J. Myanmar Acad. Arts Sci. 2019 **Vol. XVII. No.2A**

CHARACTERIZATION AND OPTICAL PROPERTIES OF THE COLEUS BLUMEI EXTRACT AS DYE SENSITIZED SOLAR CELLS (DSSC)

Khine Myint Zu[1], Swe Swe Thein[2], Yin Maung Maung[3] and Than Than Win[4]

Abstract

The natural dyes used in this research were poinsettia leaves *(Coleus Blumei).*The absorbance and energy levels of dyes solutions were characterized using UV-Vis spectrophotometer and cyclic voltammetry. From UV-Vis absorption spectrum and , it was known that combination of anthocyanin and chlorophyll with ethanol was the broader region of the visible light spectrum in the range of 400 to 700 nm compared to extracted with methanol. All dyes were measured under the different solvents and temperatures to estimate the energy of the highest occupied molecular orbital (HOMO) and the energy of lowest unoccupied molecular orbital (LUMO). Optical band gap was measured from the absorption spectrum of each dye sensitizer. Fourier transform inferred (FTIR) was used to characterize the dye active components from 4000 to 500 cm^{-1}. From FTIR results, the coleus blumei match with AMANO LIPASE (C_{11} H_9 N_3 Na O_2) compound corresponding to the carboxylic acidic group in dye solutions were observed.

Keywords: Coleus Blumei leaves, Optical Band gap energy, UV-Vis, Cyclic Voltammetry, FTIR

Introduction

Energy technology is one of the most important technologies, since the demand for energy is growing day by day. In recent year, dye–sensitized solar cells (DSSCs) have been developed as the third generation of solar cells. [Hassan K. Tajudeen etal, 2017]. DSSC is the basically a photo electrochemical devices used for the conservation of solar energy into electrical energy. [Muhamad IK et al 2015]. The sensitizing dye, as a part of photoelectrode plays a key role in absorbing, sunlight and transforming solar energy into electrical energy.[Hassan K. Tajudeen et al 2017]. Therefore, the cell performance is mainly dependent on the type of dyes used as sensitizer[NT

1. PhD candidate, Department of Physics, University of Yangon
2. Lecturer, Department of Physics, University of Yangon
3. Associate Professor, Department of Physics, University of Yangon
4. Associate Professor, Department of Physics, Mandalay University of Distance Education

Mary Rosana 2014].Natural dye has several advantages over rare metal complexes because ease of extraction with minimal chemical procedure, large absorption coefficients, low cost, non toxicity, environmentally friendly, easily biodegradable and wide availability. [NT Mary Rosana 2014]. Natural dye can easily extract from flowers, leaves, seeds and fruits.

In this research work, natural dyes were extracted from two different colors of leaves in coleus blumei (Family Lamiacae) (Kawzaw Ywet Hla). Natural dyes were extracted by using two different solvent methanol and ethanol solutions. These were characterized by UV-Vis absorption spectroscopy to observe the absorption spectra. FTIR spectral analysis was used to determine the functional group in the natural dye. Cyclic voltammetry method was used to investigate the HOMO and LUMO energies and estimate the band gap energies of natural dye.

Extraction of dye solution

The anthocyanin extraction of the mixture two different colors of coleus blumei leaves were made following procedures. Purple and pink coleus blumei leaves were washed with distilled water and kept them some time in room temperature to remove the surface water. 5g of leaves were weight and crushed adding 150 ml of 70% ethanol (w/v %) and stored overnight in the refrigerator at 4˚ C. On the following day, the extraction was mixed thoroughly by using a magnetic stirrer for two hours at 25°C, 45°C and 65°C. The extractions were filtered using 110 mm filter paper to remove solid residues. Subsequently, the extract was centrifuged at 4000 rpm using a Denley BS 400 (UK) centrifuge machine for 5 minutes to separate all residues. Similar procedures were applied by taking same amount solvents for rest extracting solutions.

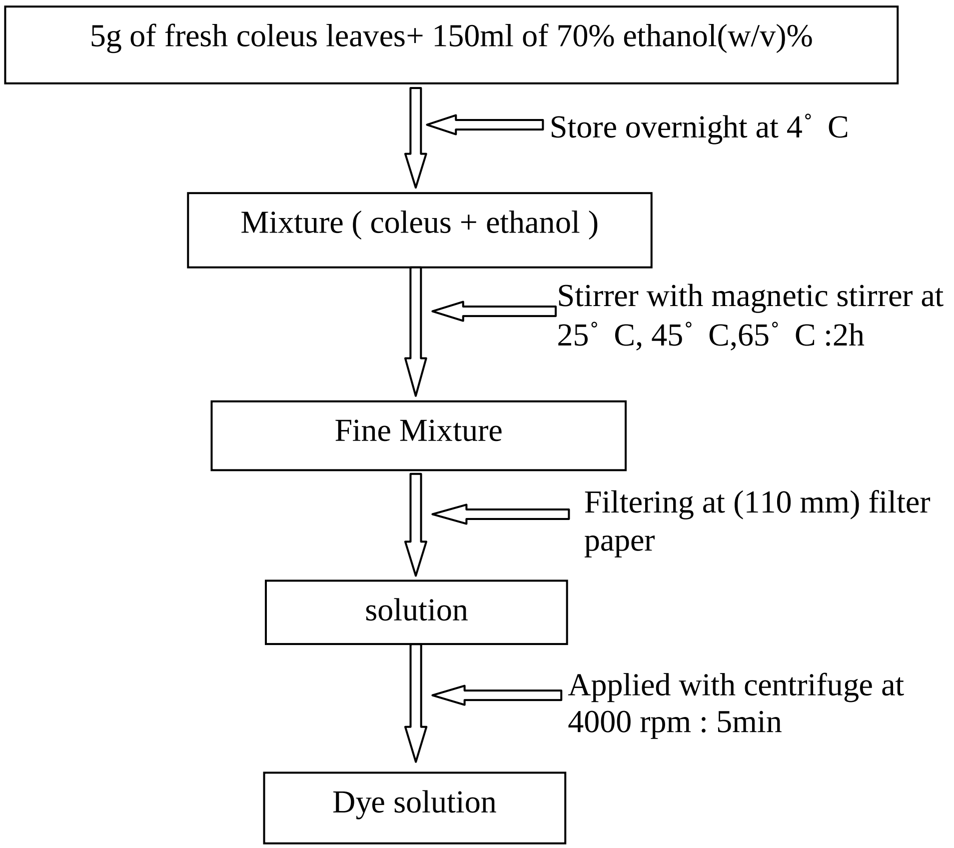

Figure 1: Block diagram of extraction of dye solution by using ethanol solvent.

Results and Discussion

UV-Analysis

UV-Vis absorption spectra analysis of poinsettia (Coleus Blumei) dye solution. Fig 2 found that the absorption peaks of dye solution of mixed Pink & Purple (Coleus Blumei) dye with ethanol 150 ml at 25˚C, 45˚C and 65˚C are 440nm (anthocyanin) and 665 nm (chlorophyll) and Fig 4 mixed Pink and Purple (Coleus Blumei) dye with methanol 150 ml at different temperatures are the same values (440 nm and 665 nm). And also the absorption peaks of dye solution at 25˚C, 45˚C and 65˚C are 400-700nm in the visible range. So the absorption peaks of these solutions at different temperatures are in UV range. The energy band gaps (E_g) of these samples at different temperatures were calculated by using Tauc Method equation and The relation between energy (hν) and (α hν)^2 for Mixed (pink & purple) Coleus dye with ethanol 150 ml at 25˚C,45˚C,65˚C, 2h are shown in Fig 3 (a,b,c) and while that of mixed (pink & purple) Coleus dye with methanol 150 ml at 25˚C, 45˚C and 65˚C , 2h are shown in Fig 5 (a,b,c).

Tauc Method ,

(α hν) =A(hν – (1)

Where, α = absorption coefficient (α = 2.303 A/ thickness)

E_g = Energy Bandgap of the material

n = order of transition (1/2,3/2,2,3)

The measured and calculated values of UV-vis for Coleus Blumei dyes at 25 ˚C, 45 ˚C and 65 ˚C with two solvents were described in Table 1(a) to (b).

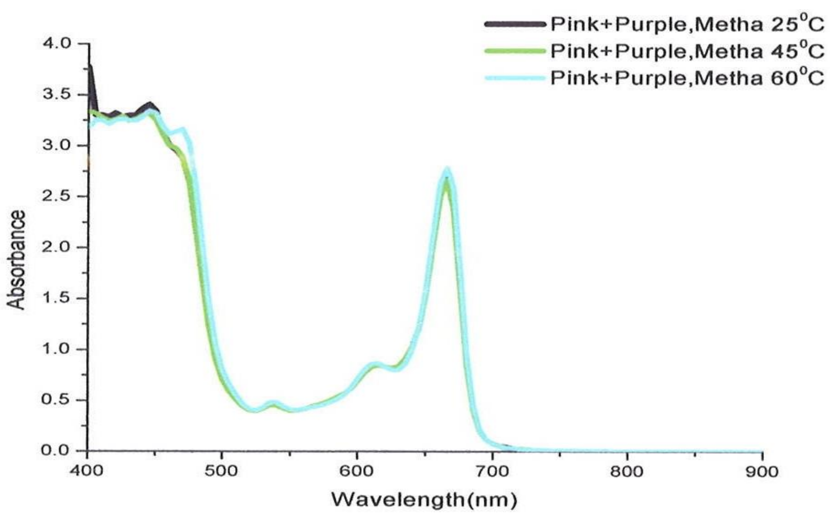

Figure 2: The absorption spectra of Mixed (Pink &Purple) Coleus at 25˚C, 45˚C and 65˚C, 2h

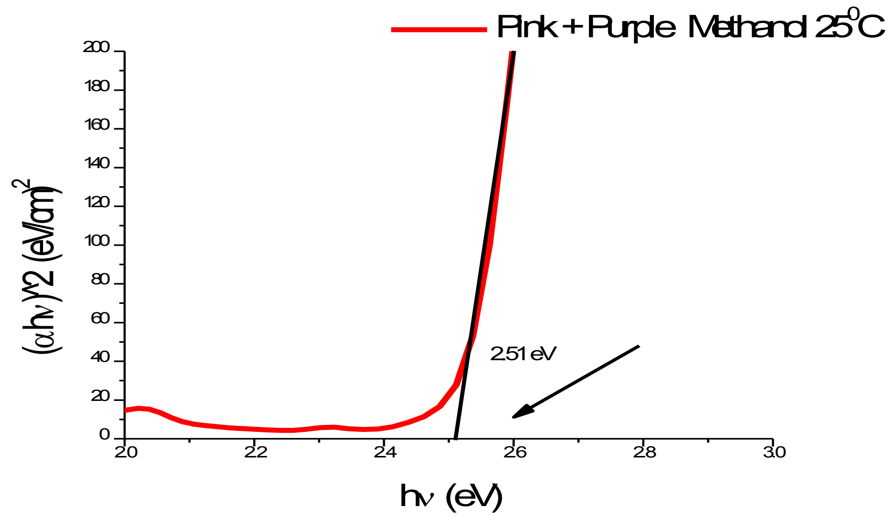

Figure 3: (a) The Cyclic Volammetry curve for Mixed Coleus (pink + purple) at 25 ˚C, 2h

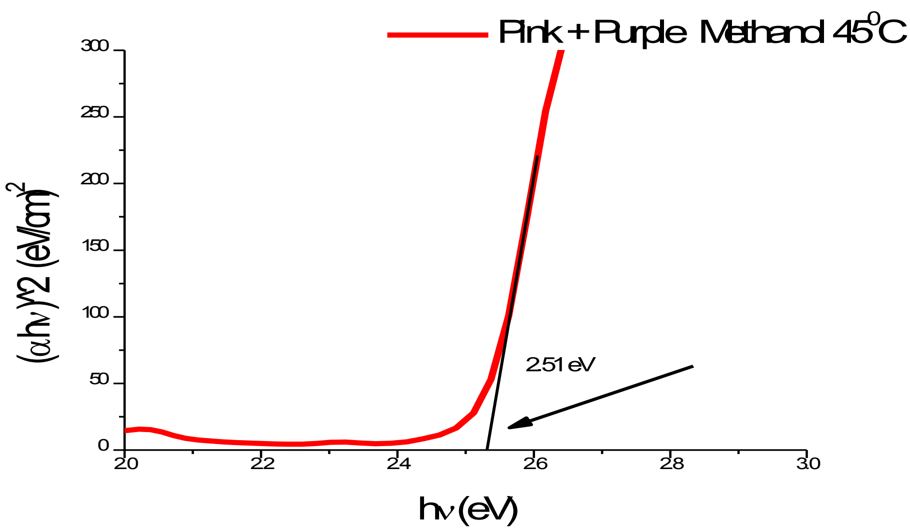

Figure 3: (b) The Cyclic Volammetry curve for Mixed Coleus (pink + purple) at 45 ˚C, 2h

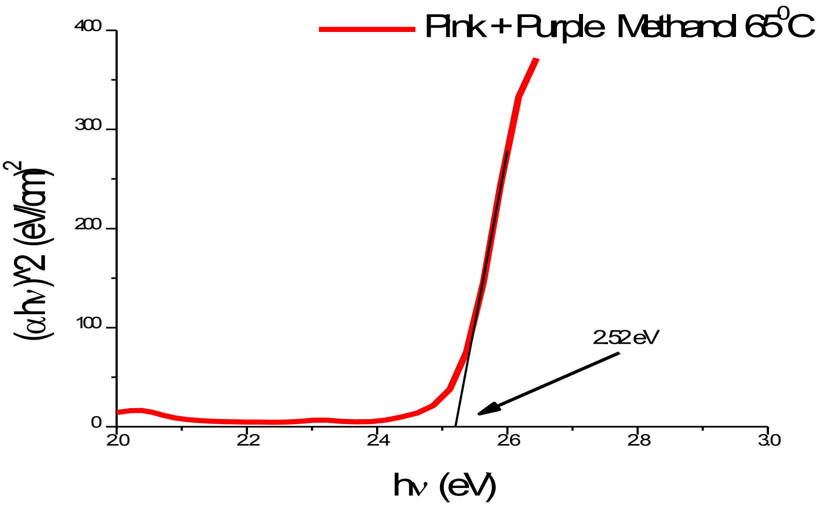

Figure 3: (c) The Cyclic Volammetry curve for Mixed Coleus (pink + purple) at 65˚C, 2h

Table 1: (a) pH level s and Energy levels for Purple Coleus with Methanol at 25˚C, 45 ˚C and 65^{0}C, 2h

Temperature (°C)	pH level	Wavelength (nm)	Energy Band gap (E_g)(eV)
25	6.60	490	2.52
45	6.34	492	2.51
65	7.70	490	2.52

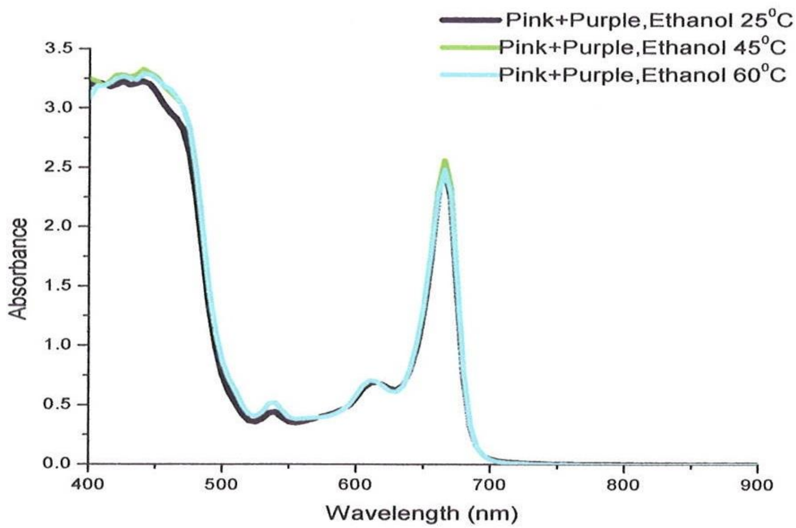

Figure 4: The absorption spectra of Mixed (Pink &Purple) Coleus at 25 ˚C, 45 ˚C and 65 ˚C, 2h

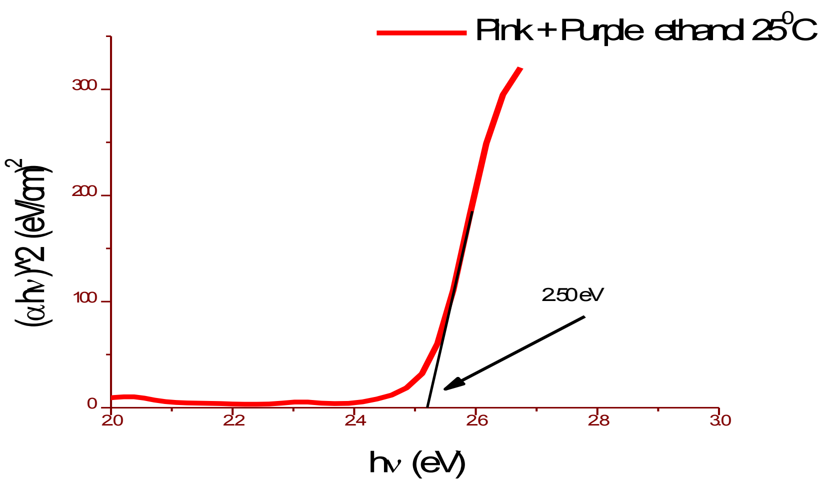

Figure 5: (a) The Cyclic Volammetry curve for Mixed Coleus (pink + purple) at 65 ˚C, 2h

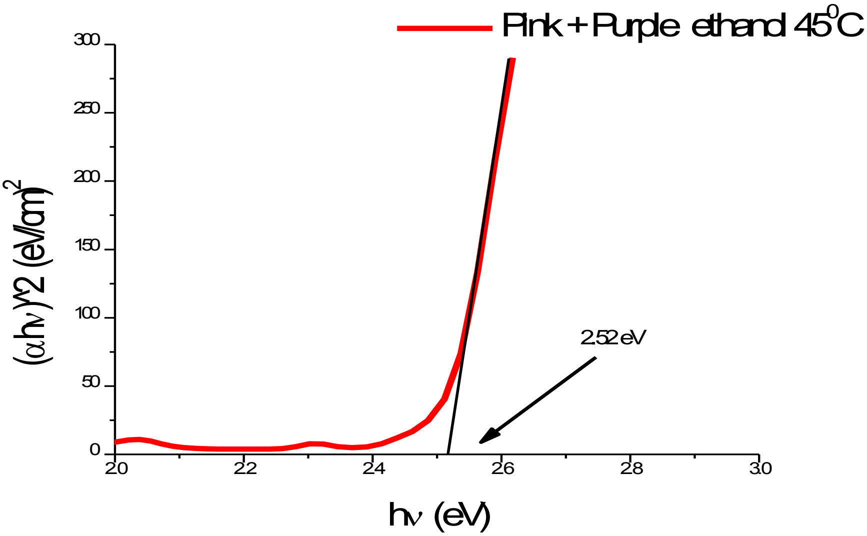

Figure 5: (b) The Cyclic Volammetry curve for Mixed Coleus (pink + purple) at 65˚C, 2h

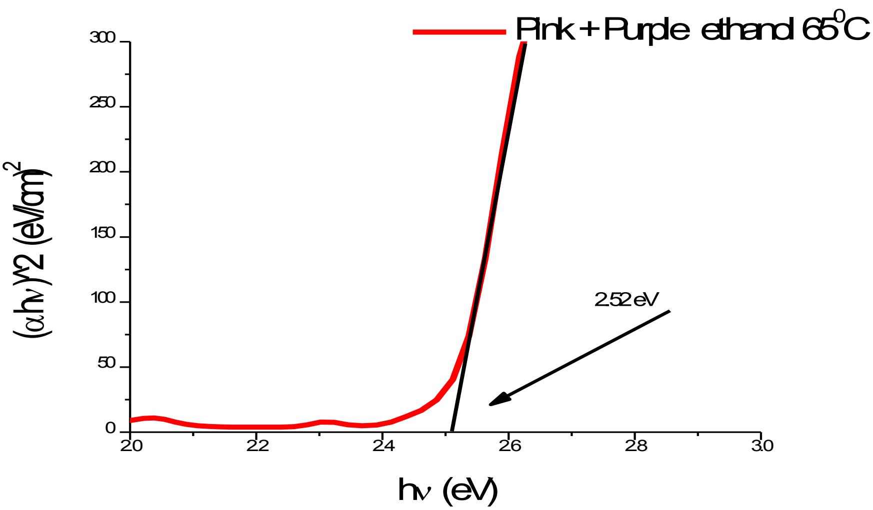

Figure 5: (c) The Cyclic Volammetry curve for Mixed Coleus (pink + purple) at 65˚C, 2h

Table 1: (b) pH levels and Energy levels for mixed (Pink &Purple) Coleus with Ethanol at 25°C, 45°Cand 65°C, 2h

Temperature (˚C)	pH level	Wavelength (nm)	Energy Band gap (E_g)(eV)
25	6.56	494	2.50
45	6.37	490	2.52
65	7.03	490	2.52

Electrochemical Properties of Natural Dye Extract

Cyclic voltammetry (CV) is very suitable method for wide range of applications. Moreover, in some area of research, cyclic voltammetry is one of the useful methods to characterize the organic material and estimate the energy band diagram. HOMO and LUMO are types of molecular orbitals. HOMO is “highest occupied molecular orbital” and LUMO is “lowest unoccupied molecular orbital”. The energy difference between HOMO and LUMO are called HOMO-LUMO gap. The difference these two orbitals can be used to predict the strength and stability of transition material complexes, as well as the colors they produce in solution.[8,13]

Electrochemical cyclic voltammetry (CV) was performed to determine the HOMO and the LUMO energy levels of the natural dyes. Fig 6 (a-c) showed the cyclic voltammograms of Pink & Purple Coleus Blumei by using methanol solvent and Fig 7 (a-c) by using ethanok solvent. In this research, the energy levels were calculated using the following equations and the calculated values were shown in Table 2(a) to 2(b).

$$E_{LUMO} = -[E^{onset} + 4.4\ ]\ eV \qquad (2)$$

$$E_{HOMO} = E_{LUMO} + E_g \qquad (3)$$

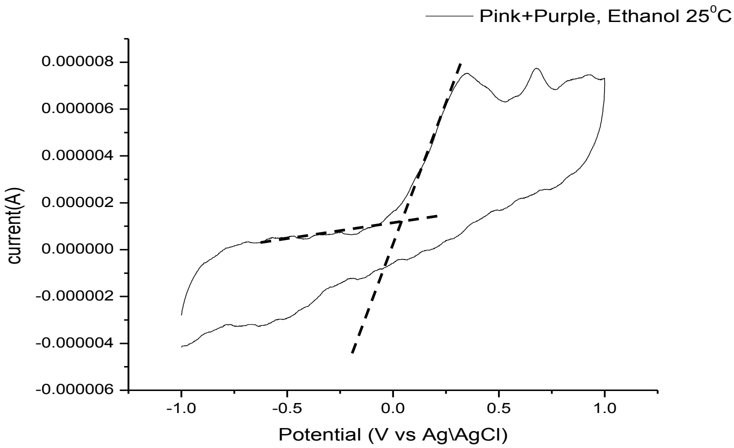

Figure 6: (a) The Cyclic Volammetry curve for (Pink + Purple) Coleus at 25˚C, 2h

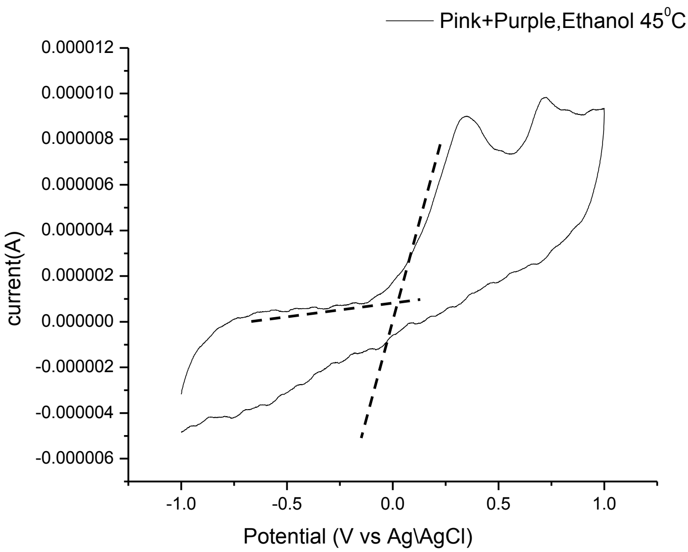

Figure 6: (b) The Cyclic Volammetry curve for (Pink + Purple) Coleus at 45˚C, 2h

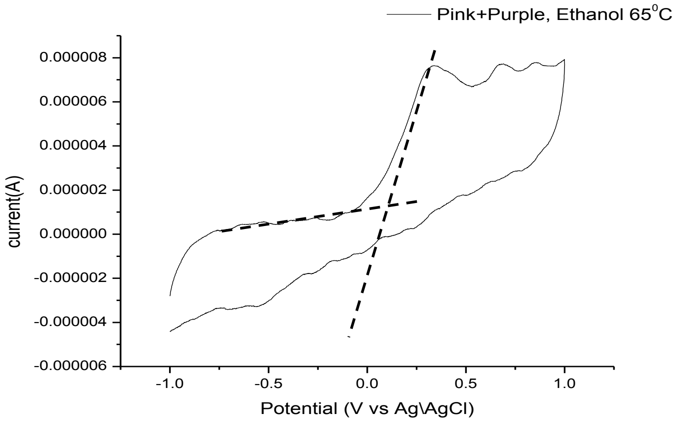

Figure 6: (c) The Cyclic Volammetry curve for (Pink + Purple) Coleus at 65˚C, 2h

Table 2: (a) Energy levels (HOMO and LUMO) for Mixed Coleus (Pink+Purple) with Ethanol at 25˚C, 45 ˚C and 65 ˚C, 2h

Temperature (˚C)	LUMO(eV)	HOMO(eV)
25	-4.36	-1.86
45	-4.34	-1.82
65	-4.32	-1.8

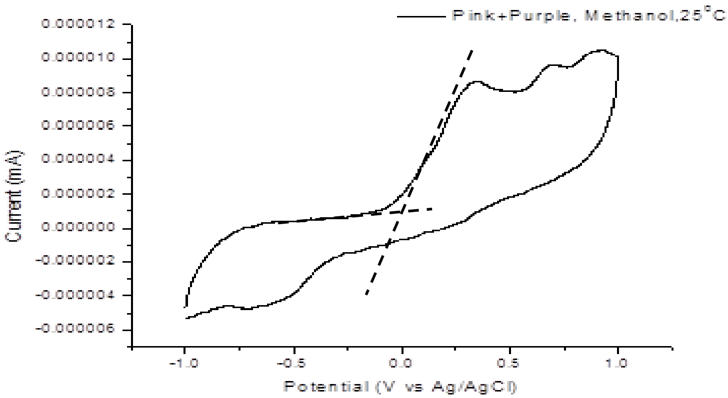

Figure 7: (a) The Cyclic Volammetry curve for (Pink + Purple) Coleus at 25˚C, 2h

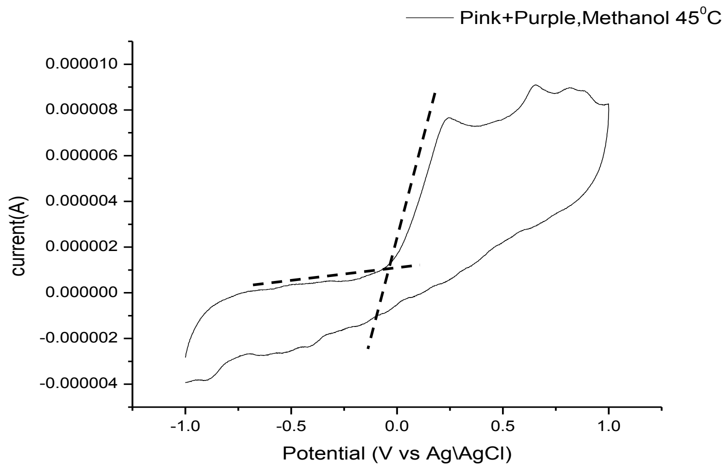

Figure 7: (b) The Cyclic Volammetry curve for (Pink + Purple)Coleus at 25˚C, 2h

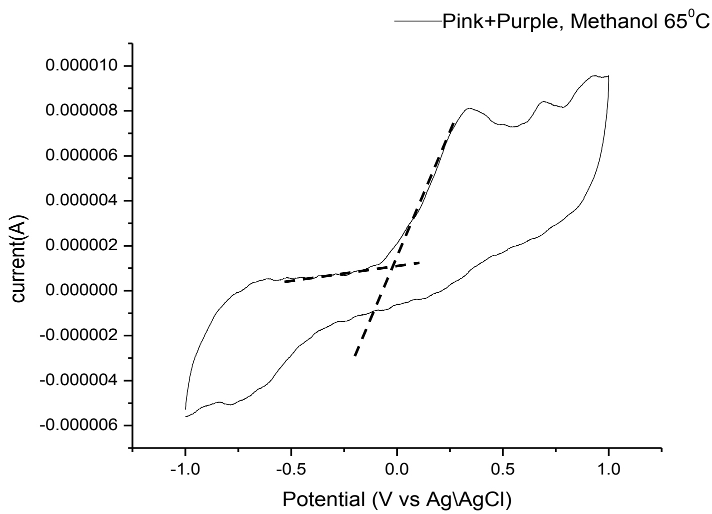

Figure 7: (c) The Cyclic Volammetry curve for (Pink + Purple) Coleus at 25˚C, 2h

Table 2: (b) Energy levels (HOMO and LUMO) for Mixed Coleus (Pink + Purple) with Methanol at 25˚C, 45 ˚C and 65 ˚C, 2h

Temperature (˚C)	LUMO(eV)	HOMO(eV)
25	-4.36	-1.85
45	-4.35	-1.84
65	-4.38	-1.86

FTIR Analysis

Fourier Transform-Infrared Spectroscopy (FTIR) is a technique used to identify organic (and in some cases inorganic) materials. This technique measures the absorption of infrared radiation by the sample material versus wavelength. The infrared absorption bands identify molecular components and structures. When a material is irradiated with infrared radiation, absorbed IR radiation usually excites molecules into a higher vibrational state. The wavelength of light absorbed by a particular molecule is a function of the energy difference between the at-rest and excited vibrational states. The wavelengths that are absorbed by the sample are characteristic of its molecular structure.[1,7,5]

Fig 8 (a) showed the FTIR spectrum of (pink + purple) coleus with methanol solvent, (b) showed the FTIR spectrum of (pink + purple) coleus with ethanol solvent. Table 3(a) showed chemical bond, chemical compound and frequencies range of pink coleus leaves by using methanol solvent, (b) showed chemical bond, chemical compound and frequencies range of pink coleus leaves by using methanol solvent.

All of dye solutions were displayed the sharp peaks frequencies range (3300 cm^{-1} - 2500cm^{-1}) indicated the presence of C-H (Alkanes) and O-H (carboxylic acids), (1640 cm^{-1}-1580 cm^{-1}) indicated the presence of N-H(Amines) and (1320 cm^{-1}-1000 cm^{-1}) indicated the presence of C-O (carboxylic acids) respectively. Therefore all dyes were corresponded to the presence of carboxylic acids groups. In additional, typical bond corresponding to C-N groups were observed. The results obtained from this research were similar as AMANO LIPASE Compound ($C_{11} H_9 N_3 Na O_2$) in FTIR library file.

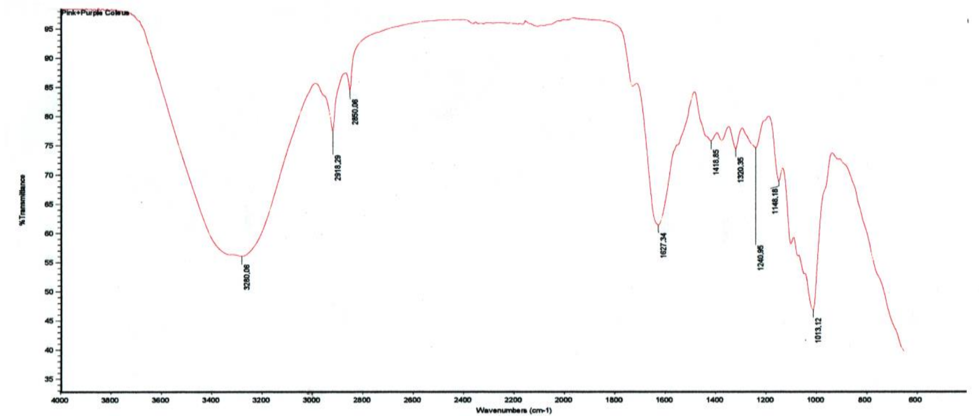

Figure 8: (a) FTIR spectrum of (Pink + Purple) Coleus leaves by using methanol solvent

Table 3: (a) Chemical Bonds, compound types & frequencies in (Pink + Purple) Coleus leaves by using methanol solvent

Bond	Compound type	Frequency range(cm^{-1})
C-H	Alkynes	3280.47 (strong, strength)
O-H	Carboxylic acid	2918.29, 2850.06 (broad, stretch)
N-H	Amines	1627.34 (bend)
C-H	Alkanes	1418.85(medium, stretch)
C-O	Alcohols, Ethers, Carboxylic acid, Esters	1013.12 (strong, stretch)

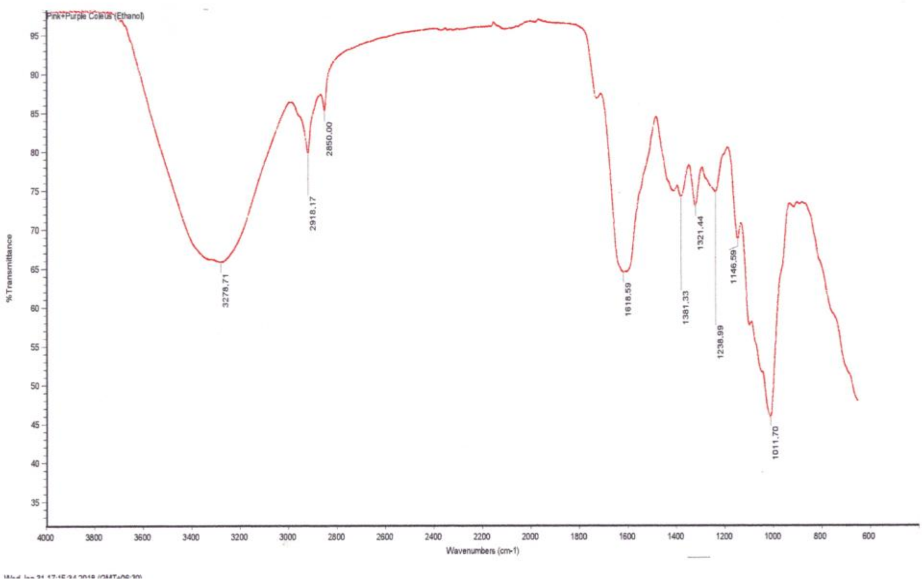

Figure 8: (b) FTIR spectrum of (Pink + Purple)Coleus leaves by using ethanol solvent

Table 3: (b) Chemical Bonds, compound types & frequencies in (Pink + Purple)Coleus leaves by using ethanol solvent

Bond	Compound type	Frequency range(cm^{-1})
C-H	Alkynes	3278.71 (strong, strength)
O-H	Carboxylic acid	2918.74, 2850.19 (broad, stretch)
N-H	Amines	1618.59 (bend)
C-H	Alkanes	1381.33(medium, stretch)
C-O	Alcohols, Ethers, Carboxylic acid, Esters	1011.70(strong, stretch)

Conclusion

The mixture of two colors of Coleus Blumei natural dyes were studied for photovoltaic applications. The maximum band gap energy was found 2.52 eV for (pink + purple) Coleus with ethanol as well as methanol solvents at 45 ^{o}C. Cyclic Voltammetry measurements were performed for these dye sensitizers to estimate their energy levels. According to the results, the largest value of LUMO was determined – 4.36 eV for (Pink+purple) Coleus with ethanol at 25 ^{o}C and – 4.38 eV with methanol at 65 ^{o}C. All types of dye solutions were pH levels round about 6, 7 and over, all of these solutions were acidic properties. The results of FTIR showed these dye solutions were AMANO LIPASE Compound which contained Carboxylic acids group. This study leads to the conclusion that dye extracted from Coleus Blumei leaves can be used as sensitizer for DSSC.

Acknowledgements

I am greatly indebted to Professor Dr Khin Khin Win, Head of Department of Physics, University of Yangon, for her kind permission.

I would also like to thank Professor Dr Aye Aye Thant, Department of Physics, University of Yangon, for her valuable advice in the preparation of this paper.

References

Arman Yusoff, N.T.R.N Kumara, Andery Lim, Piyarsiri Ekanayake and Kushan U. Tennakoon, " Impects of Temperature on the Stability of Tropical Plant Pigments as Sensitizers for Dye Sensitized Solar Cells " Journal of Biophysics, (2014), Vol.2014.

Asmaa Soheil Najm, Abu Bakar Mohamad and Norasikin A. Ludin, "The Extraction and Absorption Study of Natural Dye from Areca catechu for Dye Sensitized Solar Cell Application." International Workshop on Nanotechnology for Young Scientists, (2016),Vol.4 , pp 1-6.

Hassan K. Tajudeen etal, " Synthesis of Dye-Sensitized Solar Cells Using Chromophores from West African Plants" International journal of Science & Engineering Research, (2017) Vol.8, pp 631-635.

Hnin Ei Maung, Me Me Theint, Nyein Wint Lwin and Than Zaw Oo, " Optical Absorption and Absorption of Natural Dye Extracts on TiO_2 Scaffolds: Comparison between Green Leaf- and Red Fruit-Extracts" Journal of Material Science and Engineering, (2017), pp 166-170.

Jayaprada Rao Chunduri and Hetwi R. Shah, "FTIR Phytochemical Fingerpinting and Antioxidant Anlyses of Selected Indoor Non-Flowing Indoor Plants and Their Industrial Importance", International journal of Current Pharmaceutical Research, (2016), Vol.8, pp 37-43.

Kasim Uthman Isah, Umar Ahmadu, Adamu Idris and Isah Kimpa, " Betalain pigment as natural photosensitizers for dye-sensitized solar cells: the effect of dye pH on the photoelectric parameters". Mater Renew Sustain Energy, (2015), Vol.39, pp 1-5.

Lucia LEONAT and Gabriela SBARCEA, "Cyclic Voltammetry for Energy Levels Estimation of Organic Materials", (2013), Vol.75, pp 111-118.

Mohammed IK, Kasim Uthman ISAH, Yabagi JA , Taufiq S, "The Effect on Extracting Solvents using Natural Dye Extracts from Hyphaene hebaica for Dye-sensitized Solar Cells", Materials Science and Engineering, , (2015), Vol.5.

N.T Mary Rosana, Joshua Amarnth, K.L. Vicent Joseph, A Suresh, S. Anandan, G Saritha "Natural Sensitizers for Dye Sensitized Solar Cell Application", International Journal of Scientific & Engineering Research, (2014) Vol.5.