Supramolecular Chemistry-I

Prof. Parimal Kanti Bharadwaj

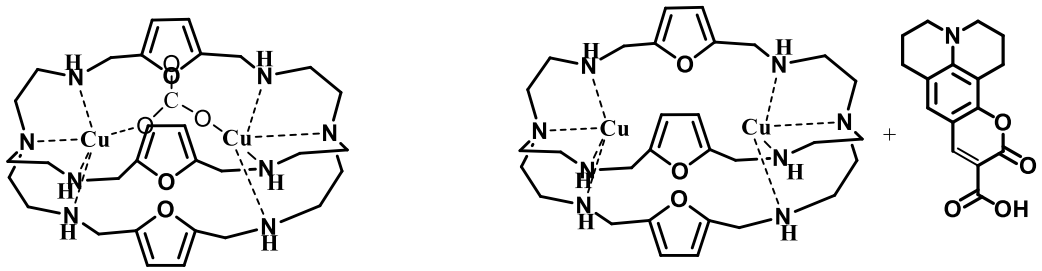
Department of Chemistry

IIT Kanpur

Week - 05

Lecture - 25

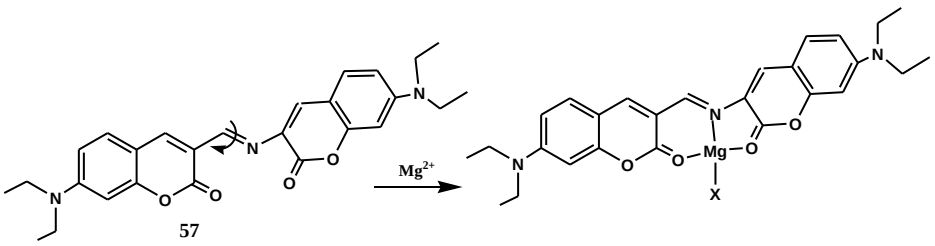
Good morning. So, in my previous class I was looking at this carbonate sensor. You take this cryptand and then make a die copper complex die copper cryptate. This die copper cryptate the distance between them distance between the two copper and the distance between this carbonate and carbonate moiety this distance is optimum. So, that carbonate forms a very strong complex with copper. So, this is the situation.



Now, when we add coumarin the coumarin binds to the copper ions. Now, let me remove this carbonate first there is no carbonate. I have only there is no carbonate I have only coumarin and this copper 2 cryptate.

So, this coumarin binds to this carboxylate coumarin derivative is called coumarin 343 . The carboxylate will bind to the copper 2 centers and since it is a negative and copper 2 is positively charged. Therefore, there is a strong attraction to bind. Then, when we excite coumarin it goes to excited state, but no fluorescence because of the interactions with paramagnetic centers it comes down to the ground state by non-radiative pathway.

So, when there is nothing only coumarin and this copper 2 cryptate no fluorescence upon excitation, but now I put carbonate in the system. Carbonate binds much better than carboxylate. The carbonate kicks out coumarin which goes outside. So, now, when I excite it gives strong fluorescence because there is nothing to quench. Therefore, this is another mechanism. And now is another excellent mechanism. Let mw draw the molecule first as follows:

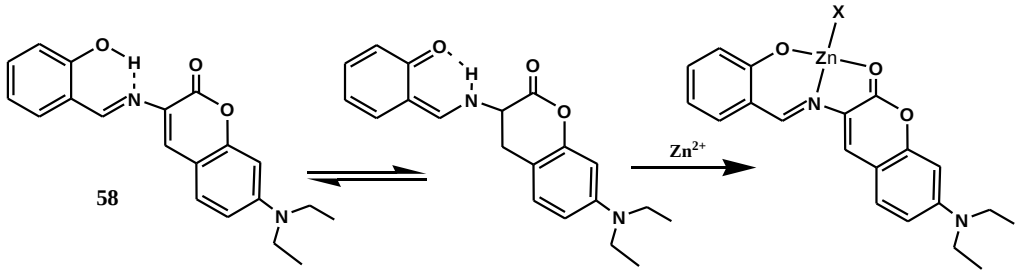


57

Here, we take two coumarin derivatives where one containing aldehyde and the other an amine. This aldehyde and amine reacts to form an imine linkage with two coumarins at the two ends.

Now upon excitation of this system, the imine double bond momentarily becomes a single bond and rotates to form the trans isomer. This rotation and changing of the isomer is a conduit to absorb the excitation energy and no emission is observed. Now, this moiety NO_2 is very specific for Mg^{2+} ion which binds strongly. Now if I excite this molecule magnesium bound double bond remains intact. This also blocks the deactivation pathway of the excited coumarin. And upon excitation, a strong emission from coumarin is observed. So, the trick is to block the useless deactivation pathway during design of the signaling system. This is quite an important result because it can detect Mg^{2+} in biosystems.

So, I encourage you all whenever you do the fluorescence not only PET, but there should be many other mechanisms which you must look into. then I am telling you another mechanism. So, different types of mechanism means your first idea is if I excite is there any pathway that it can take to deactivate? If yes, then the excited molecule will come down to the ground state without giving fluorescence. So, you have to stop that pathway.



58

The coumarin derivative shown above works on the principle of Excited State Intramolecular Proton Transfer (ESIPT). The metal free ligand shows very weak fluorescence due to ESIPT. On addition of Zn(II) ion, this process is stopped, and concomitant fluorescence enhancement is observed. When I excite this coumarin system one hydrogen is transferred from oxygen to nitrogen that is why with nitrogen now I have

a solid line and I have a dashed line with oxygen. So, whenever there is ESIPT mechanism possible that means there will be hydrogen transfer from oxygen to nitrogen and then from enol it becomes keto. So, all these things require energy. And the excited coumarin is deactivated. ESIPT stands for excited state intra molecular proton transfer. Now, I add zinc ion that will bind the way shown. Sine now hydrogen is gone and no question of excited state proton transfer. So, in absence of excited state proton transfer if I excite this coumarin I see a very strong fluorescence. What problem will happen if I put Ni^{2+} or Cu^{2+}? They will cause paramagnetic quenching and that is why Zn^{2+} is used and this is zinc specific. So, first one was stoppage of double bond rotation and here it is stoppage of intramolecular proton transfer.

So, I encourage you all that you when you do sensors for metal ions or anything or anions or neutral molecules you please look at this principle that I have shown to stop deactivation pathway. Thank you very much.