

Lighting the World with Molecules

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Keywords

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Efficient lighting and display have become important concerns in the energy-starved modern world. This has led to new paradigms in lighting and display technologies. Organic molecules provide a new class of active materials for such technologies. This article gives the basic science behind the design of such molecular materials used in displays and lighting.

1. Introduction

Human beings have endeavored to create artificial light that resembles natural sunlight for visibility in darkness. They used controlled burning of combustible substances to generate light until the discovery of the incandescent lamp (*Box 1*) which used metal filaments heated to high temperatures for producing light. Breakthrough in lighting technology appeared first with the invention of fluorescent light (*Box 1*) sources. This technology gave birth to cathode ray tubes culminating in the development of devices such as color television sets that led to a revolution in the field of entertainment and communication. The next breakthrough involved the invention of semiconductor light emitting diodes (LED). This technology provided highly efficient and convenient point source for light of different colors and found application in advertising, decoration, traffic signaling and in instrument panel indicators. Lasers based on LEDs are also widely used in low power applications. With the discovery of organic light emitting diodes (OLED), the field of lighting and displays is ushering in a new era which is expected to bring in sweeping changes both in terms of versatility and efficiency and it is widely believed that liquid crystal display (LCD) technology as well as conventional lighting technology will be largely replaced by OLEDs. This article is an introduction to the science behind organic light emitting devices.



Box 1.

In early 20th century light was generated using electricity with the help of incandescent lamps. A thin filament of a metal such as tungsten is heated using an electric current to a high temperature, typically 2000 °C, in vacuum to prevent oxidation of the film. The filament at this temperature emits light, which is close in nature to sunlight. The efficiency of an incandescent lamp is about 4% which is equivalent to about 12 Lumens/Watt. Most input energy is wasted as heat. The incandescent lamps, though still in use, have largely made way to fluorescent lamps, commonly known as tube lights. The more efficient recent versions of these are the compact fluorescent lamps (CFLs).

In tubelights an electrical discharge is set up using a gas mixture and the light emitted from the discharge which is in the near UV region is down converted into visible light using special coatings on the walls of the discharge tube known as phosphors. A tubelight yields about 100 Lumens/Watt. The discharge tubes also have loss of efficiency due to absorption of light by the walls of the container as well as incomplete transmission and opaqueness of the wall due to dust. The effective yield of visible light is thus considerably less than 100 Lumens/Watt.

2. Generating Light from Matter

To generate light from matter, we need to electronically excite matter; the excited state then emits light spontaneously while relaxing back to its electronic ground state. Electronic excitation of matter can be achieved in many different ways: (a) by application of a voltage—light generated this way is known as electroluminescence (EL); (b) by synthesizing a compound in the excited state – the light thus obtained is called chemi-luminescence, a variant of which is bioluminescence; (c) by exciting a molecule by light of one wavelength with the excited molecule emitting light of a different wavelength – this process is called photo-luminescence (PL); (d) by heating the system – the resulting light is called thermo-luminescence and (e) finally by exciting the molecules using mechanical energy which is called tribo-luminescence. Some examples of chemi-luminescence are the oxidation of luminol using hydrogen peroxide which produces 3-aminophthalate in an excited state and morphine oxidation by permanganate. Examples of bioluminescence are light emission by fireflies and many marine organisms. While the method of generating an excited state is different in each of these processes, the mechanism of light emission is the same. An excited electronic state radiatively decays to the ground state emitting light (see *Box 2*).

3. Radiative Emission – Fluorescence and Phosphorescence

In a molecule, the motion of electrons is much faster than the motion of nuclei of atoms that make up the molecule. Therefore, we can associate with each nuclear geometry various electronic states characterized by their spin and molecular quantum numbers. The plot of energy



Box 2. Black-body Radiation

A black body does not allow radiation to escape or enter. A black body is ideally conceived to be a cavity with perfectly reflecting walls and a pin hole through which the leaked light is analyzed spectroscopically (see *Figure A*). Experimental dependence of the intensity of light emitted by a black body on the wavelength at different temperatures is shown in *Figure A*. Experimental study on black-body radiation resulted in two famous laws. One is the Wien's displacement law, $T\lambda_{\max} = 2.898 \times 10^6 \text{ nm K}$ where T is the temperature of the black body and λ_{\max} is the wavelength at which the intensity is maximum. The second law is the Stefan–Boltzmann law which states that the total radiated energy per unit time per unit area, J , emitted by a black body is σT^4 , $\sigma = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$. Planck was able to obtain these laws as well as fit the black body spectrum by the revolutionary postulate of quantization. It was known from the early work on electrodynamics that an oscillating dipole emits light of frequency equal to that of the dipole oscillator. Planck assumed that black body consists of such dipole oscillators each of which is characterized by a fundamental frequency, ν . Light emitted by an oscillator of frequency ν corresponds to an energy quantum of $h\nu$, where h is now known as the Planck's constant and an oscillator can emit energy in integer number of such quanta. Planck's law can be used to estimate the temperature of a hot object, for example, the surface temperature of the Sun which is estimated to be 5800 K. Similarly, we can estimate λ_{\max} of a body, if we know its temperature. For example, humans have a λ_{\max} of 9500 nm.

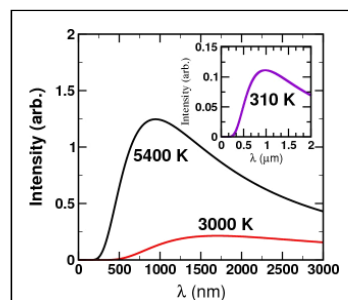


Figure A. Spectra of a black body at different temperatures. Temperature in the inset corresponds to normal body temperature of humans (note: the wavelength units in inset are microns).

of an electronic state against nuclear geometry is known as a potential energy surface (PES). PES are usually parabolic functions of nuclear coordinates for small displacements, and it is assumed that nuclear motion does not in general take a molecule from one electronic surface to another.

The approximation based on this assumption is known as the Born–Oppenheimer approximation. Within each PES, when nuclei are displaced from their equilibrium positions, the potential provides a restoring force, the consequence of which is the vibration of the molecule around the equilibrium position. The vibrational energies are quantized and the state of a molecule is characterized by the electronic and vibrational levels of the surface. Usually, the most molecules have an even number of electrons and spins on these electrons are paired in the ground state. Such a spin-paired state is called a singlet state. When all but one pair of electrons in the molecule have paired spins then the state is called a triplet state. Usually, the energy of the lowest triplet state of a molecule T_1 lies between the energy of the singlet ground state S_0 and the first excited singlet state S_1 . This is because, in the electron configuration resulting from



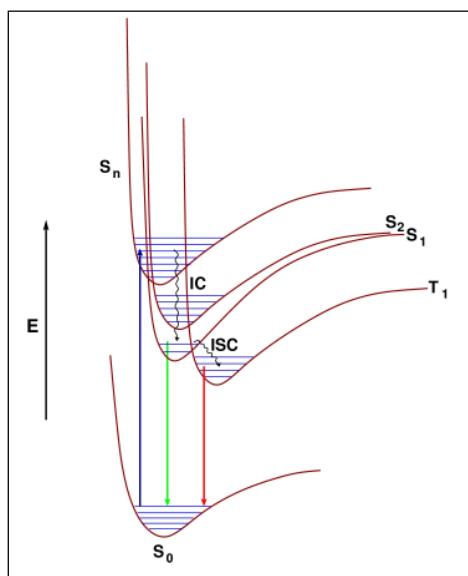


Figure 1. Illustrative singlet and triplet potential energy surfaces of a molecule. S_0 is the ground state assumed to be a singlet. S_1 and T_1 are the lowest excited singlet and lowest triplet states. Nonradiative transition from S_1 to T_1 is called intersystem crossing (ISC) while nonradiative transition from S_2 to S_1 is called internal conversion (IC). Blue arrow corresponds to Frank–Condon excitation and green arrow indicates fluorescence. Red arrow indicates phosphorescence. The energy difference between transitions shown in blue and green is known as Stoke's shift.

exciting an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), the state with parallel spin alignment of electrons in HOMO and LUMO is energetically lower, due to Hund's rule of maximum

multiplicity. This rule states that for the same distribution of electrons in orbitals, the lowest energy configuration corresponds to maximum possible parallel alignment of spins as electrons avoid each other better in this configuration than in the others. Thus T_1 will have a lower energy than S_1 .

When light of appropriate frequency falls on a molecule, the molecule absorbs the light energy and jumps from the ground state potential surface S_0 to an excited state potential surface S_n (Figure 1). This excitation involves redistribution of the electronic density which is a very rapid process and it is assumed that the nuclei do not move during the transition. This assumption of vertical transition is known as the Frank–Condon principle. Typically, an excited surface S_n is intersected by other PES, which could be singlet or triplet energy surfaces. The molecule on the surface S_n can cross to other energy surfaces. If the crossing occurs to another singlet surface, it is known as internal conversion. If the crossing is to a triplet energy surface, it is known as intersystem crossing. Internal conversion occurs due to breakdown of the Born–Oppenheimer approximation and occurs very fast, typically in a few hundreds of femtoseconds. Intersystem crossing has lower probability and occurs due to spin-orbit interactions. The energy gap between S_0 and S_1 is called the singlet gap while that between S_0 and T_1 is called the triplet gap or the spin gap. A molecule can get de-excited from the S_1 and T_1 states non-radiatively through collisions with other molecules or radiatively by emission of light. Radiative de-excitation by light emission from S_1 to S_0 is called fluorescence while light emission from T_1 is called phosphorescence. As a rule, in most molecules, fluorescence occurs from the lowest excited singlet state S_1 and seldom from other excited singlet states due to very fast internal conversion.

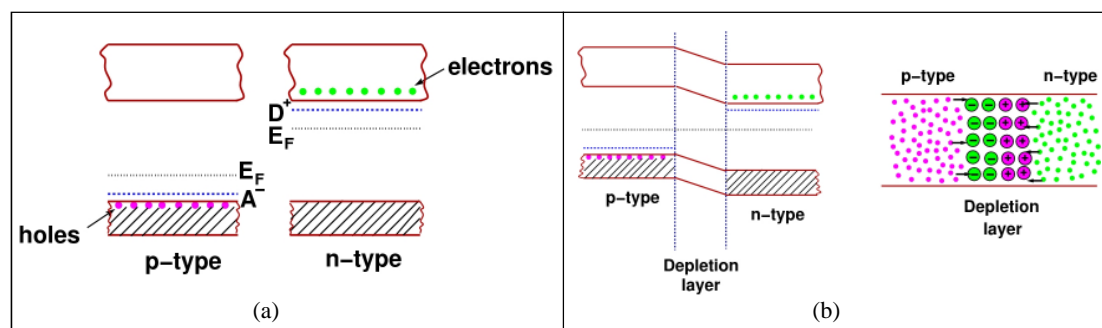


This is known as the Kasha rule. The triplet state T_1 is usually a long-lived state, due to breakdown of spin selection rule, with lifetimes ranging from a few nano seconds to a few seconds. Thus, phosphorescence is observed even after the excitation energy source is turned off.

4. Use of Semiconductors for Light Generation

With the advent of semiconductors it was possible to generate light by applying a voltage across appropriate semiconductor p-n junctions. A p-doped semiconductor has a partly vacant valence band while an n-doped semiconductor has a partly filled conduction band. So, when the two are brought together the electrons flow from the conduction band of the n-doped semiconductor to the valence band of the p-doped semiconductor. When electrons begin to diffuse from the initially neutral n-region to the initially neutral p-region, they recombine with the holes in the p-region and leave behind an uncompensated negatively charged acceptor ion. Similarly, in the n-region, there will be uncompensated positive donor ions. Thus, a space charge region whose voltage opposes the flow of electrons and holes to the p- and n-type regions, respectively, is set up and keeps majority of the electrons and holes on their respective sides. Applying a forward bias lowers the barrier and electrons flow from conduction band on the n-side to conduction band on the p-side. Simultaneously, holes flow from the valence band on the p-side to valence band on the n-side. This leads to the possibility of electrons in conduction band falling into the hole in the valence band and emitting light of frequency corresponding to the band gap. Semiconductor devices which emit light by this process are called light emitting diodes (LED) (*Figure 2*). The process of light emission called radiative electron-hole recombination does not occur in the unbiased state; since in the hole-doped region, electrons are not found in the conduction band and in the electron-doped region, holes are not found in the valence band.

Figure 2. (a) Isolated p-doped and n-doped semiconductors with separate Fermi levels. (b) Formation of the p-n junction leading to band bending and common Fermi level. On the right is shown the charges in the depletion layer.



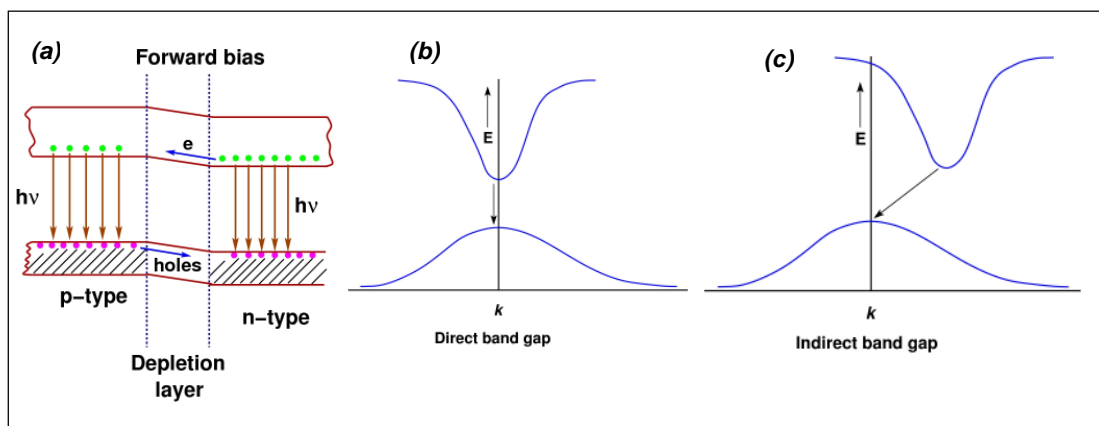


Figure 3. (a) *p-n junction under forward bias allowing electron flow into p-region and hole flow into n-region facilitating electron-hole recombination.* (b) *Schematic band diagram for a direct band gap material.* (c) *Schematic band diagram for an indirect band gap material.*

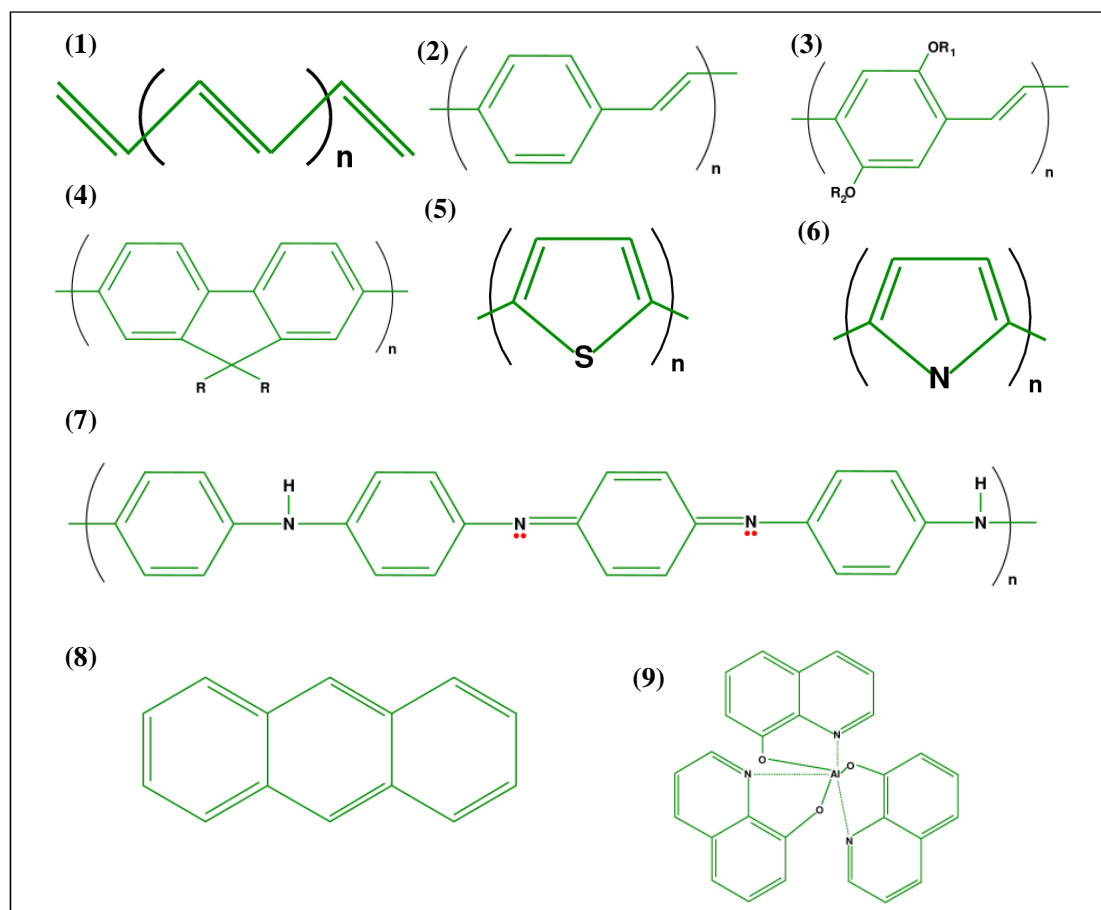
LEDs have been known for over forty years, although efficiency of light emission in GaAsP, the first material in which light emission was observed, was only 0.2%. For a semiconductor to be an efficient light emitter, it is necessary that the material should be a direct band gap material, which can be understood as follows. The emission from an excited state in any system usually occurs from the lowest energy excited state to the ground state. In many semiconductors such as silicon, the transition dipole moment for this transition is negligible because the excited state and ground state have different symmetries. In other words, the momentum of the electron in the occupied lowest energy state of the conduction band and the momentum of the highest energy empty state of the valence band are not the same and the transition dipole moment is zero since momentum is not conserved for such a transition (*Figure 3*). To conserve momentum, phonons or lattice vibrations have to take part by getting excited or de-excited and the energy gets dissipated as heat and this is not a high probability process. There exist LEDs based on direct band gap materials such as AlGaInP whose efficiency is as high as 50% in the red frequencies.

The light emitted by LEDs has a rather sharp spectral distribution; the full width at half maximum is about $1.8 k_B T$, where k_B is the Boltzmann constant. The wavelength corresponding to the spectral maximum depends upon the material used in the LED. The spectral maximum is easily shifted in GaN-based materials by using varying concentration of dopants such as Al, In, Ga and P. These materials, together with AlGaInP/GaAs almost entirely cover the visible spectrum from 300 nm to 625 nm. Together with phosphors which absorb light at higher energy and emit at a lower energy, it is possible to have LED emission almost continuously across the whole visible spectrum given that there exist thousands of phosphors which have their own characteristic emission and period for which light is emitted after excitation ceases.

5. Organic Light Emitting Diodes

Discovery of light emission from organic molecules on the application of an electric field is indeed very old. In the early 1950s it was observed by Bernanose and coworkers at University de Nancy, France that application of an AC voltage to some organic molecules (acridine orange and quinacrine) resulted in light emission. In the 1960s, scientists at Dow Chemical observed electroluminescence in doped anthracene. But, making an OLED was not possible as these materials had very poor conductivity and actual fabrication of an OLED device had to wait until the discovery of conducting polymers (*Resonance*, Vol.6, No.2, pp.62–70, 2001). The organic molecules and polymers currently being used in OLEDs are shown in *Figure 4*. What is

Figure 4. Some popular organic semiconducting polymers and molecules. 1. Polyacetylene, 2. Poly paraphenylene vinylene (PPV), 3. Substituted PPV, eg. R_1 =methyl, R_2 =2'-ethyl-hexyl, gives MEH-PPV, 4. Polyfluorene (PFO), 5. Polythiophene (PT), 6. Polypyrrole (PPy), 7. Polyaniline (PA), 8. Anthracene, 9. Tris (8-hydroxy quinolinato) Aluminium (Alq_3).



common to all these molecules is that every atom in the backbone contributes a $2p_z$ orbital to extended π -conjugation. If the atom involved in conjugation is a carbon atom, it is usually in an sp^2 hybridization and contributes one electron to π -conjugation. If the atom involved is a nitrogen atom then either one or two electrons of the atom are involved in conjugation, depending upon the chemical environment around the atom. Literally thousands of organic molecules have been tested for electroluminescence and many more are being synthesized to suit different requirements for application in OLEDs.

5.1 Mechanism of Electroluminescence

The principle behind molecular electroluminescence is very simple. In a molecular thin film or solid, an electron is injected into the LUMO at the anode and an electron is taken out from another molecule in the system at the anode from the HOMO. If the molecules are fairly densely packed then there is overlap of the MOs on neighboring molecules and under the influence of the potential difference between the electrodes, the injected electron hops towards the anode and the injected hole towards the cathode. If there are no traps in the system which can trap the injected particles, then it is possible that the electron and the hole both reside on the same molecule in the process of hopping. In this case, the electron configuration on the molecule would correspond to a hole in the HOMO and an electron in the LUMO which is nothing but an electronically excited molecule. Such an excited molecule could decay to the ground state by emitting a photon, and the process is called electroluminescence (*Figure 5*). A schematic

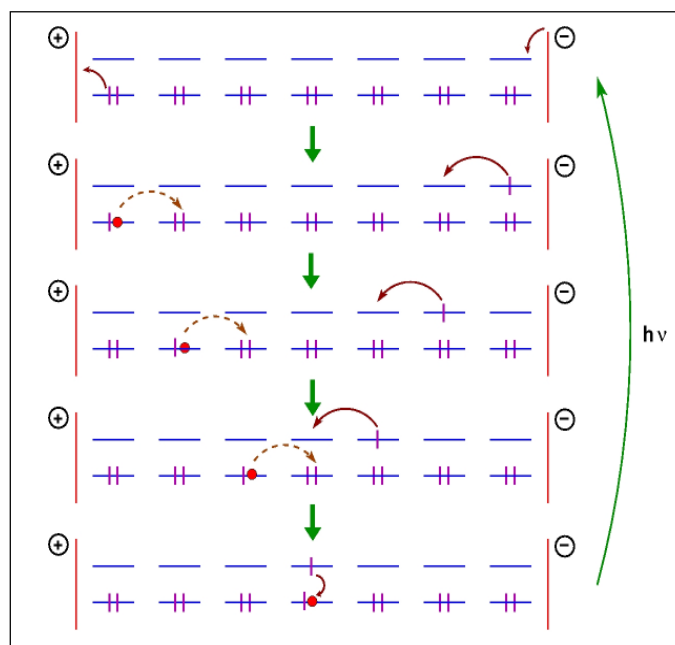


Figure 5. Schematic diagram of the electronic processes in an OLED. Top panel shows electron injection from the cathode and hole injection from the anode to the molecules at the electrode surfaces. Next three panels show hopping of the electron and hole and creation of the excited state (bottom panel). Radiative recombination of the electron and hole leads to regeneration of the initial state and emission of a photon.

Figure 6. OLED device configuration of a single layer (left) and multilayer (right) device on a glass substrate with Indium Tin Oxide (ITO) layer as the anode and calcium or magnesium layer as cathode on a glass substrate.

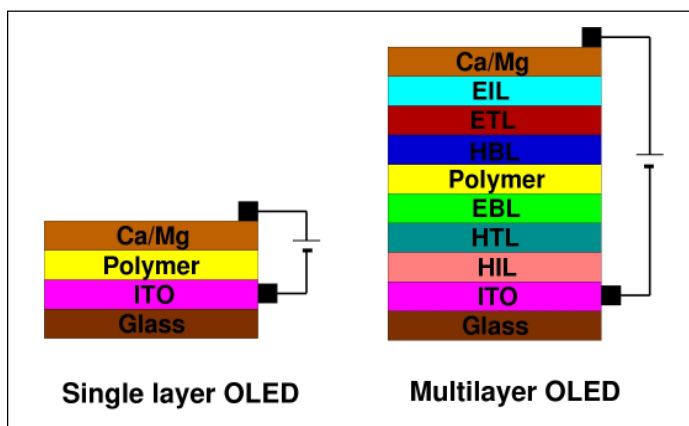


diagram of a three-layer OLED device is shown in *Figure 6*.

5.2 Efficiency of Electroluminescence

The efficiency of electroluminescent light emission from a molecular system depends upon several factors. The initial step is the process of charge injection. This occurs by a tunneling mechanism whereby an electron or a hole is injected from the corresponding electrode if the energy level of the electrode from which the electron is injected and the energy of the LUMO of the molecule involved in the process are nearly the same. Once the charges are injected they move towards opposite electrodes by hopping from molecule to molecule under the influence of the electric field. The velocity of hopping depends on the strength of the electric field, besides other parameters such as temperature, concentration of defects or impurities and closeness of packing. The velocity per unit electric field, known as the mobility in conventional semiconductors is about two orders of magnitude larger than those in organic materials. However, this is not a major hindrance for the performance of an OLED as the distance moved by a charge carrier before recombination is a few tens of nm and with mobilities in the range of $1 \text{ cm}^2/(\text{V}\cdot\text{s})$, it would take less than a microsecond for the recombination to occur. A time delay of one microsecond between switching the device and seeing the light emission cannot be perceived by human eye.

5.3 Multilayer Devices

The problem with OLEDs, however, is the mismatch in hole and electron mobilities. Hole mobilities are usually larger than electron mobilities by almost two orders of magnitude in the organics. This mismatch in mobilities, leads to large steady-state electron concentration near the cathode while hole concentration would be nearly uniform throughout the film. This results



in a recombination zone which is closer to the cathode in the device and the excitons are formed near the cathode. Such a situation is not very conducive for light emission since the exciton can break up under the influence of the large electric field near the cathode before radiative decay can occur. Therefore, it is necessary to improve the electron mobilities and shift the recombination zone more towards the center of the device. This has been achieved by fabricating multilayer devices. In a multilayer device, adjacent to the cathode is an electron injection layer (EIL) and adjacent to the anode is a hole injection layer (HIL). These layers have a closer match between the energy levels of the respective electrodes and the active orbitals of the molecules in the layers to provide better tunneling or injection efficiency. Adjacent to these HIL and EIL are the hole and electron transport layers (HTL/ETL) with higher carrier mobilities than the luminescent organic material. For an efficient OLED device, it is also important that electrons and holes be blocked from discharging against the electrodes, as far as possible. This is achieved by introducing two more layers adjacent to the central luminescent layer. These are called the electron and hole blocking layers (EBL/HBL). A schematic diagram of the multilayer OLED is shown in *Figure 6*.

5.4 Singlet to Triplet Branching Ratios

Another factor that affects the efficiency of an OLED is the fraction of the electron-hole pairs that lead to a light emitting excited state of the molecule. Since electrons and holes are spin-1/2 objects, their spin projections along an axis (say z -axis) can be up or down. This allows four different ways of injecting an electron and a hole in the system. One possibility upon electron-hole recombination leads to a state called a singlet with an antisymmetric combination of paired electron and hole spins and the remaining three combinations lead to a state called the triplet state. The ground states of these molecules are singlet and only the excited singlet recombination state has a large probability of radiative decay resulting in fluorescence. The triplet states have a very low probability of radiative decay, and radiative emission from the triplet state to the ground state, known as phosphorescence is usually weak. Thus, it appears that only 25% of the excitonic states resulting from electron-hole recombination can lead to light emission and the spin statistics seems to place an upper bound on the efficiency of OLEDs. Many experimental studies indicate that this upper limit for the OLED efficiency is breached in most systems. This shows the inadequacy of simplistic pictures which ignore the molecular details such as relative energies of the excited singlet and triplet states and the presence of internal fields due to charged impurities, applied electric field, chemical structure of the light emitting molecule and coupling between the neighboring molecules with hole and electron. It has been shown that in realistic cases, the rate of formation of singlets is higher than that of the triplets.



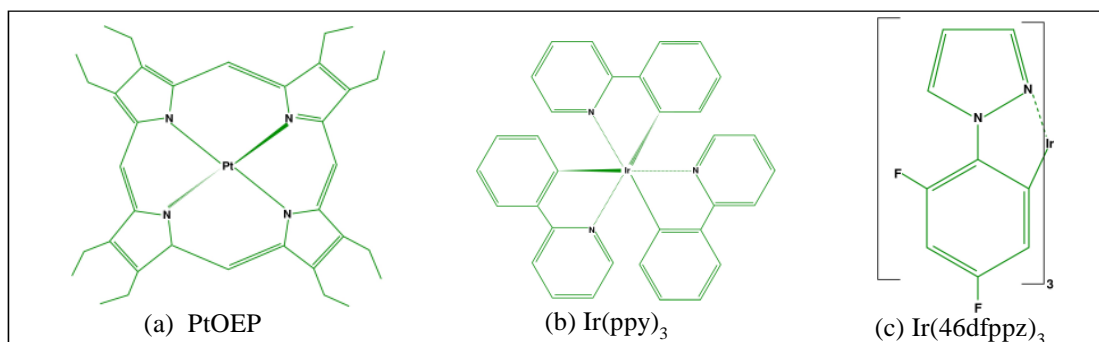


Figure 7. Some phosphorescent molecules. (a) *Platinum Octaethyl Porphyrin (PtOEP)* shows phosphorescent emission at 650 nm. (b) *Fac tris(2-phenylpyridine) iridium complex* has electroluminescent emission from a triplet state at 510 nm. (c) *A phenyl pyrazolyl iridium complex with blue phosphorescence at about 400 nm.*

5.5 Harvesting Triplets for Light Emission

There are many ways by which the triplets can be harvested for light emission. If a magnetic impurity or a heavy atom is doped into the system selectively, the triplets can be converted into light emitting singlets. It is also possible that two proximate triplet molecules can interact to give an excited singlet which could subsequently fluoresce to enhance light emission. There has been another interesting way to obtain light emission from triplets, namely, by introducing a strong phosphorescent molecule to which the triplet energy is transferred. Although phosphorescence is a slow process, due to the usually longer lifetime of triplets, the light emission is slightly delayed but is seldom an issue as long as the lifetimes are less than a few milliseconds. Indeed, this idea has already been utilized in phosphorescent organic light emitting diodes known as PhOLEDs. Currently, PhOLEDs show high efficiency for operation in the red region of the spectrum. Some of the molecules which have been used in PhOLED devices are shown in *Figure 7*.

5.6 The Kasha Rule

For technological applications, it is necessary to have OLEDs emitting light at different wavelengths. This is possible if we can design organic molecules that have strong emission at different wavelengths in the visible spectrum. To succeed in this task, it is important to understand the nature of light emitting excited states. A given molecule will have strong luminescence if the lowest singlet excited state has a large probability of radiative emission. This is because, while excitation follows the Frank–Condon principle, fluorescent emission always occurs from the lowest singlet state attained by internal conversions from the excited singlet state, according to Kasha's rule. There are a few exceptions to this rule such as the



azulene molecule, but in a large number of cases this rule is followed. Thus, for OLED applications, one needs to tailor molecules which have strong emission coefficient from the lowest excited singlet state. For a molecule to undergo an optical transition from one state to another, crudely speaking, the molecule should experience a change in dipole moment. The quantity which is a measure of this change is called the 'transition dipole moment'. The intensity of transition is proportional to the square of the transition dipole moment. For a nonzero transition dipole to be created, charge has to be redistributed when the transition occurs. The rearrangement of charge distribution is a high energy process, if the coulomb repulsion between electron density distributions is strong. It is often possible to find states whose charge density distribution is very similar to that of the ground state, but lying closer to the ground state in energy. These states have very small transition dipole to the ground state and existence of such a state just above the ground state and below the one which has a large transition dipole to the ground state makes the system very weakly fluorescent. This situation is the equivalent of indirect band gap semiconductors that we discussed above. The energy gap from the lowest energy state with a large transition dipole to the ground state is called the optical gap. Designing molecules for application in OLEDs not only requires tuning the energy gap to the state with a large transition dipole from the ground state but also ensuring that states with small transition dipoles do not lie below such a state with large transition dipole.

5.7 Tuning the Optical Gap

Tuning the optical gap of an organic system can be done in many ways. Introduction of substituent groups on a parent molecule could either blue-shift or red-shift the optical gap. Using electron donor and electron acceptor groups as substituents on the same molecule one can reduce the optical gap and increase the intensity of absorption. This is because, in the excited state, the acceptor easily accepts an electron and the donor easily donates an electron leading to a large change in charge density distribution. Introduction of such substituents also leads to red-shifting of the optical gap of the parent unsubstituted molecule. It is also possible to change the optical gap by effecting changes to the π -conjugation backbone. In *Figure 8* are shown two modifications of the Alq₃ molecule which show a shift in the optical gap to either side of the optical gap of the parent molecule.

In polymers, besides chemical substitutions, one can also control the optical gap by altering the topology of π -conjugation and the length of the π -conjugation. Topology of the conjugation can effectively reduce the repulsion between electrons in the excited state by providing alternate paths for avoiding each other. Thus, in PPV (*Figure 4*) and related polymers, the lowest singlet excited state is a state with large transition dipole moment while that in polyacetylenes, such a state is above a singlet state to which the transition dipole moment is very small. PPV class of



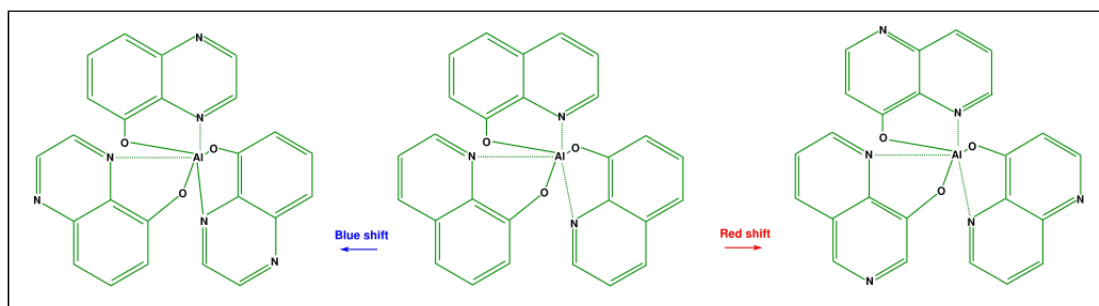


Figure 8. Substitution of nitrogen in pyridil ring leads to blue shift in emission while substitution in the phenyl ring leads to red shift in emission relative to unsubstituted Alq_3 .

molecules is widely used in OLEDs. It is also possible to tune the optical gap of a conjugated polymer by varying the conjugation length. Short oligomers have larger optical gaps than longer oligomers. The dependence of optical gap on conjugation length can be understood by drawing a parallel with the ‘particle in a box’ model. The spacing between the energy levels in this model depends inversely on the square of the box length. In a longer box, the energy gaps are smaller between the same pair of energy levels, when compared with a shorter box. Similarly, it is noticed that in longer oligomers the optical gap is smaller than in shorter oligomers. In case of aggregates of small molecules, the optical gap as well as the electroluminescent intensity depends on the way the molecules aggregate. If the molecules aggregate such that the coulombic interaction between the transition dipoles in the aggregate is attractive then the optical gap is reduced relative to the optical gap of the isolated molecule. In this aggregation the fluorescence intensity is also large. Such an aggregation is called J-aggregation. It is also possible to envisage another kind of aggregation in which the coulombic repulsion between the transition dipoles is repulsive. In such an aggregation the optical gap is larger than the optical gap of the isolated molecule and the fluorescent intensity is also very weak. Such an aggregation is called H-aggregation. It is possible to control the aggregation type by controlling the environment of aggregation and thus tune the optical gap of molecules. In recent years there has been considerable advance in using phosphorescent emission, besides fluorescent emission, in OLEDs. Exploiting both fluorescent and phosphorescent emission can, in principle, lead to a device with efficiencies close to 100%. This requires the ability to transfer the triplet excitation of the molecule to a suitable phosphorescent molecule as well as control the energy gap between the ground state, which is usually a singlet, and the lowest triplet state. Heavy transition metal or rare earth metal complexes are used to obtain strong phosphorescent emission. In *Figure 7* are shown a few popular triplet light emitting molecules. There exist a large number of molecules that have strong phosphorescent emission in the longer wavelength region of the visible spectrum. However, obtaining blue phosphorescent emitters is a challenge since high energy triplet states are usually very reactive.



5.8 Fabricating Organic Light Emitting Devices

OLEDs can be fabricated using small light emissive molecules as well as luminescent polymers. The OLEDs fabricated with small molecules are called SMOLEDs while those with polymers are called POLEDs. Small molecules widely used in SMOLEDs are Alq₃ and related systems. The polymers employed in POLEDs, to name a few, are substituted poly paraphenylene vinylenes, poly fluorenes, poly para phenylenes and poly thiophenes, depending upon the color of the light emission. Some of these are shown in *Figure 4*. Though SMOLEDs have a lead over POLEDs since the former were the first to be commercialized, the polymers have several advantages over the small molecules. Since these polymers are water soluble, fabrication of devices using such methods as lithography and inkjet printing are possible.

SMOLEDs are generally fabricated by using vacuum thermal evaporation (VTE) technique which involves periodic cleaning of the coating chamber and associated downtime losses. Besides, in the VTE technique control over uniformity and thickness is difficult for large area deposition. The organic polymers can be deposited by many techniques such as organic vapor phase deposition (OVPD) and organic vapor jet printing (OVJP). OVPD works by transporting evaporated organic materials – stored in separate, thermally controlled external cells – using inert carrier gases like nitrogen. The materials can be precisely deposited over cooled substrate of large-area by adjusting gas flow rate, pressure and temperature. Unlike with VTE, the OVPD chambers stay free of deposits, meaning less downtime, higher production and lower cost. OVJP involves highly collimated flow of organic vapor through a microscopic nozzle leading to a highly collimated gas beam which is then directed to print fine-featured organic patterns at very rapid rates.

There are also attempts to develop nanopatterning on the complete OLED layer once it has been grown, to create display systems which are a collection of large arrays of individual OLEDs. Indeed, GE demonstrated the first successful roll-to-roll manufactured OLED in March 2008. GE and other companies such as Universal Display Corporation (UDC) are pioneering the development of white OLEDs, known as WOLEDs for lighting purposes. In this effort, UDC has employed PhOLEDs to develop WOLEDs which have efficiencies in excess of 100 lumens/watt. Besides high efficiency, light emitted from WOLEDs is also bright with uniform color quality (CRI > 70 and CCT of 3900 K) and color tenability. It is also expected that with continuing efforts, the WOLEDs will also have long operational lifetimes. With advances in WOLED technologies such as the recent development of transparent WOLEDs, new niche applications in architecture and automotive lighting are around the corner.



Box 3. Units, Color Temperature, Color Rendering Index

The quality of a light bulb is measured in terms of its efficiency, quality of light and the trueness with which colors are viewed in the light. Efficiency of a light bulb is quoted in terms of lumens per watt. Higher the number, more efficient is the light source. 100% efficiency corresponds to about 280 lumens per watt. Lumen is defined in terms of candela; one candela is the luminous intensity in a given direction of a source that emits monochromatic radiation of frequency 540×10^{12} hertz that has radiant intensity of 1/683 watt per steradian of solid angle in that direction [1]. This now requires definitions of radiant intensity and luminous intensity. Radiant intensity is the total intensity of electromagnetic radiation per unit solid angle [2] while luminous intensity is the wavelength weighted power, weighted by a standardized luminosity function which takes into account the sensitivity of the eye to different wavelengths of the electromagnetic spectrum [3]. A lumen is defined as the total light emitted by a light source of one candela over a solid angle of one steradian [4]. The color temperature is the temperature of the incandescent source which is emitting light. For non-incandescent sources, apparent or correlated color temperature (CCT) is used to describe the nature of the light source [5]. A CCT of 2650–3200 K is known as warm white (yellowish) light, that between 3200 to 4000 K is neutral and above 4000 K is cool (bluish white) or also called 'daylight'. The color rendering index (CRI) represents the ability of the light source to show colors 'realistically' when compared to a standard incandescent lamp. The CRI scale ranges from 0 to 100, higher the CRI, better is the color quality. A CRI of 80 or above is required for good color quality.

6. Displays using OLEDs

Two different types of refreshing as well as turning on/off of the pixels in LCDs have been developed; they are the passive matrix displays (PMD) and active matrix displays (AMD). The AMDs are generally faster to respond, look brighter and sharper than PMDs and used where the number of pixels are large. AMDs have a thin film transistor back plane with a dedicated transistor for each pixel and delivers the right voltage to each pixel in a given row when the row is activated, thus requiring less time for refreshing as well as changing the image compared to PMDs where each pixel is addressed independently. PMDs are used in smaller displays such as digital watches and pocket calculators while AMD is used in LCD TVs and monitors. In the context of OLEDs, both PMD and AMD technologies have been developed. Active matrix OLED (AMOLED) technology has been used in many devices which use OLED displays such as digital cameras and small screen TV sets.

6.1 Comparison with Liquid Crystal Displays

There are a large variety of OLED devices which have been fabricated for different purposes. OLEDs which emit light either from the top or the bottom of the device are known. These devices also employ transparent backplanes of polycrystalline silicon for addressing the pixels in both active matrix and passive matrix configurations. There also exist transparent OLEDs



(TOLED) which use transparent materials for both electrodes. TOLEDs are especially useful in constructing three-dimensional displays as their transparency permits stacking them one on top of another. Both active matrix and passive matrix OLEDs can be fabricated on a flexible support using simple technologies discussed above. Such flexible OLEDs (FOLED) have a variety of applications in lighting large curved surface areas, such as dashboards or roof tops in cars, as well as in creating thin flexible displays that could find use in electronic newspapers.

Most commonly used color display systems in daily life are built around vacuum tubes, plasma technology and LCDs. In the last decade, vacuum tube displays have largely made way for the latter two as both these technologies have matured and provide advantages in terms of picture quality and reduced bulk of the systems. The LCD technology involves using liquid crystals which are essentially large organic molecular systems with a high degree of shape anisotropy. An ordinary molecular crystal of, say benzene, has both orientational and translational order, i.e., given the unit cell parameters of the benzene crystal and the orientation and position of a benzene molecule in the unit cell, we would know the exact positions and orientations of all the benzene molecules in the crystal. If this periodicity is broken completely, we would get a liquid phase. However, with some substances, only one of these two periodicities (translational and orientational) is completely broken. Systems in which orientational periodicity is broken are called plastic crystals; C_{60} crystals exhibit this phase. The systems in which orientational periodicity is retained but translational periodicity is broken are the liquid crystals and as the name suggests, they behave like liquids to the ordinary eye. Liquid crystals have very interesting optical properties, depending upon the orientation of the molecules; the liquid crystal is either transparent or opaque. These molecules can be oriented by the application of an electric field, thereby allowing control of opacity of a given column of liquid crystal. This is the principle used in LCD technologies.

LCD displays use back lighting and polarizers, that is a light source is always present at the base of the device and a pixel is turned on or off by either blocking or allowing this light to pass through by the use of polarizers. Because of the need for back lighting, LCDs consume more power than required and the polarizers also filter out some light. Besides, the existence of back light prevents the display from having a completely dark state; about 10% of the back light always leaks through a pixel even when the pixel is turned off. The LCD displays use the property of reorientation of the molecule to control the state of the pixel and this is usually slower than a display which uses electronic property of the system to create a display. The LCD displays also have a narrow viewing angle, which means the display has to be viewed at an angle closer to the normal to see a clear picture. The OLED displays do not have these drawbacks. They are fast since the electron-hole recombination times in OLEDs are much shorter than the reorientation times of molecules in LCDs. Thus, the response times of LCDs is 4-8 milliseconds



while that of OLEDs is of the order of 0.01 milliseconds. The OLEDs consume power only when they are turned off and there is no need for back lighting and which also implies that the 'off' state is true black. The OLED displays can be much thinner than the LCDs, besides the OLED displays can also be made to be flexible. The disadvantage of the OLEDs is that the lifetime of an OLED in the blue region is short compared to the lifetime of LCDs. However, OLEDs, which have very long lifetimes, have now been fabricated in the laboratories and if these can be commercialized then OLEDs are expected to revolutionize future of display technologies. Indeed, already SONY is marketing an 11" OLED TV (XEL-1) which is about 5 mm thick for US\$ 2,500 and has showcased a full high definition 27" OLED TV in 2007 at the Las Vegas Consumer Electronics Show. In August 2008, SONY announced a 40" OLED TV with 9.9 mm thickness which is expected to sell for US\$ 4,500 sometime in the near future. SONY, in collaboration with Max Planck Institute is working on a stacked OLED technology for display of three dimensional images. There are also other companies which have been working on various products centered on OLED technologies.

Suggested Reading

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