Computational Study of Curcumin and Its Analogues for Dye-Sensitized Solar Cell Application

Yusthinus T. Male¹, Mirella F. Maahury¹, and I Wayan Sutapa¹

¹ Chemistry Department, Faculty of Mathematics and Natural Science, Pattimura University
Jl. Ir. M. Putuhena, Ambon, Indonesia

E-mail: yusmale@fmipa.unpatti.ac.id

Abstract. Computational study of curcumin and its analogues for dye-sensitized application has been done by using Density Functional Theory (DFT) with B3LYP method at 6-31G (d) basis set. Computational shows that the structures of curcumin and its analogues are symmetrical. Analogues of curcumin are more stable than curcumin. Analogue A2 is potential to apply as active material on organic solar cell because it has small band gap (0.126 eV). Analysis of orbital populations showed that there is charge transfer from phenyl ring to middle chain (ketone).

Keywords: Curcumin, DFT, B3LYP, Energy gap, Orbital populations

1. Introduction

Organic photovoltaics are promising alternative to inorganic solar cells. Application of dye-sensitization in photovoltaics called Dye-Sensitized Solar Cell (DSSC). Natural dye has a number of advantages; low cost, widely available and non toxic materials. Fabrication of DSSC limited on its low efficiency. Much of the research in dye chemistry is devoted to the identification and synthesis of dyes matching these requirements [1,2].

One type of organic solar cell is dye sensitized nanocrystalline TiO₂ solar cells. The use of dye sensitization in photovoltaics called Dye-Sensitized Solar Cell (DSSC) [3,4]. Oligomers and monomers that absorb visible light are called chromophores and are referred to as dyes [5]. There are two kind of dye, they are natural dye and sintetic dye. Natural Dye is more favorable than sintetic dye sintetik consider abundant availability, inexpensive and non-toxic. Anthocyanin, curcumin, chlorophyll and caroten are some of natural dye.

Several studies has been conducted to obtain some potential dye as the active material in organic solar cell, i.e. using of anthocyanins from red cabbage extracts as photosensitize [6] or extracts from rosella flower (Hibiscus sabdariffa, L.). Curcumin is one of the natural dye that gives a distinctive yellow color.Stability of curcumin is
influenced by pH and light, so modifications the structure of curcumin is very important [7].

Curcumin and its analogues have been known as active materials in organic solar cell. By experimental method, many solar cell active materials has been produced but their properties could not be predicted before they were synthesized.

In this research, computational chemistry has been used to study theoretical aspect of active materials in organic solar cell. Computational chemistry is very useful to predict structure, mechanism and reaction thermodynamics so that chemists will be able to determine the structure and electronic properties of polymer organic/dyes compounds that have not been synthesized yet.

An alternative ab initio method, i.e. Density Functional Theory-DFT, was chosen in this research using Gaussian 03 software. Reliable computation of optimized geometries, energies, and electronic structures of transition metal containing system is known to require extensive consideration of electron correlation effects. The Hartree-Fock (HF) method without configuration interaction turns out to be inadequate and a treatment of electron correlation by multiconfigurational procedure is computationally expensive [7].

DFT methods are promising alternatives to the traditional ab initio methods for characterizing these systems because they include electron correlation in the exchange-correlation functional. DFT method has been proven that it is efficient enough to calculate macromolecules properties. In this research, computational method has been used to predict structure, energy, electronic spectrum and band gaps from curcumin and its analogues.

2. Methods

Density-Functional calculation were performed by using Gaussian 03 for windows with hybrid functional B3LYP (Becke’s three-parameter hybrid functional) at 6-31G(d) basis set. Input structures was drawn by Hyperchem™ 8.0; GaussView 3.07 as viewer and GaussSum 2.2 for generate Infra Red (IR) spectrum.

Input structures was hypothetical curcumin (Ao), curcumin (A) and analogues of curcumin (A1-A3), as shown in Figure 1, consecutively.
3. Results and Discussion

3.1 Geometry optimization of Curcumin and its analogues

Optimized structures of curcumin and its analogues was shown in Fig.2, while they parametric of geometry (bond, dihedral and bond lengths) can be seen in Table 1 (Appendix 1). These data shows that the geometry parameters of the phenyl rings systems (ring I and II) of curcumin and its analogues are identical. For further discussion, we only used ring I of the phenyl ring system.
Figure 2. Optimized structures
3.2 Electronic Properties of Curcumin and its Analogues

Electronic properties such as atomic charge, dipole moment, energy and the energy gap of curcumin and its analogues were shown in Table 2 (Appendix 1). From Table 2, from energy point view, it can be seen that analogues curcumin more stabilized than curcumin. Substitution of methoxy and hydroxyl groups on the phenyl ring systems generate the positive charge of C atoms. Conversely, substitution of chlorine atom on the phenyl ring lead to reduction the charges of C atoms. With calculation based on electronic structure theory, it can be shown here that incorporation of methoxy and hydroxyl substituent created red shift in the UV spectra of the complex to visible region. A good agreement between computational results and experimental data have shown the capabilities of this method to predict the properties of new active materials.

Table 2 also shown that the dipole moment values for each compound depend from kind of substituent. The main atomic orbitals of HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) have been analyzed and proven that A2 compounds has lower energy gap (0.126 eV).

3.3 Orbital Population

Molecular orbital analysis of major component of HOMO and LUMO is performed to determine the effect of the addition substituent to an excited state. Main atomic orbital populations of curcumin and its analogues are presented in Table 3 (Appendix 2). The main components of HOMO and NHOMO curcumin and curcumin analogues A1, A2 and A3 derived from p orbitals of C4 atom on the phenyl ring, while the main component comes from the LUMO p orbitals of atoms Cl in the center of the ring system. This are assigned to charge transfer from the phenyl ring to the middle of the chain.

3.4 Infra Red Frequency of Curcumin and Its Analogues

Infra red analysis showing absorption bands in region 681.75 to 1637.65 cm\(^{-1}\) (C = O), as shown in Fig.3. This results showing good agreement with experimental results.
Figure 3. IR Spectrum of curcumin (a), analogue A1 (b) and analogue A2 (c)

4. Conclusion

Computational calculations of dye compounds curcumin and its analogues shows that the structure and electronic properties of curcumin and its analogues have symmetrical properties. Curcumin analogues are more stable than curcumin. Analogue A1 has the smallest energy gap which is a promising material DSSC application. Orbital population analysis, indicate a transfer of charge from the phenyl ring to the middle chain (ketone) as well as the incorporation of substituents increase the population of $p$ orbitals of $C$ atoms substituted position.

5. Reference


