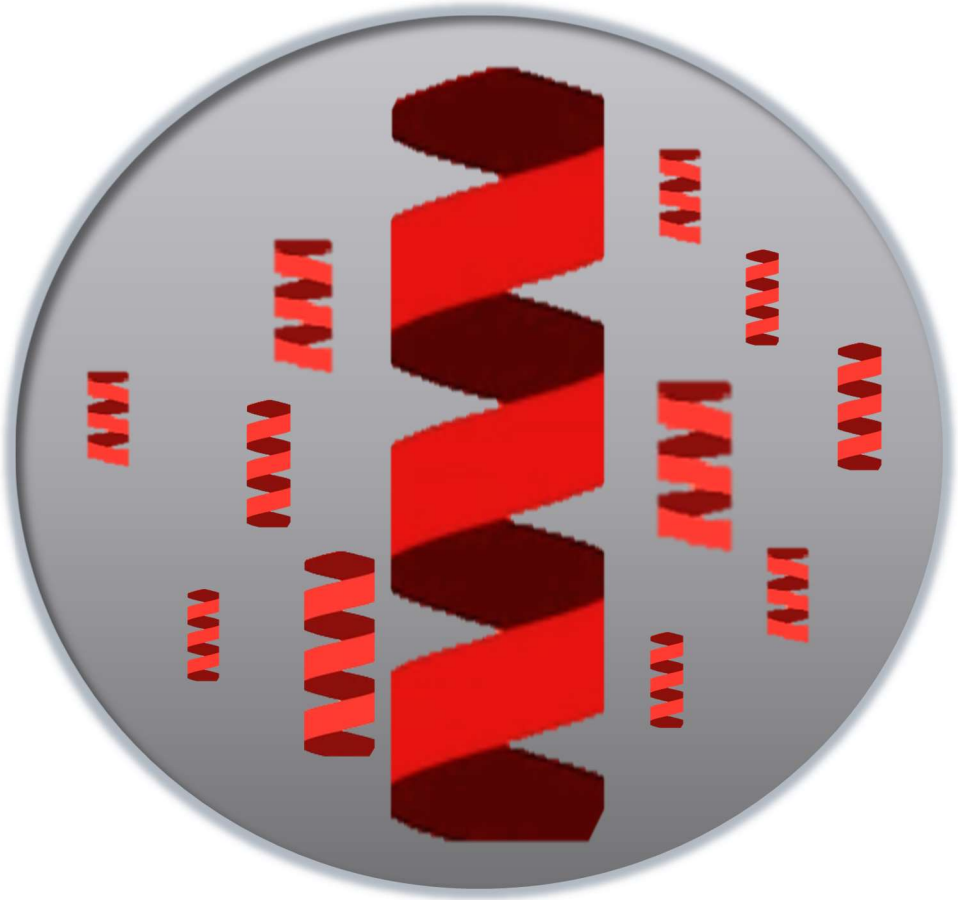
CHAPTER - 1

Introduction



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1.1 Introduction to Helical Architecture

Helical architecture is not an unfamiliar concept as it permeates many diverse natural formations with ubiquitous examples ranging from the sunflower galaxy, weather patterns, tendrils etc. at the macroscopic level to DNA double helix at the microscopic level. Nature handles the fabrication of helices with ease and elegance, while synthetic systems still struggle to imitate the size and shape of this architecture. In the field of biochemistry, helical macromolecular skeletons of nucleic acids, proteins and polysaccharides are important structural elements and their helix turns often are stabilized through hydrogen bonds, metal cations, disulfide linkages and hydrophobic interactions. The first helix postulated for a natural macromolecule was α-*Amylose*. In solution, it contains approximate, six glucose units per turn and is stabilized through hydrogen bridges connecting the three hydroxy groups.

***Figure 1.1**: Helical architecture in nature*

In the field of chemistry, the design and development of new helical structures has surfaced as an ever-demanding area of science with a scope of building some new molecules and understanding its properties and applications. In macromolecular chemistry, helically wound carbon chains are well known. Helical (+)-poly(triphenylmethyl-methacrylate) has been applied successfully as a chromatographic material for the separation of racemates.[1] Another particularly important group of helices in chemistry are the aromatic helical compounds called as helicenes. Helicenes are part of an intriguing class of polycyclic aromatic compounds formed from ortho-fused benzene or other aromatic rings that adopt a helical topology to avoid overlapping of the terminal rings resulting in helically chiral structures. In this way, simple achiral compounds upon forming helix generate helical chirality. The entire focus of our study is on aromatic helices. The synthesis of the first helical molecules dates to 1903 by Meisenheimer and Witte.

1.2 Nomenclature and the basic types of helicenes

Newman and Lednicer in 1956 introduced the term hexahelicene for phenanthro[3,4-*c*]phenanthrene[2] and added a prefix *n*, to describe the number of aromatic rings in the helical skeleton: thus pentahelicene = [5]helicene. Now based on the composition of the helical backbone, there are two types of helicenes: Carbohelicenes, which are solely composed of carbon atoms and are denoted as carbo[n]helicene formed of *n* ortho-fused benzene rings while heterohelicenes incorporate atleast one heteroatom and the general term hetero[n]helicene is used, where "hetero" refers to "aza", "bora", "oxa", "phospha", and "thia". Also, the position of the heteroatom is given by using IUPAC numbering. However, the drawback of using the same generic term is that, it can correspond to different helical systems. For example, an aza[5]helicene or pentaazahelicene may refer to a pyrido[5]helicene or to a pyrrolo[5]helicene which may be confusing. So, it is recommended to specify the type of heteroaromatic ring included in the helical scaffold.

1.2.1 *Carbohelicenes*

Carbohelicenes are also called all-benzene helicenes and contain only carbon atoms in their skeleton. These helicene molecules usually have a C_2 axis, which is not necessarily identical with the crystallographic axis. When the hydrogen atoms of the terminal benzene rings are substituted by larger substituents it leads to increased steric repulsion. With increasing n, the outer pitch only changes little. Compared to benzene, the lengths of helicenes are shorter in the inner part of the helix, whereas in the periphery they are elongated. The strain is not equally distributed inside the helicene molecule: the torsion angle between the inner bonds in the molecule is large. This induces coplanarity, whereas the terminal rings are nearly completely coplanar with bond lengths and angles similar to those of phenanthrenes.[3]

1.2.2 *Heterohelicenes*

Besides incorporating a heteroatom, heterohelicenes differ from carbohelicenes through their geometry. The bond angles of the heteroatomic moieties differ at the site of annellation. In the case of five-membered rings, a higher annellation degree is necessary to obtain an overlap of the terminal aromatic rings. For all-thiophene helices, which have not yet been synthesized, this means that eight condensed thiophene rings are necessary. In contrast to [6]helicene[4] ,the benzene and thiophene rings in heterohelicenes do not deviate strongly from planarity. The bond lengths and angles also are quite like non-annellated benzene and thiophene rings. The angles between the planes of the aromatic rings vary from -18.4 ° to + 19.9 °. For nitrogen containing helicenes, 5,10-Dihydrocarbazolo[3,4-*c*]carbazole was the first helicene synthesized (in 1927).[5]

1.2.3 *Double helicenes*

Double helicenes are composed of two fused helices which may be same or different. They can be divided into three types A, B and C based on their annellation pattern as shown in figure 1.2. Diphenanthro[3,4-c:3',4'-l]chrysene (**6**) belongs to type A. Two optically active and one meso structures theoretically are possible. The lower-melting racemic mixture and the higher-melting meso compound were obtained experimentally. The latter is thermodynamically more stable because both helix windings lie on facing molecular parts. Hexaheliceno[3,4-c]hexahelicene (**7**) is an example of type B of the double helicenes. Theoretically one meso and two optically active molecules are expected here. In the synthesis only one isomer, most probably the racemic compound, is formed exclusively. The racemic mixture should be energetically favoured because the terminal aromatic rings are situated on different sides of the molecule, with respect to the central naphthalene unit.[5]

1.2.4 *Helicenophanes*

Helicenes bearing a paracyclophane unit are called as helicenophanes. Here the terminal rings are linked by an alkyl chain giving the form of a clamped helicene. Originally helicenophanes were prepared for the determination and proof of absolute configurations.[6]

1.2.5 *Helical Metallocenes*

The helicenes can be incorporated with cyclopentadiene rings either in the body or at the termini and can be easily deprotonated to give cyclopentadienyl anion units. In this way, [4]- and [5]helicene dianions were prepared by Katz and co-workers, and subsequent reactions with metal cations produced metallocenes. The first helicene synthesized, which was bridged by a ferrocene unit, was based on the pentahelicene skeleton.[7]

1.2.6 *Bihelicenyls*

Bihelicenyls have two helicene moieties connected by a single bond. 2,2'-Bis-hexahelicyl, composed of two hexahelicyl moieties, which are connected through a single bond, occurs in a meso and two racemic configurations: the meso compound prefers a planar conformation at the central C-C single bond. For the dl isomer such a spatial arrangement is sterically unfavourable; in this case, the helicyl units are twisted around the central single bond. The d,1 isomer rearranges at its melting point to give the more stable meso compound.[5]

TYPES OF HELICENES

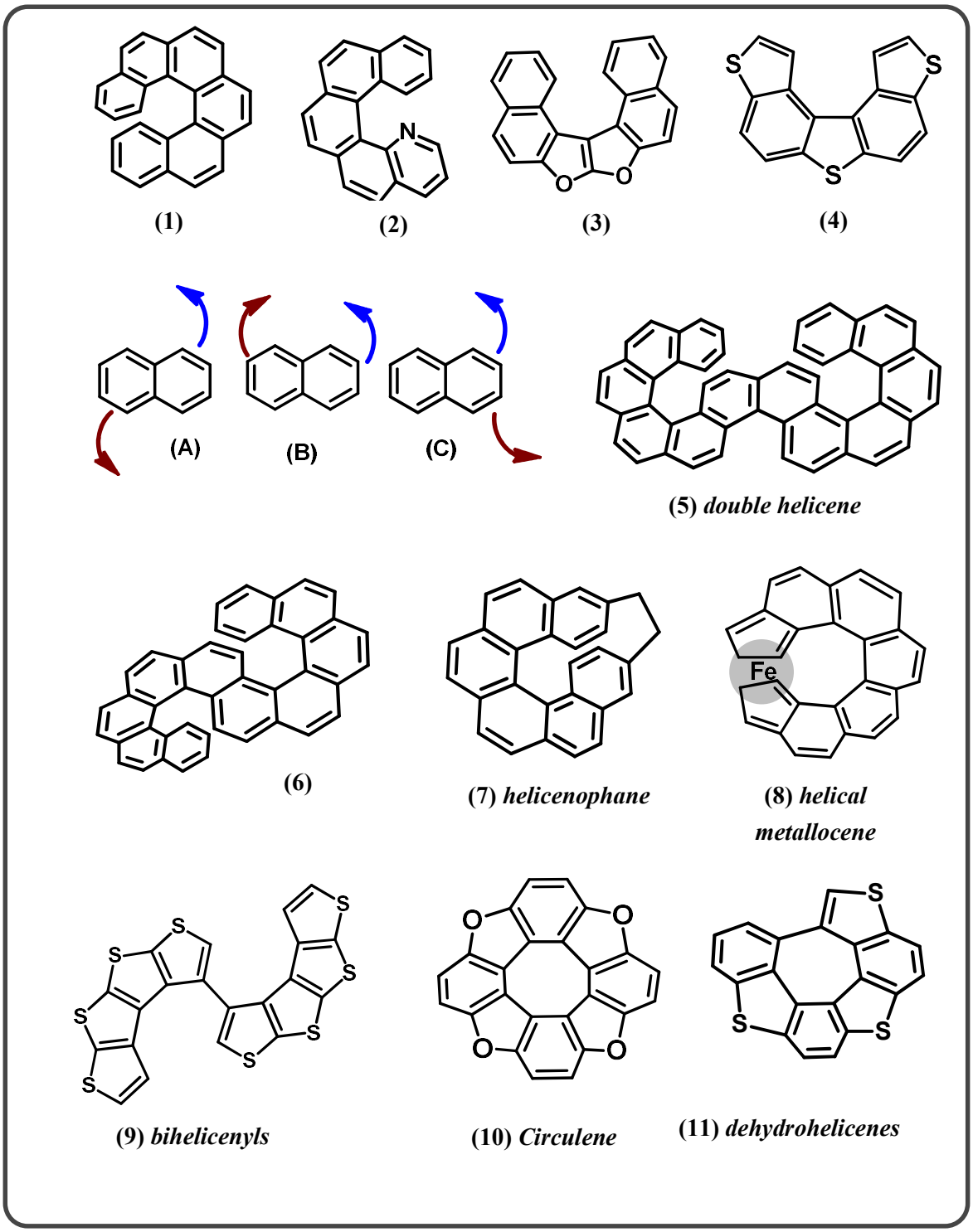


Figure 1.2: Representative examples of general types of helicenes

1.2.7 *Circulenes and dehydrohelicenes*

Circulenes are formed when the two terminal aromatic rings of a helicene are fused together. [n]circulene indicates n-condensed aromatic rings arranged in a closed macro-ring. Representatives are the bowl-shaped [5]circulene ("corannulene") and the planar [6]circulene, the latter better known by the classical name "coronene". Circulenes possess either planar, boat- or saddle-shaped aromatic skeletons based on the number of rings fused. The symmetry or helicity is strongly disturbed compared to the helicenes.[5] Dehydrohelicenes are the ones in which both the terminal rings are connected through a σ-bond.

1.3 Structural features

The most defining feature of a helical molecule is its helicity, and it arises due to steric hindrance of the terminal rings which coerces the molecule to wind in opposite directions. This renders them chiral even though they have no asymmetric carbon or other chiral centres. So according to the helicity rule proposed by Cahn, Ingold and Prelog in 1966, the molecule which spirals downwards anticlockwise is the left-handed helix and is designated as "minus" and denoted as (*M)* while the one which spirals downwards clockwise is the right-handed helix and is designated as "plus" and denoted as (*P)*.[8] Now if we keep on adding rings to the scaffold, it can be predicted that a cylindrical helix would be generated like a spring or a coil. When such a helix spirals for 360°, the distance between two ends is the helical pitch which remains constant throughout the system.

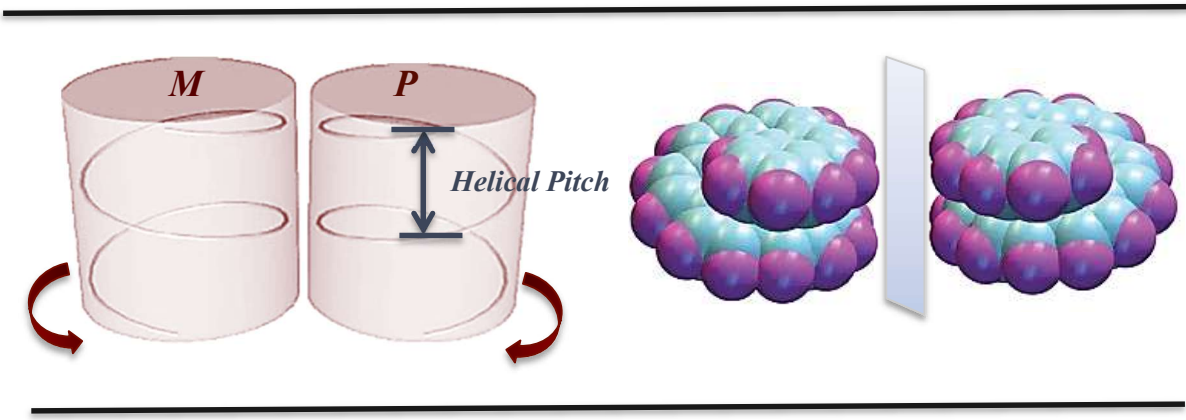


***Figure 1.3**: Schematic representation of helical pitch and a pair of (M-helicene and (P)-helicene*

The internal angle for six-membered aromatic rings like benzene or pyridine are larger (about 60º) compared to the five-membered aromatic rings like furan (about 32º), pyrrole (about 35º) and thiophene (about 45º). Hence to complete a full 360º rotation of a screw, more rings are required if they are five-membered. The exte0.nt of distortion due to non-planarity

because of helical twist can be described using two terms: *Interplanar angle* and *torsional angle*. Torsional angle is the dihedral angle between the four adjacent inner carbon atoms as shown in figure 1.4 which is influenced by the steric bulk of the functional group at C(1) position of the helical scaffold. In the case of [4]helicenes the torsional angle of **13** is greater than that of **12** due to the presence of methyl groups.

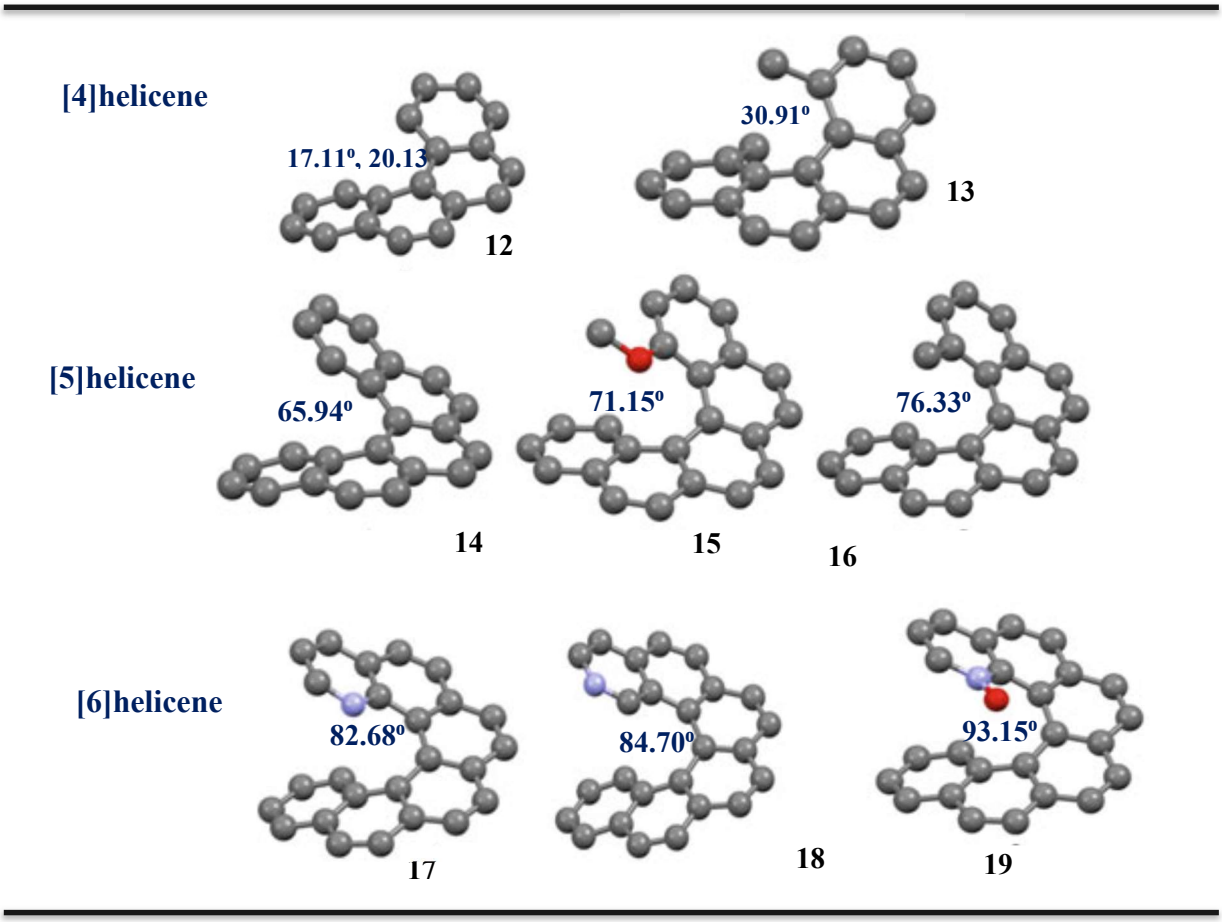


***Figure 1.4**: Torsional angles calculated from the crystal structure of [4], [5] and [6]-helicene*

For [5]helicenes, the methyl group is larger than the methoxy group, which itself is larger than H atom so the total torsional angle is **16** > **15** > **14** whereas for the [6]helicenes, the extent of distortion follows the order of **19** > **18** > **17** as the steric hindrance of O > H > lone pair of electrons. The interplanar angle (dihedral angle) is the angle between the two terminal rings. So, it is not governed by the torsional angle but by the location of the terminal rings which is affected by the length of the helical skeleton. Generally, from four benzene rings (26.7º) to six benzene rings (58.5º) the value increases and on extending the framework further, the value decreases.9

The deformation in the benzene rings of a helical skeleton is the result of the torsional strain caused by the ortho-fusion of the rings. This can be seen in the form of difference in C-C bond lengths in the inner and outer helix: the lengths of the bonds in the inner helix are

lengthened while that in the outer helix are shortened compared to the average bond length in benzene. In comparison with the rings in the helical skeleton, the two terminal ones distort least and are the most aromatic indicated by the DFT calculation. Although helicenes have a C2-symmetric axis theoretically, this is hardly found in the crystal structures. Each ring is twisted to different degrees, where the inner bond lengths and the torsional angles are different.

1.4 Properties of Helicenes

Helicenes are archetypes in chirality owing to the extended π-conjugation and helical shape. Hence the main properties of helicene are a result of these features and this separates them from other classes of polycyclic aromatic hydrocarbons.

1.4.1 *Optoelectronic /Chiroptical*

The local aromaticity of helicenes is well intact as in the case of polycyclic aromatic hydrocarbons (PAHs) inspite of having the twisted structure, due to efficient delocalization of π-electrons.[10–13] However, the extent of π-conjugation is not as good as planar PAHs. In the case of carbohelicenes, the wavelength of absorption maxima almost remains the same even when we increase the benzene rings from [4]helicene to [16]helicene. Thus, the carbohelicenes have large HOMO-LUMO gaps which could not be reduced by fusing benzene rings to the helical skeleton. In the case of heterohelicenes, the electronic structure of the system is altered due to the heteroatom. The band gaps of carbo[n]helicenes, thia[n]helicenes with alternating benzene and thiophene rings, and carbon–sulfur [n]helicenes are estimated by density functional theory (DFT) studies in gas phase: by virtue of ineffective conjugation, carbon–sulfur helicenes (4.1 eV) have the largest energy gap, while the thiahelicenes (2.5 eV) show smaller gap than that of carbohelicenes (2.9 eV).[14] In the case of heterohelicenes, most of the organic B, Si, P, N-containing helicenes display blue fluorescence due to the electron-withdrawing effect of the heteroatoms. The emission properties of the helicenes are also modified due to the large spin-orbit coupling which promotes the singlet to triplet intersystem crossing.[15] Hence along with fluorescence emission, at low temperatures, phosphorescence can also be observed. Besides, helicenes also show solid state optical properties different from the liquid state due to their unique self-assembling behaviour.

The optical property of helicenes can be altered by two general strategies: (a) by extension of the conjugated area and (b) by construction of pull–push structures, with the incorporation of donor/acceptor substituents. The latter strategy is comparatively more effective as electron donating and electron withdrawing groups could be easily incorporated into the system.[16–18] When the conjugated area in a helical system is extended like in the case of **20** where pyrene moiety is introduced to the helicene structure, the band gap could not be reduced significantly[19,20] but helicene **20** displays a Stokes shift of 296 nm resulting from the

intramolecular excimer behavior upon radiation.[21] Extending the π-conjugated area of double [6]helicene, the energy gap of **21** is greatly reduced with the λ_{max} of 525 nm in the absorption spectrum.[22] The band gap can also be reduced by introducing an antiaromatic core to the skeleton. For example, **22** with an antiaromatic as-indacene core even displays the gap of 1.48 eV.[23] Furthermore, some helicenes also show highly luminescent properties. Tetrahydrohelicene **23** shows fluorescence quantum yields of 85.3 % in CH_2Cl_2 solution and 61.8 % in film state. Helicene-like **24a–d** show quantum yields higher than 85 % both in CH_2Cl_2 solution and film state, and **24c** has nearly 100 % quantum yield in film state.[24] The study reveals that the π–π interaction between the helical cores in aggregation is prevented by the alkyl substituent, resulting in little quenching of the solid fluorescence.

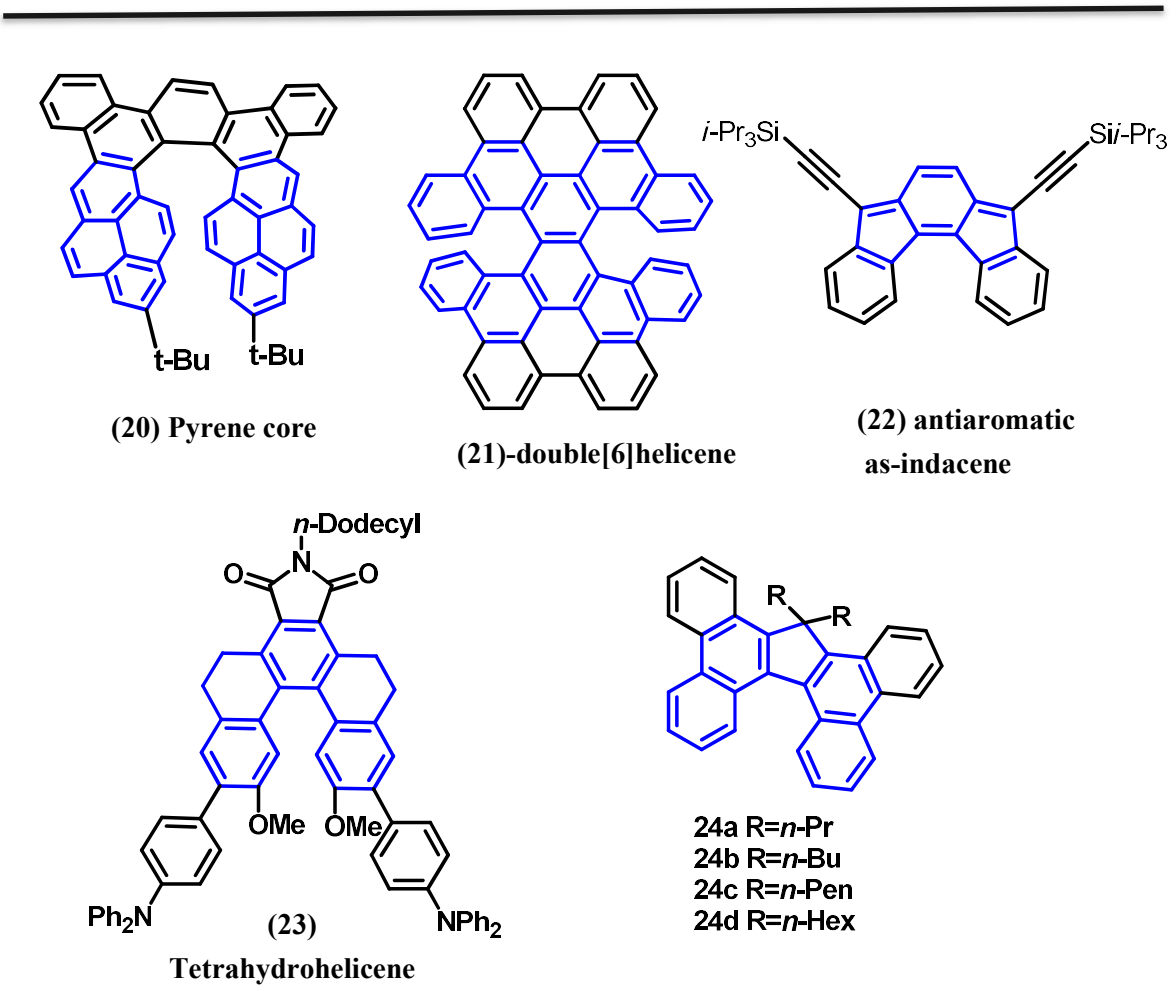


***Figure 1.5**: Representative examples of some helicenes studied for their optical properties*

1.4.2 *π-electron interaction*

Helicenes, like other polycyclic aromatic hydrocarbons, are good π-electron donors and can form charge transfer complexes with electron acceptors. It was a major milestone in helicene chemistry when this concept was first utilized in the optical resolution of [6]helicene. For example, (S)-TAPA had stronger interaction with (M)-helicenes and (R)-TAPA preferentially interacted with (P)-helicenes. Therefore, the enantiomers could be separated by recrystallization. [2,25] Also some of the electron deficient molecules like riboflavin derivatives, TABA etc. were grafted to the stationary phase for optical resolution using HPLC.

In some of the helicene aggregates, face to face π–π interactions were observed. A remarkable one-way chirality was observed in λ^5-phospha[7]helicene **25** synthesized by Nozaki group (Fig. 1.6).[26] First, the aggregation of each column was achieved by the intermolecular face-to-face π–π interactions of the helicenes bearing the same helicity with a distance of 3.35 Å; second, the columns of different helicity were alternately aligned in the crystal. This phenomenon resulted from the dipole moments of enantiomers differentiated by helicity: the column formed by (*P*)-**25** had opposite dipole moment with the one formed by (*M*)-**25**.

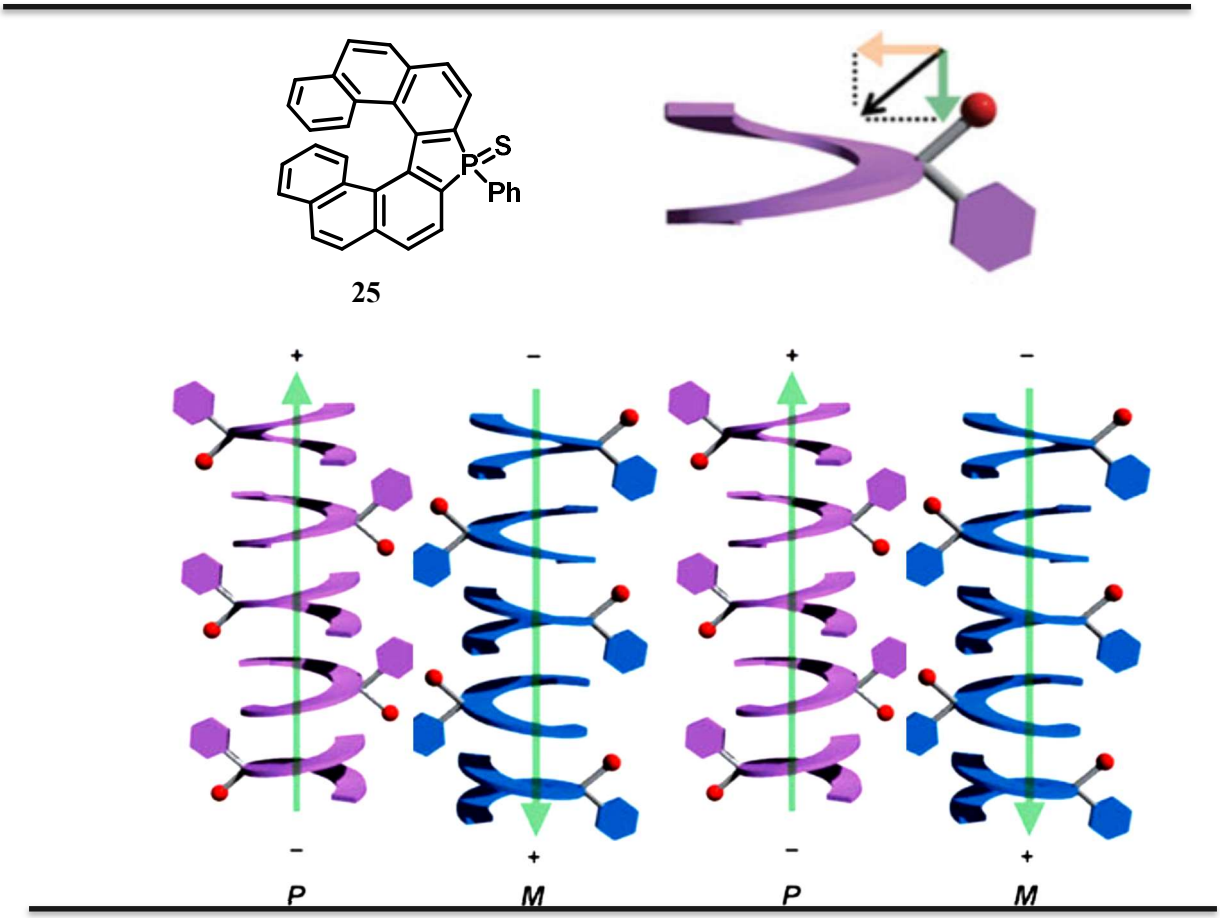


***Figure 1.6**: Schematic representation of one-way chirality*

1.4.3 *The helicity*

According to the observations inferred from ORD and CD spectroscopy, there is a general relationship between the configuration and the chirality: (*P*)-helicenes are dextrorotatory, while (*M*)-helicenes are levorotatory. Helicenes possess high specific optical rotation. In the ECD (electronic circularly dichroism) spectra, all levorotatory helicenes have positive Cotton effect at the maximum absorption wavelength, and then negative cotton effect at the shorter wavelength. [27]

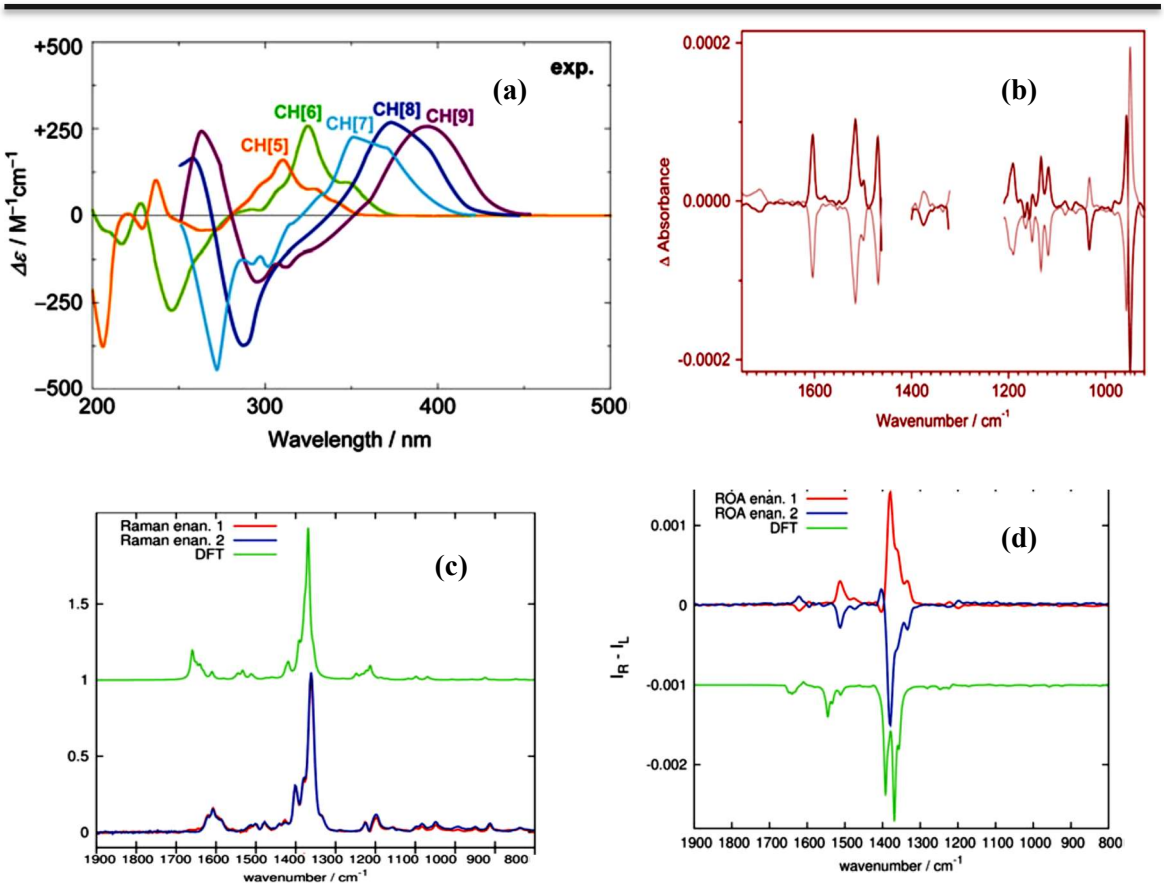


***Figure 1.7**: (a) ECD spectra of (+)-carbohelicenes (b) VCD spectra of the enantiomers of [7]helicene (c) Experimental Raman of 2-Br-hexahelicene (d) ROA of 2-Br-hexahelicene*

Vibrational circular dichroism (VCD) spectra can also be used to determine the absolute configuration.28 VCD spectra are associated with the ground states (Fig. 1.7) providing the fine vibration pattern[28] unlike the ECD spectra, which are related to the excited states displaying overlapped transitions. However, larger quantities of enantiopure samples were needed for the test than that of ECD. Recently, Raman optical activity (ROA), the other form of vibrational optical activity, was measured experimentally and interpreted by electron–phonon coupling analysis (Fig. 1.7).[29] The strongest ROA band of [7]helicene dropped in the

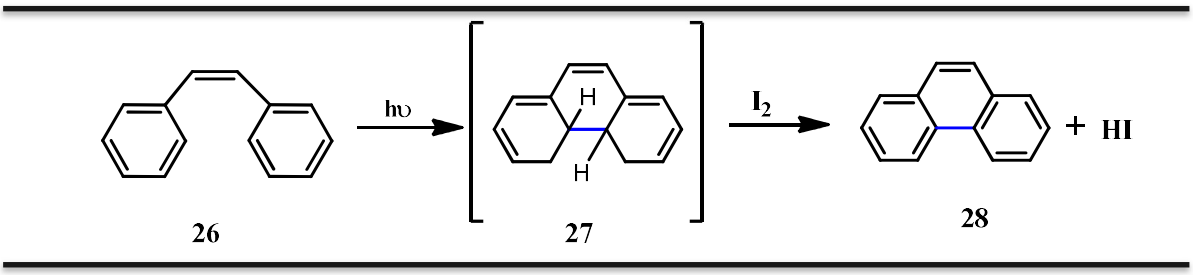
range of 1350–1400 cm^{-1}, which was associated with the bending of the H-C-C planes and the stretching of the C–C bonds.

1.5 Synthesis of Helicenes

In this section, the popular strategies to construct different helical molecules will be discussed. These strategies have been employed for the synthesis of carbohelicenes as well as heterohelicenes.

1.5.1 *Oxidative photocyclization*

Photoinduced synthetic route for helicenes was first reported in 1960s by Mallory [30] and Dietz group[31] for [4]helicenes independently and by Martin group for the synthesis of [7]helicenes. [32] It involves a two-step procedure: (1) the preparation of the stilbene precursors by the reactions between aldehyde and P-ylides [339] or Heck-type cross-coupling reactions between the aryl halides and aryl ethenes,[34] (2) radiation of the stilbene solutions in the presence of oxidants or sensitizers. Our group is actively involved in the synthesis of helicenes by this strategy hence it is important to understand the pros and cons of this method elaborately.



***Scheme 1.1**: General scheme for oxidative photocyclization*

Using this strategy [4]helicenes were easily synthesized in high yields by [1+2] procedure using Iodine as the oxidant either in benzene or cyclohexane. In the case of [5]helicenes, instead of the usual cyclization, benzo[*g,h,i*]perylene core was obtained due to over-annulation. To prevent the overannulation, Matsuda and coworkers found that the introduction of cyano groups to ethylene moieties could eliminate the degeneracy of unoccupied molecular orbitals (UMO) and stop the reaction after the first photocyclization.[35] For [6]helicene, several strategies had been investigated as [1+4][36,37] ,[2+3] [38] , [1+1+2] and [1+2+1] methods.[39] From these results, the yields were good and the regioselectivity did not seem to be a big problem. As for longer helicenes, the yield was relatively lower. Taking [7]helicene as an example, using [1+1+3] or [2+4] strategy, the yields of oxidative photocyclization were not higher than 30 %. [32,40] The [3+3] strategy was investigated: Martin and coworkers synthesized [7]helicenes from stilbene precursors **39** [32] and **40**[40,41] in 12.5 and

35 % yields respectively; Laarhoven group utilized an inert atmosphere to promote the yield up to 50 % .[38] In 1991, Katz and Liu reported a method that using Br atom as a block to improve the regioselectivity assuming the bulky atom would prevent the cyclization path from occurring at its adjacent position. As a result, the yield was greatly increased from 20 to 75 %. Recently, [2+1+1+2+1+1+2] method was proposed by Mori, Murase, and Fujita to synthesize the longest [16]helicene in 7 % yield via constructing six benzene rings in one step which was demonstrated by X-ray crystallographic study, as well as the [9]helicene. [42] This method, the photocyclization of an oligomer composed by phenylene and naphthalene units connected by vinylene groups, avoided the tedious synthesis of helicene moieties for constructing the longer one, and avoided the presence of [5]helicene unit during the cyclization to prevent the overannulation as well.

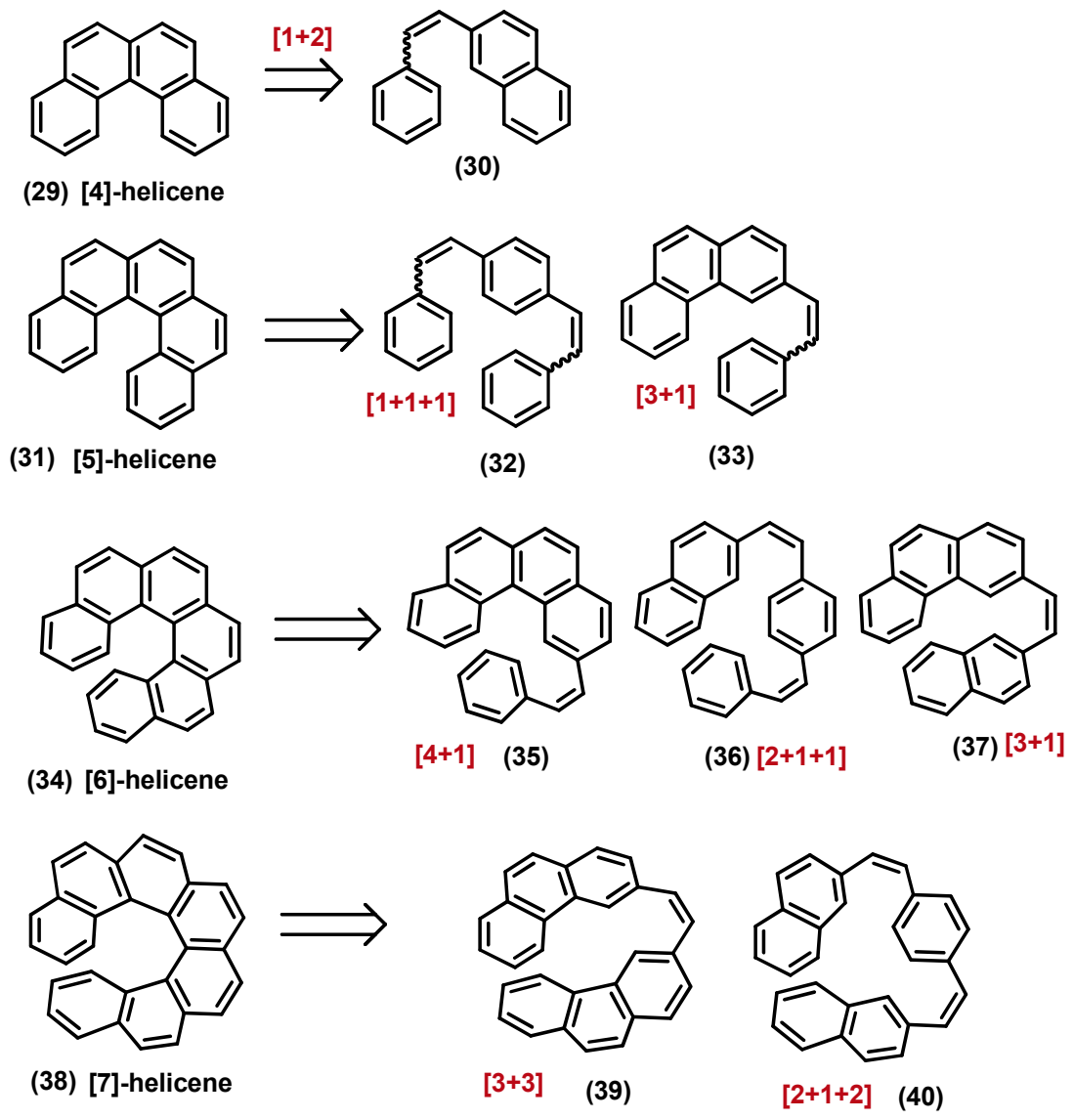
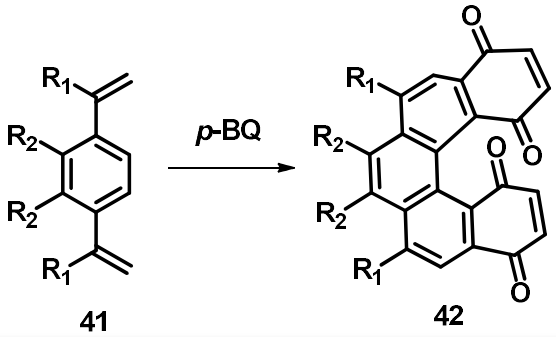


Figure 1.8: Different modes of photocyclization for the synthesis of helicenes

Although this methodology has been widely utilized, there are some limitations.[9] First, it is difficult to be used for large-scale preparation, because the photocyclization needs highly diluted solution (usually 10^{-3} M) to prevent the [2+2] intermolecular cycloaddition. If large quantity of solvent is used, safety issues should be seriously concerned, since the solvents are all extremely flammable and volatile. Second, the reaction lacks the tolerance to amino- and nitro-groups, which would accelerate the process of intersystem crossing. Third, if the difference between the polarity of the target helicene and by-products (for example, the regioisomers) is small, it is difficult to be purified. Recently, chemists found a solution–the continuous flow strategy–to solve the problem of large-scale preparation.

1.5.2 *Diels-Alder reactions*

Katz and Liu[43] for the first time synthesised helicene bis-quinone using Diels–Alder reaction in 1990. In this way for the first time large-scale synthesis of helicene bisquinones was achieved. By this strategy, [5]helicene **42** could be obtained in grams by the reaction between excess *p*-benzoquinone (12–14 equivalents) and the divinylbenzene **41**. Similarly, using the same methodology [6]- and [7]helicenes could also be prepared. Further, it was suggested that by incorporation of electron-donating functional groups on the diene precursors, the yield could be greatly enhanced.[44–46] Several useful applications of the functionalized helicenes have been reported, such as asymmetric catalysis[47], helical metal phthalocyanine derivatives[48], helical conjugated ladder polymers[49,50], chiral recognition[51,52].

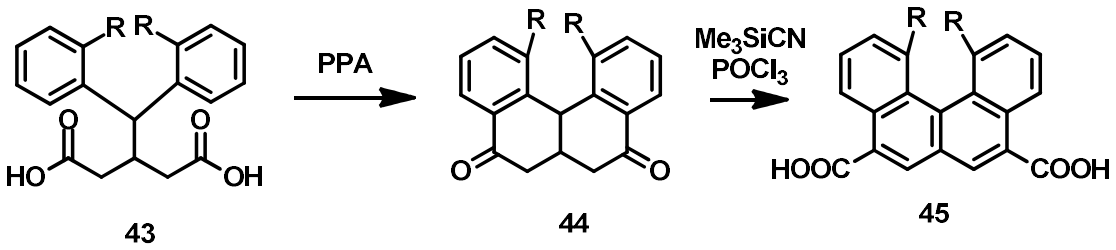


***Scheme 1.2**: General scheme of Diels alder reaction for the synthesis of [5]helicenebis-quinones*

The Diels–Alder reaction is a practical method for the preparation of symmetric helicenes, because of the efficiency, the moderate-to-good yields, and the large scale of reactions. Moreover, the substituents on dienes and dienophiles could be further modified and used as functional groups to achieve the optical resolution and change the electronic properties. The major limitation of the methodology is the limited types of dienes and dienophiles.

1.5.3 *Friedel-Crafts type reactions*

Newman and co-workers first utilized this method for the preparation of 1,12-dimethyl [4]helicene and [6]helicene in 1950s.[2,53] Yamaguchi and co-workers synthesized optically stable [4]helicenes derivatives,[54,55] in which the substituents were at the most sterically hindered positions, namely C(1) and C(12) (Scheme 1.3). The R substituents on the phenylene groups performed as blocking units that directed and facilitated the double acylation, which could be completed in one step. The subsequent addition, aromatization, and hydrolysis afforded the diacids **45** in good yields. These acid groups could be used for the optical resolution by recrystallization in the presence of quinine or chromatography after the preparation of camphorsultam derivatives.[55]



***Scheme 1.3**: Synthesis of substituted [4]helicene derivatives by FC type reaction*

Friedel–Crafts-type reaction is a useful strategy as the synthesis usually needs less than five steps and affords moderate-to-good yields. However, two points that should be taken into consideration are: (1) polar unsaturated bonds should be well designed and incorporated into the substrates; (2) to promote the regioselectivity, it would be better that the directing or blocking groups were introduced.

1.5.4 *Metal-mediated reactions*

Metal mediated reactions have become one of the most powerful methods for the preparation of helicenes due to their high efficiency, moderate to high yields, good functional group tolerance, and the ability to prepare longer helicenes. Among them, the [2+2+2] cycloisomerization is the most widely used method, in which the construction of helical skeleton could be achieved with high efficiency by different routes including platinum-catalyzed dienyne cycloisomerization, palladium-catalyzed intermolecular cyclization of arynes and alkynes, and Ni/Co-mediated intramolecular [2+2+2] cycloisomerization of triynes. By twofold [2 +2+2] cycloisomerization of triynes, longer helicenes can be synthesized.

Heterohelicenes and different helquats can also be synthesized by the similar [2+2+2] cycloisomerization method. Moreover, other types of metal-mediated reactions are also reported for the preparation of helicenes, such as Pd-catalyzed twofold Stille cross-coupling reaction, Pd-catalyzed double Suzuki-Miyaura cross-coupling, Ti-mediated McMurry coupling, intramolecular palladium-catalyzed P-arylation, Rh-catalyzed ring-closing metathesis, Fe-Mediated Scholl oxidation, Au-catalyzed hydroamination, consecutive hydroarylation reaction, and so on. [56,57]

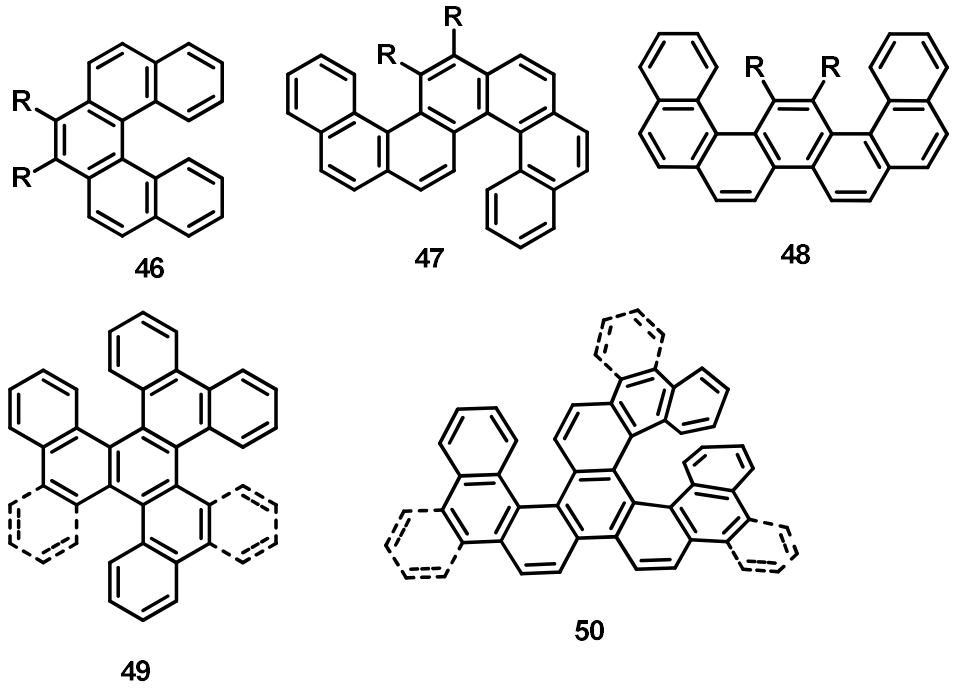


***Figure 1.9**: Helicenes synthesized by [2+2+2] cycloisomerisation*

Apart from these common synthetic protocols for the preparation of helicenes, there are some other well-known methods. Radical cyclizations[58] or cascade radical cyclizations, can be used but the regioselectivity is a major disadvantage of this method. Oxahelicenes can be prepared by oxidative coupling method[59] using BINOL analogues. Some azahelicenes can also be expediently prepared by oxidative homocouplings. Particularly, heterohelicenes including helicenium cations, azahelicenes, thiohelicenes, azabora[6]helicene, and boraoxa[6]helicene can be prepared by microwave reaction of suitable amine or salts, carbenoid coupling, Cu-mediated oxidative coupling, one-pot [4+2]benzannulation strategy[60], Pictet–Spengler reaction, double electrophilic borylation, and other heteroatom arylation reactions.

1.6 *N*-incorporating Helicenes

Nitrogen atoms can be introduced into the helicenic scaffold in many ways. Nitrogen-containing helicenes belong to the most popular class of enantioenriched helicenes. Various heterocycles (pyridyl, pyrrole, pyrazine, imidazole, thiadiazole) or triarylamines can be utilized to incorporate N-atom within a helical scaffold. *N* atom can also be part of an organic substituent (CN, NH_2, etc..) or a *N*-heteroaromatic acting as a grafted functionality onto the helical scaffold. Due to the presence of nitrogen and its lone pair of electrons, the properties of the aromatic ring can be modified. The *N*-electronegativity changes the inherent properties of the whole ring such as its electron-richness or electron-poorness, its redox potentials, its aromaticity, and its reactivity toward electrophiles and nucleophiles. The *N*-lone pair in pyridyl units is not involved in the π-conjugation and is therefore available for reactivity with other systems (basicity, oxidation, coordination), while for example in pyrroles the *N*-lone pair is engaged in ring aromaticity. These different features directly affect the photophysical and chiroptical properties of the helicene, together with other properties of azahelicenes (such as conduction, complexation, or catalysis)

1.6.1 *Pyridohelicenes*

Pyridine fused azahelicenes have many potential applications in coordination chemistry and in material science. Indeed, their transition metal complexes may show interesting properties in harvesting (visible) light and reemitting it at a wavelength that depends on the metallic ion used, thus allowing the development of light-emitting devices, chemosensors, photovoltaic dye-sensitized devices etc. In 2004, Abbate and co-workers[61] studied the X-ray structures and the chiroptical properties of monoaza[5]helicenes. In 2005, Caronna et al.[62] used the classical oxidative photocyclization of stilbene derivatives using a visible light to obtain aza or diaza[5]-helicenes. Stary and group in 2008,[63] investigated racemic aza[6]helicenes (Figure 1.10) as *N* ligands for coordination, and 1:2 Ag^I aza[6]helicene complexes were synthesized and characterized by X-ray crystallography. In 1989, Staab and co-workers[64] studied the basicity of **52** and found that the experimental pKa value was 10.3 indicating high basicity and thus acting as proton sponges due to the destabilization of the free bases because of repulsive lone pair interaction of two closely neighbouring nitrogen atoms (despite the helical topology of the molecule). Combination of helical topology and high PAs are good opportunities for enantioselective reactions of these helical nitrogen bases. Schmidt, Brédas and group[65] investigated the intersystem crossing processes in aza[5]helicene and carbo[5]-helicenes. They established that the luminescence properties can be greatly enhanced by the introduction of a nitrogen atom into the [5]helicene backbone.

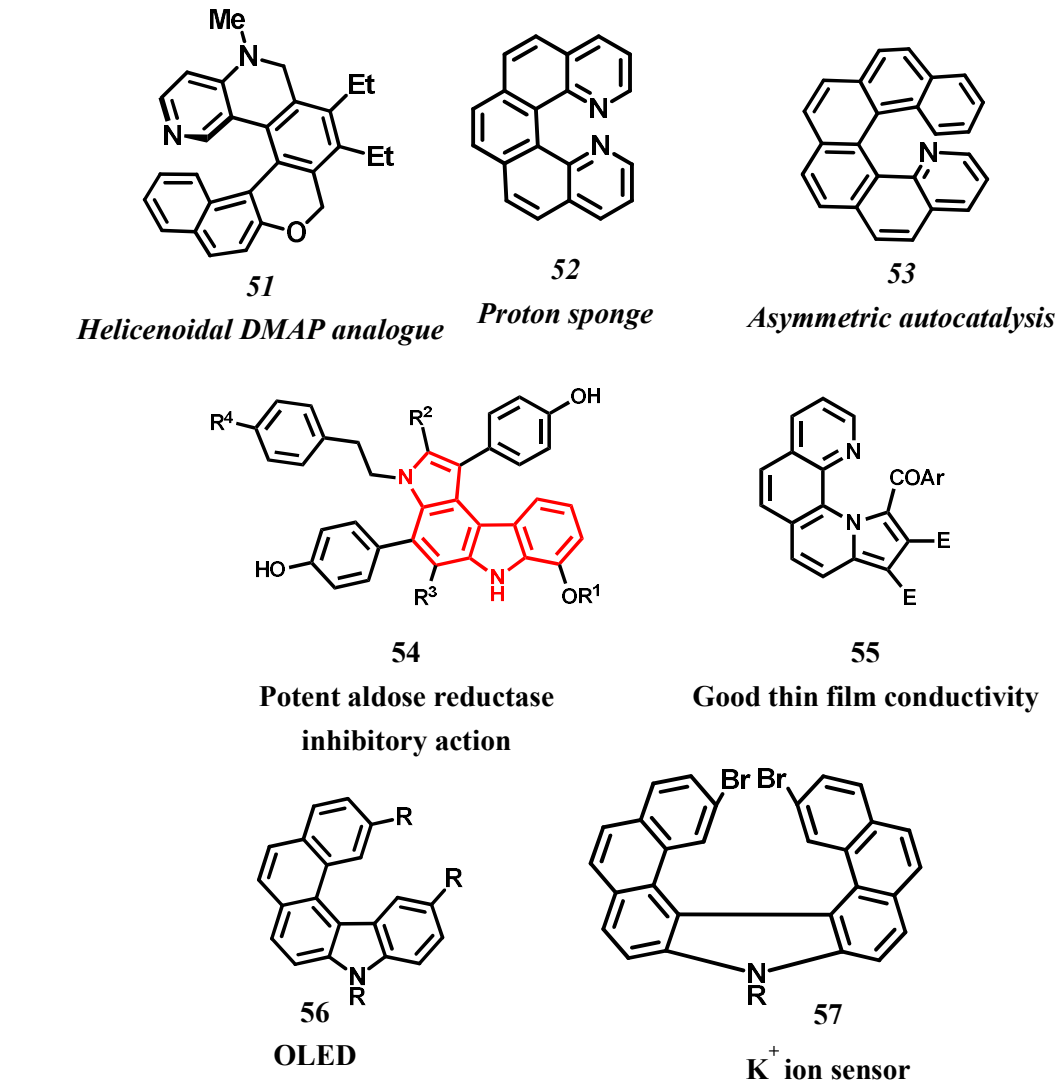


Figure 1.10: Some important N-incorporating helicenes

1.6.2 *Pyrrolohelicenes*

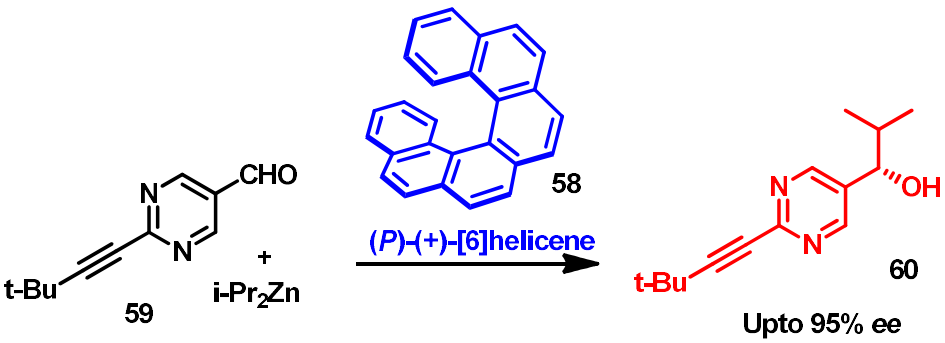
Carbazole fused heterohelicenes are called as pyrrolohelicenes. Pyrrole-incorporating PAHs are known for remarkable physical properties such as effective hole-transporting ability and bright emission. They have been used to constitute extended π-conjugated systems with a characteristic low oxidation potential.[66] However, the major challenge in the synthesis of pyrrolohelicenes is that it is more prone to racemization. For this reason, few examples of enantioenriched carbazoles have been described in the literature. Liu and group[67] in 2012 synthesized a new carbazole based di-aza[7]helicene by photocyclization strategy. The

helicene was found to be potential candidate for deep blue emitting OLED devices. In 2015, a racemic helicene bearing a chloro-quinoline and a carbazole unit was synthesised by classical oxidative photocyclization method.[68] The chloro group was then substituted with (S)-(−)- α -methyl-benzylamine substituent by a Buchwald−Hartwig coupling to give (1:1 mixture of diastereomers). The diastereomers were readily separated via standard chromatography and characterized by ECD spectroscopy. These diastereomers were configurationally stable at room temperature and no racemization was observed after heating the diastereomers at 150 °C for 12 h. Dictyodendrins, another class of tetracyclic helical compounds, were isolated from Dictyodendrilla species by Sato and co-workers in 1993. It was found that these compounds could completely inhibit telomerase at concentrations as low as 50 µg/mL. Alvarez and co-workers prepared a simplified dictyodendrin core, pyrrolo[2,3-c]carbazole, via a two-step convergent method involving Suzuki cross-coupling and 6π-electrocyclization. Moorthy *et al.*[69] synthesized helical chromenes showing photo-responsive behaviour and sensitive towards external stimuli such as acid, heat, and visible radiation.

1.7 Application of helicenes

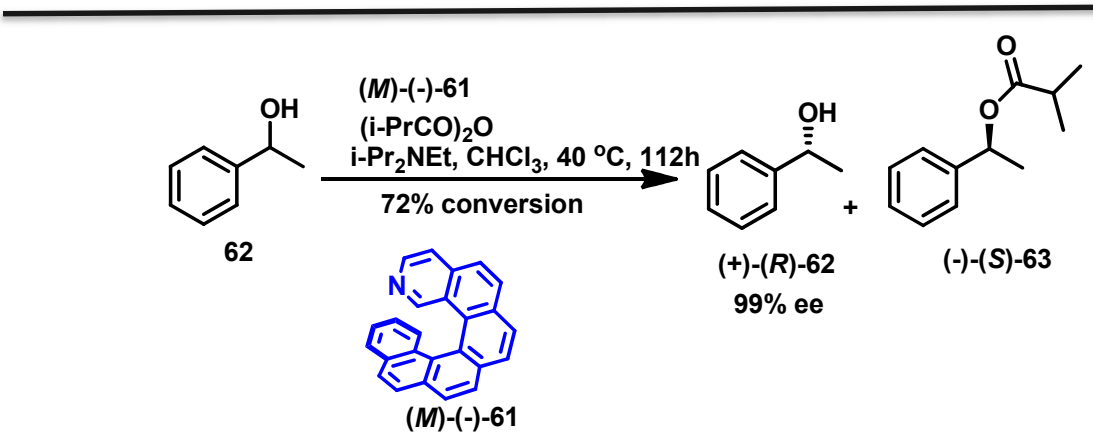
1.7.1 *Helicenes in catalysis*

The first helicene-based ligand was reported by Reetz group in 1997.[70] They synthesized 2,15-bis(diphenylphosphino)-hexahelicene (*P*Helix) in enantiomerically pure form and used it as a helical ligand for enantioselective rhodium catalyzed hydrogenation. The non-functionalized helicene **58** have been utilized by Soai and co-workers as chiral inducers for the first time in the highly enantioselective addition of diisopropylzinc to an aldehyde. Starý, Stará, and co-workers examined the catalytic activities of optically pure (*P*)-1-aza[6]helicene and (M)-2-aza[6]helicene **61** in the kinetic resolution of alcohol.[71]



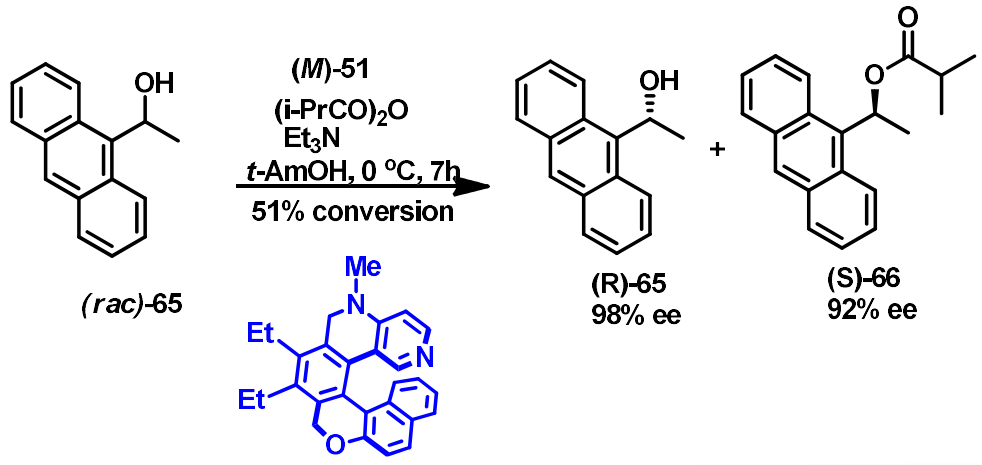
***Scheme 1.4**: Autocatalytic addition with non-functionalized helicenes as asymmetric trigger*

A helicenoidal DMAP analogue **51** was synthesized by Carbery and co-workers[72] by [2+2+2] cycloaddition and reexamined its catalytic activity for the same reaction. This organocatalyst showed higher selectivity (s = 116) in 51 % conversion rate and gave (*R*)-65 and (*S*)-66 in 98 and 92 % *ee*, respectively (Scheme 1.6). The loading of catalyst was as low as 0.5 mol%.



***Scheme 1.5**: Kinetic resolution of alcohol catalysed by 2-aza[6]helicene*

N-oxides of 1-aza[6]helicene are good catalysts for the asymmetric ring-opening of epoxides, and also show high efficiency for the asymmetric propargylation of aldehyde. The protonated 2-amino-1-aza[1]helicenes are excellent dual hydrogen bonding donor catalysts for the asymmetric addition reaction between dihydroindole and nitroalkene, and also for the asymmetric Diels-Alder reaction of nitroalkene with dienes.



***Scheme 1.5**: Kinetic resolution of alcohol catalysed by helicenoidal DMAP analogue*

1.7.2 *Helicenes in molecular recognition*

Nakazaki group synthesized the helicene crown ethers **67-68** by photochemical cyclization of stilbene-type precursors and examined their chiral recognition toward racemic amine salts **69-71.**[73] It was found that (1) the selectivity of the (*R*)-/(*S*)-enantiomer was totally reversed for the crown ethers with the same helicity; (2) the enantioselectivity of **67** was much better than that of **68**, which meant that the complementarity between the hosts and the guests was important. In 1993, Diederich and co-workers reported a new helicopodand and investigated its recognition of diacids.[74] The helicopodand had two pyridyl amino groups on the terminal rings, which could bind with the substrates bearing hydrogen bond functionalities. They observed 1:1 host–guest complexes. Diacid **73** showed the strongest binding with the helicopodand **72**, of which the binding constant was determined to be 5500 ± 810 M^{-1} by ^1H NMR titration.

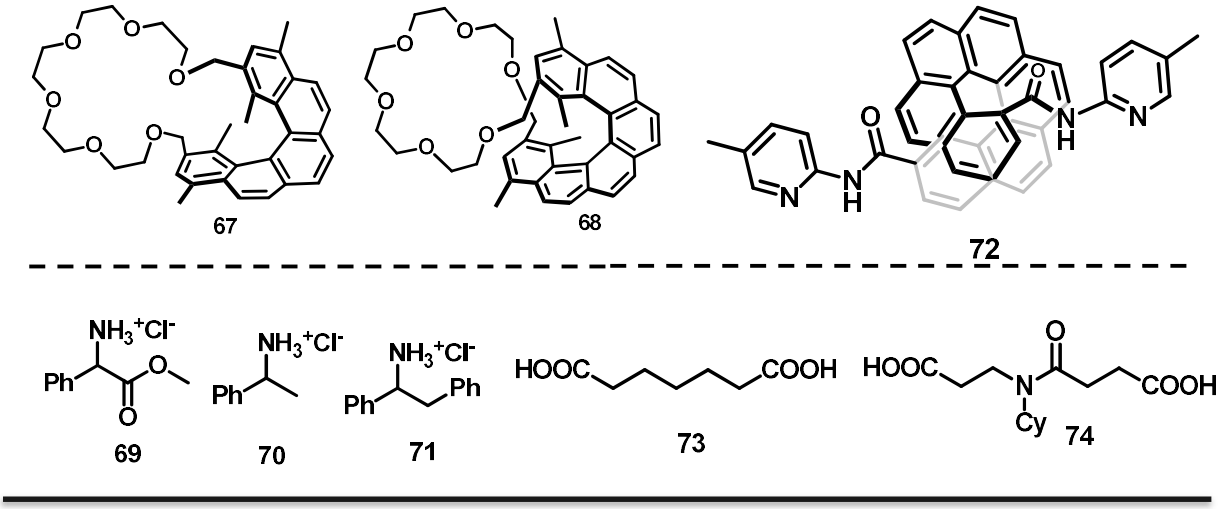


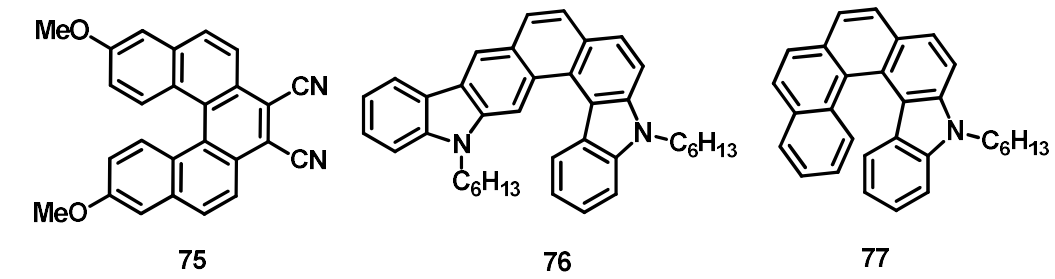
Figure 1.11: Helicene based host molecule for chiral recognition

Yamaguchi et al. described the chiral recognition between the helicene/amino-modified Si NPs and secondary alcohols. Based on the recognition that (*P*)-helicene had stronger interaction with (*S*)-alcohol, the dispersed silicon nanoparticles were aggregated in the presence of racemic alcohol, where (*S*)-enantiomer was dominated. atmosphere for 300 s for each step, and the current was promoted nearly two orders of magnitude from 0 to 49 % humidity.

1.7.3 *Helicenes in organic electronics*

Helicenes with π-conjugated skeletons are good candidates for organic electronics. Moreover, good thermal and chemical stability, strong intensity and good quantum yield of

fluorescence or phosphorescence, enables these compounds to be explored for applications in organic light emitting diodes (OLEDs) and transistors. In 2010, Sooksimuang group fabricated an OLED using Helicene **75** with a HOMO/LUMO energy gap of 2.6 eV and Tm (melting temperature) of 307 °C, Tg (glass-transition temperature) of 130 °C, and Td (decomposition temperature) of 330 °C. Later, a deep blue-emitting OLED was described by Liu and co-workers. Aza[5]helicene **76** showed good thermal stability (Tg of 203.0 °C, Td of 372.1 °C) with optical quantum yield of 9–10 %, and the HOMO/LUMO gap was determined as 2.79 eV. Fuchter, Campbell, and co-workers fabricated OFETs to detect circularly polarized lights by using the enantiomers of 1-aza[6]helicene as responsive hole-transporting material.



75 76 77

***Figure 1.12**: Reported helicenes as emissive materials*

1.8 Aim of the thesis

The main objective of this research work is to synthesize novel helical molecules with fused carbazole rings namely pyrrolohelicenes, expand their structural diversity by selective functionalization of the molecules and to study their properties so that their applications in chiral recognition, asymmetric catalysis, and organic electronics can be explored. The contents of the thesis are mainly divided into two chapters: Chapter 2 unfolds the chemistry of five-membered pyrrolohelicenes and Chapter 3 is about the chemistry of unsymmetrical hepta-helicenes. Chapter 3 is subdivided into two portions. Chapter 3A deals with the seven-membered helicenes with unsymmetrical helical scaffold and Chapter 3B is the discussion about heptahelicenes with unsymmetrical functionalization.

C**hapter 2** is subdivided in two parts **Part-I** deals with the synthesis and study of C-2 substituted pentahelicene and its functionalization. The synthesis was carried out using oxidative photocyclization strategy. However, the final helicene was found to be labile for racemization so a more sterically crowded pentahelicene was required to be developed. As per literature reports, it was known that a C-1 substituted helicene is more sterically hindered.

Hence in **Part-II**, our target was to synthesize C-1 methyl substituted pentahelicene. As expected, stereodynamically stable pentahelicene was synthesized. However, a major challenge was to separate the linear regiomer of photocyclization. This was possible by crystallization and repeated column chromatography. Both the angular and linear regiomers were fully characterized by ^{1}H-NMR spectroscopy. After success in this area, its functionalization was carried out which rendered good quality crystals of the angular regiomer. In order to improve the yield of photocyclization, a blocking group (-CN) was introduced in the helical skeleton which drastically improved the yield of angular regiomer after photocyclization. The photophysical properties of the C-2 and C-1 substituted compounds were investigated and the structural parameters were studied by single crystal XRD analysis and computational data.

Chapter 3 is about the study of pyrrolo[7]helicene and it is also subdivided in two parts. **Chapter 3A** deals with the synthesis and study of pyrrolo[7]helicene with unsymmetrical helical scaffold. The synthesis of heptahelicene was carried out as an extension of the pentahelicene. Hence double photocyclization was involved in the entire scheme. The optical properties of the heptahelicene were studied by UV-Vis, fluorescence spectra and the electrochemical properties were studied by CV analysis. The structural parameters were established by single crystal XRD data and computational analysis. The heptahelicene was further functionalized by formylation reaction which rendered two isomers. Both the isomers were characterized by ^{1}H-NMR and SCXRD data. All the compounds were explored for optical properties and resolution was attempted for the formyl derived aza[7]helicenes.

Chapter 3B is about the study of heptahelicenes with unsymmetrical functionalization. Various mono and di substituted helicene were synthesized by one-pot Wittig Heck strategy followed by photocyclization. The olefins were also synthesized by separate Wittig and Heck reaction in a sequential method and the overall yield for one-pot and sequential method was compared. One of the derivatives was an ester substituted helicene which was further hydrolysed to render aza[7]helicene carboxylic acid. All the derivatives were well characterized by spectroscopic techniques and screened for optical properties. Molecular recognition study was carried out for the aza[7]helicene carboxylic acid

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