QUANTUM MECHANICAL EVOLUTION OF FATTY ACIDS WORLD LIFE

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(Abstract)

Quantum mechanical density functional theory nonlocal gradient electron correlation interactions methods are used for investigations of various self-assembled photoactive fatty acid micelles. The micelle systems studied are based on a photoactive squarine sensitizer, an 8-oxo-guanine electron donor, cytosine, a fatty acid and its precursor (pFA) molecules. The systems include a water environment and consist of some 400 atoms and are up to about 4.5 nm in diameter. The quantum mechanical based electron correlation interactions are the source of the weak hydrogen and Van der Waals chemical bonds that are critical to the behavior of these systems. Polar solvent molecules such as water increase the strength of these bonds and thus play a central role in the self assembly and functioning of the systems studied. The distances between the separated sensitizer, precursor of fatty acid, and water molecules are comparable to Van der Waals and hydrogen bonding radii. As a result, these nonlinear quantum interactions compress the overall molecular system resulting in a smaller gap between the HOMO and LUMO electron energy levels allowing enhanced tunneling of photoexcited electrons from the sensitizer to pFA.

The most intense excited states of the photoactive fatty acid micelles are partially composed of LUMO+n states located on the fatty acid precursors when the bis(4-diphenylamine-2-phenyl)-squarine molecule is covalently attached to the 8-oxo-guanine. This coupling also promotes electron hopping (tunneling) to the pFA molecules during the most intense absorption excited state. The photoexcited electron tunnels to the waste end of the pFA molecules where it causes these molecules to split due to intense rotation and vibration of the weak chemical bond that joins the waste piece to the fatty acid section of the pFA molecule.

The most intense absorption lines of the squarine-8-oxo-guanine supermolecule were found to be shifted to the red when these molecules were associated with fatty acid micelles. In addition, the 8-oxo-guanine::cytosine-squarine supramolecule was observed to have an absorption region that covered more of the visible spectrum than a squarine-8-oxo-guanine supermolecule. The redward shift of the intense absorption lines would allow a self reproducing micelle to absorb the light in the longer wavelength region, which may have been important in the environment that life might have developed, in addition to extending the photoactive period into the earlier morning and later evening hours. That allowed better compete for such a kind of evolved photoactive micelles of Fatty Acids World life in getting the food molecules. Furthermore, one notes that the nucleotide caused wavelength shift and broadening of the absorption pattern potentially gives the nucleotides an additional valuable role, other than just a purely genetic one in the early stages of the development of life.

The main quantum mechanical research result of this paper is that life in the Earth or elsewhere in the Space could have emerged in the form of self-reproducing photoactive fatty acid micelles, which step by step evolved to nucleotide containing micelles due to an enhanced ability to absorb visible light. The nucleotide molecules and their sequences, which in the first period of evolution of fatty acid molecules were useful just for better absorbance of the light in the longer wavelength region, later in the peptide nucleic acid (PNA) or RNA World living organisms took on the role of genetic information storage.

From the information theory point of view, the nucleotide molecules sequences in the Fatty Acids World micelles carry positional information how to directly provide better relaxation electron transport along the nucleotide-sensitizer chain and in addition providing complimentary copies of that information to the next generation.

The result of self-assembly of molecules depends on the electromagnetic forces between electrons and in general is predicted by existence of the universal constants. Molecules are built from atoms therefore for the thermonuclear reactions and atom synthesis in the stars are important also the rest three fundamental forces: strong and weak nuclear interactions and gravitation (for the self-formation of stars). Universal constants of physical interactions did not changed in the Universe during last 13.73 billion years therefore the emergence of life was predicted before the time of expansion of the Universe.

(Keywords)
self-reproducing fatty acid micelles; Fatty Acids World life; life was predicted in the Universe; photoexcited electron tunneling; quantum mechanical emergence of genetic material molecules in protocells.

1. Introduction

The main idea of this article is that the life in the Earth or elsewhere in the Space could have emerged in the form of self-reproducing photoactive fatty acid micelles due to quantum mechanical interactions of molecules. As a

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consequence of this quantum mechanical origin of life we state that the emergence of life was predicted in the Universe before the time of the expansion of the Universe because the quantum mechanical universal constants of physical interactions did not changed in the Universe during last 13.73 billion years. The logical decision can be made that God fine-tuned these universal physical constants for the purpose of the emergence of life. Now is the right time to give new interpretation of Old Testament basing on the newest quantum biology scientific results.

The solution of basic questions of emergence and evolution of first living cells or protocells is tightly connected now with rapidly developing artificial living technologies in several laboratories round the world. The possibilities to synthesize artificial self-reproducing minimal cells show also on the possible ways of emergence of living protocells in the Earth or elsewhere in the Space. Due to rapid development of computers and quantum mechanical methods and program packages also exist possibilities to simulate the main processes of quantum molecular dynamics self-assembly and photosynthesis of minimal artificial cells consisting up to 2000 atoms. The main artificial cells developers are the USA scientists: Steen Rasmussen, James Bailey, Hans Ziock (Los Alamos National Laboratory - (LANL) [1-3]; Liaohai Chen (Argonne National Laboratory), and European researchers in the Center for Fundamental Living Technology at the University of Southern Denmark (Steen Rasmussen), in Italy (Pier Luigi Luisi's group at RomaTre University), Guenter von Kiedrowski at Ruhr-Universitaet Bochum, John S. McCaskill, Uwe Tangen and Patrick Wagler in Biomolecular Information Processing research group at the same university, and in the European Center for Living Technology, Venice. New synthesized programmable artificial cells or nanobiorobots are planned to be used for nanomedicine, nanoecology, and for future emerging new information technologies. Despite the really useful benefits of these artificial living technologies, one can foresee also some possible dangerous events in the case these newly created artificial living cells might self-mutate and escape to the natural biospheres. Our research group create molecular electronics logic gates regulating the photosynthesis, growth and division of artificial living cells and nanobiorobots in order to prevent the negative effects of these newly emerging artificial living bioinformation technologies. Molecular electronics and spintronics logical devices which regulate photosynthesis, self-assembling to the mobile computing structures, selectively capturing and transporting nuclear, chemical and microbial pollutants already have been quantum mechanically designed [4–8]. It have been designed variety of the molecular spintronics devices. They will regulate the photosynthesis and growth of artificial minimal living cells under conditions of external magnetic fields, while also providing a perspective for success in the synthesis of new forms of artificial living organisms [9-17].

The artificial minimal living cells that are synthesized in LANL [1-3] are only a few (4-6) nanometers in size. In their simplest form, these cells consist of a micelle which acts as the container, a light driven metabolism, and a genetic system, whose functions are all very tightly coupled. The container consists of amphiphilic fatty acid (FA) molecules that self-assemble into a micelle. The hydrophobic interior of the micelle provides an alternative thermodynamic environment from the aqueous or methanol exterior and acts as a sticking point for the photosensitizer, fatty acid precursors (pFA) (food), and the genetic material. Peptide nucleic acid (PNA) is chosen as the genetic material as it is far less polar than RNA or DNA and therefore should stick to the micelle, especially if hydrophobic chains are added to the PNA backbone. The geometric and electronic structure (without the presence of water and FA molecules) was obtained by the quantum mechanical semiempirical PM3 method implemented in GAMESS-US [18] or TURBOMOLE [19] packages installed in Linux servers cluster of our Theoretical Molecular Electronics and Spintronics research group.

The metabolism involves the photoexcitation of an electron in various photosensitizers which are stabilized by the donation of an electron from non-canonical PNA bases (for example, 8-oxo-guanine). The excited electron is in turn used to cleave a fatty acid precursor to yield another fatty acid molecule, thereby allowing the container to grow until it reaches an unstable size and divides. The artificial minimal cell could be fed PNA monomers or use an essentially identical metabolism to convert a PNA precursor monomer into a true monomer, thereby also providing the material to allow the double-stranded PNA "gene" to replicate when it undergoes a random dehybridization to yield two complementary single-stranded templates [1-3]. Finally, as the different nucleobases have different electron donor and electron relay capabilities, there is also a mechanism for natural selection, with some bases and base orderings being superior to others in their ability to facilitate the metabolism. We can define these self-replicating minimal artificial cells as PNA World life referring on the similar definitions of RNA or DNA World life.

The artificial minimal living cell contains on the order of 10^3 atoms. Due to its small size, all its processes, including its self-assembly from component molecules, its absorption of light, and its metabolism should in principle be investigated using quantum mechanical (wave) theory [9-17].

The main goal of this article is to demonstrate, by quantum mechanical methods which include electron correlation effects, the mechanism of the emergence of the simplest forms of minimal living organisms which might occur in the hot and UV-rich environment of the Earth 3.9–3.6 billion

years ago or on other planets of the Universe.

2. Procedure / Methodology

Biological molecules, supermolecules or supramolecules (micelles) are the quantum systems composed of quantum particles: nuclei (with Z charges) and surrounding electrons possessing elementary charge e=-1.602176487(40)x10^{-19} Coulomb. Elementary charge of electron is the universal constant. The electromagnetic interaction of two particles consequences on the interaction of all other quantum particles therefore we are dealing with the complex quantum many-body system. The exact many-particle hamiltonian [20] for this system is:

$$\hat{H} = -\frac{\hbar}{2}\sum_i \frac{\nabla^2_{\vec{R}_i}}{M_i} - \frac{\hbar}{2}\sum_i \frac{\nabla^2_{\vec{r}_i}}{m_i} - \frac{1}{4\pi\varepsilon_0}\sum_{i,j}\frac{e^2 Z_i}{|\vec{R}_i - \vec{r}_i|} + \frac{1}{8\pi\varepsilon_0}\sum_{i\neq j}\frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{8\pi\varepsilon_0}\sum_{i\neq j}\frac{e^2 Z_i Z_j}{|\vec{R}_i - \vec{R}_j|} \quad (1.1)$$

The masses of the nuclei M_i at the distances $\vec{R}_i$ and the electrons possess the elementary mass m_e which are at the distances $\vec{r}_i$. The reduced Planck constant is the universal constant:

$$\hbar = \frac{h}{2\pi} = 1{,}054571628\,(53) \times 10^{-34}\,\mathrm{J}\cdot\mathrm{s} = 6{,}58211899(16) \times 10^{-16}\mathrm{eV}\cdot\mathrm{s}$$

The first term of the equation 1.1 is the kinetic energy operator for the nuclei, and the second for the electrons.

The last three terms in the equation 1.1 describe the Coulomb interaction between electrons and nuclei, between electrons and other electrons, and between nuclei and other nuclei. The force between two separated electric charges is given by Coulomb's law:

$$F_C = \frac{1}{4\pi\varepsilon_0}\frac{q_1 q_2}{r^2}$$

Where q_1 and q_2 are the charges, and r is the distance between them. Likewise, ε_0 appears in Maxwell's equations, which describe the properties of electric and magnetic fields and electromagnetic radiation, and relate them to their sources.
The value of ε_0 is defined by the formula:

$$\varepsilon_0 = \frac{1}{\mu_0 c_0^2} = 8{,}854187817\ldots \times 10^{-12}\,\mathrm{A}\cdot\mathrm{s}/(\mathrm{V}\cdot\mathrm{m}) = 8{,}854187817\ldots \times 10^{-12}\mathrm{F/m}$$

where c_0 is the speed of light in vacuum and μ_0 is the magnetic constant or vacuum permeability.

All above mentioned constants: elementary charge e, reduced Planck constant, c_0 and μ_0 are universal and according to most of scientists did not changed from the beginning of the Universe.

Unfortunately quantum mechanics Schrödinger equation mathematically is not available to solve exactly. In order to find acceptable approximate eigenstates, we will need to make approximations least at two different levels [20].

Level 1: The Born-Oppenheimer approximation

The nuclei are much heavier and therefore move much slower than the electrons. We can hence 'freeze' them at fixed positions and assume the electrons to be in instantaneous equilibrium with them. In other words: only the electrons are kept as players in our quantum many body problem. The nuclei are deprived from this status, and reduced to a given source of positive charge, they become 'external' to the electron cloud. The nuclei do not move any more, their kinetic energy is zero and the first term on the hamiltonian 1.1 disappears. The last term reduces to a constant. We are left with the kinetic energy of the electron gas, the potential energy due to electron-electron interactions and the potential energy of the electrons in the (now external) potential of the nuclei. We write this formally as:

$$\hat{H} = \hat{T} + \hat{V} + \hat{V}_{ext} \quad (1.2)$$

The kinetic and electron-electron terms of 1.2 depend only on the fact that we are dealing with a quantum many-electron system [20]. This part is universal. The system-specific information (which nuclei, and on which positions) is given entirely by $\hat{V}_{ext}$

Level 2: Density Functional Theory:

Quantum mechanical electron correlation interaction density functional theory (DFT) methods *i. e.* high precision quantum mechanical simulations were used to investigate various self-assembled photoactive bioorganic systems of artificial minimal living cells [9–17]. The cell systems studied in these articles are based on peptide nucleic acid (PNA) and consist of up to 2000 atoms (not including the associated water solvent shells) and are about 8.0 nm in diameter.

The quantum simulations of single bioorganic molecules possessing closed electronic shells start from a trial geometry (Cartesian coordinates of the nuclei). Using quantum mechanical semiempirical (*e.g.* PM3, PM6), Hartree–Fock (HF) and DFT approaches in the GAMESS-US [18], TURBOMOLE [19] or ORCA [21, 22] program packages, we obtain the lowest molecular energy which parametrically depends on these coordinates. The subsequent standard geometry optimization procedure [23] minimizes the energy with respect to the nuclear positions. Special care is required to verify that the obtained optimal molecular structure is a global minimum in the phase space of the nuclear (3n-6, n being the number of atoms) degrees of freedom.

In order to obtain accurate results in investigating supermolecules, two factors need to

be accounted for: i) the quality of the density functional and ii) the quality of the molecular orbitals (extent of the phase space of the single-electron states). For simple covalently bonded molecules we chose Becke's 3 parameter exchange functional [24] with non-local Lee–Yang–Parr electron correlations [25] (DFT B3LYP). Currently, B3LYP is considered to be the most appropriate method for taking into account electron correlations in large closed-shell supermolecules in which atoms are linked by covalent bonds *i. e.* there are no Van der Waals or hydrogen bonds between atoms in a single molecule. For simulations of the self-assembly of bioorganic supramolecules in which the separate molecules are associated by hydrogen bonds or Van der Waals forces, the B3PW91, PBELYP [18, 26] and PBE [19, 20, 26] methods were used. In these two methods, exchange functionals include some electron correlation effects at larger distances that provide relatively good descriptions of the Van der Waals forces and hydrogen bonds. To obtain accurate optimal molecular geometries for single molecules, we use the 6-311G** basis set which includes (5d, 7f) polarized atomic orbitals. For self-assembly of pairs of bioorganic molecules we add diffusion orbitals of the 6-31++G** basis set (the standard tables [27] give an appropriate basis set description). The above-mentioned 6-311++G** basis set convention was adopted by John Pople and coworkers.

3. Quantum mechanical self-assembly of photoactive fatty acid micelles

We used quantum mechanical density functional theory methods that included nonlocal gradient electron correlation interactions to investigate various self-assembled photoactive fatty acid micelles. The micelle systems studied are based on a photoactive squarine sensitizer, a fatty acid and its precursor (pFA). The systems include a water environment and consist of some 400 atoms and are up to about 4.5 nm in diameter. The quantum mechanical based electron correlation interactions are the source of the weak hydrogen and Van der Waals chemical bonds that are critical to the behavior of these systems. Polar solvent molecules such as water increase the strength of these bonds and thus play a central role in the self assembly and functioning of the systems studied. The distances between the separated sensitizer, precursor of fatty acid, and water molecules are comparable to Van der Waals and hydrogen bonding radii.

As a result, these nonlinear quantum interactions compress the overall molecular system resulting in a smaller gap between the HOMO and LUMO electron energy levels allowing enhanced tunneling of photoexcited electrons from the sensitizer {either a bis(4-dimethylamine-2-phenyl)-squarine (see in the Figure 1 a movie based visualization of the last 1762 steps of the geometry optimization) or a bis(4-diphenylamine-2-phenyl)-squarine} to pFA molecule and splits it to the new released fatty acid and the head section (waste end, waste piece) of precursor of fatty acid.

The new released fatty acid joins the existing micelle, growing it and the waste end is removing out from micelle after photosynthesis. After reaching some critical size, the micelle divides into two separate smaller micelles. We can define these self-reproducing photoactive fatty acid micelles as Fatty Acid World life referring on the similar definitions of RNA or DNA World life.

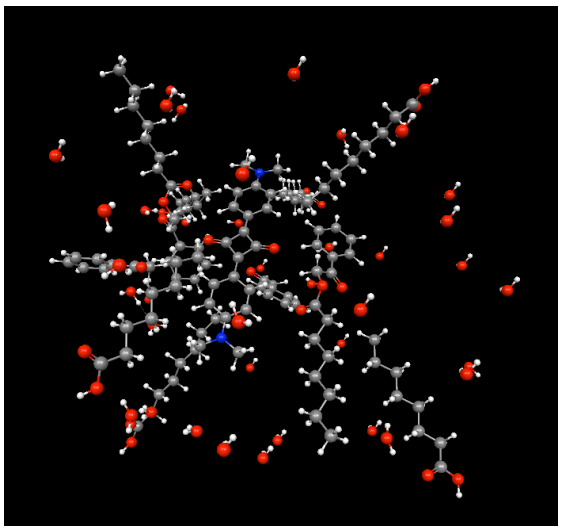

Figure 1. A movie based visualization of the last 1762 steps of the geometry optimization of a self-reproducing FA based micelle system containing a bis(4-dimehylamino-2-phenyl)-squarine molecule (in the center) that was done using semiempirical quantum mechanical method PM3. This micelle contains also two precursors of a FA, 2 waste ends of pFA, 6 FA and 37 water molecules (in total 427 atoms). Carbon atoms and their associated covalent bonds are shown as grey spheres and sticks, hydrogens - light grey, oxygens - red, nitrogens – blue.

The water molecules, which surround the entire photosynthetic complex shown in moving 1762 images were found to stabilize the system. Thereby reducing all the interatomic distances. The water molecules organized into nano ice-like substructures. It is only because of the hydrogen and Van der Waals bonds among the bis(4-dimethylamine-2-phenyl)-squarine and fatty acid, and pFA molecules, and water molecules that this system with 4.0 nm larger diameter exists. The distances among the separated sensitizer and fatty acid, and pFA molecules, and water molecules are comparable to Van der Waals and hydrogen bonding radii, and therefore we may regard the minimal cell as single electron conjugated supramolecule that we can deal with using an electron correlated model. Since bis(4-dimethylamine-2-phenyl)-squarine molecule interacts with fatty acid, and pFA molecules and with water molecules through their correlated

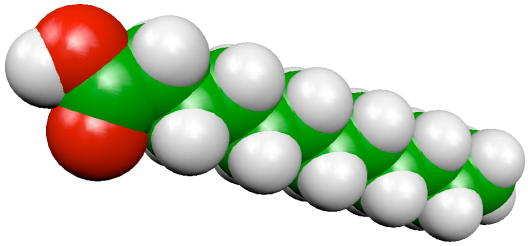

Figure 2. Van der Waals radii spheres of all atoms in fatty acid HO-CO-$(CH_2)_{10}$-CH_3. The Van der Waals spheres of carbon atoms and their associated covalent bonds are shown as green spheres, hydrogens are in light grey, oxygens – red.

electrons, intermolecular distances and surface area calculations are critical in understanding the time dependent electron tunneling processes associated with the various excited states of this micelle.

To achieve a better understanding of the quantum mechanical self-assembling process of the photoactive fatty acid micelles, it was calculated the electronic structure of fatty acid HO-CO-$(CH_2)_{10}$-CH_3 by the B3LYP method using rather a wide basis set 6-311++G** (see Figure 2).

The sum of Lowdin charges on the hydrophilic head of fatty acid and on the fragment (HO-CO-) was equal to -0.14 of electron charge. Since this molecule is neutral (the total sum of Lowdin charges = 0.00), on the rest part of the hydrophobic tail of this fatty acid the charge will be equal to +0.14 of electron charge due to a small quantum mechanical internal shift of the whole conjugated valence electron cloud from the electron-donor tail to the electron-acceptor head. An additional factor for the repulsion of fatty acid tails is that the tails are covered by positively charged hydrogen atoms.

The summary of the detailed investigations of quantum mechanical self-assembly of various fatty acid micelles and artificial minimal cells models is that fatty acids in the vacuum are not able to perform self-assembly due to the quantum dispersion forces and due to the alternating charge of the different groups -CH_2- in the tails because really these two kinds of attraction forces are small. Dispersion forces are weak Van der Waals intermolecular forces that arise from the attractive force between quantum multipoles. The more competitive electrostatic repulsion forces which destroy micelles and artificial cells in the vacuum due to the negative charges on the heads of FA and small positive charges on the FA tails, and additionally because the tails of fatty acids are covered by positively charged hydrogen atoms.

The electron correlations interactions among polar solvent (*e.g.* water, methanol) molecules, fatty acid, precursor of fatty acid, and waste ends of precursor of fatty acid molecules leads to appearing the additional attraction dispersion forces and hydrogen bonds. A hydrogen bond is a special type of quantum attractive interaction that exists among an electronegative atom and a hydrogen atom bonded to another electronegative atom and this hydrogen atom exist in two quantum states. The hydrogen bonds and Van der Waals weak chemical bonds (dispersion forces) play a critical role in the quantum mechanical electron correlations interaction based self-assembly of the photosynthetic center and functioning of the photosynthetic processes of the artificial minimal cells.

The best available method to simulate in minimal cells these Van der Waals dispersion forces and hydrogen bonds is to perform quantum mechanical non-local density functional potential calculations [8-15]. Other approaches, such as lowest level of correction (MP2) [20], multiconfiguration self consistent field (MCSCF) [20] or complete active space SCF (CASSCF) [20], in principle more suited to model dispersion forces, would not be applicable for micelles and artificial cells due to the huge computational cost.

As one can see in Figure 1 after geometry optimization these molecules self-organized to the regular structure due to accounting the quantum electron correlations interactions, *i. e.* due to the balance of weak electrostatic, hydrogen bonding and weak dispersion Van der Waals forces:

1) the bis(4-dimethylamine-2-phenyl)-squarine sensitizer molecule is in the center;

2) fatty acid molecules are oriented by their hydrophobic ends to the bis(4-dimethylamine-2-phenyl)-squarine sensitizer molecule;

3) precursor of fatty acid molecule is oriented by their hydrophilic end to the bis(4-dimethylamine-2-phenyl)-squarine sensitizer molecule;

4) most of the water molecules self-organize into clusters of nano ice-like substructures. Furthermore, all the interatomic distances between the sensitizer {either a bis(4-dimethylamine-2-phenyl)-squarine or a bis(4-diphenylamine-2-phenyl)-squarine} and the pFA molecule become reduced, *i. e.* the photosynthetic system become more compressed due to the presence of the water molecules.

To sum it up, all fatty acid micelles and artificial minimal cells, including macromolecular natural living systems, are self-assembling and achieve this based on interactions involving weak electrostatic forces (due to a small internal shift of the whole conjugated valence electron cloud from the electron-donor tail to the electron-acceptor head) and other quantum (dispersion, H-bonding) fine effects. The emergence of artificial or natural life a priori relies on the existence of these weak quantum mechanical electron correlation interactions.

The result of self-assembly of molecules depends on the electromagnetic forces between electrons and in general is predicted by existence of the universal constants: permittivity of free space, speed of light in vacuum, vacuum permeability, Planck constant, etc. (see section 2 of this article). Molecules are built from atoms therefore for the

thermonuclear reactions and atom synthesis in the stars are important also the rest three fundamental forces: strong interaction, weak interaction (also known as "strong" and "weak nuclear force") and gravitation (for the self-formation of stars). Most of physicists agree that universal constants of physical interactions did not changed in the Universe during last 13.73 ± 0.12 billion years therefore the emergence of life was predicted before the time of expansion of the Universe, *i. e.* before the time when it was the early quark matter – gluon plasma. Some physicists have explored the notion that if the fundamental physical constants had sufficiently different values, our Universe would be so radically different that intelligent life would probably not have emerged, and that our Universe therefore seems to be fine-tuned for intelligent life [28].

4. Quantum mechanical evolution of photoactive fatty acid micelles

We have performed a QM semiempirical PM3 and DFT PBE/6-31G methods for geometry optimization of photoactive fatty acid micelles using two types of squarine molecules Sq(I) and Sq(II) (see Figures 3 and 4) and precursor of fatty acid molecule: pFA – C_6H_5-CO-(CH_2)-O-CO-$(CH_2)_6$-CH_3. Fragment C_6H_5-CO-(CH_2)- represents the head section (waste end, waste piece) of the pFA which is eliminating from micelle after the photosynthesis.

The electron tunneling and associated light absorption of the most intense transitions of self-assembled artificial minimal cells as calculated by the TD DFT method differs from spectroscopic experimental results by only 0.3 or 0.2 nm, which is within the value of experiment errors [2]. This agreement implies that the quantum mechanically modeled self-assembled structures of minimal cells very closely approximate the real ones.

Part of water and waste end molecules were removed from the self-assembled fatty acid micelle shown in the Figure 1. The final self-assembled and reduced micelle is shown in the Figure 5. The spectrum calculations of this reduced micelle were performed using the time dependent (TD) DFT PBE method with the 6-31G basis set together with COSMO water solvent model installed in ORCA quantum chemical package on our research group Linux cluster. The calculated most intense spectrum line (black bar) is shown in the Figure 16.

Quantum mechanical electron correlation based simulations of the above described fatty acid micelle drawn in Figure 5 show it to be complex system, as only the entire ensemble of sensitizer, pFA, FA, and water molecules yields stable systems with a functioning photosynthetic process. Our studies show the importance of modeling as much of the full system as possible in order to obtain realistic results. Already just removing small parts of the FA, or water molecules leads to structural changes, as well as a shift in the spectroscopic values associated with the photoexcited electron tunneling from the photosensitizer {either a bis(4-dimethylamine-2-phenyl)-squarine or bis(4-diphenylamine-2-phenyl)-squarine} to the pFA molecules. Removing larger parts, e.g. more FA or water molecules leads to degradation of the fatty acid micelle. Furthermore our results show that inclusion of an ever greater fraction of the true amount of water present, as well as a greater

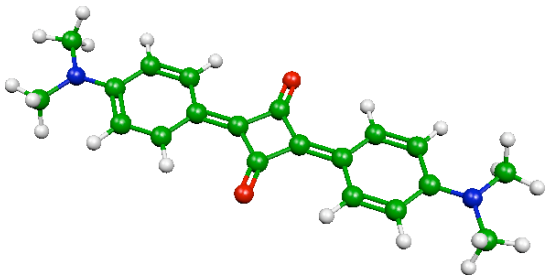

Figure 3. Image of bis(4-dimethylamine-2-phenyl)-squarine – Sq(I) molecule

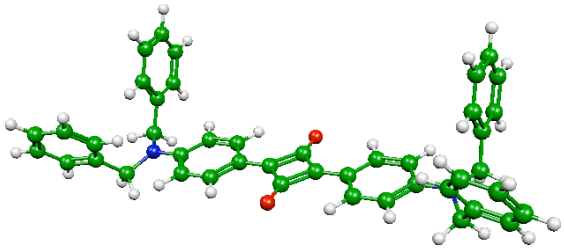

Figure 4. Image of bis(4-diphenylamine-2-phenyl)-squarine - Sq(II) molecule

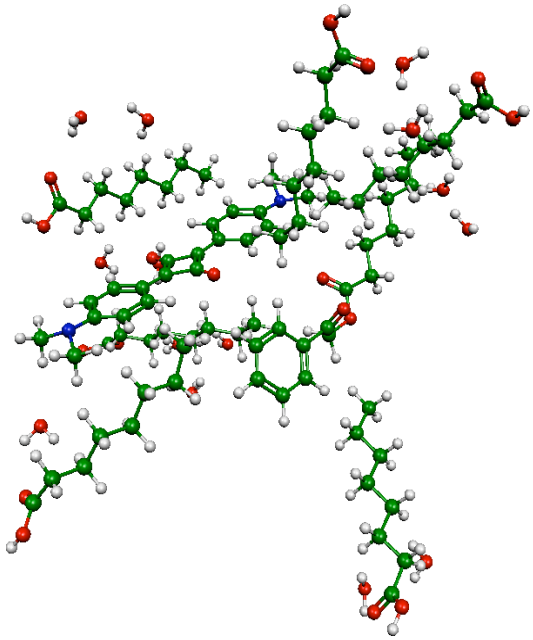

Figure 5. The last image of reduced self-assembled fatty acid micelle contains Sq(I) molecule (in the center), pFA molecule (in the bottom-left), six fatty acid molecules and 14 water molecules.

Table 1. Excitation transitions energies of a photoactive fatty acid micelle containing Sq(I) molecule, pFA molecule, six fatty acid molecules and 14 water molecules were calculated using TD DFT PBE method with the 6-31G basis set together with COSMO water solvent method in the ORCA program package. The weight of the individual excitations are given if larger than 0.01. Arrow → indicates the direction of individual electron transition from ground state HOMO-m to certain excited state LUMO+n.

Excited state #	Individual transitions HOMO-m → LUMO+n	Weight of individual transition	Energy (eV)	Wavelength (nm)	Oscillator strength (arbitrary units)
10	HOMO → LUMO	0.913	2.7	453.8	2.7235
11	HOMO → LUMO+1	0.999	2.8	450.6	0.0001
17	HOMO-1 → LUMO+1	0.99	3.0	417.7	0.0001

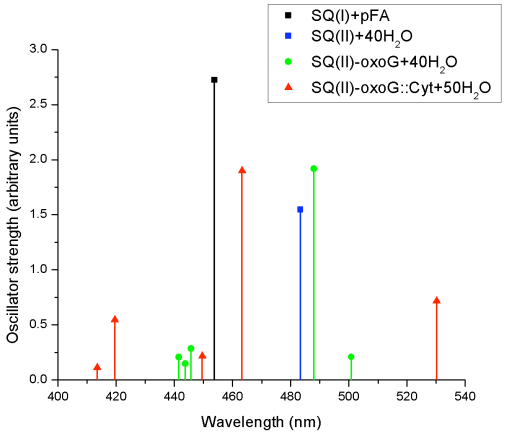

Figure 6. The intense absorption lines of the investigated squarine based derivatives: 1) minimal cell based on Sq(I) and pFA (Fig. 5) (black bar), 2) minimal cell based on Sq(II) sensitizer and pFA molecules, six fatty acid molecules and 40 water molecules (blue bar), 3) micelle based on Sq(II)-8-oxo-guanine+pFA+40 H_2O (Fig. 10) (green bars), 4) red bars represents the absorption spectrum lines of Sq(II)-8-oxo-guanine::cytosine+pFA+50 H_2O minimal cell (Fig. 13). Spectra calculated using TD DFT revPBE method with the 6-31G* basis set. The 8-oxo-guanine::cytosine-squarine supramolecule was observed to have an absorption region that covered more of the visible spectrum than a squarine-oxo-guanine supermolecule.

number of fatty acid, pFA, and nucleobase molecules to begin to approach a complete fatty acid micelle or artificial minimal cell, results in a shift of the absorption spectrum to the red for the protocell photosynthetic center, leading to an ever closer approach to the real experimental value [15]. These results indicate that the fatty acid micelle is acting as a single quantum mechanical based system. Trials with different simulation methods also show that only the QM electron correlation TD DFT simulations give results exactly comparable with spectroscopic results and all other more simplified QM methods such as local gradient DFT or *ab initio* Hartree-Fock give structures and spectra that are far from the experimentally measured ones.

It was taken from TD DFT calculations the difference of electron charge density (certain excited-state - ground-state) for the photosynthetic center of the photoactive fatty acid artificial micelle and performed the visualized the electron charge tunneling associated with certain excited state transitions (see Figures 6-8).

Spectrum of micelle given in the Figure 5 is placed in the Table 1 and in the Figure 6 (black bar: SQ(I)+pFA). The electron charge transfer trajectories in different excited states are shown in the Figures 7-9.

The most intense electron tunneling transitions of the 10th excited state should not induce metabolic photo dissociation of pFA molecule because the transferred electron cloud is located on the Sq(I) molecule (see Figure 7).

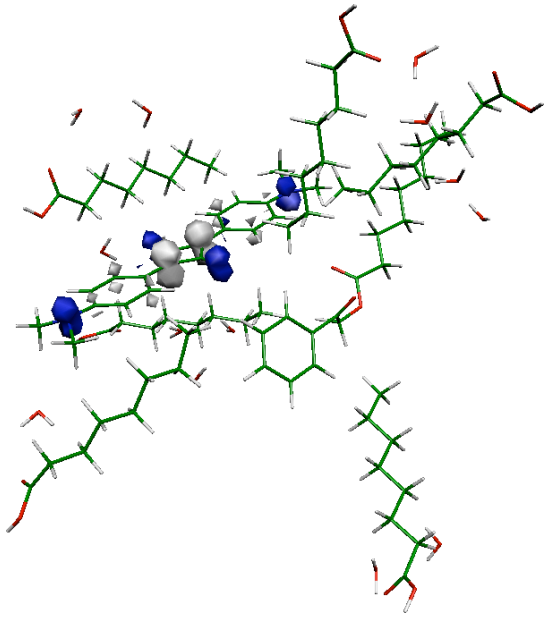

Figure 7. Visualization of the electron charge tunneling associated with the tenth excited state. The transition is from the Sq(I) to the same squarine molecule other atoms. The electron cloud hole is indicated by the dark blue color while the transferred electron cloud location is designated by the grey color. Carbon atoms and their associated covalent bonds are shown as green sticks, hydrogens are in light grey, oxygens – red, nitrogens – blue.

The electron tunneling transitions of the 11th and 17th excited states should induce metabolic photo dissociation of pFA molecule because the transferred electron cloud is located on the head (the waste piece) of pFA molecule (see Figures 8 and 9).

A similar self-assembled fatty acid micelle which contains Sq(II) sensitizer and pFA molecules, six fatty acid molecules and 40 water molecules, was investigated quantum chemically. The expectation was that the additional four aromatic rings will initiate the electron transport from Sq(II) to the pFA molecule in the most intense excited state (see blue bar in the Figure 6).

Summarizing we can state that such a micelles which possess only Sq(I) or Sq(II) sensitizers should not self-reproduce efficiently because the photosynthetic electron transitions from Sq(I) or Sq(II) to the pFA molecule are not intense and in the narrow blue light absorbance region.

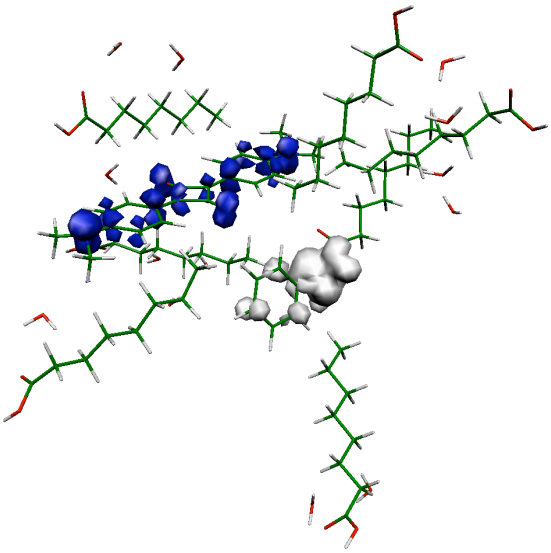

Figure 8. Visualization of the electron charge tunneling associated with the eleventh excited state. The transition is from the Sq(I) (in the center) to the pFA (in the bottom-left) molecule.

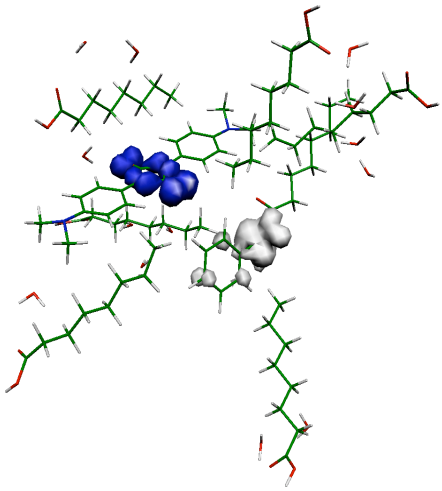

Figure 9. Visualization of the electron charge tunneling associated with the seventeenth excited state. The transition is from the Sq(I) to the pFA molecule.

The geometry optimization of modified self-assembled fatty acid micelle containing Sq(II) molecule with attached covalently 8-oxo-guanine, pFA molecule and 40 water molecules (see Figure 10) were performed by using PBELYP/3-21 with GAMESS-US package and done calculations of spectrum using TD DFT revPBE method with the 6-31G* basis set using ORCA package.

Moving figures of this article expose the self-assembly of fatty acid micelles. One can very clearly watch how due to quantum electron correlation forces and hydrogen bonding interactions (dashed lines) the water molecules are self-assembling to the nano crystals and attaching to the squarine and fatty acid molecules, how these forces compress all the complex quantum system – micelle. Only DFT nonlocal gradient methods (such as PBELYP) give the right hydrogen bonding distances comparable with experimental vales (see dashed lines in the Figures 10 and 13). The semiempirical PM3 method only partially gives the hydrogen bonding interactions therefore the supramolecule visualization program does not shows the dashed lines (see Figure 1) because the calculated hydrogen bonding distances are too large in comparison with experimental distances.

The most intense excited states of the photoactive fatty acid micelles are partially composed of LUMO+n states located on the fatty acid precursors when the Sq(II) molecule is covalently attached to the 8-oxo-guanine. This coupling also promotes electron hopping (tunneling) to the pFA molecules during the most intense absorption excited state.

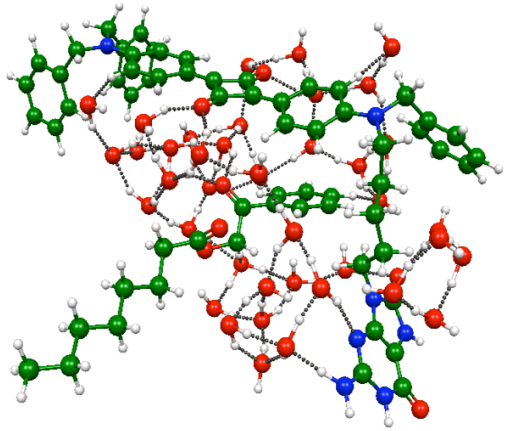

Figure 10. A movie based visualization of the last steps of the geometry optimization of a self-reproducing FA based micelle system containing a Sq(II) molecule with attached covalently 8-oxo-guanine (in the bottom-right), pFA molecule (in the bottom) and 40 water molecules. Dashed lines means the hydrogen bonds.

Table 2. Excitation transitions energies of a fatty acid micelle containing Sq(II) molecule with attached covalently 8-oxo-guanine and pFA molecule, and 40 water molecules were calculated using TD DFT revPBE method with the 6-31G* basis set in the ORCA program package. The weight of the individual excitations are given if larger than 0.1.

Excited state #	Individual transitions HOMO-m → LUMO+n	Weight of individual transition	Energy (eV)	Wavelength (nm)	Oscillator strength (arbitrary units)
8	HOMO-7 → LUMO	0.88	2.48	500.8	0.21
10	HOMO → LUMO	0.54	2.54	488.0	1.92
	HOMO-12 → LUMO	0.13			

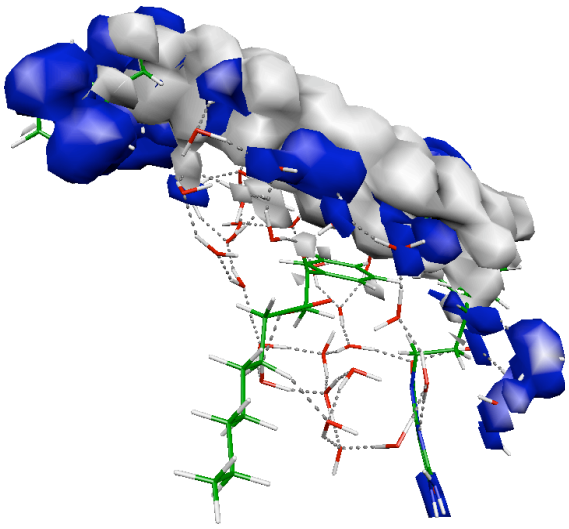

Figure 11. Visualization of the electron charge tunneling associated with the eighth excited state. The transition is from the Sq(II) (in the top) to the same Sq(II) molecule and partially to the pFA molecule (in the bottom).

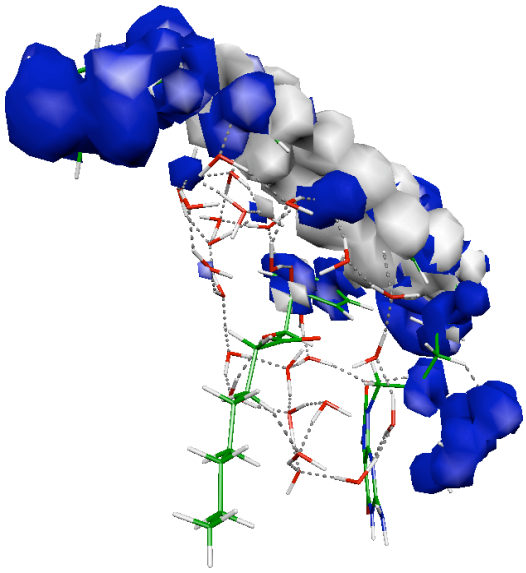

Figure 12. Visualization of the electron charge tunneling associated with the tenth excited state. The transition is from the Sq(II) (in the top) to the same Sq(II) molecule and partially to the pFA molecule (in the bottom).

The absorption spectrum of the photoactive fatty acid micelle given in the Figure 10 is detailed placed in the Table 2 and in the Figure 6 (green bars). The electron charge transfer trajectories in different excited states are shown in the Figures 11 and 12.

The electron tunneling transitions of the 8th and 10th excited states of this micelle should induce metabolic photo dissociation of pFA molecule because the transferred electron cloud is located on the head (the waste piece) of pFA molecule (see Figures 11 and 12) where it causes this molecule to split due to intense rotation and vibration of the weak chemical bond that joins the waste piece to the fatty acid section of the pFA molecule.

The intense 8th excited state is composed mainly from one individual transition HOMO-7 → LUMO with weight equal to 0.88 (see Table 2) and other individual transitions contributions are at most equal to 0.02 therefore it is possible to say that electron in this excited state most probably will tunneling from HOMO-7 to LUMO.

The most intense 10th excited state is composed mainly from two individual transitions HOMO → LUMO with weight equal to 0.54 (see Table 2), HOMO-12 → LUMO with weight equal to 0.13 and other individual transitions contributions are at most equal to 0.10 therefore it is possible to say that electron in this excited state most probably will tunneling from HOMO-m to LUMO.

The intense absorption lines (see green bars in the Figure 6) of the squarine-8-oxo-guanine supermolecule were found to be shifted to the red when these molecules were associated with simple fatty acid micelle shown in the Figure 5 (black bar) and similar micelle with Sq(II) molecule (blue bar).

The geometry optimization of more complex photoactive fatty acid micelle containing Sq(II) attached covalently to 8-oxo-guanine::cytosine supramolecule, pFA and 50 water molecules (see Figure 13) were performed by using PBELYP/3-21 with GAMESS-US package and done calculations of spectrum using TD DFT revPBE method with the 6-31G* basis set using ORCA package.

The part of absorption spectrum of the photoactive fatty acid micelle given in the Figure 13 is placed in the Table 3 and in the Figure 6 (red bars). The electron charge transfer trajectories in different excited states are shown in the Figures 14

Table 3. Excitation transitions energies of a fatty acid micelle containing Sq(II) molecule with attached covalently 8-oxo-guanine::cytosine supramolecule and pFA molecule, and 50 water molecules were calculated using TD DFT revPBE method with the 6-31G* basis set in the ORCA program package. The weight of the individual excitations are given if larger than 0.09.

Excited state #	Individual transitions HOMO-m → LUMO+n	Weight of individual transition	Energy (eV)	Wavelength (nm)	Oscillator strength (arbitrary units)
14	HOMO-9 → LUMO	0.23	2.34	530.2	0.72
	HOMO-3 → LUMO	0.2			
	HOMO → LUMO	0.19			
	HOMO-11 → LUMO	0.17			
32	HOMO → LUMO	0.36	2.68	463.3	1.9
	HOMO-14 → LUMO	0.28			

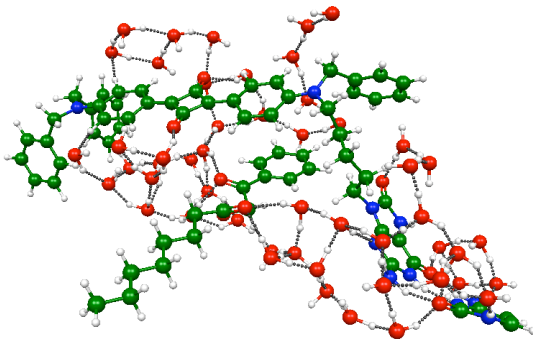

Figure 13. A movie based visualization of the last steps of the geometry optimization of a self-reproducing FA based micelle system containing a Sq(II) molecule with attached covalently 8-oxo-guanine::cytosine supramolecule (the bottom-right), pFA molecule

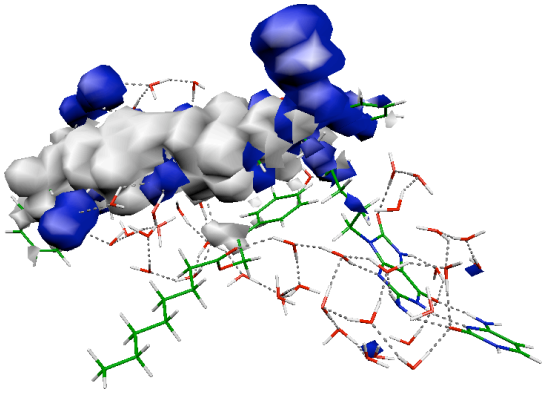

Figure 14. Visualization of the electron charge tunneling associated with the 14th state. The transition is from the Sq(II) (in the top) to the same Sq(II) molecule and partially to the pFA molecule (in the bottom).

and 15.

The electron tunneling transitions of the 14th and 32nd excited states of this micelle should induce metabolic photo dissociation of pFA molecule because the transferred electron cloud is located on the head (the waste piece) of pFA molecule (see Figures 14 and 15) where it causes this molecule to split due to intense rotation and vibration of the weak chemical bond that joins the waste piece to the fatty acid section of the pFA molecule.

The intense 14th excited state is composed mainly from four individual transitions HOMO-9 → LUMO with weight equal to 0.23 (see Table 3), HOMO-3 → LUMO with weight equal to 0.2, HOMO → LUMO with weight equal to 0.19, HOMO-11 → LUMO with weight equal to 0.17 and other individual transitions contributions are at most equal to 0.09 therefore it is possible to say that electron in this excited state most probably will tunneling from HOMO-m to LUMO.

The most intense 32nd excited state is composed mainly from two individual transitions HOMO → LUMO with weight equal to 0.36 (see Table 2), HOMO-14 → LUMO with weight equal to 0.28

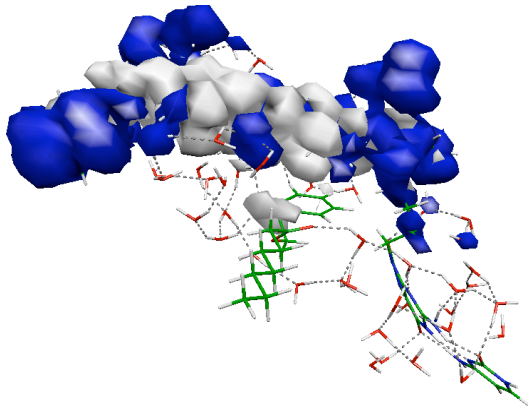

Figure 15. Visualization of the electron charge tunneling associated with the 32nd excited state. The transition is from the Sq(II) (in the top) to the same Sq(II) molecule and partially to the pFA molecule (in the bottom).

and other individual transitions contributions are at most equal to 0.09 therefore it is possible to say that electron in this excited state most probably will tunneling from HOMO-m to LUMO.

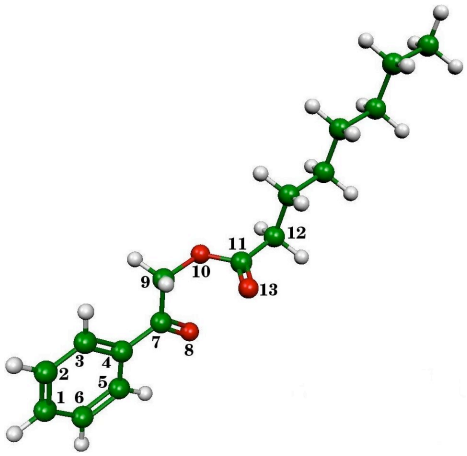

Figure 16. Geometrical structure of pFA molecule. There are numerated heavy C and O atoms from 1 to 9 in the head section (waste end, waste piece) of this molecule and from 10 to 13 in the part of FA fragment.

Summarizing it is possible to make statements concerning three our investigated photosynthetic centers of fatty acid micelles. The most intense excited states of the photoactive fatty acid micelles are partially composed of LUMO+n states located on the fatty acid precursor molecule when the bis(4-diphenylamine-2-phenyl)-squarine molecule is covalently attached to the 8-oxo-guanine. This coupling also promotes electron hopping (tunneling) to the pFA molecules during the most intense absorption excited state. The photoexcited electron tunnels to the head section (the waste piece) of the pFA molecules where it causes these molecules to split due to intense rotation and vibration of the weak chemical bond that joins the waste piece to the fatty acid section of the pFA molecule.

In order to understand process of photodissociation of pFA molecule but reduce expenses of computations it was investigated the electronic structure of single neutral pFA molecule (see Figure 16) by using B3LYP/6-311++G** method. After geometry reoptimization procedure it was obtained the electronic structure of negative ion of this molecule using unrestricted B3LYP/6-311++G** method.

Atomic Lowdin charges in Table 4 are with hydrogens summed into carbon atoms, i.e. the atomic charges of hydrogens are already added to the atomic charge of neighboring carbon atom. The sum of Lowdin charges of atoms from No 1 to 9 of neutral pFA molecule are equal to 0.274 of electron charge (e) while the sum on the same atoms in anion pFA molecule is equal to -0.620 e (see Table 4). It means that almost entire (-0.894 e) additional electron after self-consistent field procedure localizes on the waste end of pFA molecule while only -0.106 e charge of additional electron localizes on FA fragment of this molecule.

Table 4. Atomic Lowdin charges with hydrogens summed into carbon atoms of neutral and anion pFA molecules calculated by B3LYP/6-311++G** method.

Number of atom	Neutral pFA	Anion of pFA
1 C	0.035	-0.130
2 C	0.021	-0.047
3 C	0.091	0.002
4 C	-0.119	-0.146
5 C	0.035	-0.063
6 C	0.017	-0.047
7 C	0.196	0.045
8 O	-0.308	-0.490
9 C	0.307	0.257
10 O	-0.380	-0.385
11 C	0.299	0.291
12 C	0.087	0.069
13 O	-0.342	-0.370
Sum of charges on 1-9 atoms	0.274	-0.620

Data of bond orders of selected chemical bonds of neutral and anion pFA molecules are presented in Table 5.

Analysis of selected bond orders of neutral and anion pFA molecules shows that the most weakness chemical bond order is between 9th and 10th atoms in the neutral pFA molecule. The additional electron which is placed on the waste end of pFA molecule decrease the bond order from 0.772 to 0.734 between 9th and 10th atoms.

Table 5. Bond orders of selected chemical bonds of neutral and anion pFA molecules calculated by B3LYP/6-311++G** method.

Chemical bonds	Neutral pFA	Anion of pFA
9-10 C-O	0.772	0.734
7-8 C-O	1.980	2.143
10-11 O-C	1.295	1.332

It is known in molecular physics that additional electron which fall down on the molecular fragment initiate the vibrations and rotations of all chemical bonds in this fragment and it is large probability that the most weakness chemical bond between 9th and 10th atoms will be broken. This photodissociation process of pFA molecule was observed experimentally in LANL "Protocell Assembly" project [1, 2].

The new fatty acid from dissociated pFA molecule will join to minimal cell, therefore this minimal cell will grow and later spontaneously break in two new minimal cells and once again will use pFA molecules during the photo excitation processes for generation the new FA molecules, etc. This photoinduced autocatalytic bioorganic system was experimentally proved in the papers [1-3], and called in LANL "Protocell Assembly" project as minimal artificial living cell or protocell.

The most intense absorption lines of the squarine-8-oxo-guanine supermolecule were found to be shifted to the red when these molecules were associated with fatty acid micelles (see green bars situated from left to right in the Figure 6). Red bars represents the absorption spectrum lines of Sq(II)-8-oxo-guanine::cytosine+pFA(I)+50 H_2O minimal cell calculated using TD DFT revPBE method with the 6-31G basis set. In addition, the 8-oxo-guanine::cytosine-squarine supramolecule was observed to have an absorption region that covered more of the visible spectrum than a squarine-oxo-guanine supermolecule.

The redward shift of the intense absorption lines would allow a self reproducing micelle to absorb the light in the longer wavelength region, which may have been important in the environment that life might have developed, in addition to extending the photoactive period into the earlier morning and later evening hours. That allowed better compete for such a kind of evolved photoactive micelles of Fatty Acids World life in getting the food molecules. Furthermore, one notes that the nucleotide caused wavelength shift and broadening of the absorption pattern potentially gives the nucleotides an additional valuable role, other than just a purely genetic one in the early stages of the development of life.

Most probably, that appearance of the simplest self-reproducing photoactive fatty acid micelles were in the period of 3.9-3.8 billion years before, *i.e.* just after formation of stable core in the Earth. Later these photoactive fatty acid micelles evolved incorporating nucleotide molecules (most probably in the period of 3.8-3.7 billion years before), see Figure 17.

The nucleotide molecules and their sequences in the first period of evolution of Fatty Acid World were useful just for better absorbency of the light

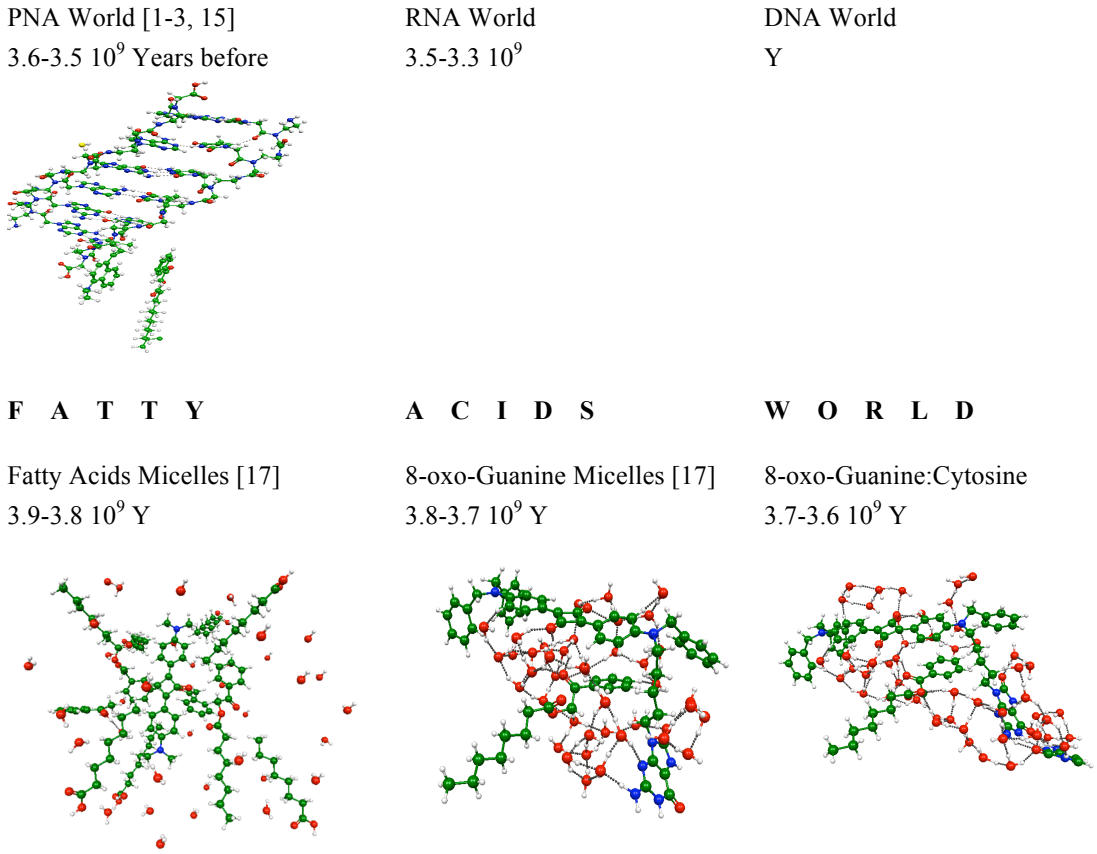

Figure 17. Demo nstration of the main results of our present and recent papers. We state that Life in the Earth or elsewhere in the Space emerged in the form of self-reproducing photoactive fatty acid micelles which step by step evolved to the nucleotide containing micelles due to better possibilities absorb the visible light.

in the longer wavelength region. Later, in the PNA or RNA Worlds, these nucleotides were used for the genetic information storage (see Figure 17). If to say strictly, from the information theory point of view, the nucleotide molecules sequences in the Fatty Acids World micelles carry positional information how to directly provide better relaxation electron transport along the nucleotide-sensitizer chain but this is not the convenient understanding of genetic information. The addition possibility of guanine::cytosine supramolecules containing fatty acid micelles to provide complimentary copies of that positional information to the next generation corresponds to the convenient understanding of genetic information.

5. Conclusions

In the proposed model, three quantum mechanical processes led to the emergence of photoactive fatty acid micelles containing an 8-oxo-guanine::cytosine base pair at the early stages of emergence of life on the Earth:

1) All macromolecular living systems, including photoactive fatty acid micelles, are self-assembling and achieve this based on interactions involving weak electrostatic forces (due to a small internal shift of the whole conjugated valence electron cloud from the electron-donor tail to the electron-acceptor head) and other quantum (dispersion, H-bonding) fine effects. The result of self-assembly of molecules depends on the electromagnetic forces between electrons and in general is predicted by existence of the universal constants. Universal constants of physical interactions did not changed in the Universe during last 13.73 billion years therefore the emergence of life was predicted before the time of the expansion of the Universe.

2) The most intense excited states of the photoactive fatty acid micelles are partially composed of LUMO+n states located on the fatty acid precursors when the bis(4-diphenylamine-2-phenyl)-squarine molecule is covalently attached to the 8-oxo-guanine. This coupling also promotes electron hopping (tunneling) to the pFA molecules during the most intense absorption excited state. The photoexcited electron tunnels to the waste end of the pFA molecules where it causes these molecules to split due to intense rotation and vibration of the weak chemical bond that joins the waste piece to the fatty acid section of the pFA molecule;

3) The most intense absorption lines of the squarine-8-oxo-guanine supermolecule were found to be shifted to the red when these molecules were associated with fatty acid micelles. In addition, the 8-oxo-guanine::cytosine-squarine supramolecule was observed to have an absorption region that covered more of the visible spectrum than a squarine-8-oxo-guanine supermolecule. The redward shift of the intense absorption lines would allow a self reproducing micelle to absorb the light in the longer wavelength region, which may have been important in the environment that life might have developed, in addition to extending the photoactive period into the earlier morning and later evening hours. This would have allowed better competition for such evolved photoactive micelles (Fatty Acids World Model) in obtaining food molecules. Furthermore, one notes that the nucleotide caused wavelength shift and broadening of the absorption pattern potentially gives the nucleotides an additional valuable role, other than just a purely genetic one in the early stages of the development of life.

The nucleotide molecules and their sequences which in the first period of evolution of fatty acid molecules were useful just for better absorbency of the light in the longer wavelength region, later in the PNA or RNA World, were used for genetic information storage. From the information theory point of view, nucleotide sequences in the Fatty Acids World micelles carry positionally information on how to directly provide better electron transport along the nucleotide-sensitizer chain and in addition providing complementary copies of that information to the next generation.

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