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Optical Absorbance and Fluorescence of Natural Dyes: Prospect of Application in Dye Sensitized Solar Cell and OLEDs.

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ABSTRACT

Optical properties (absorbance and fluorescence) total of 15 natural dye samples were investigated in the wavelength range of $\lambda = 310 - 800$ nm; using UV-Vis, Fluorescence and IR spectroscopy. The natural dye from an oven dried raw samples of either flowers or leaves of selected plants were extracted by using both the polar and non-polar solvents. Dye extracted from leaves of *Lawsonia intermis*, *Nyctanthes arbor-tristis* using cyclohexane as a solvent showed broad absorbance in the visible region from 580 nm up to 700 nm. Also dye extracted from *Callistemon citrinus* and *Gomphrena globosa* using water solvent exhibited strong absorbance from 420 up to 640 nm. Dye extracted in cyclohexane from *Lawsonia intermis*, *Nyctanthes arbor-tristis* showed intense and strong fluorescence at 350 nm, slightly broad and weak signals at 500 nm and 675 nm are also observed. Moreover, the extracts from *Gomphrena globosa* using water as a solvent showed broad and strong fluorescence at 340 - 500 nm and at near IR (700 - 800 nm), and a sharp characteristic peak at 520 nm. Therefore it is highly likely that, one of these four species could be good candidate as a sensitizer for fabricating dye sensitized solar cell and may also have high propect in organic light emitting diodes (OLEDs).

Keywords: absorbance, fluorescence, organic dye, DSSC

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INTRODUCTION

Thin film based dye-sensitized solar cells (DSSCs), which was first proposed by O'Breon and Gratzel in 1991, has been considered to be highly potential alternatives to more expensive Silicon 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), are sensitized by organo-metallic complex (dye) for absorption of light. The excited dye molecules then release electrons, by photoelectric effect, which eventually reaches to the load via TiO_2 nanocrystalline materials. With TiO_2 -based dye-sensitized solar cells, efficiencies of about 13% have been achieved using Zinc-porphyrin dye as a sensitizer in the laboratory condition [2]. Further enhancement in efficiency and durability would certainly facilitate widespread utilization of this technology.

There are a number of factors which determine the efficiency of solar cells, but the structural and optical properties of the sensitizer are clearly important ones. Zinc-porphyrin dyes, while holding the record for conversion efficiencies, have relatively low absorption coefficients. However they are 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 organic 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] and phthalocyanines [14][3-6] 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 % [15] and also for obtaining most of the above dyes 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 [16]. Identifying and extracting such dyes from plants with an appropriate solvent and separating the components present in the dye mixture with simple and cost effective methods would eventually allow to further reduce the cost of solar cell. Alternatively, these organic species which can bring about electronic transitions in the visible range can be promising in OLED applications as well. In this article, we report an investigation of optical behaviors (absorbance, fluorescence and IR) of various natural dyes.

MATERIALS AND METHODS

All the collected raw samples (either flowers or leaves), which were harvested in September, 2014, were oven dried at 40 - 50 °C for three days and crushed in a mortar to bring them into powder form. 20 gm of powder was then dipped into 100 mL of a varieties of solvents *with* differing polarity from 0.2 to 10.2, for 24 hours, to isolate organic dye molecules present in the raw samples. The trend of polarity indices among the utilized solvents is: Cyclohexane (0.2) < diethyl ether (2.8) < dichloro methane (3.1) < methanol (5.1) < water (10.2). Most of the solvents were above 95 % pure; which were purchased from Bengal Chemicals & Pharmaceuticals Ltd., India.

The extracts of all the samples were separated from their respective residues, with *Whatman1* filter paper and transferred into clean volumetric flasks, which are stored in dark room at ambient temperature (at about 20 °C). The solvent was then evaporated to obtain the dry solid dye material at the room temperature, a portion of which was used for the absorbance and fluorescence measurements. The extraction method has been summarized in Fig. 1.

For absorbance measurements, 0.01 gm of the extracted powdery samples were then redissolved in 50 mL of the solvent with which the dye was initially extracted. Absorbance of the dye samples was measured with Genesis-10 UV-Visible Spectrophotometer in the wavelength range 310 to 800 nm. The spectrometer was calibrated by measuring the concentration dependent absorbance of standard solutions at the wavelength where sample shows maximum absorbance (λ_{max}) (precaution was taken to overcome the saturation effect). Also fluorescence measurements of the respective dyes were carried with F93 Fluorospectrophotometer.

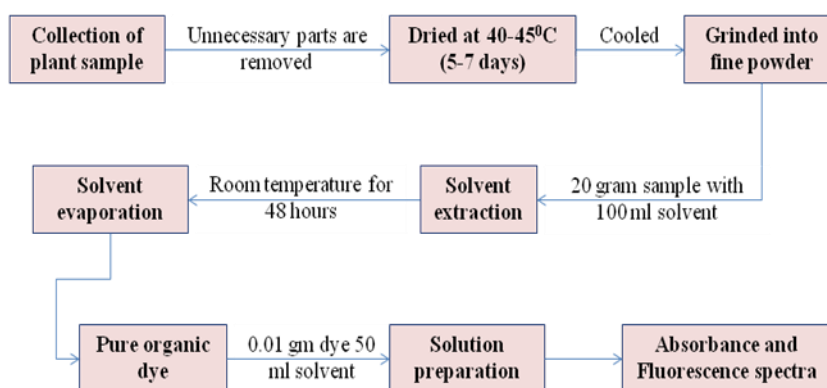


Figure 1: Schematic representation of the method for extraction and optical characterization of the natural dye samples.

RESULTS AND DISCUSSION

In Fig. 2, we present the optical absorbance spectra for fifteen natural dye samples (extracted using cyclohexane solvent) as a function of wavelength (λ) from 320 nm to 800 nm. Namely, the investigated samples were: *Berberis aristata*, *Bougainvillea glabra*, *Calendula officinalis*, *Callistemon citrinus*, *Capsicum annum*, *Chrysanthemum indicum*, *Curcuma Angustifolia*, *Dacus carota*, *Euphorbia pulcherrima*, *Gomphrena globosa*, *Lawsonia internnis*, *Malvaviscus arboreus*, *Myrica nagi*, *Nyctanthes arbor-tristis* and *Punica granatum*.

Most of these natural dye samples showed maximum absorbance at wavelength 450 nm to 500 nm, except *Chrysanthemum indicum* which show sharp decreasing trend below ~ 420 nm. While, above ~ 500 nm absorbance of all the samples decrease monotonically with increase in wavelength. While, *Nyctanthes arbor-tristis* as well as *Lawsonia internnis*, besides broader peak in the wavelength ranges 450 nm to about 500 nm, exhibit peak in between ~ 600 nm to ~ 700 nm.

The deep including three noticeable spikes in the spectra of the samples *Nyctanthes arbor-tristis* and *Lawsonia internnis*, in the wavelength region 570 - 650 nm, resembles the well known features of chlorophyll, hinting later could be one of the prominent candidates in these samples.

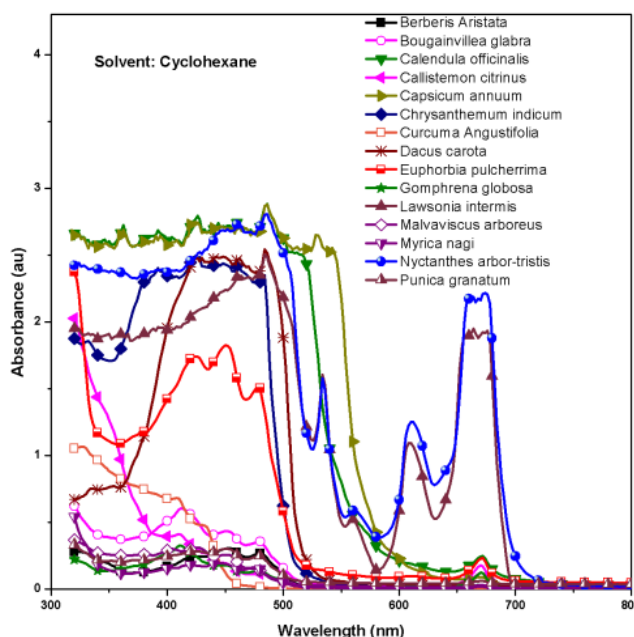


Figure 2: Absorbance as a function of radiation wavelength for various natural dye samples: *Berberis aristata*, *Bougainvillea glabra*, *Calendula officinalis*, *Callistemon citrinus*, *Capsicum annum*, *Chrysanthemum indicum*, *Curcuma angustifolia*, *Dacus carota*, *Euphorbia pulcherrima*, *Gomphrena globosa*, *Lawsonia internnis*, *Malvaviscus arboreus*, *Myrica nagi*, *Nyctanthes arbor-tristis* and *Punica granatum*.

Fig. 3 (a) - (d) show the solvent dependence of absorbance spectra for four of the total 15 samples, namely, *Lawsonia intermis* (leaves), *Nyctanthes arbor-tristis* (leaves), *Callistemon citrinus* (flower) and *Gomphrena globosa* (flower). These species were chosen due to the fact that they exhibited relatively good absorbance in the visible region of the solar spectrum. Dye extracted from *Nyctanthes arbor-tristis* and *Lawsonia intermis* using cyclohexane solvent (non polar) showed broad absorbance in the visible region up to 700 nm. Also, dye extracted from *Gomphrena globosa* and *Callistemon citrinus* using polar solvent exhibit strong absorbance in UV region to 640 nm. Therefore, these four dye species may possess high potential as a sensitizer in the dye sensitized solar cell.

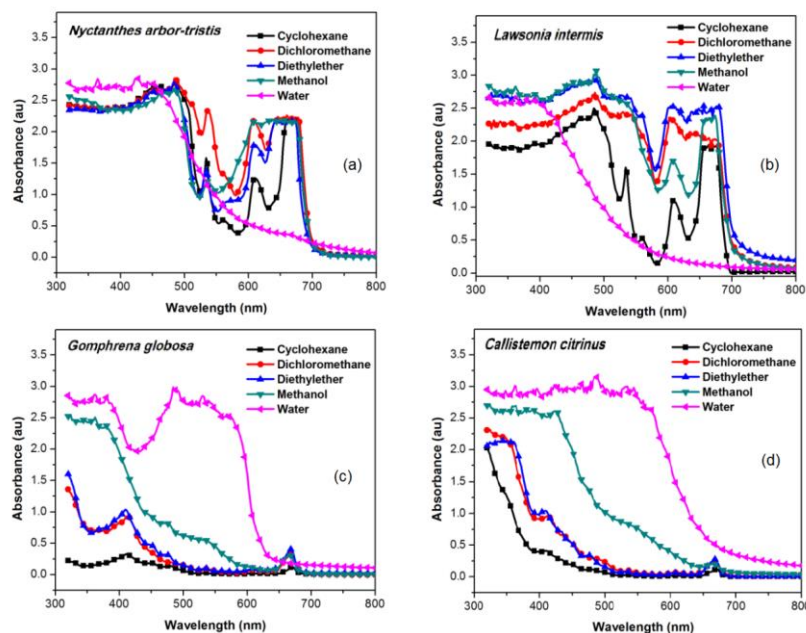


Figure 3: The solvent dependence of absorbance spectra for four dye samples extracted from *Lawsonia intermis* (leaves), *Nyctanthes arbor-tristis* (leaves), *Callistemon citrinus* (flowers) and *Gomphrena globosa* (flowers).

The appearance of fine peaks in each absorption spectrum reflect the excitation of vibrational and rotational motions of the organic compound/(s) present in the dye samples. However, as demonstrated in Fig. 3, one can notice gradual smearing out of fine structures with increase in the polarity of the solvent. The fine peak completely disappeared when water was used as a solvent. Also, although small, increasing the polarity of the solvent resulted blue shift in the absorption maxima.

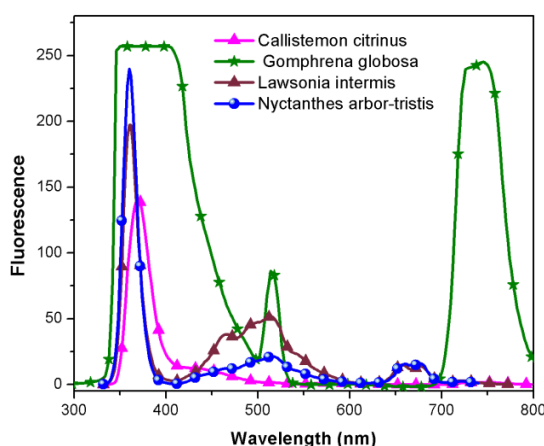


Figure 4: The fluorescence spectra of four dye samples extracted from *Lawsonia intermis* (leaves), *Nyctanthes arbor-tristis* (leaves), *Callistemon citrinus* (flowers) and *Gomphrena globosa* (flowers). Respectively, first two samples were extracted using cyclohexane and the later two samples with distilled water.

The fluorescence spectra of the *Lawsonia intermis*, *Nyctanthes arbor-tristis*, *Callistemon citrinus* and *Gomphrena globosa* were measured in respective solvents, represented in Fig. 4. The fluorescence study showed that dye extracted in polar solvent (water) from *Gomphrena globosa* showed strong emission at 300 - 500 nm and 700 - 800 nm in Uv-visible region. It also shows characteristic fluorescence of low intensity with peak at 516 nm. Dye from *Lawsonia intermis* and *Nyctanthes arbor-tristis*, which were extracted using non polar solvent (cyclohexane) and the dyes from *Callistemon citrinus* extracted using water showed almost similar fluorescence emissions. The fluorescence were found within 650 - 700 nm, 425 - 575 nm and even strong and narrow fluorescences in between 300 - 400 nm.

Comparing absorbance and fluorescence spectra of these four selected dyes, it is clear that all the four samples from *Lawsonia intermis*, *Nyctanthes arbor-tristis*, *Callistemon citrinus* and *Gomphrena globosa* shows strong absorbance from 310 (which is minimum of our study range) upto about 700 nm (Fig. 2,3) but showed strong fluorescence in UV region (between 300 - 400 nm) with maxima at 358 nm (Fig. 4). Dye from *Gomphrena globosa* also exhibit emission in the region 700 - 800 nm.

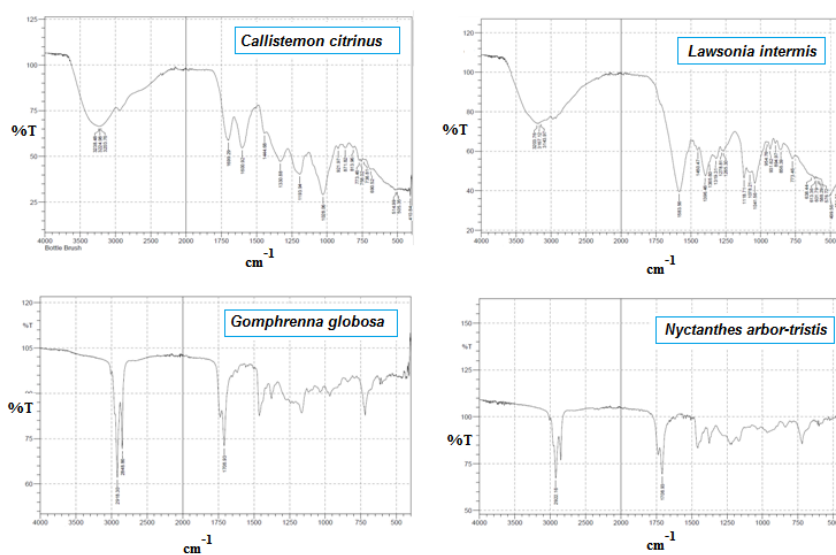


Figure 5: IR spectra dyes extracted from four plant samples *Gomphrena globosa*, *Callistemon citrinus*, *Lawsonia intermis* and *Nyctanthes arbor-tristis*, respectively.

The IR spectra from solid samples of above mentioned four dyes, extracted using respective solvents were studied using IR Prestige-21, IR spectrometer and shown in Fig. 5. Dyes extracted from both the *Gomphrena globosa* and *Callistemon citrinus* showed broad peak at 3200 cm^{-1} which is probably due to the presence of -OH group. In both the dyes peaks were also observed at around 1600 cm^{-1} . While peak at 1700 cm^{-1} was observed for *Callistemon citrinus*, which indicates that presence of C=O group under different environment. On the other hand, IR spectra of dyes extracted (with non polar solvent) from of *Lawsonia intermis* and *Nyctanthes arbor-tristis* showed almost similar IR peaks.

CONCLUSION

Investigation of absorbance and fluorescence of natural dyes extracted from leaves and flowers of plant with the prospect of using in dye sensitized solar cell were carried. Among the measured absorption spectra of natural dyes, although *Callistemon citrinus* and *Gomphrena globosa* dye extracted using cyclohexane solvent shows weak absorbance in the visible region, the absorbance of the radiation was found very good when the dyes were extracted using water solvent. While, the natural dyes from *Lawsonia intermis* and *Nyctanthes arbor-tristis* extracted in cyclohexane showed characteristic broad peak in visible region extending from 550 to 700 nm. Fluorescence study also showed that the extracted dye materials from *Gomphrena globosa*, *Callistemon citrinus*, *Lawsonia intermis* and *Nyctanthes arbor-tristis* falls in the UV region, near to the band gap of most of the semiconducting metal oxides, indicating prospect for using solar cell purposes.

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