  | Pc-Based ${}^3O_2/{}^1O_2/H_2O_2$ Sensors 199                                       |
| 5.5  | Pc-Based Neurotransmitters and Stimulants Sensors 204                               |
| 5.6  | Pc-Based Cancer Biomarker (L-Cysteine) Sensors 206                                  |
| 5.7  | Pc-Based Glucose Sensors 208  |
| 5.8  | Pc-Based Ion Sensors 210  |
| 5.9  | Pc-Based Organic Compounds Sensors 212  |
| 5.10 | Pc-Based Temperature/Pressure Sensors 219   |
| 5.11 | Conclusion 220  |
|      | Abbreviations 221   |
|      | References 223  |
|      |   |
| 6    | Application of Phthalocyanine in Electrocatalysis 227                               |
| 6.1  | Introduction 227  |
| 6.2  | Phthalocyanine for CO <sub>2</sub> Electroreduction 227                             |
| 6.3  | Phthalocyanine for ORR 255  |
| 6.4  | Phthalocyanine for OER 259  |
| 6.5  | Phthalocyanine for HER 260  |
| 6.6  | Phthalocyanine for Nitrogen Reduction Reaction (NRR) 260                            |
| 6.7  | Phthalocyanine for Electrochemical H <sub>2</sub> O <sub>2</sub> Generation 264     |
| 6.8  | Conclusion and Outlook 265  |
|      | Abbreviations 265   |
|      | References 266  |
|      |   |
| 7    | Application of Phthalocyanine in Photocatalysis 269                                 |
| 7.1  | Introduction 269  |
| 7.2  | Phthalocyanine for CO <sub>2</sub> Photoreduction 270                               |
| 7.3  | Phthalocyanine for H <sub>2</sub> O <sub>2</sub> Photosynthesis 285                 |
| 7.4  | Phthalocyanine for Photocatalytic Degradation 287                                   |
| 7.5  | Phthalocyanine for Photocatalytic Water Splitting 305                               |
| 7.6  | Conclusion and Outlook 308  |
|      | Abbreviations 309   |
|      | References 309  |
| 8    | Applications of Phthalocyanine-Based Polymeric Materials for                        |
|      | Energy Storage 313  |
| 8.1  | Introduction 313  |
| 8.2  | Metal-Ion Battery 313   |

| viii | Contents |
|------|----------|
|------|----------|

| 8.3   | Lithium-Ion Battery 314             |
|-------|-------------------------------------|
| 8.3.1 | Cathode Material 314                |
| 8.3.2 | Anode Material 316                  |
| 8.3.3 | Bipolar Electrode Material 321      |
| 8.3.4 | Interface-Modified Film 325         |
| 8.3.5 | Lithium-Sulfur Battery Catalyst 326 |
| 8.4   | Sodium-Ion Battery 328              |
| 8.4.1 | Anode Material 328                  |
| 8.4.2 | Bipolar Electrode Material 329      |
| 8.4.3 | Sodium-Iodide Battery Catalyst 332  |
| 8.5   | Potassium-Ion Battery 332           |
| 8.6   | Metal-Air Battery 335               |
| 8.7   | Li-O <sub>2</sub> Battery 336       |
| 8.8   | Li-CO <sub>2</sub> Battery 338      |
| 8.9   | Zinc-Air Battery 339                |
| 8.10  | Supercapacitor 351                  |
| 8.11  | Aqueous Electrolyte System 354      |
| 8.12  | Nonaqueous Electrolyte System 355   |
| 8.13  | Gel Electrolyte System 358          |
| 8.14  | Conclusions and Outlook 360         |
|       | Abbreviations 361                   |
|       | References 362                      |
|       |                                     |

**Index** *365*