CHAPTER-3

Dyes: Their Source, Properties and Extraction

We are making the first step out of the age of Chemistry and Physics, and into the age of Biology.

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3.1 Introduction

At the heart of a dye sensitized solar cell, as the name suggests, is the dye. The photoelectrochemical properties of dyes primarily control efficiency of solar cells. Dyes (pigments) are chemical entities that are able to absorb electromagnetic radiation in the visible range (400–780 nm). The dyes can be classified under two categories: natural or green and synthetic. The former class of dyes is present in fruits, vegetables or edible plant leaves (e.g. carotene, chlorophyll, anthocyanin etc) as well as in animal tissues (e.g. myoglobin, hemoglobin) while the latter are those synthesized artificially, for instance, quinoline yellow.

Since the advent of DSSCs, synthetic dyes have extensively been used as sensitizers with the efficiency obtained up to 15% in such cases. There are, however, concerns related to the cost and environment with these dyes. These factors thus have compelled researchers worldwide to look towards natural dyes which are present in the plant parts like roots, bark, leaves, flowers, fruits, etc. [Tennakone et al. (1997), Kumara et al. (2006), Dai et al. (2002), Hemalatha et al. (2012)]. Moreover, these dyes are abundantly available and could be easily extracted using cheap organic solvents and also the extracted dyes can be used without further purification making them a sustainable option.

Though, a number of reports for use of green dyes in solar cells is available in the literature, the research on natural dye-sensitized solar cells (N-DSSCs) still is in its infancy. The biggest challenge associated with these dyes is low efficiency of N-DSSCs as compared to that of synthetic dyes. This presents tremendous scope for the search of new and efficient dye sensitizers.

As has already been described in chapter 2, good sensitizers should have intense charge transfer absorption in the whole visible range of the solar spectrum. The factors which affect the absorption of the dye are, extraction method, extracting temperature, extraction medium, i.e., solvent, etc. [Polo et al. (2006), Wongcharee et
al. (2007)]. Thus, extraction of dyes is an important issue and in this chapter we have touched upon this point extensively.

Three dyes-Begonia, Melastoma, and Pomegranate, all belonging to anthocyanin group (as confirmed through optical studies discussed in detail in chapter 5), were used as sensitizers for the fabrication of DSSCs. The details of the dyes, their sources, extraction procedures and photochemical constituents are discussed here.

3.2 Begonia dye

The source of Begonia dye is the leaves of Begonia plant. Begonia is the sixth largest angiosperms genus with around 1,500 species [Frodin (2004)]. It is a perennial herb that belongs to the family Begoniaceae. The species grows in moist climate and is found abundantly in the Eastern Himalayas. It has asymmetric broad leaves and dark red color underneath (see Fig. 3.1). Forty five of its species are present in India [Santapau et al. (1993)]. The herb, Begonia malabarica Lam. (BM), known as Ratha soori in Tamil is found in the hilly regions of Southern India, Arunachal Pradesh and in Sri Lanka.

![Fig. 3.1: Begonia plant.](image)

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3.2.1 Photochemical constituents of BM dye

The preliminary phytochemical screening [Harborne (1976)] reveals the presence of Flavanoids, Carbohydrates, Proteins, Steroids, Resins, Tannins and Thiols. Phytochemical investigation of the various extracts of the leaves of *Begonia malabarica* Lam. (Begoniaceae) resulted in the isolation and identification of six known compounds, viz. friedelin, epi-friedelinol, β-sitosterol, luteolin, quercetin and β-sitosterol– 3-β-D-glucopyranoside [Ramesh et al. (2002)]. Fig. 3.2 shows the molecular structure of the six compounds found in the extract of BM dye.

![Molecular structure of Friedelin and Epi-Friedelinol](image)

Friedelin (C$_{30}$H$_{50}$O)

Epi-Friedelinol (C$_{30}$H$_{52}$O)
β-sitosterol

Luteolin
Fig. 3.2: Molecular structure of the phytochemical constituents of BM dye.
3.2.2 Dye extraction

As mentioned above, the leaves of BM were used for the extraction of the dye. Fresh BM leaves were taken and washed properly in de-ionized water and kept in an oven at 40 °C for 30 mins. The leaves were then crushed in an agate mortar using ethanol as extracting solvent. The ethanolic dye solution was stored in a dark container to prevent its exposure to direct sunlight. For UV-Vis, FTIR, DSC and TGA studies the dye was extracted using an automatic solvent extractor (see Fig. 3.3).

The procedure followed is:

i. Cleaning of fresh dye leaves in tap water and then in distilled water.
ii. Air drying of cleaned samples in oven at 35 °C for 24 hrs.
iii. Dye extraction of fresh samples as well as air dried samples both in ethanol and methanol using Automatic Solvent Extractor at 70 °C for 7 hrs in dark.
iv. Collection of pure extracted dye by passing the extract through refrigerated centrifuge. The system was run for 10 mins at rpm 1500-3000.
v. Evaporation of solvent of the collected extract by keeping the sample at 40 °C in an air dryer for 24 hrs.
We have attempted to extract the dye in de-ionized water as well, but the color of the extract was pale yellow and it could not stain the electrodes properly. Hence, the extract was not found suitable for DSSC application.

3.3 Melastoma dye

*Melastoma malabathricum* (MM) is among the 22 shrubs commonly found in the Southeastern Asian countries including India [Wrong (2008)]. It is found abundantly in cleared land, waste places and road sides. The plant is very common in lowland and moist areas and are used traditionally for medical purpose [Ling et al. (2009), Sharma et al. (2001)]. This plant is found copiously in Arunachal Pradesh of India commonly known as Kechi-yaying by the Adi tribes of the state [Kagyung et al. (2010)]. *M. malabathricum* has evergreen leaves and flowers throughout the year. Its fruit is classified as berries which has soft, dark purple and sweet pulp with numerous seeds (see Fig. 3.4a).

![Fig. 3.4: (a) Melastoma plant with fruits and flower (b) dye extract (c) electrodes dipped in dye.](image-url)
Its leaves, shoot and roots are prepared in various ways for treatment of various diseases according to traditional beliefs of communities/tribes as herbal medicine [Joffry et al. (2012)].

### 3.3.1 Phytochemical constituents of MM dye

Various types of phytochemical constituents have been isolated and identified from different parts of *M. malabathricum* since 1968. The presence of ellagic acid and anthocyanin (malvidin-3, 5-diglucoside) were found in the methanolic extract of its bark and aqueous extract of its flowers, respectively [Lowry (1968)]. The presence of anthocyanins (cy-3-glucoside and cy-3, 5-diglucoside) were found in *M. malabathricum* fruit extracted in water [Lowry (1968), Lowry (1976)]. Melastomic acid (5-hydroxylup-20(29)-en-28-oic-acid) were reported from the ethanolic extract of the root [Khuda et al. (1981)]. Dass and Kotoky [Dass et al. (1988)] have reported the isolation of 32-methyl-1-tritriacontanol, together with ursolic acid, p-hydroxybenzoic acid and gallic acid and kaempferol from the leaves and flowers of *M. malabathricum*. Fig. 3.5 shows the molecular structure of different constituents isolated from the fruit, leaves, flowers and bark of MM plant.
(b) Cyanidin 3, 5- diglucoside

c) Ellagic acid
d) p-Hydroxybenzoic acid
(e) Gallic acid

(f) Kaempferol

(g) Malvidin-3,5-diglcoside

Fig. 3.5: Photochemical constituents of MM dye extracted from (a, b) fruit, (c) bark, (d, e, f) flowers and leaves (g) flower.
3.3.2 Preparation of the MM dye sensitizer

All the samples were washed and cleaned prior to extraction. The outer skin of the fruit was peeled off manually. Fresh fruits were washed thoroughly and then dried in open air. 5 gm of the fruit was extracted in 10 ml of the solvents to get concentrated dye. The dye was extracted by macerating the fruit in two different solvents; de-ionized water and ethanol for 15 min. The aqueous extraction was carried out by Automatic solvent extractor at 60 °C for both media. The resulting extract was centrifuged to further remove any solid residue and used in raw form for DSSCs fabrication.

3.4 Pomegranate dye

Punicaceae is an aromatic dye which has high cyanin content. It grows wild in India, Italy, North Africa and China. The composition of pomegranate seeds is reflected by the high amount of phenolic derivatives. The compounds identified using pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) were 2-methoxy phenol, 2-methoxy-4-methyl-phenol, 2-methoxy-4-(1-propexyl)-phenol, 2-methoxy-4 vinylphenol etc. [Keheyen et al. (2006)]. The main coloring agent in the rind of pomegranate is granatonine, which is present in the alkaloid form N-methyl-granatonine, whose molecular structure is shown in Fig. 3.6 characterized by 2 condensed piperidine rings [Keheyen et al. (2006)].

![Fig. 3.6: Molecular structure of N-methyl-granatonine.](image)
The major Anthocyanins present in pomegranate juice shown in Fig. 3.7 are: Cyanidin-3-O-glucoside, Cyanidin-3, 5-di-O-glucoside, Delphinidin-3-O-glucoside, Delphinidin-3, 5-di-O-glucoside, Pelargonidin-3-O-glucoside, Pelargonidin-3, 5-di-O-glucoside [Prakash et al. (2011)].

![Chemical constituents of POM dye.](image)

- R=H; Cyanidin
- R= β-D-glucopyranosyl; Cyanidin-3-O-glucoside

![Chemical constituents of POM dye.](image)

- R=H; Delphinidin
- R= β-D-glucopyranosyl; Delphinidin-3-O-glucoside

**Fig. 3.7:** Chemical constituents of POM dye.
Pomegranate (*Punica granatum* L.) belongs to the Punicacea family. The pomegranate tree typically grows 12 to 16 feet, has many spiny branches, and can be extremely long lived, as evidenced by trees at Versailles, France, known to be over 200 years old. The leaves are glossy and lance shaped, and the bark of the tree turns gray as the tree ages. The flowers are large, red, white or variegated and have a tubular calyx that eventually becomes the fruit. The ripe pomegranate fruit can be up to five inches wide with a deep red, leathery skin; is grenade-shaped and crowned by the pointed calyx. The fruit contains many seeds (arils) separated by white, membranous pericarp, and each is surrounded by small amounts of tart, red juice (Fig. 3.8). *Punica* is a small genus of fruit-bearing deciduous shrub or small trees. Its better-known species is the Pomegranate (*Punica granatum* L.).

The flowers, fruit and root of the plant contain different alkaloids, tannin pigments (e.g. anthocyanin), organic acids (citric, malic, tartaric, ascorbic, etc.) and salts. The dye for sensitization was obtained by crushing the fresh pomegranate fruit and taking the filtrate out. No solvent was used for extraction of this dye as the seeds of fruit contain water in its yield.

![Figure 3.8: Pomegranate fruit with dye as sensitizer.](image-url)
3.5 Conclusions

The source, chemical structures of various photochemical constituents present in the dyes and extraction procedure of three natural dyes, namely, *Begonia malabarica* Lam. (BM), *Melastoma malabathricum* (MM), *Punica granatum* L. (POM) have been described. Different solvents have been used for extraction of dyes depending upon their suitability as sensitizer in DSSCs.