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Electronic transitions in two micelles system: DFT and TD-DFT approaches

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ABSTRACT

In this work, a supramolecular quantum mechanical self assembly of two minimal-protocells (micelles) containing 696 atoms is studied using density functional theory and its time dependent version. This two micelles system is initially optimized using semiempirical PM3 method. Their frontier molecular orbitals are analyzed using DFT-PBEPBE/6-311++G(d, p) method and excited states are calculated using TD-DFT//PBEPBE/6-311++G(d, p) method. The electronic transitions corresponding to these excited states are discussed. We have noticed a number of transitions which can be used for information exchange within this two micelles system.

Keywords: Quantum self assembly, minimal protocells, electronic transitions, molecular orbitals.

INTRODUCTION

The word “micelle” is the contraction of minimal protocell, which are of special interest for applications in the biotechnologies. These micelles act as the container for artificial minimal cells which are synthesized in Los Alamos National Laboratory (US) [1]. The container consists of amphiphilic fatty acid molecules that self-assemble into a micelle. The hydrophobic interior of the micelle provides an alternative thermodynamic environment from the aqueous or methanol exterior and acts as a sticking point for the photosensitizer, fatty acid precursors (food), and the genetic material. The quantum mechanical self-assembly of a system containing two micelles has been considered in this study. The electronic structure of this system has been explored by density functional theory (DFT) using the electron correlation approach. DFT has already been employed in a number of studies on various molecular systems of biological and pharmacological importance [2-8]. Apart from this, DFT has established itself as a popular tool for study of other molecular systems, such as inorganic molecules and small clusters [9-12].

Time dependent DFT (TD-DFT) is used to find excited states properties i.e. the various electronic excitations within the molecular system. It has successfully been applied for studying the nature of electronic transitions in many biomolecules [13, 14]. In this work, we have employed TD-DFT approach in order to explore electronic transitions within the two micelles system with different photosynthetic centres.

MATERIALS AND METHODS

The initial distance between the edging molecules in two micelles was kept a few times larger in comparison with the experimental van der Waals distances between organic molecules. This initial configuration has been optimized using semiempirical PM3 method. The process of geometry optimization reduced the distance between the two micelles to the experimental van der Waals distances due to Van der Waals and hydrogen bonding interactions between these micelles. The PM3 optimized structure of two micelles system has been used for single point energy calculations using DFT method with PBEPBE functional [15] and 6-311++G(d, p) basis set. The same geometry has

also been employed for TD-DFT calculations. All calculations are performed by using GAUSSIAN 09 program [16] using 20 parallel processors.

RESULTS AND DISCUSSION

This two micelles system consists of 696 atoms. It contains 45 water molecules, 14 fatty acid (FA) molecules, 2 precursor of fatty acid (pFA) molecules and two different sensitizer molecules viz. bis(4-diphenylamine-2-phenyl)-squarine (in micelle 1) and 1,4-bis(N,N-dimethylamino)naphthalene (in micelle 2) as shown in Fig. 1 which is optimized at PM3 level.

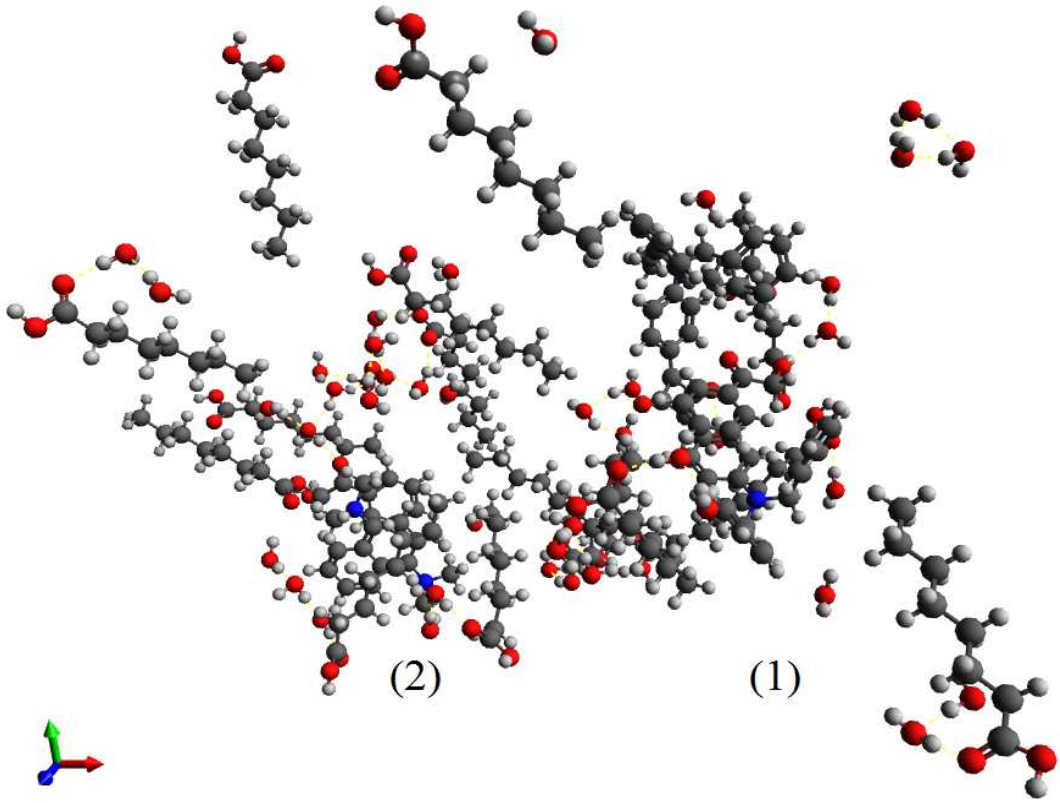

Fig. 1. PM3 optimized structure of two micelles system considered in this study. Red, dark grey, light grey and blue spheres represent O, C, H and N atoms, respectively.

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are frontier orbitals which participate in chemical reaction or interaction with other systems. Virtually, the HOMO corresponds to the ground state of the system and LUMO corresponds to its first excited state. So, any transition from HOMO to LUMO leads to the charge transfer from one region to another within the system. The HOMO-LUMO gap is important parameter to measure the chemical hardness i.e. tendency of a system to interact with other species. The smaller gap between HOMO and LUMO allows enhanced tunneling of photoexcited electrons and hence, measures the electronic transport properties. It also provides a quantitative estimate of the charge transfer interactions. For a two micelles system, the HOMO and LUMO surfaces calculated by DFT-PBEPBE/6-311++G(d, p) are shown in Fig. 2. The HOMO-LUMO gap for this two micelles system is found to be 0.1930 a. u. One can see that the HOMO is mainly located near the sensitizer molecule in micelle 2 whereas LUMO is primarily contained by sensitizer molecule in micelle 1. Therefore, the transition from HOMO to LUMO essentially corresponds to the electron density exchange between sensitizer molecules in two micelles system.

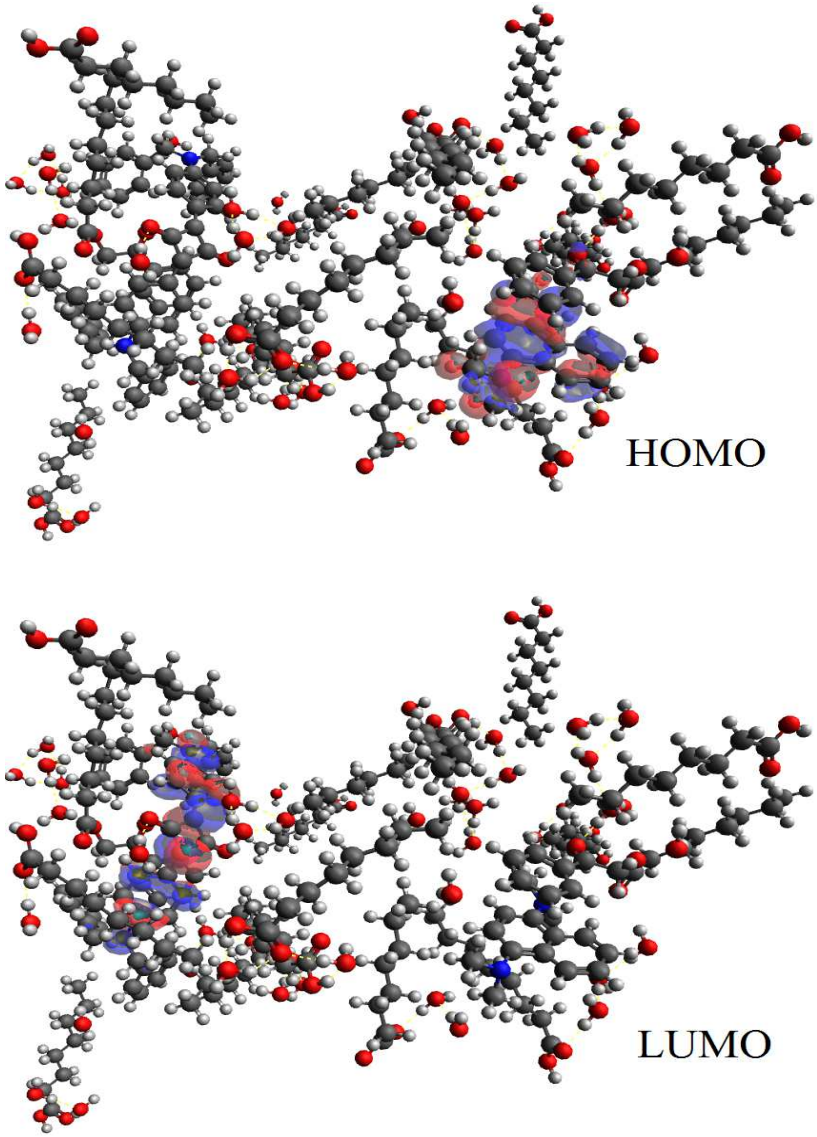

Fig. 2. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of two micelles system calculated by DFT-PBEPBE/6-311++G(d, p) method.

In order to get further insights into electronic transitions, we have calculated UV-visible spectrum of two micelles system using TD-DFT method which is shown in Fig. 3. One can note that the substantial transitions in the system are calculated at 565.21, 546.86, 473.76, 466.64 and 330.25 nm. The most prominent peak corresponds to the excitation wavelength of 546.86 nm.

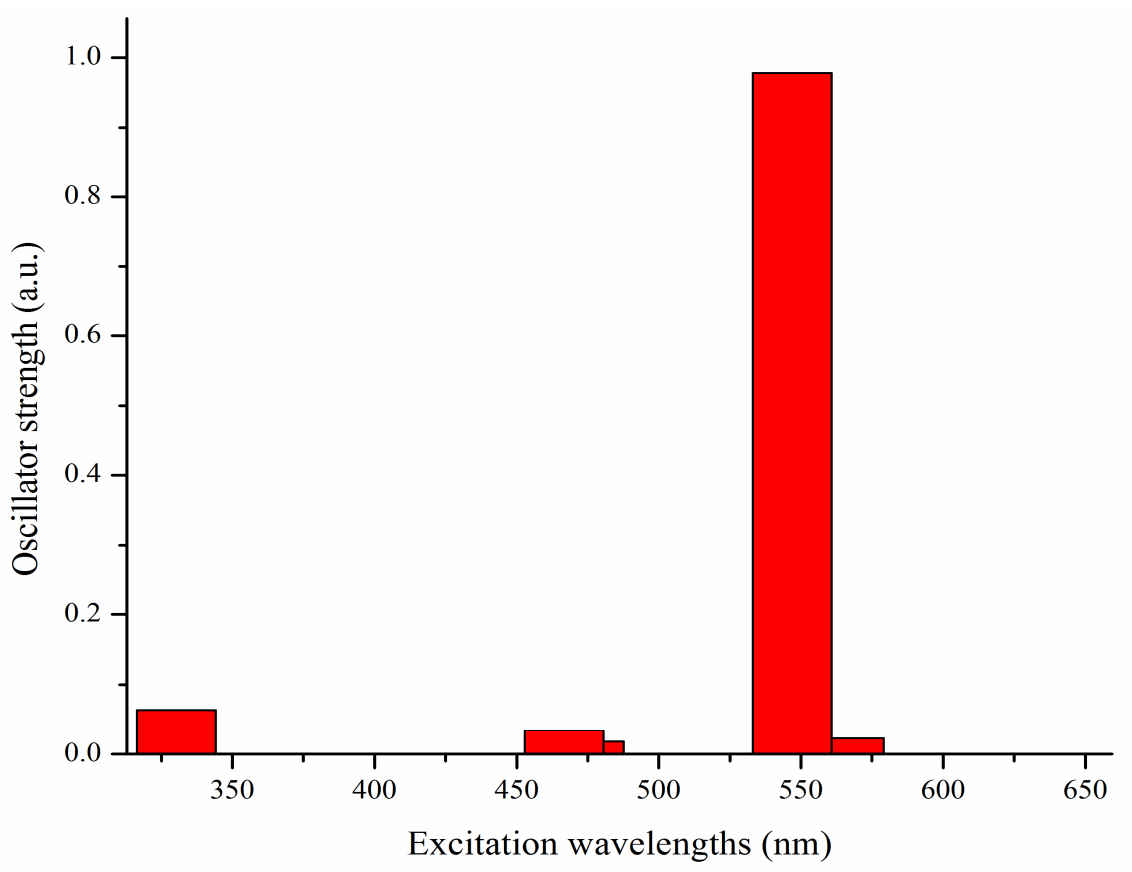

Fig. 3. UV-visible spectrum of two micelles system calculated by TD-DFT//PBEPBE/6-311++G(d, p) method.

We have analyzed electronic transitions within two micelles system up to 10 excited states as given in Table 1. Table 1 lists the vertical excitation energies (*E*), oscillator strength (*f*) and maximum excitation wavelength (λ_{max}). The oscillator strength is an important factor for the measurement of absorptivity as well as the intensity of an electronic transition i.e. how strongly the particular electronic transition is allowed. It is a dimensionless quantity defined as by the formula,

$$f = 4\ m_e\ c\ \varepsilon_0\ B/\ N_A\ e^2$$

where m_e is the mass of the electron, ε_0 the vacuum permittivity, N_A Avogadro constant, e is the elementary charge and B is the molar natural absorption coefficient integrated over the whole band units of frequency. The oscillator strength is a number usually close to zero and one. Forbidden transitions have oscillator strengths close to zero, while bands arising from electronically allowed transition show value of order of one.

Table 1. Electronic transitions in two micelles system

Excited state	Electronic transitions	Excitation energy, *E* (eV)	Oscillator strength, *f* (nm)	Excitation wavelengths, λ_{max} (nm)
1	HOMO → LUMO	1.9307	0.0000	642.17
2	HOMO→LUMO+2	2.1936	0.0228	565.21
3	HOMO-1→LUMO	2.2672	0.9778	546.86
4	HOMO-2→LUMO+1, HOMO-1→LUMO+2, HOMO+5→LUMO	2.6170	0.0179	473.76
5	HOMO-1→LUMO+2	2.6570	0.0344	466.64
6	HOMO→LUMO+2	2.7746	0.0000	446.86
7	HOMO-2→LUMO+1	3.1755	0.0000	390.44
8	HOMO→LUMO+4	3.2032	0.0000	387.04
9	HOMO-1→LUMO+3	3.2094	0.0000	386.31
10	HOMO-2→LUMO+5	3.3025	0.0633	330.25

The analysis of 1st excited state clearly indicates that it is mainly described by an electron excitation from HOMO to LUMO i.e. the electron density transfer between sensitizer molecules within two micelles systems, as mentioned earlier. Therefore, there is a possibility of information exchange from the micelle 2 to the micelle 1 and vice versa.

In order to explain electronic transitions for higher excited states, we have calculated HOMO-m and LUMO+n molecular orbitals for m, n = 1, 2, 3 and 4. These molecular orbitals are displayed in Fig. 4.

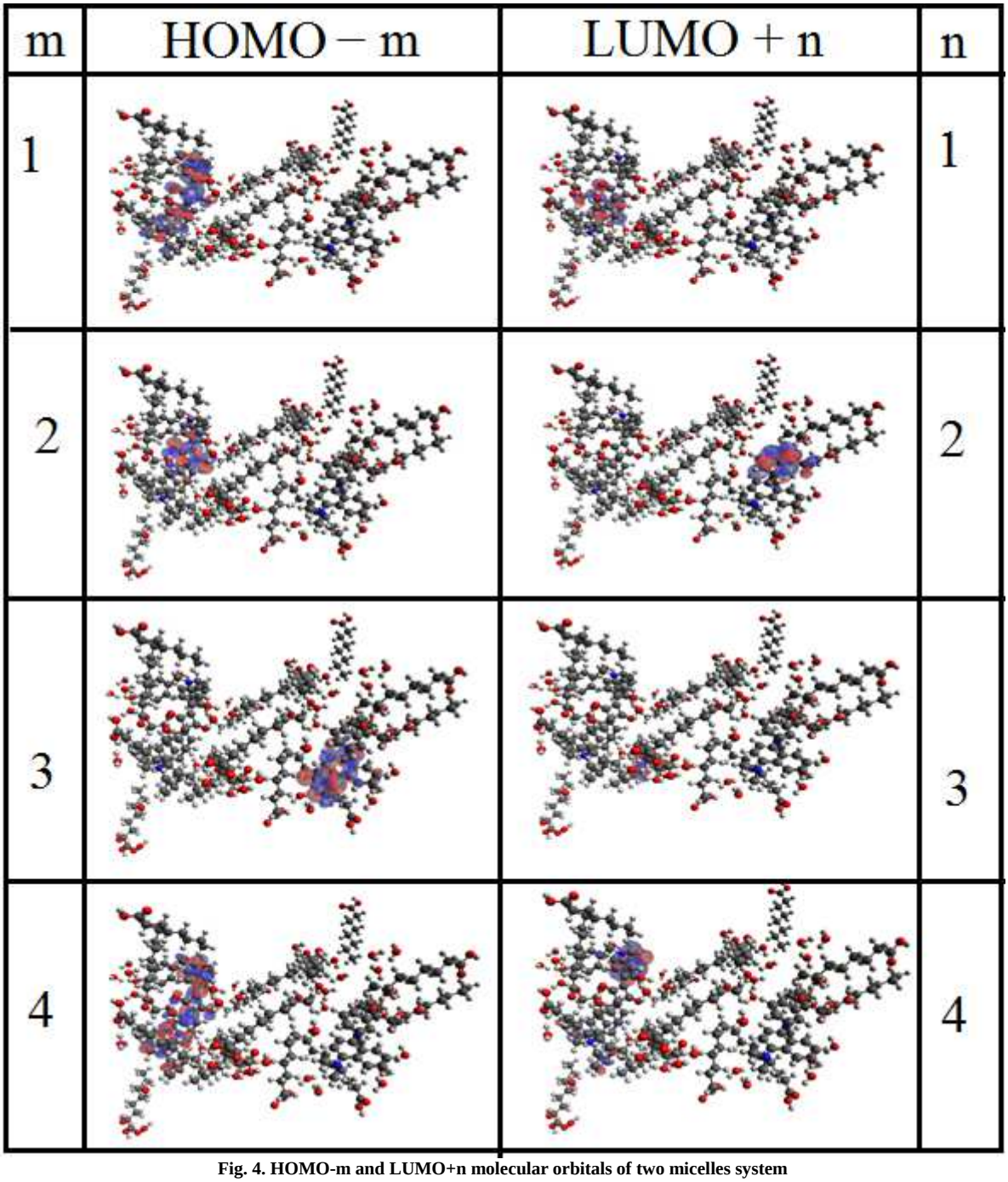

Fig. 4. HOMO-m and LUMO+n molecular orbitals of two micelles system

The second electronic transition (2nd excited state) corresponds to the transition HOMO→LUMO+2. Note that the LUMO+2 is localized near the sensitizer molecule in micelle 2. Therefore, this transition leads to the electron density localization in the micelle 2 of two micelles system. Similarly, the most intense transition (3rd excited state) corresponds to the electron density localization within micelle 1 of two micelles system (see Table 1 and Fig. 4).

The 4th excited state corresponds to the coupling of three transitions: HOMO-2→LUMO+1, HOMO-1→LUMO+2 and HOMO+5→LUMO. Out of these three transitions, HOMO-1→LUMO+2 can be used to exchange information between two micelles as it corresponds to the electron density transfer from micelle 1 to micelle 2 in two micelles system. Similar conclusion holds for the 5th excited state as it corresponds to the same transition HOMO-1→LUMO+2 (see Table 1).

For even higher excited states, 8th excited state which involves transition HOMO→LUMO+4 and leads to electron density exchange within micelles 1 and 2 in two micelles system. However, for all these excited states (from 6 to 9), the oscillator strength is essentially zero. Thus, these transitions are less likely to take place as compared to those with non-zero oscillator strengths.

CONCLUSION

We have analyzed the electronic transitions in quantum self assembly of two micelles systems using DFT and TD-DFT approaches. The self assembly contains the nonlinear electron-correlated hydrogen bonds and van der Waals interactions that result from the addition of water and fatty acids molecules. These nonlinear interactions among the atoms compress the micelles systems and resulting in the decrease in the HOMO-LUMO gap. The most intense transition has been identified and properly assigned. We have explored a number of transitions which can be used for information exchange within this two micelles system. These findings may be useful for further investigations on similar two micelles system and their applications in biotechnology.

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