



## Synthesis and applications of advanced luminescent molecules: A review

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### Abstract

Optically active advanced luminescent materials have found number of applications in the field of optoelectronics, security systems, optical imaging, and number of recording devices. Synthesis and characterization of natural or synthetic luminescent materials having biological or chemical origin are a hot topic of recent scientific studies now-a-days. Therefore, this article is designed to provide valuable information about some natural phenomenon such as the photoluminescence, fluorescence, phosphorescence, electroluminescence, cathodo-luminescence, bioluminescence, chemiluminescence, ionoluminescence, lyoluminescence, radioluminescence (scintillation), sonoluminescence and thermally stimulated luminescence and their different types. Similarly, some methods of synthesis of sodium sulphates, bis-(8 hydroxyl quinolone), mono-dispersed silica, fluorescent silica spheres, thiol-modified luminescent silica, streptavidin modified luminescent silica, iridium bisterpyridine, Eu (DBM)<sub>3</sub> as probe molecule, phenolic azo dyes, flavonoids by plant extraction via organic solvents and luciferin molecule has also been discussed along with their applications and future perspectives.

**Keywords:** Luminescence, electroluminescence, chemiluminescence, iridium bisterpyridine, sodium sulphates

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### 1. Introduction

In daily life of urban civilization, luminescence devices have become so significant that without these devices our life cannot be imagined. These devices have usage in several forms such as LED TVs, LED lamps, simple lamps, TVs, signals, displays and mobile displays etc. Luminescence devices have two common types named as (i) "incandescence" and (ii) "luminescence". The light generated from the heat energy is incandescence. If we heat any object to enough high temperature, then it will start glowing due to the heat energy, this phenomenon is known as "incandescence". For example, when the metallic or electrically powered stove's heater begin to glow "very red hot" and produce light energy. In the case of ordinary incandescent light bulb, when tungsten filament is heated upto great extent, it produces "quite white hot" light and glows brightly. The stars and sun also glows by the process of incandescence [1].

Luminescence is "cold light" generated from lower and normal temperatures. In 1888, Elkhart Weidman, a German physicist first used the word "luminescence". In Latin language the word "Lumen" means "light". Luminescent materials are the materials exhibiting this

phenomenon or in Greek language these materials are called as "Phosphors" meaning "light bearer". In 17<sup>th</sup> century, Italian alchemist "Vincentian's Casciarolo of Bologna" coined the term phosphor. He found a new stone that was perhaps barite (BaSO<sub>4</sub>) and fired it with the intention to convert the stone into some sort of noble metal. However, he could not obtain any noble metal, he discovered a very glowing material that after exposure to sunlight glows bright red in case of dark environment. A phosphor prototype zinc sulfide was prepared by Theodore sidot in 1866 which is now used in cathode ray tubes [2].

In Germany, Philip E.A. Lenard and his colleagues, worked and studied on phosphors in early 20<sup>th</sup> century. By using different host materials, they used heavy metal ions as "luminescent ions" along with different rare earth ions. In luminescence, an electron from the lowest energy state called as ground state moves towards high energy state called as excited state, then that electron emit light in the visible region by giving back the absorbed energy and as a result falls back to ground state [2].

The phenomenon of luminescence can be observed in nature like in certain deep-sea animals, various sea bacteria and fireflies and in glow-worms. Globally, it has conventionally been used in numerous fields by the different

researchers and scientists for instance in Physics, Chemistry, Archaeology, Biomedical Engineering, Geology, and in countless industrial applications for development, research and quality control [3].

As per the statement of Stoke's law, when the electromagnetic radiations fall on the material object, huge amount of energy is re-emitted and absorbed simultaneously in the form of light, having long wavelengths. This process is known as luminescence. The radiations emitted in the form of longer wavelength are the characteristics of luminescent material only. The radiations emitted by the luminescent material can be in the ultraviolet (UV), visible (VIS) and infrared (IR) region of electromagnetic spectrum. The process of cold emission or luminescence that does not include any emissions of the blackbody radiations, generally involve two basic processes: (a) the excitation of lower energy electrons to the higher energy orbitals and (b) gradual emissions of photons. The light radiations are emitted at some specific time denoted as " $\Delta c$ ", after the absorption of radiation. As a result of this process, the luminescence can further be divided into two steps (i) fluorescence and (ii) phosphorescence.

The process of luminescence can further be divided into two parts, based on the duration of emission such as (i) the type of fluorescence where  $\tau c$  is less than  $10^{-8}$ s is known as temperature independent process and (ii) the process of phosphorescence where  $\tau c$  is greater than  $10^{-8}$ s is known as temperature dependent process. The second process named as "phosphorescence" can also be divided into two parts: (a)  $\tau c < 10^{-4}$ s that is a short period (b)  $\tau c > 10^{-4}$ s that is a long period called as "thermo-luminescence". The emission in thermo-luminescence depends on  $\text{minutes} < \tau c < 4.6 \times 10^9$ , years falls in the category of long period of time. Above mentioned process is known to has its major advantage and high significance in science and latest technology [3].

Luminescence property is shown by various substances of both the organic and inorganic nature. Nevertheless, materials used in numerous luminescence applications include insulating materials having inorganic solid material, for example, quartz ( $\text{SiO}_2$ ), alkaline earth halides and alkali halides, oxides, sulphates, phosphates and several complex borates. Fluorescence is spontaneous emission as ' $\tau c < 10^{-8}$ s, thus this emission happens with radiation absorption and emission simultaneously as radiation ceases immediately. Conversely, phosphorescence is categorized by the delay in between the absorption of radiation and the time named as "t-max", to reach its full intensity [1].

After completion of excitation, for some time, phosphorescence is seen to be continued. Phosphorescence and fluorescence differentiation become difficult when there is a shorter delay time between the two. The process of phosphorescence has further been divided into two major groups depending on the duration of process such as (a)

short term phosphorescence ( $\tau c < 10^{-4}$ s) and (b) long term phosphorescence ( $\tau c < 10^{-4}$ s). Fluorescence is a temperature independent phenomenon while decay in phosphorescence mainly exhibit high temperature dependence [4].

Since ages, the phenomenon of luminescent has captivated mankind. The light from luminescent wood, glow worms, aurora borealis, rotting meat and fish are all the examples of luminescence that is naturally occurring. Unfortunately, there is no written record preserved by the primitive man of his initial observations. There are only simple pictographs of the more conspicuous environmental objects. There is a strong belief that Neanderthaler had much information about luminescence. He might see the luminous glow of bacteria growing on fish and meat. At night, a different and certain view must have trapped his keen attention. He directed all his abilities into further study of this phenomenon. In the creation of history, the light origin story is accepted by different races because light and darkness contrast is so striking and prominent. Such stories are found in Bible, Vedas (Sacred Books of Hindus) and Sri Guru Grant Sahib (Holy Scripture of Sikh Religion) [6].

In the holy writings of ancient Indian literature and epic poems, the glow produced due to fire and glow worms are frequently mentioned with the number of references. There are number of preliminary appearances that produce the manifestation of Brahma in Yoga. The Sanskrit word "Chayote" also means firefly and glow worm. In some books such as "Anugita" and "Vane Parra", these types of evidences are also mentioned [5].

Both in Japan and China, there are several prehistoric stories of mysterious fires or lights seen over fields, waters or mountains, caused by gods or scribed to dragons. Light is often emitted by sacred trees as mentioned in historic books. A painting of Ki-no Tan-yu (1602-1650) a Japanese artist, showed a poor but hardworking boy who collected various fireflies in order to study in that light in the evening, because he could not afford oil to initiate fire. Firefly collecting became very famous as a popular pastime hobby in Japan, the observation of autumn coloring. In the neighborhood of Kyoto, the festival of collecting firefly was an important event. The Buddhist sacred jewel, one of the seven treasures, called "hashi-no-tama" in Japan, is alleged to be self-luminous and to shed a brilliant light on its surroundings, a symbol of the enlightenment of Buddha's teaching [5].

The early Greeks first time observed the "Aurora borealis" and indicated the unknown process of inorganic luminescence. Blow to the eye or putting pressure on the eyeball gives light sensation as studied by the Human experiences. These effects are due to the fact that when the eyes are pressed, the fire appears to flash from it. This type of process can take place naturally in the darkness and also when the eyelids are tightly closed. The known process of phosphorescence has also been mentioned in a passage of

De Mondo. The characteristics of an ocean were explained by the Aristotle in his writing, by saying that the seas also exhalate the fire [5]. In the year 1603, some of the modern luminescent materials were introduced in the west. The Western literature also supports the preparation of first artificial phosphor at that time. The Vincenzo Casciarolo, an Italian alchemist, first time used the natural mineral barite (Barium Sulphate) during an effort to create the gold [6].

First material to be scientifically documented and showed persistent luminescence was "The Bologna stone" [7]. On 28<sup>th</sup> October 1663, observations of Robert Boyle were reported to the Royal Society of London. He started his luminescence studies with diamonds, leading to fish, flesh, shining wood and at last with element phosphorus [6]. Probably, he was the first person to describe different phenomenon in single substance (diamond) such as phosphorescence, electroluminescence thermo-luminescence and trio-luminescence. Perhaps, Mechano-luminescence (ML) was first time discovered in the caves, when human beings lived there due to the bright light generated by the different types of mineral elements. In 1605, Francis Bacon was the first person who reported discovery of ML in his writings about the "Advancement of Learning" by saying that when the hard sugar is fully scrapped with the help of knife, the sparkle or light would be produced [8].

After crushing substances such as loaf sugar, rock salt and white sugar in mortar, intense light was generated as stated by Waller in 1684 [9]. Variety of pottery materials and minerals were known to exhibit ML, by the end of the 1700s. Different substances like ruby, diamond, quartz exhibits ML reported by Wedgwood in 1792 [10]. Rock failures in earthquakes and mines emits light and it has been observed for several centuries [11].

## 2. Production and decay process

Jablonski diagram (Fig.1) is an energy state diagram that represents the excited state production and decay processes.  $S_0$ ,  $S_1$  and  $T_1$  are ground state, lowest singlet and triplet states respectively. In molecules, atom's vibronic motions generate multiple vibrational states that is present in  $S_1$  and  $T_1$  states. HOMO ([H] highest [O] occupied [M] molecular [O] orbital) and LUMO ([L] lowest [U] unoccupied [M] molecular [O] orbital) are molecular orbitals. In molecule, when the energy greater than difference of energy of HOMO-LUMO is introduced then either in  $S_1$  states, there is the generation of high vibronic state, or in states of  $S_2$  and  $S_3$ , high excited singlet states are produced. In time scale of picoseconds, there is relaxation of  $S_1$  higher vibronic states to the  $S_1$  lowest vibronic state.  $S_2$  and  $S_3$  (higher energy singlet states) relax to the ground state of  $S_1$  by means of non-radiative internal conversion processes (IC). From  $S_1$  to  $T_1$  relaxation through the process of intersystem crossing (ISC), production of triplet states occurs. Therefore, when transition of electron occurs from  $S_1/T_1$  to  $S_0$  radiative transitions occur. Spin allowed *Ashraf et al., 2020*

transition exits for few nanoseconds as the radiative transition from  $S_1$  to  $S_0$  take place. Alternatively, the transition from  $T_1$  to  $S_0$  is spin forbidden process, ranges from micro-to milliseconds and has longer duration time scale. Therefore, the emission spectrum basically looks exactly the same as that of absorption spectrum of any experimental sample.

## 3. Types of luminescence

### 3.1. Photoluminescence

Excitation of atoms in solids to a higher state and then de-excitation by generating photons in order to release energy is luminescence. Photoluminescence is the process when UV radiation of short wavelength excites the atoms in solid molecules (Fig.2) [12].

This process can further be classified as (i) intrinsic luminescence and (ii) extrinsic luminescence.

#### 3.1.1. Intrinsic luminescence

The process in which luminescence generates form pure crystals and materials is called "intrinsic luminescence". It is divided into following categories: (i) band to band type of luminescence: this type of luminescence produces band to band transition mainly due to recombination of the conduction band electron with valence band hole. Only pure materials at high temperatures can undergo this kind of luminescence. At low temperatures, it is changed into excitation luminescence. Ge and Si are examples of such materials [2] (ii) cross-luminescence: when the valence band electron recombines with that of hole, present in the core of outermost band, cross luminescence is formed. Double halides, alkali or alkaline earth halides shows this type of luminescence [13] and (iii) excitation luminescence: excitation luminescence is generated as excitation, which is produced when there is interaction between hole and excited electron moves through the crystal having some energy. Excitations are of two types. The pannier excitation is typically present in inorganic semiconductors and is produced when conduction band electron and valence band hole combine with the help of coulomb interaction. The Freckle excitation only exists when expanse of hole and the electron wave-functions is smaller to the lattice constant, and can further be found in the uranic salts, anthracite (an example of organic molecular crystal) and vanadate or tungstate (inorganic complex salts) [13].

#### 3.1.2. Extrinsic luminescence

By incorporating defects and impurities intentionally into semi-conductors, ionic crystals and phosphor luminescence is generated, termed as "extrinsic luminescence". It can be localized or un-localized. Localized type exists when both process of luminescence that is excitation and emission, are present in localized luminescent manner. Conversely, when host lattice

conduction band free electrons and valence band free holes also take participation in the process of luminescence emissions, called as un-localized extrinsic luminescence.

### 3.2. Fluorescence

Emission takes place from excited singlet state with time scale where  $\tau_c < 10^{-8}$ s is called as "fluorescence". In order to differentiate between phosphorescence and fluorescence, there is a need to study the temperature effect upon luminescence decay. Numerous kinds of luminescence are known. Some types of materials when illuminated by the light radiations of some specific wavelengths, they emit the light of different colours, through a well-known process called "fluorescence". Some types of clothes contain the chemical residues on their surface, due to the washing with chemical based detergents. These chemicals emit the light energy when stimulated by the invisible ultraviolet region of electromagnetic spectrum. Hence, clothes comprising these residual particles appears brighter due to the collective effect of fluorescence from detergent residues as well as from sunlight reflection. Fluorescent tubes having inside coat of fluorescent chemicals is another example. Inside tube, an excited vapour of mercury generates ultraviolet radiations of of 253.7 nanometer wavelengths. Electrons are excited by this powerful UV light in the phosphor fluorescent powder, resulting in emission of visible light having low heat. The process of photoluminescence can sometimes also be applied to the type of luminescence usually generated by the different colors of light [14].

### 3.3. Phosphorescence

The type of fluorescence in which electrons excited by some radiations takes more time to come back to ground state (lower energy state) by the process of decay is called "phosphorescence". It might take few hours to days. Even after excitation, radiation has been stopped but visible light is continuously emitted for some time from materials. Short persistence phosphor is the condition when time duration is short ( $10^{-4}$ sec) for phosphorescent materials [15]. If duration is longer than  $10^{-4}$ sec then it is termed as "long persistence phosphor". Phosphorescent materials are also termed as "luminous materials". Most luminous stickers, toys, watch dials and exit signs are covered with long decay phosphors.

### 3.4. Electroluminescence

With the help of applied plasmas and electric field, non-metallic gas or solid generates efficient light called "electroluminescence". It can also be produced through crystals by the passage of current through it. This occurs when electrons are excited by current which in turn occupies energy levels within the crystals. Electroluminescence will produce when this excited electron decays by emitting visible light.

### 3.5. Cathodo-luminescence

When electron beam irradiation (TV Screen and CRO Phosphors) having high energy is bombarded on materials resulting in emission of light, cathodo-luminescence is generated. It is opposite of photoelectric effect in which photon irradiation induced emission of electron. Cathode rays are termed as electrons in modern times. In evacuated tubes, electrical discharge generates electrons and when these electrons collide with the walls of the tubes light will produce [16].

### 3.6. Bioluminescence

Emission and production of the light with the help of living organism is generally termed as "bioluminescence". This phenomenon mainly occurs in the marine invertebrates and various other vertebrates. Few micro-organisms, fungi, some symbiotic organisms and terrestrial invertebrates also show this kind of luminescence [1]. Bioluminescence must not be confused with the process of phosphorescence and structural coloration, and iridescence. It is a type of chemiluminescence where chemical reaction generates light energy. Pigment (luciferin) and enzyme (luciferase) are present in anglerfish, fireflies and other light producing creatures. Oxygen reacts with this pigment to produce light in the presence of luciferase catalyst which is often facilitated by cofactors for example ATP or calcium ions. This reaction can take place either outside or inside the cell [17].

### 3.7. Chemiluminescence

Luminescence produced due to chemical reaction mostly by oxidation-reduction reaction is called as "chemiluminescence" (Fig.3). Its mechanism includes chemical energy conversion into visible light energy. Chemical bond's electrons take energy through chemical reactions. As these high energy electrons decays, light is emitted. Light is generated for some time because few of these chemical reactions occur slowly.

It is not different than incandescence, well it is dissimilar than that of more energetic chemical reactions that release more heat energy, resulting in the chemicals generally catching fire and glowing red hot. Different organisms undergo oxidation reaction and exhibit this phenomenon.

### 3.8. Ionoluminescence

Ionoluminescence is another interesting process in which inorganic and organic compounds undergo collision with fast moving ions producing light. Luminous clock dials having radioactive compounds that generates luminescence is an example of ionoluminescence. Material that exhibits luminescence like zinc sulphide is mixed with radium (radioactive material). Radiations and alpha particles are emitted as radium decays, resulting in electron excitation in materials that ultimately produce light [18].

### 3.9. Lyoluminescence

Lyoluminescence is a form of chemiluminescence. It is emission of light when already irradiated solids are dissolved in appropriate solvents. When deeply irradiated solid samples undergo dissolution in water, this clearly shows the lyoluminescent effect. The emission of light from any material usually increases by increasing the overall radiation dosage, received by any material upto a certain limit also known as "saturation value". Soups, spices, paper, powdered milk, cotton and many other gamma-irradiated substances are lyoluminescent materials. Free radical's production is the main mechanism involved in this process. With the help lyoluminescence sensitizers compounds, the intensity of lyoluminescence can be further increased by dissolution process [19].

### 3.10. Radioluminescence (Scintillation)

When radiating particles undergo collision with molecule or an atom radioluminescence occurs. It excites an electron upto the higher energy state. The extra energy is released as "photon" as the electron returns to ground state. Organic molecules present in some polymers act as radiation detectors when come in contact with the radiations like cosmic rays, gamma radiations and x-rays, thereby emitting visible light [20]. Radioactive elements emit electrons, helium nuclei (alpha particles) and gamma rays. Therefore, radioluminescence is excitation by radioactive material. When alpha particles are bombard on a phosphor or crystal, light or minute scintillation can be microscopically observed [21].

### 3.11. Sonoluminescence

Sonoluminescence is light emission via sound wave excitation including ultrasonic waves. Gaseous cavity formation in liquid due to high intensity sound wave which then quickly collapse, result in sonoluminescence. These cavities are either generated thorough cavitation process or might exit as a bubble. In laboratory, periodic manner is utilized for expansion and bursting of single bubble all over again thereby producing light with bursting every time. For this phenomenon to take place, a standing acoustic wave is established inside the liquid, and the emerging bubbles will appear on anti-node of standing pressure waves. The frequency of the resonance mainly depends upon the size and shape of the container [22]. The light flashes from the bubble for a very short period of time, approximately in between thirty five to few hundred picoseconds, having the approximate peak intensities in between 1 to 10 mW. These small size bubbles (~1 $\mu$ m) emit the radiations of light, having different wavelengths, depending upon the nature of the atmospheric gases and filled ambient fluid [23].

### 3.12. Thermally stimulated luminescence (TSL)

The "thermally stimulated luminescence" (TSL) is generally initiated by the thermal resources after the early Ashraf et al., 2020

irradiations, given to any phosphor material, by the various other sources including alpha-particles, x-rays, ultraviolet radiations, gamma rays and beta particles. TSL is the phenomenon in which solid (exposed to ionization) under rising temperature conditions emit light. Heat factor only act as stimulant in TSL [24]. Some of the conventional sources such as  $\alpha$ -rays, ionizing radiations, beta-particles, gamma-radiations, cosmic rays, ultraviolet radiations and x-rays are used as excitation means. Materials like organic solids, ceramics, glasses, plastics exhibit this phenomenon of TSL. For TSL production, three requirements should be maintained: (a) the emission is stimulated by heat (b) during radiation exposure emitting substance should absorb energy at some stage and (c) luminescent material should be semiconductor or insulator [1].

## 4. Production methods

### 4.1. Synthesis of sodium sulphates

Sodium sulphate synthesize by a technique of slow evaporation. Its saturated solution was prepared with concentration of 50g/100mL and then filtered for removing suspended particles. The fluid is moved into 2, 3 and 50mL beakers and permitted to undergo slow evaporation process. Polycrystalline samples attained after two days in the beaker which was collected, crushed, powdered and calcined at 200°C, 400°C and 600°C for 4h in furnace. Then obtained final powder was cooled and stored in dry place and pressed into pellets (80 kg/cm<sup>2</sup>). For characterization of TL and PL measurements, Na<sub>2</sub>SO<sub>4</sub> calcined at 400°C was used [25].

### 4.2. Solvothermal synthesis of luminescent bis-(8 hydroxyl quinolone)

In general synthesis, 8-hydroxyquinoline and Cd<sup>2+</sup> was used having 2:1 molar ratio mixed with water and ethanol solvent during precipitation at controlled temperatures. In order to produce normal homogeneous emulsion, oleic acid and NaOH were added into solvent with continuous stirring. Then, into this system, CdCl<sub>2</sub>.2½H<sub>2</sub>O aqueous solution was poured. Afterwards, the ethanol solution of 8-hydroxyquinoline was rapidly introduced into the solution to start the main reaction and the total volume of the mixture was kept at a certain value 30mL. Into 50mL vessel, the solution mixture was poured after stirring for about 15min., which was then treated at calculated temperature for suitable reaction time. Then, naturally at room temperature the system was cooled. The precipitates at bottom were washed twice with ethanol solution thoroughly and then re-dispersed in ethanol for future characterization and usage [26].

### 4.3. Stober synthesis of mono-dispersed silica

#### 4.3.1. Preparation of fluorescent silica spheres

Silica particles were prepared by adding a premixed ethanol solution (25 mL) containing ammonium hydroxide, tris(1,10-phenanthroline) and ruthenium(II)

chloride{[Ru(phen)<sub>3</sub>]Cl<sub>2</sub>} into a TEOS solution in ethanol (5 mL). The solution was stirred for 1h and then further solicited for 10 min. The luminescent nanospheres were washed with ethanol thrice and were isolated by centrifugation at 5000 rpm for 10 min. Under reduced pressure, the samples were dried for 1h at 100°C. Almost 80% yield was obtained at the end [27].

#### 4.3.2. Preparation of thiol-modified luminescent silica

2 mg of luminescent silica particles was dispersed in ethanol of 10mL conc. under sonication. Into this solution, 100L of MPTMS was then added. In a sealed vessel, the mixture was stirred overnight. The particles then washed with ethanol thrice and were isolated by centrifugation at 5000 rpm for 10 min. At 4°C, undissolved particles were then re-dispersed in 4 mL of phosphate buffer at pH of 7.4 [28].

#### 4.3.3. Preparation of streptavidin-modified luminescent silica

At pH 7.4, stock solution of 1mL was mixed with phosphate buffer solution of 5 mL having 0.25 mg of maleimide-labeled streptavidin. At room temperature, mixture was incubated for 2 hours under mild stirring. The streptavidin-labeled particles then washed with phosphate buffer solution thrice and were isolated by centrifugation at 5000 rpm for 10 min. At 7.4 pH, undissolved particles were then re-dispersed in phosphate buffer of 4 mL solution. Luminescence phenomenon was shown by these particles [29].

#### 4.4. Synthesis of iridium bisterpyridine

Iridium (III) chloride mixed with ligand to synthesize Ir (III) 1,2-mono-complexes and then heat at 160°C in degassed ethylene glycol for 15 min. After the reaction mixture had cooled, the resulting precipitate was filtered and washed with water, ethanol and diethyl to give the mono-terpyridine complexes 1 and 2 in modest yields (39% and 47% respectively). N,N-dimethylformamide and dimethyl sulfoxide can only solubilize the resulting mixture. <sup>1</sup>H- and <sup>13</sup>C-NMR and HR-MS are utilized for purity and structure conformation. Then further reaction between ethylene glycol ligand and mono-terpyridine complexes occurred. Two complexes 3,4 of bister pyridine was formed with reasonable yields 88% and 58% respectively.

Biphenyl phosphoryl azide (10 ml) was added into the solution of Ir (III) hydroxyl complex (3 or 4) and N,N-dimethylformamide. Excess amount of 1,8-diazabicyclo-7-ene (DBU) was added drop wise into the solution, after the mixture was cooled. Then reaction mixture was adjusted at room temperature and stirred for some days. Aqueous ammonium hexa-fluoro-phosphate was added, resulted in orange to red precipitates formation. The resulted solution was filtered, washed with water, cold ethanol and diethyl ether. DBU salt of biphenyl phosphate was only water

soluble by product produced, which is washed off with precipitated salt of hexa-fluoro-phosphate complex. Pure azides (5,6) upto 96 % was attained after recrystallization from acetonitrile diethyl ether. The successful substitution of the alcohol with azide was then confirmed by the <sup>1</sup>H-NMR shift of the methyl proton peak (0.2 ppm shift upfield), <sup>13</sup>C-NMR, infrared spectra and HR-MS spectra of the complexes showed a new peak corresponding to the characteristic azide stretch at 2100 cm for biotin-streptavidin assays [27].

#### 4.5. Synthesis of Eu (DBM)<sub>3</sub> as probe molecule

##### 4.5.1. Preparation of Eu (DBM)<sub>3</sub>phen as probe molecule

Eu<sub>2</sub>O<sub>3</sub>, DBM and phen were measured by the ratio of material to Eu DBM phen<sup>1/4</sup>1:3:1 respectively. At ambient atmosphere, Eu<sub>2</sub>O<sub>3</sub> (99.0%) dissolved in dilute HCl to form EuCl<sub>3</sub>.6H<sub>2</sub>O under heating with constant agitation. The phen (probe molecule) and Eu (DBM)<sub>3</sub> were synthesized by hydrothermal process. Firstly, DBM, EuCl<sub>3</sub>.6H<sub>2</sub>O, and phen dissolved in ethanol, then in 100 mL flask, EuCl<sub>3</sub> and DBM ethanol solutions were added. Ammonium hydroxide was added to regulate the pH with constant heating and 30 minutes of stirring reflux was applied. Secondly, solution of phen ethanol was added into this solution gradually, later heated the solution and for 3 hours and stirred the reflux. Finally, we placed the above solution at room temperature for 24 hours. Then vacuum filtration was applied. Washed the solution with ethanol and then dried at 80°C for 24 hours in drying oven [28].

#### 4.6. Synthesis of phenolic azo dyes

Suitably substituted anilines (0.01mol) were dissolved in concentrated HCl (3.5 ml) and water (20 ml), with constant stirring keeping the temperature in range of 0-5°C. Then add NaNO<sub>2</sub> solution (0.01 mol) in 10 ml water into above aniline solution with vigorous and constant stirring for 1 hour in the same temperature range. After 1 hour, reaction completeness was checked by using paper chromatogram having mobile phase of water. P-N,N-dimethyl amino-benzaldehyde solution in ethanol was used as spraying agent sprayed on dried chromatogram. In freezer, diazonium salts were kept upon reaction completion. Phenol (0.01 mol) was dissolved in 15 ml of water and 2g of K<sub>2</sub>CO<sub>3</sub> was kept in an ice bath between the temperatures of 0-5°C with constant stirring. By maintaining pH above 8, drop wise addition of diazo solution was maintained with well stirring. The reaction progress was checked by using paper chromatography with H-acid solution in alkaline media. Derivatives of 4-hydroxyazobenzene in 87-90% yields were obtained on completion of the reaction. Products then undergo filtration and oven dried at 70°C [30].

#### 4.7. Synthesis of flavonoids by plant extraction via organic solvents

The general method for flavonoids synthesis was its extraction from several plant species. Various methods were developed by scientists in order to improve the quality of extraction to achieve high purity and yield of flavonoids. Firstly, the plants were air-dried and then ground into fine powder form for extraction with the help of organic solvents (ethanol and methanol). Secondly, again organic solvents (ethyl acetate, petroleum ether, n-butyl alcohol, chloroform) were used for successive fractionation of obtained powder. Thirdly, these powdery particles were subjected to column chromatography involving Sephadex LH-20 and silica gel for efficient results.

These obtained flavonoid yield can be enhanced by different techniques like microwave, ultrasonic wave, two-phase aqueous and enzyme-assisted extraction. For determining flavonoids purity and identity, these particles then undergo high performance liquid chromatography (HPLC), thin plate chromatography (TLC), nuclear magnetic resonance (NMR) and electrospray ionization mass spectrometry (ESI-MS) analyses. As flavonoids are highly soluble in above mentioned organic solvents, so its extraction from plants yields high result. However, many plants contain less content of these flavonoids so proper isolation and extraction requires various steps, adequate time, laborious work, and plenty of organic solvents resulting in increase in production cost. So, it still has some disadvantage. Furthermore, plant tissues are of diverse nature and mostly needs different methods for processing, as a consequence, these is further increase in production cost and complications. Thus, this technique of extraction from plants is not cost-effective, so in order to lessen the production cost, alternative strategies should be attained.

Chemical synthesis is an alternative approach for flavonoid synthesis. Baker-Venkataraman and chalcone route are two methods for its synthesis. Chemical synthesis involves various steps and is complicated process, so there are only few successful and effective examples. It utilizes harmful reagents and extreme reaction conditions. Subsequent modifications and chiral synthesis further enhance its difficulty. Additionally, different intermediate products with great similarity to original product are produce due to multistep reactions resulting in purification difficulty of the desired product. Hence, it is also not economically feasible process for flavonoid production in large amounts [31].

#### 4.8. Synthesis of luciferin molecule

Green and McElroy method was used for preparing crystalline firefly molecule of luciferase. Re-crystallization should be done twice or thrice for removing contaminating enzymes in the process. 10mg of protein was taken for synthesizing these enzymes per milliliter. By McElroy and Bitler method, oxy-luciferin and crystalline luciferin Ashraf et al., 2020

enzymes were prepared. For determining concentration of these produced enzymes, measurements of optical density at 327 nm and 347 nm at neutral pH were taken. Oxy-luciferin molecule was formed when luciferase enzyme undergo reaction with light emitting pigment that was luciferin [32].

## 5. Applications

### 5.1. Applications of fluorescence

Phosphor is a substance that emits luminescence. In energy band model terms, basically few phosphors are semiconductors. These phosphors can exist in macro, micro and biological forms. Different micro and macroscopic luminescence devices are manufactured by professionals. Its basic applications are: plants specific locations have specific compounds of fluorescent nature and its careful examination and analysis gives rise to detection of various originating fungus by giving definite pattern. It also helps in studying photosynthesis phenomenon in plants by analyzing chloro-fluorescent variation at start and end of light exposure. The "fluorescence-polarization" measurements under numerous conditions, leading towards the determination of violent rotations of various diffusion constants of different proteins [33].

In fluorescence visible light emission gives valid information about the corresponding material. Thus, it seems valuable technique and has usage in various scientific fields (a) by comparing standard spectra with PL specimen spectra, impurity analysis can be done. Medical and tablet industry has wide use of this method (ii) it gives possibility for assessment and detection of numerous fluorescing compounds placed in the same type of solution and (iii) fluorometry is also useful in medicine and biology. It gives information about hormone and urine concentration, blood estimation and vitamin deficiency. It is used for strain identification (urine, blood and pus) and poison detection in chromatographic separation.

On UV interaction, specimen microscopic components exhibit PL. On this principle, fluorescence microscopes have been developed for locating and examining fine and minute structures of such specimens. Lamp inside wall has pasted phosphors. Electric discharge will generate ultraviolet light of 253.7 nanometer. Then phosphor also absorbs this ultraviolet light and via the process of emission of fluorescence, converting it into visible light. Phosphor nature defines the color of emission in lamp. In markets, various fluorescent lamp varieties are presented now-a-days. Ionizing radiations like alpha particles, UV light and electrons etc. are used for producing several luminescent materials which then emits visible light of different colors. If luminescent material is present on screen, then it has an ability to indicate the existence of field radiations. In this way, the phosphors are in the major use in watch dials and TV screen industries etc. [34].

There are two major factors that strongly influence the emission of radiations from any material object such as

(i) impurity atoms in matter and (ii) structure of solids. The PL spectrum appears to be a very good fingerprint of any specimen under observation. Therefore, the comparative analysis of any PL pattern gives us the idea about the nature of an ideal specimen to compare with the defected samples. These spectra give us very fruitful information regarding the nature and type of materials. These types of factors are usually applied in forensic sciences for the identification, detection and prosecution of crimes along with the various physiochemical properties of specimen.

If sample contains different element, then these can be differentiated with the help of characteristic radiation emitted by specific elements. Coating thickness measurement of different chemicals can be studied by analyzing characteristic emission and intensity from the emitting materials. Liquids chemical behavior can also be examined by this method [34]. It also includes the advertisements, lightening lamps, recondition equipments, data punched reader, opto-mechanical programming, indicator of position and thermo-chrome motor controllers etc. The fluorescence is most commonly used in analytical purposes for many chemical compounds in liver and kidney cells. In medico-legal works, PL selectivity and sensitivity in various micro-systems enables all the professionals to estimate the amount of amino acids, nucleic acid and proteins in body cells. Most of the blood estimation tests are using this technique for quantification and determination of various viruses and bacteria.

The process of luminescence is a structure sensitive phenomenon, capable of detecting the pattern of solid crystal lattices of different materials. The defects of crystal lattices in the host matrix can easily be determined by the examination of standard fluorescence spectra. Different types of gemstones are categorized on the basis of crystal structures, refractive indexes, specific gravities and optical properties generally named as "pleochroism". The hardness is a physical property that is usually defined by some non-linear type of Mohs scale, specified for testing the mineral hardness. Thus, these types of factors can be studied by the gemologists during the estimation, cutting and measurement of gemstones. The gemological microscopic studies of internal structure of crystals are mostly used to find the difference between natural and synthetic gemstones [22].

### 5.2. Application of bioluminescence

Bioluminescence phenomenon is adapted by many sea animals like several squid species, for the purpose of counter-illumination-camouflage, where all the animals try to match the light of overall surrounding environment. In order to match background brightness, illumination is controlled by photoreceptors in these animals. Tissues containing the bioluminescent bacteria are separated from these light producing organs. However, in one species such as "*Euprymna scallops*", the bacterial cells are the major components of the light emitted by animal bodies. In Ashraf et al., 2020

fireflies, periodic flashing in abdomens are used for attracting mates in their breeding season. In case of marine environment, the luminescence is only used for the attracting purpose in ostracods, which is a small shrimplike crustacean in oceans [23]. The process of bioluminescence is generally used for the short distance communication in the number of living organisms. However, sometimes, these types of processes are also used by the pheromones, for attracting the opposite sexes in long distance communication. Most of the marine bioluminescence has found to be light green to dark blue in coloration, while the "Black-Dragon-Fish" generally produces red glow. In this method, the red pigmented prey can also be seen by the marine fish that is found to be invisible in the deep oceanic environment. Large number of bioluminescent materials has conventionally been used in various scientific researches. Luciferase systems as reporter genes are extensively used in genetic engineering and bioluminescence imaging for research purposes [35].

### 5.3. Optically stimulated luminescence applications

Thermo luminescence dating is mostly used more commonly as compared to the radiation dosimeter. This can be defined as the accumulated radiation dosage measurement inside the tissues of nuclear researches, health care personals and various other associated workers, along with the building materials of nuclear disaster regions. From sample, grains of minerals are extracted for OSL dating treatment. These are usually divided into fine grains (4-11  $\mu\text{m}$ ) and coarse grains (100-200  $\mu\text{m}$ ). The difference between OSL and radiocarbon dating is that the former is used for dating minerals while the latter for dating organic materials. Events like "Mungo Man" (Australia's oldest human find) and mineral's last exposure to sunlight can be dated using OSL technique. For the dating purpose, the deposited geological sediments use the OSL, after the transportation of sediments by the rivers (fluvial sediments) and air (eolian sediments). In the archaeological evidences, the OSL dating is generally applied to the dating of various ceramic based materials. All the dated events represents the time of the heating of ceramic materials at extremely high temperature such as 400°C in the excess of air [36].

### 5.4. Radioluminescence applications

The radioluminescence has generally been used as light source of low-level of energy for illuminating the night signage or instruments, or in applications that generate light without energy source for long time duration. Earlier, radio-luminescent paint in instrument dials or in clock hands was used letting them readable in dark surroundings. Radioisotopes and nuclear reactors (high radiation power sources) have radio-luminescence usage. Presently, only radioisotope that is allowed to be used as light source is "tritium". It is used on emergency signs, gun sights and wristwatch etc. Small glass tube with inside phosphor



coating having tritium gas, undergo striking between phosphor molecules and beta particles, emitted from tritium. As a result of this striking, "yellow green" coloured light is emitted. Radium is substantial radiological hazard as the self-absorption by workers is a big risk therefore tritium is most commonly used because it pose insignificant threat to human health [1].

The emitted beta-particles are of low energy (5.7 Kev) thus, are not able to pass through glass tube wall. Even if they could, these particles do not have ability for penetrating human skin. The tritium is a type of gas that is usually filled in a tritium tube. If this tritium tube is broken down, the gas immediately dissipates in the air and is further diluted upto the safe level of concentrations within seconds. The approximated half-life of the tritium is 12.3 years therefore its brightness gradually declines with the passage of time. As far as the historical perspective is concerned, the copper and radium doped zinc sulphide has conventionally been used to paint the dials of various instruments, by the production of greenish glow. The phosphors comprising of zinc sulfide doped with copper and magnesium, produces yellowish orange light whereas copper doped zinc sulphide gives bluish green light [1].

### **5.5. Chemiluminescence applications**

Chemiluminescence generates white light by a non-radioactive process. It arises when enzyme-based reaction undergoes an attachment of target protein antibody to chemiluminescent substrate. This process is more delicate and sensitive as compared to colorimetric detection as the light signal is greatly amplified by enzymes, because the proteins are targeted by antibodies specifically. Methods commonly used to produce the chemiluminescence include ECL, where HRP (Horse Radish Peroxidase) oxidizes the luminal or CDP-Star®. The 1,2-dioxetane compound is dephosphorylated by using the alkaline phosphatase. To visualize the resulting bands, you can use x-ray films, which can be time-consuming and expensive or cooled CCD-based systems to generate digital images. Since many light photons are produced by chemiluminescent molecules so there is an easy detection of proteins at low levels. This is due to the right kind of image capture technology. Protein can be re-used because light is produced internally in chemiluminescence process [37]. In single protein, for highly sensitive detection, the best method is chemiluminescent western blotting. By using this technique like in CCD-based system, a dynamic wide range of images are produced permitting us to accurately and safely analyze and detect proteins pictogram or even femtogram level images [22].

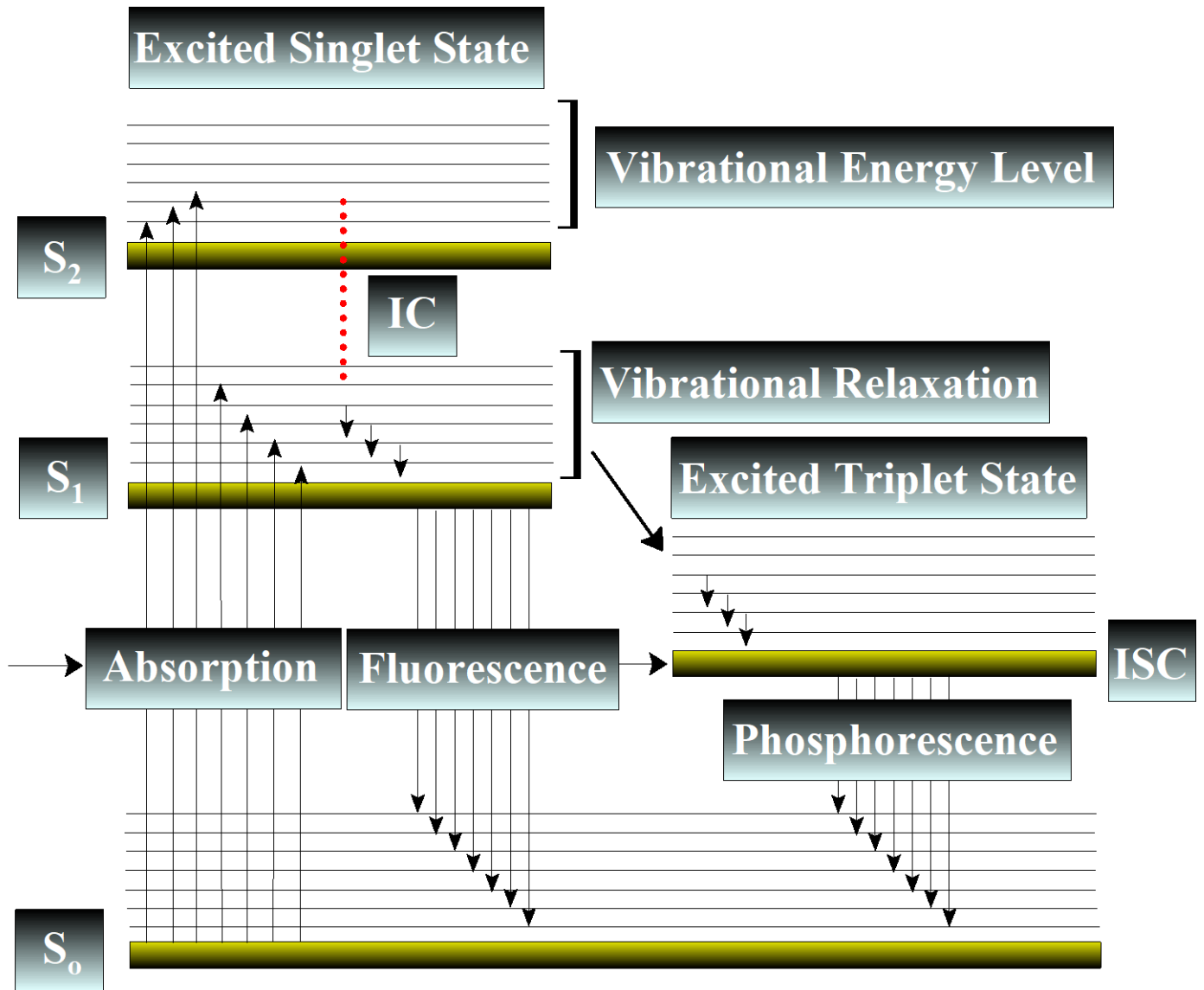


Fig.1 Jablonski Diagram

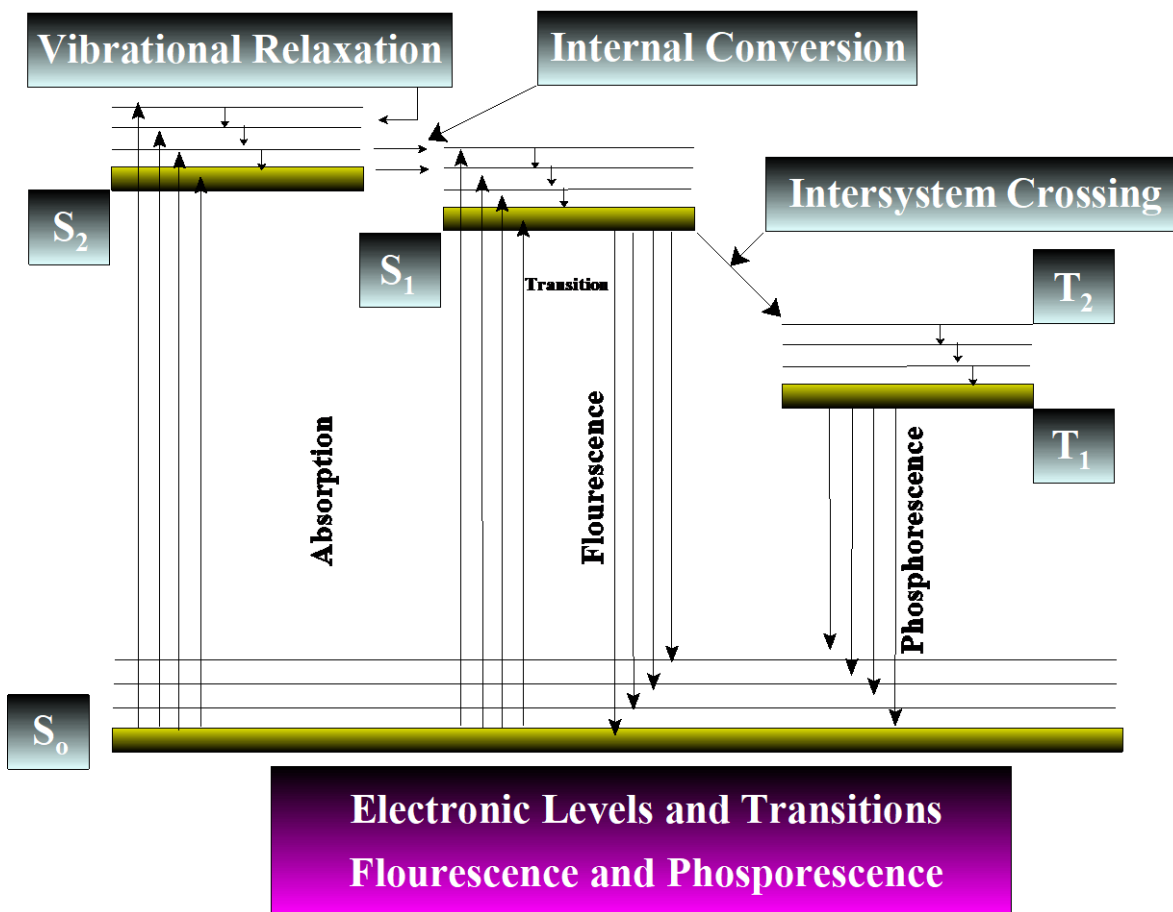


Fig.2 Process of Photoluminescence

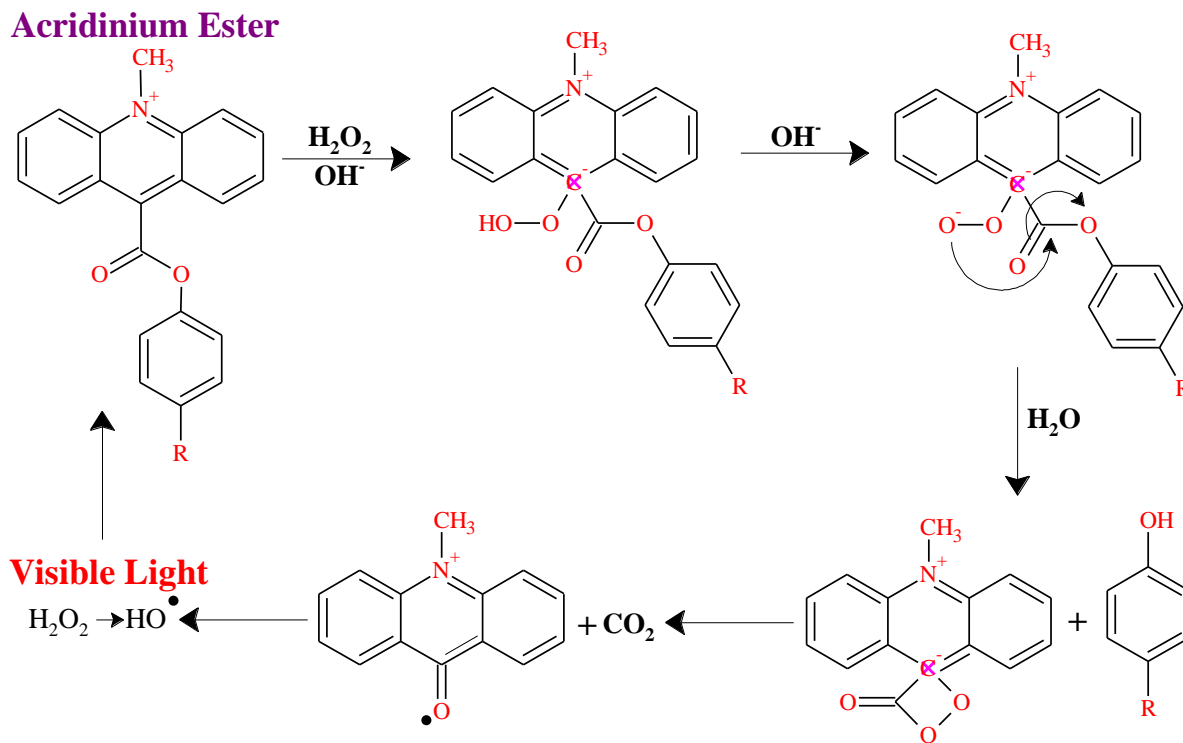


Fig.3 Process of Chemiluminescence

## Conclusions

Luminescence is "cold-body radiation" resulting in light emission spontaneously without heating. It can be caused by electrical energy, subatomic motions, chemical reactions, or by stressing a crystal. This differentiates incandescence, which is emission of light by heating, from luminescence. Historically, radioactivity was included in "radio-luminescence", but as it includes more than electromagnetic radiation so now it is considered a separate light source. A luminescence molecule plays a vital role in Biology, Chemistry, Biochemistry, Medicine and Pharmacy etc. Luminescent materials are used in aviation signs, dials, scales, navigational markings and instruments by luminescing process. Photoluminescence and bioluminescence offer great advantage. In animals, bioluminescence is used for their survival, either for communication or protection. Chemiluminescence is involved in medicine and in forensic science etc. Fluorometry is also useful in medicine and biology.

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