

Materials Chemistry
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Module - 6
Lecture - 1
Optoelectronic Materials I - OLEDs

So far in module 5, we looked at the electronic properties of materials, and in module 6 we are going to take a look at the Optoelectronic Properties of Material. Materials which combine both the optical property, as well as the electronic property together we call this is as optoelectronic properties, because most of the gadgets that we use in today's life. We couple both the optical property of a material and the corresponding electronic property of a material to harvest either information's or to harvest displays.

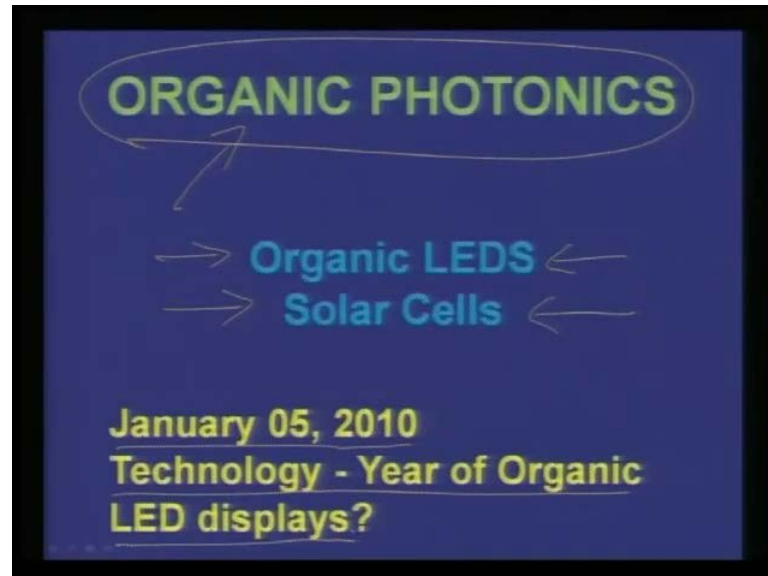
So, generally these are termed as optoelectronics and in the next few lectures I would be concentrating on some of the materials, which really stand out in today's technology which will underline the need for why we need new materials. And also I will try to explain in the next few lectures, why organic molecules plays a important role in optoelectronic devices.

Today, if you are handling any of the gadgets like iPod or cell phone or Pam computers, all the displays are more or less govern by small molecules either they are metal organic, complexes or much more easier version could be the organic molecules. So, as we looked at the genie inside a lattice, which brings in magnetism and electronic properties together. I have coined this term the genie in organic molecules there is a great potential in every organic molecule, specially when you consider optoelectronic properties. And we need to understand, what these governing properties are what are the issues that are involved in controlling optoelectronic properties.

So, when we think of organic molecules for optoelectronic applications, we can by enlarge call that area as organic photonics, in other words photonic applications that are actually initiated by using organic molecules. To stand out clearly, there are two important applications which underline the importance of organic molecules, one is called organic LEDS, and the other upcoming area is photovoltaic's or solar cells. In this

year January sorry 2010, there was a article or in conclave they decided that the technology for 2010 will be the year of LED displays.

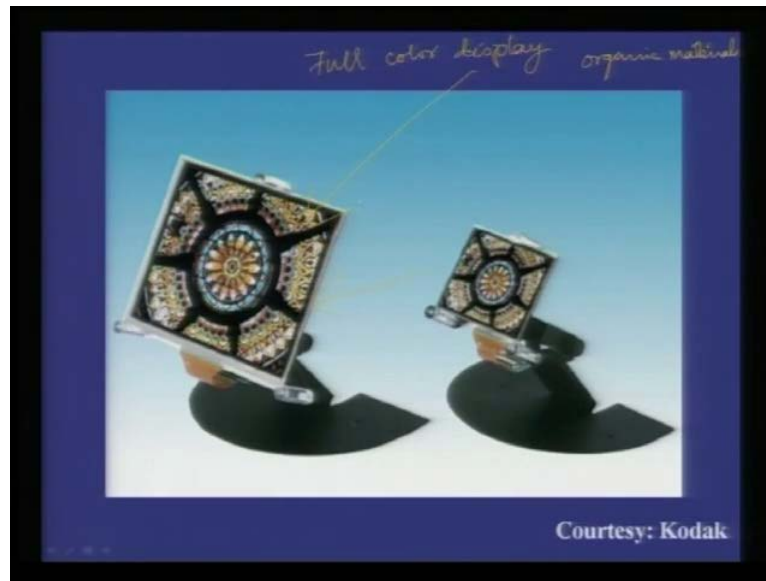
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And true to this decision made by those in the display technology, several versions of organic displays have come into picture in this year and needless to say that this technology is going to affect the landscape of photonic applications displays, in a very big way in the next 5 years. And because this year is year of LED displays, I personally thought that we should lay more emphasis an organic displays, compare to even inorganic displays. For those who are wondering, why we talk about organic displays because all the gadgets that you use currently show some sort of a LED response.

And they are all based on inorganic materials, and mainly those are governed by gallium nitrate, inorganic material based on gallium nitrate are the once which are used in photonic display materials. So, therefore, I would like to emphasis more on the use of organic.

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This cartoon tells that the more, we go for different gadgets the more we are interested in full color display. Nobody is settled with a black and white or a monochrome display those days have gone, we are looking not only for a multicolored display, but we are looking for high resolution display. So, what is this which governs a full color display, full color displays are basically initiated by the use of organic materials in today's technology. And whatever color that you are seeing is nothing, but manifestation of organic materials that are coated on the screen, whether you call it a computer display monitor or TV monitor or anything, these are all coated with choice organic materials.

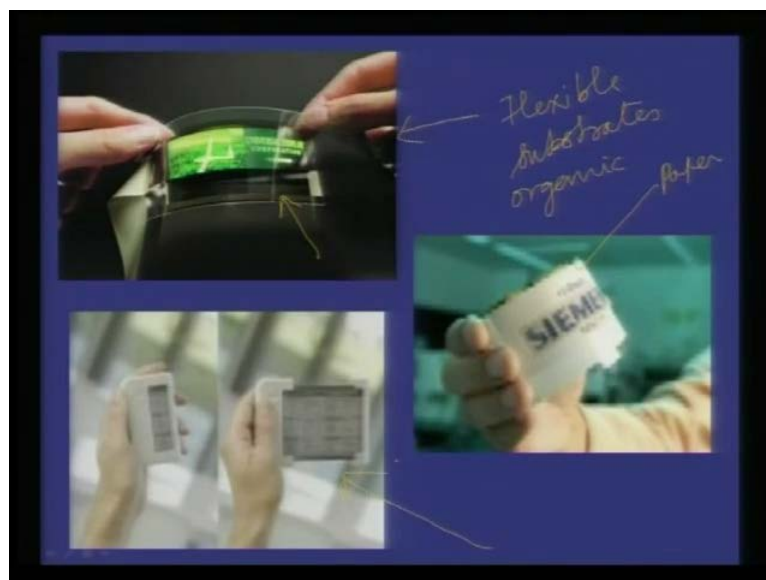
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This is the recent display, made by Sony and as you see here this is a Sony market, which is actually bringing out a new generation OLED TV this is high density TV. It looks like a computer monitor, but this is actually a TV and the whole display whatever you see here, that display here this is all projected from a organic LED screen. So, the display that is responsible for the light that is coming out of this display unit is mainly organic molecules, it is not based on gallium nitrate, but it is based on organic molecules.

So, this is almost a most recent invention and you would also see in the market 3D OLED displays are being advertised by Samsung. So, all the new generation displays have bigger screens, these can vary from 29 inch to 41 inch display screens mostly governed by organics.

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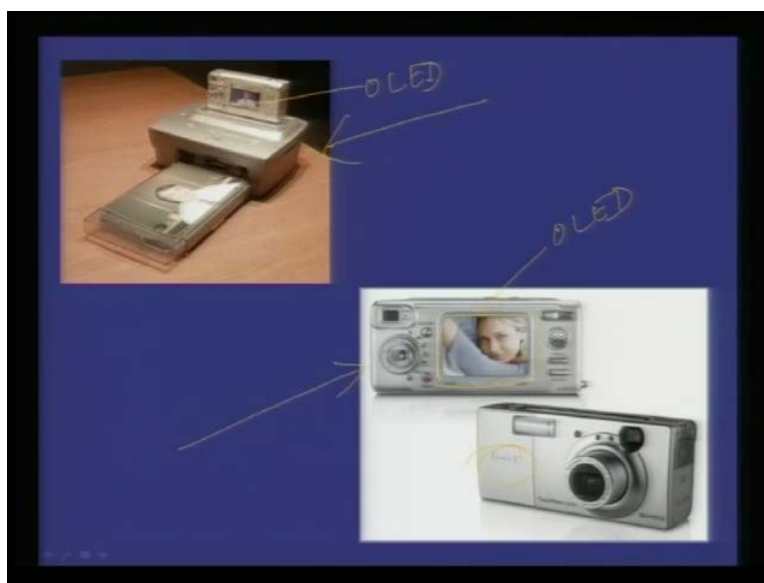


The cartoon here, shows another generation of displays that are coming these are called flexible substrates, where you can use it in variety of application even in car, windshield and so on. You can actually have some displays coming, and mainly this is coming from organic electronics, only with organics you can make such flexible displays with inorganic phosphors or inorganic photo luminescent material, it is impossible to make such flexible once.

Here is a situation where you can display on a flexible screen, this is with the paper substrate this is not this is with the polymer substrate usually it is a PET based substrate. But, here this is a paper substrate on which displays can be initiated and this is actually

brought up by Siemens, and here is another display may not be of a very high quality, but essentially tells you that you have another flexible substrate, which can be used in your pen. This is a pen holder, where you can actually pull out a screen and then you can scroll it back. So, you can just pull and scroll it back whenever you want displays are made here. So, these are flexible substrates, on which organic molecules are used for displays.

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And here is another classical example of what the organic displays can do, this is the new generation Kodak cameras that are coming digital cameras. And the beauty is the display what you get here is now made of OLED display material, and you can also see here this is also a OLED material, reason why we need OLED material. Because, you have the same sharpness, and it almost consumes 1 10TH of the power that gallium nitrate based LED will consume.

Therefore, you have a longer battery life and you get better resolution and also you can make wider screen or large area display therefore, you can do this at a very economically viable way, you can generate bigger display. So, this is catching up and in few years from now, all the displays in our electronic gadgets that we handled will all be organic.

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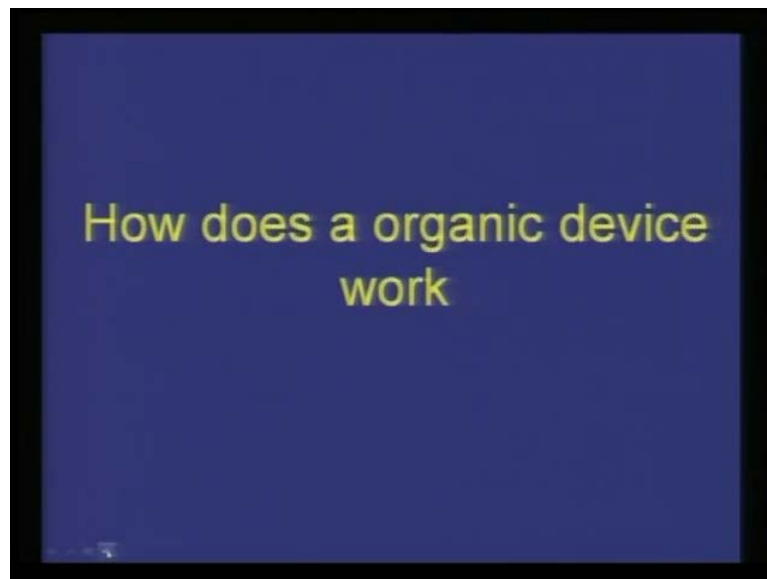
And this is an example of digital frame, now this is coming into picture you have, so many photos that you store in your cameras. And you do not know when to see it you can actually take your hard drive, from the camera and you can put in this digital frame at home, it will keep on displaying all thousands of photos that you are copying. So, this may be a good entertainment to keep the visitors occupied, when they are sitting in the living room waiting for you. And here is another OLED display from a foreign company which shows, a full color display mainly tuned from organic LEDs.

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And of course, needless to say you also have the mobile which is made of OLED and there are other applications, where you can look for OLED. This is a table lamp, made of OLED lighting and the important advantage is this gives you cool light more brightness, but it still cooler it does not irritate your eyes. And also the efficiency of this organic lamps are very high, that you can even operate with three volt battery you do not need even a AC supply, you can just do it wherever you want you get the same brightness and lot of lighting applications are also effected these stages using organic LEDS.

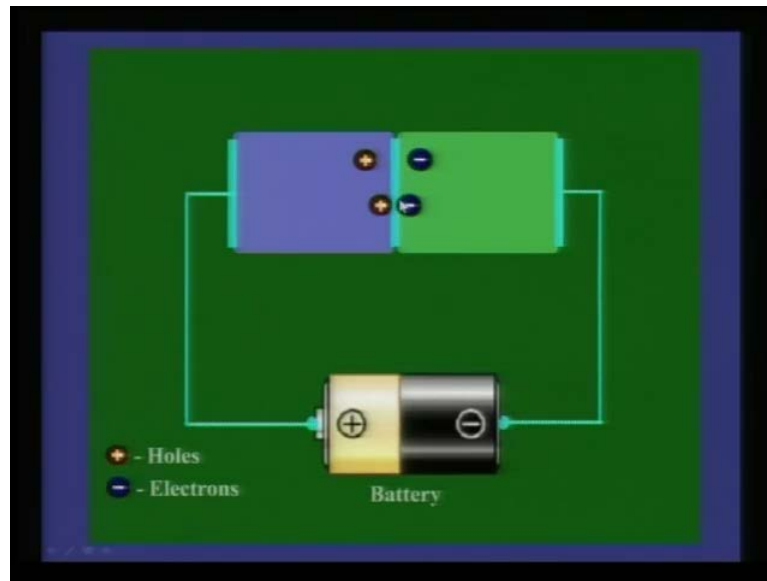
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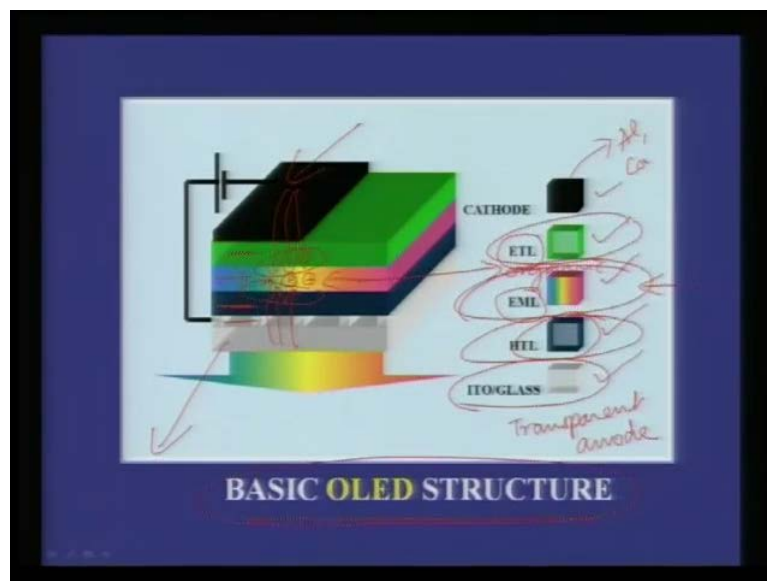
Then the whole question comes, where is my organic material in this device devices and how does the organic material work or what is the mechanism by which this organic material throws light. So, that is a good question to ask, so the question we will try to answer in the next few slides, how does a organic device works.

This is a simple example of a diode, if you have a diode and if you connect it to a battery then the electrons go from the anode material. So, the electron flows from the anode material and the sorry the holes go from the anode material, and the electron flows from the cathode. And you can see here at this interface, you have both the a holes and electrons combining and photons come out, during this excitonic recombination when the photons come out at this interlayer. So, in this animation you would see electron and a hole recombining, so at this interface if you can put a organic layer then the photon can actually excite the organic material and the decided light can be harvested.

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So, this is typically the view diagram of a basic OLED structure, where you have cathode on the top and you have a anode at the bottom. Anode is preferably a ITO Indium Tin Oxide which is coated in glass therefore, it is a transparent anode cathode can be opaque, cathode typically can be aluminum or calcium and between this there are crucial layers. But, the layer of importance to us is the organic layer, which we call this as emissive layer EML.

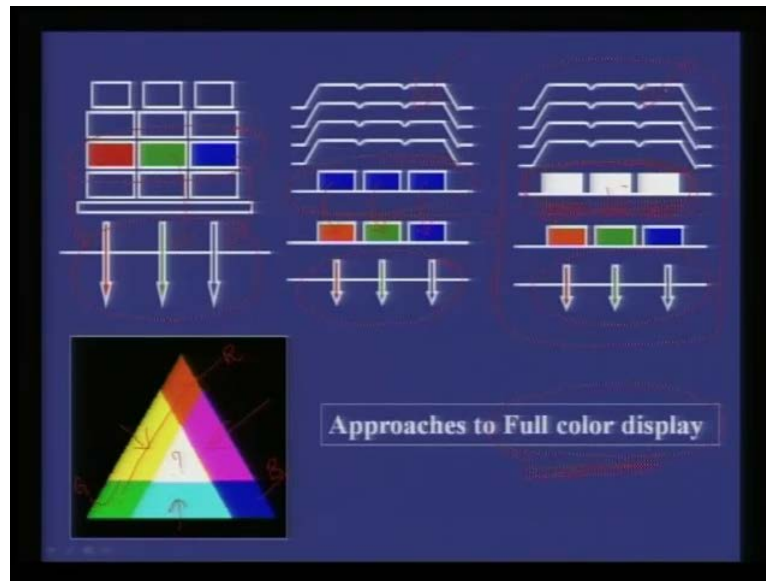
And you can sandwich this organic layer, with the electron transport layer because the electrons have to flow from here towards the emissive layer and holes have to flow from here towards the emissive layer. So, you have to control the traffic or control the mobility of the organic of the electron, as well as the holes and you should make sure that the combination of electron, and the hole both occurs at the emissive layer.

So, when there is a combination of electron hole pair which form an exciton that exciton will give a photon, which will excite in terms of your organic material. So, there are a lot of crucial issues that are involved in this, it is not a simple five layer structure which forms an OLED. Because, the number of electrons that keeps coming here and the number of holes that are going towards the emissive layer both need to be controlled, not only that the speed with which these electrons come here, and the speed with which the holes come at the emissive layer which we call it as mobility.

Mobility of the carriers also matter, so a proper recombination has to occur in this layer. If this is not effective, then the combination can happen here or the combination can happen in this region, and thereby giving some other light which is not of a desired nature. So, there are several issues involved in selecting the electron transport and the hole transport layer, and the issues related to emissive layer and also the HOMO, LUMO gap of cathode. HOMO, LUMO gap of ITO all these are crucial ingredients in designing an organic LED.

So, this is a basic structure we will come to the issues later now if I am going to put organic materials here, incidentally these are also organic materials which are polymeric in nature. So, if I am going to put organic materials here now what are all the issues that will decide, the basic performance of a LED which we can see.

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Now, there are different ways that I can harvest light from this organic LED structure, the different combinations for a full colored display I would like to touch. A basic lights basic colors are red blue and green, and combination of red blue and green gives white light, and mix of these two colors gives you yellow, mix of these two colors gives you magenta and then cyan. So, combination of RGB gives you white light therefore, you essential get a full spectrum display, when you have material which can give red light material, which can give blue material, which can give green light.

So, if you are looking for a full color display of this nature then there are three approaches. One is take a red and try to get red color as you see in this case, and green for green blue for blue, which means you are going to use three materials to get all three colors. And another one is to go for blue to red, blue to green and blue to blue down conversion, where blue is of a high energy emission therefore, you can put proper filters here and try to get from blue a down conversion to red, blue down conversion to green, blue down conversion to blue.

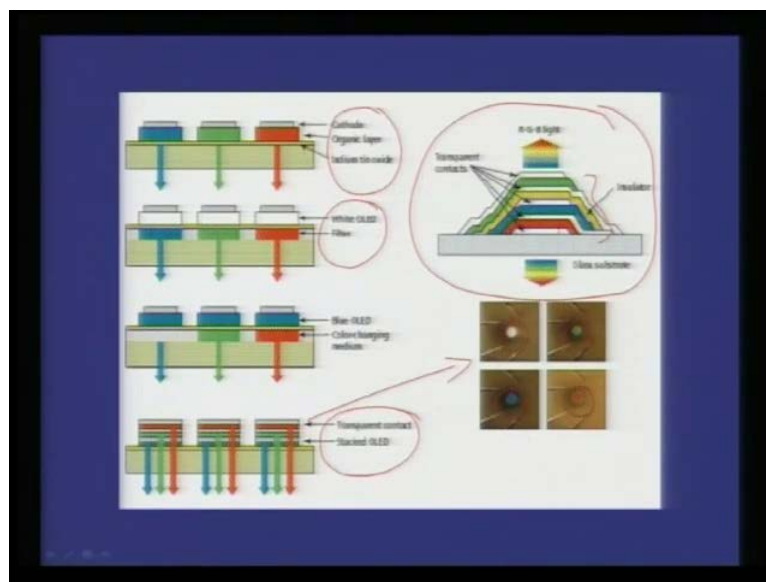
So, this is another way you can actually get your RGB colors this is another way to get a RGB color, the other approach which is of interest to us is take a white light emitting molecule. And put filter here, filter to get only red color and filter to get only green filter to get only blue color. So, your essentially having only one molecule and you are getting three different colors. So, this way you can actually minimize on your device fabrication

protocol, instead of having three materials or instead of going for down conversation you use one material which gives full colored spectrum.

But, use proper filter to get only the desired light, so this way also you can get RGB. There are different approaches, this is another approach which is popular in the market where people try to use blue and get all the colors, very few white light emitting molecules are there. White light emitting molecules can be used for full color display, as well as for white light emission for OLED lamps or for lighting applications.

Therefore, making white light emitting molecules, as do well advantage one is you can down convert it for desired lights, another thing you can use this white light molecules for even organic white light emitting lamps. So, for this reason there is special emphasis on white light emitting molecules, and companies are investing a lot of money specially for white light emission. Here, is another protocol I have already told you, so I may not run through this, but there are different ways of making a device, but need based you can actually get different displays.

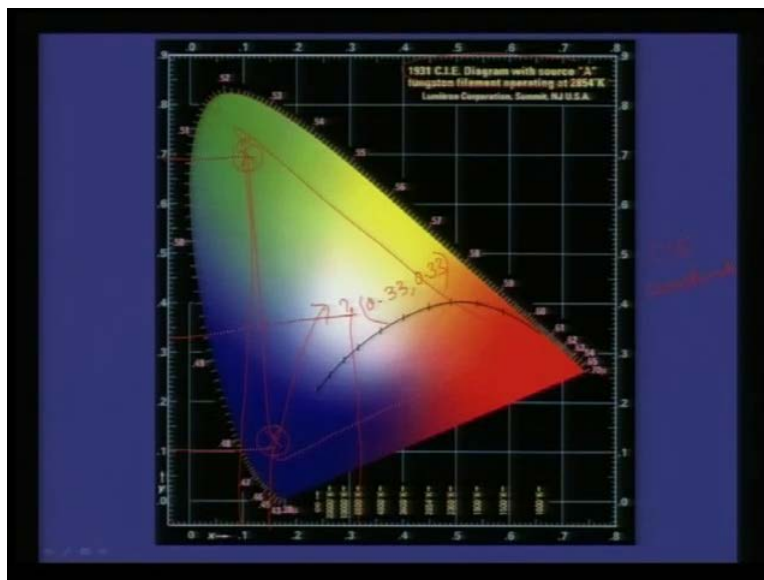
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If you preferentially activate one of the pixel, then you would get white or you would get green or you would get blue or you would get red, all from the same architecture. And in such cases you need to have stackings of this order, where you can get different pixels this is the example, that I coated in the previous slide. This is another example which I emphasis from the previous slide on white, LED and this is the stacked OLED which

gives you this sort of performance. So, you have transparent contact for all the devices that you have, but this stack OLEDs essentially will give you, the preferred light as and when you try to ask for it.

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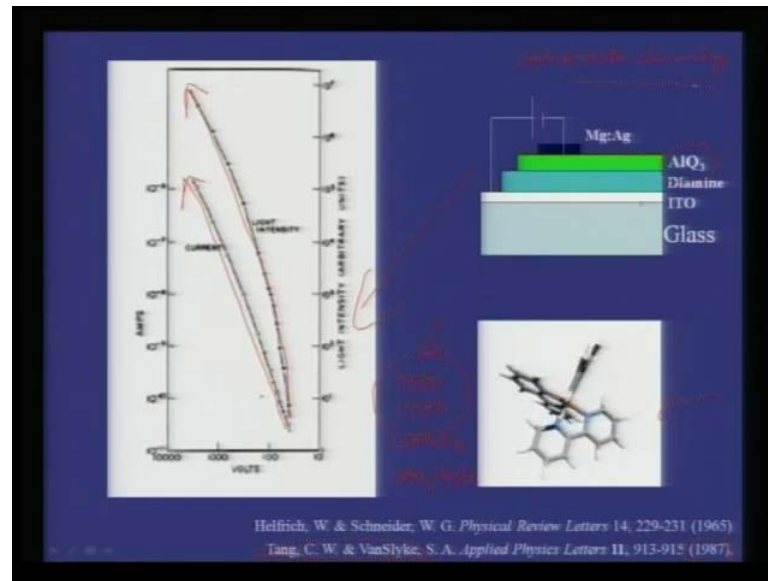


One of the things that we need to understand is how do I know, what sort of molecule it is and how do I categorize different organic molecules, and what is the number that I should resort to this is based on CIE diagram. Because, it has been accepted to represent the color of your molecular based on CIE coordinates, and CIE coordinates is actually based on a two dimensional graphical plot, which tells you the numbers.

So, if you have a number marked here then the x and y component of that will give you an idea that it is a blue light emitting molecule. If you mark something here, then you are talking about your y coordinate and x coordinate, which gives you typically a pure green one. We are actually concerned about white, and if you look at it white light emitting molecule the magic number for that comes somewhere here, and it is usually 0.33, 0.33.

So, if your x and y of your CIE coordinates is 0.33, 0.33 you are talking about a proper mix of blue green and red, together they give you a white light whose coordinates are mentioned as 0.33, 0.33. Either way if it is not matching to 0.33 then one of the colors will dominate, so this is the way you usually categorize what sort of molecule you have. So, that such a molecule if you give the CIE coordinates will immediately be you know used for a specific application.

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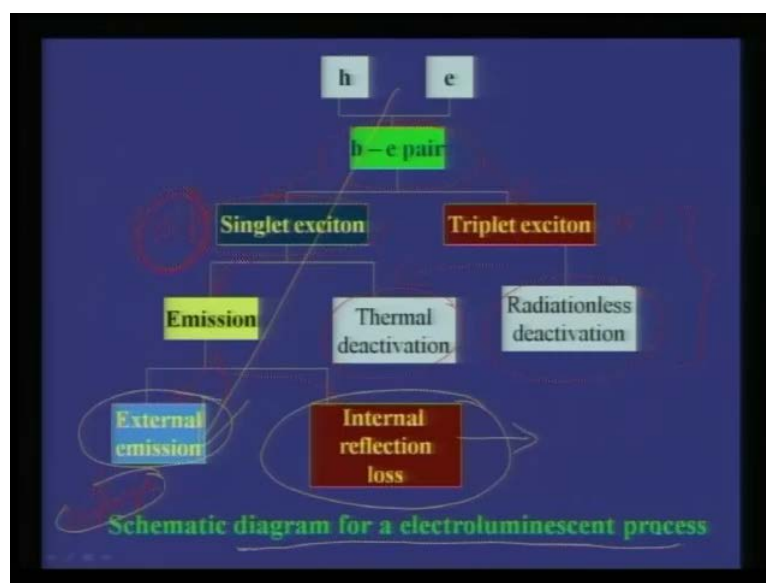


Where did it all start, we need to actually give credit for tang and vanslyk who actually brought the ALQ 3 into focus, and this is typically ALQ 3 complex which is actually in the animation. And if you make a device, such as glass ITO diamine and ALQ 3 capped with cathode, then you can see that a OLED performance occurs where with increasing voltage, you see the current and the light intensity exponentially going. This was the first demonstration as early as 1987 and I should also record, this as a historical fact.

Because, 1986 and 1987 has been a path breaking years, for most of the discoveries as far as a electronic and optoelectronic applications are concerned. As I discussed with you in module 5, I have told you how the lanthanum manganite was discovered, to show colossal magneto resistance that was in 1986 one paper came. And then 1986 also this high temperature superconductivity came into picture, where this wonder molecule was discovered, itrium barium copper oxide that was also in 1986.

And again you see here 1989, the first report on organic LED was published. Therefore these are really crucial and formative years, where many path breaking device application orientated discoveries were made in solid state materials. Therefore, this is a golden era in one sense to say, solid state chemistry came into much of focus because in solid state whether it is organic molecule or a inorganic solid, both started showing interesting properties.

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So, I will go one step further to highlight to you what exactly is happening in these compounds, why light is coming at all. As I told you, if there is a electron and hole that is combining they form a excitonic pair and this exciton pair will liberate photon, and it will die down. So, this photon can be used for activating any or promoting any molecule or exciting any molecule, so what really happens between a hole and a electron, when hole and electron combines they actually form a hole electron pair, which further leads to singlet exciton.

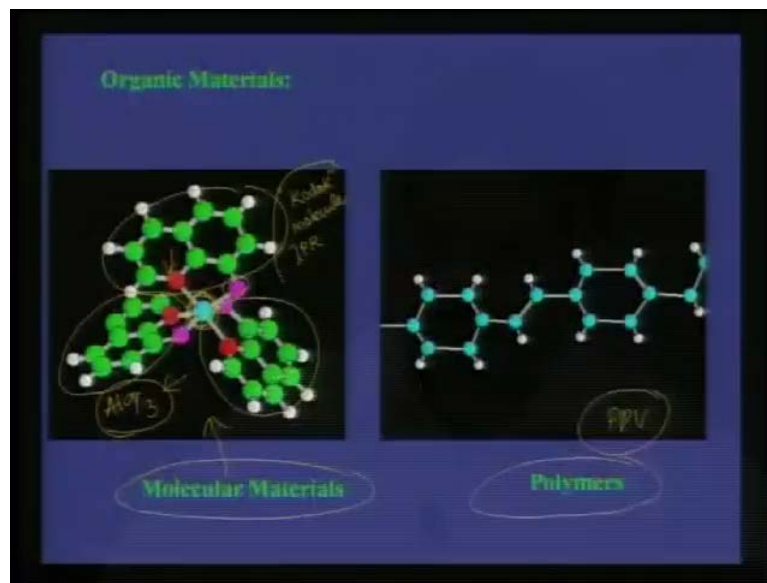
As I shared with you in while discussing organic spin walls, I told you the percentage of singlet excitons according to spin statistics is 25 percent, and triplet exciton is 75 percent, with this 25 percent comes all the light that you are harvesting from a organic molecule. Because, triplet exciton is a slow process spin forbidden, but it goes through a radiation less deactivation, but it is possible one to harvest this triplet exciton, convert it into singlet excitons. And you can try to increase on the efficiency of your excitonic emission, govern by singlets.

So, once you get a singlet exciton it can again go through a thermal deactivation which can be useless, does not really merit any attention or it can actually go through a emission process. And this emission can actually go through another two affects, one is external emission and that is what is exactly coming out as displays, but the internal reflection loss is something that we need to put up with, that is why most of the displays

you see a heating effect coming. And that is all because of the light that goes as an internal loss.

So, there are many ways that this internal loss is being minimized in this new generation display materials, but we are concerned now only about the external emission. So, this is the path way by which you get light, once you let hole and electron combined, so this is the mechanistic process for a electroluminescent device.

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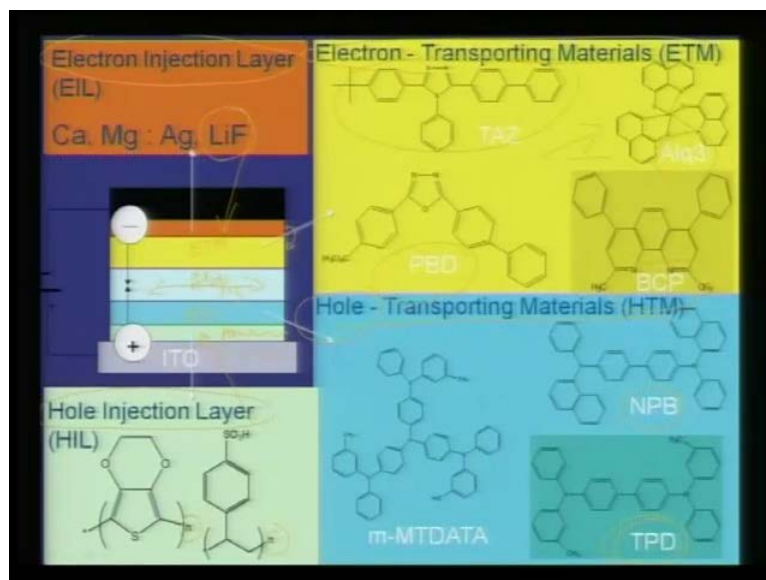
Now, what are all the organic molecules which really govern such a show or what really controls the organic displays, we can define that or we can broadly divided between two set of compounds. One those which are polymeric in nature PPV for example, is a classic example, and even now in commercial devices PPV is used will come to this later, but the other wonder molecule is the molecular material. And this is a typical example of aluminum q 3, and this is called as 8 hydroxy quinolinato aluminum 3 complex.

Popularly abbreviated as ALQ 3, and this is ALQ 3 this is the quinoline moiety and there are three such quinoline moieties, which actually coordinate to aluminum center here. And you have the coordination actually happening from nitrogen, this is a nitrogen atom and this is oxygen atom 3 oxygens actually satisfy the valency of your aluminum. Therefore, this is a electrically neutral molecule, ALQ 3 and this ALQ 3 is a wonder molecule because it was used by Kodak for the first time in device applications.

So, this is actually nick named as Kodak molecule because this molecule is also covered by IPR by Kodak company therefore, it is a proprietary molecule. And no one can in French in using aluminum Q 3 for making devices without the permission from Kodak company. So, you if you think of any organic molecule the first thing that should strike your mind is ALQ 3. In fact, the Kodak company has brought out the digital display in the cameras, which is actually made of ALQ 3 and some other hybrid molecules.

So, this is the most popular or billion dollar molecule, so to say which is actually controlling the optoelectronic applications as of now. But, there are several such molecules which are being generated, we are going to see in next few lectures a special study on this ALQ 3 or several other molecules which really govern the organic displays.

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So, having said that I have been talking to you more about ALQ 3 which is lying in this place in the device application, but there are several other organic molecules which also top up to the complexity or simplicity of this device. As I told you have a HTL that is Hole Transport Material and you also have a electron transport material. So, these are the hole injecting layers, which are mostly polymeric in nature as you see here, they are all polymeric in nature. And it is very easy to grow such polymeric films, by thermal evaporation.

So, you can make a thin layer here, to get a good support you can also use intermediate layers like this, which is mostly p dot PSS we can come to that later. And there are other

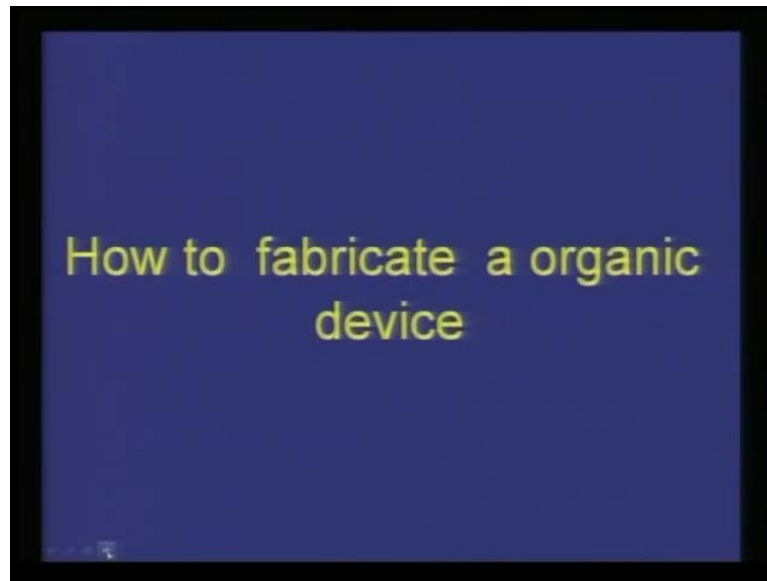
hole transporting materials, which are NPB, TPD this can also be used other than this hole injecting layers, and we also have electron injecting layer which is happening here. These are the hole injecting layers, these are the hole transport layers, the electron injecting layers are mainly coming from molecules like lithium fluoride, which are insulators.

Therefore, they help to electrons to accumulate at the cathode L i F interface and then they proceed together. So, instead of having a random electron transport across the interface, they are they act like a barrier, but this barriers are of very thin dimension, so that all the electrons that are flowing they get collected at the interface. And then they flow together, as you would see the water dashing out of the opening, flood gates from a dam. All the electrons get accumulated and they flow into the electron transport layer.

These are the popular electron transport layers, a one can think of ALQ 3 it is both a emissive layer it is also a good electron transporting layer BCP is another layer, PBD is another layer. As you would see here, mostly in this combination you can either use a purely organic molecule, small molecule or you can use a metal organic complex, where as in the hole transport materials is predominately small molecules or polymers, which are used. So, just to give you an idea what it takes to make a organic light emitting molecule, you have several combinations that are in picture. But, the grandeur of a organic LED is based on the emissive layer, so that has to be tuned properly. So, that you get all the necessary you know a display information's that you can get, so that is crucial.

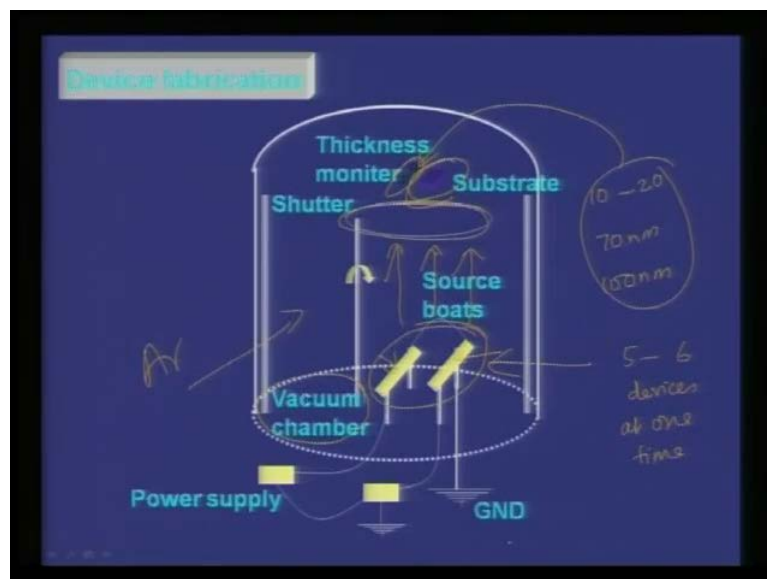
And now having discuss something about, what this molecules are and how it basically works I will spend little time on how to fabricate a organic device. Compared to the multilayer's that we discussed, in the previous module on electronic materials, organic device making efforts are rather easier comparatively, but there is a stringent protocol that is followed. Because, it has to be moister free although it can be handled at very low vacuum conditions.

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In the spin electronic application or spintronics devices I emphasize that you need absolutely a very high vacuum. But, in organic device applications you do not need very high vacuum, but a moderate vacuum of the order of 10^{-5} torr that is enough. So, in the next few slides I will discuss with you about what it takes to make a organic device.

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So, how to fabricate a organic device this is simple bell jar set up, which can be used for making this devices, and this is a vacuum chamber and in this vacuum chamber you have

source boats, which are kept here and you can heat this source boats. So, you can keep your organic molecules here, and thermally you can evaporate this, this is a shutter which is kept there, for a slow stream of this molecules to come up.

And once there is a proper flux of this organic molecules coming, then you can open the shutter and you can try to deposit in the substrate, which probably you may be able to see here. There is a substrate here and there is also a thickness monitor unit, which is a quartz balance which is kept there, which can measure the thickness of the layer that is coming in terms of angstrom, how much angstrom of the organic layer is formed per minute.

So, you can essentially control from say 10 to 20 nanometer or if you want to make a 70 nanometer thick film or a 100 nanometer thick film. It is possible for you to control the thickness using a quartz monitor that is called thickness monitor that is kept in within the chamber. So, that you can effortlessly work on the thickness of the layer that your depositing, so all it takes is to apply vacuum, and then once the required vacuum is reached then you can flush it with a some gas say argon.

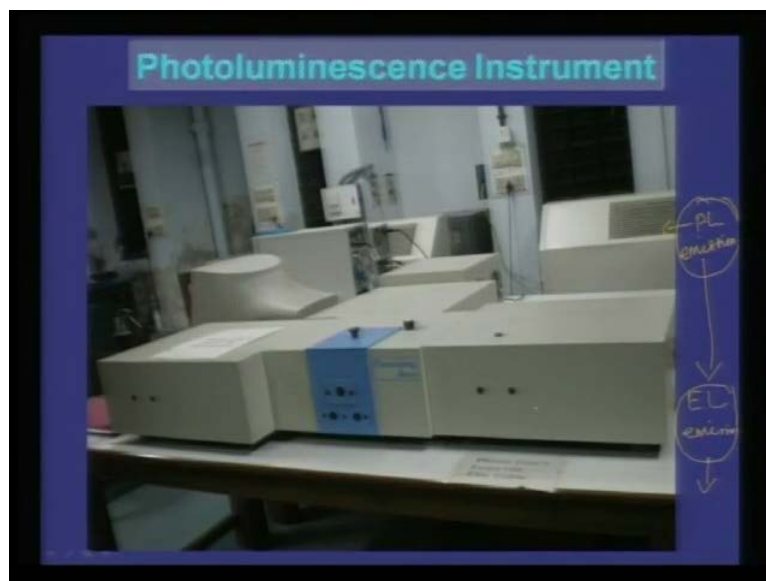
And then at optimum pressure, you can try to heat this sources and there is a steady flux of this organic molecule, which is going and it will get deposited in a substrate, in a typical experiment you can actually make 5 to 6 devices at one time. So, you can actually play with many devices, if you can go for such a protocol.

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This is typically the way the chamber looks this is a device fabrication chamber, so it may be alarming, but this is the way it is done, it involves all the other electronics in it. So, just to give a flier because it is not as easy as you see here, the machine actually looks bit more rugged as you see in this case, this is the deposition chamber in which you make the device.

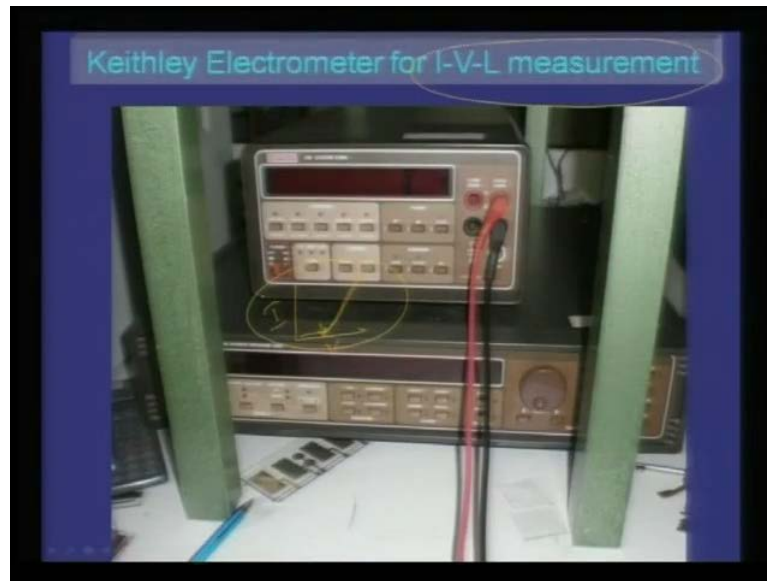
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Now, once you do the device your first idea or your temptation would be to look at the electroluminescence, but before you do the electroluminescence you also should know, what sort of color your molecule is emitting. So, that you will know what is the shift in the color when you put it in a EL device because this a machine gives you photoluminescence spectra that is your PL emission of your organic molecule, will be see. But, when you actually develop a solid state material, then the electroluminescent EL emission need not be the same as your PL emission it can be different.

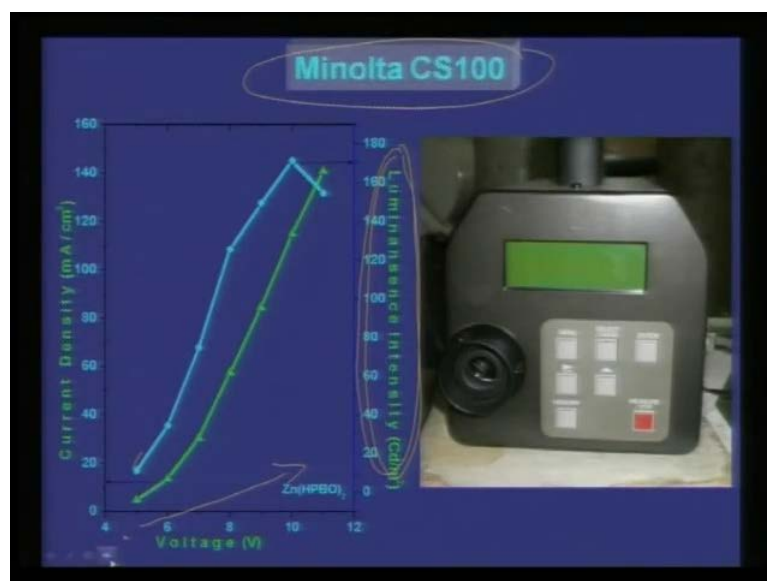
At the same time, if you can retain the same PL emission characteristics in EL emission, then you have made a real good device. In any case you will get an idea about, what the actual photo luminescent property of a material is and how you transient to make another material with a device configuration. So, this will help you in interpreting the photo physical properties of your material, so PL instrument is actually used for getting PL emission.

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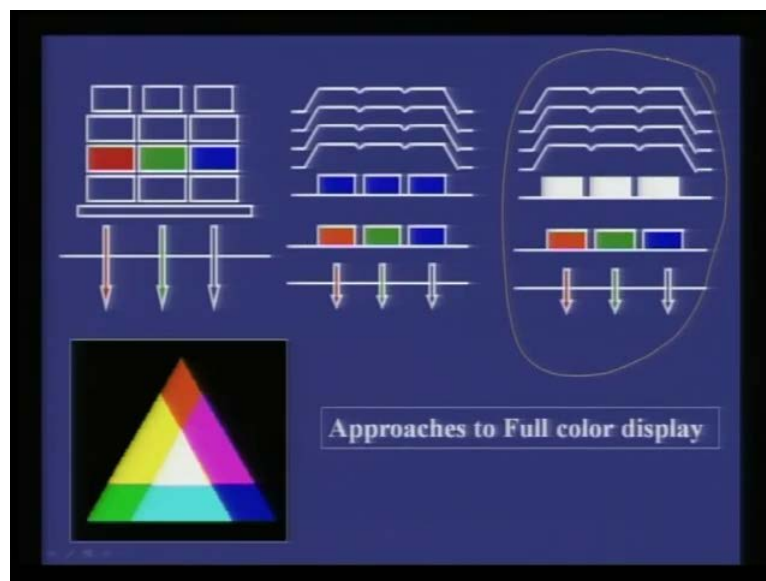
And this is I-V measurement unit, which is just unit involving multimeter and your current source, this will help you to get current versus voltage curve. So, if you are making a organic LED, your electroluminescent device typically will have some feature like this, where up to a particular voltage there will be no current and at this threshold voltage. Then you will see current flowing; that means, your electroluminescence device is going to produce light, light will start appearing as after you have applied a threshold voltage. So, this information you can get out of this I-V measurement curve.

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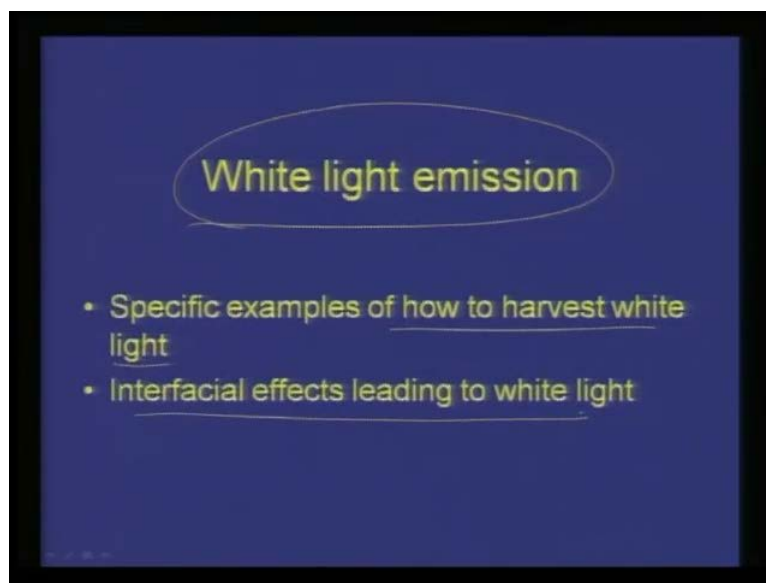
And also this Minolta CS 100 can give you, not only an idea about the current density it will also tell you, the luminescent density. As you increase the voltage, the brightness or the glow of your electroluminescent device will start increasing with increasing voltage. So, Minolta will give you the coordinates of your light output, and typically the graph will look like this we will look at it later.

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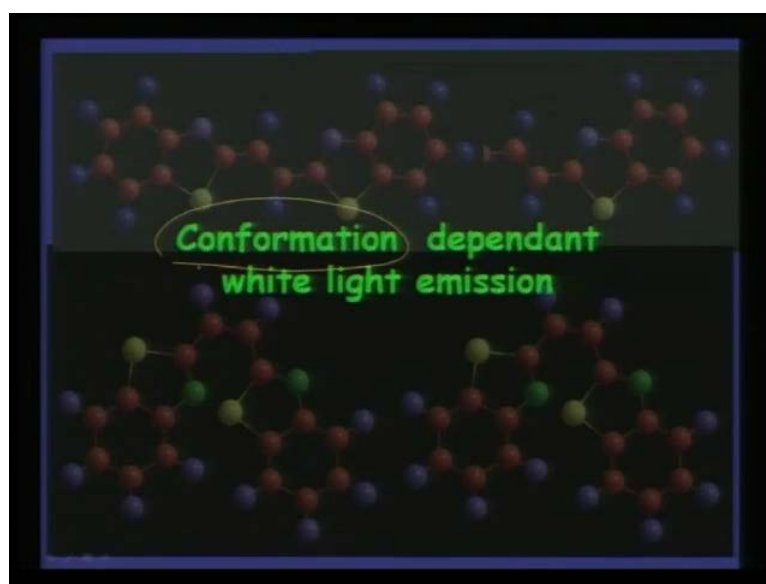


So, having said that I just want to concentrate now, on few examples and show you how organic molecules can be used to fine tune color or to understand, what is responsible for this color displays. So, I am going to take some examples in the next few slides I will tell you, what is this white light emission and with few examples as to how to harvest white light. Because, white light lighting is becoming popular, and I will also tell you white light can be engineered not just from the organic molecule, but from the EL device. The device the way you make can also be manipulated to give you white light, not necessary the white light has to come from the molecule. So, the EL device has lot of features in it which controls the light output. So, first example confirmation dependent white light emission.

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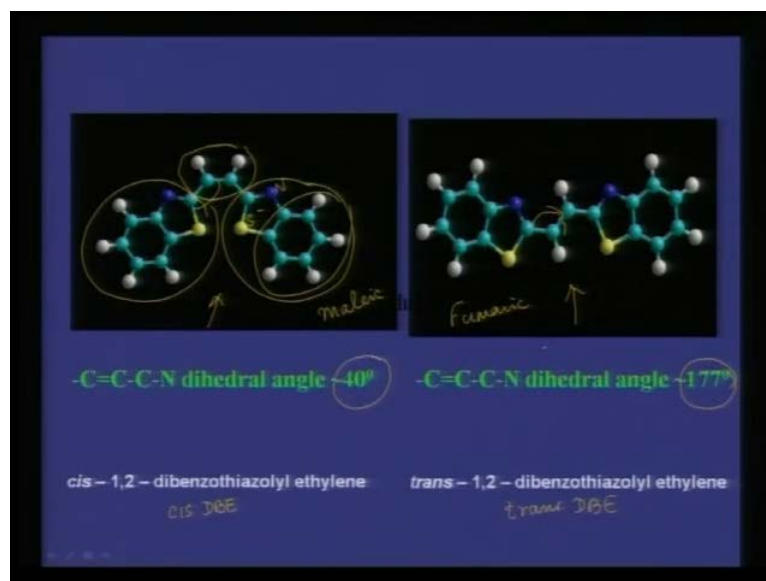


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What is this confirmation dependent I am going to show you a molecule, which is actually called dibenzo thiazolyl ethylene, there is a ethylene molecule which is actually integrating two benzothiazolyl molecules. Therefore, it is called CIS DBE for convenience I will use this abbreviation CIS DBE this is nothing, but benzothiazolyl because thiazolyl molecule is there nitrogen, sulphur is there and this your benzin ring. So, this is benzothiazolyl ethylene.

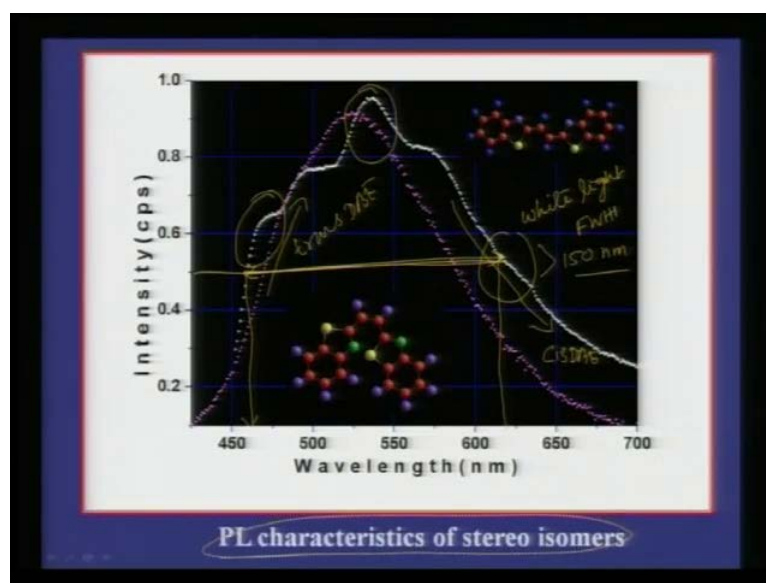
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So, two benzothiazolyl units are there which is integrated to a ethylenic double bond, in this case this is a CIS configuration therefore, you call it as CIS, DBE in this case this is trans configuration. So, you call this as trans DBE and it is easy to make both CIS and trans, if you start with malic acid and fumaric acid. So, if you start with two different starting materials you can end up with two geometrical isomers, one is CIS DBE one is trans DBE.

So, essentially they are same stereo chemically they are different, now if you look at the dihedral angle then the angle is 40 degree which means it is bent molecule. In this case it is 177 degree across the double bond, so if you look at this compound it is nearly planer whereas, in this case it is a bent molecule. So, same molecule, but with different conformers what this has to do and how it affects the EL emission.

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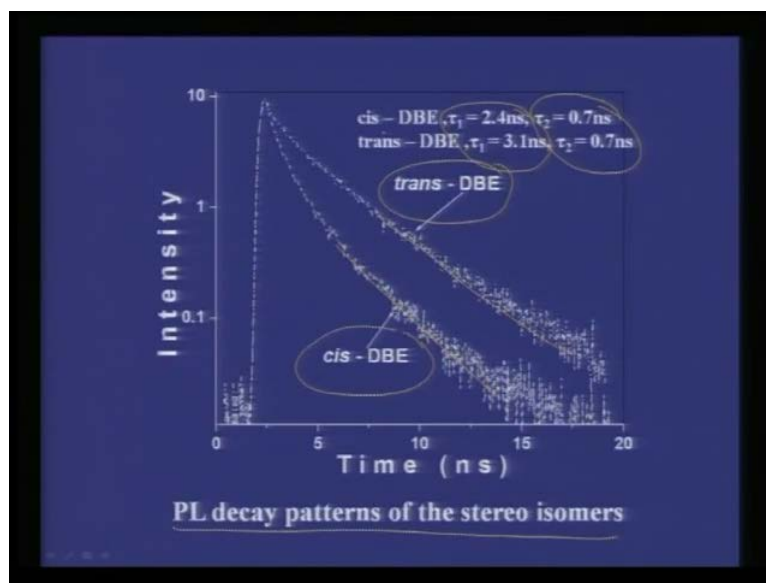


This is the photo luminescent characteristics of this stereo isomers, what you see here the white line that you see here is nothing, but your CIS DBE and you see this purple curve which is nothing, but your trans DBE. What you would immediately see is, this is a more featured emission in the case of CIS DBE, compared to Trans DBE although the broadening is there for both the molecules. You see there is a substantial broadening for the CIS DBE compared to trans DBE, so if you actually look at the full width at half maxima.

So, you are talking about the full width at half maxima somewhere here, so if you look at the full width at half maxima, it is more than 150 nanometers which means it covers part of the blue area. If blue light it covers part of green, and it also covers part of the red light emitting area, so if you have all three components are coming then there is a broad emission, which amounts to white light, typically a white light emitting molecule should have full width at half maximum which is 150 nanometers.

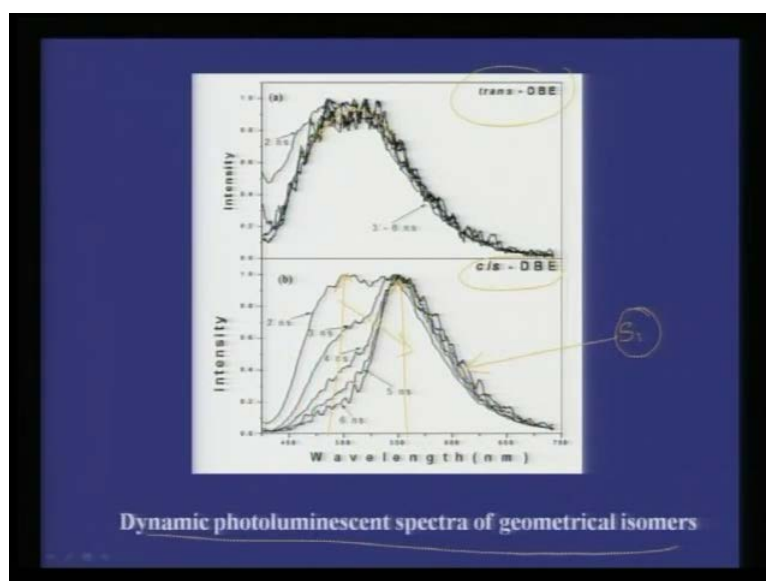
So, if it is a 150 nanometer a broad emission; that means, you have all three components in place and if they are of nearly equal intensity, then you can clearly talk about a pure white light. So, what is the question under discussion for us now, you say CIS DBE is giving white light and trans DBE is not giving white light, but both are same molecules just geometrically they are different.

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So, you can try to understand what really it takes and this is the photo luminescent decay patterns of the stereo isomers, as you would see for CIS DBE it is very, very different compared to trans DBE This can be fitted to a double exponential model where, both have nearly the same tau 2 values which is 0.7 nanoseconds, which comes somewhere here the linearity. But, you have the tau 1 values which are different, where CIS DBE has a much faster decay component compared to trans DBE.

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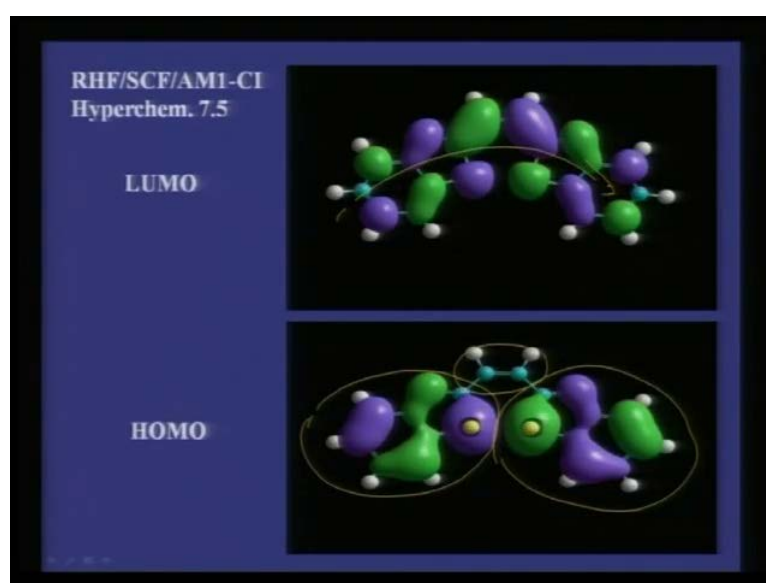


You can actually try to translate I will go to the next slide, try to translate this dynamic photo luminescent spectra of this geometrical isomers, what do you do you shine light you just pump in light. And then you excite the molecule allow that to decay for the first few nanoseconds, and keep on capturing the light that is coming out at different nanoseconds. So, you can essentially plot for different nanoseconds a emission, and you can also do that for CIS DBE.

As you could see here, CIS DBE in the first two nanoseconds the emission is here, and as you let it through to decay with different nanoseconds. You can see that the peak is shifting towards red whereas, if you look at trans DBE in the same time scale, the peak maxima is still the same. So, in one case the peak maxima keeps on going to a red shifted emission, in another case it is still the same, so; that means, there are different singlet states I will come to this issue bit more later in the slides to come.

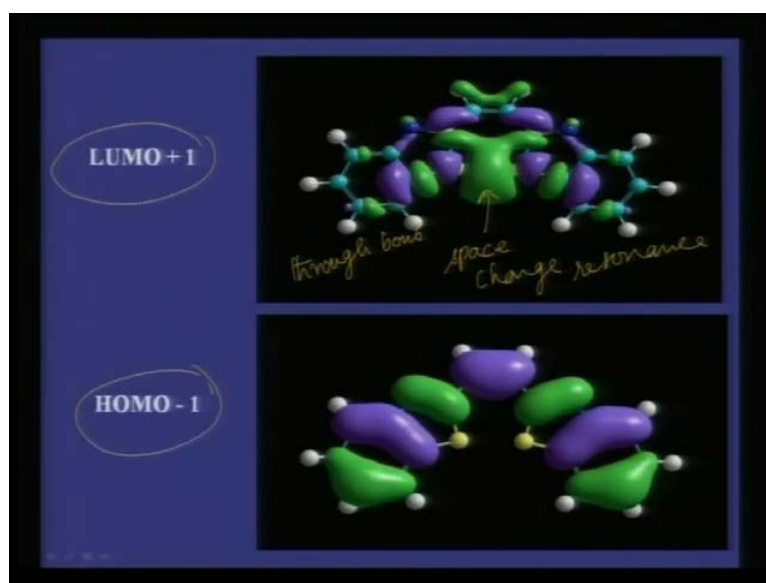
The singlet states that are responsible for this fluorescence is different or in other words there are different singlet states that are responsible for PL emission. As far as a CIS DBE is concerned whereas, for trans DBE that seems to be only one singlet which is responsible for emission. So, as a result when you let it decay only that particular chromophoric group or that singlet state is responsible for color emission. So, this much we can understand from the dynamic photo luminescence spectra.

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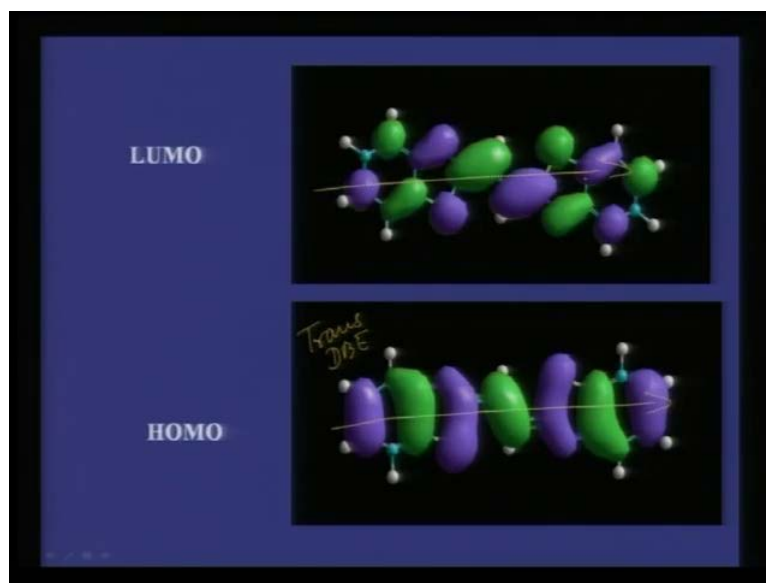
Therefore, if you do a semi empirical calculation, and try to look at what really is happening in the case of trans DBE, you would see that the homo that is the highest occupied molecular orbital. The electron density mapping shows, that the charge resonance is confined only to the benzothiazolyl ring, in the lowest unoccupied molecular orbital, the electron is actually the charge is transferred across the ring. Through the ethylenic double bond in the excited state.

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If you look at the this slide is for a CIS DBE, and this is the situation for the HOMO and this is the situation for the LUMO, and if you go to higher a levels for example, LUMO plus 1. You can see that the charge resonance is not only happening between these two rings, but also there is a space charge resonance that is happening, space charge resonance that is happening. Where there is a cris stock between two rings across the rings, not through the bound. So, you have both through bond effect and through space effect, both are contributing to the charge resonance. So, this is the situation for HOMO minus 1.

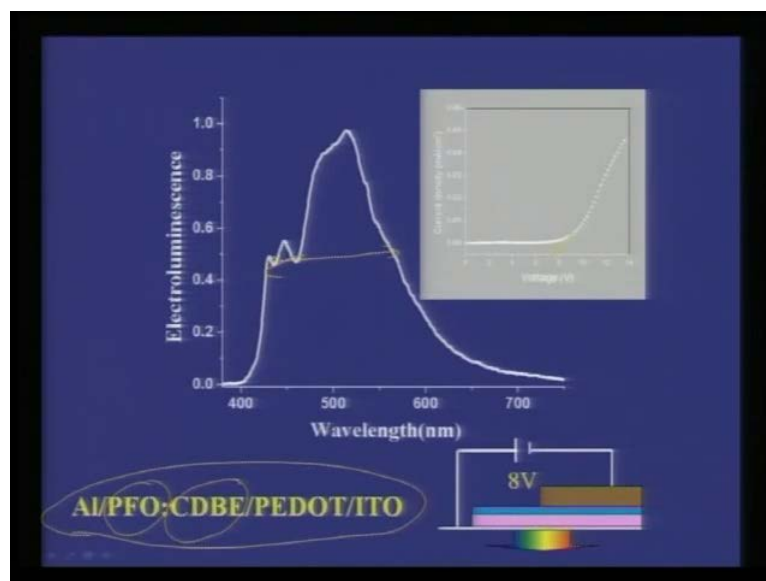
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Now, let us see what really happens to trans DBE molecule, in trans DBE you can see that in the homo the electron is delocalized and there is no significant change in the case of LUMO, it is nearly remaining the same. So, based on this one can conclude that in the case of CIS DBE, you have several singlet states which are responsible this homo plus one can contribute your LUMO can contribute to the emission. Whereas, in the case of trans DBE, the charge resonance seems to happen only via one singlet state.

As a result, you can say that the several singlet states that are involved in the CIS DBE is responsible for the wide broad emission. So, white light emission in CIS DBE is actually coming from several singlet states whereas, it is because of one singlet state which is responsible predominately for emission in trans.

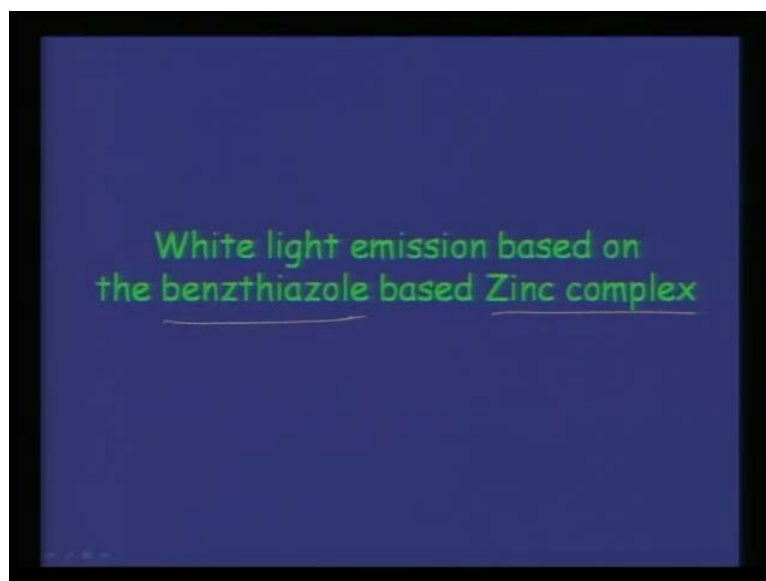
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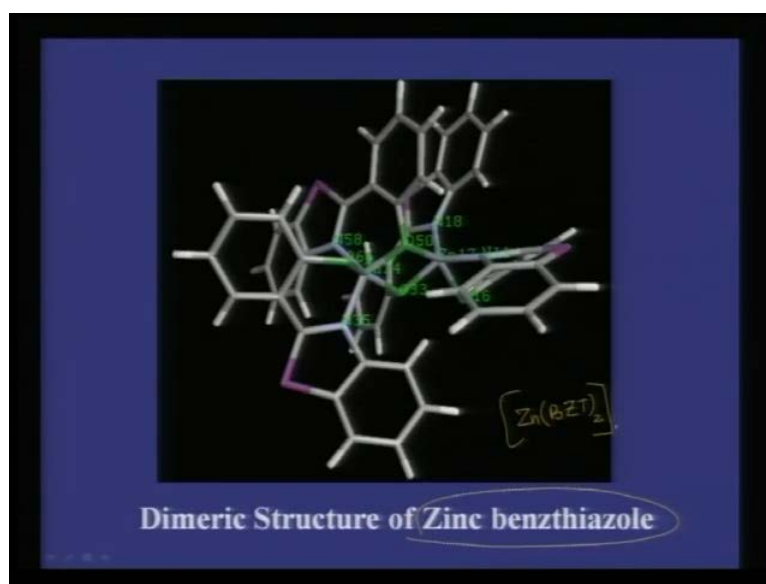
You can try to use this CIS DBE, with polyflorin substrate or matrix you can mix it and make a device of this sort, aluminum CIS DPE, p dot PSS and ITO. If you make this at 8 volt you can see the threshold is somewhere here, and at 8 volt you can see a nice device performance, which is also showing a white light. If you look at this here, it is showing a white light at approximately 8 volts, but from device point of view 8 volt is not something, which is interesting you need to go much lower. But, this is a proof of concept to say that white light can be produced with simple molecules like CIS DBE, if you can put it with the PFO matrix. So, this just to show you that small molecules can be used for engineering white light.

I am also going to give you another example, in this case it is not small molecule, but it is a zinc complex of a benzthiazole and again I can show you, that the it is not only to do with the organic molecule, but even the interface in a electroluminescence device which can be responsible for white light.

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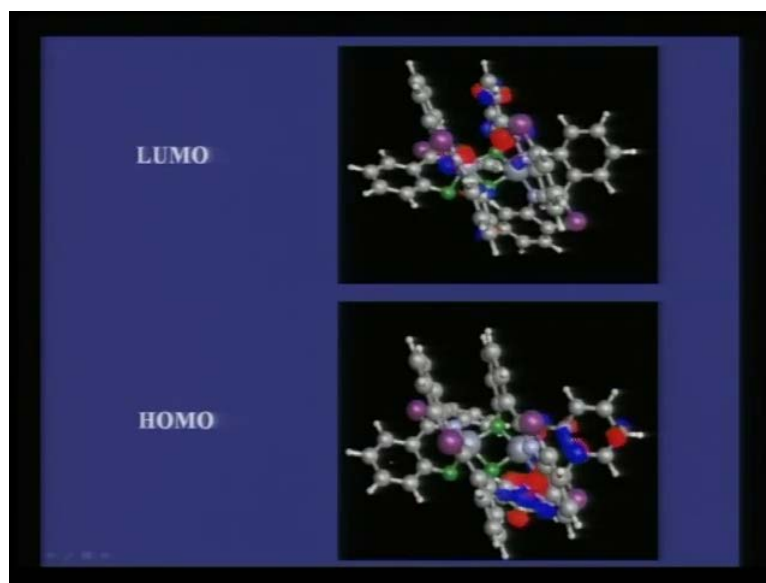


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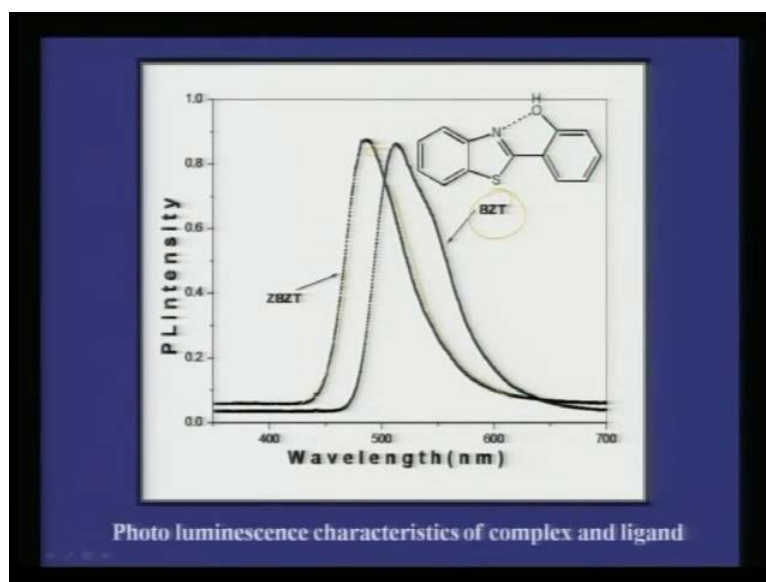
And this is the structure of Zinc benzthiazole a molecule, which actually shows a dimeric nature. So, we popularly mentioned this as a dimer like this.

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And such a dimer can throw some light and the as you see here, the electro mapping of the homo LUMO shows that the electron density is always localized in one of the organic moieties.

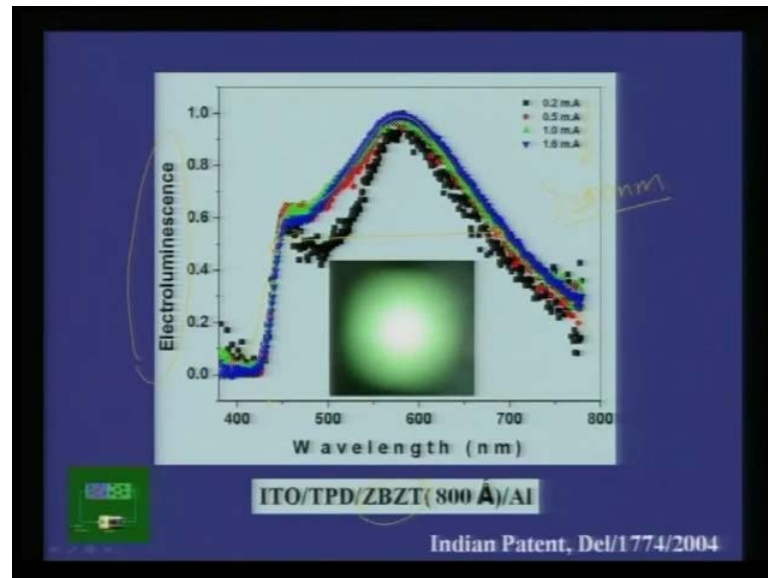
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And if you look at the photo luminescence characteristics of this complex, you can see here this is the PL emission of your BZT, which is binzthiazole. And once it is coordinated to zinc, it is blue shifted and there is a shift in the PL nevertheless the nature or the characteristics of your PL remains nearly the same, which means it is dominated

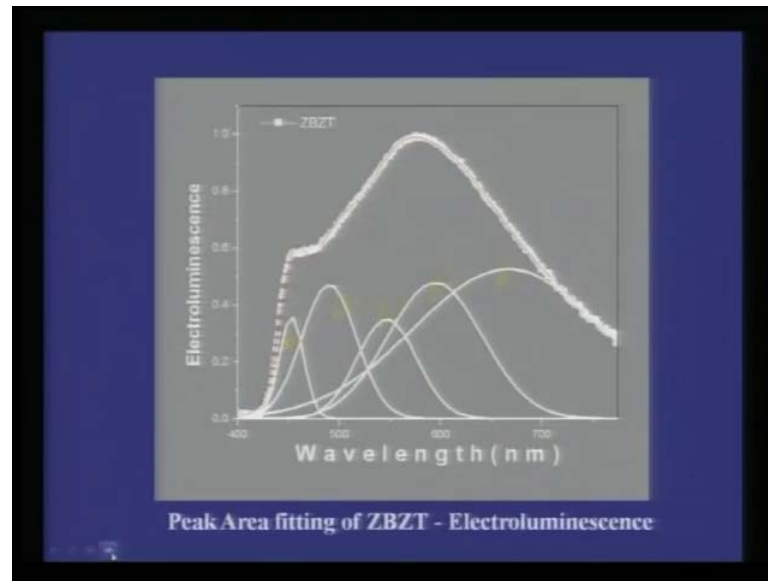
by ligand. Therefore, it is ligand to metal charge transfer which is happening in ZT BZT and this is typically the curve, I want you to retain this in your memory because I am going to show to you how the EL will look like.

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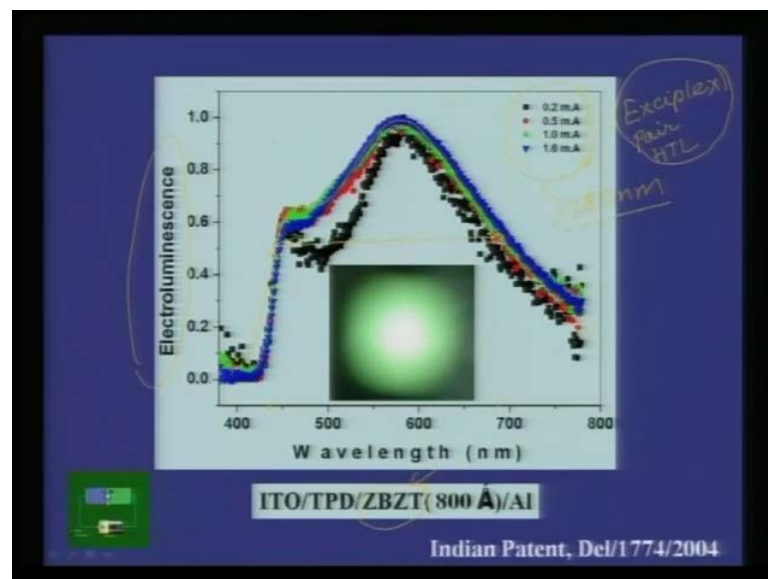
And typically a EL device looks like this, this is the electroluminescent pattern of your LED device, which has zinc benzthiazole here. And typically the thickness of this benzthiazole layer is of the order of the 80 nanometers, and at 80 nanometers despite you vary the current density, you still see a broad emission characteristics. So, if you look at the full width at half maxima you can see, it is more than this is somewhere around 430 and then this is around. So, more than 200 nanometer broadening is there when you use zinc BZT in this device configuration.

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So, where does it come from because I already told you in the previous slide that the PL emission is only of this fashion whereas, in EL it is actually going through that. So, how can we evaluate that if you deconvolute this EL spectra you can see, several you know components that are responsible for this light. And one of the way you can understand this is by varying the current density.

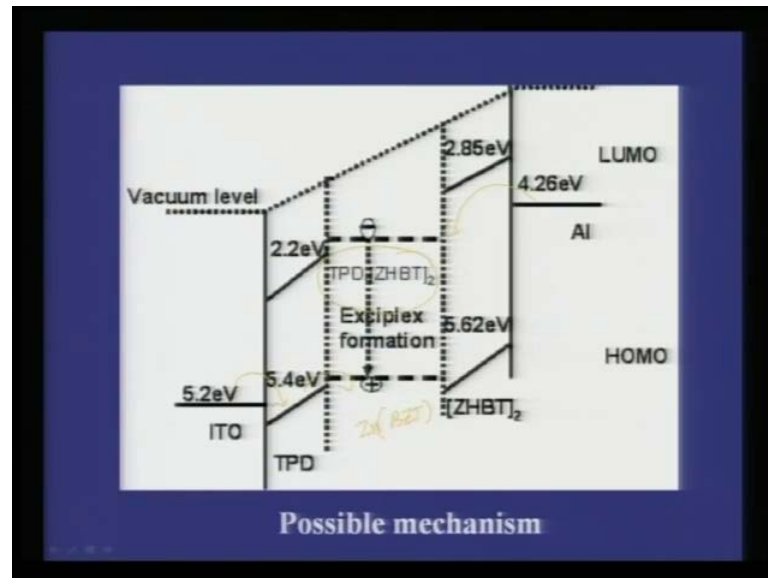
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And with all the current density values, if the EL emission is going to be same, then you call that mechanism as exciplex. So, the white light in this case is not actually coming

from zinc benzthiazole, but zinc benzthiazole can actually form a exciplex pair with your hole transport layer. And that exciplex pair will be responsible to give a white light like this.

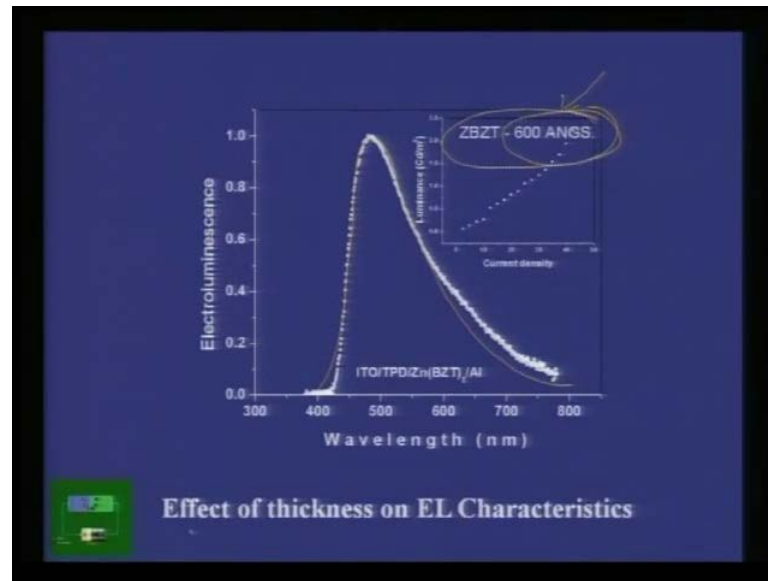
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In the next lecture I will cover those issues, but I can just sum up for today that what is this exciplex that is forming. So, ITO actually electron hole goes from here to TPD, and electro hole comes from here to the interface region that is your ZN BZT, and electron comes from aluminum to this layer. And there is a exciplex pair that is forming here, which is a columbic pair which is responsible for such a white light emission, the mechanism of which we will discuss at a later stage.

However, I should also tell you if I am going to change the ZBZT from 800 angstrom to 600 angstrom, immediately you see that this broad emission is disappearing. And the EL is resembling something of the PL of your ZN BZT therefore, the interface effects are dominant in electroluminescent devices. Therefore, one has to have a ex caution exercise over the thickness of the organic layers that you are making, if you go for thick layers then the interface dominates over the photo luminescent property of the organic molecule. So, this is a classic example to show how the thickness can alter your electroluminescent property.

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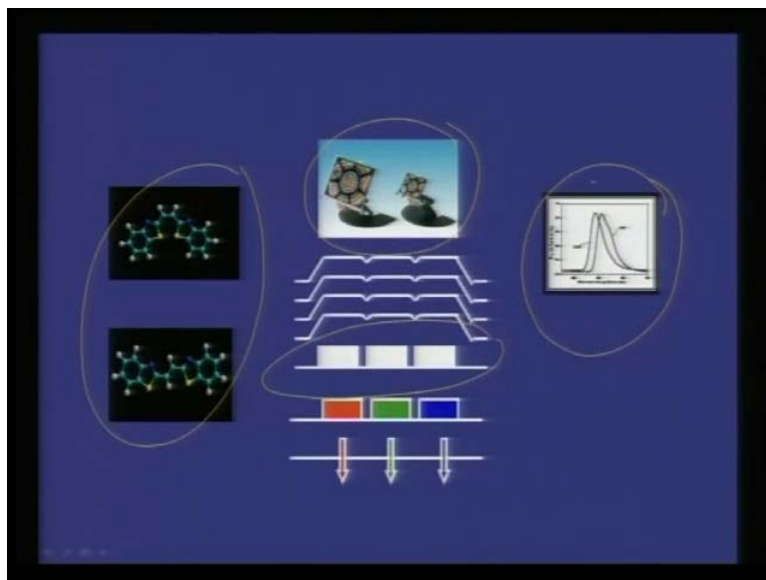


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So, to a conclude I just want to show the pixel that is coming out of this ZN BZT based LED, which clearly shows that you have a white light emission, which is having a coordinates of 0.33, 0.33. So, two examples I have given to you one is a small molecule one is a molecular complex, and both can give you board emission, but the emission that comes from this particular example, will lower the quantum efficiency. While the emission that comes from CIS DBE will contribute more to the quantum efficiency, the issues can be discussed at a later stage.

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So, I will conclude by showing that there is a great excitement in display devices and we are predominately concentrating on white light emission, examples of this white light emission I showed you two examples of a simple organic molecule, which can help you fine tune the color. And also I told you how by controlling thickness of this organic layers one can get white light or modify the light. So, I stop here for now.