

**Z ZAGADNIENÍ
FILOZOFII PRZYRODOZNAWSTWA
I FILOZOFII PRZYRODY**

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THE ROLE OF PORPHYRIN SYSTEMS IN THE EVOLUTION OF LIFE

(Summary)

In the present work the role played by porphyrin systems has been dealt with in the context of the studies on abiogenesis and early stages of the molecular evolution of life. The knowledge of this role is essential for the elucidation of the origin of the bioenergetic processes, especially those underlying the most important and ubiquitous ones in the present biosphere, i.e. photosynthesis and respiration.

In discussing this role, mainly the so called "evolutionary method" has been used along with reinterpreting the data taken from various particular branches of science (e.g. from inorganic biochemistry, molecular biophysics, organic geochemistry, exobiology, physics of the biological environment, and microbiology), and a superior "problem-unity" has been constructed. Some simple mathematical calculations have been performed as well.

The present work is divided into four chapters. The first one presents an extensive review on the occurrence and properties of porphyrin systems in the present molecular organization of life, as well as in the non-biological environment. As could be expected, it has become evident that advancement of the current investigations in particular areas of the study of porphyrin systems is unequal, and, what is more, it falls short of the needs of evolutionary biochemistry and theoretical biology. For example, tetrapyrrole complexes of with Fe, Mg, Zn, Mn, Co, Ni, and Cu ions are known to occur. However, except for the first two mentioned ones, there is only a scarce amount of data on the five remaining ones. Accordingly, very little is known about the paths of biosynthesis of them, of the physiological part they play, and above all of their comparative taxonomy. Siroheme, heme d, heme s, and the role of some Fe-porphyrins being chemically identical prosthetic groups, but functioning in the proteins performing completely different functions (e.g. heme b in cytochrome P-450

and in hemoglobin) are also poorly known entities. It may be proved the poorly determined biophysical role of certain metallocomplexes, e.g. the significance of the electronic structure of the porphyrin system and of the spin-state of the Fe^{2+} in the above mentioned heme b for the biochemical processes, and the significance of the electronic conductivity for these processes, etc.

It is interesting from the bioelectronic point of view, that semiconductor theories of photosynthesis and the action of cytochrome oxidase refer just to the electronic phenomena on the submolecular and supramolecular levels of the organization of living systems. These theories, however, may have more general significance. Namely, one may suggest an electronic role of chlorophylls, hemes, and other molecules of this type.

It should also be stressed here that there is a disproportion in the number of various types of proteins containing this same porphyrins system, e.g. the highest number of them is bound with heme b, and a very small one - with siroheme. Probably, this disproportion stems from the variety of side-groups of the porphyrin ring, which is the result of molecular evolution of these compounds.

In the second chapter an attempt is made at a reconstruction of the genesis and evolution of porphyrin systems. It has been shown there that in the course of chemical evolution the most probable way of bringing these changes about was abiosynthesis of porphyrins on aluminosilicates. In this context, a possible use of a new energy source, so far not taken into account has been suggested, namely, the electric currents modelling the telluric ones, which flew in aluminosilicates of primordial environment. The author suggests that under the influence of the telluric currents in the electronic plasma of aluminosilicates the complexes of porphyrins with Si and Al might have originated, and taken part in the next stages of biochemical evolution.

Unfortunately, the experiments simulating the probable conditions of the primordial environment carried out so far, failed to synthesize the presently known siroheme, chlorophylls, hemes, etc. It is well known that the synthesis of them in the present living forms is a complex one. In all probability, these compounds have been produced in a biogenic way, being the result of a relatively advanced molecular evolution of life. From among all these compounds siroheme seems to be the oldest one, and it seems to precede all the porphyrin compounds. However, corrinoids may be considered to precede all these compounds. It is not known what has happened in the course of the evolution of tetrapyrrole compounds on the stage between abiotically synthesized natural porphyrins and corrinoids and siroheme.

The author suggests that the evolution of porphyrin compounds has been initiated by silicoporphyrins at the stage when hypothetical carbon-siliceous protoforms of life existed. In this context, it is worth mentioning that the oldest biogenic porphyrins have been found just in quartzites (dated about 3.8 billion years), while the oldest sedimentary carbonate rocks are dated only at 3.5-3.7 billion years.

The biochemical evolution of presently known porphyrin systems seems to have proceeded both from the more to less reduced forms and of acquiring the central ions which have stronger donor or acceptor properties. In the present work, the idea that the biophysical evolution of these systems takes place has also been suggested.

Pursuing the above mentioned line of argument, a proposal is put forward that in living organisms such presently unknown porphyrin complexes, as those containing Al, Si, as well as those with transition elements (Cr, V, Ti, Sc...), and intratransition elements (lanthanides) should be searched for. The author suggests that these metalloporphyrins could perform catalytic functions or even take part in laser or maser processes involved in bioenergetics. A possible hunting-ground for these complexes could be bacteria which are able to decompose aluminosilicates, as well as the organisms which inhabit unusual and extremal environment conditions, as microorganisms in petrol, thermo- and base-philic bacteria, etc.

The enormous structural and functional diversity of porphyrin systems, in all probability, adequately reflects the adaptation of organisms to their changing environment. With this in mind, the third chapter is devoted to the role of porphyrin systems in the adaptation to changes in environment. As the author sees it, the role of these structures consisted more in helping to develop the exploitation adaptations (e.g. hemoglobins, chlorophylls), than the compensatory ones (e.g. cytochrome P-450). Moreover, it seems that the adaptational roles expressed themselves in the following three ways: i/ by changes of the type of porphyrin systems and their molecular milieu, ii/ by adjusting the concentration or the number of the porphyrin systems of the given type, and iii/ by suitable regulation of the functions of the molecules containing these systems.

This type of adaptation functions could, in the authors' view, have great significance in the reducing environment of the early pre-cambrian, because of the ability of some hemes to react to changes in the content of methane or carbon monoxide.

Taking into consideration the adaptative role of hemes in the environment where the concentration of oxygen changes, the author raised the problem of the evolution of the cooperative interactions between the sites where oxygen becomes attached. Thus, apart from the evident

existence of the biochemical adaptation, the existence of the biophysical adaptation is also postulated in the present work.

The common feature of all kinds of biochemical and, seemingly, biophysical adaptations in which porphyrin systems are involved, are the changes of chemical affinity of the macromolecule of the porphyrin-containing protein to the micromolecule of a given substrate, as well as of the protein component of the given macromolecule to the porphyrin system. These changes of affinity, being of crucial significance to the mechanisms of adaptation, are acted upon by the chemical and physical changes in the environment. Life in the course of its adaptation to the changing environment has chosen the most optimal processes. Keeping this in mind, one may understand that the biochemical pathways become adopted to some ranges of physical variables, which, in turn, enabled them to proceed optimally (e.g. in the presence of the excited state of biomolecules generated by suitable temperature, quanta of the radiation in the UV and visible range). Therefore, it is not excluded that concrete photo-emissive and photoabsorptive properties of porphyrin systems played in bio-systems the part of the factor initiating the processes involving the electromagnetic radiation in the vicinity of porphyrin compounds.

It has been also suggested, that some possible mechanisms influencing the adaptative role of porphyrin systems should be sought in the fields both of the physics of biological solid state and of bioelectronics. Consequently, when the changes of environmental temperatures are considered, the alleged pyroelectric properties of porphyrin-containing proteins should be considered, when the changed of the environmental pressure take place, the piezoelectric properties come into effect. Similarly, in the environment where electromagnetic radiation in the visible range of spectrum acts as a factor to which the living system must adopt itself, the important role is played by these properties of porphyrin systems making them a good laser material, etc.

In connection with this, a suggestion may be put forward, namely that various biochemical and biophysical adaptations in which the porphyrin systems are involved may be explained by the functions of these systems on the submolecular level of the organization of the living system.

In the search for the mechanisms of the evolution of porphyrin systems claimed above and their adaptative role, the bioelectronic model of abiogenesis and the bioplasma concept have been considered, as they are directly related to the submolecular level of organization. This has been done in the fourth chapter. Besides this, an attempt has been made at calculating and discussing the conditions

for the existence of the plasma state, as well as an evaluation of some important plasma parameters.

The most important conclusion reached in this paper is that the conditions for the existence of the plasma state in a single porphyrin systems are fulfilled only under the two following relations - binding together two essential parameters of plasma (ϵ_T - the static dielectric constant of the medium in which the electrons are transferred, m_x - the ration of the electron effective mass and its resting mass) - are simultaneously met:

$$1) \quad 25 \ll \epsilon_T m_x^{-1} \ll 65$$

and

$$2) \quad \epsilon_T m_x \approx 8.7517 \times 10^{31} \omega_p^{-2},$$

where ω_p - the plasma angular frequency.

It has also been found that the range of the values of ω_p may be assumed as:

$$2.0677 \times 10^{-4} m_x^{-1} n_0^{1/3} L^{-1} \ll \omega_p \ll 2.0677 \times 10^{-4} m_x^{-1} n_0^{2/3},$$

where: n_0 - the concentration of the electrons (in the porphyrin ring) [m^{-3}], L - the linear dimension of the system [m]. Generally speaking, the relation mentioned above shows that the range of the resonant frequencies which may be exploited by the organism broadens, if the size of the system and its subsystems increase. In this context, it has been pointed out that this relationship might be crucial for the adaptation of the living systems to the changing electromagnetic environment.

When considering the essential requirements for the existence of the plasma state in the porphyrin system, the formula expressing the optimal, as it seems, conditions for the existence of the plasma state has been reached:

$$a \omega_p m_x \left(L n_0^{-1/3} - n_0^{-2/3} \right) \gg 0,$$

where $a = 2(3\pi^2)^{1/6} m_0 h^{-1}$.

This inequality has some interesting features. For example, if the plasma state is to be maintained in a living system, it ought - and even must - to be able to increase the concentration of mobile charge carriers (which may be called catabolism in terms of biochemistry), or to increase its size (anabolism), or to change its plasma frequency, as well as the effective mass of electrons.

In analyzing the conditions for the existence of the plasma state in biostructures containing porphyrin systems, a rather disputable problem arises. Namely, if the concentration of free electrons in these structures lies in the vicinity of $1.7 \times 10^{25} \text{ m}^{-3}$, then the entropy of the degenerate electron gas should be minimal or even zero. Therefore, a suggestion has been made that bioplasma may be understood as plasma, the density of which oscillates in the border region between the nondegenerate and degenerate states. If so, the bottom limit for the linear size of such a system should be 39 \AA . Possibly, this may be an explanation why the living organism must not be smaller.

In this work, the problem of the possible existence of the superconducting plasma in the porphyrin system has been also raised. This state might act as a factor coordinating the movement of electrons in supramolecular structures.

The general conclusion following from the above considerations is that in the course of molecular evolution of life the principal function of porphyrin systems has been an electronic one, the other only being of secondary importance. As far as the methodological aspect of the present work is concerned, it must be admitted that the problems dealt with were of a very broad nature. Therefore, some simplifications and statements put implicitly were inevitable. The reconstructions which have been presented are also only of a fragmentary nature. However, these short-comings point out to the necessity of further research both in the plane of theoretical biology, and especially in its bioelectronic branch, and in such fields, as: paleobiochemistry of silicon compounds, microbiology of archaeobacteria, and many others. There are also some interesting aspects which had to be omitted in the present work, for example the evolution of magnetic properties of porphyrin compounds and its significance to the bioelectromagnetic evolution.

The author believes that in the near future the essential progress in the research of the genesis of life will depend on the taking into account the electronic model of organism as well as bioelectronic evolution. However, to bring this progress into reality, one will probably have to have at his disposal data from presently non-existent or not well-developed branches of science, such as physics and chemistry of organic and biologic semiconductors and superconductors, biophysics of archaic forms of metabolism, comparative and evolutionary biochemistry of silicon compounds, bioenergetics of processes involving organosilicon compounds, and quantum biophysics.

In spite of these short-comings it seems, that the above mentioned perspective of progress in the discussed field does not transgress the realm of admissible extrapolation.