Supramolecular Chemistry-I

Prof. Parimal Kanti Bharadwaj

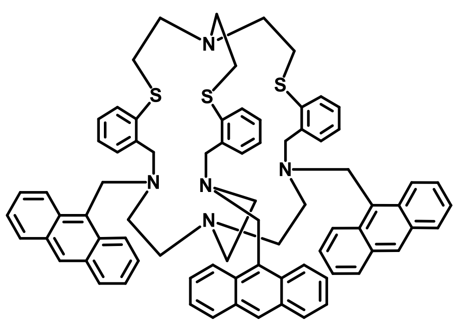
Department of Chemistry

IIT Kanpur

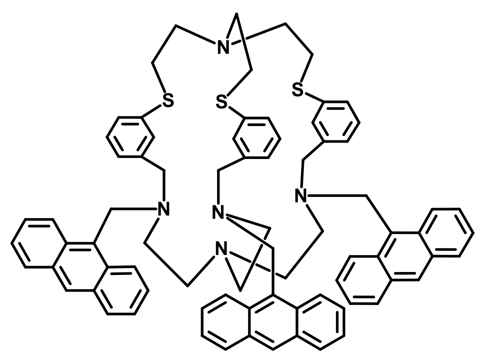
Week - 06

Lecture - 28

Hello, good morning. So, previously we talked about the particular system where one end provides NS_3 and the other end N_4. And different times we have to take care of different properties of metal ion and the compound itself. So, today I will show you other reversible systems. Anyway before I show you other reversible systems, some very important points about these systems. So, in this system what happens is the metal ion can go from one position to the other. We showed two cryptands.

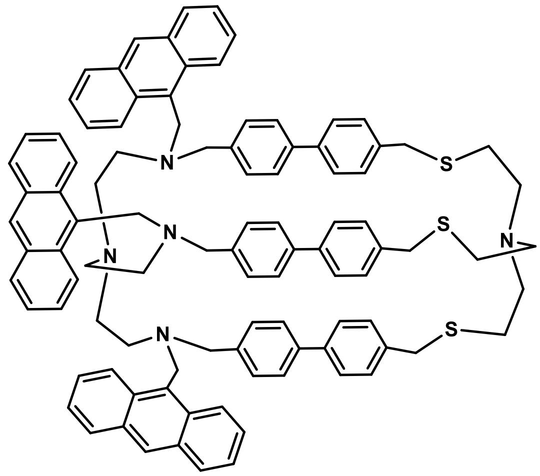


I

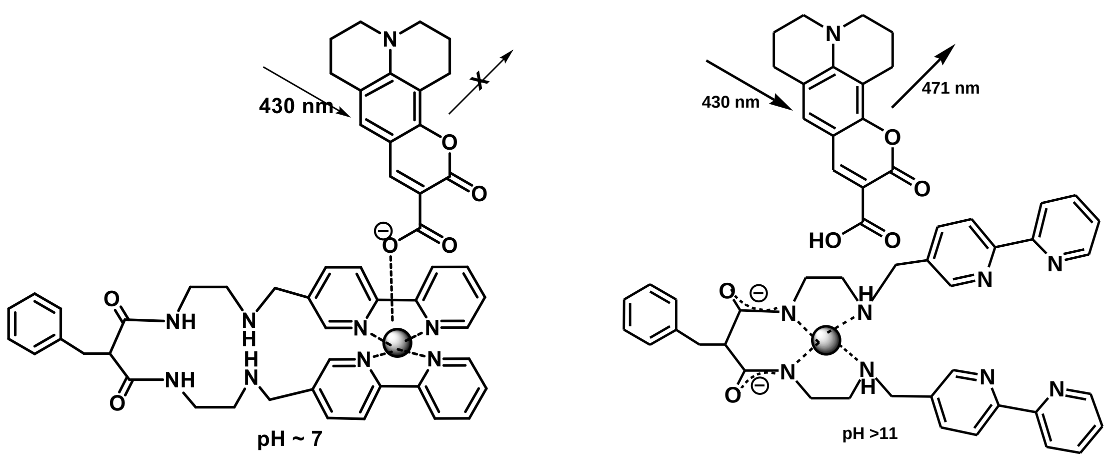


II

So, you give some energy in the in this present case, I am reducing it copper 2 to copper 1 and it is going from one end to the other. Then again upon air oxidation, it returns to the original end. This kind of systems are very important in fabricating different molecular devices, molecular machines and so on. Now, the question that comes to our mind, how long it takes from one end to the other? Well, unfortunately it takes about 18 hours for I and about 15 h for II. In II, it is meta substituted, and so the cavity is rigid so takes less time. So, more rigid cavity in this case. So, therefore, it takes less time. When we go to the next example as shown below:



Here, we have two aromatic groups instead of one and it is quite rigid. So, here the movement takes less than 30 minutes. Wonderful, Our aim will be to make it few seconds that can be possible with better designs. So, I encourage all of you to design and then you can make some interesting systems. Let us see if we can make reversibility of fluorescence with Ni^{2+} ion. At pH ~7, Ni^{2+} ion binds at the site providing 2,2'-bipyridyl



and at this site it further accepts a coumarin derivative. Since, the coumarin derivative is directly bonded to Ni^{2+}, no fluorescence is observed when coumarin is excited as square pyramidal Ni^{2+} will be paramagnetic. At pH ~11, the amide protons will be lost. The deprotonated amide N is a strong donor. So, the $Ni^{2=}$ ion will move from 2,2'-bipyridyl site to the amide site. And at this site, Ni^{2+} is quite happily bonded by square planar geometry and the coumarin is free. The free coumarin shows strong emission upon excitation. When the pH is lowered, the metal ion will move to the dipyridyl side once again and this way reversibility of fluorescence will be maintained.

Yesterday, in the previous class I showed you how mercury specific system that can detect mercury up to 3 ppb that can detect and that is very useful in detecting mercury. In Japan, there is a place called Minamata Bay which is an industrial hub. The effluent from industry contained mercury which used to go into the sea. Fishes will take that water and when human consume that fish, mercury will enter into the human body. This caused tremendous pain and eventually people used to die of mercury poisoning. So, with systems to detect mercury can be used to see whether this element entered human body.