



USING TECTONIA GRANDIS (TEAK) TO GENERATE ELECTRICITY FROM SUNLIGHT

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ABSTRACT

This paper presents theoretical studies for the suitability of natural dye, tectonia grandis (Teak) structure of (1,4,5,8-tetrahydro-2 isopentadienyl anthraquinone), to be used as photo-sensitizer for the process of photoelectric conversion in the environmentally-friendly green solar cell. The efficiency of photosensitization from natural dye is normally low, however, it can be improved by using the effect of the extracting solvent. Density functional theory (DFT) with B3LYP/6-31G (d) is used to study the photo-electrochemical properties such as the ground state geometries, excitation energy and electronic structures of the dye in different solvents. The UV-Vis absorption spectra of the dye is simulated by time dependent DFT. From the analyses of electronic and optical properties, it is found that the teak dye satisfy as a potential photosensitizer candidate for DSSCs.

Keywords: tectonia grandis, DFT, DSSCs.

INTRODUCTION

Solar energy is one of the harvesting renewable energy for solving the present and future energy crisis. For searching and developing of solar cells with low-production costs, high-energy conversion efficiency and good stability are essentially needed (Li *et al.* 2006). The nano-crystalline dye-sensitized solar cell (DSSC) is a sort of photovoltaic device that presented by O'Regan and Grätzel in 1991. Dye-sensitized solar cells (DSSCs) have been attracted a great interest in scientific research and for practical applications due to its potential advantages of being low cost, non-toxic, easy production flexibility and environmentally friendly as compared to convention silicon solar cells. Among several types of dye-sensitized solar cells, green dye-sensitized is a good applicant for use in biologically-friendly solar energy device (Liu *et al.* 2008). The dye sensitized solar cell consists of a metal oxide semiconductor photo anode, a dye sensitizer, an electrolyte and counter electrode. The performance of the cell principally depends on a dye used as a sensitizer. The photo excitation of the dye sensitizer is ensued by electron injection into the conduction band of the semiconductor during the photosensitization process. The molecule of the dye is regenerated by the redox system which itself is regenerated electrons at the counter electrode (Tai *et al.* 2011).

The dye, photosensitizer, plays an important role in absorbing sunlight and transporting electrons into the conduction band of the semiconductor, converting the energy from sunlight into electricity with photovoltaic effect in DSSCs. The metal-organic complexes, the ruthenium polypyridyl complexes (N719 and N3), have been validated to be best DSSC dye sensitizers as a result of its high efficiency (Nazeeruddin *et al.* 2005). These dyes are, however, based on expensive rare metals as well as unfriendly environment outcome. The metal-free

organic dye sensitizers, such as the natural dye, can be extracted from various parts of the vegetables, flowers, trees and even from insects. These organic dyes are easily available, inexpensive, non-toxic, environmentally friendly and fully bio-degradable for DSSCs application (Jie *et al.* 2010).

In DSSCs, several natural dye pigments such as chlorophyll, betanins, anthocynins, carotenoids and tinnins are successfully used as sensitizers. An abundance amount of research is going on to improve the efficiency of the natural dye sensitizer by using the combination of dyes, increasing on the concentration of the dye and extraction in various solvents, etc (Ananth *et al.* 2014). Apart from experimental studies of the dyes, there were theoretical studies on the dyes by performing density functional theory (DFT) and time dependent DFT (TD-DFT) calculations to investigate the suitability of the dye as a photo-sensitizer. The density functional theory has appeared to be a reliable standard device for the theoretical treatment of structures over electronic and absorption spectra. TD-DFT is a time-dependent extension of DFT which can be used to predict reliable values of the valence excitation energies with common exchange-correlation functionals (Zhang *et al.* 2009), (Xu *et al.* 2010), (Wichien *et al.* 2013).

The natural dye extracted from the leaves of teak (Tectonia Grandis) mainly contains tectoleafquinone, 1,4,5,8-tetrahydro-2 isopentadienyl anthraquinone and tinnin (K. *et al.* 2010). The authors observed an open circuit voltage (V_{oc}) of 0.61V and a short circuit photocurrent densities (J_{sc}) of 0.29mA/cm² from the DSSC sensitized with teak extract. However, there is limited work on theoretical calculations to study the performance of this dye. In our study, we theoretically investigated this 1,4,5,8-tetrahydro-2 isopentadienyl anthraquinone, which is found in the leaves of tectonia



grandis (Teak), as a dye-sensitizer by performing density functional theory and time dependent DFT calculations. We also investigated the suitability of the dye in different extraction solvents.

Computational Study

The DFT/TD-DFT study provides an insight of molecular structures and physical properties which are useful for the interpretation and prediction of optical absorption spectra of the dyes at a molecular level.

All the calculations were performed using the Gaussian 09 software package. The ground state geometries were totally optimized without any symmetry constraints at the DFT level of theory with the Becke three parameters hybrid functional and the Lee, Yang and Parr correlational functional (B3LYP) using a standard 6-31G (d) method (Lee *et al.* 1988). Time dependent DFT (TD-DFT) calculations were carried out to obtain the excitation energies and oscillation strengths for the singlet-singlet transitions at the optimized geometry in the ground state and to examine the electronic transition properties of the teak in different solvents.

RESULTS AND DISCUSSIONS

The Geometric Structures

The chemical structure and optimized geometry of the teak structure (1,4,5,8-tetrahydro-2 isopentadienyl anthraquinone) are shown in Figure-1.

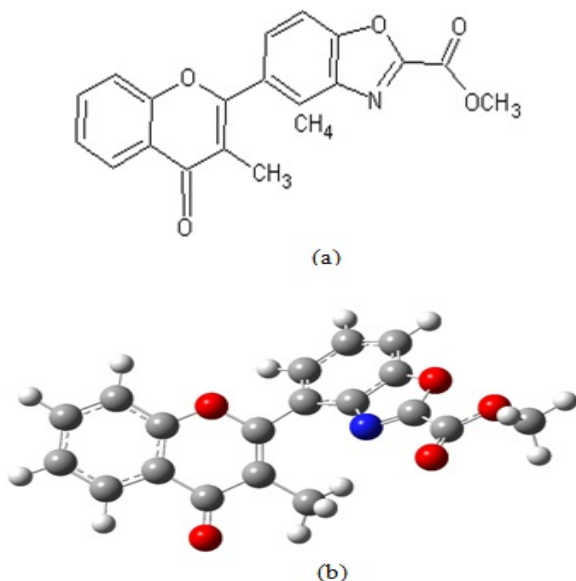


Figure-1. Structure of Teak (1,4,5,8- tetrahydro-2 isopentadienyl anthraquinone) (a) Chemical structure; (b) optimized geometrical structure.

Solvent Effects

Solvent, used in the extraction, could effect the geometry and electronic structure likewise the properties of molecule over the long-range relation between solute

molecule and solvent molecule (Zhang *et al.* 2009). The HOMO-LUMO gap of teak in different solvents for non optimized and optimized geometric are listed in Table 1. As observed in Table 1 (a) and (b), all the values of energy gap, ΔE (HOMO-LUMO), are almost the same. However, the values of energy gap after geometrical optimization were smaller than non optimized case. This indicates that the solvent effects support the stabilization of the LUMO and destabilization of the HOMO of the dyes in the optimized geometric.

Table-1. The value of the HOMO, LUMO and Energy gap.

(a) Without geometric optimization

Solvent	HOMO (eV)	LUMO (eV)	Energy gap(eV)
Vacuum	-6.40	-1.95	4.45
Ethanol	-6.48	-1.99	4.49
Methanol	-6.48	-2.00	4.48
Water	-6.48	-2.05	4.43
n-Hexane	-6.43	-1.96	4.46

(b) With geometric optimization

Solvent	HOMO (eV)	LUMO (eV)	Energy gap(eV)
Vacuum	-6.14	-2.33	3.81
Ethanol	-6.31	-2.35	3.96
Methanol	-6.31	-2.35	3.96
Water	-6.32	-2.36	3.92
n-Hexane	-6.20	-2.35	3.85

Electronic Structures

The frontier molecular orbitals (MO) energies of teak is shown in Figure-2. Although the energy gap of teak in all the solvents is almost the same, the calculated absorption spectra in ethanol (Figure-3) is the highest in the visible region as compared with other solvents. Therefore, we discuss the molecular orbitals energies of teak in ethanol. Figure-2, the result of energy levels shows that the dye extract from teak provides the conditions for photon-energy generation due to the position of the HOMO and LUMO. To completely inject the electron into the conduction band of TiO_2 , the LUMO levels of dyes must be adequately more negative than the conduction band edge of semiconductor (Ekanayake *et al.* 2013). From the suggestion that LUMO value, we can dye extract from teak leaves can achieve electron ejection and form the oxidized dyes. The comparatively large energy gaps between the LUMO of the dye and conduction band energy of semiconductor are satisfactory for efficient electron injection to the conduction band (Seksan *et al.* 2013).

The HOMO, lying at -6.31 eV, is a delocalized π orbital. The HOMO-1, lying 0.21 eV below the HOMO, is a localized π^* orbital over the entire ring. The LUMO, lying at -2.35 eV, is π^* orbital delocalized over the ring.



The LUMO+1, lying 0.26 eV above the LUMO, is π orbital mainly delocalized in the ring.

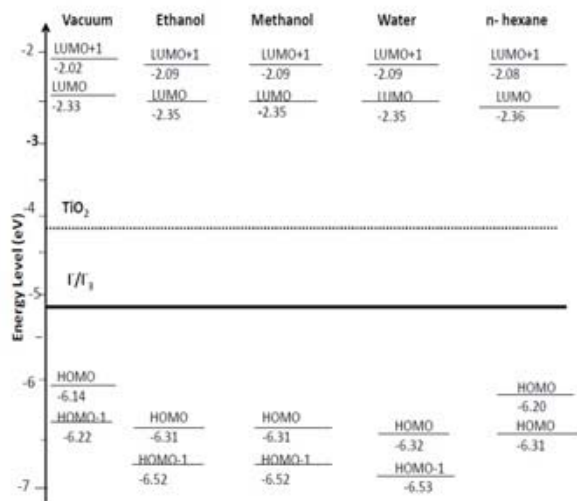


Figure-2. The calculated energy levels of Teak (1,4,5,8-tetrahydro-2 isopentadienyl anthraquinone) using B3LYP/6-31G(d) in vacuum, ethanol, methanol, water and n-hexane.

For efficient photo-to-current conversion, the microscopic information about the electronic transition in visible and near-UV region was investigated. The vertical excitation energy of oscillator strength larger than 0.01 and wavelength longer than 300 nm are listed in Table-2.

The optimized molecular structure of teak in ethanol and molecular orbital surface of HOMO-2, HOMO-1, HOMO, LUMO, LUMO+1 and LUMO+2 are shown in Figure-3. According to the optimized dye structures, the HOMO is mainly located on the donating group and the LUMO is located in electron withdrawing group through π^* type. The molecular orbital of HOMO is mainly localized on the benzylidene through π^* type. The $\pi \rightarrow \pi^*$ transition in HOMO-2 to LUMO+2 involves electron delocalization (Siriporn *et al.* 2013).

Table-2. Excitation energy (in eV), wavelength (nm) and the oscillator strength (f) of teak computed at B3LYP/6-31G(d) level with geometric optimization.

	Calculated Energy (eV)	(nm)	(f)	Composition
Vacuum	3.45	358	0.06	H \rightarrow L (54%),
	3.84	323	0.09	H-2 \rightarrow L(17%), H-1 \rightarrow L(13%)
	4.10	309	0.51	H-2 \rightarrow L(65%)
Ethanol	3.53	351	0.37	H-2 \rightarrow L(14%), H \rightarrow L (64%), H \rightarrow L+1(13%),
	3.81	325	0.19	H \rightarrow L+1 (64%), H-1 \rightarrow L+1(15%)
	3.89	318	0.74	H \rightarrow L+1(64%)
Methanol	3.57	346	0.19	H \rightarrow L (63%), H \rightarrow L+1 (24%)
	3.87	320	0.11	H-1 \rightarrow L (27%), H \rightarrow L+1(44%)
	3.96	312	0.31	H-1 \rightarrow L(27%), H-1 \rightarrow L+1 (44%)
Water	3.58	346	0.19	H \rightarrow L (63%), H \rightarrow L+1(24%)
	3.87	320	0.10	H-3 \rightarrow L (16%), H-3 \rightarrow L(15%)
	3.97	309	0.51	H-2 \rightarrow L(65%)
n-hexane	3.48	356	0.13	H \rightarrow L (60%)
	3.37	332	0.02	H-1 \rightarrow L+1(44%), H-1 \rightarrow L+1 (33%),
	3.82	324	0.11	H \rightarrow L(20%), H \rightarrow L+1(48%)

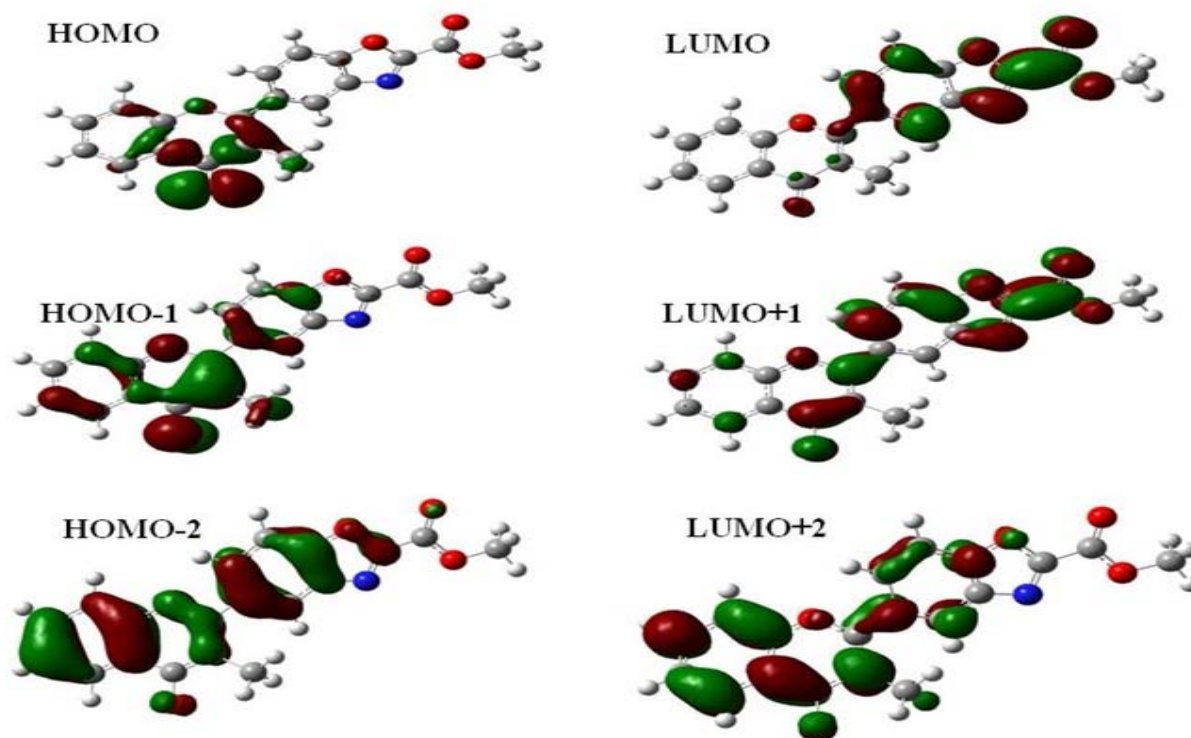


Figure-3. Molecular orbital diagram of teak (1,4,5,8- tetrahydro-2 isopentadienyl anthraquinone) in ethanol with isovalue of counter=0.03.

UV-Vis Absorption Spectra

TD-DFT theory is used to investigate the optical properties of the dye in solvents. The simulated UV-Vis absorption spectra of the dye is shown in Figure-4. As observed in the UV-Vis absorption spectra, the absorption bands of the dye in all the solvents leads to red shift in the absorption spectra. It also seen that the dye in ethanol is having the strongest absorption coefficient in the visible region as compared with other solvents. It is found that the absorption band of the dye in ethanol is centered at 351 nm in visible region.

For the teak dye, the absorption band near 351nm of simulated spectra in ethanol solvent effected from the electron transitions from the first state that is basically contributed by the two HOMOs and the final states which concern the first two LUMOs. Basically analysis over the transitions and molecular orbitals, the two absorption band of the teak dye in visible region are the $\pi \rightarrow \pi^*$ transitions. Moreover, the transitions of the absorption bands in visible region are mainly related to the energy level of the HOMO-2 \sim LUMO+1. In the transitions process, the first states are mostly related to the molecular orbitals that localized in electron acceptor groups. It can be seen that the absorptions are photoinduced electron transmission processes, in such a way the excitations generate charge separated states.

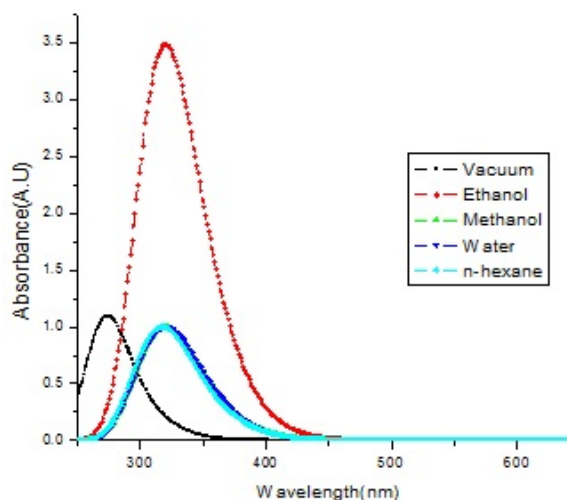


Figure-4. Simulated absorption spectra of Teak plotted to show the effect of the vacuum versus solvent effects.

CONCLUSIONS

In this work, the ground-state geometries and electronic structures of teak (1,4,5,8- tetrahydro-2 isopentadienyl anthraquinone) in various solvents were studied by using density functional theory with hybrid functional B3LYP and the excitation energy, electron transition and UV-Vis spectra were investigated by using TD-DFT methods. The high absorption coefficients in



ethanol make it more suitable for efficient light harvesting. The energy of the HOMO and LUMO is -6.31 and -2.35 eV, respectively. This shows that electron transfer from the excited dye to the TiO₂ conduction band is available.

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