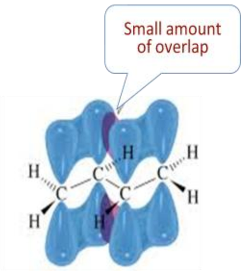
Chapter 1

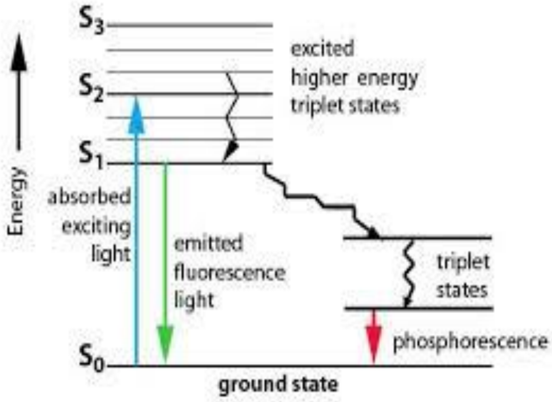
INTRODUCTION

Contents

1.1 Conjugated systems

In chemistry, a “conjugated system” means, a system of connected p-orbitals with delocalized electrons in compounds with alternating single and multiple bonds. This arrangement generally lowers the overall energy of the molecule and increases its stability. Lone pairs, radicals or carbenium ions may be part of the system. The compounds may be cyclic, acyclic, linear or hybrid. Conjugation is the overlap of one p-orbital with another across an intervening sigma bond. A conjugated system has a region of overlapping p-orbitals, bridging the interjacent sigma bond. They allow a delocalization of π-electrons across all the adjacent aligned p-orbitals. The π–electrons do not belong to one bond or atom, but rather to a group of atoms. Conjugated systems have unique properties that give rise to strong colours and the example of such system is the long conjugated hydrocarbon chain in β-carotene. When an electron in the system absorbs a photon of light of the right wavelength, it can be promoted to a higher energy level. Electrons occupying a HOMO of a sigma bond can get excited to the LUMO of that bond. This process is denoted as a σ– σ∗ transition. Likewise promotion of an electron from a π-bonding orbital to antibonding π-orbital is denoted as π-π* transition. Auxochromes with free electron pairs denoted as n have their own transitions. Hence there are following molecular electronic transitions: σ-σ*, π-π*, n-σ*, n-π* and aromatic π - aromatic π*. Sections of molecules which can undergo such detectable electron transitions can be referred to as “chromophores” since such transitions absorb “electromagnetic radiation” (light), which may be hypothetically perceived as colour somewhere in the electromagnetic spectrum. After an electron absorbs a high energy photon the system is excited electronically and vibrationally. The system relaxes vibrationally, and eventually fluoresces at a longer wavelength. This can be pictorially presented by Jablonski diagram showing different electronic transitions.





Jablonski diagram

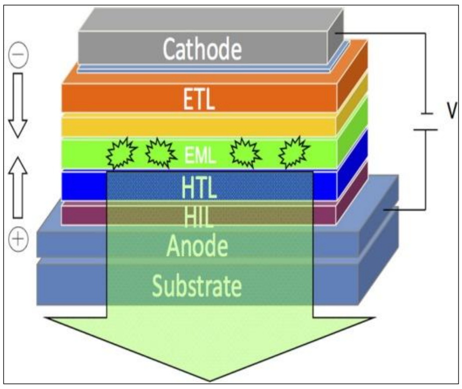
The absorption of light in the ultraviolet to visible spectrum can be quantified using ultraviolet-visible spectroscopy and the emission can be studied by florescence spectroscopy.

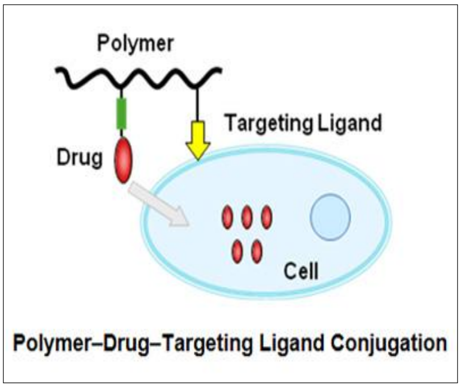
1.2 Properties of Conjugated molecules

Conjugated molecules are more stable due to sp^2-sp^2 overlap giving the “single bonds” a double bond character. They are mostly coloured and display good optical and luminescent properties. Now the reason for these compounds to be coloured and optically active is that these molecules possess double and triple bond which uses π-electron in addition to a σ-bond for bonding. π-bonds are usually weaker than σ-bonds which can be explained by significantly weaker sideways overlap of its component π-orbitals as they have parallel orientation. These less strongly bound electrons can be excited by photons with lower energy. Above 200 nm only the two lowest energy transitions, that is, $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$, are achieved as a result of the energy available from the photons. When sample molecules are exposed to light having an energy that matches a possible electronic transition within the molecule, some of the light energy will be absorbed as the electron is promoted to a higher energy orbital. As a simple rule, energetically favoured electron promotion will be from the highest occupied molecular orbital (HOMO), usually the singlet ground state, S_0, to the lowest unoccupied molecular orbital (LUMO), and the resulting species is called the singlet excited state S_1. Absorption bands in the visible region of the spectrum correspond to transitions from the ground state of a molecule to an excited state that is 40–80 kcal mol^{-1} above the ground state. Saturated hydrocarbons in particular, the lowest electronic states are more than 80 kcal mol^{-1} above the ground state, and therefore they do not absorb light in the visible region of spectrum. Such substances are not coloured. Compounds such as conjugated molecules that absorb in the visible region of the spectrum (these compounds have colour) generally have some weakly bound or delocalized electrons. In these systems, the energy difference between the LUMO and the HOMO corresponds to the energies of quanta in the visible region.[2] Many pigments make use of conjugated electron systems, such as the long conjugated hydrocarbon chain in β-carotene, resulting in a strong orange colour. With every double bond added, the system absorbs “photons” of longer wavelength (and lower energy), and the compound ranges from yellow to red in colour. As conjugated π systems become larger, the energy gap for a π - π^* transition becomes narrower, and the wavelength of light absorbed correspondingly becomes longer, which is known as red shift or bathochromic shift. Light absorbed by any molecule can be measured by spectrophotometer whereas emission can be measured by fluorimeter.

They have unique electrical properties as the electrons are able to move from one end of molecule to the other through extended π-orbitals. Conjugated materials have a backbone of continuous sp^2 hybridized carbon centres. One valance electron of each centre resides in a p_z orbital, which is orthogonal to the other three sigma bonds. All the p_z orbitals combine with each other to form a wide delocalized set of orbitals. The electrons in these delocalized orbitals have high mobility when the material is doped by oxidation, which removes some of these delocalized electrons. Thus, the conjugated π-orbitals form a one-dimentional electronic band, and the electrons within this band become mobile. Undoped conjugated materials are mostly semiconductors or insulators. Such molecules are mostly used in organic solar cells, printing electronic circuits, organic light-emitting diodes, actuators, electrochromism supercapacitors, chemical sensors and biosensors, flexible transparent display devices, electromagnetic shielding, etc. Also attempts have been made to develop materials that can possibly replace the popular transparent conductor, indium tin oxide. These type of molecules can also show electroluminescence, i.e. light emission stimulated by electric current. Due to all these properties the field of organic electronics which is concerning the design, synthesis, characterization and application of organic small molecules, oligomers or polymers that show desirable electronic properties such as conductivity is developing immensely.

Conjugated molecules also display redox behavior in presence of appropriate functional groups which can be studied by cyclic voltametry. Hence, conjugated molecules are important for wide range of applications in different fields starting from material science to biological science. As can be seen in the figure below conjugated molecules are used in the synthesis of light emitting devices as well as they are also used in the drug delivery in the biological system. The applications of these molecules will be briefly discussed in the later part of the chapter.



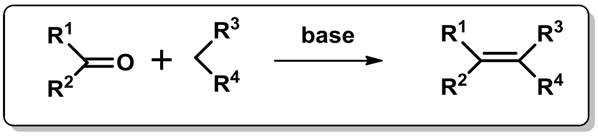


1.3 Methods for the synthesis of conjugated molecules

Conjugated molecules can be synthesized by number of methods. Few of the reported, classical key methods are as follows:

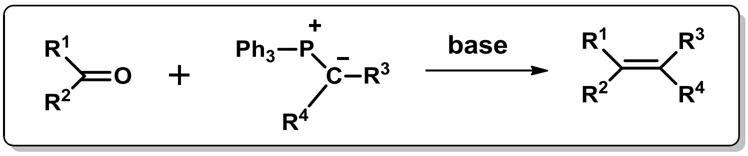
1) Knovenegal Condensation[3]

It is a nucleophilic addition of an active hydrogen compound to a carbonyl group followed by a dehydration reaction in which a molecule of water is eliminated (hence condensation). The product is often an α,β–conjugated enone. In this reaction the carbonyl group is aldehyde or a ketone. The catalyst is usually a weakly basic amine.



The active hydrogen component has the form R^3-CH_2-R^4 or R^3-CHR-R^4, for example diethyl malonate, ethyl acetoacetate or malonic acid or cyanoacetic acid or else R^3-CHR'R'', example is nitromethane.

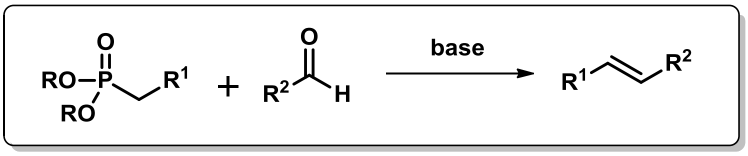
2) Wittig Reaction[3]



The Wittig reaction or Wittig olefination is a chemical reaction of an aldehyde or ketone with a triphenyl phosphonium ylide often called a Wittig reagent to give an alkene and triphenylphosphine oxide. With unstabilised ylides this results in almost exclusively *trans* product.

3) Horner-Wadsworth-Emmons reaction[3]

The Horner-Wadsworth-Emmons reaction is a chemical reaction used in organic chemistry of stabilized phosphonate carbanions with aldehyde or ketones to produce predominantly *E*-alkenes.

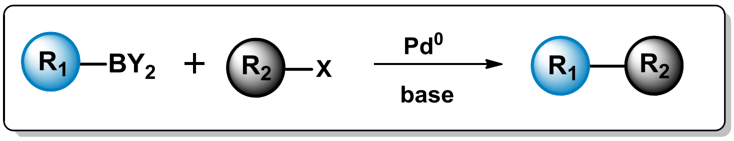


In contrast to phosphonium ylides used in the Wittig reaction, phosphonate-stabilized carbanions are more nucleophilic but less basic. Likewise, phosphonate-stabilized carbanions can be alkylated. Unlike phosphonium ylides, the dialkylphosphate salt by-product is easily removed by aqueous extraction.

Apart from the above mentioned named reactions, other palladium catalysed C-C coupling reactions are also widely used for the synthesis of conjugated molecules. The most common amongst them are described below.

4) Suzuki Reaction[3]

The Suzuki reaction is a C-C coupling reaction where the coupling partners are a boronic acid with a halide catalyzed by a palladium(0) complex. It was first published in 1979 by Akira Suzuki and he shared the 2010 Nobel Prize in Chemistry with Richard F. Heck and Ei-ichi-Negishi for their effort for discovery and development of palladium-catalysed cross couplings in organic synthesis. The general scheme for the Suzuki reaction is shown below where C-C single bond is formed by coupling a organoboron species (R_1-BY_2) with a halide (R_2-X) using a palladium catalyst and a base.



The mechanism for Suzuki reaction mainly involves three steps i.e. oxidative addition, transmetalation and reductive elimination which are shown in the **Figure 1**. The first step is the oxidative addition of palladium to the halide **2** to form organopalladium species **3**. Reaction with base gives intermediate **4**, which via transmetalation with the boron-ate complex **6** forms the organopalladium species **8**. Reductive elimination of the desired product **9** restores the original palladium catalyst **1** which completes the catalytic cycle.

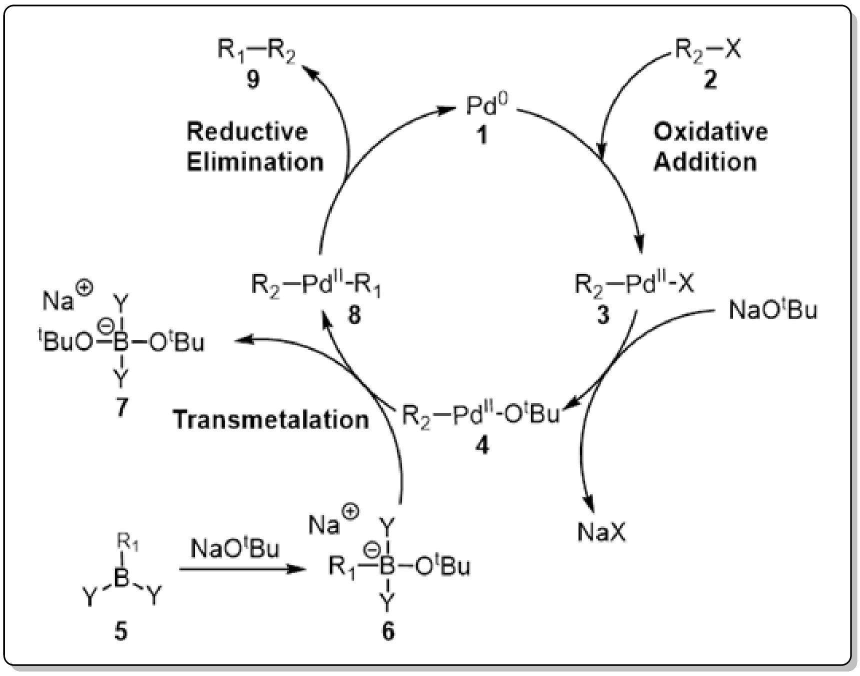
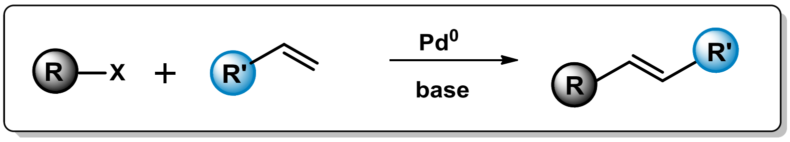


Figure 1

5) Heck Reaction[3]

The Heck reaction is the chemical reaction of an unsaturated halide (of triflate) with an alkene in the presence of a base and palladium catalyst to form a substituted alkene. The Heck reaction is of great importance, as it allows one to do substituted reactions on planar sp^2- hybridized carbon atoms. The reaction is performed in presence of an organopalladium catalyst. The halide or triflate can be an aryl, benzyl or vinyl compound and the alkene should contain at least one hydrogen and is often electron deficient.



The catalytic cycle for the Heck reaction involves a series of transformations around the palladium catalyst **Figure 2**. The palladium(0) compound required in this cycle is generally prepared *in situ* from a palladium(II) precursor. The mechanism involves first the oxidative addition of an aryl halide to palladium-ligand complex, second step is the alkene insertion followed by β-hydride elimination with the formation of new palladium-alkene π complex. This complex is decomposed in the next step. The palladium(0) compound is regenerated by reductive elimination of the palladium(II) compound by potassium carbonate in the final step.

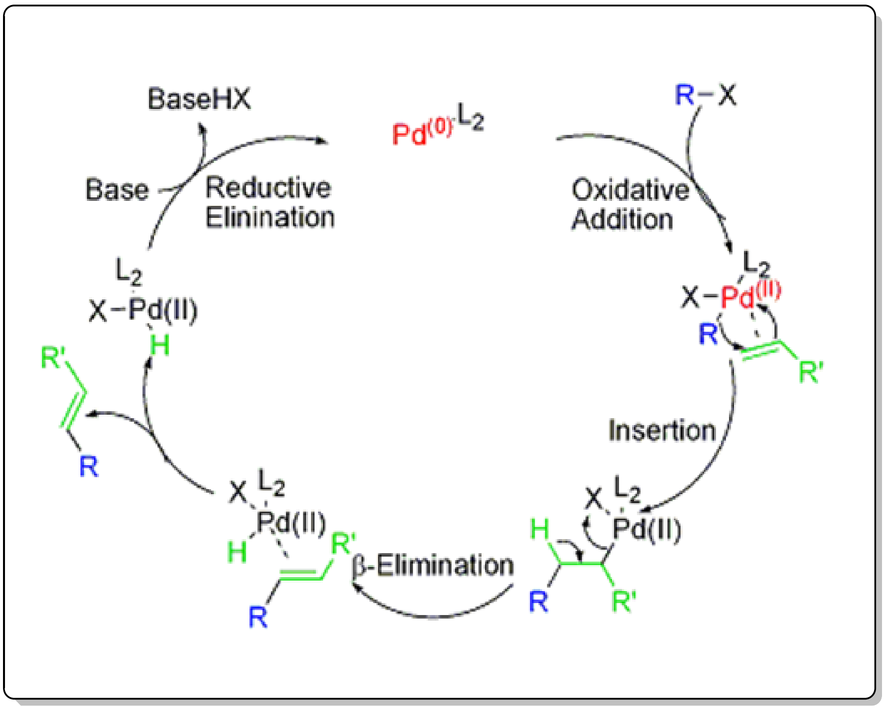
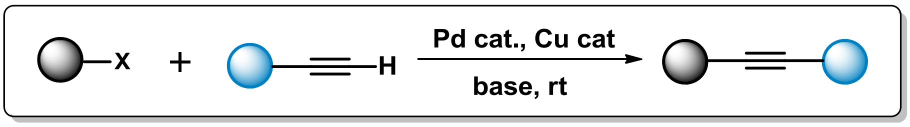


Figure 2

6) Sonogashira Reaction[3]

It is a C-C coupling reaction between a terminal alkyne and an aryl or vinyl halide catalysed by palladium and a salt of copper(I) species. The reaction can be carried out under mild conditions, such as at room temperature, in aqueous media and with a mild base.



The reaction proceeds via palladium cycle as well as copper cycle. Firstly the inactive Pd^{II} catalyst is activated by a reduction to Pd^0 compound. The active palladium complex A, reacts with aryl or vinyl halide by oxidative addition to produce a Pd^{II} intermediate, complex B. Complex B reacts in a transmetallation with the copper acetylide, complex F, which is produced in the copper cycle, to give complex C, expelling the copper halide, complex G. In the final step, complex D undergoes reductive elimination to produce the alkyne, with regeneration of the palladium catalyst. π-alkyne complex E is formed in presence of base, which makes the terminal proton on the alkyne more acidic, leading to the formation of the copper acetylide, compound F. Compound F continues to react with the palladium intermediate B, with regeneration of the copper halide G. [**Figure 3**]

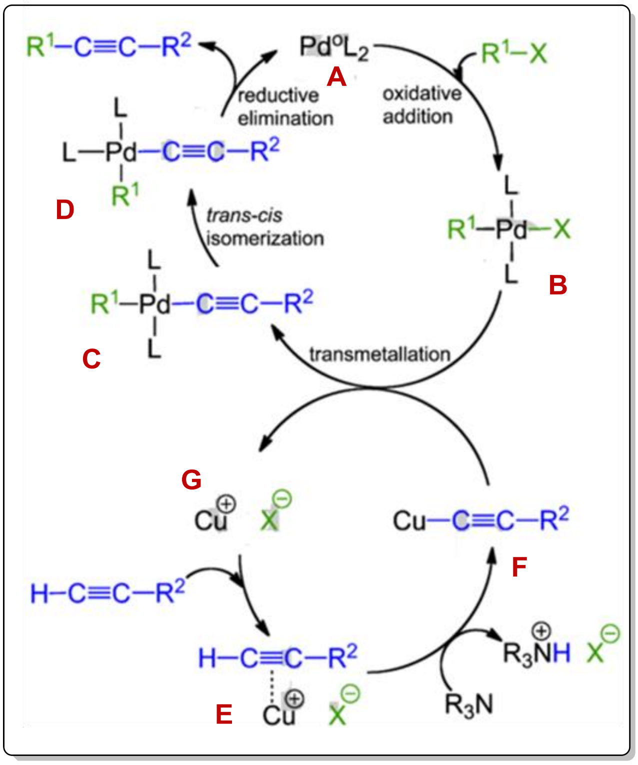


Figure 3

Apart from above mentioned methods, conjugated molecules can also be synthesized by one-pot methodologies. Recently many attempts have been made to develop efficient protocols to achieve the one-pot synthesis of useful molecules.[4] One–pot synthesis is the method in which multiple chemical transformations are performed sequentially in a single reaction vessel without intermediary purification steps. The basic advantages of one pot synthetic procedures are that it saves time and resources, reduces waste, avoids separation and purification of intermediates, it is compatible with unstable intermediates and hence in a way they are Greener Synthetic procedures. Few reports on development of one pot methodologies in organic synthesis will be presented in chapter 2. Although there are economical benefits of one-pot synthesis resulting from the fewer purification steps compensating the time and effort devoted to the optimization of a chemical process, the issues of compatibility and reliability has to be addressed.[5] As we know that the conditions for one reaction many not be favourable for the other reaction process hence we need to develop a method which can favour all the reactions, which one is planning to carry out in a one-pot synthesis. Also, one pot synthesis can be categorised in two types. One is the cascade type or tandem or domino type of reactions where the consecutive series of reactions occurs in a single reaction vessel, so the product of first reaction will undergo second reaction and so on leading to final product. Other type of one-pot reaction is the one where more than one reaction occurs on a single reactant or substrate leading to the final product. While describing one-pot methodologies it is also desirable to have measures to quantify the efficiency of the one-pot reaction cascade. The classical yield expression is not very informative or accurate in these instances as it does not reflect the fact that several bonds are formed and a number of manual operations are performed in a given one-pot cascade reaction. Therefore, Jorgensen *et al* have proposed the expression such as yield per bond formation (Y_{PBF}) and yield per manual operation (Y_{PMO}) to describe the one-pot reaction cascade,[5] where

$$Y_{PBF} = \sqrt[b]{\frac{Y}{100\%}} \; X\ 100\%$$

Y_{PBF} = yield per bond formed [%]
Y=classical yield of one-pot reaction cascade
b = number of bonds formed in one-pot reaction cascade

$$Y_{PMO} = \sqrt[nmo]{\frac{Y}{100\%}} \; X\ 100\%$$

Y_{PMO} = yield per manual operation [%]
Y=classical yield of one-pot reaction cascade
nmo= number of manual operations performed in one-pot reaction cascade

Hence, owing to the importance of one-pot synthesis we have developed three one-pot synthetic methodologies for the synthesis of conjugated molecules which will be describe in Chapter 2.

1.4 Applications of Conjugated molecules

A variety of conjugated molecules have been studied for its wide range application in different fields. Amongst the conjugated molecules oligo(phenylenevinylene) (OPVs), which correspond to the model compounds of PPVpoly(phenylenevinylene), have been extensively studied for years due to their good stability, high luminescent efficiency. They are extensively investigated π-conjugated molecules that exhibit absorption and fluorescence in the UV-visible spectral region, which can be widely tuned by chemical functionalisation and external control (e.g. solvent, temperature, pH). Further modulation of the optoelectronic properties of OPVs is possible by supramolecular aggregation, primarily driven by hydrogen bonding or π-stacking interactions. The optical and electronic properties of these molecules strongly depend upon structural features and hence can be modulated by variations in conjugation length[6–8] and donor–acceptor strengths.[6a,8b,9] Ajayaghosh *et al* have reported gelation of an oligo(*p*-phenylenevinylene) (OPV) derivative in nonpolar hydrocarbon solvents that led to a new class of functional materials, namely, π-organogels.[10] They have found that **OPV1** and **OPV2** having two hydroxymethyl groups and six dodecyloxy side chains and hexadecyloxy side chains respectively forms a self supporting soft solid from aliphatic hydrocarbon solvents **Figure 4**

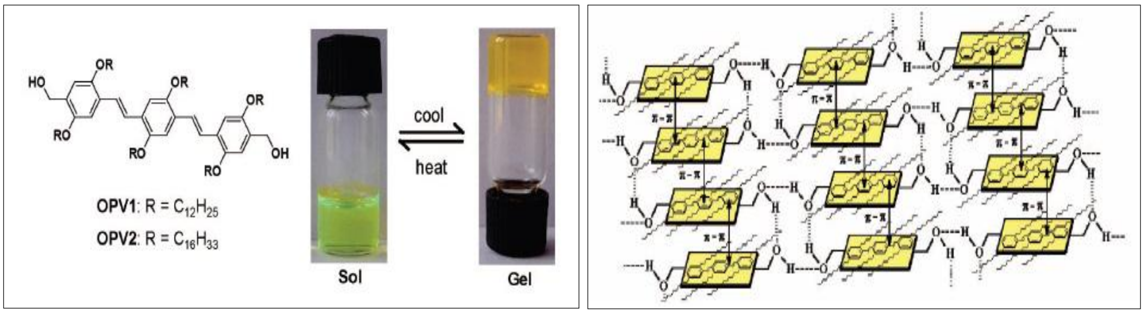


Figure 4

Hydroxymethyl groups facilitate linear H-bonded polymeric structures, which undergo π-stacking to form arrays of supramolecular polymeric structures. Hierarchical self-assembly of these structures will result in the formation of entangled networks that hold large volumes of solvents eventually resulting in the gelation of the solvents. Same group of scientist have also studied another series of OPVs with ester moiety.[11] In OPV1 the ester groups are insulated from the conjugated backbone, whereas in OPV 2-3, the ester groups are in conjugation with the OPV unit. In OPV 4 instead of ester moiety, electron-withdrawing dicyano groups were present. The colours of these molecules in powder form exhibited significant variation with the end functional groups [**Figure 5a**]. Also, the dipolar interaction of the ester moiety was shown to be effective in place of hydrogen-bond interactions, for the gelation of OPV1-3. [**Figure 5b**]

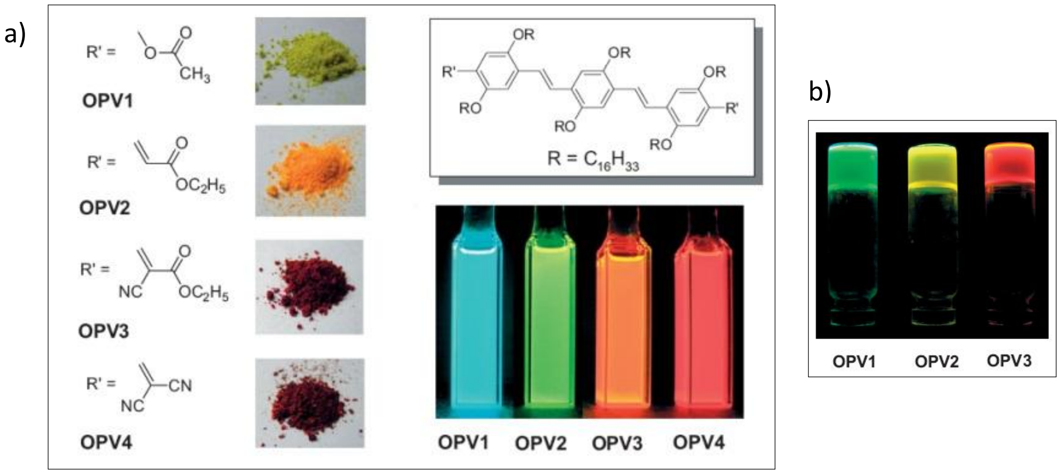
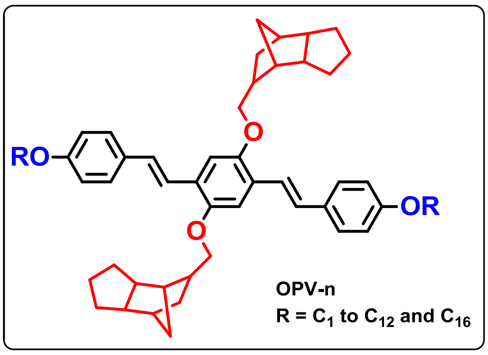


Figure 5

OPVs have also found applications in the field of liquid crystals. Jayakannan *et al* have reported a design strategy to trace the role of aromatic π-stacking and van der Waals interactions on the molecular self-organization of π -conjugated building blocks.[12] They have designed and synthesized a series of bulky oligophenylenevinylenes bearing a tricyclodecanemethylene unit in the aromatic π -core with flexible long methylene chain (*n*) 0-12 and 16 in the longitudinal position.



These OPVs were found to be liquid crystalline in nature. Polarized optical microscopic analysis confirmed the formation of cholesteric liquid crystalline (LC) phases of fan shaped textures with focal conics in OPVs with $5 \leq n \leq 9$. OPVs with longer alkyl chains (OPV-10 to OPV-12) produced a birefringence pattern consisting of dark and bright ring-banded suprastructures as shown in **Figure 6**.

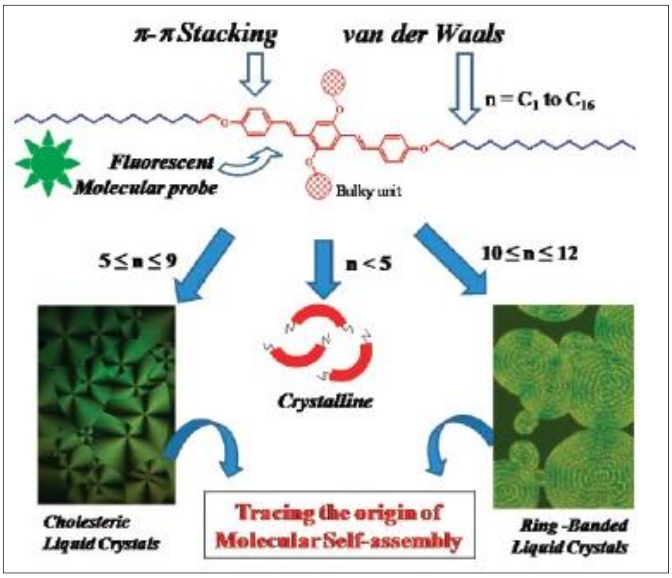


Figure 6

Apart from the above mentioned applications due to aggregations of OPVs, they are widely used as fluorescent dyes and sensors. As an example, Lippard *et al* have shown the use of bipyridyl-substituted poly(phenylenevinylene) derivative (CP1) as a turn-on fluorescent sensor for $NO_{(g)}$ in solution.[13] The action of $NO_{(g)}$ upon the CP1-Cu(II) complex reduces it to the CP1-Cu(I) complex with a concomitant 2.8-fold increase in emission intensity [**Figure 7**].

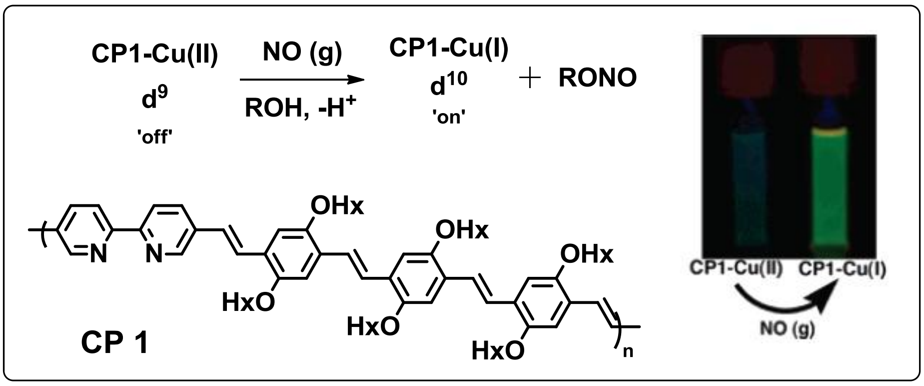


Figure 7

Apart from the above mentioned applications of conjugated molecules, another important application is as light-emitting materials in electroluminescent diodes. In 1990, Friend *et al* discovered that poly(phenylenevinylene) (PPV), and later its derivatives are capable of emitting light when subjected to low potentials and hence forth many conjugated polymers and organic materials have been used for the preparation of light emitting devices.[14] Chaieb *et al* have reported the absorption, photoluminescence and electroluminescence characteristics of substituted oligo(phenylenevinylene)s based on benzene-1,4-bis(phenylene-vinylene) with electron withdrawing or electron releasing groups on para-position of the terminal ring of the molecule. They have also used these materials as light emitting layer in electroluminescent devices. The authors have concluded that donating groups placed on both ends or in the middle of the PPV backbone result in a red-shift of the fluorescence and electroluminescence emissions. The red shift is increased with the increase of the donating effect. On the contrary substitution with the withdrawing nitro group strongly decreased the fluorescence and no light output was observed in electroluminescence. Increase in conjugation length also leads to red shift. In this context,[15] Nomura *et al* have reported the precise synthesis of chemically and analytically pure oligo(2,5-dialkoxy-1,4-phenylene vinylene)s [OPVs, alkoxy=O(CH$_2$)$_2$OSiPr$_3$] with strictly controlled repeat units (up to 15 repeat units) [**Figure 8**]. They have also synthesized OPVs with well-defined end groups by a combined olefin metathesis reaction of 2,5-dialkoxy-1,4-divinylbenzene or their derivatives with a molybdenum alkylidene complex and the subsequent Wittig-type cleavage with their dicarboxaldehyde analogues. The effects of the repeat units and the end functional groups toward their UV-Vis and the fluorescence spectra have been clearly demonstrated. They have concluded that the optical properties (in their UV-Visible and fluorescence spectra) can be modified by both conjugation repeat units and end functional groups.

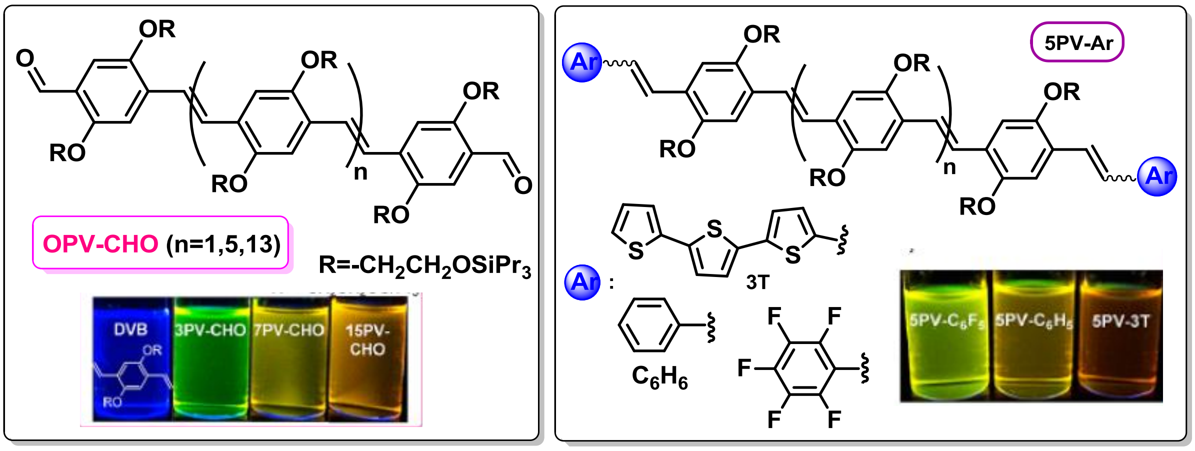


Figure 8

In the present work we have synthesized OPV derivatives by one-pot Wittig-Heck methodology[16] and studied some of molecules for their acidochromic properties, which will be described in Chapter 3, Section 1. The one-pot Wittig-Heck methodology has also been extended for the synthesis of poly(phenylenevinylene). Poly(phenylenevinylene) PPV is a very well known conducting polymer which can be processed into a highly ordered crystalline thin films. It has small optical band gap and bright yellow fluorescence which makes it a candidate in applications such as light-emitting diodes (LED) and photovoltaic devices. Moreover, PPV can be doped to form electrically conductive materials. The synthesized material of PPV has been characterized by gel permeation chromatography (GPC), thermogravimetric analysis (TGA), fluorescence spectroscopy and IR spectroscopy.

Apart from oligo(phenylenevinylene)s and poly(phenylenevinylene), many other class of conjugated compounds have been synthesized and studied for their possible applications. Amongst them we have synthesized and studied chalcone derivatives, which will be described in Chapter 3, Section 2 and Section 3. In section 2, we will be discussing about the synthesis of symmetrical bis-chalcone derivatives by mechanochemistry and studies of the synthesized derivatives as chromic compounds using UV-Visible spectroscopy and the fluorescence spectroscopy whereas in Section 3 we describe the synthesis of unsymmetrical bis-chalcone derivatives which were found to be mesomorphic in nature. The mesomorphicity of the compounds has been studied by observing the phase changes using polarizing optical microscope (POM) and differential scanning calorimetry (DSC) analysis. Another class of compounds that is explored for its specific properties is the carbazole based conjugated molecules. In Chapter 4, we will be discussing the importance of carbazole based materials in the electroluminescent devices. There we present the synthesis and characterisation of novel carbazole based molecules with different linkers. The synthesized derivatives have been studied by UV-Visible spectroscopy and fluorescence spectroscopy as well as cyclic voltammetry. The HOMO-LUMO level and optical band gap has been calculated for all the synthesized derivatives and has been compared with the reported derivatives that are used as hole transporting materials in electroluminescent devices.

1.5 References

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