Supramolecular Chemistry-I

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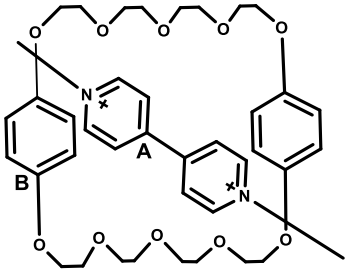
Week - 01

Lecture - 02

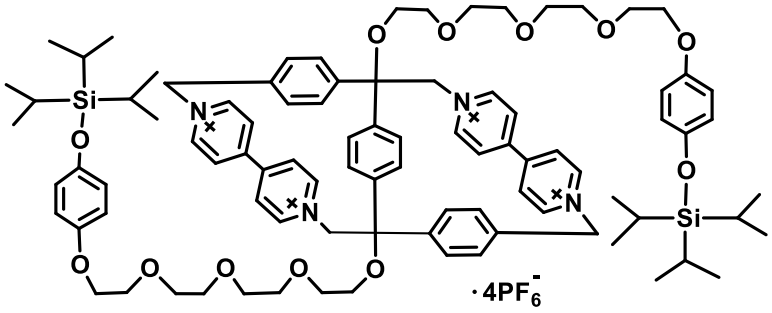
As we discussed in the previous lecture, we are trying to find out definition of supramolecular compounds. So continuing with that let me draw these pictures.

In the previous lecture, the Figure I had drawn is the following:



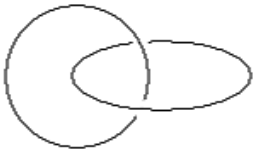
2-pseudorotaxane

This compound has one cycle, and a linear compound that goes through the cyclic compound. The oxygen atoms are electron rich; so they are electron donor and this nitrogen positively charged are electron acceptors. So they will make a complex and in common terminology, we say that this is an adduct and this particular adduct we call as pseudo-rotaxane. This is 2-pseudo-rotaxane because there are two units; one cycle and one linear chain.

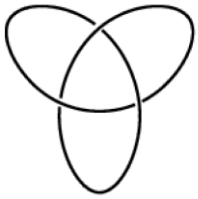


2-rotaxane

It is similar to the previous one except the linear part is quite long and at the ends we put tris-isopropyl silyl groups. Why? Because it will act like a stopper. This species we call a 2-rotaxane. So now, what we find? We find that here is a macro cycle inside this long chain organic compound. Now in the case of pseudo-rotaxane we have dawn above, can disintegrate in a particular solvent at may be higher temperature and we get the two components back. But, in case of this 2-rotaxane it will not separate as two entities because the two stoppers will not allow this macro cycle to go out. So even though in both cases, you can see that they are similar type. However, a pseudo-rotaxane is a simple adduct of two compounds and a rotaxane is a supramolecular compound because its properties are very different. The macrocycle can move along the linear component leading to interesting properties. Now we show other systems as follows:



2-catenane

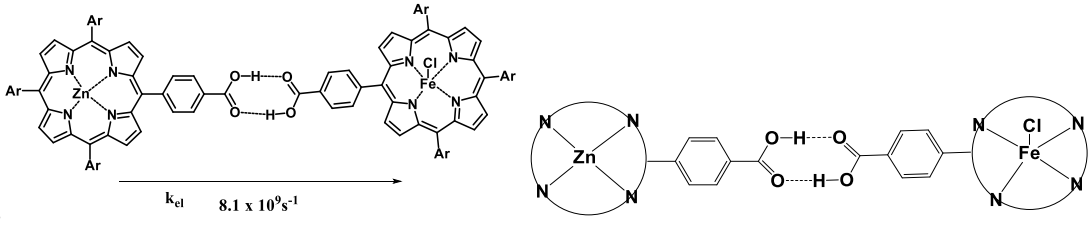


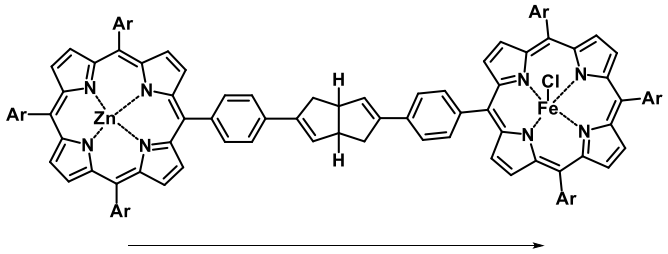
trefoil knot

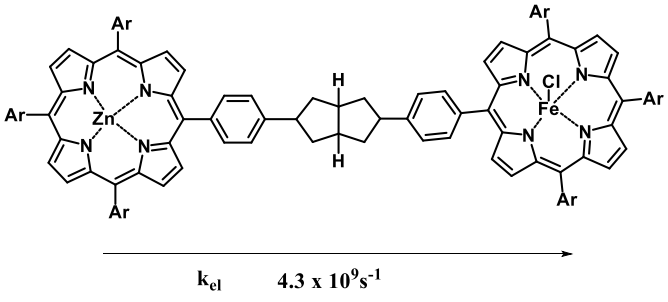
In the first system, we see two cyclic compounds are locked. They are mechanically locked forever, but there is only covalent bond here; no intermolecular forces. So, this particular compound we call as 2-catenane. It is a supramolecular compound as its properties are very different from simple macrocyclic compounds. How about the system shown in the right ? This is kind of tricky to draw, nevertheless, I can draw it. This is called a trefoil knot structure. Both these are examples of supramolecular compounds. By the way, this person Jean-Pierre Sauvage who is a student of Jean-Marie Lane and also got Nobel Prize recently for his work on catenanes. These are very important compounds. They have important properties which I will discuss as we go along.

Let me give another example as shown below: On the left side I have drawn the molecular structure. On its right is its cartoon form. Both are identical. In future we can manage with the cartoon form to save time.

1.



2. 

3. 

In these three figures, the first compound is actually a dimer where two molecules are H-bonded. So, immediately you will jump and say that this is a genuine supramolecular compound.

The second and third compounds have no intermolecular forces. And so, looks like it is a covalent compound. The third compound, is again a covalent compound. Now, we tend to comment that the first compound is a supramolecular one while the other two are simply covalent compounds. All these three compounds are what we will learn later are called molecular wires where electron transfer takes place under certain circumstances from the Zn^{2+} center to the Fe^{3+} center. You look at the electron transfer rates as given (E_{el}) for the three cases are similar. So, all these three compounds with similar electron transfer rates, are supramolecular compounds. This is a fact even only the first one has intermolecular force (here, H-bond).

So, what I have been trying to tell you is that based on electronic structure. When two molecules are associated through intermolecular forces, then we call it supramolecular but now I am saying if molecules which are big and shows properties like a supramolecular compound, then they would be called supramolecular compounds. Therefore, what is a supramolecular compound? Earlier, the definition of a supramolecular compound was based on electronic structure but nowadays it is based on the properties of the compound as well. So now, you have understood. You can say that similar situations happen in organometallic chemistry. In organometallic chemistry, you know that Wilkinson's catalyst, **$[RhCl(PPh_3)_3]$**, is an organometallic compound but it has no metal carbon bond but still it is organometallic based on its properties.

So next day, I will start talking molecular recognition. Thank you.