Supramolecular Chemistry-I

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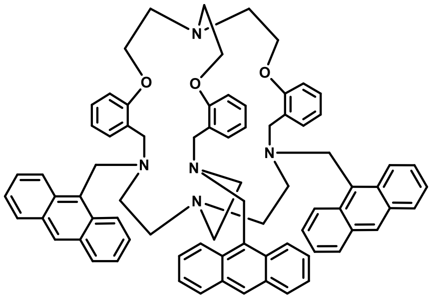
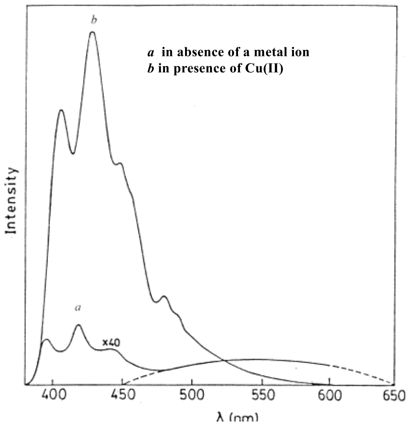
Week - 05

Lecture - 24

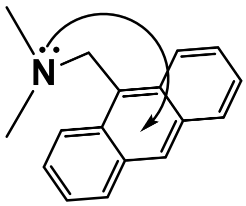
Hello, good morning again. In my previous lecture, I told you about the cryptand based fluorescence signaling systems. Today we shall discuss two more phenomena associated with fluorescence.



The first issue is known as exciplex. Exciplex stands for excited state complex. Look carefully at the following emission spectra obtained with the above system. We find a broad band centered around 550 nm in the metal-free system which is absent when Cu^{2+} is added.



This broad band around 500 nm is the exciplex band. The other band with vibrational structure is called monomer emission band. When no metal is added, the monomer emission band vanishes because of PET being operational. In that case, the nitrogen lone-pair interacts with the π-system of the fluorophore anthracene as the following figure illustrates.



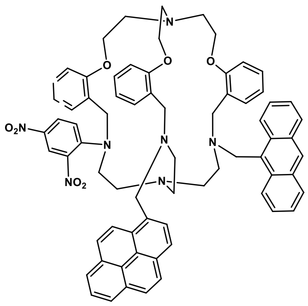
In this case, the band is broad as the fluorophore can move around the single bond easily. When a metal ion is added, the lone-pair on N is engaged to the metal through metal-nitrogen bonds and is not available for exciplex formation.

In the monomer emission, we find three bands. The middle one is called the 0-0 band and one more band on either side are vibrational structures of the monomer emission. This is for anthracene only. For other fluorophores, we get different emission band fine structures.

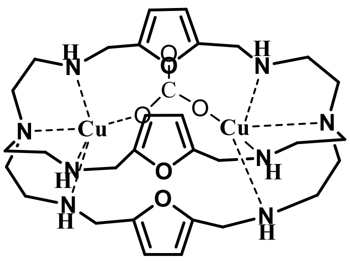
Appearance of exciplex is also very important in certain situations. I will talk about that later in some other systems ok?

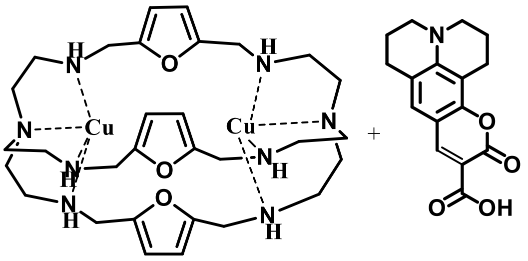
Another aspect of emission band is called excimer emission which is also very important. The term excimer is the short form of excited state dimer. So, we can have an excited state complex and excited state dimer. In a concentrated solution of the signaling system, two or more units can come together where the anthracene moieties can stack over each other giving rise to excimer. An excimer band will disappear if we dilute the system with solvents.

Another thing. For such systems where anthryl groups are present, we do excitation spectra. The excitation spectra of this system will be mirror image of absorption spectra if the compound has not decomposed under radiation meaning my compound is photo stable. Although the cryptand has poor chemo-selectivity, it has been found that when we derivatize it as shown below, the cavity becomes rigid.



When the cavity becomes rigid, it allows only Cd^{2+} ion inside the cavity and it becomes specific for Cd^{2+} ion. Now I shall describe another interesting system.





When we have the dicopper cryptate and add the coumarin derivative, it forms a complex inside the cavity through binding to the coumarin derivative. If in this situation, we excite the coumarin fluorophore, no emission spectra is observed. because copper is transition metals so quenches fluorescence. But if I allow it can take up carbonate from or you can give excess carbonate which fits perfectly here that is why it will displace coumarin. Now if we excite coumarin we can get a strong emission signal. So I will take up from this point onwards in my next class. Thank you.