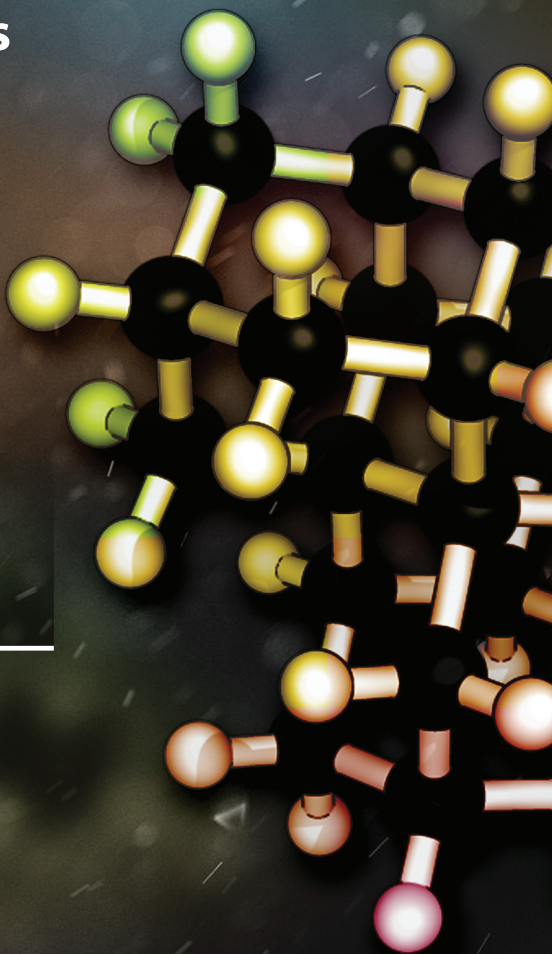


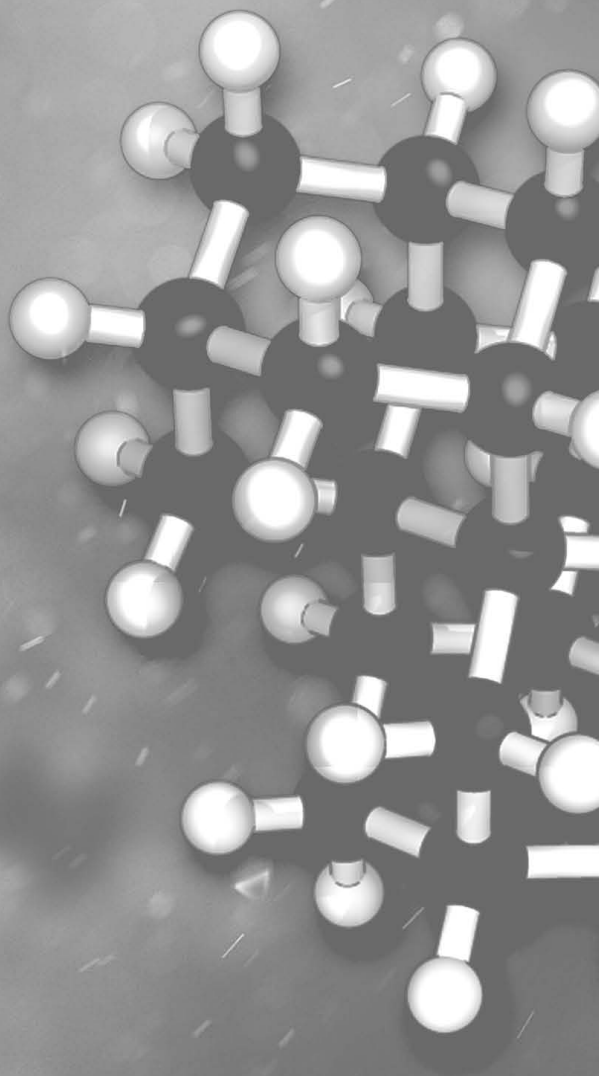
Diamondoids

Synthesis, Properties, and
Applications

Sven Stauss
Kazuo Terashima



Diamondoids



Diamondoids

Synthesis, Properties, and Applications

Sven Stauss
Kazuo Terashima

Published by

Pan Stanford Publishing Pte. Ltd.
Penthouse Level, Suntec Tower 3
8 Temasek Boulevard
Singapore 038988

Email: editorial@panstanford.com

Web: www.panstanford.com

British Library Cataloguing-in-Publication Data

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

Diamondoids: Synthesis, Properties, and Applications

Copyright © 2017 Pan Stanford Publishing Pte. Ltd.

All rights reserved. This book, or parts thereof, may not be reproduced in any form or by any means, electronic or mechanical, including photocopying, recording or any information storage and retrieval system now known or to be invented, without written permission from the publisher.

For photocopying of material in this volume, please pay a copying fee through the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA. In this case permission to photocopy is not required from the publisher.

ISBN 978-981-4745-18-5 (Hardcover)

ISBN 978-981-4745-19-2 (eBook)

Printed in the USA

Contents

<i>Symbols and Abbreviations</i>	xi
<i>Preface</i>	xiii

PART I DIAMONDOIDS: STRUCTURES, PROPERTIES, AND APPLICATIONS

1 Introduction	3
2 Structure, Nomenclature, and Symmetry of Diamondoids	9
2.1 Diamondoids and Their Relation to Other Carbon Nanomaterials	9
2.2 The Structure of Diamondoids	12
2.3 Classification of Diamondoids	14
2.4 Nomenclature and Classification of Diamondoids	18
2.4.1 The von Baeyer Naming Scheme	19
2.4.2 Nomenclature of Diamondoids Based on Dualist Graphs	22
2.4.3 Regular and Irregular Polymantanes	30
2.4.4 Formula Partition Periodic Table	31
2.5 Molecular Symmetry and Crystal Structures of Diamondoids	34
2.5.1 Molecular Symmetry of Diamondoids	35
2.5.2 Crystal Structures of Diamondoids	35
2.6 Differences between Diamondoids and Nanodiamonds	38

3	Chemical and Physical Properties and Characterization of Diamondoids	41
3.1	Chemical Properties	41
3.1.1	Thermodynamic Properties	44
3.1.2	Chemical Stability	45
3.1.3	Solubility of Diamondoids in Gases, Organic Solvents, and Supercritical Fluids	50
3.1.3.1	Solubility in organic solvents	50
3.1.3.2	Solubility in gases and supercritical fluids	53
3.1.4	Biocompatibility and Toxicity	55
3.2	Physical Properties	57
3.2.1	Electronic Properties	57
3.2.1.1	The band structure of diamondoids	58
3.2.1.2	Effect of diamondoid size on bandgap	60
3.2.1.3	HOMO-LUMO variation by functionalization of diamondoids	63
3.2.1.4	Variation of the HOMO-LUMO gap by the inclusion of small atoms inside diamondoids	64
3.3	Optical Properties	68
3.3.1	Vibrational Spectroscopy of Diamondoids	68
3.3.1.1	Infrared spectroscopy	68
3.3.1.2	Raman spectroscopy of diamondoids	68
3.4	Mass Spectrometry of Diamondoids	77
3.4.1	Nuclear Magnetic Resonance Spectroscopy of Diamondoids	77
4	Current and Future Applications of Diamondoids and Their Derivatives	81
4.1	Overview	81
4.2	Applications of Diamondoids in Oil Exploration	82
4.2.1	Formation of Diamondoids in Natural Gas Reservoirs	83
4.3	Current and Possible Future Applications of Diamondoids and Derivatives in Chemistry, Pharmaceuticals, Medicine, and Biotechnology	86

4.3.1	Applications in Chemistry	86
4.3.1.1	Host-guest chemistry	86
4.3.2	Applications of Diamondoids in Pharmaceuticals and Medicine	86
4.3.3	Current and Possible Future Applications of Diamondoids for Drug Delivery	92
4.4	Applications in Materials Science and Nanotechnology	94
4.4.1	Materials Science	94
4.4.2	Diamondoids as an Electron Source	96
4.5	Possible Future Applications of Diamondoids	100
4.5.1	Biotechnology	101
4.5.2	Quantum Computing and Communication	101
4.5.3	Magnetometry	102
4.5.4	Nanorobots and Molecular Machines	103
4.6	Summary	105

PART II ISOLATION AND ORGANIC CHEMICAL SYNTHESIS OF DIAMONDOIDS

5	Occurrence and Isolation of Diamondoids from Natural Gas and Oil Reservoirs	109
5.1	Occurrence of Diamondoids in Natural Gas and Oil Reservoirs	109
5.2	Formation of Diamondoids in Natural Sources	111
5.3	Isolation of Diamondoids from Gas and Oil	115
5.3.1	Alternative Purification Methods	116
6	Approaches for the Organic Synthesis of Diamondoids	119
6.1	A Brief History of the Isolation and Organic Synthesis of Diamondoids	120
6.2	Conventional Organic Chemical Synthesis of Diamondoids	121
6.2.1	Synthesis of Adamantane	121
6.2.2	Synthesis of Diamantane	122
6.2.3	Synthesis of Triamantane	126
6.2.4	Synthesis of Tetramantane	128
6.3	Limitations of the Organic Synthesis of Diamondoids	129

PART III NOVEL APPROACHES FOR THE SYNTHESIS OF DIAMONDOIDS BY MICROPLASMAS

7	Diamondoid Synthesis by Electric Discharge Microplasmas in Supercritical Fluids	133
7.1	Introduction	133
7.2	Generation of Plasmas in Supercritical Fluids	136
7.3	Electric Discharges in High-Pressure and Supercritical Fluid Microreactors	140
7.3.1	Investigation of Possible Diamondoid Reaction Paths by GC-MS Analysis of Intermediate Products	151
8	Synthesis of Diamondoids by Pulsed Laser Plasmas	157
8.1	Application of Pulsed Laser Plasmas in Supercritical Fluids to Nanomaterial Synthesis	161
8.2	Synthesis of Diamondoids by Pulsed Laser Plasmas	162
8.3	Micro-Raman Spectroscopy	163
8.4	Gas Chromatography–Mass Spectrometry	166
8.4.1	Synthesis of Diamantane	166
8.4.2	Possible Synthesis of Diamondoids with $n \geq 3$	167
8.4.3	Effects of Pyrolysis on Synthesized Products	172
8.5	Comparison between PLA in scCO_2 and scXe	173
8.6	Conclusions and Perspectives	174
9	Synthesis of Diamondoids by Atmospheric-Pressure Microplasmas	177
9.1	Introduction	177
9.2	Microchip Microplasma Reactors	179
9.3	Plasma Generation and Characterization	181
9.3.1	Optical Emission Spectroscopy Measurements	183
9.3.2	GC-MS Analysis of Diamantane and Reaction Intermediates	185
9.4	Summary	189

10 Conclusions and Perspectives	191
<i>Appendix</i>	193
<i>A.1 Character Code Tables of Diamondoids</i>	193
<i>Bibliography</i>	195
<i>Index</i>	221

Symbols and Abbreviations

List of Symbols

C_p	Heat capacity	
E	Energy	
E_b	Binding energy	(eV)
E_{VBM}	Valence band maximum	
F_D	Density fluctuation	
M_r	Relative molecular weight	
p	Pressure	(Pa)
p_{crit}	Critical pressure	(Pa)
T	Temperature	(K)
T_{crit}	Critical temperature	(K)
V	Volume	(m ³)
V_{appl}	Applied voltage	(kV)
$V_{\text{p-p}}$	Peak-to-peak voltage	(kV)
β	Compressibility	
κ	Heat conductivity	

List of Abbreviations

CP	Critical point
B3LYP	Becke, three-parameter Lee–Yang–Parr exchange correlation functional used for DFT
DFT	Density functional theory
DOS	Density of electronic states
GC-MS	Gas chromatography–mass spectrometry

HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
SIM	Selected ion monitoring
SXE	Soft X-ray emission

Preface

Like a modern drama, one could consider this book to consist of three main acts: In the first act, we set the stage for the topic and expose the main actors, that is, diamondoids, and their relation to other carbon nanomaterials. In the same part, we delve more deeply into the chemical and physical properties of diamondoids and give an overview of their current and possible future applications.

In the second part of the book, we, little by little, approach the main complications related to the application of especially larger diamondoids: the current approaches for obtaining diamondoids and the current attempts to obtain them by conventional chemical synthesis. In particular, we aim at demonstrating the different problems associated with the various conventional approaches.

Finally, in the third part, we present possible alternative solutions for synthesizing diamondoids from the smallest member, adamantane, using plasmas generated in supercritical fluids. Because the field of plasmas generated in such high-density fluids is still not known to a wide audience, we are first briefly presenting the properties and applications of supercritical fluids before discussing the properties of electric discharge and pulsed laser plasmas generated in supercritical fluids.

The last part of the book deals with the application of such plasmas for diamondoids in more detail before giving a final assessment of the current state of the research on diamondoids.

Molecular diamonds, commonly called diamondoids, are a very interesting class of carbon nanomaterials that can be considered the archetypical molecular building block. While still not as widely known as other carbon nanomaterials, such as carbon nanotubes and graphene, previous and current research shows that this class of

materials holds a lot of promise for many different fields of science and nanotechnology.

One of the goals in preparing this book was to introduce interested readers to the field of diamondoids; their structure, chemical, and physical properties; and the different isolation and synthesis approaches that currently exist. In addition to conventional isolation and synthesis approaches, we also introduce new ones, especially those based on electric discharge and pulsed laser plasmas generated inside supercritical fluids and at atmospheric pressure.

We hope that the present book will be useful not only as both an introductory and a reference text on diamondoids but also as an inspiration for further research on this remarkable class of nanomaterials.

This book is mainly aimed at researchers and graduate students who are curious about the field of diamondoids, that is, materials science, physics, and chemistry, but we hope that it will also be interesting for persons from other fields of science and technology.

One of our goals in writing this book was to make it an introductory text on diamondoids aimed at researchers and graduate students active in the field and at the same time to make it also a stand-alone text so that people who are not familiar with certain topics do not have to refer to the scientific literature themselves.

Special care was given to the figures and graphs. Whenever possible, we remade both graphs and figures in this book in order to avoid raster images as much as possible. In the cases where we have relied on data from other publications, we have indicated all the original data sources and references. We also tried to make the figure and table captions as self-explanatory as possible so that people who just want to flip through the book can understand the main points of an illustration or graph without having to resort to the main text.

For those readers who wish to delve more deeply into the field of diamondoids, we have compiled a comprehensive list of the current scientific literature. Especially the field of organic synthesis of diamondoids is very vast. However, for the convenience of the readers, we have limited ourselves to those references that can currently be accessed electronically.

In writing this book, we have tried to remain as general and make the contents as enduring as possible, but at the same time we also wanted to provide the reader with the latest results of the research on diamondoids. However, we are fully aware that with today's rapid pace with which science and technology advance, the contents of this book might become outdated quite rapidly. Nevertheless, we hope that this will not happen too soon and that it can serve researchers from many different backgrounds as a reference and hopefully also as an inspiration for their own research.

A very special thank-you goes to Stanford Chong for suggesting this book project and his patience and encouragement during the writing process. We are also indebted to all the staff at Pan Stanford Publishing for their efforts in bringing this book to print.

We would like to thank the following persons for their support in the work related to this book:

- Prof. Takehiko Sasaki for his help with mass spectrometry measurements and comments concerning the interpretation of the results
- Prof. Hiroshi Kataoka and Dr. Minoru Suzuki (now at Shimadzu Corp.) for their support with gas chromatography-mass spectrometry measurements and helpful discussions
- Prof. Tohru Suemoto and Prof. Motoyoshi Baba (now at Saitama University) for their help with pulsed laser ablation
- Dr. Keiichiro Urabe (now at Air Liquide) for commenting on one of the very early drafts of the manuscript
- All present and former students of the Terashima Lab for the work presented in this text

Concerning the experiments on diamondoid synthesis, we would like to thank Dr. Takaaki Tomai (now at Tohoku University), Dr. Hiroyuki Miyazoe (now at IBM Thomas J. Watson Research Center), Hirokazu Kikuchi, Sho Nakahara, Tomoki Shizuno, Fumita Oshima, Chikako Ishii, Satoshi Kato, and Koichi Kuribara. We would also like to thank Dr. David Z. Pai (Université de Poitiers) for his contribution to atmospheric-pressure diamondoid synthesis.

Since the topic of diamondoids encompasses various branches of science and readers are most probably from many different fields of science, we have tried to keep the text as self-explanatory as

possible. Especially organic chemists might find our treatment of organic synthesis too basic; however, as some of the readers (and the authors) do not have a background in organic chemistry, we hope that they can bear with us.

As any book, probably this one also contains many errors and oversights, and any mistakes in the text are entirely the responsibility of the authors. We are grateful for any feedback from the readers, and we are grateful for any feedback from the readers to point us to these.

Finally, we hope that the book can serve both as a reference text and an inspiration, both for seasoned researchers and new students, and that the field of diamondoids can grow more in the future.

This work was supported financially in part by a Grant-in-Aid for Scientific Research on Innovative Areas (Frontier Science of Interactions between Plasmas and Nano-interfaces, Grant No. 21110002) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan. The authors thank the Materials Design and Characterization Laboratory, Institute for Solid State Physics, University of Tokyo, for providing access to the pulsed laser facility.

Sven Stauss

Kazuo Terashima

Kashiwa and Tokyo, Japan