Supramolecular Chemistry-I

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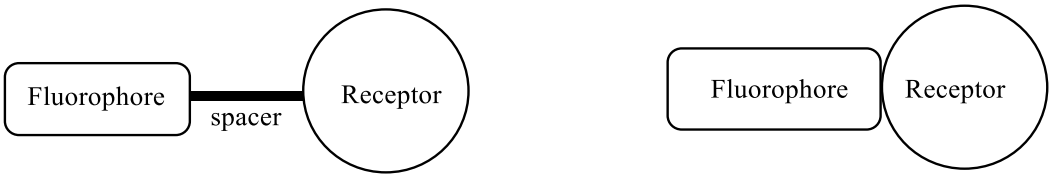
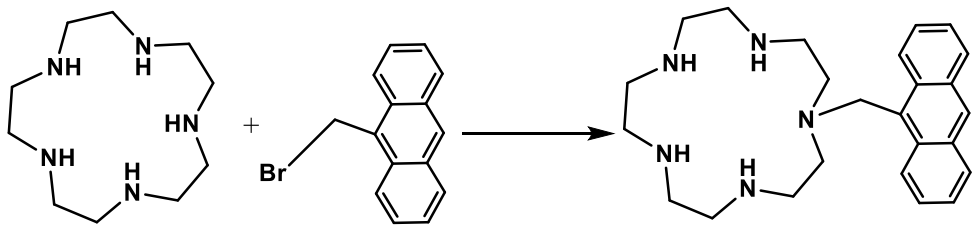
Week - 05

Lecture - 21

Good morning and welcome to the class. So, in the previous class I talked about fluorescence, what is fluorescence and all that. Today I will be discussing mechanisms of fluorescence signaling, how and on which mechanism they work and all that. The most important one we will be discussing first is called photoinduced electron transfer mechanism. In short, we say it is a PET mechanism. In a PET mechanism what happens we will mostly be discussing with spacer ok, but that is equally applicable to integrated systems as well.

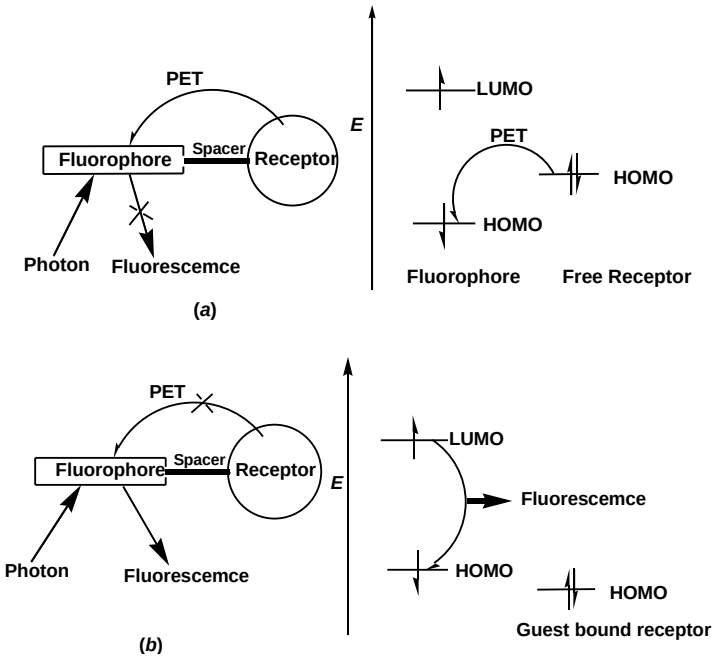


We have here a receptor, spacer and a fluorophore as one system and fluorophore receptor integrated another system. Typically, the receptor we use have one or two nitrogen's and they are attached to fluorophore through a spacer like methylene. As an example, suppose I make an aza 15-crown-5 attached to a fluorophore through a methylene spacer. My receptor is good for sodium ion due to matching size. And what is a fluorophore? Usually we take multi aromatic systems, for example, we take anthracene. Anthracene is a very good fluorophore because it can be excited at around 400 nm and it gives emission in the visible range.



We take bromomethyl derivative of anthracene, i.e., 9-bromomethyl anthracene. And in presence of a proper base and equivalent of the anthracene derivative, we can get the

anthryl group attached to this particular macrocycle. So, here is a fluorescent signaling system that will work on a PET process for the sodium ion. So, let me describe the PET process now and description will be quite easy if you take the frontier orbital diagram.

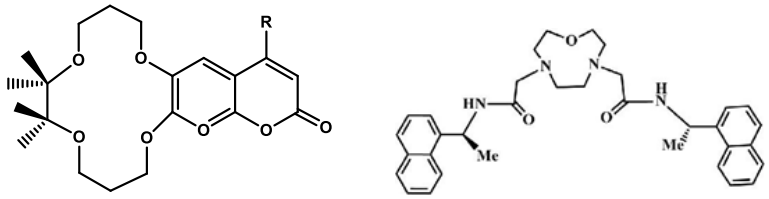


So, the frontier orbital diagram is drawn here. Here is LUMO i.e., lowest unoccupied molecular orbital and here is HOMO (highest occupied molecular orbital). The HOMO of the receptor is also shown. So, this HOMO has character of mostly the electron pair on the nitrogen. So, this is the beginning and HOMO is completely occupied. And the spacer in this case actually work to transduce or to pass the information from one component to the other alright. Now, I excite my anthracene fluorophore at a particular wavelength. Upon excitation, one of the electrons from HOMO will go to LUMO. So, one electron from the receptor lone pair will go to the HOMO of the fluorophore. This process is called PET process or photo induced electron transfer process. The single electron in the LUMO of the fluorophore comes down to the receptor HOMO giving heat radiation. And we are back to the situation as in the beginning.

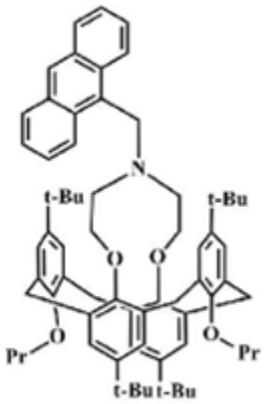
But if I put a sodium ion in the receptor cavity, sodium will engage the lone-pair because it will form chemical bond with sodium. So, what will happen to the HOMO of the receptor containing the lone pair? It will come down in energy below the energy level of the HOMO of the fluorophore. Because, when the electron density is taken out from an orbital its energy lowers because it gets stabilized. So, PET is not possible anymore. Therefore, when I excite it now this one of the one of the electrons goes to LUMO, and it comes down giving a strong fluorescence. So, this is the frontier orbital diagram of the PET process. Basically therefore, when the receptor is empty, and the fluorophore is excited we do not see emission. But

when the receptor is occupied, PET is stopped, and we see a strong emission upon excitation of the fluorophore.

Another job of a supramolecular chemist's job is to find a receptor specific for a metal ion. The receptor shown below is quite specific for lithium ion. Lithium ion is very important for patients suffering from manic depression. But, we cannot overload a patient with Li^+ ion. Depending upon the body weight, 0.6 to 1.2 millimoles of lithium will be safe for effective use. To quantify this lithium intake, we have to resort to fluorescence. Concentration of the metal inside a human body can be known from the intensity of emission.



We have here two lithium sensors where the left one has coumarin and the right one has naphthalene fluorophores. The two receptors shown here are specific for Li^+ ion without interference from Na^+ and K^+ already present in the biosystem. We can use another supramolecular synthon to fabricate another Li^+ specific sensor as shown below:



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So, thank you for today's class where I have done lithium and then a similar way we can do sodium, potassium and so on alright. Thank you.