The Chemistry of Visible Light

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Life on earth literally revolves around the sun. The sun is the ultimate source of energy for the majority of life on earth. It is solar irradiation, or light, which is the energy source for photosynthesis in plants. What most people probably are not aware of, however, is that there are a myriad of other events that can occur using light as an energy source.

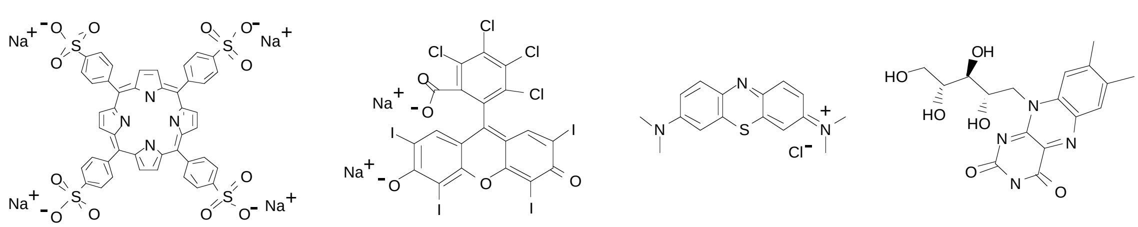
Forms of Light

A closer look at light reveals that solar radiation comes in many forms, differing in the energy they carry. Ultra-violet (UV) light is high in energy and well known here in Southern California for its harmful effects. These effects include the fading of colors by prolonged UV exposure, and more importantly, raising the risk of skin cancer. Lower energy infrared (IR) light is perceived by humans as heat. It is this radiation which keeps the earth warm, and ultimately drives the earth's weather patterns. The vision of some animals, including rattlesnakes and copperheads, is supplemented by specialized receptors that directly detect infrared radiation, thus aiding in the hunting of prey. The human eye, in contrast, can only observe this radiation with the aid of infrared cameras or converters.

The visible spectrum of light, which lies between UV and IR radiation in terms of energy, is responsible for many things including driving photosynthesis in plants, aiding in the formation of vitamin D in the skin, and allowing most animals on earth to visualize their surroundings. Visible light is also responsible for a rich variety of chemistry.

Molecules Interacting with Visible Light

Some molecules have the ability to absorb visible light, and as a result they are themselves colored. This color arises from the molecule removing those wavelengths which it absorbs, thus the reflected light is missing some of its original wavelengths. We see the color of the object as the complement of those missing colors. When a molecule absorbs visible light, it gains the energy associated with it. This molecule then exists in a higher energy state, called an excited state. If the molecule can transfer this extra energy to another molecule then it is called a photosensitizer. Many photosensitizers are organic molecules, that is to say they are composed mainly of carbon, hydrogen, nitrogen, and oxygen. These molecules are often used as dyes because they are brilliantly colored. The colors these molecules display usually arise from extensive systems of conjugated π electrons which allow them to absorb radiation in the visible region (Figure 1).



Tetrasodium-*meso*-tetra(4-sulfonatophenyl)porphine | Rose Bengal | Methylene Blue | Riboflavin (Vitamin B_2)

Figure 1. Examples of common photosensitizers

Singlet Oxygen

One possible outcome for a molecule in an exited state is to transfer its extra energy to a molecule of oxygen (O_2), causing the oxygen to be in a high energy, excited state. This excited state of oxygen is called, for reasons beyond the scope of this manuscript, singlet oxygen. Singlet oxygen is much more reactive than its low energy counterpart, ground state oxygen. It can chemically react with a number of molecules found in the body, such as the nucleic acids in DNA, the amino acids making up proteins, unsaturated fats and other biomolecules. This makes singlet oxygen toxic to living organisms. Like most things in life, there are advantages and disadvantages to the formation of singlet oxygen in the body.

Porphyria

Singlet oxygen's uncontrolled formation leads to deleterious, and very damaging effects. An example of these harmful effects is a group of diseases collectively known as the porphyrias. Porphyrias derive their name from the inability of the body to break down porphyrin and porphyrin precursors (Figure 2). Porphyrins are produced normally in the body, and they play a large role in the control of oxygen transport within the cells of healthy tissues. The result of over production in most victims of porphyria, however, is a phenomenon termed photosensitivity. The excessive amount of porphyrin in the body reaches the skin, where exposure to visible light, forming singlet oxygen, can result in pain, blistering, skin erosion, and scarring. The role of the porphyrin in this disease is based on its ability to act as a photosensitizer.

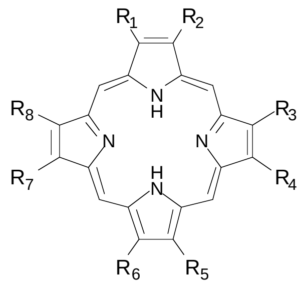


Figure 2. A generic porphyrin, where $R_{\#}$ stands for different sidechains attached to the porphyrin core.

Different types of porphyrias vary in their degree of observed phototoxicity. While most forms are genetic in origin, environmental factors such as the ingestion of certain chemicals or liver damage can contribute to the onset of the diseases. The average occurrence of porphyria in humans has been calculated to be roughly 1 per 100,000 on average, but due to its hereditary nature, there exist certain areas of the world with a much higher occurrence of these diseases. The most severe form of the disease is called congenital erythropoietic porphyria. Only about 100 cases of this most severe, and thankfully rare, type of porphyria have ever been reported, but the results of the immense overproduction of porphyrin in the body are staggering. Photomutilation usually begins appearing early in life, with the fingers, nose, and ears of the victims being the most severely affected areas of the body. The extreme over production of the porphyrin can be easily observed during the lifetime of the victim in their teeth, because the porphyrins are deposited in the dentine of the tooth. Upon irradiation with UV light a reddish fluorescence of the prophyrin can be observed. After death, the entire skeleton of the sufferer can be seen to fluoresce in an analogous fashion. The result of the most severe forms of porphyria invariably cause the sufferer to avoid light at all costs, leading to a life lived mainly in the dark, and this behavior may have played some small role in the emergence of the vampire myth.

Photodynamic Therapy

The reactivity of singlet oxygen in biological systems has been harnessed for beneficial purposes in a medical procedure known as photodynamic therapy (PDT). In this procedure photosensitizers are preferentially absorbed by tumor or cancer cells, rather than surrounding tissues. This is followed by irradiation of the tumor cells with visible light, causing singlet oxygen to be formed, hopefully killing the unwanted cells.

The advantage of PDT over other cancer therapies is its simplicity: It only requires a photosensitizer, oxygen, and light. The difficulties associated with PDT are getting the photosensitizer to localize in the tumor cells and getting the light to the tumor cells containing the photosensitizer. For these reasons PDT is most successful on surface tumors such as skin cancers, certain cancers of the eye, and esophageal cancer, where application and irradiation of the areas are facile.

While the limitations associated with PDT may seem significant, alternative methods available for fighting these tumors are typically much harsher on the patient's overall health. This motivates researchers in the field of photodynamic therapy to widen the scope of its applicability.

Singlet Oxygen at UCLA

The future of PDT will involve finding or synthesizing photosensitizers that can work with red light. This is extremely desirable because out of the colors that make up white light, red light penetrates through the body’s tissues the most easily. This phenomenon can be easily observed in a darkened room, by holding a hand over a flashlight. The hand will glow red because only red light is able to pass all the way through the tissues. With photosensitizers which can work with red light tumors which are internal, thus inaccessible to the current generation of photosensitzers, may become treatable with PDT.

In the research group of Professor Christopher S. Foote, in the Department of Chemistry and Biochemistry at UCLA, a major part of our research involves trying to utilize many of the concepts described here. In an effort to further our understanding of these processes, we are currently attempting to synthesize new and more potent photosensitizers with wider applicability for PDT, further elucidate the mechanisms by which they form singlet oxygen and other products, and continue investigations to determine how singlet oxygen reacts with different substrates.

For Further Reading:

On singlet oxygen; see Singlet O_2; Aryeh A. Frimer, Ed.; CRC Press, Inc. : Boca Raton, 1985, Vol. 1-4.

On porphyria; see *Porphyria*, Clinics in Dermatology; Michael R. Moore, Ed.; Lippincott : Philadelphia, 1985, Vol. 3. Num. 2.

On Foote group research; http://www.chem.ucla.edu/dept/Faculty/foote.html