

Phenomenon of Quantum Entanglement in a System Composed of Two Minimal Protocells

Arvydas Tamulis · Mantas Grigalavicius ·
Jonas Baltrusaitis

Received: 26 July 2012 / Accepted: 31 October 2012 /
Published online: 16 December 2012
© Springer Science+Business Media Dordrecht 2012

Abstract The quantum mechanical self-assembly of two separate photoactive supramolecular systems with different photosynthetic centers was investigated by means of density functional theory methods. Quantum entangled energy transitions from one subsystem to the other and the assembly of logically controlled artificial minimal protocells were modeled. The systems studied were based on different photoactive sensitizer molecules covalently bonded to a non-canonical oxo-guanine::cytosine supramolecule with the precursor of a fatty acid (pFA) molecule attached via Van der Waals forces, all surrounded by water molecules. The electron correlation interactions responsible for the weak hydrogen and Van der Waals chemical bonds increased due to the addition of polar water solvent molecules. The distances between the separated sensitizer, nucleotide, pFA, and water molecules are comparable to Van der Waals and hydrogen bonding radii. As a result, the overall system becomes compressed, resulting in photo-excited electron tunneling from the sensitizer (bis(4-diphenylamine-2-phenyl)-squinone or 1,4-bis(N,N-dimethylamino)naphthalene) to the pFA molecules. Absorption spectra as well as electron transfer trajectories associated with the different excited states were calculated using time dependent density functional theory methods. The results allow separation of the quantum entangled photosynthetic transitions within the same minimal protocell and with the neighboring minimal protocell. The transferred electron is used to cleave a “waste” organic molecule resulting in the formation of the desired product. A two variable, quantum entangled AND logic gate was proposed, consisting of two input photoactive sensitizer molecules and one output (pFA molecule). It is proposed that a similar process might be applied for the destruction of tumor cancer cells or to yield building blocks in artificial cells.

Keywords Quantum self-assembly · Photosynthetic centers · Minimal protocell · Minimal cell · Electron entangled molecular orbitals · Electron transfer · Quantum entangled photosynthesis · Molecular quantum entangled logical gate

A. Tamulis (✉) · M. Grigalavicius
Vilnius University Institute of Theoretical Physics and Astronomy, A. Gostauto 12, Vilnius, Lithuania
e-mail: tamulis9@gmail.com

J. Baltrusaitis
PhotoCatalytic Synthesis Group, MESA+ Institute for Nanotechnology, Faculty of Science and
Technology, University of Twente, Meander 225, P.O. Box 217, 7500 AE Enschede, The Netherlands

Introduction

Previous work on the synthesis and modeling of active components of artificial protocells has been conducted at the Los Alamos National Laboratory (LANL) in the USA (Rasmussen et al. 2003, 2008; DeClue et al. 2009; Maurer et al. 2009; Cape et al. 2011; Edson et al. 2011; Maurer et al. 2011). These studies are now continuing at the Center for Fundamental Living Technology (FLinT) and at the University of Southern Denmark (SDU).

Other LANL project used organic neutral radical molecules for quantum information processing (Tamulis et al. 2003a, b, 2004, 2007, 2008a, b; Tamuliene et al. 2004; Rinkevicius et al. 2006; Tamulis and Tamulis 2008).

The goals of the work covered in this paper are:

- i) to design the structural and optical properties of a photosynthetic artificial minimal cell and two different minimal protocells using time dependent density functional theory (TDDFT) (Marques et al. 2006) based on reasonable agreement with existing experiments at LANL;
- ii) based on that work, to design molecular quantum entangled logical gates for controlling photosynthesis in artificial minimal cells and minimal protocells and to predict the structural and optical properties of these complex systems as the basis for future synthesis and spectroscopic measurements.

Outlines of this research description:

1. The definition of a minimal cell and a minimal protocell will be formulated in section #3. We define:
 - a) a minimal cell as a self-assembled supramolecular system composed of a sensitizer molecule, a number of fatty acid molecules (FA), a precursor of the fatty acid molecules (pFA), and number of water molecules;
 - b) a minimal protocell as the self-assembled supramolecular photoactive center, composed of a sensitizer molecule, and pFA and a number of water molecules.
2. The phenomenon of quantum entanglement in a system composed of two minimal protocells will be described in section #4.

The solution of basic questions of emergence and evolution of the first living cells or protocells is tightly connected with the rapidly developing field of artificial living technologies in several laboratories around the world. The possibility of synthesizing artificial self-reproducing cells also impacts the possibility of the emergence of living protocells on the Earth or elsewhere.

In their originally conceived form, LANL's artificial cells were to consist of a micelle acting as the container, a light driven metabolism, and a genetic system, whose functions were all very tightly coupled (Rasmussen et al. 2003, 2008; DeClue et al. 2009; Maurer et al. 2009, 2011; Cape et al. 2011; Edson et al. 2011). The proposed container was to consist of amphiphilic fatty acid (FA) molecules that self-assembled into a micelle. The hydrophobic interior of the micelle was to provide an alternative thermodynamic environment from the aqueous or methanol exterior and acts as a sticking point for the photosensitizer, pFA (food), and the genetic material. Peptide nucleic acid (PNA) was initially chosen as the genetic material as it is far less polar than RNA or DNA. The different nucleotide molecules have different electron donor and electron relay capabilities, and as such, there is also a mechanism for natural selection, with some nucleotides and their orderings being superior to others in their ability to facilitate the metabolism (Rasmussen et al. 2003, 2008; DeClue et al.

2009). Practical current experimental considerations resulted in changes from the original design. Decanoic acid based self-assembling bilayer vesicles were used as the containers, and DNA as the genetic material (DeClue et al. 2009).

The active components of the systems synthesized at LANL and in the FLinT at the SDU contain on the order of 10^3 atoms. Due to this small size, all the active processes, including the self-assembly from component molecules, the absorption of light, and the metabolism should in principle be investigated using quantum (wave) theory (Tamulis et al. 2006, 2008, 2012; Tamulis and Tamulis 2007a, b, 2008; Tamulis 2008a, b, c, 2011; Tamulis and Grigalavicius 2010a, b, 2011).

The entire artificial cell might be considered to be a molecular electronics device that self-assembles according to quantum-based electron interaction potentials and that absorbs light and carries on its metabolism according to quantum electron excitation and tunneling equations. Therefore, in this picture, the photo-induced electron charge transfer in the artificial cell may be viewed as a quantum particle-wave trace.

The calculated electron charge tunneling energy of 2.753 eV (450.3 nm) associated with the eighth excited state of LANL synthesized minimal artificial living cells was investigated by Tamulis et al. (2008) and corresponds to the experimental value of 450.0 nm of the most intense absorption line (Rasmussen et al. 2008). This agreement implies that the quantum mechanically simulated self-assembled structures of such “minimal living cells” very closely approximate the realistic ones. This article uses a collection of quantum mechanical electron correlation tools and applies them to a variety of minimal protocell photosynthetic problems, while also providing a perspective for the synthesis of new forms of living organisms.

Several nonconventional systems which were designed by our research group are presented in this article. Examples of this research include the use of molecular electronics logic gates to regulate photosynthesis-like energy transduction systems, as well as to control growth and division of artificial living cells (Tamulis et al. 2003a, b, 2004, 2007; Tamuliene et al. 2004; Rinkevicius et al. 2006; Tamulis and Tamulis 2008; Tamulis 2008a, b).

Longer term goals in the use of quantum mechanical simulations might be to predict the possibility of biochemical experimental synthesis of molecular electronics and spintronics logic elements for information systems based on artificial living organisms, or for the control of nanobiorobots applied in areas such as nanomedicine and cleaning of nuclear, chemical, and microbial pollution.

Procedure/Methodology

Biological molecules, supermolecules, and supramolecules (in particular cases micelles or minimal protocells) are quantum systems composed of quantum particles: nuclei (with charges Z_i) and surrounding electrons possessing elementary charge. Due to the interactive couplings, the electromagnetic interaction of two particles has consequences on the interactions of all the other quantum particles; therefore we are dealing with a complex, quantum, many-body system. The exact many-particle Hamiltonian (Jensen 1999) for such systems is:

$$\hat{H} = -\frac{\hbar^2}{2} \sum_i \frac{\nabla_{\vec{R}_i}^2}{M_i} - \frac{\hbar^2}{2} \sum_i \frac{\nabla_{\vec{r}_i}^2}{m_e} \quad (1)$$

$$- \frac{1}{4\pi\epsilon_0} \sum_{i,j} \frac{e^2 Z_i}{|\vec{R}_i - \vec{r}_j|} + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2 Z_i Z_j}{|\vec{R}_i - \vec{R}_j|}$$

where M_i and Z_i are the masses and charges of the nuclei, the electrons possess the elementary mass m_e and elementary charge e , and \vec{R}_i and \vec{r}_i are radius vectors of nuclei and electrons.

The first term of equation 1.1 is the kinetic energy operator for the nuclei, while the second is the same, but for the j electrons associated with each nucleus i located at the distance \vec{R}_i , and the electrons possess the elementary mass m_e which are at the the electron's absolute individual locations being \vec{r}_i . the electron's absolute individual locations being \vec{r}_{ij} .

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

$$F_C = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r^2},$$

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:

$$\epsilon_0 = \frac{1}{\mu_0 c_0^2} = 8,54187817 \dots \times 10^{-12} \text{ A} \cdot \text{s} / (\text{V} \cdot \text{m}) = 8,854187817 \dots \times 10^{-12} \text{ F/m},$$

Where C_0 is the speed of light in vacuum and μ_0 is the magnetic constant or vacuum permeability.

Unfortunately the Schrödinger equation of quantum mechanics is not mathematically available for exact solution. In order to find acceptable approximate eigenstates, we will need to make approximations to at least two different levels (Jensen 1999).

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 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:

$$\hat{H} = \hat{T} + \hat{V} + \hat{V}_{ext} \quad (2)$$

The kinetic and electron-electron terms of 2 depend only on the fact that we are dealing with a quantum many-electron system (Jensen 1999). 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

Using the above approximation, 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 (Tamulis et al. 2006; Tamulis and Tamulis 2007a, b, 2008; Tamulis 2008a, b, c, 2011; Tamulis et al. 2008, 2012; Tamulis and Grigalavicius 2010a, b, 2011). The cell systems studied in these articles are based on peptide nucleic acid (PNA) and consist of up to 400 atoms (not including the associated water solvent shells) and are about 4.5 nm in diameter.

The quantum simulations of single bioorganic molecules possessing closed electronic shells start from an arbitrary geometry (Cartesian coordinates of the nuclei). Using quantum mechanical semi-empirical and DFT approaches in the GAMESS-US (Schmidt et al. 1993), TURBO-MOLE (2009) or Gaussian09 Revision A.1 (Frisch et al. 2009) program packages, we obtain the lowest molecular energy which parametrically depends on the coordinates of the nuclei. These coordinates are adjusted using the standard geometry optimization procedure (Dreizler and Gross 1990) to minimize 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 geometry optimization of the self-assembly of bioorganic supramolecules in which the separate molecules are associated by hydrogen bonds or Van der Waals forces, the RI-BP (Becke 1993) method was used. RI stands for 'Resolution of the identity' and contributes to the approximation of the above mentioned Coulomb part (Eichkorn et al. 1995). In addition, the B97d (Grimme 2006) method with Grimme long range dispersion electron corrections were used. Both of these methods include some electron correlation effects at larger distances that provide relatively good descriptions of the Van der Waals forces and hydrogen bonds. Despite the fact that in use of GGA functionals reasonable optimization results were obtained, to ensure accurate molecular orbital population in large scale systems during calculations of vertical excitations, hybrid PBE0 functional in the TD-DFT kernel was chosen. It is known that TD-DFT tends to underestimate charge transfer excitation energies when non-hybrid GGA functionals are used (Treutler and Ahlrichs 1995). Thus, excitations of the two minimal protocell systems were calculated using the PBE0 hybrid functional which has the form $\text{const1}(S + \text{PBE}(X)) + \text{const2}\cdot\text{HF} + \text{PW} + \text{PBE}(C)$ (const1 and const2 can be adjusted), where S refers to the determination of Slater-Dirac exchange energy functional, $\text{PBE}(X)$ and $\text{PBE}(C)$ are the Perdew-Burke-Ernzerhof exchange and correlation energy functionals, HF denotes the Hartree-Fock exchange and PW is the Perdew-Wang correlation functional (Adamo and Barone 1999). RI-BP and B97d methods were used together with the def-SV(P) (split valence plus polarization) (Weigend and Ahlrichs 2005) and 6-31G(d) (Ditchfield et al. 1972) basis sets respectively, whereas PBE0 was used together with the def-TZVP basis set (Weigend and Ahlrichs 2005).

Definition of Minimal Cell and Minimal Protocell

Geometry optimization using quantum mechanical methods was performed for two supramolecular systems possessing different sensitizers and other molecular components.

The first system (**1**) consisted of a 1,4-bis(N,N-dimethylamino)naphthalene) molecule, [i.e., $(\text{CH}_3)_2\text{-N-C}_{10}\text{H}_6\text{-N-(CH}_3)_2$], 12 octanoic fatty acid molecules (FA), a precursor of the fatty acid molecule (pFA) and 28 water molecules. The system studied consists of 471 atoms and is about 4.2 nm in diameter. We designated this photoactive system a minimal cell. The geometry optimization was done with the Turbomole program package using RI-BP/def-SV (P) method with Grimme dispersion correction. The final shape of (**1**) after the geometry optimization process is given in Fig. 1.

The electron correlation interactions are the source of the weak hydrogen and Van der Waals chemical bonds that are critical to the optimization behavior of this and similar systems. Polar solvent molecules, such as water, increase the strength of these bonds and play a central role in the self-assembly and functioning of the systems studied. The distances within the optimized system between the separated sensitizer, precursor of the fatty acid and water molecules are comparable to Van der Waals and hydrogen bonding radii. The water molecules that surround the entire photosynthetic complex shown in Fig. 1 were found to stabilize the system and tended to reduce most of the interatomic distances. In addition, some water molecules self-assembled into nano crystal structures while others attached to the polar ends of the FA molecules via hydrogen bonds.

As a result, these nonlinear quantum interactions compressed the overall molecular system resulting in a smaller gap between the HOMO and LUMO electron energy levels which allows enhanced tunneling of photoexcited electrons from the sensitizer (1,4-bis(N,N-

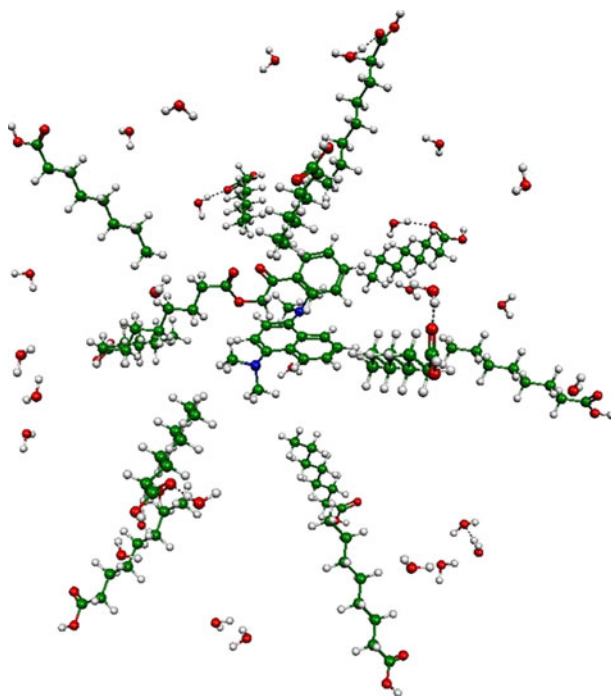


Fig. 1 Image of the final shape of the minimal cell (**1**) after geometry optimization using the RI-BP/def-SV(P) method with the Grimme dispersion correction. The system consists of a 1,4-bis(N,N-dimethylamino)naphthalene) sensitizer molecule (*center*), a pFA molecule (extending from the *left* to the *center* of the image), surrounded by 12 octanoic FA molecules and 28 water molecules. *Dashed lines* show the hydrogen bonds. Carbon atoms and their associated covalent bonds are shown as green spheres and sticks, nitrogens – *blue*, hydrogens – *gray*, oxygens – *red*

dimethylamino)naphthalene) to the pFA molecule resulting in its cleavage. The new fatty acid joins the existing minimal cell thus increasing it in size. After reaching some critical size, the minimal cell should divide into two separate smaller minimal cells.

It can be seen in Fig. 1 that during geometry optimization the molecules of the system shown self-organize into a regular structure due to 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 1,4-bis(N,N-dimethylamino)naphthalene) sensitizer molecule is in the center;
- 2) the fatty acid molecules are oriented with their hydrophobic ends pointed towards the 1,4-bis(N,N-dimethylamino)naphthalene) sensitizer molecule;
- 3) the precursor of the fatty acid molecule is oriented with its hydrophilic end associated with the 1,4-bis(N,N-dimethylamino)naphthalene) sensitizer molecule;
- 4) many of the water molecules self-organize into clusters of nano ice-like substructures. Furthermore, all the interatomic distances between the sensitizer 1,4-bis(N,N-dimethylamino)naphthalene) and the pFA molecule become reduced, i.e., the photosynthetic system becomes more compressed due to the presence of the water molecules.

We define **(1)**, a self-reproducing photoactive supramolecular system, as a minimal cell. We can define this self-reproducing photoactive minimal cell as an example of Fatty Acid World life, referring to the similar definitions of RNA or DNA World life see (Tamulis and Grigalavicius 2010b, 2011).

The results of the quantum assembly of photosynthetic supramolecular system **(2)** were obtained by using the GAMESS-US and ORCA program packages (Neese 2003, 2009) together with the DFT quantum chemical PBELYP/3-21 method and were already published, see papers (Tamulis and Grigalavicius 2010a, b, 2011). This photosynthetic supramolecular system consists of a bis(4-diphenylamine-2-phenyl)-squaraine sensitizer with a covalently attached 8-oxo-guanine::cytosine supramolecule, and a pFA molecule in an environment of 50 water molecules. The final result of the geometry optimization of this system is shown in Fig. 2.

As the geometry optimization process for system **(2)** shows, all of that system's molecules become interconnected by hydrogen bonds. Such bonds are well described by the

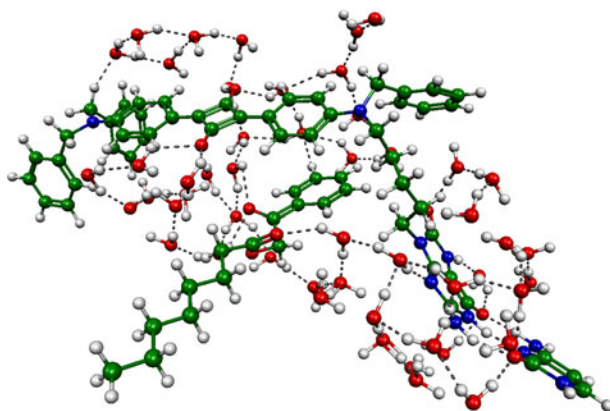


Fig. 2 Image of final structure of minimal protocell **(2)** containing a bis(4-diphenylamine-2-phenyl)-squaraine molecule with covalently attached 8-oxo-guanine::cytosine supramolecule (*the bottom-right*), a pFA molecule (*extending to the bottom-left*) and 50 water molecules

PBELYP/3-21 method used in this paper. Our DFT methods account for electron correlation interactions and if we obtain a stable and hydrogen bond - connected supramolecular system like (2), this means that system (2) really exists in nature.

We define this supramolecular photoactive center (2), composed of a sensitizer molecule, pFA and a number of water molecules, as a minimal protocell.

We propose that life first emerged in the form of such minimal protocells containing only sensitizer molecules (in this case bis(4-diphenylamine-2-phenyl)-squinare with a covalently attached 8-oxo-guanine::cytosine supramolecule), a food molecule (in this case a pFA molecule) and surrounding water molecules which organize hydrogen bonds to keep this supramolecule system together. As proposed in our earlier papers (Tamulis and Grigalavicius 2010b, 2011), later in the process of evolution these minimal protocells would have produced fatty acids and covered themselves with fatty acid envelopes to become the minimal cells of the Fatty Acid World.

The emergence of these minimal protocells and minimal cells might have happened 3.9-3.8 billion years ago, as was suggested in Tamulis and Grigalavicius (2010b), which is also in agreement with geochemical data (Mojzsis et al. 1996).

The 2000 nodes supercomputer of The University of Iowa (U.S.A.) was used for quantum mechanical investigations of the minimal cell (1) and of the system composed of two minimal protocells (3). The quantum mechanical investigations of two types of sensitizer molecules: 1,4-bis(N,N-dimethylamino)naphthalene – $(\text{CH}_3)_2\text{-N-C}_{10}\text{H}_6\text{-N-(CH}_3)_2$, and bis(4-diphenylamine-2-phenyl)-squinare as well as minimal protocell (2) were performed on the Linux servers cluster of Vilnius University Institute of Theoretical Physics and Astronomy (Lithuania).

Quantum Entanglement of Photoinduced Electron Transfer in a System Composed of Two Minimal Protocells

After the geometry optimization of the minimal fatty acid cell (1), the fatty acid molecules were removed and 8-oxo-guanine::cytosine supramolecule was covalently attached to the sensitizer 1,4-bis(N,N-dimethylamino)naphthalene molecule for a better functionality of the photosynthetic center.

The 8-oxo-guanine::cytosine supramolecule supplies a replacement electron to the sensitizer after the photoexcited electron has hopped from the sensitizer to the pFA molecule. We define this newly designed supramolecular system as a minimal protocell (1PhC). The second minimal protocell (2) is composed of a sensitizer bis(4-diphenylamine-2-phenyl)-squinare molecule attached covalently to 8-oxo-guanine::cytosine supramolecule, and pFA and water molecules, as was already mentioned in the section above.

The new photosynthetic system (3) composed of two subsystems [(1PhC) and (2)] (see Fig. 3a and b) possesses 534 atoms. The initial distance between the (1PhC) and (2) subsystems was chosen significantly larger than Van der Waals distances between supramolecules (see Fig. 3a). The geometry optimization of system (3) was performed by using the DFT method B97d and the 6-31G(d) basis set in the G09RevB.01 program package. The process of geometry optimization reduced the distance between the (1PhC) and (2) subsystems (compare Fig. 3a and b) due to Van der Waals interactions between these subsystems.

The DFT B97d method with 6-31G(d) basis set accounts for the electron correlation interactions and therefore describes the process of self-forming of hydrogen bonds. One can see in Fig. 3b many dashed lines which show hydrogen bonds. Molecular visualization

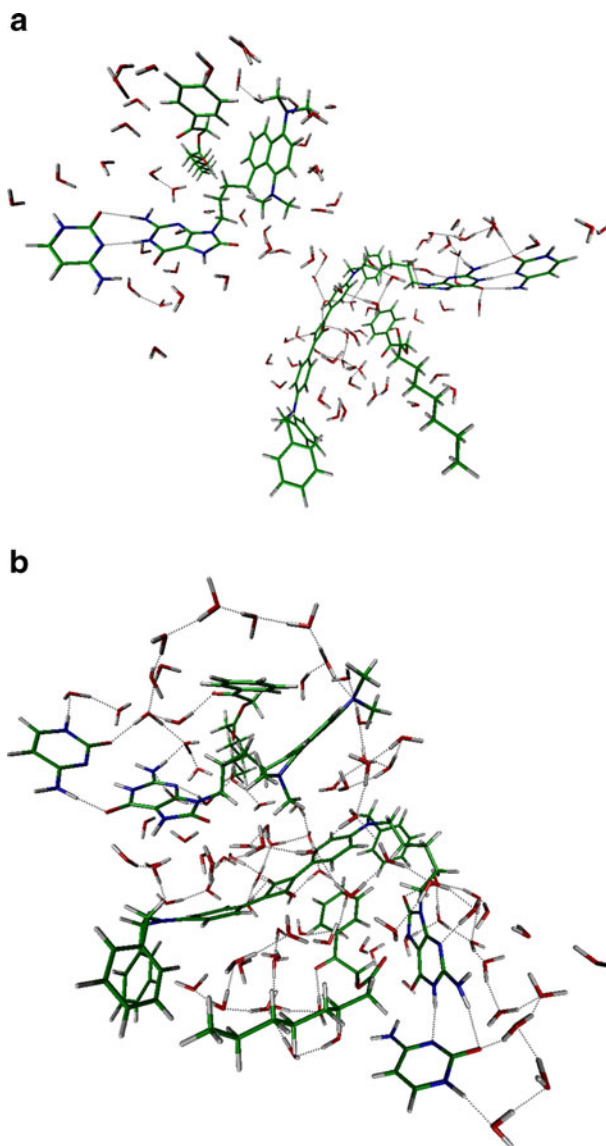


Fig. 3 **a.** Image of system (3) composed of two photosynthetic minimal protocells (1PhC) and (2) before geometry optimization. Carbon atoms and their associated covalent bonds are shown as green sticks, hydrogens – light gray, nitrogens – blue, oxygens – red. Dashed lines show the hydrogen bonds. **b.** Image of system (3) composed of two photosynthetic minimal protocells (1PhC) and (2) after geometry optimization. Geometry optimization was performed by using DFT method B97d with 6-31G(d) basis set

program Molekel¹ draws dashed lines between two atoms only if the distances correspond to the experimental values of hydrogen bonds. We can state that the appearance of many dashed lines in Fig. 3b means that the DFT B97d and other DFT methods which we use and

¹ Molecular visualization program Molekel (2012), available at <http://molekel.cscs.ch/wiki/pmwiki.php/ReferenceGuide/Introduction>

Table 1 Excitation transition energies of system (3) composed of two photosynthetic two minimal protocells (1PhC) and (2) calculated by using Turbomole PBE0 using def-TZVP basis set. The weight of the individual excitations are only given if larger than 0.1

Excited State #	Individual transitions HOMO-m \rightarrow LUMO+n	Weight of individual transition	Energy (eV)	Wavelength (nm)	Oscillator strength (arbitrary units)
4	HOMO-1 \rightarrow LUMO+1	0.894	2.63	471.2	0.00312
	HOMO \rightarrow LUMO+1	0.101			
5	HOMO \rightarrow LUMO+2	0.989	2.65	468.7	0.02940
6	HOMO \rightarrow LUMO+1	0.897	2.65	467.3	0.00028
	HOMO-1 \rightarrow LUMO+1	0.101			
8	HOMO-2 \rightarrow LUMO+1	0.998	3.00	413.5	0.00004

which account for electron correlation interactions, reasonably describe the process of self-forming of hydrogen bonds.

Optimization time sequence exposes the self-assembly of fatty acid minimal cell (1) and minimal protocell (2) and the system (3) composed of two photosynthetic minimal protocells (1PhC) and (2) given in Fig. 3a. It can be clearly seen that due to quantum electron correlation forces and hydrogen bonding interactions (dashed lines) the water molecules are self-assembling into the nano crystals and attaching to the bis(4-diphenylamine-2-phenyl)-squaraine, 1,4-bis(N,N-dimethylamino)naphthalene, 8-oxo-guanine, cytosine and pFA molecules via compression within the complex quantum system (3).

The algorithm of optimization of geometry in system (3) composed of two minimal protocells allows breaking some hydrogen bonds in the case if the total energy of the system is decreasing. Therefore in this quite complex process some hydrogen bonds

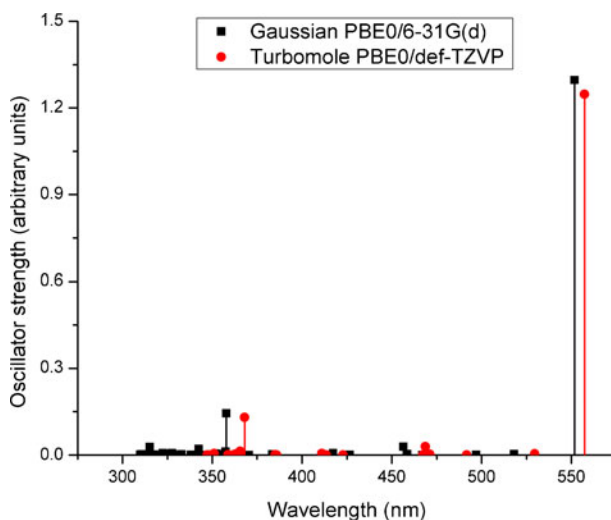


Fig. 4 The spectrum of system (3) composed of two photosynthetic minimal protocells (1PhC) and (2) calculated by using TD-DFT PBE0 method: Gaussian PBE0 with basis set 6-31G(d) and Turbomole PBE0 using def-TZVP basis set after geometry optimization

are breaking but more hydrogen bonds are being created and the entire system is compressing and lowering the total energy.

The absorption spectrum of system (3) was calculated using the final results of the atomic coordinates after the geometry optimization. The details of that spectrum are given in Table 1 and Fig. 4. The spectrum was calculated using two different programs and TD-DFT PBE0 method: Gaussian09 program package PBE0 with the basis set 6-31G(d) and Turbomole program package PBE0 with the def-TZVP basis set. Table 1 only lists the excitations which show the electron hopping from sensitizer molecules to pFA molecules.

With squaraine molecular derivatives as photosensitizers, the most intense spectral lines usually are related with electron charge redistribution in the squaraine molecules, due to the

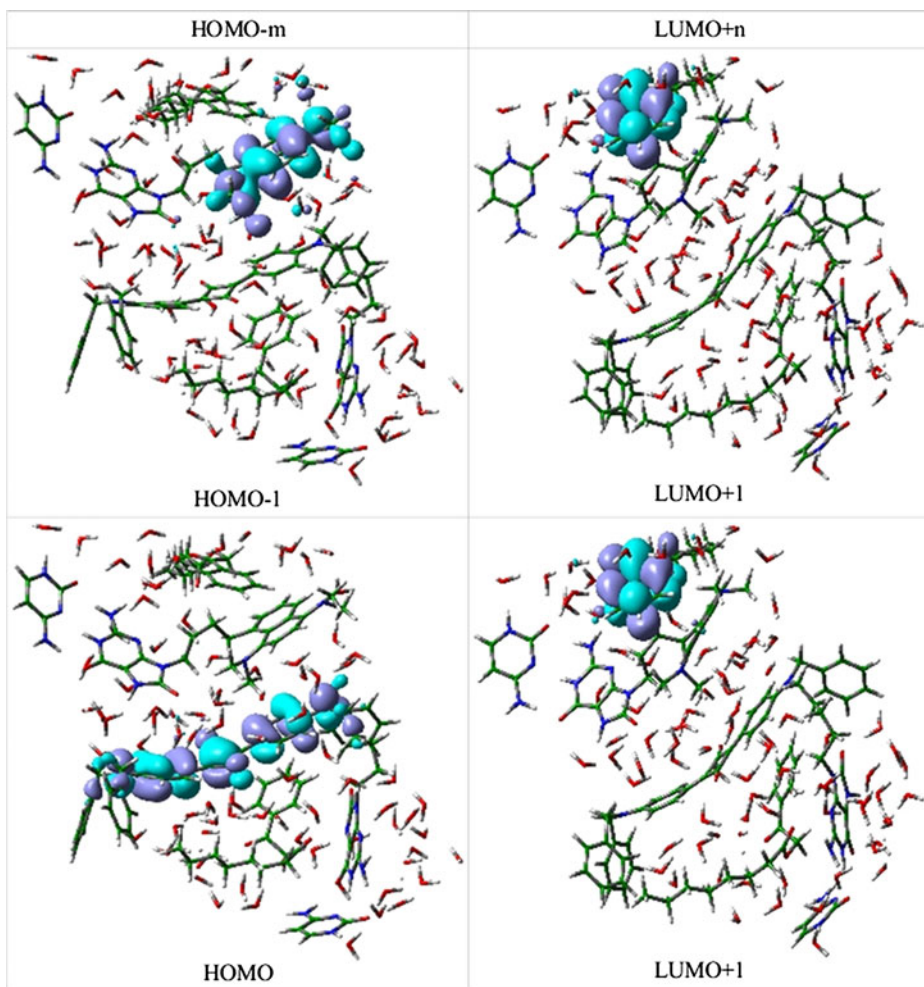


Fig. 5 HOMO-1 and HOMO (in the left) and LUMO+1 (in the right) orbitals of 4th and 6th excited states. Carbon atoms and their associated covalent bonds are shown as *green sticks*, hydrogens – *light gray*, nitrogens – *blue*, oxygens – *red*. The *light-blue parts* means positive part of wave function and blue parts means negative part

unconventional valence angles (close to 90°) in the center of these squaraine derivatives but in this article this phenomenon is not interesting.

The most interesting excitations are 4 and 6 despite the fact that they are not intense. These excitations demonstrate quantum entanglement between two photosynthetic minimal protocells (**1PhC**) and (**2**) in the system (**3**).

Analysis of the frontier orbitals HOMO-m and LUMO+n of system (**3**) in excited states 4 and 6 shows that quantum entanglement exists between the two photosynthetic centers (**1PhC**) and (**2**) (see Fig. 5). The HOMO-1 orbital is located on the subsystem (**1PhC**), while the HOMO orbital is located on (**2**) and LUMO+1 orbital is located on subsystem (**1PhC**) with different weights (see Table 1). That means that electron transition energy (and information) might be transferred at the same time (during excited states 4 and 6) from the two different photosynthetic centers (**1PhC**) and (**2**) in the system (**3**) to the subsystem (**1PhC**).

The elementary transition HOMO \rightarrow LUMO+1 of the 4th excited state (with a small weight of 0.101) through quantum entanglement has a small probability for an electron transfer from the squaraine molecule of (**2**) to the pFA molecule associated with the other (**1PhC**) subsystem (see Fig. 5).

The difference of electron charge density (certain excited states – ground state) for photosynthetic minimal protocells according to the TD DFT calculations and visualized in Figs. 6 and 7, shows the electron charge tunneling associated with certain excited state transitions. The electron cloud hole is indicated by the dark blue color while the transferred electron cloud location is designated by the gray color.

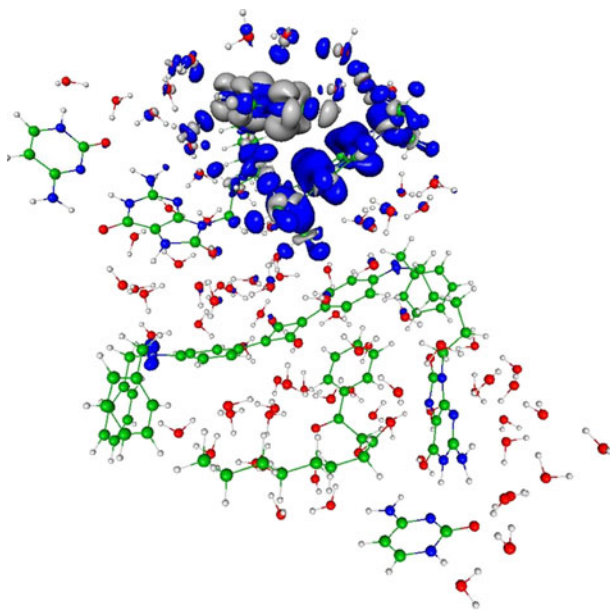


Fig. 6 Visualization of the electron charge tunneling associated with the 4th (471.2 nm) excited state. The transition is mainly from the 1,4-bis(N,N-dimethylamino)naphthalene (in the top-right) to the pFA of the (**1PhC**) subsystem (in the top), with a much smaller probability of instead being from the squaraine (in the center) to the pFA molecule of the (**1PhC**) subsystem (in the top). The electron cloud hole is indicated by the dark blue color while the transferred electron cloud location is designated by the gray color

Visualization of the electron charge tunneling associated with the 4th (471.2 nm) excited state is presented in the Fig. 6. The transition is mainly from the 1,4-bis(N,N-dimethylamino)naphthalene (in the top-right) to the pFA of the (**1PhC**) subsystem, with a much smaller probability of instead being from the squaraine to the pFA molecule of the (**1PhC**) subsystem.

Due to the elementary transition HOMO \rightarrow LUMO+1 with a small weight equal to 0.101 in the 4th excited state, one can see the small quantum entangled electron transition from squaraine molecule in subsystem (2) to the pFA molecule in subsystem (1PhC) (see Fig. 6).

These quantum entanglement calculations are performed at zero Kelvin and our final structure (**3**) is partially a result of an arbitrary initial molecule arrangement selected at the beginning of the optimization. This selection was based on our previous quantum mechanical geometry optimizations of single molecules and subsystems (**1PhC**) and (**2**). No ab initio molecular dynamics calculations to explore the conformational space were performed, since the ultimate results we are interested in - electronic excitations and charge density gradients associated with them - will be mostly determined by the proximity of the molecules that are governed by the intermolecular long range interactions, such as Coulomb and Van der Waals forces. Such interactions can be adequately described by including dispersion correction terms into our optimization. Furthermore, exploring many possible configurations of these molecules with the explicit solvent molecules using quantum mechanical studies can't be performed at the present time on these large systems.

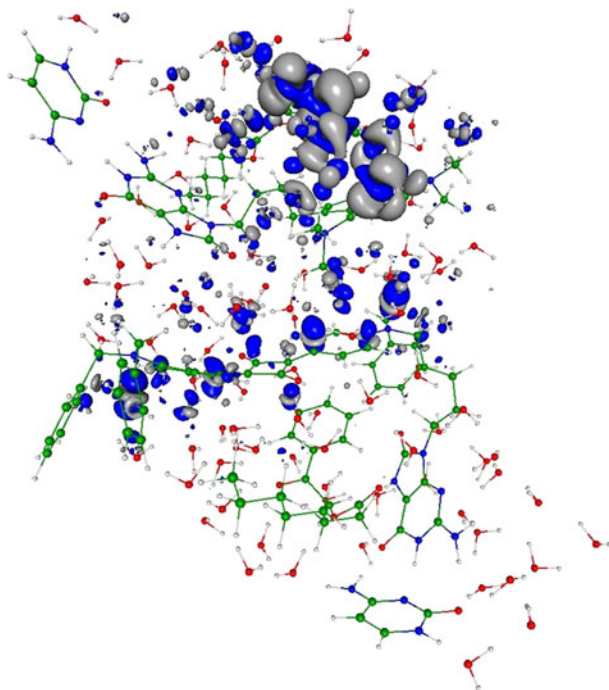


Fig. 7 Visualization of the electron charge tunneling associated with the 6th (467.3 nm) excited state. The transition is mainly from squaraine molecule (in the center) to pFA of the (**1PhC**) subsystem (in the top) and little from the 1,4-bis(N,N-dimethylamino)naphthalene (in the top-right) to the same pFA molecule of the (**1PhC**) subsystem (in the top)

Analysis of frontier orbitals HOMO-*m* and LUMO+*n* of the system (**3**) in the excited state 6 shows that there also exists an additional quantum entanglement between two photosynthetic minimal protocells (**1PhC**) and (**2**) (see Fig. 5). The orbital HOMO is located on the subsystem (**2**) while HOMO-1 is located on (**1PhC**) and LUMO+1 is located on the subsystem (**1PhC**) with different weights (see Table 1). This means that electron transition energy (and information) might be transferred at the same time (during excited state 6) from the two different photosynthetic minimal protocells (**1PhC**) and (**2**) in the system (**3**) to the minimal protocell (**1PhC**).

Due to the elementary transition HOMO \rightarrow LUMO+1 with large weight equal to 0.897 in the 6th excited state one can see the large quantum entangled electron transition from squaraine molecule in (**2**) subsystem to pFA molecule in (**1PhC**) subsystem (see Fig. 7).

Despite that the oscillator strengths associated with the quantum entangled excitations in 4th and 6th states are relatively small, this phenomenon allows to operate with information and energy transfer from one subsystem (**1PhC**) to another (**2**) and vice versa.

In summary, we can state that analysis using the time-dependent density functional theory method of calculated absorption spectrum and images of electron transfer trajectories in the different excited states, allowed to separate quantum entangled photosynthetic transitions between the neighboring minimal protocells (see Figs. 6 and 7). The excited electron was used to cleave a waste organic molecule resulting in the formation of the desired product. This means that a quantum entangled phenomenon of energy and information transfer can proceed between small (up to 10 nanometers) fatty acid minimal cells, such as the living organisms which may have existed in the first stages of the emergence and evolution of life (Tamulis and Grigalavicius 2010a,b, 2011).

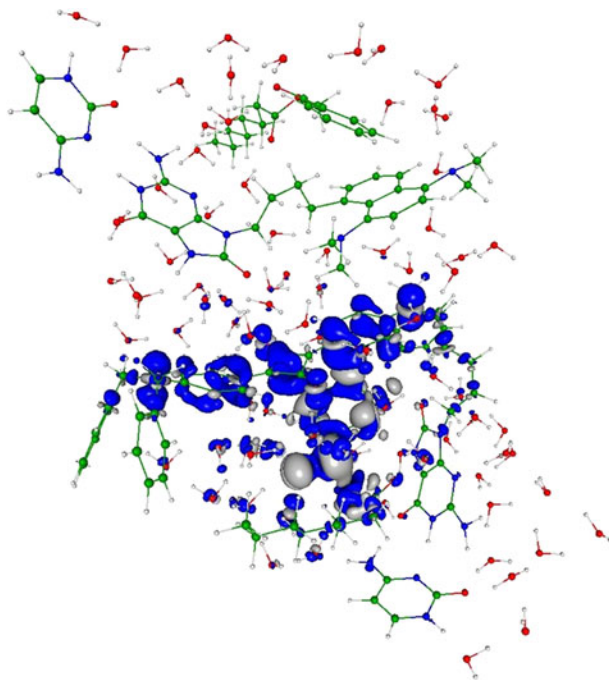


Fig. 8 Visualization of the electron charge tunneling associated with the 5th (468.7 nm) excited state. The transition is mainly from squaraine molecule (in the center) to pFA (in the center-bottom) of the (**2**) subsystem

The system (3) possesses two input photoactive sensitizer molecules in (1PhC) and in (2), i. e. containing two different variable inputs and one output (pFA molecule in (1PhC)). This logic function we define as two variable quantum entangled AND logic gate. In the future, similar processes might be applied for the destruction of tumor cancer cells or to yield building blocks in artificial cells.

The 5th and 8th transitions are associated with electron hopping from a sensitizer molecule to the pFA molecule of the same subsystem (see Figs. 8 and 9).

These research results anticipate that molecular and cellular biology science can be described with quantum physics. For example, a team of scientists at the National University of Singapore suggests that it is quantum entanglement between the electron clouds of nucleic acids in DNA that holds DNA together (Rieper et al. 2011). Rieper et al. modeled the electron clouds of nucleic acids in DNA as a chain of coupled quantum harmonic oscillators with dipole-dipole interaction between nearest neighbors resulting in a van der Waals type bonding. These authors showed that, for realistic parameters, nearest neighbor entanglement is present even at room temperature. These authors found that the strength of the single base von Neumann entropy depends on the neighboring sites, thus questioning the notion of treating single bases as logically independent units. Rieper et al. derived an analytical expression for the binding energy of the coupled chain in terms of entanglement and show the connection between entanglement and correlation energy, a quantity commonly used in our quantum chemistry calculations (Tamulis et al. 2012).

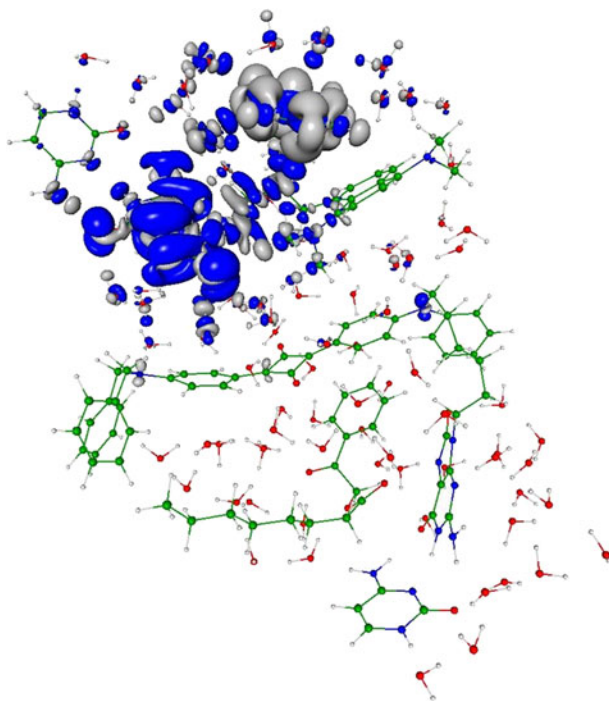


Fig. 9 Visualization of the electron charge tunneling associated with the 8th (413.5 nm) excited state. The transition is mainly from oxo-guanine molecule connected with oxo-guanine connected with 1,4-bis(N,N-dimethylamino)naphthalene (in the top-right) to the pFA molecule in the same (1PhC) subsystem

Conclusions

It is possible to make the following statements concerning our investigated model system composed of two photosynthetic minimal protocells:

- 1) Two excited states (4th and 6th) of a photoactive supramolecular system are composed of HOMO, HOMO-1 and LUMO+1 states located on two sensitizer molecules and on a fatty acid precursor molecule. This coupling promotes electron hopping (tunneling) from these sensitizer molecules to the pFA molecules in the excited states.
- 2) Analysis by our methods in the different excited states allows us to separate quantum-entangled photosynthetic transitions between neighboring minimal protocell models. This means that a quantum-entangled phenomenon of energy and information transfer exists in these model units, which might correspond to living organisms which existed in the first stages of the emergence and evolution of life (Tamulis and Grigalavicius 2010a, b, 2011).
- 3) A two variable, quantum entangled AND logic gate was modeled in the system described, which consists of two input photoactive sensitizer molecules containing two different variable inputs and one output. In future, this process might be applied to nanomedicine.

Acknowledgments Jonas Baltrusaitis was a member of the Departments of Chemistry and Chemical/Biochemical Engineering, EMRB 75 University of Iowa, Iowa City, IA 52242, USA until July 2012 and is grateful for the use of the computing facilities at the University of Iowa for the work presented. This publication was also made possible by Grant Number UL1RR024979 from the National Center for Research Resources (NCRR), a part of the National Institutes of Health (NIH). Its contents are solely the responsibility of the authors and do not necessarily represent the official views of the CTSA or NIH. The 2000 node supercomputer of the University of Iowa was used for quantum mechanical investigations of the minimal micelle (1) and system of two minimal protocells (3). The quantum mechanical investigations of minimal cell (2) were performed on the Linux servers cluster of Vilnius University Institute of Theoretical Physics and Astronomy.

Authors are grateful to USA LANL scientist Hans Ziock for the editing the text of this paper. Hans Ziock is a visiting professor at the Center for Fundamental Living Technology, The University of Southern Denmark (SDU), Campusvej 55DK5230 Odense, Denmark. H. Ziock corrected the Introduction part concerning the new aspects of the artificial cell research done in LANL and SDU.

References

- Adamo C, Barone V (1999) Toward reliable density functional methods without adjustable parameters: the PBE0 model. *J Chem Phys* 110:6158–6169
- Becke AD (1993) A new mixing of Hartree-Fock and local density-functional theories. *J Chem Phys* 98:1372–1377
- Cape JL, Monnard P-A, Boncella JM (2011) Prebiotically relevant mixed fatty acid vesicles support anionic solute encapsulation and photochemically catalyzed trans-membrane charge transport. *Chem Sci* 2:661–671
- DeClue MS, Monnard P-A, Bailey JA, Maurer SE, Collis GE, Ziock HJ, Rasmussen S, Boncella JM (2009) Nucleobase Mediated, Photocatalytic Vesicle Formation from an Ester Precursor. *J Am Chem Soc* 131:931–933
- Ditchfield R, Hehre WJ, Pople JA (1972) Self-Consistent Molecular-Orbital Methods. IX. ... Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian-Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules. *J Chem Phys* 56:2257–2261
- Dreizler RM, Gross EKV (1990) Density functional theory. Springer-Verlag, Berlin
- Edson JB, Spencer LP, Boncella JM (2011) Photorelease of primary aliphatic and aromatic amines by visible-light-induced electron transfer. *Org Lett* 13:6156–6159

- Eichkorn K, Treutler O, Öhm H, Häser M, Ahlrichs R (1995) Auxiliary basis sets to approximate coulomb potentials. *Chem Phys Lett* 242:652–660
- Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery JA Jr, Peralta JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam JM, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas Ö, Foresman JB, Ortiz JV, Cioslowski J, Fox DJ (2009) Gaussian 09, Revision A.1. Gaussian, Inc, Wallingford
- Grimme S (2006) Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J Comp Chem* 27:1787–1799
- Jensen F (1999) Introduction to computational chemistry. John Wiley & Sons, Chichester-Toronto
- Marques MAL, Ullrich CA, Nogueira F, Rubio A, Burke K, Gross EKV (2006) Time-Dependent Density Functional Theory, Lecture Notes in Physics Vol. 706, Springer, Berlin Heidelberg, ISSN 1616-6361, DOI 10.1007/b11767107
- Maurer SE, Deamer DW, Boncella JM, Monnard P-A (2009) Chemical Evolution of Amphiphiles: Glycerol Monoacyl Derivatives Stabilize Plausible Prebiotic Membranes. *Astrobiology* 9:979–987
- Maurer SE, DeClue MS, Albertsen AN, Dörr M, Kuiper DS, Ziock H, Rasmussen, Boncella JM, Monnard P-A (2011) Interactions between catalysts and amphiphilic structures and their implications for a protocell model. *ChemPhysChem* 12:828–835
- Mojzsis SJ, Arrhenius G, McKeegan KD, Harrison TM, Nutman AP, Friend RL (1996) Evidence for life on Earth before 3800 million years ago. *Nature* 384:55–59
- Neese F (2003) A spectroscopy oriented configuration interaction procedure. *J Chem Phys* 119:9428–9443
- Neese F (2009) ORCA – an ab initio, density functional and semiempirical program package, Version 2.6.04 Max-Planck-Institut fuer Bioorganische Chemie, Muelheim an der Ruhr and Universitaet Bonn
- Rasmussen S, Chen L, Nilsson M, Abe S (2003) Bridging nonliving and living matter. *Artif Life* 9:267–316
- Rasmussen S, Bailey J, Boncella J, Chen L, Collis G., Colgate S, DeClue M, Fellermann H, Goranovic G, Jiang Y, Knutson C, Monnard P-A, Mouffouk F, Nielsen PE, Sen A, Shreve A, Tamulis A, Travis B, Weronski P, Woodruff WH, Zhang J, Zhou X, and Ziock H (2008) Assembly of a minimal protocell. In Rasmussen S, M. Bedau A, Chen L, Krakauer DC, Deamer D, Packard NH, and Stadler PF (ed), *Protocells: Bridging nonliving and living matter*, Editors: S. Rasmussen, M. A. Bedau, L. Chen, D. C. Krakauer, D. Deamer, N. H. Packard, and P. F. Stadler, MIT Press, Cambridge, Massachusetts, USA, pp 125–156
- Rieper E, Anders J and Vedral V (2011) Quantum entanglement between the electron clouds of nucleic acids in DNA, arXiv:1006.4053v2 [quant-ph], Available at: <http://arxiv.org/abs/1006.4053v2>
- Rinkevicius Z, Tamulis A, Tamuliene J (2006) δ -diketo structure for quantum information processing. *Lith J Phys* 46:413–416
- Schmidt MW, Baldrige KK, Boatz JA et al (1993) General atomic and molecular electronic structure system. *J Comput Chem* 14:1347–1363
- Tamuliene J, Tamulis A, Kulys J (2004) Electronic structure of dodecyl syringate radical suitable for ESR molecular quantum computers. *Nonlinear Anal Model Control* 9:185–196
- Tamulis A (2008a) Quantum self-assembly of artificial minimal living cells and molecular electronics control. *Viva Origino* 36:10–19
- Tamulis A (2008b) Quantum mechanical control of artificial minimal living cells. *NeuroQuantology* 6:311–322
- Tamulis A (2008c) Quantum mechanical interpretation of the origin of life. In Ruksenas O (ed) *Science in the Faculty of Natural Sciences of Vilnius University, Proceedings of 5th science conference*, Vilnius, October 03, 2008, Publishing house of Vilnius University, pp 7–19
- Tamulis A (2011) Quantum Mechanical Investigations of Photosynthetic Systems of Artificial Minimal Cells Based on 8-Oxo-Guanine-Ru(bipyridine)₃2+. *J Comput Theor Nanosci* 8:624–636
- Tamulis A, Grigalavicius M (2010a) Quantum mechanical origin of genetic material in minimal protocells. *J Comput Theor Nanosci* 7:1831–1841
- Tamulis A, Grigalavicius M (2010b) Quantum mechanical evolution of fatty acids world life. *Viva Origino* 38:4–17
- Tamulis A, Grigalavicius M (2011) The Emergence and Evolution of Life in a “Fatty Acid World” Based on Quantum Mechanics. *Orig Life Evol Biosph* 41:51–71
- Tamulis A, Tamulis V (2007a) Quantum self-assembly and photoinduced electron tunneling in photosynthetic system of minimal living cell. *Viva Origino* 35:66–72

- Tamulis A, Tamulis V (2007b) Question 9: Quantum self-assembly and photoinduced electron tunneling in photosynthetic systems of artificial minimal living cells. *OLEB* 37:473–476
- Tamulis A, Tamulis V (2008) Quantum mechanical design of molecular electronics OR gate for regulation of minimal cell functions. *J Comput Theor Nanosci* 5:545–553
- Tamulis A, Tsifrinovich VI, Tretiak S, Berman GP, Allara DL (2003a) Neutral Radical Molecules Ordered in Self-Assembled Monolayer Systems for Quantum Information Processing, arXiv.org e-Print archive, Quantum Physics, available at: <http://arxiv.org/list/quant-ph/0307?100>, quant-ph/0307136 [abs, pdf], July, 2003
- Tamulis A, Tamuliene J, Tamulis V (2003b) Quantum mechanical design of photoactive molecular machines and logical devices. In: Nalwa HS (ed) *Handbook of photochemistry and photobiology*, Volume 3, Supramolecular photochemistry. American Scientific Publishers, Stevenson Ranch, pp 495–553
- Tamulis A, Tamuliene J, Tamulis V, Ziriakoviene A (2004) Quantum mechanical design of molecular computers elements suitable for self-assembling to quantum computing living systems. *Solid State Phenomena*. Scitec Publications, Switzerland, pp 97–98, 175–180
- Tamulis A, Tamulis V, Graja A (2006) Quantum mechanical modeling of self-assembly and photoinduced electron transfer in PNA based artificial living organism. *J Nanosci Nanotechnol* 6:965–973
- Tamulis A, Tsifrinovich VI, Tretiak S, Berman GP, Allara DL (2007) Neutral radical molecules ordered in self-assembled monolayer systems for quantum information processing. *Chem Phys Lett* 436:144–149
- Tamulis A, Tamulis V, Ziock H, Rasmussen S (2008) Influence of water and fatty acid molecules on quantum photoinduced electron tunnelling in photosynthetic systems of PNA based self-assembled protocells. In: Ross R, Mohanty S (eds) *Multiscale simulation methods for nanomaterials*. John Wiley & Sons, Inc, New Jersey, pp 9–28
- Tamulis A, Grigalavicius M, Medzevicius G, Krisciukaitis S (2012) Quantum Entangled Photosynthesis and OR Logic Gates Controlling Minimal Artificial Cell. *J Comput Theor Nanosci* 9:351–359
- Treutler O, Ahlrichs R (1995) Efficient molecular numerical integration schemes. *J Chem Phys* 102:346–354
- TURBOMOLE V6.0 (2009) A development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007. Available via <http://www.turbomole.com>
- Weigend F, Ahlrichs R (2005) Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design an assessment of accuracy. *Phys Chem Chem Phys* 7:3297–3305