Supramolecular Chemistry-I

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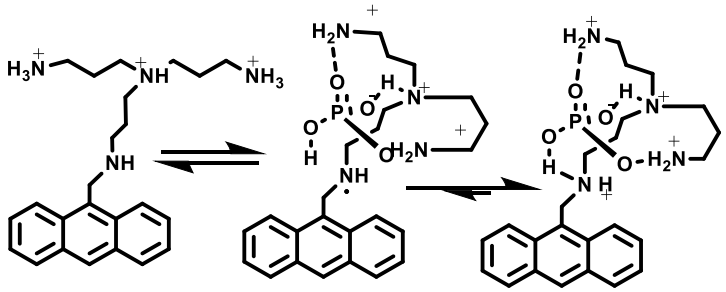
Week - 06

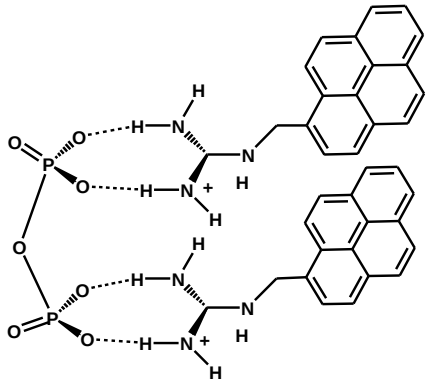
Lecture – 27

Welcome back to the class. So, what did I do in the last class that we have synthesized a dye if you will or a fluorescent signaling system that can detect up to 3 ppb of Hg^{2+} in water and that particular dye has almost 100 percent cell viability up to a very concentrated solution. So, this experiment that I described in my previous lecture we call it in vitro studies. In case of a in vivo study, we can take up the case of a person poisoned with something, say arsenic. Then we would like to know how much arsenic went into the body? For this, we have to synthesize an arsenic specific fluorescence signaling system. Then we can progress like the case of mercury poisoning case. And since it is specific for arsenic, other metal ions present in the body will not interfere with the experiments.

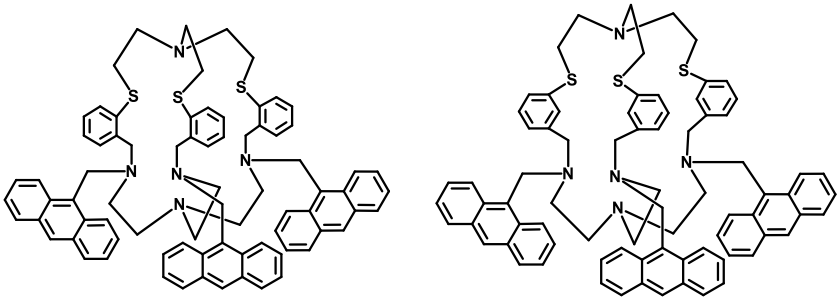
Similarly, for each metal ion, we need to have a specific receptor that can be connected to a fluorophore and we follow the procedure elaborated in my previous lecture. How about anions ? In oxidative phosphorylation cycle, phosphate and pyrophosphate are important metabolites and their concentration in vivo can indicate the physiological condition. So, we need to find out receptors for anions.



The phosphate anion, HPO_4^{2-} receptor is shown above. Here, the fluorophore is anthracene, and the PET mechanism is operational. The phosphate anion binds to the receptor stopping the PET and showing a strong fluorescence. So, phosphate can be detected. For pyrophosphate anion, $P_2O_7^{4-}$ we have a new receptor, as shown below:

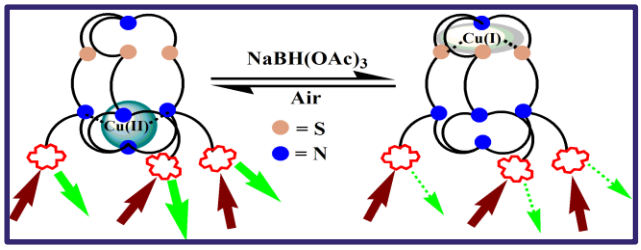


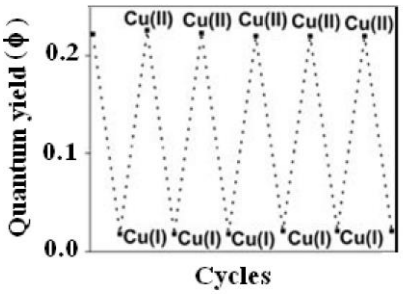
Here, a guanidinium moiety is connected to a pyrene ring. Why pyrene ring ? Because, pyrene rings have a great tendency to stack giving rise to excimer band (excimer = excited state dimer) as it has a large π-surface. Two of these systems connect to one pyrophosphate unit through hydrogen bonding. There will be no PET possible as the relevant N atom is protonated. But two of these systems will come together due to H-bonding interactions with one pyrophosphate anion and the two pyrene units will form stacking leading to an excimer band when pyrene is excited. This will help detect the pyrophosphate anion. We now want to make reversible fluorescence signaling. But how ? If you recall, when a metal ion can come out of a cryptand cavity and go inside again under some circumstances, we can make reversible fluorescence signaling. Here we show an excellent system. I have two cryptands as follows:



I want my fluorescent signaling system reversible with transition metals ok ?

In these cryptands, Cu^{2+} ion binds the tren moiety that supplies four N donors while the NS_3 moiety prefers to bind Cu^{+} ion. So, this knowledge we had alright? So, we went ahead and made these two fluorescent signaling systems.These two are PET sensors. When Cu^{2+} ion is bonded to four N donors, the PET is blocked and we get a strong emission.





Next, we reduce the Cu^{2+} to Cu^{+} with a mild reducing agent, $NaBH(OAc)_3$. We have seen that this can reduce copper +2 to copper +1 state. Now as soon as we give this reducing agent after sometime what happens? All copper +2 is converted into copper +1 and being copper +1 they move to the other end having NS_3 donors. So, now PET takes place and emission is gone. Now we leave it in the air. In air, copper +1 is not very stable in THF medium. So, copper +1 will be oxidized to copper +2 again. As soon as it goes to copper +2 it moves to the end having 4 N donors. The again, lone pair of N will be engaged to copper +2 blocking PET and we see strong fluorescence. So, chemically we can reduce copper 2 to copper 1 and it goes from one end of the cavity to the other end. So, we see strong fluorescence when in one end and when in the other we see no fluorescence. So, we can get a reversible fluorescence signaling system. So, these things are very important for making molecular machines. So, I stop here today and next time I will from this point onwards I will elaborate again and go to other systems. Thank you very much.