Prominence of Using Betalain and Cubebin as Natural Dye Sensitizers for the Design of Eco-Friendly DSSC's

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ABSTRACT: Globally, the steady increase in 5% of energy per year has urged the need of alternative sources of renewable energy and has become a top challenge. The PV technology has become the most promising technology in harvesting the solar-energy. The use of natural pigments has become a viable alternative to expensive and rare Ruthenium dyes because of its low cost, easy attainability, abundance in supply of raw materials and no environment threat.   In this paper, we investigate the performance of Dye Sensitized Solar Cells (DSSCs) based on natural dyes extracted from Indian medicinal plants. Herein, Cubebin and Betalain dyes are extracted from fresh *Ocimum tenuiflorum and Piper nigrum*. FT-IR, FT-Raman, Photoluminescence and UV–visible light absorption characteristics of the dyes are used to identify the characteristic peaks of the extracted dyes. Features of the electronic absorption spectrum in the visible and near-UV regions were assigned based on TD-DFT calculations. These dyes are used as photo sensitizer for fabrication of TiO_2 photo-anode based dye sensitized solar cells (DSSCs). The photo-voltaic characteristics of the developed DSSCs are measured under simulated solar light. The solar to electric conversion efficiencies for the cubebin and betalain and mixed dye based solar cells are estimated as 0.39% and 0.38% respectively. The highest conversion efficiency for natural photo sensitizers based solar cell is attributed due to the absorption of wider range of solar spectrum.

KEYWORDS: DSSC, Energy, Solar Cells, Betalain, Cubecin, Photovoltaic, *Ocimum tenuiflorum, Piper nigrum*

1. INTRODUCTION

The research on solar cells has emerged as an alternative source of energy due to its emphasis over the usage of burning fossil fuels which has drastic harmful influence to the environment. Solar cells make use of inexhaustible sunlight as a free source of energy. The development of efficient solar cells will decrease mankind's dependence on fossil fuels that can significantly protect our natural resources. The research on solar cells made its impact as a vital technology among the various renewable sources of energy [1-2]. Solar cells based on the single silicon crystals were the first generation devices that evidenced the highest photon to current conversion efficiency. The high cost of production and installation of first generation solar cells make various researchers introduce the second generation solar cell devices made-up of semiconductor thin films. The unsatisfactory efficiency challenges of the second generation solar cells has led the path to the usage of pigments in the third generation solar cells popularly known as Dye sensitized solar cells (DSSCs). These devices are similar to plant photosynthesis that mechanizes the energy from the absorbed sunlight [3-7].

A dye-sensitized solar cell is usually composed of a dye capped nano-crystalline porous semiconductor electrode, a metal counter electrode, and a redox electrolyte mediating electron transfer processes that occurs in the cell. The performance of the cell primarily depends on the material and the quality of the semiconductor electrode and naturally extracted or synthesized stable sensitizer dyes. Even though several wide band-gap metal oxide semiconductors are employed in the DSSCs, TiO_2 and ZnO were the most predominantly and successfully used semiconductors [8-10].

The sensitizer plays a key role in absorbing light. Today, Ru (II) polypyridyl complexes were reported to obtain the highest efficiency. Unfortunately, the paucity of Ru metal and the difficulties in the ruthenium complex preparation have made the DSSCs as most expensive solar cells. To design the low-cost and good stability DSSCs, the search for potential alternative metal complex sensitizers urge to evaluate various organic dyes and natural dyes that were extracted from plants to explore their possibilities as photo-sensitizers. However, these dyes have been fraught with complications like synthetic routes and low yield. On the other hand, the natural dyes found in flowers, leaves, and fruits of plants can be extracted by simple procedures and can be employed in DSSCs. The natural dyes have advantages with resemblance in functionalities of organic dyes and their easy availability, non-toxicity, complete biodegradability and temperature compatibility [11-14].

Several Natural dyes namely tannin, carotene, anthocyanin, Betalain and chlorophyll have been extensively investigated as sensitizers in dye-sensitized solar cells [15-17].

Solar cells are the main photo-devices that achieve the conversion of light energy into electrical energy. In particular, the solar cells based on photosynthesis principle of plants and algae, have great potential for the development of stable DSSCs. An efficient solar cell sensitizer should demonstrate i) strong adsorption to the semiconductor surface through anchoring groups, ii) intense absorption in the visible part of the spectrum, iii) proper energy level alignment of dye excited state and the conduction band edge of the semiconductor, as well as the redox level of the electrolyte and the ground state of the dye, iv) fast charge transfer from the dye to the substrate, with low loss of photoelectrons, and v) electrochemical and thermal stability. In the attempt to find dyes satisfying these requirements, a large number of different molecules have been synthesized and characterized. The extraction and purifications of new dyes from plants and other materials are time and resource consuming. In spite of the importance, the computational studies were undertaken to evaluate the efficiency of the compounds as a promising alternative analysis. The interest for dye modeling and for more complex dye-substrate computational studies has been steadily increasing [18-23]. Achieving accurate results is challenging because of the size of the system, which in many cases consists of a relatively large number of atoms. In this context, density functional theory (DFT) and time dependent DFT (TD- DFT) methods have been applied to large molecules with reasonable accuracies of a few tenths of an eV, allowing for the description not only for the absorption spectrum of the dye but also for the more complex system consisting of the dye and the TiO_2 clusters. The dye bonding on the nanoparticle, the alignment of the energy levels of the two sub-systems, the transfer of the electron from the dye to the cluster can be successfully calculated by means of a DFT approach (24).

In this paper, we report the performance of dyes extracted from the leaves of siddha medicinal plants such as *Ocimum Tenuiflorum* and *Piper Nigrum*. The fabrication and electro- optical characterization of DSSCs by using Betalains and Cubebin as TiO_2 sensitizers were reported. Based on theoretical calculations the absorption onto the substrate, the matching of the absorption spectra, the energy level alignment, Photo luminescence properties and the charge transfer were discussed and the pigments were emphasized as sensitizers by comparing with experimental data. To the best of our knowledge, this is the first report on the usage of Betalains and Cubebin dyes as sensitizers for TiO_2 based dye-sensitized solar cells (DSSCs).

2. EXPERIMENTAL METHODS

The basic chemical structure of the pigment Betalain extracted from *Ocimum Tenuiflorum* and the cubebin pigment extracted from *Piper Nigrum* were shown Figure.1.

Preparation of Natural Photosensitizers

The medicinal plants of *Ocimum tenuiflorum* and *Piper nigrum* were collected from Kolli hills of Salem, Tamilnadu, India. The leaves were washed several times with distilled water to remove the dust particles and the residual moisture was removed under sun-dried condition. The dried leaves were crushed using mortar and pestle. The crushed powder was mixed with ethanol and the solution is left undisturbed in dark at room temperature. After one week, the residual parts were filtered out and the resultant is used as dye solutions.

Cell Assembly

The TiO_2 porous film electrode was prepared by using the sol-gel method, starting from the commercial Titanium (IV) oxide, anatase, nanopowder < 25nm, from Sigma-Aldrich. The pure TiO_2 paste was prepared by mixing 1 g of the commercial P25 TiO_2 powder (Degussa) with 0.1 ml of acetyl acetone, 0.4 ml of Triton X-100, and 0.2 g of polyethylene glycol in 5 ml of a mixture of water and ethanol. A conductive glass sheet of 1.5 cm² was immerged in acetone for 48 h to remove impurities. A plastic adhesive tape was fixed on the four sides of conductive glass sheet to restrict the thickness and the area of about 1·1 cm² of TiO_2 film was prepared by spreading the TiO_2 paste onto the conductive glass by using a glass rod. Finally, the glass sheet was inserted at 450 °C for 30 minutes and cooled to a temperature of 80–90 °C, the conductive glass of solidified TiO_2 was immerged in dye sensitizer alcohol solution for 48 hours to absorb the dye on TiO_2 porous film adequately, the other impurities were washed up with anhydrous ethanol and dried in moisture-free air.
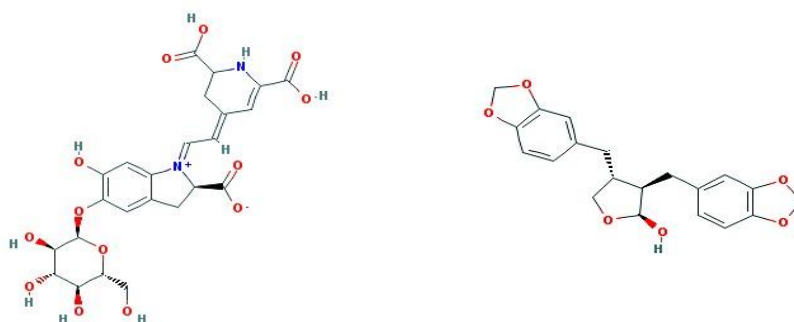

Figure 1: The 2D chemical structure of the pigments extracted from *Ocimum tenuiflorum* and *Piper nigrum.* a. Betalain b. Cubebin

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After that, a TiO₂ porous film electrode was prepared. Platinum coated FTO glass was used as electrode, followed by drying at 400ºC for 30 minutes. The electrolyte solution for DSSCs was prepared by dissolving KI (0.5 M) and I$_2$ (0.05 M) in mixed solvents of ethylene glycol and acetonitrile (4:1 in the volume ratio). The iodide electrolyte solution was placed at the edges of the plates. The liquid was drawn into the space between the electrodes by capillary action. Two binder clips were used to hold the electrodes together.

Characterization and Measurements

The photo anodes were characterized by using a UV–Visible Spectrophotometer (UV-2550, Shimadzu), a Field Emission Scanning Electron Microscope equipped by an energy dispersive X-ray analyzer (FESEM-EDX, JEOL, JSM-6400), and a BET surface area analyzer (Autosorb-1, Quanta chrome). The photoluminescence (PL) spectra of the samples were analyzed with a Fluorescence Spectrophotometer (Hitachi F-4500FL Spectrophotometer, Japan).The photovoltaic properties of the prepared DSSCs, i.e. short circuit current (J_{SC} in mA/cm²), open circuit voltage (V_{OC} in mV), fill factor (FF), and efficiency (ή in %) were determined from the I–V curve obtained by using a LOT-Oriel solar simulator (Model LS0100- 1000, 300W Xe Arc lamp Power SupplyLSN251 equipped

with AM 1.5 filter, 100mW/cm²) respectively, with 0.5 and 1 cm² of illuminated active area.

Theoretical Studies

The molecular structures of Betalain and cubebin were studied by using Gaussian9 and were optimized. The Density Functional Theory (DFT) studies were carried out with the B3LYP exchange-correlation functional and the 6-31G (d) basis set. The stability of optimized structures and zero-point corrections on the total energies were obtained by performing vibrational analysis. Using the TD-DFT, the molecular orbitals and electronic transitions were calculated in solvent (acetonitrile) by employing the polarizable continuum model (PCM) with the same B3LYP functional. The basis sets on the heavier atoms were augmented by diffuse functions via 6-31+G (d) for better evaluation of electronic states.

3. RESULTS AND DISCUSSION

The absorption spectra of dyes betalain and cubebin from *Ocimum tenuiflorum* and *Piper Nigrum* ethanol extract were shown in Figure.2 (a,b).
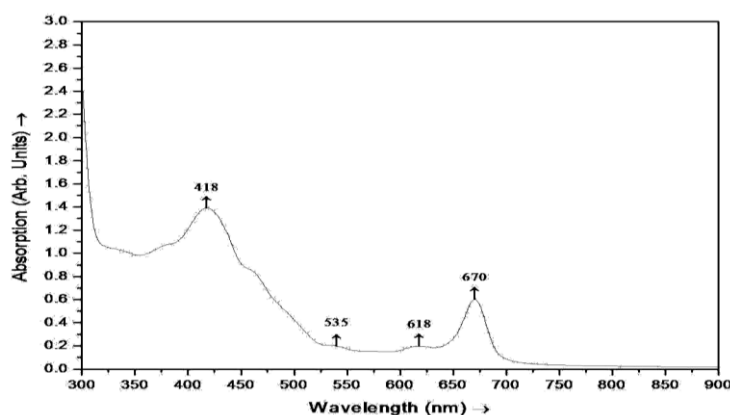

Figure.2 (a): The absorption spectra of dyes from medicinal plants a. betalain dye from *Ocimum tenuiflorum*
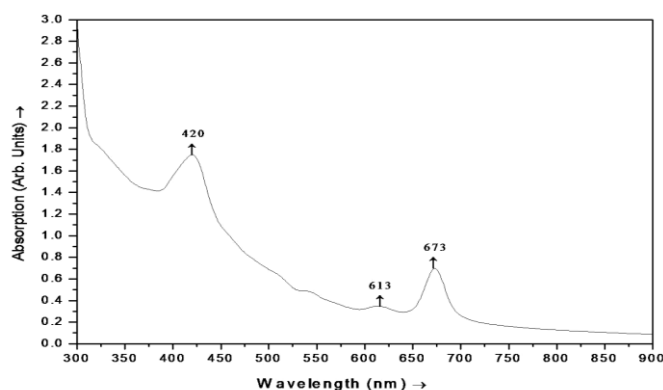

Figure.2 (b): The absorption spectra of dyes from medicinal plants b. Cubebin dye from *Piper nigrum*

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From the absorption spectra, we have evidenced that the dyes used in the study absorb the light in the visible spectrum that satisfies the primary criteria for their use as sensitizers in DSSCs [24-26]. To be more specific, cubebin extract from *Piper nigrum* exhibited the broad absorption band in the range of 420–673 nm and besides showed a sharp absorption peak at 670 nm. Both the dyes, Betalain and Cubebin exhibited the common peak at 670 nm which is in consideration with the characteristic absorption band of chlorophyll. *Piper nigrum* absorbs in the wide range of 410–600 nm with an absorption peak at 420 nm. The differences and variations in the absorption characteristics of dyes can be attributed to the different colors of the extracts due to respective pigments present in them.

Photoluminescence of Green Sensitizers

To recall photoluminescence is a process in which a chemical compound absorbs a photon (electromagnetic radiation), thus transitioning to a higher electronic energy state, and then radiates a photon back out, returning to a lower energy state. Ultimately, available chemical energy states and allowed transitions between states (and therefore wavelengths of light preferentially absorbed and emitted) are determined by the rules of quantum mechanics [27]. In this respect, there may be a correlation between the phenomenon of photoelectron emission and the photoelectric property in a natural dye based DSSC system. Figure 3 shows the emission intensity of dye Betalain extracted from *Ocimum tenuiflorum* and Cubebin from *Piper nigrum*.

The emission intensity of the dye namely betalain from *Ocimum tenuiflorum* has exhibit PL intensity of 672.5 nm and 870 nm and cubebin from *Piper nigrum.* In general, the PL intensity increases with increasing number of emitted electrons resulting from recombination between excited electrons and holes. Particularly, the PL intensity decreases more in the presence of a metal that can capture excited electrons and exhibit conductivity, via the relaxation process. Both of the compounds exhibit very good absorption and Photoluminescence property.

Theoretical Analysis of FT-IR and FT-Raman Spectra of Photosensitizers

The theoretically predicted FT- IR and FT-Raman spectra using B3LYP/6-311 G (d,p) method and the observed experimental FT-IR and FT-Raman spectra were observed in the range of 4000 cm^{-1} to 500 cm^{-1} are shown in Figure 4(a)and (b). The respective FT-IR spectra and FT-RAMAN spectra were recorded in the range from 4000 to 400 cm^{-1}.

The c l o s e examination of the spectra reveals that they exhibit broad absorption frequency in the range 4000 cm^{-1} to 500 cm^{-1} with a wide and strong band which attributed to the –OH stretching and due the wide variety of hydrogen bonding between OH groups. The molecule Betalain exhibits a sharp peak at 2000 cm^{-1} and Cubebin shows peak around 3744 cm^{-1} associated with the symmetric and asymmetric –C–H–stretching vibrations of CH and CH$_3$ groups. The

signal characteristics bands of C=O (carbonyl) stretching vibration at 1600–1750 cm^{-1} can also be observed due to presence of some aromatic esters. Hence, the IR spectra of extracts contains band that can be assigned due to the coloring components found in the extracts. Betalain contains methyl groups and cubebin containing C-H groups are generally referred to as electron donating substituent in the aromatic ring system. Absorption arising from C–H stretching in the alkenes occur in the region 3000–2840 cm^{-1}. The lowering of the wave numbers from the normal values is due to the intermolecular charge transfer (ICT) from the dimethyl group to the hydroxyl group via π conjugation system.

The changes in intensity of the CH$_3$ stretching mode are also due to the influence of electronic effects resulting from hyper conjugation of methyl group with nitrogen atom and the aromatic ring system. Thus the hyper conjugation of methyl group, causing changes in intensity in IR, clearly indicates that methyl hydrogen is directly involved in the donation of electronic charge. The asymmetric and symmetric bending vibrations of methyl group normally appear around 1446 and 1375 cm^{-1} respectively. The relatively large value of intensity in IR and Raman wave numbers of the rocking modes suggests the presence of hyper conjugation. The twisting and torsion vibrations are identified below 503 cm^{-1}, which are also supported by the computed wave numbers.

The ring modes which are found to be active in both IR and Raman spectra enable the Betalain molecule to be an effective π conjugation system. Because of the existence of one directional charge transfer from the donor to the acceptor through the single–double bond conjugated path induces large variations of both the molecular dipole moment and the molecular polarizability during the same vibrations, thus gaining the activity of both IR and Raman at the same time. The simultaneous activation of IR and Raman ring modes also supports the charge transfer interaction between CH$_3$ and the Benzene ring which also plays an important role in the DSSC activity.

Electronic Structures and Electrochemical Properties

According to the intra-molecular electron transfer mechanism of dyes in the DSSCs, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the dye should be lower and higher, respectively, than that of electrolyte and conduction band of semiconductor (TiO$_2$). The electron distribution of HOMO is mainly located in the electro-donor to the π-conjugated linker while subjecting to sun light irradiation, and the electron transfer proceeds from the electron-donor to the electron-acceptor through the π- conjugated linker. The electron distribution of LUMO is delocalized in electron acceptor to the π -conjugated linker and it could inject the electron from the excited dye to the conduction band of semiconductor.

Theoretically, the dye absorbs photon from the sun light and result in broad band absorption extended from visible to IR region [28-29]. The electron-donating

ability of the electron-donor in D- π -A dyes has the   tendency to influence the electrochemical properties.
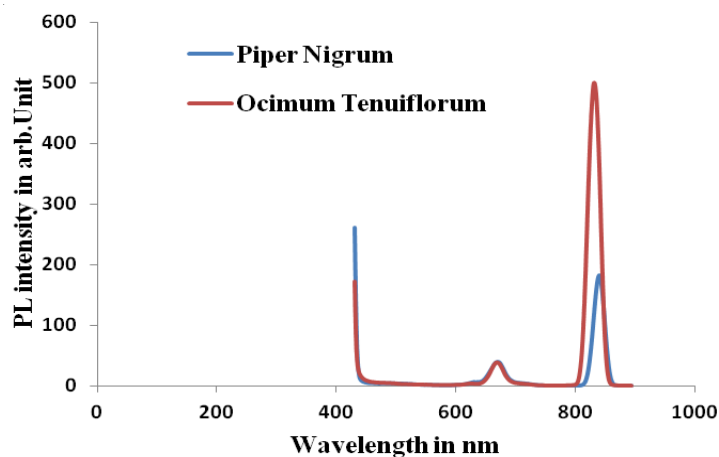

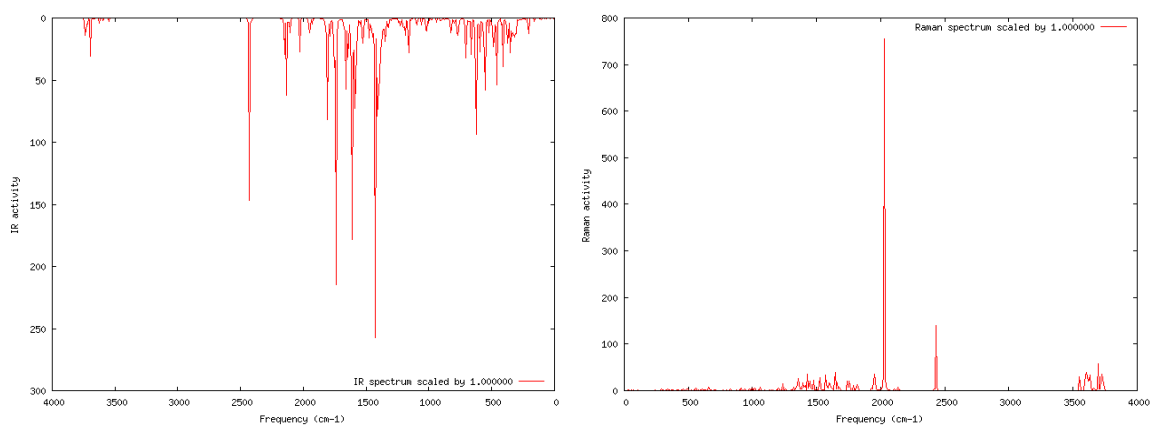**Figure 3: Photoluminescence Spectra for Green Sensitizers**

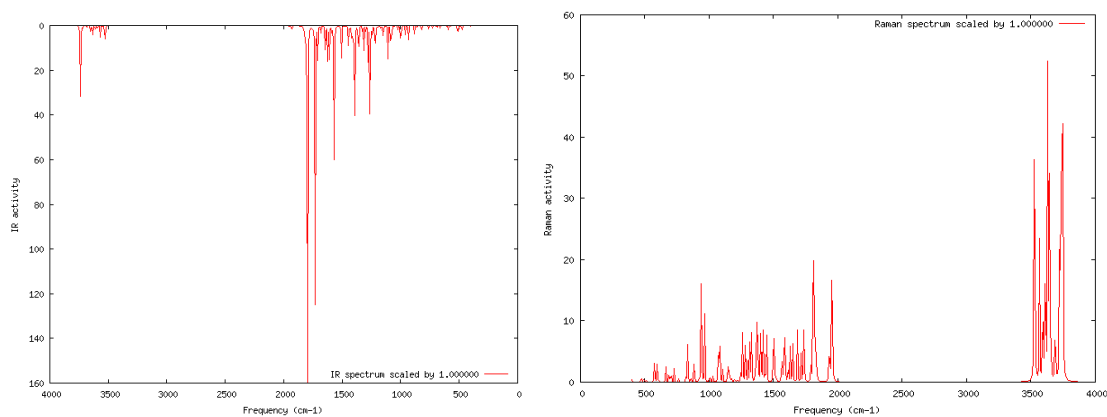**Figure 4 (a) Theoretical FT-IR and FT-Raman Spectra of Betalain**

Figure 4 (b) Observed FT-IR and FT-Raman Spectra of Cubebin

Table.1: Frontier molecular orbital's energies (eV) and energy gap (eV) for studied dyes using 6-11++G ** level of theory.

Compound	HOMO (eV)	LUMO (eV)	Energy gap in
Betalain	- 4.75	-1.95	2
Cubebin	- 4.52	- 1.63	2

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A D- π -A dye with a stronger electron-donating group should give a high HOMO when compared to that of electrolyte and conduction band of semiconductor (TiO$_2$). The electron distribution of HOMO is mainly located in the electro-donor to the π -conjugated linker while subjecting to sun light irradiation and the electron transfer proceeds from the electron-donor to the electron- acceptor through the π-conjugated linker. The electron distribution of LUMO is delocalized in that with a weaker electron-donor. The calculated HOMO, LUMO and related band gap for dyes are reported in Table 1.

Electronic Absorption Spectra

The time-dependent density functional theory (TD-DFT) method has been performed to calculate the electronic absorption spectra of these dyes. Two major absorption peaks have been obtained for natural dyes in the visible region. Computational analysis has indicated that a dye with stronger electron donating group enhances the HOMO energy as compared to a weaker electron-donating group. Betalain is assigned to the intra-molecular charge transfer band at 670–770 nm and the Cubebin absorption peak are associated with the n ⟶π transition of the entire molecule. The π-conjugated linkers with electron-withdrawing substituent have been shown to generate a slightly blue-shifted absorption band as compared to those without any substituent. The Benchmark calculations have been performed to evaluate the best functional group for correctly predicting the absorption spectra of the dyes employed in this study, and in particular the low-energy transitions. The excitation energies, oscillator strengths, and the contributing configurations for the most relevant first three states of Betalain and Cubebin dyes using DFT methods with 6-311++G** basis set were reported in Table 2.

The results showed that the wavelength of the peak maximum (λ_{max}) of ICT spectra is significantly shifted in Betalain pigment λ_{max} values was calculated to be 725 nm, 918 nm and 1101 nm respectively. Comparisons between the calculated and experimental spectra of a dye of similar structure of Betalain predicted that λ_{max} obtained from TD-DFT calculation to be 725 nm in excellent agreement with the experimentally observed value of 670 nm. Furthermore, the calculated absorption wavelengths of Betalain and Cubebin at 6-311++G** level of theory are in good agreement with the corresponding experimental value. Both the natural dyes show intense narrow absorption bands, but as a consequence of the extended π-system of Betalain, its absorption maximum is shifted to 725 nm as compared to Cubebin (λ_{max}= 250 nm).

The absorption spectra of Betalain shows a strong optically allowed band at 670.25 nm, corresponding to the HOMO/LUMO transition, and a less intense band at 725.87 nm. The absorption spectra display good absorption maxima for Betalain as compared to the corresponding transition in Cubebin irrespective of the DFT functional used. As shown in Table.2 and Figure 5 (a, b) the first absorption band for Betalain is in the near IR region 725.87 nm.

The frontier orbital's (HOMO and LUMO) analyses were paid much attention as they play significant role in the stability of the compounds. Establishment of difference in the energies of the HOMO and LUMO and their band gap in eV envisages the compounds excitement which fascinates the pigments capability as potential sensitizers. The calculated HOMO and LUMO energy levels and their band gaps in the terms of eV were reported in the Table.1.

The LUMO of the dyes need to be higher than the conduction band edge of TiO$_2$, for an effective injection of charge into conduction band of TiO$_2$. The computational generated energy levels of HOMO and LUMO of Betalain were -4.75 eV and -1.95 eV, respectively, where as the energy levels of HOMO and LUMO of Cubebin were -4.52 eV and -1.63 eV, respectively.

The calculated band gaps of Betalain and Cubebin were 2.70 eV and 2.89 eV, respectively (Table 1). It is observed the band gap of Betalain is less in comparison with cubebin, which is considered as favorable for efficient absorption of solar energy.

The results of electron distribution of natural transition orbitals (NTO) as reported in Figure.6 and Figure.7 clearly indicate that the studied Betalain and Cubebin dyes are potent sensitizers for DSSCs.

Table 2: Absorption wavelength (nm) and oscillator strength (f) calculated by using 6-311++G basis set for acceptor dyes.**

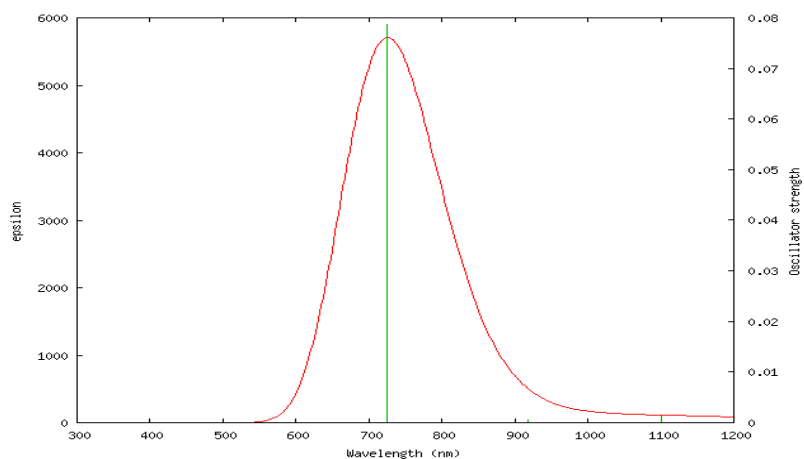| BASIS SET	Betalain Pigment				Cubebin pigment			
	Wave length (nm)	F (LHE)	MO contribution	MO coefficient	Wave length (nm)	F (LHE)	MO contribution	MO coefficient
6-311 ++G**	1101	0.0013	144 ->145	0.63	251	0.1075	93 -> 95	0.61
	918	0.0005	143 ->145	0.24	249	0.063	94 -> 96	0.60
	725	0.0787	142->145	0.23	245	0.0002	94 -> 95	0.70

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Figure.5a: The UV-Vis absorption spectra of Betalain calculated by 6-311++G basis set.**
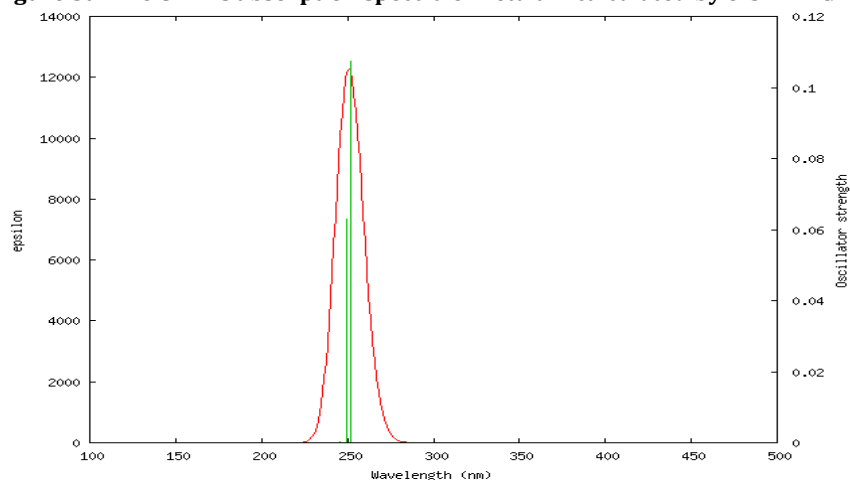

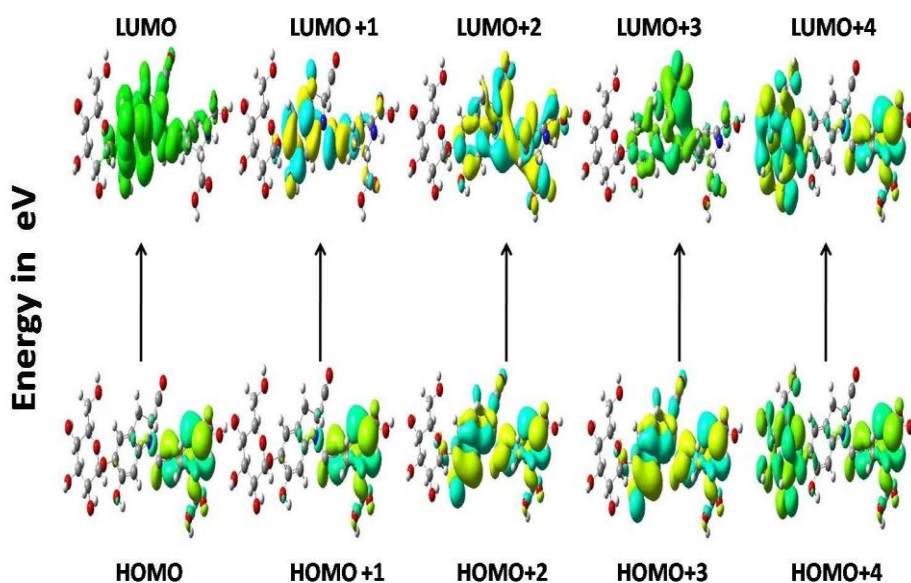**Figure.5b: The UV-Vis absorption spectra of Cubebin calculated by 6-311++G** basis set.**

Figure 6: Schematic diagram of the NTO's of Betalain calculated at the 6-311++G level of theory. The surfaces are generated with an isovalue at 0.02**
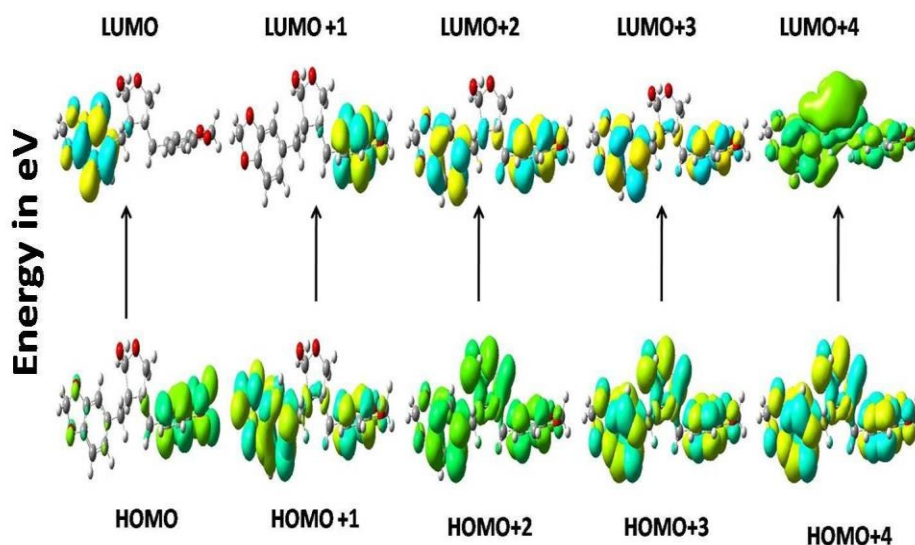
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Figure 7: Schematic diagram of the NTO's of Cubecubin calculated at the 6-311++G level of theory. The surfaces are generated with an isovalue at 0.02**

The movement of electron charge density distributed mainly on the donor units before light irradiation and to the acceptor units after light irradiation favors the electron injection from dye molecules to the conduction band edge of TiO_2. It is observed that the electron density moves from donor moiety towards the anchoring group in all the transitions of both Betalain and Cubebin dyes. This feature of dyes results in directional electron transfer to the conduction band of TiO_2. The anchoring group in Betalain and Cubebin exhibited considerable contribution to the LUMOs which lead to a strong electronic coupling with TiO_2 surface thus improved the electron injection efficiency. This would subsequently enhances the short-circuit current density J_{SC}. Thus the resulting excited states of both dyes are strongly coupled to the TiO_2 surface due to charge delocalization involving the anchoring hydroxyl group.

The NTO orbitals of all transitions computed for Betalain and Cubebin are included in Figure 6 and 7 based on the TD-DFT calculation at 6-311++G** level of theory. The NTO analysis yields an unambiguous donor–acceptor pair for most cases, thus facilitating the assignment of the nature of the electronic transition. The most prominent transitions in UV-Vis range have been analyzed. It can be clearly seen that HOMO is localized to a great extent on the Betalain core, which is associated with the π-framework of the Betalain ring. One can notice a similar pattern for the charge density distribution in the NTO's of both Betalain and Cubebin. It is interesting to note that in the excited state there is a clear charge transfer towards the acceptor moiety. In Betalain, there is a further clear accumulation of charge on the anchoring group. This charge accumulation has a pronounced effect in the charge injection into the CB of the electrode. TD-DFT calculations on Cubebin dye (Table 2) reveal an intense absorption at 250.25nm (f=0.613) associated with the π-π*

electronic transition. This transition corresponds to excitation from HOMO-LUMO responsible for the facile charge flow from the cubebin core to the anchoring group. As discussed, in these transitions the initial states are mainly related to the MOs that are localized on electron donor groups, while the final states are mainly related to the MOs that are localized on electron acceptor groups. This indicates that the absorptions are photo induced electron transfer processes, thus the excitations generated were the charge separated states.

It is instructive at this point to attempt an estimation of the light harvesting efficiency of the dyes under investigation. LHE can be computed using equation (1)

$$LHE = 1 - 10^{-f} \qquad (1)$$

Where, f is the computed oscillator strength of the electronic transition. The computed LHE values are listed in Table.3 for the first n-π* transition for both Betalain and Cubebin. This photo physical property reveals the electron density to concentrate on the electron-donor, which is the main chromophore responsible to the sensitization of photo-to-current conversion processes. The results of this theoretical investigation will help to design and develop more efficient natural dyes for the DSSC applications.

Photovoltaic Performance

Current-voltage curve measurements are the most central way to characterize the photovoltaic (PV) device performance. The solar cell efficiency is determined by its current-voltage (I-V) characteristics under standard illumination conditions. A standard solar spectrum of air mass 1.5 (AM 1.5) with an intensity (the power of incident light) of 100 m W /cm^2 also referred to as 1 sun, is used for solar cell characterization. The performance of dye-sensitized solar cells was evaluated in terms of short circuit current density J_{SC}, open circuit voltage V_{OC}, fill factor *FF* and efficiency η % which are shown in Table 3 and the Current –Voltage curve in
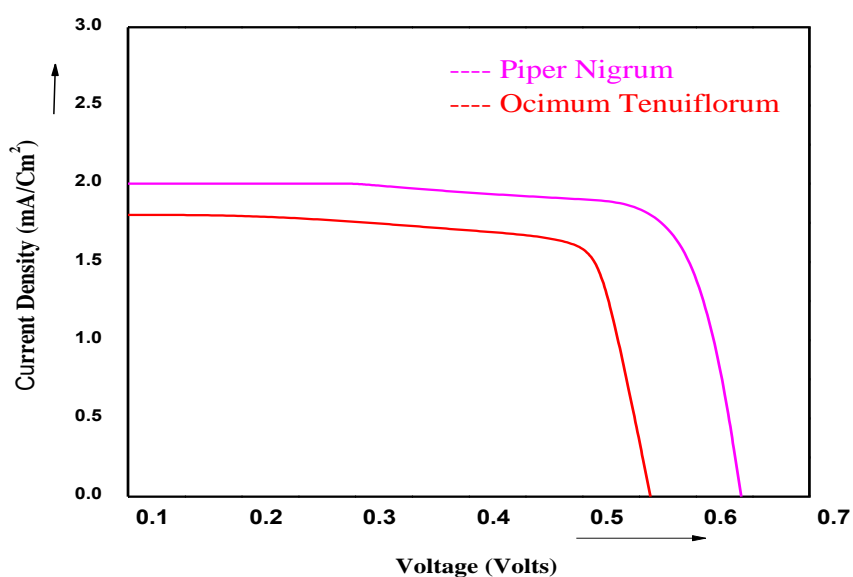
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Figure 8. Current –Voltage characteristics of *Piper nigrum and Ocimum tenuiflorum*

Table.3: Characteristics of DSSC

Name of the Photosensitizer	J_{sc} (mA /cm^2)	V_{oc} (mV)	FF	η%	References for comparison of η%	
Piper Nigrum	1.8	0.56	0.725	0.392	Beta Betaxanthin Betanin	0.19 (Ref 26) 0.07
					Water extract (hydrochloric acid)	0.119(Ref 30)
					Water extract (HCL) Water extract (ascorbic acid)	0.402 0.106
					Purified methanol extract (hydrochloric acid)	0.048
Ocimum Tenuiflorum	1.72	0.5	0.797	0.38		

The fill factor and efficiency were calculated under a stimulated illumination with a light intensity of 100 mW/cm^2. The FF of the DSSC was calculated using the equation,

$$FF = I_{max} V_{max} / I_{sc} V_{sc} \quad ------ (2)$$

The incident photon – to – current (IPCE) efficiency (ή) was calculated using the equation

$$ή \, (\%) = I_{max}$$

$$V_{max} / P_{inc} \quad -------- (3)$$

Where I_{max} and V_{max} are the current and voltage obtained at the maximum power point on the photovoltaic power output curve and P_{in} is the power density of the incident radiation respectively. In principle, the maximum I_{sc} of a dye-sensitized solar cell is determined by how well the absorption window of the dye overlaps with the solar spectrum. The overall photo conversion efficiency (η) is calculated from the integral photocurrent density (J_{SC}), the open circuit photocurrent (V_{OC}), the fill factor (FF) of the cell, and the intensity of the incident light (Pin).

It is clearly shown in the Table 3 that there is a close resemblance of the photo current conversion efficiency curve with the absorption spectrum of the respective dye providing clear evidence of the sensitization of photocurrent. In this study, among the two natural dyes, the betalain dye extracted from the *Ocimum tenuiflorum* is shown to be promising dyes for photovoltaic's. The solar conversion efficiency of the dye based DSSC sensitized from *Ocimum tenuiflorum* can reach 0.392% under irradiation of 100 mW/cm^2, which is the highest photo signal in this study. These two natural photosensitizers applied in TiO$_2$ based DSSC are thus suitable to improve the efficiency of eco-friendly energy devices. The efficiency of natural dye-

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sensitized solar cells is determined by a number of factors that include selection of the appropriate natural dye, quantitatively significant stable electronic anchorage of the dye to the surface of the metal oxide nanostructure, choice of photo anode, counter electrodes, electrolyte and solvent system. It is therefore highly desirable to standardize these critical factors in the context of making natural dye-sensitized solar cells a commercially viable option. The advantages of natural dyes as photo sensitizer are large absorption coefficients, high light- harvesting efficiency, no resource limitations, low cost, simple preparation techniques and eco-friendly. Although the efficiencies obtained with these natural dyes are still below the current requirements for large scale practical applications, these interesting explorations of fabrication of dye-sensitized solar cell using dyes obtained from bio-resources invoked participation of researchers around the globe to engage in research to search for new sources of natural dye systems that are stable, non-toxic, biocompatible and have desirable optoelectronic properties. Some serious efforts in natural dye sensitizers may spring up a perspective of commercial feasibility for inexpensive and environmentally friendly dye-sensitized solar cells.

CONCLUSION

As the DSSC are the promising alternative for the development of new generation solar cells, the use of natural pigments has become a viable alternative resource for the development of third generation solar cells. In this work we report that the successful conversion of visible light into electricity was achieved by employing the dyes Betalain and cubecin extracted from *Ocimum tenuiflorum* and *Piper nigrum.* These extracted dyes were characterized by UV–Vis absorption spectra, Photoluminescence and photo electrochemical properties of the DSSC. I-V characteristics curves were measured and the photo electrochemical properties were investigated. The highest efficiency was obtained for DSSC fabricated with TiO_2 sensitized by Betalain dye extracted from Ocimum *tenuiflorum.*

REFERENCES

[1]. Awodibo Michael, Boyo Adenike, Oluwole Surukite, Abudusalami Ibrahim and Boyo Henry., 2013, Construction of Dye Sensitized Solar Cell with Bouganvilla,Cordia Sebestena and Talinium Triangulare Flower, Journal of Natural Sciences Research. 3, 5-10.

[2]. Cherepy, N. J., G.P. Smestad, M. Gratzel and J. Z. Zang., 1997. Ultrafast Electron Injection: Implications for a Photoelectrochemical Cell Utilizing an Anthocyanin Dye-Sensitized TiO_2 Nanocrystalline Electrode, J. Phys. Chem.B, 101:9342-9351.

[3]. Efurumibe,E.L., Asiegbu, A.D., Onuu,M.U., 2012, Mathematical modelling of electron transport through the anode (TiO_2) of a standard dye-sensitized solar cell Asian J. Applied Sci. 5:33-42.

[4]. Gratzel, M., 2004. Dye-sensitized solar cells, Journal of Photochemistry and Photobiology C: Photochemistry Reviews, 4:145-153.

[5]. Hao, S., J. Wu, Y. Huang and J. Lin., 2006. Plant Seeds-Based Dye-Sensitized Solar Cells, Solar Energy, 80: 209-214.

[6]. Idu, M. and H. I. Onyibe., 2007. Medicinal plants of Edo State, Nigeria. Res. J. Med.Plant, 1: 32-41.

[7]. Chou,C.S., Chou,F.C., Kang, J.Y., 2012. Preparation of ZnO-coated TiO_2 electrodes using dip coating and their applications in dye-sensitized solar cells, Powder Technology, 215-216, 38-45.

[8]. Senthil, T.S., Muthukumarasamy, N., Velauthapillai, D.,Agilan, S.,Thambidurai,M., Balasundaraprabhu, R., 2011, Natural dye (cyanidin 3-O-glucoside) sensitized nanocrystalline TiO_2 solar cell fabricated using liquid electrolyte/quasi-solid-state polymer electrolyte, Renewable Energy, 36(9), 2484–2488.

[9]. Ratna Chauhan, Reena Kushwaha, and Lal Bahadur, 2011. Study of Light Harvesting Properties of Different Classes of Metal-Free Organic Dyes in TiO_2 Based Dye-Sensitized Solar Cells, International Journal of Photo energy, 2011, 9-12.

[10]. Kanmani,S.S., Ramachandran, K., 2012. Synthesis and characterization of TiO_2/ZnO core/shell nanomaterials for solar cell applications, Renewable Energy, 43, 149–156.

[11]. Michael, A., Adenike,B., Surukite, O., Ibrahim, A., Henry, B, 2013, Construction of Dye Sensitized Solar Cell with Bouganvilla,Cordia Sebestena and Talinium Triangulare Flower, Journal of Natural Sciences Research 3 (5)13-24.

[12]. O'Regan,B., Gratzel, M., 1991., A Low-Cost, High-Efficiency Solar Cell Based on Dye-Sensitized Colloidal TiO2 Films. Nature, 353, 6346, 737–740.

[13]. Kamat, P.V., Schatz, G.C., 2009, Nanotechnology for next generation solar cells. Journal of Physical Chemistry C, 113(35), 15473–15475.

[14]. Jiao,T.F., Wang, Y., Zhang, Q. R, 2013, Preparation and photocatalytic property of gold nanoparticles by using two bolaform cholesteryl imide derivatives,, Journal of Dispersion Science and Technology, 34(2), 1675–1682.

[15]. C. Sandquist, J.L. McHale, Improved efficiency of betanin-based dye-sensitized solar cells, Journal of Photochemistry and Photobiology A 221 (2011),90–97.

[16]. Fernando., J.M.R.C., Senadeera, G.K.R., 2008, Natural anthocyanins as photo sensitizers for dye sensitized solar cells, Current Science, 95(5):663-666.

[17]. Mark A. Kelm and Muraleedharan G. Nair. Mosquitocidal Compounds and a Triglyceride, 1,3-Dilinoleneoyl 2-palmitin, from Ocimum sanctum, J.Agric. Food Chem., 1998, 46 (8), 3092–3094,

[18]. Bhawana Rathi, Sameksha Koul, R. L Khosa (2013). Journal of Natural Remedies, 2320-3358, Vol 13.

[19]. Polo, A.S., Iha, N.Y.M., 2006, Blue sensitizers for solar cells: natural dyes from Calafate and Jaboticaba Journal of Solar Energy Materials and Solar Cells, 80, 209–214.

[20]. Feng, J., Jiao, Y., Ma, W., Nazeeruddin,M.K., Grätzel, M., Meng,S., 2013, First principles design of dye molecules with ullazine donor for dye sensitized solar cells, The Journal of Physical Chemistry C, 117 (8) 3772–3778.

[21]. Chen, Z., Li,F., Huang,C., 2007, Current Organic Chemistry, Organic D-π-A dyes for dye-sensitized solar cell, Current Organic Chemistry, 11(14), 1241–1258.

[22]. Ranjitha, S., Aroulmoji,V., Mohr, T., Anbarasan, P.M., Rajarajan, G., 2014. Structural and spectral properties of 1 2-dihydroxy-9 10-anthraquinone Dye Sensitizer for Solar Cell Applications, Acta Physica Polonica A 126: 6. 833-839 9.

[23]. Mohr,T., Aroulmoji, V., Samson Ravindran,R., Müller, M., Ranjitha, S., Rajarajan, G., Anbarasan, P.M., 2014. DFT and TD-DFT study on Geometries, Electronic Structures and Electronic Absorption of Some Metal Free Dye Sensitizers for Dye Sensitized Solar Cells, Spectrochim Acta A Mol Biomol Spectroscopy 135: 1066-1073.

[24]. Ranjitha, **S**, Rajarajan, G, Gnanendra, T.S, Anbarasan, P.M., Aroulmoji, V., 2015 Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 149(5) 997–1008.

[25]. Matsuda, H., Kawaguchi, Y., Yamazaki, M., Hirata, N., Naruto, S., Asanuma, Y. Kaihatsu, T.Kubo, M., 2004. Melanogenesis Stimulation in Murine B16 Melanoma Cells by *Piper nigrum* Leaf Extract and Its Lignan Constituents, Biological & Pharmaceutical Bulletin, 27(10), 1611-1616.

[26]. Dongshe Zhang a, Suzanne M. Lanier a, Jonathan A. Downing a,ason L. Avent a,b, June Lumc, Jeanne L. McHalea,2008, Betalain pigments for dye-sensitized solar cells, Journal of Photochemistry and Photobiology A: Chemistry 195, 72–80

[27]. Liu, T.M., Chu,S.W., Sun, C.K., Lin,B.L., Cheng,P.C., Johnson,I., 2001, Multi- photon confocal microscopy using a femtosecond Cr:forsterite laser. Scanning 23, 249- 254.

[28]. Shimatani, K., Tajima, H., Komino, T., Ikeda, S., Matsuda, M., 2005. The electroluminescence spectrum of chlorophyll a, Chem. Lett.34, 948.

[29]. Geetha,M., Suguna, K., Anbarasan, P.M., Aroulmoji, V., 2014, Preparation and Characterization of Tailored TiO_2 Nano Particles Photoanode for Dye Sensitized Solar Cells, International journal Advanced Science & Engineering,1(1), 1-5.

[30]. Corneliu I. Opreaa, Anca Dumbravˇab, Irina Enacheb,c, Adrian Georgescua, Mihai A. Girtu, 2012, A combined experimental and theoretical study of natural betalain pigments used in dye-sensitized solar cells, Journal of Photochemistry and Photobiology A: Chemistry 240 (2012) 5– 13.