Reviews

Supramolecular systems as a bridge between nonliving and living matter*

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A comparison of the structures and functions of synthetic and biological supramolecular systems, consideration of the principles of matter sophistication during the evolution, and analysis of the energy profile of the basic hierarchical elements in the structural organization of matter allowed one to conclude that supramolecular systems have their own niche in the above hierarchy and precede biological systems, which are a community of functionally differentiated supramolecular systems formed from biomolecules. Therefore, supramolecular systems can be regarded as a sort of a "bridge" between nonliving and living matter. Other issues of matter evolution were considered.

Key words: supramolecular systems, biological systems, evolution of matter, origin of life.

The phenomenon[1] and origin of life,[2] as well as the evolution of matter as a whole (including the evolution of biological and social systems[3—5]), are the issues intriguing mankind for centuries.

At present, the transformation of matter from the Big Bang till now is regarded as a continuous process called Big History in the English version and Universal History in the Russian version.[3] In this continuous process, three main steps can be distinguished: (1) prebiological evolution on the whole (from the Big Bang till the origin of life), (2) biological evolution (until *Homo sapiens* has appeared), and (3) social evolution (evolution of a human society) (Fig. 1).

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The intriguing point of the Big History is the origin of life, when inanimate matter transformed itself into living one. The totality of recent scientific data suggests a key role of supramolecular systems in the process under consideration, though leaving this intriguing point still unanswered.

In the last few decades, the novel scientific concept "supramolecular systems" has been derived from supramo-

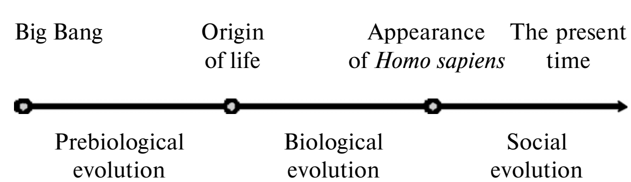

Fig. 1. Schematic representation of Big History.

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lecular chemistry,[6] a new branch of chemistry created in 1978 by the French scientist J.-M. Lehn, the Nobel Prize winner and the Foreign Member of the Russian Academy of Sciences.

According to the definition by J.-M. Lehn "supramolecular chemistry is a chemistry beyond molecules that describes complex associates of two or more chemical species held together by intermolecular forces"; *i.e.*, supramolecular systems are complex molecular (polymolecular) structures due to intermolecular noncovalent interactions. All of the known noncovalent (intermolecular) interactions are taken into account, with particular emphasis given to hydrogen bonding, cation—n(π) interactions, and hydrophobic effects.[7]

Relatively weak intermolecular noncovalent bonds can form sufficiently stable structures (supramolecular systems). The prerequisites for this include (1) preorganization of the constituents (molecules) of a supramolecular system, (2) multiplicity (or, in other words, a multipoint character) of binding of these constituents, and (3) cooperative actions of binding forces.[7]

As a result, molecules attracted by intermolecular forces combine into two types of supramolecular systems. One type includes stoichiometrically definite, mainly bimolecular structures called "supermolecules". A classic example is the acetic acid dimer, which was termed "supermolecule" as early as the 1930s. The other type includes polymolecular systems called "supramolecular ensembles". Examples are micelles formed by amphiphilic compounds under the action of hydrophobic effects. On the whole, sufficiently generalized data on the design, synthesis, architecture, and functions of supramolecular systems are cited in the literature (see, *e.g.*, Refs 6, 8, and 9).

Intensive investigations into the chemistry of supramolecular systems in the last 30 years have led one to the conclusion in the title: supramolecular systems can be regarded as a sort of a bridge between nonliving and living matter. This conclusion is based on three approaches:

(1) comparison of the structures and functions of synthetic and biological supramolecular systems;

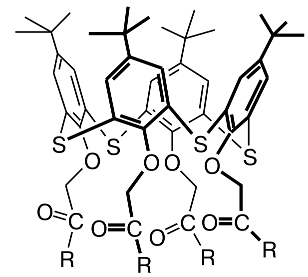
(2) consideration of the principles of matter sophistication during the evolution;

3) analysis of the energy profile of the hierarchy of the basic elements of the structural matter organization.

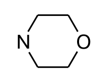
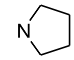
Comparison of the structures and functions of synthetic and biological supramolecular systems

It is essential that supramolecular chemistry was developed in two ways involving (1) a study of synthetic supramolecular systems and (2) a study of natural supramolecular systems produced by biological objects themselves. A comparison of the properties of synthetic and natural supramolecular systems allows one to conclude that both types of systems have the same properties (functions) and structures. Let us consider the main data obtained for synthetic supramolecular systems.

To date, receptors for all main types of substrates (both organic and inorganic cations, anions, and neutral molecules) have been synthesized. Data on the receptor properties of some functionalized calix[4]arenes **1—8** for metal cations are shown in Fig. 2.[10—12]*



1—8

Compound	R	Compound	R
1	—NHCH$_2$Ph	**7**	
2	—NHPh		
3	—NH(CH$_2$)$_7$Me		
4	—NH(CH$_2$)$_{11}$Me	**8**	
5	—NH(CH$_2$)$_{17}$Me		
6	—NHNH$_2$		

All the receptor systems are the so-called host—guest structures. Receptor (host) molecules can add or sometimes accommodate substrate (guest) molecules.

Receptors can manifest high selectivity; *i.e.*, they tend toward "molecular recognition". This implies that molecules recognize each other by virtue of intermolecular interactions, without any damage to the structures of their partners, that is they exchange molecular information. It is essential that information is created and stored at the molecular level and read out at the supramolecular level without any damage to the molecules themselves or their covalent bonds.

In molecular recognition, the so-called complementarity principle is implemented. The complementarity may be both spatial (the interacting groups approach each other at distances sufficient for their interactions) and functional (*e.g.*, if one component bears a proton-donating group, while the other in an appropriate position bears a proton-withdrawing group, and *vice versa*); *i.e.*, all the necessary conditions for the best bonding between the components of a system are met. This is nothing else than

* A number of examples cited in this paper was taken from our study of the supramolecular chemistry of calixarenes. This was done to demonstrate that a set of key (for the topic of this review) properties such as receptor nature, molecular recognition, transportation, and catalysis occur even within a narrow class of compounds (*e.g.*, such as calixarenes).[13]

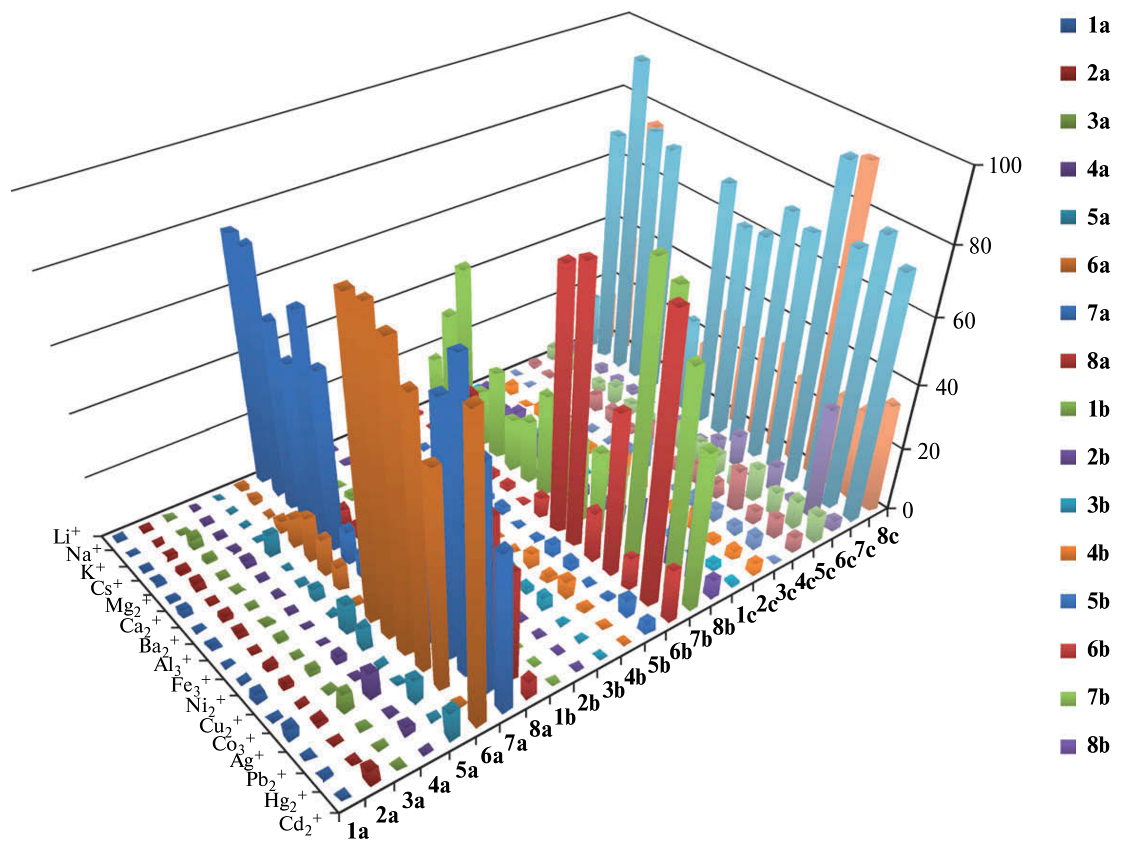
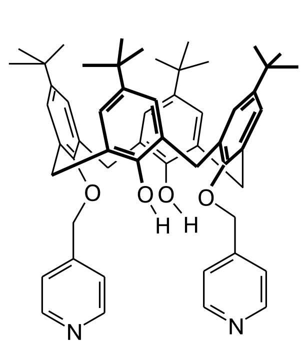


Fig. 2. Degree of extraction (%) of metal cations with thiacalix[4]arene derivatives **1**—**8**, where **a** is a *cone*, **b** is a *partial cone*, and **c** is *1,3-alternate*.

the basics of Emil Fischer´s "lock and key" model, which is well known in enzymology.

Apart from synthetic receptors of all main types of substrates, synthetic transport vehicles have been designed. Receptors can transport substrates across membranes or channels. In a system capable of molecular recognition, the transportation will be selective. For instance, out of a library of structurally related compounds, calixarenes transport only one that has been recognized[14,15] (Fig. 3).



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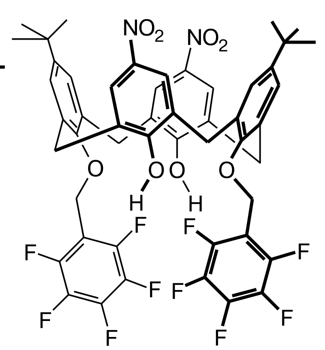

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Synthetic supramolecular systems can act as efficient catalysts, which has been illustrated with generally accepted, so-called biomimetic reactions that simulate processes in living organisms; the reaction rate constants increase by five to six orders of magnitude in the presence of supramolecular catalysts. Interestingly, the kinetic patterns in these cases correspond to those in enzymatic processes.[16]

A great role in the formation of supramolecular systems is played by hydrogen bonds. In such systems, it is usually impossible to distinguish between receptors and substrates nor understand which components are hosts and guests. The interacting molecules are equal partners, so it is more correct to discuss supramolecular relations between them.

Let us consider particular hydrogen-bonded systems. The acetic acid dimer consisting of two acetic acid molecules linked by two hydrogen bonds, has already been mentioned as an example of a supermolecule. This structure is so stable that acetic acid exists as a dimer even in the vapor phase. However, some molecules can form more than two (three or more) hydrogen bonds and have several sites for their formation. For instance, look at the system melamine—cyanuric acid[17] (Fig. 4). Depending on the conditions, the system produces ribbon or rosette structures or their combinations. Ribbons are supramolecular ensembles with unknown numbers of the starting molecules in their polymolecular structure. Rosettes are super-

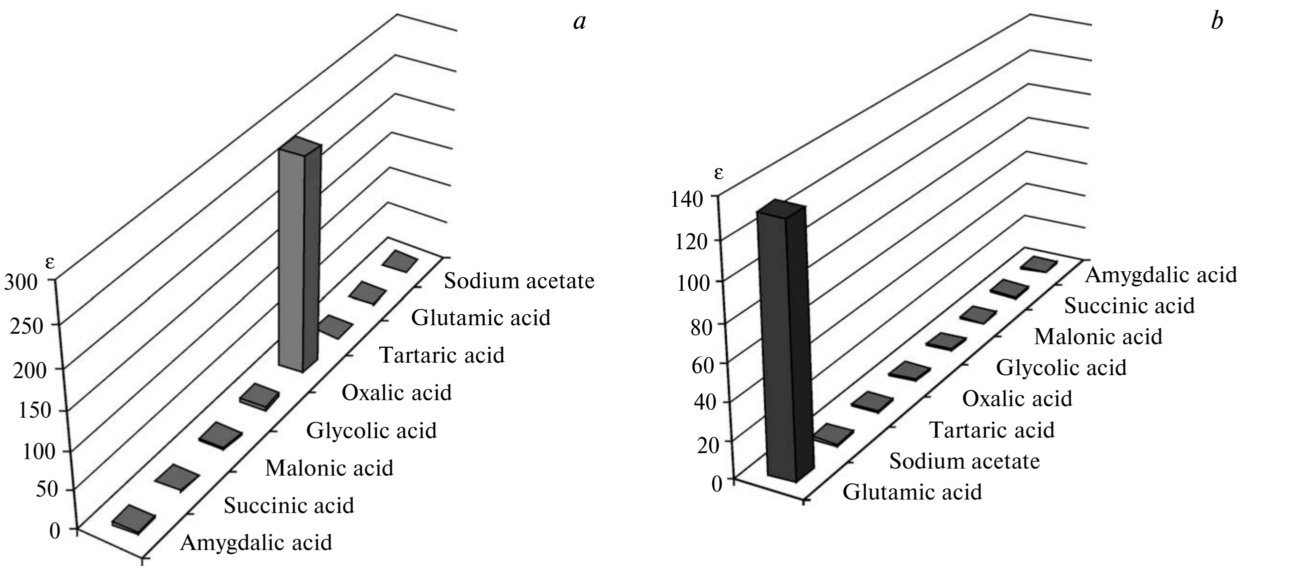


Fig. 3. Flux enhancement factors ($\varepsilon = j_i/j_0$) for substrates penetrating across a liquid membrane in the presence of calixarenes **9** (*a*) and **10** (*b*).

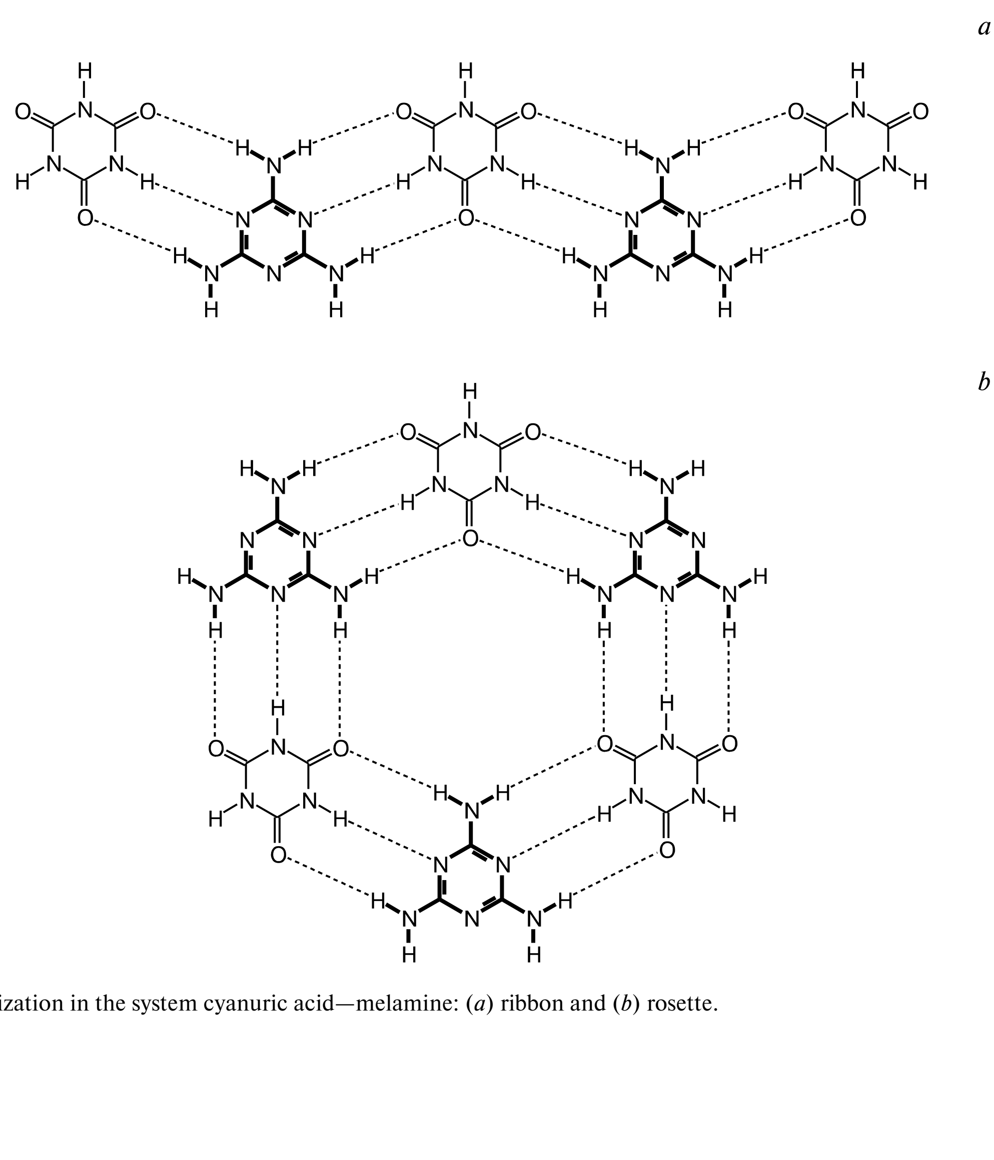


Fig. 4. Self-organization in the system cyanuric acid—melamine: (*a*) ribbon and (*b*) rosette.

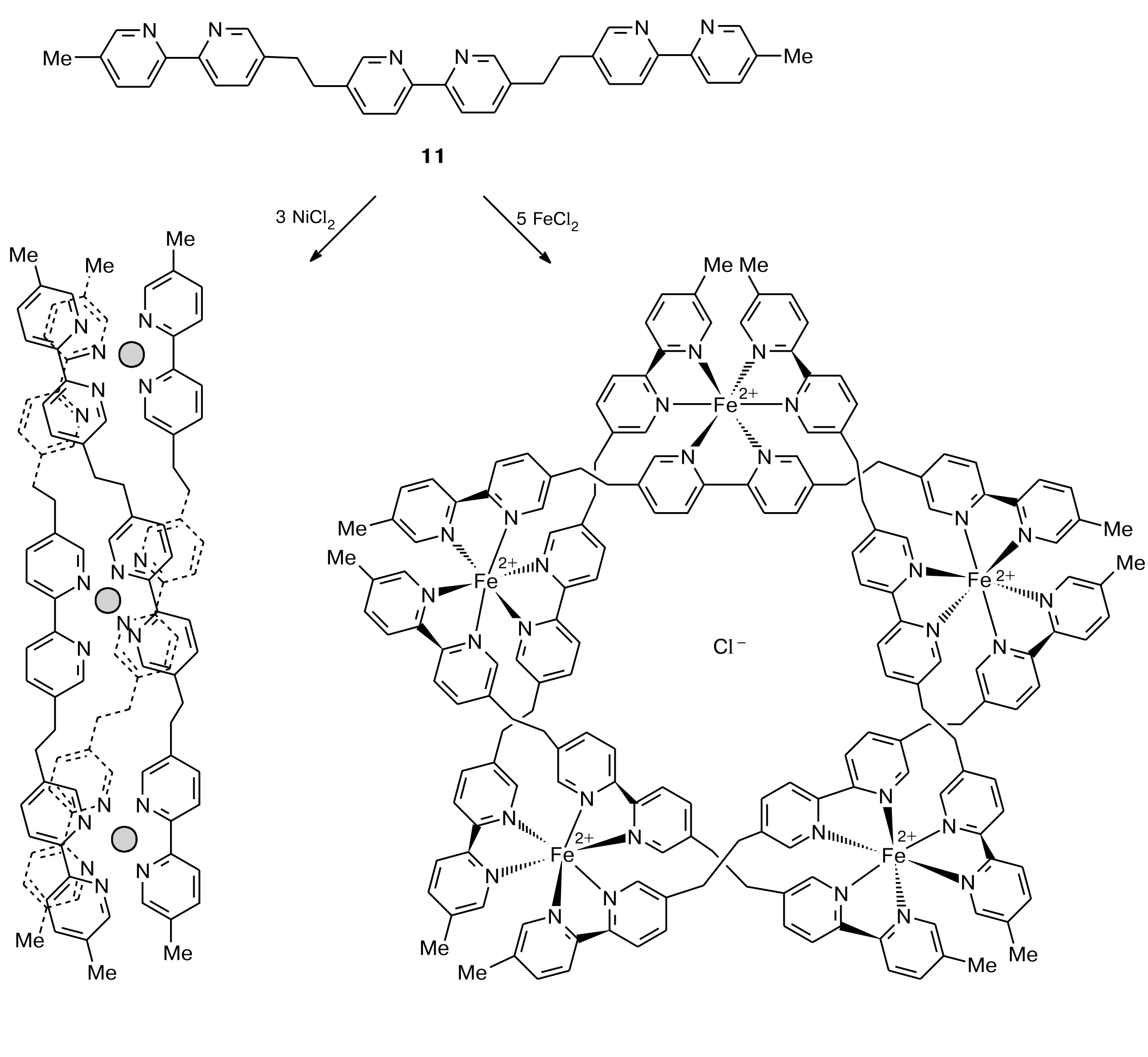
molecules with well-defined numbers and structures of the starting molecules. It is worth noting that molecules spontaneously gather to form such structures; *i.e.* self-assembly or self-organization takes place. This example is not unique because the phenomenon is very common.

Very complicated self-organization may result from cation—*n*-electrons interactions.[18,19] For instance, a reaction of multiunit ligand **11** containing several *n*-electron sites with nickel (Ni^{2+}) dichloride gives a triple helix, while a similar reaction with iron (Fe^{2+}) dichloride affords a star-shaped structure (Scheme 1). In the latter case, the ligand molecules are intertwinned. All these compounds are formed in quantitative yields.

It should be noted that the molecules of ligand **11** react with a singly charged copper cation to give a double helix.[18] On the whole, the helical structure is not a rare case among supramolecular systems and is usual for certain structures of interacting components. This is the so-called class of "helicates".[6,8,9]

Self-organization of the so-called amphiphiles (compounds combining a polar head and a nonpolar tail) gives rise to various structures depending on the structure of amphiphiles and the conditions of the process. These include normal spherical micelles (spheres with polar groups directed outward and the tails inward); normal cylindrical micelles (cylinders with the same orientation of amphiphilic molecules); inverted spherical micelles (spheres with tails directed outward and polar groups gathered inside); vesicles (spheres made up of amphiphiles arranged in a double layer in which polar groups are both outside and inside and tails are directed toward each other); planar bilayers (amphiphiles with tails directed toward each other and polar groups on both sides of the bilayer, which may be closed on itself). The main driving force in the

Scheme 1



formation of the above structures are hydrophobic effects. In our context, vesicles and bilayers are of greatest interest.

Thus, it can be inferred that organic molecules of synthetic origin (not necessarily biomolecules) can undergo supramolecular association by intermolecular noncovalent interactions to give supramolecular systems. In the resulting couples, one molecule will be a receptor for the other (a substrate). Receptor—substrate interactions can be selective, which allows molecular recognition and underlies molecular informatics. Supramolecular systems can function as transport vehicles and catalysts. Molecular recognition can provide selective transportation and catalysis. All these properties and functions pertain to supramolecular systems as such, regardless of any biological objects.

Note that the architecture and functions of such key structures in biological systems as, *e.g.*, DNA or cell membranes, are typically supramolecular (Figs 5, 6).

Two DNA chains are hydrogen-bonded in the nucleotide base pairs adenine—thymine and guanine—cytosine (see Fig. 5). The double-helix structure of DNA is known. It has been demonstrated that double and triple helices of long molecules held together in a supramolecular system is a supramolecular standard and that the double helix of DNA is a specific case of such supramolecular structures. The function of information storage and translation is effected according to the already known mechanism. Information is stored at the molecular level and read out at the supramolecular level.[17]

A plasmatic membrane is an amphiphilic bilayer with other included structures (see Fig. 6). Phospholipids, the main constituents of membranes, are typical amphiphiles; the functions of these inclusions (receptors, channels) are also supramolecular. So, cell membranes are supramolecular both structurally and functionally.

After the consideration of separate elements of biological systems, it is expedient to go into the structures and functions of a cell, an elementary unit of every living creature on the Earth. Because we are lacking in reliable knowledge of the protocell, let us consider its simpler modern version, namely, a prokaryotic cell.

According to the current concepts, every prokaryotic cell has four main structural—functional subsystems, each of which is indispensable for the life of the cell as a whole:[20]

(1) the outer cytoplasmatic membrane (the planar bilayer membrane is made up of amphiphilic molecules of lipids and proteins), which acts as a semipermeable barrier in the interaction of the cell interior with the environment;

(2) genetic machinery (DNA);

(3) biosynthetic machinery (mRNA, ribosomes, and tRNA);

(4) metabolic machinery (enzymes, whose selectivity is due to molecular recognition).

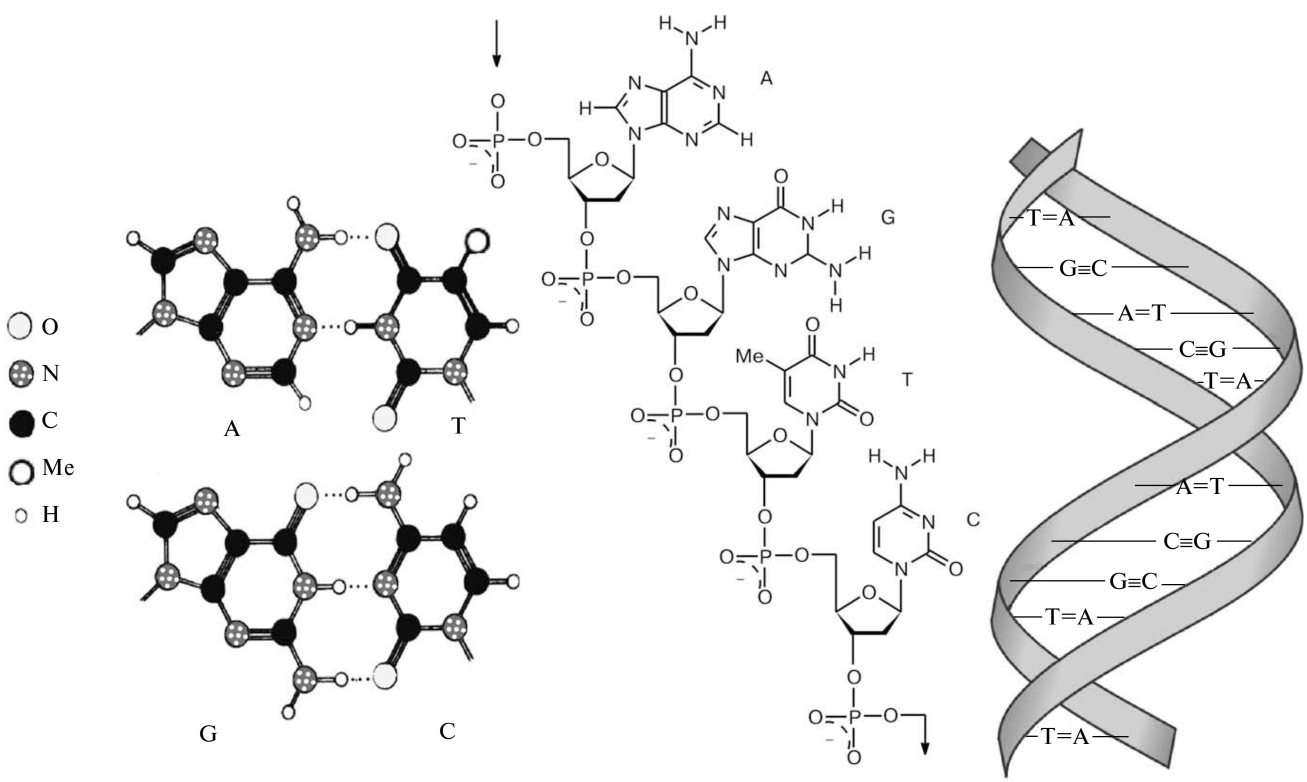


Fig. 5. Supramolecular structure of DNA (A is adenine, G is guanine, T is thymine, and C is cytosine).

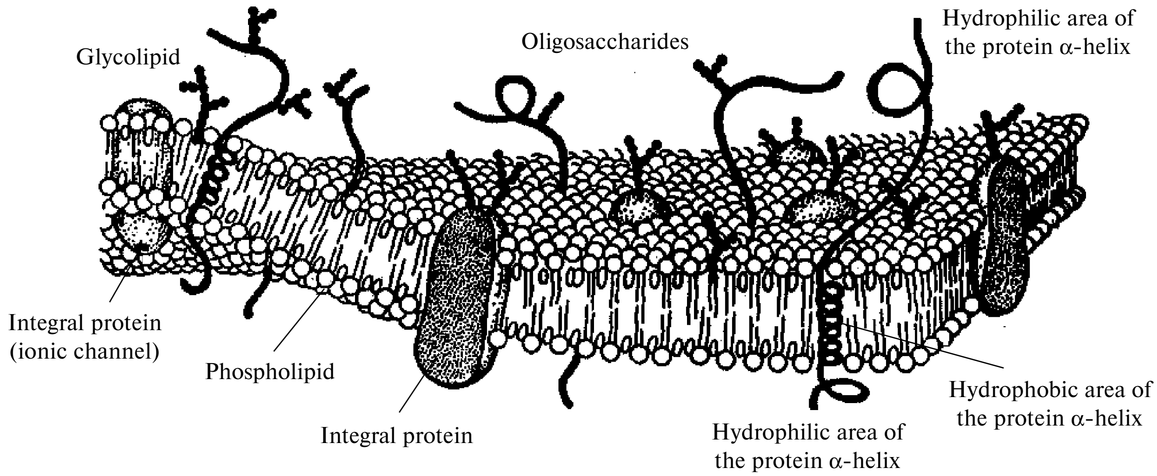


Fig. 6. Supramolecular structure of a cell membrane.

Each subsystem is supramolecular, though having different structures and different functions. However, only their combination and cooperation make the cell viable.

It is absolutely clear that supramolecular systems were derived from molecules during the evolution and could not originate in biological systems. On the contrary, it is supramolecular systems that gave rise to biological systems. This is suggested by the logics of matter sophistication during the evolution, which will be discussed below and becomes more evident from a subsequent energy analysis. The obvious conclusion drawn from the above consideration is that supramolecular systems organized themselves into biological systems. As shown with a prokaryotic cell as an example, only a community of interrelated and interdependent (but structurally and functionally differentiated) supramolecular systems can produce a viable biological system (cell). It should be noted that the idea of the importance of supramolecular biomolecular systems as the basis for biological systems is currently expressed by other researchers as well (see, *e.g.*, Ref. 21).

Now it will be useful to look at the hierarchical structure diagram of the basic elements involved in structural organization of matter (Fig. 7).[22]

The first level is represented by elementary particles. The second level is represented by atoms built from elementary particles. The third level is represented by molecules built from atoms by covalent bonding. The fourth level is that of supramolecular systems. Molecules are held together by intermolecular noncovalent bonds to form supramolecular systems (supermolecules or supramolecular ensembles). The final level is that of biological systems, which can be regarded as an interdependent community of functionally differentiated supramolecular systems.

The first important conclusion that can be made in this context is that supramolecular systems have their own level and, consequently, their niche in the hierarchy of the basic elements of structural matter organization. The ten-

Elementary particles	p n e	
Atoms	a b c	
Molecules	A(a—a) B(a—b) C(b—c) Covalent bonds	
Supramolecular systems	A...A A...B	Supermolecules
	A...B...C ⋮ ⋮ C...A Noncovalent (intermolecular) bonds	Supramolecular ensembles
Biological systems	Community of structurally and functionally differentiated supramolecular systems	

Fig. 7. Schematic hierarchy of the basic elements in the structural organization of matter.

dency of molecules to form supramolecular systems is not their ordinary property but is the property bringing matter organization to a qualitatively new level.

The second important conclusion refers to biological systems. This conclusion is not only, and even is not so much, that supramolecular systems (with participation of biomolecules) provide the basis for biological systems but also that biological systems themselves constitute a basic element of structural matter organization. This conclusion will be confirmed after the energy profile of structural matter organization is examined.

Particular emphasis should be placed on the phenomenon of self-organization. The term "self-organization" was introduced when science came across spontaneous formation of complex ordered structures. Their complexity, ordering, and spontaneous formation were surprising. However, everything in nature occurs spontaneously and the degrees of complexity and ordering and formation of a particular species depend on the level of structural organization of the resulting species and the balance of forces determining its formation. Why the resulting supramolecular structure can be a triple helix in one case and a five-pointed star in another case (as illustrated above) depends on the particular properties of interacting species (*e.g.*, the Ni^{2+} and Fe^{2+} cations). In both cases, the same process (self-organization) takes place, yielding different products from different starting compounds because of their different properties. When considering self-organization as spontaneous formation of higher-level or/and higher-order systems compared to the starting systems, one can conclude that self-organization is a fundamental property of matter, which is inherent in all levels of structural matter organization.

According to the previous conclusion, biological systems result from self-organization of supramolecular systems. Supramolecular systems result from self-organization of molecules. Molecules result from self-organization of atoms. Atoms result from self-organization of elementary particles. Thus, sequential self-organization of the simpler systems gives rise to more complex systems. Let us consider the principles of matter sophistication.

Principles of matter sophistication during the evolution

A study of matter evolution suggests that the evolution of the Universe proceeds from simpler to more complex forms.[23] Otherwise, there would be no mankind. Elementary particles, atoms, molecules, supramolecular systems, biological systems, and mankind are the increasingly complex forms of matter during its evolution. The directive definite principles[23] in this process are (1) relay-type transformation of matter; (2) precedence of simpler forms to more complex ones; (3) strictly successive sophistication of matter.

Following these principles confirms the scheme displaying the hierarchy of the basic elements of structural matter organization, in which supramolecular systems have their own niche.

Analysis of the energy profile of the hierarchy of structural matter organization

Interesting results are obtained while analyzing the relative changes in the energy levels of structural matter organization (energy profile of the hierarchy of structural matter organization,[24] Fig. 8). This can be done by assessing the specific energies of formation of matter objects of a given level from objects of the preceding lower level (*i.e.*, the energies of formation of atoms from elementary particles per elementary particle, the energies of formation of molecules from atoms per atom, and the energies of formation of supramolecular systems from molecules per molecule). Of course, exact evaluation is fundamentally impossible because of a large scatter of the values. Fortunately, this is not required since we want to know the character of changes, dealing simply with the orders of the corresponding quantities.

With consideration of the aforesaid, the energy for atoms is taken to be 10^6 eV (see Fig. 8, *a*). This value is of the same order of magnitude as the binding energies of nucleons in atomic nuclei per nucleon.[25] The binding energies of the bonds between electrons and atomic nuclei (*ca.* 10 eV) can be ignored. The binding energies for molecules (*m*) and supramolecular systems (*ss*) are taken to be 10 and 1 eV (these values corresponds to the energies of covalent[26] and intermolecular bonds,[7] respectively).

These data are compared in Fig. 8, in which the axis *x* may be regarded as a unidirectional arrow of time (evolution, matter sophistication). It can be seen in Fig. 8 that

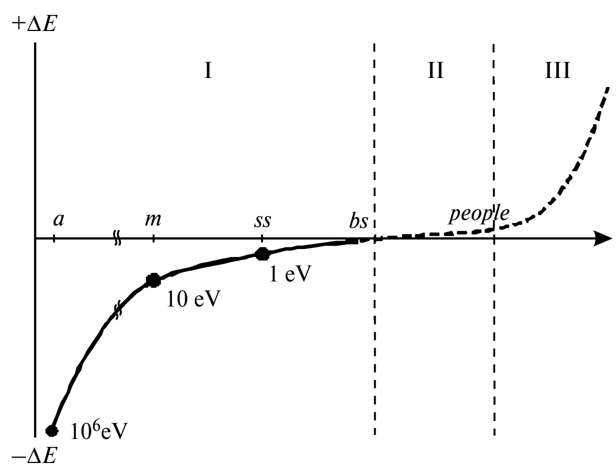


Fig. 8. The energy profile of the hierarchy of the basic elements in the structural organization of matter: (I) prebiological evolution, (II) biological evolution, and (III) social evolution.

the formation of atoms, molecules, and supramolecular systems is exothermic. The liberated energy is consumed by the environment: these are thermodynamically open systems. Atoms, molecules, and supramolecular systems are stable structures in equilibrium state. They require no energy supply from the environment for their existence. In the sequence of matter transformations from elementary particles to supramolecular systems, the energies of formation of the corresponding structures decrease from the preceding level to the next one, approaching zero. This would seem to indicate the end of matter evolution.

However, the pattern changes with appearance of systems that exist and function (and they can exist only as long as they function) by consuming energy from the environment. These systems are biological systems (*bs*). The development of such systems initiates the qualitatively new, biological step of evolution leading to *Homo sapiens* (*people*) and then to a human society. During social evolution, the energy consumption increases incessantly. The fact that biological systems naturally follow the tendency found in prebiological systems suggests that biological systems are a basic element for structural matter organization.

Two arising questions are: (1) what are the nature and causes of the transition from prebiological evolution to biological one and (2) what is the character of energy changes during the biological and social periods of matter evolution.

What happened to supramolecular systems and why did they (of course, systems based on biomolecules) begin to live? Lying beyond the scope of this paper and being controversial,[1,5,27] these questions will be side-stepped here; it should only be mentioned that biological systems are treated as thermodynamically open nonequilibrium systems in the steady state.

As shown by A. I. Zotin and A. A. Zotin,[28] the energy changes during the biological and social periods of matter evolution are exponential (however, the energy per gram of a biological object is calculated). Of particular interest is the fact that the pattern remains unchanged when moving from animals through people to a human society, despite power generation from the environment in these periods. If power is wanted, it must be generated. This power generation/consumption increases exponentially and, according to some estimations, will reach a critical value in 2130. To that time, generated power will be 1% of the solar energy reaching the surface of the Earth. Note, however, that although the exponential character of power generation is undoubted, there are alternative estimates of the ratio of generated power to the solar energy reaching the surface of the Earth.[29]

On the whole, the above consideration allows one to formulate some principles of matter evolution.

Along with the principles of sophistication and self-organization, which have already been discussed, the principle of sequential level-forming properties is also valid. Some explanations to this principle are required because important conclusions follow from it.

The questions as to how and which way matter develops itself have been answered: by self-organization, spontaneously, from simpler to more complex forms. Another arising question is: what is the reason for matter evolution? Neither self-organization nor sophistication of matter provides an answer to this question. Both processes are not the driving forces of matter transformation. In this case, self-organization and sophistication are the form and result, respectively, of the action of these forces.

Let us reveal the actual driving forces of matter transformation processes. For generalized consideration, they can be defined as the properties or ability of objects of a given level of structural matter organization to form objects of the next level. In their essence, these properties (forces) differ at different levels. For instance, elementary particles have the tendency to form atoms resulting from the formation of atomic nuclei (nuclear forces) followed by their interactions with electrons. Atoms are capable of covalent bonding by the known mechanism of pairing electrons with antiparallel spins, so they tend to unite into molecules. Molecules can be united through intermolecular noncovalent bonds into supramolecular systems. Supramolecular systems tend to form biological systems. It is essential that each higher level of matter organization is a new level of information, which determines the formation of the next level of matter (and information). Thus, the principle of sequential level-forming properties includes two conditions: (1) objects of each level of structural matter organization have the tendency (ability) to form objects of the next level and (2) each new level corresponds to a new level of information that allows the formation of each next level.

One can notice the following strict sequence. The formation of atoms is due to the properties of elementary particles. Whenever elementary particles are formed, atoms will be formed. The formation of molecules is due to the properties of atoms. Whenever atoms are formed, molecules will be formed. The formation of supramolecular systems is due to the properties of molecules. Whenever molecules are formed, supramolecular systems will be formed. The formation of biological systems is due to the properties of supramolecular systems. Whenever supramolecular systems are formed, biological systems will be formed and hence life will originate.

Thus, the origin of life is predetermined under appropriate conditions mainly depending on the conditions of existence and functioning of supramolecular systems and their stability and sensitivity to temperature and other factors. Supramolecular systems are responsible for the viability of biological systems. Rephrasing Engels´ thought, one can say that life is a form of existence of supramolecular systems.

Of course, the idea that the origin of life is predetermined has been expressed earlier. Here are A. Lima-de-Faria´s words (1988):[30] "Biological evolution exists because it was inevitable. In the infancy of the Universe, the proton, the neutrino, and the boson possessed those qualities that made subsequent evolution of plants and animals inevitable". However, this does not diminish the importance of the conclusions made in the present review.

Thus, this study demonstrated that supramolecular systems are the acme of the prebiological evolution of matter. The properties of supramolecular systems are indispensable for the formation and existence of biological systems. Indeed, biological systems cannot exist without molecular recognition. However, molecular recognition is possible only on a supramolecular basis because a molecule should be recognized without its degradation. This can be done only through noncovalent bonding. In industry, non-destructive methods are used for testing materials. Molecular recognition can be called a non-destructive molecular test. Biological systems cannot be represented without DNA or translation of genetic information. Remember that DNA has a supramolecular structure and genetic information is read out at a supramolecular level. The same is true for biomembranes, ionophores, and other biological structures.

To sum up, supramolecular systems are a bridge between nonliving and living matter. Moreover, supramolecular systems is the basis for life.

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