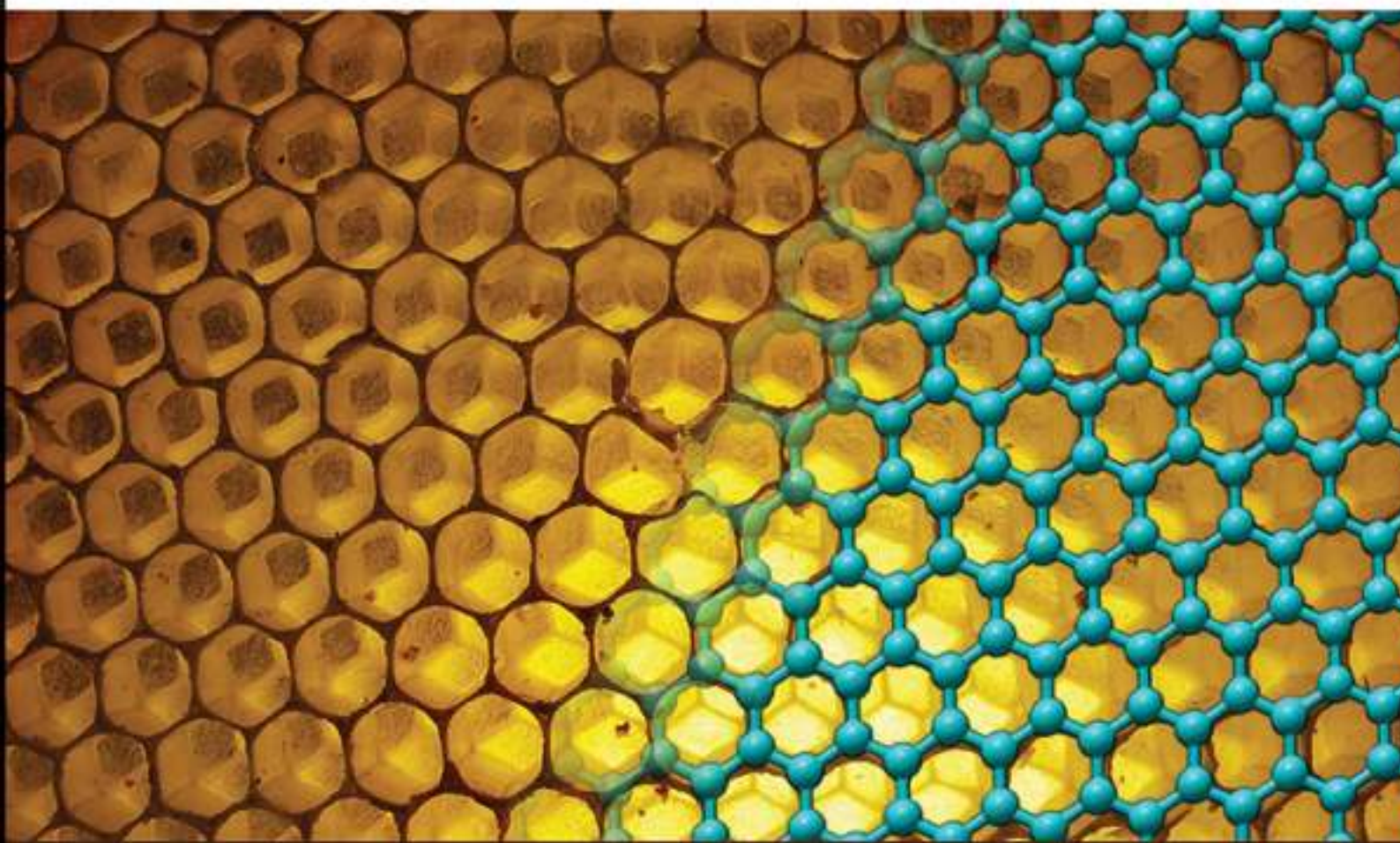


Organic Nanomaterials

Synthesis, Characterization, and Device Applications

EDITED BY **Tomás Torres and Giovanni Bottari**



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ORGANIC NANOMATERIALS

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Edited by

TOMÁS TORRES

Departamento de Química Orgánica
Facultad de Ciencias
Universidad Autónoma de Madrid
Madrid, Spain *and* IMDEA Nanociencia
C/Faraday 9
Ciudad Universitaria de Canto Blanco
Madrid, Spain

GIOVANNI BOTTARI

Departamento de Química Orgánica
Facultad de Ciencias
Universidad Autónoma de Madrid
Madrid, Spain *and* IMDEA Nanociencia
C/Faraday 9
Ciudad Universitaria de Canto Blanco
Madrid, Spain

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PREFACE

In the last decade, much progress has been made in the field of organic nanomaterials. Recent developments in nanoscience and nanotechnology have driven this field forward, thus allowing the preparation of novel materials with controlled morphology and well-defined properties, with clear and exciting technological applications. The new insights into the optoelectronic properties of molecules, together with the recent development of techniques such as scanning probe microscopy, among many others, have pushed chemists to design novel molecular and supramolecular functional architectures. The implications range from the basic molecular self-assembly of complementary organic systems, which constitute an important part of the so-called “bottom-up approach” to exciting new applications of pure organic or hybrid materials, like the ones expected for low dimensional carbon nanostructures, such as fullerenes, nanotubes, and graphenes, or the recent developments in molecular photovoltaics, for example, in nanostructured hybrid materials for energy conversion and storage. The aim of this book entitled *Organic Nanomaterials: Synthesis, Characterization, and Device Applications*, is to present an appropriate and representative coverage of these materials, which constitute one of the most actively pursued fields of science.

This book contains 26 chapters, which have been rationally organized in five main parts. The first part is concerned with introductory and general chapters on nanomaterials and self-assembled nanostructures. Christensen and Tomalia propose a classification strategy for well-defined, soft-matter nanoscale building blocks (Chapter 1), Schenning and González-Rodríguez analyze the role of hydrogen bonding in the nanoscale organization of π -conjugated materials (Chapter 2), and Amabilino reviews some interesting aspects of chiral, organic nanomaterials (Chapter 3). An overview of a class of biochemical nanomaterials is given

by Javakhishvili and Hvilsted (Chapter 4), followed by thorough studies of self-assembled porphyrin nanostructures and their potential applications by Shelnett and Medforth (Chapter 5); finally, electron-transfer functions of nonplanar porphyrins are studied by Fukuzumi and Kojima (Chapter 6).

The second part of the book consists of a series of chapters devoted to carbon nanostructures ranging from fullerenes (including endohedral fullerenes) and carbon nanotubes to graphene, which report on properties, theoretical studies, and applications. The supramolecular aspects of receptors for the molecular recognition of fullerenes are described by Canevet, Pérez, and Martín (Chapter 7), whereas covalent, donor–acceptor ensembles based on phthalocyanines and carbon nanostructures, including graphene, are reviewed by Bottari, Urbani, and Torres (Chapter 8). Breakthroughs in the photophysics of carbon nanotubes are covered by two excellent contributions addressing (a) the photoinduced electron-transfer properties of supramolecular carbon nanotube materials decorated with photoactive sensitizers, outlined by D’Souza, Sandanayaka, and Ito (Chapter 9), and (b) the study of the interactions of porphyrins and phthalocyanines with carbon nanotubes, which is presented by Bartelmeß and Guldi (Chapter 10). The next two chapters are dedicated to endohedral fullerenes, namely to the synthesis of systems encapsulating helium, dihydrogen, and water, by Murata, Murata, and Komatsu (Chapter 11), and to fundamental and applied aspects of endohedral metallofullerenes by Akasaka and co-workers (Chapter 12). In these two interesting chapters, the authors present new insights into the chemistry and properties of endohedral fullerenes. This block of the book mainly devoted to carbon nanostructures is closed with an excellent update on electrochemical characterization and potential applications of carbon materials by Echegoyen and co-workers (Chapter 13),

followed by a theoretical approach to solvating insoluble carbon nanostructures by molecular dynamics by Calvaresi and Zerbetto (Chapter 14).

The third group of chapters focuses on different aspects of some inorganic materials, self-assembled monolayers, organic field effect transistors, and molecular self-assembly at solid surfaces. Thus, the topic of inorganic metal capsules with redox-active guests is treated by Macdonell and Cronin (Chapter 15), whereas the following two chapters developed by Huskens and co-workers (Chapter 16) and by Laromaine and Mace (Chapter 17) review the use of stimuli-responsive monolayers and self-assembled monolayers as model biosurfaces, respectively. Finally, the low-dimensionality effects in organic field effect are described by Biscarini and co-workers (Chapter 18), and the block is well-complemented by the growth of organic nanomaterials by molecular self-assembly at solid surfaces, which is developed by Gallego, Otero, and Miranda (Chapter 19).

The fourth part of the book consists of a series of chapters dealing with different areas involving both biological aspects and nanomaterials. In this part, Vélez reports on the interesting area of biofunctionalized surfaces (Chapter 20), whereas Fabbro, Da Ros, and Prato describe carbon nanotube derivatives as anticancer drug delivery systems (Chapter 21), with a special attention to the medical applications of different kinds of carbon nanotube-based nanomaterials. Closing this section, a study on porous nanomaterials for biomedical applications is outlined by De Cola and co-workers (Chapter 22), whereas Foldvari and co-workers report on nanoparticle design for gene therapy (Chapter 23).

The book ends with three comprehensive applied chapters, as examples of the potential use of organic nanostructured materials in nanoscience, which are devoted to sensors and molecular photovoltaics. This part starts with a chapter by Ratera, Tárraga, Molina, and Vecianna which discusses the sensing of Hg(II) ions in water (Chapter 24), and it is followed by two chapters on the main fields of organic solar cells, namely, organic nanomaterials for efficient bulk heterojunctions by Troshin and Sariciftci (Chapter 25), and mesoscopic dye-sensitized solar cells by Nazeeruddin, Ko, and Grätzel (Chapter 26).

Most chapters end with a summarizing conclusion that also serves as an abstract. The combined authors of the chapters give a good representation of the organic nanomaterials, although with different styles as is often the case in multi-author books.

Finally, and most importantly, we are indebted to all the authors for all their efforts in the preparation of their contributions, which we hope the readers will appreciate.

The editors would like to dedicate this book to the memory of our colleague and friend Christian G. Claessens, who recently passed away.

TOMÁS TORRES
GIOVANNI BOTTARI

*Universidad Autónoma de Madrid, Spain
April 2013*

CONTRIBUTORS

Takeshi Akasaka, Life Science Center of Tsukuba Advanced Research Alliance, University of Tsukuba, Tsukuba, Ibaraki 305-8577, Japan; *and* College of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, China

David B. Amabilino, Institut de Ciència de Materials de Barcelona, Consejo Superior de Investigaciones Científicas, Campus Universitari de Bellaterra, 08193 Cerdanyola del Vallès, Catalonia, Spain

Idiko Badea, College of Pharmacy and Nutrition, University of Saskatchewan, Saskatoon, Saskatchewan, S7N 5C9, Canada

Juergen Bartelmeß, Department of Chemistry and Pharmacy, Interdisciplinary Center for Molecular Materials (ICMM), Friedrich-Alexander-Universität Erlangen-Nürnberg, 91058 Erlangen, Germany

Mario Barteri, Department of Chemistry, Università “La Sapienza”, 00195, Rome, Italy

Fabio Biscarini, Università degli Studi di Modena e Reggio Emilia, Dipartimento di Scienze della Vita, via Campi 183, I-41125, Modena Italy and Consiglio Nazionale delle Ricerche (CNR), Istituto per lo Studio dei Materiali Nanostrutturati (ISMN), 40129 Bologna, Italy

Giovanni Bottari, Departamento de Química Orgánica, Facultad de Ciencias, Universidad Autónoma de Madrid, 28049 Madrid, Spain; *and* IMDEA Nanociencia, C/Faraday 9, Ciudad Universitaria de Canto Blanco, E28049 Madrid, Spain

Matteo Calvaresi, Dipartimento di Chimica “G. Ciamician”, Università di Bologna, 40126 Bologna, Italy

David Canevet, Laboratoire MOLTECH-Anjou, 49045 ANGERS Cedex 01, France

Stefano Casalini, Consiglio Nazionale delle Ricerche (CNR), Istituto per lo Studio dei Materiali Nanostrutturati (ISMN), 40129 Bologna, Italy

Massimiliano Cavallini, Consiglio Nazionale delle Ricerche (CNR), Istituto per lo Studio dei Materiali Nanostrutturati (ISMN), 40129 Bologna, Italy

Jørn B. Christensen, Department of Chemistry, University of Copenhagen, DK-2100 Copenhagen, Denmark

Tobias Cramer, Consiglio Nazionale delle Ricerche (CNR), Istituto per lo Studio dei Materiali Nanostrutturati (ISMN), 40129 Bologna, Italy

Leroy Cronin, School of Chemistry, University of Glasgow, Glasgow, G12 8QQ, United Kingdom

Tatiana Da Ros, Center of Excellence for Nanostructured Materials (CENMAT), INSTM—Unit of Trieste, Dipartimento di Scienze Chimiche e Farmaceutiche, Università degli Studi di Trieste, 34127 Trieste, Italy

Luisa De Cola, Université de Strasbourg, Institut de Science et d’Ingénierie Supramoléculaires (ISIS), 67083 Strasbourg, France

André Devaux, Department of Chemistry, University of Fribourg, CH- 1700 Fribourg, Switzerland

McDonald Donkuru, College of Pharmacy and Nutrition, University of Saskatchewan, Saskatoon, Saskatchewan, S7N 5C9, Canada

Francis D’Souza, Department of Chemistry, University of North Texas, Denton, TX 76203-5017, United States

Lourdes E. Echegoyen, Department of Chemistry, University of Texas at El Paso, El Paso, TX 79968, United States

Luis Echegoyen, Department of Chemistry, University of Texas at El Paso, El Paso, TX 79968, United States

Mahmoud Elsbahy, School of Pharmacy, University of Waterloo, Waterloo, Ontario, N2L 3G1, Canada. *Current affiliations*: Department of Pharmaceutics, Faculty of Pharmacy, Assiut University, Assiut, Egypt; *and* Laboratory for Synthetic-Biologic Interactions, Department of Chemistry, Texas A&M University, College Station Texas, 77842, United States

Chiara Fabbro, Center of Excellence for Nanostructured Materials (CENMAT), INSTM—Unit of Trieste, Dipartimento di Scienze Chimiche e Farmaceutiche, Università degli Studi di Trieste, 34127 Trieste, Italy. *Current affiliation*: Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari di Venezia, 30123 Venezia, Italy

Lai Feng, Department of Physical Science and Technology, School of Energy, Soochow University, Suzhou, Jiangsu 215006, China; *and* Life Science Center of Tsukuba Advanced Research Alliance, University of Tsukuba, Tsukuba, Ibaraki 305-8577, Japan

Marianna Foldvari, Canada Research Chair in Bionanotechnology and Nanomedicine, Waterloo Institute of Nanotechnology, School of Pharmacy, University of Waterloo, Waterloo, Ontario, N2L 3G1, Canada

Shunichi Fukuzumi, Department of Material and Life Science, Graduate School of Engineering, Osaka University and ALCA (JST), 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan; *and* Department of Bioinspired Science, Ewha Womans University, Seoul 120-750, Korea

José M. Gallego, Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, 28049 Madrid, Spain

Michael Grätzel, Laboratory of Photonics and Interfaces (LPI), Ecole Polytechnique Federale de Lausanne, CH-1015 Lausanne, Switzerland

Dirk M. Guldi, Department of Chemistry and Pharmacy, Interdisciplinary Center for Molecular Materials (ICMM), Friedrich-Alexander-Universität Erlangen-Nürnberg, 91058 Erlangen, Germany

Jurriaan Huskens, Department of Science and Technology, Molecular Nanofabrication Group, MESA⁺ Institute for Nanotechnology, University of Twente, 7500 AE Enschede, Netherlands

Søren Hvilsted, Danish Polymer Centre, Department of Chemical and Biochemical Engineering, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark

Osamu Ito, CarbonPhotoScience Lab., Kita-Nakayama 2-1-6, Izumi-ku, Sendai, 981-3215, Japan

Irakli Javakhishvili, Danish Polymer Centre, Department of Chemical and Biochemical Engineering, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark

Pascal Jonkheijm, Department of Science and Technology, Molecular Nanofabrication Group, MESA⁺ Institute for Nanotechnology, University of Twente, 7500 AE Enschede, Netherlands

Jaeyung Ko, Department of New Material Chemistry, Korea University, Jochiwon, Chungnam 339-700, Korea.

Takahiko Kojima, Department of Chemistry, Faculty of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennoudai, Tsukuba, Ibaraki 305-8571, Japan

Koichi Komatsu, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

Anna Laromaine, Institut de Ciència dels Materials de Barcelona, ICMAB-CSIC, Campus UAB, 08193 Bellaterra, Spain

Francesca Leonardi, Consiglio Nazionale delle Ricerche (CNR), Istituto per lo Studio dei Materiali Nanostrutturati (ISMN), 40129 Bologna, Italy

Fang-Fang Li, Department of Chemistry, University of Texas at El Paso, El Paso, TX 79968, United States

Xing Lu, State Key Laboratory of Material Processing and Die & Mould Technology, College of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, China; *and* Life Science Center of Tsukuba Advanced Research Alliance, University of Tsukuba, Tsukuba, Ibaraki 305-8577, Japan

Henning Lülf, Université de Strasbourg, Institut de Science et d'Ingénierie Supramoléculaires (ISIS), 67083 Strasbourg, France

Andrew Macdonell, School of Chemistry, University of Glasgow, Glasgow, G12 8QQ, United Kingdom

Charles R. Mace, Diagnostics For All, 840 Memorial Drive, Cambridge, MA 02139, United States

Nazario Martín, Facultad de Ciencias Químicas, Departamento de Química Orgánica, Universidad Complutense de Madrid, 28040 Madrid, Spain; *and* IMDEA Nanociencia, Ciudad Universitaria de Cantoblanco, E28049 Madrid, Spain

Craig J. Medforth, REQUIMTE/Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, 4169-007 Porto, Portugal

Rodolfo Miranda, Departamento de Física de la Materia Condensada, Facultad de Ciencias, Universidad Autónoma de Madrid, 28049 Madrid, Spain

Pedro Molina, Departamento de Química Orgánica, Facultad de Química, Universidad de Murcia, Campus de Espinardo, E-30100 Murcia, Spain

Michihisa Murata, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

Yasujiro Murata, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

Shigeru Nagase, Fukui Institute for Fundamental Chemistry, Kyoto University, Sakyo-ku, Kyoto 606-8103, Japan

Mohammad Khaja Nazeeruddin, Laboratory of Photonics and Interfaces (LPI), Ecole Polytechnique Federale de Lausanne, CH-1015 Lausanne, Switzerland; *and* University, Jochiwon, Chungnam 339-700, Korea

Roberto Otero, Departamento de Física de la Materia Condensada, Facultad de Ciencias, Universidad Autónoma de Madrid, 28049 Madrid, Spain

Emilio M. Pérez, IMDEA Nanociencia, Ciudad Universitaria de Canto Blanco, E28049 Madrid, Spain

Eko Adi Prasetyanto, Université de Strasbourg, Institut de Science et d'Ingénierie Supramoléculaires (ISIS), 67083 Strasbourg, France

Maurizio Prato, Center of Excellence for Nanostructured Materials (CENMAT), INSTM—Unit of Trieste, Dipartimento di Scienze Chimiche e Farmaceutiche, Università degli Studi di Trieste, 34127 Trieste, Italy

Imma Ratera, Department of Molecular Nanoscience and Organic Materials, Institut de Ciència de Materials de Barcelona (ICMAB-CSIC)/CIBER-BBN, Campus de la UAB, 08193 Bellaterra, Spain

David González-Rodríguez, Nanostructured Molecular Systems and Materials Laboratory, Departamento de Química Orgánica, Universidad Autónoma de Madrid, 28049 Madrid, Spain

Atula S. D. Sandanayaka, School of Materials Science, Japan Advanced Institute of Science and Technology (JAIST), Nomi, Ishikawa, 923-1292, Japan

Niyazi Serdar Sariciftci, Linz Institute for Organic Solar Cells (LIOS), Physical Chemistry, Johannes Kepler University of Linz, A-4040 Linz, Austria

Satoru Sato, Life Science Center of Tsukuba Advanced Research Alliance, University of Tsukuba, Tsukuba, Ibaraki 305-8577, Japan

Francesca A. Scaramuzzo, Department of Science and Technology, Molecular Nanofabrication Group, MESA⁺

Institute for Nanotechnology, University of Twente, 7500 AE Enschede, Netherlands

Albertus P. H. J. Schenning, Laboratory for Functional Organic Materials and Devices, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands

John A. Shelnett, Department of Chemistry, University of Georgia, Athens, GA 30602, United States

Yuta Takano, Life Science Center of Tsukuba Advanced Research Alliance, University of Tsukuba, Tsukuba, Ibaraki 305-8577, Japan

Alberto Tárraga, Departamento de Química Orgánica, Facultad de Química, Universidad de Murcia, Campus de Espinardo, E-30100 Murcia, Spain

Donald A. Tomalia, NanoSynthons LLC, The National Dendrimer and Nanotechnology Center, 1200 N. Fancher Avenue, Mount Pleasant, MI, 48858, United States

Tomás Torres, Departamento de Química Orgánica, Facultad de Ciencias, Universidad Autónoma de Madrid, 28049 Madrid, Spain; *and* IMDEA Nanociencia, C/Faraday 9, Ciudad Universitaria de Canto Blanco, E28049 Madrid, Spain

Pavel A. Troshin, Institute for Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow Region, 142432, Russia

Maxence Urbani, Departamento de Química Orgánica, Facultad de Ciencias, Universidad Autónoma de Madrid, 28049 Madrid, Spain

Jaume Veciana, Department of Molecular Nanoscience and Organic Materials, Institut de Ciència de Materials de Barcelona (ICMAB-CSIC)/CIBER-BBN, Campus de la UAB, 08193 Bellaterra, Spain

Marisela Vélez, Instituto de Catálisis y Petroleoquímica, Consejo Superior de Investigaciones Científicas, Campus de Cantoblanco, 28049 Madrid, Spain

Ronald Verrall, Department of Chemistry, University of Saskatchewan, Saskatoon, Saskatchewan, S7N 5C9, Canada

Adrián Villalta-Cerdas, Department of Chemistry, University of Texas at El Paso, El Paso, TX 79968, United States

Michio Yamada, Department of Chemistry, Tokyo Gakugei University, Koganei, Tokyo 184-8501, Japan

Francesco Zerbetto, Dipartimento di Chimica “G. Ciamician”, Università di Bologna, 40126 Bologna, Italy

A PROPOSED TAXONOMY AND CLASSIFICATION STRATEGY FOR WELL-DEFINED, SOFT-MATTER NANOSCALE BUILDING BLOCKS

JØRN B. CHRISTENSEN AND DONALD A. TOMALIA

1.1 INTRODUCTION

The field of nanoscience has evolved explosively over the last two decades, generating a vast number of nanoscale structures and objects. These nanoconstructs may be derived from covalently bound molecules in the classical chemical sense or they may be supramolecular, self-assembled structures. That withstanding, in either case “well-defined nanostructures/objects” may be formed from the smaller discrete building blocks (i.e., atoms, small molecules, monomers, polymers, etc.) if certain “bottom-up” assembly processes are involved that ensure structure control of critical nanoscale design parameters (CNDPs) such as (a) size, (b) shape, (c) surface chemistry, (d) flexibility/rigidity, (e) architecture, and (f) composition. These resulting discrete, homogeneous nanostructures/objects constitute an important category of nanomaterials and are distinguished from other heterogeneous nano-assemblies by expressing well-defined interrelationship patterns and quantized stoichiometries with each other [1, 2]. The quantized stoichiometries and interparticle relationships exhibited by these well-defined nano-entities are a consequence of their structure-controlled precursor building blocks and their ability to transfer important critical atomic design parameters (CADPs) or critical molecular design parameters (CMDPs) to the nanoscale level. This structural information is routinely transferred with high integrity to higher complexity in biological systems via certain evolutionary/genealogical aufbau strategies as described in Figure 1.8 and 1.1. Joyce [3, 4] has clearly demonstrated (a) the importance of these genealogical/evolutionary aufbau

patterns involving well-defined nanoscale building blocks such as proteins, RNA, and DNA and (b) their ultimate role in the diversification of life.

In the case of abiotic systems, unique structure controlled synthetic strategies and construction rules are usually involved in the formation of these well-defined nanostructures/objects. The importance of understanding these bottom-up construction rules and aufbau patterns cannot be overstated. They will be invaluable for developing classification and taxonomy schemes to define key nano-building blocks (i.e., nano-elements), as well as their hybridization pathways to (i.e., nano-compounds/assemblies) and synthetic evolution to higher complexity in the nanoscale region. In many respects, our present insights are similar to previous historical growth phases in traditional chemistry during the nineteenth century that led to the Mendeleev Periodic Table in 1869. In essence, the patterns and categorization of atomic elements in Mendeleev’s periodic table constituted an elegant classification or taxonomy for all the known atomic elements [5, 6]. Mendeleev’s seminal atomic element taxonomy [7] has provided powerful insights and critical information useful for *a priori* predictions of elemental physicochemical behavior, as well as chemical reactivity, stoichiometries, assembly patterns, and so on, leading to the formation of traditional small molecular structures and assemblies as illustrated in Figure 1.2. The idea of classifying atomic elements or small molecules according to chosen criteria of similarity features or as a function of their interrelationships patterns/trends is not new. In fact, Swedish botanist Carl von Linnæus (1707–1778), the “father of taxonomy,” initiated such a

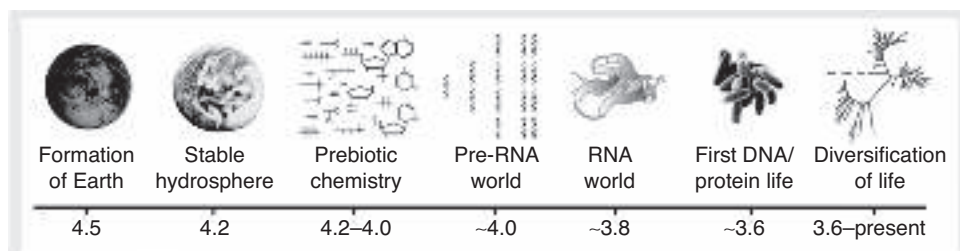


FIGURE 1.1. Timeline of events associated with the early history of life on Earth, with approximate dates in billions of years before the present [4]. Reprinted with permission of Macmillan Publishers Ltd., 2002.

systematic classification for the plant and animal kingdoms over 100 years earlier than Mendeleev, wherein he used a taxonomy scheme to classify biological entities.

These scientific classifications have been described by Mayr and Bock [8] as “the arrangement of well-defined entities” into a hierarchical series of nested classes. A class (i.e., taxon) is defined as “collection of similar entities.” Such a taxon consists of collections of entities that share certain similarity features consisting of attributes or traits in common. Similar or related classes at one hierarchical level are combined comprehensively into more exclusive classes at the next lower taxon level to more specifically narrow down the entity description. This process is demonstrated by a

Linnaean classification downward from broader taxa to more specific taxa involving diverse entities such as humans, dogs, wolves, or bacteria as described in Figure 1.3. Variations of the Linnaean taxonomy system have been used to classify a wide range of biological diversity. Many of these classifications are less familiar to chemists and physical scientists; however, they are generally known by biologists and life scientists. Extensive classifications have been reported for complexity at the submicron scale level (e.g., viruses [9,10]) and progress to higher levels of complexity at the micron-scale/macroscale level to include bacteria [11], yeasts [12], fungi [13], plants, and animals as illustrated in Figure 1.3. Presently these taxonomies and classifications are well established for entities

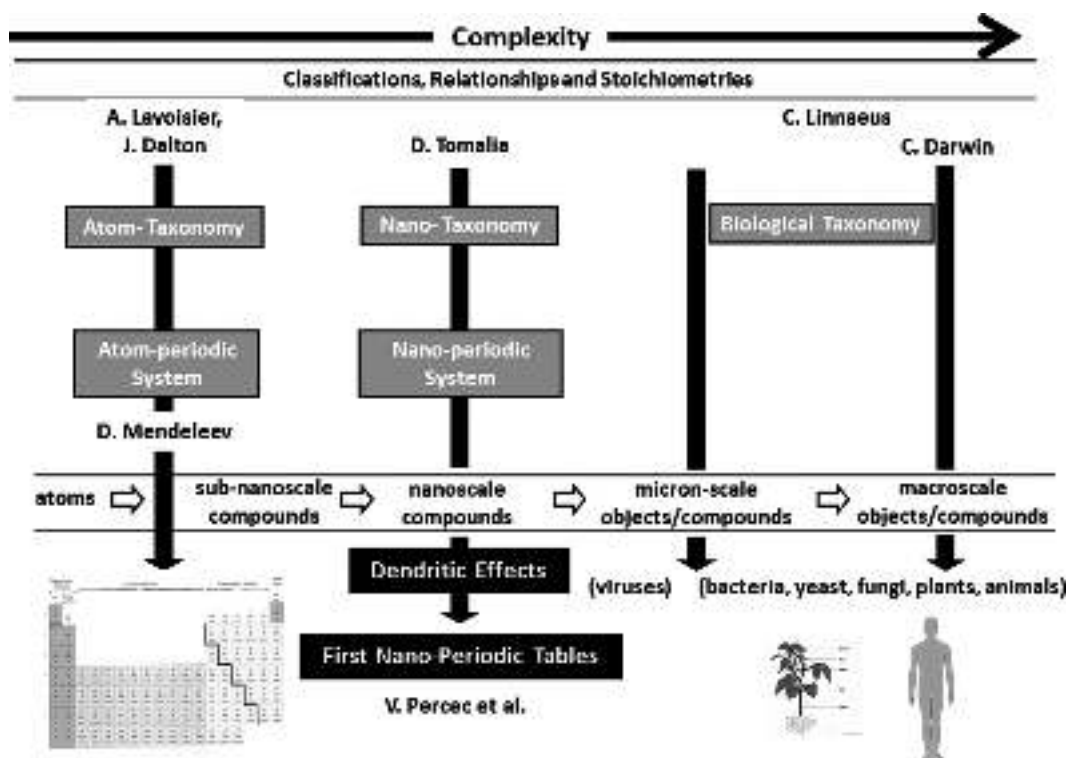


FIGURE 1.2. A comparison of taxonomies at the picoscale, nanoscale, and micron scale/macroscale as a function of hierarchical complexity.

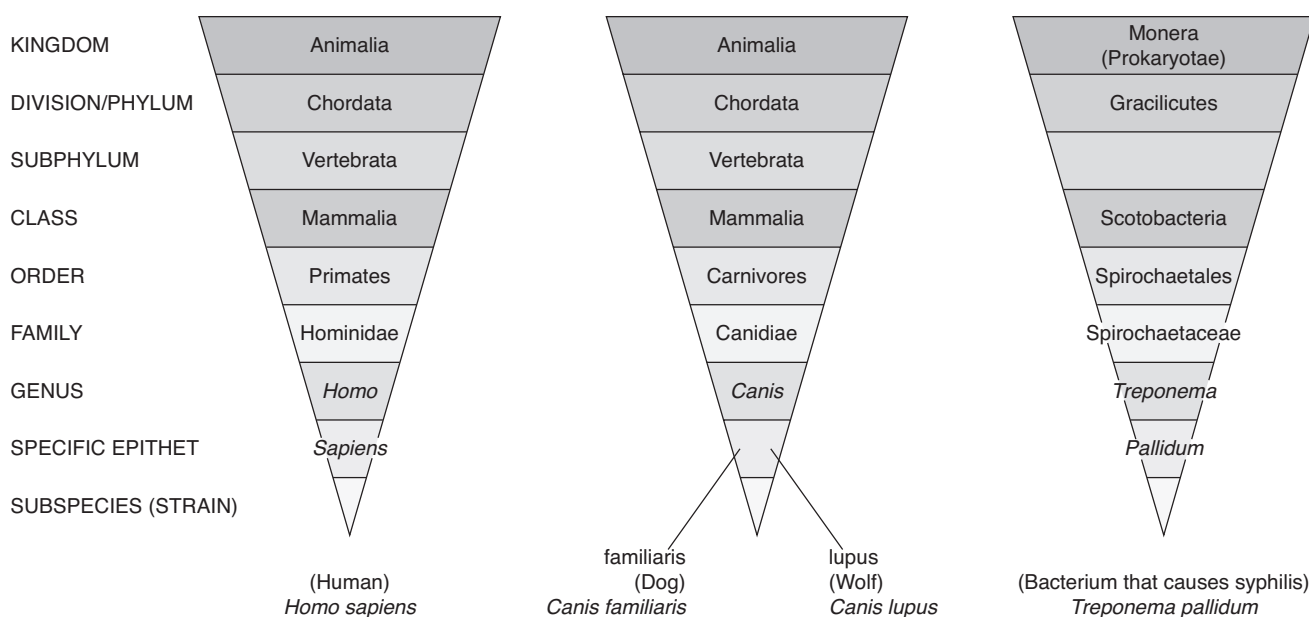


FIGURE 1.3. Linnaean classification of several diversified examples such as a human, a dog, a wolf, and a bacterium [11]. Image reproduced with permission of Copyright John Wiley & Sons.

at the atomic/molecular level as well as higher complexity at the micron/macroscale. However, relatively little has been reported concerning classifications/taxonomies of structures and assemblies at the nanoscale level.

It is widely accepted that well-defined genealogy and evolutionary precursors played a critical role in the development of taxonomies at the micron-scale/macroscale levels [3, 4]. Similarly, it will be of high importance to define analogous taxa for well-defined module/entities at the picoscale, molecular, and nanoscale levels. It is proposed that the CHDPs for these well-defined precursors may very well provide appropriate criteria for evaluating bottom-up construction pathways, roles, and classification schemes for higher-complexity nano-building blocks as described in Figure 1.4. Historically, it is widely recognized that seminal atomic element classifications were critical in the ultimate evolution of an atomic periodic table/system by Mendeleev in 1869 [7]. Based on recent progress reported toward development of a similar nano-periodic system [2] and first examples of nano-periodic tables, a suitable taxonomy strategy appears to be both critical and timely.

In this chapter, we propose further steps toward the development of a universal nano-classification system. This account should be considered a “work in progress” and involves the use of “critical hierarchical design parameters” (CHDPs), namely, (a) sizes, (b) shapes, (c) surface chemistries, (d) flexibility/rigidity, (e) architectures, and (f) elemental compositions as described in Figure 1.4. It is proposed that these CHDPs should be considered as classification criteria (i.e., taxa) and used according to Linnaean

principles for classifying various “aufbau precursors” to the 12 hard/soft nano-element categories described later in Section 1.7 (Figure 1.17). It is widely recognized that Linnaean taxonomy principles have been used successfully for classifying evolutionary/genealogical hybrids arising from fundamental entities in biological systems. In a similar manner, at the nanoscale it should be possible to use these CNDP-based taxa as classification criteria for defining future hybridizations of these nano-element categories into anticipated new libraries of nano-compounds and nano-assemblies. Finally, it is proposed that using these CNDPs according to Linnaean classification criteria should be considered as an approach for generating a specific taxonomy-based nomenclature.

1.2 ADAPTATION OF LINNAEAN TAXONOMY PRINCIPLES TO A NEW NANO-CLASSIFICATION SCHEME

Successful Linnaean-like taxonomies have been demonstrated for important soft nano-element categories and nano-compounds and their assemblies. Most noteworthy is the extensive classification of [S-4]-type proteins (Section 1.2.2). Secondly, the development of taxonomies for the combination (i.e., hybridization) of [S-4]-type protein subunits or [S-5]-type viral capsids with [S-6]-type RNA or DNA nano-elements to produce [S-6:S-4] or [S-6:S-5]-type viral nano-compounds, respectively, has been demonstrated as described in Section 1.2.3.

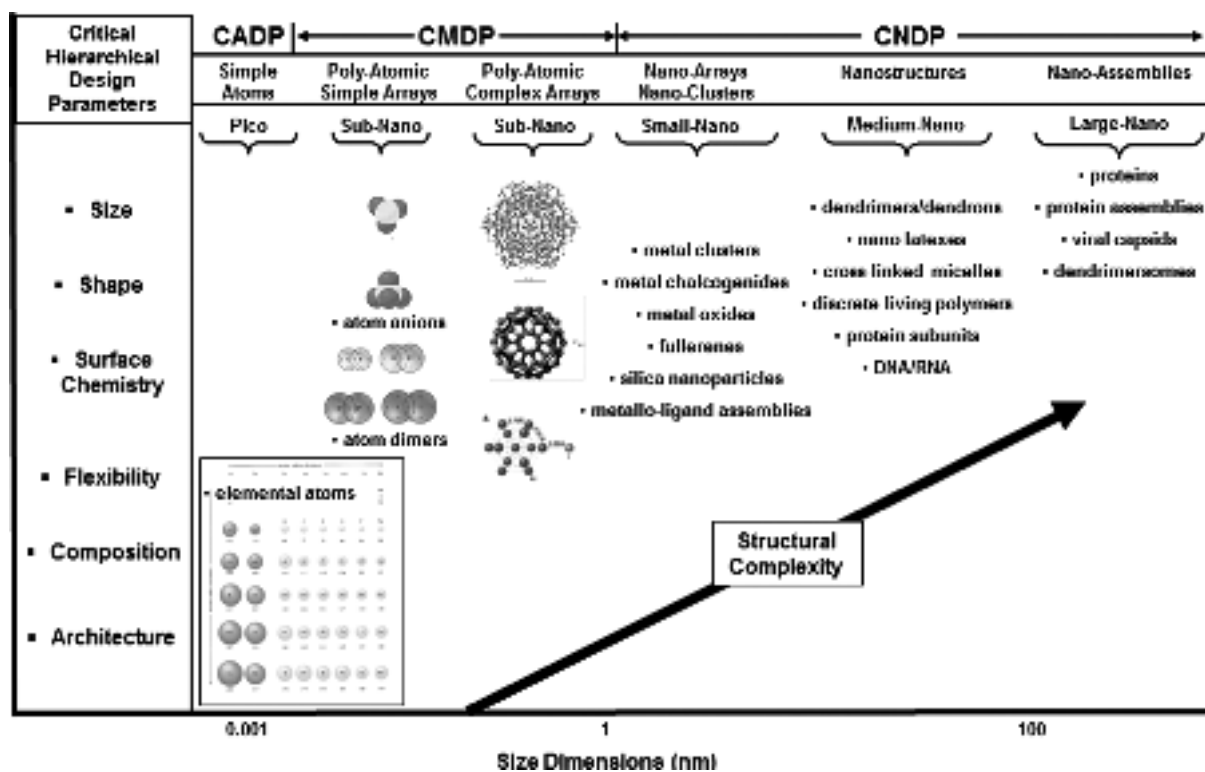


FIGURE 1.4. Critical hierarchical design parameters (CHDPs): (a) size, (b) shape, (c) surface chemistry, (d) flexibility/rigidity, (e) architecture, and (f) elemental composition for various hierarchical structures as a function of dimensions (i.e., atomic-picoscale level (CADP), molecular-subnanoscale (CMDP), and nanometric-nanoscale (CNDP)).

1.2.1 Taxonomy of Biological Structures and Organisms

The term *taxonomy* [Greek *taxis*, arrangement or order, and *nomos*, law or nemein, to distribute or govern] is defined as the science of biological classification. In a broader sense, this taxonomy concept involved the use of a protocol that provides three key features, namely: (a) identification, [the process of determining that a particular organism belongs to a recognized taxon; (b) classification [arrangement of organisms into similar groups or taxa] and (c) nomenclature [the branch of taxonomy concerned with the assignment of names to taxonomic groups in agreement with published rules]. These three parameters have been used routinely for describing classifications and relationships between various biological organism/entities residing in the higher-complexity dimensions of the micron scale–macroscale (i.e., 0.1 μm to meters) [14]. At least eight taxonomic parameters were deemed necessary for defining the higher complexity of micron-scale–macroscale biological systems. They are widely recognized and recalled with the mnemonic “*Do kings play chess on fine grained sand?*” and include the following eight hierarchical parameters: (1) domain, (2) kingdom, (3) phylum, (4) class, (5) order, (6) family, (7) genus, (8) species [15].

A dominant feature that differentiates biological classification (taxonomy) from most other classification systems is *evolution*. The similarity between biological structures or organisms placed in a common taxon is not arbitrary. It is the result of shared descent from their nearest common ancestor. As such, these classifications require an evaluation of evolutionary stages and intrinsic genealogy that precedes each entity classification. In essence, these eight classification parameters not only capture similarities and differences, but also integrate critical biological entity features/properties such as (a) homogeneity, (b) size, (c) morphology/shape, (d) behavior/function, (e) flexibility/rigidity, (f) architecture, and (g) elemental composition as important evolutionary/genealogical selection criteria for these classifications [16]. Such Linnaean-inspired concepts have been studied extensively by essentially every generation of naturalist during the past 200 years, including Charles Darwin. Modified versions of these Linnaean taxonomic criteria and classifications presently serve as the “gold standard” for classifying all biological hierarchy/diversity residing in the micron–meter size range. Such taxonomy concepts have provided a universal and versatile system for classifying all micron-scale–macroscale biological entities (i.e., certain viruses, bacteria, fungi, plants, animals, etc.) and laid the

foundation for modern biological taxonomy/classifications and nomenclature. This well-defined taxonomic scheme has served to organize, simplify, and unify wide ranges of diversity and complexity at the micron-scale and macroscale within biology. Most importantly, this well-defined taxonomic system has provided a critical, quantitated protocol for analyzing important patterns, trends, and relationships between classified biological entities. More contemporary modifications have involved the use of molecular level (i.e., DNA/RNA-based) data as a means for classification.

1.2.2 Protein Taxonomies

The nanoscale class of protein structures/assemblies has been proposed as a well-defined soft nano-element category designated as [S-4] based on its quantized

CNDPs [2] (see Section 1.7.1). A structural classification of proteins (SCOP) was first pioneered as early as 1995 by Murzin et al. [17]. More recently, a very comprehensive protein taxonomy based on secondary structure was reported [18]. This taxonomy is generated automatically by computer and based solely on secondary protein structure. It takes the form of a cladogram/dendrogram-based “similarity tree” in which proteins with similar secondary structure occupy neighboring leaves. This taxonomy is largely in agreement with SCOP and is a multidimensional classification scheme based on homologous sequences and full three-dimensional structure, as well as information about the chemistry and evolution of the protein. A “similarity tree” based on this taxonomy is as illustrated in Figure 1.5. Much like dendrimer architecture, a similarity tree is heuristically composed of multiple dendron-like domains that are all connected to a central core

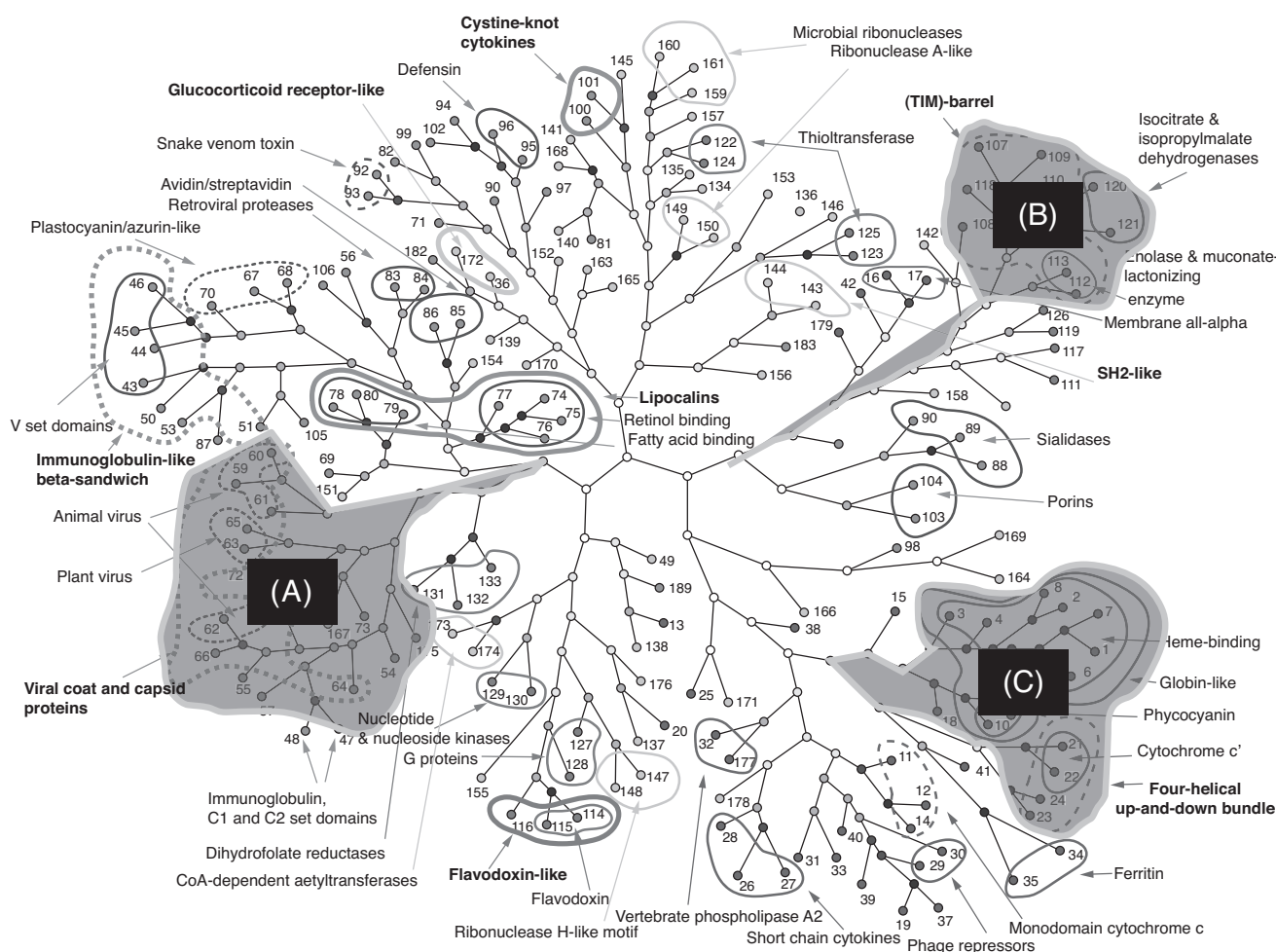


FIGURE 1.5. A similarity tree derived from 183 diverse proteins are examined and classified into various cladograms or similarity domains designated by clusters of protein structures exhibiting similar features or functional properties. For example, domain (A) is associated with proteins that self-assemble into viral coats/capsids, domain (B) includes a cluster of proteins associated with enzymes and biological catalysts and domain (C) identifies specific protein types associated with oxygen transport properties [18]. Reprinted with permission of Macmillan Publishers Ltd., 1999.

of information. These dendron-like domains are referred to as cladograms or dendrograms. The central core contains conserved structural information that feeds into these various cladograms. Based on the hybridization of structural information that is connected to this conserved core, one observes branches of similar yet diverse protein features. As noted in the similarity tree (Figure 1.5), the various cladograms connected to the core serve to cluster similar features into specific domains (i.e., domains (A), (B), and (C)). These domains may be associated with specific properties/functions of interest. Thus, based on secondary protein structure, this taxonomy proved to be a versatile protein classification scheme for evolving differentiating cladograms that associated certain protein types with various biological structural or functional roles. For example, cladogram (A) identifies certain proteins that self-assemble to produce viral coats and capsids as opposed to cladogram (B), which defines clusters of proteins associated with a biological catalysis function (i.e., enzymes, etc.), or cladogram (C), which identifies specific protein types associated with oxygen transport properties (i.e., ferritin, heme-type binding proteins). It is readily apparent that such a taxonomy based on secondary protein structure provides a simple scheme for classifying a large database of complex information. Successful use of such Linnaean taxonomic principles for micronscale/macroscale plants/animals and now nanoscale protein molecules provides optimism for recognizing common features in each of these dimensionally differentiated hierarchical domains. These taxonomic differentiations should be suitable for defining ordered classes and ultimately evolving versatile and useful nomenclatures just as Mendeleev's periodic table of atomic elements led to a classification scheme (i.e., taxonomy) and a universal nomenclature for the elements and their resulting compounds.

1.2.3 Virus Taxonomies

Based on their quantized, well-defined CNDPs, viral capsids have been proposed as an important soft nano-element category designated as [S-5] [2, 19]. As described in Section 1.8.3, they are derived from the stoichiometric self-assembly of category [S-4]-type protein subunits. Viruses, in turn, have been proposed as stoichiometric nano-compounds that are derived from the self-assembly of either [S-4]-type protein subunits around [S-6] RNA or DNA cores (i.e., [S-6]-type nano-elements) or the self-assembly of viral capsids around these RNA/DNA [S-6]-type cores. Meanwhile, an invaluable classification system has been introduced by Baltimore [9] that places viruses into one of seven groups based on an analysis of parameters such as (a) their core nucleic acid type (i.e., DNA or RNA), (b) strandedness (i.e., single strand versus double strand), (c) sense, and (d) method of replication [20] (see Section 1.9.3, Figure 1.31). Such DNA/RNA-driven taxonomy has produced invaluable assistance in the classification and determination of evolutionary

termini (i.e., dead ends) confirming extinction or evolutionary gaps raising expectations for biological entities yet to be discovered [21, 22]. On the other hand, a more Linnaean-type taxonomy has been developed for viruses (i.e., the LHT System). This taxonomy is based on a comparison of physico chemical features such as (a) core nucleic acids (i.e., DNA/RNA), (b) symmetry (i.e., helical, icosahedral or complex), (c) presence of envelope components, (d) diameter of capsids, (e) number of capsids, and so on [23] (see Section 1.9.3; Figure 1.30).

1.3 HOW DOES NATURE TRANSFER STRUCTURAL INFORMATION FROM A LOWER HIERARCHICAL LEVEL TO HIGHER COMPLEXITY?

The clustering of similar secondary protein structure as observed in the similarity tree (Figure 1.5), suggests that critical features are conserved and transferred up the hierarchy ladder to produce the higher complexity observed at the nanoscale in cladograms (A), (B), and (C) above. As such, one must ask: *Are there conserved critical hierarchical design parameters that maintain informational integrity and robustness when transferred to higher complexity?* Anecdotal evidence supports the notion that certain critical design parameters at the atomic, molecular, nanoscale, and microscale level can effectively transfer important structural information to higher hierarchical complexity. Many well-known examples of molecular self-assembly, genetic expression, and evolution clearly demonstrate these principles. The critical role of atoms and molecular level monomers (i.e., alpha-amino acids) is clearly illustrated in Figure 1.6a. As demonstrated in the protein taxonomy (Figure 1.5) it appears that secondary/tertiary structure is far better conserved than specific protein sequence. It is well known that secondary/tertiary protein structures are directly dependent on CNDPs such as (a) size, (b) shape, (c) surface chemistry, and (d) flexibility/rigidity. A clear example is readily illustrated by the conservation of nanoscale protein (i.e., collagen) secondary/tertiary structure throughout its respective hierarchical micron-scale self-assembly steps to produce biological tendons as shown in Figure 1.6b.

In 1917, D'Arcy Thompson (1860–1948) published a seminal biological treatise entitled *On Growth and Form* [16]. This work provided deep insights and answers to the question above. It clearly articulated the importance of preferred and controlled “critical micron-scale/macroscale design parameters” (CMicDPs) such as (a) size, (b) shape, (c) surface function, (d) flexibility/rigidity, (e) architecture, and (f) atomic composition features in the successful evolution of all biological structures and organisms. As early as 1990–1993, it was stated that analogous “critical atomic, molecular and

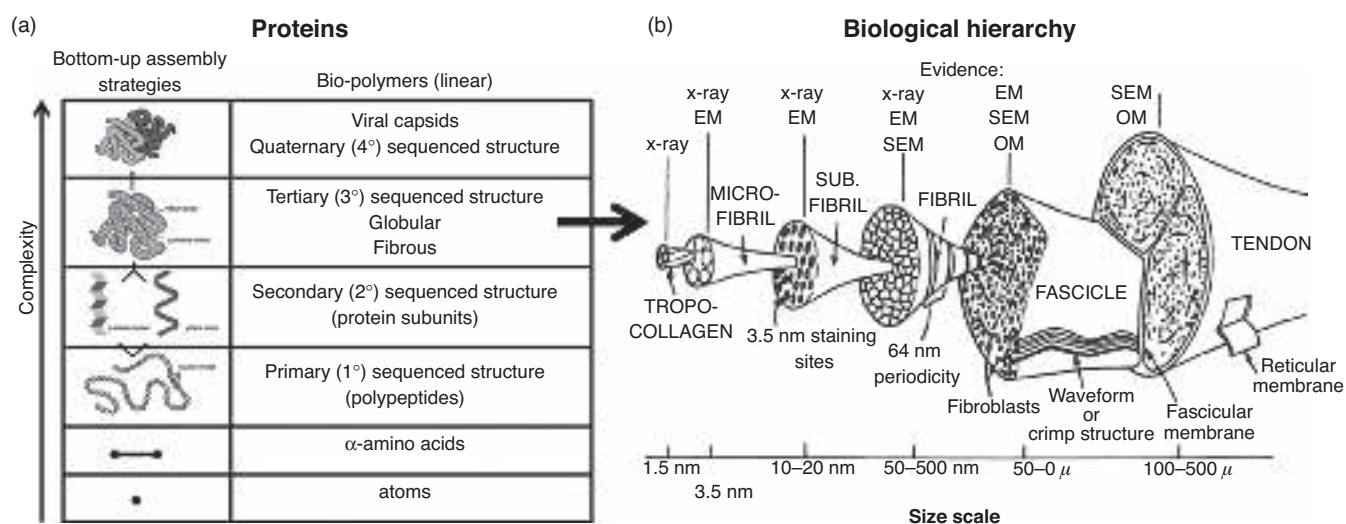


FIGURE 1.6. (a) Bottom-up synthesis of proteins with symmetry-breaking events from atoms and monomers leading to self-organization complexity. (b) Bottom-up assembly of the fibrous protein, collagen, through six symmetry-breaking levels to produce new emerging properties associated with tendon. Reproduced with permission of Eric Baer.

nanoscale design parameters” were conserved and inextricably associated with the transfer of information in all well-defined structures throughout the atomic to microscale hierarchical continuum [24, 25].

1.4 THE USE OF CLADOGRAMS FOR CLASSIFICATIONS OF WELL-DEFINED BIOLOGICAL (MICRON SCALE/MACROSCALE), ATOMIC (PICOSCALE), AND NANOSCALE BUILDING BLOCKS

1.4.1 Taxonomy of Biological Entities

Cladograms (i.e., dendrograms) as illustrated in Figure 1.5 for nanoscale proteins and in Figure 1.7 for macroscale animals (i.e., vertebrae) have been used traditionally for defining evolutionary (i.e., precursor-type) relationships and pathways leading to clusters of similar entities based on several pervasive criteria. In Figure 1.7, the vertebrate classifications (i.e., cladograms) are based on similar evolutionary and genealogical features such as sizes, shapes/morphologies, and functions resulting from hybridization to produce certain well-defined families of organisms. Prior to the advent of DNA sequencing, nearly all cladogram-based biological systematics involved the use of morphology or shape data classifications for defining genealogy and evolutionary pathways. Presently, both molecular and morphological systematics are used extensively for this purpose [11]. Many of these issues have been examined in detail by Zuckerkandl and Pauling [26].

1.4.2 Taxonomy of Atomic Elements

Nearly concurrently, Lavoisier [1743–1794; *Traite Elementaire de Chimie* (1789)], Prout [1754–1844; *Law of Definite Proportions* (1797)], Dalton [(1766–1844; *Law of Multiple Proportions/New System of Chemical Philosophy* (1808))], and others began the classification of less complex hierarchical entities such as the atomic elements. This activity led to Mendeleev’s (1834–1907) seminal periodic element proposal wherein he classified and organized known elements according to their periodic properties and chemical behavior. This led to a taxonomic framework (i.e., Mendeleev Periodic Table) that could be adapted to and interpreted according to the earlier Linnaean template for biological structures and organisms. For example, the elements were organized into domains of reactive versus inert types (i.e., unsaturated versus saturated valence shells), vertical elemental groups (i.e., metals, metalloids, and nonmetals; Groups I–VIII), inorganic type elementals versus organic, horizontal periods (i.e., atomic weights), mono-isotope versus poly-isotopic elements, and so on. Rich [27] refers to such a periodic taxonomy as a view of the relationship patterns that exist among the elements. Similarly, one can visualize a crude taxonomy for the atomic elements based on the well-known mnemonic and classical Linnaean taxonomy template used for classifying biological structures/organisms as described in Figures 1.8 and 1.9.

The elements are different aggregates of the atoms of primordial hydrogen.

—Prout’s Hypothesis (1815)

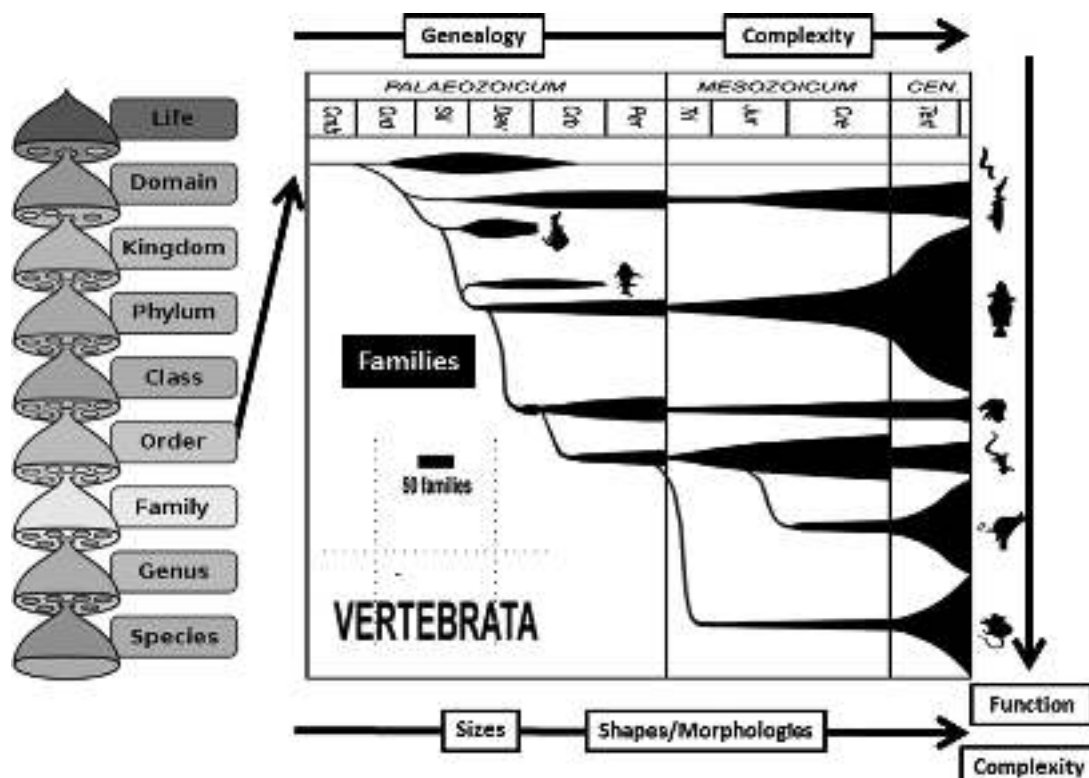


FIGURE 1.7. A cladogramic (i.e., dendrogramic) classification of the Vertebrata order into families using Linnaean taxonomy principles according to sizes, shapes (i.e., morphologies), function, genealogy, and complexity. The darkened dimension bar represents approximately 50 families.

Based on genealogical and evolutionary principles described for the formation of heavier atomic elements from lighter elements [28], one may view Niels Bohr's seminal perspective of the Mendeleev Periodic Table as an evolutionary cladogram for tracing the transformation and evolution of light to heavier atomic elements as shown in Figure 1.8. Based on a Linnaean template, the classification of elements into families based on genealogy or electron shells (i.e., periods) in the context of sizes, shapes, function (i.e., surface chemistry), and complexity is readily apparent.

In general, the Mendeleev Periodic Table has evolved and been viewed as a very articulate taxonomic account of all the known atomic elemental building blocks. Most notable during this periodic table development was the emergence of certain patterns/trends (i.e., vertical elemental groups and horizontal periods) that contained a number of empty positions. These unoccupied elemental positions within these taxonomic patterns suggested the existence of yet undiscovered elements with properties that could be extrapolated from the property patterns/trends of the surrounding elements. Without the benefit of knowing or understanding anything about atomic structure, electronic theory, or quantum mechanics, Mendeleev provided a powerful predictive taxonomic concept that still remains rational and consistent with accepted

contemporary understanding of atomic structure and their physicochemical properties.

Furthermore, it is now recognized that the Mendeleev Periodic Table provides a very rich taxonomy for classifying and predicting important CADPs [25] such as (a) size, (b) shape, (c) reactive/inert surface chemistry, (d) flexibility/polarizability and (e) architecture. These periodic trends and property patterns are as described in Figure 1.8 and 1.9. It is obvious, that hybridization of these various co-reactive atomic elements would produce their own unique and differentiated cladograms of small molecule structures and assemblies.

Such an approach might prove to be an interesting template for organizing and classifying various aufbau-type precursors leading to well-defined nano-building blocks (i.e., nano-element categories) as well as their subsequent hybridization into nano-compounds and assemblies. These issues will be discussed later in Section 1.7.1.

1.4.3 In Quest of a Taxonomy for Nonbiological Nanoscale Structures and Assemblies

Hierarchical taxonomies are widely recognized and used routinely for building blocks as small as picoscale atomic elements and well-defined biological structures as well as for

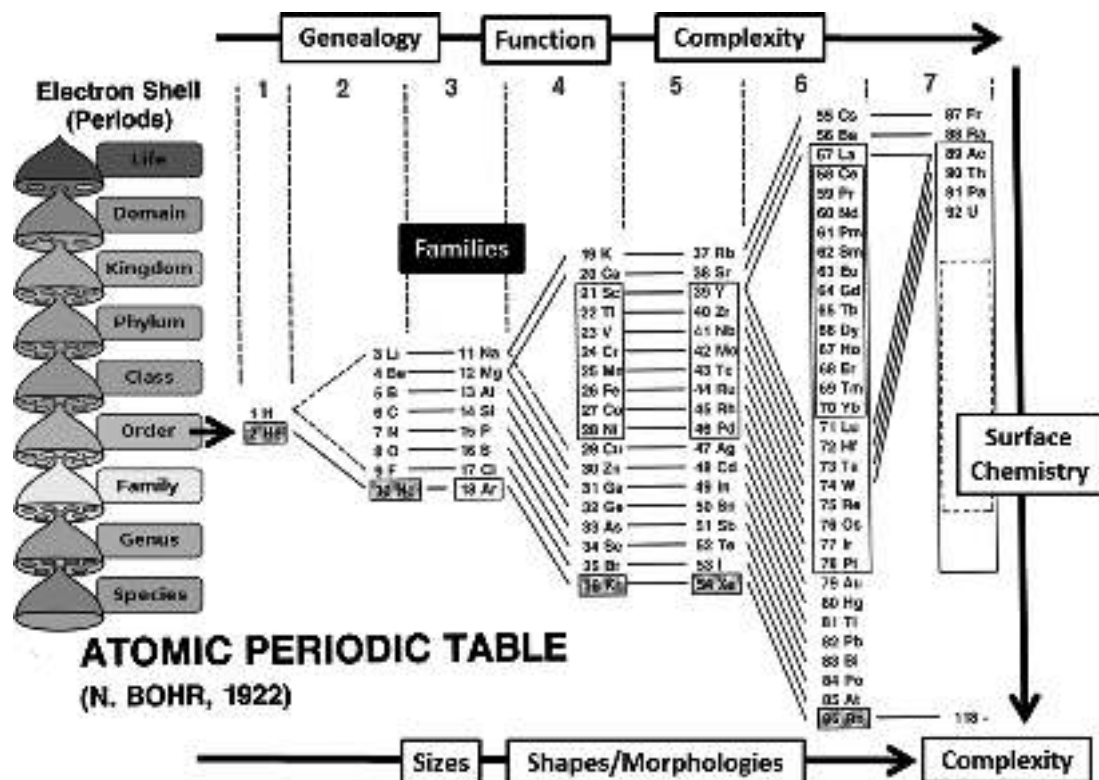


FIGURE 1.8. Linnaean taxonomy categories wherein the “order classification” of the elements is presented in a Bohr-type periodic-type cladogram associated with atomic elemental families that are defined as a function of CADPs that include; vertical periods of electronic shells [(i.e., sizes, orbital shapes, flexibility/rigidity, surface chemistry (reactivity))] and horizontal classes of electronic shells (i.e., sizes, reactivities, increasing masses, etc.).

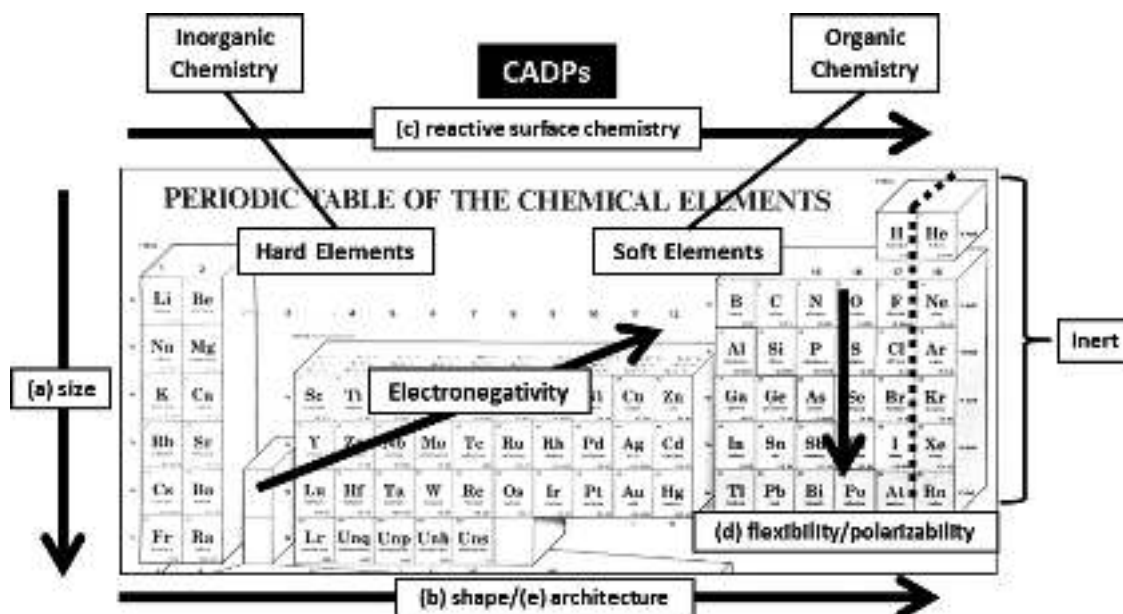


FIGURE 1.9. Structure-controlled critical atomic design parameters (CADPs) for atomic elements classified in a Mendeleev periodic table as a function of (a) size, (b) shape, (c) reactive surface chemistry, (d) flexibility/polarizability, (e) architecture, and (f) elemental composition.

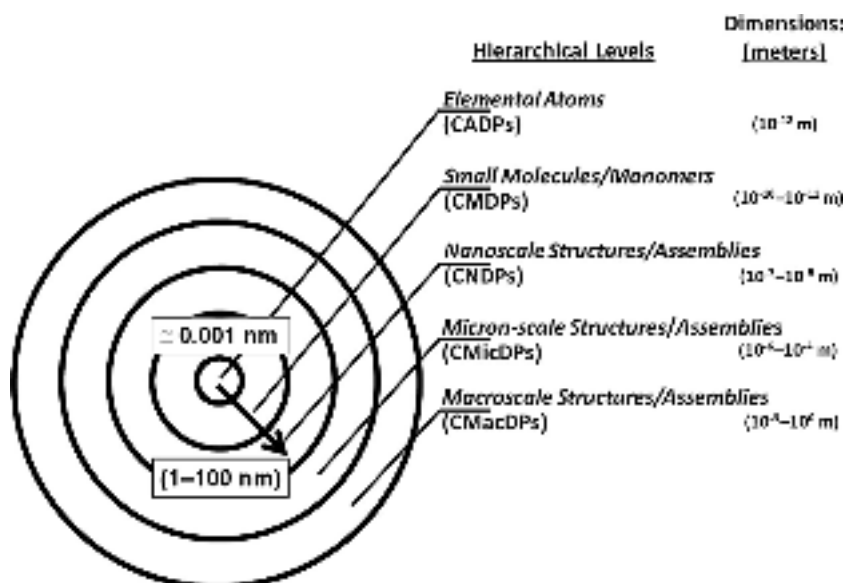


FIGURE 1.10. Concentrically, nested hierarchical levels used to illustrate conservation of critical module design parameters (i.e., sizes, shapes, surface chemistries, flexibilities, and architectures) as a function of their hierarchical levels (i.e., CADP→CMDP→CNDP→CmicDP→CMacDP) associated with their respective dimensions [31].

organisms as large as micron/meter scale. With the exception of biological-type taxonomies offered recently for proteins [29] and for viruses [20] based on messenger DNA/RNA precursors and genealogy, relatively little attention has been focused on nonbiological structures, assemblies, or entities in the 1 to 100-nm dimensional region. As shown in Figure 1.10, this nanoscale region is bracketed by well-demonstrated taxonomies for the atomic elements (i.e., the Mendeleev Periodic Table), as well as by Linnaean-type taxonomies for the micron-scale–macroscale region. As such, it seems plausible to expect a continuum of conserved CHDPs to connect these two hierarchical levels.

It is noteworthy that in spite of enormous activity in the nanotechnology field during the past several decades, only highly specific/limited strategies have been proposed [30]; however, no such universal Linnaean-type taxonomic scheme has been suggested for classifying and unifying well-defined nanostructures, assemblies, or clusters until recently.

1.4.3.1 Taxonomy of Nanostructure/Assemblies

(a) *Dendrimers/Dendrons as a Window to a Nanoscale Taxonomy.* Recently, we described the use of dendrons/dendrimers as a window to a new nano-periodic system for defining quantized, discrete categories of nano-building blocks (i.e., nano-elements) [31]. They may be thought of as heuristic, core-shell-type atom mimics that share many atom-like combining properties with atoms to yield stoichiometric nano-compounds. Based on more than 12,000 published references in the literature, it has been clearly demonstrated

that dendrons/dendrimers are structure controlled nanoscale constructs that exhibit quantized critical nanoscale design parameters (CNDPs) such as (a) size, (b) shape, (d) flexibility/rigidity, and (e) architecture. A variety of dendrimer surface reactions or guest–host assemblies have been shown in the literature to produce stoichiometric nano-compounds including (a) dendrimer–dendrimer, (b) dendrimer–protein, (c) dendrimer–fullerene, and (d) dendrimer–metal nanocluster structures, to mention a few [2]. Meanwhile, as part of this comparison, dendrimers have been shown to exhibit heuristic cladogram properties similar to the atomic elements as illustrated in Figure 1.11, where they are displayed according to the Niels Bohr format. Further comparisons can be made by projecting the first three generations of a dendrimer in a Mendeleev-type periodic format [1] as shown in Figure 1.12.

1.5 HEURISTIC MAGIC NUMBER MIMICRY AT THE SUBATOMIC, ATOMIC, AND NANOSCALE LEVELS

Many legendary scientists have made profound historical statements concerning the importance of number theory to the periodicity of matter. The following are just a small sampling:

- John Dalton (1803): “Atoms combine in simple numerical ratios.”
- Prout’s Hypothesis published anonymously in (1815): “The elements are different aggregates of the atoms of primordial hydrogen.”

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