Colours in our life: From aesthetics to functions

Dr S. Sivaram

Abstract

Colours have fascinated human beings from times immemorial. Simply stated they have made our lives colourful in multifarious areas. This article elaborates on the journey of colours through the generations. It also discusses the role of colours from aesthetics to functional applications.

Introduction

Colours are ubiquitous in our lives; they are everywhere around us, from the sky to the ocean blue, to the hues of the flowers to the green of the grass. They make our food enticing and our apparels enchanting. The world of art without a palette of colours is unimaginable. They make or break our moods, yellow for comfort, blue for trust, red for energy, white for perfection and drive sales of products and brands. At a sub-conscious levels, colours evoke strong emotions, associations and responses in all living beings. It is, therefore, not surprising that the market for synthetic dyes and organic pigments is valued at US$ 15 billion and growing at 6% per annum.

In spite of such widespread occurrence and use, the origins of colours remained a mystery for a long time. The earliest use of colours can be seen in Egyptian paintings dating back to 1000 BCE. The cave paintings of Ajanta (200 BCE to 500 CE) used highly refined water soluble pigments based on Kaolin, lamp black, Glauconite (green), ochre (yellow) and lapis lazuli (blue). Early natural philosophers like Democritus, and Aristotle inquired into the origin of colour. Pliny the Elder, in his magnum opus, Naturalis Historia, published in 77 CE provided a rich collection of facts and thoughts on the subject drawn from his study of botany, zoology, mineralogy and geology.

Early colours were based on pigments derived from inorganic materials, such as Prussian Blue (discovered in 1706), Cobalt Blue (discovered in 1807), and ultramarine blue (discovered in 1826). These were the source of vivid blues used by painters such as van Gogh and Renoir to create timeless masterpieces [1].

The first organic molecule to be used as a colouring material was synthetic indigo, first synthesized by Adolph von Bayer (1835-1917, Nobel Prize 1905). It is also interesting to note that an unintended consequence of the "Indigo Riots" that took place in Bengal, India in 1859 resulted in indigo becoming the first chemical to be manufactured in a chemical plant (BASF, 1897). This marked the beginning of the organized chemical industry in Western Europe [2].

Our understanding that colours result when light interacts with matter is due to Isaac Newton who put forth this idea in 1672. When light interacts with

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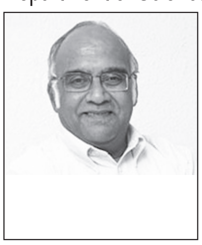

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matter, several processes can occur. The light can be absorbed, transmitted, reflected, refracted, diffracted or scattered. The fundamental physics of these events were unravelled by Lord Rayleigh (1842-1919, Noble Prize 1904). Albert Einstein (1879-1955, Noble Prize 1921) and C.V. Raman (1888-1970, Noble Prize 1930). Colour is, therefore, not physical but pure perception. To perceive colour, you need three things: a source of light, an object with which the light can interact and the angle at which the viewer observes the light emanating from the object. Water in a glass is colourless, but in an ocean it appears blue. Also depending on the depth, the colour of water in a sea ranges from light blue to deep blue.The sea is seen as blue because the water absorbs the longer wavelengths of red and reflects and scatters the blue, which comes to the eye of the viewer. The colour of the sea is also affected by the colour of the sky, reflected by particles in the water; and by algae and plant life in the water, which can make it look green; or by sediment, which can make it look brown. No wonder, Pablo Picasso once asked, "I want to know one thing. What is colour?"

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Colours and our ability to produce them from a variety of materials, organic or inorganic, natural or synthetic continue to fascinate scientists. The recent buzz about the discovery of a new shade of blue by a research team at Oregon State University is an example of how much science yet remains to be explored. The scientist have created a never before seen shade of blue derived from three elements, Yttrium, Indium and Manganese, which absorbs uv light and is stable at very high temperatures. $YInO_3$ is an off white color material. $Yin_{0.98}Mn_{0.02}O_3$ is blue. With increasing Mn content, the colour becomes darker and darker [3]. The compound $YMnO_3$ is a black colour material. Small evaluation quantities of this pigment are available from Shepherd Color Co., Cincinnati, USA (http://www.shepherdcolor.com/YInMn/) at a jaw-dropping price of US $ 1000 per kg.

This happens to be the first new blue pigment discovered after 200 years indicating that chemistry still holds many secrets waiting to be unraveled!

From Aesthetics to functions

Organic and inorganic colour forming substances are being increasingly looked at as advanced materials, capable of unique and useful functions, beyond mere aesthetics. This has led to a resurgence of research and development in this area and has led to many advances that have significant applications in medicine, energy harvesting devices, displays and lighting systems, nutraceutical and pharmaceutical adjuvants as well as printing inks. We discuss below a few of these functional applications of colour.

Dye sensitized solar Cells (DSSC)

Since its discovery in 1990, DSSC's have emerged as a major non-silicon based device for harvesting solar energy and its conversion to electricity [4]. Interaction of light with matter is one of the most profound concepts in science; the colours in our material world, both, natural and manmade is an exquisite manifestation of this science. Our ability to create energy out of light also exploits the same phenomenon. DSSC consists of five components, namely, a transparent conductive oxide (TCO) substrate, a nanostructured n-type semiconductor (TiO_2), a visible-light absorber dye, an electrolyte and a counter electrode. With the key idea of mimicking the natural photosynthesis, DSSCs are being pursued as eco-friendly devices, which could be easily fabricated. In a dye-sensitized solar cell, upon absorption of light, dye molecules reach an excited state with an appropriate energy level alignment of all the components. This causes charge separation at the interface between the dye-sensitized semiconductor and the electrolyte. While electrons are injected into the conduction band (CB) of the semiconductor (usually titanium dioxide, TiO_2) and transported to the conductive electrode, the regeneration of the oxidized dye takes place at the counter electrode by means of an electron-donor species (typically a liquid electrolyte based on the redox couple iodide/triiodide). Light with high enough energy excites the electrons in the dye molecule.The excited electrons diffuse into the semiconducting TiO_2 and are transported out of the cell. This leaves a positive "electron hole" in the dye molecule. The separation of the excited electron and the "hole" create a voltage. The process is schematically illustrated in Fig 1. The energy conversion efficiency has progressively improved from a mere 1% in the early nineties to about 14% today, thanks to the discovery of bet-

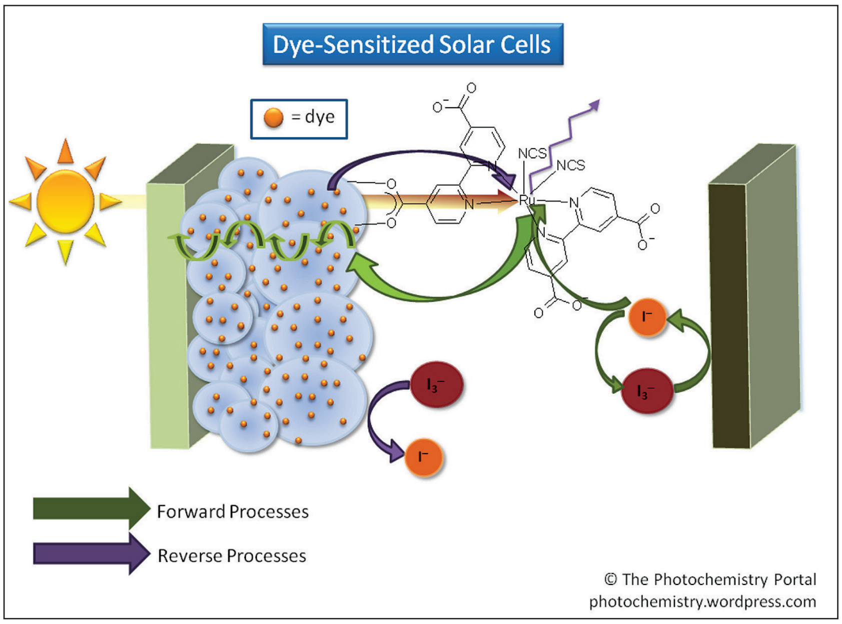

Fig 1: Schematics of the operation of a DSSC

ter and better dyes. Research is in progress to improve the efficiency of light absorption at a molecular level by modification of ruthenium complexes, which are the work horse dyes for the present generation of DSSC's (Fig 2) [5]. The unique features of a DSSC are that they are flexible, wearable, and printable and can harvest energy out of even diffuse lights. Major applications are in portable devices, building integrated photovoltaics and in the Internet of things (IoT) applications. Many companies are active in this area, namely, G24, UK; Donjin Semichem, Korea; 3G Solar, Israel; Dyetec Solar, USA; and Fukikura and Nissha Corp, Japan. A more detailed description of the science and technology behind DSSC and their commercial readiness is beyond the scope of this article. The interested reader may refer to the references cited [6].

Organic colours and natural dyes

Organic colours are fat-soluble pigments responsible for the myriad colours of plant leaves, fruits and flowers, as well as for the colour of feathers, crustacean shells, fish flesh and skin, etc. They are naturally occurring and hence are safe for human consumption. Apart from imparting colours to the foods we consume, they also act as critical dietary supplements. Carotenoids constitute one of the largest segments of organic colours with a market of US $ 1.5 billion (2014) [7]. Foods, drinks, animal nutrition products, pharmaceuticals and cosmetics are some of the most important end users of caretonoids. Phthalocyanins, extracted from Spirulina is the most important naturally occurring blue colour, which is, used as a natural food colour. In combination with natural yellow and red pigments, the naturally occurring blue pigment can be used to produce vibrant green and purple colours. Anthraquinones obtained from madder roots are the basis of red alizarin dyes. Several sulfur dyes can be synthesized from almond shells or rosemary leaves, which are waste biomass. Archroma offers them under the trade name Earth Colors[8].

Nevertheless, natural organic colors are small volume specialties, which are high priced and yet not affordable or technically viable for application in conventional dyeing applications. Natural colours do not match the vibrancy of the synthetic and are weakly binding to surfaces. They are unsuitable for use with synthetic fibres. Interestingly, there is no white pigment or color that you can obtain from nature!

Colours without dyes or pigments

The possibility that we can impart color without using a dye or a pigment is inspired by nature, where objects and species exhibit vibrant colours without any added ingredient. Colours found in fruits, flowers, insects and other living species are functional in that they protect them from predators, provide camouflage and facilitate pollination, mating and procreation. The wings of a butterfly, the feathers of a peacock, the glitter effects of marble berry fruit are exquisite examples of surface nanostructures perfected through long evolutionary cycles. Advanced techniques of microscopy that can image surfaces on a nanometer scale are re-

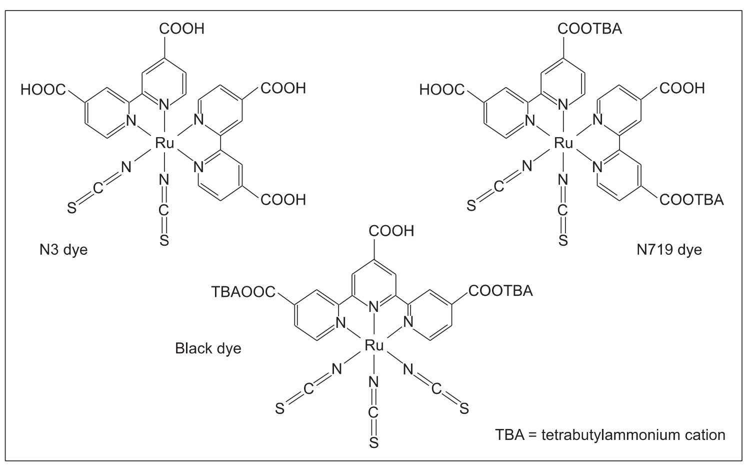

Fig 2: Some ruthenium dyes currently in use in DSSC's

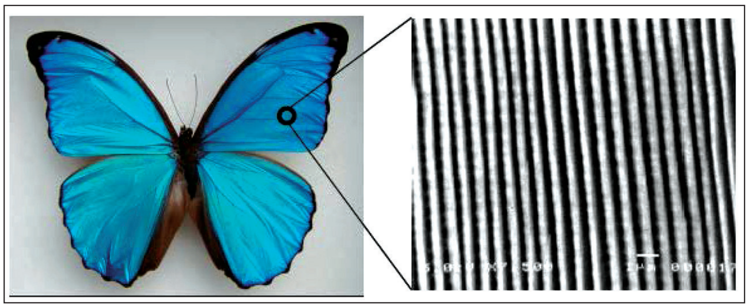

Fig 3: Ordered nanostructure gratings on the surface of the butterfly responsible for its colour

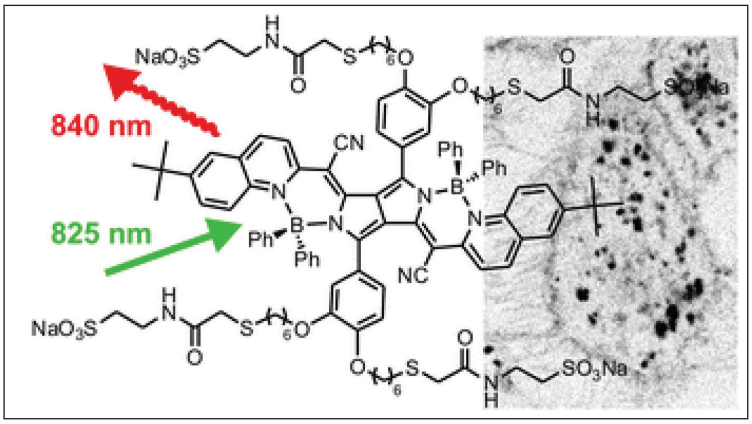

Fig 4: Near Infra red absorbing dyes (700-900 nm) Pyrrolopyrrole cyanine dyes

vealing to us the secrets of nature. The striking colors of butterfly wings come from light diffracting off the ordered microstructure of their scale (Fig 3). The iridescent colours of many natural objects are due to ordered stacks of nanocellulose fibres. Synthetic surfaces with similar optical effects can be now created in the laboratory. Such colours are permanent and will never fade. A startup company in New Zealand has produced colourfast wools by "dyeing" them with gold and silver nanoparticles, exploiting the well-known size dependent surface plasmon emissive properties of nanoparticles (http://www.noblebond.co.uk). The molecular basis of colour, which has been the mainstay of this science, is giving way to a structural basis. Future advances in this area are likely to both exciting and disruptive.

Near Infra red dyes based on diketopyrrolopyrroles

Diketopyrrolopyrrole (DPP) pigments have been widely used in inks, paints, and plastics since it was first discovered in early 1970s. The DPP-based materials were exploited for its optical, electrical and fluorescent properties and good charge carrier mobility. More recently, their applications In organic photovoltaic functional materials have been explored [9]. Fluorescent dyes are the basis for a broad range of modern techniques in life and material sciences. Pyrrolopyrrole cyanine (PPCys) dyes have long fluorescence lifetimes (3-4 ns), photostable and are a new class of near IR dyes which have found wide applications in both in vivo and in vitro imaging applications of biological materials [10] (Fig 4). Their optical properties are marked by strong NIR absorption and fluorescence and hardly any absorption in the visible range with high fluorescence quantum yields. PPCys are attractive candidates for labelling applications or as selective NIR absorbers. These outstanding photophysical properties make PPCys one of the most promising NIR dyes for medical imaging applications.

Summary

Colours are an integral part of our world, both, animate and inanimate and have fascinated humankind for centuries. They have stimulated human inquiry and creativity since time immemorial, from the ancient Egyptian paintings on palmyra leaves to contemporary technologies used for harvesting energy out of the sun and gaining a glimpse of the innermost functioning of human cells and organs. Colours, which have fascinated us for their sheer beauty and aesthetics are now becoming functional and an integral part of our continuing understanding of how light interacts with matter, a quest that began over three hundred and fifty years ago.

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