

World Scientific Series on Carbon Nanoscience

HANDBOOK OF CARBON NANO MATERIALS

Volume 1

Synthesis and Supramolecular Systems

Editors

Francis D'Souza

Karl M. Kadish

World Scientific Series on Carbon Nanoscience

HANDBOOK OF CARBON NANO MATERIALS

Volume 1

Synthesis and Supramolecular Systems

Editors

Francis D'Aluza
Wichita State University, USA

Karl M. Kadish

University of Houston, USA



 World Scientific

NEW JERSEY • LONDON • SINGAPORE • BEIJING • SHANGHAI • HONG KONG • TAIPEI • CHENNAI

Published by

World Scientific Publishing Co. Pte. Ltd.

5 Toh Tuck Link, Singapore 596224

USA office: 27 Warren Street, Suite 401-402, Hackensack, NJ 07601

UK office: 57 Shelton Street, Covent Garden, London WC2H 9HE

British Library Cataloguing-in-Publication Data

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

HANDBOOK OF CARBON NANO MATERIALS

Volume 1: Synthesis and Supramolecular Systems

Copyright © 2011 by World Scientific Publishing Co. 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-13 978-981-4327-81-7 (Set)

ISBN-10 981-4327-81-6 (Set)

ISBN-13 978-981-4350-20-4 (Vol. 1)

ISBN-10 981-4350-20-6 (Vol. 1)

Typeset by Stallion Press

Email: enquiries@stallionpress.com

Printed by Fulisland Offset Printing (S) Pte Ltd. Singapore

HANDBOOK OF CARBON NANO MATERIALS

Volume 1
Synthesis and Supramolecular Systems

Preface

This *Handbook of Carbon Nanomaterials* celebrates the 25th anniversary of the discovery of Fullerenes, then known as Buckyballs. Since their discovery in 1985, fullerenes as well as carbon nanotubes and graphenes, two closely related carbon allotropes, have taken up a solid place in modern science and technology as evidenced by the awarding of two Nobel Prizes — the first, in Chemistry, was given in 1996 to Robert F. Curl Jr., Sir Harold Kroto and Richard E. Smalley for the discovery of fullerenes and the second, in Physics, was awarded in 2010 to Andre Geim and Konstantin Novoselov for the isolation of graphene using Scotch tape as a tool. Since 1985, more than 100,000 scientific papers have been published on topics devoted to fullerenes, carbon nanotubes and related materials and there is no doubt that these types of carbon nanomaterials, with their unique structures and properties, will continue to find many new applications in all areas of science and technology.

The present *Handbook of Carbon Nanomaterials* consists of 23 chapters in two volumes which, as a whole, summarize current work and the latest developments in the field of carbon nanomaterials as seen through the eyes of more than three dozen leading researchers from around the world. The topics covered in this two volume set of books can be divided into four general areas. The first deals with the chemistry of fullerenes and carbon nanotubes, including organic functionalization, reactivity, perfluoroalkylation and fullerenes linked to photosensitizers. The second covers the chemistry and physics of endohedral fullerenes. The third major area of coverage involves molecular and supramolecular chemistry of fullerenes and carbon nanotubes while the fourth includes topics related to photoinduced energy and electron transfer. Finally, applications of fullerenes, carbon nanotubes and graphenes as applied to organic molecular electronics, polymers composites, thermal conductive materials, photovoltaics and sensing are presented.

This Handbook was written as a hands on reference guide for scientists working in the fields of chemistry, physics, materials science, polymer science, solid-state physics, nanotechnology or supramolecular science. The coverage of topics presented is both in-depth and comprehensive, and when combined with the perspectives for future research given by the contributing authors makes this book an invaluable reference source which should be considered essential reading for both students and advanced researchers in the field.

The editors would like to acknowledge all of the contributors for their timely submission of the state-of-the-art review topics; We also acknowledge NSF, Kansas-EPSCoR, ACS-PRF (to FD) and the Robert A Welch Foundation (to KMK) for financial support; last but not least, the staff of World Scientific Publishing Co are acknowledged for their immense help in bringing out this publication in a timely manner.

Francis D'Souza
Wichita, KS, USA

Karl M. Kadish
Houston, TX, USA

December 18, 2010

List of Contributors*

Takeshi Akasaka

University of Tsukuba
Tsukuba, Ibaraki, Japan
E-mail: akasaka@tara.tsukuba.ac.jp
Chapter 5

Olga V. Boltalina

Colorado State University
Fort Collins, CO 80523, USA
Email: olga.boltalina@colostate.edu
Chapter 4

Peter D.W. Boyd

The University of Auckland
Auckland 1142, New Zealand
Email: pdw.boyd@auckland.ac.nz
Chapter 11

John W. Connel

NASA Langley Research Center
Hampton, VA 23681, USA
E-mail: john.w.connell@nasa.gov
Chapter 22

Juan Luis Delgado

Universidad Complutense
Madrid, Spain
Chapter 10

Francis D'Souza

Wichita State University
Wichita, KS 67260, USA
Email: Francis.DSouza@wichita.edu
Chapter 21

Luis Echegoyen

University of Texas at El Paso
El Paso, TX 79968, USA
E-mail: echegoyen@utep.edu
Chapter 10

Fernando Fernández-Lázaro

Universidad Miguel Hernández
Alicante, Spain
Chapter 19

Salvatore Filippone

Universidad Complutense
Madrid, Spain
Chapter 2

Tsuyohiko Fujigaya

Kyushu University
Fukuoka 819-0395, Japan
Chapter 8

*Full Contact Information for authors can be found on the title page of each chapter.

Shunichi Fukuzumi

Osaka University
Osaka 565-0871, Japan
Email: fukuzumi@chem.eng.
osaka-u.ac.jp
Chapter 16

Paris E. Georghiou

Memorial University of
Newfoundland
St. Johns, Canada
Email: parisg@mun.ca
Chapter 12

Sayata Ghose

National Institute of Aerospace
Hampton, VA 23666, USA
Chapter 22

David González-Rodríguez

Universidad Autónoma
Madrid, Spain
Chapter 3

Dirk M. Guldi

Friedrich-Alexander-Universität
Erlangen-Nürnberg
Erlangen, Germany
Email: guldi@chemie.uni-erlangen.de
Chapter 20

Uwe Hahn

Universidad Autónoma de Madrid
Madrid, Spain
Chapter 3

Maria Antonia Herrero

Universidad de Castilla-La Mancha
Ciudad Real, Spain
Chapter 9

Ali Hosseini

The University of Auckland
Auckland 1142
New Zealand
Chapter 11

Piétrick Hudhomme

Université d'Angers
Angers, France
Email: pietrick.hudhomme@univ-
angers.fr
Chapter 17

Julien Iehl

Université de Strasbourg et CNRS
Strasbourg Cedex 2, France
Chapter 1

Hiroshi Imahori

Kyoto University
Kyoto, Japan
Email: imahori@scl.kyoto-u.ac.jp
Chapter 18

Osamu Ito

CarbonPhotoScience
Sendai, Japan
Email: ito@tagen.tohoku.ac.jp
Chapters 14, 15

Marta Izquierdo

Universidad Complutense
Madrid, Spain
Chapter 2

Chang Yi Kong

Clemson University
Clemson, SC 29634, USA
Chapter 22

Włodzimierz Kutner

Polish Academy of Sciences
Warsaw, Poland
E-mail: wkutner@ichf.edu.pl
Chapter 21

Igor V. Kuvychko

Colorado State University
Fort Collins, CO 80523, USA
Chapter 4

Helge Lemmetyinen

Tampere University of
Technology
Tampere, Finland
Chapter 13

Yi Lin

National Institute of Aerospace
Hampton, VA 23666, USA
E-mail: yi.lin@nianet.org
Chapter 22

Nazario Martín

Universidad Complutense de
Madrid
Madrid, Spain
Email: nazmar@quim.ucm.es
Chapters 2, 10

Ángel Martín-Domenech

Universidad Complutense
Madrid, Spain
Chapter 2

Luis Martín-Gomis

Universidad Miguel Hernández
Alicante, Spain
Chapter 19

Aurelio Mateo-Alonso

Albert-Ludwigs-Universität
Freiburg
Freiburg i. Brsg, Germany
Chapter 20

Jackson D. Megiatto, Jr.

New York University
New York 10003, USA
Email: jackson.megiatto@nyu.edu
Chapter 7

Mohammed J. Meziani

Clemson University
Clemson, SC 29634, USA
Chapter 22

Shigeru Nagase

Institute for Molecular Science
Okazaki, Aichi, Japan
E-mail: nagase@ims.ac.jp
Chapter 5

Naotoshi Nakashima

Kyushu University
Fukuoka 819-0395, Japan
Email: nakashima-tcm@mail.
cstm.kyushu-u.ac.jp
Chapter 8

Jean-François Nierengarten

Université de Strasbourg et CNRS
Strasbourg Cedex 2, France
Email: nierengarten@chimie.u-
strasbg.fr
Chapter 1

Angy L. Ortiz

Clemson University
Clemson, SC 29634, USA
Chapter 10

Piotr Pieta

Polish Academy of Sciences
Warsaw, Poland
Chapter 21

Maurizio Prato

Università di Trieste
34127 Trieste, Italy
Email: prato@units.it
Chapter 9

Christopher A. Reed

University of California
Riverside CA 92521, USA
Chapter 11

Slava V. Rotkin

Lehigh University
Bethlehem, PA 18015, USA
E-mail: rotkin@lehigh.edu
Chapter 23

Ángela Sastre-Santos

Universidad Miguel Hernández
Alicante, Spain
E-mail: asastre@umh.es
Chapter 19

David I. Schuster

New York University
New York, 10003, USA
E-mail: david.schuster@nyu.edu
Chapter 7

Natalia B. Shustova

Colorado State University
Fort Collins, CO 80523, USA
Chapter 4

Steven Stevenson

University of Southern Mississippi
Hattiesburg, MS, 39406, USA
Email: Steven.Stevenson@usm.edu
Chapter 6

Steven H. Strauss

Colorado State University
Fort Collins, CO 80523, USA
Email: steven.strauss@colostate.edu
Chapter 4

Ya-Ping Sun

Clemson University
Clemson, SC 29634, USA
E-mail: syaping@clemson.edu
Chapter 22

Toshikazu Takata

Tokyo Institute of Technology,
Tokyo, 152-8552, Japan
Chapter 15

Yasuhiko Tanaka

Kyushu University
Fukuoka 819-0395, Japan
Email: ttakata@polymer.titech.ac.jp
Chapter 8

Leilei Tian

Clemson University
Clemson, SC 29634, USA
Chapter 22

Nikolai V. Tkachenko

Tampere University of Technology
Tampere, Finland
Email: nikolai.tkachenko@tut.fi
Chapter 13

Tomás Torres

Universidad Autónoma de Madrid
Madrid, Spain
Email: tomas.torres@uam.es
Chapter 3

Tomokazu Umeyama

Kyoto University
Kyoto 615-8510, Japan
Chapter 18

Maxence Urbani

Université de Strasbourg et CNRS
Strasbourg Cedex 2, France
Chapter 1

John D. van Paauwe

The University of Auckland
Auckland 1142, New Zealand
Chapter 11

Ester Vazquez

Universidad de Castilla-La Mancha
Ciudad Real, Spain
Chapter 9

L. Monica Veca

Clemson University
Clemson, SC 29634, USA
Email: lveca@clemson.edu
Chapter 22

Wei Wang

Clemson University
Clemson, SC 29634, USA
Chapter 22

Mateusz Wielopolski

Friedrich-Alexander-Universität
Erlangen-Nürnberg
Erlangen, Germany
Chapter 20

René M. Williams

Universiteit van Amsterdam
Amsterdam, The Netherlands
E-mail: r.m.williams@uva.nl
Chapter 17

Michio Yamada

Tokyo Gakugei University
Tokyo, Japan
Chapter 5

Contents of Volumes 1 and 2

Volume 1 – Synthesis and Supramolecular Systems

1. Chemistry with Fullerene Building Blocks
Julien Iehl, Maxence Urbani and Jean-François Nierengarten
2. New Reactivity in Fullerene Chemistry
Marta Izquierdo, Salvatore Filippone, Ángel Martín-Domenech and Nazario Martín
3. Phthalocyanine Functionalized Carbon Nanostructures
Uwe Hahn, David González-Rodríguez and Tomás Torres
4. Perfluoroalkylation of Fullerenes
Olga V. Boltalina, Igor V. Kuvychko, Natalia B. Shustova and Steven H. Strauss
5. New Vistas in Endohedral Metallofullerenes
Michio Yamada, Takeshi Akasaka and Shigeru Nagase
6. Metallic Oxide Clusters in Fullerene Cages
Steven Stevenson
7. Synthesis of Electron Donor-[60]Fullerene Multi-Ring Interlocked Systems
Jackson D. Megiatto, Jr. and David I. Schuster
8. Solubilized Carbon Nanotubes and Their Redox Chemistry
Naotoshi Nakashima, Yasuhiko Tanaka and Tsuyohiko Fujigaya
9. Recent Advances in Covalent Functionalization and Characterization of Carbon Nanotubes
Maria Antonia Herrero, Ester Vazquez and Maurizio Prato

10. Reactions and Retro-reactions of Fullerenes
Angy L. Ortiz, Luis Echegoyen, Juan Luis Delgado and Nazario Martín
11. Porphyrin-Fullerene Supramolecular Chemistry
*Peter D.W. Boyd, Ali Hosseini, John D. van Paauwe
and Christopher A. Reed*
12. Supramolecular Hosts for Pristine Fullerenes
Paris E. Georghiou

Volume 2 Electron Transfer and Applications

13. Dynamics of Photoinduced Charge Transfer of Fullerene Based Donor–Acceptor Systems: From Solution to Organized Molecular Films
Nikolai V. Tkachenko and Helge Lemmetyinen
14. Photoinduced Electron Transfer Between Fullerenes and Electron-Donors Through Molecular Bridges
Osamu Ito
15. Photoinduced Electron Transfer Processes of Fullerene Rotaxanes
Toshikazu Takata and Osamu Ito
16. Electron Donor–Acceptor Nanohybrids and Their Application to Light–Energy Conversion
Shunichi Fukuzumi
17. Energy and Electron Transfer in Photo- and Electro-Active Fullerene Dyads
Pi  trick Hudhomme and Ren   M. Williams
18. Fullerenes for Photoelectrochemical and Photovoltaic Devices
Hiroshi Imahori and Tomokazu Umeyama
19. Fullerenes as Photosensitizers in Photorefractive Materials
*  ngela Sastre-Santos, Luis Mart  n-Gomis
and Fernando Fern  ndez-L  zaro*

20. Functionalized Fullerene Derivatives in Organic Molecular Electronics
Mateusz Wielopolski, Aurelio Mateo-Alonso and Dirk M. Guldi
21. Preparation, Properties, and Application of Polymer Composites of Carbon Nanotubes
Piotr Pieta, Francis D'Souza and Włodzimierz Kutner
22. Thermal Conductive Materials Based on Carbon Nanotubes and Graphene Nanosheets
L. Monica Veca, Wei Wang, Yi Lin, Mohammed J. Meziani, Leilei Tian, John W. Connel, Sayata Ghose, Chang Yi Kong and Ya-Ping Sun
23. Electronic Properties of DNA-SWNT Hybrids: From Charge Separation to Optical Sensing
Slava V. Rotkin

Contents

<i>Preface</i>	xiii
<i>List of Contributors</i>	xv
<i>Contents of Volumes 1 and 2</i>	xxi
1 / Chemistry with Fullerene Building Blocks	1
<i>Julien Iehl, Maxence Urbani and Jean-François Nierengarten</i>	
1. Introduction	1
2. Fullerene Building Blocks for Porphyrin Synthesis	2
3. Fullerene Building Blocks for Dendrimer Synthesis	6
3.1. Divergent synthesis	8
3.2. Convergent synthesis	10
4. Click Chemistry with Fullerene Building Blocks	16
4.1. Click chemistry with fullerene mono- and bis-adducts	16
4.2. Click chemistry with fullerene hexa-adducts	22
5. Conclusions and Perspectives	28
References	28
2 / New Reactivity in Fullerene Chemistry	33
<i>Marta Izquierdo, Salvatore Filippone, Ángel Martín-Domenech and Nazario Martín</i>	
1. Introduction	33
2. Regioselective Intramolecular <i>cis-1</i> Cycloadditions to Fullerenes	34
2.1. Intramolecular nucleophilic addition of phenols	35
2.2. Intramolecular nucleophilic addition of alcohols and thiols	37
3. Fuller-1,6-enynes: New and Versatile Building Blocks in Fullerene Chemistry	38
3.1. The Pauson–Khand reaction on [60]fullerene	39
3.2. Thermally induced [2+2] cyclizations from fuller-1,6-enynes	45
3.3. Thermally induced intramolecular ene reaction of fuller-1,6-enynes: synthesis of fulleroallenes	46

3.4. Theoretical study of the thermal intramolecular reactions of fuller-1,6-enynes	47
4. Catalytic Enantioselective Cycloadditions: Chiral Fullerenes	49
References.	55

3 / Phthalocyanine Functionalized Carbon Nanostructures 59

Uwe Hahn, David González-Rodríguez and Tomás Torres

1. Introduction	59
2. Phthalocyanine-Fullerene Assemblies.	60
2.1. Covalent phthalocyanine-fullerene systems.	61
2.2. Non-covalent phthalocyanine-fullerene systems	75
3. Phthalocyanine-CNT Assemblies.	83
3.1. Covalent phthalocyanine-carbon nanotube systems	84
3.2. Non-covalent phthalocyanine-carbon nanotube systems	89
4. Conclusions and Perspectives	93
Acknowledgments	94
References.	94

4 / Perfluoroalkylation of Fullerenes 101

*Olga V. Boltalina, Igor V. Kuvychko, Natalia B. Shustova
and Steven H. Strauss*

1. Methods of Synthesis	102
1.1. General remarks	102
1.2. <i>In situ</i> formation of PFAFs in an arc generator or mass spectrometer	103
1.3. Synthesis of PFAFs: reactions with metal trifluoroacetates.	105
1.4. Synthesis of PFAFs: reactions with perfluoroalkyl iodides	107
1.4.1. Reactions with CF_3I	108
1.4.2. Reactions with $\text{R}_\text{F}\text{I}$ ($\text{R}_\text{F} = \text{C}_2\text{F}_5, \text{C}_3\text{F}_7, \text{C}_4\text{F}_9, \text{C}_6\text{F}_{13},$ and $\text{C}_{12}\text{F}_{25}$)	112
2. Methods of Isolation and Characterization.	115
2.1. Selective syntheses of PFAFs.	115
2.2. Purification methods	119
2.3. Characterization	123
2.3.1. Mass spectrometry	123
2.3.2. Vibrational and UV-vis spectroscopy	125
2.3.3. NMR spectroscopy	127
2.3.4. X-ray crystallography	128

3. Physical Properties	134
4. Electrochemical Properties	135
5. Chemical Properties	137
6. Conclusions and Perspectives	139
References.	139

5 / New Vistas in Endohedral Metallofullerenes 145

Michio Yamada, Takeshi Akasaka and Shigeru Nagase

1. Introduction	146
2. Cage Frameworks, Positions, and Movements of Encaged Species	147
2.1. Monometallofullerenes.	147
2.2. Dimetallofullerenes	149
2.3. Clusterfullerenes	153
3. Electronic Properties of Pristine Endohedral Metallofullerenes	154
4. Chemistry of Endohedral Metallofullerenes	156
4.1. Bis-silylation	156
4.2. Electrophilic carbene addition.	160
4.3. 1,3-Dipolar cycloaddition.	165
4.4. Nucleophilic addition.	168
4.5. Diels–Alder reaction.	170
4.6. Radical reaction.	173
5. Electronic Tuning by Chemical Functionalization.	175
6. Conclusions and Perspectives	180
Acknowledgments	180
References.	180

6 / Metallic Oxide Clusters in Fullerene Cages 185

Steven Stevenson

1. Introduction	186
2. Synthesis	188
2.1. Historical perspective on oxometallic fullerene (OMF) and metallic nitride fullerene (MNF) synthesis	188
2.2. Electric-arc synthesis of OMFs	189
3. Isolation	191
3.1. Stir and Filter Approach (SAFA) for $\text{Sc}_4\text{O}_2@\text{C}_{80}$ and $\text{Sc}_4\text{O}_3@\text{C}_{80}$	192
3.2. Selective precipitation method using Lewis acids	196
3.2.1. Isolation of a Stage 1 metallofullerene (<i>e.g.</i> , $\text{Sc}_4\text{O}_3@\text{C}_{80}$)	198

3.2.2. Isolation of a Stage 2 metallofullerene (<i>e.g.</i> , $\text{Sc}_2\text{O}@\text{C}_{82}$)	199
4. Reactivity	200
4.1. Reactivity comparison with other fullerenes	200
4.2. Reactivity comparison to electrochemical band gap	201
5. UV Characterization	203
6. Conclusions and Perspectives	203
Acknowledgments	203
References.	203
 7 / Synthesis of Electron Donor-[60]Fullerene Multi-Ring Interlocked Systems	 207
<i>Jackson D. Megiatto, Jr. and David I. Schuster</i>	
1. Introduction	207
2. Electron Transfer Reactions in Artificial Photosynthetic Systems	209
3. Supramolecular Artificial Photosynthesis — Catenanes and Rotaxanes	210
4. Synthesis of Ferrocene- C_{60} -Rotaxane	216
5. Synthesis of Zn(II)-Porphyrin-“Stoppered”- C_{60} -Rotaxane.	221
6. Synthesis of Zn(II)-Porphyrin- C_{60} -[2]Catenates	224
7. Structural Characterization	226
8. Synthesis of [3]Catenates	228
9. Conclusion and Perspectives	238
References.	240
 8 / Solubilized Carbon Nanotubes and Their Redox Chemistry	 245
<i>Naotoshi Nakashima, Yasuhiko Tanaka and Tsuyohiko Fujigaya</i>	
1. Introduction	245
2. Characterizations of Individually Solubilized Carbon Nanotubes.	247
3. Individual Solubilization of SWNTs Using Surfactant Micelles	247
4. DNA/Carbon Nanotube Hybrids	249
5. Individual Solubilization of SWNTs Using Functional Aromatic Molecules	251
6. Nanotube/Polymer Composites	254
7. Redox Reaction and Determination of Electronic States of Carbon Nanotubes.	254