Supramolecular Chemistry-I

Prof. Parimal Kanti Bharadwaj

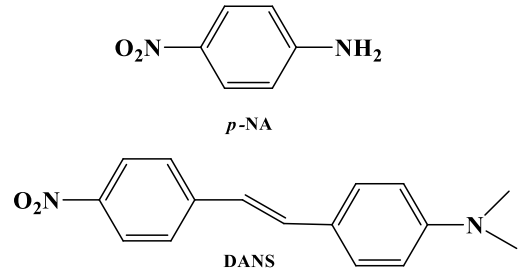
Department of Chemistry

IIT Kanpur

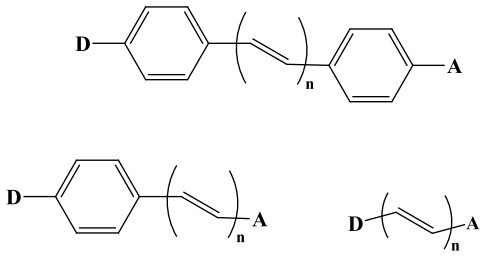
Week - 07

Lecture - 34

Welcome back to the class. See, I told you that for second order optical nonlinearity, i.e., for higher β value, we need donor one side, acceptor one side and in the middle aromatic π system. And as we increase the π system, the value of β will increase. For example, this para nitro aniline in acetone gives 8 into 10 to the power minus 30 ESU unit. There is a unit into 10 to the power minus 30 unit ok.

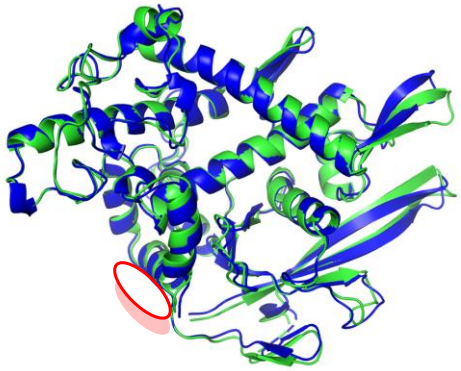


The static quadratic nonlinearity of *p*-NA measured in acetone was found to be $8x10^{-30}$ esu while that of DANS in chloroform was $55x10^{-30}$ esu using 1907 nm light.



So, compared to *p*NA, DANS has a longer π-system and hence about 7 times larger β value. Once you increase the π-system in a molecule its β value increases, but there is one caution something called trade off. What happens? As we increase the π-system, its absorption maximum will come to the longer and longer wavelength. This will interfere some of the β emission. This aspect is known as trade-off between second order nonlinearity/higher absorption. It will always give less β value. This is also the reason for choosing metals like Zn^{2+} or Cu^{+} ion while measuring nonlinearity because these metal ions do not absorb any visible radiation and they are colorless. So, this is enough I will as

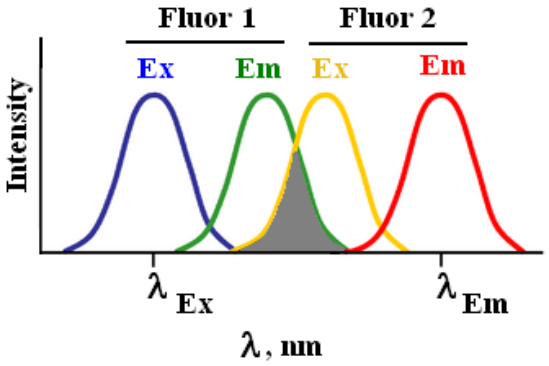
I told already I will give you one or two some typical references from where you can know further. My idea of teaching this course always has been I introduce you to the main features of the current supra molecular chemistry and any of you might be interested in a particular area then with the references you can go ahead. Now, I will tell you the last part of this with light. I will tell you now a very important phenomenon called Förster (Fluorescence) Resonance Energy Transfer or in short, FRET.



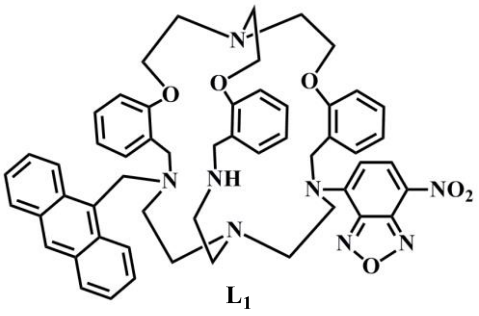
Let's see the problem first. I have shown here a protein. Its active site, i.e., the site where biochemical reaction takes place is in the interior. The protein consists of amino acids and here it forms helices, β-sheets, turns, etc. The amino acids, tyrosine (Tyr), tryptophan (Trp), and phenylalanine (Phe) are fluorescence active amino acids that are present in different numbers. What is my problem? I want to know how my protein (enzyme) is functioning? To know that I put a fluorophore molecule at the surface of the protein shown by red circle. I am using the term protein. But they are also metalloenzymes.

The fluorophore we attached at a precise position. This is possible because we know the structure of the protein or metalloenzyme. So, we know the distance between the active site and the fluorophore probe attached at the surface of the protein. Suppose, there is a tryptophan near the active site. Tryptophan is fluorescence active amino acid. When the enzyme is working, this tryptophan molecule will take certain orientation and when the protein is not working tryptophan will take a different orientation.

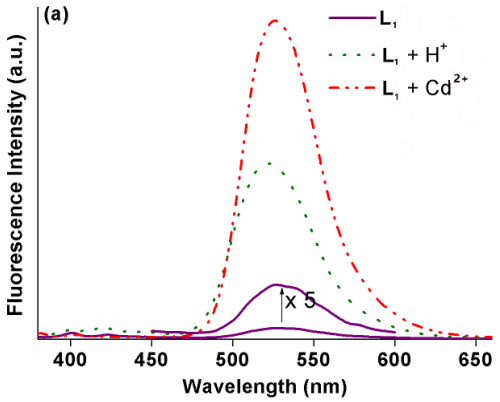
Now the phenomenon of FRET. Our present system has two chromophores. If we excite the probe, it will emit radiation. If there is an overlap between the emission band of the probe with the absorption band of the tryptophan, then there will be a resonance energy transfer and we will see emission of tryptophan. Let us see by a diagram:



As per this diagram, if we excite fluor1 then Fluor2 will emit. So, emission spectra of one fluorophore means natural fluorophore, emission spectra of natural fluorophore and absorption spectra of my fluorophore they have some overlap, they have some overlap this is blackened. In that case energy will be transferred from this excited state to the fluorophore 2. I will tell you again: there are two fluorophores fluorophore 1, fluorophore 2. If the emission spectra of fluorophore 1 overlaps with the absorption spectra of fluorophore 2, then there will be energy transfer from fluorophore 1 to fluorophore 2. That means fluorophore 2 is excited and it will give emission. This is called Förster resonance energy transfer in short FRET. This process of FRET works in solution phase. Most importantly, efficiency of FRET will depend upon the distance between the two fluorophores and the two fluorophores must be oriented properly. So from the intensity of emission after FRET will give us valuable insights about the orientation of the fluorophore at the active site because we know the orientation of the fluorophore we attached at the surface of the protein. FRET can be studied quite well in cryptand based systems.



L_1



In presence of Cd^{2+} which will go inside the cavity, will stop PET and give a strong emission from anthracene upon excitation. But, if there is another fluorophore nearby which has an overlap of its absorption band with the emission band of anthracene, FRET

will occur and emission due to this nitro containing fluorophore and no anthracene emission. This is shown in the Figure on the right.

So, I will stop and start this topic again tomorrow in my next class. Thank you very much.