

Fundamentals and Applications of Supramolecular Chemistry
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Week 12
Lecture 56

W12L56_Applications in Photophysical processes

So, hello, everybody.

In this last week of the course on Supramolecular Chemistry, we are going to look at some important applications. And to start with, we are going to explore the applications of photophysics.

So, in the previous lectures, we have looked at the different photochemical procedures where the excitation is brought about by light, and then organic transformations are achieved. Now, we are going to look at photoexcitation processes that lead to different photophysical processes, which bring about changes in the luminescent profiles of the samples. We can have both radiative processes as well as non-radiative processes.

So, in photoexcitation, we can have different processes; we can have photophysical processes and photochemical processes. For example, secondary charge separation, isomerization reactions, and dissociation.

These kinds of photochemical reactions can take place in the excited state, where the charge can be transferred from the donor molecule to the acceptor molecule, as has also been observed in the process of photosynthesis.

We can have trans-cis isomerization in the presence of light, and we can also have dissociative processes such that the weak bonds in the molecule can break.

In the photophysical properties, we have examined the concepts of fluorescence and phosphorescence, which are luminescent processes. We also have the non-radiative processes, which are the electron transfer and energy transfer processes as well.

So, what is important is that we can have either fluorescence or phosphorescence processes. These are important in sensing and signaling, whereas the chemical reactions of the excited state of photochemical processes are significant in the fields of application to molecular switches and photocatalysis.

So, we can now look at how this process of energy transfer is important because we are also going to look at the applications of these photophysical properties in molecular

wires.

And before we go into the applications of molecular wires, we will see how the process of energy transfer is a nonradiative process. This is the non-radiative transfer of excitation energy before the sample can undergo luminescence by removing the excess energy in the form of photons of reduced frequency.

So, we have this energy transfer process, which is actually a non-radiative process that involves the transfer of excitation energy by non-radiative means. So, this energy transfer mechanism operates by a Förster type, which involves the electrostatic interactions between the donor and the acceptor.

These are the electrostatic interactions between the donor and the acceptor, and the number 2 is the Dexter type, which is the exchange energy of the electrons.

So, we can look at these processes more carefully now. So, say we have got the excited state of the donor, this is the HOMO, and this is the LOMO. So, we have now promoted the electron, and it now interacts with the acceptor, which is in the singlet state, and there is now a singlet-to-singlet Förster energy transfer.

So, this will now de-excite, and this will now undergo photoexcitation. So, this comes back to the ground state, and then this goes into the excited state.

So, you have this kind of Förster energy transfer from the donor to the acceptor. So, we can say that a $D^* + A$ is going to $D + A^*$, where the spin multiplicity is the same for the donor and the acceptor.

We can also have the Dexter energy transfer, where we have photoexcitation. Now we have both these electrons, $1A$, and now there is an exchange. So, this electron goes here, and this electron goes here.

So, there is an electron exchange. So, this is now the $1A^*$. This is the singlet-to-singlet Dexter energy transfer. We can also have another case where we have the triplet excited donor; these have the same spin orientation, which is a triplet state, and this interacts with the acceptor again. So, this goes here; this is an electron exchange now happening.

This is the triplet-to-triplet Dexter energy transfer. So, this will lead to the formation of the ground state of the donor and the triplet state for the acceptor, which is the excited state. So, this is an acceptor, this is the donor triplet, and this is the acceptor triplet.

So, this is a triplet-to-triplet Dexter energy transfer that can operate. So, in all these processes, there is a transfer of energy without the release of photons.

In the Coulombic, it is purely electrostatic, and the extent of energy transfer depends upon the separation between the donor and the acceptor. And it actually occurs at very short distance separations, which decides the efficiency of the process.

Overall, these processes lead to the quenching of the luminescent processes. For example, it leads to the quenching of fluorescence or phosphorescence in the materials of interest. So, we can actually look at some examples to understand these photoexcitation processes more closely.

Therefore, for example, we can look at electron transfer processes. And we can also look at energy transfer processes in covalent and non-covalent systems. For example, we can take a zinc porphyrin chromophore. We have a zinc porphyrin. This is the Zn^{2+} , and here it is connected to a 5-membered ring.

So, we have this one, this one, this one, and this one; this is an iron-chloro bond. So, this is iron in the +3 oxidation state. So, this is a covalent backbone connected by a covalent backbone, the two chromophores. This is a zinc porphyrin, and this is the Fe^{3+} chromophore. Now we can compare the same system.

We can see this particular arrangement, where it is connected via a non-covalent backbone. The non-covalent interactions are purely hydrogen bonded. These are modular components: Zn^{2+} as well as Fe^{3+} .

And on photo excitation, when there is $h\nu$ and photo excitation, there is an electron transfer to the Fe^{3+} center, which leads to the formation of the Fe^{2+} center. This electron transfer process happens on photo excitation and is responsible for creating the charge separation between the donor and the acceptor.

So, now this electron transfer takes place either by the covalent backbone or by the non-covalent backbone, and this electron transfer process is quite efficient. If I were to consider this A, and this system is B, it is 4.3×10^9 for B and it is 8.1×10^9 for A.

So, you can see that even the supramolecular motif is as efficient as the covalent backbone in transferring the electron from the donor to the acceptor and therefore creating the necessary charge transfer, which we refer to as a secondary charge transfer.

And these electron transfer processes are important in different applications. For example, electron transfer processes are important in photosynthesis and also in the design of a diode material.

So, we see that this electron transfer process takes place in a very efficient manner. Similarly, we can also take an example where we can look at a system that involves the energy transfer process. When we interact with binaphthyl, this is in an anthracenyl moiety, in the presence of an acid and a base.

So, here what happens is that this gets protonated, and then there are hydrogen bonds that it forms with the ether. So, when you do the photoexcitation here, $h\nu$, this is followed by energy transfer. This is the non-radiative energy transfer from the binaphthyl unit to the anthracenyl unit.

And this leads to the luminescence of the anthracenyl moiety, whereas it quenches the fluorescence of the binaphthyl moiety. So, in the absence of this complexation or supramolecular hydrogen bonding association, what will happen is that the binaphthyl will exhibit fluorescence.

But that is quenched because of this complexation, and the energy transfer process now happens from binaphthyl to anthracenyl, which now releases a photon of energy $h\nu'$, and that is responsible for the luminescence of the anthracenyl moiety in solution.

And it is a very sensitive process because if we now replace a methyl with biphenyl, no complexation takes place because of the steric mismatch. So, with this background, we can now go and look at the application of this in molecular wires. We can take an example. In a molecular wire, the concept is that you have a donor and an acceptor, and there must be a pathway for electron transfer or conduction.

This process must take place, and it has to happen rapidly because electronic flow is the opposite of current flow. To start with, J. Marie-Lehn's group has addressed this problem by preparing a large number of carotenoid complexes, which he calls caroviologens. These caroviologens have been made. Let us look at one particular example of this caroviologen.

We have the methylated pyridine. So, the thickness is comparable to the length of the wire. This particular caroviologen has been formed, and it contains alternating single and double bonds; therefore, it has been observed to function as a molecular wire. And interestingly, you can see that these are the hydrophilic groups, and this is the hydrophobic backbone. And because this has both polar and non-polar parts, it is something that is relevant in the transfer of signals in cells across the bilayers.

So, if there has to be a signaling mechanism between the intracellular and the outer or extracellular region via these bilayers, then the viologens have both the hydrophobic part as well as the hydrophilic part.

This particular example serves to illustrate that electron transfer processes or current flow are very important in understanding different biological pathways.

So, in the next class, we will look in more detail at the functional aspects of these systems as molecular wires.

Thank you.