Fundamentals and Applications of Supramolecular Chemistry
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Lecture 57

W12L57_Molecular Wire and Cable, Molecular Switches and Non linear optical (NLO) materials

So, let us now continue the discussion. We were looking at the design of a molecular wire, where we have the hydrophobic backbone and the hydrophilic ends as well. In order to explore the properties of molecular wires, namely, suitable electron conducting pathways, these molecular entities were incorporated into, for example, bilayers that are very important in biological self-assembly processes.

We already looked at the fact that ions need to move from intracellular to extracellular and vice versa. Therefore, these signaling pathways involve the transfer of potentials, the movement of current, and it is important to see whether the communication between these different boxes or regions can be facilitated by systems that can actually provide the necessary conduction pathways for electrons to move from one region to the other.

So, in this regard, a very interesting set of experiments was performed.

So, to look at the function of the electronic conductivity pathway, transmembrane conductivity experiments were performed. And these were performed in dihexadecyl phosphate, which is $[CH_3-(CH_2)_{15}-O]_2-(P=O)-OH$.

So, what has been observed is that when we have these particular bilayers and we add this particular molecule consisting of the molecular wire here, we have $K_3[Fe(CN)_6]$, which is an electron acceptor, and we have a donor, which is sodium dithionite. So, this functions as a reducing agent; therefore, it will get oxidized, and this is the acceptor because it is going to accept the electrons.

So, this is the electron acceptor, and this is the electron donor. It is to be kept in mind now that we are performing this experiment in the presence of the zwitterion.

So, only if you have this particular molecular wire, is there no enhancement in the electrical conductivity. So, what I mean to say is that if I were to take this particular A only, if I take A only as the molecular wire, that means I only have the positive ends; we have this bipyridyl moiety, where we have the methyl groups, then these positive charges will neutralize the negative charges on the phosphate and therefore, there will be no conductivity that will take place.

So, the negative charges on the vesicles will neutralize the positive charges on the pyridinium ions, and no conductivity will be observed.

However, when we take small amounts of this zwitterion B, an enhancement in conductivity takes place, by 4 to 8 times. And this enhancement in conductivity takes place because now we have an internal oxidizing agent that is going to get reduced, and we have an external reducing agent.

So, this is an external reducing agent that is going to get oxidized. So, this releases the electron; the electron is picked up by this molecular wire, it is transferred; this is the conducting pathway. Then it reaches the acceptor end, which is the internal oxidizing agent, and eventually tends to get reduced.

So, the electron acceptor property functions here; therefore, this is the facile conducting pathway. In this way, the electrons are able to move from the extracellular to the intracellular region, or there is a current flow from the intracellular to the extracellular chamber.

So, these facile conducting pathways exist; therefore, this particular B-zwitterion functions as an electron conductor or as a molecular wire. This is one very important application of this particular system, which actually contains alternating single and double bonds, which are called the caroviologens.

So, these caroviologens, which function as molecular wires, having zwitterionic behavior, are able to conduct this process in a very facile way.

Keeping this application in mind, the next thing was that if you have a molecular wire, we would also like to protect the molecular wire using some particular insulation, which is referred to as a molecular cable.

So, a molecular cable was also designed that can actually insulate the molecular wire. Let us look at one particular example of this. Okay. So now you can see a pretty long structure that effectively tells you that we have these molecular cables, and it is a three-stranded molecular cable, designed by Jean-Marie Lehn, to actually contain the caroviologens.

So, you have these caroviologens, this molecular wire here. So, this molecular wire, which is present inside, can be insulated using these three standard molecular cables because the caroviologens are delicate.

As you know, the molecular wires are delicate entities, and therefore, you can actually cover them with these molecular cables so that they stay protected.

So, we see we can actually design very complex molecules to function as molecular wires as well as molecular cables. The next application we can look at is a molecular switch.

So, let us take this particular example where this system functions as a molecular switch. This system is very popular; it has been studied and investigated in detail. This is a methyl, and this is a methyl.

So, this is the open state of the system, and this is in equilibrium with the closed state; this is the methyl = -R2, and this is the closed state. Now, in the closed state, you can see that we have this rearrangement of the electron density, and this gives rise to the closed state.

Now the closed state is obtained when you irradiate with 365 nanometer light, which is UV light, and when you irradiate it with 600 nm or greater, which is visible light, it gives rise to the open state. And we can have two different case studies.

So, this behaves as a donor and this behaves as an acceptor when R1 is equal to this particular moiety, which is the donor, and this is the acceptor. So, there are some very interesting properties of these molecular switches. And so, you are able to access, first of all, the two stable states as a function of wavelength.

So, the switching on and off process is completely reversible, depending on the wavelength of light you use. If you use UV light, it will go to the closed state; if you shine visible light, it will come back to the open state.

And the electronic properties of the two states are also very different. For example, you can see here that the closed state contains a fully conjugated bridge. So, you see the alternating single, double, single, double, single, double, single bonds.

This kind of conjugation pathway is present. This is a nice conjugation pathway that exists in the closed state, a fully conjugated system. Therefore, this allows for effective electronic communication from R1 to R2.

So, if R1 is a donor group and R2 is an acceptor group, the donor group is able to push electron density, and the acceptor group is able to accept electron density via this conjugation pathway. That makes this closed state a very interesting situation where electronic communication can take place between the donor and the acceptor groups.

And also when R1 and R2 are the same, for example, here both of them are positively charged. This conjugation pathway effectively insulates the two positively charged species as well; that is, they stay away from each other in the case of case 1, where both are positively charged.

And so, this is a very interesting case of a molecular switch, and what happens is that this electronic communication, essentially between the donor and the acceptor, constitutes a push-pull system, and this push-pull system is very important.

Because these kinds of molecules exhibit NLO properties, which are called the non-linear optical response, this is essentially characterized, to start with, by a large magnitude of the hyperpolarizability of the system of interest.

And this actually happens, in the case of the molecular switch in the closed state, where there is very facile electronic communication, extensive polarization from one end to the other, because there is a donor part and an acceptor part.

Therefore, this creates a ground state charge separation between the donor and acceptor units. So, in the ground state, you now have a high magnitude of the dipole moment. Therefore, this molecule, which has a high magnitude of the dipole moment, can now interact with the external electric fields.

This external electric field can now polarize the electron density in the molecule. Now, in addition to polarizing it in a linear fashion, non-linear responses are also present, and this has to be incorporated into the overall polarization of the sample, out of which the non-linear response becomes important.

That is reflected in the large magnitude of the hyperpolarizability coefficient, which can actually be computed for a system of interest as well. So, now to start with, let us look at the basic principle of an NLO material. The NLO response is also referred to as second harmonic generation, and effectively, this phenomenon causes the doubling of the frequency of the incident light.

So, if you shine light of a frequency nu, what comes out is the frequency 2nu. For example, these NLO experiments are actually done on powdered samples.

Using the Kurtz-Perry technique on powdered samples, where you take a glass capillary, fill it with the powdered sample, which can be organic or inorganic material, you shine light of 1064 nm, and what comes out is the green light of 532 nm, indicating second harmonic generation that is present in the material of interest.

And so, what we can now see is that when you actually shine a light of a particular frequency, omega, the extent of polarization in the molecule, mu, which is a function of the frequency, has actually not only a linear component but also a nonlinear component as well. And so, to start with, the linear component is alpha(ij)*omega, but now when you subject it to very intense fields, for example, lasers, the extent of polarization, which is induced in the sample, is non-linear. Ok.

And this is because the overall polarization is asymmetrical in nature, and because it is asymmetrical in nature, it now contains, in addition to the linear polarization, the non-linear terms, such that we can now refer to the dipole moment μ, which is equal to the ground state dipole moment + α_{ij} (E) + β_{ijk} + the gamma term, and these are the non-linear terms.

This is the linear response, and β and γ are referred to as the first and second order hyperpolarizability. So, these are the first and second order hyperpolarizability terms. This beta term is actually the second harmonic generation term or the NLO response.

In order to get a nonlinear optical response, it is also relevant that the arrangement in the solid must be non-centrosymmetric. If the arrangement of the molecules is such that there is a center of inversion in the crystal, then the overall polarization is equal to 0, and therefore, there will not be any such SHG response.

Now, going back to the previous term here, you can see that we can write E = cos(wt). So, that will make it μ_0 + α(ij) and the electric field is equal to E(0)cos(wt) + 1/2 β ijk $(E_0)^2 \cos^2(wt)$ + 1/6 γ. E 0 cube cos cube (wt), and now we know that cos square (wt) is equal to half plus half cos 2wt.

Therefore, we now see that the electromagnetic radiation contains a component that is oscillating at 2w or twice the frequency. So, this oscillating frequency is twice the magnitude or double the magnitude of the incident frequency, and therefore, you will see now that if the frequency is double, this leads to lambda being half the initial value.

So, that is what happens when you have 1064 nm; what comes out is now 532 nm green light. So, the wavelength is half, the frequency is double, and that is the origin of the SHG response. And so, what is also very important is the design of NLO materials.

So, if you are going to have materials that do not have a high magnitude of the hyperpolarizability coefficient, that is beta, then they are not going to function as efficient NLO materials, number one. Number 2, we also need to arrange the molecules in a non-centrosymmetric fashion.

So, the design of an NLO material is that number 1 is large polarization, and number 2 is the non-centrosymmetric arrangement. So, if you are able to have these two conditions satisfied, then we can elicit a very efficient response for a material to exhibit NLO activity.

There are different ways in which this NLO response has been achieved, and people have tried to design a system that exhibits marked polarization.

So, if you want to see marked NLO effects, then the design of the system has to be such that overall, when you excite the molecule, there is a large charge separation created, there is a sufficient amount of polarization in the material, and we need to have large changes in mu and a small energy gap between the ground and the excited state. So, in this regard, people have designed different kinds of systems which we call push-pull systems.

The molecular switch was one such example, but we can take more examples. For example, we can have a donor system, and we can have communication with an acceptor system. For example, we can take this as one system. And now we can increase the conjugation. So, this can push electron density; this is the donor, and this is the acceptor, and we can increase the conjugation here as well.

A can be of different types. It can be an electron-withdrawing group, like an aldehyde; it can be a cyano; it can be a protonated pyridine; or it can be a strongly electron-withdrawing cyano or a nitro group.

So, these can be my acceptor moieties, and these are my donor functionalities, which you see here. These function as efficient push-pull systems, and to start with, the molecule is expected to have a high polarizability.

But now, if this molecule, which has a high polarizability, arranges in the solid state in a way that the dipoles align in a non-centrosymmetric way, or they orient in a parallel fashion, then this will give a large bulk polarization and a large bulk dipole moment.

But if they arrange in a centrosymmetric way, then the dipole moments will simply be equal to 0, and the overall bulk polarization P will be equal to 0.

So, in a crystal, if you have the opposite arrangement of these dipoles, then you will not be able to get any overall SHG activity. Although at the molecular level you might have designed a very efficient push-pull system, the arrangement simply makes it centrosymmetric, and therefore, you are not able to elicit a good SHG response.

So, you can have a molecule that can have, for example, polymorphs, where one polymorph can have a non-centrosymmetric arrangement and the other polymorph can have a centrosymmetric arrangement, and one is SHG active while the other is SHG inactive.

That is what makes the design of SHG materials extremely challenging and interesting because it is not in solution, but in the solid state that we are trying to look for the SHG property as well.

And the idea is always to be able to align the dipoles in a non-centrosymmetric manner so that you can extract or utilize the hyperpolarizability contained in the molecule of interest.

With this, we come to the close of the discussion of SHG materials. In the remaining lectures, we will look at some other aspects of supramolecular chemistry as well.

Thank you.