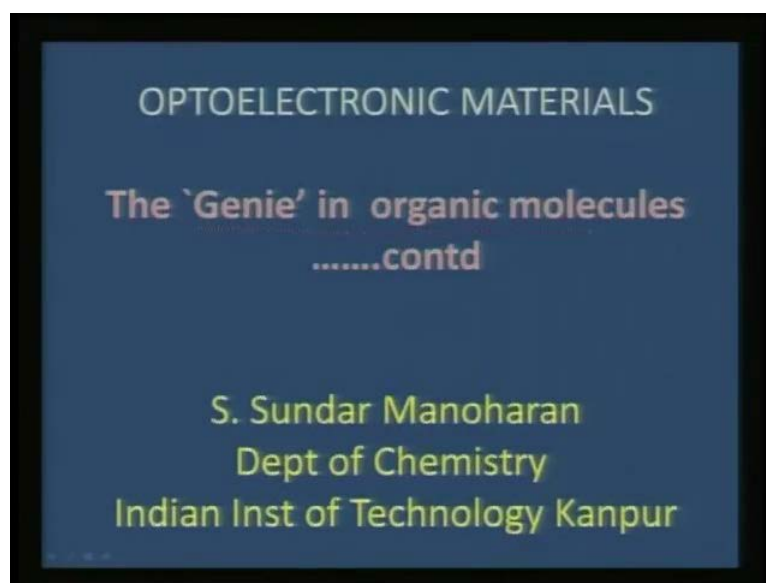


Materials Chemistry
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Module - 6
Lecture - 2
Optoelectronic Materials II – OLEDs

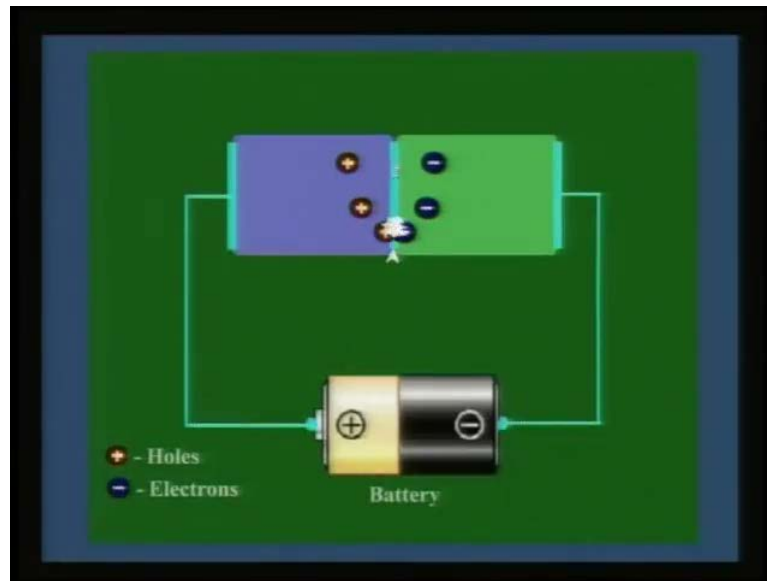
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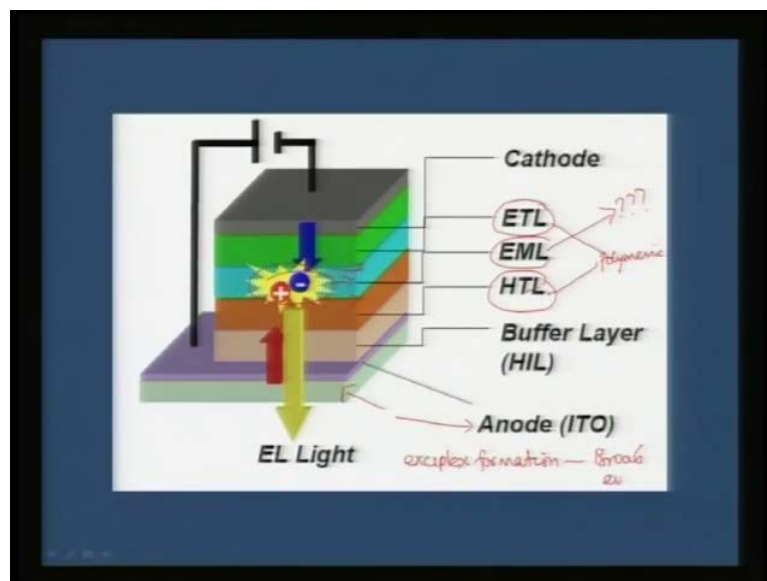
In today's lecture, I am going to continue on Optoelectronic Materials. In the last lecture, we saw about the Genie in organic molecules, the organic molecules have special potential to find applications in organic LED's and this is what we have seen in the last class. And I am going to continue giving some examples of how this organic molecule can be used to fine tune organic LED's and also how this can be used to modulate the displayed device properties. So, in the next few slides, I just want to recap on whatever I have told in the first lecture.

Just to keep in perspective, what we are discussing as I told you, this is a simple demonstration of a diode, where holes come from here and electrons come from the cathode. And when they combine together, they form exciton pair and they release a photon and that photon, when it is in the middle layer, which is an emissive layer, then the photon can excite the organic molecule as a result, we can get the desired light.

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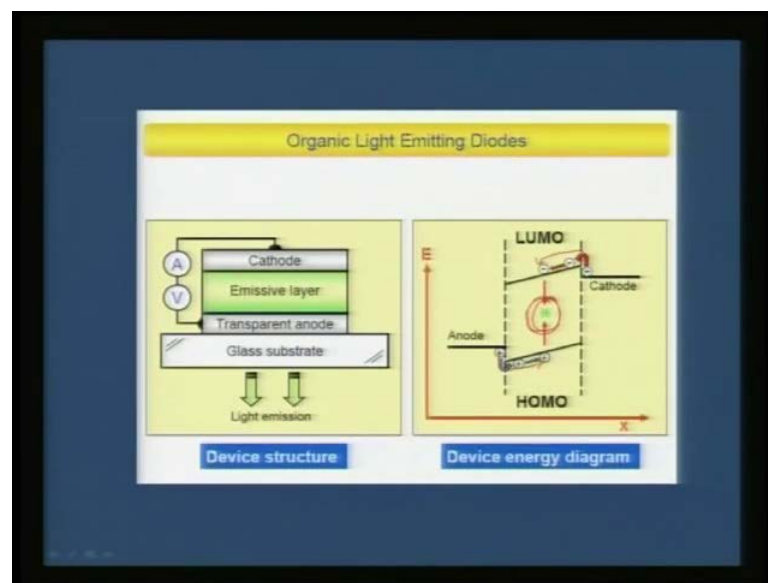
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And also in the last class, in the last lecture, I touched on the basics of a organic L E D where, I told that this is a transparent anode, which is called indium tin oxide, which is a transparent electrode and then you have a buffer layer to help grow a hole transport layer and this is the emissive layer and this is the electron transport layer. Now, hole transport layer and electron transport layers can be polymeric in type or they can also be small organic molecules, but we are actually talking about, the organic molecules here, which are called popularly as emissive layers.

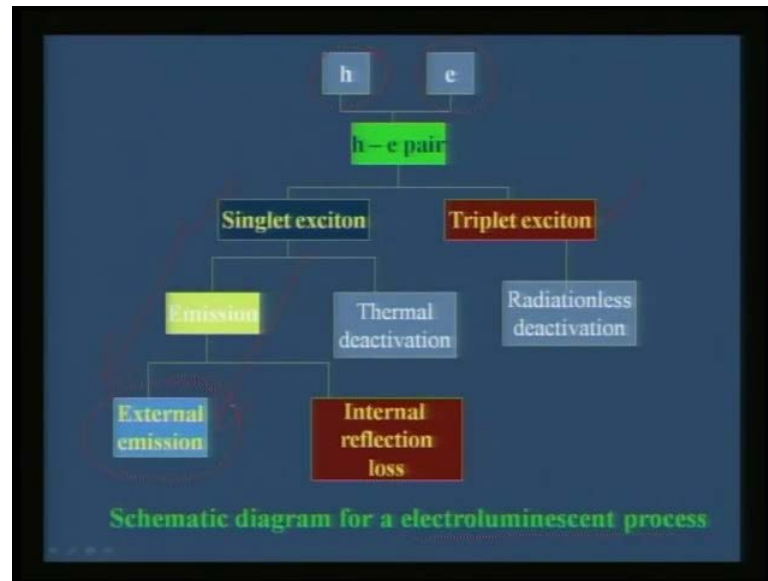
So, at the recombination zone, which is your, which is the emissive layer, if you can bring the number of holes and number of electrons together to recombine at this interface, then you get the desired light, which is due to the emissive layer. So, this is a basic principle of a the organic L E D, there are different issues that, we can understand in the last lecture, I told you how to get white light emission and also I told you, how these interfaces are important. Because of this interfaces, I also showed you another example of, how exciplex formation can lead to broad emission that is white light, I showed you an example, which we will further see today.

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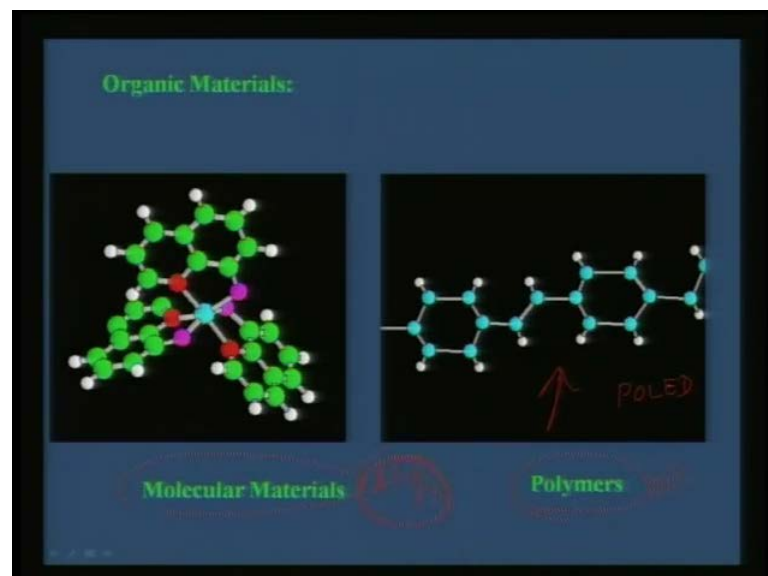
So, what is important here is, how this hole can easily come to the emissive layer and how the electrons can come to the emissive layer and thereby they form the excitonic state, which can release a photon here. So, the number of holes, that you generate the speed with which the holes travel, the number of electrons, you generate and then speed with which you moderate electrons, all are important in order to harvest the desired light at the emissive layer, which forms the fundamental principle for organic light emitting diode.

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I also told you about the mechanism, what exactly happens to electroluminescent process, because you have a hole and a electron combining to form a singlet exciton, it can also form triplet exciton. But, singlet excitons are the ones, which ultimately are going to give the external emission, which we see in terms of light output in the O L E D device therefore, we are more concerned about this protocol, how we can harvest the light from a singlet exciton.

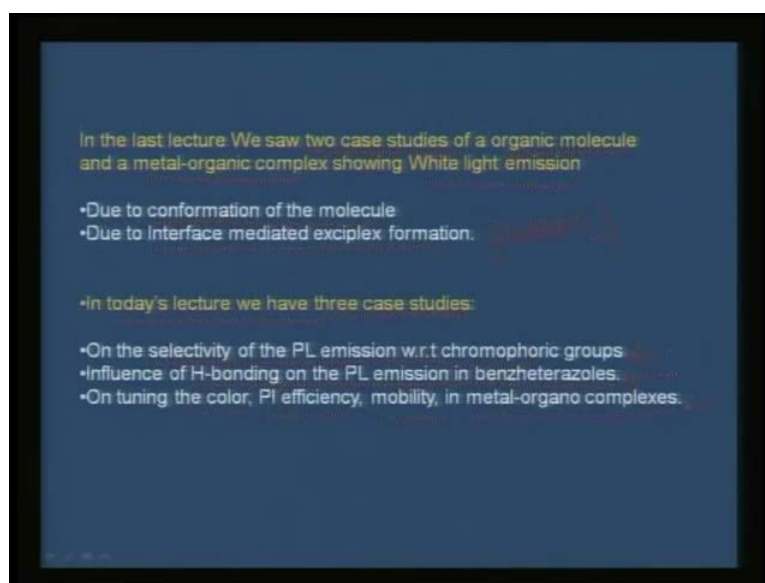
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And also I told you in the last class, there are 2 basic organic class of compounds namely molecular materials, which are based on A I Q 3 or polymers, which hold this display technology. By and large it has been observed that, this molecular materials are more rugged and it can withstand the thermal issues, therefore from thermal stability point of view small molecules have been used, till now for commercial oled devices, whereas polymers are slightly degradable.

They are sensitive to both light and air and other issues, nevertheless there is a great potential with polymer, because you can go for large area display material. So, much of work is actually going into polymeric L E D, which call it as P O L E D polymer L E D. So, we will come to this issue later, but we saw in the last class that, there are 2 class of compounds.

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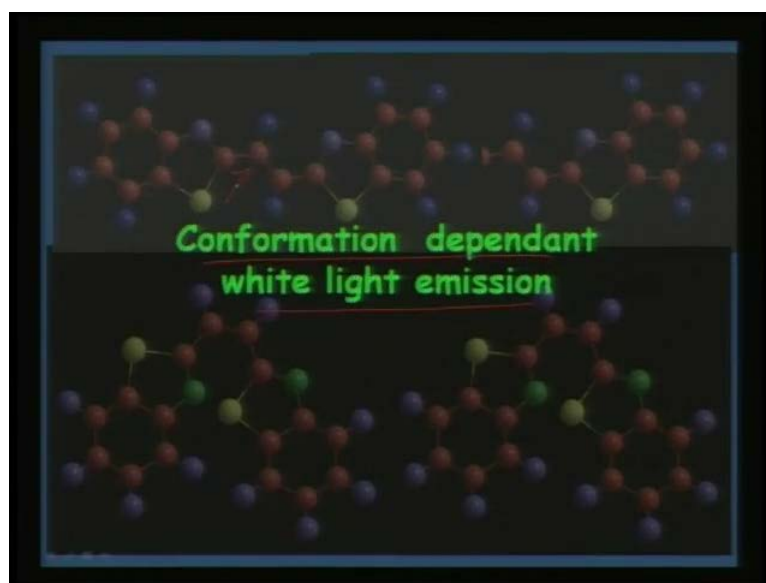
And in the last lecture, we saw 2 case studies, of a organic molecule and a metal organic complex, they show white light emission and I also discussed with you about, why this white light emission is coming. In the case of organic molecule, I showed you that, it is due to confirmation of the molecule, if it is in CIS form, then it shows and I also showed from metal organic complex, that is zinc B Z T complex, I showed, how exciplex mediated white light emission can come.

In today's lecture, I am going to present to you 3 case studies, again showing the potential of what all is buried inside a organic molecule, which can show fundamental

properties and it is very easy for us to moderate the light emission in oled devices. If we understand the solid state properties of this organic molecules, because the organic molecules in solution gives a entire different picture, when you consider against the solid state properties.

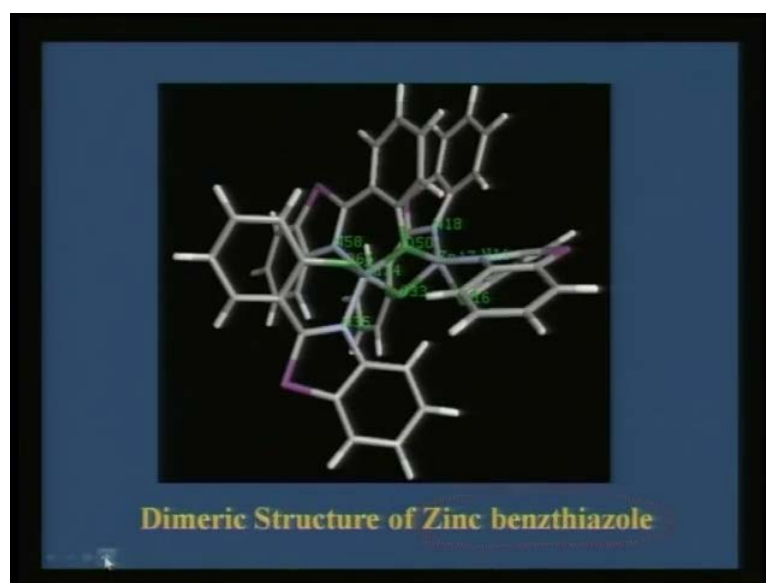
So, once we study the P I emission in solid state, we can get to understand, what sort of device that, we can anticipate from this group of molecules, first I am going to talk to about selectivity of P I emission with different chromophoric groups in the organic molecules, so this is one example. And as a passing thought, I am also going to give a brief example on hydrogen bonding on the P I emission in benzheterazoles, how hydrogen bonding can play, in tuning the P I properties. And on tuning the colour P I efficiency mobility, how we can use metal organic complexes, to vary the p l emission. So, these 3 will be the basis for today's lecture, as I told you in the last class.

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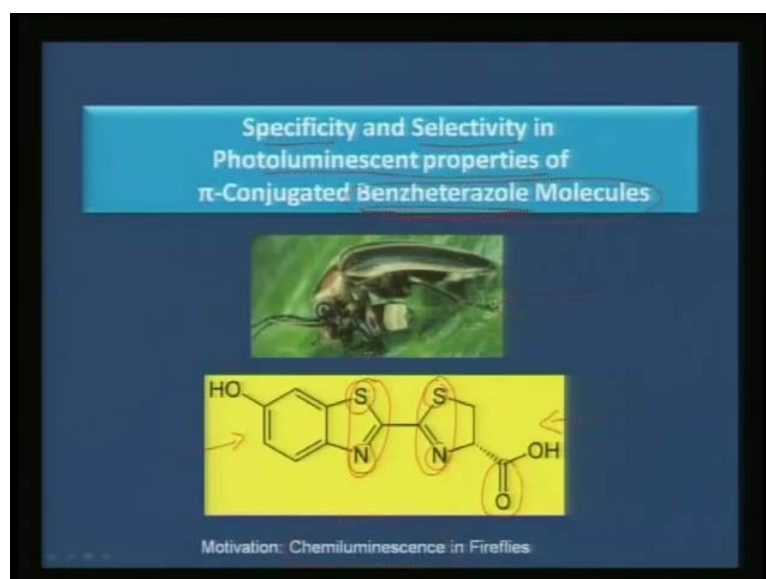
If I have the confirmation dependent white light emission, either if it is a Trans D B or CIS D B molecule, how we can tune the white light emission.

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And in the last lecture, I also showed to you about, zinc benz thiazole, how in when you make a device out of it, how the interface is actually helping in white light emission.

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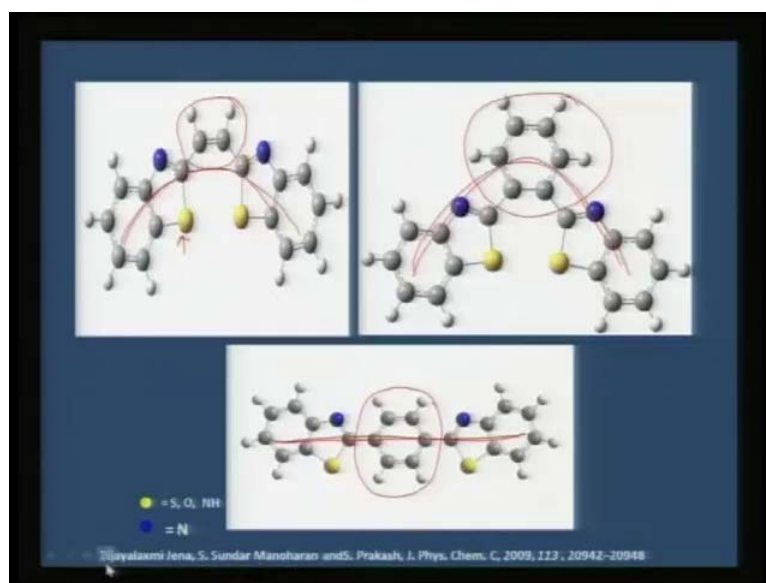
Now, in today's class, I am going to talk to you about specificity and selectivity on the photoluminescent properties of pi conjugated benzheterazole molecules. Why we are laying more emphasis on benzheterazoles, because this is a class of compound, which we all see in everyday life. If you remember this is nothing but the cartoon of a firefly, which we all have seen and specially during winter days or in dark environment, you will

see this firefly glowing and it gives light and then it puts off it gives light and puts off this is nothing but a classic example of chemiluminescence.

When there is chemiluminescence, there is a oxidation reduction process, which is going on, which actually is responsible for this light emission and it this is a enzymatic catalyzed, enzyme catalyzed reaction. So, therefore, the enzyme is called luciferase, because it helps in helping the molecule to glow. So, what is the molecule, that is responsible, it is actually called luminol or luciferase molecule, because in this molecule, the functional groups or the chromophoric groups, that are responsible for strong emission, comes from this benzothiazole moiety.

So, this is important, in fact, it is very difficult to isolate this molecule, therefore one can actually try to prepare several of this benzothiazole based molecules to see and to understand, what is exactly responsible for the fine tuning of colours. So, with this in perspective, we have actually chosen, a range of benzheterazole molecules and tried to understand, what is the role of this functional groups and the chromophoric groups, that are present in the molecules, which will help in fine tuning the light emission. So, to this end, I am going to pick out some molecules and then try to show you by playing around with different combinations, how we can fine tune the colour.

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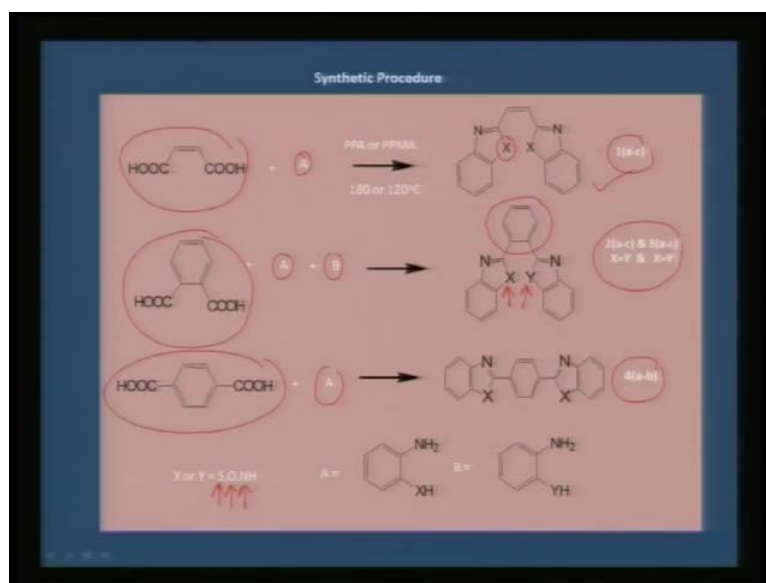


For example, this is a example of 2 benzheterazole molecules, this can be nitrogen and sulphur or nitrogen oxygen of nitrogen, nitrogen. So, you can call this as a

benzoheterazole in general or benzothiazole, if it is sulphur, benzoxazole, if it is oxygen benzimidazole, if it is nitrogen. Now, when you have 2 of this, these are planar molecules and you can try to have a extended pi conjugation by introducing a linked molecule, such as ethylene or you can have a linker molecule, such as phenyl group.

So, either ethylene or phenyl group can be used to provide a extended pi conjugation, so in this case, how does the electron density really moderate and how we can try to control the P I emission, it is in such pi conjugated systems. Another way of looking into it keep both the benzothiazole moieties away from each other not in closer proximity, therefore you can have a linker like this and substitute the benzothiazole in 1 4 position, so electron pathway will be in this direction. So, if it is either this way or this way or this way, how does the electron delocalization in this molecules, which is going to affect the P I emission is what to be studied.

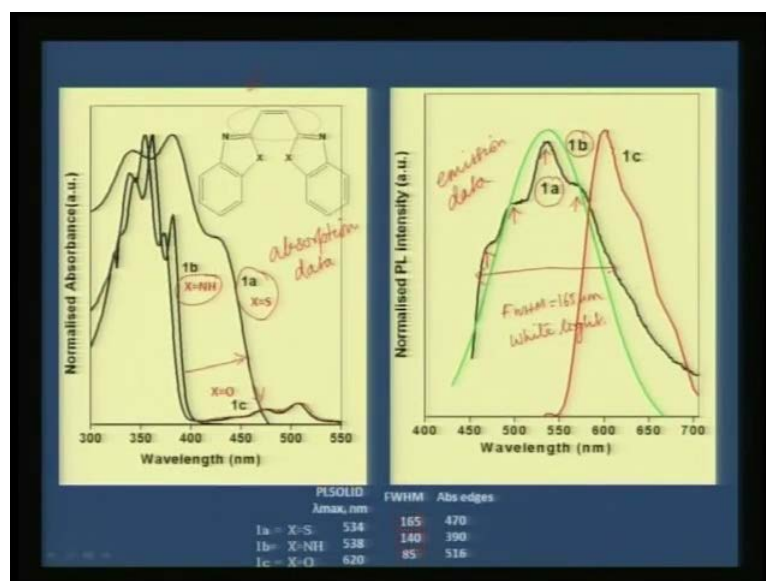
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Now, as a general protocol synthesis of this is very important and if you are really interested to know how we make this sort of molecules, it is very easy, we can try to make mallic acid or we can try to take carboxylic acid with the carbonyl, carboxyl groups in adjacent position or you can actually have the carboxylic group in the paraposition. Now a or you can either add this with a or with a and b or with a now in this case, if it is a for example, you can actually generate 3 series of compounds based on x x can be either sulphur or oxygen or nitrogen.

Therefore, you can call this either as thiazole or oxazole or imidazole, similarly, we can actually try to add here, we can try to put, either one thiazole and one oxazole or one thiazole and one imidazole, therefore you can get a mixed ligand complexes with benzene as a phenyl moiety as your linker or we can actually go for other combinations. Therefore, we are going to generate say 4 sets of molecules and we will try to see generally, what is the nature of the P I emission, to understand how this chromophoric groups are going to alter the issue, for example, let us take the case of the absorption.

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This is the absorption data of 1 a molecule and this is the emission spectra of the one series, now if you see here you can very well understand, that if it is a thiazole based molecule. In thiazole, you see the bandage is shifted by over 70 nanometers, it is more towards the visible region, in case of thiazole species and imidazole is blue shifted here, you can see that, imidazole is having a bandage at 400 nanometer. Now, if you go for oxazole interestingly oxazole has a sharp band edge, somewhere around 400, but then you can see that, it is actually tailing and extending up to 550.

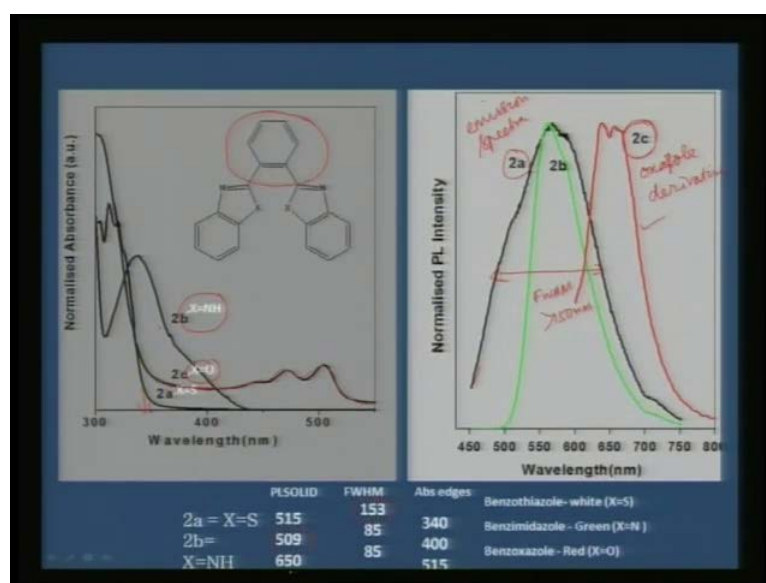
So, oxazoles seemingly have a extended optical band edge, compared to thiazole and imidazole, but distinctly you can see, there is a large shift between the thiazole and oxazole, when compared to thiazole compounds. So, what is this implication on the emission data, if you look at the emission, you can very clearly see, that this one a

molecule, has a fine structure emission structure, which is more resolved and you see several satellite features coming, along with a peak maxima which is coming at 550.

Now, compared to that, if you look at 1 b molecule, which is nothing but your imidazole, imidazole gives a broad emission peak and 1 c compound, which is oxazole is clearly red shifted. So, we can see from here, 1 which is absorbing at the visible region or which has a bandage more towards visible is actually showing a featured emission, in which if you actually look at the full width at half maxima is around 165, so 165 nanometer, which means this is more like a white light emitting molecule.

Whereas, if you look at the imidazole although, it is showing a one peak the full with half maxima is considerably less and oxazole component shows a very narrow emission and it is more preferentially in the red region. So, we can clearly understand, that the thiazole moieties seemingly have a wide spread in the emission feature and it is also showing, fine structures in terms of emission.

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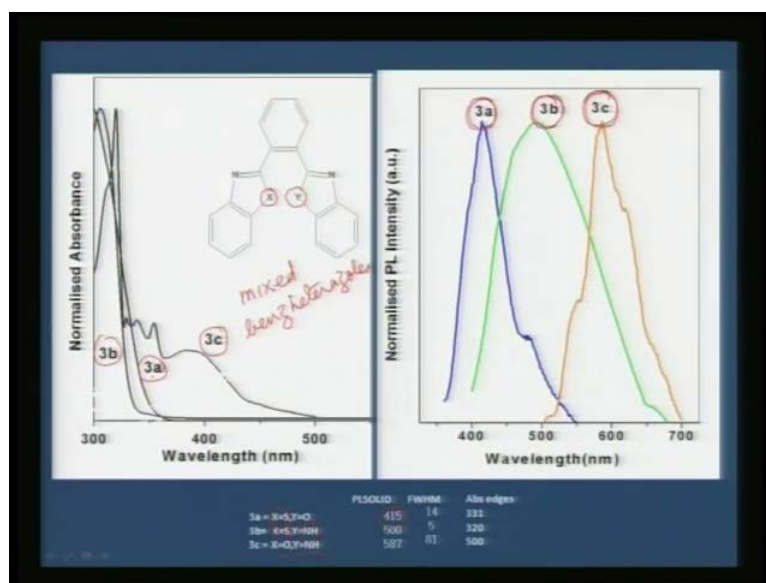
Now we will look at another group of compound, the 2 series where you are actually instead of having a alkyne linker, you are going to have a phenyl linker, if you have a phenyl linker then the situation, now remains the same. As far as oxazole is concerned, you see here oxazole after a sharp bandage here around 330 nanometres, you see that, there is a tailing and this extends up to the entire visible region.

Oxazole seemingly is having its having a bandgap, which is much much lower, as a result, you can again see in the emission feature, that the 2 C molecule, which is nothing but your oxazole derivative. Oxazole derivative again showing a red emission, compared to the thiazole and imidazole case, when you look at the bandage of imidazole, when you have pi electron, you can clearly see that the imidazole is extending pi bandage up to 450 or so while thiazole is actually showing a blue shifted emission, which is reverse of the one series compound.

Nevertheless, you can see here the emission spectra of 2 a molecule, again shows a full width at a half maxima, which is 153 nanometer, which means even the 2 a molecule, that is thiazole molecule shows a white light emission full width at half maxima, which is greater than 150 nanometer. So, what is peculiar in both the cases, 1 series and 2 series, thiazoles are showing a featured emission and it is also showing a near white light emission.

Whereas, if you look at oxazole, whether it is with the phenyl linker or with the alkyne linker, you would see that it is showing a preferred red emission, imidazole on the other hand always shows a green emission, you can see here imidazole always shows a green emission. So, this seems to be characteristic of all the benzheterazoles.

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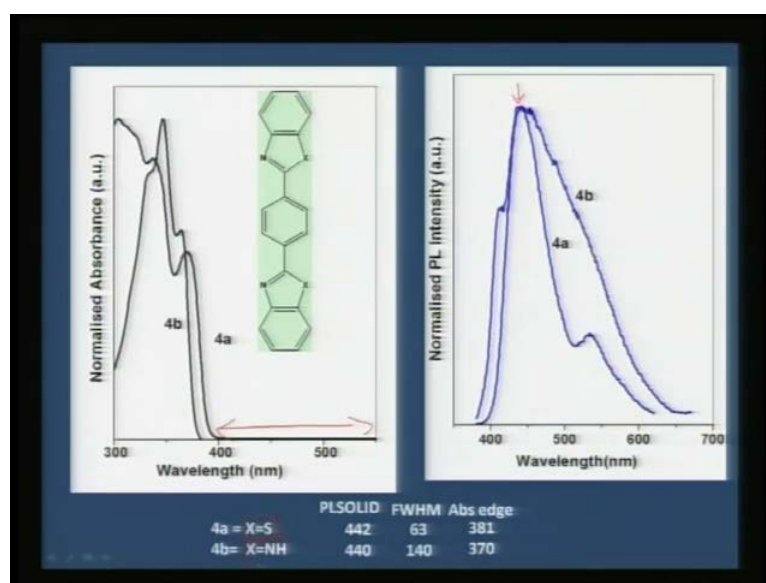


Now, if you go to 3 series where you are going to actually play around with your x in other words this is a mixed benzheterazoles, you would see, the same feature coming for

3 C molecule. Whereas, where 3 C is involving a oxazole and a imidazole ring, you can see that the bend bandage is extending up to 500 nanometer whereas, 3 A and 3 B molecules are predominantly those, which have thiazole and which shows a strong blue shifted emission.

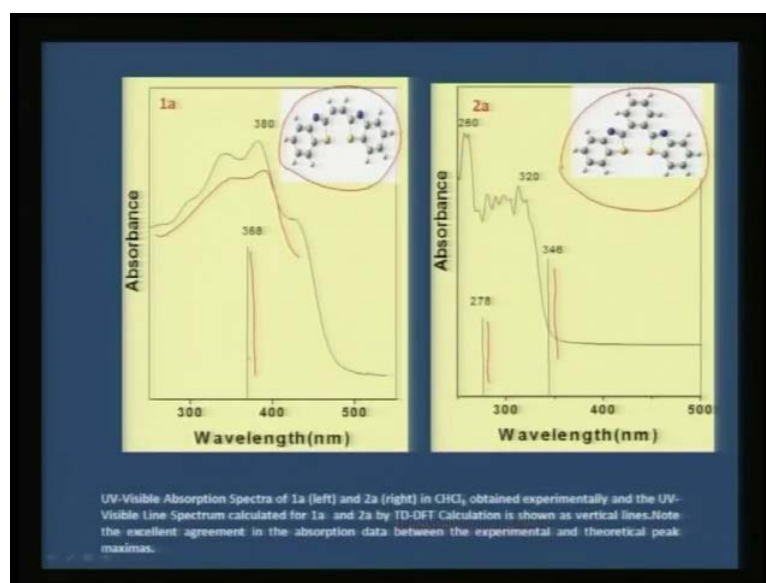
Now, if you look at the 3 C molecule again, wherever oxazole is involved, you see these are red shifted therefore, it is showing a orange colour whereas, if you have the 3 v molecule, which involves imidazole again you see a green emission. And in the case of sulphur and oxygen combination, oxazole and thiazole you see a near u v emission coming somewhere around 410 nanometres or so what is peculiar in this case is when oxazole is present. Oxazole predominantly contributes to red shifted emission whereas, sulphur shows more preference to blue and imidazoles usually show preference to green colour.

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And the same is true, for the 4 series also, if you are going to keep the benzheterazole rings, away from each other, not in closer proximity, then you can see, that there is no tailing of this bandage and there is no tailing here. And you can also see that these have sharp bandages below 400 nanometre and you can also see that the emission spectras are more concerted towards blue region. So, this is quite true of both the thiazole as well as imidazole moieties.

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If you look at the absorption spectra, you can actually do a density functional calculation DFT calculation and if you try to generate the UV-Visible spectra, to see whether this is matching with the experimental data. One would find, that there is an excellent agreement of the theoretical prediction of this UV-Visible spectra with the experimental value. This is the experimental curve and what you see here is a one-line spectrum and here, you see a two-line spectrum, exactly resembling that of the experimental data.

Why we do not see all these featured emissions, because when we are calculating the UV-Visible spectra, you are actually considering only one molecule whereas, in the experiments, you actually consider 100 of molecules together. So, when you have hundreds of molecules in solid state, when they are packed together, then you would see a featured emission whereas, when you do a calculation for a single molecule, you see the most predominant emission, which is mentioned. So, we can say that, the theoretical analysis goes well with the experimental data, therefore whatever structure that we are predicting, due to optimization of this geometry is nearly the same, as that of what we observe in the experiments.

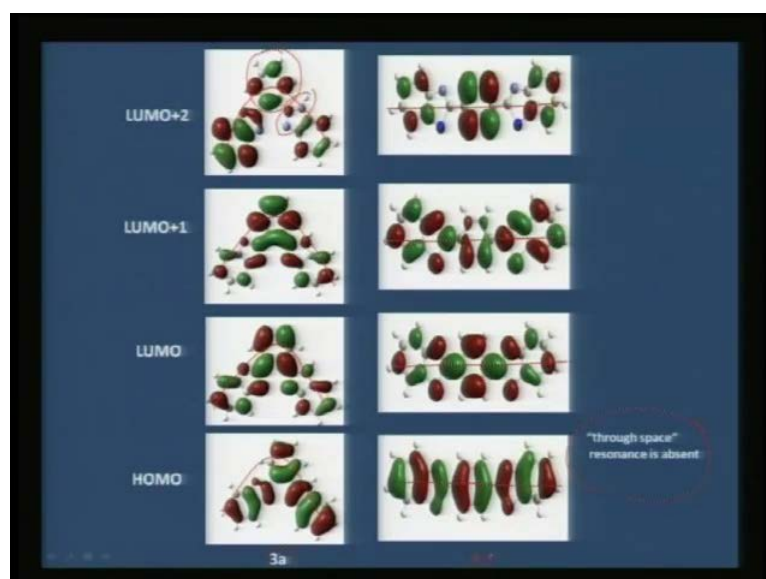
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Selected Calculated Excitation Energies(E), Wavelength(λ) and Oscillatory Strength (f) for low lying Singlet(S_n) States for 1a and 2a compound

Molecule	Excited States	Molecular Orbital / ΔE (eV)	f	λ (nm) (Cal, Exp)
1a	S5	LUMO-HOMO / 3.36	0.9814	(368, 382)
2a	S5	LUMO-HOMO / 3.57	0.6282	(346, 320)
	S19	LUMO-HOMO-1 / 4.44 LUMO+1-HOMO	0.3721	(278, 260)

And these are some of the energies and the oscillator strength of these molecules, which are calculated specifically, we have studied 1 a and 2 a compounds, because we would like to see whether, we can make some correlation and try to understand. Why 1 a and 2 a molecules among the series of compounds, that we are studying are standing out and why they have specifically a white emitting properties, that is the whole notion and these are some of the data's, that one can arrive at by doing the calculations.

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Now, just to give a visual picture of what this calculations mean, if you look at the frontier molecular orbital and if we use this b3lyp program, which with this subset, if you have this bases set. Then this is the sort of charge resonance picture that evolves, when you consider 1 a molecule remember, 1 a molecule is nothing but 2 benzothiazole groups coupled by ethylene linker and 2 a molecule is nothing but 2 benzothiazole groups, coupled by a phenyl linker.

So, this is what we mean and if you look at the frontier molecular orbitals, you can see in the case of HOMO, that is highest occupied molecular orbital, the charge resonance is spread around the ring and this also involves the alkyne moiety, ethylene moiety. And if you look at the lowest unoccupied molecular orbital, again you see in the excited state, the charge resonance is spread along the ring and even so in the case of LUMO.

And if you look at one of the higher excited states lumo plus 2, you would see, the charge resonance is now confined more to the benzothiazole rings and also you would see, the charge resonance is actually mediating across the sulphur bonds or sulphur atoms. Why, because sulphur atoms are much bigger and they carry lone pair of electrons therefore, the charge resonance is not only through the bond, but also through the space.

So, you have a through space resonance, in the case of sulphur atoms, which is peculiarly absent in the case of imidazole or oxazole you would not see the same picture, if you look at oxazole or imidazole compounds. Now, this is not only true in the case where you have sulphur sulphur in adjacent positions, in SIS positions with a ethylene linker, suppose you try to push it away by introducing a phenyl linker.

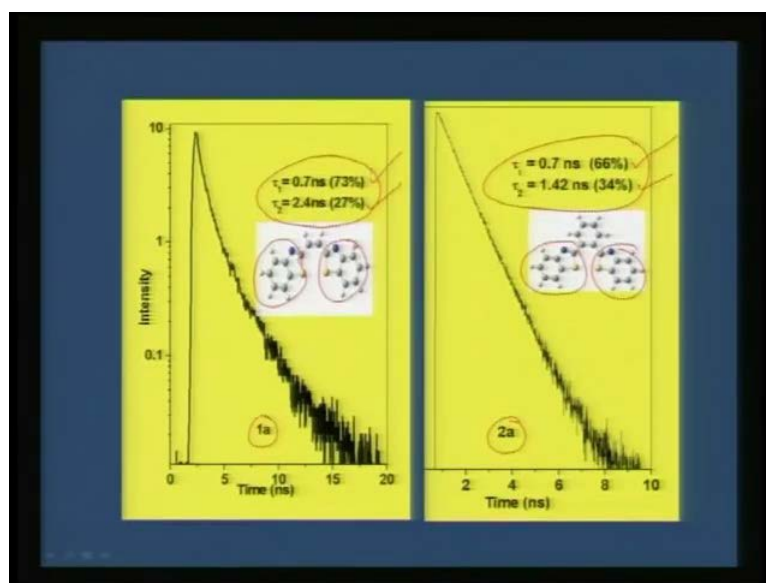
Then even in terms of phenyl linker, you would see here, the charge resonance is through the bond across the linker molecule and it is the same as in the case of 1 a compound and when you come here to LUMO plus 2. Again, you see that in this case the charge is confined more to the benzothiazole rings and also you would see that the charge resonance is across the sulphur atoms. Therefore, the bigger the atom and more the charge density in other words, because of the availability of the lone pair of electrons, now you have the charge resonance is spread through the space.

So, when you have a through space and through bond resonance, then you would see a very different emission phenomena happening, because there is more of charge

delocalization as a result, you would have a broad emission coming into picture. So, the broad emission that, we talk about, broad emission is mainly due to the through space and through bond resonance, that is typical of only sulphur compound, compared to imidazole and oxazole.

Now, if you take 3 a compound as I told you 3 a compound is not having thiazole ring, in one case, it is actually imidazole and in one case, it is actually thiazole ring, if you have such a combination, you would see that, there is through bond resonance here and also here. But, this resonance is actually sorry, its localized and it is not spread throughout the ring and same is the case for a 4 a molecule also, you can see that charge resonance is across the ring and it is across the ring here and there is no through space resonance. Therefore, through space resonance is absent in the case of 3 a and 4 a molecule and as a result.

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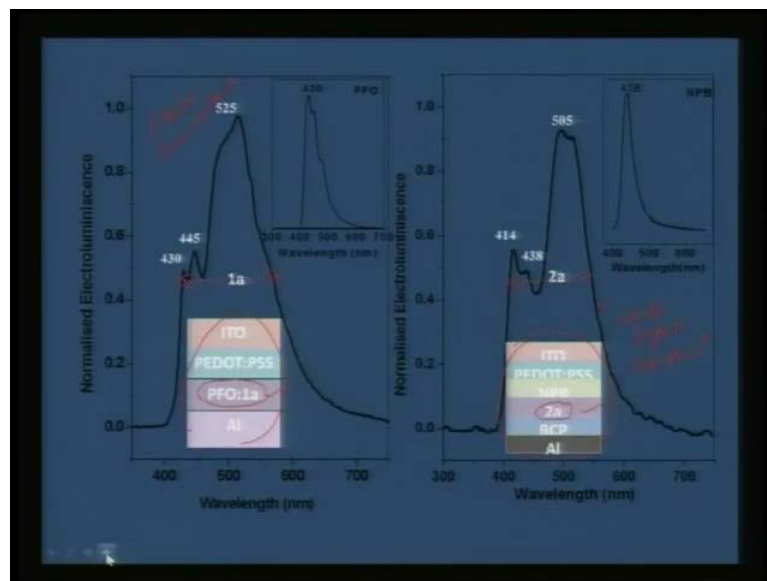
We can sort of make a general conclusion, that the featured emission for thiazoles is mainly, because of a extended charge resonance, which is spread throughout the ring, which brings down the HOMO LUMO gap. And because the HOMO LUMO gap is smaller the emission is now involving, the blue green and red region as a result your full width at a half maxima is always above 150 nanometres.

So, these sulphur based molecules or thiazole based molecules can act as potential ligands, for a extended charge localization as a result, they are good candidates for white

light emission compared to imidazole and oxazole compounds. We can get some more clues, when you look at the 1 a and 2 a compound, what is different here is only the linker, that is the ethylene linker or the phenyl linker. You would see the time decay curves, if you look at the time decay curves and you fit it to a double exponential decay model.

Then you would see both has a same component, that is 0.7 nanosecond time decay, which mainly comes from the thiazole molecules, which we can conclude, because both have a common tau 1 value and the tau 2 seems to be coming from the linker. In this case, it is 0.142 seconds, it is comparatively faster for a aromatic linker, compared to ethylene linker. So, we can have a guess as to what is the molecule or what is the functional group or the chromophoric group, that is responsible for this time decay, the fast decay components seems to be coming from the benzothiazole as compared to the linker groups.

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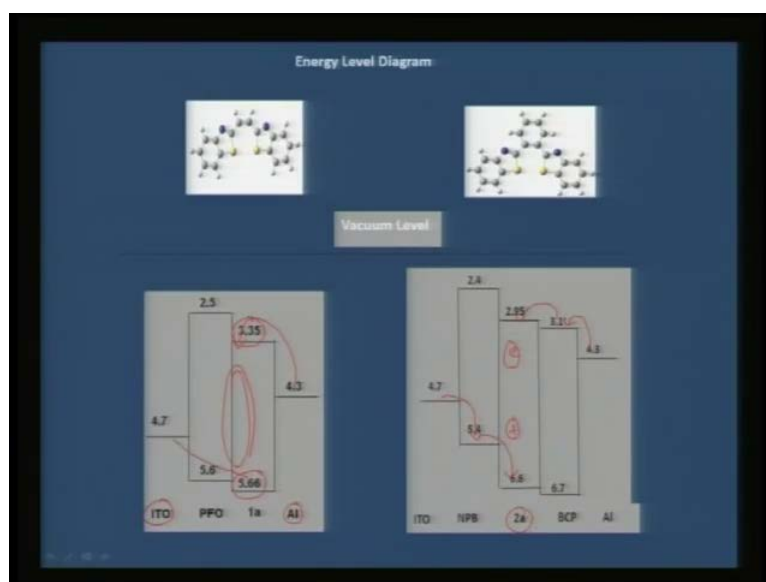


And we can also extend this case, now to make devices for example, we have made 2 devices using, 1 a compound and 2 a compound, because of all the compounds, I have told you, that only these 2 compounds seemingly view white light emission. As a result, we can try to make emissive layer, either depositing exclusive 2 a compound layer or we can mix it with P F O as a matters, if you are unable to effectively deposit this in a thin

film situation. Now, whatever be the case whether it is spin coated with the P F O 1 a composite or whether it is vacuum sublimated, thermal evaporated layer.

One would see, whatever be the device configuration, you can see almost a similar feature is seen in the electroluminescence, this is the electroluminescence data. And one could see that, the full width at half maxima is nearly one is nearly 150 nanometres as a result in both cases you would see, there is a white light emission coming out of these devices. So, conceptually we can make some logical conclusion or summary to say that benzothiazole molecules preferentially show white light emission.

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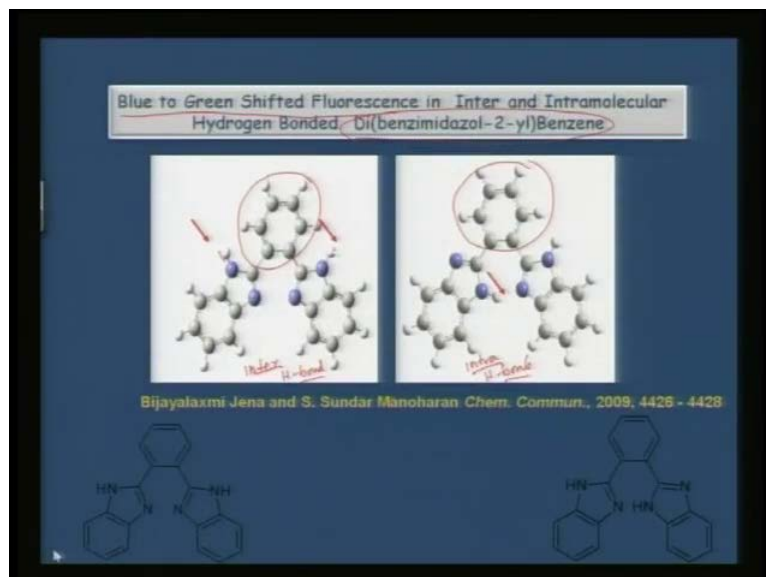


And the devices that, we have made has this sort of an energy level picture, which really falls well, because your HOMO LUMO level has to be compatible to I T O and to the cathode and which exactly happens therefore, the holes are injected this way and electrons are injected this way, therefore the combination exactly appears at this interface. And similarly, in the case of 2 a compound, you can see that the holes can come easily and then electrons can go this way therefore, the electron hole pair can actually have the fusion occurring here.

And therefore, you can get the white light emission, so as your choosing a molecule one should also know, that the HOMO level and the LUMO level should be comparable to the adjacent layers, otherwise you would not get the right set of devices. And

incidentally in the case of 1 a and 2 a compound, we have a excellent match where the device falls in picture and as a result we can harvest a white light emission.

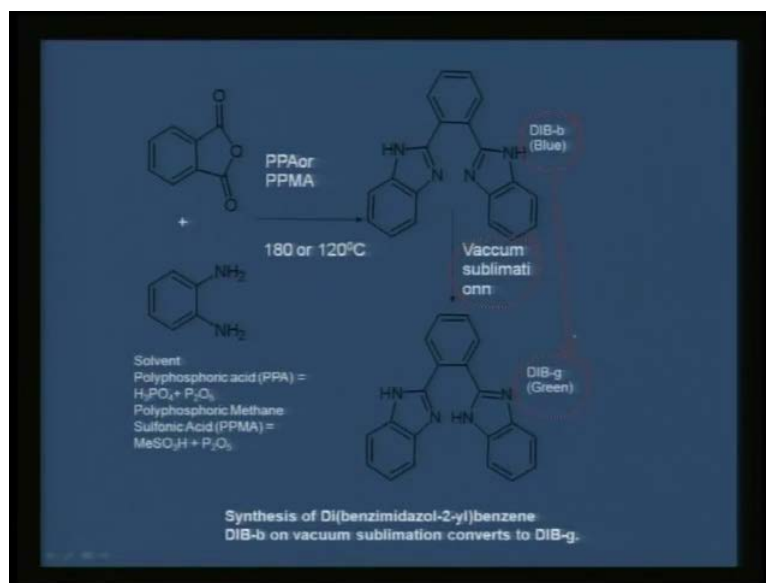
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Now, as a passing thought, I would like to sort of give another small idea about, what really happens, if hydrogen bond exists in this sort of molecules, take the case of same phenyl linker, but in this case not benzothiazole, we are actually having imidazole moieties. So, this is imidazole moiety, now this imidazole can actually have the N H groups facing outward or the N H group 1 N H group facing inward.

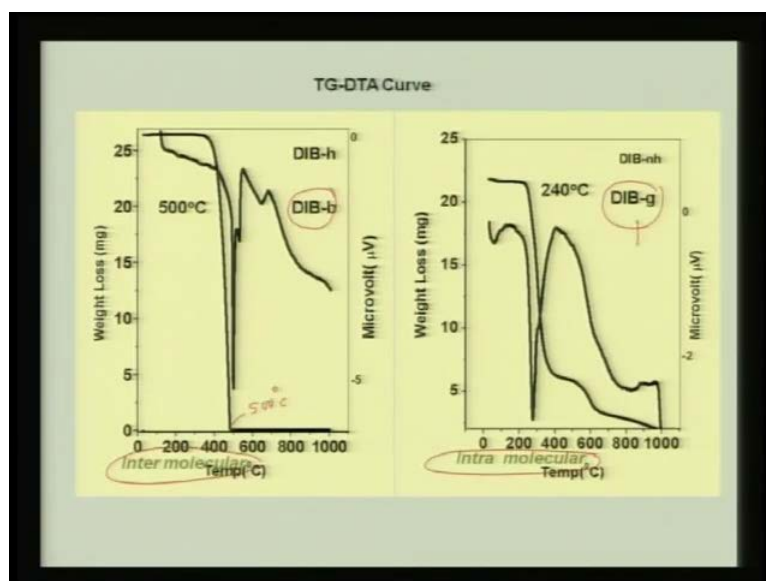
So, depending on that, I can either talk about the possibility of a inter molecular hydrogen bonding or I can talk about intramolecular hydrogen bonding, both are possible. In such cases, you can actually expect different sort of P l properties and that is exactly what happens, there is a blue to green shifted fluorescence, when you have a inter or a intramolecular hydrogen bonding and I will show you as a quick representation.

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How this happens, now if you take the synthesis part as you synthesize this molecule one would actually come end up with D I B, that is dibenzimidazolyl benzene and this compound, we mark it B, because it gives blue colour. Now, if this blue colour compound, if you try to vacuum sublimate, what happens on vacuum sublimation, you get a compound, which is actually showing green in colour. So, this is a simple sublimation process, but during sublimation a blue colour compound goes to a green colour compound, which is of interest to us and we can try to see what really happens.

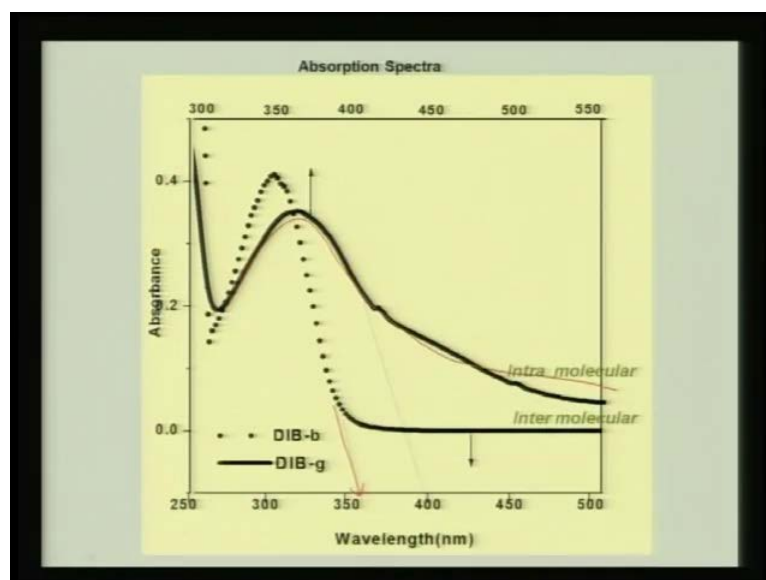
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Now, you can take these blue colour compounds, which we call it as D I B b and you can take this green colour compound, if you look at the thermal analysis, you can clearly see the one, which is having inter molecular hydrogen bonding. Suddenly collapses and then the molecule undergoes a 100 percent weight loss and this happens somewhere around 500 degree C, when you have intermolecular hydrogen bonding whereas, in the intramolecular hydrogen bonding, which is the case of the green emitting molecule.

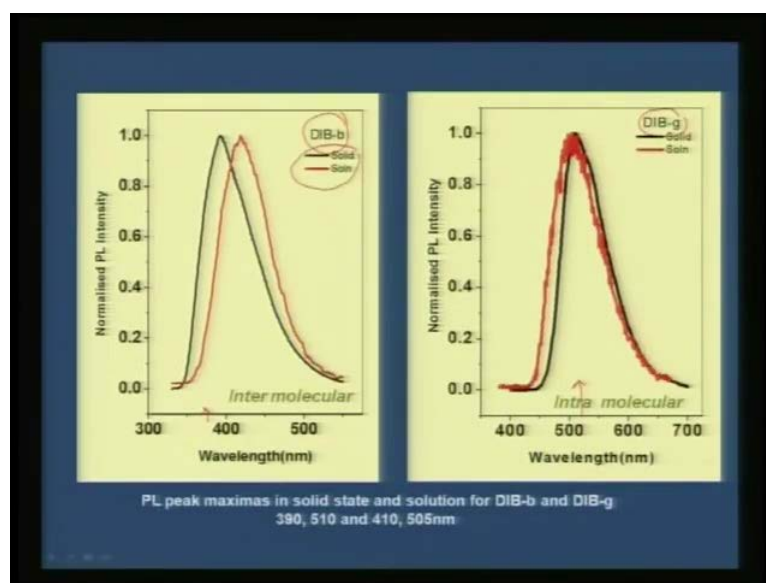
You can see that, there is a sharp fall around 400, but then it extends down up to 1000 degree, which means, the intramolecular hydrogen bonded compound is more thermally stable compared to intermolecular hydrogen bonded compound. And because of this hydrogen bonding network the solid state property of these 2 compounds will vary.

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As a result, you would see what happens to the absorption spectra, the intramolecular hydrogen bonded 1, absorbs up to 450 or so whereas, the intermolecular hydrogen bonded shows a very sharp optical bandage and that is narrow at 350 nanometres. And because of this reason, you would also see that the emission spectra is very clearly different.

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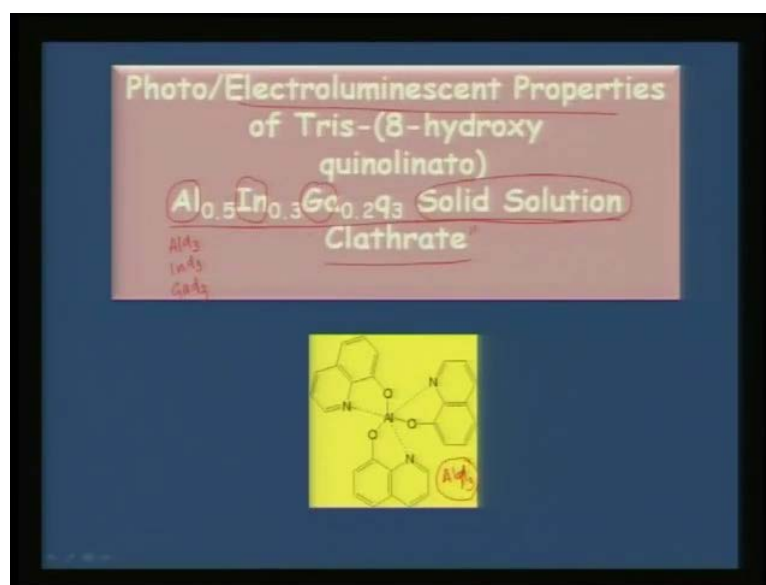


And what is the difference here, you can see here, the blue emitting molecule is showing your emission spectra, somewhere around 380 nanometres, whereas, in the case of green emitting molecule, the emission spectra is somewhere around 520 nanometres. And if you compare the solid and the solution spectra, emission spectra of the intermolecular hydrogen bonded molecule, you can see that, there is a collapse of this intermolecular hydrogen bonding, once you put it in solution as a result, there is a red shifted emission.

In solution compared to blue emission in the solid state whereas, there is no such feature present in the case of intramolecular the solvation does not seem to affect. So, this is a classic example to show that, hydrogen bonding controls the P I emission, even if it is a small molecule, you can have a precise fine tuning of colour, if you can hold the hydrogen bonding, which will decide the a P I emission.

So, we have seen 2 case studies in one case, I have shown you a spectrum of molecules and I have tried to impress upon you, how the sulphur based compounds lead preferentially to white light emission. And I have shown you, some examples including devices as to why they show white light emission and also, I have shown you in the second case, how hydrogen bonding can affect the P I property.

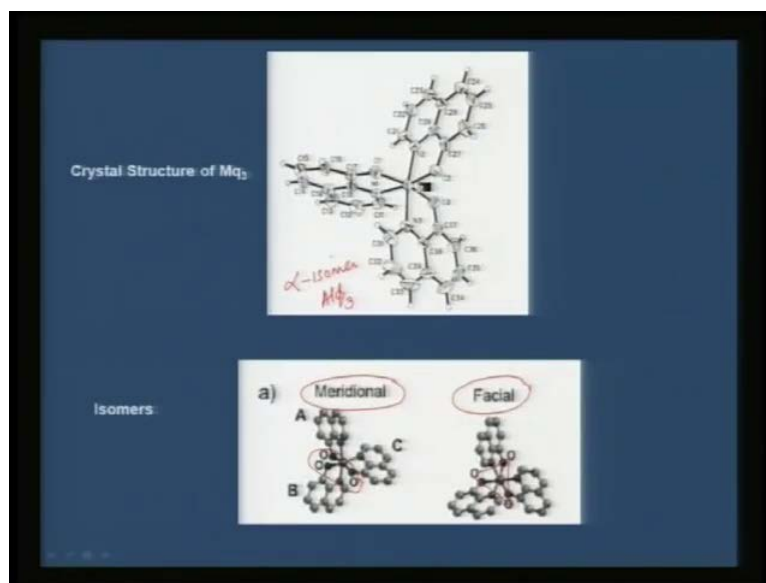
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In the third case that, I want to present today, before I close is the photo and electroluminescent properties of a quinoline complex and this is called as a solid solution clathrate. I want to share with you here the excitement, because all of us know that, this is the most famous molecule called Alq₃ molecule, which has 3 quinoline units bonded to this, it forms octahedral complex. And this Alq₃ molecule is one of the well known emissive layer in organic LED, because it is also used in today's display devices including those display in digital cameras.

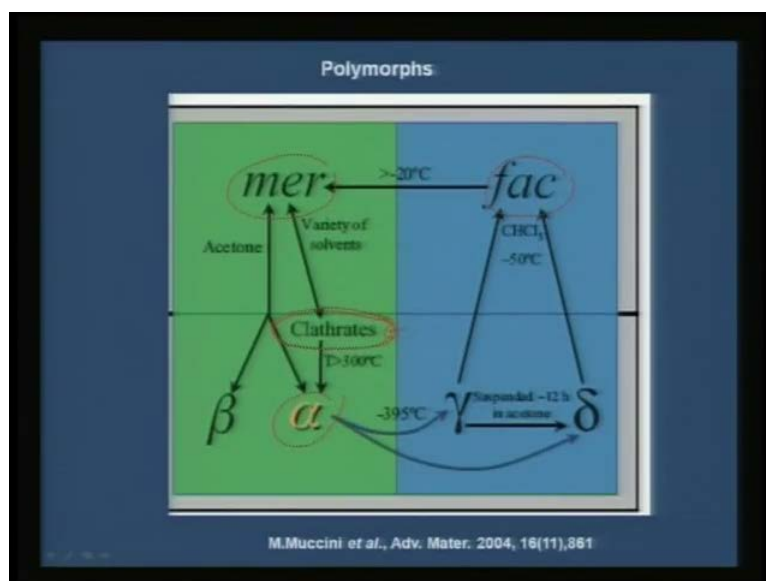
Now, Alq₃ cannot just be the only molecule, we need to look for newer molecules for new properties. So, therefore, what will happen suppose, I take aluminium indium gallium these are in the same group, therefore if I form Alq₃ indium q₃ gallium q₃ is it possible for me to make 1 complex, having 3 metal ions in the same complex. And this is possible only if there are some number of molecules in a single unit cell, then you can distribute atomically all these 3 atoms and in that case, you can get all 3 atoms in 1 molecule, which we call it as solid solution. And this is possible, because there is one polymer, which is called as a clathrate, clathrate is a caged structure or it is a larger molecule with stackings and I will show you some of the features of it.

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This is a typical crystal structure of a alpha isomer of A 1 q 3 and even in A 1 q 3, there are different polymers and this is typically the x ray crystal structure of a A 1 q 3 alpha isomer. And the A 1 q 3 can either be in meridional form or facial form meridional isomer has a structure a core structure, which has 2 oxygen's in close proximity against 1 away from this 2 oxygen's or this 3 oxygen's can be equidistant ok. So, based on the way this oxygen's are arranged, either you can categorize this as facial isomer or meridional isomer.

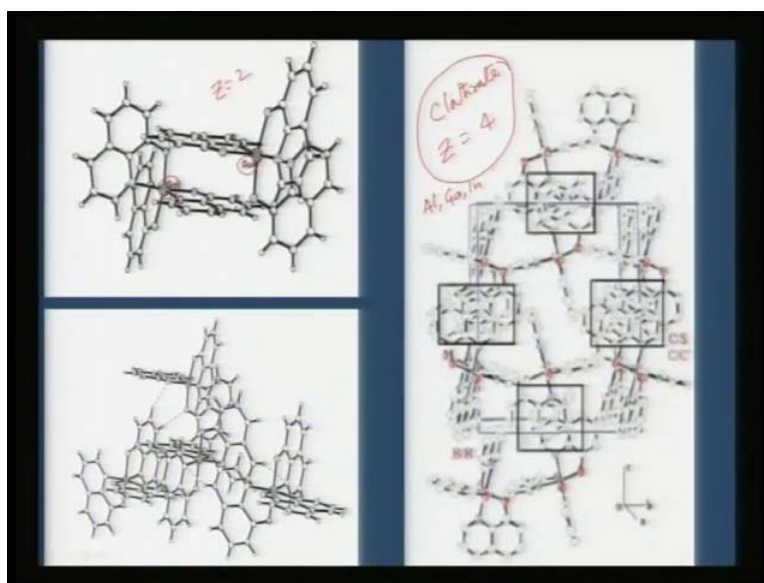
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But, there is also one other phase, which is called as clathrate and this clathrate phase is a low temperature phase, if you try to heat this clathrate actually if you sublime then you come across the alpha form or these are all categorized as meridional forms and there is another form called facial form. So, there can be inter conversion from meridional to facial or you can sublime or you can suspend in acetone and you can realize either alpha gamma or delta form.

And you also have this crucial polymer, which is called clathrate, which is actually made out of $Al\ 1\ q\ 3$ complex stacked with several of the solvent molecules therefore, this has a bigger crystal structure compared to the alpha isomers or the mer or facial isomer. So, we can actually try to look at the clathrate form and see, if you can make all 3 atoms in a single molecule.

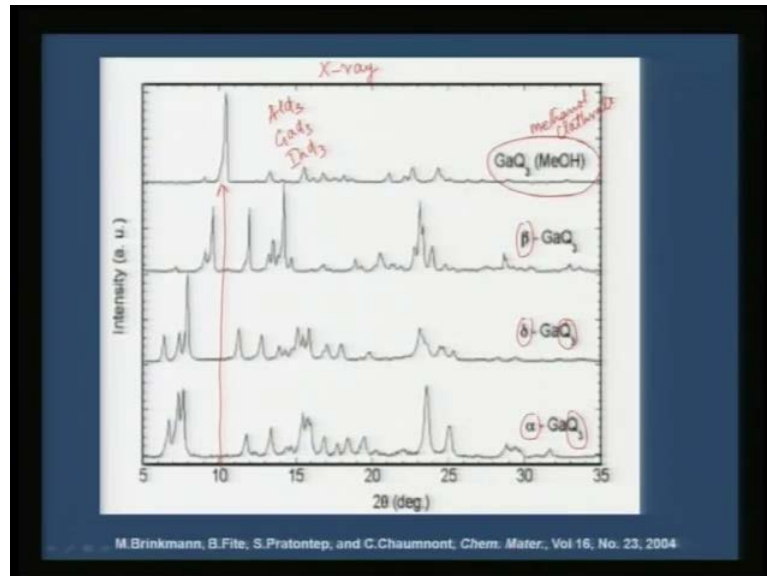
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So, if you look at the alpha form, here z is equal to 2, so suppose you have gallium $q\ 3$, you can see 2 gallium atom sitting in this picture and this is the situation for a clathrate. You can see, there are 4 molecules of clathrate sitting in a cage structure and this is by and large a bigger 1, therefore there is a possibility, if in a single unit cell, it is possible to put aluminium gallium and indium together in atomic level precision and how can we diagnose that, if you take the x ray diffraction peak. The alpha isomer typically, looks like this the delta isomer and the beta isomer, they all have a characteristic pattern, but

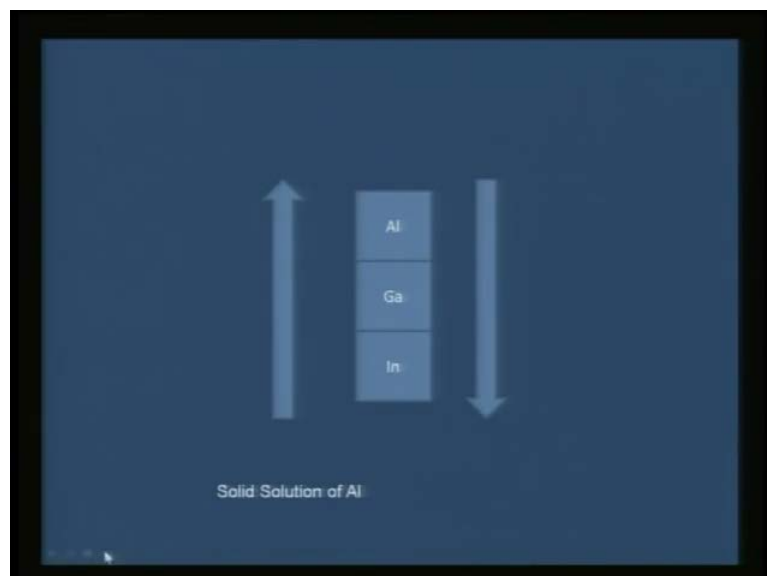
essentially they all have only 3 quinoline moieties, but the way the solid state packing goes, they all differ from each other.

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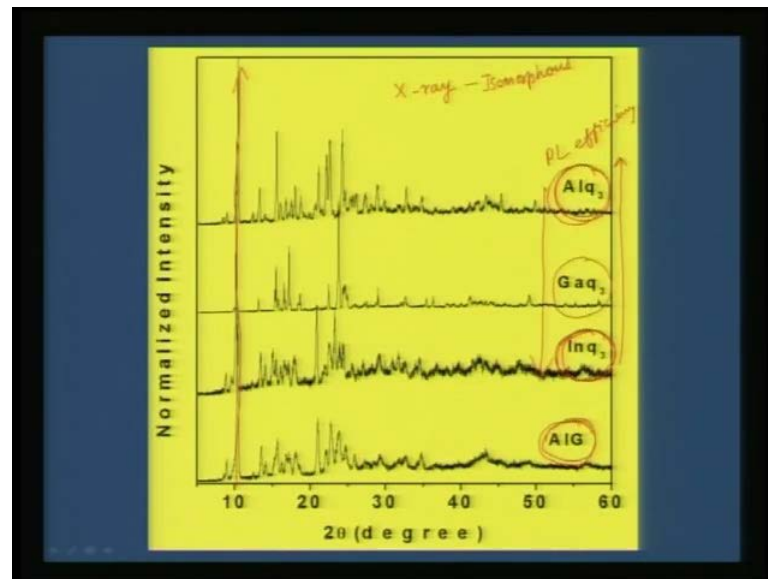
Therefore, they are called as different polymers, but if you look at the clathrate, this is called methanol clathrate. The methanol clathrates have rather a very simple x ray pattern, which has a 100 percent peak somewhere around 10. Now, if you have a 10 degree peak, then you can carefully try to look at A 1 q 3 clathrate, gallium q 3 clathrate, indium q 3 clathrate and try to see whether, they all have the same x ray peak.

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And therefore, we can try to look at what is the order of this solid solutions.

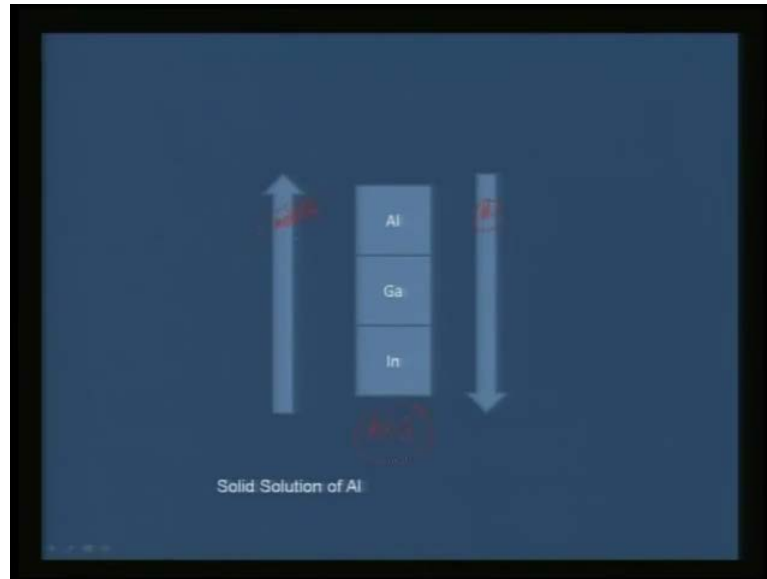
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I will show you the x ray peak, the x ray diffraction data of Alq₃, gallium q₃, indium q₃ and the solid solution, if you see here all these peaks have, a common 100 percent peak at 10 degree, which means principally, they are all x ray isomorphous. And because they are x ray isomorphous, it is possible to have all the 3 atoms together in same molecule, why we are looking at it.

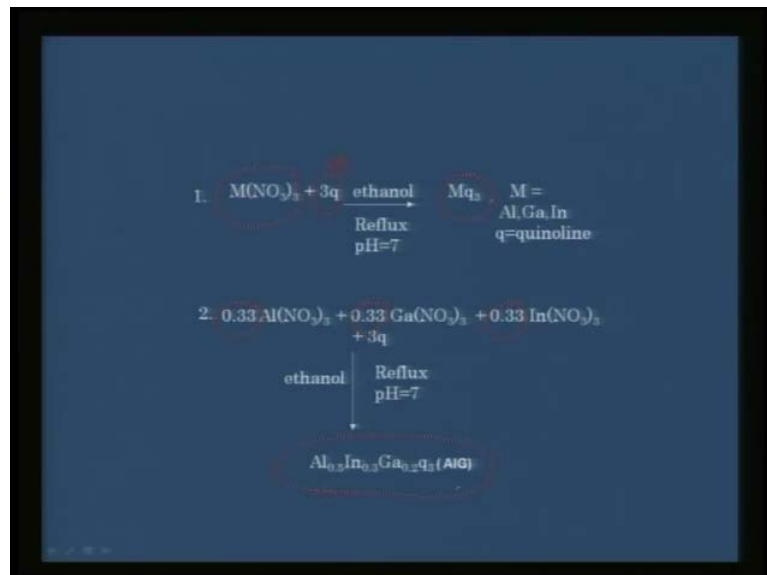
If you look at the aluminium q₃, this has more P l efficiency, compared to indium q₃, because as you go down the series the P l efficiency goes down. Whereas, if you look at the mobility as you go up the series the mobility decreases in other words mobility of the charge carrier is much better in indium q₃ whereas the P l efficiency is low. Whereas, in this case P l efficiency is much better in aluminium whereas, the charge mobility is comparatively less, because of the ionic size and because of the electro positive character, so as result now we need to look at 2 things.

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One P I efficiency goes down, as you go down the group and the ionic mobility of the charged carriers goes down as you go up the series. So, you need a compromise, as a result one can go for a solid solution, which will have both P I and mobility values in a compromising ratio and for this reason, we can try to prepare these complexes.

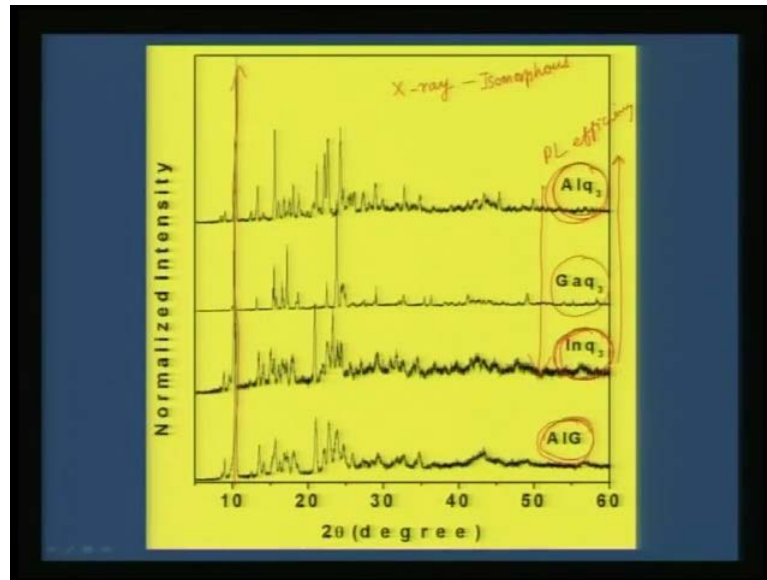
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How do we prepare such complex individual complexes, you can prepare by taking the nitrate and this is hydroxyquinoline, so if you reflex this at a optimum condition, then you get aluminium q 3 or indium q 3 or gallium q 3. Now, if you want to prepare a solid

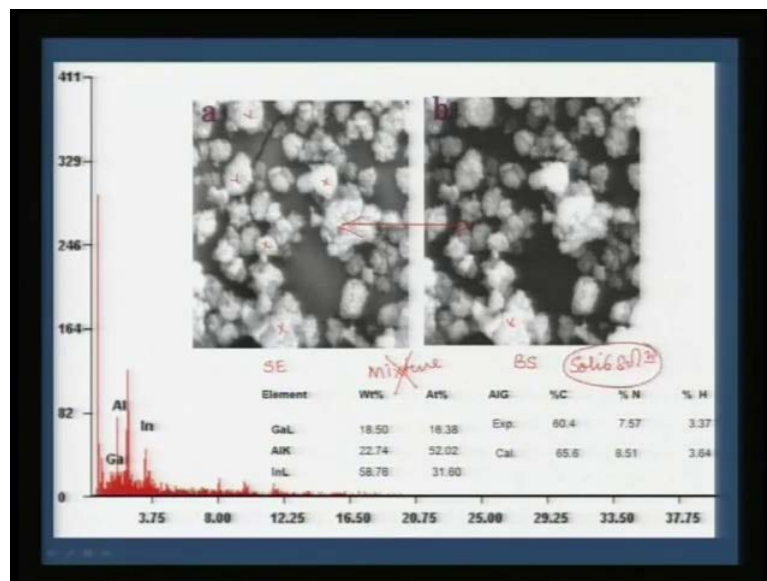
solution, what you do, you take this in stoichiometric proportion, if you reflex it then you get this compound as you see although, you take 0.3 0.3 0.3. In net you seem to get only this sort of compound as a solid solution, which means this is the most preferred stoichiometry, at which the solid solution can be stable.

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So, you can see the x ray pattern is exactly matching with the individual compounds.

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How do we know that this is a solid solution, you can take the secondary electron image and the back scattered image. Secondary electron when back scattered image will give you clue, whether it is a simple mixture of all the 3 complex together image, you will see they are all in different colours in black and grey resolution, they will all be in different shades.

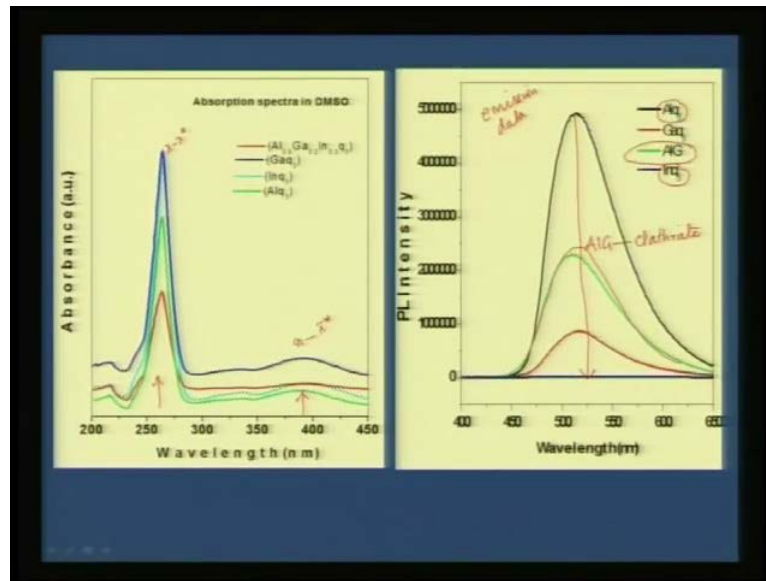
But, what you see here from this picture to this picture almost the colour contrast is exactly the same therefore, this is not a mixture of 3 complex, but this is a solid solution. And because it is a solid solution, the stoichiometry at this point is going to be the same at this point, the stoichiometry in any given place will be the same and that is the simple definition of a solid solution precursor.

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Now, we have tried to refine, this data as you see here Alq₃ and AlG₃, they show the similar x ray pattern and we can do the rietveld analysis and we can see that, both are crystallizing in monoclinic form and these are the structural datas.

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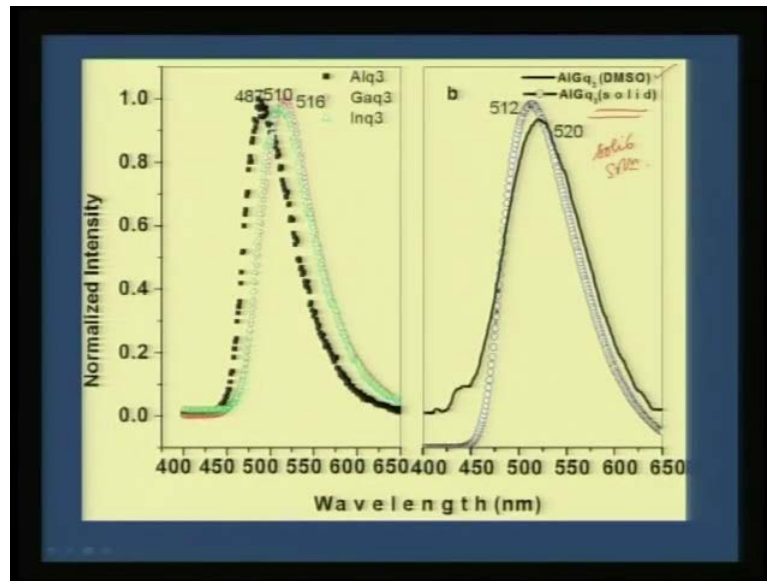


But, what is interesting that, I would like to point out to you is the absorption spectra, you can see that the absorption spectra of the $(Al_{0.3}Ga_{0.7})_3(In_{0.3})_3$ and $(Al_{0.3})_3$ they all show similar feature, which means the π to π^* transition and the n to π^* transition, you can see is happening at around 260 nanometer and somewhere around 380 nanometer.

This is due to n to π^* transition and this is due to π to π^* transition and it is all the same for both the solid solutions and individual molecules, but interesting point here is the emission data. If you see the emission data, we exactly have got, what we anticipated, because $(Al_{0.3})_3$ and $(In_{0.3})_3$, they have a very sharp change in the PL intensity. $(Al_{0.3})_3$ is highly luminescence compared to $(In_{0.3})_3$ whereas, if you prepare a solid solution, which involves all 3 atoms together, then you can see that it is exactly placed in the middle.

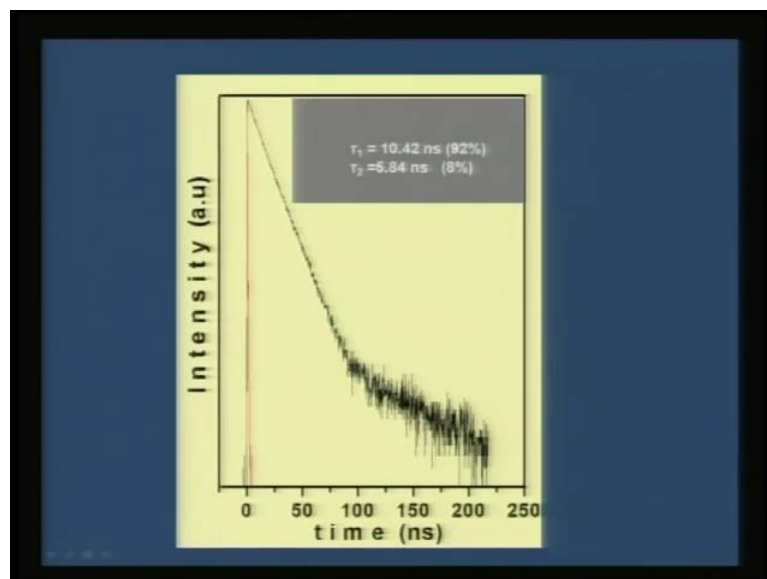
So, this is your $(Al_{0.3}Ga_{0.7})_3(In_{0.3})_3$, which means I am able to now make a compromise between the mobility of charge carriers and the PL intensity by bringing all 3 metal ions together in a single compound and this is possible only, because it has a clathrate feature. So, by knowing the crystal structure by knowing the x ray pattern, it is possible to fine tune to get the right composition, which will have dual property of both the mobility as well as the PL emission in one single form.

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That if it is Alq3 gallium or indium, they have preferred emission feature and if it is DIG in solid it exactly comes between these solids indicating, that these are really the solid solution. And the solid solution seems to be very typical of its structure and therefore, you do not see much of a change whether, you record it in solid or in liquid form.

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And you can also try to fit this to a two double exponential decay, you can see 2 components, tau 1 and tau 2 and mostly coming from the quinoline moieties.

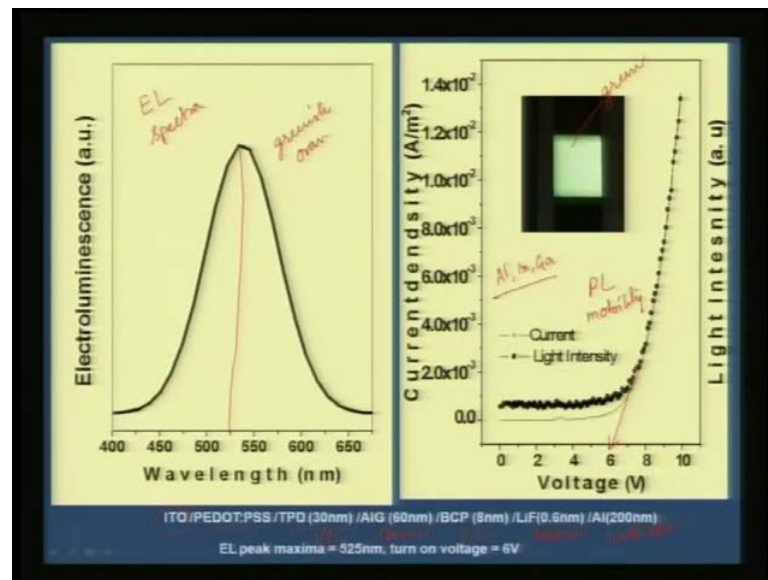
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Properties	Alq ₃	Gaq ₃	Inq ₃	AlG
Abs. λ_{max} (nm)	264	264	264	264
PL λ_{max} (nm)	487	516	510	512(520)
PL FWHM (nm)	67	72	75	90(100)
PL quantum eff.	1	0.08	0.002	0.42
$E_{red, onset}$ (eV)	-1.81	-1.85	-1.88	-1.83
$E_{exc, onset}$ (eV)	1.27	1.20	1.16	1.22
HOMO (eV)	-6.16	-6.12	-6.06	-6.14
LUMO (eV)	-2.99	-2.95	-2.92	-2.97

The PL quantum yield is reported relative to the Alq₃ and it is taken to be $\Phi_{PL}(\text{Alq}_3) = 1$ for clarity.

And these are all some of the data, that we can agree upon and try to see, how the solid solution is performing in comparison to the individual molecules, you can see that the absorption is placed somewhere, closer to indium and gallium. And then the P I is exactly mid placed between aluminium and gallium complex and so is all the HOMO LUMO values everything is recorded, which clearly shows that, such a solid solution can be achieved.

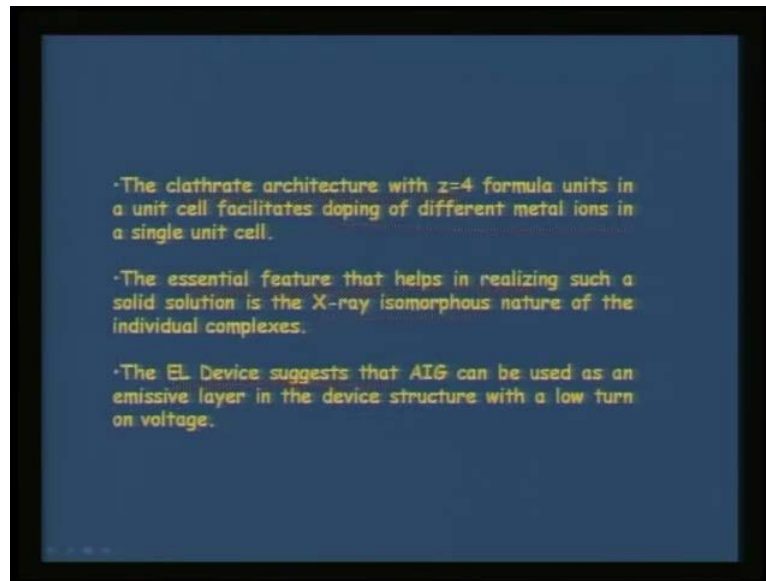
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Now, this is the electroluminescence data E L spectra of a device, which you can make with I T O as your anode, then P dot P S S as the buffer layer T P D as your whole transport layer and this is the emissive layer and then you have the electron transport layer and this is the barrier and this is your cathode. So, in a device configuration like this, you can see that A I G is giving a nearly good green emission and one can see, that the current and the light intensity curves are going hand in hand with a turn on a voltage somewhere around 6 volts.

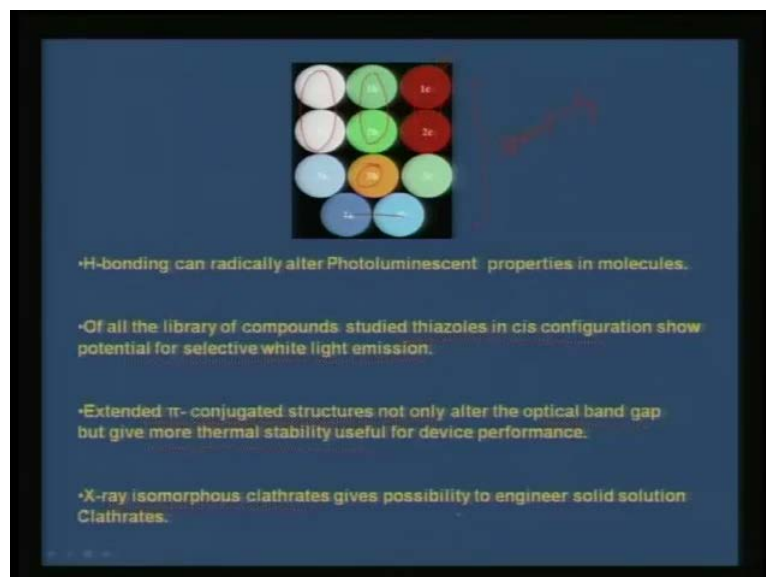
Fairly good one and one can achieve a compromise between P I and mobility, if one can actually play around with the amount of aluminium, indium and gallium that you can take in a single solid solution. And you this is the E L spectra, which shows that, this is nearly a greenish orange emission, that is coming out of this E L spectra.

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So, what do we see here, the clathrate architecture with z is equal to 4 formula unit in a unit cell facilitates doping of different metal ions in a single unit cell. The essential feature that helps in realizing, such a solid solution is the x ray isomorphous nature the E L device suggest, that A I G can be used as a emissive layer in the device structure with the low turn on voltage.

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Having said this, I just want to make some quick summary, in the first place, we looked at the specificity of these aromatic compounds benzheterazole and I have shown you, that 1 a and 2 a preferentially shows white light. The imidazoles show green and the oxazoles show red emission and combination of thiazole and oxazole or thiazole and imidazole leads to either orange or to blue.

So, with this notion one can say that, there is a very definite way more like a thumb rule, one can try to exercise in rationally preparing, the desired organic compounds, that will give you a preferred emission. And of all the library of compound studied thiazoles in CIS configuration show selective white light emission, extended Pi conjugated structures not only alter the bandgap, but they give more thermal stability useful for device performance. And lastly I have shown an example where x ray isomorphous clathrates can help us engineer solid solution clathrates to get a compromise between P l emission and mobility of the charge carriers. So, I stop here with these examples and I will try to discuss in the next lecture, how inorganic phosphors can be used for display technology.