Supramolecular Chemistry-I

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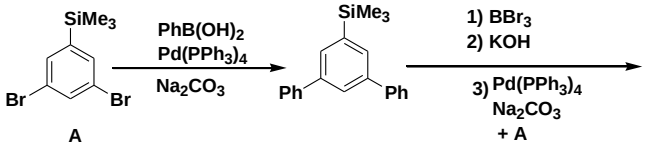
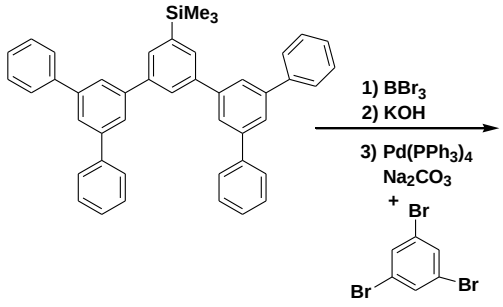
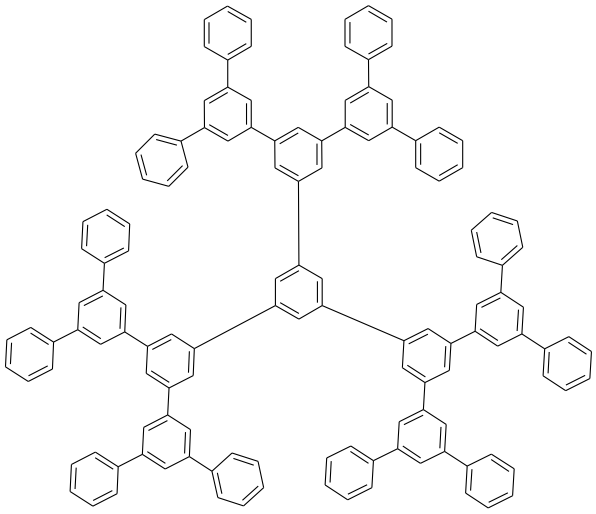
Week - 04

Lecture - 20

Good morning. So, I just mentioned that we can synthesize a dendrimer adopting a divergent method. Today, I shall discuss the convergent method. In the convergent method has been adopted where the branched polymers are grown from "outside in" i.e., if four identical units converge on a single core unit forming four covalent bonds, then a first-generation dendrimer is formed:







The repeat branching units can allow high guest uptake and the core experience the unique microenvironment provided by the dendrimer branching units to enable one to study the effects of microenvironment on the guest inclusion.

We have been discussing different supra molecular synthons. Let us just recapitulate for some 5-10 minutes. First we discussed macrocycles. In macrocycles we used crown ethers and different other macrocycles for example, aza macrocycles, thia macrocycles, azathia macrocycles, etc. Then we took macrocycles with pendant arms, 1 or 2 arms and these are called lariat ethers when the macrocycle is a crown ether. But generally, we use this term pendant arms. Then we discussed macrobicycles that is cryptands and cyclophanes. So, after cryptands of different kinds, we mentioned sperands. Sperands have spherical shapes and are very rigid structurally. We did calixarenes, cyclodextrins, cucurbiturils, rotaxanes, catenanes, entangled structures and finally dendrimers. So, we did several items which are called supramolecular synthons. So, with these supra molecular synthons we will now use them in different supramolecular situations ok?

Our aim is to extract some useful properties out of these systems. So, we can make use of them because you have understood that unless we can make use of the compounds that we are making those compounds will be rather useless ones. So, from today onwards I will start usefulness of these compounds in different situations.

Fluorescence, sometimes also known as luminescence, is an important technique. This is an important technique through which we connect to the microscopic world. Whatever is happening in the microscopic world we can monitor that by fluorescence with purposely built systems. And you know that fluorescence is a very sensitive tool—the reason I will explain to you. The sensitivity comes from the mode of measuring the emission spectra. If you are measuring UV visible absorption spectrum, are not very accurate because we measure the amount absorbed with respect to the solvent. Fluorescence is extremely sensitive because we are measuring the entire radiation generated by the molecules when it comes down to the ground state from the excited state.

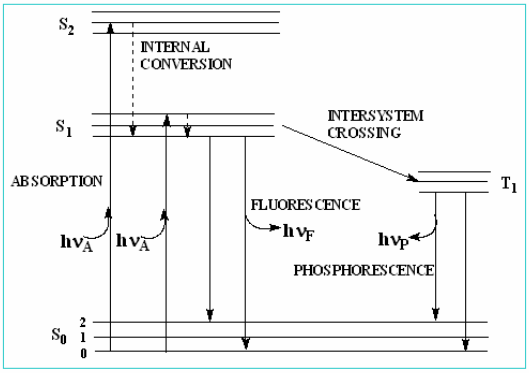


Figure: Jablonski diagram

Before we talk about fluorescence the most important thing about fluorescence that we have to write a diagram that is called Jablonski diagram. Let me write a simple form of the Jablonski diagram as shown above. So, here is your electronically ground state (S_0); this is electronically first excited state (S_1) and second excited state (S_2); these are vibrational levels first electronically first excited state. So, when we excite the molecule with radiation will it will go to these excited states. Molecules reach the state S_2 , will come down to the S_1 state called internal conversion. So, upon excitation molecules can populate S_1 as well as S_2 states but eventually through internal conversion they all come to the S_1 state. Now there is another state which I am coming to later is called the T_1 state or the triplet state. This state gets populated from the state by a process called intersystem crossing.

Molecules from the S_1 state will come down to the S_0 state giving fluorescence. Molecules from the triplet state can also come down to the ground state giving phosphorescence. So, this Jablonski diagram I have here is approximate and actually it is really a complex one. Now the question is does it mean that all molecules will give fluorescence? Usually fluorescence lifetime is 10^{-8}-10^{-10} seconds. But, any molecule if we excite they will be excited to say first excited state that is called absorption spectroscopy. What happens to those molecules? Do they give fluorescence? No, because in those cases their lifetime is almost 10^{-12} seconds or less. These molecules come down to the ground state via non-radiative pathways giving off heat. So, fluorescence is a property of molecule which we call fluorophores. That is why not all molecules give fluorescence, but only certain molecules give fluorescence we call them fluorophores. How about phosphorescence? Phosphorescence is a much-delayed process because transition is from triplet to singlet state. Since, spin multiplicity is changing that is why that is a difficult process. So, before phosphorescence comes fluorescence has already taken place. Another important thing, that when I have written the lines I tried to put them vertical. Why vertical? Because this axis gives us an idea about nuclear separation of atoms in the fluorophore during transition. Because nuclear nuclei are very big compared to electrons. So, nuclei are slow moving, but electrons are very tiny particles they move fast. Therefore, we assume that the nuclei are stationary while electronic transition are occurring. This is called the Franck-Condon principle.

So, you have to know this Jablonski diagram. I do not expect you to know in detail, but at least some salient features of the Jablonski diagram. Now we see how to make use of this fluorescence phenomenon in purposely built systems.

I will start mechanism of sensing in my next class. Thank you very much.