## **Contents**

|   | Hydi | rogen Bonding Motifs: New Progresses                      | 1  |
|---|------|---|----|
|   | Dan- | Wei Zhang, Hui Wang and Zhan-Ting Li                      |    |
|   | 1.1  | Hydrogen Bonding: The Basic Aspects                       | 1  |
|   |      | 1.1.1 Definition  | 1  |
|   |      | 1.1.2 Hydrogen Bonding Donors and Acceptors               | 2  |
|   |      | 1.1.3 The Strength of the Hydrogen Bond                   | 3  |
|   |      | 1.1.4 Hydrogen Bonding Formed by a Single Functional      |    |
|   |      | Group   | 5  |
|   | 1.2  | Intramolecular Hydrogen Bonding                           | 13 |
|   |      | 1.2.1 The O-H···X Hydrogen Bonding                        | 13 |
|   |      | 1.2.2 The N-H···X Hydrogen Bonding                        | 14 |
|   | 1.3  | Intermolecular Hydrogen Bonding                           | 24 |
|   |      | 1.3.1 Double Hydrogen Bonding                             | 24 |
|   |      | 1.3.2 Triple Hydrogen Bonding                             | 25 |
|   |      | 1.3.3 Quadruple Hydrogen Bonding                          | 27 |
|   | 1.4  | Conclusion  | 33 |
|   | Refe | rences  | 34 |
|   |      |   |    |
| 2 | Und  | erstanding of Noncovalent Interactions Involving Organic  |    |
|   | Fluo | rine  | 37 |
|   | Piyu | sh Panini and Deepak Chopra                               |    |
|   | 2.1  | Introduction  | 37 |
|   |      | 2.1.1 Why Fluorine Is So Special?                         | 39 |
|   | 2.2  | Debate on Participation of Fluorine as a Hydrogen Bond    |    |
|   |      | Donor: Overview of the Weak X-H···F-C; $X = N$ , O, C     |    |
|   |      | Hydrogen Bond   | 40 |
|   | 2.3  | Inputs from Other Interactions Involving Organic Fluorine | 53 |
|   |      | 2.3.1 Insight into Halogen–Halogen Interactions Involving |    |
|   |      | Fluorine  | 53 |
|   |      |   |    |

viii Contents

|   |      | 2.3.2   | Insights into Halogen Bond Formation Involving Fluorine (C–F···X; $X = \text{Halogen}, N, O, S$ ) | 57  |
|---|------|---------|---|-----|
|   | 2.4  | Conclu  | sions   | 61  |
|   |      |         |   | 62  |
|   |      |         |   | ٠.  |
| 3 |      |         | onding in Supramolecular Crystal Engineering Wang and Qi-Yu Zheng                                 | 69  |
|   | 3.1  |         | action  | 69  |
|   | 3.2  |         | I Engineering Strategies  | 71  |
|   |      | 3.2.1   | Supramolecular Synthons and Retrosynthesis  | 71  |
|   |      | 3.2.2   | Reticular Synthesis   | 72  |
|   | 3.3  | Hydro   | gen Bonding   | 73  |
|   |      | 3.3.1   | Definition and Scopes   | 73  |
|   |      | 3.3.2   | Description of Hydrogen Bonding Motifs:   |     |
|   |      |         | The Graph Sets  | 74  |
|   |      | 3.3.3   | Hydrogen Bonding Rules  | 75  |
|   | 3.4  | Interpe | enetration  | 75  |
|   | 3.5  | Hydro   | gen Bonding Structures  | 77  |
|   |      | 3.5.1   | Discrete Hydrogen Bonding Capsules  | 77  |
|   |      | 3.5.2   | 1D Infinite Hydrogen Bonding Nanotubes  | 84  |
|   |      | 3.5.3   | 2D and 3D Borromean Arrayed Organic Crystals  | 90  |
|   |      | 3.5.4   | 2D → 3D Parallel Polycatenated Structures   | 93  |
|   |      | 3.5.5   | 3D Interpenetrated dia and pcu Frameworks   | 95  |
|   |      | 3.5.6   | Unusual Aggregation Phase of Water Molecules  | 96  |
|   | 3.6  |         | eations   | 99  |
|   |      | 3.6.1   | Crystal Engineering of Solid State Photochemical  |     |
|   |      |         | Reactions   | 99  |
|   |      | 3.6.2   | Gas Adsorption and Separation   | 103 |
|   |      | 3.6.3   | Crystal Engineering of Pharmaceutical Cocrystals  | 105 |
|   | Refe | rences  |   | 107 |
|   |      | _       |   |     |
| 4 |      |         | onding-Mediated Self-assembly of Aromatic   |     |
|   |      |         | ular Duplexes   | 115 |
|   |      | -       | and Chuan-Feng Chen   | 115 |
|   | 4.1  |         | uction  | 115 |
|   | 4.2  | 4.2.1   | mide-Based Molecular Duplex Strands   | 116 |
|   |      | 4.2.1   | Oligoamide-Based Molecular Duplex Strands   | 116 |
|   | 4.3  |         | Applications  | 118 |
|   | 4.3  | 4.3.1   | nydrazide-Based Molecular Duplex Strands  | 122 |
|   |      | 4.3.1   | From Supramolecular Zipper to Quadruple Hydrogen-Bonded Heterodimer                               | 123 |
|   |      | 4.3.2   | Strict Self-complementary Oligohydrazide-Based  | 123 |
|   |      | 7.5.2   | Duplexes  | 124 |
|   |      |         | Duplenes  | 14  |

Contents ix

|   |       | 4.3.3 Shuttle Movement                                  | 125 |
|---|-------|---|-----|
|   |       | 4.3.4 Mutual Responsive Low Molecular Mass Organic      |     |
|   |       | Gelators  | 127 |
|   |       | 4.3.5 Supramolecular Substitution                       | 127 |
|   |       | 4.3.6 Amide-Urea-Based Molecular Duplexes               | 128 |
|   |       | 4.3.7 "Hao" Templated Molecular Duplex                  | 131 |
|   | 4.4   | "Covalent Casting" Strategy-Based Molecular Duplexes    | 131 |
|   | 4.5   | Other Molecular Duplex Strands                          | 133 |
|   | 4.6   | Conclusions and Outlook                                 | 135 |
|   | Refe  | rences  | 135 |
| 5 | Hydi  | rogen Bonding-Driven Anion Recognition                  | 137 |
|   | Lipir | ng Cao, Jie Zhao, Dong Yang, Xiao-Juan Yang and Biao Wu |     |
|   | 5.1   | Introduction  | 137 |
|   | 5.2   | Amide-Based Anion Recognition                           | 138 |
|   | 5.3   | Urea-Based Anion Recognition                            | 149 |
|   | 5.4   | Pyrrole-Based Anion Recognition                         | 164 |
|   | 5.5   | CH Donor-Based Anion Recognition                        | 175 |
|   | 5.6   | OH-Based Anion Recognition                              | 178 |
|   | 5.7   | Conclusion  | 181 |
|   | Refe  | rences  | 181 |
| 6 |       | nation of Hydrogen-Bonded Self-assembled Structures     |     |
|   |       | olar Solvents   | 187 |
|   | -     | atim Banerjee and Carsten Schmuck                       |     |
|   | 6.1   | Introduction  | 187 |
|   | 6.2   | Nucleobase Pairing and Nanostructure Formation in Water | 188 |
|   | 6.3   | Self-sorting/Orthogonal Self-assembly                   | 193 |
|   | 6.4   | Supramolecular Polymers                                 | 201 |
|   | 6.5   | Supramolecular Gels in Aqueous and Polar Organic Media  | 207 |
|   | 6.6   | Vesicles, Bilayers, Micelles Through H-Bonding          | 214 |
|   | Refe  | rences  | 224 |
| 7 | _     | rogen Bonded Capsules: Chemistry in Small Spaces        | 227 |
|   |       | uan Liu and Julius Rebek Jr                             |     |
|   | 7.1   | Why Study Encapsulated Molecules?                       | 227 |
|   | 7.2   | The Capsules and Their Contents                         | 228 |
|   |       | 7.2.1 The Tennis Ball                                   | 228 |
|   |       | 7.2.2 The Softball                                      | 230 |
|   |       | 7.2.3 A Cylindrical Capsule                             | 23  |
|   |       | 7.2.4 The Volleyball                                    | 23  |
|   | 7.3   | What's It Like Inside the Capsules?                     | 23  |
|   | 7.4   | How Do Molecules Get In and Out of the Capsules?        | 234 |
|   | 7.5   | Amplified Intermolecular Forces                         | 23  |

x Contents

|   | 7.6   | Arrangements in Encapsulation Space:                       | 237 |
|---|-------|--|-----|
|   |       | New Stereochemistry  | 237 |
|   |       | 7.6.1 Social Isomers                                       | 237 |
|   |       | 7.6.2 Single Molecule Solvation                            |     |
|   |       | 7.6.3 Isotope Effects                                      | 239 |
|   |       | 7.6.4 Constellations                                       | 240 |
|   |       | 7.6.5 Diastereomers  | 242 |
|   | 7.7   | Chiral Spaces  | 243 |
|   | 7.8   | Reactivity   | 245 |
|   | 7.9   | Conclusion   | 246 |
|   | Refe  | rences   | 247 |
| 8 | -     | rogen Bonded Organic Nanotubes                             | 249 |
|   |       | Li Hou   |     |
|   | 8.1   | Introduction   | 249 |
|   | 8.2   | Strategies for the Construction of Hydrogen Bonding-Driven |     |
|   |       | Organic Nanotubes  | 250 |
|   | 8.3   | Nanotubes from Hydrogen Bonding-Induced Helical            |     |
|   |       | Structures   | 251 |
|   | 8.4   | Nanotubes from Tubular Molecules                           | 254 |
|   | 8.5   | Nanotubes from Hydrogen Bonded Rod-like                    |     |
|   |       | Molecular Units  | 256 |
|   | 8.6   | Nanotubes from Hydrogen Bonded Cyclic Molecules            | 258 |
|   |       | 8.6.1 Nanotubes from Hydrogen Bonded Cyclic Peptides       | 258 |
|   |       | 8.6.2 Nanotubes from Hydrogen Bonded Cyclic Ureas          | 26  |
|   | 8.7   | Nanotubes from Hydrogen Bonded Wedge- or Sector-like       |     |
|   |       | Molecules  | 262 |
|   | 8.8   | Conclusions and Outlooks                                   | 265 |
|   |       | rences   | 265 |
|   |       |  |     |
| 9 |       | onding-Assisted One-Pot Macrocyclization for Rapid         |     |
|   |       | struction of H-Bonded Macrocyclic Aromatic Foldamers       | 269 |
|   |       | qiang Zeng   |     |
|   | 9.1   | Introduction   | 269 |
|   | 9.2   | Concept Formulation  | 27  |
|   | 9.3   | Aryl Amide Macrocycles                                     | 274 |
|   |       | 9.3.1 Non-fivefold Symmetric Aryl Amide Macrocycles        | 274 |
|   |       | 9.3.2 Fivefold Symmetric Aryl Amide Macrocycles            | 27  |
|   |       | 9.3.3 Highly Selective Production of Strained Aromatic     |     |
|   |       | Hexamers   | 288 |
|   |       | 9.3.4 Chemo- and Regio-Selective Demethylations            | 292 |
|   | 9.4   | Macrocycles Containing Non-amide Linkages                  | 293 |
|   | - • • | ,  |     |

Contents xi

|    | 9.5                                    | Mechanism of One-Pot Macrocyclization                   | 2 |  |
|----|--|---|---|--|
|    |  | 9.5.1 Variable Functionalizations Around the Pentameric | _ |  |
|    |  | Periphery   | 2 |  |
|    |  | 9.5.2 A Chain-Growth Mechanism Underlying the           | _ |  |
|    |  | Formation of Aromatic Pentamers                         | 3 |  |
|    |  | 9.5.3 A Non-chain Growth Mechanism Underlying           |   |  |
|    |  | the Formation of Strained Aromatic Hexamers             |   |  |
|    |  | and Heptamers   | 3 |  |
|    | 9.6                                    | Conclusion  | 3 |  |
|    | Refer                                  | ences   | 3 |  |
| 10 | Hydr                                   | ogen-Bonded Supramolecular Polymers                     | 3 |  |
|    | Chen Lin, Tangxin Xiao and Leyong Wang |   |   |  |
|    | 10.1                                   | Introduction  | 3 |  |
|    | 10.2                                   | Hydrogen-Bonding Building Blocks                        | 3 |  |
|    | 10.3                                   | Hydrogen-Bonded Main-Chain Supramolecular Polymers      |   |  |
|    |  | Constructed by Low-Molecular-Weight Monomers            | 3 |  |
|    | 10.4                                   | Hydrogen-Bonded Supramolecular Polymers Constructed     |   |  |
|    |  | by High-Molecular-Weight Conventional Polymers          |   |  |
|    |  | that Are Functionalized by Hydrogen-Bonded Motifs       | 3 |  |
|    |  | 10.4.1 Telechelic Supramolecular Polymers               | 3 |  |
|    |  | 10.4.2 "Side-Chain" Supramolecular Polymer Networks     | 3 |  |
|    | 10.5                                   | Supramolecular Polymers Constructed by Orthogonal       |   |  |
|    |  | Hydrogen Bonding-Driven Self-assembly and Other         |   |  |
|    |  | Non-covalent Interactions                               | 3 |  |
|    | 10.6                                   | Conclusions   | 3 |  |
|    | Refer                                  | rences  | 3 |  |