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ORIGINAL ARTICLE

The supramolecular chemistry between eastern philosophy and the complexity theory

Omar Pandoli · Gian Piero Spada

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Abstract How supramolecular chemistry interplays between the eastern philosophy and the complexity theory relationship? From which point could we start to speak about the fundamental self-organization process that seems to be "the driving force that lead up to the evolution of the biological word from the inanimate matter"? We think the best way is to focus on the core, and move around a core concept: the self-processes in Nature are the starting point for the whole organic world. Taking suggestion from the old eastern philosophy and observing the recent western theory in this paper we will evidence some analogies between the two apparent different thoughts and show that both approaches want to know more about the emerging of life from inanimate matter. In this perspective we underline that Supramolecular Chemistry, investigating the emerging behaviour or properties of the whole complex system, has a central role to understand the spontaneous evolution of Nature. If the self-organization is a conveyor belt of non-animated to animated complex matter, what are the gears of this engine of Nature able to generate Life and new living beings? We cannot provide a definitive answer to this question, however we can recall some acutely relevant research. In this paper we introduce, first, some basic principles of the ancient eastern philosophy in synergy with the modern science of the complexity. Second, the theories dealing with autopoietic systems and dissipative structures, will be presented in order to compare biological and social mechanisms with the (organic) chemistry world. Finally, we report on a few aspects of supramolecular chemistry of guanosine derivatives and their implications in material sciences, medicine and nanotechnology.

Keywords Supramolecular chemistry · Complexity theory · Eastern philosophy · Guanosine · Self-assembly · Adaptative system

Introduction

The pleasure and, simultaneously, the difficulty in writing this paper has been the oxymoron of thinking and operating in a circular way. Where to start to speak about the fundamental self-organization process? From which cardinal points we should begin? We suggest that the best way is to focus on the core, and move around a paramount concept: the self-processes in Nature are the starting point for the whole organic world. Eigen, a pioneer of the study of self-organized systems, said: 'Self-organization is driving force that lead up to the evolution of the biological word from the inanimate matter' [1, 2].

In this paper we want to show some analogies between the eastern philosophy and the theory of the complexity and the effort of the modern science to gain information about the emerging of life from inanimate matter. In all of this we thought that the Supramolecular Chemistry through the observation, bottom-up, of the single molecule, and the approach top-down to study the emerging behaviour of the

O. Pandoli (✉)
Dipartimento di Chimica, Università di Ferrara,
Via Borsari 46, 44100 Ferrara, Italy
e-mail: omar.pandoli@unife.it

Present Address:
O. Pandoli
Institute of Micro/Nano Science Technology, Shanghai Jiao
Tong University, Shanghai, People's Republic of China

G. P. Spada
Dipartimento di Chimica Organica "A. Mangini", Alma Mater
Studiorum – Università di Bologna, Via San Giacomo 11,
40126 Bologna, Italy

whole complex system, it could have a central role to understand the self-process phenomena of Nature.

Coming back to the first question, one could argue: if the self-organization is a conveyor belt of the non-animated to animated complex matter, what are the gears of this engine of Nature able to generate Life and new living beings? We cannot provide a definitive answer to this question however, we can recall some acutely pertinent research. In this paper we introduce, first, some basic principles of the ancient eastern philosophy in synergy with the modern science of the complexity and spontaneity of the evolution of Nature. Second, the theories dealing with autopoietic systems and dissipative structures will be presented in order to compare biological and social mechanisms with the (organic) chemistry world. Finally, we report on a few aspects of supramolecular chemistry of guanosine derivatives and their implications in material sciences, medicine and nanotechnology.

The holistic view in eastern philosophy

In 1975 Capra, in the Book "The Tao of Physics. An Exploration of the Parallels Between Modern Physics and Eastern Mysticism," explored the relationship between the concepts of modern physics and the basic ideas of Eastern mysticism [3, 4]. He reminds us that Schrödinger, the pioneer of quantum mechanics, was deeply influenced by Eastern philosophy.

In 1990 Shimizu reported that the principle of self-organisation enables the connection of oriental thoughts to western thoughts [5]. More recently Jones and Culliney found the roots of the essential ideas of the science of complexity/chaos in the social ordering principle of *li* (organisation or rites/decorum) in Confucius's Analects [6].

Chinese philosophy has a history spanning several thousand years; its origins are often traced back to the "I Ching" (simplified Chinese: 易 经, pinyin: *Yì Jīng*), "Classic of Changes" or "Book of Changes", one of the oldest of the Chinese classic texts [7].

The first character 易 *Yì* is a verb, it means "to change" or "to exchange/substitute one thing for another". The second character 经 *Jīng* here means "classic text", derived from its original meaning of "regularity" or "persistency", implying that the text describes the "Ultimate Way" which will never change throughout the flow of time. The book is a system of symbols used to identify patterns in random events. The text describes an ancient system of cosmology and philosophy that is intrinsic to ancient Chinese cultural beliefs. This cosmology is centred on the idea of the dynamic balance of opposites, the evolution of events as a process; the acceptance of the inevitability of change. This system is attributed to King Wen around 1,000 years B.C. The "Book of Changes" evolved in stages over the next eight centuries, but the first recorded reference is in 672 B.C. [8].

During the VI century B.C. the greatest Chinese philosophers, such as Confucius (simplified Chinese: 孔夫子; pinyin: *Kǒng Fūzǐ*, literally "Teacher") and Laozi (simplified Chinese: 老子; pinyin: *Lǎozǐ*, literally "Old Master") were influenced and inspired even to the point of recording explanations, sentences and theories. From here the "I Ching", an ancient compendium of divination, became a heavily respected book of wisdom.

Confucius' thoughts have been developed into a philosophy known as Confucianism. His philosophy emphasized personal and governmental morality, correctness of social relationships, justice and integrity, common sense, and practical knowledge. Into the "I Ching" is told that Confucios was close to the river and he said: 'All flows and slides like this river, without pauses, day and night' [7]. This is the idea of the change. The sage that accepts and practices this understanding does not look any more at singularity, but the eternal, immutable law operating in every change. Within this philosophy the primordial forces are unstoppable, the course of becoming circular continues uninterrupted. The reason being that, between the primordial forces born ever a new tension state, a gradient that maintains the forces in movement and the push and the pull to unify the differences, therefore generating continuously.

Laozi is a central figure in Taoism (also spelled "Daoism"). Into the Taoism (Daoism) there are two key concepts: (a) *Zìrán* (simplified Chinese: 自然; pinyin: *zìrán*) that literally means "self so, so of its own, so of itself" and thus "naturally, spontaneously, freely, in the course of events, of course, doubtlessly", and (b) *Wúwéi* (simplified Chinese: 无为; pinyin: *wúwéi*) that literally means "without action" and is often included in the paradox *wéiwúwéi*: "action without action" or "effortless doing". The Taoism's basic concept was the observation of Nature and the discovery of its *Way*, or *Tao*. At the same time the man, according to Taoism, should follow the natural order, acting spontaneously and trusting in their intuitive knowledge.

In the words of Huai Nan Tzu, a philosopher of the II century B.C., 'He who conforms to the course of the Tao, following the natural process of Heaven and Earth, finds it easy to manage the whole word' (cited in ref. [3]).

The idea of cyclic pattern in the motion of the *Tao* was given a definite structure by the introduction of the polar opposites *yīn* and *yáng*. They are the two poles, two polar forces, which set the limits for the cycles of change. In Chinese philosophy, the concept of *yīn*/*yáng* (simplified Chinese: 阴, pinyin: *yīn* and simplified Chinese: 阳, pinyin: *yáng*), is often used to describe how seemingly disjunct or opposing forces are interconnected and interdependent in

Fig. 1 The Tao/Dao

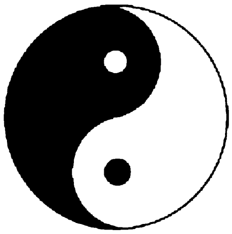


Fig. 2 Combination of yáng and yīn in four pairs diagrams and eight trigrams

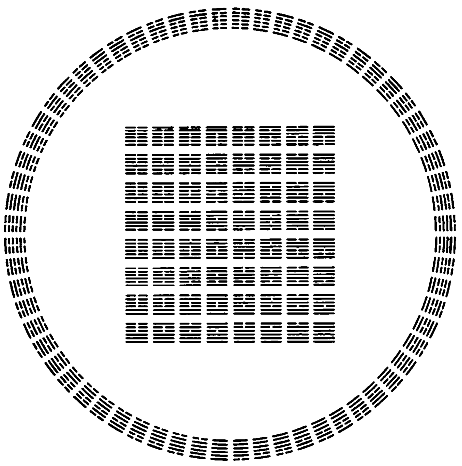


Fig. 3 Two regular arrangements of the 64 hexagrams

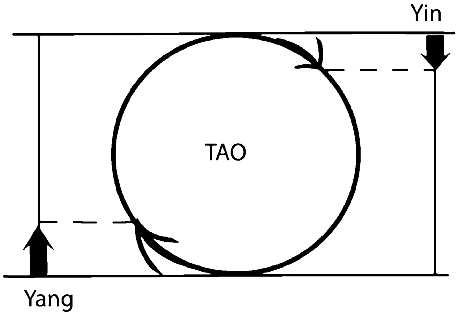


Fig. 4 Dynamic unit of a polar opposites

the natural world, giving rise to each other in turn. The dynamic interplay character of *yīn* and *yáng* is illustrated by the ancient Chinese symbol called *T'ai-chi T'u*, or "Diagram of the Supreme Ultimate" (Fig. 1).

The dynamic diagram of the *yīn* and *yáng* suggest a continuous cyclic movement: 'The yang returns cyclically to its beginning, as the yin attains its maximum and gives place to the yáng' (cited in ref. [3]).

Into "I Ching", *yīn e yáng* are represented by broken and solid lines, *yīn* is broken (- -) and *yáng* is solid (—). The whole system of hexagrams is built up naturally from these two lines. The *yáng* represents the light (force of the sky, the man), while the *yīn* represents the dark (force of the land, the woman). These are combined in diagram then into trigrams, which are more *yáng* or more *yīn* depending on the number of broken and solid lines (e.g. ☰ is heavily *yáng*, while ☷ is heavily *yīn*) (Fig. 2).

The trigrams were combined in pairs to obtain sixty-four hexagrams and arranged as illustrated in Fig. 3: a square of eight times eight hexagrams and a circular sequence. These two representations are one of the most common.

The property's *Tao* is to maintain the universe in a continuing state of tension between the polar dynamic forces. Into the "I Ching" the changes are thoughts as natural processes and almost similar with the idea of Life. In this case the life is based on the opposed poles of activity and receptivity. This opposed poles support the tension and they manifest themselves as changes, or transformations of a vital process. If this tension or gradient, give up, there would be life no longer. If life stops, also the contrasts would be cancelled, and the dead of the universe will be the natural consequence. Fortunately the gradient of these tensions is constantly generated from life's own changes.

As explained Capra, 'the dynamic unity of polar opposites can be illustrated with a simple example of a circular motion and its projection. Suppose you have a ball going round a circle. If this movement is projected on to a screen, it becomes an oscillation between two extreme points. In any projection, the circular movement will appear as an oscillation between two opposite points' [3]. The two motions, one ascending and another descending, represent transformation and alteration, respectively. This oscillation shows us how the opposites change their shapes: the solid line *yáng* become the broken line *yīn* and vice-versa into unified way (Fig. 4).

Capra wrote into the "The Tao of Physics"'s epilogue: 'In contrast to the mystic, the physicist begins his enquiry into the essential nature of things by studying the material world. Penetrating into ever deeper realms of matter, he has become aware of the essential unity of all things and events. More than that, he has also learnt that he himself and his consciousness are an integral part of this unity. Thus the mystic and the physicist arrive at the same conclusion, one starting from the inner realm, the other from the outer world. The harmony between their views confirms the ancient Indian wisdom that BRAHMAN, the ultimate reality without, is identical to ATMAN, the reality within' [3].

Complexity theory and creative evolution of the life

The complexity theory covers one of most important page of the contemporary philosophy and scientific thought. This theory has brought about an interdisciplinary scientific field which studies the common properties within the complex systems of nature, society and science. This scientific field referred to as “Complexity Science” (Fig. 5) is a new approach to science that studies how relationships between parts (components, elements or agents) give evidence to the collective behaviours of any system and how that system interacts, and forms relationships with its environment [9]. We can define the complexity theory, among other definitions, as the interdisciplinary study of the emergent phenomena associated to “adaptative complex systems”.

In this framework equal contributions came from philosophers and scientists: neurobiologists, neurophysiologists, information technologists, chemists, epistemologists, philosophers of mind, sociologists, anthropologists, physicists, mathematicians and economists.

According to Gershenson postdoctoral fellow of the Vrije Universiteit Brussel and the New England Complex Systems Institute, ‘Uncertainty and subjectivity should no longer be viewed negatively, as the loss of the absolute order of mechanicism, but positively, as factors of creativity, adaptation and evolution. The science of complexity is based on a new way of thinking that stands in sharp contrast to the philosophy underlying Newtonian science, which is based on reductionism, determinism, and objective knowledge. Determinism was challenged by quantum mechanics and chaos theory. Systems theory replaced reductionism by a scientifically based holism. Cybernetics and post-modern social science showed that knowledge is intrinsically subjective. These developments are being integrated under the header of complexity science’ [10, 11].

The reductionism movement however, attempts to understand these complex systems by breaking them down into their smallest possible or discernible elements, and then, by understanding those elemental properties, they may obtain information about the behaviour of the whole system. This approach was in total contrast with the thinking revered at the beginning of the XX century by the work of philosophers, such as Henri Bergson, Pierre Teilhard de Chardin, Alfred North Whitehead and Smuts.

Later on, a different approach again came about. In 1926 Smuts, military leader and philosopher, coined the word “holism” [12]. Holism (from *Mλoςholos*, a Greek word meaning “all, entire, total”) is the idea that all the properties of a given system (physical, biological, chemical,

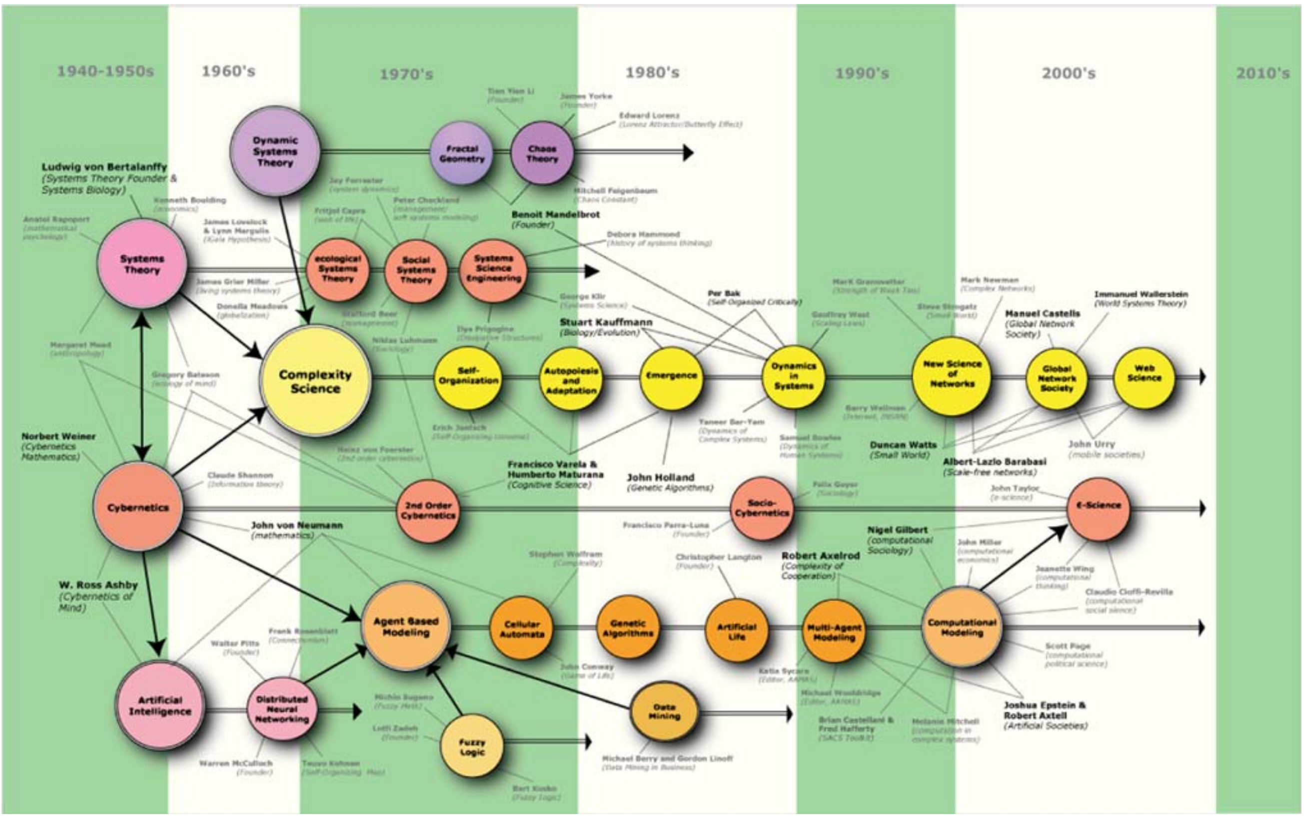


Fig. 5 Map of complexity science by Castellani [9]. This is a file from the Wikimedia CommonsGNU free documentation license

social, economic, mental, linguistic, etc.) cannot be determined or explained by its component parts alone. Instead, the system as a whole determines how the parts behave. Also, the philosopher Morin tells us: ‘In opposition to reduction, complexity requires that one tries to comprehend the relations between the whole and the parts. The knowledge of the parts is not enough, the knowledge of the whole as a whole is not enough, if one ignores its parts; one is thus brought to make a come and go in loop to gather the knowledge of the whole and its parts. Thus, the principle of reduction is substituted by a principle that conceives the relation of whole-part mutual implication’ [13].

In 1973 von Bertalanffy, an Austrian biologist known as one of the founders of General Systems Theory (GST) attempted to provide alternatives to conventional models of organization [14].

The GST emphasizes holism over reductionism and the concept of organism over mechanism. The GST considers the living system open system unlike the mechanical newtonian’s closed system. The open system interacts directly with own environment exchanging matter, energy and information through a boundary. This boundary, that in biology is identified with a cell membrane, limits an system’s internal space over the wider external environment. The input-output’s flow through the boundary determines a strong influences on the system itself and produces effects that can never be controlled or predicted. Different systems coupled form a network of input-output relations and can communicate each other inside a new supersystem. Now the subsystems all together form the supersystem in which they are not more independent but act in coherence with the others under the coordination of the supersystem.

According to Gershenson ‘This mutual implication means that not only the behaviour of the whole is determined by the properties of its parts (upwards causation), but the behaviour of the parts is, in some degree, constrained by the properties of the whole (downward causation)’ [10, 11, 15].

The basic question of the complexity science is the following: what are the characteristics of the dynamic–adaptative complex systems?

At the moment there is no robust theoretical answer, but the scientists are intuitively looking for the answer to this question. The idea or the fundamental basics are that the adaptative systems evolve toward an intermediate region between order and chaos: the so-called “edge of chaos” [16].

The edge of chaos is the optimum zone between two opposite positions: from one side there is a system with a rigid order not able to undergo any modification without self destructing (e.g. crystalline states of NaCl or the totalitarian societies); and on the other side, is an irregular system or chaotic state (such as a gas or anarchy, from Greek *αναρχία*, anarchía, “without ruler”), where each component of the system is independent and the spontaneous organization is avoid. Only the equilibrium on the edges of chaos seems to have the right combination of elements for the spontaneous self-organization [17].

In 1996 the psychologist and electrical engineer Holland and others at the interdisciplinary Santa Fe Institute (SFI) in USA introduced an important concept to the “complex adaptive system” [18].

A complex adaptive system is also called “multi-agents system” in which the components of the system are considered single agent: ignorant or selfish. In the first case, the ignorant agent operates with spontaneous actions of trial and error to reach own utility or goal. In this case, it acts without to follow an outline of rules of his wider environment. In the second case the self-fish agent operates, at the beginning, locally without the cooperation of his neighbourhood but, step by step his action changes something in the whole system with a global effect [19]. This spontaneously global effect comes, or emerges, from a mutual adaptation of the single agents that became a community of cooperative agents.

These adaptive processes can be affected by feedback mechanisms. A positive feedback can amplify the multiple casual contacts and accentuates changes that lead to a continuous “divergence-emergence” from a starting point. The negative feedback reduces or suppresses the internal or external influences and stabilizes the previous global configuration maintaining its normal course of operation (Fig. 6).

‘Positive and negative feedback work together in living system, but this dynamic equilibrium cannot ever maintains the growth, nor can it ensure its survival. Even though the living system is trying the best to maintain its viability, this effort, nonetheless, cannot counterbalance or defeat the

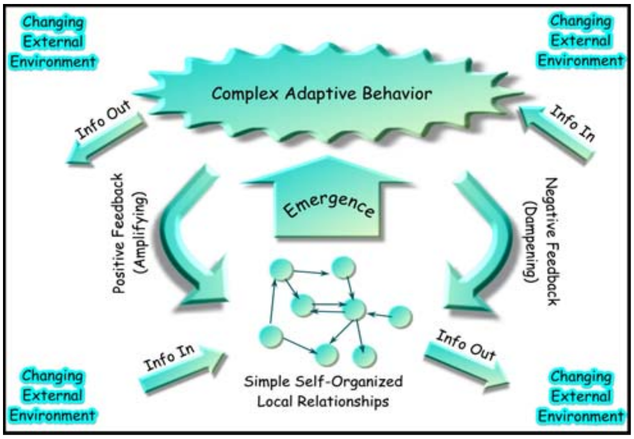


Fig. 6 A way of modelling a complex adaptive system. A system with high adaptive capacity exerts complex adaptive behavior in a changing environment. This is a file from the Wikimedia CommonsGNU free documentation license

entropically increasing trend. The system gradually and continuously loses its integration and proper functioning, which eventually results in the system's expire' [20].

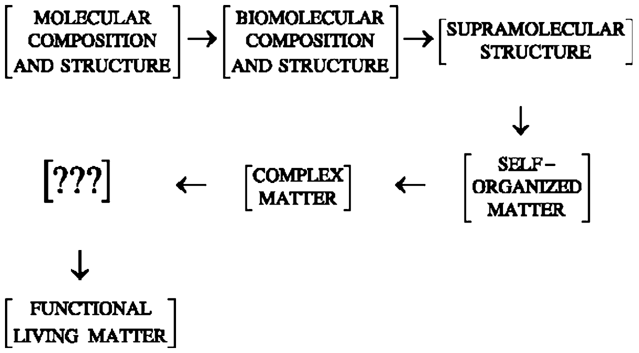
Shortly, there are some common features to all complex systems: the agents or components of a system may be "hardware" (molecules, physical processor, cells, people) or "software" (virtual unit); the interactions between the components must respect the equilibrium state at the "edge of the chaos"; if there is a unique agent that governs the behaviour of the whole, the system can not be complex, because the description can be reduced to the leader (the absence of hierarchy pyramid); the adaptive interactions with the external environment, by transferring matter, energy, digital information and shape, learning and casual factors, can influence the subsystem and the whole system that may co-evolve and develop different strategies, such as, symbiosis, cooperation, communication, etc. [17].

From these characteristics it is possible to classify the system as follow: (a) minimally complex systems where natural no-biological systems, such as, crystals, clouds, rivers, elemental particles and the galaxy (neglecting life) have not adaptive interactions with their environment; (b) medium complex systems, such as, complex artifacts, computers, digital virus, some prebiotic systems, such as, virus and ribosomes, may present adaptive interactions and may show new and unpredictable behaviours (innocent emergence); at least (c) high complex systems, such as, all the biosphere's systems, from bacterias to human population are all adaptive and are associated to emergent phenomena, such as, life, brain, social organization, ecosystem, culture, economy, etc. [17].

In 1944, the Schrodinger's question "What is life?" inspired and motivated a scientific and intellectual challenge of scientists and scholars [21]. Schrodinger tried to understand the structures of the biomolecules and said: 'there must have been something into life's mechanism that prevent the degradation of the life, there must have been a irreversible phenomenon' (cited in ref. [3]).

After 62 years, Jortner in a fascinating review summarized the scientific issues to describe the origin of terrestrial life [22, 23]. Into the Scheme 1, the same author, showed us a hypothetical linear progress from the inanimate matter to the functional living matter where the attributes marked by question marks are still unknown and can be deeply understood comprising all the phenomena bounded to self-organization processes.

The review recalled and described, in a holistic (collective) view, the conceptual framework and its milestones of functional living matter [22, 23]: (a) Oparin's idea that living matter originated from inanimate matter [24]; (b) the central role of self-organization (self-assembly) which leads to the evolution of a 'complex biological matter' [1, 2, 25–30]; (c) the ideas of the biologist Morowitz on complex matter [31, 32]; (d) the metabolism as net of chemical reactions [33]; (e) the concept of Maturana and Varela 's autopoietic system [34] and (f) Prigogine's dissipative structures [35–37]. These milestones are shortly recalled in the following.



Scheme 1 Adapted from reference [22, 23]

(a) In 1929, the Russian biochemist Oparin in his classic book "Origin of Life" explained the first comprehensive version of the idea that living matter originated from inanimate matter by a continuous evolutionary process [24]. Oparin called it "molecular evolution", and today it is commonly referred to as prebiotic evolution. In the words of Luisi [38]: 'Starting from small molecules, compounds with increasing molecular complexity and with emergent novel properties would have evolved, until the most extraordinary of emergent properties—life itself—originated' (cited in ref. [4]).

(b) The concept of self-organization (or self-assembly) is a process of attraction and repulsion in which the internal organization of a system, normally an open system, increases in complexity without being guided or managed by an outside source. It has been developed with the main contributions by Eigen [1, 2], Yates [25], Lehn [26–30] and Heckl [39], and relies on six basic ingredients: (i) 'molecular structure formation of either living or non-living matter is driven by multiple molecular interactions and operates on a huge diversity of possible structural combinations; (ii) before the biological evolution, the chemical evolution took place, performing a selection on molecular diversity, leading to the embedment of structural information in chemical entities with a balance of exploitation and exploration; (iii) the implementation of the concepts of molecular information pertains to information storage at the molecular level and the retrieval, transfer and processing of information at the supramolecular level; (iv) the formation of supramolecular structures is induced by molecular recognition based on non-covalent intermolecular interactions. This includes self-organization, which allows adaptation and design at the supramolecular level; (v) self-organization involves selection in addition to design at the supramolecular level, and may allow the target driven selection of the fittest, leading to biologically active substances; (vi) self-organizing systems typically (but not always) display emergent properties, i.e. properties that cannot be reduced to the properties of the single parts' (cited in ref. [22]).

(c) Morowitz provided a unified description of living matter [31, 32]: 'Life is that property of matter that results in the cycling of bioelements in aqueous solution, ultimately driven by radiant energy to attain maximum complexity' (cited in ref. [4]).

This definition implies the same consideration of the General System Theory, in which the open system is well defined from the external environment by a boundary. Inside the micro-environment the system can produce several and different molecules that can be integrated into the membrane. In water the emergent life of the biological complex matter involves coupled chemical reactions of homogenous and/or heterogeneous bioelements (building blocks) with a support of radiant energy. These cyclical coupled reactions take place inside the biological microreactor system protected by its own membrane. When the internal volume increases for an increasing production of biomaterials, the membrane may reach a breaking point. In this growth process the stabilizing forces are no longer able to maintain the membrane's integrity, and the vesicle breaks up into two or more smaller bubbles (bifurcation point).

Morowitz also emphasized that the growth and the replication of the vesicles are possible only with a constant flow of matter and energy with the external environment through the membrane. The internal structures and the boundary are subject to thermal decay over the time, so that to preserve their existences they have to stay struggle far from the equilibrium through a continual processing of matter and energy with own environment.

(d) The term metabolism is derived from the Greek word *Μεταβολισμός*, "Metabolismos", for "change" or "overthrow", it is the sum of biochemical processes involved in life.

As suggested by the general system theory, if we look at the cell as a whole it is characterized by a boundary (the cell membrane) which discriminates the system "itself" and its environment. Within this boundary, there is a network of chemical reactions (the cell metabolism) by which the system sustains itself. Every simple living system has a complex network of metabolic processes that works ceaselessly transporting nutrients in and waste out of the cell, and continually using food molecules to build proteins and other cell components. From the simplest to the complex living organisms (microrganisms, plants, animals, people) we can recognize on the cell the minimal biological element to process the life.

In the words of the microbiologist Margulis [33]: 'Metabolism, the incessant chemistry of self-maintenance, is an essential feature of life (…) Through ceaseless metabolism, through chemical and energy flow, life continuously produces, repairs, and perpetuates itself. Only cells, and organisms composed of cells, metabolize. Wherever we see life, we see networks' (cited in ref. [4]).

Also, as suggested Von Bertalanffy, a group of systems coupled via different input-output relations forms a network, as well the ecosystem's organisms create a network of relationships in terms of food webs [14]. In this case the network transforms and replaces the components in other building blocks to continually generate itself during the time. In this case, the couples phenomenon of the systemic life to create and destroy, to born and die, are the keys to preserve the web of life.

(e) In 1973 the biologists Maturana and Varela introduced the term "Autopoiesis" [34]. Literally it means "self-creation" (from the Greek *αυτό*, "auto", for self and *ποίησις*, poiesis, for "creation or production"), and expresses a fundamental relationship between structure and function. The dynamic process of self-generation is the central core of the autopoiesis theory to identify the life into natural system. This theory unifies the two essential features of the life mentioned above: the physical boundary and the metabolic network.

'An autopoietic machine is a machine organized (defined as a unity) as a network of processes of production (transformation and destruction) of components which: (i) through their interactions and transformations continuously regenerate and realize the network of processes (relations) that produced them; and (ii) constitute it (the machine) as a concrete unity in space in which they (the components) exist by specifying the topological domain of its realization as such a network' [34].

With this definition Maturana and Varela help us to understand that a virus is not alive because it is not able to reproduce itself with own metabolism but it needs an autopoietic machine of another living system.

(f) If the Biological theory of autopoiesis identifies the fundamental characteristic of the life, as well the philosophical and physical-chemical thoughts reached the same meaning to describe the life.

According to Morin, 'the self-organization process of living system depends on its environment to draw energy, matter and information: indeed, it constitutes an organization that works to maintain itself, it degrades energy by its work, therefore it must draw energy from its environment' [13].

'A dissipative structure, as described by the chemist Prigogine [35–37], is an open system that maintains itself in a state far from equilibrium, yet is nevertheless stable: the same overall structure is maintained in spite of an ongoing flow and change of components' (cited in ref. [4]).

From the Prigogine point of view, a complex system, called in his theory dissipative structure, has an intrinsic nature to change in other new structures (mutation) with a constantly support of matter, energy and information's flow. Inside an open system, such as a cellular structure, the cellular metabolism uses a continual flow of energy to avoid the die of the cell, or the equilibrium state. This means that a cell, described as open system, operates far from the equilibrium state and need a constant resource input and output with its environment to stay alive and renew itself. This dynamic process is one of the more fascinating theory that could explain the emergence of new ordered structures with the constant incoming of energy and matter's flow.

The increasing of matter and energy inside the system can bring to a point of instability, known as a "bifurcation point", where new forms of order and new structures may emerge. This creativity (generation of new forms) at the point of instability can be seen as a spontaneous process to understanding the emergence and the evolution of the life. In 1982 the biochemist Lehninger argued that 'living organisms preserve their internal order by taking from their surroundings free energy, in the form of nutrients or sunlight, and returning to their surroundings an equal amount of energy as heat and entropy' [40].

Prigogine emphasized saying: 'Life is a clear example of order far from thermodynamic equilibrium. Into the universe, the order floats into a disorder sea' [36].

Supramolecular chemistry as a science of informed matted and the creativity of auto-organization

According to Desiraju 'for a long time chemists tried to understand nature at a level that was purely molecular—they considered only structures and functions involving strong covalent bonds, but some of the most important biological phenomena do not involve making and breaking covalent bonds—the linkages that connect atoms to form molecules. Instead, biological structures are usually made from loose aggregates that are held together by weak, non-covalent interactions. Because of their dynamic nature, these interactions are responsible for most of the processes occurring in living systems' [41, 42].

The slow shift towards this new approach began in 1894, when Emil Fischer proposed that an enzyme interacts with its substrate as a key does with its lock in which molecular recognition is implicit in the lock-and-key model.

After 75 years, the term "supramolecular chemistry" was coined on 1969 by Lehn in his study of inclusion compounds and cryptands. The award of the 1987 Nobel Prize in Chemistry to Pedersen, Cram and Lehn represented the formal arrival of the subject on the chemical scene. Lehn defined supramolecular chemistry as 'the chemistry of the intermolecular bond' [26]. Just as molecules are built by connecting atoms with covalent bonds, supramolecular compounds are built by linking molecules with intermolecular interactions. Supramolecular structures are the result of not only additive but also cooperative interactions, and their properties generally follow from their supramolecular features.

According to Lehn 'three main themes line the development of supramolecular chemistry: the first one, molecular recognition, relies on design and pre-organization and implements information storage and processing. The second, the investigation of self-organization and self-processes in general, relies on design; it implements programming and programmed systems. The third, emerging phase, introduces adaptation and evolution, based on self-organization through selection in addition to design, and implements chemical diversity and 'informed' dynamics' [27, 28].

Molecular recognition-directed self-organization, making use of hydrogen bonding, donor–acceptor, and metal coordination interactions for controlling the processes and holding the components together, has given access to a range of supramolecular entities of truly impressive architectural complexity, which otherwise would have been too difficult to construct as well as interlocked mechanically linked compounds. The control provided by recognition processes allows the development of advanced functional supramolecular materials and supramolecular devices for application in emerging areas of supramolecular photonics, electronics, ionics, sensors and non-linear optics.

A self-organization process may be considered to involve three main steps: (i) molecular recognition for the selective binding of the basic components or "agents", (ii) growth through sequential and eventually hierarchical binding of multiple agents in the correct relative disposition, and (iii) termination of the process that specifies the end point and signifies that the process has reached completion. 'These self-processes directed via the molecular information stored in the covalent framework of the components and read out at the supramolecular level through specific interaction/recognition patterns, may be defined processing algorithms. They thus represent the operation of programmed chemical systems, and are of major interest for supramolecular science, engineering and biological evolution' [29]. For the study of biological evolution these processes represent progressive steps to study (receptor–protein binding, drug design, protein folding) and control the self-organization of large and complex supramolecular architectures through natural-molecular programming.

At least, in the recent years the dynamic nature of the supramolecular chemistry has become an interesting research field [30]. Indeed, supramolecular chemistry is intrinsically a "dynamic chemistry" in view of the lability of the non-covalent interactions connecting the molecular components of a supramolecular entity. The resulting ability of supramolecular species to reversibly dissociate and associate, deconstruct and reconstruct allows them to incorporate, decorporate and rearrange their molecular components with the emergence of new unforeseen structure-function. This dynamic character is at the basis of the generation of the highly complex architectures held together by weak bonds and highly pressured from external stimuli of the surrounding environment.

Moreover the "Dynamic Combinatorial Chemistry" (DCC), defined as a combinatorial chemistry under thermodynamic control, was extensively reviewed by Otto where they shown all the powerful application of this methodology [43].

The unique advantage of dynamic combinatorial chemistry over traditional combinatorial chemistry is the fact that library members that engage in non-covalent interactions are favoured over their less strongly interacting counterparts. This makes DCLs attractive tools to screen for compounds that play a role in molecular recognition of some kind. At present, the main applications are: '(i) identification of the most stable structure in mixtures of structures with different conformational properties (foldamers) (Fig. 7a), (ii) selection of aggregates between library members that can take place through intermolecular non-covalent interactions (Fig. 7b), it has real potential for the discovery of self-assembling molecules including interlocked architectures and new soft materials, (iii) selection of a host or receptor by a guest (Fig. 7c), (iv) selection of a guest or ligand by a host (Fig. 7d)' [43].

Detailed understanding of the dynamic processes becomes crucial to use supramolecular assemblies to influence reaction chemistry, selectively encapsulate small molecules, or create new nanodevices. Increasingly, the focus is on application of these molecules to other chemistry problems: selective substrate binding, trapping reactive intermediates or protecting unstable species, and influencing reaction chemistry within assembly cavities [44]. In a recent critical review dedicated to Sauvage, Stoddart point out the importance of the supramolecular synthesis to building up new complex mechanically interlocked molecules (MIMs) [45]. Finding inspiration from the ancient art it has been possible to create new beautiful structures, such as catenanes, rotasanes, borromean rings and Solomon knots. With the supramolecular approaches it will possible increase the creativity of the chemists to impacts new application fields like molecular electronics, nanoactuators, bioimaging, nanofluidics, gas storage and drug delivery. 'The time is now ripe for creative and efficient templated synthesis.... ...The chemists would do best to embrace the complexity that is associated with integrated systems and respond to their emergent properties in all-encompassing manner' [45].

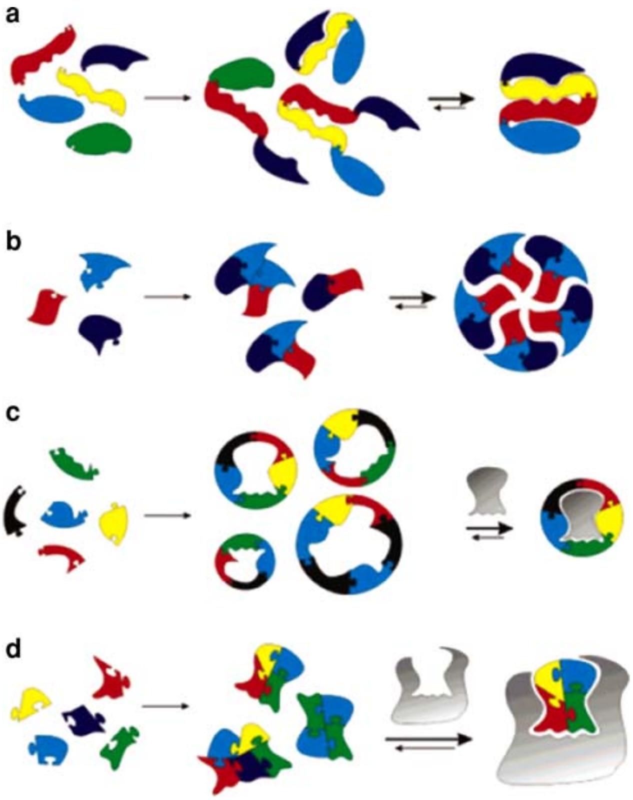


Fig. 7 Different ways of selecting specific members of a dynamic combinatorial library on the basis of noncovalent interactions: **a** selection of foldamers driven by internal noncovalent interactions; **b** selection of self-assembling molecules on the basis of noncovalent interactions between different library members; **c** selection of a host by a separately introduced guest; **d** selection of a guest by a separately introduced host. Adapted from reference [43]

The case of guanosine

In this section we summarize some results reported by Davis [46], Lehn [47], Rowan [48] and Spada [49, 50] that describe the supramolecular chemistry, selectivity, reversibility and emergence property of guanine derivatives [51].

Davis and colleagues conducted a self-sorting study in CD_2Cl_2 to illustrate how the cation dictates the self-assembly patterns for two isomer of guanosine [46]. The different informations stored into the molecular structure is based only in the transposition of an oxygen and nitrogen atom; this simple positional change in molecular structure leads to significant differences in the supramolecular organization and cation selectivity for the two assemblies. Both **G 1** and **isoG 2** can further aggregate by cation-stabilized stacking of hydrogen-bonded layers. Thus, **G 1** forms a hexadecamer composed of four stacked G-quartets, while **isoG 2** gives a sandwich decamer (**isoG 2**)$_{10}\cdot M^+$ (Fig. 8).

An equimolar mixture of the two isomers in CD_2Cl_2, in the absence of cations, formed a mixture of hydrogen-bonded species. Addition of Ba^{2+} to this mixture gave quantitative formation of two discrete hydrogen-bonded complexes, four G tetramers stacking around two Ba^{2+} ions, (**G 1**)$_{16}Ba^{2+}$, and a sandwich complex of two **isoG** pentamers around a Ba^{2+} ion, (**isoG 2**)$_{10}Ba^{2+}$, were formed.

These experiments demonstrated the dynamic role of cation in expressing the hydrogen-bonding and base-stacking information embedded in the nucleoside monomers. Both **G 1** and **isoG 2** self-associate essentially quantitatively upon addition of Ba^{2+} picrate. The two isomers, each with its own unique hydrogen bonding pattern, are completely sorted into structures composed of G-quartets and isoG pentamers, provided a Ba^{2+} cation is available to direct self-recognition.

This self-sorting illustrated that a cation is needed to template formation of distinct assemblies in solution from this mixture of nucleosides. This experiment is an example of the equilibrium shifting that characterizes dynamic non-covalent chemistry.

Ghoussoub and Lehn were able to control the mesoscale dynamic sol–gel interconversion, i.e., from a disordered guanine solution to gel-forming ordered G-quartet architectures, through reversible cation binding and release [47]. However, a great challenge remains to control the switching between two or more highly ordered guanine-based. We reported the tunable interconversion between discrete supramolecular assemblies from a lipophilic guanosine, (Fig. 9) i.e., G-ribbons and G-quartet columns, fuelled by cation complexation and release [52].

We have shown the ionic modulation of the reversible interconversion between two highly ordered supramolecular motifs of a guanosine derivative. This “supramolecular dynamer” can be of importance as a model system to mimic the formation-annihilation of G-quartet-based architectures, which might be of biological significance, in the frame of nucleic acid telomerase. Otherwise by exploiting the information stored in the molecule, in particular, its pre-programmed propensity to undergo self-recognition and self-association pathways, in combination with the reversibility of its self-assembly under external stimuli such as temperature or chemical environment, it is possible to implement molecule-sized prototypes of dynamic chemical devices for future data storage.

To exploit an emergence property of a wired supramolecular structure, the two different H-bonded ribbons formed by self-assembly of lipophilic 2´-deoxyguanosine (in the absence of cations) has been considered: ribbon A has a net dipole, whereas ribbon B contains no dipole. The use of nanoribbons A formed from deoxyguanosine units in the design of molecular electronic nanodevices has been recently proposed (Fig. 10).

Self-assembled nanoribbons obtained from drop casting were used to interconnect gold nanoelectrodes fabricated by electron beam lithography (Fig. 11) and diode and FET have been obtained [50].

Stuart Rowan and co-worker reported a self-assembly on the surface of a ditopic monomers guanine **G2nG** [48]. The guanine linked with a linear alkyl spacer result in the formation molecular-sized bands on HOPG when adsorbed from a water/DMSO solution. Moreover, demonstrated that

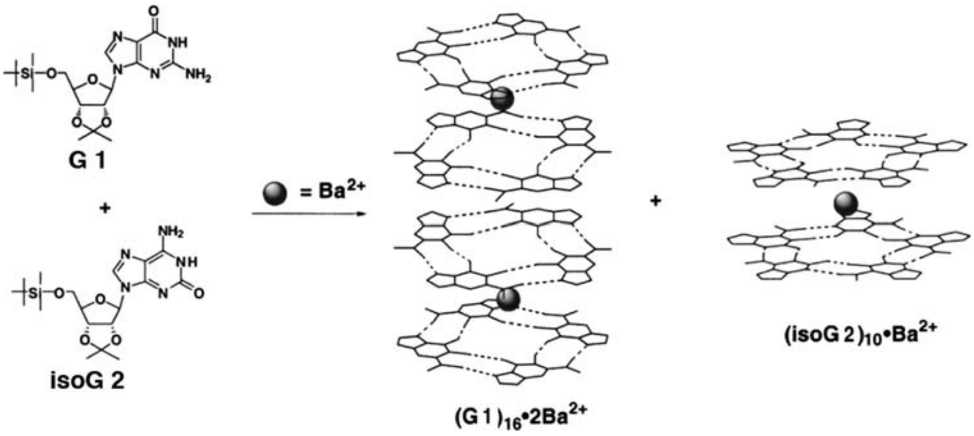


Fig. 8 The isomers **G 1** and **isoG 2** self-sort in the presence of barium picrate to give discrete complexes

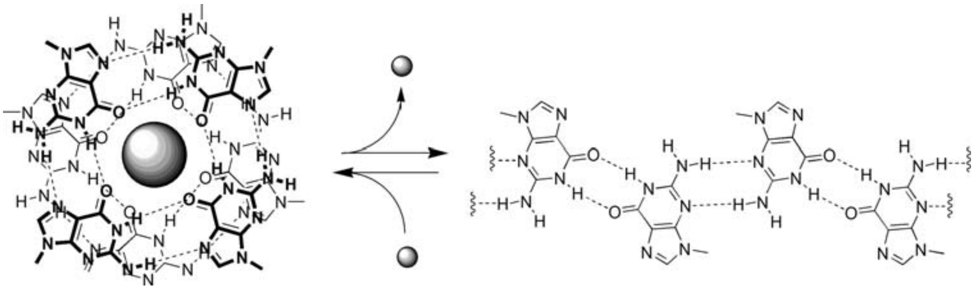


Fig. 9 Reversible interconversion of the supramolecular assemblies of guanine moieties fueled by cation complexation and release: the metal templated octamer and G-ribbon

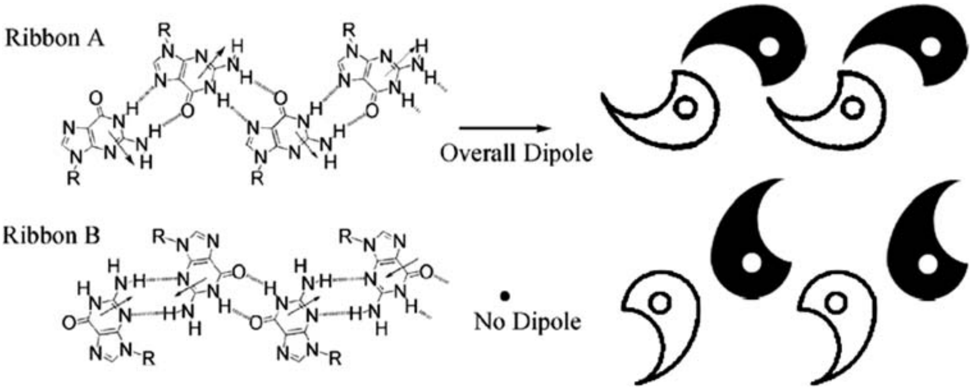


Fig. 10 Without templating cations, lipophilic deoxyguanosine self-assemble into two different hydrogen-bonded ribbons and exploit different supramolecular properties

the assemblies are composed of bands with widths that can be systematically varied by simply changing the length of the core-spacer hydrocarbon unit. Furthermore, this concept has been extended into using these assemblies as scaffolds to supramolecular graft hydrophilic groups onto HOPG. This is an important consideration if regular repeatable banding structures are targeted for the surface scaffolds, either to control a second molecular layer deposition in the space, or to storage information above the surface, or to direct a bio-mineralization from organic matrix as happen in Nature. Supramolecular chemistry at the interface plays a defining role in the "bottom-up" approach to nanoarchitectures which have a myriad of potential technological applications in areas such as nanoelectronics, biological coatings, and catalytic processes.

Molecular components are able to generate multicomponent architectures in absence of ions, but in the presence of ions they can also create new hybrid organic–inorganic complex systems. Regarding to sensitivity to perturbation of a system, with the modification of internal and external factors, such as the molecular design, the concentration of the building block, the change of the solvent, the presence of different kind of ions and the implementation of external power energy, it's possible to obtain a huge adaptation and diversity to build up a new generation of complex informed matter.

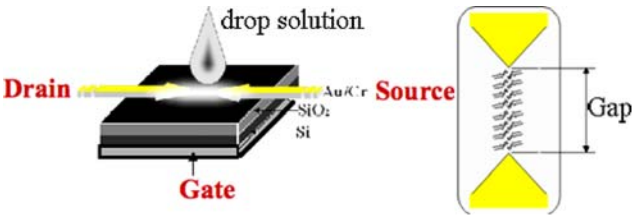


Fig. 11 The preparation of the nanodevice. Adapted from reference [50]

Moreover, because self-assembly is a strategy for organizing matter at the nano to micrometer scale, the areas where it will be employed in the future will be, inter alia: crystallization science, robotic and manipulation, nanoscience and technology, microelectronics and netted system [53].

At the end, we want to recall two important issues from Desiraju and Hosseini. 'In any supramolecular assembly, a large number of intermolecular interactions is possible—but only a few are actually observed. The weakness of these interactions makes it difficult to predict supramolecular structures and means that, in solution, supramolecular structures are not always stable over time. But this flexibility also means that they are frequently favoured in important mechanisms, notably in biological reactions and in crystallization processes, where the ability to form short-lived states and to perform easily trial-and-error corrections is essential' [42]. In fact, Hosseini added that the probability to predict exactly a supramolecular structure is very low, but only using all our various techniques we can verify the advanced hypothesis [54]. Considering moreover from the Complex Theory that we can never truly control or predict the effects of the internal and external environment of a open system, our idea to manage new supramolecular entities "is not to control them but play with them". The complex system's adaptation process as a trigger can absorbs the external negative/positive effects and propagates into the emerged regime. In this process the co-evolution of the system agents under the influence of the external environment could explain the emergence of the self-organized complex systems in any context: physical, chemical, biological, psychological or social. For instance, inside the LC display the electric field controls the orientation of ferroelectric liquid crystal for different colour pixels. In this case the trigger is a electric field that plays in harmony with the whole system to move in synergy all the components of the multiagents system. The light in optoelectronic, the magnetic force in spintronic field, the mechanical and electric force in mechatronic and so on, are all clever triggers to change, with global effect, supramolecular open systems. If we cannot to control or predict, we must use the best trigger to move the whole system in harmony with their surrounding.

According to Laozi, 'when the interior motion is in harmony with the surrounding environment all can develop without friction and continue during the time. Under this easy and simple alteration all the things evolve to reach the perfection. Human being have a place in the Tao but are not particular exalted. They are simply things among things. Because of their desires and their unique capacity to think, act intentionally, and alter their nature, human tend to forsake their proper place and upset the natural harmony of the Way' (cited in ref. [55]).

Final remarks

All living system must die (bifurcation) and reborn (re-organise) on cycles of bird and death. The whole tandem natural phenomena, such us day & night, anabolism & catabolism, apoptosis & autopoiesis, agonist & antagonist muscles, or the transformation from *yīn to yáng* & *yáng* to *yīn*, show the evolution process of the organic world.

We can make the same consideration for the tandem self-organization processes. If one hand, the self-organization based on design implements "re-cognition & pre-organization"; on the other hand the second tandem process based on selection implements "adaptation & co-evolution". Design and selection are two faces of the same coin that can help us to study the dynamic systems of higher complexity through the tandem self-processes (Fig. 12).

In light of this, the basic research of the supramolecular chemistry based on self-organization is running in four directions. In each of them the self-organization process is implicit into the transformation, replication and self-maintaining of live or alive matter. It is involved in Maturana and Varela's autopoietic system, in Prigogine's dissipative structure, in the hierarchical complex matter and in the interlocking webs of life. In the holistic view, all living systems are open-systems, these "re-active" systems are opened to its own environment exchanging matter, energy and information through different communication channels.

As mentioned before, the dark *yīn* (broken line) and bright *yáng* (solid line), two polar opposites and complementary entities, form a symmetric diagram arrangement called the *Tao*. Furthermore, they can be combined in four pair, in eight trigrams and in 64 hexagrams. So that we could make a similar consideration for Guanosine derivatives, as polar entities that support complementary moieties (donor and acceptor groups) enables to self-assemble in dimers, trimers, tetramers and in multi-hierarchical systems, such as octamers, dodecamers, hexadecamers and polymeric structures (Fig. 13) [49, 51].

"Smart" complex matter presents a higher emergent property than the resultant sum of the single molecular constituents, therefore a multi-agent system (or multi-component architectures) in response to the environment's

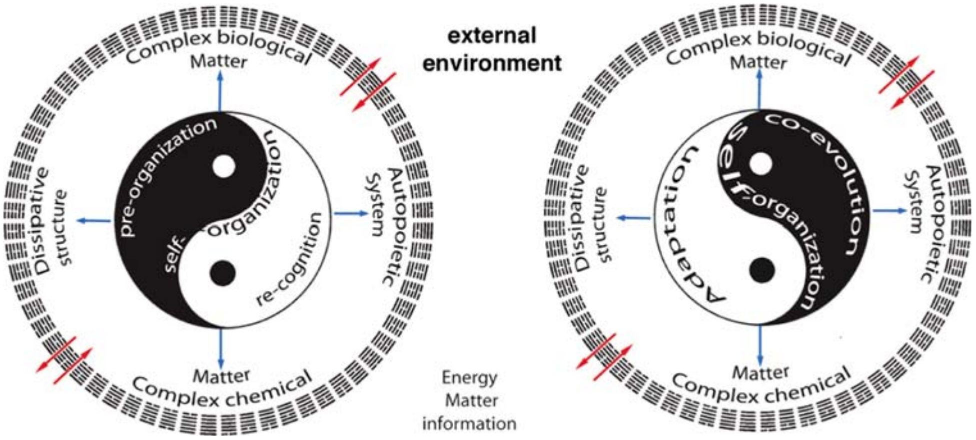


Fig. 12 Tandem self-organization process based on design and on selection implement recognition & pre-organization and adaptation & co-evolution, respectively

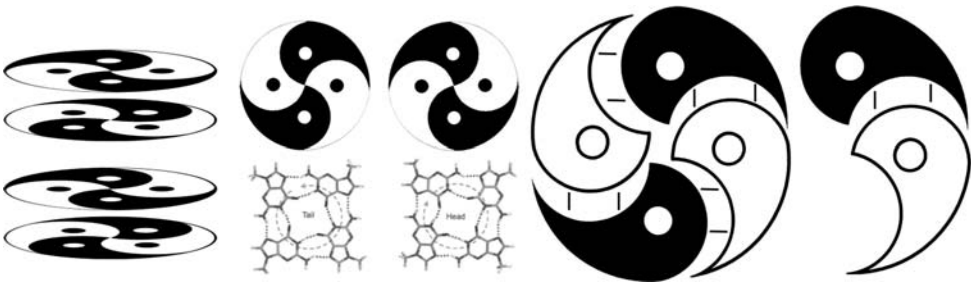


Fig. 13 Guanosine derivatives in different multi-hierarchical configurations

Fig. 14 "Dinamic duo". (Produced by Arte in Mobile, Ghana, Niger, Senegal for Arco'08 http://www.aecidarteinvisible.com)

input achieves a set of conditions and constrains (adaptativity and cooperativity) with its neighbours leading up to a balanced eco-system from organic chemistry to biological chemistry. Therefore "smart" supramolecular matter, which features depend on molecular information, is by nature a "dynamic chemical complex matter" that evolves by communication processes reaching a "biological complex matter" connected spatially and temporally to its surrounding (or web of life).

A deeply understanding of the "natural creativity of dynamic-informed self-process" based on design and selection will help us to discover new spontaneous forms of order which lead to development and evolution of our living systems. This dynamic unity of polar processes can be also represented in an artistic painting as in Fig. 14.

How the *Tao* of polar opposites, or complementary phenomena can work each other to preserve itself in a wider environment and evolve during the time?

We can image one way to unfold the evolution of the matter under the pressures of the external environment and the arrow of the time (Fig. 15). We could ride toward the centre of a double spiral. Our path during the spiral doesn't stop inside the deep centre but starts again from the end of the levo-rotatory rice to dextro-rotation reaching again the starting point of our ride. While we walk down to our way the cycle unfolds during the time and under the external pressure of the environment. During this evolution the spiral shows itself and changes from a circular shape to a linear shape with a double direction. This shows us two-way riding on the same street, but if we could push and open the zipper until now united (a bifurcation point), we have joined a single path in the same direction of the arrow of time (Fig. 15). The path is paved by self-organization, covering a full range of self-processes that determine the internal build-up of the complex systems, as well as its external connection to the environment.

According to "*I Ching*", when the "trigrams" combine each other to form the 64 "exagrams" they move in a double motion: one clockwise during the time it sums and expands causing the past; the second, opposite, shrinks and folds counter clockwise over time, through which are formed the seeds of the future. Knowledge of this second movement gives us the knowledge of the future. In a metaphor: 'if you understand how the tree is contracted in the seed, one can deploy the future of the seed that becomes a tree' (cited in ref. [7]).

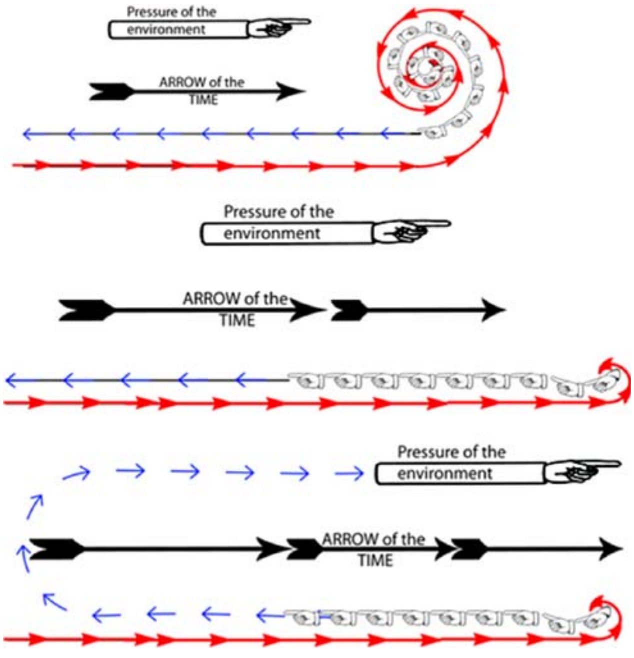


Fig. 15 Double spiral under the external pressure and the arrow of the time

The book of the changes "I Ching" reflects the ceaseless transformation of all things and situation. It is designed to reach the laws that represent the changes taking place within the "exagrams". Even and when you can fully deduct these laws, you will have a sufficient vision of becoming and will be able to understand the past and the future in equal measure to take account of our actions.

Examples of "included cycles" are the course of the day, the course of the year, and all natural phenomena in the organic world. These cyclic phenomena run each other until to returned back to the starting point. The cyclical self-organization changes are what occur in the living world and the third form of change without return (at bifurcation point) is related to the phenomena of chance (evolution).

All the self-processes (e.g. self-generating, self-producing, self-poetic, self-organizing) are cycling phenomena whom occur in tandem with one another. Consequently, with the Blaise Pascal words, we should conceive the circular relations: 'one cannot know the parts if the whole is not known, but one cannot know the whole if the parts are not known'.

At the same time Calvino wrote on "Le città invisibili": 'Marco Polo descrive un ponte, pietra per pietra. – Ma qual è la pietra che sostiene il ponte? – chiede Kublai Kan. – Il ponte non è sostenuto da questa o quella pietra, – risponde Marco Polo, – ma dalla linea dell'arco che esse formano. Kublai Kan rimane silenzioso, riflettendo. Poi soggiunse: – Perché mi parli delle pietre? E' solo dell'arco che m'importa. Marco Polo risponde: – Senza pietre non c'è arco [56].

(Translation: Marco Polo describes a bridge, stone by stone. – But what is the stone that supports the bridge? – Asks Kublai Kan. – The bridge is not supported by this or that stone, – answered Marco Polo – but by the line of which they form. Kublai Kan remains silent, reflecting. Then said: – Why you speak about the stones? It is only the arch that I am interesting. Marco Polo replies: – Without stones there is no arc)'.

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