Available online at www.pelagiaresearchlibrary.com

Pelagia Research Library

Advances in Applied Science Research, 2014, 5(1):8-12

ISSN: 0976-8610
CODEN (USA): AASRFC

Absorbance of natural and synthetic dyes: Prospect of application as sensitizers in dye sensitized solar cell

Bhim P. Kafle[1], Babu R. Pokhrel[2], Rajendra Gyawali[1], Ananda. Kafle[1], Tirtha M. Shrestha[1], Ramita Shrestha[1] and Ravi. M. Adhikari

[1]*Kathmandu University, Dhulikhel, Kavre, Nepal*
[2]*Patan Multiple Campus, Tribhuvan University, Kathmandu, Nepal*
[3]*Angstrom Technologies, Kentuki, USA*

ABSTRACT

Optical transmittance of various natural organic- and synthetic (commercial)- dyes has been measured in the wavelength range of 310-900 nm. The pure natural dye from raw samples of either flower or root of plants were extracted and dried following standard method. Then the powder of both natural and synthetic dyes were dissolved in ethanol for transmittance measurements by UV-Visible spectrometric technique. In the visible region of electromagnetic radiation, all the natural dye samples show poor absorbance, except Maharanga bicolor. While the synthetic dyes, specifically, Green-VS, Patent-Blue and Black-ADLI show strong absorbance over the wide range in the visible spectrum, demonstrating the prospect of utilizing in the fabrication of dye sensitized solar cells. Uniquely, a natural dye extracted from root of herb Maharanga bicolor shows characteristic peak at around 500 nm, associated with rovibronic transitions.

Key words: absorbance, dye, Maharanga bicolor, Green VS, Patent Blue, Black ADLI, solar cell

INTRODUCTION

The conversion of solar energy to electricity utilizing solar cells represents one of the most promising and environmentally friendly methods to energy production. As a result, there have been huge efforts in a wide variety of solar cell technologies. Among the most widely used solar cells, silicon based solar cells are in the foremost. However, large-scale utilization is hindered by the production costs of solar cells, due to the rigorous process of obtaining pure silicon from silicon oxide. Thin film based dye-sensitized solar cells (DSSCs), which was first proposed by O'Breon and Gratzel in 1991, appear to be highly potential alternatives to more expensive solar cell technologies because of their high light-to-electricity conversion efficiencies, inexpensive production cost, and ease of fabrication [1].

In DSSCs, a thin film of nano-particles of metal oxide, mostly titanium oxide (TiO_2) or zinc oxide (ZnO), is synthesized on top of conducting glass electrode. The films of compound semiconducting material of metal oxide, which are in the order of hundreds nanometer to micro- meter thick, are sensitized by metal complex dye for absorption of light. The excited dye then releases electron, by photoelectric effect, which eventually reaches to the load via TiO_2 or ZnO nanocrystalline nanocrystals. With TiO_2-based dye-sensitized solar cells, efficiencies of up to 11% have been obtained using standard ruthenium polypyridyl complexes as a sensitizer in the laboratory condition[1]. While, very recently, slightly improvement in efficiency (12%) was reported with the Zn porphyrin dye. Further improvements in efficiency and durability would certainly facilitate widespread utilization of this technology.

There are a number of factors determining the efficiency of solar cells, but the structural and physical properties of the sensitizer are clearly important ones. Zinc-porphyrin dyes, while holding the record for conversion efficiencies, have relatively low extinction coefficients. They are also considered to be expensive, and difficult to synthesize. With a view to the limited metal-complex resources, metal free organic dyes have attracted considerable attention in recent years owing to their excellent flexibility in terms of molecular tailoring: Motivated by the possibility of finding a replacement for metal-complex dyes, a number of chromophores, including coumarins [3], indulines [4] oligoenes[5] merocyanines [6] hemicyanines [7] oligothiophenes [8], functionalized thiophenes [9], squaraines [10], benzothiadiazoles [11], perylenetetracarboxylic acid derivatives [12], diphenylaminostyrenes [13], phthalocyanines [14] and some other dyes such as anthocyanin [15-19] have been studied, with varying degrees of success. However, for the most efficient of these sensitizers, the overall conversion efficiency is limited to 4-7.5% [20] and also for obtaining most of the above dies one should follow rigorous methods of synthesis and purification.

It has been known that plants and bacteria capture solar energy using porphyrin-based chromophores for converting it into chemical energy [21]. Extracting such dyes from plants with a appropriate solvent and separating components (compounds) present in the dye mixture with simple and cost effective methods would eventually allow to further reduce the cost of solar cell fabrication.

In this article, we report on investigation of absorbance of various natural dyes and also of synthetic dyes (acidic), which have been traditionally used in wool coloring. We will also shed a light on the spectroscopic feature of the measured photoabsorption spectra.

MATERIALS AND METHODS

Extraction of the natural dye from plants (either flowers, roots or barks) was carried out. The collected samples were dried by diffused solar radiation by letting open for 2-3 days in a room, and crushed in a mortar to bring them into powder form. Certain amount of the powder was then dipped in ethanol (95%; purchased from Bengal Chemicals & Pharmaceuticals Ltd., India) for 24 hours for allowing to liberate dye molecules present in the sample. The extracts were filtered and dried in low temperature. A known weight of the extract of both natural and synthetic dyes were then dissolved in ethanol for absorption measurements (precaution was taken to overcome the saturation effect). The synthetic dyes were purchased from Hindustan Ciba Geigy Ltd. Absorbance of the dye was measured on Genesis-10 UV-Visible Spectrophotometer in the wavelength of 310 to 900 nm. The spectrometer was calibrated by measuring the concentration dependent absorbance of standard solutions at three different regions: UV, visible and near-IR. Fig. 1 shows, as an example, concentration dependent absorbance of cuppersulphate ($CuSO_4$) solution recorded at 810 nm wavelength in which $CuSO_4$ shows maximum absorbance.

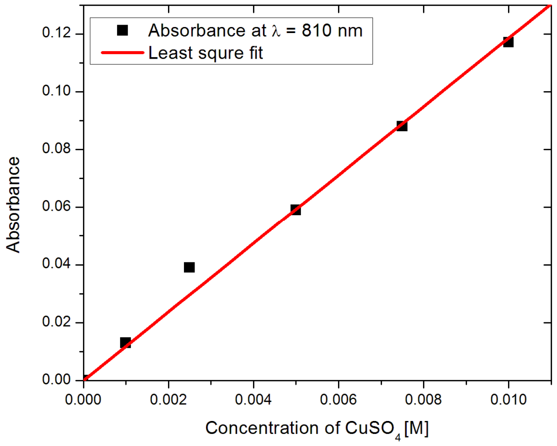

Figure 1. Calibration of spectrophotometer by measuring absorbance of $CuSO_4$ solutions of various known concentrations with radiation of 810 nm

Solid line represents the least square fit

RESULTS AND DISCUSSION

In Fig. 2, we present the absorbance as a function of radiation wavelength for different natural dye samples: Hibiscus-rosa-sinensis, Cysanthemum (Marigold), brassica nigra (Mustard), Tagetes erecta (Godawari) and Terminalia arjuna. Ethanol was used as a solvent to extract from raw samples and also to prepare the solution from the extracted one. While all the samples show strong absorbance with peak around 340 nm, Tagetes erecta shows rather broader peak but start to fall from ca. 425 nm. As all the natural dyes from present measurements found to have poor absorbance in the visible region, they may not be suitable for solar cell purposes.

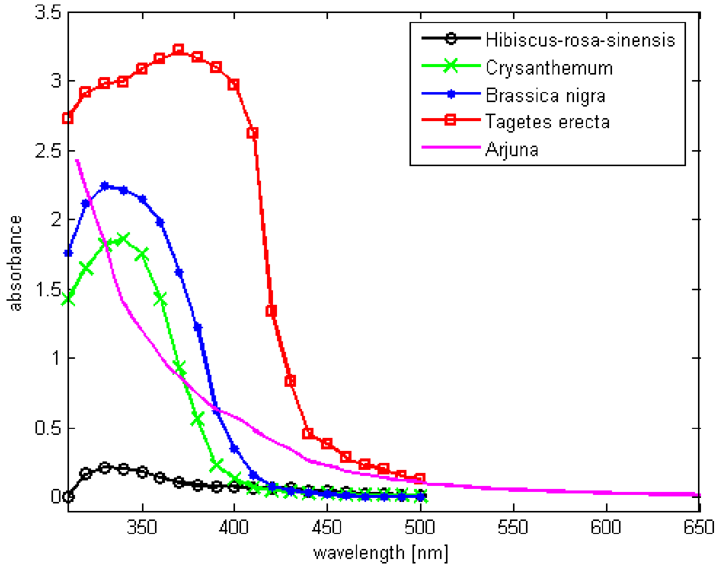

Fig. 2, absorbance as a function of radiation wavelength for natural dye samples: Hibiscus-rosa-sinensis (open circle), Cysanthemum (cross), brassica nigra (solid squre), Tagetes erecta (open square) and Terminalia arjuna (solid line).

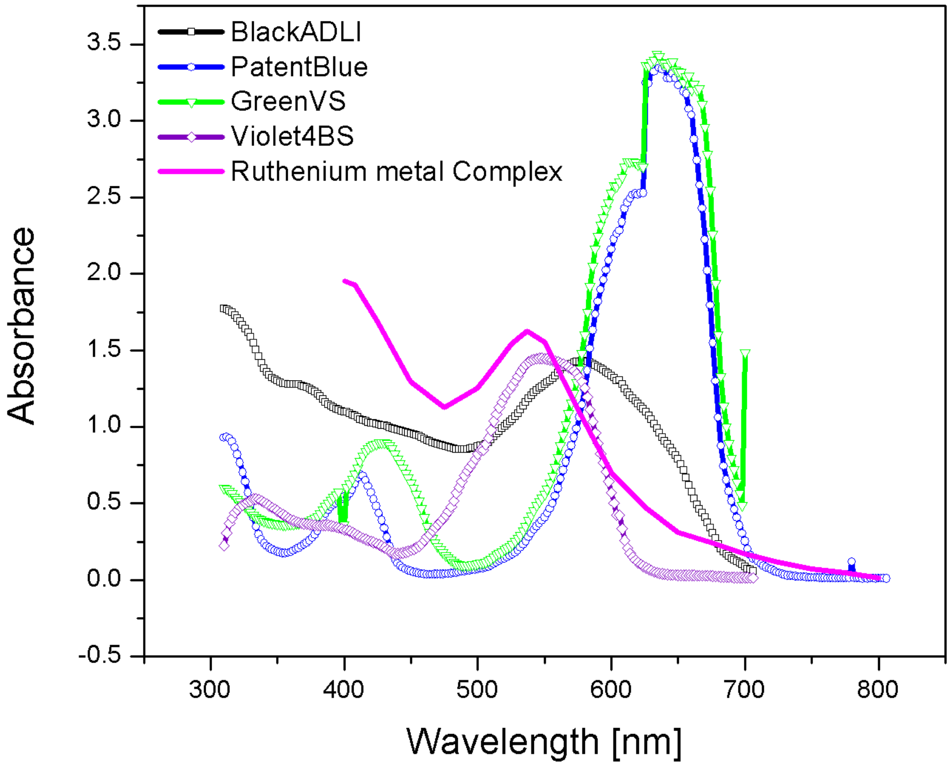

Fig. 3. The electronic absorption spectra of various synthetic dye samples, in the wavelength range of 300 - 900 nm. BlackADLI (open square), PatentBlue (open circle) GreenVS (open triangle) Violet4BS (open diamond), Solid curve is of Ruthenium dye [22]

Also, presented in Fig. 3 are electronic absorption spectra of various synthetic dyes recorded in the wavelength range of 310 nm to 900 nm. Ethanol was used as a solvent. As indicated in the figure, among all the samples, the *GreenVS* and *PatentBlue* exhibited superior absorbance in the visible region (around 550 nm to 700 nm). Interestingly, both dyes behave similarly in this region and show maximum absorbance at 650 nm with a FWHM around 60 nm. The *Violet4BS* shows absorbance peaking at 540 nm with FWHM of ca. 60 nm. On the other hand, *BlackADLI* shows fairly good absorbance in wide region extending from UV to visible region of electromagnetic spectrum (300 nm to 700 nm), with two major peaks at around 310 and 575 nm. The *Yellow2GLNI* shows the weakest response in the visible region among the studied samples. Also included is the action spectrum of Ruthenum dye complex, Z917, (represented by solid line) for comparison taken from Ref. [22], which have been common dye for DSSCs due to its good absorbance in the visible region.

In the present situation, although we are unable to specify the exact molecule (chromophore) responsible for absorption of light, we may shade some light on the basis of their color. All of the spectrum presented in Fig. 3 are of synthetic acidic dyes. As Anthraquinone derivatives generally form blue dyes, basic structure of the Patent Blue is of *Anthraquinone* type and expected to be synthesized from chemical intermediates which form anthraquinone-like structures as their final state [23]. The *Green VS* may be derivative of Triphenylmethane since the later generally forms yellow or green dyes.

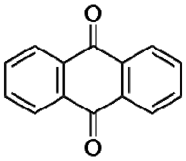

Fig. 4. Chemical structure of anthraquinone

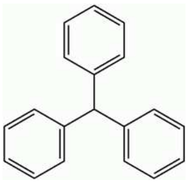

Fig. 5. Chemical structure of Triphenylmethane

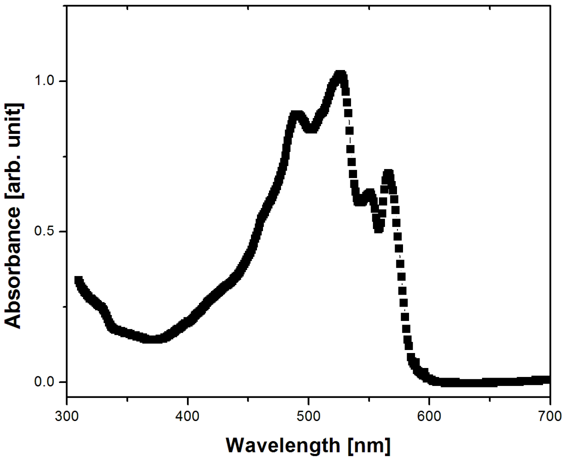

Fig. 6. The electronic absorption spectrum of Maharanga bicolor dye, prepared in hexane as a solvent, in the wavelength range of 310-700 nm

Fig. 6. The electronic absorption spectrum of Maharanga bicolor dye (extracted from root of Maharanga bicolor herb and dissolved in hexane) in the wavelength range of 310- 900 nm. Note that hexane is a nonpolar solvent with polarity index of zero. Curve around 310 nm appear to be falling side of the peak in the UV region. Besides, it also demonstrates another broad peak centering around 510 nm with full FWHM of around 110 nm. Although measurements were in liquid phase, surprisingly, rotational-vibrational peaks are noticeably visible indicating vibrational and rotational transitions accompanied with electronic transitions.

CONCLUSION

Among the measured absorption spectra of natural dyes, although Tagetes erecta shows better absorbance in the visible region its absorbance spectrum false rapidly after 420 nm reaching around only 10 percent at 450 nm. While, Maharanga bicolor shows broad peak in visible region extending from 400 to 600 nm, indicating prospect for using solar cell purposes. More interestingly although measurements were carried out in liquid phase (hexane as a solvent), surprisingly, rotational-vibrational peaks are noticeably visible. This may be due to minimal solvenyt effect as the polarity index of hexane is zero. The appearance of such peaks may be understood as an indication of vibrational and rotational transitions accompanied with electronic transitions.

On the other hand, the synthetic dyes, specifically, Green-VS, Patent-Blue, and Black-ADLI show strong absorbance over the wide range in the visible spectrum, demonstrating the prospect of utilizing in the fabrication of dye sensitized solar cells.

Acknowledgement
B. Kafle would like to thank to University Grant Commission (UGC) Nepal and Third Word Academy of Science (TWAS) for supporting for this research project.

REFERENCES

[1] B. O'Regan, Michael. Gratzel, *Nature* **1991,** 353, 737 – 740.
[2] Aswani Yella, Hsuan-Wei Lee, Hoi Nok Tsao, Chenyi Yi, Aravind Kumar Chandiran, Md.Khaja Nazeeruddin, Eric Wei-Guang Diau, Chen-Yu Yeh, Shaik M Zakeeruddin, Michael Grätzel, *Science*, **2011**, 334, 629-633.
[3] Hara, K.; Sayama, K.; Ogha, Y.; Shinpo, A.; Suga, S.; Arakawa, H. *Chem. Commun.* **2001**, 569–570.
[4] Horiuchi, T.; Miura, H.; Sumioka, K.; Uchida, S. *J. Am. Chem. Soc.* **2004**, *126*, 12218–12219.
[5] Kitamura, T.; Ikeda, M.; Shigaki, K.; Inoue, T.; Anderson, N. A.; Ai, X.; Lian, T.; Yanagida, S. *Chem. Mater.* **2004**, *16*, 1806–1812.
[6] Sayama, K.; Hara, K.; Mori, N.; Satsuki, M.; Suga, S.; Tsukagoshi, S.; Abe, Y.; Sugihara, H.; Arakawa, H. *Chem. Commun.* **2000**, 1173–1174.
[7] Wang, Z.-S.; Li, F.-Y.; Huang, C.-H. *Chem. Commun.* **2000**, 2063–2064.
[8] Koumura, N.; Wang, Z.-S.; Mori, S.; Miyashita, M.; Suzuki, E.; Hara, K. *J. Am. Chem. Soc.* **2006**, *128*, 14256–14257.
[9] Hagberg, D. P.; Yum, J.-H.; Lee, H.; De Angelis, F.; Marinado, T.; Karlsson, K. M.; Humphry-Baker, R.; Sun, L.; Hagfeldt, A.; Gratzel, M.; Nazeeruddin, M. K. *J. Am. Chem. Soc.* **2008**, *130*, 6259–6266.
[10] (a) Li, C.; Wang, W.; Wang, X.; Zhang, B.; Cao, Y. *Chem. Lett.* **2005**, *35*, 554–555. (b) Burke, A.; Schmidt-Mende, L.; Ito, S.; Gratzel, M. *Chem. Commun.* **2007**, 234–236.
[11] Velusamy, M; Thomas, K. R. J.; Lin, J. T.; Hsu, Y.-C.; Ho, K.-C. *Org. Lett.* **2005**, *7*, 1899–1902.
[12] Shibano, Y.; Umeyama, T.; Matano, Y.; Imahori, Y. *Org. Lett.* **2007**, *9*, 1971–1974.
[13] Xu, W.; Peng, B.; Chen, J.; Liang, M.; Cai, F. *J. Phys. Chem. C* **2008**, *112*, 874–880.
[14] He, J.; Benko, G.; Korodi, F.; Polivka, T.; Lomoth, R.; Akermark, B.; Sun, L.; Hagfeldt, A.; Sundstrom, V. *J. Am. Chem. Soc.* **2002**, *124*, 4922–4932
[15] Jude O. Ozuomba and Azubuike J. Ekpunobi, *Der Chemica Sinica*, **2013**, 4(3):137-143
[16] Jayant Gandhi, Rajesh Dangi, Jagdish Chandra Sharma, Nikhil Verma and Shipra Bhardwaj, *Der Chemica Sinica*, **2010**, 1 (3): 77-83
[17] Jude O. Ozuomba1, Laeticia U. Okoli and Azubuike J. Ekpunobi, *Advances in Applied Science Research*, **2013**, 4(2):60-69
[18] P. Sevvanthi, A. Claude*, C. Jayanthi and A. Poiyamozhi, *Advances in Applied Science Research*, **2012**, 3 (6):3573-3580
[19] D. S. Bhavsar, *Advances in Applied Science Research*, **2012**, 3(3), 1250-1254
[20] Sule Erten-Ela, M. Deniz Yilmaz, Burcak Icli, Yavuz Dede, Siddik Icli, and Engin U. Akkaya, *Org. Lett.*, **2008**, 10 (15), 3299-3302.
[21] Wayne M. Campbell, Kenneth W. Jolley, Pawel Wagner, Klaudia Wagner, Penny J. Walsh, Keith C. Gordon, Lukas Schmidt-Mende, Mohammad K. Nazeeruddin, Qing Wang, Michael Gra1tzel, and David L. Officer, *J. Phys. Chem. C*, **2007** 111, 11760.
[22] Feifei Gao, Yuan Wang,Dong Shi, Jing Zhang, Mingkui Wang, Xiaoyan Jing, Robin Humphry-Baker, Peng Wang,Shaik M. Zakeeruddin, and Michael Gra¨ tzel, *J. AM. CHEM. SOC* **2008** *130*, 10720–10728.
[23] http://en.wikipedia.org/wiki/Acid_dye#Structures; accessed on 20/10/1013.