Paradigm shift of functions of organic dyes and pigments

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Abstract: Color plays an important role in adding value to textile products. Organic dyes and pigments have traditionally been used to color the textile world, in fact the word dyes is almost synonymous to textile. However, in the last two decades there has been a major shift of interest on organic dyes and pigments. These types of materials are now finding a lot of interest in opto-electronic device application like solar energy, solar cells, diodes etc. The main reason for the current shift of application of organic dyes and pigment is based on factors like cost, electronic property and most important is that the whole technology including processing and functioning is environmentally friendly. This work intent to give a review of some of organic dyes and pigments which have crossed over from coloring textile to become organic electronic materials. Some of the chemical modifications done to improve on optoelectronic properties will be briefly discussed.

Keywords: Dyes, Pigment, opto-electronic materials, electronic properties

1. INTRODUCTION

The impact of climate change is no longer a theory but a reality and many people across the world have experienced difficult times in the recent past. Floods have become a phenomenon in some parts of the world good example in the Philippians, drought and associated food shortage is now common in many parts of Africa, environmental caused diseases are now threatening life in many parts of the world. One major cause of all this suffering is pollution of environment by industrial activities. Concerted efforts are now being taken by various governments and other organizations to minimize the pollution from industries. More than 70% of industries across the world depend on oil to power their production. The use of oil produces a lot of fumes which contribute immensely to environmental deterioration. Not only alternative clean sources of power are currently being highly demanded but also appliances that consume less power. Solar power has been identified as a major source of power and holds a great potential of conserving the environment if it can be efficiently utilized.

The first solar cell was developed in the bell laboratory in USA by Chapin et al in 1954 using silicon material (Chapin et al., 1954). Ever since Chapin discovery various studies have been undertaken by various researchers to improve on the efficiency of the solar cell which has seen to the successful commercialization of silicon based solar cells. However due to the complexity of processing and the cost of silicon, the solar cells overall cost has been very expensive making it unaffordable. Efforts to find alternative materials which can replace silicon so as to overcome its limitation became successful in 1991 when Gratzel et al (O'Regan & Gratzel et al., 1991) invented the first solar cell using ruthenium dye. The dye was used to sensitize the solar cell and thus the technology is called Dye sensitized solar cell (DSSC). However, like the silicone development of ruthenium dye requires complex process which made the solar cell expensive. Efforts to reduce the cost have seen the introduction of organic dyes into the electronic world. Organic electronic dyes are cheap in price and their processing is simple, also other electronic application of these organic materials in areas like sensor, light emitting diodes, among others have been developed. In the last couple of years organic materials have been intensively researched as they are believed to hold the keyto cheap solar cells and other electronic applications (Kim et al., 2004; Liang et al., 2007). Initially general organic dyes which had little or no significance in the textile industry were used however as time went by some important textile dyes both synthetic and natural dyes have joined the band wagon and are now playing a significant role in solar cell generation and electronic devices which use low power. This review is indented to give a brief overview of these dyes. We have also done some work on this dye of which we would like to show case.

2. THE SOLAR CELL TECHNOLOGY AND OPTOELECTRONICS

Conversion of light into electricity requires three distinct processes: light absorption generates an electronically excited state, separation of the excited states into electrons and protons, transfer of electrons. In a DSSC set up, the light absorption is done by the dyes while $TiO_2$is used as a semiconductor to separate the electrons from the excited state and transfer them to the conduction band where they are directed to the load. To increase the surface area and maximize electron transfer, the semiconductor in form of nanoparticles are sintered onto the transparent electrode, then coated with a single monolayer coverage of dye. The thinner the dyes layer the higher the light absorption. Furthermore, every light- absorbing dye molecule is directly attached to the semiconductor to optimize charge separation. Completing the circuit in a DSSC is typically accomplished with a redox electrolyte, almost always iodide/triiodide as illustrated in Fig. 1.

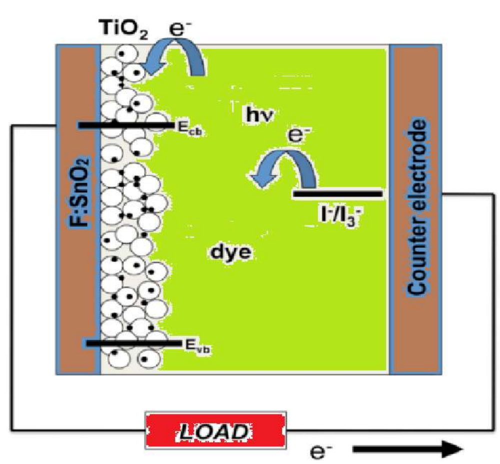

Figure 1 The components and electron transfer processes in a typical dye-sensitized TiO_2 solar cell

One important factor that governs the performance of a solar cell is the absorption spectrum of the organic semiconductors or the dye molecules used for device fabrication. In an ideal situation, the solar cell absorption spectrum should completely cover the region of terrestrial solar irradiation (Winder & Sariciftci, 2004). Therefore, the development of novel dye molecules with appropriate absorptive properties for photon harvesting has become an important area to explore. Dyes which have maximum absorption in the maximum irradiation region of the solar as illustrated in Fig. 2 are highly recommended.

3. DYES FROM TEXTILESUSED FOR DSSC AND OPTOELECTRONIC APPLICATION

There are various textile dyes which in the past few years have found a lot of application in solar cell and other optoelectronic applications. The list is quite long but this report will focus on a few important once which have received a lot of interest among researchers. Some of these dyes include Phthalocyanine, Porphyrines and perylenediimides.

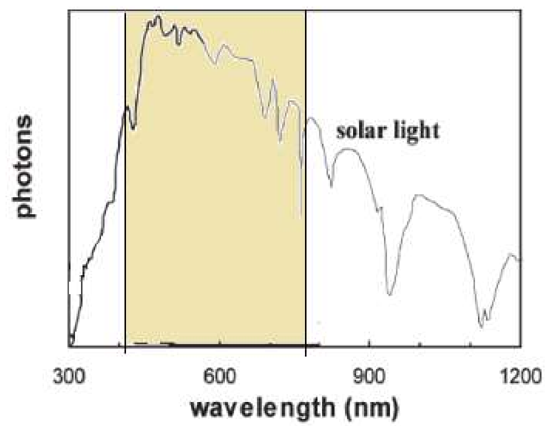

Figure 2 Normalized absorption spectra of typical perylenediimide dyes and the spectrum of solar irradiance

Common characteristics of these classes of dyes used in electronic application is their strong conjugation due to extended π-system, absorption in high wavelength region which make them good light harvesters and good light emission properties. These properties are required both for solar cell and optoelectronic applications. The listed organic dues their good optoelectronic properties now find wide application in solar cell devices, light emmiting diodes, sensors and many other optoelectronic applications.

3.1. Phthalocyanine

Phthalocyanine is an intensely blue-green-coloured aromatic macrocyclic compound that is widely used in dyeing. Phthalocyanines form coordination complexes with most elements of the periodic table as shown in Fig. 3. These complexes are also intensely colored and also are used as dyes or pigments. Phthalocyanine are good materials for solar cell due to their suitable properties which include strong red and near-IR absorbance, high extinction coefficients, good thermal, chemical, and photolytic stability, and easy tuneability through rational design of the macrocyclestructure (Cid et al., 2009; Eu et al., 2008).

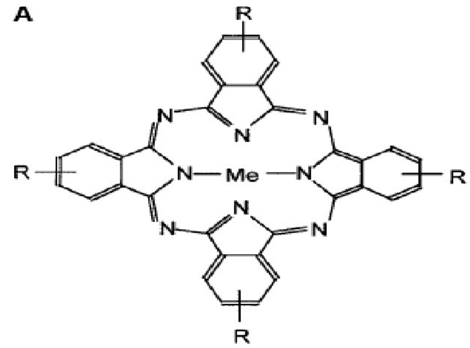

Figure 3 Structure of phthalocyanine dyes; Reactive blue 38: Me = Ni, R = $-SO_3H$ or $–SO_2$-NH-D, D = phenylen unit with reactive group; Reactive Blue 15: Me = Cu, R = $-SO_3Na$ or $–SO_2$-NH-$C_6H_3SO_3Na$-NH-$C_3N_3ClNH_2$.

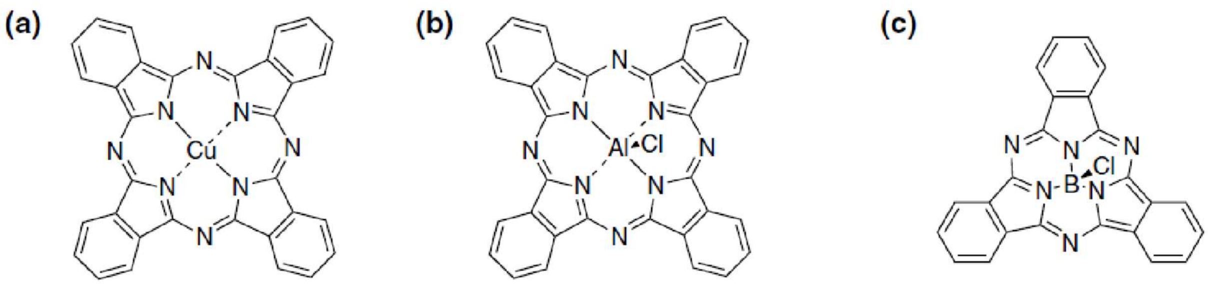

Figure 4 Derivatives of phthalocyanine dyes

The pioneer work of organic solar cell done by Tang (Tang, 1986) reported in 1986 used phthalocyanine with a C60 to make hetero-junction bilayer organic solar cell, the efficiency was very low however over the years continued research has seen significant improvement. Fig. 4 shows some of derivatives which have been studied (Walter et al., 2010).

3.2. Porphyrins

Porphyrins are a group of organic compounds, many naturally occurring. They are highly conjugated systems. As a consequence, they typically have very intense absorption bands in the visible region and may be deeply colored (Gouterman. 1978). Porphyrin dyes are active dyes for polyamide fibers and as cationic dyes for wool, polyamide, polyacrylic, and cellulose fibers.

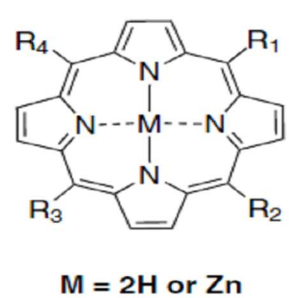

Figure 5 Structure of porphyrins dyes

Porphyrins are one of the first organicdyes that were studied as possible dyes to replace the expensive ruthenium complex dye for

DSSC (Kay et al., 1994) and interest in these dyes has continued to grow. The performance of Porphyrine dyes based DSSC has continually been improved and recently efficiency of up to 11% has been reported making porphyrines a possible alternative for ruthenium dye. Porhyrines have also been widely used in a range of applications, such as molecular electronics (Tsuda et al., 2003; Lash & Chandrasekar, 1996), solar energy conversion (Hasobe et al., 2005), photochemical water splitting (Darwent et al., 1982; Funyu et al., 20030 and donor-acceptor systems.

3.3. Perylenediimide dye

Perylenediimides (PDI) constitute a group of high- performance pigments with red to black shades, depending on the fine details of chemical structure and on molecular packing in the solid state. PDI-based pigments are used predominately in fiber applications and in high- grade industrial paints, particularly in carpet fibers and in the automobile industry, they produce high quality and/or durability of the colors. Perylene imides are well-known as chemically, thermally, and photophysically stable dyes (Ego et al., 2003). Together with phthalocynines they were the first organic dyes which were tested for DSSC. Ever since concerted effort has been made to see the successful utilization of this dye in electronic appliances. Also, PDI have been utilized in various optical devices like organic field-effect transistors (OFETs) and light-emitting diodes (OLEDs). These dyes have also been used in electrophotography (xerographic photoreceptors), fluorescent light collectors, and lasers (Liu et al., 2004, O'Neil et al., 1992).

3.3.1. Our work on PDI

The electronic properties of perylene-3,4;9,10- bis(dicarboximide) chromophores can be tailored by changing substituents on the perylene chromophores, yielding a family of n-type and p-type materials (Zhao et al., 1999; Lukas et al., 2002). Currently PDI is the most researched organic dye for solar cell and other electronic device application, the reason being this is the only organic dye which can be used as electron donor (p-type) and electron acceptor (n-type). As compared to other organic materials which are only p-type, PDI stands a high chance of maximum utilization in many areas of application. However, the dye has inherent stacking problem which has greatly limited its potential applications. Much research has been done to solve this challenge and significant achievement has been reported. Our group has also been involved in studying the self-assembly behavior of aggregation constrained PDI dye. We have used a bulky nanoparticle to sterically hinder the aggregation forces as per the molecular structure in Fig. 6.

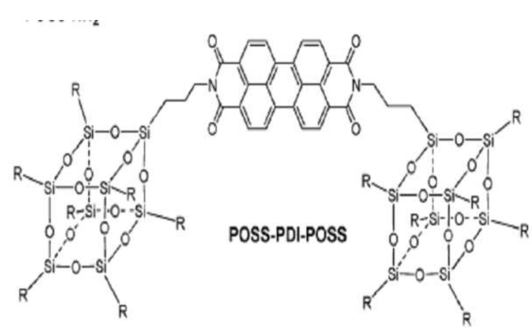

Figure 6 PDI dye modified with bulky nanoparticle POSS

Due to the nodes at the imides nitrogen, the bulky nanoparticle did not have any significant effect on the solution optoelectronic properties as reflected in Fig. 7. Both the absorption and fluorescence spectrum resembled the characteristic PDI chromophore in solution. However, significant straining of aggregation was achieved which enabled development of solid crystal structure with enhanced optoelectronic properties like fluorescence. Our molecular structure is tended to have good properties which are believed to be required for DSSC application and we believe better efficiency will be achieved when applied. Also, the achieved highly ordered crystal can find many other applications in optoelectronics.

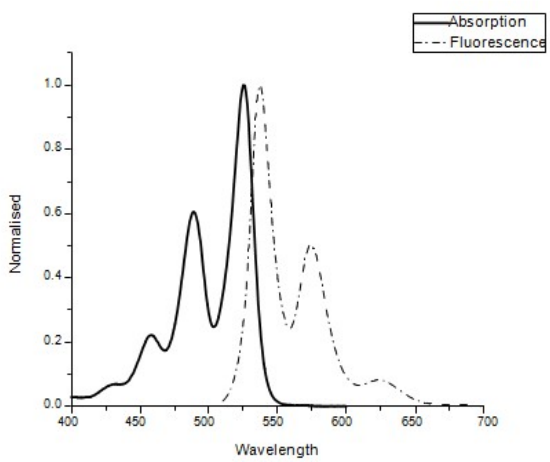

Figure 7 Absorption spectra and emission spectra of PDI dyes in chloroform

4. NATURAL DYES

Natural dyes found in flowers, leaves, and fruits have traditionally been extracted by simple procedures and used to dye textile products for a long time. The advent of synthetic dyes almost saw complete disappearance of natural dyes but due to environmental concerns, natural dyes have been gaining a lot of interest in the textile world. These types of dyes are cheap, non-toxic, and completely biodegradable. Apart from textiles natural dyes have been gaining significant attention in the electronic world, specifically for DSSC application. Already several natural dyes have been investigated for light generation good examples include cyanin (Sirimanne et al., 2006), carotene (Gomez-Ortiz et al., 2010), tannin (Espinosa et al., 2005), and chlorophyll (Kumara et al., 2006). So far, the best DSSC efficiency of 7.6% for natural dyes. This achieved efficiency is very promising to the development of natural dye sensitized DSSC.

5. FUTURE OUTLOOK

It is now clear that both natural and synthetic dyes are set for a major shift in their area of application. It’s just a matter of time that the full commercialization of DSSC made from organic dyes will be realized. Since a lot of research is being undertaken, we anticipate more textile dyes to join the electronic world. Already major companies are keen on adapting this emerging technology especially the digital world are already embracing appliances made of organic dyes. Samsung and LG are already in the market and within a short time major shift is expected. The challenge is, textile dyes are now joining a more lucrative field, will we be able to compete favorably?

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