

Edited by Hisashi Yamamoto and Takashi Kato

# Molecular Technology

Materials Innovation

Volume 3

Molecular Technology

# **Related Titles**

Yamamoto, H., Kato, T. (eds.)

# Molecular Technology Volume 1: Energy Innovation

2018 ISBN: 978-3-527-34163-4

Yamamoto, H., Kato, T. (eds.)

# Molecular Technology Volume 2: Life Innovation

2018 ISBN: 978-3-527-34162-7

Yamamoto, H., Kato, T. (eds.)

# Molecular Technology

Volume 4: Synthesis Innovation

2019 ISBN: 978-3-527-34588-5

# Molecular Technology

Materials Innovation

Edited by Hisashi Yamamoto and Takashi Kato

Volume 3



#### Editors

#### Hisashi Yamamoto

Chubu University Molecular Catalyst Research Center 1200 Matsumoto Kasugai 487-501 Aichi Japan

#### Takashi Kato

University of Tokyo Department of Chemistry and Biotechnology 7-3-1 Hongo, Bunkyo-ku 113-8656 Tokyo Japan

#### Cover

fotolia\_VAlex and fotolia\_monsitj

All books published by **Wiley-VCH** are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Library of Congress Card No.: applied for

# British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

# Bibliographic information published by the Deutsche Nationalbibliothek

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <http://dnb.d-nb.de>.

© 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Boschstr. 12, 69469 Weinheim, Germany

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photoprinting, microfilm, or any other means – nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

 Print ISBN:
 978-3-527-34161-0

 ePDF ISBN:
 978-3-527-80273-9

 ePub ISBN:
 978-3-527-80272-2

Cover Design Adam-Design, Weinheim, Germany Typesetting SPi Global, Chennai, India Printing and Binding

Printed on acid-free paper

10 9 8 7 6 5 4 3 2 1

## Foreword by Dr. Hamaguchi

Molecular Technology is a newly developed research field supported through Japan Science and Technology Agency (JST) research funding programs. These programs aim to establish an innovative research field that harnesses the characteristics of molecules to enable new scientific and commercial applications. It is our great pleasure to publish this book, with the ambition that it will develop both an understanding of and further support for this new research field within the research and student community.

٧

Molecular Technology as introduced in this book began in 2012 as a research area within JST's Strategic Basic Research Programs. JST is an advanced network-based research institution that promotes state-of-the-art R&D projects and leads the way in the co-creation of future innovation in tandem with wider society. JST develops a wide range of funding programs related to the promotion of scientific and technological innovation, which include strategy planning, target-driven basic research, and promotion of research and development.

Various research projects focused on Molecular Technology are currently underway within JST's Strategic Basic Research Programs, including

- the team-based research program " CREST (Core Research for Evolutionary Science and Technology)" and
- the individual research program " PRESTO (Precursory Research for Embryonic Science and Technology)".

Dr. Yamamoto (CREST) and Dr. Kato (PRESTO) manage the Molecular Technology research area as research supervisors.

In addition, JST's Strategic International Collaborative Research Program promotes research projects in the area of Molecular Technology, including ongoing cooperation with *L'Agence nationale de la recherche* (The French National Research Agency, ANR).

A wide range of researchers from the young to seniors across fields from green science, life science, and energy are participating in successful research aimed at establishing the new field of Molecular Technology. They are already producing excellent research results and it is our hope that these will develop into technologies capable of initiating a new era in energy and green and life sciences.

# vi Foreword by Dr. Hamaguchi

I encourage you to read not only researchers in related fields but also look more broadly to researchers working in other fields. Inspired by this book, I look forward to emerging new research fields and seeds toward future innovation.

> *Michinari Hamaguchi* Japan Science and Technology Agency President

## Foreword by Dr. Noyori

As an affiliated institution of the Japan Science and Technology Agency (JST), the Center for Research and Development Strategy (CRDS) navigates the latest global trends in science, technology, and innovation to aid the Japanese government in formulating its national strategies. *Molecular Technology* is the outcome of a research project born of a CRDS Strategic Proposal realized under the excellent editorial supervision of Hisashi Yamamoto and Takashi Kato. To them and to the scientists who have made major advances in molecular technology through their uninhibited research I extend my heartfelt congratulations and respect.

The significance of molecular science in all areas of scientific endeavor is certain to increase. Accurate understanding of molecular assemblies and molecular complexes is essential for comprehending the elaborate workings of natural phenomena and of the genesis and mechanisms of materials and life functions. Now, more than ever, science must be seen as a single entity, a comprehensive whole. Mathematical science and the most advanced technologies of observation and information help us explore the essence of materials and substances in a way that brings together all fields of science. It is the nature of molecular science to continually advance and expand. Using the metaphor of light, we can say that molecules behave in the manner of both "waves and particles."

The traditional separation of science into physics, chemistry, and biology no longer applies. Neither does it make any sense to maintain those seemingly self-contained subdivisions of organic chemistry, inorganic chemistry, physical chemistry, or polymer chemistry. So long as specialized groups and rigid educational systems cling to outdated perceptions, the more important it is to encourage an "anti-disciplinary" type of science in which diverse fields converge rather than conventional interdisciplinary or transdisciplinary attempts to link diverse fields.

Molecular technology, while firmly grounded in fundamental scientific knowledge, aims for practical applications within contemporary society. Johann Wolfgang von Goethe once said, "Knowing is not enough; we must apply. Willing is not enough; we must do." Technology with no practical application is meaningless to society. Researchers should not hesitate to set their own themes and topics of exploration in academia where self-determination holds strong and creativity wins the highest respect. Researchers must show ingenuity in the pursuit of their chosen mission even as they fulfill their duty to pursue science-based technology for society. Never forget that it is by no means advisable to function purely as a support for activities that industry should actually undertake on its own.

The creative outcomes of the Molecular Technology Project launched in 2013 in conjunction with new collaborations are certain to lead to a wide range of innovations and to make significant contribution to achieving the Sustainable Development Goals (SDGs) of the United Nations' 2030 Agenda.

Science is one; and the world is one. Those who will follow us have a responsibility to the world after 2030 and it is my hope that new generations will pioneer revolutionary molecular technology that will bring science and humanity ever closer together. Brain circulation and international collaboration are essential to achieving these goals. V. S. Naipaul, winner of the 2001 Nobel Prize in Literature, once noted that knowing what you wanted to write was three-quarters of the task of writing. Humanity's future is to be found in the unbounded imagination of the young and in their ability to support the challenges they undertake.

December 2017

*Ryoji Noyori* Tokyo, Japan

# Preface

Chemical science enables us to qualitatively change existing science and technology by purposefully designing and synthesizing molecules and creating the desired physical, chemical, and biological functions of materials and drugs at molecular level. In 2012, we have started a big funding project in Japan, "Molecular Technology" (Establishment of Molecular Technology toward the Creation of New Functions [CREST], and Molecular technology and new functions [PRESTO]), and numerous research groups in Japan have joined the project in diverse research areas. All of these are typical transdisciplinary research projects between chemistry and various other research areas. In other words, molecular technology is the brand-new scientific discipline. In principle, most of the proposed projects try to solve the big bridge between chemistry and other basic science and technology. We thus propose a good model for this bridge, which can make valuable contribution to human welfare.

Between JST and ANR we initiated a number of international collaboration projects in molecular technology in 2014. Since then, 12 new projects have been started. The projects provide quite unique opportunity for collaboration between Japan and France and active research groups have participated with very close discussions on molecular technology between the two countries. We are sure this project will provide close contacts between the research groups of Japan and France for otherwise impossible discoveries. Overall, this international collaboration will be a new entry for even more important discoveries in future.

In 2016, we started the discussion to bring out a new and comprehensive book on molecular technology for the benefit of all the researchers in the world to provide typical and leading examples in molecular technology. Overall, researchers of 15 CREST, 50 PRESTO, and 12 INTERNATIONAL groups have contributed to this book. This book covers extremely diverse areas of molecular technology, from materials to pharmaceuticals.

> *Hisashi Yamamoto* Chubu University, Supervisor of CREST

*Takashi Kato* The University of Tokyo, Supervisor of PRESTO

# Contents

- 1 Control of Electronic Property of C<sub>60</sub> Fullerene via Polymerization 1 Nobuvuki Aoki
- 1.1 Introduction 1
- 1.1.1 History of Polymerization of C<sub>60</sub> Fullerene 1
- 1.1.2 Electronic Property of Pristine  $C_{60}$  and n-Type FET Action 4
- 1.2 Polymerization of  $C_{60}$  Fullerene 5
- 1.2.1 Photo-irradiation 5
- 1.2.2 Doping Effect Using Alkali Metal and Superconductivity 8
- 1.2.3 High-Pressure and High-Temperature Application 9
- 1.2.4 Plasma and EB Irradiation 11
- 1.2.5 Low-Energy EB Irradiation 12
- 1.3 Summary 14 Acknowledgments 14 References 14
- 2 Flapping Molecules for Photofunctional Materials 17 Shohei Saito
- 2.1 Introduction 17
- 2.1.1 Motivation 17
- 2.1.1.1 Hybridization of Rigidity and Flexibility 17
- 2.1.2 Background 18
- 2.1.2.1 How to Change Photophysical Properties by Changing Conformation of Molecules *18*
- 2.1.3 Flapping Fluorophore 19
- 2.2 Viscosity Imaging Technique 23
- 2.2.1 Molecular Design of Chemical Viscosity Probes 23
- 2.2.2 Flapping Viscosity Probe 24
- 2.2.2.1 Synthesis 24
- 2.2.2.2 Fluorescence and Excited-State Dynamics 27
- 2.2.2.3 Polarity-Independent Viscochromism 29
- 2.2.2.4 Monitoring the Epoxy Resin Curing 31
- 2.3 Light-Removable Adhesive 32
- 2.3.1 Polymer and Supramolecular Approach 33

xii Contents

- 2.3.2 Liquid Crystal Approach 33
- 2.3.3 Light-Melt Adhesive 36
- 2.3.3.1 Requirements for Applications 36
- 2.3.3.2 Materials Design 38
- 2.3.3.3 Adhesive Performance 38
- 2.3.3.4 Working Mechanism 42
- 2.4 Conclusion 44 References 44

#### 3 Catechol-Containing Polymers: A Biomimetic Approach for Creating Novel Adhesive and Reducing Polymers 53 Hiroshi Yabu

- 3.1 Background 53
- 3.1.1 Adhesive Proteins of Mussels 53
- 3.1.2 Bio-Based Catechol-Containing Polymers 53
- 3.1.3 Synthetic Polymers Containing Catechol Moieties 56
- 3.1.4 Toward Biomimetic Molecular Technology 59
- 3.2 Advanced Adhesives and Surface Modification Agents 60
- 3.3 Reducing Agents for Creating Nanoscale Metallic Structures 62
- 3.4 Application as Proton-Conductive Thin Films 66
- 3.5 Templates for Carbon Materials 66
- 3.6 Summary 66
  - References 67
- 4 Development of Ultra-microfabricating Polymeric Materials and Its Self-assembly Technology 71
  - Teruaki Hayakawa
- 4.1 Introduction 71
- 4.2 Perpendicular Orientation of High-*χ*BCP Microphase-Separated Domains *7*2
- 4.2.1 Challenges in Perpendicular Orientation of High- $\chi$ BCP 72
- 4.2.2 Solvent Annealing Method 74
- 4.2.3 Top-Coat Method 75
- 4.2.4 Perpendicular Orientation by Molecular Structure Design 75
- 4.2.4.1 Development of Perpendicular Orientation High- $\chi$ BCP Using Silicon-Containing Polymer 75
- 4.2.4.2 Development of a Perpendicular Oriented High- $\chi$ BCP by Using a Polysiloxane Derivative 77
- 4.3 Conclusions 82 Acknowledgments 82 References 82
- 5 Molecular Simulations of Deformation and Fracture Processes of Crystalline Polymers 85 Yuji Higuchi
- 5.1 Introduction 85
- 5.2 Coarse-Grained Molecular Simulations 87

- 5.2.1 Deformation and Fracture Processes of Glass Polymers and Elastomers 87
- 5.2.2 Molecular Simulation of Polymer Crystallization 90
- 5.3 Deformation and Fracture Processes of Semicrystalline Polymers on the Molecular Scale 92
- 5.3.1 Deformation and Fracture Process 92
- 5.3.2 Discussion 97
- 5.3.2.1 Comparison of Simulation Results 98
- 5.3.2.2 Degradation and Mechanical Properties of Polymers 99
- 5.3.2.3 Future Work *100* 5.4 Conclusions *101* References *101*
- 6 A Tale of Chirality Transfer, Multistep Chirality Transfer from Molecules to Molecular Assemblies, Organic to Inorganic Materials, Then to Functional Materials 107 Reiko Oda, Emilie Pouget, Thierry Buffeteau, Sylvain Nlate, Hirotaka Ihara, Yutaka Okazaki, and Naoya Ryu
- 6.1 Introduction 107
- 6.2 Chirality Induction and Chirality Transfer 107
- 6.2.1 Notion and Examples of Chirality Induction and Chirality Transfer *108*
- 6.2.2 From Molecule to Molecule 108
- 6.2.3 From Molecule to Self-assembled Systems 109
- 6.2.4 From Molecular Assemblies to Molecules *109*
- 6.2.5 Inorganic Chiral Structures 110
- 6.2.6 Characterization Methods of Chiral Assemblies 111
- 6.2.7 Aim of This Chapter 112
- 6.3 Molecular and Supramolecular Chirality from Gemini-Tartrate Templates *112*
- 6.3.1 Gemini-Tartrate Amphiphiles 112
- 6.3.1.1 Formation of Gels with Chiral Nanoribbon Structures 112
- 6.3.1.2 Specific Recognition Between Dication Amphiphiles and Tartrates *114*
- 6.3.1.3 Conformation of Tartrate Ions in Solution, Micellar Aggregates, and Twisted Ribbons 115
- 6.3.1.4 Induction of Chiral Conformation in the Cationic Amphiphile 116
- 6.3.1.5 Effect of Enantiomeric Excess Studied by ECD, VCD, and XRD 118
- 6.3.2 Organic–Inorganic Nanohelices 122
- 6.3.2.1 Chirality of Silica Nanohelices Evidenced by VCD 123
- 6.3.3 Silica Nanohelices as Platform to Organize Non-chiral Objects 125
- 6.3.3.1 Induction of CD on Non-chiral Dye 125
- 6.3.3.2 Gold Nanoparticles Forming 3D Helical Superstructures with Controlled Morphology and Strong Chiroptical Property 127
- 6.4 Conclusion 128 References 130

xiv	Contents

<ul> <li><i>Nagahir Contrology Cells</i>, <i>International 10, July Mathematics</i>, <i>University of the second systems</i>, <i>International 11, July Mathematics</i>, <i>International 11, July Mathematical 11, July Mathematics</i>, <i>Internationa</i></li></ul>	7	Solution Plasma Reactions and Materials Synthesis 137
<ul> <li>Nugumo Sano Sano 137</li> <li>Solution Plasma 138</li> <li>Materials Synthesis by Solution Plasma 139</li> <li>Noble Metal Nanoparticles 141</li> <li>Noble Metal Nanoparticles 144</li> <li>Bimetallic and Alloy Nanoparticles 144</li> <li>Bimetallic and Alloy Nanoparticles 145</li> <li>Metal Carbide, Boride, and Sulfide 150</li> <li>Carbon Materials 152</li> <li>Metal Carbide, Boride, and Sulfide 150</li> <li>Carbon Materials 152</li> <li>Metal Carbide, Boride, and Sulfide 150</li> <li>Carbon Materials 152</li> <li>Metal Carbide, Boride, and Sulfide 150</li> <li>Carbon Materials 158</li> <li>Composite Materials 160</li> <li>Sano Molecular Weight Biopolymer 158</li> <li>Composite Materials 160</li> <li>Metal Nanoparticle/Carbon Composite 161</li> <li>Sano Metal Nanoparticle/Metal Oxide Composite 161</li> <li>Sano Metal Nanoparticle/Metal Oxide Composite 161</li> <li>Metal Nanoparticle/Metal Oxide Composite 163</li> <li>Polymer/Carbon Composite 163</li> <li>Metal Nanoparticle/Biopolymer Composite 163</li> <li>Metal Nanoparticle/Biopolymer Composite 163</li> <li>Summary and Future Challenge 163</li> <li>High-Precision Tools and Measurements 164</li> <li>Carbon Computers 173</li> <li>Satoshi Maeda, Yu Harabuchi, and Kenichiro Saita</li> <li>Introduction 173</li> <li>Methodology 174</li> <li>Metal Artificial Force Induced Reaction Method 174</li> <li>Search for Potential Crossing Points 177</li> <li>Results and Discussion 178</li> <li>Aldol Reaction 179</li> <li>Caisen Rearrangement 180</li> <li>Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184</li> <li>Search for Cluster Structures by AFIR 187</li> </ul>		Nagabiro Saito
<ul> <li>Schution Plasma 138</li> <li>Note Metal Nanoparticles 141</li> <li>Noble Metal Nanoparticles 141</li> <li>Noh-noble Metal Nanoparticles 144</li> <li>Bimetallic and Alloy Nanoparticles 145</li> <li>Metal Oxide 147</li> <li>Metal Carbide, Boride, and Sulfide 150</li> <li>Carbon Materials 152</li> <li>Metal Carbide, Boride, and Sulfide 150</li> <li>Carbon Materials 152</li> <li>Mesoporous Silica 158</li> <li>Composite Materials 160</li> <li>Sale Low Molecular Weight Biopolymer 158</li> <li>Composite Materials 160</li> <li>Metal Oxide/Carbon Composite 160</li> <li>Metal Nanoparticle/Carbon Composite 161</li> <li>Metal Nanoparticle/Mesoporous Silica Composite 163</li> <li>Metal Nanoparticle/Mesoporous Silica Composite 163</li> <li>Metal Nanoparticle/Mesoporous Silica Composite 163</li> <li>Metal Nanoparticle/Mesoporous 163</li> <li>Metal Nanoparticle/Mesoporous 163</li> <li>Metal Nanoparticle/Mesoporous 5164</li> <li>Metal Nanoparticle/Mesoporous 5163</li> <li>Metal Nanoparticle/Mesoporous 5164</li> <li>Summary and Future Challenge 163</li> <li>High-Precision Tools and Measurements 164</li> <li>Carbon Maeda, Yu Harabuchi, and Kenichiro Saita</li> <li>Introduction 173</li> <li>Methodology 174</li> <li>Multicomponent Algorithm (MC-AFIR) 175</li> <li>Single-Component Algorithm (MC-AFIR) 175</li> <li>Single-Component Algorithm (MC-AFIR) 176</li> <li>Search for Potential Crossing Points 177</li> <li>Results and Discussion 178</li> <li>Aldol Reaction 179</li> <li>Claisen Rearrangement 180</li> <li>Co-catalyzed Hydroformylation 181</li> <li>Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184</li> <li>Base-Mediated Boryl</li></ul>	71	Caparal Introduction 127
<ul> <li>3. Solution Flasma 135</li> <li>Materials Synthesis by Solution Plasma 139</li> <li>7.3.1 Noble Metal Nanoparticles 141</li> <li>7.3.2 Non-noble Metal Nanoparticles 144</li> <li>7.3.3 Bimetallic and Alloy Nanoparticles 145</li> <li>7.3.4 Metal Oxide 147</li> <li>7.3.5 Metal Carbide, Boride, and Sulfide 150</li> <li>7.3.6 Carbon Materials 152</li> <li>7.3.7 Mesoporous Silica 158</li> <li>7.3.8 Low Molecular Weight Biopolymer 158</li> <li>7.3.9 Composite Materials 160</li> <li>7.3.9.1 Noble Metal Nanoparticle/Carbon Composite 161</li> <li>7.3.9.2 Metal Oxide/Carbon Composite 161</li> <li>7.3.9.3 Metal Nanoparticle/Metal Oxide Composite 161</li> <li>7.3.9.4 Metal Nanoparticle/Metal Oxide Composite 163</li> <li>7.3.9.4 Metal Nanoparticle/Metal Oxide Composite 163</li> <li>7.3.9.5 Metal Nanoparticle/Metal Oxide Composite 163</li> <li>7.4.5 Summary and Future Challenge 163</li> <li>7.4.1 Highly Controllable Synthesis of Materials 163</li> <li>7.4.2 High-Precision Tools and Measurements 164</li> <li>7.4.3 Computational Simulation 165</li> <li>7.4.4 Large-Scale Synthesis 165 References 166</li> </ul> 8 Global Reaction Route Mapping Strategy: A Tool for Finding New Chemistry in Computers 173 Satoshi Maeda, Yu Harabuchi, and Kenichiro Saita 8.1 Introduction 173 8.2 Methodology 174 8.2.1 Artificial Force Induced Reaction Method 174 8.2.2 Multicomponent Algorithm (MC-AFIR) 175 8.2.3 Single-Component Algorithm (SC-AFIR) 176 8.3.1 Aldol Reaction 178 8.3.2 Passerini Reaction 179 8.3.3 Claisen Rearrangement 180 8.3.4 Co-catalyzed Hydroformylation 181 8.3.5 Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184 8.3.7 Search for Cluster Structures by AFIR 187	7.1	Solution Diagma 129
<ul> <li>7.3.1 Noble Metal Nanoparticles 141</li> <li>7.3.2 Non-noble Metal Nanoparticles 144</li> <li>7.3.3 Bimetallic and Alloy Nanoparticles 145</li> <li>7.3.4 Metal Oxide 147</li> <li>7.3.5 Metal Carbide, Boride, and Sulfide 150</li> <li>7.3.6 Carbon Materials 152</li> <li>7.3.7 Mesoporous Silica 158</li> <li>7.3.8 Low Molecular Weight Biopolymer 158</li> <li>7.3.9 Composite Materials 160</li> <li>7.3.9.1 Noble Metal Nanoparticle/Carbon Composite 160</li> <li>7.3.9.2 Metal Oxide/Carbon Composite 161</li> <li>7.3.9.3 Metal Nanoparticle/Metal Oxide Composite 161</li> <li>7.3.9.4 Metal Nanoparticle/Metal Oxide Composite 161</li> <li>7.3.9.5 Metal Nanoparticle/Metal Oxide Composite 163</li> <li>7.4 Metal Nanoparticle/Biopolymer Composite 163</li> <li>7.4 Summary and Future Challenge 163</li> <li>7.4.1 Highly Controllable Synthesis of Materials 163</li> <li>7.4.2 High-Precision Tools and Measurements 164</li> <li>7.4.3 Computational Simulation 165</li> <li>7.4.4 Large-Scale Synthesis 165 References 166</li> </ul> 8 Global Reaction Route Mapping Strategy: A Tool for Finding New Chemistry in Computers 173 Satoshi Maeda, Yu Harabuchi, and Kenichiro Saita 8.1 Introduction 173 8.2 Methodology 174 8.2.1 Artificial Force Induced Reaction Method 174 8.2.2 Multicomponent Algorithm (MC-AFIR) 176 8.2.3 Single-Component Algorithm (SC-AFIR) 176 8.3.2 Passerini Reaction 178 8.3.1 Aldol Reaction 178 8.3.2 Passerini Reaction 179 8.3.3 Claisen Rearrangement 180 8.3.4 Co-catalyzed Hydroformylation 181 8.3.5 Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184 8.3.7 Search for Cluster Structures by AFIR 187	7.2	Matariala Synthesia by Colution Dlasma 120
<ul> <li>7.3.1 None Nictal Nanoparticles 141</li> <li>7.3.2 Non-noble Metal Nanoparticles 144</li> <li>7.3.3 Bimetallic and Alloy Nanoparticles 145</li> <li>7.3.4 Metal Oxide 147</li> <li>7.3.5 Metal Carbide, Boride, and Sulfide 150</li> <li>7.3.6 Carbon Materials 152</li> <li>7.3.7 Mesoporous Silica 158</li> <li>7.3.9 Composite Materials 160</li> <li>7.3.9.1 Noble Metal Nanoparticle/Carbon Composite 160</li> <li>7.3.9.2 Metal Oxide/Carbon Composite 161</li> <li>7.3.9.3 Metal Nanoparticle/Metal Oxide Composite 161</li> <li>7.3.9.3 Metal Nanoparticle/Metal Oxide Composite 161</li> <li>7.3.9.4 Metal Nanoparticle/Mesoporous Silica Composite 161</li> <li>7.3.9.5 Metal Nanoparticle/Biopolymer Composite 163</li> <li>7.3.9 Metal Nanoparticle/Biopolymer Composite 163</li> <li>7.3.9 Metal Nanoparticle/Biopolymer Composite 163</li> <li>7.3.9 Metal Nanoparticle/Biopolymer Composite 163</li> <li>7.4 Summary and Future Challenge 163</li> <li>7.4 Summary and Future Challenge 163</li> <li>7.4 High-Precision Tools and Measurements 164</li> <li>7.4.2 High-Precision Tools and Measurements 164</li> <li>7.4.4 Large-Scale Synthesis 165 References 166</li> </ul> 8 Global Reaction Route Mapping Strategy: A Tool for Finding New Chemistry in Computers 173 Satoshi Maeda, Yu Harabuchi, and Kenichiro Saita 8.1 Introduction 173 8.2 Methodology 174 8.2.1 Artificial Force Induced Reaction Method 174 8.2.2 Multicomponent Algorithm (MC-AFIR) 175 8.2.3 Single-Component Algorithm (SC-AFIR) 176 8.3.1 Aldol Reaction 178 8.3.2 Passerini Reaction 179 8.3.3 Claisen Rearrangement 180 8.3.4 Co-catalyzed Hydroformylation 181 8.3.5 Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184 8.3.7 Search for Cluster Structures by AFIR 187	7.5 7.2.1	Natellals Sylicitesis by Solucion Plasma 139
<ul> <li>7.3.2 Non-noble Metal Nanoparticles 144</li> <li>7.3.3 Bimetallic and Alloy Nanoparticles 145</li> <li>7.3.4 Metal Oxide 147</li> <li>7.3.5 Metal Carbide, Boride, and Sulfide 150</li> <li>7.3.6 Carbon Materials 152</li> <li>7.3.7 Mesoporous Silica 158</li> <li>7.3.8 Low Molecular Weight Biopolymer 158</li> <li>7.3.9 Composite Materials 160</li> <li>7.3.9.1 Noble Metal Nanoparticle/Carbon Composite 160</li> <li>7.3.9.2 Metal Oxide/Carbon Composite 161</li> <li>7.3.9.3 Metal Nanoparticle/Metal Oxide Composite 161</li> <li>7.3.9.3 Metal Nanoparticle/Mesoporous Silica Composite 161</li> <li>7.3.9.4 Metal Nanoparticle/Biopolymer Composite 163</li> <li>7.3.9.6 Polymer/Carbon Composite 163</li> <li>7.4 Summary and Future Challenge 163</li> <li>7.4 Summary and Future Challenge 163</li> <li>7.4.1 Highly Controllable Synthesis of Materials 163</li> <li>7.4.2 High-Precision Tools and Measurements 164</li> <li>7.4.3 Computational Simulation 165</li> <li>7.4.4 Large-Scale Synthesis 165 References 166</li> </ul> 8 Global Reaction Route Mapping Strategy: A Tool for Finding New Chemistry in Computers 173 Satoshi Maeda, Yu Harabuchi, and Kenichiro Saita 8.1 Introduction 173 8.2 Methodology 174 8.2.1 Artificial Force Induced Reaction Method 174 8.2.2 Multicomponent Algorithm (MC-AFIR) 175 8.2.3 Single-Component Algorithm (SC-AFIR) 176 8.3.1 Aldol Reaction 178 8.3.2 Passerini Reaction 178 8.3.2 Passerini Reaction 179 8.3.3 Claisen Rearrangement 180 8.3.4 Co-catalyzed Hydroformylation 181 8.3.5 Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184 8.3.7 Search for Cluster Structures by AFIR 187	7.5.1	Noble Metal Nanoparticles 141
<ul> <li>7.3.5 Binteratic and Andy Nanoparticles 143</li> <li>7.3.4 Metal Oxide 147</li> <li>7.3.5 Metal Carbide, Boride, and Sulfide 150</li> <li>7.3.6 Carbon Materials 152</li> <li>7.3.7 Mesoporous Silica 158</li> <li>7.3.8 Low Molecular Weight Biopolymer 158</li> <li>7.3.9 Composite Materials 160</li> <li>7.3.9.1 Noble Metal Nanoparticle/Carbon Composite 161</li> <li>7.3.9.2 Metal Oxide/Carbon Composite 161</li> <li>7.3.9.3 Metal Nanoparticle/Metal Oxide Composite 161</li> <li>7.3.9.4 Metal Nanoparticle/Metal Oxide Composite 161</li> <li>7.3.9.5 Metal Nanoparticle/Metal Oxide Composite 163</li> <li>7.4 Metal Nanoparticle/Biopolymer Composite 163</li> <li>7.4.9 Polymer/Carbon Composite 163</li> <li>7.4.9 High-Precision Tools and Measurements 164</li> <li>7.4.3 Computational Simulation 165</li> <li>7.4.4 Large-Scale Synthesis 165 References 166</li> </ul> 8 Global Reaction Route Mapping Strategy: A Tool for Finding New Chemistry in Computers 173 Satoshi Maeda, Yu Harabuchi, and Kenichiro Saita  1. Introduction 173 8.2 Methodology 174 8.2.1 Artificial Force Induced Reaction Method 174 8.2.2 Multicomponent Algorithm (MC-AFIR) 175 8.3.3 Results and Discussion 178 8.3.1 Aldol Reaction 178 8.3.2 Passerini Reaction 179 8.3.3 Claisen Rearrangement 180 8.3.4 Co-catalyzed Hydroformylation 181 8.3.5 Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184 8.3.7 Search for Cluster Structures by AFIR 187	7.3.2	Non-noble Metal Nanoparticles 144
<ul> <li>7.3.4 Metal Okte 147</li> <li>7.3.5 Metal Carbide, Boride, and Sulfide 150</li> <li>7.3.6 Carbon Materials 152</li> <li>7.3.7 Mesoporous Silica 158</li> <li>7.3.8 Low Molecular Weight Biopolymer 158</li> <li>7.3.9 Composite Materials 160</li> <li>7.3.9.1 Noble Metal Nanoparticle/Carbon Composite 160</li> <li>7.3.9.2 Metal Oxide/Carbon Composite 161</li> <li>7.3.9.3 Metal Nanoparticle/Metal Oxide Composite 161</li> <li>7.3.9.4 Metal Nanoparticle/Metal Oxide Composite 161</li> <li>7.3.9.5 Metal Nanoparticle/Mesoporous Silica Composite 163</li> <li>7.3.9.6 Polymer/Carbon Composite 163</li> <li>7.4 Summary and Future Challenge 163</li> <li>7.4 Summary and Future Challenge 163</li> <li>7.4.1 Highly Controllable Synthesis of Materials 163</li> <li>7.4.2 High-Precision Tools and Measurements 164</li> <li>7.4.3 Computational Simulation 165</li> <li>7.4.4 Large-Scale Synthesis 165 References 166</li> </ul> 8 Global Reaction Route Mapping Strategy: A Tool for Finding New Chemistry in Computers 173 Satoshi Maeda, Yu Harabuchi, and Kenichiro Saita 8.1 Introduction 173 8.2 Methodology 174 8.2.1 Artificial Force Induced Reaction Method 174 8.2.2 Multicomponent Algorithm (MC-AFIR) 175 8.3 Single-Component Algorithm (SC-AFIR) 176 8.2.4 Search for Potential Crossing Points 177 8.3 Results and Discussion 178 8.3.1 Aldol Reaction 178 8.3.2 Passerini Reaction 179 8.3.3 Claisen Rearrangement 180 8.3.4 Co-catalyzed Hydroformylation 181 8.3.5 Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184 8.3.7 Search for Cluster Structures by AFIR 187	7.3.3	Matal Oxida 147
<ul> <li>7.3.6 Metal Carbide, Boride, and Sunde 150</li> <li>7.3.6 Carbon Materials 152</li> <li>7.3.7 Mesoporous Silica 158</li> <li>7.3.9 Composite Materials 160</li> <li>7.3.9.1 Noble Metal Nanoparticle/Carbon Composite 160</li> <li>7.3.9.2 Metal Oxide/Carbon Composite 161</li> <li>7.3.9.3 Metal Nanoparticle/Metal Oxide Composite 161</li> <li>7.3.9.4 Metal Nanoparticle/Metal Oxide Composite 161</li> <li>7.3.9.5 Metal Nanoparticle/Metal Oxide Composite 163</li> <li>7.3.9.6 Polymer/Carbon Composite 163</li> <li>7.3.9.6 Polymer/Carbon Composite 163</li> <li>7.4 Summary and Future Challenge 163</li> <li>7.4.1 Highly Controllable Synthesis of Materials 163</li> <li>7.4.2 High-Precision Tools and Measurements 164</li> <li>7.4.3 Computational Simulation 165</li> <li>7.4.4 Large-Scale Synthesis 165 References 166</li> </ul> 8 Global Reaction Route Mapping Strategy: A Tool for Finding New Chemistry in Computers 173 Satoshi Maeda, Yu Harabuchi, and Kenichiro Saita 8.1 Introduction 173 8.2 Methodology 174 8.2.1 Artificial Force Induced Reaction Method 174 8.2.3 Single-Component Algorithm (MC-AFIR) 175 8.3.3 Claisen Rearrangement 180 8.3.4 Co-catalyzed Hydroformylation 181 8.3.5 Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184 8.3.7 Search for Cluster Structures by AFIR 187	7.3.4	Metal Oxide 147
<ul> <li>7.3.6 Carbon Materials 152</li> <li>7.3.7 Mesoporous Silica 158</li> <li>7.3.8 Low Molecular Weight Biopolymer 158</li> <li>7.3.9 Composite Materials 160</li> <li>7.3.9.1 Noble Metal Nanoparticle/Carbon Composite 161</li> <li>7.3.9.2 Metal Oxide/Carbon Composite 161</li> <li>7.3.9.3 Metal Nanoparticle/Metal Oxide Composite 161</li> <li>7.3.9.4 Metal Nanoparticle/Mesoporous Silica Composite 161</li> <li>7.3.9.5 Metal Nanoparticle/Mesoporous Silica Composite 163</li> <li>7.3.9.6 Polymer/Carbon Composite 163</li> <li>7.4.9 Might Controllable Synthesis of Materials 163</li> <li>7.4.2 High-Precision Tools and Measurements 164</li> <li>7.4.3 Computational Simulation 165</li> <li>7.4.4 Large-Scale Synthesis 165 References 166</li> </ul> 8 Global Reaction Route Mapping Strategy: A Tool for Finding New Chemistry in Computers 173 Satoshi Maeda, Yu Harabuchi, and Kenichiro Saita 8.1 Introduction 173 8.2 Methodology 174 8.2.1 Artificial Force Induced Reaction Method 174 8.2.2 Multicomponent Algorithm (MC-AFIR) 175 8.2.3 Single-Component Algorithm (SC-AFIR) 176 8.3.1 Aldol Reaction 178 8.3.1 Aldol Reaction 178 8.3.2 Passerini Reaction 179 8.3.3 Claisen Rearrangement 180 8.3.4 Co-catalyzed Mukaiyama Aldol Reaction 184 8.3.5 Earch for Cluster Structures by AFIR 187	7.3.5	Carbon Materials 152
<ul> <li>7.3.7 Mesoporous Slica 138</li> <li>7.3.8 Low Molecular Weight Biopolymer 158</li> <li>7.3.9 Composite Materials 160</li> <li>7.3.9.1 Noble Metal Nanoparticle/Carbon Composite 161</li> <li>7.3.9.2 Metal Oxide/Carbon Composite 161</li> <li>7.3.9.3 Metal Nanoparticle/Metal Oxide Composite 161</li> <li>7.3.9.4 Metal Nanoparticle/Mesoporous Silica Composite 161</li> <li>7.3.9.5 Metal Nanoparticle/Biopolymer Composite 163</li> <li>7.4 Summary and Future Challenge 163</li> <li>7.4 Summary and Future Challenge 163</li> <li>7.4.1 Highly Controllable Synthesis of Materials 163</li> <li>7.4.2 High-Precision Tools and Measurements 164</li> <li>7.4.3 Computational Simulation 165</li> <li>7.4.4 Large-Scale Synthesis 165 References 166</li> <li>8 Global Reaction Route Mapping Strategy: A Tool for Finding New Chemistry in Computers 173 Satoshi Maeda, Yu Harabuchi, and Kenichiro Saita</li> <li>8.1 Introduction 173</li> <li>8.2 Methodology 174</li> <li>8.2.1 Artificial Force Induced Reaction Method 174</li> <li>8.2.2 Multicomponent Algorithm (MC-AFIR) 175</li> <li>8.2.3 Single-Component Algorithm (SC-AFIR) 176</li> <li>8.3.1 Aldol Reaction 178</li> <li>8.3.1 Aldol Reaction 178</li> <li>8.3.2 Passerini Reaction 179</li> <li>8.3.3 Claisen Rearrangement 180</li> <li>8.4 Co-catalyzed Hydroformylation 181</li> <li>8.3.5 Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184</li> <li>8.3.6 Base-Mediated Borylation with a Silylborane 184</li> </ul>	7.3.6	Carbon Materials 152
<ul> <li>7.3.8 Low Molecular Weight Biopolymer 158</li> <li>7.3.9 Composite Materials 160</li> <li>7.3.9.1 Noble Metal Nanoparticle/Carbon Composite 161</li> <li>7.3.9.2 Metal Oxide/Carbon Composite 161</li> <li>7.3.9.3 Metal Nanoparticle/Metal Oxide Composite 161</li> <li>7.3.9.4 Metal Nanoparticle/Metal Oxide Composite 163</li> <li>7.3.9.5 Metal Nanoparticle/Biopolymer Composite 163</li> <li>7.3.9.6 Polymer/Carbon Composite 163</li> <li>7.4 Summary and Future Challenge 163</li> <li>7.4.1 Highly Controllable Synthesis of Materials 163</li> <li>7.4.2 High-Precision Tools and Measurements 164</li> <li>7.4.3 Computational Simulation 165</li> <li>7.4.4 Large-Scale Synthesis 165 References 166</li> <li>8 Global Reaction Route Mapping Strategy: A Tool for Finding New Chemistry in Computers 173 Satoshi Maeda, Yu Harabuchi, and Kenichiro Saita</li> <li>8.1 Introduction 173</li> <li>8.2 Methodology 174</li> <li>8.2.1 Artificial Force Induced Reaction Method 174</li> <li>8.2.2 Multicomponent Algorithm (MC-AFIR) 175</li> <li>8.2.3 Single-Component Algorithm (SC-AFIR) 176</li> <li>8.4 Search for Potential Crossing Points 177</li> <li>8.3 Results and Discussion 178</li> <li>8.3.1 Aldol Reaction 179</li> <li>8.3.2 Passerini Reaction 179</li> <li>8.3.3 Claisen Rearrangement 180</li> <li>8.4 Co-catalyzed Hydroformylation 181</li> <li>8.3.5 Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184</li> <li>8.3.6 Base-Mediated Borylation with a Silylborane 184</li> <li>8.3.7 Search for Cluster Structures by AFIR 187</li> </ul>	7.3.7	Mesoporous Silica 158
<ul> <li>7.3.9 Composite Materials 160</li> <li>7.3.9.1 Noble Metal Nanoparticle/Carbon Composite 161</li> <li>7.3.9.2 Metal Oxide/Carbon Composite 161</li> <li>7.3.9.3 Metal Nanoparticle/Mesoporous Silica Composite 161</li> <li>7.3.9.4 Metal Nanoparticle/Mesoporous Silica Composite 163</li> <li>7.3.9.5 Metal Nanoparticle/Biopolymer Composite 163</li> <li>7.3.9.6 Polymer/Carbon Composite 163</li> <li>7.4 Summary and Future Challenge 163</li> <li>7.4 Summary and Future Challenge 163</li> <li>7.4.1 Highly Controllable Synthesis of Materials 163</li> <li>7.4.2 High-Precision Tools and Measurements 164</li> <li>7.4.3 Computational Simulation 165</li> <li>7.4.4 Large-Scale Synthesis 165 References 166</li> <li>8 Global Reaction Route Mapping Strategy: A Tool for Finding New Chemistry in Computers 173 Satoshi Maeda, Yu Harabuchi, and Kenichiro Saita</li> <li>8.1 Introduction 173</li> <li>8.2 Methodology 174</li> <li>8.2.1 Artificial Force Induced Reaction Method 174</li> <li>8.2.2 Multicomponent Algorithm (MC-AFIR) 175</li> <li>8.2.3 Single-Component Algorithm (SC-AFIR) 176</li> <li>8.2.4 Search for Potential Crossing Points 177</li> <li>8.3 Results and Discussion 178</li> <li>8.3.1 Aldol Reaction 179</li> <li>8.3.2 Passerini Reaction 179</li> <li>8.3.3 Claisen Rearrangement 180</li> <li>8.3.4 Co-catalyzed Hydroformylation 181</li> <li>8.3.5 Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184</li> <li>8.3.6 Base-Mediated Borylation with a Silylborane 184</li> <li>8.3.7 Search for Cluster Structures by AFIR 187</li> </ul>	7.3.8	Low Molecular Weight Biopolymer 158
<ul> <li>7.3.9.1 Noble Metal Nanoparticle/Carbon Composite 160</li> <li>7.3.9.2 Metal Oxide/Carbon Composite 161</li> <li>7.3.9.3 Metal Nanoparticle/Metal Oxide Composite 161</li> <li>7.3.9.4 Metal Nanoparticle/Mesoporous Silica Composite 163</li> <li>7.3.9.5 Metal Nanoparticle/Biopolymer Composite 163</li> <li>7.3.9.6 Polymer/Carbon Composite 163</li> <li>7.4.5 Summary and Future Challenge 163</li> <li>7.4.1 Highly Controllable Synthesis of Materials 163</li> <li>7.4.2 High-Precision Tools and Measurements 164</li> <li>7.4.3 Computational Simulation 165</li> <li>7.4.4 Large-Scale Synthesis 165 References 166</li> <li>8 Global Reaction Route Mapping Strategy: A Tool for Finding New Chemistry in Computers 173 Satoshi Maeda, Yu Harabuchi, and Kenichiro Saita</li> <li>8.1 Introduction 173</li> <li>8.2 Methodology 174</li> <li>8.2.1 Artificial Force Induced Reaction Method 174</li> <li>8.2.2 Multicomponent Algorithm (MC-AFIR) 175</li> <li>8.2.3 Single-Component Algorithm (SC-AFIR) 176</li> <li>8.2.4 Search for Potential Crossing Points 177</li> <li>8.3 Results and Discussion 178</li> <li>8.3.1 Aldol Reaction 179</li> <li>8.3.2 Passerini Reaction 179</li> <li>8.3.3 Claisen Rearrangement 180</li> <li>8.3.4 Co-catalyzed Hydroformylation 181</li> <li>8.3.5 Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184</li> <li>8.3.6 Base-Mediated Borylation with a Silylborane 184</li> </ul>	7.3.9	Composite Materials 160
<ul> <li>7.3.9.2 Metal Oxide/Carbon Composite 161</li> <li>7.3.9.3 Metal Nanoparticle/Metal Oxide Composite 161</li> <li>7.3.9.4 Metal Nanoparticle/Mesoporous Silica Composite 163</li> <li>7.3.9.5 Metal Nanoparticle/Biopolymer Composite 163</li> <li>7.3.9.6 Polymer/Carbon Composite 163</li> <li>7.4 Summary and Future Challenge 163</li> <li>7.4.1 Highly Controllable Synthesis of Materials 163</li> <li>7.4.2 High-Precision Tools and Measurements 164</li> <li>7.4.3 Computational Simulation 165</li> <li>7.4.4 Large-Scale Synthesis 165 References 166</li> <li>8 Global Reaction Route Mapping Strategy: A Tool for Finding New Chemistry in Computers 173 Satoshi Maeda, Yu Harabuchi, and Kenichiro Saita</li> <li>8.1 Introduction 173</li> <li>8.2 Methodology 174</li> <li>8.2.1 Artificial Force Induced Reaction Method 174</li> <li>8.2.2 Multicomponent Algorithm (MC-AFIR) 175</li> <li>8.2.3 Single-Component Algorithm (SC-AFIR) 176</li> <li>8.2.4 Search for Potential Crossing Points 177</li> <li>8.3 Results and Discussion 178</li> <li>8.3.1 Aldol Reaction 178</li> <li>8.3.2 Passerini Reaction 179</li> <li>8.3.3 Claisen Rearrangement 180</li> <li>8.3.4 Co-catalyzed Hydroformylation 181</li> <li>8.3.5 Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184</li> <li>8.3.6 Base-Mediated Borylation with a Silylborane 184</li> <li>8.3.7 Search for Cluster Structures by AFIR 187</li> </ul>	7.3.9.1	Noble Metal Nanoparticle/Carbon Composite 160
<ul> <li>7.3.9.3 Metal Nanoparticle/Metal Oxide Composite 161</li> <li>7.3.9.4 Metal Nanoparticle/Mesoporous Silica Composite 163</li> <li>7.3.9.5 Metal Nanoparticle/Biopolymer Composite 163</li> <li>7.3.9.6 Polymer/Carbon Composite 163</li> <li>7.4 Summary and Future Challenge 163</li> <li>7.4.1 Highly Controllable Synthesis of Materials 163</li> <li>7.4.2 High-Precision Tools and Measurements 164</li> <li>7.4.3 Computational Simulation 165</li> <li>7.4.4 Large-Scale Synthesis 165 References 166</li> <li>8 Global Reaction Route Mapping Strategy: A Tool for Finding New Chemistry in Computers 173 Satoshi Maeda, Yu Harabuchi, and Kenichiro Saita</li> <li>8.1 Introduction 173</li> <li>8.2 Methodology 174</li> <li>8.2.1 Artificial Force Induced Reaction Method 174</li> <li>8.2.3 Single-Component Algorithm (MC-AFIR) 175</li> <li>8.2.3 Single-Component Algorithm (SC-AFIR) 176</li> <li>8.2.4 Search for Potential Crossing Points 177</li> <li>8.3 Results and Discussion 178</li> <li>8.3.2 Passerini Reaction 179</li> <li>8.3.3 Claisen Rearrangement 180</li> <li>8.3.4 Co-catalyzed Hydroformylation 181</li> <li>8.3.5 Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184</li> <li>8.3.7 Search for Cluster Structures by AFIR 187</li> </ul>	7.3.9.2	Metal Oxide/Carbon Composite 161
<ul> <li>7.3.9.4 Metal Nanoparticle/Mesoporous Silica Composite 161</li> <li>7.3.9.5 Metal Nanoparticle/Biopolymer Composite 163</li> <li>7.4 Summary and Future Challenge 163</li> <li>7.4.1 Highly Controllable Synthesis of Materials 163</li> <li>7.4.2 High-Precision Tools and Measurements 164</li> <li>7.4.3 Computational Simulation 165</li> <li>7.4.4 Large-Scale Synthesis 165 References 166</li> <li>8 Global Reaction Route Mapping Strategy: A Tool for Finding New Chemistry in Computers 173 Satoshi Maeda, Yu Harabuchi, and Kenichiro Saita</li> <li>8.1 Introduction 173</li> <li>8.2 Methodology 174</li> <li>8.2.1 Artificial Force Induced Reaction Method 174</li> <li>8.2.2 Multicomponent Algorithm (MC-AFIR) 175</li> <li>8.2.3 Single-Component Algorithm (SC-AFIR) 176</li> <li>8.2.4 Search for Potential Crossing Points 177</li> <li>8.3 Results and Discussion 178</li> <li>8.3.1 Aldol Reaction 179</li> <li>8.3.2 Passerini Reaction 179</li> <li>8.3.4 Co-catalyzed Hydroformylation 181</li> <li>8.3.5 Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184</li> <li>8.3.6 Base-Mediated Borylation with a Silylborane 184</li> <li>8.3.7 Search for Cluster Structures by AFIR 187</li> </ul>	7.3.9.3	Metal Nanoparticle/Metal Oxide Composite 161
<ul> <li>7.3.9.5 Metal Nanoparticle/Biopolymer Composite 163</li> <li>7.3.9.6 Polymer/Carbon Composite 163</li> <li>7.4 Summary and Future Challenge 163</li> <li>7.4.1 Highly Controllable Synthesis of Materials 163</li> <li>7.4.2 High-Precision Tools and Measurements 164</li> <li>7.4.3 Computational Simulation 165</li> <li>7.4.4 Large-Scale Synthesis 165 References 166</li> <li>8 Global Reaction Route Mapping Strategy: A Tool for Finding New Chemistry in Computers 173 Satoshi Maeda, Yu Harabuchi, and Kenichiro Saita</li> <li>8.1 Introduction 173</li> <li>8.2 Methodology 174</li> <li>8.2.1 Artificial Force Induced Reaction Method 174</li> <li>8.2.2 Multicomponent Algorithm (MC-AFIR) 175</li> <li>8.2.3 Single-Component Algorithm (SC-AFIR) 176</li> <li>8.2.4 Search for Potential Crossing Points 177</li> <li>8.3 Results and Discussion 178</li> <li>8.3.1 Aldol Reaction 179</li> <li>8.3.2 Passerini Reaction 179</li> <li>8.3.4 Co-catalyzed Hydroformylation 181</li> <li>8.3.5 Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184</li> <li>8.3.6 Base-Mediated Borylation with a Silylborane 184</li> <li>8.3.7 Search for Cluster Structures by AFIR 187</li> </ul>	7.3.9.4	Metal Nanoparticle/Mesoporous Silica Composite 161
<ul> <li>7.3.9.6 Polymer/Carbon Composite 163</li> <li>7.4 Summary and Future Challenge 163</li> <li>7.4.1 Highly Controllable Synthesis of Materials 163</li> <li>7.4.2 High-Precision Tools and Measurements 164</li> <li>7.4.3 Computational Simulation 165</li> <li>7.4.4 Large-Scale Synthesis 165 References 166</li> <li>8 Global Reaction Route Mapping Strategy: A Tool for Finding New Chemistry in Computers 173 Satoshi Maeda, Yu Harabuchi, and Kenichiro Saita</li> <li>8.1 Introduction 173</li> <li>8.2 Methodology 174</li> <li>8.2.1 Artificial Force Induced Reaction Method 174</li> <li>8.2.3 Single-Component Algorithm (MC-AFIR) 175</li> <li>8.2.3 Single-Component Algorithm (SC-AFIR) 176</li> <li>8.2.4 Search for Potential Crossing Points 177</li> <li>8.3 Results and Discussion 178</li> <li>8.3.1 Aldol Reaction 179</li> <li>8.3.2 Passerini Reaction 179</li> <li>8.3.3 Claisen Rearrangement 180</li> <li>8.3.4 Co-catalyzed Hydroformylation 181</li> <li>8.3.5 Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184</li> <li>8.3.6 Base-Mediated Borylation with a Silylborane 184</li> <li>8.3.7 Search for Cluster Structures by AFIR 187</li> </ul>	7.3.9.5	Metal Nanoparticle/Biopolymer Composite 163
<ul> <li>7.4 Summary and Future Challenge 163</li> <li>7.4.1 Highly Controllable Synthesis of Materials 163</li> <li>7.4.2 High-Precision Tools and Measurements 164</li> <li>7.4.3 Computational Simulation 165</li> <li>7.4.4 Large-Scale Synthesis 165 References 166</li> <li>8 Global Reaction Route Mapping Strategy: A Tool for Finding New Chemistry in Computers 173 Satoshi Maeda, Yu Harabuchi, and Kenichiro Saita</li> <li>8.1 Introduction 173</li> <li>8.2 Methodology 174</li> <li>8.2.1 Artificial Force Induced Reaction Method 174</li> <li>8.2.2 Multicomponent Algorithm (MC-AFIR) 175</li> <li>8.2.3 Single-Component Algorithm (SC-AFIR) 176</li> <li>8.2.4 Search for Potential Crossing Points 177</li> <li>8.3 Results and Discussion 178</li> <li>8.3.1 Aldol Reaction 179</li> <li>8.3.2 Passerini Reaction 179</li> <li>8.3.4 Co-catalyzed Hydroformylation 181</li> <li>8.3.5 Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184</li> <li>8.3.6 Base-Mediated Borylation with a Silylborane 184</li> <li>8.3.7 Search for Cluster Structures by AFIR 187</li> </ul>	7.3.9.6	Polymer/Carbon Composite 163
<ul> <li>7.4.1 Highly Controllable Synthesis of Materials 163</li> <li>7.4.2 High-Precision Tools and Measurements 164</li> <li>7.4.3 Computational Simulation 165</li> <li>7.4.4 Large-Scale Synthesis 165 References 166</li> <li>8 Global Reaction Route Mapping Strategy: A Tool for Finding New Chemistry in Computers 173 Satoshi Maeda, Yu Harabuchi, and Kenichiro Saita</li> <li>8.1 Introduction 173</li> <li>8.2 Methodology 174</li> <li>8.2.1 Artificial Force Induced Reaction Method 174</li> <li>8.2.2 Multicomponent Algorithm (MC-AFIR) 175</li> <li>8.2.3 Single-Component Algorithm (SC-AFIR) 176</li> <li>8.2.4 Search for Potential Crossing Points 177</li> <li>8.3 Results and Discussion 178</li> <li>8.3.1 Aldol Reaction 179</li> <li>8.3.2 Passerini Reaction 179</li> <li>8.3.4 Co-catalyzed Hydroformylation 181</li> <li>8.3.5 Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184</li> <li>8.3.6 Base-Mediated Borylation with a Silylborane 184</li> <li>8.3.7 Search for Cluster Structures by AFIR 187</li> </ul>	7.4	Summary and Future Challenge 163
<ul> <li>7.4.2 High-Precision Tools and Measurements 164</li> <li>7.4.3 Computational Simulation 165</li> <li>7.4.4 Large-Scale Synthesis 165 References 166</li> <li>8 Global Reaction Route Mapping Strategy: A Tool for Finding New Chemistry in Computers 173 Satoshi Maeda, Yu Harabuchi, and Kenichiro Saita</li> <li>8.1 Introduction 173</li> <li>8.2 Methodology 174</li> <li>8.2.1 Artificial Force Induced Reaction Method 174</li> <li>8.2.2 Multicomponent Algorithm (MC-AFIR) 175</li> <li>8.2.3 Single-Component Algorithm (SC-AFIR) 176</li> <li>8.2.4 Search for Potential Crossing Points 177</li> <li>8.3 Results and Discussion 178</li> <li>8.3.1 Aldol Reaction 179</li> <li>8.3.2 Passerini Reaction 179</li> <li>8.3.4 Co-catalyzed Hydroformylation 181</li> <li>8.3.5 Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184</li> <li>8.3.6 Base-Mediated Borylation with a Silylborane 184</li> <li>8.3.7 Search for Cluster Structures by AFIR 187</li> </ul>	7.4.1	Highly Controllable Synthesis of Materials 163
<ul> <li>7.4.3 Computational Simulation 165</li> <li>7.4.4 Large-Scale Synthesis 165 References 166</li> <li>8 Global Reaction Route Mapping Strategy: A Tool for Finding New Chemistry in Computers 173 Satoshi Maeda, Yu Harabuchi, and Kenichiro Saita</li> <li>8.1 Introduction 173</li> <li>8.2 Methodology 174</li> <li>8.2.1 Artificial Force Induced Reaction Method 174</li> <li>8.2.2 Multicomponent Algorithm (MC-AFIR) 175</li> <li>8.2.3 Single-Component Algorithm (SC-AFIR) 176</li> <li>8.2.4 Search for Potential Crossing Points 177</li> <li>8.3 Results and Discussion 178</li> <li>8.3.1 Aldol Reaction 179</li> <li>8.3.2 Passerini Reaction 179</li> <li>8.3.3 Claisen Rearrangement 180</li> <li>8.3.4 Co-catalyzed Hydroformylation 181</li> <li>8.3.5 Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184</li> <li>8.3.6 Base-Mediated Borylation with a Silylborane 184</li> <li>8.3.7 Search for Cluster Structures by AFIR 187</li> </ul>	7.4.2	High-Precision Tools and Measurements 164
<ul> <li>7.4.4 Large-Scale Synthesis 165 References 166</li> <li>8 Global Reaction Route Mapping Strategy: A Tool for Finding New Chemistry in Computers 173 Satoshi Maeda, Yu Harabuchi, and Kenichiro Saita</li> <li>8.1 Introduction 173</li> <li>8.2 Methodology 174</li> <li>8.2.1 Artificial Force Induced Reaction Method 174</li> <li>8.2.2 Multicomponent Algorithm (MC-AFIR) 175</li> <li>8.2.3 Single-Component Algorithm (SC-AFIR) 176</li> <li>8.2.4 Search for Potential Crossing Points 177</li> <li>8.3 Results and Discussion 178</li> <li>8.3.1 Aldol Reaction 179</li> <li>8.3.2 Passerini Reaction 179</li> <li>8.3.3 Claisen Rearrangement 180</li> <li>8.3.4 Co-catalyzed Hydroformylation 181</li> <li>8.3.5 Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184</li> <li>8.3.6 Base-Mediated Borylation with a Silylborane 184</li> <li>8.3.7 Search for Cluster Structures by AFIR 187</li> </ul>	7.4.3	Computational Simulation 165
References1668Global Reaction Route Mapping Strategy: A Tool for Finding New Chemistry in Computers173 Satoshi Maeda, Yu Harabuchi, and Kenichiro Saita8.1Introduction173 8.2Methodology174 8.2.1Artificial Force Induced Reaction Method174 8.2.2Multicomponent Algorithm (MC-AFIR)175 8.2.3Single-Component Algorithm (SC-AFIR)176 8.2.4Search for Potential Crossing Points177 8.3Results and Discussion178 8.3.1Aldol Reaction179 8.3.3Claisen Rearrangement180 8.3.4Co-catalyzed Hydroformylation181 8.3.5Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction184 8.3.6Base-Mediated Borylation with a Silylborane184 8.3.7Search for Cluster Structures by AFIR	7.4.4	Large-Scale Synthesis 165
<ul> <li>Global Reaction Route Mapping Strategy: A Tool for Finding New Chemistry in Computers 173 Satoshi Maeda, Yu Harabuchi, and Kenichiro Saita</li> <li>Introduction 173</li> <li>Methodology 174</li> <li>Methodology 174</li> <li>Artificial Force Induced Reaction Method 174</li> <li>Artificial Force Induced Reaction Method 174</li> <li>Subscript Single-Component Algorithm (MC-AFIR) 175</li> <li>Single-Component Algorithm (SC-AFIR) 176</li> <li>Search for Potential Crossing Points 177</li> <li>Results and Discussion 178</li> <li>Aldol Reaction 179</li> <li>Claisen Rearrangement 180</li> <li>Co-catalyzed Hydroformylation 181</li> <li>Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184</li> <li>Base-Mediated Borylation with a Silylborane 184</li> <li>Search for Cluster Structures by AFIR 187</li> </ul>		References 166
New Chemistry in Computers173Satoshi Maeda, Yu Harabuchi, and Kenichiro Saita8.1Introduction1738.2Methodology1748.2.1Artificial Force Induced Reaction Method1748.2.2Multicomponent Algorithm (MC-AFIR)1758.2.3Single-Component Algorithm (SC-AFIR)1768.2.4Search for Potential Crossing Points1778.3Results and Discussion1788.3.1Aldol Reaction1798.3.3Claisen Rearrangement1808.3.4Co-catalyzed Hydroformylation1818.3.5Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction1848.3.6Base-Mediated Borylation with a Silylborane1848.3.7Search for Cluster Structures by AFIR187	8	Global Reaction Route Mapping Strategy: A Tool for Finding
Satoshi Maeda, Yu Harabuchi, and Kenichiro Saita8.1Introduction 1738.2Methodology 1748.2.1Artificial Force Induced Reaction Method 1748.2.2Multicomponent Algorithm (MC-AFIR) 1758.2.3Single-Component Algorithm (SC-AFIR) 1768.2.4Search for Potential Crossing Points 1778.3Results and Discussion 1788.3.1Aldol Reaction 1798.3.2Passerini Reaction 1798.3.3Claisen Rearrangement 1808.3.4Co-catalyzed Hydroformylation 1818.3.5Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 1848.3.6Base-Mediated Borylation with a Silylborane 1848.3.7Search for Cluster Structures by AFIR 187		New Chemistry in Computers 173
<ul> <li>8.1 Introduction 173</li> <li>8.2 Methodology 174</li> <li>8.2.1 Artificial Force Induced Reaction Method 174</li> <li>8.2.2 Multicomponent Algorithm (MC-AFIR) 175</li> <li>8.2.3 Single-Component Algorithm (SC-AFIR) 176</li> <li>8.2.4 Search for Potential Crossing Points 177</li> <li>8.3 Results and Discussion 178</li> <li>8.3.1 Aldol Reaction 178</li> <li>8.3.2 Passerini Reaction 179</li> <li>8.3.3 Claisen Rearrangement 180</li> <li>8.3.4 Co-catalyzed Hydroformylation 181</li> <li>8.3.5 Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184</li> <li>8.3.6 Base-Mediated Borylation with a Silylborane 184</li> <li>8.3.7 Search for Cluster Structures by AFIR 187</li> </ul>		Satoshi Maeda, Yu Harabuchi, and Kenichiro Saita
<ul> <li>8.2 Methodology 174</li> <li>8.2.1 Artificial Force Induced Reaction Method 174</li> <li>8.2.2 Multicomponent Algorithm (MC-AFIR) 175</li> <li>8.2.3 Single-Component Algorithm (SC-AFIR) 176</li> <li>8.2.4 Search for Potential Crossing Points 177</li> <li>8.3 Results and Discussion 178</li> <li>8.3.1 Aldol Reaction 178</li> <li>8.3.2 Passerini Reaction 179</li> <li>8.3.3 Claisen Rearrangement 180</li> <li>8.3.4 Co-catalyzed Hydroformylation 181</li> <li>8.3.5 Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184</li> <li>8.3.6 Base-Mediated Borylation with a Silylborane 184</li> <li>8.3.7 Search for Cluster Structures by AFIR 187</li> </ul>	8.1	Introduction 173
<ul> <li>8.2.1 Artificial Force Induced Reaction Method 174</li> <li>8.2.2 Multicomponent Algorithm (MC-AFIR) 175</li> <li>8.2.3 Single-Component Algorithm (SC-AFIR) 176</li> <li>8.2.4 Search for Potential Crossing Points 177</li> <li>8.3 Results and Discussion 178</li> <li>8.3.1 Aldol Reaction 178</li> <li>8.3.2 Passerini Reaction 179</li> <li>8.3.3 Claisen Rearrangement 180</li> <li>8.3.4 Co-catalyzed Hydroformylation 181</li> <li>8.3.5 Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184</li> <li>8.3.6 Base-Mediated Borylation with a Silylborane 184</li> <li>8.3.7 Search for Cluster Structures by AFIR 187</li> </ul>	8.2	Methodology 174
<ul> <li>8.2.2 Multicomponent Algorithm (MC-AFIR) 175</li> <li>8.2.3 Single-Component Algorithm (SC-AFIR) 176</li> <li>8.2.4 Search for Potential Crossing Points 177</li> <li>8.3 Results and Discussion 178</li> <li>8.3.1 Aldol Reaction 178</li> <li>8.3.2 Passerini Reaction 179</li> <li>8.3.3 Claisen Rearrangement 180</li> <li>8.3.4 Co-catalyzed Hydroformylation 181</li> <li>8.3.5 Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184</li> <li>8.3.6 Base-Mediated Borylation with a Silylborane 184</li> <li>8.3.7 Search for Cluster Structures by AFIR 187</li> </ul>	8.2.1	Artificial Force Induced Reaction Method 174
<ul> <li>8.2.3 Single-Component Algorithm (SC-AFIR) 176</li> <li>8.2.4 Search for Potential Crossing Points 177</li> <li>8.3 Results and Discussion 178</li> <li>8.3.1 Aldol Reaction 178</li> <li>8.3.2 Passerini Reaction 179</li> <li>8.3.3 Claisen Rearrangement 180</li> <li>8.3.4 Co-catalyzed Hydroformylation 181</li> <li>8.3.5 Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184</li> <li>8.3.6 Base-Mediated Borylation with a Silylborane 184</li> <li>8.3.7 Search for Cluster Structures by AFIR 187</li> </ul>	8.2.2	Multicomponent Algorithm (MC-AFIR) 175
<ul> <li>8.2.4 Search for Potential Crossing Points 177</li> <li>8.3 Results and Discussion 178</li> <li>8.3.1 Aldol Reaction 178</li> <li>8.3.2 Passerini Reaction 179</li> <li>8.3.3 Claisen Rearrangement 180</li> <li>8.3.4 Co-catalyzed Hydroformylation 181</li> <li>8.3.5 Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184</li> <li>8.3.6 Base-Mediated Borylation with a Silylborane 184</li> <li>8.3.7 Search for Cluster Structures by AFIR 187</li> </ul>	8.2.3	Single-Component Algorithm (SC-AFIR) 176
<ul> <li>8.3 Results and Discussion 178</li> <li>8.3.1 Aldol Reaction 178</li> <li>8.3.2 Passerini Reaction 179</li> <li>8.3.3 Claisen Rearrangement 180</li> <li>8.3.4 Co-catalyzed Hydroformylation 181</li> <li>8.3.5 Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184</li> <li>8.3.6 Base-Mediated Borylation with a Silylborane 184</li> <li>8.3.7 Search for Cluster Structures by AFIR 187</li> </ul>	8.2.4	Search for Potential Crossing Points 177
<ul> <li>8.3.1 Aldol Reaction 178</li> <li>8.3.2 Passerini Reaction 179</li> <li>8.3.3 Claisen Rearrangement 180</li> <li>8.3.4 Co-catalyzed Hydroformylation 181</li> <li>8.3.5 Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184</li> <li>8.3.6 Base-Mediated Borylation with a Silylborane 184</li> <li>8.3.7 Search for Cluster Structures by AFIR 187</li> </ul>	8.3	Results and Discussion 178
<ul> <li>8.3.2 Passerini Reaction 179</li> <li>8.3.3 Claisen Rearrangement 180</li> <li>8.3.4 Co-catalyzed Hydroformylation 181</li> <li>8.3.5 Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184</li> <li>8.3.6 Base-Mediated Borylation with a Silylborane 184</li> <li>8.3.7 Search for Cluster Structures by AFIR 187</li> </ul>	8.3.1	Aldol Reaction 178
<ul> <li>8.3.3 Claisen Rearrangement 180</li> <li>8.3.4 Co-catalyzed Hydroformylation 181</li> <li>8.3.5 Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184</li> <li>8.3.6 Base-Mediated Borylation with a Silylborane 184</li> <li>8.3.7 Search for Cluster Structures by AFIR 187</li> </ul>	8.3.2	Passerini Reaction 179
<ul> <li>8.3.4 Co-catalyzed Hydroformylation 181</li> <li>8.3.5 Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184</li> <li>8.3.6 Base-Mediated Borylation with a Silylborane 184</li> <li>8.3.7 Search for Cluster Structures by AFIR 187</li> </ul>	8.3.3	Claisen Rearrangement 180
<ul> <li>8.3.5 Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184</li> <li>8.3.6 Base-Mediated Borylation with a Silylborane 184</li> <li>8.3.7 Search for Cluster Structures by AFIR 187</li> </ul>	8.3.4	Co-catalyzed Hydroformylation 181
<ul><li>8.3.6 Base-Mediated Borylation with a Silylborane 184</li><li>8.3.7 Search for Cluster Structures by AFIR 187</li></ul>	8.3.5	Lanthanide-Ion-Catalyzed Mukaiyama Aldol Reaction 184
8.3.7 Search for Cluster Structures by AFIR <i>187</i>	8.3.6	Base-Mediated Borylation with a Silylborane 184
4	8.3.7	Search for Cluster Structures by AFIR 187
8.3.8 The Paternò–Büchi Reaction <i>188</i>	8.3.8	The Paternò–Büchi Reaction 188

- 8.3.9 Minimum Energy Conical Intersection Structures of 1,3-Butadiene and Benzene *189*
- 8.3.10 Application of SMF/SC-AFIR for Medium-Sized Molecules 189
- 8.3.11 Ultrafast Nonradiative Decay in Organometallic Complex 191
- 8.3.12 Photochemical Ligand Substitution Reactions of *fac*-[Re<sup>I</sup>(bpy)(CO)<sub>3</sub>PR<sub>3</sub>]<sup>+</sup> 192
- 8.4 Concluding Remarks 194 Acknowledgments 194 References 194
- 9 Computational Molecular Technology Toward Macroscopic Chemical Phenomena: Red Moon Methodology and Its Related Applications 201

Masataka Nagaoka, Masayoshi Takayanagi, Norio Takenaka, Yuichi Suzuki, Kentaro Matsumoto, Nobuaki Koga, Sandhya Karakkadparambil Sankaran, Purushotham Uppula, and Yukichi Kitamura

- 9.1 Introduction 201
- 9.2 Methodology 202
- 9.2.1 What Today's Chemists Want and Need to Consider 202
- 9.2.2 Red Moon Methodology A Recent Computational Molecular Technology 205
- 9.2.2.1 Molecular Description of Complex Chemical Reaction Systems 205
- 9.2.2.2 Red Moon Method A Rare Event-Driving Methodology of Necessity (Red Moon) 206
- 9.2.2.3 Algorithmic Procedure of Red Moon Method 208
- 9.2.3 A Set-Up Using Conventional Computational Molecular Technology 209
- 9.2.3.1 Reaction Scheme Quantum Chemistry (QC) and Experiment 209
- 9.2.3.2 Molecular Mechanical (MM) Force Fields 210
- 9.3 Applications 211
- 9.3.1 Ethylene Coordinative Chain Transfer Polymerization Mechanism on (Pyridylamide)Hf(IV) Catalyst 211
- 9.3.1.1 Active Site Opening Mechanism in Ion Pair of (Pyridylamide)Hf(IV) Catalyst: An Associative Mechanism 211
- 9.3.1.2 Ion Pair Structure and Its Molecular Mechanical (MM) Force Fields 211
- 9.3.1.3 Propagation Reaction on the Active Site of (Pyridylamide)Hf(IV) Catalyst 213
- 9.3.2 Propylene Polymerization Reaction Mechanism on C2 Symmetric  $[H_2Si(Ind)_2ZrCH_3]^+$  and  $[H_2Si(Ind)_2ZrCH_3]^+[CH_3B(C_6F_5)_3]^-$  213
- 9.3.2.1 Energetics of Propylene Insertion into Active Catalyst  $H_2Si(Ind)_2ZrCH_3^+$  – Enantioselectivity and Regioselectivity 214
- 9.3.2.2 Reaction Mechanism of cis and trans Approach of Counter Anion  $[CH_3B(C_6F_5)_3]^-$  on the Various Stereoisomers 215
- 9.3.2.3 Toward Propagation Reaction on the Active Site of the Catalyst Ion Pair  $[(CH_3)_2Si(Ind)_2ZrCH_3]^+[CH_3B(C_6F_5)_3]^-$  217
- 9.3.3 Aromatic Polyamide Polymerization 220

xvi Contents

- 9.3.3.1 Microscopic Clarification of the MPD/TMC Mixing Ratios for the Interfacial Polycondensation Reaction Process [20] 220
- Water Permeability and Fidelity of the Membrane Model 224 9.3.3.2
- 9.3.3.3 Characteristics of Red Moon Method and Its Possibility 226
- 9.4 Lithium Ion and Sodium Ion Batteries 226
- 9.4.1 Strong Sensitivity to Small Structural Difference of Electrolyte Molecules on the Solid-Electrolyte Interphase (SEI) Film Formation 228
- 9.4.2 Microscopic Additive Effect on Solid-Electrolyte Interphase (SEI) Film Formation in Sodium Ion Batteries 228
- 9.5 Summary and Conclusions 231 Acknowledgments 232 References 232

#### 10 Multi-timescale Measurements with Energetic Beams for Molecular Technology 235 Masaki Hada and Taiki Hoshino

- 10.1 Introduction 235
- Time-Domain Measurements 236 10.2
- Femtosecond Optical Pump–Probe Studies 236 10.2.1
- 10.2.2 Femtosecond X-ray and Electron Pulse Sources 238
- 10.2.3 Structural Dynamics Revealed by X-ray or Electron Probes 243
- 10.3 Time-Correlation Measurements 248
- Introduction of X-ray Photon Correlation Spectroscopy 248 10.3.1
- Principle of XPCS 249 10.3.2
- 10.3.3 Example 250
- 10.3.4 Particle Diffusion 251
- 10.3.5 Surface Fluctuation of Fluids 252
- 10.3.6 Summary and Perspective 255 References 257
- 11 Single Molecule Magnet for Quantum Information Process' 263

Tadahiro Komeda, Keiichi Katoh, and Masahiro Yamashita

- 11.1 Introduction 263
- 11.2 Synthesis and Magnetic Properties of Double-Decker SMM 265
- 11.3 Device Applications of SMM for Spintronic Operations 269
- Scanning Tunneling Microscopy (STM) and Spectroscopy (STS) 11.4 Phthalocyaninato–Terbium(III) Multiple-Decker Complexes 273
- Film Formation on Metal Substrates 274 11.4.1
- 11.4.2 Bonding Configuration of Pc Molecule 275
- 11.4.3 Molecule Films of Double-Decker Phthalocyaninato-Tb(III) Complexes: Bonding Configuration and Film Structure 276
- 11.4.4 Hetero-ligand Double-Decker Molecule 281
- Triple-Decker Molecule 283 11.4.5
- 11.4.6 Double- and Triple-Decker Pc and Kondo Behavior 286

- 11.4.7 Ligand Effect on the Kondo Behavior 291
- 11.4.8 Molecular Ordering and Kondo Resonance 293
- 11.5 Summary and Future Scope 296 Acknowledgments 298 References 298

#### 12 Molecular Technology for One- and Two-Dimensional Materials on Surfaces 305

Shigeki Kawai and Kazukuni Tahara

- 12.1 General Introduction 305
- 12.1.1 Scanning Tunneling Microscopy 305
- 12.1.2 Atomic Force Microscopy in Ultrahigh Vacuum Environment 306
- 12.1.3 High-Resolution Imaging with a Functionalized Tip Measurement at Low Temperature in Ultrahigh Vacuum Environment *310*
- 12.1.4 Scanning Probe Microscopy at Liquid/Solid Interface 313
- 12.2 On-Surface Chemical Reaction 314
- 12.2.1 General Info About the On-Surface Chemical Reaction 314
- 12.2.2 Ultrahigh Vacuum Environment 314
- 12.2.3 Thermal-Assisted On-Surface Reaction in UHV 318
- 12.2.4 Local Probe-Assisted On-Surface Reaction in UHV 320
- 12.2.5 Chemical Reactions at the Liquid/Solid Interface 325
- 12.2.5.1 Carbon–Carbon Bond Formation Reactions 325
- 12.2.5.2 Dynamic Imine Formation Reactions 329
- 12.2.5.3 Condensation of Boronic Acids 333
- 12.3 Conclusion and Perspective 336 Acknowledgments 336 References 337

Index 343

# Control of Electronic Property of C<sub>60</sub> Fullerene via Polymerization

1

Nobuyuki Aoki

1

Chiba University, Graduate School of Science and Engineering, Department of Materials Science, 1-33 Yayoi, Inage, Chiba 263-8522, Japan

## 1.1 Introduction

#### 1.1.1 History of Polymerization of C<sub>60</sub> Fullerene

Fullerenes, the spherical cage molecules composed of carbon atoms, were discovered by Kuroto and Smalley coworkers in 1985 [1]. After the development of a large-scale synthesis method by Kraetschmer et al. in 1990 [2], they became usable not only in vacuum but also in atmospheric conditions. C<sub>60</sub> is the most popular molecule in the fullerenes composed of 60 carbon atoms as shown in Figure 1.1a. It has semiconductor characteristics having a bandgap. The experimental values have been shown as typically 1.5-1.8 eV for the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gap [3, 4]; however, the value varies within the range of 1.43-2.35. The electrical properties of fullerene are based on the bandgap. It shows n-type semiconductor characteristics; the activation energy is less than half of the bandgap and is close to the half value only at high temperatures. At around room temperature, the activation energy is in the range of 100-200 meV, which relates to activation from the donner-like state within the optical gap [5]. The transport properties are strongly affected also by the orientation state of the crystalline fullerene. On decreasing the temperature from room temperature, the first kink of the conductivity is observed at around 260 K related to the restriction of the orientation angle of rotation of  $C_{60}$  molecules [6]. The second kink at 90 K relates to the glass transition of the orientation angle.

The conductivity drastically falls by several orders of magnitude, mostly becoming insulating due to absorption of oxygen molecules [7]. This is due to the formation of deep level trap sites lying 0.7 eV below the bottom of the conduction band. Therefore, most of the transport measurements of the semiconducting properties are done in vacuum conditions. An inert atmosphere such as argon, nitrogen, or helium also helps maintain the conductivity. If the sample was exposed in air once, heating at 160–180 °C in vacuum is necessary to recover the conductivity by desorbing oxygen from the thin film of fullerene [8].

#### 2 1 Control of Electronic Property of C<sub>60</sub> Fullerene via Polymerization

Crystalline  $C_{60}$  fullerene exhibits face centred cubic (fcc) structure due to van der Waals interaction. Intermolecular interactions change the electrical and optical properties. A possibility of intermolecular coupling was observed first by photo-irradiation using laser light [9]. UV–visible light illumination read the photopolymerization of the  $C_{60}$  molecules in oxygen-free condition since oxygen hinders the reaction by forming photoexcited triplets [10]. Such a process occurs only above 260 K since a random orientation of the rotation is essential for the polymerization process.

Photo-transformation takes place by [2+2] cycloaddition reaction mechanism [11], where faced double molecular bonds are broken and a four-member ring is formed as shown in Figure 1.1a.

Such a dimer structure is called "dumbbell type" polymerization. For the occurrence of the polymerization reaction, the following requirements can be summarized:

- (i) The  $C_{60}$  molecules should be situated close enough to each other (an application of pressure assists this situation).
- (ii) They must be rotating freely.
- (iii) Their double bonds must be faced in parallel.
- (iv) Certain external energy that opens the double bond must be applied (photoexcitation, thermal agitation, plasma, electron beam [EB] absorption, pressure application, etc.).
- (v) A four-atom carbon ring is formed.

After forming the intermolecular bonding, the mean intermolecular length, typically 1.0 nm in fcc structure, shortens to 0.01–0.03 nm. And then, the free rotation of the molecule stops, and solubility in polar organic solvents such as toluene, xylene, hexane, and so on is lost. For the photochemical reaction between  $C_{60}$  molecules, the following reaction scheme is proposed [11]. Although the [2+2] cycloaddition of neutral  $C_{60}$  molecules is thermally forbidden due to the Woodward–Hoffmann rules, this type of reaction is photochemically allowed between an excited and a ground state molecule. The interaction of the singly occupied  $\pi^*$ -orbital of the photoexcited molecule with the unoccupied  $\pi^*$ -orbital of the ground state molecule, as well as the interaction of the singly and doubly occupied  $\pi$ -orbitals gives rise to a symmetrically allowed and energetically favorable transition state. The simplified orbital interactions of two C=C double



**Figure 1.1** Structural model of a  $C_{60}$  fullerene molecule (a) and a fullerene dimer having a dumbbell structure (b).

1.1 Introduction 3



**Figure 1.2** Schematic of the photochemical reaction (a) and energy diagrams of frontier orbital interactions of reactants in [2+2] cycloaddition reactions (b).

bonds are illustrated in Figure 1.2. Such a polymerization process in a solid or a thin film of  $C_{60}$  can also take place by other means: application of high pressure at high temperature, intercalation of alkali metals, plasma treatment, EB irradiation, and so on. If a negative ion reacts with a neutral ground state molecule, the interaction of the singly occupied and the vacant  $\pi^*$ -orbitals results in a lower energy transition state, similarly to the photochemical mechanism.

For the intermolecular bond formation, two types of possibilities are proposed. In one configuration, the two C atoms shared by the two adjacent hexagons in a  $C_{60}$  are covalently bonded to the C atoms that are shared by the two hexagons in the adjacent  $C_{60}$  (66/66 bond); in another, the two C atoms shared by a hexagon and a pentagon in a  $C_{60}$  are bonded to the adjacent  $C_{60}$  (66/65 bond) shown in Figure 1.3b. It is known that the 66/66 bond is more stable thermodynamically than the 66/65 one; therefore, the 66/65 one must be a very rare case [12, 13]. However, existence of a  $C_{60}$  polymer composed of 66/65 bonds (Figure 1.3b) is the only model to explain the metallic property of the polymer having a two-dimensional rhombohedral (rh) structure realized by high temperature and high pressure application [14].

Hence, we can control the electrical properties of  $C_{60}$  fullerene depending on the polymerized structure. In this chapter, after showing the basic electrical properties of a pristine  $C_{60}$  fullerene, various kinds of polymerization regimes and the electrical properties will be introduced.

1 Control of Electronic Property of C<sub>60</sub> Fullerene via Polymerization



Figure 1.3 (a) 66/66 and (b) 66/65 bonding structures.

#### 1.1.2 Electronic Property of Pristine C<sub>60</sub> and n-Type FET Action

The first  $C_{60}$  field effect transistor (FET) was reported by Paloheimo et al. [15] in 1993 and developed by Haddon et al. [16] in 1995. They clarified that  $C_{60}$  FET works as an n-type transistor and exhibits fairly good carrier mobility around  $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . The highest mobility is more than  $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  as reported by Li et al. in 2012 [17]. The properties are severely dependent on the environment. After being exposed in air or oxygen, the conductance suddenly drops and it becomes almost insulating [7]. Therefore, most of the transport experiments are performed in vacuum conditions. The conductance also depends on temperature, so that there might be a large amount of charge trapping states, in other words donor-like states, in the pseudo gap of  $C_{60}$  FET [18]. In general, these states usually come from structural disorders at crystalline defect or grain boundary, as well as from polaronic disorders introduced by guest impurities. The latter would be an effect of oxygen adsorption, by which the conductance decreases drastically. Therefore, transport measurements of a C<sub>60</sub> FET require an oxygen-free environment such as vacuum or inert gas, or covering by a passivation layer [19]. Figure 1.4 shows typical current–voltage (I-V) curve and transfer curves of a  $C_{60}$ thin film FET. The FET structure is fabricated on a SiO<sub>2</sub> layer of heavily doped Si wafer. The electrical contacts are performed by Au. The channel length and width are 5 and 100  $\mu$ m, respectively. The field effect mobility,  $\mu$ , in the low field region can be estimated from the following equation [20]:

$$\mu = \frac{I_{\rm D}L}{C_{\rm ox}W\left\{V_{\rm DS}(V_{\rm GS}-V_{\rm T})-\frac{1}{2}V_{\rm DS}^{2}\right\}}$$

where  $I_{\rm D}$  is the drain current, L is the channel length, W is the channel width,  $C_{\rm OX}$  is the gate capacitance of oxide layer,  $V_{\rm DS}$  is the drain voltage,  $V_{\rm GS}$  is the gate voltage, and  $V_{\rm T}$  is the threshold voltage. Considering the threshold voltage to be 15 V, the mobility is estimated as 0.1 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>.

The temperature dependence of a  $C_{60}$  FET shows nearest neighbor hopping, which depends on  $T^{-1}$  at temperatures lower than room temperature. However, below 100 K, variable range hopping (VRH) has been observed in the conductance of  $C_{60}$  FET [21]. In this transport regime, the conductance drops with decreasing temperature depending on the following relation:

 $\sigma \propto \exp(-T^{-1/4})$ 

1.2 Polymerization of C<sub>60</sub> Fullerene 5



**Figure 1.4** Typical transistor curves of a  $C_{60}$  thin film FET (a). Transfer curve and estimated mobility (b).

This relationship indicates that the transport is three dimensional in the thin film of  $C_{60}$  since the suffix of *T* can be obtained from 1/(d + 1) where *d* is the dimensionality of electron transport of the system. In general, conduction carriers in VRH can transport by hopping among electronic states at Fermi level ( $E_F$ ), which enables us to estimate the density of charge trapping states in the pseudo gap of  $C_{60}$  thin film.

# 1.2 Polymerization of C<sub>60</sub> Fullerene

#### 1.2.1 Photo-irradiation

Photopolymerization of C<sub>60</sub> thin film under visible or UV irradiation was confirmed first by Rao et al. in 1993 [9]. The reaction was confirmed using UV-visible light from a Hg arc lamp or an Ar ion laser having a wavelength of 488 nm on  $C_{60}$  thin films of thickness of several hundred nanometers on a Si substrate. One typical evidence of the photopolymerization is a peak shift of  $A_{g}(2)$ mode in the Raman scattering spectrum, which corresponds to the pentagonal pinch mode of the  $C_{60}$  molecule [22]. The peak occurs at 1469 cm<sup>-1</sup> before the light irradiation and shifts to 1460 cm<sup>-1</sup> after the irradiation. The mechanism of photo-transformation is based on [2+2] cycloaddition reaction [11]. A 1D polymer chain of C<sub>60</sub> molecules having an orthorhombic crystal structure is proposed for this photopolymer. The polymerization reaction occurs within a temperature range between 260 and 400 K without applying pressure. The lower limit is due to the necessity of free rotation of  $\mathrm{C}_{60}$  molecules. On the other hand, the upper limit is restricted by a depolymerization process due to an increase in thermal vibrations. Therefore, the intermolecular bonding is broken by heating to more than 473 K so that the photopolymer reversibly returns to the monomer [23]. The activation energy for the depolymerization process is approximately 1.25 eV [22]. For the photopolymerization, light having photon energy greater than the bandgap energy of the  $C_{60}$  molecules is necessary. Existence of long

#### 6 1 Control of Electronic Property of C<sub>60</sub> Fullerene via Polymerization

chains of more than 20  $C_{60}$  molecules was confirmed by laser desorption mass spectrum from  $C_{60}$  thin film after sufficient UV–visible light irradiation [9]. Figure 1.5a shows typical Raman shift peaks of  $A_g(2)$  mode of a  $C_{60}$  thin film. The peak occurs at 1469 cm<sup>-1</sup> before irradiation; however, it shifts to 1460 cm<sup>-1</sup> after green laser irradiation for 10 minutes. On the other hand, no significant peak shift can be confirmed; Raman peaks of a solid single crystal before and after laser light irradiation are shown in Figure 1.5b. In the case of the thin film, the peak shift occurs very easily even during the irradiation for Raman spectroscopy. In other words, it is very difficult to obtain a Raman peak of the pristine  $C_{60}$  thin film at 1469 cm<sup>-1</sup>. In the case of photopolymerization, it is basically difficult to obtain long chain polymers. The polymer chain is mainly of short-range oligomers such as dimer or tetramers. The  $A_g(2)$  peak position shifts to further lower frequency through progress of the polymerization reaction of  $C_{60}$ . The shoulder at 1453 cm<sup>-1</sup> can be assumed as the peak corresponding to a polymer higher than a dimer (e.g. trimer). Generally, no long-range order can



**Figure 1.5** Typical peak shifts of  $A_g(2)$  mode before (black) and after (gray) laser irradiation of a thin film (a) and a single crystal (b).

be observed in the photopolymer of the thin film unlike in pressure-induced polymerization.

A  $C_{60}$  photopolymer still shows semiconducting electric property [24]. The evolution of gate voltage dependences of a  $C_{60}$  thin film FET with laser light irradiation is shown in Figure 1.6. The FET sample has a  $C_{60}$  thin film of 50 nm thickness and the electric contacts occur underneath the thin film, forming a bottom contact structure. In the case of such an FET, the ON current of the FET decreases with increasing dose of the green laser beam. Consequently, a decrease in the mobility was confirmed. In this sample structure, since a laser beam was irradiated from the top of the thin film, photopolymerization takes place from the surface of the film. Therefore, at the bottom of the film, the molecules must be polymerized partially and then such a disorder affects the decrease of the mobility.

Basically, polymerization by photo-irradiation is never perfect in the bulk region of a C<sub>60</sub> thin film and a solid of a single crystal since the dimerization of two C<sub>60</sub> molecules hinders successive, long-chained, photo-polymerization. However, polymerization at the surface of a thin film shows different behavior. 2D-rhombohedral rinks of C<sub>60</sub> molecules were confirmed on a thin film after irradiation with UV-visible light (photon energy: 2-4 eV, light intensity:  $3-4 \text{ W cm}^{-2}$ ) for 400 hours at room temperature in vacuum [25]. The resistivity was of the order of  $10^3 \Omega$  cm. More recently, we also observed the formation of two-dimensional polymer films synthesized on a  $C_{60}$  thin film after sufficient irradiation with optical vortex (OV) laser light [26]. Figure 1.7 shows the atomic force microscope image of the surface of the irradiated region. A film having a thickness of 1 nm can be confirmed on the grains in a  $C_{60}$  thin film. The coverage on the surface depends on the dose of the laser light. Such a film reminds us of a 2D polymer phase having te- and rh-structures. When we placed two electrodes on the irradiated region after the irradiation, we confirmed no gate voltage dependence of current through the sample, which suggested a metallic property (sufficient amount of carriers exist in a sample without applying a gate voltage). Surprisingly, the current can be confirmed even in air since a  $C_{60}$  thin film becomes insulating immediately after being exposed in air. The mechanism is still under discussion; however, the experimental results suggest that even



**Figure 1.6** Typical effect of photopolymerization on transfer curves of a  $C_{60}$  FET (a). The mobility decreases as well as the ON current incrementing the dose (b).

1 Control of Electronic Property of C<sub>60</sub> Fullerene via Polymerization



Figure 1.7 AFM image of C<sub>60</sub> thin film out of (a) and within (b) the OV irradiated region.



Figure 1.8 Schematic view of OV irradiation on a  $C_{60}$  thin film and the electrical measurement within the irradiated region using Au wires after the irradiation (a). Two terminal transfer curves at different bias voltages (b). No gate voltage dependence was observed.

photo-polymerization may provide a metallic 2D polymer at the surface of thin films after sufficient irradiation (Figure 1.8).

#### 1.2.2 Doping Effect Using Alkali Metal and Superconductivity

Doping into C<sub>60</sub> fullerene molecules is accompanied by 3-D intercalation of alkali, alkali earth, and rare earth metals forming compounds [27]. Owing to the intercalation, electrons can be delivered into the unoccupied band whose lattice can store up to six electrons, without forming the chemical bond unlike the conventional covalently-bonded semiconductors such as Si.  $A_x C_{60}$ , where X can be changed from one to six in stoichiometric ratio, which has different characteristics depending on the number of X. A<sub>1</sub>C<sub>60</sub> and A<sub>3</sub>C<sub>60</sub> show metallic property while the other structures have semiconducting property. Especially, A<sub>3</sub>C<sub>60</sub> compound is well known to exhibit superconducting property at low

8

temperature. The critical temperatures of  $K_3C_{60}$  and  $Rb_3C_{60}$  are 19.8 and 30.2 K at normal pressure, respectively [28]. On the other hand, the  $A_1C_{60}$  (A = K, Rb, or Cs) compound shows different behavior. It is reported that the crystal has an orthorhombic structure and the C60 molecules have a covalent bond with each other one dimensionally. X-ray diffraction pattern of the material shows good agreement with the calculated atomic position of orthorhombic phase with [2+2] cycloaddition below 350 K [29]. The mechanism of the formation of intermolecular bonds is explained by ion-induced [2+2] cycloaddition [30]. Such a structure can be obtained via the following process; alkali ions such as K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup>, which are larger than the tetrahedral space of fcc  $C_{60}$ crystal, can form a doped structure with one ion per octahedral position. The compound takes a NaCl (fcc) structure at high temperatures (e.g. more than 420 K for  $KC_{60}$ ). It can be balanced by Coulomb interaction between A<sup>+</sup> and  $C_{60}$ and a slight distortion of the crystal. The structure undergoes first-order phase transition into a body-centered orthorhombic structure. The structure is formed by the distortion of the fcc lattice without diffusing the metal ion out from the crystal. And then, [2+2] cycloaddition takes place and the one-dimensional polymer is formed. This polymerization scheme is basically similar to a process in high-pressure application; however, the dimensionality of the polymerized crystal is different. The fcc structure is not stable at room temperature and transits into an orthorhombic polymer phase. A single crystal of  $(KC_{60})_N$  was grown; it was a few millimeters long and the degree of polymerization exceeded 100 000 [31]. At low temperatures such as liquid nitrogen temperature, the crystal forms a superstructure by dimerization within the 1D crystal.

#### 1.2.3 High-Pressure and High-Temperature Application

As mentioned above, depolymerization process occurs at more than 200 °C in normal pressure; however, application of pressure with heating brings about the other phases of polymerization. Iwasa et al. reported the first polymerization with a rhombohedral (rh-phase) structure in 1994 [32]. They heated  $C_{60}$  crystals up to 1073 K by applying a pressure of 4–8 GPa. The other phases, orthorhombic (or-phase) and tetragonal (te-phase), were confirmed in latter experiments [33]. Their crystalline structures have been determined by X-ray diffraction patterns. Successive transition was observed from fcc structure to 1D- (or-phase) or 2D- (te- and rh-phase) polymerized phase by increasing the temperature and applying pressure. A mixture of rh- and te- phases is formed at 2-4 GPa and 673–1073 K, and a pure rh-phase at 4–8 GPa and the same temperatures [34]. By applying pressure, the intermolecular distance is decreased and the regularity of rotation angle is restricted; therefore, the crystalline structure changes from fcc to simple cubic (sc) phase, which is a more restricted structure. Since such a restriction of rotation angle hinders the formation of intermolecular bond by [2+2] cycloaddition process, polymerization does not progress in the sc phase. However, by increasing the temperature, the transition in the sc phase is suppressed and it returns to the fcc phase again, and then the angular disorder of the rotation also reappears. Therefore, higher order polymerization such as the teand rh-phase can be obtained at high pressure and high temperature conditions. Typically, more than 5 GPa and 973 K are necessary for the formation of the rh-phase [34].

Since rh-polymer phase has 2D and a hexagonal symmetry, the crystal exhibits a hexagonal or triangular shape. On the other hand, the te-phase polymer shows a square-shaped crystal. Makarova et al. show the transport properties of each polymer [35]. Both te- and rh-polymers show semiconducting characteristics; the resistance increases with decreasing temperature. However, an rh-phase sample synthesized at 7–8 GPa and 973–1073 K shows metallic property; the resistance decreases with decreasing temperature (Figure 1.9).

Okada and Oshiyama showed the results of the first principles calculation of band structures of the rh-polymer phase [36], which is composed of normal 66/66 bonds and has a bandgap at the Fermi energy as shown in Figure 1.10. Therefore, there is still room for discussion on the mechanism; however, the only clear mechanism is that of an rh-phase polymer having 66/65 bonds. Metallic band structures are suggested in both cases of ABA and ABC staking of rh-phase polymer layers of 66/65 bonds.

If a  $C_{60}$  crystal is heated at over 1273 K in 5 GPa, the cages of  $C_{60}$  molecules are broken and become amorphous carbon [37].

The peak shifts of  $A_g(2)$  mode in Raman spectrum in the different polymer structures are summarized by Rao et al. [38]. However, the suggested peak assignments of the Raman shift in each phase include ambiguity. It is difficult to obtain a pure sample having a single polymer phase, as multiple phases are usually involved in it. Therefore, in the early stages of the experiments, mixed peaks were occasionally misassigned in the spectrum. The most reliable experimental result shown by Meletov et al. is that a peak wave number of  $A_g(2)$  mode in pure rh-phase of  $C_{60}$  crystal appears at 1408 cm<sup>-1</sup> as shown in Figure 1.11 [39]. They prepared the single crystal of rh-phase sample by applying a high pressure of 5 GPa at 773 K. By heat treatment at more than 523 K for 0.5 hour, the peak height at 1408 cm<sup>-1</sup> decreased and then peaks corresponding to the 2D-te-phase and the 1D-or-phase began to appear as shown in Figure 1.11. After thermal treatment at 548 K for 0.5 hour, these peaks also disappeared and only a peak of 1469 cm<sup>-1</sup> corresponding to the  $C_{60}$  monomer finally remained. Even at



**Figure 1.9** Scanning electron microscope image of polymeric  $C_{60}$  crystal having rh-phase (a) and temperature dependences of the resistivity (b) [35].