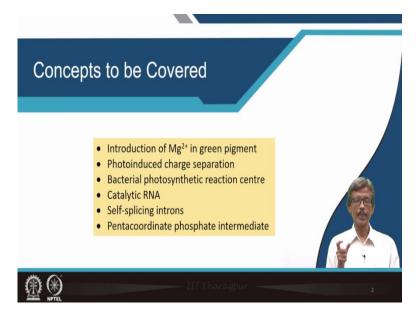
Biological Inorganic Chemistry Professor Debashis Ray Department of Chemistry Indian Institute of Technology, Kharagpur Lecture 28 Module 06: Phosphate Metabolism and Cellular Signaling Photoreception and Enzymes

Good morning everybody. So, we are here reached up to lecture number 28. So, almost 50 percent we are covering for this particular course. So, now we will talk about the photo reception as well as some enzymes. So, why this photo reception and what does it mean because we are not talking here in this particular lecture title is that what are the metal ions, so, we will be considering magnesium two plus.

(Refer Slide Time: 0:52)

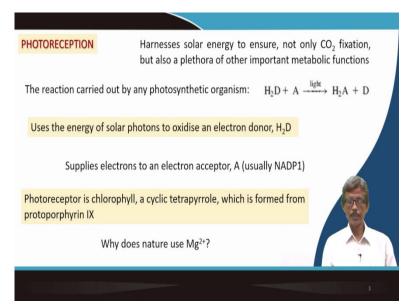


So, we all know that is we will be talking about the chlorophyll, the plant pigment as the nature's best known plant pigment, which is due to the magnesium, then what you can see that you have the h nu is falling on the lip of the green plants and you can have the corresponding photo induced charge separation, then these are related to something which is you can have the corresponding photosynthetic bacteria we call the cyanobacteria cyan is the color.

So, cyanobacteria, so, blue green algae, so, blue green algae can have the similar type of reaction center, then little bit complicated thing is that, whether the magnesium can be involved for getting some catalytic RNA self-splicing introns also and finally, what we are knowing and what we are talking about, because, we are talking about the magnesium ion

coordination and then also the corresponding chemistry the main group chemistry rather based on the phosphorus center because the phosphorus is also with that of other triphenylphosphine type of thing or the phosphates are very good ligands for your magnesium center.

(Refer Slide Time: 2:02)



So, how we can receive or the reception you can put for your h nu, it can basically harness or harnesses the solar energy to ensure not only for CO2 fixation, but also many types of very useful reactions and the metabolic functions as that it can give you the fruits the food material for our survival also. So, we are dependent on very much on the nature mother nature as well as on these green plants.

So these reactions which are being carried out by the photosynthetic organism, what is that fundamental reaction what we are talking about? So, in terms of the corresponding reaction and the chemists, the biochemist or anybody, when you talk about the action as well as the reaction, we write everything as reaction not action. So, action definitely is there, but we are talking about the reactions when we do reagents or mixing we get some reaction, but, if you look at the top, what molecule I have written over there only the CO 2 fixation.

So, the CO2 fixation in terms of this photosynthesis is also a task to ask for your global environmental problem solve salvation or the solve. So, the particular simple reaction is that you have the light you have the photon you have the h nu, you have two species like H 2 D n plus a.

So, H 2 D is the donor and a is the acceptor converting to h two A and D. So, this is the fundamental and the very basic reaction where H 2 D is nothing but why it is donor is donor in terms of electron donor. So, you must have something where you can have the electron donor and which can use the energy of these photons well, he knew and we all know why our plant lives are green in color, because it can absorb something it can absorb the red and blue color in the spectrum.

So, we will show also the what is the corresponding a visible spectrum or a green solution and what we can extract in ether. So, if you can have the green leaf you can extract it out you can separate it out in a corresponding separating funnel and you get a very good green solution and if you put that solution within the keyword of the spectrophotometer you can get the around the corresponding and can record the corresponding spectra, four different varieties chlorophyll A or chlorophyll B.

So, right now, what you see here is that, that you can have the electron donor H two D and how it can be converted to H 2 A and the removal of that thing that means, not only the electron in terms of your hydrogen basically attached hydrogen also that basically the electron donor when it is giving electron it is getting oxidized. So, H 2 D is getting oxidized to give you D and A will be reduced to H 2 A.

So, not only electron transfer though we are defining these donor and acceptors also in terms of electron donor and electron acceptor most of the time we talk this basically fast because the electron transport is taking place in the first step, then you can have the proton transport. So, the triggering thing what we initiate reaction by moving for your electron transfer, then follow up the accent is your proton transport.

So, which can supply also to the electron acceptor, so, what is a is nothing but your NADPH or NADP 1. So, nicotinamide adenine dinucleotide phosphate, so, again some phosphate groups are they are they are they are good at electron acceptor and they can supply energy to the system. So, one such example of this chlorophyll let us see, let us take that chlorophyll and that chlorophyll basically is made up of a typical leg and we know now what is that leg and which is tetrapyrrole.

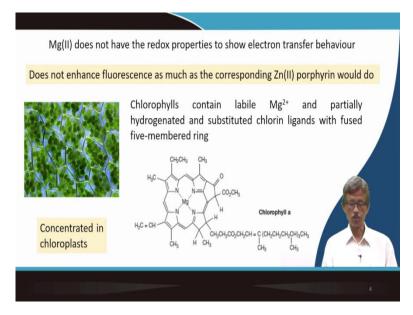
So four pyrrole units we will take 1, 2, 3, 4 and in linear fashion if you attach them with a methylene bridge, CH two bridges, so you get a linear tetrapyrrole unit but you have to move it you have to connect it to get a garland so garland around magnesium so if you put a garland

around magnesium, we know for nitrogens of the pyrrole centers, pyrrole functions can come and bind to your magnesium center.

That is why it gives you a protoporphyrin nine one variety there are large varieties of these things, some kind is present in our blood, some is present in b2b and b2c some is present in factor for 30 in many cases in cytochromes also, so we will discuss if our time permits only. So, in this particular case, you had the cyclic tetrapyrrole and you will grab basically the magnesium.

So, why does nature use magnesium two plus, why not other metal ions which is available in our body, in the nature in the plants and everywhere in the soil also, because through root basically the plants are taking up this magnesium and magnesium is definitely the micronutrient. But when we are adding fertilizers we do not add magnesium we are talking in terms of phosphorus, we are talking in terms of potassium we are talking in terms of corresponding phosphorus, but we never give magnesium because if some soil is deficient in magnesium, we have to supply magnesium because magnesium is the most important thing to give you the corresponding green vegetation.

(Refer Slide Time: 7:29)



So, why nature is using magnesium the bivalent magnesium or magnesium in oxidation state 2 or Mg 2 and bromine 2 also be right does not have the redox properties it cannot oxidize magnesium to 2 magnesium three plus or magnesium 2 for a reduction to magnesium 1 plus. So, these redox silent. So, that silence in terms of electron transfer is basically a very stumbling block initially when people identified first.

So, around 150 years back when people identified fast and thought up the presence of magnesium in the plant life that how you can manage the electron transfer behavior since we have to talk in terms of the electron transfer behavior and whatever reaction we are writing over here is in terms of only the electron transfer and also the corresponding fluorescence behavior does not enhance the fluorescence as much as the corresponding gene to porphyrin in can do.

If you have a synthetically prepared for fire in a laboratory basically we can make many such porphyrin in chemistry and porphyrin coordination chemistry is very rich some people are working on porphyrin chemistry and they say that we can also go for some mimicking of all these things and they are studying the bio inorganic chemistry, they claim basically, but is far away from your typical biological thing.

So, this magnesium thing can if you substitute it and you simply run the fluorescence, you measure the fluorescence only do not bother about something else. So, we will find the zinc is the much more superior metal ion element in terms of its corresponding fluorescence enhancement or the typical fluorescence behavior. So, what are these picture or what is this figure?

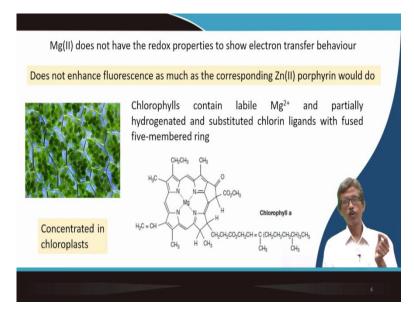
So, try to understand it is you are studying from your school days from class five and class six where we have first came to know about chloroplasts. So, how these thing is getting concentrated within the chloroplast and you see the nice motive basically all are like your graphene structure, hexagons side by side hexagons.

So, it is basically a graphene sit like arrangement, because you have the corresponding cell boundary. So, the hexagonal cell boundaries there within which you have the green pigment within the chloroplast basically it is there. So, there we basically but if you see these green pigment or the green chloroplast, to me basically you also try to understand in that way that I am looking at to the magnesium because our ultimate goal is to see where your magnesium is because the magnesium is your catalytic site.

So, it is not very inert one and is not giving a very static complexation reaction, but is level it is binding and then the next moment it can remove also and partially hydrogenated some of the ring can be partially hydrogenated in this particular case of this particular structure. So, what is there basically, so, you see, now, we can correlate what you have learned in your class the six and what you are learning here now, that now we can correlate the entire chlorophyll molecule in terms of a chemists eye what nature is seeing because is the corresponding microscopic picture you have the slice of that corresponding section you draw got it from the leaf and you are see under the microscope and you take the photograph also and it has been taken from the Wikipedia page.

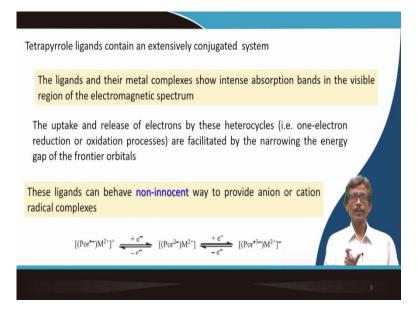
So, you will get it every time everywhere even if you have the in the understanding that okay let us see what that say structure is then ultimately what chemistry is interested to know about the corresponding magnesium and corresponding big macro cyclic link like that of your portfolio. So, many substitutions are there and many varieties that basically they are attending on the substitutions and all these things and particularly not only for buildings also but you can have also the cyclopentadienyl at the right hand side top.

(Refer Slide Time: 11:25)



So, you have the tetrapyrrole ligand system in your hand and it is extensively conjugated. So, if you have not noticed you see once again that you have double bond, single bond double bond single bond double bond like the keratin. So, it is basically in a cyclic so, you can have the ring current also when you can move basically if sometimes we in organic chemistry reaction mechanisms, we ride the movement of the double bonds. So, basically is the localized system. So, you can move one double bond from one point to the other.

(Refer Slide Time: 11:57)



So, basically that particular one is giving an extensive conjugation. So, that extensive conjugation is basically helping us to see the color within the visible region or in visible range. So, since you are looking at the green color, so, and you are not seeing something where the magnesium is not a transient midline, it can go for your DD transition, but something is happening from the ligand part so like and is so interesting and so, beautiful is that the ligand is responsible for the absorption of the electromagnetic radiation and in the visible region you see some color.

So, when you go for these two reactions the H 2 D to H 2 A, we have seen that the uptake and release of electrons by these heterocycles also can take place. So, you can have the corresponding oxidation or reduction process if it is highly delocalized system. So, if you can put one extra electron to the system that means purified in itself the ligand itself which can be in the reduced form or it can also be oxidized so it is electron deficient or electron deficient molecule.

So, whether it can sustain you can have the corresponding stable form after the addition of one electron or after removal of one electron that also we can see. So, basically that is being facilitated by narrowing the energy gap of the frontier orbitals. So, it is possible if you only change the corresponding energy gap of the different frontier orbiters that means you have the conjugation that means, your pi star levels are going closer, closer and closer.

So, that is why you can have the different frontier orbitals as the pi star levels and all these if you can bring down the pi star level close to the pi level, your energy is not going for the UV

range when the gap is more your energy is more so, it is in the range, but if you come down to a lower level, you have the corresponding or packet for your transition is will fall on the visible range.

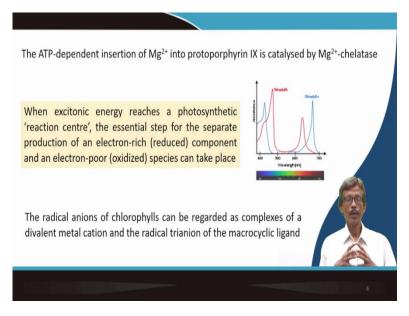
So, you get a color putting in for that particular. So, what does it mean now that you can go for a redox reaction and that redox reaction is basically driven or centered on the corresponding ligand part. So, in that way, what we can define which is written in blue, blue said wording as the non-innocent that is that it can supply electron or it can take up electron also in terms of his redox behavior, it is non innocent.

So, it can take up and it can give up electron also giving you the corresponding oxidized form or the reduced form of the corresponding ligand. So, now, what we see here is that of your corresponding form that you profile in is there one dot minus is that you are able to reduce it. So, when you have the profile neutral ligand and the magnesium two plus is coordinating the overall charge on the complex which is in the square bracket, the square bracket charge would be two plus which is the charge of the metal ion, because the ligand is not balancing or counter balancing any kind of charge, what you can have for the magnesium two plus center.

So, overall you get that is a portfolio net portfolio net negatively charged one with a dot and that means, the extra electron water you can have bound to your magnesium which is m two plus bivalent and metal ion. So, that can further accept one more electron to give you a paired net electron where you can have the two negative charge and having no charge overall charge on the complex and the farther one where you will have the qualified in can have three negative charges one period that is why one unpaired electron is not swaying the three charges and one extra electron you can So, an overall charge on the complex is minus one.

So, between the neutral complex and the monopod additive complex and the mono negative complex you can have three different species the way you can transfer the electron.

(Refer Slide Time: 16:01)



So, the magnesium insertion within the macrocyclic ligand is basically triggered again by the ATP molecules and one magnesium two plus chelatase can be responsible for the insertion of the magnesium within it. And now, if you run the corresponding visible spectrum that way we saw the extract it in ether or any other good organic solvent even chloroform also can do depending upon the extractability of the left what is your source.

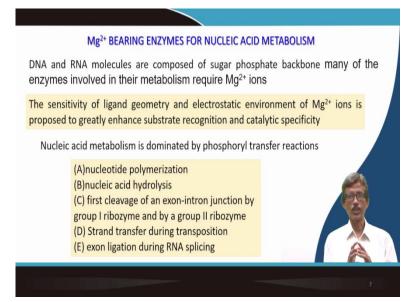
Then you run the corresponding spectrum the wavelength versus absorbance if you plot, so, 400 to 700 nanometer you see for the chlorophyll A the red line, so, if these are too close and chlorophyll B to this moving there, so, that is most interesting also and sometime close to that of your 400 nanometer band, we call it as a solid band.

The solid band is due to the transition within the corresponding macro cyclic ring only. So, when the excitonic energy the energy required for your excitation of the purified end ring, which we are moving to RC the reaction center, we can have some reaction center we can have the water oxygen center in photosystem two, so, that is a different reaction center which we call as a WOC but this is RC only the reaction center where your energy is getting absorbed.

So, you can have the electron reach the reduced component and an electron poor oxidized species can take place. So, while one is accepting and if the electron transport is taking place from one species to the other, so, the species which is accepting electron will be electron rich and the species which is transferring electron will be electron poor.

So, the radical anion basically we have seen now that the radical enhanced can be formed and these radicals announced of these chloroform can be regarded as complexes of the divalent metal cation or the metal cation and the radical trianion of the macrocytic ligand what you have written in terms of the reactions.

(Refer Slide Time: 18:00)



Then, we can see now, about the corresponding metabolism in nucleic acids. So, we are moving directly from the photosystems. So, that is one part of this particular class where we are talking magnesium in plant species. Now, we can go to the nucleic acids the DNA and RNA molecules, the more sophisticated molecules we talk in terms of your biological world, or the bio organic chemistry also talk that there is only nucleic acids because, we do not know much about the nucleic acids and its involvement and interaction and the coordination with the middle and centers. So, two varieties of molecules always consider one is your DNA molecule and another is your RNA molecule.

And now, we already know that while you are studying magnesium in all these classes, because we have seen that the magnesium is needed and that magnesium is so useful that it can take off not only the other donor groups like the carboxylates from the protein and or the corresponding sugar and, but it can also take care of the phosphate groups are the phosphate addition or the phosphate removal.

So, the phosphate the ligand is plenty at the line and is available like your portfolio ending in the chlorophyll. So, the phosphates are available the phosphate groups are available then how it can coordinate. So, the ligand geometry because you can have the big protein say huge molecule and you know that the, if the protein is coming it can have the different fold you can have some little bit closing or it can have the open particular structure.

And you can have is not that on the fingertips, you will get all the donor groups, but you can have in between you can have all the donor groups available. So, how these donor groups will be available from here say three of the donor groups that are available from this man and another three from the same. So, if we bring these two ends within the protein envelope and try to take up this magnesium at the center.

So, how these bonds will be forming? If you allow six bonds already we have seen in some other example, in other slide that magnesium is giving you six bonds to that particular metal ion center, but it is not that all these bonds are of same type and within the same regular geometry like a typical or a perfect octahedron. So, we may not get a perfect octahedron but it can be a distorted one and that distortion is also helpful for us also if it is more distorted, you get some weakness of the bond some weaker bonds will be forming and the reactivity can be enhanced.

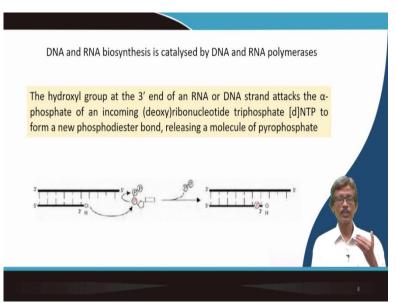
So, basically what happens here if you can go for a particular ligand geometry and the electrostatic environment that means, that donor atom environment around the magnesium center is greatly enhanced, enhance the substrate recognition and catalytic specificity. So, that particular geometry if something is opening up from the regular octahedral geometry, so, the substrate can enter through that particular site and will try to interact with the magnesium center.

So, similarly during the metabolism the nucleic acid metabolism is dominated by this particular type of phosphoryl group transfer reaction. So, the PGT So, do not worry about the least of these reactions it is can be on the basis at what we can understand what we can know even people are working or researching on it is the very the highest level of information is what people can have, but at least try to know what are the basic thing you can think of and you can formulate it out of these.

So, there are five such very useful reactions. One we all know that the DNA polymerization reaction, so, nucleotide polymerase chain reaction, again it is magnesium dependent and you can have the corresponding phosphoryl transfer reaction. So, these are the two things we always consider then the hydrolysis of the nucleic acid then the cleavage of the exon intron junction.

So, some junction the nomenclature is there one is the exon and in turn x is the external part and it is the internal part for the ribosomes, then strand transport during transposition to DNA to RNA transposition, so we all know and the DNA splicing also.

(Refer Slide Time: 22:32)



So, all these things are dependent on the presence of the magnesium as well as the phosphate and the phosphate group transfer. So, if we know that we all know you are hearing all the time even for the time when we are talking much about the viruses. So, the polymerase is the polymerase chain reactions we all know. So, the polymerase chain reaction is some reaction which is taking place in a cascade way or the chain way.

So, what does it mean about the different polymerases. So, these follow the polymerization reactions or the polymers is what they are and is important for the bio synthesis or our biological thing or the biological world basically, in our body also, how we go for the synthesis that bio synthesis all these two important classes of molecules, one is the DNA and another is the RNA the nucleic acids, NA is the nucleic acids, the deoxy and the other one is not deoxy one.

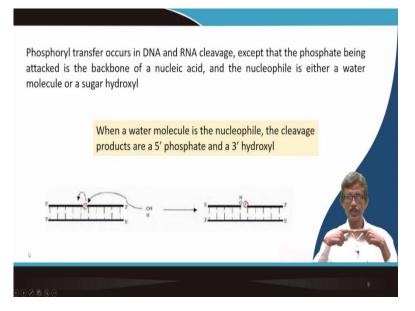
So, you have the corresponding hydroxyl group attached to the 3 prime position or 3 dash positions. So, the 3 prime positions of an RNA and DNA strand basically can be attached that basically always and all we know that the OH is a good nucleophile like your water molecule, what are itself can be a good nucleophile after deprotonation the water converting to your hydroxide ion and that hydroxide ion HO minus can be also a very good nucleophile So, that can attack the corresponding alpha phosphate group of the DNA and RNA.

Similarly, the 3 prime part that means the hydroxyl and the intact hydroxyl not the OH minus is basically can attack that phosphate group of an incoming deoxy ribonucleotide triphosphate that is the DNTP. So, deoxy ribonucleotide triphosphate like your ATP and ADP, you have a new nomenclature, try to remember what is that so, is the sugar is the deoxy form deoxy, but sugar, ribose sugar.

Sugar your ribose so immediately you should know all these nicely that you had the ribose sugar, which is in a deoxy form for that also we need something when you go for the DNA synthesis part, the ribose sugar is there that we can go for the deoxy. So, and again some catalytic thing is there are an enzymes out there.

So, deoxyribose nucleotides are there, so you get that triphosphate. So, what does it mean basically, we are talking so, it is very much similar to that of your ATP molecule. So, whether we can go for a new phosphodiester bond or whether we will be able to claim it. So, these are the two things we are studying everywhere every time during all these classes. So, if you are able to go for a new phosphodiester bond and releasing a molecule of pyrophosphates.

So, diester bond is forming and you can have the PP, PI is your inorganic phosphate and ion but you can have the pyrophosphates, so, two units of this bio phosphate.



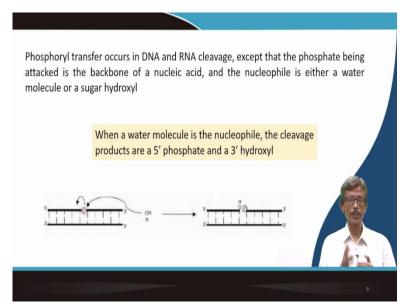
(Refer Slide Time: 25:39)

So, if you look at this particular molecule nicely here, the diagram the cartoon diagram, so, you can have the three primary random 5 primers, so, the two strands basically you can have, so, these two strands when in your hand and you are bringing something that means that that

is the rectangular part, the sugar part, pentagon is the sewer rectangular part is the base, the nucleotide base and the PPP is that three phosphate unit.

So, how you take up and things So, if you have the cleavage, PP unit, you are able to remove it, so, one P can be inserted within this particular chain.

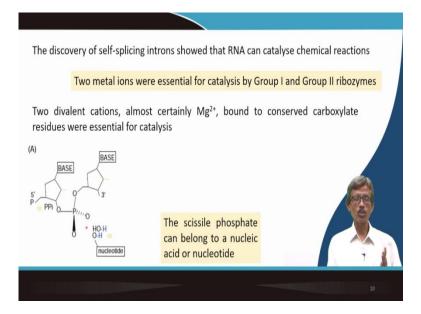
(Refer Slide Time: 26:12)



So, this is one kind of reaction. So, similarly, another kind of reaction can take place when the phosphoryl transfer occurs in DNA and RNA cleavage and when the phosphate being attacked in the backbone of the molecule, and you can have the super hydroxyl function and that when water molecule is the nucleophile, every time we are talking in the language I am saying now, the cleavage products are five prime phosphate and three prime hydroxyl.

So, you break it and you will end up with that particular thing. So, you see, we are showing the phosphate backbone, so, phosphate backbone is there. So, it is basically the tip is that phosphate backbone and how you claim it. So, that particular strand is getting cleaved by only one molecule.

(Refer Slide Time: 26:55)



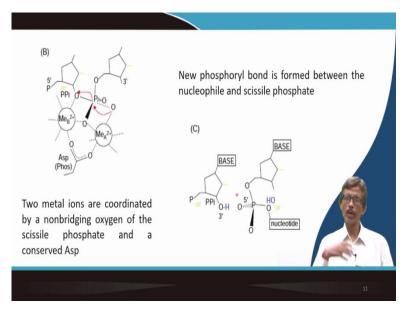
So, that way we see that self-splicing introns So, you have to have the cutting splicing we are cutting, so, the discovery of self-splicing introns, show that RNA can catalyze many chemical reactions, since, we are seeing some reaction where we are baking this particular thing that the phosphate linkage we can break in the from the chain.

So, whether many chemical reactions because the RNA world is now a bigger world and people start thinking started thinking that our life and our world has been started from the RNA molecules only. So, is the idea is that the RNA world you have. So, two metal ions were essential for this particular catalysis for the group one and group two ribozyme. So, ribose sugars are they are an enzyme and that ribose gone to kind of giving that coined the name as the ribosome which are not basically different from your RNA catalysts.

So, you have the divalent cations and almost suddenly the magnesium two plus is there and the carboxylated residues along with the phosphate residue. So, what do you get basically, that you get here the base base is there along with that base you have the pentagon sugar and the phosphate unit.

So, these are the very basic units and how the nucleotides are coming along with that of your I OH and or the H OH and also because the alcohol and can also be transiently pour donated to giving you that another and at that point, so, the scissile phosphate can belong to a nucleic acid or a nucleotide. So, like that what I was just saying that you have the phosphate backbone, but that can be cut.

(Refer Slide Time: 28:35)



Then what do you find in some other examples that to metal ions you can have, so, 2 magnesium centers you can have and you can bring one phosphate units and that phosphate unit since the phosphate groups has many oxygens center unlike your hydroxide function, so, it can bleach to metal ions and you can activate the catalytic site.

Similarly, in this particular case, ultimately how do you get A to B to C. So, new phosphoryl bond is formed between the nucleophile and the phosphate unit. So, like in the previous all cases, that you take the phosphate from one side and bring the phosphate to the other side. So, that is the fundamental reaction and that is the most important reactions what you can have.

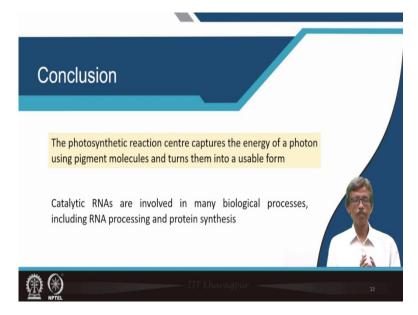
<text><text><equation-block><text><text>

(Refer Slide Time: 29:14)

So, in all these DNA polymerase is the new DNA chain directly on the preexisting DNA template we form and three prime hydroxyl group is important and they are definitely a class of metal enzymes therefore, and that typically required the function from the two magnesium two plus ions for the DNA and two DNA n plus one. So, one unit increase.

So, you have these m two plus m two plus units and all these groups are there and that is basically functioning in the DNA polymerase. So, DNA polymerase once you listen it once you understand it you would obviously know that okay magnesium is there. So, for the function of the DNA polymerase reactions for the phosphodiester bond formation over there, we require the corresponding involvement of the magnesium ion.

(Refer Slide Time: 29:58)



So two things we have considered one is the photosynthetic part the photosynthetic reaction center, which is capturing h nu and we get the pigment molecules, which is useful for your glucose synthesis. And then the catalytic RNAs, the ribozymes, we have, and they are involved in many important biological reactions. And they are also involved in RNA processing and new types of our new categories of proteins.

(Refer Slide Time: 30:25)



And references you start with the chlorophyll, access it from the chlorophyll and then you go the related other pages in Wikipedia and the book we have clicked on. So, thank you very much for your attention.