Supramolecular Chemistry-I

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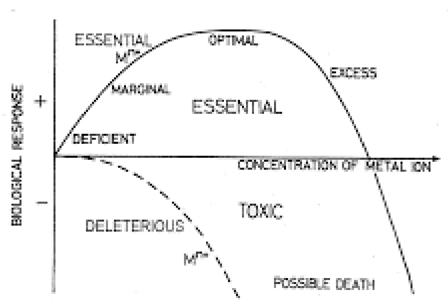
Week - 05

Lecture - 23

Welcome to the class. So, we have been discussing alkali metal sensing. Now, we come to an important one- transition metal sensing. I want you to have an idea about these metal ions. What do they do in biology? Sodium ion and potassium ions are very important and so are some of the transition metals like copper, zinc, iron, and so on. These are some of the essential transition metal ions.

These are called Bertrand curves for essential metal ions and they perform many essential biological functions. I will show you today one curve, it is in bio-inorganic chemistry, but that is fine. I am showing you a curve for a particular metal ion.



Biological response dependence on the concentration of an essential nutrient (solid curve) and of a deleterious substance (dashed curve)

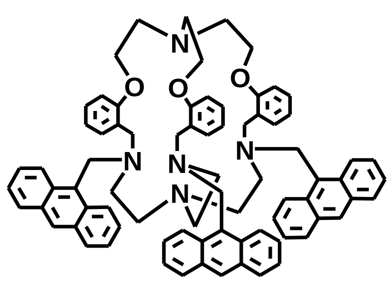
Say this is the curve for copper. So, when copper is in very small amount, there will be copper deficiency. It also gives an optimum range for this metal in a biosystem. But when copper is present in excess, then that might lead to Wilkinson's disease, Parkinsonian, so many problems. So, we cannot have very small amount of copper, then it will be copper deficiency. We cannot have large excess of copper in our body, then we can have disease. You must have heard about this one. This curve is called Bertrand curve. Each metal has its own unique Bertrand curve. I just want to emphasize that essential metal ions within a concentration window function properly in biology. Through fluorescence, we can detect if there is excess or less amount of a transition metal is present. So, that is why this is very important. Now, I will tell you the problems with transition metals. Transition metals especially paramagnetic ones quench fluorescence very effectively. Quench means if something gives fluorescence, then if transition metal is there, it will quench that and we do not see any emission. If we want to put a transition metal and then we see strong fluorescence, then that is very important and you will be glad to know that in the world, we are the first from IIT Kanpur who made systems where transition metal induced fluorescence enhancement was possible. Since then, many people have done.

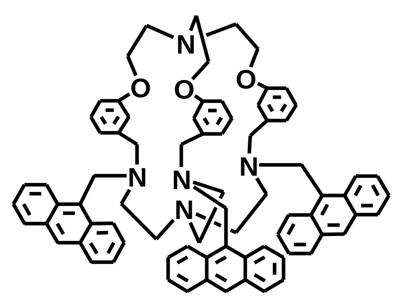
There are several mechanisms to account for the quenching. These are:

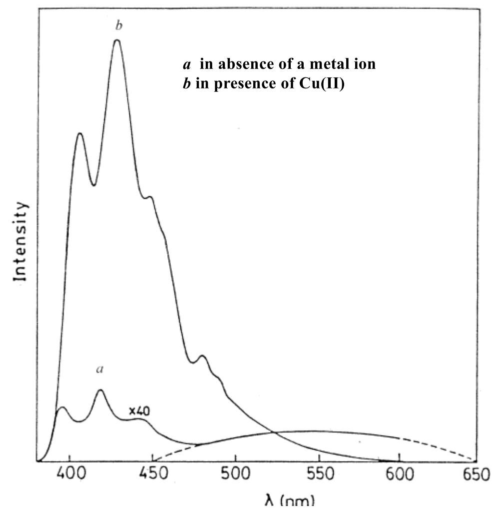
1. Conversion of electronic energy through collisions. But we generally take 10^{-7} M solution. So, the collision probability will be low.
2. High spin-orbit coupling can quench emission.
3. Then number three is redox perturbation. Transition metals are redox active. So, redox perturbation can also quench fluorescence.
4. Perturbation by paramagnetic means unpaired electrons.
5. Formation of charge transfer complexes and
6. Transfer of electronic energy to the metal ion to and from metal ions or ion. So, these are some of the mechanisms of quenching for transition metals.

   All these means that metal receptor interaction is very high and metal fluorophore communication should be very low.

   So, to alleviate these problems, we synthesized the following systems for transition metal induced fluorescence enhancement by transition metal ions.







We earlier talked about the characteristics of metal binding by cryptands that is when metal is inside the cavity, it is covered from all sides. So, it is isolated from surroundings and the anthryl group is outside. So, anthracene cannot interact with metal inside the cavity. Therefore, we see a very strong fluorescence upon excitation. Since then, instead of anthracene, we have done with pyrene, coumarins, etc. Depending upon what wavelength we want, we can choose the fluorophore. So, fluorophore is just reporter here. It reports to us, what is happening in the microscopic world.

One problem is that the cryptand receptor has poor chemo selectivity. I stop here today and next time I will do more of this. We take a look at directly take a look at these things again. Thank you very much. Thank you.