With Forewords by

Jean-Marie Lehn Nobel Laureate Janine Benyus President of Biomimicry Institute

# Bioinspiration and Biomimicry in Chemistry

**Reverse-Engineering** Nature

Edited by Gerhard F. Swiegers

### BIOINSPIRATION AND BIOMIMICRY IN CHEMISTRY

# BIOINSPIRATION AND BIOMIMICRY IN CHEMISTRY

## **REVERSE-ENGINEERING NATURE**

Edited by

Gerhard F. Swiegers



Copyright © 2012 by John Wiley & Sons, Inc. All rights reserved

Published by John Wiley & Sons, Inc., Hoboken, New Jersey Published simultaneously in Canada

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, (978) 750-8400, fax (978) 750-4470, or on the web at www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008, or online at http://www.wiley.com/go/permission.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor author shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services or for technical support, please contact our Customer Care Department within the United States at (800) 762-2974, outside the United States at (317) 572-3993 or fax (317) 572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic formats. For more information about Wiley products, visit our web site at www.wiley.com.

#### Library of Congress Cataloging-in-Publication Data:

Bioinspiration and biomimicry in chemistry : reverse-engineering nature / edited by Gerhard F. Swiegers. p. cm.
Includes bibliographical references and index.
ISBN 978-0-470-56667-1 (cloth)
1. Biomimicry. 2. Biomimetics. 3. Biomedical engineering. 4. Biomedical materials. I. Swiegers, Gerhard F. QP517.B56B478 2012 610.28-dc23
2011049801

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

Dedicated to Crawford Long, William Thomas Green Morton, and Wilhelm Röntgen

	Foreword Jean-Marie Lehn				
	Foreword Janine Benyus Preface				
Pre					
Co	ntributo	rs		XXV	
1.	in Che	mistry	<b>the Concept of Biomimicry and Bioinspiration</b> and Gerhard F. Swiegers	1	
	1.1	What is 1	Biomimicry and Bioinspiration?	1	
	1.2	Why See	k Inspiration from, or Replicate Biology?	3	
		1.2.1	Biomimicry and Bioinspiration as a Means of Learning from Nature and Reverse-Engineering from Nature	3	
		1.2.2	Biomimicry and Bioinspiration as a Test of Our Understanding of Nature	4	
		1.2.3	Going Beyond Biomimicry and Bioinspiration	4	
	1.3 Other Monikers: Bioutilization, Bioextraction, Bioderivation and Bionics		5		
	1.4	Biomimi	cry and Sustainability	5	
	1.5	Biomimi	cry and Nanostructure	7	
	1.6	Bioinspiration and Structural Hierarchies			
	1.7	Bioinspiration and Self-Assembly			
	1.8	Bioinspir	ation and Function	12	
	1.9		erspectives: Drawing Inspiration from the Complex hat is Nature	13	
		Reference	es	14	

2.			<b>If-Assembly I: Self-Assembled Structures</b> <i>py, Christopher Richardson, and Jack K. Clegg</i>	17	
	2.1	Introduc	ction	17	
	2.2	Molecul	lar Clefts, Capsules, and Cages	19	
		2.2.1	Organic Cage Systems	21	
		2.2.2	Metallosupramolecular Cage Systems	24	
	2.3			28	
	2.4	Self-Ass	sembled Liposome-Like Systems	30	
	2.5	Ion Cha	nnel Mimics	32	
	2.6	Base-Pa	iring Structures	34	
	2.7	Molecular Clefts, Capsules, and CagesI2.2.1Organic Cage Systems22.2.2Metallosupramolecular Cage Systems2Enzyme Mimics and Models: The Example of Carbonic Anhydrase2Self-Assembled Liposome-Like Systems3Ion Channel Mimics3Base-Pairing Structures3DNA–RNA Structures3Bioinspired Frameworks3Conclusion4References4spired Self-Assembly II: Principles of Cooperativity poinspired Self-Assembly Systems4Allosteric Cooperativity5Effective Molarity5Chelate Cooperativity5Interannular Cooperativity5Stability of an Assembly6			
	2.8	Bioinspi	ired Frameworks	38	
	2.9	Conclusion		41	
		Referen	ces	41	
3.	in Bio	inspired	Self-Assembling Systems	47	
	3.1	Introduc	ction	47	
	3.2	Statistic	al Factors in Self-Assembly	48	
	3.3	Alloster	ic Cooperativity	50	
	3.4	Effectiv	e Molarity	52	
	3.5	Chelate	Cooperativity	55	
	3.6	Interann	ular Cooperativity	60	
	3.7	Stability	of an Assembly	62	
	3.8	Conclus	sion	67	
		Referen	ces	67	
4.		-	olecular Machines enson, Andrew I. Share, and Amar H. Flood	71	
	4.1	Introduc	stion	71	
		4.1.1	Inspirational Antecedents: Biology, Engineering, and Chemistry	72	

	4.1.2	Chemical Integration	75		
	4.1.3	Chapter Overview	77		
4.2	Mechar	nical Effects in Biological Machines	78		
	4.2.1	Skeletal Muscle's Structure and Function	78		
	4.2.2	Kinesin	79		
	4.2.3	F <sub>1</sub> -ATP Synthase	80		
	4.2.4	Common Features of Biological Machines	82		
	4.2.5	Variation in Biomotors	83		
	4.2.6	Descriptions and Analogies of Molecular Machines	83		
4.3	Theoret	ical Considerations: Flashing Ratchets	83		
4.4	Sliding	Machines	86		
	4.4.1	Linear Machines: Rotaxanes	86		
	4.4.2	Mechanistic Insights: Ex Situ and In Situ			
		(Maxwell's Demon)	89		
	4.4.3	Bioinspiration in Rotaxanes	93		
	4.4.4	Molecular Muscles as Length Changes	93		
4.5	Rotary	Motors	102		
	4.5.1	Interlocked Rotary Machines: Catenanes	103		
	4.5.2	Unimolecular Rotating Machines	104		
4.6	Moving	Larger Scale Objects	104		
4.7	Walking	g Machines	106		
4.8	Ingenio	us Machines	109		
	4.8.1	Molecular Machines Inspired by Macroscopic			
		Ones: Scissors and Elevators	109		
	4.8.2	Artificial Motility at the Nanoscale	109		
	4.8.3	Moving Molecules Across Surfaces	110		
4.9	Using S	Synthetic Bioinspired Machines in Biology	111		
4.10	Perspective				
	4.10.1	Lessons and Departures from Biological Molecular Machines	114		
	4.10.2	The Next Steps in Bioinspired Molecular			
		Machinery	115		
4.11	Conclus	sion	116		
	References				

X CONTENTS
------------

5.	. Bioinspired Materials Chemistry I: Organic–Inorganic Nanocomposites Pilar Aranda, Francisco M. Fernandes, Bernd Wicklein, Eduardo Ruiz-Hitzky, Jonathan P. Hill, and Katsuhiko Ariga			121	
	5.1	Introduc	ction	121	
	5.2	Silicate- Systems	Based Bionanocomposites as Bioinspired	122	
	5.3	Bionanc	ocomposite Foams	124	
	5.4	Biomimetic Membranes			
		5.4.1 5.4.2	Phospholipid–Clay Membranes Polysaccharide–Clay Bionanocomposites as Support for Viruses	126 127	
	5.5	Hierarch	hically Layered Composites	129	
	5.5	5.5.1	Layer-by-Layer Assembly of Composite-Cell Model	129	
		5.5.2	Hierarchically Organized Nanocomposites for Sensor and Drug Delivery	130	
	5.6	Conclus	sion	133	
		Referen	ces	134	
6.	Bioinspired Materials Chemistry II: Biomineralization as Inspiration for Materials Chemistry139Fabio Nudelman and Nico A. J. M. Sommerdijk				
	6.1	Inspirati	ion from Nature	139	
	6.2	Learning from Nature			
	6.3	Applying Lessons from Nature: Synthesis of Biomimetic and Bioinspired Materials			
		6.3.1 6.3.2 6.3.3	Biomimetic Bone Materials Semiconductors, Nanoparticles, and Nanowires Biomimetic Strategies for Silica-Based Materials	147 151 157	
	6.4		-	160	
		Referen	ces	160	
7.		p <b>ired Ca</b> l F. Swieg	<b>talysis</b> gers, Jun Chen, and Pawel Wagner	165	
	7.1	Introduc	ction	165	

7.2	A Gene	ral Description of the Operation of Catalysts	168		
7.3	A Brief History of Our Understanding of the Operation of Enzymes				
7.3	7.3.1	Early Proposals: Lock-and-Key Theory, Strain Theory, and Induced Fit Theory	170		
	7.3.2	The Critical Role of Molecular Recognition in Enzymatic Catalysis: Pauling's Concept of Transition State Complementarity	170		
	7.3.3	The Critical Role of Approach Trajectories in Enzymatic Catalysis: Orbital Steering, Near Attack Conformers, the Proximity Effect, and Entropy Traps	172		
	7.3.4	The Critical Role of Conformational Motion in Enzymatic Catalysis: Coupled Protein Motions	172		
	7.3.5	Enzymes as Molecular Machines: Dynamic Mechanical Devices and the Entatic State	173		
	7.3.6	The Fundamental Origin of Machine-like Actions: Mechanical Catalysis	174		
7.4	Representative Studies of Bioinspired/Biomimetic Catalysts				
	7.4.1	Important General Characteristics of Enzymes as a Class of Catalyst	177		
	7.4.2	Bioinspired/Biomimetic Catalysts that Illustrate the Critical Importance of Reactant Approach Trajectories	178		
	7.4.3	Bioinspired/Biomimetic Catalysts that Demonstrate the Importance and Limitations of Molecular Recognition	182		
	7.4.4	Bioinspired/Biomimetic Catalysts that Operate Like a Mechanical Device	187		
7.5		lationship Between Enzymatic Catalysis and logical Homogeneous and Heterogeneous is	192		
7.6	Selected High-Performance NonBiological Catalysts that Exploit Nature's Catalytic Principles				
	7.6.1	Adapting Model Species of Enzymes to Facilitate Machine-like Catalysis	194		
	7.6.2	Statistical Proximity Catalysts	201		

	7.7	Conclusi Principle	on: The Prospects for Harnessing Nature's Catalytic s	203
		Referenc	es	204
8.			phiphiles and Vesicles and Bart Jan Ravoo	209
	8.1	Introduct	ion	209
	8.2	Synthetic Vesicles	e Amphiphiles as Building Blocks for Biomimetic	210
	8.3	Vesicle F	Fusion Induced by Molecular Recognition	216
	8.4	Stimuli-H	Responsive Shape Control of Vesicles	224
	8.5	Transme	mbrane Signaling and Chemical Nanoreactors	231
	8.6	Toward I Subcomp	Higher Complexity: Vesicles with partments	239
	8.7	Conclusi	on	245
		Referenc	es	246
9.		-	faces I: Gecko-Foot Mimetic Adhesion	251
	9.1	The Hier	archical Structure of Gecko Feet	251
	9.2 Origin of Adhesion in Gecko Setae			252
	9.3	1 7 7		
9.4 Fabrication of Synthetic Dry Adhesives		on of Synthetic Dry Adhesives	254	
		9.4.1	Polymer-Based Dry Adhesives	254
		9.4.2	Carbon-Nanotube-Based Dry Adhesives	278
	9.5	Outlook		284
		Referenc	es	286
10.		pired Sur	faces II: Bioinspired Photonic Materials	293
	10.1	Structura	l Color in Nature: From Phenomena to Origin	293
	10.2	Bioinspir	red Photonic Materials	296
		10.2.1 10.2.2	The Fabrication of Photonic Materials The Design and Application of Photonic	297
			Materials	298

				CONTENTS	xiii
	10.3	Conclusi	on and Outlook		317
		Referenc	es		319
11.	Wolfgan		nciples in Macromolecular Science er, Marlen Schunack, Florian Herbst, and lamagatta		323
	11.1	Introduct	tion		323
	11.2	Polymer	Synthesis Versus Biopolymer Synthesis		325
		11.2.1 11.2.2 11.2.3	Features of Polymer Synthesis "Living" Chain Growth Aspects of Chain Length Distribution in Sy	vnthetic	325 326
			Polymers: Sequence Specificity and Templa		328
	11.3	Biomime	etic Structural Features in Synthetic Polymers	S	330
		11.3.1	Helically Organized Polymers		330
		11.3.2	$\beta$ -Sheets		333
		11.3.3	Supramolecular Polymers		334
		11.3.4	Self-Assembly of Block Copolymers		337
	11.4	Movement in Polymers			343
		11.4.1	Polymer Gels and Networks as Chemical Motors		343
		11.4.2	Polymer Brushes and Lubrication		346
		11.4.3	Shape-Memory Polymers		349
11.5 Antibody-Like Binding and Enzyme-Like Catalysis					
		in Polymeric Networks			352
	11.6	Self-Hea	ling Polymers		355
		Referenc	es		362
12.			ities and Bioinspired Receptors Ivan Jabin, and Olivia Reinaud		367
	12.1	Introduction			367
	12.2	Mimics of the Michaelis-Menten Complexes of Zinc(II) Enzymes with Polyimidazolyl Calixarene-Based Ligands			368
		12.2.1	A Bis-aqua Zn(II) Complex Modeling the A Site of Carbonic Anhydrase	Active	369
		12.2.2	Structural Key Features of the Zn(II) Funne Complexes	el	371