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Full Length Research

Study of electronic and transport properties of melanin structure using Density Functional Theory

Suleiman A. B[1*], Mansur Sa'id[2], Babaji G.[3], Galadanci G. S. M.[3] and Taura L. S.[4]

[1]Department of Physics, Federal University, Dutse, Nigeria.
[2]Department of Physics, Yusuf Maitama Sule University Kano, Nigeria.
[3]Department of Physics, Bayero University, Kano, Nigeria.
[4]Departmrnt of Physics, Sule Lamido University, Kafin Hausa, Nigeria.

*Corresponding author. Email: suleiman_abdussalam@yahoo.com; Tel: +2348039644595.

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ABSTRACT: Organic semiconductors are a relatively new member of the semiconductor family and composed of molecules containing carbon, hydrogen, and another element. Melanin is a pigment that colours skin, eyes and hair and it could soon be facing a new generation of biologically friendly electronic devices in applications such as medical sensor and tissue stimulation treatment. The need to find the correct solvent for the melanin still remains challenged. In this work the electronic properties of eumelanin was studied under gas phase and solution, using Integral Equation Formalism Polarizable Continuum Model (IEFPCM) using different solvent. Total energy, Homo-Lumo energy gaps and density of states were reported. Gaussian09 code which uses density functional theory as the working principle was used to study the electronic and transport properties of melanin structure. Three exchange functional: HF (HF), GGA (PBE) and Hybrid (B3LYP) were used at different basis set of 3-21G, 6-31G, and 6-311G. It was found that at the 6-311G level for the three exchange functional, the total energy of -2981.03028, -2996.839821 and -3000.227297 eV respectively. However, HOMO-LUMO energy gap in gas phase was improved to be 2.65 eV and 2.79 eV, 2.65 eV in DMSO and Acetonitrile respectively. It was concluded that DMSO solvent is more efficient for melanin compound. However, it is recommended to increase the level of approximation.

Keywords: Bandgap, DFT, DOS, HOMO, LUMO.

INTRODUCTION

Melanin as pigment was identified to have other functions apart from been a bio-macromolecules, it is found to be among the organic semiconductors. It can be found mostly in; human skin, hair, inner ear and even brain. It was identified to be black or brown depending on the composition and structural differences. Melanin can either be eumelanin (with Nitrogen attached between carbons) or Pheomelanin (with Sulfur attached between carbons) or neuromelanin (Prota, 1980). Not only biologist, melanin attracted much of the attention of biophysicists due to the fact that a part from biological functions, melanin exhibits an interesting physical property such as high electrical conductivity leading to the suggestion that they could act as amorphous organic semiconductors (McGinness, 1972). Its threshold switching behavior revealed that it can be used for electronic devices.

Synthetic Melanin has attracted condense matter community. Due to its physical and biochemical behaviour and its possibilities of combining amorphous semiconductor with that of broadband monotonic absorption from UV-vis to NIR (Near Infrared). Also, it can be converted from photons into phonons (Meredith et al., 2006). Different devices can be produced from the synthetic melanin such as chemi-sensors, new generation solar cells and many other bioelectronics devices. Also, it signals the possibilities of acting as an effective radiation sensitizer that could improve spectral range and efficiency of superconducting transition-edge bolometers (Seppa, 2001).

Sheliakina et al. (2018) reported that melanin is an

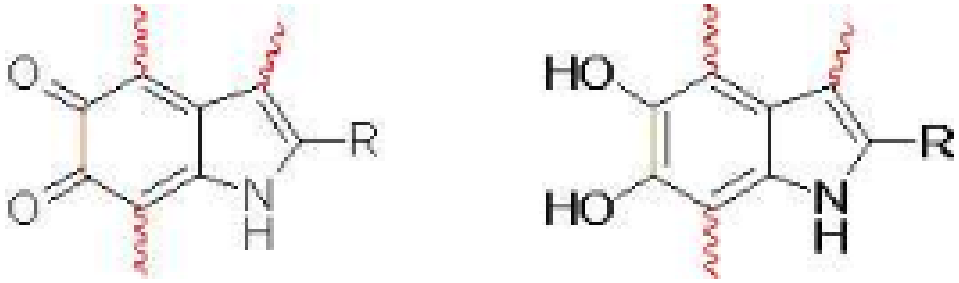

Figure 1. The building blocks of eumelanin. R represents a COOH group in DHICA and a H in DHI. Squiggly lines indicate sites of attachment to the extended polymer and possibly to proteins. The details of these attachments in the total complex structure are not known.

electronic-ionic hybrid conductor, rather than the amorphous organic semiconductor, which opens up new opportunities in bioelectronics given its biocompatibility. Although the overall composition of eumelanin is reasonnably understood, the exact structure remains ambiguous.

Two major types of melanin are pheomelanin and eumelanin. It is well-known that eumelanin, the black-brown variety of melanin, results from the oxidative polymerization of two building blocks, 5,6-dihydroxyindole (DHI) and 5,6-dihydroxyindole 2-carboxylic acid (DHICA). The monomer structure as shown in Figure 1, with polymerisation points (Giacomantonio, 2005) is thought to link randomly with each other and some precursors to form oligomers and polymers. The monomer molecules can be in various oxidation states as such, melanin is not a conventional, single, well defined molecule, but rather, a heterogeneous mixture of similar macromolecules made from random linkages of these basic structural units. *In vivo*, melanins also exist intermixed with other molecules such as proteins.

There have been many attempts in applying melanin in various devices in order to improve the performance of the devices. McGinness et al. (1974) modified 'thio-capped gold nanoparticles with melanin' in order to combine magnetic properties and biocompatibility. Giacomantonio (2005) reported that water plays vital role in studying charge transport mechanisms and suggests that proper control of hydration needed. McGinness et al. (1974) report the DC conductivity of $10^5 S/cm$ at room temperature and suggest that melanin can may be a future semiconductor and also report the switching behaviour similar to that observed in some inorganic amorphous semiconductors. Baraldi et al. (1979) report the DC conductivity of 1012 S/cm at room temperature after five minute steady state flow of current. Dielectric spectroscopy study on the synthetic powder of melanin report that the two main hopping polarization observed was due to water assisting and the distance between the hopping decreases as the temperature increases. Photoconductivity measurement on natural melanin shows that the amplitude of photocurrent increased by more than one order of magnitude with an increase in hydration from 3 to 40 weight percent adsorbed water (Giacomantonio, 2005).

Selvaraju et al. (2016) reported that substituents can change the electronic characteristics of these molecules, hence changing their optoelectronic properties and the energy gap 2.50eV (Baraldi et al., 1979).

The primary advantage of ab initio methods is the accuracy with which calculations are performed. To the degree that a researcher needs to know a property that most accurately matches experimental data or that most approximates a theoretical prediction, the ab initio method is chosen. Ab initio methods are used by researchers to study the properties of molecules which are of great importance in pharmaceutical industry, materials science and in drug designing. Gaussian package program was used by several researchers to study the compounds of pharmaceutical interest, industrial chemicals, NLO materials and etc (Frisch et al., 2009).

However, search for suitable solvent for melanin is still remains challenging. It was reported that ammonia solution yielded rather homogenous film in microscale (Abbas et al., 2009). Also, Abbas et al. (2009) reported that melanin dissolved in dimethyl sulfoxide methanol (DMSO) solution in a concentration of 0.2 mg/ml. Thus, the objective of this research is to study the electronic properties of eumelanin under gas phase and then in solution using Integral Equation Formalisms Polarizable Continuum Model (IEFPCM) using different solvent. Total energy, Homo-Lumo energy gaps, and Density of state were reported.

COMPUTATIONAL PROCEDURE

Gaussian 09 software package (Frisch et al., 2009) was used by many researchers to study molecular, electronics, phonons, vibration spectra (IR, Raman, NMR and UV-Vis), Phonons, potential energy surface, thermodynamics properties (heat reactions and energy activation) and other observable properties (dipole moment, polarizability, etc.). The programme uses density functional theory and with highest accuracy in determining the ground state energy which most accurately matches experimental data. The

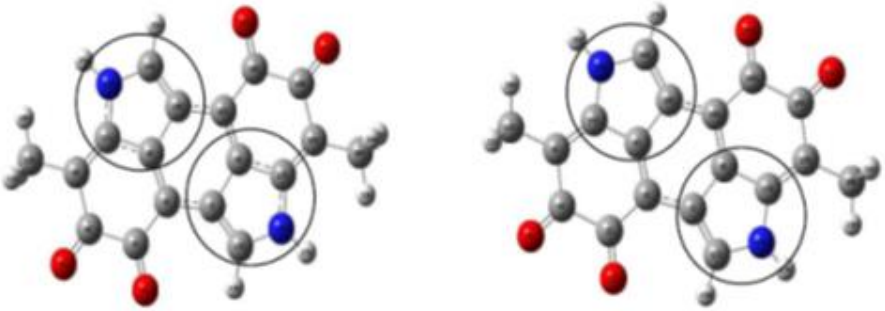

Figure 2. Structure of melanin molecule (a) Before optimization (b) After optimization with B3LYP/6-311G.

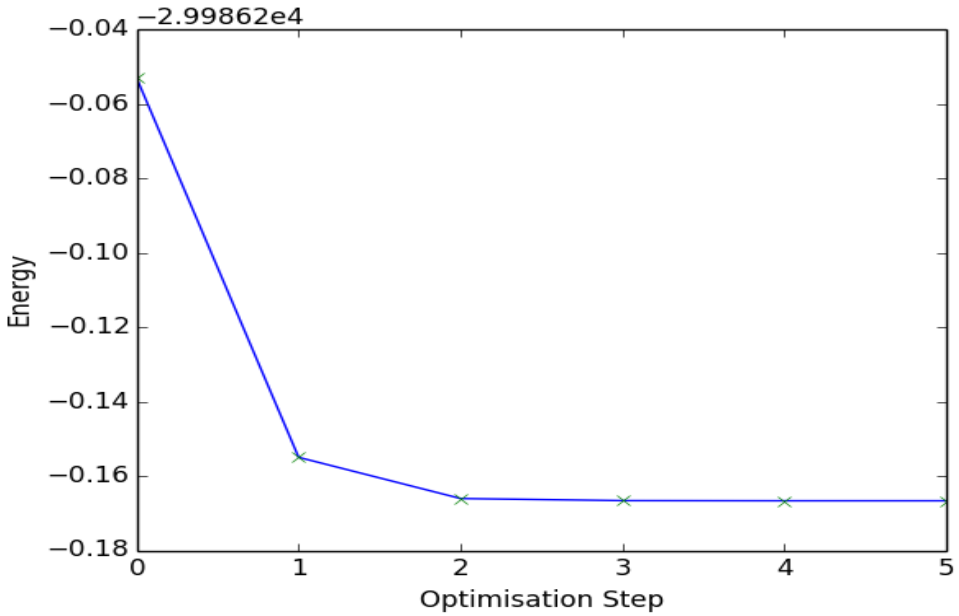

Figure 3. Geometry optimization steps vs Relative energy at B3LYP/6-311G level.

structure of melanin was sourced from Ligand expo (www.http://ligandexpo.rcsb.org). The geometry was optimized using the basis sets; 3-G, -311G and 6-311G and Hatree Fock (HF) exchange and correlation functional. The result of the structure optimizations were recorded. Similar optimizations were performed with Generalized Gradient Approximation (GGA) and Hybrid approximation (HA). The results were also tabulated.

However, solvent search calculation was performed using Integral Equation Formulation Polarizable Continuum Model (IEFPCM ICP) and different solvents; Acetone (C_3H_6O), Acetonitrile (C_2H_3N), Aniline ($C_6H_5NH_2$), Benzene (C_6H_6), Carbon tetrachloride (CCl_4), Chlorobenzene (C_6H_5Cl), Chloroform ($CHCl_3$), Cyclohexane (C_6H_{12}), Dichloroethane (CH_2Cl_2), Diethlyether ($(C_2H_5)_2O$), DMSO ($(CH_3)2SO$), Heptane (C_7H_{16}), Menthol ($C_{10}H_{20}O$) and Toluene ($CH3NO_2$). The HOMO-LUMO energies were recorded and energy gaps were calculated. Density of state (DOS) was utilized to further understanding the structural behaviour of the melanin molecule. This was also used to determine the electron population of the structure.

RESULT AND DISCUSSION

Figure 2 showed the geometry structure of melanin molecules. The structure was optimized systematically due to the limitation of working environment. The disappearrance of double bond between carbon and nitrogen was due to the effect of optimization at DFT/B3LYP.

The geometry optimization technique is like sliding down from the top of the hill. Figure 3 shows how the energy of the molecule is changing with the change in step and it was

Table1. Variation of energy with change in the basis set at different exchange functional.

S/N	Basis Set	Total Energy XC (HF) (eV)	Total Energy XC (PBE) (eV)	Total Energy XC (B3LYP) (eV)
1.	3-21G	-2964.9789	-2983.394342	-2983.394402
2.	6-31G	-2980.41389	-2996.234493	-2999.592476
3.	6-311G	-2981.03028	-2996.839821	-3000.227297

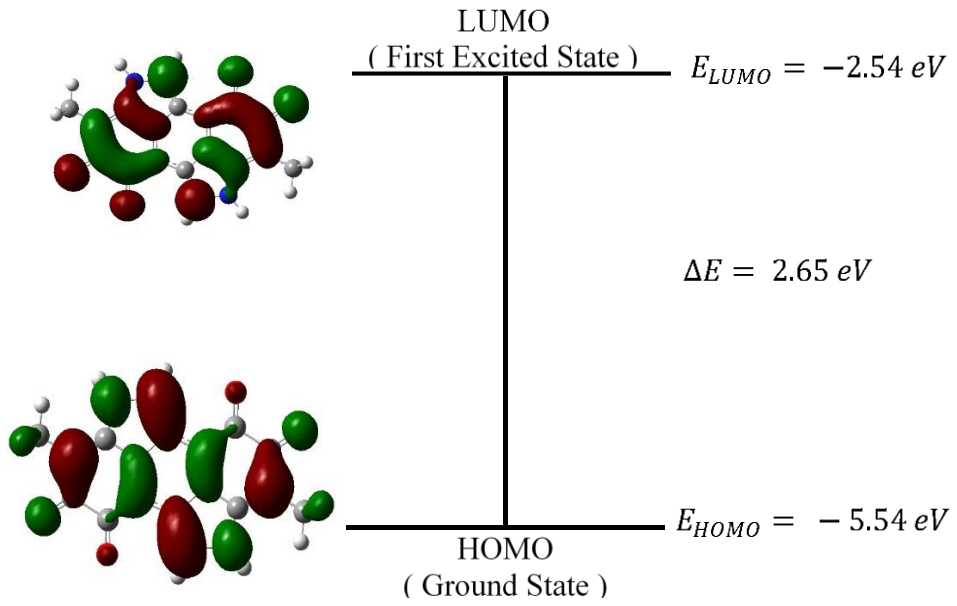

Figure 4. Isosurfaces of the HOMO and LUMO for Melanin. The red regions correspond to negative values, while the green regions correspond to positive values. at B3LYP/6-311G level.

was observed that the structure almost stabilized at step 2 but for consistency the programme allows up to five steps before it reach the convergence. This characterized that the structure is in ground state as expected.

The total energy for the three exchange and correlation approximations were tabulated in Table 1. For each approximation and the basis set; 3-21G, 6-31G and 6-311G is set and each time the total energy was recorded. It was observed that as the basis set increase the total energy of the system is approaching the ground state. Also, it can be seen that the accuracy of B3LYP is greater than that of PBE and HF as expected. For this reason, the final geometry at B3LYP/6-311G was chosen for other calculation of the electronics properties.

The geometry optimization was performed on a gas phase medium. Figure 4 shows the frontier molecular orbital at gas phase of melanin structure. In the HOMO region there were more positive molecular orbital than that of the negative ones with an estimation of energy of -5.54eV. This indicates that there is every possibility of electrons to transfer from the higher valance band to the lower conduction band. Also, at LUMO there is equal number of positive and negative molecular orbital with energy of -2.54eV and the energy band gap 2.65eV.

The scout out for the right solvent for the melanin quiescently requires to be elaborated. Gaussian code enables investigation of more solvent by considering the energy gap. The energy gap of HOMO–LUMO explains the eventual charge transfer interaction within the molecule, which influences the biological activity of the molecule. The HOMO is located over the group and the LUMO is located below the group. The HOMO→ LUMO transition implies an electron density transferring throughout the structure. Furthermore, moving from the gas phase to the solvent phase, the increasing value of the energy gap and molecule becomes more stable as shown in Table 2. Consequently, the lowering of the HOMO–LUMO band gap is essentially a consequence of the large stabilization of the LUMO. This is due to the strong electron-acceptor ability of the electron acceptor group.

Table 2 above shows the result for the search of solvent of melanin performed using B3LYP/311G on the following solvents as contains in the Gaussian09. For each solvent the result of frontier molecular orbital (Highest Occupied Molecular Orbital (HOMO), Lowest Unoccupied Molecular Orbital (LUMO)) and Band Gap were shown. It was

Table2. Variation of energy with change in the basis set at different exchange functional.

C_3H_6O	C_2H_3N	$C_6H_5NH_2$	C_6H_6	CCl_4	C_6H_5Cl	$CHCl_3$	C_6H_{12}	CH_2Cl_2	$(C_2H_5)_2O$	$(CH_3)2SO$	C_7H_{16}	$C_{10}H_{20}O$	$CH3NO_2$	$(CH_2)_4O$	Theoretical (**eV)	Experimental (***eV)
HOMO																
-5.03	**-5.03**	-5.07	-5.13	-5.14	-5.08	-5.09	-5.14	-5.05	-5.06	**-5.02**	-5.14	-5.03	-5.03	-5.06	**-5.44**	**-5.55**
LUMO																
-3.10	**-2.38**	-2.96	-3.82	-3.82	-2.95	-3.92	-3.91	-3.83	-3.83	**-2.24**	-3.83	-3.29	-3.82	-3.83	**-2.70**	**-2.74**
Energy Gap																
1.93	**2.65**	2.11	1.31	1.32	2.13	1.17	1.23	1.22	1.23	**2.79**	1.31	1.74	1.21	1.23	**2.70**	**2.85**

(Selvaraju et al 2016, Morresi et al 2010). *(Selvaraju et al. 2016).

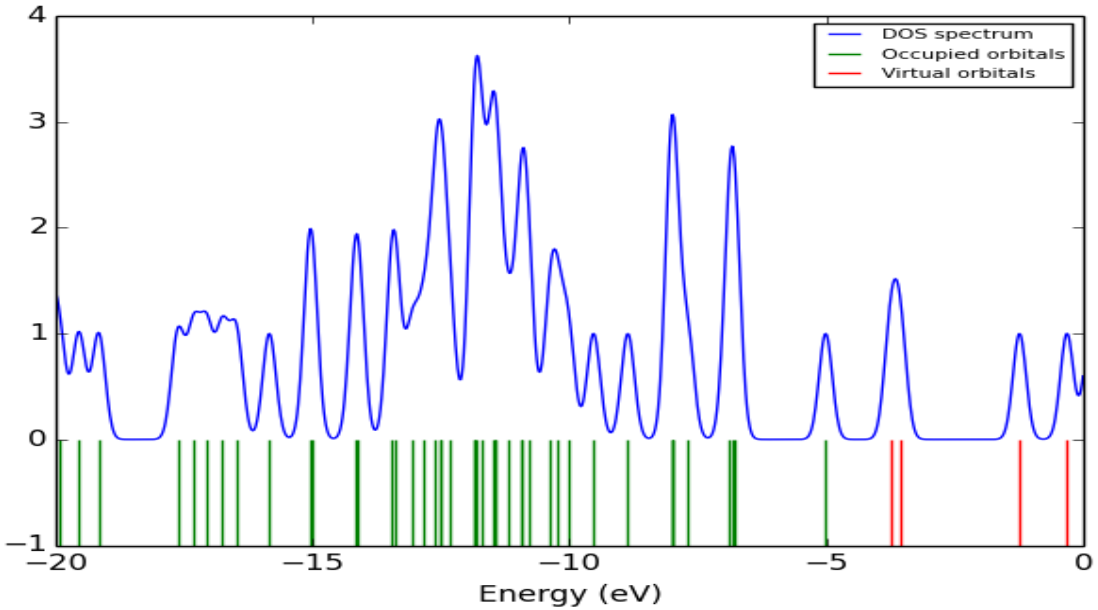

Figure 5. Density of state spectrum of melanin at B3LYP/6-311G level.

observed that DMSO has the band gap of 2.79 eV which is in agreement with the result obtained by Selvaraju et al. (2016) and Morresi et al. (2010). Also, Acetonitrile has the band gap of 2.65 eV which lags the literature by 0.05eV.

Figure 5 shows the electron population density of melanin structure. Three different levels of the spectrum were observed; DOS spectrum (blue), Occupied orbitals spectrum (green) and Virtual

spectrum (red). From the Figure 5, it shows that that there are more electrons at the occupied state and distributed over the large area of the highest conduction band. This shows that the conductivity of the electron can be classified as that of the semiconductor.

Conclusion

Melanin is an organic material which was predicted to be a promising semiconductor and has many potential applications in nanotechnology such as in medical sensor and tissue stimulation treatment. Density functional theory approach was used to report the result of geometry optimization and ground state energy of the structure. Effect of approximation and basis were reported. Frontier molecular orbital result at gas phase and solvents were shown and the best energy gap of 2.79, and 2.65 for the solvent DMSO and Acetonitrile respectively. 2.65eV energy gap was found in gas phase medium. DOS, occupied orbital spectrum and virtual orbital spectrum of the electron formation were observed. It was suggested that melanin pigment can be extracted and used in nanoscale devices.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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