

Fundamentals and Applications of Supramolecular Chemistry
Deepak Chopra
Department of Chemistry
IISER Bhopal
Week 07
Lecture 35

W7L35_ Stimuli Driven Processes in Artificial Molecular Machines

So, hello, everybody. Now, let us go to the next lecture this week, and today we are going to continue our discussion on stimuli-guided processes.

We are also going to discuss the supramolecular aspects related to the applications of photochemistry in the design of new molecular entities or supramolecular entities that can possibly function as, for example, artificial molecular machines. So, let me write this down: stimuli-guided processes.

We are continuing that further, and today we are going to look at some fundamental aspects of supramolecular photochemistry, which can be extended to the understanding of artificial molecular machines. And here we would like to start with a definition of a supramolecular device.

So, we have here a supramolecular device where different components are present in this arrangement of functional groups forming a molecule. There are different components present in this arrangement via specific functional groups that form a molecule, such that each particular component has a specific function.

So, a supramolecular device now contains these different components, which are made up of different functional groups that make up this molecule. This is essentially a very large molecule, and the individual molecular components have specific properties such that these properties are intrinsic to the system.

And also, it is to be kept in mind that this entire complex system, which contains different molecular components made up of different functional groups, is essentially stabilized by a network of intramolecular hydrogen bonds.

So, there exist non-covalent interactions between the different molecular components or the functional groups that stabilize the arrangement of the molecules in this complex system. So, overall, the system is fairly complex; it is a large molecule, it contains different functional groups, and each component has a specific function.

Overall, there exist intermolecular hydrogen bonds or pi...pi stacking interactions, and different kinds of non-covalent interactions that stabilize these components in that particular complex system.

And obviously, these non-covalent interactions are weak, so we should be able to actually control these intermolecular interactions depending on different kinds of movement of molecular components within this particular complex system.

So, as I told you, the idea is to look at the application of a certain stimulus and then use it in the applications of artificial molecular machines. And in this regard, it must be kept in mind that when you talk about a machine, a machine is an entity that takes in a certain input of energy and then gives out work. This work can be in the form of chemical work, electrical work, or mechanical work.

So, what is a machine? A machine performs work; it can be chemical, electrical, or mechanical work. And the efficiency is very important for a machine. It is the work output divided by the work input multiplied by 100%.

And in the performance of the machine, we have to keep in mind that the waste processes must be minimized, such as heating or generating chemical byproducts that have to be removed continuously. So, the heating and generation of chemical products or byproducts during the operation of these machines can actually reduce the efficiency of the machine.

So instead of employing chemical energy, it would be nice if we could employ photons, that is, photochemical processes, or we could employ electrons, that is, electrochemical processes, to perform work.

And so, keeping in mind that we are going to combine the concept of machines and apply it to that of a supramolecular device where essentially every component of this complex system plays a very, very important role. However, if on the application of an external stimulus, the functionality of the complex system is identified with the entire molecule itself.

Now this is important; initially, we were saying that to function as a supramolecular device, we give some stimuli, and there are specific regions of the complex system, specific functional groups, or specific molecular components that actually respond to it. But instead of that, if the entire molecule responds to the stimulus, it means the functionality of the complex system is governed by the entire molecule.

Then this refers only to the function of a large molecule. So, we have to differentiate between processes that involve large molecules and processes that involve supramolecular arrangements of molecules.

And so, if there is a stimulus and the entire functionality depends upon the entire molecule itself, that means you are not able to essentially deconvolute the contribution of the individual components; then this is the case of a large molecule that is being activated, compared to a supramolecular device where only the specific components are being activated.

So, let us take this up with our cartoon representation. For example, we have different components that are identified as follows.

So, in this case, this is a molecule that contains two components: component 1 and component 2. Overall, this is a complex molecule, and this arrow represents a bridging ligand, a covalent spacer, or a non-covalent spacer as well. So, these are the possibilities, and now we can have photochemical activation, which can give rise to these processes.

So, now you see it is either this particular component, one that is being photochemically activated, or two; but in this case, it is the entire molecule that is being activated. So, this is a reference to the large molecule, and this is a supramolecule.

This is how we distinguish between the two entities. We can take another example. The star here indicates an electronically excited state. We can have another case where we actually put an electron into the system; it can lead to this species, or it can have this covalent association, or the backbone, or this. We can also remove an electron.

It can form this kind of species, and we can also have, with the application of light, a charge transfer process where an electron can be transferred from one side to the other, or we can have these processes. So, this is called a charge transfer state.

And this is also a charge-separated excited state, which we also call the primary separation. So now you have an electronic transition, from, say, a donor part of the component to the acceptor part of the component, within the same molecule. That is, we call it a charge transfer process, which happens in the presence of light.

It can either be, from "this is the donor" to "this is the acceptor," "this is the donor" to "this is the acceptor," and "this is the primary separation," which we call the charge-separated excited state. And it is important to keep in mind that now, when you generate the charge transfer excited state, different processes can take place.

And these kinds of entities that are actually affected by light are referred to as chromophores. So, chromophores are the important functional units or structural building blocks that must be present, which are sensitive to light, and these photochemically active components can now undergo different photochemical processes. They can now undergo different photochemical processes; for example, let us start with the basic concepts.

So, we now have S_0 , which is the ground electronic state, and S_1 , which is the excited singlet state. So, we now have the electrons. This is the ground state, this is the excited state, and this is the energy; it is increasing. We first have a particular frequency, say $h\nu_1$.

So, we have the electron that goes to the excited state, and then de-excitation to the ground state results in the process of fluorescence, where we now have the frequency of the emitted light that is less than the frequency of the incident light.

So, we refer to this process as fluorescence, which can take place. But then we can have the process of intersystem crossing, where we now go to the triplet state, which is characterized by both electrons being unpaired. This is the excited triplet state, and from this state, you can actually have back intersystem crossing, or you can have the phenomenon of phosphorescence.

This is now referred to as, say, I refer to this as $h\nu_5$. Now, following the process of fluorescence, the electron that has now been excited to S_1 can undergo two different processes.

We can now have an electron transfer to another acceptor molecule. So, we can have this, and now there is a low-lying acceptor molecule. The electron is now transferred, and from here we can have the emission back to the ground state; this I represent by $h\nu_3$.

So, this represents the fluorescence coming from the acceptor molecules. So, there is now a transfer of the electron to a low-lying acceptor, which then emits the photon and returns to the ground state with frequency $h\nu_3$, responsible for the fluorescence of the acceptor, in comparison to the fluorescence of the initial species from which the excitation occurred.

We can also have an excitation transfer; that means before the electron de-excites to the ground state, that energy is transferred to another acceptor, which can now emit light and come back to the ground state, and this results in the fluorescence, $h\nu_4$, of the external acceptor.

So, all these photochemical processes can take place; we can have first the fluorescence, then electron transfer, followed by fluorescence happening at a lower frequency from the low-lying acceptor.

We can also have the excitation transfer, which we also call the energy transfer process, resulting in the promotion of the electrons from the ground state of the acceptor to the excited state, followed by de-excitation or emission of luminescence, which corresponds to fluorescence occurring from the external acceptor.

And all this takes place at different frequencies. So, all these photochemical processes are very important when it comes to trying to understand the supramolecular photochemistry of fairly complex systems.

So, keeping these things in mind, it is now relevant to look at some specific examples where we can apply the concept of supramolecular photochemistry to understand the behavior of artificial molecular machines.

Now, in this regard, let us look at the first example where we now have a system that functions as a plug socket model. So, here we have the bi-naphtho crown ether. This has the crown ether moiety, and we have the bi-naphtho unit. This is the anthracenyl benzyl ammonium species.

Now, what happens is that when you add an acid, trifluorosulfonic acid here, this particular hydrogen gets protonated, and it forms a new species, where essentially there occurs threading, where the anthracenyl moiety now forms a new chemical entity, and you can see here that this new chemical entity has hydrogen bonds that stabilize this particular 1:1 complex.

And in this particular state, if you shine light now, then there will be a transfer of energy. This energy is now taken up by this binaphtho unit, and then there is a transfer of energy from the binaphtho unit to the anthracenyl unit, followed by the emission of light, which happens at a different frequency, ν' , which is less than that of ν .

So, this tells you that during the process of complexation, there occurs quenching of the fluorescence of the dibenzo unit, and the fluorescence that you observe is now at a lower frequency coming from the anthracenyl moiety. And now, when you actually add a base, tri-butyl tertiary amine, this proton will be scavenged, de-threading will take place, and it will again return to the initial state.

That means there will be no further connection between the plug and the socket. So, this in-and-out state is very interesting, and this tells you about the fact that we can monitor the movement of the machinery, which means the anthracenyl moiety enters the socket via the acid-base mechanism.

So, this reversibility can be established by monitoring this threading mechanism via photo-induced energy transfer, where we have the quenching of the binaphthyl fluorescence and the sensitization of the fluorescence of the anthracenyl unit that is linked to the ammonium ion.

So, this change in the fluorescence profile occurs because this dethreading mechanism is controlled by the base, and the threading is controlled by the acid. So, this kind of

acid-base stimuli controls the movement of the species.

Now, we can take another example, another very interesting example, where we have this particular unit, where you see the starting configuration is where there are strong hydrogen bonds between this dibenzo-18-crown-6 and the corresponding 4,4'-bipyridinium unit.

We have put these bulky stoppers here, and they prevent the movement of this dibenzo-18-crown-6 out of this particular region. So, this is like a stopper that we put here. Now, when you add a base, the addition of a base deprotonates this hydrogen, and once it deprotonates, then you destroy the charge-assisted hydrogen bonds.

When you destroy the charge-assisted hydrogen bonds, there is a movement of this macrocycle from this particular station, say S1, to this particular station, say S2.

Why? Because now this particular configuration stabilizes the crown ether, by charge transfer interactions. So, now you see it comes here. And at this stage, if you now add the acid, if you again protonate this NH, then what will happen is that this is now a protonated species, and you can again have the species that is formed here.

Now, if you want to reset this process, you will have to destabilize this particular entity. Now, the destabilization of this entity can be achieved by the electrochemical reduction of this bipyridinium unit, or you can perform the oxidation of the crown ether molecule.

So, if you do the reduction, then this positive charge will go away, this will now become a free radical, there will be an electron here, and that will destabilize the charge transfer interactions, and then this will again go back to the initial configuration.

Or if you oxidize this crown ether, it will have a positive charge. There will be repulsions between these two entities, and it will again go back to the initial configuration. So, you can always set these entities depending upon the different species which are present and you can control these processes.

So, you started with a base and then you had a movement of this particular crown ether and now you can again bring it back to the initial state by electrochemical reduction or by oxidation of the crown ether moiety.

And the last example, we can see a much more complicated case where we now have this kind of an arrangement, where we have got different cationic species. So, we have the starting arrangement, where the crown ether is more stabilized by the pyridinium unit.

This is slightly less positive because of the methyl groups. We have this electron rich system, we have the photosensitizer and we have the stopper here. The starting

configuration is shown here between two stations A1 and A2.

First is the transfer of the electron from the photosensitizer to this particular A1 station. So, you can see that this creates the radical cation and now this is an unstable species or a little less stable species.

So, this can lead to now, a process which we call as ring displacement. So, this leads to ring displacement. Because now, it is going to be more stabilized, in this particular region, and the photosensitizer will transfer the electron, becomes P⁺.

There are two competing processes; one is the ring displacement and the deactivation of the excited state by the transfer of electron back to the initial position. Now at this particular state again you can have a electronic reset, where the electron can now go back from A1- back to the photosensitizer. If this happens, then again this will be a less stable arrangement.

This will be followed by a nuclear reset, where it now comes back to the initial configuration. So, you see that there are different processes which are involved here.

So, you start first with photochemical activation, photosensitizer, transfer of electron, reduction at the A1 station. Then you have a molecular movement, because this stabilizes the charge transfer interactions now, and then there is a back transfer of the electron to the photosensitizer, that is the electronic reset, and then we have a nuclear reset.

And we can control this process of movement, this intramolecular mechanism, between the two stations A1 and A2, with the de-excitation pathway. So, these examples tell us that whenever you have a stimulus, say in the form of light, followed by movement of electrons, and these molecular movements can control the conversion of light energy to mechanical energy.

So, in all these processes we have conversion of light to mechanical energy. So, with this we would like to complete this lecture. I hope you have been able to appreciate stimuli guided processes and in the next week we will now go on to the other topics of discussion as well.

Thank you.