**Supramolecular Chemistry-I**

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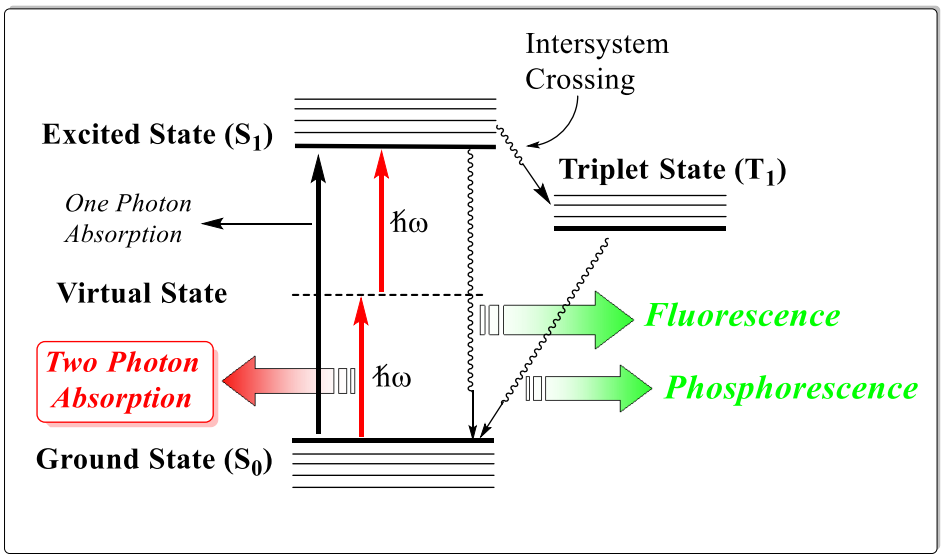
**Week - 07**

**Lecture - 33**

So, in the previous lecture, I was talking about various aspects of second order optical nonlinearity and molecules. You remember we talked about supra molecular synthons, macrocycles, calixarenes, cucurbituril, cryptands, and so on. There were many, I spent several lectures on those. So, each of those compounds have been derivatized with donors and acceptors. Basic thing is we have to make donors and π-acceptors that could be three dimensional. Even better, we can use phthalocyanine, porphyrins or simple aza macrocycles. So, all these compounds can be derivatized to have D-π-A systems and they will all give second order optical nonlinearity. So, my request to you will be you study these things in details. Their use of I will now discuss. One very important property of second order optical nonlinearity is known as SHG that stands for second harmonic generation. Suppose we take a second order optically active compound. Now if I allow an electromagnetic radiation of frequency $\upsilon_1$ through the compound then we can produce a radiation of frequency of $\upsilon_2$ coming out. This frequency will be twice that of $\upsilon_1$. That is called second harmonic generation. Of course, some other radiations of multiple of $\upsilon_1$ frequency can be produced with much lower intensity. This means if I put a light of 500 nanometer which is in the visible range, we can generate 250 nanometer light which is in the UV range. This will be very useful in several modern applications like laser spectroscopy, defense, optical telecommunication, etc.

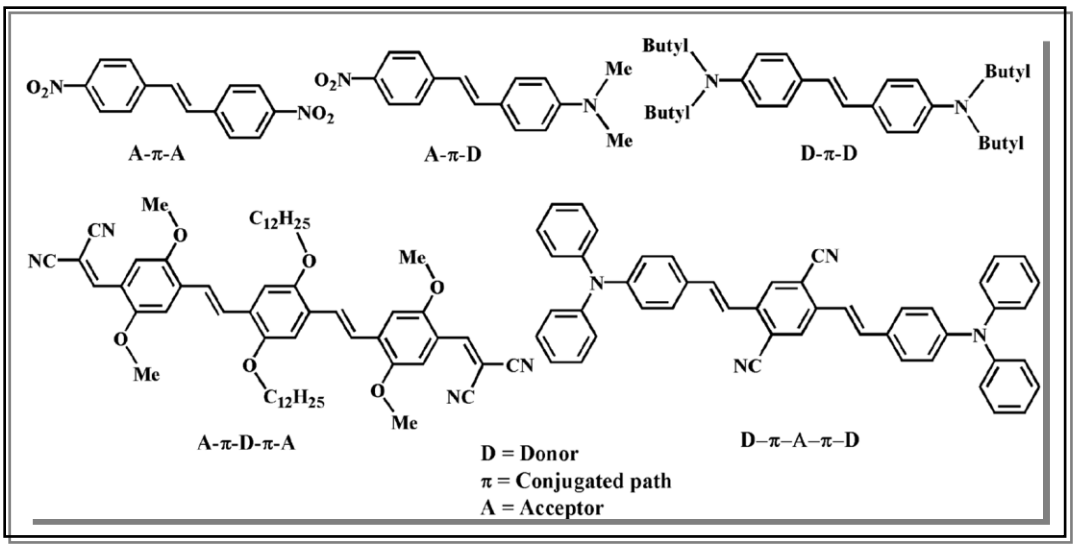
Third order NLO is again very important. Third order NLO can be useful in optical switching, optical data storage, mapping of cells, etc. While for manifestation of second order NLO activity the compound must be crystallizing in non-centrosymmetric space group but for third order NLO activity, there is no restriction for the compound to crystallize in non-centrosymmetric space group. That means whether it crystallizes in centrosymmetric or non centrosymmetric does not matter it will always show third order optical NLO activity. Third order NLO activity is measured in terms of two photon absorption cross section. This phenomenon is shown below by a diagram:

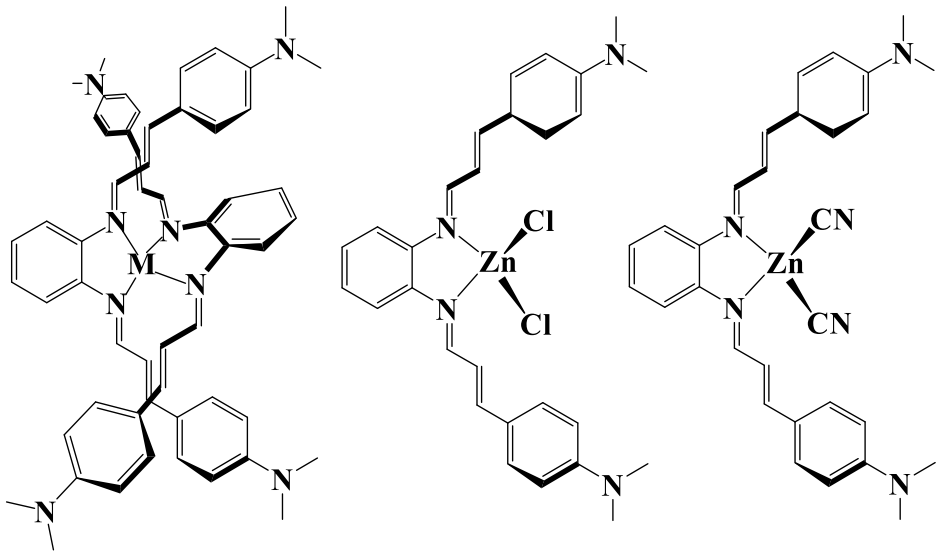



Two-photon absorption (TPA) involves the excitation of molecular species from the ground state ($S_0$) to the first excited singlet state ($S_1$) or to the second excited singlet state ($S_2$) by simultaneous absorption of two photons (Scheme 1.1). The efficiency of a molecule at the optical frequency $\omega/2\pi$ of this process is determined by measuring two-photon absorption cross-section, $\sigma^{(2)}$ value, which is related to the imaginary part of the second hyperpolarizability, $\gamma(-\omega;\omega,\omega,-\omega)$, by Eqn. 5.1 and its unit is GM (1 GM = $10^{-50}$cm$^4$.s.photons$^{-1}$. molecule$^{-1}$).

$$\sigma^{(2)} = \frac{8\pi^2\hbar\omega^2}{n^2c^2} L^4 \,\mathrm{Im}\,\gamma\left(-\omega;\omega,\omega,-\omega\right) \ldots\ldots \text{(Eqn. 5.1)}$$

where ħω is the energy of incoming photons, c the speed of light, *n* is the refractive index of the medium and *L* corresponds to local field factor. Sigma 2 is the two-photon absorption cross-section. A strategy for the design of molecules exhibiting large two-photon absorption (TPA) cross-section, was developed on the basis of symmetric charge transfer from the ends of a conjugated system to the middle, or *vice versa*. Upon excitation, a substantial symmetric intramolecular charge re-distribution takes place in these molecules resulting in high TPA cross-section. The search for molecular guidelines to obtain with symmetric D–π–D, A–π–D–π–A, and D–π–A–π–D conjugated structural motifs. The TPA phenomenon has focused mostly on organic dipolar, quadrupolar and octupolar molecules, dendrimers and porphyrins.



**1. M = $Zn(ClO_4)_2$** **3** **4**

**2. M = $Cu(BF_4)$**

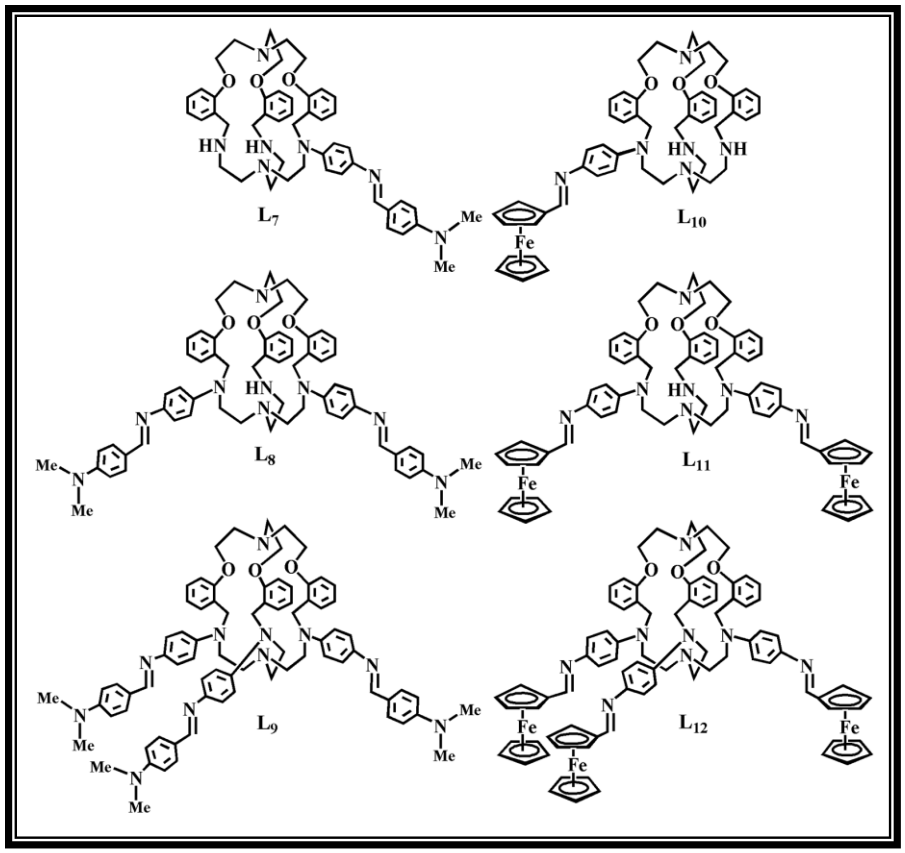
$\sigma^{(2)}(1) = 10736$

$\sigma^{(2)}(2) = 10198$

$\sigma^{(2)}(3) = 1769$

$\sigma^{(2)}(4) = 1700$

We always take $Zn^{2+}$ and $Cu^{+}$ as these ions do not show any absorption in the visible range. Otherwise, wrong values for TPA will get.


L7
L10
L8
L11
L9
L12