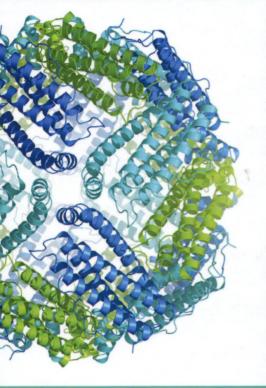
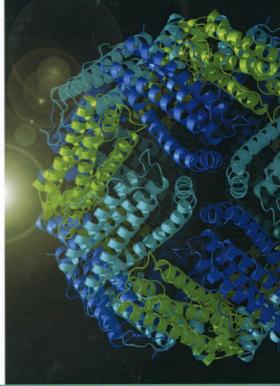
Coordination Chemistry in Protein Cages

Principles, Design and Applications





Edited by
Takafumi Ueno
Yoshihito Watanabe

With a foreword by Harry B. Gray, California Institute of Technology



Copyright © 2013 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:

Coordination chemistry in protein cages principles, design, and applications / edited by Takafumi Ueno, Yoshihito Watanabe.

pages cm

Includes index.

ISBN 978-1-118-07857-0 (cloth)

Protein drugs.
 Protein drugs-Physiological transport.
 Carrier proteins.
 Ueno, Takafumi,
 editor of compilation.
 Watanabe, Yoshihito, editor of compilation.

RS431.P75C66 2013

615.1'9-dc23

2012045122

Printed in the United States of America

ISBN: 9781118078570

10 9 8 7 6 5 4 3 2 1

CONTENTS

Poleword				
Prefa	Preface			
Cont	ribu	ntors	xvii	
PART	ΓI	COORDINATION CHEMISTRY IN NATIVE PROTEIN CAGES		
ľ	Nan	Chemistry of Nature's Iron Biominerals in Ferritin Protein ocages beth C. Theil and Rabindra K. Behera	3	
j	1.1	Introduction	3	
]	1.2	Ferritin Ion Channels and Ion Entry	6	
		1.2.1 Maxi- and Mini-Ferritin	6	
		1.2.2 Iron Entry	7	
1	1.3	Ferritin Catalysis	8	
		1.3.1 Spectroscopic Characterization of μ-1,2 Peroxodiferric		
		Intermediate (DFP)	8	
		1.3.2 Kinetics of DFP Formation and Decay	12	
1	1.4	Protein-Based Ferritin Mineral Nucleation and Mineral Growth	13	
1	1.5	Iron Exit	16	
i	1.6	Synthetic Uses of Ferritin Protein Nanocages	17	
		1.6.1 Nanomaterials Synthesized in Ferritins	18	

		1.6.2 Ferritin Protein Cages in Metalloorganic Catalysis and Nanoelectronics	19
		1.6.3 Imaging and Drug Delivery Agents Produced in Ferritins	19
	1.7		20
	,	Acknowledgments	20
		References	21
2	Mol	ecular Metal Oxides in Protein Cages/Cavities	25
	Achii	n Müller and Dieter Rehder	
	2.1		25
	2.2	Vanadium: Functional Oligovanadates and Storage of VO ²⁺ in	
		Vanabins	26
	2.3	Molybdenum and Tungsten: Nucleation Process in a Protein	• 0
		Cavity	28
		Manganese in Photosystem II	33
		Iron: Ferritins, DPS Proteins, Frataxins, and Magnetite Some General Remarks: Oxides and Sulfides	35 38
	2.6	References	38
PAI	RT II	DESIGN OF METALLOPROTEIN CAGES	
3		Novo Design of Protein Cages to Accommodate	
	Met	al Cofactors	45
	Flav	ia Nastri, Rosa Bruni, Ornella Maglio, and Angela Lombardi	
	3.1		45
	-		45
	-	Introduction	45 47
	-	Introduction De Novo-Designed Protein Cages Housing Mononuclear	47
	3.2	Introduction De Novo-Designed Protein Cages Housing Mononuclear Metal Cofactors De Novo-Designed Protein Cages Housing Dinuclear Metal Cofactors	47 59
	3.23.33.4	Introduction De Novo-Designed Protein Cages Housing Mononuclear Metal Cofactors De Novo-Designed Protein Cages Housing Dinuclear Metal Cofactors De Novo-Designed Protein Cages Housing Heme Cofactor	47 59 66
	3.2	Introduction De Novo-Designed Protein Cages Housing Mononuclear Metal Cofactors De Novo-Designed Protein Cages Housing Dinuclear Metal Cofactors De Novo-Designed Protein Cages Housing Heme Cofactor Summary and Perspectives	47 59 66 79
	3.23.33.4	Introduction De Novo-Designed Protein Cages Housing Mononuclear Metal Cofactors De Novo-Designed Protein Cages Housing Dinuclear Metal Cofactors De Novo-Designed Protein Cages Housing Heme Cofactor Summary and Perspectives Acknowledgments	47 59 66 79 79
	3.23.33.4	Introduction De Novo-Designed Protein Cages Housing Mononuclear Metal Cofactors De Novo-Designed Protein Cages Housing Dinuclear Metal Cofactors De Novo-Designed Protein Cages Housing Heme Cofactor Summary and Perspectives	47 59 66 79
4	3.2 3.3 3.4 3.5	Introduction De Novo-Designed Protein Cages Housing Mononuclear Metal Cofactors De Novo-Designed Protein Cages Housing Dinuclear Metal Cofactors De Novo-Designed Protein Cages Housing Heme Cofactor Summary and Perspectives Acknowledgments	47 59 66 79 79
4	3.2 3.3 3.4 3.5 Gen Mat	Introduction De Novo-Designed Protein Cages Housing Mononuclear Metal Cofactors De Novo-Designed Protein Cages Housing Dinuclear Metal Cofactors De Novo-Designed Protein Cages Housing Heme Cofactor Summary and Perspectives Acknowledgments References eration of Functionalized Biomolecules Using Hemoprotein rices with Small Protein Cavities for Incorporation of	47 59 66 79 79 80
4	3.2 3.3 3.4 3.5 Gen Mat	Introduction De Novo-Designed Protein Cages Housing Mononuclear Metal Cofactors De Novo-Designed Protein Cages Housing Dinuclear Metal Cofactors De Novo-Designed Protein Cages Housing Heme Cofactor Summary and Perspectives Acknowledgments References eration of Functionalized Biomolecules Using Hemoprotein	47 59 66 79 79
4	3.2 3.3 3.4 3.5 Gen Mat	Introduction De Novo-Designed Protein Cages Housing Mononuclear Metal Cofactors De Novo-Designed Protein Cages Housing Dinuclear Metal Cofactors De Novo-Designed Protein Cages Housing Heme Cofactor Summary and Perspectives Acknowledgments References eration of Functionalized Biomolecules Using Hemoprotein rices with Small Protein Cavities for Incorporation of	47 59 66 79 79 80
4	3.2 3.3 3.4 3.5 Gen Mat	Introduction De Novo-Designed Protein Cages Housing Mononuclear Metal Cofactors De Novo-Designed Protein Cages Housing Dinuclear Metal Cofactors De Novo-Designed Protein Cages Housing Heme Cofactor Summary and Perspectives Acknowledgments References eration of Functionalized Biomolecules Using Hemoprotein rices with Small Protein Cavities for Incorporation of actors shi Hayashi Introduction	47 59 66 79 79 80 87
4	3.2 3.3 3.4 3.5 Gen Mat Cofa	Introduction De Novo-Designed Protein Cages Housing Mononuclear Metal Cofactors De Novo-Designed Protein Cages Housing Dinuclear Metal Cofactors De Novo-Designed Protein Cages Housing Heme Cofactor Summary and Perspectives Acknowledgments References eration of Functionalized Biomolecules Using Hemoprotein rices with Small Protein Cavities for Incorporation of actors shi Hayashi	47 59 66 79 79 80

			CONTENTS	vii
	4.4	Conversion	on of Myoglobin into Peroxidase	95
		4.4.1	Construction of a Substrate-Binding Site Near the	-
			Heme Pocket	95
		4.4.2	Replacement of Native Heme with Iron Porphyrinoid	
			in Myoglobin	99
		4.4.3	Other Systems Used in Enhancement of Peroxidase	
			Activity of Myoglobin	100
	4.5	Modula	tion of Peroxidase Activity of HRP	102
	4.6		bin Reconstituted with a Schiff Base Metal Complex	103
	4.7		ctase Model Using Reconstituted Myoglobin	106
		4.7.1	Hydrogenation Catalyzed by Cobalt Myoglobin	106
		4.7.2	A Model of Hydrogenase Using the Heme Pocket of	
			Cytochrome c	107
	4.8	Summa	ry and Perspectives	108
			vledgments	108
		Referen		108
5		The second of the second of	gn of Protein Cages for Alternative	
		ymatic Fu		111
	Nich	olas M. Ma	rshall, Kyle D. Miner, Tiffany D. Wilson, and Yi Lu	
	5.1	Introduc	etion	111
	5.2		uclear Electron Transfer Cupredoxin Proteins	112
	5.3			116
	5.4		ic Copper Proteins	118
		5.4.1	Type 2 Red Copper Sites	118
		5.4.2	Other T2 Copper Sites	120
		5.4.3	Cu, Zn Superoxide Dismutase	121
		5.4.4	Multicopper Oxygenases and Oxidases	122
	5.5	Heme-E	Based Enzymes	124
		5.5.1	Mb-Based Peroxidase and P450 Mimics	124
		5.5.2	Mimicking Oxidases in Mb	125
		5.5.3	Mimicking NOR Enzymes in Mb	127
		5.5.4	Engineering Peroxidase Proteins	128
		5.5.5	Engineering Cytochrome P450s	129
	5.6	Non-He	eme ET Proteins	131
	5.7	Fe And	Mn Superoxide Dismutase	132
	5.8	Non-He	eme Fe Catalysts	133
	5.9	Zinc Pro	oteins	134
	5.10	Other N	Metalloproteins	135
		5.10.1	Cobalt Proteins	135
		5.10.2	Manganese Proteins	136
		5.10.3	Molybdenum Proteins	137
		5.10.4	Nickel Proteins	137

		5.10.5	Uranyl Proteins	138
		5.10.6	Vanadium Proteins	138
	5.11		ry and Perspectives	139
		Rrefere	nces	142
PA	RT III		RDINATION CHEMISTRY OF PROTEIN MBLY CAGES	
6	Meta	l-Directe	ed and Templated Assembly of Protein	
	-		res and Cages	151
	F. Akij	Tezcan		
	6.1	Introduc	ction	151
	6.2	Metal-I	Directed Protein Self-Assembly	152
		6.2.1	Background	152
		6.2.2	Design Considerations for Metal-Directed Protein	
			Self-Assembly	153
		6.2.3	Interfacing Non-Natural Chelates with MDPSA	155
		6.2.4	Crystallographic Applications of Metal-Directed	
			Protein Self-Assembly	159
	6.3		Templated Interface Redesign	162
		6.3.1	Background	162
		6.3.2	Construction of a Zn-Selective Tetrameric Protein	
			Complex Through MeTIR	163
		6.3.3	Construction of a Zn-Selective Protein Dimerization	166
	6.1	C	Motif Through MeTIR	166 170
	6.4		ry and Perspectives	170
		Referen	vledgments	171
		Keleieli	ices	1/1
7	Catal	ytic Rea	actions Promoted in Protein Assembly Cages	175
	Takafı	ımi Ueno	and Satoshi Abe	
	7.1	Introdu	ction	175
	7.1	7.1.1	Incorporation of Metal Compounds	176
		7.1.2	Insight into Accumulation Process of Metal Compounds	177
	7.2		as a Platform for Coordination Chemistry	177
	7.3		ic Reactions in Ferritin	179
		7.3.1	Olefin Hydrogenation	179
		7.3.2	Suzuki-Miyaura Coupling Reaction in Protein Cages	182
		7.3.3	Polymer Synthesis in Protein Cages	185
	7.4		nation Processes in Ferritin	188
		7.4.1	Accumulation of Metal Ions	188
		7.4.2	Accumulation of Metal Complexes	192

		CONTENTS	ix
	7.5	Coordination Arrangements in Designed Ferritin Cages	194
	7.6	Summary and Perspectives	197
		Acknowledgments	198
		References	198
8	Meta	l-Catalyzed Organic Transformations Inside a Protein	
		old Using Artificial Metalloenzymes	203
	V. K. I	K. Praneeth and Thomas R. Ward	
	8.1	Introduction	203
		Enantioselective Reduction Reactions Catalyzed by Artificial	200
		Metalloenzymes	204
		8.2.1 Asymmetric Hydrogenation	204
		8.2.2 Asymmetric Transfer Hydrogenation of Ketones	206
		8.2.3 Artificial Transfer Hydrogenation of Cyclic Imines	208
	8.3	Palladium-Catalyzed Allylic Alkylation	211
	8.4	Oxidation Reaction Catalyzed by Artificial Metalloenzymes	212
		8.4.1 Artificial Sulfoxidase	212
		8.4.2 Asymmetric <i>cis</i> -Dihydroxylation	215
	8.5	Summary and Perspectives	216
		References	218
PA	RT IV	APPLICATIONS IN BIOLOGY	
9	Selec	tive Labeling and Imaging of Protein Using Metal Complex	223
	Yasuto	ka Kurishita and Itaru Hamachi	
	9.1	Introduction	223
	9.2	Tag-Probe Pair Method Using Metal-Chelation System	225
		9.2.1 Tetracysteine Motif/Arsenical Compounds Pair	225
		9.2.2 Oligo-Histidine Tag/Ni(II)-NTA Pair	227
		9.2.3 Oligo-Aspartate Tag/Zn(II)-DpaTyr Pair	230
		9.2.4 Lanthanide-binding Tag	235
	9.3	Summary and Perspectives	237
		References	237
10	Mole	cular Bioengineering of Magnetosomes for Biotechnological	
		cations	241
	Atsust	ni Arakaki, Michiko Nemoto, and Tadashi Matsunaga	
	10.1	Introduction	241
	10.2	Magnetite Biomineralization Mechanism in Magnetosome	242
		10.2.1 Diversity of Magnetotactic Bacteria	242

CONTENTS

		10.2.2	Genome and Proteome Analyses of Magnetotactic	
			Bacteria	244
		10.2.3	Magnetosome Formation Mechanism	246
		10.2.4	Morphological Control of Magnetite Crystal in	
			Magnetosomes	250
	10.3	Functio	nal Design of Magnetosomes	251
		10.3.1	Protein Display on Magnetosome by Gene Fusion	
			Technique	252
		10.3.2	Magnetosome Surface Modification by In Vitro System	255
		10.3.3	Protein-mediated Morphological Control of Magnetite	
			Particles	257
	10.4	Applica	ation	258
		10.4.1	Enzymatic Bioassays	259
		10.4.2	Cell Separation	260
		10.4.3	DNA Extraction	262
		10.4.4	Bioremediation	264
	10.5	Summa	ry and Perspectives	266
		Acknov	vledgments	266
		Referen	nces	266
11	RT V		ICATIONS IN NANOTECHNOLOGY Nanoparticles for Hybrid Inorganic—Organic	
11	Mate	_	Nanoparticles for Hybrid morganic-Organic	275
			wise Lunan Masaki Ushida and Trayon Doualas	213
	Snejai	n Qazı, Ja	nice Lucon, Masaki Uchida, and Trevor Douglas	
	11.1	Introdu	ction	275
	11.2	Biomin	eral Formation in Protein Cage Architectures	277
		11.2.1	Introduction	277
		11.2.2	Mineralization	278
		11.2.3	Model for Synthetic Nucleation-Driven Mineralization	279
		11.2.4	Mineralization in Dps: A 12-Subunit Protein Cage	279
		11.2.5	Icosahedral Protein Cages: Viruses	282
		11.2.6	Nucleation of Inorganic Nanoparticles Within	200000000000000000000000000000000000000
			Icosahedral Viruses	282
	11.3		er Formation Inside Protein Cage Nanoparticles	283
		11.3.1	Introduction	283
		2 (2) (2)		~ ~ ~
		11.3.2	Azide–Alkyne Click Chemistry in sHsp and P22	285
		11.3.3	Atom Transfer Radical Polymerization in P22	285 287

			CONTENTS	Xi	
	11.4	Coordir	nation Polymers in Protein Cages	292	
		11.4.1	Introduction	292	
		11.4.2	, ,		
			by Preforming Complexes	292	
		11.4.3	Coordination Polymer Formation from Ditopic Ligands		
			and Metal Ions	295	
		11.4.4			
			Hsp-Phen-Fe	296	
	11.5		ry and Perspectives	298	
			vledgments	298	
		Referen	ices	298	
12	Nano	particles	s Synthesized and Delivered by Protein in the Field of		
	Nano	technolo	ogy Applications	305	
	Ichiro	Yamashit	a, Kenji Iwahori, Bin Zheng, and Shinya Kumagai		
	12.1	Nanopa	article Synthesis in a Bio-Template	305	
		12.1.1	NP Synthesis by Cage-Shaped Proteins for		
			Nanoelectronic Devices and Other Applications	305	
		12.1.2	Metal Oxide or Hydro-Oxide NP Synthesis in the		
			Apoferritin Cavity	307	
		12.1.3	Compound Semiconductor NP Synthesis in the		
			Apoferritin Cavity	308	
		12.1.4	NP Synthesis in the Apoferritin with the Metal-Binding		
			Peptides	311	
	12.2	Site-Dia	rected Placement of NPs	312	
		12.2.1	Nanopositioning of Cage-Shaped Proteins	312	
		12.2.2	Nanopositioning of Au NPs by Porter Proteins	313	
	12.3	Fabrica	tion of Nanodevices by the NP and Protein Conjugates	317	
		12.3.1	Fabrication of Floating Nanodot Gate Memory	318	
		12.3.2	Fabrication of Single-Electron Transistor Using Ferritin	321	
		Referen	ices	326	
13	Engi	neored "	Cages" for Design of Nanostructured		
15				329	
	Inorganic Materials Patrick B. Dennis, Joseph M. Slocik, and Rajesh R. Naik				
	13.1	Introdu	ction	329	
	13.2		Binding Peptides	331	
	13.3		e Protein Cages	332	
	13,4		hock Proteins	334	
	13.5		cric Protein and Carbohydrate Quasi-Cages	340	
	13.6		ary and Perspectives	346	
		Referen		347	

PART VI COORDINATION CHEMISTRY INSPIRED BY PROTEIN CAGES

14	Metal-Organic Caged Assemblies Sota Sato and Makoto Fujita		
	14.2	Construction of Polyhedral Skeletons by Coordination Bonds	355
		14.2.1 Geometrical Effect on Products	356
		14.2.2 Structural Extension Based on Rigid, Designable	
		Framework	358
		14.2.3 Mechanistic Insight into Self-Assembly	366
	14.3	Development of Functions via Chemical Modification	366
		14.3.1 Chemistry in the Hollow of Cages	367
		14.3.2 Chemistry on the Periphery of Cages	368
	14.4	Metal-Organic Cages for Protein Encapsulation	370
	14.5	Summary and Perspectives	370
		References	371
Ind	ex		375