

QUANTUM SELF-ASSEMBLY OF ARTIFICIAL MINIMAL LIVING CELLS AND MOLECULAR ELECTRONICS CONTROL

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(Abstract)

Artificial minimal living cells and their substructures are quantum mechanically self-assembling due to competition of weak electrostatic forces and weak attraction Van der Waals dispersion forces, and hydrogen bonds originated due to electron correlation interactions among biological and water molecules. The best available method to simulate in minimal cells these weak electrostatic and Van der Waals dispersion forces, and hydrogen bonds is to perform quantum mechanical non-local density functional potential calculations of artificial minimal living cells consisting of around 400 atoms. The cell systems studied are based on peptide nucleic acid and are 3.0 – 4.5 nm in diameter. The electron tunneling and associated light absorption of most intense transitions as calculated by the time dependent density functional theory method differs from spectroscopic experiments by only 0.3 nm, which are within the value of experiment errors. This agreement implies that the quantum mechanically self-assembled structure of artificial minimal living cells very closely approximate the realistic ones.

Analysis of time dependent density functional theory method calculated absorption spectrum and images of electron transfer trajectories in the different excited states allow to separate two different logically controlled functions of molecular device consisting of guanine-cytosine-PNA-1,4-dihydroquinoxaline-1,4-bis(N,N-dimethylamino)naphthalene supermolecule and Van der Waals bonded precursor of fatty acid molecule. These two different logically controlled functions of artificial minimal living cells are: 1) initiation of metabolic fatty acid production in five excited states or 2) initiation of gene dehybridization in one excited state. This designed supermolecule works in the artificial minimal cell as molecular electronics classic OR logic function (Boolean logics OR gate).

(Keywords)

quantum self-assembly of supramolecules; artificial minimal living cells; photoexcited electron tunneling; molecular electronics logical gate

1. Introduction

Artificial living technologies are rapidly developing in several laboratories around the world: in USA (Steen Rasmussen, James Bailey, Hans Ziock, Los Alamos National Laboratory (LANL) [1]; Liaohai Chen, Argonne National Laboratory), in Italy (Pier Luigi Luisi's group at RomaTre University), in Germany (John S. McCaskill, Guenter von Kiedrowski, Ruhr-Universitaet Bochum; Patrick Wagler, Protostream GmbH), and in European Center for Living Technology (headquarter in Venice).

New creating nano biorobots are planned to be used for nanomedicine, nanoecology, and for future emerging new information technologies. Despite of really useful benefits of these artificial living technologies one can foresee also some possible dangerous events in the case if these new creating artificial living cells might self-mutate and escape to the natural biospheres. We are creating molecular electronics logic gates regulating the photosynthesis, growing and dividing of artificial living cells and nanobiorobots in the order to prevent the negative affects of these new emerging artificial living information technologies. The molecular electronics and spintronics logical devices which regulate photosynthesis, self-assembling to the mobile computing structures, selectively capturing and transporting nuclear, chemical and microbial pollutions already were quantum mechanically designed [3-8].

The artificial minimal living cells (LANL scientists call them as protocells) that are synthesized in USA Los Alamos National Laboratory (LANL) [1, 2] 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 (in [1] and this paper) or methanol (in paper [2]) 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. It is also capable of undergoing the same Watson-Crick pairing and replication as RNA and DNA (see Figure 1). PNA is similar to DNA but has a peptide-based backbone, as opposed to DNA's sugar-phosphate backbone.

The first main goal of this article is to report the results of quantum mechanical (QM) modeling of the self-assembly and charge transfer in a minimal protocell [1] that might have implications for the first living organism on the Earth [2] around 3.8-3.5 billion years ago. The climate in the Earth at that time was hot with intense UV radiation therefore PNAs might were the most suitable for genome of minimal living cells in comparison with RNA or DNA. This article uses a collection of quantum mechanical tools and applies them to a variety of protocell photosynthetic problems, while also providing a perspective of the requirements for success in the synthesis of new forms of living organisms.

Figure 1 and other figures in this article was done by Molekel software [9].

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, 2]. 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.

The artificial minimal living cell contains on the order of 103 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 [10-14].

Usually self-reproducing artificial living cells that are creating in LANL and in other laboratories (see for example, <http://www.istpace.org/index.html>) do not have the nanosize electronics tools which might be able to regulate the growth and multiplication. It is important to have possibility to stimulate or prevent uncontrolled multiplication of artificial living organisms by installing different molecular electronics devices. The second main goal of this paper is by using quantum mechanical experiments to predict the possibility of biochemical experimental synthesis of molecular electronics controlled artificial minimal living cells or nanobiorobots which might be used for nanomedicine and nanoecology. It is presented in this paper the quantum mechanically designed molecular electronics OR logical gate for the the regulation of artificial minimal living cell functions.

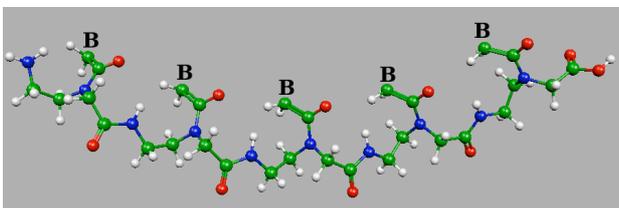


Figure 1. PNA has a peptide-based backbone. Carbon atoms and their associated covalent bonds are shown as green spheres and sticks, hydrogens are in light grey, oxygens – red, nitrogens – blue. B means attached nucleobase molecule.

2. Procedure/Methodology

We used quantum mechanical electron correlation interactions density functional theory (DFT) methods (*i.e.* high precision quantum mechanical simulations) to investigate various self-assembled photoactive bioorganic systems of artificial minimal living cells [4-8]. The cell systems studied are based on peptide nucleic

acid (PNA) and consisted of up to 400 atoms (not including the associated water solvent shells) and are up to 3.0-4.2 nm in diameter.

The chemical formulas of the molecules used in the simulated version of minimal cell are sensitizers: **1**) 1,4-bis(N,N-dimethylamino)naphthalene – $(\text{CH}_3)_2\text{-N-C}_8\text{H}_6\text{-N-(CH}_3)_2$ and 1,4-dihydroquinoxaline – $\text{C}_8\text{H}_7\text{N}_2$, canonic nucleobase **2**) cytosine – $\text{C}_4\text{H}_5\text{N}_3\text{O}$, **3**) precursor of fatty acid – $\text{C}_6\text{H}_5\text{-CO-(CH}_2\text{)-O-CO-(CH}_2\text{)}_3\text{-CH}_3$, **4**) head (the waste piece) of the precursor of fatty acid – $\text{C}_6\text{H}_5\text{-CO-CH}_3$, **5**) and fatty acid – $\text{HO-CO-(CH}_2\text{)}_3\text{-CH}_3$ (see Figure 2).

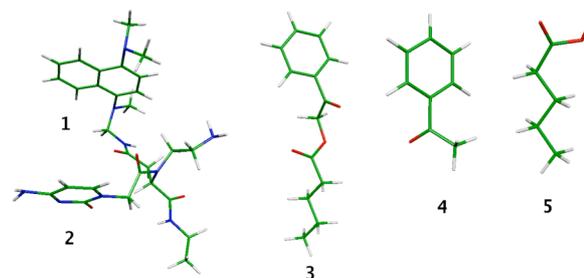


Figure 2. The molecules used in the simulated version of minimal cell are fragment of PNA supermolecule with attached **1**) 1,4-bis(N,N-dimethylamino)naphthalene, and **2**) cytosine molecules, and **3**) precursor of fatty acid, and **4**) head (the waste piece) of the precursor of fatty acid, **5**) and fatty acid molecules. Carbon atoms and their associated covalent bonds are shown as green sticks, hydrogens are in light grey, oxygens – red, nitrogens – blue.

Our quantum simulations of single bioorganic molecules possessing closed electronic shells start from a trial geometry (Cartesian coordinates of the nuclei). Using restricted Hartree-Fock (HF) and a density functional theory (DFT) approaches in the Gaussian 03 [15], GAMESS-US [16] or ORCA [17, 18] program packages, we obtain the lowest molecular energy, which depends on these coordinates parametrically. A subsequent standard geometry optimization procedure [15-20] 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 [21] with non-local Lee-Yang-Parr electron correlations [22] (DFT B3LYP), and PBEPBE [15, 17, 18, 23], and PBELYP [16, 23] models. Currently, the B3LYP method is considered to be the most appropriate method to take into account electron correlations in large closed-shell supermolecules of which atoms are linked by covalent bonds (*i.e.*, there are no Van der Waals nor hydrogen bonds between atoms in a single molecule) [24, 25]. For simulations of the self-assembly of bioorganic supramolecules in which the separate molecules are associated by hydrogen bonds or Van der Waals forces we used PBEPBE [15, 17, 18, 23], and PBELYP [16, 23] methods. 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 [26] give the appropriate basis set description).

The above-mentioned 6-311++G** basis set convention was adopted by John Pople and coworkers. The basis set structure is given for the whole molecule, rather than a particular atom. The notation also emphasizes the split valence (SV) nature of these sets. Symbols like n-ijG or n-ijkG are encoded as follows: n – the number of primitives for the inner shells; ij or ijk – the number of primitives for contractions in the valence shell. The ij notation describes sets of valence double zeta quality and ijk, sets of valence triple zeta quality. Generally, in the basis sets derived by Pople's group, the s and p contractions belonging to the same "electron shell" (*i.e.* corresponding formally to the same principal quantum number n) are folded into an sp-shell. In this case, the number of s-type and p-type primitives is the same, and they have identical exponents. However, the coefficients for the s- and p-type contractions are different. The symbol "*" is used to indicate when Pople's basis sets are augmented with d- or f-type polarization functions: n-ijG* or n-ijkG* when this is done only for heavy atoms; and n-ijG** or n-ijkG** when done for all atoms together with p-functions for hydrogen atoms.

The basis sets are also frequently augmented with the so-called diffuse functions. These are very shallow Gaussian basis functions, which more accurately represent the "tail" portion of the atomic orbitals, which are distant from the atomic nuclei. These additional basis functions can be important when considering anions and other large, "soft" molecular systems. These gaussians have very small exponents and decay slowly with distance from the nucleus. The diffuse gaussians are usually s- and p-type, however sometimes diffuse polarization functions are also used. Diffuse functions are necessary for a correct description of anions and weak bonds (*e.g.* hydrogen bonds) and are frequently used for calculation of properties such as dipole moments, polarizabilities, *etc.* The inclusion of diffuse functions is indicated with the "+" sign: n-ij+G or n-ijk+G when one diffuse s-type and p-type gaussian with the same exponent is added to a standard basis set for heavy atoms; and n-ij++G or n-ijk++G when one diffuse s-type and p-type Gaussian is added for heavy atoms together with one diffuse s-type gaussian for hydrogen atoms. Table 1 lists the availability of diffuse and polarization functions and the range of applicability for each built-in Gaussian03 [15], GAMESS-US [16] and ORCA [17, 18] program packages basis set we use.

Quantum modeling of the self-assembly of nanostructures in PNA based minimal living cells was performed using the software we developed for building PNA double helices.

The geometries of the constituent molecules and their pairs were individually optimized using the PBELYP [16, 23] method with the 6-311++G** basis set implemented

in the GAMESS-US program package which is installed in dual processor Opteron servers Linux cluster of our Theoretical Molecular Electronics and Spintronics research group and with the PBEPBE method [16, 23] using the 6-311++G** basis set [26] implemented via the Gaussian03 program package on the LANL SGI Altix 3000 machine.

Table 1: The function availability and range of applicability for each built-in basis set in Gaussian03 [15], GAMESS-US [16] and ORCA [17, 18] program packages.

Basis set	Applies to atoms	Polarization functions	Diffuse functions
3-21G	H-Xe	* or **	+
6-31G	H-Kr	(3df,3pd)	++
6-311G	H-Kr	(3df,3pd)	++

3. Quantum Mechanical Self-Assembly of Artificial Minimal Living Cell

For the reasons of better understanding of the self-assembling process of artificial minimal cell it was calculated electronic structure of fatty acid HO-CO-(CH₂)₆-CH₃ (see Figure 3) by PBEPBE method using rather wide basis set 6-311++G*. Sum of Mulliken charges on the hydrophilic head of fatty acid and on the first -CH₂ chain (HO-CO-(CH₂-) is equal to -0.14 of electron charge. Since this molecule is neutral (total sum of Mulliken charges = 0.00) therefore on the rest part of the hydrophobic tail of this fatty acid charge will be equal to +0.14 of electron charge due to a small quantum mechanical internal shift of whole conjugated valence electron cloud from electron-donor tail to electron-acceptor head. Additional factor for the repulsion of tails of fatty acids is that this tail is covered by positively charged hydrogens. The Van der Waals radii spheres of all atoms in this fatty acid are drawn in the Figure 3 below.

The summary of our detailed investigations of quantum mechanical self-assembly of various micelles and artificial minimal cells models [8] 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 -CH₂- 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

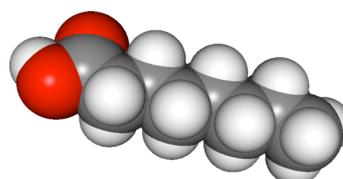


Figure 3. Van der Waals radii spheres of all atoms in fatty acid HO-CO-(CH₂)₆-CH₃. The Van der Waals spheres of carbon atoms and their associated covalent bonds are shown as grey spheres and sticks, hydrogens are in light grey, oxygens – red.

tails, and additionally because the tails of fatty acids are covered by positively charged hydrogen atoms.

The electron correlations interactions among polar solvent (water) molecules, PNA, fatty acid, precursor fatty acid, and waste ends of precursor 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 living 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 [3-8]. Other approaches, such as lowest level of correction (MP2), multiconfiguration self consistent field (MCSCF) or complete active space SCF (CASSCF), in principle more suited to model dispersion forces, would not be applicable for minimal cells due to the huge computational cost.

The distances between the separated sensitizer, precursor 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 system resulting in a smaller gap between the HOMO and LUMO electron energy levels and photoexcited electron tunneling occurs from the sensitizer (either a 1,4-bis(N,N-dimethylamino)naphthalene or 1,4-dihydroquinoxaline) to pFA molecules [6-8]. For example, the average distance among photoelectron donor and photoelectron acceptor fragments in the modeled photosynthetic system without water molecules is approximately equal to 5.6 Å (the smallest interatomic distance is equal to 4.83 Å) while the average distance among photoelectron donor and photoelectron acceptor is equal to 3.5 Å in the minimal cell with real water molecules presented in the Figure 4 (the smallest interatomic distance is equal to 2.58 Å).

It have been done quantum mechanical PBEPBE/3-21G [23] method geometry optimization (*i.e.* self-assembly) procedure using GAMESS-US [16] package starting from randomly displaced various molecules shown in Figure 2 that are components of LANL minimal cell [1, 2]. As one can see in the Figure 4 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 cytosine-PNA hydrophilic fragment covalently bonded to a 1,4-bis(N,N-dimethylamino)naphthalene sensitizer molecule are in the center;
- 2) six 5-carbon fatty acid molecules are oriented by their hydrophilic ends to the cytosine-PNA fragment covalently bonded to a 1,4-bis(N,N-

- dimethylamino)naphthalene sensitizer molecule;
- 3) two precursor fatty acid molecules (pFA) (in the top-left and top-right) are oriented by their hydrophilic ends the cytosine-PNA fragment covalently bonded to a 1,4-bis(N,N-dimethylamino)naphthalene sensitizer molecule;
- 4) two the waste pieces of the pFA molecules are oriented by their hydrophilic ends to the cytosine-PNA fragment covalently bonded to a 1,4-bis(N,N-dimethylamino)naphthalene sensitizer molecule;
- 5) most of the water molecules self-organize into clusters of nano ice-like substructures. Furthermore, all the interatomic distances between the 1,4-bis(N,N-dimethylamino)-naphthalene sensitizer and the pFA molecule become reduced, *i.e.* the photosynthetic system become more compressed due to the presence of the water molecules;

All the macromolecular living systems (not only these our investigating artificial minimal cells) are self-assembling based on competition of weak electrostatic forces (due to small internal shift of whole conjugated valence electron cloud from electron-donor tail to electron-acceptor head) and other quantum (dispersion, H-bonding) fine effects. Emergency of natural life or artificial life is *a priori* predicted due to the existence of these weak quantum mechanical electron correlations interactions.

It have been performed calculations of optimal electronic structure and spectra of this photosynthetic center using time dependent (TD) DFT PBEPBE method [23] with the 6-31G basis set together with COSMO water solvent model using ORCA package [17, 18, 27] installed on our research group dual processor Opteron servers Linux cluster. It was taken from these calculations the difference of electron charge density (certain excited-state - ground-state) for the photosynthetic center of artificial minimal living cell [1, 2] which consists of conjugated cytosine-PNA-1,4-bis(N,N-dimethylamino)naphthalene supermolecule, six fatty acid, two pFA molecules, and two the waste pieces of the pFA molecules and performed the visualized the electron charge tunneling associated with certain excited state transitions (see Figure 4).

Electron charge tunneling energy equal to 2.753 eV (450.3 nm) associated with the eighth excited state shown in Figure 4 correspond to experimental value equal to 450.0 nm of the most intense absorption line [2]. This agreement implies that the quantum mechanically self-assembled structures of minimal living cells very closely approximate the realistic ones.

Quantum mechanical electron correlation experiments of self-assembly of above described artificial minimal living cells show that these cells are complex systems because only entire ensemble of PNA, and sensitizer, and pFA, and FA and water molecules is stable and therefore it is able to perform quantum photosynthetic processes. Removing the small part of nucleobase, FA and water molecules leads to the structural changes in comparison with realistic structures and difference in comparison with the spectroscopic values of photoexcited electron tunneling from sensitizer

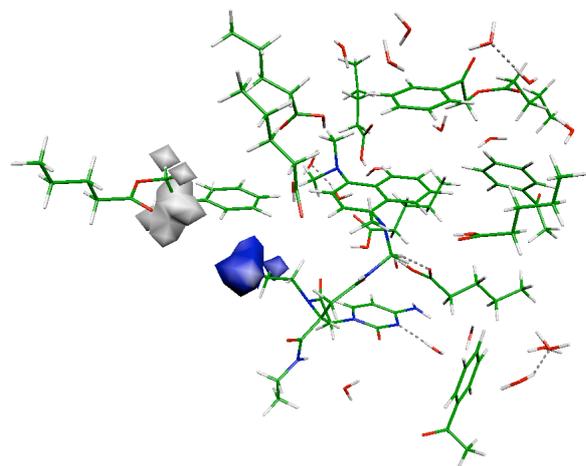


Figure 4. Image of a photosynthetic system consisting of a cytosine-PNA fragment covalently bonded to a 1,4-bis(N,N-dimethylamino)naphthalene sensitizer molecule (in the center), six 5-carbon fatty acid molecules, two pFA molecules (in the left and top-right), and two the waste pieces of the pFA molecules and water molecules that were optimized using the PBEPBE/3-21G method. Visualization of the electron charge tunneling associated with the eighth excited state. The transition is from the conjugated cytosine-PNA fragment-1,4-bis(N,N-dimethylamino)naphthalene supermolecule (in the center-left) to the one of the pFA molecules (in the left). The electron cloud hole is indicated by the dark blue color while the transferred electron cloud location is designated by the grey color.

(1,4-bis(N,N-dimethylamino)naphthalene to pFA molecules. Quantum mechanical electron correlation experiments of self-assembly of artificial minimal living cells removing the main part of nucleobase, and FA and water molecules leads to the degradation of these cells. We can state what the inclusion of ever more water, and fatty acid, and pFA molecules, and waste pieces of the pFA molecules and nucleobase molecules in the different artificial minimal living cells results in a shift of the absorption spectrum to the red for the artificial protocell photosynthetic center, leading to an ever closer approach to the real experimental value and indicates the measure of the complexity of this quantum complex system, *i.e.* a minimal protocell.

As it was underlined before, the second main goal of this article is to demonstrate the *ab initio* quantum mechanical processes of minimal cells such as photoexcited electron tunneling from photoelectron donor molecule to photoelectron acceptor molecule. The most general quantum mechanical theory reality of this complex nonlinear bioorganic system is that according of quantum uncertainty the cloud of photoelectron hole possesses some asymmetrical delocalization while mainly is localized on conjugated with sensitizer supermolecule. Electron cloud also due to quantum uncertainty is partially delocalized while the largest probability to find this photoelectron is on the waste end of pFA molecule.

The quantum reality of nanometer size bioorganic systems is different in comparison with our meter size world and even in comparison with micrometer size bacteria world.

It is important to say that only quantum mechanical electron correlation TD-DFT experiments with minimal

living cells gives results exactly comparable with spectroscopic results and all other more simplified quantum mechanical methods such as local gradient DFT or *ab initio* Hartree-Fock gives structures and spectra far from the experimentally measured.

The corresponding of experimental absorption spectra peaks and our quantum mechanically calculated confirm that our chosen method of designing single electron nano photocells might be useful not only for artificial living organisms but also for wide implementation in the nano photodevices, and molecular computers.

4. Quantum Mechanical Design of Molecular Electronics OR Gate for the Regulation of Artificial Minimal Living Cell Functions

We used TD DFT PBEPBE method [23] with the 6-31G basis set together with COSMO water solvent method [27] in the ORCA program package which is installed on our Linux cluster to calculate the absorption spectra and the relative positions of the HOMO and LUMO eigenvalues of Schrodinger equation of various separate different sensitizer molecules: 1,4-bis(N,N-dimethylamino)naphthalene, and 1,4-dihydroquinoxaline, and 7,8-dimethylisoalloxazine that were previously our investigated by less accurate DFT methods [4]. Analysis and comparison of the results showed that these sensitizers are good candidates for use in artificial minimal cells because their HOMO electron energy levels are energetically high enough relative to the LUMO electron energy level of the pFA molecule and their absorption spectra are in the visible region.

Geometry optimization of artificial logically controlled photosynthetic system consisting of guanine-cytosine-PNA fragment (left-bottom of Figure 5) with covalently bonded two sensitizers: 1,4-dihydroquinoxaline and 1,4-bis(N,N-dimethylamino)naphthalene molecules and Van der Waals dispersion forces bonded precursor of fatty acid molecule (in the right-top of figure), and surrounded by hundreds of real water molecules was performed by semiempirical quantum mechanical PM3 method. Later most of water molecules are removed and geometry of this minimal cell was reoptimized by DFT PBEPBE/6-31G methods ORCA package [17, 18] on our research group Linux cluster.

It have been performed calculations using TD DFT PBEPBE method [23] with the 6-31G basis set together with COSMO water solvent model using ORCA package [17, 18, 27] installed on our Linux cluster of the difference of electron charge density (excited-state - ground-state) for the photosynthetic center of logically controlling artificial minimal living cell which consists of conjugated guanine-cytosine-PNA-1,4-dihydroquinoxaline-1,4-bis(N,N-dimethylamino)naphthalene supermolecule and Van der Waals dispersion forces bonded pFA molecule, and surrounded by real water molecules.

The absorption spectrum of this photosynthetic system is detailed placed in the Table 2 and electron charge transfer trajectories in different excited states are shown in the Figures 6-12).

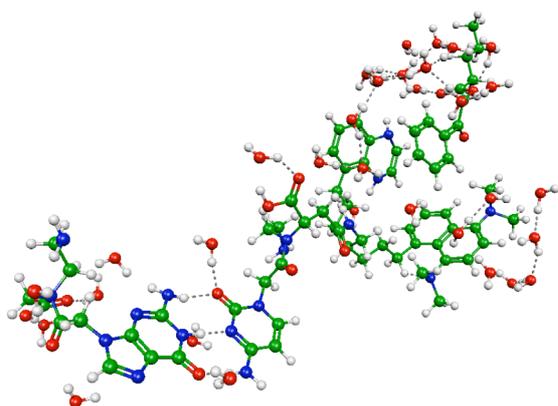


Figure 5. Molecular electronics OR logic gate installed in photosynthetic center of minimal cell consists of: guanine-cytosine-PNA-1,4-dihydroquinoxaline-1,4-bis(N,N-dimethylamino)-naphthalene supermolecule and Van der Waals dispersion forces bonded pFA molecule (in the top-right, between the sensitizer molecules) surrounded by real water molecules environment. The 1,4-dihydroquinoxaline and 1,4-bis(N,N-dimethylamino)-naphthalene are covalently bounded to the PNA via a molecular insulator bridges.

The electron tunneling transitions of the 13th, 17th, and 23th, 24th, 26th excited states should induce metabolic photodissociation of pFA molecule because the transferred electron cloud is located on the head (the waste piece) of pFA molecule (see Figures 7, 8 and 10-12).

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 6) by using B3LYP/6-311G method. After geometry reoptimization procedure it was obtained the electronic structure of negative ion of this molecule using unrestricted B3LYP/6-311G method

Atomic Mulliken charges in Table 3 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 Mulliken charges of atoms from No 1 to 9 of neutral

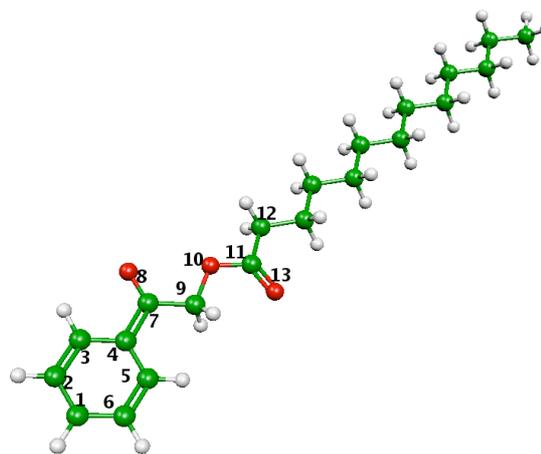


Figure 6. Geometrical structure of pFA molecule. There are numerated heavy C and O atoms in the waste end of this molecule and in the part of FA fragment.

pFA molecule are equal to +0.282 of electron charge (e) while the sum on the same atoms in anion pFA molecule is equal to -0.632 e (see Table 3). It means that almost entire (-0.914 e) additional electron after self-consistent field procedure localizes on the waste end of pFA molecule while only -0.086 e charge localizes on FA fragment of this molecule.

Chemical bond orders in quantum chemistry are equal to values of non diagonal elements of condensed to chemical bonds all electrons matrix multiplied by two. Data of selected chemical bonds of neutral and anion pFA molecules are presented in Table 4.

Analysis of selected bond orders of neutral and anion pFA molecules shows that the most weakness chemical bond order is between ninth 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 0.297 to 0.260 between ninth and 10th atoms.

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 ninth and 10th atoms

Table 2. Excitation transitions energies of a photosynthetic center of logically controlling artificial minimal living cell which consists of conjugated guanine-cytosine-PNA-1,4-dihydroquinoxaline-1,4-bis(N,N-dimethylamino)naphthalene supermolecule and Van der Waals dispersion forces bonded pFA molecule, and surrounded by real water molecules were calculated using TD DFT PBE/PBE method with the 6-31G basis set together with COSMO water solvent method in the ORCA program package. 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)
13	HOMO-1 → LUMO	0.999	2.176	569.7	0.00015
16	HOMO → LUMO+12	0.999	2.320	534.4	0.00011
17	HOMO-4 → LUMO	0.999	2.370	523.2	0.00006
19	HOMO → LUMO+13	0.998	2.427	510.9	0.00032
23	HOMO-6 → LUMO	0.999	2.542	487.7	0.00029
24	HOMO-7 → LUMO	0.999	2.561	484.2	0.00022
26	HOMO → LUMO+14	0.986	2.606	475.7	0.00010

will be broken. This photodissociation process of pFA molecule is observing experimentally in LANL "Protocell Assembly" project.

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

Table 3. Atomic Mulliken charges with hydrogens summed into carbon atoms of neutral and anion pFA molecules calculated by B3LYP/6-311G method.

Number of atom	Neutral pFA	Anion of pFA
1 C	0.048	-0.108
2 C	0.001	-0.086
3 C	0.100	-0.028
4 C	-0.141	-0.124
5 C	0.099	-0.030
6 C	-0.014	-0.104
7 C	0.280	0.183
8 O	-0.340	-0.486
9 C	0.249	0.151
10 O	-0.467	-0.461
11 C	0.534	0.531
12 C	-0.022	-0.039
13 O	-0.391	-0.411
Sum of charges on 1-9 atoms	0.282	-0.632

Table 4. Bond orders of selected chemical bonds of neutral and anion pFA molecules calculated by B3LYP/6-311G method.

Chemical bonds	Neutral pFA	Anion of pFA
9-10 C-O	0.297	0.260
7-8 C-O	1.322	1.277
10-11 O-C	0.376	0.455

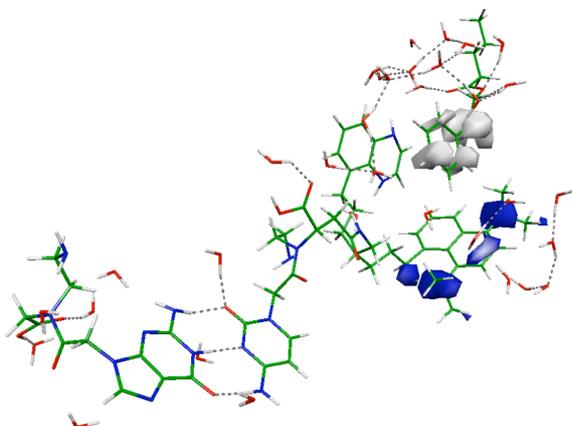


Figure 7. Electron charge transfer transition for the thirteenth excited (569.7 nm) state is from the guanine-cytosine-PNA-1,4-bis(N,N-dimethylamino)naphthalene supermolecule HOMO-1 to the pFA molecule LUMO calculated by TD-DFT PBEPBE/6-31G method. The electron cloud hole is indicated by the dark blue color while the transferred electron cloud location are designated by the grey color.

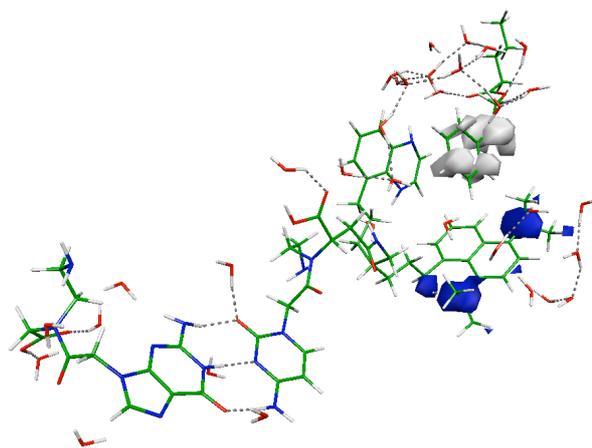


Figure 8. Electron charge transfer transition for the seventeenth excited (523.20 nm) state is from the guanine-cytosine-PNA-1,4-bis(N,N-dimethylamino)naphthalene supermolecule HOMO-4 to the pFA molecule LUMO calculated by TD-DFT PBEPBE/6-31G method.

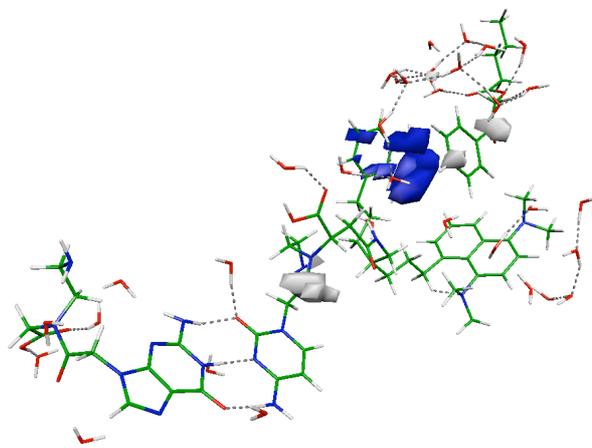


Figure 9. Electron charge transfer transition for the nineteenth excited (510.9 nm) state is from the guanine-cytosine-PNA-1,4-dihydroquinoxaline supermolecule HOMO to the cytosine and pFA molecules LUMO+13 calculated by TD-DFT PBEPBE/6-31G method.

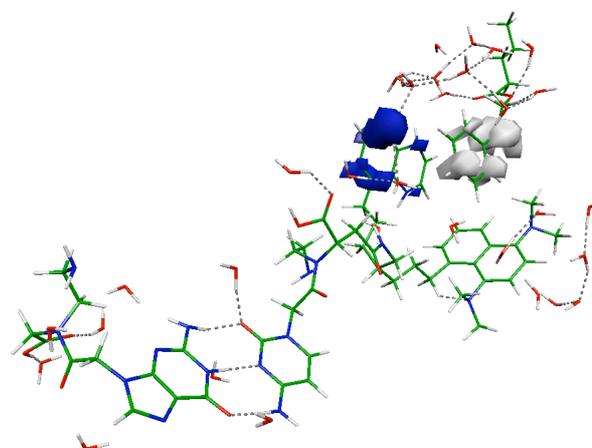


Figure 10. Electron charge transfer transition for the twenty third excited (487.7 nm) state is from the guanine-cytosine-PNA-1,4-dihydroquinoxaline supermolecule HOMO-6 to the pFA molecule LUMO calculated by TD-DFT PBEPBE/6-31G method.

papers [1, 2], and called in LANL "Protocell Assembly" project as minimal artificial living cell.

The electron tunneling transition of the 19th excited state should induce metabolic photodissociation of pFA molecule and photodissociation of hydrogen bonds of nucleotide base pair in the guanine-cytosine-PNA fragment in the same time because the part of transferred electron cloud is located on the head (the waste piece) of pFA molecule and another part of transferred electron cloud is located on the cytosine molecule of cytosine-PNA fragment (see Figure 9). The phenomenon when the part of transferred electron cloud is located on the head (the waste piece) of pFA molecule and another part of transferred electron cloud is located on the cytosine molecule might be explained by quantum uncertainty of wave function of entire supramolecule but this case (19th excited state) is not interesting for the reasons of the construction of molecular electronics classic logic function (Boolean logics gate) while might be used for the construction of molecular quantum computing gate.

The electron tunneling transition of the 16th excited state should induce photodissociation of hydrogen bonds of nucleotide base pair in the guanine-cytosine-PNA

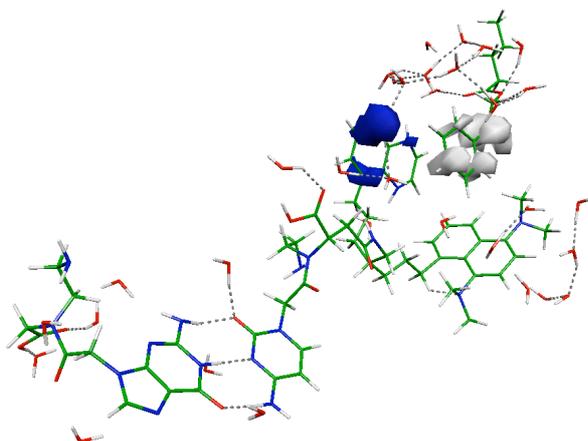


Figure 11. Electron charge transfer transition for the twenty fourth excited (484.2 nm) state is from the guanine-cytosine-PNA-1,4-dihydroquinoxaline HOMO-7 to the pFA molecule LUMO calculated by TD-DFT PBEPBE/6-31G method.

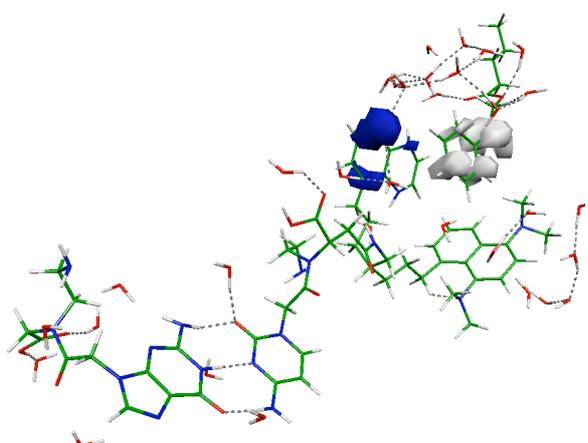


Figure 12. Electron charge transfer transition for the twenty sixth excited (475.7 nm) state is from the guanine-cytosine-PNA-1,4-dihydroquinoxaline supermolecule HOMO to the pFA molecule LUMO+14 calculated by TD-DFT PBEPBE/6-31G method.

fragment because the transferred electron cloud is located on the cytosine molecule of guanine-cytosine-PNA fragment (see Figure 13).

Quantum mechanical B3LYP/6-31+G* and PBEPBE/6-31+G* calculations of model system consisting of guanine-cytosine surrounded by 101 water molecule (see Figure 14) shows that the placement of additional negative electron charge leads to the enlargement of interatomic distances of hydrogen bonds and to the reducing of the bond orders of the guanine-cytosine hydrogen bonds [28].

The additional electron located on cytosine in the sixteenth excited (534.4 nm) state should destroy the hydrogen bonds of nucleotide base pair guanine-cytosine and initiate the PNA gene dehybridization in the artificial minimal living cells. The geometry reoptimization of negatively charged model system guanine-cytosine in the surrounding 51 water molecules cluster in the excited states were done by using Turbomole program package [29] and led to the breaking of hydrogen bonds of

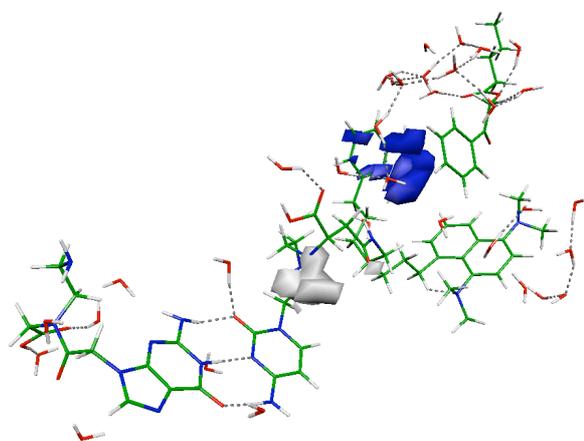


Figure 13. Electron charge transfer transition for the sixteenth excited (534.4 nm) state is from the guanine-cytosine-PNA-1,4-dihydroquinoxaline supramolecule HOMO to the cytosine molecule LUMO+12 calculated by TD-DFT PBEPBE/6-31G method.

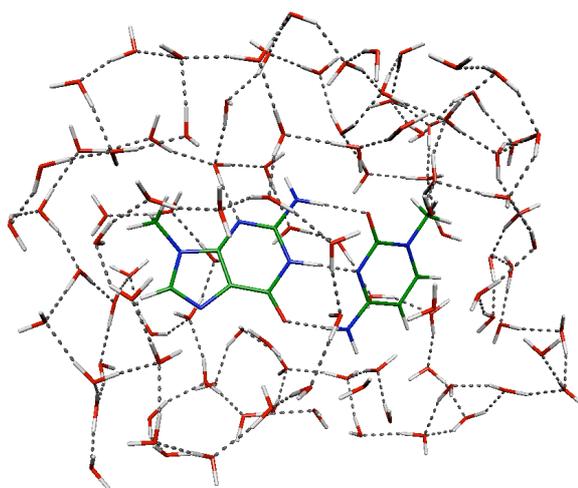


Figure 14. The hydrogen bonds of nucleotide base pair guanine-cytosine and among 101 water molecules cluster are marked by dashed lines. Carbon atoms and their associated covalent bonds are shown as green sticks, hydrogens are in light grey, oxygens – red, nitrogens – blue.

guanine-cytosine [28] while the geometry optimization in the sixteenth excited (534.4 nm) state of entire supermolecule shown in the Figure 13 is still too expensive. This PNA gene photoinduced dehybridization in the minimal cells not yet experimentally done in LANL "Protocell Assembly" project.

Analysis of digits of 6th column in Table 2 shows that most oscillator strengths of photoexcited electron transitions (in 13th, 23th, 24th excited states) initiating metabolic lipid production are more intense in comparison with the oscillator strength photoexcited electron transition (in 16th excited state) initiating gene dehybridization.

Analysis of TD DFT calculated absorption spectrum characteristics in the Table 2 show that in this supramolecule all the weights of individual transitions are approximately equal to 1. It means that enough to draw only one figure for the representation of certain transition because the superposition of another elementary transition with significantly small weight does not significantly affect on this transition. Images of electron transfer trajectories (see Figures 10, 11, 13-15 and 16) in the different excited states allow to separate two different logically controlled functions of molecular device consisting of guanine-cytosine-PNA-1,4-dihydroquinoxaline-1,4-bis(N,N-dimethylamino)naphthalene supermolecule and Van der Waals bonded pFA molecule. These two different logically controlled functions of artificial minimal living cells are:

- 1) initiation of metabolic fatty acid production in the excited states 13th, 17th and 23th, 24th, 26th or
- 2) initiation of gene dehybridization in the 16th excited state.

In other words one should be able to initiate the metabolic fatty acid production illuminating this artificial minimal cell by wavelengths: 569.7 nm, 523.2 nm, 487.7 nm, 484.2 nm, 475.7 nm or one should be able initiate the gene dehybridization illuminating this artificial minimal cell by wavelength equal to 534.4 nm.

It can be stated that our quantum mechanically installed guanine-cytosine-PNA-1,4-dihydroquinoxaline-1,4-bis(N,N-dimethylamino)naphthalene supermolecule works in the artificial minimal living cell as molecular

electronics classic OR logic function, *i.e.* Boolean logics OR gate (see Figure 15).

This OR molecular electronics logical gate is for selected stimulation of the photosynthesis or the self-reproduction of artificial minimal living cells which should be ease to synthesize it and install in these artificial minimal living cells for investigations of the efficiency of their functionality. Our research is on the way for total prevention of the photosynthesis and self-reproduction of artificial minimal living cells by installing molecular electronics AND logic gate and using external magnetic fields with molecular spintronics ControlNot gate [30].

5. Conclusions

Artificial living cells and their substructures are self-assembling due to electron correlation interactions among biological and water molecules which leads to appearing of the quantum mechanical repulsion weak electrostatic forces (due to internal shift of whole conjugated valence electron cloud from electron-donor tail to electron-acceptor head) and the quantum mechanical attraction Van der Waals dispersion forces and hydrogen bonds. Dispersion forces are weak intermolecular forces that arise from the attractive force between quantum multipoles. A hydrogen bond is a special type of quantum attractive interaction that exists between an electronegative atom and a hydrogen atom bonded to another electronegative atom and this hydrogen atom exist in two quantum states. The best method to simulate these Van der Waals dispersion forces and hydrogen bonds is to perform quantum mechanical non-local density functional potential calculations of artificial minimal living cells consisting of around 400 atoms. The cell systems studied are based on peptide nucleic acid and are 3.5 – 4.5 nm in diameter. The electron tunneling and associated light absorption of most intense transitions as calculated by the time dependent density functional theory method differs from spectroscopic experiments by only 0.3 nm, which are within the value of experiment errors. This agreement implies that the quantum mechanically self-assembled structure of artificial minimal living cells very closely approximate the realistic ones.

Analysis of TD DFT calculated absorption spectrum and images of electron transfer trajectories in the different excited states allow to separate two different logically controlled functions of molecular device consisting of guanine-cytosine-PNA-1,4-dihydroquinoxaline-1,4-bis(N,N-dimethylamino)naphthalene supermolecule and Van der Waals dispersion forces bonded pFA molecule. These two different logically controlled functions of minimal cells (protocells) are:

- 1) initiation of metabolic lipid production in the excited states 13th, 17th and 23th, 24th, 26th or
- 2) initiation of gene dehybridization in the 16th excited state.

It is possible to initiate the metabolic lipid production illuminating this artificial minimal cell by wavelengths: 569.7 nm, 523.2 nm, 487.7 nm, 484.2 nm, 475.7 nm or it is possible to initiate the gene dehybridization illuminating this artificial minimal cell

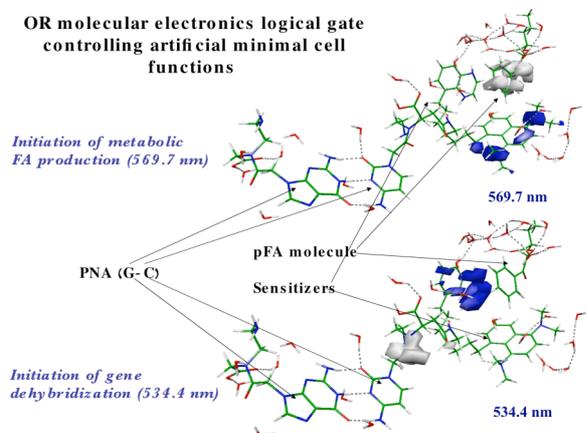


Figure 15. The summarizing picture of the OR molecular electronics logical gate for selected stimulation of the photosynthesis or the self-reproduction of artificial minimal living cells.

by wavelength equal to 534.4 nm.

Our quantum mechanically installed guanine-cytosine-PNA-1,4-dihydroquinoxaline-1,4-bis(N,N-dimethylamino)naphthalene supermolecule works in the artificial minimal cell (protocell) as molecular electronics classic OR logic function (Boolean logics OR gate).

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