



Photoferroelectricity in di-phenylalanine peptide nanotubes

V.S. Bystrov*

Institute of Mathematical Problems of Biology, Keldysh Institute of Applied Mathematics of RAS, 142290, Pushchino, Russia

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ABSTRACT

Molecular modeling and computational analysis are carried out for photo-induced and photo-luminescence effects in di-phenylalanine (FF) peptide nanotubes (PNT) using quantum-chemical semi-empirical approach PM3 in unrestricted Hartree-Fock (UHF) and restricted (RHF) approximation. HyperChem package tool is applied. The data obtained from the main photo-ferroelectric phenomena (the values of the forbidden band gap E_g and its shift under an applied electrical field, “red” shift of the photo-luminescence after photo-excitation) are compared with phenomenological thermodynamic theory of photo-ferroelectricity based on the Landau-Ginzburg-Devonshire expansion. The data computed are in good agreement with those obtained within phenomenological thermodynamic description. It means that the proposed quantum description and computational analysis throw new light on our understanding of these important phenomena and could serve as a new theoretical and modeling basis for investigation of photoferroelectricity in such peptide tubular molecular nanostructures and other related systems.

1. Introduction

The tubular nanostructures and properties of the self-assembled di-phenylalanine peptide nanotubes (FF PNT) are in the focus of many investigators at the last time and are intensively studied [1–13]. Especially, the polarization and piezoelectric properties were wide investigated: were established the strong piezoelectricity and switching peculiarities, obtained and confirmed ferroelectric properties [14–19], investigated phase transition at the $T \sim 150^\circ\text{C}$ and established Currie-Weiss law in the phase transition vicinity with Currie-Weiss constant $C_{Wb} \sim 260\text{ K}$. All these unique properties were corroborated by computer molecular modeling and calculations [18,19]. Moreover, the investigated phase transition was firstly predicted namely by computer molecular dynamics simulation [10,18,19] and performed detailed computational molecular modeling allowed to clarify many of ferroelectric properties [20] of FF PNT at the molecular nanoscale level. Nevertheless, one feature is not enough investigated. It is possibilities of the optical and photoferroelectric phenomena in this FF PNT. Some peculiarities of such effects were recently considered in the work [21], where reported about a blue photoluminescence phenomena with red shifting, and several light-induced effects was studied in Ref. [22].

In this work computer molecular modeling and computational analysis of possible photoferroelectric phenomena in the FF PNT were presented, based on our recent computer simulation, molecular-mechanical and quantum-chemical calculations of the FF PNT structures

and properties [14–19], using HyperChem molecular modeling package [23] with quantum semi-empirical PM3 method and several others calculations. Physical mechanism of these photoferroelectric phenomena was described early by Fridkin V.M [24,25] based on the general thermodynamic approach [20,26] and had a phenomenological description [20,26]. Now this approach could be joined and with so-called a bioferroelectricity [19,27] (which are inherent in many organic and biological molecules and compounds) on the common atomic-molecular basis with quantum electron properties taken into account.

2. Computational and models details

2.1. Main computational approaches and details

The molecular modeling and quantum-chemical calculations using Hartree-Fock restricted and unrestricted (RHF/URF) approaches in semi-empirical PM3 method using HyperChem 8.01 package are presented. The determination of total optimized energy of each studied molecular models and corresponding energy values for electron molecular orbital, such as, Low Unoccupied Molecular Orbital (LUMO) - E_{LUMO} and Highest Occupied Molecular Orbital (HOMO) - E_{HOMO} , were performed. These calculations were made, firstly, for initial preliminary optimized models in zero electric field and then for several simulated values of the external applied electric field E (using for this aim a special option in HyperChem software [23]). The applied electric

* Group of Computer Modeling of Nanostructure, Dept. of Prospective Information Technology, Institute of Mathematical Problems of Biology, Keldysh IAP RAS, Vitkevicha Str., 1., Pushchino, 142290, Russia.

E-mail addresses: vsbys@mail.ru, bystrov@ua.pt.

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field had their component E_z along the main c -axis of the nanotube. The main features of such computational approach was elaborated early and were described in Refs. [14–19]. More details are presented below in our published papers for other similar systems [28–32].

For a deeper understanding and further detailed studies of the molecular structure FF PNT, and the possible mechanisms of their self-organization, self-assembly and phase transitions in their structures, the molecular computer modeling and a detailed study of their structural and physical properties (including electronic structure and the electronic quantum levels, the electrical properties, etc.) was conducted, including the dynamics of their behavior in an electric field and a changes with temperature. These studies were carried out by various methods of molecular modeling with self-consistent structural (geometrical) optimization and molecular dynamics (MD) simulations using mainly HyperChem software package version 7.52 and 8.01 [23]. The main results of example for full data computed for RHF case is presented in [Supplementary Materials section S1](#), and in [S2](#) are shown examples of the main images.

2.2. Main used computational methods and approaches

Currently, there are already exist a wide arsenal of various computer software packages that allow for molecular modeling. In this paper has been used already well and enough tested and approved in the several our studies of other similar systems [28–32] software package HyperChem [23]. It combines several of the most important methods, such as methods based on classical Newton physics - the methods of the molecular mechanics (MM, such as BIO CHARMM), used for systems with a fixed effective charges of atoms, and the quantum-chemical methods (QM), when explicitly taken into account the electronic subsystem with all its quantum properties. It was used in a very broad range of the most modern approximations – from the *ab initio* methods (“from first principles”) and density functional theory (DFT), up to a large set of the different effective semi-empirical methods. These QM methods are the self-consistent field (SCF) Hartree-Fock (HF) calculations as based on *ab initio* and DFT, as well as for the semi-empirical methods (such as PM3), in both restricted Hartree-Fock (RHF) and unrestricted Hartree-Fock (UHF) approximations.

In HyperChem is also possible to perform the wide calculations and the molecular dynamics (MD) simulations, as well to simulate the application of an external electric and magnetic fields, and to optimize the geometrical structure of the molecular system under the influence of these fields. These features are just necessary for us in these studies.

The performed work was used all of the various numerical methods, and combinations thereof. Our experience has shown that for such organic molecular systems of the type as PNT or PVDF, including in its structure mainly carbon atoms (C), oxygen (O), nitrogen (N), fluorine (F), phosphorus (P) and hydrogen (H), very good and fast method is a quantum-chemical semi-empirical method PM3 (parameterization number 3). PM3, developed by Stewart [33–36], is based on the so-called “neglect of diatomic differential overlap (NDDO)” approximation, with several modifications and with the choice of a wide number of parameters to reproduce experimental quantities. For PVDF and FF PNT, the most accurate HF calculations are based on the HF Hamiltonian of the full molecular system, with valence double electron wavefunctions including correlation interactions on d-polarization functions for C and F atoms, and p-polarization functions for H atoms. However, using DFT calculations for all similar system with a higher level of accuracy usually required a very long time and a large amount of computer memory. PM3 generally is the most accurate and rapid QM computational method, utilizing several experimental parameters to simplify the calculation process [25]. Therefore, we tried to compare the calculated data with faster and simpler semi-empirical quantum-chemical methods, such as PM3 approximation.

It works very effectively, both important for the description and quantum calculations of the electronic subsystem cases, as in the RHF

and UHF. We often use both of these approaches to clarify and confirm the convergence of the computed data. Method PM3, especially in the UHF approximation is often the most convenient and rapid method for calculating the redistribution of the total charge of the system (including their quantum interactions in the redistribution of the electronic wave functions) and the polar dipole properties of this molecular system that is just and necessary for us in this work for the calculations of the molecular structure consisting of carbon, oxygen, nitrogen and hydrogen. In some cases, for more complex models of the studied structures, we use a combination of techniques - combining quantum calculations (QM) based on the PM3, with MM methods. One of the most appropriate of the MM methods set, was proved BIO CHARMM method. To test calculations and results at the higher level of the accuracy we also used various approximations of the DFT methods. But in a reasonable and efficient combination of them with semi-empirical methods, we obtain the most good practical results.

The key point of the whole approach of the computerized molecular modeling is a numerical optimization of the structure of the investigated system, which is based on the finding the minimum of the system total energy, or - the generalized potential energy surface (PES) of the system. This fully self-consistent process of the searching for the optimal structure is its self-organization into the energetically most favorable form and structure. The optimization of molecular geometry is executed using the Polak–Ribere (conjugate gradient) algorithm, which determines an optimized geometry at the minimum energy point (using PES) [23].

In our particular case FF PNT, the key point is the precisely formation of this self-consistent (self-assembly) stable molecular structure (in various environmental conditions - temperature, electric field), corresponding to the minimum energy of the whole system. Furthermore, as we have shown on the basis of this performed simulation, the main point is the formation of the hydrogen bonds and the quantum mechanical ordering of the entire system of the dipoles emerging molecular structure. Namely, due to the nonlinear quantum interaction there is arisen much greater (than it would be in the case of a simple summation), the total dipole moment of the entire system - spontaneous polarization, sharply oriented with the preferred direction. And this non-linear effect of the cooperative dipole ordering is one of the main characteristic properties of the ferroelectrics.

2.3. . Main model details

As it was previously established, in their main ferroelectric phase (at the room temperature) FF PNT reveals very strong piezoelectric effect, high polarization (directed along the PNT tube main axis) and high coercive field, restricted the polarization switching in this state [10,11]. One of the most promising developed molecular computational models of such FF PNT structure is presented on [Fig. 1](#) [10,18,19]. As result, the dependence of the polarization from electric field computed from this model ([Fig. 2](#)) leads to high coercive field $E_c \sim 45$ MV/cm (with initial zero field polarization $P_0 \sim 0.04$ C/m²), which can not switch the polarization.

Thus, inside PNT exist strong intrinsic electric field along c -axis, which must influence on the photo-excited electrons and holes in this dielectric (or semiconductor) materials. One of the well defined analysis of the basic principles of the followed photoferroelectric phenomena nature was made in book [24]. Based on these approaches we suppose that all related phenomena must be observed and described similarly in this case in FF PNT.

3. Analysis, results and discussions

First, if it is followed from analysis of high polarization field inside FF PNT and high coercive field [18], the corresponding electronic orbitals E HOMO and E LUMO must be shifted in this intrinsic electrical field and the values of forbidden zone gap E_g must changed too, in

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