

Contents

Foreword *xiii*

- 1 Out-of-Equilibrium (Supra)molecular Systems and Materials:
An Introduction** *1*
Nicolas Giuseppone and Andreas Walther
- 1.1 General Description of the Field *1*
- 1.1.1 Background, Motivation, and Interdisciplinary Nature of the Topic *1*
- 1.1.2 From Equilibrium Self-Assembly to Far-From-Equilibrium
Self-Organization *5*
- 1.1.3 From Responsive Materials to Adaptive and Interactive Materials
Systems with Life like Behavior *7*
- 1.1.4 An Outlook on Challenges Ahead *9*
- 1.2 Description of the Book Content *10*
Acknowledgments *14*
References *14*
- 2 Learning from Embryo Development to Engineer
Self-organizing Materials** *21*
*Anis Senoussi, Yuliia Vyborna, Hélène Berthoumieux, Jean-Christophe Galas,
and André Estevez-Torres*
- 2.1 The Embryo is a Material Capable of Chemical and Morphological
Differentiation *22*
- 2.2 Pattern Formation by a Reaction–Diffusion Turing Instability *24*
- 2.2.1 Short Mathematical Analysis of the Turing Instability in a Two-species
System *26*
- 2.2.2 Turing Patterns *In Vivo* *27*
- 2.2.3 Turing Patterns *In Vitro* *28*
- 2.2.4 Simpler than Turing: Reaction–Diffusion Waves *In Vitro* *29*
- 2.2.4.1 Min Protein Waves *29*
- 2.2.4.2 DNA/Enzyme Waves *31*
- 2.3 Pattern Formation by Positional Information *32*
- 2.3.1 Models of Positional Information *32*
- 2.3.1.1 Equilibrium Model: Cooperativity *34*

2.3.1.2	Reaction-only Mechanism: Temporal Bistability	34
2.3.1.3	Reaction–Diffusion Mechanism: Spatial Bistability	35
2.3.2	Positional Information <i>In Vivo</i> : Patterning of the <i>Drosophila</i> blastoderm	35
2.3.3	Positional Information <i>In Vitro</i>	36
2.3.3.1	DNA Strand Displacement Patterns	36
2.3.3.2	PEN DNA/Enzyme Patterns	38
2.3.3.3	Transcription–Translation Patterns	39
2.4	Force Generation and Morphogenesis in Reconstituted Cytoskeletal Active Gels	40
2.4.1	Cytoskeletal Filaments and Molecular Motors, the Building Blocks of Active Gels	41
2.4.2	Active Gel Theory for a 1D System	42
2.4.3	Active Structures Generated by Cytoskeletal Systems <i>In Vitro</i>	45
2.4.3.1	Gliding Filaments	45
2.4.3.2	Aster Formation	45
2.4.3.3	Contractions	46
2.4.3.4	Active Flows	46
2.4.3.5	Corrugations	47
2.4.3.6	Vesicle and Droplet Deformation and Movement	47
2.5	Conclusion and Perspectives	48
	Acknowledgment	49
	References	50

3 From Clocks to Synchrony: The Design of Bioinspired Self-Regulation in Chemical Systems 61

Annette F. Taylor

3.1	Introduction	61
3.2	Bioinspired Behavior: Insight from Models	62
3.3	Feedback and Clocks	63
3.3.1	Clock Reactions	65
3.3.2	Autocatalysis in a Closed Reactor	66
3.4	Maintaining Systems Far from Equilibrium	69
3.5	Kinetic Switches	71
3.6	Design of Oscillators	72
3.7	Waves and Patterns	74
3.7.1	Fronts, Waves, and Spirals	74
3.7.2	Stationary Concentration Patterns	76
3.8	Synchronization and Collective Behavior	77
3.9	Materials Systems	78
3.9.1	Coupled Reactions and Materials	78
3.9.2	Feedback in Polymerization and Precipitation Processes	79
3.10	Conclusions	81
	References	82

4	<i>De novo</i> Design of Chemical Reaction Networks and Oscillators and Their Relation to Emergent Properties	91
	<i>Sergey N. Semenov</i>	
4.1	Introduction	91
4.2	The Role of Out-of-Equilibrium Conditions in the Emergence of CRN Properties and Functions	94
4.3	The Role of Stoichiometry, Connectivity, and Kinetics for CRNs	96
4.4	Design Guidelines and Network Motifs	98
4.5	Examples of <i>De novo</i> Designed CRNs in Well-Mixed Solutions	107
4.6	Recent Advances in the Design of Flow Systems	112
4.7	Examples of <i>De novo</i> Designed Reaction–Diffusion Networks	112
4.8	Autocatalysis as an Emergent Property of CRNs	116
4.9	Future Challenges and Directions in Designing CRNs	119
	References	120
5	Kinetically Controlled Supramolecular Polymerization	131
	<i>Kazunori Sugiyasu</i>	
5.1	Introduction	131
5.2	Thermodynamic Models for Supramolecular Polymerization	134
5.3	Supramolecular Polymerization Under Kinetic Control	136
5.4	Living Supramolecular Polymerization	139
5.5	Seeded Supramolecular Polymerization Coupled with Chemical Reactions	147
5.6	Equipment-Controlled Supramolecular Polymerizations	151
5.7	Crystallization-Driven Self-Assembly and Other Systems	153
5.8	Conclusion	157
	References	158
6	Chemically Fueled, Transient Supramolecular Polymers	165
	<i>Michelle P. van der Helm, Jan H. van Esch, and Rienk Eelkema</i>	
6.1	Introduction	165
6.2	Nonlinear Behavior: A Lesson from Biology	167
6.3	Walking Uphill in the Energy Landscape	169
6.4	The Nature of the Chemical Fuel	171
6.5	Chemically Fueled, Transient Supramolecular Polymerization Systems	172
6.6	Conclusion and Outlook	184
	References	185
7	Design of Chemical Fuel-Driven Self-Assembly Processes	191
	<i>Krishnendu Das, Rui Chen, Sushmitha Chandrabhas, Luca Gabrielli, and Leonard J. Prins</i>	
7.1	Introduction	191
7.2	Chemically Fueled Self-Assembly	191

7.3	Transient Signal Generation Using Gold Nanoparticles	197
7.4	Self-Assembly Under Dissipative Conditions	199
7.5	Out-of-Equilibrium Self-Assembly	201
7.6	Toward Chemical Fuel-Driven Self-Assembly	205
7.7	Outlook	209
	References	210
8	Dynamic Combinatorial Chemistry Out of Equilibrium	215
	<i>Kai Liu and Sijbren Otto</i>	
8.1	Introduction	215
8.2	Kinetic Control in DCC	217
8.2.1	Introducing Irreversible Reactions into DCLs	217
8.2.1.1	Irreversible Reactions Acting on a Specific Library Member	218
8.2.1.2	Irreversible Reactions Acting on Multiple DCL Members	221
8.2.2	Kinetically Trapped Self-Assembly in DCC	223
8.2.3	Phase Changes in DCC	225
8.2.4	DCC Under Non-equilibrium Conditions	228
8.3	Dissipative DCC	230
8.3.1	Chemically Fueled DCC	231
8.3.2	Light-Driven DCC	231
8.4	Conclusions and Outlook	234
	References	236
9	Controlling Self-Assembly of Nanoparticles Using Light	241
	<i>Tong Bian, Zonglin Chu, and Rafal Klajn</i>	
9.1	Introduction	241
9.2	Nanoparticle Surface-Functionalized with Photoswitchable Molecules	242
9.2.1	Azobenzene-Functionalized Nanoparticles	242
9.2.2	Spiropyran-Functionalized Nanoparticles	247
9.3	Assembling Nanoparticles Using Photodimerization Reactions	251
9.4	(De)protonation of Nanoparticle-Bound Ligands Using Photoacids/Photobases	253
9.5	Light-Induced Adsorption of Photoswitchable Molecules	256
9.5.1	Photoswitchable Host–Guest Inclusion Complexes on Nanoparticle Surfaces	256
9.5.2	Nonselective Adsorption of Photoswitchable Molecules	259
9.6	Phase Transitions of Thermoresponsive Polymers Induced by Plasmonic Nanoparticles	261
9.7	Light-Induced Chemical Reduction of Nanoparticle-Bound Ligands	263
9.8	Irreversible Self-Assembly of Nanoparticles	265
9.9	Extension to Microparticles	266
9.10	Summary and Outlook	268
	References	269

10	Photoswitchable Components to Drive Molecular Systems Away from Global Thermodynamic Minimum by Light	275
	<i>Michael Kathan and Stefan Hecht</i>	
10.1	Introduction	275
10.2	Thermodynamic vs. Photodynamic Equilibria	277
10.3	Manipulating Chemical Reactions and Equilibria with Light	281
10.4	From Shifting Equilibria to Continuous Work Powered by Light	287
10.5	Light to Control Assembly and Create Order	296
10.6	Conclusion: From Remote Controlling to Driving Processes	297
	References	299
11	Out-of-Equilibrium Threaded and Interlocked Molecular Structures	305
	<i>Massimo Baroncini, Alberto Credi, and Serena Silvi</i>	
11.1	Introduction	305
11.1.1	Metastable, Kinetically Trapped, and Dissipative Non-equilibrium States	307
11.1.2	Energy Inputs	309
11.1.2.1	Chemical Energy	309
11.1.2.2	Electrical Energy	310
11.1.2.3	Light Energy	310
11.1.3	Mechanically Interlocked Molecules and Their Threaded Precursors	311
11.2	Pseudorotaxanes	312
11.2.1	Semirotaxane-Based Molecular Reservoirs	313
11.2.2	Supramolecular Pumps	315
11.3	Rotaxanes	319
11.3.1	Molecular Ratchets	319
11.3.2	Generation of Non-equilibrium States by Autonomous Energy Consumption	322
11.4	Catenanes	324
11.4.1	Molecular Switches and Energy Ratchets	325
11.4.2	Autonomous Chemically Fueled Catenane Rotary Motors	327
11.5	Conclusions	331
	Acknowledgments	332
	References	332
12	Light-driven Rotary Molecular Motors for Out-of-Equilibrium Systems	337
	<i>Anouk S. Lubbe, Cosima L.G. Stähler, and Ben L. Feringa</i>	
12.1	Introduction	337
12.2	Design and Synthesis of Light-driven Rotary Motors	339
12.3	Tuning the Properties of Molecular Motors	342
12.4	Molecular Motors as Out-of-Equilibrium Systems	346
12.5	Single Molecules Generating Work on the Nanoscale	348

12.5.1	Molecular Stirring	349
12.5.2	Amplifying Motor Function	350
12.6	Immobilization	352
12.6.1	Surface-Attached Molecular Motors	352
12.6.2	3D Networks	355
12.7	Liquid Crystals and Polymer Doping	358
12.7.1	Liquid Crystals	358
12.7.2	Polymer Doping	361
12.8	Self-assembled Systems	364
12.9	Conclusion	368
	References	369
13	Design of Active Nanosystems Incorporating Biomolecular Motors	379
	<i>Stanislav Tsitkov and Henry Hess</i>	
13.1	Introduction	379
13.2	Active Nanosystem Design	381
13.3	Biological Components of Active Nanosystems	384
13.3.1	Microtubules	385
13.3.2	Kinesin	387
13.3.3	Dynein	388
13.3.4	Actin Filaments	388
13.3.5	Myosin	389
13.4	Interactions Between Components of Active Nanosystems	389
13.4.1	Filament Response to External Load	390
13.4.2	Motor–Filament Interactions	390
13.4.3	Filament–Filament Interactions	392
13.4.4	Filament–Cargo Interactions	392
13.4.5	Motor–Surface Interactions	393
13.5	Implementations of Active Nanosystems	393
13.5.1	Delivering Cargo in Active Nanosystems	394
13.5.2	Sensing Using Active Nanosystems	396
13.5.2.1	Biosensors	396
13.5.2.2	Surface Characterization	396
13.5.2.3	Force Measurements	397
13.5.3	Controlling the Behavior of Active Nanosystems	397
13.5.3.1	Passive Control	397
13.5.3.2	Active Control	398
13.5.4	Extending the Lifetime of Active Nanosystems	398
13.5.5	Higher-Order Structure Generation	399
13.5.6	Simulating Active Nanosystems in the Inverted Motility Configuration	399
13.5.7	Active Nanosystems Employing the Native Motility Configuration	401
13.5.7.1	Biological Importance	401
13.5.7.2	Active Nanosystems	401

13.5.8	Active Nematic Gels	403
13.6	Conclusion	403
	References	403
	Index	423

