CHAPTER 1

Introduction: The Concept of Biomimicry and Bioinspiration in Chemistry

TIMOTHY W. HANKS

Department of Chemistry, Furman University, Greenville, South Carolina, USA

GERHARD F. SWIEGERS

Intelligent Polymer Research Institute and ARC Center of Excellence for Electromaterials Science, University of Wollongong, Wollongong, NSW 2522, Australia

1.1 WHAT IS BIOMIMICRY AND BIOINSPIRATION?

The idea of looking to Nature to solve problems is undoubtedly as old as humanity itself. Observations of Nature, particularly of its biological face, have impacted the development of every facet of human society, from basic survival tactics to art, and from fashion to philosophy. Indeed, as a part of the biosphere ourselves, we cannot help but frame our conceptual understanding of ourselves and our environment in terms of biology. *Bioinspiration* and *biomimicry*, then, are ancient processes that take advantage of millions of years of evolutionary experimentation to help us address the many challenges that affect human well-being.

The term *biomimetics* was suggested by Schmitt in the early 1960s and was listed in Webster's dictionary as early as 1974. Webster's dictionary defined the concept as "The study of the formation, structure, or function of biologically produced substances and materials (as enzymes or silk) and biological mechanisms and processes (as protein synthesis or photosynthesis) especially for the purpose of synthesizing similar products by artificial mechanisms that mimic natural ones."[1]

While there are many historical examples that fit this definition, the formalization of the concept occurred only in the late 20th century. This formalization was

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significant in that it arguably represented a key paradigm shift in which the chemistry community changed its focus from molecular composition to the morphology and function of molecular and supramolecular structures.

While *biomimicry* formally involves a direct replication of processes or techniques that are employed by Nature, *bioinspiration* involves a more indirect "drawing of ideas" from Nature. Here Nature serves as a rich and readily accessible source of new concepts and approaches. Of particular interest are approaches that have the potential to help solve intractable and challenging problems. *Bioinspiration* is mostly concerned with understanding the principles that underlie natural processes and then applying these principles in nonbiological settings. Benson, Share, and Flood describe the principle as follows in Chapter 4, "Bioinspired Molecular Machines":

> Bioinspiration is described as understanding the fundamental aspects of some biological activity and then recasting it in another form. Consider the Wright brothers' research program, where lift, control, and propulsion were all accepted elements of bird flight. The first two elements were recast in similar forms as wing shape and wing warp, whereas the latter was completely replaced with an engine-driven propeller. It is illustrative that propulsion was generated using very different means.

The distinction between biomimicry and bioinspiration is, however, not clear-cut. There are many shades of overlap between these two concepts. For example, a deliberate and systematic mimicry of techniques employed by Nature within systems that are far removed from Nature could be considered to be either biomimicry or bioinspiration. A good illustration of this is given by Hoffmann in his masterly exposition in Chapter 14, "Biomimicry in Organic Synthesis." He says:

> When the targets of natural product synthesis become even more complex in the 21st century, it is evident that the strategies and methods used in the last century reach their limits. Hence, organic chemistry is faced in the 21st century with the necessity to substantially increase the efficiency of syntheses by turning to new strategies. Combined with better synthesis methods, this should reduce the number of steps necessary to reach complex target structures. . . . Natural products are synthesized by Nature in the living cells from simple starting materials. . . . When new strategies for synthesis of such compounds are needed, it is obvious and advantageous to ask how Nature synthesizes such molecules in the process of biosynthesis. This raises the hope that Nature has found, through the process of evolution, an efficient route for the synthesis of a particular natural product, a route that could serve as a model for in vitro synthesis. Thus, knowledge of a biosynthetic pathway for a natural product of interest could serve as a guideline to develop a "biomimetic" synthesis. This line of thought could be expected to open reasonable approaches to the synthesis of a natural product, or at least provide a much better synthetic route than used before.

The formal distinctions between biomimicry and bioinspiration can therefore blur and become difficult to separate. For this reason, this book assigns the same weight and importance to both topics. It is left up to the reader to decide whether a particular experiment is best considered as biomimicry or bioinspiration.

1.2 WHY SEEK INSPIRATION FROM, OR REPLICATE BIOLOGY?

1.2.1 Biomimicry and Bioinspiration as a Means of Learning from Nature and Reverse-Engineering from Nature

Perhaps the key reason for studying biomimicry and bioinspiration is to learn from Nature. Biological entities and processes have evolved over billions of years to achieve forms and functions that are often remarkable, both for their efficacy and their efficiency. Humanity has a lot to learn from Nature.

Zhu and Gu in Chapter 10, "Bioinspired Surfaces II: Bioinspired Photonic Materials," put it very succinctly:

> Nature provides inexhaustible wealth to humankind [and this is the reason to learn from it].

In Chapter 6, "Bioinspired Materials Chemistry II: Biomineralization as Inspiration for Materials Chemistry," Nudelman and Sommerdijk state it thus:

> Living organisms are well known to exploit the material properties of amorphous and crystalline minerals in building a wide range of organic–inorganic hybrid materials for a variety of purposes, such as navigation, mechanical support, protection of the soft parts of the body, and optical photonic effects. The high level of control over the composition, structure, size, and morphology of biominerals results in materials of amazing complexity and fascinating properties that strongly contrast with those of geological minerals and often surpass those of synthetic analogs. It is no surprise, then, that biominerals have intrigued scientists for many decades and served as a source of inspiration in the development of materials with highly controllable and specialized properties. Indeed, by looking at examples from the biological world, one can see how organisms are capable of manipulating mineral formation so as to produce materials that are tailor-made for their needs.

Finally, Benson and colleagues make the amusing note that we do not need an alien civilization to land on Earth in order to undertake technological development by reverse-engineering. We can reverse-engineer from Nature. That is, indeed, the very basis of biomimicry and bioinspiration. They state in Chapter 4, "Bioinspired Molecular Machines":

> A variation on this last notion of bioinspiration has a healthy life in our fertile cultural imagination—revisited in fiction and urban legend alike. The proposition has been made that the explosion in technological development over the past century or so came about when humanity reverse-engineered technology that was originally fabricated by advanced alien species. While absurd as an account of modern civilization, this sequence of events is somewhat analogous to chemistry's use of bioinspiration, which takes cues from Nature's mature "technology."

1.2.2 Biomimicry and Bioinspiration as a Test of Our Understanding of Nature

It has often been said that one only truly understands a principle or a system if one is able to apply it in a functionally operational way, in a setting of one's own making. Much of the work described in this book is dedicated to this concept. It asks: Do we properly understand Nature's principles? If we do, then we should be able replicate, in at least some small measure, the feats of biology. If we cannot, then our understanding is necessarily and unambiguously incomplete. The experiment leaves little leeway for self-delusion. As noted by Benson, Share, and Flood in Chapter 4:

> Here, the direct question to be answered once the machine has been made is: "Does it move?" Or, in the parlance of the Wright brothers, "Does it fly?"

Seen in this light, bioinspiration and biomimicry can also be considered to be a test of our understanding of Nature. Indeed, every experiment is, effectively, a measure of our understanding. Swiegers, Chen, and Wagner have stated it thus in Chapter 7, "Bioinspired Catalysis":

> Every winged aircraft and putative aircraft ever built comprises nothing less than a test of the builder's understanding of the underlying principle by which birds fly, namely, the law of the aerofoil.

1.2.3 Going Beyond Biomimicry and Bioinspiration

A question that arises is: what, in the fullness of time, is the ultimate purpose of biomimicry and bioinspiration? According to several commentators, this "ultimate purpose" is not merely to emulate Nature or achieve capacities similar to those enjoyed by Nature, but rather to go beyond Nature into a man-made realm that surpasses Nature. Nobel Laureate Jean-Marie Lehn is perhaps the foremost proponent of this approach. He describes it thus in his Foreword to this book:

> Chemistry and in particular supramolecular chemistry entertain a double relationship with biology. Numerous studies are concerned with substances and processes of a biological or *biomimetic* nature. The scrutinization of biological processes by chemists has led to the development of models for understanding them on a molecular basis and of suitably designed effectors for acting on them. On the other hand, the challenge for chemistry lies in the development of *abiotic*, nonnatural systems, figments of the imagination of the chemist, displaying desired structural features and carrying out functions other than those present in biology with comparable efficiency and selectivity. Not limited by the constraints of living organisms, abiotic chemistry is free to invent new substances and processes. The field of chemistry is indeed broader than that of the systems actually realized in Nature.

1.3 OTHER MONIKERS: BIOUTILIZATION, BIOEXTRACTION, BIODERIVATION, AND BIONICS

Bioinspiration and biomimicry however, are arguably not the only descriptors of our interaction with Nature. There are several distinct approaches for making use of facts learned by observing the biosphere. The most obvious is to use natural materials directly; what we might call *bioutilization*. When the natural component of interest is too dilute for our purposes as harvested, such as natural products to be used in pharmaceuticals, they must be *bioextracted*. This technique has long been a major approach to exploiting the bounty of the biosphere and will continue to play a major role in society.

It is, moreover, often the case that a product of Nature does not meet our needs in the initially extracted form or that the extraction process may not be economically feasible. *Bioderived* materials are the result of modifying Nature's offerings to provide enhanced performance. The optimization and production of bioderived products has arguably been the key tool for the transformation of human society for centuries. For example, the development of organic chemistry from its origins in dye chemistry to its current key role in the pharmaceutical, plastics, and many other industries is largely a result of the modification of products found in Nature.

In addition to extracting and modifying natural materials for our own purposes, we have long strived to reproduce biological form and function. There are many examples of such efforts, including attempts by the Chinese to make artificial silk more than 3000 years ago, the invention of Velcro based on the hooked seeds of the burdock plant, and dry adhesive tape based on the surface morphology of gecko feet.[2] The term *bionics* was introduced by Steele, in late 1958, to promote the study of biological systems for solving physical problems. Bionics was originally defined as "the science of systems which have some function copied from Nature," but perhaps as a result of the TV series *The Six Million Dollar Man*, and recent interest in the brain/machine interface, the term has largely come to mean "biological electronics." While specific interfaces between living systems and electronics may indeed have some of the features of the original definition, we will largely avoid the use of the term here to avoid confusion.

1.4 BIOMIMICRY AND SUSTAINABILITY

In order to rationally exploit the products and processes of Nature for our own purposes, it is necessary to deconstruct very complex systems in order to decipher the underlying physical, chemical, and biological processes that result in the natural phenomena we wish to emulate. This process of deducing and exploiting the fundamental laws that govern the universe has proved to be a powerful strategy for technological development. Indeed, while modern science and technology has its origins in Nature, many of the products we surround ourselves with show little, or only superficial, resemblance to naturally occurring materials. The sheer number of humans on the planet and our ability to manipulate energy on a scale unlike anything found in the biosphere means that we have created (and continue to create) environments that are radically different from those produced by Nature. All biological systems impact their surroundings, but the unprecedented scale and rate of our activities has outstripped the capacity of the biosphere to adapt using its evolutionary approach. Our efforts to provide ourselves with comfort, security, and even amusement are often highly detrimental to the rest of the biosphere and ultimately to ourselves. Plastics are generally not degraded by the usual biological processes and their mass is not readily recycled. Sediment disruption from mining and concentration of particular elements in fabrication processes can lead to areas that are highly toxic to life forms, including our own. Pesticides, industrial waste, and pharmaceutical products can make their way into the environment, causing mutations or cellular disruptions in plants and animals. It has been clear now for some decades that the industrialization of society with scant regard for the larger biosphere has serious consequences.

The term biomimicry has been used since at least 1976 as a synonym for biomimetic,[3] but it has more recently been linked to environmentalism with the publication of *Biomimicry: Innovation Inspired by Nature*[4] by Janine Benyus and through the popularization of the idea through the work of the Biomimicry Institute.[5] Benyus's book focuses on nine core concepts derived from the study of the natural world:

Nature runs on sunlight.
Nature uses only the energy it needs.
Nature fits form to function.
Nature recycles everything.
Nature rewards cooperation.
Nature banks on diversity.
Nature demands local expertise.
Nature curbs excesses from within.
Nature taps the power of limits.

From this perspective, biomimicry becomes a strategy for not only taking advantage of Nature to produce novel structures and processes, but also as a way to combat the negative environmental impacts of current practices. New developments toward sustainable agriculture practices parallel these ideas, but there is movement within the science and engineering communities that embraces these ideas as well. A recent review[6] highlights some of the activities in the chemical engineering research and education establishments to develop programs that not only take advantage of the technological insights afforded by Nature, but also strategies for integrating industrial processes with those of the biosphere. Likewise, recent texts have explored the role that biomimicry might play in architecture[7, 8] and urban planning.[9] As human population continues to increase and resources become scarce, a biomimetic approach to organizing our cities offers a strategy for long-term survival.

In the interests of providing a balanced view, we should note that the "green" biomimetic approach described above is not without critics. Kaplinsky argues that humans too are part of Nature and that our technical achievements and physical constructs are not only on par with those of evolution, but are "natural" in the same way that the building of shelters by other animals are natural.[10] The interdependence of Nature is such that the activities of one species necessarily impact the environment of others, and while the activities of humans are dramatically larger than those of any other species, the basic principle is the same. Kaplinsky agrees that there is much to be learned from Nature, but he points out that biological designs are by no means completely optimized, even for the unique microenvironment of a given species. Evolution has produced amazing structures and strategies over the eons, but the process is exceedingly slow. Conversely, humans are able to learn, adapt, and innovate on a time scale that is very brief compared to evolutionary processes.

Kaplinsky takes issue with other ideas of the green biomimicry viewpoint. In effect, he proposes that it is possible to get carried away with the wonders of Nature, while ignoring the less palpable aspects. For example, at the risk of being overly cynical, he notes that "the fossil fuels that supply our energy are, after all, nothing but waste products of Nature that escaped its supposedly miraculous recycling process." Moreover, while Nature may "reward cooperation," it also rewards competition, parasitism, violence, and some of the most underhanded, nefarious behaviors imaginable. Indeed, the entire biosphere is a battle zone of species engaged in all-out physical, chemical, and biological warfare in a relentless struggle for resources. This battle is carried out over multiple size and temporal regimes where the primary difference between winners and losers is reproduction and whether the "recycling" commences soon or somewhat later.

Clearly, Nature is not inherently benign—a fact not lost on the defense establishment, which is concerned not only with the implications of bioweapons, but also about the ways in which biomimetics will impact areas of the warfare system from fuels to robotics.[11] Biomimicry offers tremendously powerful strategies, but also demands responsible development in order to provide benefits while mitigating potential damage. The biomimetic approach does, however, inherently encourage an examination of how a particular structure or process fits into its surroundings and may thereby assist in the development of sustainable approaches to technological and industrial development.

1.5 BIOMIMICRY AND NANOSTRUCTURE

The concept of biomimicry has been explored in a wide range of fields and attempts have been made to apply the "lessons of Nature" in a number of ways, some of them in unexpected fields. For example, Thompson uses biomimicry to propose approaches to personnel management[12] and a recent report describes a bioinspired approach to credit risk analysis.[13] While computational models have been applied extensively to biological systems, biomimetic principles have also been successfully directed toward problems in computer science, such as systems management,[14] control systems and robotics,[15] and distributed computing algorithms.[16] However, by far the most active fields making use of bioinspiration and biomimicry are those of chemistry and materials science.[17] This comes as no surprise, since there has always been a close relationship between biology and chemistry. What has changed in recent years, and is reflected in the content of this book, is the level of complexity that is involved in the biomimicry. This complexity shows itself in many ways, but particularly in material morphology across multiple size regimes—structural hierarchy-and in the new field of nanotechnology.

In 1994, the U.S. National Research Council issued a report outlining the potential offered by biological hierarchical structures to materials scientists.[18] They noted that while Nature has a relatively limited range of materials to work with, composites with astoundingly diverse properties result through structural control over multiple length scales.

Hierarchical materials systems in biology are characterized by:

- Recurrent use of molecular constituents (e.g. collagen), such that widely variable properties are attained from apparently similar elementary units
- Controlled orientation of structural elements
- Durable interfaces between hard and soft materials
- Sensitivity to—and critical dependence on—the presence of water
- Properties that vary in response to performance requirements
- Fatigue resistance and resiliency
- Controlled and often complex shapes
- Capacity for self-repair

The report goes on to describe specific examples of natural materials with unique properties and technological challenges that could potentially be met by mimicking key features. Yet the actual realization of the examples offered is difficult, as it requires not only understanding the material's composition and properties at the different length scales, but also the ways in which they work together to provide the properties of interest.

In 2010, the U.S. National Nanotechnology Initiative reached its 10th anniversary, with more than $14 billion directed toward the development of new technologies.[19] Worldwide, more than $50 billion (U.S.) has been spent by the public and private sectors, with many nations instituting formal nanotechnology programs. The global focus on nanotechnology has accelerated the ongoing development of imaging and analytical tools that bridge the gap between the traditional chemistry size regime and that of biology. From the "top–down" perspective, these tools permit ever-higher resolution for probing of material structure. From the "bottom–up" perspective, they give insight into the organization of molecules into increasingly larger and more elaborate assemblies.

Optical and electron microscopes provide striking and appealing images of natural structures that can take us from very large to very small (nanometer) length scales. At the small end though, the scanning probe microscope (SPM) family of instruments are key tools that help nanoscience and biology combine to provide a unique biomimetic perspective.[20]

Beginning with the scanning tunneling microscope and later the more biologically relevant atomic force microscope (AFM), SPMs involve the rastering of a very sharp tip (on the order of 10 nm in radius of curvature) across a surface. The tip is affixed to a cantilever, which undergoes deflection in response to surface topography (in the case of simple AFM) or other forces. A recent review on the use of AFM in the study of amyloids illustrates the power of scanning probe technologies to provide a variety of detailed information.[21]

AFM and other SPM technologies are tremendously powerful tools for examining the surfaces and interfaces found in both synthetic and biological materials. It is the surface of a material, or a component within a composite, that determines whether another environmental actor will adhere or simply slip away. Surfaces are responsible for the ways in which light is absorbed and reflected, giving an object its color. Surfaces are where an object is first subject to wear and corrosion. In atomically homogenous nanoparticles, the surface atoms experience forces different from those in the bulk and may have distinctly different chemical behavior.

In Chapters 9 and 10, inspiration is taken from different types of biological surfaces. In a sweeping and detailed exposition, Qu, Li, and Dai examine, in Chapter 9, the issue of dry adhesion using the gecko foot as inspiration. They discuss recent progress and the potential of synthetic mimics of this incredible structural design. In Chapter 10, Zhu and Gu consider the phenomenon of structural color, which involves the use of nanopatterned surfaces to generate bright and vividly colored surfaces. Their inspiration is the wings of the Morpho butterfly and related structures, which achieve vibrant color by means of interference effects due to their surface and near-surface structures.

1.6 BIOINSPIRATION AND STRUCTURAL HIERARCHIES

Throughout Chapters 9 and 10, the importance of structural hierarchy on surface properties is demonstrated. The gecko's toes, for example, are covered arrays of hair-like structures called *setae*, which are in turn split into even finer structures. This concept of increasing effective surface area is not restricted to increasing adhesive forces. In Chapter 13, Della Pelle and Thayumanavan present examples where functional arrays can be used for light-harvesting and drug delivery. Some arrays may be thought of as large two-dimensional surfaces that are roughened into the third by the attachment of ever smaller structures. Dendridic structures, also discussed in Chapter 13, are better conceptualized as polymers that grow from simple molecules into increasingly bifurcated three-dimensional arrays through the coupling of monomers with connectivity greater than two.

In Chapter 8 Himmelein and Ravoo look at amphiphilic bilayer "surfaces" that have effectively been bent until they form hollow vesicles. At their most basic, these vesicles are composed of a homogenous collection of amphiphiles—molecules containing a hydrophilic head group and a lipophilic tail. At their most complex level, they are the elaborate architectures that define the cell walls in living organisms. The phospholipid-based cell wall is a highly sophisticated, dynamic structure complete with functional components that enable the cell not only to retain its contents but also to transport nutrients and waste, to respond to chemical and physical stimuli, and to perform other functions. Synthetic vesicles used in commercial applications are far less ambitious in their function, mainly serving to encapsulate drugs or other species. However, through biomimicry, more complex structures are being developed by adding molecular recognition elements to the surface, introducing subcompartments, and introducing "smart" stimulus–response capability. The relative ease with which different regions of the vesicle may be modified makes these structures interesting platforms for the development of nanoscale devices.

Nature produces much more than interesting surfaces and pseudosurfaces. There is a tremendous interest in bioinspired composite materials in which the synergism between materials with different physical properties and different size scales leads to useful macroscopic physical properties, as well as to important biological and chemical features.[22] For example, both the aging of the world's population and ongoing violent conflicts are driving the search for synthetic materials that can be used to replace human tissue. The challenges of tissue engineering and regenerative medicine are as great as the need for high volume abiological replacements.[23] Some applications in this field require materials with good mechanical strength, while others demand constructs that are soft and extensively vascularized. The majority of materials must be biocompatible, meaning not only nontoxic and acceptable to the immune system, but also with the proper mechanical properties to interface with natural tissue. Sometimes the requirements for a particular application seem almost absurd in light of previous generations of synthetic materials, yet Nature shows they are possible. For example, an implanted neural electrode should be very soft and highly hydrated, yet capable of conducting electricity. Ideally, it would act as a cellular scaffold that minimizes the inflammatory response generated by the insertion of the electrode and would encourage the directional growth of neurons through the controlled release of chemical, electrical, and perhaps viscoelastic cues. Biocompatible hydrogels are under development that may be able to fulfill all of these functions.[24]

Chapters 5 and 6 review biomimetic materials in which the inorganic aspects of biology are exploited. In Chapter 5, Aranda, Fernandes, Wicklein, Ruiz-Hitzky, Hill, and Ariga discuss the formation, properties, and applications of organic–inorganic hybrid materials, which can provide strength *and* fracture resistance due to clever structural hierarchy and control of component interfaces. In Chapter 6, Nudelman and Sommerdijk present a class of synthetic materials inspired by biomineralization. There are countless examples in Nature where organisms extract inorganic ions from their environment to create relatively hard structures with both striking macroscopic shapes and microscopic structures that provide properties critical to the organism. Sommerdijk illustrates how lessons learned from these structures can be applied to the construction of new ceramics and semiconductors. Throughout this chapter, an emphasis is placed on the importance of considering not only the structures of biological models, but also the processes that lead to their formation.

1.7 BIOINSPIRATION AND SELF-ASSEMBLY

Biological processes generally take place under mild conditions and in aqueous solution. Not only are these conditions quite different from those of traditional materials synthesis, the dynamical behavior of the resulting products is also quite different. Synthetic structures are generally conceived as being in their final, complete form at the end of the fabrication process, while supramolecular biological structures derive much of their functionality from their spatial organization. They are also dynamic, responding to environmental cues to change both shape and activity. To achieve this, biological systems rely on a combination of relatively strong covalent bonds for their primary structure and both directional and nondirectional weak interactions for higher level structure and assemblies.[25] The primary mechanism for the construction (and deconstruction) of biological entities is one of self-assembly, where the basic building blocks of a superstructure are guided into place by strategic positioning of the functional groups that give rise to the weak interactions. The ability to build structures with atomic precision is also a goal of nanoscience and considerable effort is being applied toward designing the self-assembling building blocks that lead to useful superstructures.

Self-assembly inevitably generates defects in a structure. While “defects” are the origin of a property of interest in some materials, even in those cases it is necessary to be able to control the number and locations of defects. Fully reversible systems operate under thermodynamic control, allowing defects to be repaired, but this is a slow process and only provides access to structures at the global thermodynamic minimum. The first limitation can be problematic in biology, but is even more so in the industrial world, where high throughput is not only desirable, but may determine the ultimate feasibility of a given process. The second limitation is also important, because many interesting structures lie at local thermodynamic minima. Biology shows that such structures may be accessed by “assisted self-assembly,” where reaction conditions or biocatalysts provide viable pathways to kinetic structures.[26]

An alternative to thermodynamic self-assembly is “kinetic” or “nonequilibrium” self-assembly. Here the system cascades through a series of steps to end up at the kinetically favored product, which would typically not lie at the global thermodynamic minimum. In such processes, each step sets up the next, leaving the system with little option but to traverse a pathway that seems almost predetermined, much like the pathway that is followed when a line of dominos is toppled. Nonequilibrium processes of this type are believed to be common in biology. For example, the remarkable rapidity with which proteins fold is consistent with this process being largely a nonequilibrium one.

Self-assembly is a general theme that necessarily runs throughout this text, but the topic is addressed in detail in Chapters 2 and 3. In Chapter 2, Lindoy, Richardson, and Clegg provide an overview of self-assembly in polymeric, metal-organic, and other nonbiological systems that generate structures that have “biological” features and functions. The authors provide specific examples of self-assembled structural elements that may lead to novel applications. In Chapter 3, Ercolani and Schiaffino discuss the role of cooperativity in biological and abiological systems.

Cooperativity is an important feature in molecules that display allosteric responses and can provide selectivity in binding events for sensors and stimuli-responsive constructs. Cooperativity is particularly important in nonequilibrium self-assembly processes, which are path and time dependent.

In Chapter 11, Binder, Schunack, Herbst, and Pulamagatta expand on the self-assembly theme in a discussion of the dynamic behavior of biomimetic polymers. As with biological polymers such as proteins, these synthetic polymers display dynamic changes in their higher order structure, including folding and coiling into predefined shapes. Elements of self-assembly and molecular recognition are also found in Chapter 4, by Benson, Share, and Flood, with an examination of bioinspired molecular machines. Here, self-assembly is required for both the initial formation of the machines and to drive the switching between individual states. The harnessing of biology to design nanoelectromechanical systems has the potential to lead to systems with not only hierarchical structure but also hierarchical mechanical motion.[27]

1.8 BIOINSPIRATION AND FUNCTION

In biology, structure is intimately coupled to function. Natural structures are exquisitely engineered to operate within the chemical and energetic constraints of the biological environment and therefore often incorporate highly efficient or even unexpected (from the synthetic viewpoint) functions. For example, polymer science has provided us with products that have excellent mechanical properties, but when polymeric products fail they are usually nonrecyclable (at least by biological mechanisms) and their primary purpose is irreversibly compromised. Conversely, biological composites feature mechanisms for restoring functionality after sustaining damage. Recent efforts to develop self-healing polymers and polymer composites are taking the initial steps toward low-maintenance, high-durability products and devices.[28] The challenge in this area is to refine the biological inspiration so that it will work with synthetic processes. Biological repair requires a dynamic and relatively elaborate support infrastructure; it is often slow (days to months) compared to the needs of synthetic materials (minutes to perhaps hours).[29]

Bioinspired functionality is a theme woven throughout this text, but possibly the field where Nature's functional molecules inspire the greatest respect from those developing their synthetic counterparts is that of catalysis. Enzymes are highly efficient and can display extraordinary selectivity by orienting substrates, stabilizing intermediates, and other processes that are not yet fully understood.[30] In Chapter 7, Swiegers, Chen, and Wagner explain how the conformational dynamics of enzymes is an integral part of their catalytic function and how biomimetic catalysts can make use of conformational flexing to replicate natural efficiencies.

Natural compounds have long been a source of inspiration for the pharmaceutical and related health care industries. Tremendous effort has gone into the total synthesis of natural products as well as into preparing derivatives that might show superior performance.[31] In Chapter 14, Hoffmann looks at functionality from the perspective of process rather than from a largely structure/function viewpoint. Biomimetic and cascade reactions in synthetic organic chemistry, for instance, are able to produce target molecules with high step, atom, and redox efficiencies. This approach to the production of pharmaceutically and industrially important compounds ties into the green promise of biomimicry. Comparisons of our current abilities with those of biological systems gives us a benchmark of our progress and ideas for further refinement.

Biological organisms live in complex environments and survive by collecting quantitative and qualitative information about the changes around (and within) them. Like biological structures, the sensing function is hierarchical and takes place on the subcellular level on up to macroscopic sensors with sensing processes triggering responses across different size and temporal regimes.[32]

In Chapter 12, Le Gac, Jabin, and Reinaud use the example of synthetic receptors based on calix[6]arene-based receptors as biomimics of molecular and ion-pair recognition elements. The low toxicity and versatility of this platform places it alongside crown ethers and cyclodextrins as some of the most important classes of macrocycle with a myriad of potential uses.[33]

1.9 FUTURE PERSPECTIVES: DRAWING INSPIRATION FROM THE COMPLEX SYSTEM THAT IS NATURE

In the final chapter of this work, Cady, Robinson, Smith, and Swiegers briefly explore some future perspectives in the field of bioinspiration and biomimicry in chemistry. These include an examination of the big picture of life itself, its origin and its character. They show that life in Nature comprises an extraordinarily complicated web of interconnected interactions that displays properties which are characteristic of so-called complex systems, including emergence, evolution, autonomy, and others.

The field of complex systems science studies the way in which multiplicities of independent elements interact with each other to create chains of action and reaction that lead to amplified and/or unique outcomes. Examples include family trees (chains of procreation), weather systems (chains of interacting weather events), traffic patterns on intersecting highways (chains of automobile movements), and economic behavior (in, for example, the chains of mutually beneficial transactions on stock exchanges). The most important complex system, at least to us, involves the way that biochemical entities interact with each other to create life itself (chains of biochemical events). A future perspective that is just beginning to emerge in bioinspiration and biomimicry is to understand and replicate the processes at play. In biology, this field is called *systems biology*. The corresponding new and emerging field of *systems chemistry* aims to study and apply the same concepts to chemistry.

The significance of these studies is that they go beyond mere chemistry and have implications in a host of other fields, including some of those mentioned previously, like information technology (self-improving computer programs), social interactions and human behavior (e.g., criminology, sociology, ethics), and economics (the phenomenon of "economic growth"). As such, they offer the prospect of unifying science and improving the human experience.

This book provides a perspective on how the study of Nature has had a profound impact on the disciplines of chemistry and materials science. It is a story that is thousands of years old, yet we are still in the introductory chapter. The inspiration that will be gleaned from the earthly biosphere over the coming years is vast and we may never discover all of its secrets, much less elucidate the web of synergistic interactions that makes it all work. It is breathtaking to realize that our world is but one among a vast number of likely worlds, many of which will surely have evolved their own biospheres with their own unique materials and interconnected processes. In the fullness of time bioinspiration and biomimicry may ultimately grow to encompass an interplanetary aspect. Perhaps this will one day turn out to be the best justification for humankind to reach for the stars.

REFERENCES

1. Harkness, X. X. *IEEE Eng. Med. Biol*. **2004**, *23,* 20.
2. Vincent, J. F. V.; Bogatyreva, O. A.; Bowyer, A.; Paul, A.-P. *J. R. Soc. Interface* **2006**, *3,* 471.
3. Busch, D. H. *Abs. Papers Am. Chem. Soc*. **1976**, *Suppl. 1*, 1.
4. Benyus, J. M. *Biomimicry: Innovation Inspired by Nature*, William Morrow, New York, 1997.
5. http://www.biomimicryinstitute.org/.
6. Garcia-Serna, J.; Perez-Barringon, L.; Cocero, M. J. *Chem. Eng. J*. **2007**, *133,* 7.
7. Ginatta, C. *ARCHITECTURE Without Architecture: Biomimicry Design*, VDM Verlag Dr. Müller GmbH & Co. KG, Saarbrucken, Germany, 2010.
8. Gruber, P. *Biomimetics in Architecture: Architecture of Life and Buildings*, Springer, New York, 2011.
9. Spiegelhalter, T.; Arch, R. A. *The Sustainable City VI: Urban Regeneration and Sustainability* (Eds. Brebbia, C. A.; Hernandez, S.; Tiezzi, E.), Wit Press, Southampton, UK, 2010.
10. Kaplinsky, J. *Architectural Design* **2006**, *76,* 66.
11. *Bio-inspired Innovation and National Security* (Eds. Armstrong, R. E.; Drapeau, M. D.; Loeb, C. A.; Valdes, J. J.), National Defense University Press, Washington DC, 2010.
12. Thompson, K.; Bonk, C. J.; Cross, J. *Bioteams: High Performance Teams Based on Nature's Most Successful Designs*, Meghan Kiffer Press, Tampa, FL, 2008.
13. Yu, L.; Wang, S.; Lai, K. K.; Zhou, L. *Bio-Inspired Credit Risk Analysis: Computational Intelligence with Support Vector Machines*, Springer, New York, 2008.
14. Nakrani, S.; Tovey, C. *Bioinspir. Biomim*. **2007**, *2,* S182.
15. Passino, K. M. *Biomimicry for Optimization, Control and Automation*, Springer-Verlag, London, 2005.
16. Afek, Y.; Alon, N.; Barad, O.; Barkai, N.; Bar-Joseph, Z. *Science* **2011**, *331,* 183.

17. Sanchez, C.; Arribart, H.; Guille, M. M. G. *Nature Materials* **2005**, *4,* 277.

18. Tirrell, D. A. (coord.) *Hierarchical Structures in Biology as a Guide for New Materials Technology*, National Material Advisory Board, The National Academic Press, Washington DC, 1994.

19. Sargent, J. F. Jr. *The National Nanotechnology Initiative: Overview, Reauthorization, and Appropriations Issues*, Congressional Research Service, Washington DC, 2011.

20. Casuso, I.; Rico, F.; Scheuring, S. *J. Mol. Recog*. **2011**, *24,* 406.

21. Gosal, W. S.; Myers, S. L.; Radford, S. E.; Thomson, N. H. *Prot. Pept. Lett*. **2006**, *13,* 261.

22. *Biomimetics, Learning from Nature* (Ed. Mukherjee, A.), InTech, Vukovar, Croatia, 2010.

23. Schenke-Layland, K. *Adv. Drug Deliv. Rev*. **2011**, *63,* 193.

24. Guiseppi-Elie, A. *Biomaterials* **2010**, *31,* 2701.

25. Mohammed, J. S.; Murphy, W. L. *Adv. Mater*. **2009**, *21,* 2361.

26. Hirst, A. R.; Roy, S.; Arora, M.; Das, A. K.; Hodson, N.; Murray, P.; Marshall, S.; Javid, N.; Sefcik, J.; Boekhoven, J.; van Esch, J. H.; Santabarbara, S.; Hunt, N. T.; Ulijn, R. V. *Nature Chemistry* **2010**, *2,* 1089.

27. Huang, T. J.; Flood, A. H.; Brough, B.; Liu, Y.; Bonvallet, P. A.; Kang, S.; Chu, C.-W.; Guo, T.-F.; Lu, W.; Yang, Y.; Stoddart, J. F.; Ho, C.-M. *IEEE Trans. Autom. Sci. Eng*. **2006**, *3,* 254.

28. Blaiszik, B. J.; Kramer, S. L. B.; Olugebefola, S. C.; Moore, J. S.; Sottos, N. R.; White, S. R. *Annu. Rev. Mater. Res*. **2010**. *40,* 179.

29. Vincent, J. F. V. *Proc. Inst. Mech. Eng. H: J. Eng. Med*. **2009**, *223,* 919.

30. Deuss, P. J.; den Heeten, R.; Laan, W.; Kamer, P. C. J. *Chem. Eur. J*. **2011**, *17,* 4680.

31. Beghyn, T.; Deprez-Poulain, R.; Willand, N.; Folleas, B.; Deprez, B. *Chem. Biol. Drug Des*. **2008**, *72,* 3.

32. Johnson, E. A. C.; Bonser, R. H. C.; Jeronimidis, G. *Philos. Trans. R. Soc. A* **2009**, *367,* 1559.

33. Sansone, F.; Baldini, L.; Casnati, A.; Ungaro, R. *New J. Chem*. **2010**, *34,* 2715.