Heteroatomic and Organometallic Helicenes: Synthesis and Chirooptical Properties

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General information
General Information

Helix is a fundamental structure that builds our nature. We can find different kinds of helices in our world such as tornado, stem of trumpet flower in daily life, or DNA, proteins at the molecular level. Helicene is one kind of molecules containing a helical structure, and unlike other helical molecules, the helical structure of a helicene is made-up of ortho-fused aromatic rings constituting an inherently chiral $\pi$-conjugated system.

![Figure 1: Structure of M-carbo[6]helicene](image)

This special structure gives helicenes unique properties such as very high optical rotation and very strong circular dichroism signal. Based on these properties, the helicene may potentially be used for applications such as chiral-wave guides, chiral sensors, chiral switches, or for 3D-imaging.$^1$

Metal-based helicenes or metallahelicenes are a very new kind of helicenes for which we can introduce the knowledge of organometallics into organic helicene chemistry. Introducing metals into a helicene backbone can have many advantages: easiness in synthesis, probability in constructing various different structures, novel properties due to the metallic center, facility for tuning the properties of the helicene, etc.$^2$

My PhD work is related to the metal-based helicenes, metallahelicenes and heterohelicenes, and focuses on the chiroptical properties and the applications of these helicenes. The work is mainly separated into three parts.

The first topic is to synthesize some iron-ethynyl-helicene complexes, and to study their redox tuning of the chiroptical properties. These complexes contain one or two redox iron centers linked with a helicene unit through a C≡C bond. The chiroptical properties, including UV-vis, ECD, optical rotation, IR, VCD, Raman and ROA, are studied with changing the redox states of the iron center.

![Figure 2: The example of the structure of iron-ethynyl-helicene in this topic.](image)
The second topic of my work is to synthesize ruthenium-bis-ethynyl-helicene-DTE complexes containing one redox center (Ru) and one photochromic center (DTE). This molecule shows a ruthenium bridge linking the helicene unit and DTE unit in each side through C≡C bonds. The redox-triggered switching and light-triggered switching are studied by UV-vis and ECD spectroscopies, showing species dual switching activity.

![Figure 3](image1.png)

Figure 3: The example of the structure of ruthenium-bis-ethynyl-helicene-DTE complex in this topic.

The third topic of my work is to synthesize a series of platinahelicenes and their corresponding borahelicenes. Ortho-platination and ortho-borylation reaction are used for synthesizing these compounds. In this topic, the optical and chiroptical properties are studied and comparison is made towards different numbers of the helicene cycles, different numbers of the heterocycles/metallacycles. The luminescence property and circularly polarized luminescence is also studied for these compounds. Besides, a new method using a chiral sulfoxide as a chiral ligand for the resolution of some platinahelicenes is described.

![Figure 4](image2.png)

Figure 4: The examples of the structures of platina[10]helicene and bisbora[6]helicene in this topic.

Reference

Chapter 1

General introduction on helicenes
Chapter 1 General introduction on helicenes

Abstract: for this chapter, I will mainly review helicenes, their synthesis and their optical and chiroptical properties and their photophysics, together with a few applications. Since the helicenes have already been reviewed for several times, here I will briefly talk about the story of helicenes but mainly focused on the recent researches on helicenes.

§1 Chirality and helicene

§1.1 Chirality

Chirality is the property of any object that cannot be superimposable to its mirror-image. In chemistry, the molecules belonging to $C_n$, $D_n$, $I$, $O$ or $T$ group are chiral. The chirality of a chiral molecule can come from one or more different sorts of chirality, such as central chirality, planar chirality, axial chirality, etc. Isomers with identical constitution but with different arrangement of the atoms in space are called stereoisomers. When two stereoisomers are related as mirror images, they are a pair of enantiomers, otherwise, diastereoisomers. It is noteworthy that a molecule containing more than one chiral elements may also be achiral by forming a meso compound.

Central chirality is quite common in chiral molecules, and in most cases, central chirality needs a chiral center (asymmetric atom). The most important chiral center is sp$^3$-hybrid carbon atom with four different groups (or asymmetric carbon). The chirality of this chiral center can be denoted as $R/S$ according to the Cahn-Ingold-Prelog (C-I-P) priority rules. Most of the small biological molecules such as monosaccharides, amino-acids and steroids contain this asymmetric carbon, and only one chirality ($R$ or $S$) is bioactive. Similarly, some sp$^3$-hybrid phosphorus or nitrogen with different groups can also be chiral. Besides according to C-I-P priority rules, lone pair can also be counted as one group, thus some molecule such as sulfoxide can be chiral also. Another common chiral center is octahedral metal center coordinated by three bidentate ligands with propeller shape, and $\Lambda/\Delta$ is used to denote this chirality.

Besides, there are some other chirality, for example axial chirality, planar chirality and helical chirality. Helicenes and their derivatives belong to the helical chirality (Figure 1.1).

Helical chirality is a kind of inherent chirality, and we denote the chirality as $P$ or $M$. $P$ for the right-handed helix, and $M$ for the left-handed helix. For example, in nature the A-DNA and B-DNA employ $P$ helix while Z-DNA employs $M$ helix. Most of $\alpha$-helix for proteins is $P$ helix.
§1.2 Helicenes

Helicenes are the most important artificial examples of helical chirality. A helicene is constituted of ortho-fused aromatic rings, usually benzene rings, and displays a helical shape. Judging from the number of ortho-fused rings \((n)\), normally, when \(n \leq 4\), the molecule is planar. When \(n > 4\), because of the steric hindrance of two terminal rings, the molecule is no longer planar and forms helical shape, and at this time, the molecule is named as \([n]helicene\). The chirality of helicenes is denoted as \(P/M\) according to their respective right-handed or left-handed helical chirality. The requirement for the aromatic rings on helicene is not restricted and heterocycles can be involved. In fact, lots of helicenes contain substructures like thiophene, pyridine, furan, etc., and can be simply named as thiahelicenes, azahelicenes or oxahelicenes. Besides, by introducing a metallacycle into the ortho-fused helicene backbone, one can form metallahelicenes (Figure 1.2).

![Some examples of carbohelicenes (shown in P-enantiomer).](image)

![The two enantiomers of carbo[16]helicene as mirror-image.](image)

The history of helicenes synthesis can be retraced back to the year of 1903 during which the first two helicenes have been synthesized. These are aza[5]helicenes with a pyridazine (Figure 1.4a) or a pyrrole (Figure 1.4b) ring in the middle instead of benzene rings.\(^2\) The first carbo[4]helicene was reported later in 1912,\(^3\) and the first carbo[5]helicene in 1918.\(^4\) Then, more than 30 years later, \(i.e.\) in 1955, carbo[6]helicene and its resolution was published par Newman \(et\ al.,\)^\(^5\) and this was the first
example of a non-racemic helicene. Later on, in 1967 Martin et al. synthesized carbo[7]helicene and photocyclization was first introduced into helicenes synthesis. Using this method, carbo[8]helicene and carbo[9]helicene were published in 1968, and carbo[13]helicene in 1969, carbo[11]helicene, carbo[12]helicene and carbo[14]helicene in 1975. When the number of the ring becomes bigger than 13, the helicene molecule starts to have three layers, and this will gravely limit the synthesis. Only recently, the carbo[16]helicene (Figure 1.3) was synthesized by Fujita et al., and it is the longest helicene having been reported to date.

In 1971 and 1974, the first reviews on helicene were published by Wynberg and by Martin respectively. Later on, many other researchers reviewed the helicenes and their derivatives with different direction from synthesis, properties to applications.

\[\text{Figure 1.4 The first helicenes synthesized in 1903.}\]

\section{1.3 Heterohelicenes and helicene derivatives}

Other types of carbohelicenes, azahelicenes, or thiahelicenes, are also found, such as for example phosphahelicenes obtained by introducing a phosphole ring into the helicene, PAH-containing helicenes obtained by combining the PAHs (polymaromatic hydrocarbons) and helicenes together, or helicene-containing macromolecules.

Indeed, by introducing a phosphole ring into the helicene backbone, one can form a phosphahelicene. In 1993, the first phosphahelicene was synthesized; this was a phospha[5]helicene (Figure 1.5a) reported by Gladiali et al. and Wild et al. separately with different synthetic routes. Unfortunately, this helicene showed configurationally unstability and was considered as non-chiral compound at room temperature. Besides, Wild et al. also described the first arsenahelicene in the same category (Figure 1.5b). Recently, Tanaka et al. and Nozaki et al. published several phospha[7]helicenes with five-membered phosphole in middle (for example, Figure 1.5c), and these helicenes showed good optical properties. Marinetti et al. synthesized a series of phosphahelicenes with the phosphole unit laying on the external edge (for example, Figure 1.5d), and these helicenes showed good efficiency in enantioselective catalysis.
In addition, there are several macromolecules with special structure containing helicene moiety, and they are interesting in both fundamental researches and applications, such as for example some PAHs and their derivatives containing non-planar π-system. There are some pioneering works on the synthesis of helicene-containing PAHs.\textsuperscript{20} For example, in 2011, Li and Müllen \textit{et al.} published a core-extended terrylene derivatives containing two [5]helicene moieties, and showed two diatereoisomers of this molecule (homochiral and hetereochiral \textbf{Figure 1.6a}).\textsuperscript{21} In 2015, Kamikawa \textit{et al.} published a double [5]helicene derivative showing diatereoselectivity in the synthesis with only homochiral compound synthesized (\textbf{Figure 1.6b}).\textsuperscript{22} This compound also showed relatively high racemization barrier for a [5]helicene (Gibbs free energy of activation $\Delta G^\neq$ at 31.8 kcal·mol\textsuperscript{-1} at 300 K). In 2015, Itami \textit{et al.} published the first PAH containing [6]helicene moieties, and this molecule showed two diatereoisomers (homochiral and heterochiral, \textbf{Figure 1.6c}) with high isomerization barrier between them.\textsuperscript{23} Besides, due to the unique structure, it showed special π-π stacking in the solid state.

Besides, there are some other macromolecules containing helicene moieties. For example, in 1999 Katz \textit{et al.} combined four non-racemic [7]helicene moieties with a phthalocyanine core,\textsuperscript{20d} and synthesized two macromolecules with Cu or Ni atom in the center. These molecules showed non-

![Figure 1.7 Example of phthalocyanine-based helicene macromolecules.](image)

§1.4 Helicene-based metal complexes

Helicene-based metal complexes are a very important class in helicene chemistry and have been reviewed by our group recently. Another important series of helicene-based metal complexes are the helicenic metalloccenes, and pioneering work was achieved by Katz et al. between the 1970s and the 1990s. The first helicene iron complex was published in 1979, and this complex is a [5]helicene dimer bridged by two Fe atoms coordinated in the both terminal rings (Figure 1.8a). Later on, in 1982, they published another longer helicene with two terminal rings of a [7]helicene coordinating one Fe atom (Figure 1.8b), and the X-ray structure was received in 1983, showing the ferrocene-like structure for the iron center. In 1986, the enantioriched form of this [7]helicene complex was synthesized, showing huge specific rotation and circular dichroism signal. Later on, they used the similar methodology to synthesize a series of ferrocene or colbatocenium based helicene monomers, dimers or oligomers with the metal center as the linker (for example, Figure 1.8c).
Recently, Thiel et al. synthesized a series of dibenzo[c,g]fluorene-based complexes with \( \eta^5 \)-coordination of different transition metals (for example, Figure 1.9a and b),\(^{28}\) and these [5]helicene complexes showed electrochemical properties and catalytic properties. However, due to the low racemization barrier, the enantiopure form of these complexes cannot be obtained. In 2011, Urbano and Carreño et al. published a [4]helicene-based ferrocene complex which showed planar chirality (Figure 1.9c).\(^{29}\) Besides, some theoretic researches indicated the possibility to form some intramolecular helicenic metallocenes, for example the metallocenes that Cr, Mo, W or Pt atom trapped by the two terminal rings of carbo[7]helicene (Figure 1.9d),\(^{30}\) or Fe atom trapped by a [10]helicene constituted of cyclopentadiene (Figure 1.9e).\(^{31}\)

Works on \( \eta^6 \)-coordination on helicenes also have been done in 2012 by Alvarez et al., who used a \([\text{C}_5\text{Me}_5\text{Ir}]\) unit to coordinate the helicene backbone.\(^{32}\) Three different helicene complexes with different position for the coordination were synthesized, and the complex showed haptotropic rearrangement of the Ir atom on the helicene backbone from the third ring to the first ring (for example, Figure 1.10a). Besides, they also synthesized the [6]helicene with two Ir atoms coordinated, as well as the complex with [CymemeRu] unit (Figure 1.10b). An earlier computational research by Sola et al. exhibited the mechanism of this kind of haptotropic rearrangement on a carbo[4]helicene, indicating that the rearrangement processes with the metal preferring to bind to the outer rings which are less substituted and more aromatic.\(^{33}\)
Another big type of helicene-based organometallic complex is the helicene with a cyclometallated ring. If this cyclometallated ring is ortho-fused into the helicene backbone, then this type of complex can be called metallahelicene. Our group published several works on metallahelicenes. For example, the first metallahelicene published was a platina[6]helicene (Figure 1.11a) in 2010. In 2015, our group published a roll-over cycloplatinated complex containing a [6]helicene unit (Figure 1.11b) and acting as an acid-base triggered chiroptical switch. The metallahelicenes will be discussed in detail in Chapter 4.

Besides these two big types of organometallic helicene complexes, there are some other helicene-based complexes with transition metal coordinated by heteroatoms from helicene. For example, in 2014, Marinetti et al. synthesized some helicene-based phosphole gold complexes, showing good enantioselective catalysis (Figure 1.12a). Similarly, Hashmi et al. published some helicene-based phosphane gold complexes, showing good luminescent properties (Figure 1.12b). Besides, Garcia et al. published some helicene-based cyano complexes, showing interesting isomerization (Figure 1.12c).
Our lab also published some helicene-based complexes coordinated by phosphorus atom or nitrogen atom. For example, some aza[4]helicene or aza[6]helicene-based phosphole Cu and Pd complexes (Figure 1.13a and b), showing interesting stereochemistry at metal centers (for square planar Pd\textsuperscript{II} center, the chirality can be induced by the helicene units, while for the Cu\textsuperscript{I} tetrahedral center, there is no induction).\textsuperscript{38} In 2013, our lab published a helicene-capped N,P,N,P,N-helicands within a Cu\textsuperscript{I} helicate, exhibiting impacted chiroptical properties by ligand to ligand charge transfers (LLCT).\textsuperscript{39} In 2014, our lab published an aza[6]helicene platinum complex with two chlorine ligands displaying the \textit{cis}/\textit{trans} isomerism controlled by the chirality of the azahelicene ligand (different reactivities between racemic and enantiopure helicenes toward platinum) (Figure 1.13c).\textsuperscript{40}

![Figure 1.12 Some other examples of organometallic helicene complexes.\textsuperscript{19e,36,37}](a) (b) (c)

![Figure 1.13 Some helicene-based complexes studied by our group.\textsuperscript{38,39,40}](a) (b) (c)

§1.5 Helicene synthesis

Before the introduction of photocyclization, the synthesis of helicene was difficult and limited the development of helicene chemistry. For example it took 10 steps to synthesize the carbo[6]helicene,\textsuperscript{5c} and for each helicene, the synthetic method was lacking any general method. The photocyclization helped the development of helicene chemistry for its simplicity and efficient regioselectivity. Photocyclization as a use to construct \textit{ortho}-fused aromatic cycles was published in 1964 by Mallory \textit{et al.}\textsuperscript{41} Later on, Martin \textit{et al.} started to introduce this method for helicene synthesis, and diminished the steps for helicene synthesis. For example, it only needs 4 steps for synthesizing carbo[6]helicene.\textsuperscript{7} With this photocyclization reaction, Martin \textit{et al.} could synthesize up to carbo[14]helicene.\textsuperscript{6-9} The milestone in helicene synthesis is the synthesis of carbo[16]helicene \textit{via} six
photocyclizations in one-step, which was achieved in 2015 by Fujita et al.,\textsuperscript{10} and this example showed that this old powerful method is still not outdated.

Oxidative photocyclization, contains three steps: first, the cis/trans isomerization takes place under the irradiation; then, the cyclization takes place on the stilbene derivative, and a 1,3-cyclohexadiene ring is formed; subsequent oxidation takes place by catalytic amounts of iodine, and two hydrogen atoms are removed by I\textsubscript{2}, forming phenanthrene derivative (Scheme 1.1). The I\textsubscript{2} will reduced to HI which can regenerate I\textsubscript{2} by reacting with oxygen. Note that stoechiometric amounts of I\textsubscript{2} can also be used but in the presence of a HI scavenger such as propylene oxide and under inert atmosphere.\textsuperscript{13}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{scheme1.png}
\caption{Oxidative photocyclization for synthesizing phenanthrene derivatives.}
\end{figure}

For synthesizing longer helicenes, the design of the starting stilbene derivatives is quite important. For example, by starting from [4]+[3]+[4] precursor with two photocyclization, it showed 52\% of yield to get the carbo[13]helicene, while by starting from [6]+[6] precursor with one photocyclization,\textsuperscript{42} the carbo[13]helicene cannot be obtained due to the steric hindrance (Scheme 1.2). Besides, for synthesizing carbo[7]helicene, if by starting from [3]+[3], carbo[7]helicene can be obtained, while if by starting from [2]+[4], the major compound is a [4]helicene dimer (Scheme 1.3).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{scheme2.png}
\caption{Two methods of photocyclization for synthesizing carbo[13]helicene.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{scheme3.png}
\caption{Two strategies for synthesizing carbo[7]helicene.}
\end{figure}
In 1998, Pérez and Guitián *et al.* published a new method starting from arynes via palladium-catalyzed intermolecular [2+2+2] cyclotrimerization (*Scheme 1.4*), and this reaction appeared as a powerful method for constructing a $D_3$ symmetric chiral core. With this method, they synthesized some molecules containing [4]helicene, [5]helicene even [7]helicene moieties.\textsuperscript{43,44}

![Scheme 1.4 Palladium catalyzed [2+2+2] cyclotrimerization.\textsuperscript{44}]

In the same year, Starý and Stará *et al.* published the intramolecular [2+2+2] reaction to synthesize helicene-like molecules containing seven-membered oxacycles catalyzed by CpCo(CO)$_2$ (*Scheme 1.5*).\textsuperscript{45} This reaction showed an intramolecular [2+2+2] reaction starting from triynes. Later, they applied this method to synthesize carbo[5], [6] and [7]helicene derivatives by either Co or Ni as catalysts.\textsuperscript{131} This method was also used to synthesize helicene-like paraquats named helquats by Teplý *et al.*\textsuperscript{46}

![Scheme 1.5 Palladium catalyzed [2+2+2] cyclotrimerization.\textsuperscript{45}]

In 1990, Katz *et al.* developed a new method by introducing the Diels-Alder reaction to construct a [5]helicene derivative with paraquinones as the terminal rings (*Scheme 1.6*).\textsuperscript{47,48} Later on in 2000, they used the same method to synthesize [7]helicene derivatives.\textsuperscript{49}

![Scheme 1.6 Palladium catalyzed [2+2+2] cyclotrimerization.\textsuperscript{47}]

Besides, there are still many other methods to synthesize helicenes and are reviewed in many articles.\textsuperscript{13a-k}
§1.6 Resolution

In the early research, recrystallization was used for some helicenes such as carbo[n]helicenes that can crystallize in enantiopure form, and then by picking the crystals one by one, those researchers could obtain the enantiopure helicenes, and were able to study their chiroptical properties further. This method requires the helicenes to be conglomerates and spontaneously crystallize into pure enantiomers. However, when the pair is true racemate, to get the enantiopure compound is quite difficult.\(^{50}\)

The first resolution of carbo[6]helicene was performed by Newman \textit{et al.}, who used auxiliary TAPA (\(\alpha\)-(2,4,5,7-tetranitro-9-fluorenylideneaminoxy)-propionic acid, \textbf{Figure 1.14}) which formed, through the \(\pi-\pi\) stacking between the helicene and TAPA, diastereoisomers of different solubilities.\(^{5}\)

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{tapa.png}
\caption{The structure of TAPA.}
\end{figure}

The pioneering work for the resolution of helicene by chromatography was done by Klemm and Reed in 1959.\(^{51}\) In their work, the silica gel impregnated with TAPA was used as the stationary phase, and carbo[5]helicene could be partially resolved. Later on in the 1970s, Mikeš and Gil-Av \textit{et al.} started to use the high performance liquid chromatography (HPLC) for helicene resolution. In 1976, they used the silica gel coated with TAPA or its homologues as the stationary phase and successfully separated the two enantiomers from [5]helicene to [14]helicene.\(^{52}\) This system also showed good resolution for some heterohelicenes published by Wynberg \textit{et al.}\(^{53}\) Besides, binaphthyl-2,2’-diyl hydrogen phosphate (BPA)\(^{54}\) and riboflavin\(^{55}\) were also found as good candidates for the coating reagent for helicene resolution by HPLC. Recently, our group and Yashima \textit{et al.} showed the good resolution of helicene derivatives including metallahelicenes by HPLC with riboflavin derivatives as the chiral stationary phase.\(^{56}\)

§1.7 Racemization

Because the chirality is caused by the steric hindrance of the two terminal rings, the latter is very important for studying the racemization. Normally, for [4]helicenes, this steric hindrance is not big enough to keep the helicene within one configuration, and two enantiomers can interconvert into each other is very fast, so that we usually consider most of the [4]helicenes as non chiral compounds. When the ring number is \(n \geq 6\), due to the enough big steric hindrance, these helicenes are configurationally stable at room temperature.
The first racemization phenomenon was recorded by Newman et al. who found that the carbo[6]helicene undergoes partial racemization at melting point at 234 ~ 250 °C. The first study on racemization was done by Newman et al. in 1963 on 1-fluoro-12-methyl[4]helicene (Figure 1.15a), and this [4]helicene showed a relatively high racemization apparent activation energy $E_a$ ($E_a$ can be considered as racemization enthalpy of activation $\Delta H^\neq$ at not too high temperature) at 31.3 kcal·mol$^{-1}$ due to the steric hindrance caused by the fluoro and methyl groups in the ortho-position, and it is configurationally stable at room temperature. Later on, in 1969, Wynberg et al. studied the racemization of two thia[6]helicenes, and these two helicenes showed racemization Gibbs free energy of activation $\Delta G^\neq = 23.7$ and 22.0 kcal·mol$^{-1}$ at 298 K respectively, and this 1.7 kcal·mol$^{-1}$ difference causing 18 times of difference in racemization rate. In 1970, Goedicke and Stegemeyer studied the racemization process of the carbo[5]helicene and it showed $\Delta H^\neq = 22.9$ kcal·mol$^{-1}$ and $\Delta G^\neq = 24.1$ kcal·mol$^{-1}$ = 293 K. The mechanism of the racemization of carbo[5]helicene was also proposed in this publication, which occurred through a non-aromatic bridged intermediate. The study of carbo[6]helicene made by Martin et al. in 1972 showed much higher racemization barrier with $\Delta H^\neq = 33.8$ kcal·mol$^{-1}$ and $\Delta G^\neq = 37.0$ kcal·mol$^{-1}$ at 478 K, indicating very negligible racemization at room temperature. The systematic study on the racemization of carbo[7] to [9]helicenes was done in 1974, showing that both $\Delta H^\neq$ and $\Delta G^\neq$ at 290 K of these helicenes are around 40 kcal·mol$^{-1}$. This result shows that starting from carbo[7]helicene to carbo[9]helicene, the racemization barrier is not increased, although the number of rings is increased. This result indicated another racemization mechanism, and it was proposed by Lindner in 1975 and later on by Haufe et al. and Grimme and Peyerimhoff with computational study in 1996. This racemization process undergoes a twisted face-to-face $C_s$ transition states for those helicenes. In 1986, Kawazura et al. studied the racemization of some thiahelicenes (Figure 1.15a and b) and they also proposed the $C_s$ transition state for the racemization of thiahelicenes. In 2009, Starý et al. complemented the data of carbo[11]helicene, with $\Delta G^\neq = 37.5$ kcal·mol$^{-1}$ at 503 K, and the calculated result showed that the $C_s$ form was an intermediate meso compound during the racemization process.

![Figure 1.15 Some helicenes for racemization studies.](image-url)
Besides, the study on the substituted carbo[6]helicene revealed that when positions 1 and/or 16 (Figure 1.17a) are substituted by methyl groups, much higher racemization barriers than non-substituted carbo[6]helicene were obtained, while for the positions 2 and 15, there is small effect, and for the position 3, 4, 13, and 14, there is no effect. Gaucher, Prim et al. studied the effect caused by the different heteroatoms that leads to the different racemization barrier. With the change from oxygen atom to sulfur atom (Figure 1.17b), the barrier increased from 9 to 20 kcal·mol$^{-1}$.  

Figure 1.17 (a) The position of carbo[6]helicene; (b) the helicenes studied by Gaucher, Prim et al.

§2 Chiroptical properties

In the chiroptical properties, two very important factors for characterizing one chiral compound are the circular birefringence and the circular dichroism. This two factors are the two aspects (real part and imaginary part) of refractive index $\tilde{n}$. For a chiral substance, the refractive index $\tilde{n}$ is different for the left-handed and right-handed circularly polarized light, and this results in the phenomena of the circular birefringence (i.e. optical rotation) and the circular dichroism (see Appendix).

§2.1 Optical rotation and electronic circular dichroism

The optical rotation corresponds to the rotation of the plane of a linearly polarized light through a chiral substance. It is caused by the circular birefringence that two circularly polarized light showed different speed in a chiral medium.
Usually, specific rotation and molar rotation (which takes into account the molecular weight, see Appendix) are used to quantify the phenomenon of optical rotation. For helicenes both specific and molar rotation are very huge, and upon the extension of $\pi$-conjugation when forming bigger helicenes, the specific and molar rotation will increase.

Table 1.1 lists the specific rotation and molar rotation from carbo[6] to [9]helicene in sodium D line (589.3 nm)."
§2.2 Vibrational circular dichroism and Raman optical activity

Vibrational circular dichroism, or VCD, is a good experiment to study the chiroptical properties. However, few literatures have been published focusing on VCD of helicene. Recently, [7]helicene, 2-bromo[6]helicene and 5-aza[6]helicene were studied experimentally and theoretically (Figure 1.19). Because of lack of systematic studies, not too much conclusion can be drawn, and only several characteristic features can be reached.

According to the work on 2-bromo[6]helicene (Figure 1.20) done by Abbate et al., several
helical sense-responsive features can be found in the mid-IR region. Three major regions were found. First, the bands above 1400 cm\(^{-1}\) showing alternated sign with most intense features are attributed to CC stretching, possessing fairly large \(g\) factor up to \(10^{-4}\). This vibration mode was also discovered in the case of 5-aza[6]helicene\(^{74}\) and carbo[7]helicene.\(^{72}\) Second, the bands between 1400 and 1100 cm\(^{-1}\) showing monosignated feature (positive for \(M\)-helicene) correspond to in-plane HCC bending modes with moderate intensity. Third, the bands below 1100 cm\(^{-1}\) shows negative broad feature for \(M\)-helicene.

Similarly, some pioneering works of Raman Optical Activities (ROA) for several helicenes were also published recently. In 1971, Barron already theoretically predicted that carbo[6]helicene might show large Rayleigh optical activity.\(^{75}\) But until 2009, the first publication on ROA for helicene was published by Liegéois and Champagne on carbo[6]helicene and tetrathia[7]helicenes, and it theoretically showed that for the \(P\)-helicene, the most of the ROA signals were negative.\(^{76}\)

Actually ROA measurements are usually prevented by strong luminescence of the molecules and for this reason only few experimental results have been reported. Furthermore the ROA spectra use an incident wavelength at 532 nm for which most of the time the helicenes absorb; we then call the phenomenon Resonance Raman spectroscopy. The first publication of experimental ROA spectrum for helicenes was published by Abbate, Tommasini \textit{et al.} in 2013 (Figure 1.21).\(^{77,78}\) In this paper, the 2-bromo[6]helicene was studied, and the two major bands, G band and D band were put forward. This two bands are originated from the vibrational modes of graphene.\(^{78}\) Normally, taking 2-bromo[6]helicene for example, the G band has high wavenumbers at around 1658 cm\(^{-1}\), while for D band occurs at around 1368 cm\(^{-1}\) (Figure 1.22).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{roa_spectra.png}
\caption{The experimental (upper, \(P\) for blue, \(M\) for red) and calculated (lower) ROA spectra of 2-bromo[6]helicene.\(^{77}\)}
\end{figure}
2.3 Circularly polarized luminescence

The phenomenon of circularly polarized luminescence (CPL) is caused by the ability of a chiral compound in generating different left-handed and right-handed polarized lights. It is similar to the CD but in emission instead of absorption. The dissymmetry factor $g_{\text{Lum}}$ is used for quantify the CPL, and $I_L$ and $I_R$ are the intensities of left-handed and right handed polarized emission; its maximum values are -2 and +2.

$$g_{\text{Lum}} = \frac{2I_L - I_R}{I_L + I_R}$$

In 2001, Katz et al. described the first helicene (Figure 1.23) displaying CPL. This helicene showed positive CPL signal for $P$ enantiomers and negative CPL signal for $M$ enantiomer. Due to the unique structure of this helicene making aggregation in solution, the $|g_{\text{Lum}}|$ was relatively high up to 0.01.\textsuperscript{79} In 2011, Takeuchi and Tanaka et al. also took the advantage of aggregation and published another helicene (Figure 1.24a) showing specially trimeric aggregation, and the $|g_{\text{Lum}}|$ of CPL was 0.035\textsuperscript{80}. Later on in 2012 they published a [7]helicene with triphenylene units (Figure 1.24b) which had the $|g_{\text{Lum}}|$ around 0.03 even at low concentration.\textsuperscript{17b} In 2014, a special S-shaped azahelicene dimer (Figure 1.24c) was synthesized with $g_{\text{Lum}}$ at 0.028, however its monomer showed glum less than 0.001.\textsuperscript{81} This interesting phenomenon may also be due to the aggregation of this S-shaped molecule.
Figure 1.23 The first example of helicene in CPL study.\textsuperscript{79}

![Chemical Structures](image)

Figure 1.24 Selected helicenes which have been studied on CPL spectroscopy with special aggregations.

There are also several examples for the helicene without these special aggregations. Although compared with the helicenes with aggregations, these helicenes showed relatively small $|g_{\text{lum}}|$ value of CPL, it reflects that small molecule like helicene itself can also have a CPL signal. In 2003, Venkataraman \textit{et al.} published two non-aggregated azahelicenes (Figure 1.25) with $|g_{\text{lum}}|$ at 0.001 and 0.0008.\textsuperscript{82} In 2012, Hiroto and shinokubo \textit{et al.} reported an azahelicene (Figure 1.26a) with $|g_{\text{lum}}|$ at 0.003.\textsuperscript{83} In 2013, Nozaki \textit{et al.} reported a sila[7]helicene (Figure 1.26b) with strong fluorescence and high quantum yield, and this helicene showed the $|g_{\text{lum}}|$ at 0.0035.\textsuperscript{84} In 2015, Hasobe \textit{et al.} showed an [7]helicene fused by asymmetric 1,2-dialkyl-substituted quinoxaline (Figure 1.26c) with the $|g_{\text{lum}}|$ at 0.004.\textsuperscript{85} In 2014, our group reported the CPL activity of platinahelicenes (see Figure 1.11) which displayed circularly polarized phosphorescence at room temperature and could reach $|g_{\text{lum}}|$ values as high as $10^{-2}$.\textsuperscript{35} In 2015, we also reported two helicene rhenium complexes corresponding to the first chiral rhenium complexes with CPL activity, and these two helicenes showed the $|g_{\text{lum}}|$ around 0.003.\textsuperscript{86} Besides, our group also published the first example in switching of CPL which will be discussed in §3.1.
§3 Applications

§3.1 Chiroptical switching

Molecular switches are a kind of molecules which can respond to the external stimulus, change from one state to another state reversibly, and modify the output signals. According to the external stimuli, molecular switches can be divided into several kinds such as light-, pH-, redox-, coordination-, temperature-, host-guest-triggered switches, etc. When the output signals are chiroptical signals, we can name this kind of switches the chiroptical switches. The chiroptical switches can also be divided into several kinds such as ECD switches, VCD switches, CPL switches, etc., according to their chiroptical properties.

Due to their huge chiroptical properties, helicenes are good candidates to be used as chiroptical switches. There exist already helicene-based redox-triggered chiroptical switches, pH-triggered chiroptical switches as well as light-triggered chiroptical switches published recently. Our lab also
worked on the helicene-based chiroptical switches, for example the ruthenium-based redox-triggered switches.\textsuperscript{91} The redox-triggered switches and the light-triggered switches will be described in detail in Chapters 3 and 4.

The first examples of helicene-based pH-triggered switches were published by our group in 2014.\textsuperscript{92} This molecule is a helicene-grafted vinyl-osmium complex, and by using either HCl or NEt\textsubscript{3}, we can change this molecule to the carbene-osmium form (Scheme 1.7).

\textbf{Scheme 1.7} Helicene-based pH-triggered switch published by our group.\textsuperscript{92}

Later on in 2015 our group published another two helicene-based pH-triggered switches (Scheme 1.8).\textsuperscript{35} For these switches, by adding HBF\textsubscript{4} or Na\textsubscript{2}CO\textsubscript{3}, we can change the states between the pyridine form or pyridinium form, and accordingly the optical rotation, ECD spectrum and CPL spectrum could be changed. Especially, these two compounds are the first examples of switching the CPL (Figure 1.28).

\textbf{Scheme 1.8} helicene-based pH-triggered switches published by our group.\textsuperscript{35}
Figure 1.28 The switching of CPL based on these two helicenes.\textsuperscript{35} (a) Switching the fluorescence wavelength of a CPL-active organic helicene. (b) Switching the $g_{\text{hum}}$ value in an organometallic helicene.

§3.2 Racemic helicenes as emitters

Helicenes, especially those heterohelicenes containing nitrogen, boron, phosphorus or silicon atoms have good luminescence properties and are therefore good candidates for light-emitting device such as OLEDs. Not only enantiopure helicenes were studied for luminescence (or CPL) properties, but the racemic helicenes or some configurationally unstable \[4\]helicenes or \[5\]helicenes were also used as emitters. Compared with other planar PAHs these helicene-based emitters showed good solubility and reduced aggregation due to the non-planar structure, and this solved the difficulties for the low solubility of PAHs and also avoided the $\pi-\pi$ stacking when made for OLEDs. For example, in 2002 Venkataraman \textit{et al.} published some a series of azahelicenes with strong emission (for example, Figure 1.29a).\textsuperscript{93} Later on in 2011 Nakamura \textit{et al.}\textsuperscript{94} and in 2015 Wagner \textit{et al.}\textsuperscript{95} published two similar \[4\]helicenes with phosphorus or boron atom in center respectively as green emitters (Figure 1.29b and c), and showed high emission properties with quantum yields of 0.83 and 0.81 respectively. These two helicenes showed two isostructural different types of emitters (B-doped and P-doped). In 2012, Nakamura \textit{et al.} published a \[6\]helicene combining nitrogen and boron atom together, and this azaborahelicene showed unique properties that when it is in racemate form, it shows $p$-type semiconductivity, while when it is in enantiopure form, it shows $n$-type semiconductivity (Figure 1.29d).\textsuperscript{96} Recently, Liu \textit{et al.} published some diazahelicenes (for example, Figure 1.29e) with good solubility and high decomposition temperature, and they applied one of them to make a deep-blue-emitting OLED,\textsuperscript{97} and in 2014, Chen \textit{et al.} published a series of tetrahydro\[5\]helicene-based dye molecules with full-color emission, and some of them showed high quantum yield up to 0.51.\textsuperscript{98}
Other than these heterohelicene bearing emitters, are PAH derivatives that display strong emission. For example, in 2013 Yamato et al. published some pyrene-cored blue light emitter bearing one or two [4]helicene moieties (for example, Figure 1.30a and b). In 2015, Pascal et al. showed two highly luminescent molecules with the combination between mesobenzathrone with [6]helicene (for example, Figure 1.30c).

In addition, in 2012 Vauthey et al. published some [4]helicene cations, showing fluorescence in the near infrared region with quantum yield ranging between 2 and 20% (for example, Figure 1.31a). Chen et al. also reported this year a tetrahydro[5]helicene derivative, showing acid-base stimulated fluorescence switching (for example, Figure 1.31b).

§3.3 Molecular tweezers

Due to the unique helical structure, helicenes can be used as molecular tweezers, and the two
terminal rings play the role of the two arms. For example, the work of Katz et al. showed the [7]helicene tweezer behavior toward Fe atom (Figure 1.8b)\textsuperscript{25}, as well as the computational studies on helicenic metallocenes mentioned before (Figure 1.9d, e).\textsuperscript{30,31} In 2007, Deb et al. published the computational study toward to the carbo[7]helicene which showed interaction between the two terminal rings with Na\textsuperscript{+}, K\textsuperscript{+}, Cs\textsuperscript{+} or benzene rings (Figure 1.32a).\textsuperscript{103} In 2012, Fuchter et al. showed experimentally that the weak coordination between the carbo[7]helicene and Ag\textsuperscript{+} was found either through NMR experiment or crystallography.\textsuperscript{104} Recent research by Markrlik et al. showed the formation of carbo[6]helicene-Ag\textsuperscript{+} complex in the gas phase as well as in the solid phase,\textsuperscript{105} or carbo[6]helicene-Tl\textsuperscript{+} complex in the gas phase.\textsuperscript{106} In 2015, Álvarez et al. published a [6]helicene connected to two coronannulenes in the terminal rings (Figure 1.32b), and this molecules behaved as a big tweezer toward C\textsubscript{60} molecules.\textsuperscript{107}

\begin{center}
\includegraphics[width=0.8\textwidth]{figure1.32}
\end{center}

\textbf{Figure 1.32} Some examples of molecular tweezers.\textsuperscript{103,107}

\section*{3.4 Molecular Recognition}

Due to their good luminescence properties, some helicenes have potential to be used as luminescent sensors for molecular recognition. For example in 2001, Reetz et al. published that enantiopure 2,15-dihydroxy[6]helicene (HELIXOL, Figure 1.33a) had the capability in discriminating enantiomeric forms of amines and amino alcohols from fluorescence quenching, and this HELIXOL could be treated as an enantioselective fluorescent sensor.\textsuperscript{108} In 2013, Sasaki et al. showed the enantioselective binding and chiral recognition between 1,14-dimethyl[5]helicene-spermine ligand (Figure 1.33b) and B-DNA or Z-DNA.\textsuperscript{109}

\begin{center}
\includegraphics[width=0.8\textwidth]{figure1.33}
\end{center}

\textbf{Figure 1.33} Some helicenes in molecular recognition.\textsuperscript{108,109}
With this chiral recognition property, helicene can also be used for the resolution of racemic compounds. In 2012, Yamaguchi et al. published a silica nanoparticle graphed with a conformationally stable [4]helicene derivative (Figure 1.34a), and this nanoparticle could kinetically resolve some aromatic alcohols. This type of nanoparticle also showed the recognition to some double helix oligomers. In 2014, our group and Yashima et al. published an acetylene polymer bearing optical active [6]helicene moiety (Figure 1.34b), and this polymer showed a high chiral recognition toward 1,1′-binaphthyl derivatives.

![Figure 1.34 Some helicene derivatives for chiral recognition and resolution.](image)

### §3.5 Asymmetric Catalysis

The unique helical structure of helicene makes it possible for enantiopure helicene to be used in some asymmetric catalysis, and this was reviewed recently by Marinetti et al. Although the history of helicene lasts for more than 100 years, due to the limitation in synthesizing large amounts, the first publication in the application of helicene in catalysis appeared in 1997, by Reetz et al. who synthesized 2,15-bis(diphenylphosphino)[6]helicene (P-Helix, Figure 1.35a) as ligand for catalysis. This ligand was treated with [Rh⁺(COD)₂]BF₄⁻ to form the P-Helix-Rh⁺(COD)BF₄⁻ and was used in enantioselective hydrogenation of itaconic acid ester. Later on in 2000, they showed that this P-Helix had excellent performance in the kinetic resolution in Pd-catalyzed allylic substitution. In 2001, Katz et al. prepared a bis[5]helicenediol ligand ([5]HELOL, Figure 1.35b), and treated it in the addition of Et₂Zn to aryl aldehydes. In 2003, Yamaguchi et al. developed a bishelicenol phosphite ligand (Figure 1.35c) and also applied it in the Rhodium catalyzed hydrogenation of itaconate. This ligand displays three different chiralities (helicene moiety, axial chirality and R group), and a matched/mismatched phenomenon was observed.

![Figure 1.35 Some examples of helicenes applied in catalysis.](image)
In 2001, Soai et al. used enantioenriched carbo[5]helicene or carbo[6]helicene as catalysts in 2001,\textsuperscript{117} and later on thia[7]helicene in 2006\textsuperscript{118} for addition of \textsuperscript{3}Pr\textsubscript{2}Zn to aryl aldehyde (Soai Reaction, Scheme 1.9). The Mechanism of Soai Reaction is autocatalytic,\textsuperscript{119} and the helicenes were the chiral initiator; the reaction appeared extremely efficient even by starting from enantioenriched helicene with e.e. less than 1%. Besides, some azahelicene N-oxides also showed the asymmetric catalysis in addition of aryl aldehydes by allenyltrichlorosilane.

![Scheme 1.9 Soai Reaction.117,118](image)

From 2014, Marinetti et al. also published several helicene-based catalysts by using enantiopure phosphahelicenes or phosphole-bearing helicenes. For example, by connecting with gold metal, those helicenes (Figure 1.36) can be used as enantioselective catalysts in the enyne cycloisomerization (Scheme 1.10).\textsuperscript{19c} Later on in 2015, they published the enantioselective allene cyclization by using gold bearing helicenes with similar structure (Scheme 1.11).\textsuperscript{120}

![Figure 1.36 Some examples of phosphole-based helicene published by Marinetti et al.19c](image)

![Scheme 1.10 helicene-based gold complex in enantioselective enyne cycloisomerization.19c](image)

![Scheme 1.11 helicene-based gold complex in enantioselective allene cyclization.120](image)

\textbf{§4. Conclusion}

To sum up, in this chapter, I mainly presented the most important types of helical chiral compounds, the helicenes. I discussed the preparation of helicene from synthesis and resolution. The
use of photocyclization has been a major synthetic method for synthesizing helicenes, and the use of TAPA has been a milestone in the resolution of helicene, while more common techniques involve HPLC separations. Besides, I also presented the chiroptical properties of helicenes. For example, helicenes have large optical rotations, and significant ECD signals. I also discussed recent research hotspots in helicenes chemistry like VCD, ROA and CPL. Finally, I discussed the applications of helicenes like chiroptical switches, light emitters, molecular tweezers, molecular recognition as well as catalysis. We will see in the next chapters that helicenes are good models for chiroptical switching and circularly polarized luminescence.

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Chapter 2

Iron-ethynyl-helicenes: redox-tuning of the chiroptical properties
Chapter 2 Iron-ethynyl-helicenes: redox-tuning of the chiroptical properties

Abstract

In this chapter, three iron complexes 1a, 1b and 1c were synthesized and fully characterized. Their electrochemical properties were characterized by cyclic voltammetry, and showed two redox states for each complex 1a,b (1a and [1a]⁺, 1b and [1b]⁺) and three states for 1c (1c, [1c]⁺ and [1c]²⁺), and the oxidized states showed paramagnetic property according to EPR and SQUID experiments. Redox-triggered switching activity was studied by UV-vis and ECD spectroscopies in an optically transparent thin-layer electrochemical (OTTLE) cell. The compounds also showed tunable response upon chemical oxidation in infrared (IR), vibrational circular dichroism (VCD), Raman and Raman Optical Activity (ROA) spectroscopies as well as polarimetry at different wavelengths including the telecommunication region.

§1 Introduction on helicene-based redox-triggered chiroptical switches

§1.1 Organic helicene-based redox-triggered switches

Nowadays, molecular switches are of interest in many field including molecular motors, molecular computers and molecular recognition.¹ As mentioned in Chapter 1, helicenes or helicene-like molecules have the potential of making efficient chiroptical switches. For example, the helicene, if redox-active, it can be used as a redox-triggered chiroptical switch.¹ This kind of switch can display a response to an external potential change. By modulating the value of the potential, it can reversibly change from one redox state to another redox state by gaining or losing one or more electrons. Accordingly, the optical properties, as well as chiroptical properties, can also change, and due to this electrochromic property, the switch can convert the electrical stimulation to optical and chiroptical signals. Spectroelectrochemistry² has been often used in studies of these redox-triggered chiroptical switches.

Scheme 2.1 General scheme of a redox-triggered switch containing two redox state A and B.

Based on the different designs of the skeleton, different redox-switchable helicene-like molecules can be synthesized. For example, in 2001, Suzuki et al. published a switch adopting a dihydro[5]helicene/binaphthyl system.³ In this system, the two states, the dihydro[5]helicene state and binaphthyl state, can switch to each other by breaking or reforming the central C–C bond via a two-electron redox process (Scheme 2.2). Meanwhile, from the structural point of view, the chirality of the molecule can reversibly switch between the helical chirality and the axial chirality. Correspondingly, the ECD spectrum exhibits drastic changes. Notably, the variation of Δε value
reaches 140 L·mol\(^{-1}\)·cm\(^{-1}\) at 290 nm.

![Diagram](image.png)

**Scheme 2.2 Example of the dihydro[5]helicene-based redox-triggered switch.**

Based on this result, this group has later on developed several other dihydro[5]helicene-based redox-triggered switches, and some of them show multi-input/multi-output response property or four-way-output response property.\(^4\)

Teplý *et al.* published another helicene-based switch by introducing electron-accepting viologen-type structure into a helicene which shows three redox states from the dicaticonic state, to the monocationic radical state, then to the neutral state by two successive reduction processes (**Scheme 2.3**).\(^5\) Accordingly, the ECD spectrum shows modification and generation of new active bands in the visible and near-IR region. Besides, ON/OFF switching or positive/negative switching in ECD spectroscopy can be observed with several measurement cycles on an appropriately chosen readout wavelength. This example shows an innovative combination between the redox-active unit and chiral unit: for common helicenes, reversibility and bistability are usually not good enough to be treated as switches, while by fusing or connecting a redox-active unit, reversibility and bistability can be largely improved.

![Diagram](image.png)

**Scheme 2.3 Redox process of viologen-type [5]helicene.**

In 2010 by Rajca *et al.* published a thiahelicene as a redox-triggered chiroptical switch.\(^6\) This helicene contains seven *ortho*-fused thiophene rings, and by an oxidation process, it can go from neutral state to radical cationic state (**Scheme 2.4**). This switch also showed a big modification in the ECD spectrum between the two redox states as measured by spectroelectrochemistry. Interestingly, the life-time of the radical cationic state has been examined by EPR spectroscopy. By chemical oxidation with NOPF\(_6\), this radical cationic species can exist at room temperature with a half-life time around 15 ~ 20 min, and obvious degradation occurred during the cycling experiment.
The works based on carbohelicene derivatives were also published by Avarvari and Crassous et al.\(^7\) and Diederich and Crassous et al.,\(^8\) who respectively introduced a redox-active ethylenedithio-tetrathiafulvalene (EDT-TTF) or a quinone unit fused to [6]helicene respectively (Figure 2.1). Both EDT-TTF and quinone units are designed with fusion and efficient \(\pi\)-conjugation to the helicene backbone.

![Scheme 2.4 Redox process of the thio[7]helicene.](image)

From Avarvari’s work, the EDT-TTF-based helicene shows two reversible redox states from neutral state to radical cationic state. In the spectroelectrochemistry experiment, the ECD spectrum shows changes in the visible and near-infrared region between these two states and shows good reversibility (Figure 2.2). Besides, the crystal structure of this compound has also been studied and it may have the potential to make a chiral conductor.

![Figure 2.1 EDT-TTF-based redox-active helicene (a); quinone-based redox-active helicene (b).](image)

![Figure 2.2 The ECD spectra of EDT-TTF-based helicene (red: reduced state, blue: oxidized state).](image)

The Diederich’s work shows that the quinone-based helicene has two redox states from neutral state to radical anionic state by gaining one electron. Similarly, in spectroelectrochemistry, the ECD
spectrum shows large changes in the bisignated helicene band between two redox states and reveals good reversibility. Besides, the elemental lithium was used as chemical reductant for reaching the radical anionic state and the molecule formed a radical anionic lithium complex with two oxygen atoms chelating the lithium atom. By electron nuclear double resonance (ENDOR) spectroscopy study, this radical complex also exhibits the property of chiral recognition the enantiomeric pair of binaphthyl-diphosphine oxide (Figure 2.3).

**Figure 2.3** The chiroptical switching and chiral recognition of quinone-based helicene.

### §1.2 Helicene-based redox switches with metal centers.

Introducing redox-active metal centers into a helicene is also a good method to reach the redox-triggered switches. In 1993, Katz *et al.* has studied the redox property of a cobaltocene-bearing [9]helicene oligomer (Figure 2.4a). This preliminary work showed that the oligomer can be electrochemically reduced from CoIII to CoII and re-oxidized under air. The corresponding ECD spectrum showed the changes (Figure 2.4b). Unfortunately, the study of the switching activity was not continued, although various kinds of potentially redox-switchable helicenes containing cobaltocene or ferrocene unit had been synthesized by Katz *et al.* at that time.

![Figure 2.4](image-url)

**Figure 2.4** Cobaltocene-bearing [9]helicene oligomer (a); and its ECD spectra of the redox process (b).

After around one decade, our group started to investigate the metal-based helicene complexes systematically, and in 2012 a ruthenium-based helicene complex was developed, which showed redox-switchable chiroptical properties. This was the first example of helicene-based chiroptical redox-triggered switch containing metal center, and it shows big modulation of the ECD spectrum in visible and near-infrared regions, as well as excellent reversibility. From a synthetic point of view, this molecule shows simple strategy by starting from an enantiopure ethynyl-functionalized organic helicene and a ruthenium complex as a precursor for hydroruthenenation (Scheme 2.5). Besides, similar architecture can also be used as an acid-base chiroptical switch. Indeed, our lab synthesized a similar
[6] helicene-based vinyl-osmium complex in 2014, showing strong modification in ECD spectroscopy as well as IR spectroscopy.\textsuperscript{12}

\[
\text{Scheme 2.5 Synthetic route for the ruthenium-vinylhelicene.}
\]

This strategy gives a general synthetic route for different types of metal-based redox-switchable helicenes by simply connecting the helicene unit and the metal complex unit. This kind of helicenes can benefit not only from the advantages of reversibility and bistability of the metal center, but also inheriting the significant chiroptical properties of the helicene. In this chapter, we are seeking new metal-based redox-switchable helicenes with good reversibility and bistability, and besides, we will study the chiroptical properties not only in the electronic region but also in the vibrational region.

\section*{§1.3 The (\(\eta^2\)-dppe)(\(\eta^5\)-CsMes)Fe–C≡C– building block}

The reversibility and the bistability are both very important for redox-triggered chiroptical switches, and still a big difficulty for helicene-based switches. Usually, for a pair of redox states of a helicene-based switch, only the starting state is stable and the counterpart state is not so stable with either low life-time or high sensitivity to air or water, and normally this counterpart can only be obtained \textit{in situ}, chemically or electrochemically, from the starting state, and cannot last for a long time. This short-coming usually shortens the number of cycles and makes some long-time experiment (\textit{e.g.} VCD experiment) not accessible, thus is disadvantageous for both the study and the application of this kind of switches.

For us, we want to find some redox-switchable metal-based building blocks with good reversibility and bistability for synthesizing our helicene-based switches. Here we present a good candidate, (\(\eta^2\)-dppe)(\(\eta^5\)-C\(_5\)Me\(_5\))Fe–C≡C– building block.\textsuperscript{13} This building block usually possesses two stable redox states: Fe\(^{II}\) neutral state and Fe\(^{III}\) cationic state, that can reversibly switch to each other by losing or gaining one electron using electrochemistry (\textbf{Scheme 2.6}). The complex in its Fe\(^{II}\) neutral state can be synthesized by organometallic chemistry and is stable in the solid state under air. The Fe\(^{III}\) cationic state can be obtained from the Fe\(^{II}\) neutral by one chemical oxidation and is stable under argon at least for several weeks. This life-time is long enough for the fundamental study of this oxidized state as well as for increasing the redox cycling numbers.

The good interaction between the redox-switchable building block and the helicene is also quite important, and this building block can connect an aryl ligand \textit{via} a C≡C bond, and shows good interaction by \(d\pi\)-conjugation between the iron center and the ethynyl-aryl ligand. The aryl ligand can be considered as a non-innocent ligand because it is also involved into the redox process due to the
good interaction.\textsuperscript{13} Lapinte et al. and Paul et al. have thoroughly studied this building block, and the properties of both states (NMR, UV-Vis, near-IR, mid-IR, EPR, fluorescence, to molecular orbitals, molecular polarizabilities, functional aryl group effects, magnetic properties).\textsuperscript{14}

\[
\begin{array}{c}
\text{Fe}^\text{II} \quad \text{Fe}^\text{III} \\
\begin{array}{c}
\text{Ph}_2\text{P} \quad \text{PPh}_2 \\
\text{Ar}
\end{array}
\end{array}
\]

\textbf{Scheme 2.6} Redox states of \((\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}–\text{C}≡\text{C}–\) building block linking with aryl group.

From a synthetic point of view, complexes containing this Fe building block are not complicated to be synthesized.\textsuperscript{15} Usually, one can synthesize the complex in its neutral state starting from \((\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{FeCl}\) and aryl-substituted acetylene (Ar–≡–H) in the presence of NaPF\textsubscript{6} in the solvent mixture of CH\textsubscript{3}OH and THF under argon. After the reaction, a vinylidene cationic complex is formed as the intermediate. Then, by reacting with the base \(t\text{-BuOK}\), this intermediate can be deprotonated in the \(\beta\)-position and form the target neutral \(\text{Fe}^\text{II}\) species (Scheme 2.7). The cationic \(\text{Fe}^\text{III}\) state can be obtained by reacting with chemical oxidant such as FcPF\textsubscript{6} or iodine.

\[
\begin{array}{c}
\text{Fe}^\text{II} \quad \text{Fe}^\text{III} \\
\begin{array}{c}
\text{Ph}_2\text{P} \quad \text{PPh}_2 \\
\text{Ar}
\end{array}
\end{array}
\]

\textbf{Scheme 2.7} Synthetic route for the iron complex in \(\text{Fe}^\text{II}\) state.

The mechanism for forming the vinylidene intermediate is: 1) Cl\textsuperscript{−} is discoordinated from \(\text{Fe}(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}\) with the help of a polar solvent and reacts with Na\textsuperscript{+} from NaPF\textsubscript{6}, forming NaCl precipitate, while \(\text{Fe}(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)^+\) cation is generated; 2) \(\pi\) orbital of ethynyl group coordinates to the newly generated \(\text{Fe}(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)^+\), forming a \(\pi\) coordinated complex; 3) this \(\pi\) coordinated complex isomerizes to vinylidene complex via a [1,2]-\(\sigma\) hydrogen transfer, forming the vinylidene intermediate (Scheme 2.8).

\[
\begin{array}{c}
\text{Fe}^\text{II} \quad \text{Fe}^\text{III} \\
\begin{array}{c}
\text{Ph}_2\text{P} \quad \text{PPh}_2 \\
\text{Ar}
\end{array}
\end{array}
\]

\textbf{Scheme 2.8} Mechanism of the reaction to generate vinylidene complexes 3.

The neutral state shows closed shell singlet with 18 e\textsuperscript{−} for the Fe center, while the cationic state shows open shell doublet with 17 e\textsuperscript{−} for the Fe center. This indicates that the cationic species is a radical cation with one unpaired electron, and can exhibit special magnetic property. If the molecule contains multiple Fe centers, the mixed-valence state can be reached, and some of them, displaying
good interaction, can be applied as molecular wires. The magnetic properties for the molecules containing multiple Fe\textsuperscript{III} centers are also interesting to study. For example by adapting different linking spacer, the interaction between these Fe\textsuperscript{III} centers behaves different, and mainly can be classified to three cases: paramagnetic interaction, ferromagnetic interaction or antiferromagnetic interaction.

§1.4 Design of our complexes

Based on the knowledge above, we have designed three iron-based helicenes: [4]helicene-ethynyl-[Fe\textsuperscript{II}] 1a, [6]helicene-ethynyl-[Fe\textsuperscript{II}] 1b and [6]helicene-bis(ethynyl-[Fe\textsuperscript{II}]) 1c (Figure 2.5) in neutral state forms. The building block (\(\eta^2\)-dppe)(\(\eta^5\)-C\textsubscript{5}Me\textsubscript{5})Fe–C≡C– is connected on the 2-position of helicene terminal ring. Non-chiral 1a has been designed for the comparison with the chiral [6]helicenes 1b and 1c, and also due to the easy synthesis of the [4]helicene ligand, 1a can also be used for optimizing the reaction and measurement conditions. 1b contains one iron center and 1c contains two iron centers, and this two complexes have been designed for studying the chiroptical switching properties, and by comparing these two complexes with different numbers of iron centers, we can study the influence on the chiroptical properties. Besides, 1c can exhibit three redox states from neutral Fe\textsuperscript{II}-Fe\textsuperscript{II} state, to radical cationic Fe\textsuperscript{II}-Fe\textsuperscript{III} mixed valence state, then to fully oxidized dicationic Fe\textsuperscript{III}-Fe\textsuperscript{III} state, and different redox states may have different chiroptical properties. Also 1c is interesting for studying the magnetic interaction between the two iron centers.

![Figure 2.5 The designed iron-based redox-switchable helicenes 1a, 1b and 1c.](image)

§2 Synthesis

§2.1 Synthesis of neutral species

The ligands 2-ethynyl[4]helicene 2a, 2-ethynyl[6]helicene 2b and 2,15-diethynyl[6]helicene 2c, and the iron complex precursor Fe(\(\eta^2\)-dppe)(\(\eta^5\)-C\textsubscript{5}Me\textsubscript{5})Cl\textsuperscript{18} were prepared according to the literature. Enantiopure P-2b and M-2b, P-2c and M-2c were resolved by preparative chiral HPLC separation.\textsuperscript{11}

The three neutral species 1a, 1b or 1c were synthesized referring to the method mentioned in §1.4. Fe(\(\eta^2\)-dppe)(\(\eta^5\)-C\textsubscript{5}Me\textsubscript{5})Cl reacts with the free ethynylhelicene ligands 2a, 2b or 2c under argon in the presence of NaPF\textsubscript{6} for 48 hours to generate positively charged iron vinylidene complexes 3a,
3b or 3c with PF$_6^-$ as the counter-anion, and these vinylidene complexes can respectively generate the target neutral species 1a, 1b and 1c in the acetylide form by the deprotonation process with the help of t-BuOK (Scheme 2.9). The vinylidene intermediates 3a, 3b or 3c are quite sensitive towards air or water, while the acetylides 1a, 1b and 1c show relatively high stability in air in the solid state or in solution under inert atmosphere.

![Scheme 2.9 Synthetic route to the neutral species 1a, 1b and 1c.](image)

In this chapter, we have synthesized non-chiral iron helicene complex 1a, racemic complexes rac-1b and rac-1c (unless emphasized, hereafter in this chapter, “rac-” will be omitted), as well as enantiopure complexes P-1b and M-1b, P-1c and M-1c, by starting from the non-chiral ligand (2a), the racemic ligands (rac-2b and rac-2c) and enantiopure ligands (P-2b and M-2b, P-2c and M-2c) respectively with totals yields around 51-77%. These compounds were characterized by high-resolution mass spectrometry (See Experimental Part) and NMR spectroscopies. Red single crystals of 1a, 1b and 1c were grown by slow diffusion of pentane vapors into dichloromethane solutions under inert atmosphere and the structures were solved by X-ray diffraction.

§2.2 X-ray studies

Complex 1a crystallized in the non-centrosymmetric $P2_12_12_1$ space group (Figure 2.1). From the bond angles of P1-Fe1-P2, P1-Fe1-C37 and P2-Fe1-C37 which are close to 90°, one can clearly see that the iron center adopts an octahedral geometry and shows a piano stool structure with 2 phosphorus and 1 carbon atoms coordinating for each direction, pair-wise perpendicular, and $\eta^5$-
C$_5$Me$_5$ occupying the other three directions. The [4]helicene shows a helical structure with helical curvature (the dihedral angle between the planes of two terminal rings of the helicene) of 22.3°, and together with the space group, we can conclude that 1a is crystallized as a conglomerate form, and each single crystal of 1a is chiral, showing same P or M helix. This result is not contradictory with the consideration that 1a exhibits non-chiral in solution, as explained in §2.3. Selected bond angles and distances are depicted in Table 2.1. Compared with the C≡C bond of ethyne (1.203 Å), this CC bond here is much longer (1.232 Å), indicating the delocalization of the π orbital to the helicene plane as well as Fe atom. Small distortion of the Ar−C≡C−Fe bonds was observed (the angles of C39−C38−C37 and C38−C37−Fe1 are deviated from 180°), which may be caused by the steric hindrance between the helicene rings and bulky Fe building block.

![Figure 2.6: Molecular structure of 1a.](image)

**Table 2.1** Selected bond distances and bond angles for 1a.

<table>
<thead>
<tr>
<th>Bond distance (Å)</th>
<th>Bond angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe1−C37</td>
<td>1.880(4)</td>
</tr>
<tr>
<td>Fe1−P1</td>
<td>2.166(1)</td>
</tr>
<tr>
<td>Fe1−P2</td>
<td>2.178(1)</td>
</tr>
<tr>
<td>C37−C38</td>
<td>1.232(5)</td>
</tr>
<tr>
<td>C38−C39</td>
<td>1.419(5)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond angle (°)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>P1−Fe1−P2</td>
<td>86.08(4)</td>
</tr>
<tr>
<td>P1−Fe1−C37</td>
<td>87.3(1)</td>
</tr>
<tr>
<td>P2−Fe1−C37</td>
<td>83.1(1)</td>
</tr>
<tr>
<td>Fe1−C37−C38</td>
<td>175.5(3)</td>
</tr>
<tr>
<td>C37−C38−C39</td>
<td>173.2(4)</td>
</tr>
</tbody>
</table>

The complex 1b crystallized in the non-centrosymmetric $P2_1$ space group (Figure 2.7). Selected bond angles and distances are depicted in Table 2.2. This monoclinic space group with one twofold screw axis indicates that the molecule also crystallizes in the conglomerate form. Although the single crystal was obtained from the racemic solution, all the helicenes in this single crystal display $M$ stereochemistry. The iron center also shows the octahedral geometry with $η^5$-C$_5$Me$_5$ occupying the three directions. Compared to the helical curvature of 1a, that of the 1b is much bigger, which is 53.1°, and this value is normal for [6]helicenes.\(^1\) Similar to 1a, 1b also exhibits the delocalization of the
C≡C bond and small distortion of Ar–C≡C–Fe.

Figure 2.7: Molecular structure of M-1b.

Table 2.2 Selected bond distances and bond angles for 1b.

<table>
<thead>
<tr>
<th>Bond distance (Å)</th>
<th>Bond angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe1–C37</td>
<td>1.890(4)</td>
</tr>
<tr>
<td>P1–Fe1–P2</td>
<td>86.10(5)</td>
</tr>
<tr>
<td>Fe1–P1</td>
<td>2.189(1)</td>
</tr>
<tr>
<td>P1–Fe1–C37</td>
<td>85.0(1)</td>
</tr>
<tr>
<td>Fe1–P2</td>
<td>2.171(1)</td>
</tr>
<tr>
<td>P2–Fe1–C37</td>
<td>85.5(1)</td>
</tr>
<tr>
<td>C37–C38</td>
<td>1.217(6)</td>
</tr>
<tr>
<td>Fe1–C37–C38</td>
<td>173.6(4)</td>
</tr>
<tr>
<td>C38–C39</td>
<td>1.433(6)</td>
</tr>
<tr>
<td></td>
<td>C37–C38–C39</td>
</tr>
</tbody>
</table>

The complex rac-1c crystallized in the centrosymmetric triclinic $P\overline{1}$ space group (Figure 2.8), and selected bond angles and distances are depicted in Table 2.3. Contrary to 1b, the space group of 1c shows that it crystallized as a $P$ and $M$ racemate form. Besides, a $C_2$ axis exists in this molecule which is perpendicular to the helicene axis. This symmetry element facilitated the characterization of this complex. The helical curvature for the [6]helicene of 1c is 60.5°, and this value is quite big among [6]helicenes.\textsuperscript{19} It may be caused by the steric hindrance of the two bulky iron building blocks. From the value of the bond angles and distances, the delocalization of both C≡C bonds and small distortion of both Ar–C≡C–Fe bonds can also be observed in the crystal structure. The smaller C$_3$Me$_3$ groups are in the direction along the helicene, while the bigger dppe groups are in the direction against the helicene for avoiding the big steric hindrance. The distance between the two Fe atoms is 10.8 Å.
Figure 2.8: Molecular structure of 1c (P-enantiomer was selected).

Table 2.3 Selected bond distances and bond angles for 1c.

<table>
<thead>
<tr>
<th>Bond distance (Å)</th>
<th>Bond angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe1–C37</td>
<td>1.892(4)</td>
</tr>
<tr>
<td>Fe1–P1</td>
<td>2.187(2)</td>
</tr>
<tr>
<td>Fe1–P2</td>
<td>2.170(2)</td>
</tr>
<tr>
<td>C37–C38</td>
<td>1.211(6)</td>
</tr>
<tr>
<td>C38–C39</td>
<td>1.420(5)</td>
</tr>
<tr>
<td>Fe1–P2</td>
<td>2.178(2)</td>
</tr>
<tr>
<td>P1–Fe1–P2</td>
<td>85.96(6)</td>
</tr>
<tr>
<td>P1–Fe1–C37</td>
<td>88.9(2)</td>
</tr>
<tr>
<td>P2–Fe1–C37</td>
<td>83.8(2)</td>
</tr>
<tr>
<td>Fe1–C37–C38</td>
<td>173.6(5)</td>
</tr>
<tr>
<td>C37–C38–C39</td>
<td>172.3(6)</td>
</tr>
<tr>
<td>Fe2–C66</td>
<td>1.888(4)</td>
</tr>
<tr>
<td>Fe2–P3</td>
<td>2.178(2)</td>
</tr>
<tr>
<td>Fe2–P4</td>
<td>2.175(2)</td>
</tr>
<tr>
<td>C66–C65</td>
<td>1.228(6)</td>
</tr>
<tr>
<td>C65–C57</td>
<td>1.423(6)</td>
</tr>
<tr>
<td>P3–Fe2–P4</td>
<td>86.26(5)</td>
</tr>
<tr>
<td>P3–Fe2–C66</td>
<td>84.0(1)</td>
</tr>
<tr>
<td>P4–Fe2–C66</td>
<td>85.5(1)</td>
</tr>
<tr>
<td>Fe2–C66–C65</td>
<td>177.5(4)</td>
</tr>
<tr>
<td>C66–C65–C57</td>
<td>175.0(4)</td>
</tr>
</tbody>
</table>

§2.3 NMR spectroscopy

NMR samples of 1a, 1b and 1c were prepared in CD$_2$Cl$_2$, and $^1$H NMR (Figure 2.9, Figure 2.10 and Figure 2.11), $^{13}$C NMR, $^{31}$P NMR spectroscopies were measured, as well as 2D NMRs ($^1$H–$^1$H COSY, HMQC and HMBC) for peak assignment. It is worth noting that the samples should be prepared carefully under argon, avoiding any oxidation processes, because trace oxidation can cause some shifts and broadening of some peaks. Indeed from the literature, the oxidation process can generate some paramagnetic species, and due to the relatively fast electron exchange reaction between the compound and oxidized species, NMR shows averaged single set of signals of them, thus from the spectra some large or small shift and broadening of the peaks can be discovered if any oxidation processes have happened.
Figure 2.9 The $^1$H NMR spectrum (400 MHz) of 1a in CD$_2$Cl$_2$ at 25 °C.

Figure 2.10 The $^1$H NMR spectrum (400 MHz) of 1b in CD$_2$Cl$_2$ at 25 °C.
Figure 2.11 The $^1$H NMR spectrum (400 MHz) of 1c in CD$_2$Cl$_2$ at 25 °C.

All the peak assignments for 1a, 1b and 1c in $^1$H NMR and $^{13}$C NMR spectroscopy were done (see Experimental Part). For the [4]helicene 1a, the chemical shift of helicene protons ranges from 9 to 7 ppm, while for [6]helicenes 1b and 1c, from 8 to 6.5 ppm. The characteristic peak of 15 protons from C$_5$Me$_5$ have chemical shifts around 1.5 ppm as a singlet. In $^{13}$C NMR, the most intense peaks are the 5 aromatic carbons and 5 peripheral carbons of the C$_5$Me$_5$ group around 88 ppm and 10 ppm. Besides, the $\alpha$-carbon (Ar−C≡C$_\alpha$−Fe) of the ethynyl group shows a broad peak in 144.26 for 1a, while for 1b and 1c this peak cannot be found due to the long relaxation time $T_2$ from the connecting iron. The $\beta$-carbon of the ethynyl group shows also a broad peak (121.50 for 1a, 121.97 for 1b and 122.03 for 1c).

Interestingly, diastereotopy phenomenon on the symmetric dppe ligand was found for 1b and 1c. In the $^1$H NMR spectrum of 1a, 2 sets of peaks between 3 to 1.5 ppm were found for the 4 CH$_2$ protons from dppe, thus 2 of them for the endo-position and the rest 2 for the exo-position (Figure 2.12), and in this case, no diastereotopy phenomenon was found. However, in the spectra of 1b and 1c, 4 sets of peaks in this region were found, namely, each proton has a distinct peak. So in these two case, diastereotropic phenomenon was found. Diastereotropic phenomenon is caused by the induced chirality influencing on two symmetric but magnetically equivalent protons, and these two protons become chemically inequivalent due to the chirality. Here, due to the chirality from helicene, two symmetric CH$_2$ are not chemically equivalent and show their own chemical shifts. Similarly, the protons from the phenyl rings display the same phenomenon as well. In the $^{13}$C NMR, without the
disturbance of endo-/exo-position, this phenomenon is clearer: we found two peaks for CH₂ carbons for 1b and 1c, while one peak for 1a.

![Figure 2.12](image) (a) The endo- and exo-positions.

In $^{31}$P NMR spectrum we can also find this diastereotopy phenomenon (Figure 2.13). 1a has a single peak at 99.56 for the two phosphorus of dppe, while 1b and 1c show two broad peaks (99.41 and 95.55 for 1b; 99.93 and 95.40 for 1c).

![Figure 2.13](image) The $^{31}$P NMR spectra (162 MHz) of 1a, 1b and 1c in CD$_2$Cl$_2$ at 25 °C.

This diastereotopy phenomenon indicates that 1a appears as a non-chiral molecule, while 1b and 1c are chiral. For 1b and 1c, there is no doubt, while for 1a, this result seems opposite to the result from X-ray diffraction experiment that the helicene unit shows chirality in crystals. Certainly, this two results should not be contradictory with each other: the racemization of the [4]helicene between P- and M-isomers can exist for 1a, and in crystals this racemization is blocked, while in solution it occurs in relatively fast speed. Therefore, 1a can be treated as a non-chiral compound in solution.

§2.4 Cyclic voltammetry studies

The iron center is redox-active and can exist in its Fe$^{II}$ neutral state and Fe$^{III}$ cationic state, so that the neutral Fe$^{II}$ species 1a and 1b can switch to their mono-radical cationic Fe$^{III}$ states [1a]$^+$ and [1b]$^+$ by losing one electron (Scheme 3.10).
More complicated, for neutral species 1c, because it has two iron centers, 1c can switch to the mono-radical cationic state $[1c]^+$ and then to di-radical cationic state $[1c]^{2+}$ by losing one more electron (Scheme 2.11).

The cyclic voltammetry (CV) experiment of 1a, 1b and 1c were measured in CH$_2$Cl$_2$ solution in the presence of NBu$_4$PF$_6$ salt with concentration around 0.2 mol·L$^{-1}$ at 25 °C under inert atmosphere. The results show that 1a and 1b have a reversible one-electron oxidation wave at $-0.64$ V (vs. Fe$^+/Fe^0$) and $-0.60$ V respectively, while 1c displays two close reversible one-electron oxidation waves at $E_{[1c]^{2+}/[1c]^+} = -0.64$ V and $E_{[1c]^+/1c} = -0.55$ V (Figure 2.14).

**Figure 2.14** The cyclic voltammograms of 1a, 1b and 1c with scan rate of 0.2 V·s$^{-1}$. 
The difference between the 2 oxidation potentials \( \Delta E = E_{[1c]^+/[1c]} - E_{[1c]^{-2+}/[1c]^{-1+}} \) of 1c is 0.09 V, which is very close, and it suggests that the two Fe centers are oxidized almost at the same time. By calculation, we found the existence of disproportionation from the mono-cationic species \([1c]^+\) to 1c and \([1c]^{-2+}\) (Equation 2.1), with an equilibrium constant \( K \) as 0.029 (Equation 2.2), namely, maximum percentage for \([1c]^+\) in solution is 75%.

\[
2[1c]^+ \rightleftharpoons 1c + [1c]^{-2+} \tag{Equation 2.1}
\]
\[
K = \frac{[1c][[1c]^{-2+}]}{[[1c]^+]^2} = \exp\left(-\frac{\Delta EF}{RT}\right) \tag{Equation 2.2}
\]

§2.5 Synthesis of oxidized species and characterization

As mentioned above, the iron center shows good bistability, so it is possible to synthesize and characterize the oxidized species. The oxidized species \([1a]^+\), \([1b]^+\) and \([1c]^{-2+}\) were obtained by chemical oxidation from the neutral species 1a, 1b and 1c. Considering the results from the cyclic voltammograms, the neutral species can be oxidized at relatively low potential, and here we used I\(_2\) as the chemical oxidant.\(^{21}\) Mixing the solution of neutral complexes 1a, 1b or 1c in CH\(_2\)Cl\(_2\) and the I\(_2\) solution in CH\(_2\)Cl\(_2\) under inert atmosphere we can get the oxidized species nearly instantaneously with the change of color from red to black, and from the precipitation by adding degassed ether we can obtain to the pure solid \([1a]^+,\Gamma, [1b]^+,\Gamma\) and \([1c]^{-2+},2\Gamma\) respectively with nearly quantitative yield (Scheme 2.12). It is worth to note that with further addition of I\(_2\), the counter-ion \(\Gamma\) can react with I\(_2\) to form I\(_3^-\). Although rather stable in the solid state, it is worth to mention that the formed oxidized species are sensitive to oxygen with time. The oxidized species can gradually take some decomposition process in solution under air, and the C≡C bond can be cut, forming a diamagnetic cationic carbonyl iron complex (Figure 2.15).\(^{14e}\) Therefore, the manipulation should better be done under inert atmosphere. Besides, this reaction can also be performed in situ by adding appropriate I\(_2\) solution to avoid less decomposition by oxygen (for example, NMR measurement can be done by adding I\(_2\) solution just before the measurement). The enantiopure P- and M-\([1b]^+,\Gamma\), and P- and M-\([1c]^{-2+},2\Gamma\) were also synthesized using the same method by starting from the enantiopure neutral species of P- and M-1b or 1c.

![Figure 2.15 The oxidized cationic carbonyl iron complex.](image)
§2.6 NMR, EPR, SQUID measurement and spin density calculation

$^1$H NMR was measured for $[1a]^{+}\Gamma$, $[1b]^{+}\Gamma$ and $[1c]^{-2+}2\Gamma$ in CD$_2$Cl$_2$ under argon (Figure 2.16, Figure 2.17, and Figure 2.18). Because of the paramagnetic behavior, all these three compounds show very big shifts of proton peaks in a range from $+35$ ppm to $−70$ ppm, and the peaks more or less become broad. Notably, for $[1c]^{-2+}2\Gamma$, the proton peaks also show very big shifts indicating the cationic complex exhibits paramagnetic property as triplet state, *vide infra.*$^{17a}$ For all oxidized complexes, the most intense peak comes from the protons of C$_5$Me$_5$ in around $−10$ ppm. The protons from helicene rings, especially from the ring directly connected to the iron center, show the most shielded and deshielded shifts. This big range of shift indicates the electron spin from the iron center is delocalized to the helicene ligand and mostly affects to the two first phenyl rings.
Figure 2.16 The $^1$H NMR spectrum (400 MHz) of [1a]$^+\Gamma$ in CD$_2$Cl$_2$ at 25 °C.

Figure 2.17 The $^1$H NMR spectrum (400 MHz) of [1b]$^+\Gamma$ in CD$_2$Cl$_2$ at 25 °C.
In collaboration with Dr. Olivier Cador and Dr. Frédéric Paul (ISC Rennes), the EPR spectroscopy for $[1\text{a}]^{+},\Gamma$, $[1\text{b}]^{+},\Gamma$ and $[1\text{c}]^{-2+}$ was measured at low temperature in the solid state. The signals are anisotropic with the average $g$ factors of 2.131, 2.092 and 2.117 respectively (Figure 2.19). These values are bigger than the $g$ factor of free electron (2.0023), indicating the compounds are not purely organic radicals, and the radical electron is mainly localized in the metal atom. These results are in agreement with the literature.$^{14g}$

Superconducting quantum interference device (SQUID) measurement was performed for $[1\text{a}]^{+},\Gamma$, $[1\text{b}]^{+},\Gamma$ and $[1\text{c}]^{-2+},2\Gamma$. For $[1\text{a}]^{+},\Gamma$ and $[1\text{b}]^{+},\Gamma$, the $\chi_M T$ values were found to be constant, while for $[1\text{c}]^{-2+},2\Gamma$, the curve shows a constant value above 70 K (approximately twice as high as
for the mono-iron species [1b]\(^{+}\), \(\Gamma \) i.e. 0.75 vs. 0.38 cm\(^{-3}\) K \(\cdot\) mol\(^{-1}\),) and the value decreases slightly upon cooling from 70 to 2 K, which is characteristic of a very small anti-ferromagnetic interaction between the unpaired spins \((J \sim -2\) cm\(^{-1}\)).

Figure 2.20 SQUID measurement for [1a]\(^{+}\), \(\Gamma \) (orange), [1b]\(^{+}\), \(\Gamma \) (red) and [1c]\(^{2+}\) (green) from 2 K to 300 K.

B3LYP/SV(P) calculations for the electron spin density were performed for [1b]\(^{+}\) (Figure 2.21) and [1c]\(^{2+}\) (Figure 2.22) on the low-energy optimized structures (For [1b]\(^{+}\) there are two low-energy optimized structures [1b-1]\(^{+}\) and [1b-2]\(^{+}\)). This calculation shows the delocalization of the spin in each atom of one molecule. For [1b]\(^{+}\), the results show that the integrated spin density is mainly localized in the iron center with \(\Delta \rho = \rho^a - \rho^b\) around 1. Besides, the C≡C bond and first two helicene rings are involved in the delocalization of spin density with alternation of the sign of \(\Delta \rho\). The ligand dppe and the ligand C\(_5\)Me\(_5\) are less involved. For [1c]\(^{2+}\), because the two electron spins can be in the same sign or in the opposite signs, so it can have two states: the singlet state and the triplet state, and here only the singlet state of was calculated. A similar result is observed with two iron which displayed the strongest electron-spin density (\(\Delta \rho 1.07\)), and the peripheral four benzene rings as well as the C≡C bond are also involved.

Figure 2.21 The calculated electron spin density of [1b]\(^{+}\).
The calculated electron spin density of $[1c]^{-2+}$ (singlet state).

From the results above, one can clearly conclude that all the $[1a]^+$, $[1b]^+$ and $[1c]^{-2+}$ are paramagnetic. $[1c]^{-2+}$ can be treated as a diradical dication, and the two Fe centers can be treated as non-interacting in room temperature.

§3 Optical and chiroptical properties

We studied the optical and chiroptical properties of the three complexes 1a, 1b and 1c such as UV-vis spectroscopy, electronic circular dichroism (ECD) spectroscopy, infrared spectroscopy, vibrational circular dichroism (VCD) spectroscopy, Raman spectroscopy, Raman Optical Activity (ROA), as well as optical rotation.

§3.1 UV-vis spectroscopy

The UV-vis spectra were recorded for all neutral acetylide complexes 1a, 1b and 1c in CH$_2$Cl$_2$ with the concentration around 1 × 10$^{-4}$ mol·L$^{-1}$ (Figure 2.23), and selected bands are depicted in Table 2.4. Both the ligands and the complexes have strong bands below 300 nm ($\varepsilon > 5 \times 10^4$ L·mol$^{-1}$·cm$^{-1}$). Compared with the ligands, the iron complexes form new bands in the lower-energy region between 350 nm and 600 nm. For 1b and 1c, one can find two distinct bands in this region, the higher-energy band at around 392 nm and the lower-energy band at around 468 nm.
Table 2.4 Selected UV-Vis data for \(1a\), \(1b\), \(1c\), [\(1a\)]\(^+\), [\(1b\)]\(^+\), [\(1c\)]\(^+\) and [\(1c\)]\(^\cdot\cdot\cdot\)\(^2\).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Wavelength, nm ((\varepsilon), (10^3) (\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1a)</td>
<td>240 (65); 283 (50); 294 (48); 323 (sh, 20); 431 (11.8); 492 (sh, 7.6)</td>
</tr>
<tr>
<td>(1b)</td>
<td>240 (71); 267 (57); 319 (28); 351 (sh, 16.8); 392 (sh, 10.0); 468 (sh, 6.9)</td>
</tr>
<tr>
<td>(1c)</td>
<td>238 (sh, 73); 270 (50); 322 (22); 350 (sh, 16.5); 393 (sh, 13.4); 462 (sh, 9.6)</td>
</tr>
<tr>
<td>[(1a)](^+)</td>
<td>240 (77); 278 (sh, 59); 288 (63); 324 (sh, 27); 390 (6.0); 412 (5.7); 492 (4.2); 762 (5.2)</td>
</tr>
<tr>
<td>[(1b)](^+)</td>
<td>243 (74); 269 (65); 317 (31); 417 (sh, 4.2); 440 (3.7); 518 (2.7); 776 (4.4)</td>
</tr>
<tr>
<td>[(1c)](^+)(^a)</td>
<td>243 (75); 273 (51); 332 (sh, 21); 418 (9.8); 497 (6.5); 792 (3.6)</td>
</tr>
<tr>
<td>[(1c)](^\cdot\cdot\cdot)(^2)</td>
<td>248 (82); 274 (56); 422 (5.6); 513 (3.8); 767 (5.5)</td>
</tr>
</tbody>
</table>

\(^a\)The data of \(1c\)\(^+\) are calculated by deconvolution (\textit{vide infra}).

Figure 2.23 The UV-Vis spectra of neutral species \(1a\) (yellow), \(1b\) (red) and \(1c\) (green).

UV-Vis spectra were also measured for the oxidized species [\(1a\)]\(^+\),[\(1b\)]\(^+\),[\(1c\)]\(^+\) and [\(1c\)]\(^\cdot\cdot\cdot\)\(^2\),\(2\Gamma\) (Figure 2.24) with selected bands depicted in Table 2.4. Counter ion \(\Gamma\) has no absorption longer than 250 nm, so the spectra of [\(1a\)]\(^+\),[\(1b\)]\(^+\),[\(1c\)]\(^+\) and [\(1c\)]\(^\cdot\cdot\cdot\)\(^2\),\(2\Gamma\) obtained can be considered as the spectra of the cations [\(1a\)]\(^+\), [\(1b\)]\(^+\) and [\(1c\)]\(^\cdot\cdot\cdot\)\(^2\). Comparing with the neutral complexes, the three oxidized species show additional low-energy bands in the visible region and in the near-infrared region. These new bands have a vertex at around 762 ~ 792 nm with a tail down to 900 nm. Meanwhile, the region from 350 nm to 550 nm decreased to nearly half the intensity compared with neutral species.
The UV-Vis spectra of oxidized species $[1a]^+$, $[1b]^+$ (yellow), $[1b]^+$ (red) and $[1c]^{-2+},2I^-$ (green) can be recorded equally by using optically transparent thin-layer electrochemical (OTTLE) cell. The advantage of this OTTLE cell is that we can perform the electrochemistry during the spectrum measurement, so that we can record the spectrum during the redox process. In our experiment, considering the volatility of CH$_2$Cl$_2$ that forms bubbles during the measurement, we selected 1,2-dichloroethane as the solvent, and $^n$Bu$_4$NPF$_6$ was chosen as the electrolyte in the concentration around 0.2 mol·L$^{-1}$. A platinum wire pseudo-reference electrode was used as the reference.

Each spectrum of $[1a]^+$, $[1b]^+$ and $[1c]^{-2+}$ was measured by applying a potential of +0.4 V (vs. Pt wire) on the solution neutral species respectively, while by applying a reverse potential of −0.4 V, these three cationic species turned back to the starting neutral species $1a$, $1b$ and $1c$. Besides, by increasing the voltage stepwise, we also investigated the evolution of this oxidation process. This evolution was also reproduced by I$_2$ titration.

During the oxidation process, $1a$ and $1b$ showed simultaneously several increases or decreases of all the bands with several identical isosbestic points. Typically, we can find a huge decrease of the bands between 350 - 550 nm, and the increase of the bands between 550 - 900 nm for both complexes (Figure 2.25 and Figure 2.26).
Figure 2.25 (a) Electric oxidation process of 1a; (b) I₂ titration oxidation process of 1a.

Figure 2.26 (a) Electric oxidation process of 1b; (b) I₂ titration oxidation process of 1b.

Meanwhile, although 1c showed a decrease of the bands between 350 - 550 nm, and the increase of the bands between 550 - 900 nm, the typical isosbestic point around 550 nm could not be found (Figure 2.27). The typical vertex of the low-energy bands around 700 - 800 nm showed some shift during this process (the band raised at 792 nm, then shifted to 767 nm during the stepwise oxidation). This phenomenon is due to the formation of mono-oxidized intermediate species [1c]⁺ during the oxidation process. The two oxidation potentials from 1c to [1c]⁺, and from [1c]⁺ to [1c]⁻²⁺ are close according to the CV measurement, so that there is equilibrium between 1c, [1c]⁺ and [1c]⁻²⁺ according to Equation 2.2, and the pure [1c]⁺ curves cannot be directly measured due to this disproportionation.
Figure 2.27 (a) Electric oxidation process of 1c; (b) I$_2$ titration oxidation process of 1c.

Although the spectrum of [1c]$^+$ cannot be directly measured, it can be deconvoluted. For a given oxidation percentage $x$ (when there is only neutral species 1c, $x = 0\%$, while only fully oxidized species [1c]$^{-2+}$, $x = 100\%$) and given the equilibrium constant $K$ defined in Equation 2, the percentage of each species in solution $n_{1c}(x)$, $n_{[1c]^+}(x)$ and $n_{[1c]^{-2+}}(x)$ can be calculated (Figure 2.28).

\[
n_{1c} = 1 - x + \frac{1 - \sqrt{1 - (16K - 4)(x^2 - x)}}{8K - 2}
\]

\[
n_{[1c]^+} = -\frac{1 - \sqrt{1 - (16K - 4)(x^2 - x)}}{4K - 1}
\]

\[
n_{[1c]^{-2+}} = x + \frac{1 - \sqrt{1 - (16K - 4)(x^2 - x)}}{8K - 2}
\]

Figure 2.28 Percentage of each species in solution according to the given oxidation percentage $x$.

Accordingly, from 0\% to 35\%, we considered the reaction mainly the oxidation from 1c to [1c]$^+$, and the generation of [1c]$^{-2+}$ can be ignored, while from 65\% to 100\%, mainly the oxidation from [1c]$^+$ to [1c]$^{-2+}$. In this two regions, we found their own isosbestic points respectively in the oxidation evolution. On the contrary, in the region between 35\% to 65\%, the disproportionation cannot be ignored. Equation 2.3 shows the way we calculated the spectrum of [1c]$^+$, according to the given $x$ value and the obtained spectra of neutral species $S_{1c}$ and fully oxidized species $S_{[1c]^{-2+}}$.

\[
S_{[1c]^+} = \frac{S(x) - n_{1c}(x)S_{1c} - n_{[1c]^{-2+}}(x)S_{[1c]^{-2+}}}{n_{[1c]^+}(x)}
\]  
\[
\text{Equation 2.3}
\]

From this, we deconvoluted the spectrum of mono-oxidized species $S_{[1c]^+}$ (Figure 2.29).
Figure 2.29 Deconvolution of UV-Vis spectrum of \([1c]^+\).

The oxidation evolution for \(1c\) shows that the two bands as shoulder peaks at 393 nm and 462 nm for \(1c\) continuously decrease and shifts bathochromically to 418 nm and 497 nm respectively in the \(1c\) to \([1c]^+\) process, and keeps on decreasing in the \([1c]^+\) to \([1c]^{2+}\) process. Similarly, a low-energy band forms at 792 nm in the \(1c\) to \([1c]^+\) process, then increases continously and shifts hypsochromically to 767 nm in the \([1c]^+\) to \([1c]^{2+}\) process.

Redox reversibility was also investigated for these three complexes using spectr electrochemistry by measuring the UV-vis response and alternating the potential in a fixed wavelength. For example, we chose the absorption band at 767 nm of the oxidized species for our investigation. By oxidizing the neutral species \(1\) at +0.4 V (vs. Pt wire), the absorption \(\varepsilon\) increased from 0 to around 4000 L·mol\(^{-1}\)·cm\(^{-1}\), and by reversing the potential to −0.4 V, the absorption decreased to the origin. Five cycles of this process were done for each species (Figure 2.30).

\[\varepsilon\] (L·mol\(^{-1}\)·cm\(^{-1}\))
\[0\]
\[25\]
\[50\]
\[75\]
\[100\]

Figure 2.30 The redoxing reversibility measured by the absorption at 767 nm for \(1a\), \(1b\) and \(1c\) by alternating the potential of +0.4 V and −0.4 V vs. Pt wire.

§3.2 Optical rotations

The optical rotation of enantiopure species \(P\)- and \(M\)-1b and \(P\)- and \(M\)-1c, as well as oxidized species \(P\)- and \(M\)-[1b]\(^+\),\(\Gamma\) and \(P\)- and \(M\)-[1c]\(^{-2+}\),\(2\Gamma\) were measured for the sodium line (\(\lambda_D = 589.3\))
nm) with the concentration around $1 \times 10^{-4}$ mol·L$^{-1}$ in CH$_2$Cl$_2$, and the data of specific rotation $[\alpha]_{D}^{23}$ and molar rotation $[\phi]_{D}^{23}$ of $P$-helicene are listed in Table 2.5.

**Table 2.5** Selected optical rotation data for 1a, 1b and 1c.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$[\alpha]_{D}^{23}$ (°·cm$^3$·dm$^{-1}$·g$^{-1}$)</th>
<th>$[\phi]_{D}^{23}$ (°·cm$^2$·dmol$^{-1}$)</th>
<th>$[\phi]_{D}^{23}$ cacl. (°·cm$^2$·dmol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P$-1b</td>
<td>+3810</td>
<td>+35800</td>
<td>43073$^a$</td>
</tr>
<tr>
<td>$P$-1c</td>
<td>+5132</td>
<td>+79700</td>
<td>83843</td>
</tr>
<tr>
<td>$P$-[1b]$^+$,$I^-$</td>
<td>+924</td>
<td>+9858</td>
<td>-</td>
</tr>
<tr>
<td>$P$-[1c]$^{2+}$,$2I^-$</td>
<td>+497</td>
<td>+8991</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ Boltzmann averaged value for [1b-1]$^+$ and [1b-2]$^+$. 

Comparing with the molar rotation for organic [6]helicenes$^{18}$ that is around $1 \times 10^4$·°·cm$^2$·dmol$^{-1}$, the molar rotation of neutral species $P$-1b and $P$-1c appears extremely huge. This may be due to the anomalous dispersion because the measurement was taken in the tail of the UV-Vis absorption band. Therefore, the optical rotation is not the result only of the circular birefringence, but of the combined effect of circular birefringence and circular dichroism. Both the molar rotation of 1b and 1c were calculated theoretically by Dr. Monika Srebro (Wracław University) and Prof. Jochen Autschbach (Buffalo University), and the values agree well with the experimental values. Upon oxidation, the specific and molar rotation are significantly decreased and the values for $P$-[1b]$^+$,$I^-$ and $P$-[1c]$^{2+}$,$2I^-$ appear similar to those of organic [6]helicenes,$^{18}$ although here again the compounds absorb at 589 nm (contrary to organic [6]helicenes).

§3.3 ECD spectroscopy

ECD spectra were measured for the neutral species $P$- and $M$-1b and $P$- and $M$-1c, the oxidized species $P$- and $M$-[1b]$^+$ and $P$- and $M$-[1c]$^{2+}$ in CH$_2$Cl$_2$ with the concentration around $5 \times 10^{-5}$ mol·L$^{-1}$. The evolution of the oxidation process was either followed by spectroelectrochemistry in an OTTLE cell$^1$ or by chemical oxidation using iodine. Selected bands are given in Table 2.6.
The ECD spectra of both neutral species 1b and 1c show the classical bisignate Cotton effect at between 230 nm and 400 nm (Figure 2.31). Complex P-1b displays a negative band at and 274 nm followed by a positive band at 332 nm, while P-1c shows a negative band at 293 nm and a positive band at 337 nm. This negative and then positive bisignate shape can mainly be attributed to the typical helicene $^1$B$_a$ band (higher energy) and $^1$B$_b$ band (lower-energy). The sign of $^1$B$_a$ band and $^1$B$_b$ band allows us to determine the absolute configuration of P- and M-enantiomers of helicene. Comparing with the starting ligand P-2b, $^1$B$_b$ band of P-1b shows slightly hypsochromic shift (from 334 nm to 332 nm, a shoulder peak from 355 nm to 353 nm), and the intensity decreased ($\Delta \varepsilon$ from +195 L·mol$^{-1}$·cm$^{-1}$ to +138 L·mol$^{-1}$·cm$^{-1}$). In the lower-energy region, P-1b shows additional bands at 397 nm ($\Delta \varepsilon$ +28 L·mol$^{-1}$·cm$^{-1}$) and 505 nm ($\Delta \varepsilon$ +18 L·mol$^{-1}$·cm$^{-1}$) with a tail down to 630 nm. Similarly, 1c also shows the $^1$B$_a$ band at 293 nm and $^1$B$_b$ band at 337 nm. Compared with the $^1$B$_b$ band of the starting ligand P-2c, that of neutral complex P-1c shows relatively low intensity of $\Delta \varepsilon$ (+101 L·mol$^{-1}$·cm$^{-1}$, comparing with +320 L·mol$^{-1}$·cm$^{-1}$ for P-2c). At 506 nm, one can see an additional band at with intensity of +68 L·mol$^{-1}$·cm$^{-1}$. Note that the shoulder peaks probably originate from the vibronic structure (CC stretching vibrational modes).

### Table 2.6 Selected ECD data for 1a, 1b and 1c.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Wavelength, nm ($\Delta \varepsilon$, L·mol$^{-1}$·cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P$-$1b$</td>
<td>247 (−117); 274 (−94); 300 (−33); 332 (+138); 360 (+90); 397 (+28); 505 (+18)</td>
</tr>
<tr>
<td>$P$-$1c$</td>
<td>241 (−72); 259 (+28); 293 (−138); 337 (+101); 387 (+78); 506 (+68)</td>
</tr>
<tr>
<td>$P$-$[1b]^+$</td>
<td>253 (−149); 302 (−33); 338 (+126); 360 (+119); 420 (+14); 490 (+4); 590 (−7); 770 (+6)</td>
</tr>
<tr>
<td>$P$-$[1c]^+$</td>
<td>241 (−81); 277 (−65); 300 (−122); 363 (+162); 433 (+32); 508 (+36); 602 (−3); 795 (+9)</td>
</tr>
<tr>
<td>$P$-$[1c]^{-2+}$</td>
<td>242 (−60); 279 (−51); 303 (−110); 362 (−202); 427 (−46); 490 (−18); 579 (−16); 773 (+20)</td>
</tr>
</tbody>
</table>

*The data of [1c]$^+$ is calculated by deconvolution.*
Figure 2.31 CD spectrum of P- and M-1b, P- and M-1c and their P-ligands.

From the TDDFT calculations, one can find that the main low-energy transition for both 1b and 1c is mainly caused by the HOMO/LUMO transition. For both 1b and 1c, the HOMO mainly lies on the iron centers, C≡C bonds as well as the first two rings of helicene, and the LUMO totally lies on the helicene (Figure 2.32 and Figure 2.33). The calculated contributions of this transition for the two low-energy optimized structures 1b-1 and 1b-2 are 96.0% and 97.4%, and this contribution is 95.9% for 1c. This low-energy transition for both 1b and 1c can be described as metal-ligand to ligand charge transfer (MLLCT).

Figure 2.32 HOMO and LUMO of two low-energy optimized structures of 1b.
By oxidizing the \(P-1b\) to \(P-[1b]^+\), \(\text{B}_b\) bands become bathochromically shifted (from 332 nm to 338 nm, the shoulder peak from 353 nm to 360 nm), while the \(\Delta \varepsilon\) of the original MLLCT decreases to \(4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}\). Meanwhile, two additional bands appear in the lower-energy region (visible to near-infrared): one at 590 nm with a negative \(\Delta \varepsilon = -7 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}\), and the other one at 770 nm with \(\Delta \varepsilon = +6 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}\). The curves of evolution for the oxidation process from \(P-1b\) to \(P-[1b]^+\) were recorded by \(I_2\) titration, and it shows spontaneous increasing or decreasing of all the peaks with several distinct isosbestic points, indicating the compound is stable during the oxidation process.

Oxidized \(P-[1c]^{-2+}\) shows the increase of the typical \(\text{B}_b\) band with maximum absorption of \(+202 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}\) at 372 nm and in the lower-energy region (wavelength bigger than 400 nm), the oxidation behavior is quite similar with that of \(P-1b\) except some small red or blue shifts and stronger intensity. However, the oxidation process has different speed in different wavelength due to the intermediate species \(P-[1c]^+\). Still, some clear isosbestic points can be found in the ECD spectra, for example, the isosbestic point at around 660 nm showing the oxidized \(P-[1c]^{-2+}\) changing sign from negative to positive.
TDDFT calculations show that the band between 700 and 900 nm is mainly caused by two transitions, the transition from the highest occupied β orbital (MO246/β) to lowest unoccupied β orbital (MO247/β) and the transition from the second highest occupied β orbital (MO245/β) to lowest unoccupied β orbital (MO247/β) for both two optimized structures of [1b]⁺ with the contribution of 45.8% and 32.9% for [1b-1]⁺, and 23.6% and 58.8% for [1b-2]⁺. For [1c]⁻²⁺ this band is mainly caused by the highest occupied β orbital (MO406/β) to the lowest unoccupied β orbital (MO407/β) transition with contribution of 49.4%.

**Figure 2.35** (a) I₂ titration oxidation of P-1c; (b) Lower-energy region.

**Figure 2.36** Selected MOs for two low-energy optimized structures of [1b]⁺.
Figure 2.37 Selected MOs for low-energy optimized structure of [1c]$^{2+}$.

The ECD spectrum of [1c]$^+$ can also be deconvoluted according to Equation 3.3, and this species also shows typical helicene bisignate shape between 230 to 400 nm. The low-energy band appears at 795 nm which is red-shifted but around half of the intensity compared with [1c]$^{2+}$.

Figure 2.38 (a) Deconvolution of CD spectrum of [1c]$^+$; (b) Deconvolution of CD spectrum of [1c]$^+$ in lower-energy region.

Redox reversibility of enantiopure 1c and 1b were also investigated by ECD spectroscopy at a fixed wavelength by alternating the potential between $+0.4$ V and $–0.4$ V (vs. Pt wire). By choosing different wavelengths, one can obtain either ON/OFF switching or positive/negative switching respectively. For example, by choosing the 589 nm of $P$-1b, we reached a positive/negative switching (Figure 2.39a), and by choosing the 767 nm of $M$-1c, we reached a ON/OFF switching (Figure 2.39b), while by choosing the 372 nm of $M$-1c, we reached a switching in maximum change of $\Delta \varepsilon$ (120 L·mol$^{-1}$·cm$^{-1}$, Figure 2.39c). These results highlight the efficient redox-triggered chiroptical switching activity of these new helicene-ethynyl-iron complexes.
The redoxing reversibility of $P-1b$ and $M-1c$ measured in different wavelengths by alternating the potential between +0.4 V and −0.4 V vs. Pt wire.

§3.4 Absorption, CD and optical rotation at 1.54 μm

The wavelength at around 1.54 μm (1540 nm) is very important for the telecommunication transmission. This wavelength is in the C band (conventional band, 1530 nm to 1565 nm) of silica fibers, which offers the lowest attenuation loss (about 0.26 dB·km$^{-1}$).24 Besides, optical amplifiers are also available for operating in this band. Here we report the results we obtained in this region with the collaboration of Dr. Goulch'en Loas and Prof. Marc Vallet (Physics Department, University of Rennes 1).

First, the absorption spectra from 900 to 3000 nm in the near infra-red (NIR) region were measured for the neutral species $1b$ and $1c$ in CH$_2$Cl$_2$ with the concentration around 10$^{-5}$ mol L$^{-1}$, and the oxidation process was also measured by chemical oxidation with I$_2$ titration (Figure 2.40 and Figure 2.41).

Figure 2.40 The NIR spectra of $1b$ with I$_2$ titration process to $[1b]^+$ (from red to black).
Figure 2.41 The NIR spectra of 1c with I$_2$ titration process to [1c]$^{2+}$ (from red to black).

In this NIR region, despite of the disturbance of solvent peaks, some useful information is obtained. Complex 1b shows almost no absorption between 900 and 3000 nm. With the process of titration, a weak band appears at 1860 nm, and at the end of the titration, 1b is fully converted into [1b]$^+\Gamma$, this band has increased to a maximum value with $\varepsilon = 168$ L·mol$^{-1}$·cm$^{-1}$. Complex 1c shows a similar behavior as 1b, and the fully oxidized dicationic species [1c]$^{2+}2\Gamma$ displays a similar weak absorption at 1862 nm with $\varepsilon = 256$ L·mol$^{-1}$·cm$^{-1}$. At 1.54 $\mu$m wavelength, both 1b and 1c show no absorption, while [1b]$^+\Gamma$ and [1c]$^{2+}2\Gamma$ have absorptions with $\varepsilon = 58$ and 93 L·mol$^{-1}$·cm$^{-1}$ respectively.

The CD signals and optical rotation have been measured at 1.54 $\mu$m by using a home-made CD and optical rotation detectors, and the data are listed in Table 2.7. From these results, we can conclude that the band around 1860 nm for the oxidized species is CD active and shows a weak CD signal at 1.54 $\mu$m with negative sign for the $M$-enantiomers. More interestingly, the optical rotation at 1.54 $\mu$m of both 1b and 1c shows complete inversion of the sign from $-$ to $+$ upon oxidation without changing the chirality of the molecules. To the best of our knowledge, this is the first time that a helicene changes its optical rotation’s sign while its structure and stereochemistry keep their integrity.
Table 2.7 The absorption $\varepsilon$, molar rotation $[\phi]_{D}^{23}$ and circular dichroism $\Delta \varepsilon$ of $M\text{-}1b$, $M\text{-}1c$, $M\text{-}[1b]^+,\Gamma$ and $M\text{-}[1c]^{-2+},2\Gamma$ measured at 1.54 $\mu$m.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\varepsilon$ (L·mol$^{-1}$·cm$^{-1}$)</th>
<th>$\Delta \varepsilon$ (L·mol$^{-1}$·cm$^{-1}$)</th>
<th>$[\phi]_{D}^{23}$ ($^\circ$·cm$^2$·dmol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1b</td>
<td>0</td>
<td>0</td>
<td>-2370</td>
</tr>
<tr>
<td>1c</td>
<td>0</td>
<td>0</td>
<td>-4010</td>
</tr>
<tr>
<td>$[1b]^+,\Gamma$</td>
<td>58</td>
<td>-0.098</td>
<td>+4380</td>
</tr>
<tr>
<td>$[1c]^{-2+},2\Gamma$</td>
<td>93</td>
<td>-0.076</td>
<td>+10080</td>
</tr>
</tbody>
</table>

§3.5 IR and VCD spectroscopies

Similar to the investigation of the electronic transitions by the UV-Vis and ECD spectroscopies, we have also studied the vibrational transitions. This study was done by two different techniques: vibrational absorption and Raman scattering. For vibrational absorption, we studied the IR spectroscopy and VCD spectroscopy.$^{25}$

Each measurement of IR and VCD was performed in CD$_2$Cl$_2$ in the same time, and we recorded the spectra of $P\text{-}1b$ and $M\text{-}1b$ (Figure 2.42a), $P\text{-}1c$ and $M\text{-}1c$ (Figure 2.42b), as well as $P\text{-}[1b]^+,\Gamma$ and $M\text{-}[1b]^+,\Gamma$ (Figure 2.43a), $P\text{-}[1c]^{-2+},2\Gamma$ and $M\text{-}[1c]^{-2+},2\Gamma$ (Figure 2.43b) from 2200 to 1300 cm$^{-1}$. The region between 1450 to 1400 cm$^{-1}$ is not accessible for 1b and $[1b]^+,\Gamma$, because of the solvent absorption. This study was conducted in collaboration with Dr. Juan Casado (Malaga University).

![Figure 2.42](image.png)

Figure 2.42 (a) The VCD spectra (up) and IR spectra (down) for $P\text{-}1b$ (red solid) and $M\text{-}1b$ (blue dashed); (b) The VCD spectra (up) and IR spectra (down) for $P\text{-}1c$ (red solid) and $M\text{-}1c$ (blue dashed).
Figure 2.43 (a) The VCD spectra (up) and IR spectra (down) for $P$-$[1b]^+\Gamma$ (red solid) and $M$-$[1b]^+\Gamma$ (blue dashed); (b) The VCD spectra (up) and IR spectra (down) for $P$-$[1c]^{-2+}\cdot2\Gamma$ (red solid) and $M$-$[1c]^{-2+}\cdot2\Gamma$ (blue dashed).

In the IR spectra, the most appealing band is the C≡C stretching band occurring around 2000 cm$^{-1}$. The neutral complexes 1b and 1c show a single absorption at 2050 cm$^{-1}$ and 2046 cm$^{-1}$ respectively. After the oxidation to $[1b]^+\Gamma$ and $[1c]^{-2+}\cdot2\Gamma$ this peak shifts to 1990 cm$^{-1}$ and 1987 cm$^{-1}$. Besides, both complexes $[1b]^+\Gamma$ and $[1c]^{-2+}\cdot2\Gamma$ show a new peak at 1953 cm$^{-1}$ and 1952 cm$^{-1}$, that may originate from coupling with other vibrational modes (Fermi coupling). This bathochromic shift can be explained by the delocalization of positive charge through the whole molecule resulting the longer C≡C bond (Scheme 2.13). This C≡C stretching vibration is also VCD active with a positive band for $P$-$1b$ and $P$-$1c$ and a negative one for $M$-$1b$ and $M$-$1c$ in the VCD spectra and the wavenumber of this band in VCD spectra agrees well with the result from the IR spectra. When the complexes are oxidized, a bisignate band appears, a strong positive peak followed by a weak negative peak at higher wavenumber for $P$-$1b$ and $P$-$1c$. The wavenumbers are 1993 cm$^{-1}$ and 2033 cm$^{-1}$ for $P$-$[1b]^+\Gamma$, and 1996 cm$^{-1}$ and 2032 cm$^{-1}$ for $P$-$[1c]^{-2+}\cdot2\Gamma$. The IR peak around 1952 cm$^{-1}$ for both two oxidized helicenes appears VCD inactive.

![Scheme 2.13](image)

Scheme 2.13 The resonance structures for the oxidized species $1^+$.  

The changes in the absorption of the C≡C stretching band before and after oxidation are also very interesting. In the IR spectra, the $\varepsilon$ of 1b decreases from 1400 to 270 L·mol$^{-1}$·cm$^{-1}$ when 1b is oxidized, while the $\Delta\varepsilon$ increased from 0.1 to 1.5 L·mol$^{-1}$·cm$^{-1}$. Accordingly, the dissymmetry factor
g (g = \Delta \varepsilon / \varepsilon) changes from $7 \times 10^{-3}$ for 1b at 2050 cm\(^{-1}\) to $6 \times 10^{-3}$ for [1b]\(^+\),\(\Gamma\) at 1993 cm\(^{-1}\), increasing around 85 times. Similarly, when 1c is oxidized to [1c]\(^2+\),2\(\Gamma\), the \(\Delta \varepsilon\) increases from 0.27 to 3 L\(\cdot\)mol\(^{-1}\)\(\cdot\)cm\(^{-1}\), and the dissymmetry factor g increased from to $3 \times 10^{-4}$ to $1 \times 10^{-2}$. Comparing with the dissymmetry factor g of other chiral compounds usually less than $10^{-3}$, these values are quite big. This increase shows that the C=C bond in the oxidized state is more VCD active and has more rotational strength, which means that it is more magnetically allowed.\(^{25}\)

Typical helicene signals of the skeleton vibration can be found between 1600 and 1400 cm\(^{-1}\). For the region around 1600 cm\(^{-1}\), a strong peak at 1599 cm\(^{-1}\) for both 1b and 1c in the IR spectra, and a medium peak at 1573 cm\(^{-1}\) for 1b and 1569 cm\(^{-1}\) for 1c are observed, which is related to the CC stretching correlated to the G modes in the Raman spectroscopy (vide infra). In the VCD spectra, a bisignate signal appears and is well correlated with the IR spectra: negative band at 1598 cm\(^{-1}\) followed by the positive band at 1575 cm\(^{-1}\) for P-1b and negative band at 1592 cm\(^{-1}\) followed by the positive band at 1568 cm\(^{-1}\) for P-1c. The vibration of the in-plane HCC bendings coupled to CC stretchings in the inner or in the out periphery of the helicene as mentioned by Abbate et al.,\(^{27}\) can also be observed in these two molecules however with opposite signs: positive band at 1612 cm\(^{-1}\) for P-1b, and two positive bands at 1603 cm\(^{-1}\) and 1616 cm\(^{-1}\) for P-1c. When the complexes are oxidized, this region appears weak to medium with multiple peaks for [1b]\(^+\),\(\Gamma\) and [1c]\(^2+\),2\(\Gamma\) in the IR spectra. Weak bands were also observed in VCD spectra and an obvious negative band can be observed at 1602 cm\(^{-1}\) for P-[1b]\(^+\),\(\Gamma\) and 1600 cm\(^{-1}\) for P-[1c]\(^2+\),2\(\Gamma\) and positive band at 1572 cm\(^{-1}\) and 1573 cm\(^{-1}\) for P-[1b]\(^+\),\(\Gamma\) and P-[1c]\(^2+\),2\(\Gamma\) respectively, which are correlated with the CC stretching of the G modes (vide infra).

Meanwhile, in the region between 1500 and 1400 cm\(^{-1}\), two identical groups of peaks can be found around 1480 cm\(^{-1}\) and 1430 cm\(^{-1}\). For neutral 1b the first group contains three peaks at 1497 cm\(^{-1}\), 1484 cm\(^{-1}\) and 1476 cm\(^{-1}\), and the second group contains one peak at 1434 cm\(^{-1}\), while for 1c, the first group has one peak at 1487 cm\(^{-1}\) and second group contains one peak at 1433 cm\(^{-1}\). In the VCD spectra, similar negative doublet at around 1500 cm\(^{-1}\) was observed for P-1b as Abbate et al. mentioned,\(^{27}\) and for P-1c it becomes bisignated with negative band at 1504 cm\(^{-1}\) and positive band at 1487 cm\(^{-1}\). Besides, another bisignated band was observed 1438 cm\(^{-1}\) as negative peak and 1430 cm\(^{-1}\) as positive peak for P-1c, however due to the apparatus, this region is not accessible for 1b. When 1b and 1c was oxidized, the two groups of peaks can still be observed, and the main peaks are at 1485 cm\(^{-1}\) and 1437 cm\(^{-1}\) for [1b]\(^+\),\(\Gamma\) and 1485 cm\(^{-1}\) and 1436 cm\(^{-1}\) for [1c]\(^2+\),2\(\Gamma\) in the IR spectra. While in the VCD spectra, the peaks at this region are quite weak, however for P-[1c]\(^2+\),2\(\Gamma\), an identical bisignate band can be found at 1435 cm\(^{-1}\) as negative peak and at 1428 cm\(^{-1}\) as positive peak, and comparing with neutral P-1c, this bisignate band is red shifted.
§3.6 Raman and ROA spectroscopies

Raman spectroscopy and ROA experiments\(^{28}\) were performed for the enantiopure neutral species \(P-1b\) and \(M-1b\) (Figure 2.44a), \(P-1c\) and \(M-1c\) (Figure 2.44b), as well as the oxidized species \(P-[1b]^+\cdot\Gamma\) and \(M-[1b]^+\cdot\Gamma\) (Figure 2.45a), \(P-[1c]^{2+}\cdot2\Gamma\) and \(M-[1c]^{2+}\cdot2\Gamma\) (Figure 2.45b) in CD\(_2\)Cl\(_2\) with the laser Raman excitation at 532 nm. For each pair of enantiomers, the Raman spectra appear similar and the ROA spectra show mirror-image relationships.

![Figure 2.44](image1)

**Figure 2.44** (a) The ROA spectra (up) and Raman spectra (down) for \(P-1b\) (red solid) and \(M-1b\) (blue dashed); (b) The ROA spectra (up) and Raman spectra (down) for \(P-1c\) (red solid) and \(M-1c\) (blue dashed).

![Figure 2.45](image2)

**Figure 2.45** (a) The ROA spectra (up) and Raman spectra (down) for \(P-[1b]^+\cdot\Gamma\) (red solid) and \(M-[1b]^+\cdot\Gamma\) (blue dashed); (b) The ROA spectra (up) and Raman spectra (down) for \(P-[1c]^{2+}\cdot2\Gamma\) (red solid) and \(M-[1c]^{2+}\cdot2\Gamma\) (blue dashed).

Similarly, we start to investigate the C≡C bond first. This bond is also Raman active, and in Raman spectra, it relates to the peak at 2048 cm\(^{-1}\) for \(1b\) and 2050 cm\(^{-1}\) for \(1c\). In the ROA spectra,
the corresponding peak can also be observed at the same wavenumber and is negative for $P$-$1b$ and $P$-$1c$ while positive for $M$-$1b$ and $M$-$1c$ with medium intensity. When the complexes are oxidized, a bathochromic shift is also observed, and is shifted to 1988 cm$^{-1}$ for $[1b]^+\cdot I^-$ and 1990 cm$^{-1}$ for $[1c]^{-2+}\cdot 2I^-$, and the sign of the peak is remained.

In Raman spectra of polyaromatic hydrocarbons, the most important bands are G bands and D bands. For helicenes, the G bands are usually at around 1600 cm$^{-1}$ and the D bands at around 1350 cm$^{-1}$. For neutral $P$-$1b$, strong G bands can be found as strongest in the Raman spectrum with the main peak at 1580 cm$^{-1}$, and in ROA spectrum, it shows the strongest negative peaks at 1574 cm$^{-1}$ with two shoulder peaks at 1600 cm$^{-1}$ and 1544 cm$^{-1}$. The D band is the second strongest band in both Raman and ROA spectra, and for $P$-$1b$, the main peak shows same shift at 1354 cm$^{-1}$ in Raman spectra and in ROA spectra, apart from this main peak which is negative, another shoulder peak can be found at 1396 cm$^{-1}$. For the neutral $P$-$1c$, the results are quite similar. The main peak of G bands was found as also the strongest peak but as a doublet at 1596 cm$^{-1}$ and 1568 cm$^{-1}$ in the Raman spectrum, and second strongest negative peaks at 1596 cm$^{-1}$ with shoulder at 1568 cm$^{-1}$ in the ROA spectrum. D bands shows the main peak at 1354 cm$^{-1}$ in Raman spectrum, and the same shift but the strongest intensity in ROA spectrum, the same shoulder peak is also observed at 1396 cm$^{-1}$ with medium intensity. When the complexes are oxidized, the G bands and D bands show less modifications in the shift of the bands but some changes in the intensity in the Raman spectra, while in the ROA spectra, these two bands become broad compared with the sharp peaks of the neutral species.

§4 Conclusion

In conclusion, three helicene-based iron complexes in their neutral state 1a, 1b and 1c and in their cationic oxidized state $[1a]^+\cdot I^-$, $[1b]^+\cdot I^-$ and $[1c]^{-2+}\cdot 2I^-$ have been synthesized. The electrochemical property has been studied by cyclic voltammetry, and the magnetic property of their cationic state has been studied by EPR and SQUID experiments, showing paramagnetic character. Switching properties has been studied by UV-vis and ECD spectroscopies, showing very good bistability and reversibility. By choosing the different wavelength in ECD spectroscopy, we have reached ON/OFF switch and positive/negative switch. We also have studied the tuning upon oxidation, and the results shows that the optical rotation in 589 nm and 1.54 μm changes dramatically, and especially in 1.54 μm, it is the first time that the optical rotation changes the sign while the molecular structure and stereochemistry keep their integrity. Besides, in the infrared region, IR and VCD, Raman and ROA spectroscopies have been studied, and this is the first case of helicene in studying the tuning upon oxidation. Some significant modifications have been observed. Especially for VCD spectra that $[1c]^{-2+}\cdot 2I^-$ exhibits extremely huge $g$ value up to 0.01 for the C≡C stretching. Now, we are focusing in studying the magnetochirality for these helicene complexes.
References


Chapter 3

Ruthenium-bis-ethynyl-helicene-DTE complexes: dual switching activity
Chapter 3 Ruthenium-bis-ethynyl-helicene-DTE complexes: dual switching activity

Abstract

In this chapter, we describe the synthesis of a ruthenium-bis-alkynyl derivative linked to a helicene moiety and a dithienylethene unit. This molecule exhibits a dual switching properties: light-triggered switching property from an open state $4o$ to a closed state $4c$, and the redox-triggered switching property from reduced state $4o$ to oxidized state $[4o]^{+}$. The closed state $4c$ shows a unique switching property since when it is oxidized to the first oxidation state, it isomerizes to $[4o]^{+}$. Based on this result, we can use this molecule as a “NOR” logic gate. The UV-vis and ECD spectra have been studied and are described in details.

§1 Introduction

§1.1 Helicene-based light-triggered chiroptical switches

Chapter 3 mainly talks about the helicene-based redox-triggered switches, and with appropriate designs, helicene can also be used as the light-triggered chiroptical switches. There are several kinds of photochromic units that can be applied to light-triggered switches; and the most widely used photochromic unit is the dithienylethene (DTE) and it has been widely reviewed. Below are described examples of DTE-based photo-active helicene molecules treated as light-triggered chiroptical switches.

As early as 2001, Branda et al. started to study the DTE-based photochromic helicene derivatives, and reported a photochromic switch with a thia[7]helicene form as the closed state. This helicene showed a DTE unit in the open form with each side of the ethene linked to a 1-methylnaphtha[2,1-b]thiophene. This special structure, when irradiated at 410 nm, underwent ring closing reaction and formed a [7]helicene derivative as the closed state. It also showed the reversibility under an irradiation longer than 458 nm, and reformed the open state. Besides, despite the fact that the helicene’s closed state generated is racemic, the UV-vis spectroscopy showed the significant changes between the open state and the closed state.

Later on in 2005, they reported a chiral light-triggered switch for which the closed state was also a DTE-based thia[7]helicene derivative, but with a stereoselective ring closing process (Scheme 3.2).
Indeed, a terminal bulky chiral group was introduced into each of the terminal rings, which enabled the ring closing reaction from one side rather than from the other side, and it preferentially generated one diastereoisomer rather than the other. Although the photostationary state, when irradiating at 400 nm, was 40% for the closed state, the selectivity demonstrated that only one diastereoisomer of the closed state was generated according to the NMR spectroscopy. This good stereoselectivity resulted in the large change in ORD spectra between the open state and the closed photostationary state. The $\Delta[\alpha]$ reaches 9698° between the open form and closed photostationary state at 373 nm. Modification on the ECD spectrum were also observed.

![Diagrams](image)

**Scheme 3.2** Example of DTE-based [7]helicene as a photochromic switch.

In 2007, Yokoyama et al. published a DTE-based system in which a thia[5] or [7]helicene was generated in the closed state. In these systems, a chiral methoxymethoxyethyl group was introduced in both two examples as a stereogenic center, in order to obtain the stereoselectivity during the photochemical ring closing reaction. Both of these two cases described on **Scheme 3.3** showed high changes in optical rotation, despite the closed state was only reached as a photostationary state and stereoselectivity was not efficient. Besides, they also discovered that the percentage of the photostationary state, as well as the diastereomeric excess ($d.e.$) value of the ring closing reaction were varied according to the different type of the solvent.

![Diagrams](image)

**Scheme 3.3** Two examples of Yokoyama’s DTE-based helicenes.

Examples of non-DTE-based photochromic helicene derivatives have also been reported. For example, Moorthy et al. introduced the chromene unit into a helicene which exhibits two photochromic states, a colorless closed state and a red open state. For example, they synthesized a [6]helicene derivative bearing a chromene unit with two phenyl rings in the ortho position, and ring
opening reaction occurred for this helicene under UV irradiation, forming a \([5]\)helicene derivative containing a quinonoid unit with red color (Scheme 3.4). This open state, under either heating, or under acidic condition, or upon visible irradiation, reformed the starting closed state. By taking the advantage of the steric hindrance generated from the helicene unit, the open state, unlike normal chromene derivatives undergoing ring closing reaction at room temperature, showed very good stability. Because of these properties above, this molecule was treated as an “INHIBIT” logic gate function.

Scheme 3.4 Example of Moorthy’s chromene-based helicene.

Wang et al. introduced an azobenzene unit into the helicene backbone, and synthesized an enantiopure \([5]\)helicene derivative.⁶ This helicene showed a special photochromic property with \(cis\)-\(trans\) isomerization of the azobenzene unit between two photostationary states under the irradiation using different wavelengths (Scheme 3.5). Optical rotation changed significantly between these two photostationary states. In addition, a thin film of polycarbonate containing 2 wt % of this compound was prepared; it exhibited a similar photochromic property as in solution. Besides, the electrochemically active imide group introduced made this molecule a redox-triggered switch, and by reducing this molecule to a radical anion, it showed response in ECD spectroscopy. This is the only example of helicene-based light-triggered/potential-triggered dual-mode chiroptical switch.

Scheme 3.5 Example of Wang’s helicene-based dual chiroptical switch.
§1.2 Ruthenium and DTE based light-triggered/potential-triggered dual switches

Complexes with a ruthenium(II) center coordinated by two η²-dppe ligands and connecting with one or two arylethynyl ligands have been widely studied. Such kind of molecule shows good redox reversibility between the reduced Ru(II) state and the oxidized Ru(III) state. Besides, during the oxidation process, not only the ruthenium center is oxidized but also its ligands, especially the arylethynyl ligand which shows a good electronic interaction with the ruthenium center. Thus, such kind of ligand is described as a non-innocent ligand. Because of this non-innocence property, optical properties can consequently be modulated by changing the redox state of the ruthenium center, especially because the arylethynyl is a chromophore.

As mentioned before, DTE unit is a good chromophore and has good photochromic properties. By combining the DTE unit with the ruthenium center through a C≡C bond, we can generate a potential-triggered/light-triggered dual switch, either by stimulating the oxidation state from the potential, or by stimulating the open/closed state from the irradiation. Because the DTE unit becomes a non-innocent ligand, redox-state change will also have an influence on the DTE unit.

Important works on this topic have been performed by Rigaut et al., Chen et al., and by some other groups. For example, in 2013, Rigaut et al. have published a molecule with two ruthenium centers connected by a DTE unit (Figure 3.1). This molecule is treated as a molecular transport junction, and exhibits special electrochromic and photochromic properties. Interestingly, the DTE unit can undergo ring closing reaction by either the irradiation or the electrolysis. Consequently, this molecule can be viewed as an “OR” electronic logic gate with irradiation (UV) and electrolysis (E) as input and the conductance as output.

![Figure 3.1](image-url)

Figure 3.1 (a) The DTE molecule bearing two ruthenium centers set in nanogap; (b) The truth table of this “OR” logic gate.

During the oxidation process, the DTE unit may undergo automatic cyclization reaction (from open state to closed state) or cycloreversion reaction (from closed state to open state) without irradiation. Whether a DTE unit undergoes a cyclization or cycloreversion depends on the design of molecule. Some of them shows cyclization as in Rigaut’s example reported above, while there are also several cases for the cycloreversion or for both. In 2003, Branda et al. published an example of DTE derivatives showing cycloreversion reaction upon oxidation (Scheme 3.6).
cycloreversion occurred not upon fully oxidation of all the molecules, but happened with only catalytic amount of molecules oxidized. The mechanism was proposed showing that the oxidized species plays as a catalyst (Scheme 3.7): when trace of the closed molecules M-closed is oxidized to the M⁺-closed, it will automatically undergo the cycloreversion to M⁺-open, then another molecule M-closed will transfer one electron to M⁺-open, forming M⁺-closed and the M⁺-open will form M-open.

![Scheme 3.6 The example of DTE derivative reported Branda et al.](image)

![Scheme 3.7 Mechanism of electrochroism in DTE reported by Branda et al.](image)

§1.3 Design of the complex

In collaboration with Prof. Stéphane Rigaut and Dr. Lucie Norel, and based on the study above, in order to synthesize a dual chiroptical switch, we decided to introduced a helicene unit to the ruthenium/DTE dual switch, taking benefits from the good optical and chiroptical properties of the helicene. The target molecule 4o (Figure 3.2) was designed with these three units: a photochromic unit DTE, a redox unit ruthenium center with two 1,2-bis(diphenylphosphino)ethane (dppe) ligands and a chiroptical unit [6]helicene. Both the DTE unit and the helicene unit are linked to the Ru(η²-dppe)₂ center via C≡C bond respectively, and they are placed in the trans position.

![Figure 3.2 The molecule [6]helicene-Ru(η²-dppe)₂-DTE 4o.](image)

Besides, as mentioned before, both the [6]helicene ligand and the DTE ligand in 4o act as non-innocent ligands, so that these two chromophores will be influenced by the changes in the redox state, and depending on the redox state they will exhibit different optical properties. In addition, since there
is a communication between the helicene and the DTE units through the ruthenium-bisethynyl bridge, the open/closed state of the DTE unit will also have influence on the helicene unit, and correspondingly, the chiroptical properties of the helicene unit will be changed according to the different state of DTE unit. Furthermore, the helicene unit may also give chiral induction for the ring closing reaction of the DTE unit, so that DTE unit may also exhibit chiroptical property. Therefore, the three units of this molecule are well combined, and should be considered as a united ensemble rather than three simply linked units in the two switching processes.

§2 Synthesis

§2.1 Synthesis of 4o

The strategy for synthesizing such a large molecule is considered as two steps of complexation between the ruthenium precursor and two arylethynyl ligands. The ligand 2-ethynyl[6]helicene 2b was prepared according to the literature, and its pure enantiomers P-2b and M-2b were obtained by resolution using preparative chiral HPLC. The DTE ligand 5o was synthesized in collaboration with Rigaut's group. The open form of this DTE ligand was chosen for the easy handling in the synthesis. The first complexation reaction was performed between the ruthenium precursor [Ru(dppe)Cl]OTf and the ligand 2-ethynyl[6]helicene 2b (Scheme 3.8) in degassed CH$_2$Cl$_2$ solution at 25 °C, forming a vinylidene cationic complex 6. Then for the second complexation reaction, 6 reacted with the DTE ligand 5o with 5 equivalent of NaPF$_6$ and NEt$_3$ in darkness to form the yellow target complex 4o. The total yield of these two complexation reactions was 70~84%.

By starting from the racemic ligand rac-2b, we got the racemic complex rac-4o (unless emphasized, hereafter in this chapter, “rac-” will be omitted), and by starting from the enantiopure ligands P-2b and M-2b we were able to obtain the enantiopure complexes P-4o and M-4o respectively.

Scheme 3.8 Synthetic route for 4o.
Notably, for the second complexation, there are several cascade steps that occurred in this one-pot reaction (Scheme 3.9): first, the vinylidene complex 6 was deprotonated by NEt₃ and generated a neutral helicene acetylide complex 7-1; then this helicene acetylide complex released the Cl⁻ with the help of NaPF₆, generating a 16 electron cationic species 7-2 with PF₆⁻ as the counter-anion; alkynyl ligand 5o coordinated to the empty orbital of ruthenium center, and formed a 18 electron π-coordinated complex 7-3; then, [1,2]-σ hydrogen transfer occurred and 7-3 isomerized to vinylidene cationic complex 7-4; finally, another equivalent of NEt₃ deprotonated the vinylidene complex 7-4 again, and the target complex 4o was generated. The final complex 4o was purified by a short alumina column chromatography after this one-pot reaction.

Scheme 3.9 Mechanism for the one-pot reaction for synthesizing 4o from 6.

After the synthesis, complex 4o was characterized by high-resolution mass spectrometry, which showed correct exact mass of this complex. Complex 4o was characterized by NMR spectroscopies. Deep yellow single crystals were grown by diffusion pentane vapors into the 4o solution in CH₂Cl₂ in darkness and the crystal structure was characterized by X-ray diffraction.

§2.2 X-ray

Complex 4o crystallized in the centrosymmetric $P\bar{1}$ space group (Figure 3.3), and some
important bond lengths and bond angles are listed in Table 3.1. From the structure, the ruthenium center displays octahedral geometry and with the two C≡C bonds in the trans-position, and the two bulky dppe ligands separating the helicene unit and DTE unit in two sides. Some distortions were found. First, some distortion along the C≡C bond of the helicene unit was observed. Compared with the angles along Ru–C≡C–DTE (Ru1–C81–C82 and C81–C82–C83) almost close to 180°, the angles along Ru–C≡C–[6]helicene show large deviations, especially the C1–C2–C3 angle being around 167°. This huge distortion is caused by the steric hindrance between the [6]helicene unit and dppe ligands. Second, because of this steric hindrance, the octahedral ruthenium center also shows distortion. The average number between four angles of P–Ru1–C1 is 91.6°, which is larger than the average number 88.4° of P–Ru1–C81, indicating that the four P–Ru bonds diverge from the octahedral positions and slope slightly to the DTE side. Besides, the helicity for the helicene unit (dihedral angle between two terminal helicene rings) is 45.1°, and compared with [6]helicene iron complex 1b of 53.1°, this angle becomes smaller. The dihedral angle between two thiophenes from the DTE unit is 54.6° in this open form due to the steric hindrance from the two methyl groups. Besides, we also clearly found that although the compound crystallized in the racemic form, the stereochemistry of open DTE unit is related with the stereochemistry of the helicene: they show the same chirality in one molecule, i.e. when the chirality of helicene is M, the chirality of open DTE unit is also M.

Figure 3.3 Structure of 4o (only P enantiomer is shown; the 8 phenyl groups from dppe ligands are shown in wireframe style for clarity).
Table 3.1 Important bond distances and bond angles for 4o.

<table>
<thead>
<tr>
<th>Bond distance (Å)</th>
<th>Bond angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru1–P1</td>
<td>2.366(1)</td>
</tr>
<tr>
<td>Ru1–P2</td>
<td>2.375(1)</td>
</tr>
<tr>
<td>Ru1–P3</td>
<td>2.347(1)</td>
</tr>
<tr>
<td>Ru1–P4</td>
<td>2.335(1)</td>
</tr>
<tr>
<td>Ru1–C1</td>
<td>2.067(4)</td>
</tr>
<tr>
<td>C1–C2</td>
<td>1.214(6)</td>
</tr>
<tr>
<td>C2–C3</td>
<td>1.441(6)</td>
</tr>
<tr>
<td>Ru1–C81</td>
<td>2.047(4)</td>
</tr>
<tr>
<td>C81–C82</td>
<td>1.216(6)</td>
</tr>
<tr>
<td>C82–C83</td>
<td>1.412(6)</td>
</tr>
<tr>
<td>dating (1)</td>
<td></td>
</tr>
<tr>
<td>P1–Ru1–P2</td>
<td>81.19(4)</td>
</tr>
<tr>
<td>P3–Ru1–P4</td>
<td>82.55(4)</td>
</tr>
<tr>
<td>P1–Ru1–C1</td>
<td>98.4(1)</td>
</tr>
<tr>
<td>P2–Ru1–C1</td>
<td>98.5(1)</td>
</tr>
<tr>
<td>P3–Ru1–C1</td>
<td>86.5(1)</td>
</tr>
<tr>
<td>P4–Ru1–C1</td>
<td>83.1(1)</td>
</tr>
<tr>
<td>P1–Ru1–C81</td>
<td>86.3(1)</td>
</tr>
<tr>
<td>P2–Ru1–C81</td>
<td>83.0(1)</td>
</tr>
<tr>
<td>P3–Ru1–C81</td>
<td>91.9(1)</td>
</tr>
<tr>
<td>P4–Ru1–C81</td>
<td>92.2(1)</td>
</tr>
<tr>
<td>Ru1–C1–C2</td>
<td>173.1(3)</td>
</tr>
<tr>
<td>C1–C2–C3</td>
<td>166.6(4)</td>
</tr>
<tr>
<td>Ru1–C81–C82</td>
<td>179.7(3)</td>
</tr>
<tr>
<td>C81–C82–C83</td>
<td>178.4(4)</td>
</tr>
</tbody>
</table>

§2.3 NMR

NMR sample of 4o was prepared in CD$_2$Cl$_2$ under inert atmosphere, and $^1$H NMR, $^{13}$C NMR, $^{19}$F NMR and $^{31}$P NMR spectroscopies, as well as 2D NMR measurements (H-H COSY, HMQC and HMBC), were measured in darkness. All the peaks in $^1$H NMR and $^{13}$C NMR were assigned (see experimental part). The $^1$H NMR spectrum is shown in Figure 3.4.
Figure 3.4 The $^1$H NMR spectrum (500 Hz) for 4o in CD$_2$Cl$_2$ at 298 K.

In the $^1$H NMR, the helicene protons are mostly deshielded with most of the peaks having chemical shifts around 8 to 7.6 ppm. The CH$_2$ protons from dppe have signals between 3 to 2 ppm which appear as multiple broad peaks due to the combination between the splits by phosphorus and ruthenium, and similar steric difference (exo- and endo-) and diastereotopy phenomenon as found for 1b and 1c in previous chapter. The typical two CH$_3$ from the DTE unit have distinct chemical shifts at 2.02 and 1.87 ppm. In $^{13}$C NMR, similar diastereotopy phenomenon, combined with steric difference, was also found: each type of carbons (ipso-, ortho-, meta- and para-) from eight phenyl ring are divided into four groups, with each group showing triplet with different coupling constant (ipso-, ortho- and meta-) or singlet (para-). The $\beta$-carbon from the two C≡C bonds display chemical shifts at 119.24 and 107.19 ppm, while the $\alpha$-carbon cannot be seen due to the long relaxation time because of ruthenium. The CH$_2$ peaks also show the diastereotopy phenomenon, and were found at 32.62 and 31.42 ppm as broad multiplet. The two CH$_3$ carbon from DTE unit can be found at 14.90 and 14.67 ppm respectively. In $^{31}$P NMR, two phosphorus peaks were found at 54.44 and 51.38 respectively as triplet (coupling constant $J = 23$ Hz), this result is similar as the [6]helicene iron complex 1b and 1c, also due to the diastereotopy phenomenon. In $^{19}$F NMR, each CF$_2$ from DTE unit has a distinct peak, and in this case, we have not observed the diastereotopy phenomenon, and this may be due to the far distance between the CF$_2$ and helicene chiral unit.
§3 Switching properties
§3.1 Photochromic property

We first studied the light-triggered switching property of 4o. By irradiating at 365 nm under the UV lamp, the yellow solution of the complex 4o in open state can turn to the close state as a dark green complex 4c (Scheme 3.10). By irradiating under the red light of 650 nm, this green 4c can turn back to the starting yellow open state 4o. The irradiation time varies, depending on the concentration and the power of the lamp.

![Scheme 3.10 Photochromic switching between 4o and 4c.](image)

Notably, the closed DTE unit generated two chiral centers at α-position of two thiophenes respectively, and because of photochemical electrocyclic reaction rule, conrotatory products are the only products, so that two methyl groups are in the two sides of the DTE plane, thus, the chirality of the α-carbon can be both R or both S. Consequently, molecule 4c can have two diastereoisomers $P,R,R$-4c (or $M,S,S$-4c) and $P,S,S$-4c (or $P,R,R$-4c).

![Figure 3.5 A pair of diastereoisomers $P,R,R$-4c and $P,S,S$-4c.](image)

This switching process can be monitored by the NMR spectroscopy. By using the UV light at 365 nm, irradiating the NMR tube prepared with 4o dissolved in CD$_2$Cl$_2$ with concentration around 5 × 10$^{-2}$ mol·L$^{-1}$, the open form 4o started to convert to 4c, and this process was monitored by $^1$H NMR, $^{31}$P NMR, as well as $^{19}$F NMR, according to the ratio of integration for some special peaks of 4o and 4c. Typically, in $^1$H NMR spectroscopy (Figure 3.6), the peaks two methyl groups in DTE at 2.02 and 1.87 ppm decreased and 4 peaks at 2.19, 2.18, 2.16 and 2.15 ppm increased upon the irradiation, and these 4 peaks indicate the existence of two diastereoisomers of 4c and the ratio between these two diastereoisomers is close to 1:1, showing low stereoselectivity. After sufficient
irradiation, normally 30 minutes, the peaks of \( \text{4o} \) decreased to less than 2%, so that we can consider \( \text{4o} \) can almost fully convert to \( \text{4c} \) under 365 nm. Similarly, \( \text{4c} \) turned back to \( \text{4o} \) with more than 98% of conversion after sufficient irradiation at 650 nm, although this process took 2 days’ irradiation due to the high concentration. This result indicated that this light-triggered switching process is very efficient from one state to the other with full conversion.

![Chemical structure and NMR spectra](image)

**Figure 3.6** The \(^1\)H NMR spectrum (400 Hz) for \( \text{4c} \) in CD\(_2\)Cl\(_2\) at 298 K.

The UV-vis spectra of this switching process was also investigated. This measurement was done in the CH\(_2\)Cl\(_2\) solution with concentration around \( 1 \times 10^{-4} \) mol·L\(^{-1} \) by gradual irradiation at 365 nm (Figure 3.7), and selected bands are listed in Table 3.2. Because of the low concentration, this closing process only need several minutes to go to the full conversion. Besides, by irradiating at 650 nm for half an hour, we recovered the spectrum of \( \text{4o} \).
Table 3.2 Selected UV-Vis data for 4o, 4c, [4o]^+ and [4o]^{++}.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Wavelength, nm (ε, 10^3·L·mol^{-1}·cm^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>4o</td>
<td>245 (86); 318 (42); 347 (37); 406 (11.6); 445 (sh, 7.5)</td>
</tr>
<tr>
<td>4c</td>
<td>240 (82); 318 (42); 345 (sh, 28); 381 (18); 440 (sh, 7.7); 679 (27)</td>
</tr>
<tr>
<td>[4o]^+</td>
<td>267 (84); 360 (sh, 18); 388 (sh, 11); 422 (7.3); 450 (6.6); 490 (sh, 4.3); 525 (3.4); 620 (1.7); 1272 (22)</td>
</tr>
<tr>
<td>[4c]^{++}</td>
<td>657; 964</td>
</tr>
</tbody>
</table>

"Because [4c]^+ is not stable and cannot be generated in pure form, some typical values without ε are read from the oxidation process of 4c.

Figure 3.7 Evolution curves from 4o (yellow) to 4c (green) by gradual irradiation at 365 nm.

The solution of 4o in CH2Cl2 shows a yellow color, and in the UV-vis spectrum, 4o exhibits a high energy band at 245 nm with ε bigger than 8 × 10^4·L·mol^{-1}·cm^{-1}, and longer wavelength shoulders at 318 and 347 nm. Besides, a band in the visible region at 406 nm with shoulder at 445 nm and tailing down to 500 nm can also be found. This band may probably be attributed to the ligand-metal to ligand charge transfer (LMLCT) as mentioned for the helicene iron complex 1b in the previous chapter. Above 500 nm until 2000 nm, there is no absorption found.

Step-wise irradiation has been studied, and the spectra of this evolution showed spontaneous changes for several bands with several identical isosbestic points, indicating that this process is quite clean. Particularly, a huge absorption band at 679 nm with ε around 2 × 10^4 L·mol^{-1}·cm^{-1} has arisen for 4c, which can be attributed to the intraligand charge transfer (ILCT) centered in the closed form of DTE unit. Besides, some modulation between 300 and 450 nm can also be found, and typically, the band at 347 nm for 4o has decreased a lot. Switching cycling has also been studied by monitoring the absorption at 679 nm. The solution has been irradiated at 365 nm or 650 nm, and the absorption has been recorded. A total of 5 cycles has been made and they show good reversibility (Figure 3.8).
In conclusion, 4o shows a good reversibility for the light-triggered switching process, and the study at UV-vis spectroscopy shows good response.

§3.2 Cyclic voltammetry

After studying the light-triggered switching process, we started to study the redox-triggered one. Before studying it, the electrochemical properties were investigated. Both the open state 4o and the closed state 4c were studied by cyclic voltammetry (CV). The CV measurements were performed in CH$_2$Cl$_2$ solution under inert atmosphere in darkness. NBu$_4$PF$_6$ was used as the electrolyte with concentration around 0.2 mol·L$^{-1}$.

First, the open state 4o shows a reversible oxidation wave with $E_{[4o]^+/4o} = +0.45$ V (vs. SCE, thereafter), and an irreversible oxidation wave with $E_{[4o]^{2+}/[4o]^+} = +1.31$ V. The first reversible oxidation occurs at the ruthenium center, and the second irreversible oxidation may probably occur at the ligand itself. Besides, the ligands are non-innocent and they also have some contribution to the first oxidation.

By irradiating the 4o solution at 365 nm stepwise, we have achieved the evolution curves of the
cyclic voltammograms from \(4o\) to \(4c\) (Figure 3.10). The first oxidation of \(4o\) becomes slightly shifted to lower potential, and the second oxidation of \(4o\) also shows a slight shift to lower potential, and a reduction wave appears. Besides, a new oxidation wave appears between these two peaks.

![Figure 3.10](image-url) \(\text{Figure 3.10}\) The evolution curves of cyclic voltammograms of \(4o\) to \(4c\) (yellow to green) by gradual irradiation at 365 nm with scan rate of 0.2 V·s\(^{-1}\).

For the close state \(4c\), it has three distinct oxidation waves, and the cyclic voltammograms were measured for each oxidation wave respectively. The first two waves are reversible with \(E_{\text{[4c]}}^{+\text{/4c}} = +0.36\) V and \(E_{\text{[4c]}}^{2\text{+/4c}} = +0.80\) V (vs. SCE). While, for the third oxidation wave, it exhibits reversibility at high scanning rate (Figure 3.11a and b), but irreversibility in low scanning rate (Figure 3.11c). In the low scanning rate of 0.06 V·s\(^{-1}\), only oxidation peak can be found with oxidation potential at +1.16 V, but by increasing the scanning rate, the reduction peak starts to appear. This result indicates that \([4c]^{3+}\) can be generated but is not stable in solution.

![Figure 3.11](image-url) \(\text{Figure 3.11}\) The cyclic voltammograms of each oxidation wave of \(4c\) with different scan-rates: (a) first oxidation with scan-rates from 0.06 V·s\(^{-1}\) to 0.6 V·s\(^{-1}\); (b) second oxidation with scan-rates from 0.06 V·s\(^{-1}\) to 0.6 V·s\(^{-1}\); (c) third oxidation with scan-rates from 0.06 V·s\(^{-1}\) to 2 V·s\(^{-1}\).

Based on the experiment above, the first reversible oxidation processes of both \(4o\) and \(4c\)
(Scheme 3.11 and Scheme 3.12) are interesting for us and it is worth trying to study their electrochromic properties.

\[
\begin{align*}
\text{Scheme 3.11 Redox process of 4o.} \\
\text{Scheme 3.12 Redox process of 4c.}
\end{align*}
\]

§3.3 Electrochromic properties of 4o

The first oxidation process of the open state has two states: the reduced state \(4o\) and the first oxidized state \([4o]^+\), and this switching process can be investigated by spectroelectrochemistry at UV-Vis-NIR region. The measurement was performed in optically transparent thin-layer electrochemical (OTTLE) cell at 25 °C using 1,2-dichloroethane as the solvent, 0.2 mol·L\(^{-1}\) of NButPF\(_6\) as electrolyte and Pt wire as the pseudo-reference electrode. The evolution curves of this oxidation process was recorded stepwise by gradual increase of the potential from \(-0.2\) V to +0.6 V vs. Pt wire (Figure 3.12), and some typical bands of \([4o]^+\) are listed in Table 3.2.
For the neutral state \(4o\), the maximum absorption wavelength is around 500 nm, while for \([4o]^+\), this maximum absorption wavelength can increase to 1550 nm. The biggest change is therefore a huge band appearing centered at 1272 nm with \(\varepsilon\) around \(2.2 \times 10^4\ \text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}\) during the oxidation process. This band can be attributed to the ligand to metal-ligand charge transfer (LMLCT). Furthermore, \([4o]^+\) has continuous weak absorption from 500 nm until to the band at 1272 nm. Besides, the bands centered at 318 nm and 347 nm as well as 405 nm for \(4o\) has decreased during the oxidation process.

§3.4 Electrochromic properties of 4c

As the study for the open state \(4o\), we also studied the two redox states for \(4c\), the reduced state \(4c\) and the first oxidation state \([4c]^+\). The electrochromic property has also been studied by spectroelectrochemistry in OTTLE cell, and he evolution curves of this oxidation process was recorded stepwise by gradual increase of the potential from \(-0.2\) V to \(+0.6\) V vs. Pt wire (Figure 3.13).
Interestingly, the spectroelectrochemistry shows us an unanticipated result, since two steps are appearing in this oxidation process. At the beginning of the oxidation process, the ILCT band centered in the DTE unit decreases and the vertex of this peak shifts hypsochromically from 679 nm to 657 nm. Meanwhile a new broad band is generated at 964 nm with tails further than 1800 nm out of the window of the measurement. At this step, the curves changed with two distinct isosbestic points at 543 nm and 778 nm appearing at the two ends of the ILCT band. Besides, from the ammeter of the potentiostat, a big positive current is detected, indicating this process is an oxidation process. Then, when the oxidation process continues, a shoulder peak at around 1272 nm starts to be generated, and the peak centered at 964 nm reached to the maximum absorption and then starts to decrease, and at this step, the ammeter shows no obvious current even though the spectra changes dramatically. And finally this process has finished until the shoulder peak at 1272 nm reaches to the maximum around $2 \times 10^4 \text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$, and the peaks at 657 nm and 964 nm almost have disappeared in the weak flat absorption. From the changes of spectra and response of the ammeter, we can consider the second step undergoes a non-oxidation process.

Besides, comparing the final spectrum of the oxidation process of 4c (Figure 3.14, purple solid), we have found that it is quite similar as the spectrum of $[4o]^+$ (Figure 3.14, purple dashed) with the same absorption at 1272 nm. From this result, we can conclude that these two steps are first the oxidation step that generates $[4c]^+$ from 4c with two peaks at 657 nm and 964 nm under the external potential, and second step is $[4c]^+$ that isomerizes to $[4o]^+$.

More interestingly, by reducing this oxidized compound, we discovered the curve (Figure 3.14, yellow solid) did not agree with 4c (Figure 3.14, green dashed) but with 4o (Figure 3.14, yellow dashed), and the ILCT absorption of DTE unit between 500 and 800 nm almost disappeared. More interestingly, by irradiation at 365 nm for 1 min, this ILCT band can be regenerated and the curve
(Figure 3.14, green solid) was similar to 4c again. This regeneration of starting 4c further proves the result above. From this result, we considered that 4c undergoes a cycloreversion reaction upon oxidation.

Figure 3.14 Curves starting from 4o with: 1st step, irradiation under 365 nm (4c, green dashed); 2nd step, adding potential to +0.6 V (purple solid); 3rd step, adding potential to −0.2 V (yellow solid); 4th step, irradiation under 365 nm (green solid) with comparison of 4o (yellow dashed) and [4o]⁺ (purple dashed).

Compared with Rigaut’s example with two ruthenium centers showing cyclization upon oxidation, our case with one ruthenium center shows cycloreversion upon oxidation, indicating the number of ruthenium centers has a big influence on the behavior of DTE. For studying the mechanism of this cycloreversion reaction, we tried to keep the potential as low as possible to keep it in the first process, avoiding the second non-oxidation process, however all the efforts were tried but failed. But, one phenomenon is very interesting that in lower potential, the second non-oxidation process goes slower than in higher potential. This result indicated that the isomerization from [4c]⁺ to [4o]⁺ was not a simple reaction, but related with the potential, and we propose this isomerization processed from [4c]⁺ to [4o]⁺ as a dication catalyzed reaction similar as the Branda’s example14 (Scheme 3.13). In the solution, traces of dicationic species [4c]²⁺ are generated due to the disproportionation from [4c]⁺, and this [4c]²⁺ is not stable and transforms to [4o]²⁺. Since \( E^{\text{ox}}_{4o^{2+/4o^{+}}} \) is much higher than \( E_{4c^{2+/4c^{+}}} \), one positive charge is immediately transferred from [4o]²⁺ to a neighboring [4c]⁺ before it starts to be decomposed, and new [4o]⁺ and [4c]²⁺ are generated. This newly formed [4c]²⁺ again transforms to [4o]²⁺ and starts a new cycle. In higher external potential, the system can generate more [4c]²⁺ from [4c]⁺ and make this catalytic process faster. Therefore, this mechanism can explain why this isomerization is faster at higher external potential though this isomerization is non-oxidation process.
§3.5 Three-state cycling and logic gate

From here, we can conclude and summarize the photochromic property and electrochromic property of complex 4 (Scheme 3.14). First, 4o and 4c are a pair of photochromic states by light triggering at 650 nm and 365 nm respectively. 4o and [4o]$^+$ are a pair of electrochromic states by potential triggering at its first oxidation potential, and 4c and [4c]$^+$ are also a pair of electrochromic states by potential triggering at its first oxidation potential. However, for the pair of 4c and [4c]$^+$, the oxidized state [4c]$^+$ can isomerize to [4o]$^+$.

Based on the result above, we designed a three-state cycling process: 1) Starting from 4o, by irradiation at 365 nm to generate 4c; 2) Oxidizing 4c to form [4o]$^+$ at +0.6 V (vs. Pt wire); 3) Reducing [4o]$^+$ back to 4o at −0.4 V (vs. Pt wire) (Scheme 3.15).

We made 5 cycles of this process, and we fixed the wavelength at 679 nm and 1272 nm to study...
the changes of absorption according to the different stimuli. For the 679 nm the signal shows OFF→ON→OFF, and for the 1272 nm the signal shows OFF→OFF→ON. Degradation was found during this process, and after 5 cycles around 50% degradation happened. This degradation may be due to the degradation of the oxidized species [4o]$^{2+}$ during the process.

**Figure 3.15** Five switching cycles between 4o, 4c and [4o]$^{+}$ at 679 nm (black) and 1272 nm (red).

Besides, based on this unique photochromic and electrochromic property, this molecule can be treated as an optical logic gate at 679 nm. First, the open state 4o is set to the close state 4c by irradiation at 365 nm. We have defined that the open state 4o with low absorption at 679 nm as “0”, and closed state 4c with high absorption at 679 nm as “1”. The output can be measured by the absorption. Two inputs have been introduced: irradiation at 650 nm (hv) and external potential at +0.6 V then −0.4 V vs. Pt wire (E). These two inputs can be defined as “0” and “1” representing the presence and absence of each input. Either irradiation (1,0) or external potential (0,1) or together (1,1) can trigger the ring opening reaction of 4c (1), and form the low absorption species 4o (0). So, we can treat this process as an “NOR” logic gate. This result is similar to the result from the Rigaut’s work, however, the difference is that for them, the logic gate is “OR” and for us the logic gate is “NOR”. This difference is mainly caused by the different behavior of the ring closing/opening reaction at high potential.

**Figure 3.16** (a) The symbol of “NOR” logic gate; (b) The truth table of “NOR” logic gate.

§3.6 Switching property in ECD

Having systematically studied the switching properties of 4o, we started to study the chiroptical switching properties of 4o by ECD spectroscopy. The photochromic property was measured in a normal UV cell in CH$_2$Cl$_2$ with concentration around $1 \times 10^{-4}$ mol·L$^{-1}$, and the electrochromic
property of both 4o and 4c was measured in OTTLE cell with the same conditions as for UV-vis spectroscopy. Some selected bands of \( P-4o \), \( P-4c \) and \( P-[4o]^+ \) are listed in Table 3.3.

**Table 3.3** Selected UV-Vis data for \( P-4o \), \( P-4c \) and \( P-[4o]^+ \).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Wavelength, nm (( \varepsilon, 10^3 \cdot \text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P-4o )</td>
<td>247 (−180); 278 (−82); 303 (−29); 313 (+19); 335 (sh, +84); 351 (+100); 403 (+48); 445 (+46)</td>
</tr>
<tr>
<td>( P-4c )</td>
<td>245 (−185); 275 (−93); 303 (+35); 343 (+120); 397 (+50); 448 (+40); 679 (+3)</td>
</tr>
<tr>
<td>( P-[4o]^+ )</td>
<td>343 (+39); 360 (+108); 418 (+18); 450 (+19); 525 (+8)</td>
</tr>
</tbody>
</table>

The ECD spectrum of \( P-4o \) (Figure 3.17) shows typical helicene bisignate bands: two peaks for the negative band (\( 1B_a \) band) at 247 nm and 278 nm followed by positive band (\( 1B_b \)) at 335 nm and 351 nm. The sign of these two bands is well agreed with its starting ligand \( P-2b \), indicating the typical helicene band is well agreed with the absolute configuration. Besides, compared with \( P-2b \), \( P-4o \) shows additional positive bands in lower energy region at 403 nm (\( \Delta \varepsilon +48 \cdot \text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1} \)) and 445 nm (\( \Delta \varepsilon +46 \cdot \text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1} \)) with a tail down to 500 nm. These two bands, in agreement with the UV-vis result, are also considered as LMLCT.

![Figure 3.17 ECD spectra of the open state \( P-4o \) (yellow solid), \( M-4o \) (yellow dashed), the closed state \( P-4c \) (green solid) and \( M-4c \) (green dashed).](image)

After the irradiation at 365 nm for several minutes, \( P-4o \) can completely convert into \( P-4c \), and the ECD spectrum can be measured. On one side, compared with the spectrum of \( P-4o \), the closed state \( P-4c \) also shows the typical helicene bisignate bands with some slight changes at \( 1B_a \) band and \( 1B_b \) band. Typically, the intensity of \( 1B_b \) band increases from +100 to +120 L·mol\(^{-1}\)·cm\(^{-1}\). These changes of typical helicene bands indicate that the modulation on the structure of DTE unit does have influence on the chiroptical properties of helicene unit, which further proves that the whole molecule is a united ensemble.
On the other side, the huge ILCT absorption band centered at 679 nm in UV-vis spectrum, centered in the DTE unit, appears CD active with $\Delta \varepsilon$ small around $+3 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ for $P$-enantiomer. Although the signal is small, it corresponds to an induced circular dichroism, and this phenomenon illustrates that the chirality of the helicene unit can influence on the DTE unit through the ruthenium bridge, even though the distance is long and the ruthenium center with two dppe ligands is bulky.

Then, we have studied the redox switching properties of the open state $4o$ (Figure 3.18). This redox-triggered switching process shows that the oxidized state $[4o]^+$ has severe changes compared with the starting $4o$. First, the $1B_8$ band of $[4o]^+$ is red shifted from 351 to 360 nm. The LMLCT band between 400 to 500 nm decreased dramatically from $\Delta \varepsilon$ around 50 L·mol$^{-1}$·cm$^{-1}$ to around 20 L·mol$^{-1}$·cm$^{-1}$. Besides, new band forms at 525 nm ($\Delta \varepsilon +8 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) with a tail down to 560 nm. These results indicate that this redox-triggered switching process is more efficient than the light-triggered switching process when considering the modulation of the ECD spectra.

![Figure 3.18](image.png)

**Figure 3.18** ECD spectra of the open state $P\cdot4o$ (yellow solid), $M\cdot4o$ (yellow dashed), the open oxidized state $P\cdot[4o]^+$ (brown solid) and $M\cdot[4o]^+$ (brown dashed).

Similarly, we have also studied the oxidation process of the closed state $4c$, and the result is as was expected: the oxidation process finished with the spectrum of $[4o]^+$. This result further improve the isomerization process from $[4c]^+$ to $[4o]^+$ (Figure 3.19). Besides, it is hard to discover the intermediate of $[4c]^+$, which may be because the difference between $[4o]^+$ and $[4c]^+$ is no so big, just like the difference between $4o$ and $4c$. 

Figure 3.19 ECD spectra of the close state \( P-4o \) (green solid) and \( M-4o \) (green dashed), the oxidized curve \( P-[4o]^+ \) (brown solid) and \( M-[4o]^+ \) (brown dashed) and their evolution curves

§4 Conclusion

In this chapter, we have synthesized a ruthenium-bis-ethynyl-helicene-DTE complex in the neutral open state 4o, and this molecule is among the rare examples of helicenes which show dual switching activity towards both irradiation and potential. Its switching properties have been studied in detail by UV-vis and ECD spectroscopies, and the neutral closed state 4c shows an interesting cycloreversion reaction upon oxidation. This special electrochromic property enable us to apply this molecule as a “NOR” logic gate. Furthermore, interesting induced circular dichroism coming from the DTE response was observed in 4c despite the fact that the chiral helicene moiety is placed far from it, thus emphasizing the efficient electronic communication through the ruthenium center.
References


Chapter 4

Platinahelicenes and borahelicenes: synthesis, chiroptical and luminescence properties
Chapter 4 Platinahelicenes and borahelicenes: synthesis, chiroptical and luminescence properties

Abstract

In this chapter, we describe the synthesis of platinahelicenes of different lengths, incorporating one or two Pt(II) centers (8b–8d), and the corresponding borahelicenes (9a–9d). Their UV–vis spectra, ECD spectra, optical rotation, luminescence, as well as circularly polarized luminescence (CPL) have been measured, showing interesting difference between them with comparison between 1) the boron atom and the platinum atom, 2) one metal/boron center or two metal/boron centers and 3) different lengths of helicenes. Besides, resolution through a chiral sulfoxide as chiral auxiliary ligand has been used for obtaining enantiopure platinahelicenes.

Figure 4.1 The designs of platinahelicenes and borahelicenes.

§1 Introduction

§1.1 Review on metallahelicenes

A metallahelicene can be defined as a helicene in which one or more carbon atoms of the helicene backbone are replaced by metal atoms. Unlike the helicene complexes mentioned in the previous chapters that metal atom is incorporated at the periphery of the helicene, the metallahelicene enable the metal atom to be directly involved in the construction of the helicene backbone, which helps the better interaction between the metal atom orbitals and the π-conjugated helicene backbone. Besides, metal center can also be easily tuned by coordination chemistry as well as organometallics, or by redox activity, which helps to modify the properties of the helicene conveniently.

The first publication reported on the metallahelicene was platina[6]helicene 8a synthesized by our group in 2010. With the introduction of a platinum atom by ortho-metallation, the PtII center was involved in the helicene backbone and the metallacycle became one of the ortho-fused rings. The helicene complex 8a was synthesized by ortho-metallation (Scheme 4.1) from the ligand 10a, and
the design of 10a here is very important and artful from the synthetic point of view: the pyridin-2-yl group is linked on the position 1 of a carbo[4]helicene backbone, making it possible to undergo the ortho-metallation on the position 2 of the carbo[4]helicene directed by the nitrogen atom, forming an azaplatinacycle, and then this newly formed azaplatinacycle, fused with the pyridine ring, become two additional ortho-fused rings on the [4]helicene backbone, thus forming a [6]helicene. So in this strategy, by starting from carefully designed ligand and appropriate metallation reaction, it is possible not only to introduce a metal atom to the helicene backbone but also furnishes additional helicene rings. Besides, in organometallic chemistry, ortho-metallation has been already well-investigated, and is readily accessible and easily manipulated. Generally, there are two methods for synthesizing these platinahelicenes with acetoacetate (Acac) chelating ligand (Scheme 4.1). In the beginning, our group adopted the first synthetic route starting from K₂PtCl₄ and the ligand 10a to first form a dimer with two bridging Cl, and then by reacting with 2,4-pentadione in basics condition to form the target Acac complex 8a. Later on, we switched into the second synthetic route starting from Pt(dmso)₂Cl₂ and the ligand 10a, forming an intermediate complex with dmso and Cl as the ligand, then to react it with Na(Acac) to form the target 8a. It is worth noting that by using the second synthetic route, we can introduce some chiral auxiliaries by replace the dmso to some chiral sulfoxides, which can make it possible for resolution of two stereoisomers of helicene.

**Scheme 4.1** Two synthetic methods for the ortho-fused platinahelicene.

The preliminary studies on 8a also showed that it displays very good chiroptical properties, for example high molar rotation \( [\alpha]_D^{23} = +1300 \, ^\circ \cdot \text{cm}^2 \cdot \text{dmol}^{-1} \cdot \text{g}^{-1} \), \( [\phi]_D^{23} = +8170 \, ^\circ \cdot \text{cm}^2 \cdot \text{dmol}^{-1} \) \((\pm 5\%)\) \((C = 2.85 \times 10^{-3} \, \text{mol} \cdot \text{L}^{-1} \text{in CH}_2\text{Cl}_2)\) and a strong typical helicene ECD spectrum. Besides, it displays a red phosphorescence at room temperature with quantum yield up to 10%.

Later on, based on this strategy, our group synthesized a series of platinahelicenes with different length ([6] or [7]) or different functional groups on the helicene backbone (OCH₃, F or H) (Figure...
4.2), and systematically studied their absorption, chiroptical properties and luminescence properties.\textsuperscript{1a,3a}

![Figure 4.2 Different types of metallahelicenes synthesized from our lab.](image)

A new platinahelicene dimer, bis(platina[6]helicene) with a Pt(III)–Pt(III) scaffold bridged by benzoate was also synthesized from our lab.\textsuperscript{3a,4} This helicene showed a new structure adopting two helicene units face to face with a perpendicular Pt–Pt bond linking together (Scheme 4.2). In this case, it illustrated that the organometallics have a potential to construct some special structures that organic chemistry can hardly access to. Besides, in this case, a special isomerization process from the heterochiral \((P,M)\) to the homochiral \((P,P\) and \(M,M)\) was observed at high temperature due to the steric hindrance, and the homochiral enantiomer showed much higher signals in both molar rotation and CD spectrum due to \(\sigma–\pi\) conjugation.

![Scheme 4.2 The isomerization from heterochiral to homochiral of bis(platina[6]helicene).](image)

Our group also synthesized some metallahelicenes other than platinahelicenes, for example, the iridahelicene with two [6]helicene units sharing one iridium atom (Figure 4.3).\textsuperscript{1a}

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Figure 4.3 Iridahelicene (stereochemistry (P,P,A)) synthesized from our lab.

In 2012, Sierra et al published a similar work, and they synthesized an osma[6]helicene, the first \(d^4\)-metallahelicene (Scheme 4.3). In this work, despite only the racemic form of this helicene was studied, the NICS(0) calculation was performed for the first time for this type of metallahelicenes for studying the aromaticity of each cycle. The result showed that with the complexation, the aromaticity of each cycle appeared more or less smaller than the starting pyridyl[4]helicene ligand, especially for the cycles closer to the metallacycle. Meanwhile the metallacycles showed some aromaticity even though it was relatively weak. This result demonstrated that the metallacycle is also involved in the whole helicene \(\pi\)-conjugated system, and the addition of this metallacycle showed the tuning of all the other cycles along the helicene.

\[
\begin{align*}
\text{Scheme 4.3 Synthesis of osma[6]helicene with calculation of NICS(0) for each helicene backbone ring.}
\end{align*}
\]

§1.2 Design of my work

Based on the publication mentioned above, we decided to introduce more rings on the helicene backbone as well as put more than one platinum atoms in order to study the synthetic method, the resolution, as well as optical and chiroptical properties of platinahelicenes with one and with two Pt atoms. Besides, circularly polarized luminescence has been studied in this work for the first time. Three new platinahelicenes, namely, platina[8]helicene 8b, bisplatina[6]helicene 8c and bisplatina[10]helicene 8d have been designed (Figure 4.1, first line). Helicene 8b contains eight fused rings, and the second ring is an azaplatinacycle, and compared with the platina[6]helicene 8a, it has two more \textit{ortho}-fused benzene rings than \textit{8a}. Complex 8c shows a symmetric structure with two azaplatinacyles in the second and fourth ring of a [6]helicene, and 8d showed an extension of an

Studying the series of platinalahelicenes is not enough, and we have also designed the same series of borahelicenes by using boron atom to replace the platinum atom.

Recently, Murakami et al. reported a new simple strategy for synthesizing the azaborole cycle derivatives by starting from 2-phenylpyridine with two steps: first, cycloborylation reaction between the 2-phenylpyridine with BBBr$_3$ and NPr(Et)$_2$, to form a B$_2$B-dibromo-azaborole derivative, then this compound can react with AIR$_3$, using alkyl group to replace the bromo groups, forming a B$_2$B-dialkyl-azaborole derivative (Scheme 4.4). This method takes advantage of the directing nitrogen atom and makes the electrophilic aromatic borylation in the ortho-position, forming the azaborole cycle. In addition, the final compound dialkyl-azaborole derivatives show strong fluorescence both in the solid state and in solution with high quantum yields, and are expected to be potent light-emitting materials with low-lying LUMO energy level.$^6,7$

![Scheme 4.4 Synthetic route for the azaborole derivative.](image)

Taking advantage of this simple synthetic method, as well as good the fluorescence properties of the azaborole cycle, we have also designed a series of borahelicenes containing different numbers of helicene cycles and different numbers of boron atoms: bora[6]helicene 9a, bora[8]helicene 9b, bisbora[6]helicene 9c and bisbora[10]helicene 9d (Figure 4.1, second line). These four helicenes show similar structures as the previous platinalahelicenes 8a, 8b, 8c and 8d, and can be considered as counterparts of those platinalahelicenes. Comparative study can be done between these helicenes with different heterocycles from synthetic methods, structures, chiroptical properties, to luminescence properties.

§2 Synthesis

§2.1 Synthesis of ligands

According to Scheme 4.1, the synthesis of monoplatinahelicenes 8a,b, and of monoborahelicenes 9a,b starts from the preliminary synthesis of ligands 10a,b 11a,b (Figure 4.4). All these four ligands contain one 2-pyridyl group linked to the position 1 of [4] or [6]helicene moieties. Among them, 10a and 11a were synthesized according to the previous work from our group,$^3$ and 10b and 11b were synthesized by adopting a similar synthetic method. Notably, 10a and 11a can be treated as non-chiral molecules since the racemization barrier is relatively small and they easily invert at room temperature.$^{1a}$ As for 10b and 11b, both of them contain a [6]helicene moiety,
which is configurationally stable even at 200 °C due to the high racemization barrier ($\Delta G^{\neq} > 37$ kcal mol$^{-1}$).\textsuperscript{8}

Figure 4.4 The ligands of platinahelicenes and borahelicenes (some of them are shown in $M$-form).

For 8c and 9c the corresponding ligand is 1,8-di(pyridine-2-yl)naphthalene 10c, and it was synthesized according to the literature.\textsuperscript{9} This ligand contains two phenylpyridine moieties in each side so that two ortho-platination or cycloborination can take place. The corresponding ligands for 8d - 9d are 10d - 11d, and both of them contain a [6]helicene moiety and the two pyridyl groups are linked to the position 1 and 16. They are also configurationally stable. The synthesis of these two ligands is similar to the synthesis of ligands 10a,b.

For the borahelicenes, the methoxy group linked to the helicene moieties was replaced by fluoro group due to the synthetic requirement. Indeed, during the synthesis of borahelicenes, BBr$_3$ was used and it can deprotect the methoxy group. As a consequence, the chemically inert fluoro group was used instead.

Similarly to the literature methods for synthesizing 10a - 11a by a Wittig reaction followed by photocyclization,\textsuperscript{3} the ligands 10b - 11b were also synthesized by this method. A Wittig reactions starting from the benzo[c]phenanthrylmethyl-phosphonium bromide\textsuperscript{10} and either 2-methoxy-5-(pyridine-2-yl)benzaldehyde or 2-fluoro-5-(pyridine-2-yl)benzaldehyde yielded stilbene derivatives 12b and 13b in 80% and 92% yield respectively (Scheme 4.5). Then photocyclization in a highly diluted toluene solution under irradiation by a mercury lamp with in situ oxidation using catalytic amounts of iodine under air and using irradiation by a mercury lamp, generated the target ligands 10b and 11b in 70% and 56% yield respectively. Notably, 10b and 11b were synthesized in racemic forms (i.e. as a mixture of the two $P$ and $M$ enantiomers). The methoxy or fluoro group was introduced here to block this position so that the photocyclization can only happen at one side of the phenyl ring, therefore, the pyridyl group is ensured to be placed at the right position. The total yield of these two ligands is around 50%. 

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Ligands 10d and 11d were synthesized in a similar way: by starting from naphtha-2,7-diyl bis-triphenyolphosphonium bromide and the corresponding benzaldehydes, and performing double Wittig reactions in both sides to get the stilbene derivatives 12d and 13d in 91% and 95% yield respectively. Then, double photocyclizations were used under irradiation by a mercury lamp and in the presence catalytic amounts of iodine in a highly diluted toluene solution to form the ligands 10d and 11d in the racemic form in 19% and 11% yield respectively. Because of the steric hindrance, the total yield of these two ligands is much lower compared with the monopyridyl ligand 10b and 11b. However, considering that preparation of the starting bis-triphenyolphosphonium bromide is much easier than the starting benzo[c]phenanthrylmethyl-phosphonium bromide, these yields are acceptable.
Single crystals were grown by slow diffusion of pentane vapors into CH2Cl2 solutions of the diverse racemic compounds (10b, 10d, 11d), and their structures were resolved by X-ray diffraction.

The ligand rac-10b crystallized in the centrosymmetric $P2_1/a$ space group (Figure 4.5), with the presence of both $P$ and $M$ enantiomers in the unit cell. The structure shows the [6]helicene moiety linked to a pyridyl ring with a dihedral angle of 45.3° for avoiding big steric hindrance. Besides, the nitrogen atom is on the outer side of the molecule. The helicity (angle between the two terminal rings of the helix) for the [6]helicene unit is 48.1°, which is in accordance with normal [6]helicenes.\textsuperscript{11}

![Figure 4.5 The crystal structure of P-10b.](image)

The dipyridyl[6]helicene ligand 10d crystallized (Figure 4.6a) in the centrosymmetric $P\overline{1}$ space group. The structure is quite similar to ligand 10b, but with one more pyridyl group and one more methoxy. The helicity of the [6]helicene moiety 10d is 36.9°, which is relatively small and may be caused by the $\pi-\pi$ stacking of the each terminal pyridyl ring with the helicene backbone (centroid-centroid distances between the pyridyls and the second fused phenyls: 3.52 Å). Similarly, the two nitrogen atoms are also in the outer side.

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Figure 4.6 The crystal structure of 10d (a) and 11d (c) together with their supramolecular arrangement in the solid state (b and d).

The other dipyridyl[6]helicene ligand 11d crystallized (Figure 4.6c), in the same $P\overline{1}$ space group as 10d. Besides, the nitrogen atoms are also in the outer side. The helicity of the [6]helicene moiety is even smaller than that of 11d, which is 31.9° due to stronger $\pi-$ $\pi$ interactions (centroid-centroid distances between the pyridyls and the second fused phenyls: 3.38 Å).

Although ligands 10d and 11d crystallize in the same space group, their supramolecular arrangement is different. Indeed, in 10d, homochiral supramolecular columns formed of only $M$ or $P$ helices are formed (Figure 4.6b), while in 11d, heterochiral supramolecular columns formed of alternated $M$ or $P$ helices are observed (Figure 4.6d).

§2.2 Synthesis of platina[8]helicene 8b

Racemic platina[8]helicene 8b was synthesized as follows: first, reaction between the ligand 10b and a platinum source Pt(dms)2Cl2, in refluxing toluene and under basic conditions (Na2CO3) afforded the sulfoxide intermediate rac-14b in 81% yield. Then the ligand exchange reaction from dimethylsulfoxide and chloride to $\eta^2$-acetonate by reacting with sodium acetylacetonate yielded rac-8b in 95% yield. Similar as for the synthesis of 8a, in this cycloplatination, the size of the helicene increased from [6]helicene (10a) to [8]helicene (8a) thanks to the cycloplatination also.
8b was fully characterized by $^1$H NMR, $^{13}$C NMR as well as 2D NMRs, and all the peaks were assigned (see experimental part). From the $^1$H NMR spectrum of 8b (Figure 4.7), we can clearly find that the protons ($6'$-proton in the pyridyl group and 3-proton in the helicene unit) closer to the Pt atom showed the satellites peaks split by the $^{195}$Pt atom. The two symmetric CH$_3$ groups of Acac ligand also showed different shifts in the $^1$H NMR, due to the different chemical environment induced by the square-planar Pt center and helicene unit.

![Figure 4.7 The $^1$H NMR spectrum (400 MHz) of 8b at 298 K in CDCl$_3$.](image)

To obtain the enantiopure $P$- and $M$-8b, there are several methods: by starting from enantiopure ligand 10b, or performing the enantiomeric resolution of rac-8b. But these methods need preparative chiral HPLC, which is expensive. Straightforward method was used in our group for resolving this platininghelicene, simply changing the sulfoxide from dimethylsulfoxide to other chiral enantiopure sulfoxide, for example, enantiopure $R$- or $S$-methyl($p$-tolyl)sulfoxide (mtso). Indeed, there are several
publications focusing on the resolution of planar-chiral platinacycles by a chiral sulfoxide. Besides, methyl(p-tolyl)sulfoxide also shows high chemical and configurational stability. No obvious decomposition or racemization occurred when heating in toluene at 110 °C for 24 hours. Through this method, the first cycloplatination step no longer generates a pair of enantiomers but a pair of diastereoisomers, and we have the chance to separate these two diastereoisomers by taking advantage of their different chemical or physical properties.

Herein we describe the synthetic route starting from enantiopure (R,R)-Pt(mtso)₂Cl₂ reacted with the racemic ligand rac-10b to generate a pair of diastereoisomers (M,R)-15b and (P,R)-15b. The reaction condition is similar as that of rac-14b, and yellow mixture of diastereoisomers was obtained after a short column chromatography. The ¹H NMR spectrum showed that (M,R)-15b and (P,R)-15b were formed in a 1:1 ratio by judging the methoxy group in the helicene unit or the methyl group directly linking to the S atom (Figure 4.8).

\[ (R,R)-\text{Pt(mtso)}_2\text{Cl}_2 + \text{Na}_2\text{CO}_3, \text{toluene, 110 }^\circ\text{C} \rightarrow \begin{cases} (M,R)-15b \\ (P,R)-15b \end{cases} \]

**Scheme 4.8** Synthesis of two diastereoisomers (M,R)-15b and (P,R)-15b as intermediates for resolution.

Further resolution was undertaken by column chromatography followed by crystallization. (M,R)-15b and (P,R)-15b have slightly different Rf values in the thin layer silica chromatography, so that by carefully prepared silica gel column chromatography with the mixture of heptane and ethyl acetate (3:1) as eluent, followed by the crystallization step, we obtained enantiomerically and diastereomerically pure (M,R)-15b and (P,R)-15b as single red crystals with respective yields of 33% and 18%. This method enabled us to obtain the two enantiopure helicenes in a hundred-milligram-scale. Both (M,R)-15b and (P,R)-15b were fully characterized by ¹H NMR, ¹³C NMR, as well as 2D NMRs, and all the peaks were assigned. The pure ¹H NMR spectra of both (M,R)-15b and (P,R)-15b

**Figure 4.8** The crude ¹H NMR spectrum (400 MHz) of reaction for forming (M,R)-15b and (P,R)-15b in CDCl₃.
were obtained (Figure 4.9 and Figure 4.10). From the spectra, we clearly found the split of 6’-proton in the pyridyl group by the \(^{195}\)Pt, forming two satellite peaks in the two sides. Besides, the three different methyl groups in each compound showed distinct shifts respectively, which can help us to identify the ratio between these two diastereoisomers during the resolution experiment.

Figure 4.9 The \(^1\)H NMR spectrum (400 MHz) of \((P,R)-15b\) at 298 K in CDCl\(_3\).
Figure 4.10 The $^1$H NMR spectrum (400 MHz) of (M,R)-15b at 298 K in CDCl$_3$.

(M,R)-15b displays lower solubility compared with (P,R)-15b, and by slow diffusion of pentane vapors into a CH$_2$Cl$_2$ solution of the initial mixture of diastereoisomers, we obtained single crystals of (M,R)-15b, while suitable single crystals of (P,R)-15b were grown by diffusion of heptane vapor into an ethyl acetate solution (Figure 4.11).
The X-ray structure of (M,R)-15b shows that the complex crystallized in the non-centrosymmetric P2₁ space group. The eight ortho-fused cycles including the platinacycle incorporated within the helical backbone can be seen clearly from the structure, and the helicity (the dihedral angle between two terminal rings) is 11.4°. This value is relatively small compared with normal other [8]helicenes, and it may be due to the intramolecular π-π stacking (centroid-to-centroid distances of 3.465 Å between the pyridyl ring and the 7th benzene ring). The platinum center shows a slightly distorted square planar structure with the sulfoxide and the chlorine respectively in the trans-position of nitrogen atom and carbon atom in the helicene ligand due to the strong trans effect. Besides, because of the steric hindrance between the methyl group of sulfoxide and the helicene moiety, the tolyl group is in the opposite direction from the helicene, which also makes the unique supramolecular organization from the X-ray structure: along the x axis, the helicene forms intermolecular π-π stacking, and this intermolecular π-π stacking, together with the intramolecular π-π stacking, may lead to the low solubility and becomes the driving force for the efficient diastereoselective crystallization process.¹
c

The isomer (P,R)-15b crystallized in the non-centrosymmetric P2₁2₁2₁ space group and from the structure, we also found eight ortho-fused cycles with a small helicity of 15.0°. Intramolecular π-π stacking was also found with centroid-to-centroid distance 3.717 Å between the pyridyl ring and the 7th benzene ring. Compared with the structure of (M,R)-15b, (P,R)-15b shows no supramolecular organization, and the tolyl group is in the same direction of the helicene moiety.
The final enantiopure complexes $P$- and $M$-$8b$ were obtained by respectively reacting the enantiopure $(P,R)$-$15b$ or $(M,R)$-$15b$ with sodium acetylacetonate in toluene at 110 °C, and the chiral sulfoxide and chloride were replaced by the bidentate $\eta^2$-acetoneate with yields around 95%. No racemization was observed during this reaction and the compound is stable in refluxing toluene.

![Scheme 4.9 Synthetic route for the enantiopure $M$-$8b$ or $P$-$8b$.](image)

Single crystals of $rac$-$8b$ were also grown by slow diffusion of pentane vapor into a CH$_2$Cl$_2$ solution, and the structure was obtained by X-ray diffraction studies.

![Figure 4.12 The crystal structure of $8b$ (for clarity, the solvent molecule is removed).](image)

The compound $rac$-$8b$ crystallized in the centrosymmetric $P\bar{1}$ space group. From the X-ray structure, the helicity of $8b$ is 15.0°. This value is similar as the $(P,R)$-$15b$, however is also relatively small compared with normal carbo[8]helicene$^{11}$ due to the strong intramolecular $\pi$-$\pi$ stacking between the terminal rings (centroid-to-centroid distances of 3.557 Å between the pyridyl ring and the 7th benzene ring).

§2.3 Synthesis of bisplatina[6]helicene $8c$

The synthetic route for bisplatina[6]helicene $8c$ demonstrates a simple strategy without using photocyclization, which is sometimes a limitation for helicene synthesis, yielding $8c$ in hundred-milligram scale. The starting ligand 1,8-di(pyridine-2-yl)naphthalene $10c$ (Scheme 4.10) can be easily prepared according to the literature through simple Stille Coupling in gram scale.$^9$ Then, this simple molecule reacts with two equivalents of a platinum source, and forms two ortho-fused platinacycles, together with the two naphthalene rings and two terminal pyridyl rings, forming a complex with six ortho-fused rings, thus, the [6]helicene. Only one case of similar strategy has been
published for synthesize an organic [6]helicene derivative due to the limitation of organic chemistry. However, for organometallic chemistry, the ortho-metallation reaction makes this strategy more applicable.

\[
\begin{align*}
\text{Scheme 4.10 Synthesis route to 10c.}
\end{align*}
\]

To synthesize 8c, we can also take the advantage of using the chiral sulfoxide as a chiral auxiliary ligand for resolution. The bisplatinum[6]helicene 8c was synthesized starting from the ligand 1,8-di(pyridine-2-yl)naphthalene 10c which reacted with either non-chiral Pt(dmso)2Cl2 or chiral \( (R,R) \)-Pt(mtso)2Cl2 by using two cycloplatinations to generate either the racemic \( \text{rac-14c} \) with dimethylsulfoxide and chloride as the ligands, or a pair of diastereoisomers \( (M,R,R)-15c \) and \( (P,R,R)-15c \) with chiral methyl(p-tolyl)sulfoxide and chloride as the ligands. Interestingly, compared with the synthesis of 15b for which a 1:1 diastereoisomeric ratio was obtained, the \( (P,R,R)-15c \) / \( (M,R,R)-15c \) ratio is around 1.5:1 based on the integration of the 6'-proton in pyridyl group from the \(^1\)H NMR (Figure 4.13). This phenomenon indicates that this cycloplatination shows diastereoselectivity, which is quite rare in cycloplatination reactions when taking place at high temperature such as in refluxing toluene.

\[
\begin{align*}
\text{Scheme 4.11 Synthesis the pair of diastereoisomeric (M,R,R)-15c and (P,R,R)-15c.}
\end{align*}
\]

\[
\begin{align*}
\text{Fig. 4.13 The crude \(^1\)H NMR spectrum (400 MHz) of reaction for forming (M,R,R)-15c and (P,R,R)-15c at 298 K in CDCl}_3.
\end{align*}
\]
Single crystals were grown by slow diffusion of pentane vapors into a CHCl$_3$ solution of the diastereoisomeric mixture, and the crystals of pure (P,R,R)-15c were obtained due to their lower solubility. (P,R,R)-15c crystallized in the non-centrosymmetric $P2_12_12_1$ space group, and the structure shows six ortho-fused rings with helicity of 58.8° (Figure 4.18). This helicity shows good agreement with the value of normal [6]helicenes.$^{11}$ As the structure of (P,R)-15b, each tolyl group shows the same direction with the helicene, and a $C_2$ axis exists in this molecule. Besides, due to the trans effect, the sulfoxide is always in the trans-position of the nitrogen atom. The supramolecular organization of (P,R,R)-15c shows that the existence of intermolecular $\pi-\pi$ stacking between the neighboring helicenes, and this may cause the low solubility of (P,R,R)-15c.

![Figure 4.14](image_url) The crystal structure of (P,R,R)-15c and its supramolecular organization along the x axis.

Diastereoisomeric resolution was performed by crystallization taking advantage of different solubilities between (M,R,R)-15c and (P,R,R)-15c. Indeed, by simply using appropriate quantity of mixed solvent of heptane and CHCl$_3$ (3:1), (P,R,R)-15c precipitated from the solution with a 34% yield, while the mother liquors contained mainly (M,R,R)-15c. Diastereoisomerically pure (M,R,R)-15c was also obtained by careful silica column chromatography followed by crystallization in mixed solvent of heptane and CHCl$_3$ (3:1) with 33% yield. Notably, both (M,R,R)-15c and (P,R,R)-15c showed a loss of diastereomeric purity around 30% in the refluxing toluene for 72 hours, forming a mixture of both diastereoisomers, and this racemization rate is higher than the normal helicene for example platina[6]helicene 8a which shows almost no racemization in refluxing toluene. This easier racemization is due to the more open structure of the helicene.$^{1c}$

Both (M,R,R)-15c and (P,R,R)-15c were characterized by $^1$H NMR, $^{13}$C NMR as well as 2D NMRs, and all the peaks were assigned. Similar with the two diastereoisomers of platina[8]helicene 15b, these two diastereoisomers also showed different shifts of two methyl groups on the sulfoxide respectively in $^1$H NMR (Figure 4.15 and Figure 4.16). Besides, the satellite peaks of 6'-proton due to the split of $^{195}$Pt were also found for both compounds. In addition, the less peaks from the integrals in $^1$H NMR for both (M,R,R)-15c and (P,R,R)-15c indicates that these two compounds are $C_2$ symmetric.
Figure 4.15 The $^1$H NMR spectrum (400 MHz) of ($P,R,R$)-15c at 298 K in CDCl$_3$.

Figure 4.16 The $^1$H NMR spectrum (400 MHz) of ($M,R,R$)-15c at 298 K in CDCl$_3$. 
The final complexes \textit{rac-8c}, \textit{M-8c} and \textit{P-8c} were obtained by reacting the pure \textit{rac-14c}, (\textit{M,R,R})-15c or (\textit{P,R,R})-15c respectively with sodium acetylacetonate in toluene at 110 °C (\textbf{Scheme 4.12}). For the stability of enantiopure \textit{P} or \textit{M-15c}, a long half-life was observed around 19 days at 100 °C in 71% to 80 % yield.

\begin{scheme}{Scheme 4.12}{Synthetic route for the enantiopure \textit{M-8c} or \textit{P-8c}.}
\end{scheme}

\textit{8c} was fully characterized by \textit{1}H NMR, \textit{13}C NMR, as well as 2D NMRs, and all the peaks were assigned. The \textit{1}H NMR (\textbf{Figure 4.17}) appeared very simple due to the \textit{C}_2 symmetry of the molecule, and the satellites split by \textit{195}Pt was clearly found for the 6'-protons.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.17.png}
\caption{The \textit{1}H NMR spectrum (400 MHz) of \textit{8c} at 298 K in CDCl3.}
\end{figure}

Single crystals of \textit{8c} were also obtained by slow diffusion of pentane vapor into a CH\textsubscript{2}Cl\textsubscript{2} solution of \textit{rac-8c}, and the crystal structure was obtained by X-ray diffraction (\textbf{Figure 4.18}). The [6]helicene moiety of \textit{8c} shows a similar structure compared that of (\textit{P,R,R})-15c with the helicity of 51.2° which is smaller than that of (\textit{P,R,R})-15c.
Figure 4.18 The crystal structure of 8c (only P-enantiomers is shown; for clarity, the solvent molecule is removed).

§2.4 Synthesis of bisplatina[10]helicene 8d

Similarly to bisplatina[6]helicene 8c, the bisplatina[10]helicene 8d was synthesized by adopting the double cycloplatination. The intermediate rac-12d was obtained by reacting the ligand 10d with 3 equivalent of non-chiral Pt(dmso)₂Cl₂ with 6 equivalent of Na₂CO₃ in toluene at 110 °C, with 84% yield (Scheme 4.13).

![Scheme 4.13 Synthesis of intermediate rac-14d.]

Single crystals of rac-14d were obtained by slow diffusion of pentane vapors into a CH₂Cl₂ solution, and the structure was solved by X-ray diffraction. This intermediate crystallized in the centro-symmetric C2/c space group (two P and M helices in the unit cell), and the structure shows ten ortho-fused rings with intramolecular π-π stacking between the last 4 terminal rings in each side (ring 1, 2, 3 and 4 with ring 7, 8, 9 and 10, numbering see Scheme 4.13). Because of this, the helicity of 10d is only 18.7°. Besides, the distance between two platinum atoms is 4.83 Å. The supramolecular organization shows assemblies of alternated P and M helices (Figure 4.13).
Figure 4.19 The crystal structure of rac-12d (only the M enantiomer is shown). Supramolecular organization along the z axis.

Note that when we tried the reaction between 10d and the chiral \((R,R)\)-Pt(mtso)\(_2\)Cl\(_2\), a very low yield was obtained and purification was difficult. This may be due to the big steric hindrance of the two methyl(p-tolyl)sulfoxides. So for this compound, resolution with the help of a chiral auxiliary appeared difficult, and we used the preparative chiral HPLC for the resolution, and obtained the enantiopure \(P\)- and \(M\)-14d (see Experimental Part).

The final complex 8d, both racemic form or enantiopure form, was afforded by adopting the same method: reacting the 14d (\(rac\), \(M\) or \(P\)) with sodium acetylacetonate in toluene at 110 °C respectively in around 57% yield (Scheme 4.14).

8d was fully characterized by \(^1\)H NMR, \(^{13}\)C NMR, as well as 2D NMRs, and all the peaks have been assigned. The \(^1\)H NMR (Figure 4.20) shows less proton peaks, indicating that 8d possesses a symmetric structure. Typically, 8d shows the satellite peaks of 6’-protons in the two pyridyl groups due to the coupling with \(^{195}\)Pt.
The 1H NMR spectrum (400 MHz) of 8d at 298 K in CDCl₃.

Single crystals of P-8d were obtained by slow diffusion of pentane vapors into CH₂Cl₂ solution of racemic 8d, and the structure was resolved by X-ray diffraction. The complex P-8d crystallized in the non-centrosymmetric P2₁ space group. The helicity of this [10]helicene is 22.0°. Besides, π-π stacking can also be observed in this molecule between the 4 terminal rings in each side. The distance between the two Pt atoms is 5.94 Å, almost 1 Å bigger than the value in 14d.

The crystal structure of P-8d.
§2.5 Synthesis of borahelicenes

Other than the platinahelicenes, we also synthesized borahelicenes as counterparts in order to study their chiroptical and emission properties. The synthetic routes for 9a-d are almost the same as in the literature: first the borylation between the ligands with BBr₃ in the presence of a base (3 equivalent of N¹Pr(Et)₂) at 0 °C then at 25 °C to form intermediates 16a-d with one or two newly formed azaborole cycles (Scheme 4.15). The bromide groups then were replaced by methyl groups by reacting these intermediates with trimethyl aluminum to afford the final borahelicenes 9a-d in racemic form. The M and P enantiopure borahelicenes were obtained by preparative chiral HPLC (see Experimental Part).

These four compounds were fully characterized by NMR studies, and ¹H NMR, ¹³C NMR, ¹¹B NMR, ¹⁹F NMR, as well as 2D NMRs were made for these four compounds. The spectra of ¹H NMR are shown in Figure 4.22, Figure 4.23, Figure 4.24 and Figure 4.25 for these four compounds respectively. From the ¹H NMR spectra, the most interesting peaks are the protons of two methyl groups directly linking to the boron atom. Because of the helical chirality, the protons in the different
methyl groups are diastereotopic and show different shifts. For example, 9a shows the shifts at 0.37 and 0.09 for these two methyl groups; 9b shows −0.40 and −0.43; 9c shows 0.31 and 0.10; 9d shows 0.06 and −0.52. These methyl groups exhibit more deshielded in the shorter helicenes 9a and 9c, while more shielded for the longer 9b and 9d. 11B NMR also shows the similar phenomenon that 9a and 9c are more deshielded at 0.3 and 0.5 while 9b and 9d are more shielded at −0.7 and −0.6. 19F NMR for 9a, 9b and 9d all show doublet due to the coupling with the 3-proton on the helicene ring with a coupling constant around 8 Hz. Meanwhile, for the peaks of 3-proton in 1H NMR, the doublet with the same coupling constant is found. Besides, both 9c and 9d shows less proton peaks due to the C2 symmetry of these two molecules.

![The 1H NMR spectrum (400 MHz) of 9a at 298 K in CDCl3.](image)

**Figure 4.22** The 1H NMR spectrum (400 MHz) of 9a at 298 K in CDCl3.
Figure 4.23 The $^1$H NMR spectrum (400 MHz) of 9b at 298 K in CDCl$_3$.

Figure 4.24 The $^1$H NMR spectrum (400 MHz) of 9c at 298 K in CDCl$_3$. 
Single crystals of \textit{rac-9c} and \textit{rac-9d} could be obtained by slow diffusion of pentane vapors into \(\text{CH}_2\text{Cl}_2\) solutions and the structures were solved by X-ray diffraction. Compound \textit{rac-9c} crystallized in the centro-symmetric \textit{I2/a} space group (with the \textit{P} and \textit{M} helices present), and the structure shows a \textit{C}_2 symmetry. The helicity of this compound is 53.1° which is normal for a [6]helicene. The C11--B1 and the B1--N1 bond-lengths are 1.60 and 1.62 Å respectively. The B--C shows normal value compared with common boron compounds (~1.6 Å) while B--N shows a relatively longer value compared with some common boron-nitrogen compounds (1.4 to 1.5 Å) but in reasonable range. For the B--N bond, if this bond is not strong enough, decoordination and coordination can occur and this process can cause the racemization. Besides, for this structure, the short lengths of C--B bond or B--N bond causes the [6]helicene more open compared with the bisplatinahelicene \textit{8c}, which leads to the low configurational stability in solution at room temperature. Actually, 25% loss of optical rotation was observed for this compound, when keeping the enantiopure \textit{M-9c} or \textit{P-9c} in \(\text{CH}_2\text{Cl}_2\) solution after one week at room temperature. So for the measurement in solution, the solution needs to be newly prepared.

Complex \textit{rac-9d} crystallized in the centro-symmetric \textit{P\bar{1}} space group, which is same as \textit{8d}. The helicity of this molecule is quite small, \textit{i.e.} 2.6° which may be caused by the strong \(\pi-\pi\)-stacking between the 4 terminal rings of each side. Besides, the distance between two boron atoms is 6.19 Å.
The supramolecular arrangement of rac-9c and rac-9d is similar, with heterochiral supramolecular columns formed of alternated $M$ or $P$ helices (Figure 4.26).

![Figure 4.26](image)

**Figure 4.26** The crystal structures of rac-9c (only the $P$ enantiomer is shown) and rac-9d (only the $M$ enantiomer is shown).

![Figure 4.27](image)

**Figure 4.27** Supramolecular arrangement of rac-9c along the x axis.

§3 Optical and chiroptical Properties

§3.1 UV-vis spectroscopy

Having obtaining the series of platinahelicenes and borahelicenes in both racemic form and enantiopure form, we started to measure their optical and chiroptical properties, as well as the ligand 10b to 10d (the UV-vis, optical rotation and ECD data of 8a and the UV-vis data of its ligand 10a is published by our group according to the literature³, and here we use these data for comparison). First, the UV-vis spectra of them have been investigated. These spectra were measured in CH$_2$Cl$_2$ solution with concentration around 10$^{-5}$ mol·L$^{-1}$. The selected bands are listed in Table 4.1.
Table 4.1 Selected UV-Vis data for 8a, 8b, 8c, 8d, 9a, 9b, 9c, 9d, 10a, 10b, 10c and 10d.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Wavelength, nm (ε, 10^3·L·mol^{-1}·cm^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>8a platina[6]helicene</td>
<td>255 (61); 294 (34); 316 (34); 346 (34); 435 (sh, 7.1); 452 (7.8)</td>
</tr>
<tr>
<td>8b platina[8]helicene</td>
<td>234 (68); 260 (45); 281 (40); 318 (sh, 30); 335 (sh, 26); 369 (13); 467 (5.0)</td>
</tr>
<tr>
<td>8c bisplatina[6]helicene</td>
<td>255 (42); 290 (34); 326 (sh, 18); 389 (21); 433 (11); 471 (6.6)</td>
</tr>
<tr>
<td>8d bisplatina[10]helicene</td>
<td>240 (61); 264 (50); 297 (46); 374 (sh, 16); 423 (8.1); 447 (6.8); 480 (5.3)</td>
</tr>
<tr>
<td>9a bora[6]helicene</td>
<td>236 (40); 262 (23); 285 (sh, 26); 294 (27); 306 (25); 326 (sh, 13); 343 (8.9); 359 (8.4); 377 (5.8); 398 (4.2)</td>
</tr>
<tr>
<td>9b bora[8]helicene</td>
<td>233 (48); 265 (46); 313 (sh, 24); 324 (25); 352 (sh, 15); 371 (sh, 11); 405 (2.1); 427 (1.4)</td>
</tr>
<tr>
<td>9c bisbora[6]helicene</td>
<td>255 (33); 288 (16); 354 (15); 374 (13); 391 (12)</td>
</tr>
<tr>
<td>9d bisbora[10]helicene</td>
<td>269 (57); 336 (29); 393 (sh, 8,0); 414 (3.8); 440 (2.8)</td>
</tr>
<tr>
<td>10a pyridyl[4]helicene</td>
<td>387 (1020); 316sh (17100); 292 (43300)</td>
</tr>
<tr>
<td>10b pyridyl[6]helicene</td>
<td>265 (42); 270 (sh, 41); 310 (22); 320 (20); 339 (16); 399(sh, 0.8); 422 (0.3)</td>
</tr>
<tr>
<td>10c dipyridynaphthalene</td>
<td>236 (34); 306 (11)</td>
</tr>
<tr>
<td>10d dipyridyl[6]helicene</td>
<td>233 (44); 269 (48); 320 (24); 353 (13); 427 (0.2)</td>
</tr>
</tbody>
</table>

The UV-vis spectra of the platinahelicenes are shown in Figure 4.28, and their corresponding ligand are shown in Figure 4.29. The ligand 10b displays a typical spectrum for a [6]helicene derivative showing an intense high-energy band at 265 nm and several bands between 300 and 350 nm with intensities around 2 × 10^4·L·mol^{-1}·cm^{-1} and a tail down to 450 nm. After the cyplatination, the platina[8]helicene 8b shows a red shift for the lower energy band from 422 to 467 nm with a tail down to 510 nm. This red shift is mainly caused by the elongation of the π plane of the helicene backbone from a [6]helicene to a [8]helicene. Similarly, ligand 10d also shows the typical spectrum for [6]helicene derivative with intense high-energy bands at 233 and 269 nm and a tail down to 450 nm. The double cycloplatinations in 10d have increased the π fused core to a [10]helicene and accordingly the lowest-energy band occurs at 480 nm with a tail down to 520 nm. The changes from ligand 10c to bisplatina[6]helicene 8c are even more striking. While ligand 10c has only two moderate absorption bands in the UV region, after the double cycloplatinations to obtain 8c, several strong bands can be observed in the visible region from 380 to 500 nm. These bands originate from the interaction between the two Pt atoms and the π-orbital of the ligand.1c

Making transverse comparison between the platinahelicenes, for example the comparison between platina[6]helicene 8a and bisplatina[6]helicene 8c, we can find that 8c with two Pt incorporated within the helicene backbone shows higher intensity in the absorption at visible region
than for 8a having only one Pt atom, and the lowest energy band is more red-shifted. In addition, by comparing 8a and 8b, we can find that upon adding two additional terminal helicene rings, the lowest-energy band shifts from 452 nm to 467 nm, indicating the effect of the elongation of the \( \pi \) system. Besides, going from 8b to 8d, which exhibits even longer \( \pi \) conjugation and one more Pt atom, the lowest-energy band can still be red-shifted, and the intensity can be increased.

![Figure 4.28](image)

**Figure 4.28** The UV-vis spectra of platinahelicenes 8a (yellow), 8b (orange), 8c (pink) and 8d (red).

![Figure 4.29](image)

**Figure 4.29** The UV-vis spectra of ligands 10a (yellow), 10b (orange), 10c (pink) and 10d (red).

The UV-vis spectra of the four borahelicenes are shown in **Figure 4.30**. Compared with the platinahelicenes, these borahelicene shows less intense absorption bands. In addition, by comparing bora[6]helicene 9a and bisbora[6]helicene 9c, we can find the similar maximum value of absorption around 420 nm, and the lowest-energy band is around 395 nm. However, 9c shows stronger absorption (around one time higher than 9a in the visible region), and this may be due to the absorption of two borazole cycles. For the longer helicenes 9b and 9d, two typical strong absorption
bands can be found around 265 nm and 324 nm for $9b$, and 269 nm and 336 nm for $9d$. Additional lower-energy bands are also found at 427 and 440 nm for $9b$ and $9d$ respectively. These values are bigger than the smaller helicenes $9a$ and $9c$ due to the more extended $\pi$-conjugation.

**Figure 4.30** The UV-vis spectra of borahelicenes $9a$ (light blue), $9b$ (dark blue) $9c$ (light green) and $9d$ (dark green).

§3.2 Optical rotations

The optical rotations were measured for all the platinahelicenes $8b$ to $8d$, intermediate platinahelicenes $15b$ and $15c$, and borahelicenes $9a$ to $9d$, as well as the ligand $10b$ in CH$_2$Cl$_2$ with the concentration around $10^{-3}$ to $10^{-4}$ mol·L$^{-1}$, and the data for specific rotation $[\alpha]_{D}^{23}$ and molar rotation $[\phi]_{D}^{23}$ are listed in Table 4.2. Notably, the bisbora[6]helicene $9c$ was measured in the newly prepared solution due to the configurational unstability. Indeed, around 25% loss of optical rotation was observed for the compound keeping in CH$_2$Cl$_2$ solution after one week at room temperature due to the racemization. The configurational instability was not observed for the other borahelicenes at room temperature. TDDFT calculation for the optical rotations with the method of BHLYP/SV(P) for some of compounds are also listed in Table 4.2.
First, from this table, one can observe that some of the [6]helicenes, *i.e.* the ligand P-10b, the platina[6]helicenes P-8a and P-8c, as well as the diastereoisomers (M,R,R)-13c and (P,R,R)-13c, show almost similar molar rotations around +9000 °·cm²·dmol⁻¹, which is also in accordance with the value of regular organic [6]helicenes.¹¹ On the contrary, the two bora[6]helicenes P-9a and P-9c show relatively small molar rotations, around +5000 °·cm²·dmol⁻¹, which may be caused by the more open helenic structure due to the azaborole cycle, and this more open structure also causes the configurational instability of P-9c.

Second, the platina[8]helicenes (M,R)-13b, (P,R)-13b or P-8b show also almost similar molar rotation values around 2×10⁴ °·cm²·dmol⁻¹, which is also in accordance with the regular organic [8]helicenes.¹¹ Interestingly, the molar rotation increased dramatically around 1.5 times from the ligand [6]helicene P-10b to the platina[8]helicenes, indicating that the simple complexation can modulate significantly the chiroptical property. Besides, the calculated molar rotation values for the platina[8]helicenes agree reasonably well with the experimental values, while for the ligand P-10b, the calculated value is overestimated.¹⁶

Finally, for the bisplatina[10]helicene P-8d and the bisbora[10]helicene P-9d, the molar rotation values are relatively high, up to 3×10⁴ °·cm²·dmol⁻¹, probably due to the high extension of the π system as well as intramolecular π-π stacking interactions (inducing a small pitch of ~ 3.5-4 Å).

### §3.3 ECD spectroscopy

The ECD spectra of both *M* and *P* enantiomers of the platinahelicenes 8b to 8d and the

<table>
<thead>
<tr>
<th>Compound</th>
<th>[α]D²³ (°·cm²·dm⁻¹·g⁻¹)</th>
<th>[β]D²³ (°·cm²·dmol⁻¹)</th>
<th>[θ]D²³ calc. (°·cm²·dmol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-8a</td>
<td>+1300</td>
<td>+8170</td>
<td>+9982</td>
</tr>
<tr>
<td>P-8b</td>
<td>+3090</td>
<td>+22500</td>
<td>+23300</td>
</tr>
<tr>
<td>P-8c</td>
<td>+1030</td>
<td>+8950</td>
<td>+9982</td>
</tr>
<tr>
<td>P-8d</td>
<td>+3145</td>
<td>+35500</td>
<td>-</td>
</tr>
<tr>
<td>P-9a</td>
<td>+1394</td>
<td>+5060</td>
<td>-</td>
</tr>
<tr>
<td>P-9b</td>
<td>+3010</td>
<td>+14000</td>
<td>-</td>
</tr>
<tr>
<td>P-9c</td>
<td>+1438</td>
<td>+5210</td>
<td>-</td>
</tr>
<tr>
<td>P-9d</td>
<td>+5317</td>
<td>+32100</td>
<td>-</td>
</tr>
<tr>
<td>P-10b</td>
<td>+1906</td>
<td>+8290</td>
<td>+16400</td>
</tr>
<tr>
<td>(M,R)-15b</td>
<td>-2430</td>
<td>-19900</td>
<td>-24000</td>
</tr>
<tr>
<td>(P,R)-15b</td>
<td>+2350</td>
<td>+19200</td>
<td>+19100</td>
</tr>
<tr>
<td>(M,R,R)-15c</td>
<td>-1123</td>
<td>-11800</td>
<td>-9800</td>
</tr>
<tr>
<td>(P,R,R)-15c</td>
<td>+916</td>
<td>+9616</td>
<td>+4337</td>
</tr>
</tbody>
</table>

* Optical rotation was measured for the newly prepared solution.
borahelicenes 9a to 9d have been measured in CH₂Cl₂ solution with concentration around 10⁻⁵ mol·L⁻¹. Notably, the ECD spectra for 9c has been measured on freshly prepared solutions for avoiding the racemization. The data of the P-enantiomers are listed in Table 4.3 and the ECD spectra depicted in Figure 4.31 and Figure 4.32.

Table 4.3 Selected UV-Vis data for P-8a, P-8b, P-8c, P-8d, P-9a, P-9b, P-9c and P-9d.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Wavelength, nm (Δε, L·mol⁻¹·cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-8a platina[6]helicene</td>
<td>252 (−161); 282 (sh, +30); 309 (+61); 342 (+89); 391 (+9.4)</td>
</tr>
<tr>
<td>P-8b platina[8]helicene</td>
<td>245 (+73); 280 (−123); 303 (sh, −79); 335 (sh, −8.0); 372 (+168); 468 (+4.1)</td>
</tr>
<tr>
<td>P-8c bisplatina[6]helicene</td>
<td>243 (−85); 295 (+109); 323 (−3.8); 345 (+15); 377 (+22); 430 (−3.5); 447 (+9.4); 472 (+21)</td>
</tr>
<tr>
<td>P-8d bisplatina[10]helicene</td>
<td>240 (+72); 280 (−176); 322 (+49); 340 (−9.7); 274 (sh, +76); 394 (+119); 436 (sh, +74); 493 (+15)</td>
</tr>
<tr>
<td>P-9a bora[6]helicene</td>
<td>237 (−95); 296 (sh, +89); 307 (+110); 397 (−8.7)</td>
</tr>
<tr>
<td>P-9b bora[8]helicene</td>
<td>267 (−116); 307 (−77); 340 (sh, +122); 353 (+159); 379 (sh, +100); 427 (−4.8)</td>
</tr>
<tr>
<td>P-9c bisbora[6]helicene</td>
<td>277 (+71); 303 (−4.8); 358 (sh, +15); 374 (+20); 392 (sh, +16)</td>
</tr>
<tr>
<td>P-9d bisbora[10]helicene</td>
<td>251 (−95); 268 (−165); 294(+59); 331 (−47); 379 (+249); 439 (−7.9)</td>
</tr>
</tbody>
</table>

The ECD spectrum of platina[8]helicene P-8b shows typical helicene bisignate bands: ¹Bₐ band at 280 nm with negative sign and ¹B₀ band at 372 nm with positive sign. Compared with the platina[6]helicene P-8a, P-8b appears more red-shifted (ca. 30 nm). This is due to the elongation of the π system. Besides, the ¹B₀ band of P-8b is much stronger than that of P-8a. In addition, a small positive tail is found at 468 nm for P-8b, which corresponds to the lowest-energy band in the UV-vis spectrum, showing this band is ECD active. However, such band is not found for P-8a. The red shift, high intensity of the ¹B₀ band, together with the small positive lowest-energy band make the molar rotation of 8b much bigger than 8a.

For bisplatina[6]helicene 8c, the typical helicene bisignate bands and the overall shape is quite different compared with organic [6]helicene derivatives. Strong positive band are found at 295 nm, and there are some weak bands with positive or negative sign between 320 and 430 nm. Besides, a moderately intense band with lowest energy is found at 472 nm, which also agrees with the result of UV-vis spectrum. Besides, compared with P-8b, this band shows much higher intensity for P-8c with Δε around +21 L·mol⁻¹·cm⁻¹.

For the bisplatina[10]helicene P-8d, the bisigned bands were also found, and compared with P-8a or P-8b it appeared red-shifted which may be due to the longer π system. The shape of ¹B₀ is broad with two identical shoulder peaks in two sides. The intensity of the maximum value of ¹B₀ band appeared lower compared with that of P-8b. In addition, a lowest-energy band with positive sign has
been found at 493 nm with moderate intensity, which is more red-shifted than the smaller helicene 8c.

![Figure 4.31 The ECD spectra of platinahelicenes P-8a (yellow), P-8b (orange), P-8c (pink) and P-8d (red).](image)

The ECD spectra of borahelicenes also show quite different characteristics compared with platinahelicenes (Figure 4.32). For the bora[6]helicene P-9a one can find the bisignated bands with negative sign at 237 nm and positive sign at 307 nm. In the visible region, however, a negative band was found for this P-enantiomers at 397 nm with intensity of $-8.7 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$. This negative band may cause the lower molar rotation value of 9a compared with 8a.

For the bisbora[6]helicene P-9c, similarly to P-8c, one cannot find the typical bisignated bands of helicenes, however an intense band at 277 nm is displayed, similarly to P-8c but with some blue shift. A positive band with moderate intensity can be found at 374 nm with two identical shoulder peaks in each side. For P-9c, no negative lowest-energy band is found in this case.

Bora[8]helicene P-9b shows the typical bisignated bands: a set of negative bands at 267 and 307 nm, and a positive band at 353 nm with two identical shoulder peaks in each side. Besides, a negative lower-energy band is also found at 427 nm, causing the smaller value of molar rotation.

For the bisbora[10]helicene P-9d, the $^1\text{B}_a$ band is not so typical with two negative bands at 268 and 331 nm and a positive band at 294 nm in middle. However, for the $^1\text{B}_b$ band, it shows strong intensity with $\Delta\varepsilon$ at $+249 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$, which is twice higher compared with the other [10]helicene P-8d, and this band is also more red-shifted when compared with P-9a and P-9b. In this case, a low-energy negative band is also observed at 439 nm.

Note that the shoulders observed in several spectra probably originate from vibronic progressions (C=C stretchings).
Figure 4.32 The ECD spectra of borahelicenes $P\text{-}9\text{a}$ (light blue), $P\text{-}9\text{b}$ (dark blue) $P\text{-}9\text{c}$ (light green) and $P\text{-}9\text{d}$ (dark green).

§3.4 Luminescence and CPL

The luminescence measurements have been performed by Gareth Williams’ group (Durham University, England), and all the eight helicenes were measured at 298 K as well as at 77 K. The results are summarized in Table 4.4 and the emission are displayed in Figure 4.33 and Figure 4.34.

From the results, one can see that the emission of the four platinahelicenes is a red phosphorescence around 640 nm at 298 K, while the emission of borahelicenes is a blue fluorescence around 430 nm at 298 K. The quantum yields showed interesting results: when the helicene becomes longer, the quantum yield is decreased (comparing $8\text{a}$ and $8\text{b}$, $8\text{c}$ and $8\text{d}$, $9\text{a}$ and $9\text{b}$, $9\text{c}$ and $9\text{d}$), while when the helicene contains two Pt or B atoms, the quantum yield is increased (compare $8\text{a}$ and $8\text{c}$, $8\text{b}$ and $8\text{d}$, $9\text{a}$ and $9\text{c}$, $9\text{b}$ and $9\text{d}$). One explanation for the lower quantum yield of longer [8] or [10]helicenes may be the intramolecular $\pi-\pi$ stacking, which can quench the emission in both cases of fluorescence and phosphorescence. In addition, by introducing more azaboracycles or azaplatinacycles increases the emission. Besides, for the bisbora[6]helicene $9\text{c}$, the quantum yield is very high up to 0.49, which is quite rare in helicenes. At low temperature, similarly to other helicenes, all four borahelicenes started to show phosphorescence in the longer wavelength with relaxation times around 1 s.
Table 4. Emission data for P-8a, P-8b, P-8c, P-8d, P-9a, P-9b, P-9c and P-9d.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Emission λ_{max} nm (298 K)(^a)</th>
<th>τ_{lum} ns (298 K)</th>
<th>Φ (298 K)(^c)</th>
<th>Emission λ_{max} nm (77 K)(^b)</th>
<th>τ_{lum} (77 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>8a</strong></td>
<td>644</td>
<td>21 000</td>
<td>0.10</td>
<td>592, 638, 691 (sh)</td>
<td>45 μs</td>
</tr>
<tr>
<td><strong>8b</strong></td>
<td>648</td>
<td>16 500</td>
<td>0.056</td>
<td>598, 644</td>
<td>32 μs</td>
</tr>
<tr>
<td><strong>8c</strong></td>
<td>633, 673</td>
<td>18 700</td>
<td>0.13</td>
<td>608, 664, 727</td>
<td>28 μs</td>
</tr>
<tr>
<td><strong>8d</strong></td>
<td>637, 663</td>
<td>31 000</td>
<td>0.079</td>
<td>614, 667, 730 (sh)</td>
<td>61 μs</td>
</tr>
<tr>
<td><strong>9a</strong></td>
<td>404, 425, 450 (sh)</td>
<td>4.1</td>
<td>0.21</td>
<td>396, 417, 443, 471 (fluo); 543, 581, 626 (phos)</td>
<td>7.2 ns (fluo); 1.1 s (phos)</td>
</tr>
<tr>
<td><strong>9b</strong></td>
<td>435, 458</td>
<td>5.3</td>
<td>0.069</td>
<td>427, 454, 484, 516 (fluo); 546, 593, 643 (phos)</td>
<td>7.3 ns (fluo); 1.2 s (phos)</td>
</tr>
<tr>
<td><strong>9c</strong></td>
<td>427</td>
<td>3.2</td>
<td>0.49</td>
<td>397, 415, 443, 474 (sh) (fluo); 556, 604, 654 (phos)</td>
<td>3.9 ns (fluo); 620 ms (phos)</td>
</tr>
<tr>
<td><strong>9d</strong></td>
<td>443, 471, 502, 541</td>
<td>5.5</td>
<td>0.074</td>
<td>437, 464, 496, 532 (fluo); 554, 599, 657 (phos)</td>
<td>7.3 ns (fluo); 1.1 s (phos)</td>
</tr>
</tbody>
</table>

\(^a\) Measured in CH\(_2\)Cl\(_2\) at 298 K. \(^b\) Measured in diethyl ether-isopentane-ethanol (2 :2 :1 v/v). \(^c\) Measured using [Ru(bpy)\(_3\)]Cl\(_2\) as the standard.

The circularly polarize luminescence (CPL) experiments have been performed by Gilles Muller’s group (San José University, USA) for the enantiopure platinahelicenes 8a-8c, and the enantiopure borahelicenes 9a-9d, as well as for the enantiopure ligand 10b. The measurement has been done in the degassed CH\(_2\)Cl\(_2\) solution and the results are shown in Figure 4.33 and Figure 4.34.

![Figure 4.33](image_url)  
**Figure 4.33** The CPL spectra (upper) and the luminescent spectra (lower) for both enantiomers of platinaheliene 8a (λ_{ex} = 452 nm), 8b (λ_{ex} = 452 nm) and 8c (λ_{ex} = 459 to 469 nm), and the ligand 10b (λ_{ex} = 371 to 282 nm).
For platinahelicenes the $P$-enantiomers show positive signals while the $M$-enantiomers show negative signals, as well as the ligand 10b. The $g_{\text{lum}}$ for 8a is $-0.011/+0.013$ for two enantiomers, and is the biggest among these compounds. For 8b and 8c the $g_{\text{lum}}$ are $-0.005/+0.004$ and $-0.0005/+0.0005$ respectively. The ligand 10b shows $g_{\text{lum}}$ values of $-0.0008/+0.0008$. Note that bisplatina[10]helicene 10d displayed too low CPL activity to be measured experimentally.

For the borahelicenes, the $g_{\text{lum}}$ are $+0.001/-0.0013$, $+0.0013/-0.0014$, $+0.0010/-0.0014$ and $-0.0006/+0.0006$ for $M$-9a/$P$-9a, $M$-9b/$P$-9b, $M$-9c/$P$-9c and $M$-9d/$P$-9d respectively. Note that the sign of borahelicenes are interesting. For 9a, 9b and 9c, the positive signal is for the $M$-enantiomers while the negative signal is for the $P$-enantiomers, which is opposite to the platinahelicenes, the ligand 10b as well as the bora[10]helicenes 9d. This result may have some relationship with the negative sign for the lowest-energy band in ECD for some of borahelicenes.

These results clearly demonstrate that our heteroatomic and organometallic helicene solutions in CH$_2$Cl$_2$ solution exhibit an active CPL signal, showing clearly that the emitted light is polarized in the opposite direction from the two enantiomers. However, the positive CPL sign is not always related to the $P$ stereochemistry of the helicene, it actually also depends on the sign of the lower energy absorption band.

Figure 4.34 The CPL spectra (upper) and the luminescent spectra (lower) for both enantiomers of platinahelene 9a ($\lambda_{\text{ex}} = 395$ nm), 9b ($\lambda_{\text{ex}} = 405$ to 409 nm), 9c ($\lambda_{\text{ex}} = 405$ nm) and 9d ($\lambda_{\text{ex}} = 420$ nm).

Except for platina[6]helicene 8a which displays a $|g_{\text{lum}}|$ of $\sim 10^{-2}$, the CPL results of these helicenes are quite small ($10^{-4}$-$10^{-3}$), but of the same order of magnitude as other known helicenes (see Chapter 1).
§4 Conclusion

To sum up, we have synthesized a series of platinahelicenes 8a-d and borahelicenes 9a-d. Both racemic and enantiopure form of these compounds were obtained. During the synthesis, an efficient crystallization process combined with chromatography of diastereomeric cycloplatinated complexes bearing chiral methyl tolyl sulfoxide ligand 15b and 15c was developed. This method allowed us to obtained the enantiopure mono-platinahelicene 8b and bis-platinahelicene 8c respectively in good scale (hundreds-milligram-scale). The optical and chiroptical properties, including UV-vis spectroscopy, ECD spectroscopy, optical rotation, luminescence and CPL activity, have been studied and comparison between these two series of helicenes have been made. Both platinahelicenes and borahelicenes shows good CPL activity, and for platinahelicenes, they showed circularly polarized phosphorescence in room temperature for helicene for the first time, especially 8a that it displays the highest $|g_{\text{lum}}|$ value of the order of $10^{-2}$.

Reference


General conclusion
General Conclusion

During these three years, I have worked on metallic helicenes and heteroatomic helicenes, on their optical and chiroptical properties, as well as on their applications. Three topics have been done, and they are 1) the iron-ethynyl-helicene complexes, 2) the ruthenium-bis-ethynyl-helicene-DTE complexes, and 3) the platinahelicenes and the borahelicenes.

In the first topic, I have synthesized three helicene-based iron complexes in their neutral state and in their cationic oxidized state. Switching properties have been studied by UV-vis and ECD spectroscopies, exhibiting very good bistability and reversibility. ON/OFF switch and positive/negative switch were reached by choosing the different wavelength in ECD. The tuning of chirooptical properties upon oxidation have also been studied in the telecommunication region of 1.54 μm, and it is the first time that we found the change of the sign in the optical rotation without changes of the molecular structure and stereochemistry. In the infrared region, IR and VCD, Raman and ROA spectroscopies have been studied, and this is the first case in studying the tuning upon oxidation. In the VCD spectra, huge g values up to 0.01 were found.

In the second topic, a ruthenium-bis-ethynyl-helicene-DTE complex was synthesized, and this molecule shows a rare example of helicene which show dual switching activity towards both irradiation and potential. The switching properties have been studied in detail by UV-vis and ECD spectroscopies, and the neutral closed state shows an interesting cycloreversion reaction upon oxidation. This special property enabled us to apply this molecule as a “NOR” logic gate.

In the third topic, a series of platinahelicenes and borahelicenes have been synthesized. An efficient crystallization process combined with chromatography of diastereoisomeric complexes with a chiral sulfoxide ligand was developed for the platinahelicenes resolution in large scale (hundreds-milligram-scale). The optical and chirooptical properties, including UV-vis spectroscopy, ECD spectroscopy, optical rotation, luminescence and CPL activity, have been studied and comparison between these two series of helicenes have been made. Both platinahelicenes and borahelicenes show strong luminescence and good CPL activity, and the platinahelicenes displayed circularly polarized phosphorescence at room temperature, with highest $|g_{\text{lum}}|$ value up to $10^{-2}$. 

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Experimental part
Experimental part

General information

All experiments were performed under an atmosphere of dry argon using standard Schlenk techniques. Commercially available reagents were used as received without further purification. Solvents were freshly distilled under argon from sodium/benzophenone (tetrahydrofuran, diethyl ether) or from phosphorus pentoxide (pentane, dichloromethane). Irradiation reactions were conducted using a Heraeus TQ 150 mercury vapor lamp. Preparative separations were performed by gravity column chromatography on basic alumina (Aldrich, Type 5016A, 150 mesh, 58 Å) or silica gel (Merck Geduran 60, 0.063-0.200 mm) in 3.5-20 cm columns. $^1$H, $^{11}$B, $^{13}$C, $^{19}$F and $^{31}$P NMR spectra were recorded on a Bruker AM300, AV400 or AV500. Chemical shifts of $^1$H and $^{13}$C NMR were reported in parts per million (ppm) relative to Me$_4$Si as external standard. $^{31}$P NMR downfield chemical shifts were expressed with a positive sign, in ppm, relative to external 85% H$_3$PO$_4$ and were decoupled from the proton. Assignment of proton atoms is based on $^1$H-$^1$H COSY experiment. Assignment of carbon atoms is based on HMBC, HMQC and DEPT-135 experiments. Mass analyses were performed by the CRMPO, University of Rennes 1. Elemental analyses were performed by the CRMPO, University of Rennes 1. Specific rotations (in deg cm$^2$ g$^{-1}$) were measured in a 1 dm thermostated quartz cell on a Perkin Elmer-341 polarimeter. Electronic Circular dichroism (in M$^{-1}$ cm$^{-1}$) was measured on a Jasco J-815 Circular Dichroism Spectrometer (IFR140 facility - Biosit - Université de Rennes 1), adapted with an extended wavelength option to 1100 nm for NIR-CD. UV-vis-NIR spectroscopy was conducted on a Varian Cary 5000 spectrometer.

$(\eta^2$-dppe)$($\eta^5$-C$_5$Me$_5$)$FeCl$, 2-ethynyl-carbo[4]helicene,$^2$ 2-ethynyl-carbo[6]helicene 1a,$^2$ 2,15-bis-ethynyl-carbo[6]hexahelicene 1b,$^3$ compound 5o,$^4$ benzo[c]phenanthrylmethyl-phosphonium bromide,$^5$ (naphthalene-2,7-dimethyl)bis(triphenylphosphonium bromide),$^6$ 1,8-di(pyridin-2-yl)naphthalene,$^7$ R,R-Pt(mtso)$_2$Cl$_2$,$^8$ and Pt(dmso)$_2$Cl$_2$,$^8$ were prepared according to previously described procedures.

§1 Synthesis

Complex 1a

[Diagram of complex 1a]

In a Schlenk tube, 275 mg of $(\eta^2$-dppe)$($\eta^5$-C$_5$Me$_5$)$FeCl$ (0.44 mmol), 101 mg of 2-ethynyl[4]helicene 2a (0.4 mmol) and 100 mg of NaPF$_6$ (0.6 mmol) were suspended in a mixture of 4 mL of degassed CH$_3$OH and 1 mL of THF under argon. The suspension was stirred at 25 °C for 48
hours. Then the solvent was removed under vacuum and the residue was dissolved in a minimum amount of CH₂Cl₂ under argon, then diethyl ether was added into the solution to form a heavy brown precipitate of vinylidene complex 3a. The vinylidene complex 3a was filtered under argon, washed with 5 mL of diethyl ether and dried under vacuum. Then the vinylidene complex together with 68 mg of t-BuOK (0.6 mmol) were suspended in 5 mL of THF under argon, and the reaction mixture was stirred at 25 °C for 4 hours and the reaction mixture turned from black to dark red. Filtration was performed under argon and the solvent of filtrate was removed. The residue of filtrate was redissolved in a minimum amount of CH₂Cl₂ and degassed CH₃OH was added to the solution to form the product as a heavy red precipitate. The precipitate was filtered off, washed with 5 mL of degassed CH₃OH and dried under vacuum to form the final product (175 mg, 52%) as red powder. Dark red single crystals could be grown by slow diffusion of n-pentane vapors into a CH₂Cl₂ solution of the product.

¹H NMR (400 MHz, CD₂Cl₂, 298 K), δ = 9.03 (d, J = 8.4 Hz, 1H, H₁), 8.71 (s, 1H, H₁), 8.00 (dd, J = 7.8 Hz, J = 1.3 Hz, 1H, H₀), 7.98-7.91 (m, 4H, Hₜₚ-ortho), 7.86 (d, J = 8.5 Hz, 1H, H₁), 7.79 (d, J = 8.5 Hz, 1H, H₁), 7.77 (d, J = 8.4 Hz, 1H, H₁), 7.73 (d, J = 8.3 Hz, 1H, H₁), 7.63 (d, J = 8.4 Hz, 1H, H₁), 7.59 (t, J = 7.3 Hz, 1H, H₁), 7.54 (ddd, J = 8.3 Hz, J = 6.8 Hz, J = 1.3 Hz, 1H, H₁), 7.44-7.37 (m, 2H, Hₜₚ-para), 7.36-7.30 (m, 8H, 4Hₜₚ-ortho and 4Hₜₚ-meta), 7.30-7.25 (m, 6H, 4Hₜₚ-meta and 2Hₜₚ-para), 7.19 (d, J = 8.4 Hz, 1H, H₁), 2.77 (m, 2H, −CH₂−), 2.08 (m, 2H, −CH₂−), 1.49 (s, 15H, CH₃Cₚ).

¹³C{¹H} NMR (100 MHz, CD₂Cl₂, 298 K), δ = 139.28 (d, J = 24 Hz, 2Cₜₚ-ipso), 138.00 (d, J = 44 Hz, 2Cₜₚ-ipso), 134.54 (t, J = 4 Hz, 4Cₜₚ-ortho), 134.37 (t, J = 4 Hz, 4Cₜₚ-ortho), 133.77 (Cₜₚ), 131.68 (Cₚ), 131.08 (C¹₂c), 130.99 (C¹₂a), 130.29 (C⁴ₚ), 129.56 (C²), 129.37 (2Cₜₚ-para), 129.23 (2Cₜₚ-para), 129.17 (C³), 128.72 (C⁹), 128.43 (C¹), 128.14 (C⁴), 128.11 (C¹₂), 127.73 (t, J = 4 Hz, 4Cₜₚ-meta), 127.63 (C⁵), 127.47 (t, J = 4 Hz, 4Cₜₚ-meta), 127.36 (C⁸), 127.30 (C⁷), 126.57 (C¹₂b), 126.25 (C¹), 125.77 (C¹₀), 124.70 (C⁶), 121.50 (broad, −C=C−Fe), 88.24 (5Cₚ), 31.09 (m, 2C, −CH₂−), 10.32 (5CH₃Cₚ).

³¹P NMR (162 MHz, CD₂Cl₂, 298 K), δ = 99.56. HRMS-ESI+: m/z calcd for C₅₆H₅₀P₂⁵⁺Fe: 840.27317 [M⁺]; found: 840.2723.

Complex 1b

Rac-1b: In a Schlenk tube, 138 mg of (η²-dppe)(η²-C₅Me₃)FeCl (0.22 mmol), 70 mg of racemic 2-ethynyl[6]helicene rac-2b (0.2 mmol) and 50 mg of NaPF₆ (0.3 mmol) were suspended in a mixture of 4 mL of degassed CH₃OH and 1 mL of THF under argon. The suspension was stirred at 25 °C for 48 hours. Then the solvent was stripped off and the residue was dissolved in a minimum amount of
CH₂Cl₂ under argon, then diethyl ether was added to form a dark brown precipitate of vinylidene complex rac-3b which was filtered under argon, washed with 5 mL of diethyl ether and dried under vacuum. Then the vinylidene complex rac-3b together with 34 mg of t-BuOK (0.3 mmol) were suspended in 5 mL of THF under argon, and the reaction mixture was stirred at 25 °C for 4 hours during which the color turned from black to dark red. After filtration under argon, the residue was redissolved in a minimum amount of CH₂Cl₂ and degassed CH₃OH was added to the solution to form the product as a heavy red precipitate. The precipitate was filtered, washed with 5 mL of degassed CH₃OH and dried under vacuum to form the final product (116 mg, 62%) as a red powder. Dark red single crystals could be grown by slow diffusion of n-pentane vapors into a CH₂Cl₂ solution of the product.

**P-1b and M-1b**: The same procedure applied to enantiopure ligands P-2b and M-2b enantiomers gave P-1b and M-1b with 51 and 56% respective yields.

¹H NMR (400 MHz, CD₂Cl₂, 298 K), δ 8.04 (d, J = 8.1 Hz, 1H, H₇), 7.99 (d, J = 8.1 Hz, 1H, H₁⁰), 7.98 (d, J = 8.1 Hz, 1H, H₉), 7.94 (d, J = 8.1 Hz, 1H, H₇), 7.80 (d, J = 8.5 Hz, 1H, H₈), 7.78 (d, J = 8.8 Hz, 1H, H₁¹), 7.72 (d, J = 8.5 Hz, 1H, H₈), 7.68 (d, J = 8.8 Hz, 1H, H₁²), 7.66 (d, J = 7.5 Hz, 1H, H₁³), 7.64 (d, J = 7.5 Hz, 1H, H₁⁶), 7.62-7.58 (m, 2H, Hph-ortho), 7.55 (d, J = 8.4 Hz, 1H, H₇), 7.51-7.35 (m, 7H, 4Hph-ortho, 2Hph-meta and 1Hph-para), 7.31 (t, J = 7.4 Hz, 1H, Hph-para), 7.28-7.19 (m, 3H, 2Hph-meta and 1Hph-para), 7.16 (t, J = 7.5 Hz, 1H, H₁⁴), 7.13-7.06 (m, 2H, Hph-ortho), 7.01-6.91 (m, 5H, 4Hph-meta and 1Hph-para), 6.84 (s, 1H, H₁), 6.75 (d, J = 8.4 Hz, 1H, H₇), 6.73 (t, J = 7.5 Hz, 1H, H₁⁵), 2.34 (m, 1H, −CH₂−), 2.17 (m, 1H, −CH₂−), 1.95 (m, 1H, −CH₂−), 1.78 (m, 1H, −CH₂−), 1.29 (s, 15H, CH₃CP*)

¹³C {¹H} NMR (100 MHz, CD₂Cl₂, 298 K), δ 140.80 (d, J = 26 Hz, Cph-ipsos), 138.07 (d, J = 22 Hz, Cph-ipsos), 137.84 (dd, J = 37 Hz, J = 6 Hz, Cph-ipsos), 136.99 (dd, J = 36 Hz, J = 4 Hz, Cph-ipsos), 135.20 (d, J = 10 Hz, 2Cph-ortho), 134.78 (d, J = 9 Hz, 2Cph-ortho), 133.63 (d, J = 8 Hz, 2Cph-ortho), 133.33 (d, J = 8 Hz, 2Cph-ortho), 133.29 (C₈a), 131.94 (C₁²a), 131.81 (C₆a), 131.50 (C₁₀a), 130.97 (C¹⁶c), 130.11 (C₁₆a), 129.75 (C₃ and Cph-para), 128.83 (Cph-para), 128.73 (C₆a and Cph-para), 128.65 (C² and Cph-para), 128.41 (broad, C¹), 128.33 (C¹⁶b), 128.18 (C₁²), 128.03 (C₁⁶), 127.93 (C¹⁶d), 127.88 (C₅), 127.80 (C¹₃), 127.66 (d, J = 7 Hz, 4Cph-meta), 127.45 (C⁷), 127.34 (C₁⁰), 127.12 (d, J = 8 Hz, 2Cph-meta), 127.09 (d, J = 8 Hz, 2Cph-meta), 126.94 (C⁹), 126.85 (C₆), 126.69 (C₈), 126.56 (C¹₁), 125.79 (C¹₄), 124.58 (C¹₆c), 124.57 (C¹₅), 123.88 (C⁶), 121.97 (broad, −C≡C−Fe), 87.87 (5CPh*), 31.84 (dd, J = 35 Hz, J = 11 Hz, −CH₂−), 30.26 (dd, J = 29 Hz, J = 13 Hz, −CH₂−), 10.30 (CH₃CP*).

³¹P NMR (162 MHz, CD₂Cl₂, 298 K), δ 99.41 (broad), 95.55 (broad).

HRMS-ESI⁺: m/z calcd for C₆₄H₅₄P₂⁵⁶Fe: 940.30447 [M⁺]; found: 940.3044.

**Complex 1c**
Rac-1c: In a Schlenk tube, 137.5 mg of \((\eta^2\text{-dppe})(\eta^4\text{-C}_5\text{Me}_5)\text{FeCl}\) (0.22 mmol), 37.6 mg of racemic 2,15-diethynyl[6]helicene rac-2c (0.1 mmol) and 50.4 mg of NaPF\(_6\) (0.3 mmol) were suspended in a mixture of 4 mL of degassed CH\(_2\text{OH}\) and 1 mL of THF under argon. The suspension was stirred at 25 °C for 48 hours. Then the solvent was stripped off and the residue was dissolved in a minimum amount of CH\(_2\text{Cl}_2\) under argon, then diethyl ether was added into the solution to form a dark brown precipitate of vinylidene complex 3c which was filtered under argon, washed with 5 mL of diethyl ether and dried under vacuum. Then the vinylidene complex 3c together with 24.7 mg of t-BuOK (0.22 mmol) were suspended in 5 mL of THF under argon, and the reaction mixture was stirred at 25 °C for 4 hours during which the color turned from black to dark red. After filtration under argon, the precipitate was redissolved in a minimum amount of CH\(_2\text{Cl}_2\) and degassed CH\(_2\text{OH}\) was added to the solution to form the product as a dark red precipitate which was filtered, washed with 5 mL of degassed CH\(_2\text{OH}\) and dried under vacuum to form the final product (120 mg, 77%) as a red powder. Dark red single crystals could be grown by slow diffusion of n-pentane vapors into a CH\(_2\text{Cl}_2\) solution of the product.

P-1c and M-1c: The same procedure applied to enantiopure ligands P-2c and M-2c enantiomers gave P-1c and M-1c with 68 and 77% respective yields.

\(^1\text{H NMR} (400 \text{ MHz}, \text{CD}_2\text{Cl}_2, 298 \text{ K}), \delta \) 7.98 (d, J = 8.1 Hz, 2H, H\(_2\) and H\(^\text{P}^{\text{ortho}}\)), 7.90 (d, J = 8.1 Hz, 2H, H\(^\text{P}^{\text{ortho}}\) and H\(^{\text{P}^{\text{ortho}}}\)), 7.65 (d, J = 7.3 Hz, 4H, H\(^\text{P}^{\text{ortho}}\)), 7.51 (s, 4H, H\(^\text{P}^{\text{ortho}}\) and H\(^{\text{P}^{\text{ortho}}}\)), 7.50 (d, J = 7.3 Hz, 4H, H\(^\text{P}^{\text{ortho}}\)), 7.46 (t, J = 7.3 Hz, 2H, H\(^\text{P}^{\text{para}}\)), 7.41 (d, J = 7.5 Hz, 4H, H\(^\text{P}^{\text{ortho}}\)), 7.37 (t, J = 7.3 Hz, 4H, H\(^\text{P}^{\text{meta}}\)), 7.33 (d, J = 8.2 Hz, 2H, H\(^\text{P}^{\text{para}}\) and H\(^{\text{P}^{\text{para}}}\)), 7.29 (t, J = 7.4 Hz, 2H, H\(^\text{P}^{\text{para}}\)), 7.21 (t, J = 7.4 Hz, 4H, H\(^\text{P}^{\text{meta}}\)), 7.17 (t, J = 7.5 Hz, 2H, H\(^\text{P}^{\text{para}}\)), 7.06 (d, J = 7.4 Hz, 4H, H\(^\text{P}^{\text{ortho}}\)), 6.97 (t, J = 7.5 Hz, 4H, H\(^\text{P}^{\text{meta}}\)), 6.93 (t, J = 7.3 Hz, 4H, H\(^\text{P}^{\text{meta}}\)), 6.91 (s, 2H, H\(^\text{P}^{\text{para}}\) and H\(^{\text{P}^{\text{para}}}\)), 6.87 (t, J = 7.3 Hz, 2H, H\(^\text{P}^{\text{para}}\)), 6.71 (d, J = 8.2 Hz, 2H, H\(^\text{P}^{\text{para}}\) and H\(^{\text{P}^{\text{para}}}\)), 2.37 (m, 2H, –CH\(_2\)–), 2.22 (m, 2H, –CH\(_2\)–), 1.94 (m, 2H, –CH\(_2\)–), 1.73 (m, 2H, –CH\(_2\)–), 1.35 (s, 30H, CH\(_3\)C\(_{\text{P}}\)\(^\text{a}\)).

\(^{13}\text{C}\{^1\text{H}\} \text{ NMR} (100 \text{ MHz}, \text{CD}_2\text{Cl}_2, 298 \text{ K}), \delta \) 141.08 (d, J = 26 Hz, 2C\(^{\text{P}^{\text{ipso}}}\)), 137.94 (d, J = 22 Hz, 2C\(^{\text{P}^{\text{ipso}}}\)), 137.79 (d, J = 40 Hz, 2C\(^{\text{P}^{\text{ipso}}}\)), 137.07 (d, J = 36 Hz, 2C\(^{\text{P}^{\text{ipso}}}\)), 135.37 (d, J = 11 Hz, 4C\(^{\text{P}^{\text{ortho}}}\)), 134.86 (d, J = 9 Hz, 4C\(^{\text{P}^{\text{ortho}}}\)), 133.48 (d, J = 7 Hz, 4C\(^{\text{P}^{\text{ortho}}}\)), 133.17 (d, J = 9 Hz, 4C\(^{\text{P}^{\text{ortho}}}\)), 132.94 (C\(^{\text{8a}}\)), 131.51 (C\(^{\text{6a}}\) and C\(^{\text{10a}}\)), 130.80 (C\(^{\text{16a}}\) and C\(^{\text{16c}}\)), 129.73 (2C\(^{\text{P}^{\text{para}}}\)), 129.51 (C\(^3\) and ...
C\(^{14}\), 128.77 (2C\(^{\text{Ph-paran}}\), 128.57 (4C\(^{\text{Ph-paran}}\), C\(^{1}\) and C\(^{16}\)), 128.45 (C\(^{4a}\) and C\(^{12a}\)), 128.08 (C\(^{16b}\) and C\(^{16d}\)), 127.91 (C\(^{2}\), C\(^{5}\), C\(^{12}\) and C\(^{15}\)), 127.62 (d, J = 7 Hz, 8C\(^{\text{Ph-meta}}\)), 127.35 (d, J = 8 Hz, 4C\(^{\text{Ph-meta}}\)), 127.18 (d, J = 9 Hz, 4C\(^{\text{Ph-meta}}\)), 127.09 (C\(^{7}\) and C\(^{10}\)), 126.94 (C\(^{4}\) and C\(^{13}\)), 126.24 (C\(^{8}\) and C\(^{9}\)), 123.78 (C\(^{6}\) and C\(^{11}\)), 122.03 (broad, 2C, −C≡C−Fe), 87.82 (10C\(^{\text{Cp*}}\)), 31.97 (dd, 2C, J = 35 Hz, J = 10 Hz, −CH\(_2\)−), 31.81 (dd, 2C, J = 29 Hz, J = 13 Hz, −CH\(_2\)−), 10.40 (10CH\(_3\)\(^{\text{Cp*}}\)).

\(^{31}\)P NMR (162 MHz, CD\(_2\)Cl\(_2\), 298 K), δ 99.93 (broad), 95.40 (broad).

HRMS-ESI+: m/z calcd for C\(_{102}\)H\(_{92}\)P\(_4\)Fe\(_2\): 1552.48429 [M\(^+\)]; found: 1552.4846.

**Complex [1a]**

42 mg of 1a (0.05 mmol) was dissolved in 4 mL of THF, and 0.25 mL of degassed I\(_2\) solution (0.1 mmol·L\(^{-1}\) in CH\(_2\)Cl\(_2\)) was added with a micro-syringe. The reaction was stirred at 25 °C for 16 hours and then 10 mL of degassed pentane was added to form a heavy brown precipitate. The precipitate then was collected by filtration under argon and washed by pentane twice to afford the product as a brown solid (45 mg, 93%).

\(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\), 298 K): δ 31.7 (broad, 1H, \(H^{\text{hexilene}}\)), 21.4 (broad, 1H, \(H^{\text{hexilene}}\)), 13.0 (d, J = 6.5 Hz, 1H, \(H^{\text{hexilene}}\)), 10.17 (d, J = 7.2 Hz, 1H, \(H^{\text{hexilene}}\)), 10.05 (s, 1H, \(H^{\text{hexilene}}\)), 7.95 (s, 2H, \(H^{\text{Ph-paran}}\)), 7.38 (broad, 6H, \(H^{\text{ethylene}} \times 2\) and \(H^{\text{Ph-ortho}} \times 4\)), 6.69 (s, 4H, \(H^{\text{Ph-meta}}\)), 6.20 (s, 2H, \(H^{\text{Ph-par}}\)), 5.85 (broad, 1H, \(H^{\text{hexilene}}\)), 4.07 (s, 1H, \(H^{\text{hexilene}}\)), 3.77 (s, 4H, \(H^{\text{Ph-meta}}\)), 3.56 (d, J = 7.1 Hz, 1H, \(H^{\text{hexilene}}\)), 2.16 (broad, 4H, \(H^{\text{Ph-ortho}}\)), −2.9 (broad, 2H, \(H^{\text{ethylene}}\)), −10.2 (broad, 15H, \(CH_{3}\)\(^{\text{Cp*}}\)), −25.6 (broad, 1H, \(H^{\text{hexilene}}\)), −30.3 (broad, 1H, \(H^{\text{hexilene}}\)), −69.3 (broad, 1H, \(H^{\text{hexilene}}\)).
Complex \([1b]^+\Gamma\)

\[
\begin{array}{c}
\includegraphics[width=0.5\textwidth]{complex_1b.png}
\end{array}
\]

*Rac-[1b]*\(^+\Gamma\): 18.8 mg of 1b (20 μmol) was dissolved in 4 mL of THF, and 0.1 mL of a degassed \(I_2\) solution (0.1 mmol·L\(^{-1}\) in \(CH_2Cl_2\)) was added with a micro-syringe. The reaction was stirred at 25 °C for 16 hours and then 10 mL of degassed pentane was added to form a dark brown precipitate. The precipitate was then collected by filtration under argon and washed twice with pentane to afford the product as a brown solid (20.5 mg, 96%).

\(^1\)H NMR (400 MHz, \(CD_2Cl_2\), 298 K): \(\delta\) 33.4 (broad, 1H, \(H_\text{helicene}\)), 20.2 (broad, 1H, \(H_\text{helicene}\)), 14.5 (broad, 1H, \(H_\text{ethylene}\)), 13.0 (broad, 1H, \(H_\text{helicene}\)), 10.7 (broad, 2H, \(H_\text{Ph-ortho}\)), 9.97 (s, 2H, \(H_\text{helicene}\)), 8.94 (s, 1H, \(H_\text{helicene}\)), 8.52 (s, 1H, \(H_\text{Ph-para}\)), 8.22 (s, 1H, \(H_\text{helicene}\)), 8.10 (s, 1H, \(H_\text{Ph-ortho}\)), 8.05 (s, 1H, \(H_\text{helicene}\)), 7.69 (s, 1H, \(H_\text{helicene}\)), 7.36 (s, 1H, \(H_\text{helicene}\)), 7.31 (s, 1H, \(H_\text{Ph-para}\)), 6.69 (s, 1H, \(H_\text{helicene}\)), 6.57 (s, 2H, \(H_\text{Ph-meta}\)), 6.30 (s, 3H, \(H_\text{Ph-para} \times 1\) \& \(H_\text{Ph-meta} \times 2\)), 6.07 (s, 1H, \(H_\text{Ph-para}\)), 5.28 (broad, 2H, \(H_\text{Ph-ortho}\)), 4.81 (s, 1H, \(H_\text{helicene}\)), 4.13 (s, 1H, \(H_\text{helicene}\)), 3.80 (s, 2H, \(H_\text{Ph-meta}\)), 3.67 (s, 2H, \(H_\text{Ph-meta}\)), 2.75 (broad, 2H, \(H_\text{Ph-ortho}\)), 0.90 (broad, 2H, \(H_\text{Ph-ortho}\)), 0.46 (broad, 1H, \(H_\text{ethylene}\)), −3.8 (broad, 1H, \(H_\text{ethylene}\)), −10.4 (broad, 15H, \(CH_3Cp^+\)), −23.3 (broad, 1H, \(H_\text{helicene}\)), −31.5 (broad, 1H, \(H_\text{helicene}\)), −66.8 (broad, 1H, \(H_\text{helicene}\)).

Complex \([1c]^{2-}\Gamma\)

\[
\begin{array}{c}
\includegraphics[width=0.5\textwidth]{complex_1c.png}
\end{array}
\]

15.5 mg of 1c (10 μmol) was dissolved in 4 mL of THF, and 0.1 mL of a degassed \(I_2\) solution (0.1 mmol·L\(^{-1}\) in \(CH_2Cl_2\)) was added by micro-syringe. The reaction was stirred at 25 °C for 16 hours and then 10 mL of degassed pentane was added to form a dark brown precipitate. The precipitate was then collected by filtration under argon and washed twice with pentane to afford the product as a brown solid (17 mg, 94%).

\(^1\)H NMR (400 MHz, \(CD_2Cl_2\), 298 K): \(\delta\) 33.4 (broad, 2H, \(H_\text{helicene}\)), 21.9 (broad, 2H, \(H_\text{helicene}\)), 16.7 (broad, 2H, \(H_\text{ethylene}\)), 14.8 (s, 2H, \(H_\text{helicene}\)), 10.3 (broad, 4H, \(H_\text{Ph-ortho}\)), 8.60 (s, 2H, \(H_\text{Ph-para}\)), 7.10 (s, 2H, \(H_\text{Ph-para}\)), 6.67 (s, 4H, \(H_\text{Ph-meta}\)), 5.84 (s, 2H, \(H_\text{Ph-para}\)), 5.60 (s, 6H, \(H_\text{Ph-para} \times 2\) \& \(H_\text{Ph-meta} \times 4\)),
4.72 (broad, 4H, $H_{\text{Ph-ortho}}$), 3.78 (s, 4H, $H_{\text{Ph-meta}}$), 3.57 (s, 4H, $H_{\text{Ph-meta}}$), 2.89 (broad, 4H, $H_{\text{Ph-ortho}}$), 1.80 (broad, 2H, $H_{\text{ethylene}}$), 0.96 (s, 2H, $H_{\text{helicene}}$), 0.75 (broad, 4H, $H_{\text{Ph-ortho}}$), −5.6 (broad, 2H, $H_{\text{ethylene}}$), −8.8 (broad, 2H, $H_{\text{ethylene}}$), −10.5 (broad, 30H, $CH_3Cp^*$), −22.9 (broad, 2H, $H_{\text{helicene}}$), −30.9 (broad, 2H, $H_{\text{helicene}}$), −67.5 (broad, 2H, $H_{\text{helicene}}$).

**Complex 6**

\[ \text{Rac-6: In a Schlenk tube, 325mg of } \left[(\eta^2-\text{dppe})_2\text{RuCl}\right]\text{OTf (0.30 mmol) and 109 mg of racemic rac-2b (0.31 mmol) were suspended in 10 mL of degassed CH}_2\text{Cl}_2 \text{ under argon. The suspension was stirred at 25 °C for 48 hours. After the reaction, 40 mL of diethyl ether was added into the solution to form a heavy brown precipitate. The precipitate was filtered under argon and washed by 10 mL of diethyl ether and dried under vacuum to form the product as brown solid (413 mg, 96%).} \]

**P-6:** The reaction was started as described for racemic product, using 108 mg of \left[(\eta^2-\text{dppe})_2\text{RuCl}\right]\text{OTf (0.10 mmol) and 37 mg of P-2b (0.105 mmol), and the product was isolated as a brown solid (125 mg, 87%).} \]

**M-6:** The reaction was started as described for racemic product, using 108 mg of \left[(\eta^2-\text{dppe})_2\text{RuCl}\right]\text{OTf (0.10 mmol) and 37 mg of M-2b (0.105 mmol), and the product was isolated as a brown solid (128 mg, 89%).} \]

**Complex 4o**

\[ \text{Rac-4o: 28.7 mg of rac-6 (20 μmol), 9.4 mg of 5o (20 μmol) and 16.8 mg of NaPF}_6 \text{ (100 μmol) were added into a Schlenk tube under argon in darknes, and 5 mL of CH}_2\text{Cl}_2 \text{ was injected. The reaction mixture was stirred for 5 min, after which 14 μL of NEt}_3 \text{ (100 μmol) were injected. Then, the Schlenk tube was well-covered with aluminum foil, preventing from the irradiation of the sunlight,} \]

VII
and the reaction mixture was stirred at 25 °C for 72 h. The solvent was then stripped off and the residue was purified by basic alumina column chromatography (CH₂Cl₂) under darkness to afford the product as a yellow solid (30.2 mg, 88%) 

**P-40:** The reaction was started as described for racemic product, using 28.7 mg of **P-6** (20 µmol), and the product was isolated as a brown solid (33 mg, 96%).

**M-40:** The reaction was started as described for racemic product, using 28.7 mg of **M-6** (20 µmol), and the product was isolated as a brown solid (28 mg, 82%).

**1H NMR (500 MHz, CD₂Cl₂, 298 K):** δ 8.03 (d, J = 8.2 Hz, 1H, H²⁸), 8.00 (d, J = 8.2 Hz, 1H, H²⁹), 7.97 (d, J = 8.2 Hz, 1H, H³¹), 7.94 (d, J = 8.2 Hz, 1H, H³²), 7.88 (d, J = 8.5 Hz, 1H, H³⁵), 7.82 (d, J = 8.5 Hz, 1H, H³⁶), 7.76 (d, J = 8.6 Hz, 1H, H³¹), 7.73 (d, J = 8.6 Hz, 1H, H³¹), 7.67 (d, J = 8.4 Hz, 1H, H³¹), 7.66 (d, J = 8.1 Hz, 1H, H³¹), 7.65 (dd, J = 8.2 Hz, J = 1.2 Hz, 1H, H³¹), 7.58 (dt, J = 8.1 Hz, J = 1.6 Hz, 2H, H³¹), 7.43–7.38 (m, 4H, H³), 7.39 (t, J = 8.1 Hz, 2H, H³²), 7.38–7.31 (m, 8H, H³), 7.35 (s, 1H, H³¹), 7.31 (tt, J = 8.2 Hz, J = 1.4 Hz, 1H, H³¹), 7.18 (t, J = 7.4 Hz, 2H, H³³), 7.16 (t, J = 7.3 Hz, 2H, H³³), 7.12 (ddd, J = 8.0 Hz, J = 6.9 Hz, J = 1.1 Hz, 1H, H³¹), 7.09–7.06 (m, 4H, H³), 7.04 (t, J = 7.5 Hz, 2H, H³³), 6.96 (t, J = 7.6 Hz, 4H, H³⁴), 6.95 (t, J = 7.6 Hz, 4H, H³⁴), 6.83 (dd, J = 8.1 Hz, J = 1.5 Hz, 1H, H³¹), 6.80 (t, J = 7.5 Hz, 2H, H³³), 6.79 (m, 1H, H³¹), 6.77 (t, J = 7.6 Hz, 4H, H³⁴), 6.72 (s, 1H, H³¹), 6.61 (t, J = 7.6 Hz, 4H, H³⁴), 6.27 (s, 1H, H³⁴), 2.78 (broad, 2H, H³¹), 2.42 (broad, 4H, H³¹), 2.30 (broad, 2H, H³¹), 2.02 (s, 3H, H³¹), 1.87 (s, 3H, H³¹).

**13C {¹H} NMR (100 MHz, CD₂Cl₂, 298 K):** δ 142.39 (C³¹), 142.38 (t, J = 15.3 Hz, C³¹), 141.89 (C³¹), 138.56 (t, J = 20 Hz, 2C, C³¹), 137.69 (t, J = 19 Hz, 2C, C³¹), 136.56 (t, J = 19 Hz, 2C, C³¹), 136.25 (C³¹), 135.76 (t, J = 20 Hz, 2C, C³¹), 134.82 (t, J = 5 Hz, 4C, C³¹), 134.70 (t, J = 5 Hz, 4C, C³¹), 134.45 (t, J = 5 Hz, 4C, C³¹), 133.87 (C³¹), 133.75 (t, J = 5 Hz, 4C, C³¹), 133.43 (C³¹), 131.90 (C³¹), 131.82 (C³¹), 131.64 (C³¹), 131.63 (t, J = 15.3 Hz, C³¹), 130.97 (C³¹), 130.48 (C³¹), 130.10 (C³¹), 129.42 (2C, C³¹), 129.31 (C³¹), 129.16 (2C, C³¹), 129.06 (2C, C³¹), 128.97 (C³¹), 128.91 (2C, C³¹), 128.60 (2C, C³¹), 128.45 (C³¹), 128.26 (C³¹), 128.09 (3C, C³¹), 127.70 (C³¹), 127.54 (t, J = 4 Hz, 4C, C³¹), 127.47 (C³¹), 127.34 (t, J = 4 Hz, 4C, C³¹), 127.27 (t, J = 4 Hz, 4C, C³¹), 127.12 (t, J = 4 Hz, 4C, C³¹), 126.96 (C³¹), 126.94 (C³¹), 126.84 (C³¹), 126.82 (C³¹), 126.75 (C³¹), 126.70 (C³¹), 126.68 (C³¹), 126.35 (C³¹), 125.94 (2C, C³¹), 124.67 (C³¹), 124.56 (C³¹), 124.36 (C³¹), 124.12 (C³¹), 122.04 (C³¹), 123.11 (C³¹), 119.24 (C³¹), 107.19 (C³¹), 32.62 (broad, 2C, C³¹), 31.42 (broad, 2C, C³¹), 14.90 (C³¹), 14.67 (C³¹). Peaks of C³¹, C³¹, C³¹, C³¹ and C³¹ are too broad to be found in the spectrum due to splitting by ruthenium, phosphorus or fluorine.

**19F NMR (377 MHz, CD₂Cl₂, 298 K):** δ −109.9 (broad, 2F), −110.2 (broad, 2F), −132.1 (quint, J = 5.3 Hz, 2F).

**31P {¹H} NMR (162 MHz, CD₂Cl₂, 298 K):** δ 54.44 (t, J = 23 Hz, 2P), 51.38 (t, J = 23 Hz, 2P).
HRMS-ESI$^+$ (m/z) calcd. for C$_{103}$H$_{76}$F$_6$P$_4$S$_2$$^{103}$Ru ([M]$^+$) 1716.32812, found 1716.3295.

**Complex 4c**

In an NMR tube, 10 mg of 4o were dissolved in 0.5 mL of CD$_2$Cl$_2$, and this tube was irradiated under a UV lamp (365 nm, 4 W) upon stirring for 30 min. As observed by NMR experiment, full conversion from 4o to 4c (> 98%) was obtained.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$, 298 K): δ 8.03 (d, $J = 8.2$ Hz, 1H, $H^{i8}$), 8.01 (d, $J = 8.2$ Hz, 1H, $H^{i9}$), 7.98 (d, $J = 8.2$ Hz, 1H, $H^{i10}$), 7.93 (d, $J = 8.2$ Hz, 1H, $H^{i7}$), 7.90 (d, $J = 8.5$ Hz, 1H, $H^{i5}$), 7.84 (d, $J = 8.5$ Hz, 1H, $H^{i6}$), 7.74 (d, $J = 8.6$ Hz, 1H, $H^{i12}$), 7.71 (d, $J = 8.6$ Hz, 1H, $H^{i11}$), 7.70 (d, $J = 8.4$ Hz, 1H, $H^{i4}$), 7.64 (d, $J = 8.4$ Hz, 1H, $H^{i16}$), 7.63 (d, $J = 7.6$ Hz, 1H, $H^{i13}$), 7.55 (broad, 2H, $H^P^{i9}$), 7.46–7.40 (m, 10H, $8 \times H^{P3}$, $2 \times H^{P20}$), 7.25–7.19 (m, 8H, $4 \times H^{P4}$, $4 \times H^{P5}$), 7.10 (t, $J = 7.3$ Hz, 1H, $H^{i4}$), 7.07 (t, $J = 7.4$ Hz, 2H, $H^{P5}$), 7.00 (t, $J = 7.4$ Hz, 8H, $H^{P4}$), 6.90 (ddd, $J = 8.4$ Hz, $J = 4.8$ Hz (this J value is due to the two diastereoisomers), $J = 1.4$ Hz, 1H, $H^{i13}$), 6.90–6.87 (m, 4H, $H^{P3}$), 6.82 (t, $J = 8.0$ Hz, 2H, $H^{P5}$), 6.80 (t, $J = 7.4$ Hz, 4H, $H^{P4}$), 6.78 (ddd, $J = 8.6$ Hz, $J = 6.9$ Hz, $J = 1.4$ Hz, 1H, $H^{i15}$), 6.71 (d, $J = 5.6$ Hz (this J value is due to the two diastereoisomers), 1H, $H^{i11}$), 6.65 (t, $J = 7.6$ Hz, 4H, $H^{P4}$), 5.32 (broad, 1H, $H^{P1}$), 2.76 (broad, 2H, $H^{P1}$), 2.44 (broad, 4H, $H^{P1}$), 2.28 (broad, 2H, $H^{P1}$), 2.19 (d, $J = 3.1$ Hz (this J value is due to the two diastereoisomers), 3H, $H^{D17}$ or $D15$), 2.16 (d, $J = 2.9$ Hz (this J value is due to the two diastereoisomers), 3H, $H^{D17}$ or $D15$). Peak of C$^{D12}$ and C$^{D21}$ is expected as a broad peak hidden at the aromatic region. Peaks of C$^{H18}$ are too broad to be found in the spectrum due to splitting by ruthenium or phosphorus.

$^{13}$C{$^1$H} NMR (125 MHz, CD$_2$Cl$_2$, 298 K): δ 137.76 (td, $J = 21$ Hz, $J = 8$ Hz (this J value is due to the two diastereoisomers), 2C, C$^{Po2}$), 137.07 (td, $J = 20$ Hz, $J = 5$ Hz (this J value is due to the two diastereoisomers), 2C, C$^{Po2}$), 135.56 (td, $J = 19$ Hz, $J = 4$ Hz (this J value is due to the two diastereoisomers), 2C, C$^{Po2}$), 135.76 (td, $J = 21$ Hz, $J = 6$ Hz (this J value is due to the two diastereoisomers), 2C, C$^{Po2}$), 134.87 (m, 4C, C$^{P3}$), 134.66 (t, $J = 5$ Hz, 4C, C$^{P3}$), 134.14 (m, 4C, C$^{P3}$), 133.44 (C$^{H16a}$), 133.36 (m, 4C, C$^{P3}$), 131.87 (C$^{H12a}$), 131.80 (C$^{H6a}$), 131.61 (C$^{H10a}$), 130.93 (C$^{H16c}$), 130.02 (C$^{H16a}$), 129.43 (2C, C$^{P5}$), 129.36 (2C, C$^{P5}$), 129.24 (2C, C$^{P5}$), 129.21 (C$^{H4a}$), 129.02 (C$^{H3}$), 128.90 (2C, C$^{P5}$), 128.37 (C$^{H16b}$), 128.07 (C$^{H16d}$), 128.04 (4C, C$^{H2}$, C$^{H13}$, C$^{H15}$ and C$^{H12}$), 127.97 (C$^{H16}$),
127.81 (m, 6C, C\textsuperscript{1H}, C\textsuperscript{H1} and C\textsuperscript{P4}), 127.55 (t, J = 4 Hz, 4C, C\textsuperscript{P4}), 127.45 (C\textsuperscript{H10}), 127.43 (t, J = 4 Hz, 4C, C\textsuperscript{P4}), 127.27 (t, J = 4 Hz, 4C, C\textsuperscript{P4}), 127.10 (C\textsuperscript{H4}), 126.96 (C\textsuperscript{H8} and C\textsuperscript{H9}), 126.76 (C\textsuperscript{H11}), 126.30 (C\textsuperscript{H14}), 124.67 (C\textsuperscript{H15} and C\textsuperscript{H16}), 124.50 (C\textsuperscript{H16c}), 121.74 (C\textsuperscript{H17}), 32.50 (broad, 2C, C\textsuperscript{P1}), 31.32 (broad, 2C, C\textsuperscript{P1}), 26.03 (broad, 2C, C\textsuperscript{D15} and C\textsuperscript{D17}). Most of peaks from DTE unit are too broad to be found in the spectrum.

\textsuperscript{19}F NMR (377 MHz, CD\textsubscript{2}Cl\textsubscript{2}, 298 K): \(\delta = -111.0\) (very broad, 2F), \(-111.7\) (broad doublet, \(J = 250\) Hz, 1F), \(-114.8\) (broad doublet, \(J = 250\) Hz, 1F), \(-132.5\) (dd, \(J = 238\) Hz, \(J = 20\) Hz, (this \(J\) value is due to the two diastereoisomers), 1F), \(-133.5\) (dd, \(J = 238\) Hz, \(J = 21\) Hz, (this \(J\) value is due to the two diastereoisomers), 1F).

\textsuperscript{31}P{\textsuperscript{1}H} NMR (162 MHz, CD\textsubscript{2}Cl\textsubscript{2}, 298 K): \(\delta = 53.47\) (m, 2P), 50.47 (m, 2P).

HRMS-ESI\textsuperscript{+} (m/z) calcd. for C\textsubscript{103}H\textsubscript{76}F\textsubscript{6}P\textsubscript{4}S\textsubscript{2}Ru ([M]\textsuperscript{+}) 1716.32812, found 1716.3301.

**Ligand 10b**

583 mg of benzo[c]phenanthrylmethyl-phosphonium bromide (1.0 mmol) were suspended in 20 mL of dried THF under argon and cooled to \(-78\) °C. After addition of \(n\)-butyl lithium (0.63 mL, 1.6 mol·L\textsuperscript{-1} in hexanes), the obtained red mixture was stirred for 5 min at \(-78\) °C and then for 30 min at room temperature. 213 mg of 2-methoxy-5-(pyridin-2-yl)benzaldehyde (1.0 mmol), dissolved in 5 mL of dried THF was added dropwise to the suspension cooled again to \(-78\) °C. The orange heterogeneous mixture was stirred at \(-78\) °C for 5 min then at room temperature for 2 h. The solvent was removed under vacuum and the product was purified by silica gel column chromatography (heptane:CH\textsubscript{2}Cl\textsubscript{2} = 9:1, v/v) to afford the stilbene derivative 12b as a white solid (350 mg, 80%; mixture of cis and trans). Then, 545 mg of 12b was dissolved in 2 L of toluene and 30 mg of catalytic amount of I\textsubscript{2} were added. The solution was irradiated for 18 h under a Heraeus TQ 150 mercury vapor lamp. The solvent was removed under vacuum and the residue was purified by silica gel column chromatography (heptane:CH\textsubscript{2}Cl\textsubscript{2} = 2:1, v/v) to afford the product as a yellow solid (380 mg, 70%).

\textsuperscript{1}H NMR (400 MHz, CD\textsubscript{6}D\textsubscript{6}, 340 K), \(\delta = 8.68\) (d, \(J = 8.6\) Hz, 1H, \(H^5\)), 7.81 (broad, 1H, \(H^6\)), 7.81 (d, \(J = 8.6\) Hz, 1H, \(H^6\)), 7.75 (AB system, \(J = 8.2\) Hz, 1H, \(H^8\)), 7.74 (AB system, \(J = 8.2\) Hz, 1H, \(H^7\)), 7.64 (dd, \(J = 8.3\) Hz, \(J = 0.9\) Hz, 1H, \(H^{13}\)), 7.59 (d, \(J = 8.5\) Hz, 1H, \(H^{12}\)), 7.55 (d, \(J = 8.2\) Hz, 1H, \(H^9\)), 7.36 (d, \(J = 8.6\) Hz, 1H, \(H^{16}\)), 7.29 (d, \(J = 8.2\) Hz, 1H, \(H^{10}\)), 7.22 (d, \(J = 8.5\) Hz, 1H, \(H^{11}\)), 7.05 (broad d, \(J = 8.2\) Hz, 1H, \(H^{2}\)), 7.04 (ddd, \(J = 7.9\) Hz, \(J = 6.8\) Hz, \(J = 1.1\) Hz, 1H, \(H^{14}\)), 6.54 (ddd, \(J = 8.6\) Hz, \(J =
6.8 Hz, \( J = 1.4 \) Hz, 1H, \( H^5 \)), 6.46 (broad t, 1H, \( H^6 \)), 6.43 (d, \( J = 8.2 \) Hz, 1H, \( H^7 \)), 6.25 (ddd, \( J = 7.4 \) Hz, \( J = 4.8 \) Hz, \( J = 1.1 \) Hz, 1H, \( H^3 \)), 5.70 (d, \( J = 7.8 \) Hz, 1H, \( H^3 \)), 3.54 (s, 3H, –OCH\( _3 \)).

\(^1^3\text{C}\{^1\text{H}\} ^{\text{NMR}} (100 \text{ MHz}, \text{C}_6\text{D}_6, 340 \text{ K}), \delta 159.33 (C^2), 155.81 (C^4), 148.16 (C^6), 133.43 (C^8), 132.90 (C^{12a}), 132.63 (C^1), 132.06 (C^8a), 131.71 (C^{6a}), 130.72 (C^{10}), 130.39 (C^2), 130.05 (C^{16c}), 129.17 (C^{16a}), 127.69 (C^{16b}), 127.46 (C^{12}), 127.20 (C^6), 127.16 (C^{13}), 126.76 (C^{10}), 126.66 (C^{16c}), 126.61 (C^{16}), 126.31 (C^{16d}), 126.22 (C^7), 126.10 (C^11), 125.49 (C^6), 125.24 (C^9), 124.77 (C^{6a} and C^{14}), 123.60 (C^{15}), 121.20 (C^5), 120.53 (C^3), 118.55 (C^5), 105.20 (C^3), 55.16 (–OCH\( _3 \)).

**Ligand 10d**

838 mg of (naphthalene-2,7-dimethyl)bis(triphenylphosphonium bromide) (1.0 mmol) was suspended in 40 mL of dry THF under argon and cooled to −78 °C. 0.88 mL of n-butyllithium (2.5 mol·L\(^{-1}\) in hexane, 2.2 mmol) was added, and the reaction mixture was stirred for 5 min at −78 °C and then for 30 min at room temperature and the reaction turned to red. Then the reaction mixture was cooled to −78 °C again and 426 mg of 2-methoxy-5-(2-pyridinyl)benzaldehyde (2.0 mmol) dissolved in 5 mL of dry THF was added dropwise. The reaction was stirred at −78 °C for 5 min then at room temperature for 2 h. The solvent was removed under vacuum and the product was purified by short silica gel column chromatography (CH\(_2\)Cl\(_2\)) to afford the stilbene derivative 12d as a yellow solid (498 mg, 91%, cis and trans). Then this 498 mg of 12d (0.91 mmol) were dissolved in 3 L of toluene together with 10 mL of THF and 30 mg of catalytic iodine. The solution was irradiated under a mercury lamp for 16 h. Then the solvent was removed and the residue was purified by silica gel column chromatography (heptane:CH\(_2\)Cl\(_2\) = 2:1, v/v) and then washed by small amounts of acetone to afford the product as a yellow solid (95 mg, 19%).

\(^1\text{H}\) NMR (400 MHz, C\(_6\)D\(_6\), 345 K): \( \delta 8.53 (d, J = 8.6 \) Hz, 2H, \( H^6 \)), 7.94 (d, \( J = 4.7 \) Hz, 2H, \( H^6 \)), 7.58 (d, \( J = 8.2 \) Hz, 2H, \( H^{10} \)), 7.35 (d, \( J = 8.2 \) Hz, 2H, \( H^8 \)), 7.29 (d, \( J = 8.6 \) Hz, 2H, \( H^8 \)), 7.23 (d, \( J = 8.1 \) Hz, 2H, \( H^2 \)), 6.54 (d, \( J = 8.1 \) Hz, 2H, \( H^3 \)), 6.35 (broad t, 2H, \( H^3 \)), 6.22 (dd, \( J = 7.4 \) Hz, \( J = 4.7 \) Hz, \( J = 1.1 \) Hz, 2H, \( H^3 \)), 5.68 (d, \( J = 7.7 \) Hz, 2H, \( H^3 \)), 3.66 (s, 6H, –OCH\( _3 \)).

\(^{13}\text{C}\{^1\text{H}\} ^{\text{NMR}} (100 \text{ MHz}, \text{C}_6\text{D}_6, 345 \text{ K}): \delta 158.63 (C^2), 155.82 (C^4), 148.11 (C^6), 132.84 (C^8), 131.52 (C^1), 131.40 (C^{13}), 131.28 (C^8), 129.39 (C^2), 129.28 (C^{12}), 128.19 (C^{14}), 126.42 (C^5), 126.00 (C^9 and C^{11}), 125.67 (C^{10}), 124.93 (C^7), 121.95 (C^6), 120.15 (C^3), 118.33 (C^5), 104.91 (C^3), 55.39 (–OCH\( _3 \)).
584 mg of ([4]helicene-2-methyl)triphenylphosphonium bromide (1.0 mmol) was suspended in 20 mL of dry THF under argon and cooled to −78 °C. 0.44 mL of n-butyllithium (2.5 mol·L⁻¹ in hexane, 1.1 mmol) was added, and the reaction mixture was stirred for 5 min at −78 °C and then for 30 min at room temperature and the reaction turned to red. Then the reaction mixture was cooled to −78 °C again and 201 mg of 2-fluoro-5-(2-pyridinyl)benzaldehyde (1.0 mmol) dissolved in 5 mL of dry THF were added dropwise. The reaction was stirred at −78 °C for 5 min then at room temperature for 2 h. The solvent was removed under vacuum and the product was purified by short silica gel column chromatography (CH₂Cl₂) to afford the stilbene derivative 13b as a yellow solid (391 mg, 92%, cis and trans). Then, 391 mg of 13b (0.92 mmol) were dissolved in 3 L of toluene together with 10 mL of THF and 30 mg of catalytic iodine. The solution was irradiated under mercury lamp for 16 h. Then the solvent was removed and the residue was purified by silica gel column chromatography (heptane:CH₂Cl₂ = 2:1, v/v) to afford the product as yellow solid (220 mg, 56%).

\[^1\text{H} \text{NMR}\ (400 \text{ MHz}, \text{C}_6\text{D}_6, 333 \text{ K}): \delta 8.29 \text{ (d, } J = 8.6 \text{ Hz, } 1\text{H, } H^6), 7.74 \text{ (broad, } 1\text{H, } H^5), 7.73 \text{ (d, } J = 8.1 \text{ Hz, } 1\text{H, } H^8), 7.72 \text{ (d, } J = 8.6 \text{ Hz, } 1\text{H, } H^6), 7.68 \text{ (d, } J = 8.1 \text{ Hz, } 1\text{H, } H^7), 7.61 \text{ (d, } J = 7.9 \text{ Hz, } 1\text{H, } H^{13}), 7.56 \text{ (d, } J = 8.6 \text{ Hz, } 1\text{H, } H^{12}), 7.53 \text{ (d, } J = 8.2 \text{ Hz, } 1\text{H, } H^9), 7.28 \text{ (d, } J = 8.2 \text{ Hz, } 1\text{H, } H^{10}), 7.26 \text{ (d, } J = 8.6 \text{ Hz, } 1\text{H, } H^{16}), 7.19 \text{ (d, } J = 8.6 \text{ Hz, } 1\text{H, } H^{11}), 7.03 \text{ (ddd, } J = 7.9 \text{ Hz, } J = 6.9 \text{ Hz, } J = 0.9 \text{ Hz, } 1\text{H, } H^{14}), 6.87 \text{ (broad, } 1\text{H, } H^2), 6.79 \text{ (dd, } J_{HF} = 9.3 \text{ Hz, } J = 8.3 \text{ Hz, } 1\text{H, } H^3), 6.52 \text{ (dd, } J = 8.6 \text{ Hz, } J = 1.5 \text{ Hz, } 1\text{H, } H^{15}), 6.47 \text{ (broad, } 1\text{H, } H^4), 6.24 \text{ (ddd, } J = 7.4 \text{ Hz, } J = 4.7 \text{ Hz, } J = 0.9 \text{ Hz, } 1\text{H, } H^5), 5.64 \text{ (d, } J = 7.8 \text{ Hz, } 1\text{H, } H^3).\]

\[^{13}\text{C} \{^1\text{H}\} \text{ NMR}\ (100 \text{ MHz, } \text{C}_6\text{D}_6, 333 \text{ K}): \delta 159.57 \text{ (d, } J_{CF} = 251 \text{ Hz, } C^4), 159.07 \text{ (C}^2), 148.66 \text{ (C}^6), 136.26 \text{ (d, } J_{CF} = 4 \text{ Hz, } C^1), 134.13 \text{ (C}^4), 133.39 \text{ (C}^{12a}), 132.68 \text{ (C}^{8a}), 132.08 \text{ (C}^{6a}), 131.23 \text{ (C}^{10a}), 130.90 \text{ (d, } J_{CF} = 4 \text{ Hz, } C^{10c}), 130.51 \text{ (d, } J_{CF} = 9 \text{ Hz, } C^2), 129.25 \text{ (C}^{16a}), 128.40 \text{ (C}^{16b}), 128.23 \text{ (C}^2), 128.10 \text{ (C}^6), 127.94 \text{ (C}^{16c}), 127.69 \text{ (C}^{13}), 127.54 \text{ (C}^{10b}), 127.38 \text{ (C}^6), 126.95 \text{ (C}^{16d}), 126.69 \text{ (C}^{16d}), 126.63 \text{ (C}^{11}), 126.57 \text{ (C}^7), 125.70 \text{ (C}^{8b}), 125.47 \text{ (C}^{14}), 124.30 \text{ (C}^{15}), 123.02 \text{ (d, } J_{CF} = 16 \text{ Hz, } C^{13}), 121.08 \text{ (C}^3), 119.50 \text{ (C}^5), 119.49 \text{ (d, } J_{CF} = 7 \text{ Hz, } C^3), 110.37 \text{ (d, } J_{CF} = 20 \text{ Hz, } C^3).\]

\[^{19}\text{F} \text{ NMR}\ (377 \text{ MHz, } \text{C}_6\text{D}_6, 333 \text{ K}): \delta -123.8 \text{ (dd, } J_{HF} = 9.3 \text{ Hz, } J_{HF} = 6.5 \text{ Hz}).\]

HRMS-ESI⁺ (m/z) calcd. for C₃₁H₁₉NF ([M+H]⁺) 424.1496, found 424.1491.
Ligand 11d

1.68 g of (naphthalene-2,7-dimethyl)bis(triphenylphosphonium bromide) (2.0 mmol) were suspended in 40 mL of dry THF under argon and cooled to −78 °C. 1.76 mL of n-butyllithium (2.5 mol·L⁻¹ in hexane, 4.4 mmol) was added, and the reaction mixture was stirred for 5 min at −78 °C and then for 30 min at room temperature and the reaction turned to red. Then the reaction mixture was cooled to −78 °C again and 805 mg of 2-fluoro-5-(2-pyridinyl)benzaldehyde (4.0 mmol) dissolved in 5 mL of dry THF were added dropwise. The reaction was stirred at −78 °C for 5 min then at room temperature for 2 h. The solvent was removed under vacuum and the product was purified by short silica gel column chromatography (CH₂Cl₂) to afford the stilbene derivative 13d as a yellow solid (989 mg, 95%, cis and trans). Then, 523 mg of 13d (1.0 mmol) were dissolved in 3 L of toluene together with 10 mL of THF and 30 mg of catalytic iodine. The solution was irradiated under a mercury lamp for 16 h. Then the solvent was stripped off and the residue was purified by silica column chromatography (heptane:CH₂Cl₂ = 2:1, v/v) and then washed by small amounts of acetone to afford the product as a yellow solid (57 mg, 11%).

¹H NMR (400 MHz, C₆D₆, 333 K): δ 8.14 (d, J = 8.6 Hz, 2H, H⁵ and H¹₂), 7.86 (broad, 2H, H⁶' and H⁸'), 7.53 (d, J = 8.2 Hz, 2H, H⁶ and H⁸), 7.27 (d, J = 8.2 Hz, 2H, H⁷ and H¹₀), 7.17 (d, J = 8.6 Hz, 2H, H⁶ and H¹¹), 7.06 (t, J = 7.2 Hz, 2H, H⁶ and H¹⁵), 7.14 (dd, 3JHF = 9.5 Hz, J = 8.2 Hz, 2H, H³ and H¹³), 6.30 (t, J = 7.6 Hz, 2H, H'² and H'⁶), 6.20 (ddd, 2H, J = 7.4 Hz, J = 4.7 Hz, J = 1.1 Hz, H'⁶' and H'⁸'), 5.58 (d, J = 7.8 Hz, 2H, H'⁷ and H'⁸').

¹³C {¹H} NMR (100 MHz, C₆D₆, 333 K): δ 159.61 (d, JCF = 252 Hz, 2C, C⁴ and C¹³), 158.20 (2C, C² and C²'), 148.83 (2C, C⁶ and C⁸'), 134.83.18 (d, JCF = 3 Hz, 2C, C¹ and C¹⁶), 133.60 (2C, C⁴ and C⁴'), 132.12 (C⁶a), 131.78 (2C, C⁶a and C¹⁰a), 129.76 (d, 3JCF = 9 Hz, 2C, C² and C¹⁵), 128.96 (C¹⁶c), 128.67 (d, 3JCF = 4 Hz, 2C, C¹⁶a and C¹⁶c), 126.73 (2C, C⁷ and C¹⁰), 126.62 (2C, C⁶ and C¹¹), 126.58 (2C, C⁸ and C⁹), 126.08 (2C, C¹⁶b and C¹⁶d), 124.67 (d, 2JCF = 16 Hz, 2C, C⁴a and C¹²a), 120.69 (d, 3JCF = 6 Hz, 2C, C⁵ and C¹²), 120.72 (2C, C⁴' and C⁸'), 119.41 (2C, C⁶' and C⁸'), 110.02 (d, 2JCF = 20 Hz, 2C, C³ and C¹¹).

¹⁹F NMR (377 MHz, C₆D₆, 333 K): −124.2 (m).

HRMS-ESI⁺ (m/z) calcd. for C₃₆H₂₁N₂F₂ ([M+H]⁺) 519.16728, found 519.1671.
**Complex 14b**

A mixture of 178 mg of 10b (0.41 mmol), 260 mg of Pt(dmso)$_2$Cl$_2$ (0.62 mmol) and 87 mg of Na$_2$CO$_3$ (0.82 mmol) in 10 mL of toluene was refluxed overnight under argon. The cooled reaction mixture was concentrated under vacuum and was purified by column chromatography (silica gel, V$_{chloroform}$/V$_{ethyl acetate}$ = 10:1) to afford the product (245 mg, 81%) as a yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$, 298 K): δ 8.74 (dd, $J = 4.9$ Hz, $J = 2.8$ Hz, 1H), 8.35 (d, $J = 8.6$ Hz, 1H), 7.99 (AB system, $J = 8.0$ Hz, 1H), 7.98 (AB system, $J = 8.0$ Hz, 1H), 7.94 (d, $J = 7.9$ Hz, 1H), 7.89 (d, $J = 8.6$ Hz, 1H), 7.86 (d, $J = 8.1$ Hz, 1H), 7.75 (s, 1H), 7.65 (d, $J = 8.6$ Hz, 1H), 7.58 (d, $J = 8.1$ Hz, 1H), 7.31 (d, $J = 8.6$ Hz, 1H), 7.26 (m, 1H), 7.21 (d, $J = 8.5$ Hz, 1H), 6.67 (ddd, $J = 8.5$ Hz, $J = 6.8$ Hz, $J = 1.3$ Hz, 1H), 6.56–6.48 (m, 2H), 5.58–5.52 (m, 1H), 4.07 (s, 3H), 3.67 (s, 3H).

**Complex 15b**

A suspension of 527 mg of 10b (1.21 mmol), 1040 mg of R,R-Pt(mtso)$_2$Cl$_2$ (1.81 mmol) and 194 mg of Na$_2$CO$_3$ (1.83 mmol) in 10 mL of toluene was refluxed under argon overnight, and concentrated under vacuum. Long column chromatography (silica gel, V$_{heptane}$/V$_{ethyl acetate}$ = 3:1) was taken carefully, to afford the P,R-15b (first eluent, 330 mg, 33%) as a yellow powder, and the crude M,R-15b (166 mg, 18%) was afford by recrystallization from second eluent of column chromatography as orange crystals.

$^1$H NMR of P,R-15b (400 MHz, CDCl$_3$, 298 K): δ 8.90 (ddd, $J = 5.8$ Hz, $J = 1.8$ Hz, $J = 0.6$ Hz, $^1$H satellites: $^3J_{Pt-H} = 34$ Hz, 1H, $H^6$), 8.32 (d, $J = 8.6$ Hz, 1H, $H^5$), 8.21 (d, $J = 8.5$ Hz, 2H, $H^\text{ortho}$), 7.97 (AB system, $J = 8.2$ Hz, 1H, $H^7$), 7.96 (AB system, $J = 8.2$ Hz, 1H, $H^7$), 7.86 (d, $J = 8.6$ Hz, 1H, $H^6$), 7.84 (d, $J = 8.2$ Hz, 1H, $H^6$), 7.79 (s, $^1$H satellites: $^3J_{Pt-H} = 50$ Hz, 1H, $H^1$), 7.65 (d, $J = 7.9$ Hz, 1H, $H^1$), 7.61 (d, $J = 8.6$ Hz, 1H, $H^{12}$), 7.58 (d, $J = 8.5$ Hz, 2H, $H^{para}$), 7.57 (d, $J = 8.2$ Hz, 1H, $H^{10}$), 7.29 (d, $J = 8.6$ Hz, 1H, $H^{11}$), 7.07 (d, $J = 8.5$ Hz, 1H, $H^{16}$), 6.56 (ddd, $J = 7.2$ Hz, $J = 5.8$ Hz, $J = 1.6$ Hz).
Hz, 1H, $H^5$), 6.51 (ddd, $J = 8.1$ Hz, $J = 7.2$ Hz, $J = 1.8$ Hz, 1H, $H^4$), 6.32 (ddd, $J = 8.5$ Hz, $J = 6.9$ Hz, $J = 1.3$ Hz, 1H, $H^{15}$), 6.10 (ddd, $J = 7.9$ Hz, $J = 6.9$ Hz, $J = 1.1$ Hz, 1H, $H^{14}$), 5.55 (ddd, $J = 8.1$ Hz, $J = 1.6$ Hz, $J = 0.6$ Hz, 1H, $H^3$), 4.06 (s, 3H, $–OCH_3$), 3.71 (s, 3H, $–SOCH_3$), 2.58 (s, 3H, Ar$CH_3$).

$^{13}$C{$^1$H} NMR of $P,R$-**15b** (100 MHz, CDCl$_3$, 298 K): $\delta$ 167.10 (C$^2$), 155.88 (C$^4$), 147.68 (C$^6$), 144.59 (C$^2$), 143.32 (C$^{para}$), 141.35 (C$^{ipso}$), 135.85 (C$^4$), 134.56 (C$^1$), 132.14 (C$^{8a}$), 131.94 (C$^{12a}$), 131.78 (C$^{6a}$), 131.17 (C$^{10a}$), 129.86 (C$^{meta}$), 128.54 (C$^{16c}$), 128.10 (C$^{12}$), 128.00 (C$^{13}$ and C$^{16b}$), 127.63 (C$^{16e}$), 127.40 (C$^8$), 127.06 (C$^{16c}$), 127.00 (C$^3$), 126.42 (C$^{ortho}$), 126.37 (C$^{10}$), 126.12 (C$^9$), 125.55 (C$^{16}$), 125.26 (C$^{14}$), 125.13 (C$^{11}$), 124.19 (C$^{16d}$), 123.45 (C$^{16d}$), 122.91 (C$^{4a}$), 121.72 (C$^5$), 118.14 (C$^5$), 118.10 (C$^3$), 111.38 (C$^3$), 56.34 ($–OCH_3$), 49.80 ($–SOCH_3$), 21.71 (Ar$CH_3$).

$^1$H NMR of $M,R$-**15b** (400 MHz, CDCl$_3$, 298 K): $\delta$ 8.89 (ABMX system, $^{195}$Pt satellites: $3J_{Pt-H} = 34$ Hz, 1H, $H^6$), 8.29 (d, $J = 8.6$ Hz, 1H, $H^8$), 8.11 (d, $J = 8.4$ Hz, 2H, $H^{ortho}$), 8.06 (dd, $J = 8.0$ Hz, $J = 0.9$ Hz, 1H, $H^{15}$), 7.99 (AB system, $J = 8.2$ Hz, 1H, $H^6$), 7.97 (AB system, $J = 8.2$ Hz, 1H, $H^3$), 7.88 (d, $J = 8.6$ Hz, 1H, $H^6$), 7.78 (d, $J = 8.1$ Hz, 1H, $H^3$), 7.70 (d, $J = 8.5$ Hz, 1H, $H^{12}$), 7.61 (d, $J = 8.1$ Hz, 1H, $H^{10}$), 7.41 (ddd, $J = 8.0$ Hz, $J = 6.9$ Hz, $J = 1.1$ Hz, 1H, $H^{14}$), 7.33 (d, $J = 8.5$ Hz, 1H, $H^{11}$), 7.31 (d, $J = 8.4$ Hz, 2H, $H^{meta}$), 7.20 (d, $J = 8.5$ Hz, 1H, $H^{16}$), 7.17 (s, $^{195}$Pt satellites: $3J_{Pt-H} = 52$ Hz, 1H, $H^3$), 6.71 (dd, $J = 8.5$ Hz, $J = 6.9$ Hz, $J = 1.3$ Hz, 1H, $H^{15}$), 6.53 (ABMX system, 1H, $H^3$), 6.51 (ABMX system, 1H, $H^6$), 5.53 (ABMX system, 1H, $H^3$), 3.90 (s, 3H, $–OCH_3$), 3.81 (s, 3H, $–SOCH_3$), 2.39 (s, 3H, Ar$CH_3$).

$^{13}$C{$^1$H} NMR of $M,R,R$-**15b** (100 MHz, CDCl$_3$, 298 K): $\delta$ 166.89 (C$^2$), 155.83 (C$^4$), 147.72 (C$^6$), 146.45 (C$^3$), 143.33 (C$^{para}$), 141.88 (C$^{ipso}$), 136.06 (C$^4$), 134.55 (C$^1$), 132.27 (C$^{12a}$), 132.24 (C$^{8a}$), 131.74 (C$^{6a}$), 131.31 (C$^{10a}$), 129.91 (C$^{meta}$), 128.72 (C$^{16a}$), 128.54 (C$^{13}$), 128.36 (C$^{12}$), 128.07 (C$^{16b}$), 127.48 (C$^8$), 127.06 (C$^{16e}$ and C$^{16c}$), 126.99 (C$^5$), 126.46 (C$^{10}$), 126.15 (C$^9$), 125.97 (C$^{ortho}$), 125.95 (C$^{14}$), 125.93 (C$^{16}$), 125.20 (C$^{11}$), 124.99 (C$^{15}$), 124.14 (C$^6$), 123.35 (C$^{16d}$), 122.76 (C$^{4a}$), 121.56 (C$^5$), 118.09 (C$^5$), 117.97 (C$^3$), 112.25 (C$^3$), 56.06 ($–OCH_3$), 49.34 ($–SOCH_3$), 21.52 (Ar$CH_3$).

**Complex 8b**

![Complex 8b](image)

*Rac-8b*: A mixture of 74.2 mg of **14b** (0.1 mmol), 12.8 mg of sodium 2,4-pentanedionate (0.015 mmol) in 10 mL of toluene was refluxed for 18 hours under argon. The cooled reaction mixture was concentrated under vacuum and was purified by column chromatography (silica gel, chloroform) to afford the product (68.3 mg, 95%) as a yellow solid.

XV
**P-8b and M-8b:** The same procedure applied to enantiopure complexes \( P,R-15b \) and \( M,R-15b \) enantiomers gave \( P-8b \) and \( M-8b \).

\(^{1}H\) NMR (400 Hz, CDCl₃, 298 K): \( \delta \) 8.38 (d, \( J = 8.5 \) Hz, 1H, \( H^5 \)), 8.23 (ddd, \( J = 5.8 \) Hz, \( J = 1.7 \) Hz, \( J = 0.6 \) Hz, \(^{195}\)Pt satellites: \( \delta J_{Pt-H} = 35 \) Hz, 1H, \( H^6 \)), 8.00 (AB system, \( J = 8.3 \) Hz, 1H, \( H^8 \)), 7.99 (AB system, \( J = 8.3 \) Hz, 1H, \( H^8 \)), 7.92 (d, \( J = 8.2 \) Hz, 1H, \( H^8 \)), 7.84 (d, \( J = 8.5 \) Hz, 1H, \( H^8 \)), 7.74 (d, \( J = 8.0 \) Hz, 1H, \( H^{13} \)), 7.65 (d, \( J = 8.2 \) Hz, 1H, \( H^{10} \)), 7.48 (d, \( J = 8.5 \) Hz, 1H, \( H^{12} \)), 7.31 (d, \( J = 8.5 \) Hz, 1H, \( H^{15} \)) 7.21 (d, \( J = 8.5 \) Hz, 1H, \( H^{16} \)), 7.16 (ddd, \( J = 8.0 \) Hz, \( J = 6.9 \) Hz, J = 1.1 Hz, 1H, \( H^{15} \)), 6.91 (s, \(^{195}\)Pt satellites: \( \delta J_{Pt-H} = 46 \) Hz, 1H, \( H^5 \)), 6.61 (ddd, \( J = 8.5 \) Hz, \( J = 6.9 \) Hz, \( J = 1.3 \) Hz, 1H, \( H^{15} \)), 6.51 (ddd, \( J = 8.3 \) Hz, \( J = 7.3 \) Hz, \( J = 1.7 \) Hz, 1H, \( H^8 \)), 6.42 (ddd, \( J = 7.3 \) Hz, \( J = 5.8 \) Hz, \( J = 1.5 \) Hz, 1H, \( H^8 \)), 5.49 (ddd, \( J = 8.3 \) Hz, \( J = 1.5 \) Hz, \( J = 0.6 \) Hz, 1H, \( H^8 \)), 5.42 (s, 1H, \(-CH_{Acac}\)), 4.12 (s, 3H, \(-OCH_3\)), 2.00 (s, 3H, \(-CH_3\)), 1.98 (s, 3H, \(-CH_3\)).

**Complex 14c**

A mixture of 28.2 mg of 1,8-di(pyridin-2-yl)naphthalene (0.1 mmol), 101.3 mg of Pt(dmsoc)_2Cl_2 (0.24 mmol) and 42.4 mg of Na_2CO_3 (0.4 mmol) in 15 mL of toluene was refluxed under argon for 12 hours. The cooled reaction mixture was concentrated under vacuum and was purified by flash chromatography (silica gel CH_2Cl_2) to afford the product (46 mg, 51%) as a yellow solid.

\(^{1}H\) NMR (400 MHz, CDCl₃, 298 K): \( \delta \) 9.48 (d, \( J = 5.8 \) Hz, 2H), 8.38 (d, \( J = 8.5 \) Hz, 2H), 7.62 (d, \( J = 8.5 \) Hz, 2H), 7.53–7.48 (m, 4H), 7.06–6.98 (m, 2H), 3.71 (s, 6H), 3.67 (s, 6H).

**Complex 15c**

A suspension of 85 mg of 1,8-di(pyridin-2-yl)naphthalene (0.30 mmol), 370 mg of \( R,R-\)
Pt(mtso)₂Cl₂ (0.64 mmol) and 100 mg of Na₂CO₃ (0.94 mmol) in 10 mL toluene was refluxed under argon overnight, and concentrated under vacuum. Column chromatography (silica gel, V<sub>heptane</sub>: V<sub>ethyl acetate</sub> = 1:1) was performed carefully to afford the to afford the M,R,R-15e (first eluent, 25 mg, 8%) as a yellow powder, mixture of M,R,R-15e and P,R,R-15e (second fraction, 11:9, 82 mg, 26%), and mixture of M,R,R-15e and P,R,R-15e (third eluent, 1:3, 65 mg, 21%). The third fraction was dissolved in minimum solvent of CHCl₃ and precipitated by heptane:CHCl₃ (V:V = 3:1) and then washed by heptane:CHCl₃ (V:V = 3:1) to afford P,R,R-15e (48 mg, 15%) as a yellow powder. The complex mixture could be recycled and resolved again.

¹H NMR of P,R,R-15e (400 MHz, CDCl₃, 298 K): δ 9.58 (dd, J = 5.9 Hz, J = 1.6 Hz, ¹⁹⁵Pt satellites: 3J<sub>Pt-H</sub> = 30 Hz, 2H, H<sup>6'</sup> and H<sup>6</sup>), 8.17 (d, J = 8.5 Hz, 2H, H<sup>3</sup> and H<sup>4</sup>), 8.06 (d, J = 8.4 Hz, 4H, H<sup>endo</sup>), 7.47 (dd, J = 8.1 Hz, J = 7.4 Hz, J = 1.6 Hz, 2H, H<sup>5</sup>' and H<sup>4</sup>''), 7.38 (d, J = 8.5 Hz, 2H, H<sup>3</sup>' and H<sup>5</sup>'), 7.32 (d, J = 8.1 Hz, 2H, H<sup>5</sup> and H<sup>6</sup>''), 7.29 (d, J = 8.4 Hz, 4H, H<sup>meta</sup>), 7.03 (dd, J = 7.4 Hz, J = 5.9 Hz, J = 1.3 Hz, 2H, H<sup>6</sup>' and H<sup>5</sup>''), 3.77 (s, 6H, −SOCH₃), 2.36 (s, 6H, ArCH₃).

¹³C{¹H} NMR of P,R,R-15e (100 MHz, CDCl₃, 298 K): δ 166.77 (C<sup>5</sup>' and C<sup>2</sup>'), 149.96 (C<sup>6</sup>' and C<sup>6</sup>'), 148.03 (C<sup>2</sup> and C<sup>7</sup>), 143.57 (C<sup>para</sup>), 140.63(C<sup>ipso</sup>), 139.27 (C<sup>4</sup>' and C<sup>4</sup>'), 136.92 (C<sup>1</sup> and C<sup>8</sup>), 131.56 (C<sup>4d</sup>a), 130.81 (C<sup>4b</sup> and C<sup>5</sup>), 130.66 (C<sup>3</sup> and C<sup>6</sup>), 130.12 (C<sup>meta</sup>), 125.83 (C<sup>8a</sup>), 125.62 (C<sup>ortho</sup>), 123.38 (C<sup>3b</sup> and C<sup>3a</sup>), 120.53 (C<sup>5b</sup>' and C<sup>5a</sup>'), 49.37 (−SOCH₃), 21.53 (ArCH₃).

¹H NMR of M,R,R-15e (400 MHz, CDCl₃, 298 K): δ 9.63 (dd, J = 6.0 Hz, J = 1.6 Hz, J = 0.6 Hz, ¹⁹⁵Pt satellites: 3J<sub>Pt-H</sub> = 32 Hz, 2H, H<sup>6'</sup> and H<sup>6</sup>), 8.24 (d, J = 8.4 Hz, 4H, H<sup>ortho</sup>), 7.70 (d, J = 8.4 Hz, 2H, H<sup>3</sup> and H<sup>4</sup>), 7.57 (dd, J = 8.3 Hz, J = 7.2 Hz, J = 1.6 Hz, 2H, H<sup>5</sup>' and H<sup>4</sup>''), 7.51 (dd, J = 8.3 Hz, J = 7.2 Hz, J = 1.6 Hz, 2H, H<sup>5</sup>' and H<sup>4</sup>''), 7.43 (d, J = 8.4 Hz, 4H, H<sup>meta</sup>), 7.38 (d, J = 8.4 Hz, 2H, H<sup>3</sup>' and H<sup>5</sup>'), 7.05 (dd, J = 7.2 Hz, J = 6.0 Hz, J = 1.5 Hz, 2H, H<sup>6</sup>' and H<sup>5</sup>''), 3.78 (s, 6H, −SOCH₃), 2.47 (s, 6H, ArCH₃).

¹³C{¹H} NMR of M,R,R-15e (100 MHz, CDCl₃, 298 K): δ 166.76 (C<sup>5</sup>' and C<sup>2</sup>'), 149.79 (C<sup>6</sup>' and C<sup>6</sup>'), 148.88 (C<sup>2</sup> and C<sup>7</sup>), 143.94 (C<sup>para</sup>), 140.64(C<sup>ipso</sup>), 139.55 (C<sup>4</sup>' and C<sup>4</sup>'), 137.20 (C<sup>1</sup> and C<sup>8</sup>), 131.71 (C<sup>3</sup> and C<sup>6</sup>), 131.62 (C<sup>4d</sup>a), 130.95 (C<sup>4b</sup> and C<sup>5</sup>), 130.32 (C<sup>meta</sup>), 126.03 (C<sup>ortho</sup>), 125.62 (C<sup>8a</sup>), 123.30 (C<sup>3b</sup> and C<sup>3a</sup>), 120.55 (C<sup>5b</sup>' and C<sup>5a</sup>'), 49.81 (−SOCH₃), 21.65 (ArCH₃).

**Complex 8c**

Rac-8c: A mixture of 17 mg of 14c (0.019 mmol) and sodium 5.9 mg of 2,4- pentanedionate (0.048 mmol) in 10 mL of toluene was refluxed for 2 hours under argon. The cooled reaction mixture
was concentrated under vacuum and was purified by column chromatography (silica gel, dichloromethane) to afford the product (13 mg, 80%) as a yellow solid.

**P-8c**: A mixture of 21 mg of *P,R,R-15c* (0.02 mmol), 5.9 mg of sodium 2,4-pentanedionate (0.048 mmol) in 10 mL of toluene was refluxed for 2 hours under argon. The cooled reaction mixture was concentrated under vacuum and was purified by column chromatography (silica gel, CH₂Cl₂) to afford the product (13 mg, 75%) as a yellow solid.

**M-8c**: A mixture of 22 mg of *M,R,R-15c* (0.021 mmol), 5.9 mg of sodium 2,4-pentanedionate (0.048 mmol) in 10 mL of toluene was refluxed for 2 hours under argon. The cooled reaction mixture was concentrated under vacuum and was purified by column chromatography (silica gel, CH₂Cl₂) to afford the product (13 mg, 71%) as a yellow solid.

**1**H NMR (400 MHz, CDCl₃, 298 K): δ 8.92 (ddd, *J* = 5.8 Hz, *J* = 1.6 Hz, *J* = 0.6 Hz, **1**⁵Pt satellites: **3**J_{Pt-H} = 34 Hz, 2H, *H⁶* and *H⁹*), 7.73 (d, *J* = 8.1 Hz, 2H, *H⁵* and *H⁶*), 7.64 (d, *J* = 8.1 Hz, 2H, *H⁴* and *H⁷*), 7.32 (ddd, *J* = 8.3 Hz, *J* = 7.3 Hz, *J* = 1.6 Hz, 2H, *H⁴* and *H⁷*), 7.18 (ddd, *J* = 8.3 Hz, *J* = 1.2 Hz, *J* = 0.6 Hz, 2H, *H⁵* and *H⁶*), 6.90 (ddd, *J* = 7.3 Hz, *J* = 5.8 Hz, *J* = 1.2 Hz, 2H, *H⁴* and *H⁷*), 5.53 (s, 2H, −CH₂Acac), 2.06 (s, 6H, −CH₃Acac), 2.05 (s, 6H, −CH₃Acac).

**1**³C{**1**H} NMR (100 MHz, CDCl₃, 298 K): δ 186.12 (C=O), 184.77 (C=O), 168.80 (C² and C⁵), 147.20 (C⁶ and C⁹), 146.30 (C² and C⁵), 136.95 (C⁴ and C⁷), 135.84 (C¹ and C⁸), 131.52 (C⁴a), 130.30 (C⁴ and C⁷), 127.06 (C³ and C⁶), 126.12 (C⁸a), 123.35 (C⁴ and C⁷), 119.67 (C⁶ and C⁹), 102.81 (−CH₂Acac), 28.37 (−CH₃Acac), 27.38 (−CH₃Acac).

**Complex 14d**

A suspension of 30 mg of 10d (0.055 mmol), 70 mg of Pt(dmso)₂Cl₂ (0.17 mmol) and 35 mg of Na₂CO₃ (0.33 mmol) in 5 mL toluene was refluxed under argon overnight, and concentrated under vacuum. Column chromatography (silica gel, ethyl acetate) was performed to afford the product (52 mg, 84%) as a yellow powder.

**1**H NMR (400 MHz, CDCl₃, 298 K): δ 8.87 (ddd, *J* = 5.7 Hz, *J* = 1.7 Hz, *J* = 0.6 Hz, **1**⁵Pt satellites: **3**J_{Pt-H} = 32 Hz, 2H, *H⁶* and *H⁹*), 8.34 (s, **1**⁵Pt satellites: **3**J_{Pt-H} = 52 Hz, 2H, *H⁵* and *H¹⁴*), 8.06 (d, *J* = 8.5 Hz, 2H, *H⁸* and *H¹²*), 7.94 (d, *J* = 8.2 Hz, 2H, *H⁸* and *H⁴*), 7.70 (d, *J* = 8.2 Hz, 2H, *H⁵* and *H⁴*), 7.32 (d, *J* = 8.5 Hz, 2H, *H⁸* and *H¹¹*), 6.47 (ddd, *J* = 7.2 Hz, *J* = 5.7 Hz, *J* = 1.6 Hz, 2H, *H⁸* and *H¹¹*), 5.68 (ddd, *J* = 8.0 Hz, *J* =
1.6 Hz, \( J = 0.6 \) Hz, 2H, \( H^6^\prime \) and \( H^7^\prime \)), 4.21 (s, 6H, \(-\text{OCH}_3\)), 3.97 (s, 6H, \(-\text{SOCH}_3\)), 3.60 (s, 6H, \(-\text{SOCH}_3\)).

\[ ^{13}C\{^{1}H\} \text{ NMR (100 MHz, CDCl}_3, 298 K): \delta 166.84 (C^2^\prime \) and C^3^\prime), 156.31 (C^4 \) and C^{13}, 148.12 (C^6 \) and C^6^\prime), 145.02 (C^2 \) and C^15), 135.67 (C^4^\prime \) and C^4^\prime), 132.81 (C^1 \), C^6^a \) and C^16), 131.16 (C^8^a), 130.48 (C^16c), 127.37 (C^8 \) and C^9) 126.76 (C^7 \) and C^10), 125.63 (C^{16a} \) and C^{16e}), 124.45 (C^{4a} \) and C^{12a}), 124.38 (C^6 \) and C^{11}), 123.82 (C^{16b} \) and C^{16d}), 122.65 (C^5 \) and C^{12}), 118.58 (C^5^\prime \) and C^5^\prime), 117.39 (C^3 \) and C^3^\prime), 111.09 (C^3 \) and C^{14}), 55.26 (\(-\text{OCH}_3\)), 48.39 (\(-\text{SOCH}_3\)), 46.57 (\(-\text{SOCH}_3\)).

**Complex 8d**

A mixture of 20 mg of 14d (0.018 mmol), 5 mg of sodium 2,4-pentanedionate (0.04 mmol) in 2 mL toluene was refluxed for 2 hours under argon. The cooled reaction mixture was concentrated under vacuum and was purified by column chromatography (silica gel, chloroform) to afford the product (11 mg, 57%) as a yellow solid.

\[ ^{1}H \text{ NMR (400 MHz, CDCl}_3, 298 K): \delta 8.31 (\text{ddd, } J = 5.8 \text{ Hz, } J = 1.6 \text{ Hz, } J = 0.5 \text{ Hz, } ^{195}\text{Pt satellites: } ^3J_{\text{Pt-H}} = 32 \text{ Hz, } 2H, H^6^\prime \) and H^6^\prime), 7.90 (d, \( J = 8.2 \) Hz, 2H, H^8 \) and H^9\)), 7.86 (d, \( J = 8.5 \) Hz, 2H, H^5 \) and H^12\)), 7.65 (d, \( J = 8.2 \) Hz, 2H, H^7 \) and H^10\)), 7.21 (d, \( J = 8.5 \) Hz, 2H, H^5 \) and H^11\)), 7.04 (s, 2H, H^5 \) and H^12\)), 6.44 (\text{ddd, } J = 8.3 \text{ Hz, } J = 7.2 \text{ Hz, } J = 1.6 \text{ Hz, } 2H, H^6^\prime \) and H^5^\prime), 6.38 (\text{ddd, } J = 7.2 \text{ Hz, } J = 5.8 \text{ Hz, } J = 1.5 \text{ Hz, } 2H, H^8 \) and H^5\)), 5.51 (\text{ddd, } J = 8.3 \text{ Hz, } J = 1.5 \text{ Hz, } J = 0.5 \text{ Hz, } 2H, H^5 \) and H^5^\prime), 5.48 (s, 2H, \(-\text{CH}_3\)Acac), 4.00 (s, 6H, \(-\text{OCH}_3\)), 2.04 (s, 6H, \(-\text{CH}_3\)Acac), 2.02 (s, 6H, \(-\text{CH}_3\)Acac).

\[ ^{13}C\{^{1}H\} \text{ NMR (100 MHz, CDCl}_3, 298 K): \delta 185.52 (C=O), 183.07 (C=O), 168.34 (C^2 \) and C^2^\prime), 155.20 (C^4 \) and C^{13}), 145.53 (C^2 \) and C^15), 145.29 (C^8 \) and C^6\)), 134.18 (C^4^\prime \) and C^4^\prime), 132.39 (C^{6a} \) and C^{10a}), 131.31 (C^1 \) and C^16), 130.33 (C^{16c}), 129.89 (C^8\prime), 126.27 (C^8 \), C^9 \) and C^{16a} \) and C^{16e}), 125.73 (C^7 \) and C^{10}), 123.47 (C^{4a} \) and C^{12a}), 122.48 (C^5 \) and C^{12}), 122.41 (C^{16b} \) and C^{16d}), 122.06 (C^6 \) and C^{11}), 117.54 (C^5 \) and C^5\prime), 117.12 (C^3 \) and C^{3\prime}), 108.76 (C^3 \) and C^{14}), 102.09 (\(-\text{CH}_3\)Acac), 55.06 (\(-\text{OCH}_3\)), 28.40 (\(-\text{CH}_3\)Acac), 27.53 (\(-\text{CH}_3\)Acac).

HRMS-ESI\(^+\) (m/z) calcd. for C_{48}H_{38}N_{2}O_{6}^{195}\text{Pt}_2 ([M]\(^+)\): 1128.20201, found 1128.2020.
Compound 16a

259 mg of 11a (0.80 mmol) and 173 μL of NPr$_2$Et (1.0 mmol) were suspended in 0.2 mL of CH$_2$Cl$_2$ at 0 °C and 3 mL of a BBr$_3$ solution (1 mol·L$^{-1}$ in CH$_2$Cl$_2$) were added into the suspension. The reaction was then stirred at 25 °C for 24 hours. Then the reaction was quenched by saturated Na$_2$CO$_3$ solution and was extracted with CH$_2$Cl$_2$. The organic layer was washed with water, dried over MgSO$_4$ and concentrated. The resulting solid was collected by filtration and washed with ether to afford the product as a yellow solid (365 mg, 93%).

$^1$H NMR (400 MHz, CDCl$_3$, 298 K): δ 8.95 (d, $J = 5.6$ Hz, 1H), 8.26 (d, $J = 8.6$ Hz, 1H), 8.05 (d, $J = 8.3$ Hz, 1H), 8.03 (d, $J = 8.1$ Hz, 1H), 7.97 (d, $J = 8.3$ Hz, 1H), 7.96 (d, $J = 8.6$ Hz, 1H), 7.95 (d, $J = 8.3$ Hz, 1H), 7.85 (d, $^3 J_{HF} = 8.5$ Hz), 7.52 (ddd, $J = 8.1$ Hz, $J = 6.9$ Hz, $J = 1.0$ Hz, 1H), 7.40 (ddd, $J = 8.2$ Hz, $J = 7.6$ Hz, $J = 1.4$ Hz, 1H), 7.30 (ddd, $J = 7.6$ Hz, $J = 5.6$ Hz, $J = 0.9$ Hz, 1H), 7.25 (ddd, $J = 8.3$ Hz, $J = 6.9$ Hz, $J = 1.1$ Hz, 1H), 6.48 (d, $J = 8.2$ Hz).

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$, 298 K): δ 161.85 (d, $^1 J_{CF} = 262$ Hz), 155.68, 143.79, 141.49, 133.08, 132.13, 130.23, 129.33, 128.53, 128.45, 127.65 (d, $^4 J_{CF} = 2$ Hz), 126.96, 126.77, 126.52, 126.34 (d, $^3 J_{CF} = 4$ Hz), 125.87 (d, $^4 J_{CF} = 2$ Hz), 124.64 (d, $^4 J_{CF} = 2$ Hz), 124.40 (d, $^2 J_{CF} = 17$ Hz), 122.70, 122.00, 120.41 (d, $^3 J_{CF} = 8$ Hz), 112.37 (d, $^2 J_{CF} = 21$ Hz). Signal of the carbon directly connected to boron cannot be found.

$^{11}$B NMR (128 MHz, CDCl$_3$, 298 K): δ −1.4 (broad). $^{19}$F NMR (377 MHz, CDCl$_3$, 298 K): −114.6 (d, $^3 J_{HF} = 8.5$ Hz).

Compound 9a

49.3 mg of 16a (0.10 mmol) were suspended in 0.5 mL of dry toluene under argon, and 100 μL of AlMe$_3$ solution (2 mol·L$^{-1}$ in toluene) were added dropwise into the suspension. The reaction mixture was stirred at 25 °C for 30 min and was quenched by 5 mL of water. Then the reaction mixture was extracted with 10 mL of ethyl acetate, and the organic layer was washed with 10 mL of water, dried over MgSO$_4$, and concentrated under vacuum. The residue was purified by silica gel
column chromatography (CH₂Cl₂) to afford the product as a pale yellow solid (35 mg, 96%).

^1^H NMR (400 MHz, CDCl₃, 298 K): δ 8.43 (ddd, J = 5.7 Hz, J = 1.5 Hz, J = 0.7 Hz, 1H, H^f^), 8.26 (d, J = 8.5 Hz, 1H, H^g^), 8.12 (d, J = 8.5 Hz, 1H, H^l^), 8.00 (d, J = 8.6 Hz, 1H, H^j^), 7.99 (d, J = 8.0 Hz, 1H, H^d^), 7.94 (d, J = 8.6 Hz, 1H, H^i^), 7.87 (d, J = 8.5 Hz, 1H, H^p^), 7.64 (d, 3^J^HH = 8.9 Hz, 1H, H^i^), 7.47 (ddd, J = 8.0 Hz, J = 6.9 Hz, J = 1.0 Hz, 1H, H^k^), 7.22 (ddd, J = 8.3 Hz, J = 7.4 Hz, J = 1.5 Hz, 1H, H^j^), 7.15 (ddd, J = 8.5 Hz, J = 6.9 Hz, J = 1.3 Hz, 1H, H^l^), 7.10 (ddd, J = 7.4 Hz, J = 5.7 Hz, J = 1.1 Hz, 1H, H^p^), 6.57 (d, J = 8.3 Hz 1H, H^i^), 0.37 (s, 3H, –CH₃), 0.09 (s, 3H, –CH₃).

^1^B NMR (128 MHz, CDCl₃, 298 K): δ 0.3 (broad).

^13^C {^1^H} NMR (100 MHz, CDCl₃, 298 K): δ 174.04 (broad, C^2^), 160.26 (d, 1^J^CF = 259 Hz, C^4^), 156.64 (C^2^), 141.48 (C^6^), 137.15 (C^4^), 132.47 (C^6a^), 131.94 (C^8a^), 130.56 (C^12a^), 128.62 (C^12^), 128.41 (C^8^), 128.11 (C^6^), 127.24 (d, 4^J^CF = 2 Hz, C^1^), 126.61 (C^7^), 126.34 (d, 3^J^CF = 4 Hz, C^12c^), 126.21 (C^11^), 126.10 (C^10^), 125.64 (d, 4^J^CF = 2 Hz, C^6^), 124.82 (d, 4^J^CF = 2 Hz, C^12b^), 122.78 (d, 2^J^CF = 17 Hz, C^6a^), 122.13 (C^5^), 120.45 (d, 3^J^CF = 8 Hz, C^5^), 119.71 (C^6^), 111.47 (d, 2^J^CF = 17 Hz, C^3^), 9.58 (broad, –CH₃), 8.95 (broad, –CH₃).

^19^F NMR (377 MHz, CDCl₃, 298 K): −120.4 (d, 3^J^HF = 8.9 Hz).

HRMS-ESI⁺ (m/z) calcd. for C_{25}H_{20}N_{11}F_{13}B ([M+H]^+) 364.16673, found 364.1671.

**Compound 16b**

169 mg of 11b (0.40 mmol) and 121 µL of N^0^Pr₂Et (0.70 mmol) were suspended in 0.1 mL of CH₂Cl₂ at 0 °C and 2 mL of a BBr₃ solution (1 mol·L⁻¹ in CH₂Cl₂) were added into the suspension. The reaction was then stirred at 25 °C for 24 hours. Then the reaction was quenched with saturated Na₂CO₃ solution and was extracted with CH₂Cl₂. The organic layer was washed with water, dried over MgSO₄ and concentrated. The resulting solid was collected by filtration and washed with ether to afford the product as a yellow solid (189 mg, 80%).

^1^H NMR (400 MHz, CDCl₃, 298 K): δ 8.43 (ddd, J = 5.6 Hz, J = 1.7 Hz, J = 0.6 Hz, 1H), 8.35 (d, J = 8.5 Hz, 1H), 8.20 (d, J = 8.1 Hz, 1H), 8.12 (d, J = 8.2 Hz, 1H), 8.12 (d, J = 8.1 Hz, 1H), 8.10 (d, J = 8.5 Hz, 1H), 7.92 (d, J = 8.2 Hz, 1H), 7.58 (dd, J = 8.1 Hz, J = 1.2 Hz, 1H), 7.45 (s, 2H), 7.45 (d, 3^J^HF = 8.7 Hz), 7.17 (ddd, J = 8.1 Hz, J = 6.9 Hz, J = 1.0 Hz, 1H), 7.07 (ddd, J = 8.0 Hz, J = 7.4 Hz, J = 1.7 Hz, 1H), 7.02 (ddd, J = 7.4 Hz, J = 5.6 Hz, J = 1.4 Hz, 1H), 6.90 (d, J = 8.5 Hz), 6.63 (ddd, J = 8.5 Hz, J = 6.9 Hz, J = 1.2 Hz, 1H), 5.42 (d, J = 8.0 Hz).

^13^C {^1^H} NMR (100 MHz, CDCl₃, 298 K): δ 161.79 (d, 1^J^CF = 261 Hz), 154.08, 142.71, 140.87, XXI
133.01, 132.03, 131.98, 131.89, 128.95, 128.79, 128.72, 128.52 (d, $^3J_CF = 4$ Hz), 128.15, 127.93, 127.34, 127.32, 127.11, 127.07, 126.72 126.98, 126.03 (d, $^4J_CF = 3$ Hz), 125.22, 125.11, 124.88, 123.64 (d, $^4J_CF = 2$ Hz), 123.15 (d, $^2J_CF = 17$ Hz), 121.37, 120.73 (d, $^3J_CF = 8$ Hz), 120.02, 112.09 (d, $^2J_CF = 21$ Hz). Signal of the carbon direct connecting with boron cannot be found. $^{11}$B NMR (128 MHz, CDCl$_3$, 298 K): $\delta$ –2.3 (broad).

$^{19}$F NMR (377 MHz, CDCl$_3$, 298 K): –115.3 (d, $^3J_{HF} = 8.7$ Hz).

**Compound 9b**

148 mg of 16b (0.25 mmol) was suspended in 1 mL of dried toluene under argon, and 400 μL of AlMe$_3$ solution (2 mol·L$^{-1}$ in toluene) were added dropwise into the suspension. The reaction mixture was stirred at 25 °C for 30 min and was quenched with 10 mL of water. Then the reaction mixture was extracted with 20 mL of ethyl acetate, and the organic layer was washed with 20 mL of water, dried over MgSO$_4$, and concentrated under vacuum. The residue was purified by silica gel column chromatography (CH$_2$Cl$_2$) to afford the product as a pale yellow solid (93 mg, 80%).

$^{1}$H NMR (400 MHz, CDCl$_3$, 298 K): $\delta$ 8.34 (d, $J = 8.6$ Hz, 1H, $H^6$), 8.15 (d, $J = 8.1$ Hz, 1H, $H^7$), 8.10 (d, $J = 8.1$ Hz, 1H, $H^8$), 8.09 (d, $J = 8.2$ Hz, 1H, $H^9$), 8.00 (d, $J = 8.6$ Hz, 1H, $H^6$), 7.87 (d, $J = 5.7$ Hz, 1H, $H^9$), 7.86 (d, $J = 8.2$ Hz, 1H, $H^{10}$), 7.52 (d, $J = 8.0$ Hz, 1H, $H^{13}$), 7.44 (d, $J = 8.6$ Hz, 1H, $H^{14}$), 7.39 (d, $J = 8.6$ Hz, 1H, $H^{12}$), 7.21 (d, $^3J_{HF} = 8.9$ Hz, 1H, $H^7$), 7.11 (ddd, $J = 8.0$ Hz, $J = 6.9$ Hz, $J = 1.0$ Hz, 1H, $H^{14}$), 7.01 (d, $J = 8.6$ Hz, 1H, $H^{16}$), 6.88 (ddd, $J = 8.2$ Hz, $J = 7.4$ Hz, $J = 1.7$ Hz, 1H, $H^{15}$), 6.82 (ddd, $J = 7.4$ Hz, $J = 5.7$ Hz, $J = 1.4$ Hz, 1H, $H^{16}$), 6.57 (ddd, $J = 8.6$ Hz, $J = 6.9$ Hz, $J = 1.4$ Hz, 1H, $H^{15}$), 5.62 (d, $J = 8.2$ Hz, 1H, $H^5$), –0.40 (s, 3H, –CH$_3$), –0.43 (s, 3H, –CH$_3$).

$^{11}$B NMR (128 MHz, CDCl$_3$, 298 K): $\delta$ –0.7 (broad).

$^{13}$C NMR (100 MHz, CDCl$_3$, 298 K): $\delta$ 173.32 (broad, $C^2$), 160.23 (d, $^1J_{CF} = 256$ Hz, $C^4$), 155.38 ($C^2$), 140.39 ($C^6$), 136.42 ($C^4$), 132.49 ($C^8$), 131.89 ($C^{12a}$), 131.82 ($C^{6a}$), 131.77 ($C^{10a}$), 128.50 ($C^{16a}$), 128.45 ($C^{16e}$), 128.41 ($C^{16b}$), 128.22 ($C^3$), 127.81 ($C^5$), 127.72 ($C^{13}$), 127.13 ($C^7$), 126.98 (2C, $C^8$ and $C^9$), 126.94 ($C^{10}$), 126.42 ($C^{16c}$), 125.84 ($C^{14}$), 125.38 (2C, $C^{11}$ and $C^{16}$), 125.18 ($C^6$), 124.87 ($C^{15}$), 123.86 ($C^{16d}$), 121.47 (d, $^2J_{CF} = 16$ Hz, $C^{1h}$), 120.90 (d, $^3J_{CF} = 8$ Hz, $C^5$), 119.29 ($C^3$), 119.13 ($C^5$), 111.10 (d, $^2J_{CF} = 16$ Hz, $C^3$), 10.23 (broad, –CH$_3$), 7.91 (broad, –CH$_3$).

$^{19}$F NMR (377 MHz, CDCl$_3$, 298 K): –121.0 (d, $^3J_{HF} = 8.9$ Hz).

HRMS-ESI$^+$ (m/z) calcd. for C$_{33}$H$_{24}$NF$^{11}$B ([M+H]$^+$) 464.19803, found 464.1982.

XXII
Compound 16c

282 mg of 1,8-di(2-pyridyl)naphthalene (1.0 mmol) and 518 μL of N’Pr₂Et (3.0 mmol) were suspended in 1 mL of CH₂Cl₂ at 0 °C and 10 mL of a BBr₃ solution (1 mol·L⁻¹ in CH₂Cl₂) were added into the suspension. The reaction was then stirred at 25 °C for 24 hours. Then the reaction was quenched with 1 mL of ethanol and the insoluble material was collected by filtration and washed with CH₂Cl₂ to afford the product as a yellow solid (345 mg, 56%).

Compound 9c

311 mg of 16c (0.50 mmol) was suspended in 4 mL of dried toluene under argon, and 2 mL of a AlMe₃ solution (2 mol·L⁻¹ in toluene) were added dropwise into the suspension. The reaction mixture was stirred at 25 °C for 30 min and then was quenched with 10 mL of water. Then the reaction mixture was extracted with 30 mL of ethyl acetate, and the organic layer was washed with 5 mL of water, dried over MgSO₄, and concentrated under vacuum. The residue was purified by silica gel column chromatography (CH₂Cl₂) to afford the product as a white solid (179 mg, 99%).

¹H NMR (400 MHz, CDCl₃): δ 8.54 (d, J = 5.6 Hz, 2H, H₆' and H₆'″), 7.97 (d, J = 7.7 Hz, 2H, H₄ and H₅), 7.82 (d, J = 7.7 Hz, 2H, H₃ and H₆), 7.65 (t, J = 7.8 Hz, 2H, H₄' and H₄'″), 7.24 (t, J = 6.7 Hz, 2H, H₅' and H₅'″), 7.10 (d, J = 8.2 Hz, 2H, H₃' and H₃'″), 0.31 (s, 6H, −CH₃), 0.10 (s, 6H, −CH₃).

¹¹B NMR (128 MHz, CDCl₃): δ 0.5 (broad).

¹³C {¹H} NMR (100 MHz, CDCl₃): δ 175.23 (broad, 2C, C² and C⁰), 157.04 (2C, C²' and C²'″), 142.24 (2C, C⁰ and C⁰′), 137.72 (2C, C⁴ and C⁴′), 132.86 (C⁴a), 131.58 (2C, C⁴ and C⁵), 127.21 (2C, C⁴ and C⁵), 126.00 (2C, C⁴ and C⁵), 124.12 (C⁸a), 123.26 (2C, C⁴' and C⁴'″), 119.65 (2C, C⁴' and C⁵'″), 9.77 (broad, 2C, −CH₃), 9.07 (broad, 2C, −CH₃).

HRMS-ESÍ+: (m/z) calcd. for C₂₄H₂₅N₂¹¹B₂ ([M+H]⁺) 363.21983, found 363.2206.
Compound 16d

51.9 mg of 11d (0.10 mmol) and 52 μL of NPr₂Et (0.30 mmol) were suspended in 0.1 mL of CH₂Cl₂ at 0 °C and 0.9 mL of a BBr₃ solution (1 mol·L⁻¹ in CH₂Cl₂) was added into the suspension. The reaction was then stirred at 25 °C for 24 hours. Then the reaction was quenched with 0.1 mL of ethanol and the insoluble material was collected by filtration and washed by CH₂Cl₂ to afford the product as a yellow solid (58 mg, 68%).

HRMS-ESI⁺: (m/z) calcd. for C₃₆H₁₈N₂F₂Br₁₁B₂ ([M–Br]⁺) 774.91687, found 774.9185.

Compound 9d

43 mg of 16d (0.05 mmol) was suspended in 0.5 mL of dried toluene under argon, and 200 μL of a AlMe₃ solution (2 mol·L⁻¹ in toluene) were added dropwise into the suspension. The reaction mixture was stirred at 25 °C for 30 min and was quenched with 5 mL of water. Then the reaction mixture was extracted with 20 mL of ethyl acetate, and the organic layer was washed with 10 mL of water, dried over MgSO₄, and concentrated under vacuum. The residue was purified by silica gel column chromatography (CH₂Cl₂) to afford the product as a pale yellow solid (29 mg, 97%).

¹H NMR (400 MHz, CDCl₃, 298 K): δ 8.25 (d, J = 8.2 Hz, 2H, H₈ and H₉), 8.00 (d, J = 8.2 Hz, 2H, H₇ and H₁₀), 7.98–7.96 (m, 2H, H₆′ and H₆″), 7.65 (d, J = 8.5 Hz, 2H, H₅ and H₁₂), 7.47 (d, J = 8.5 Hz, 2H, H₆ and H₁₁), 7.14 (dd, J_HF = 8.8 Hz, J = 8.0 Hz, 2H, H₃ and H₁₄), 6.90–6.83 (m, 4H, H₄′, H₄″ and H₅′, H₅″), 5.38–5.34 (m, 2H, H₃′ and H₃″), 0.06 (s, 6H, −CH₃), −0.52 (s, 6H, −CH₃).

¹¹B NMR (128 MHz, CDCl₃, 298 K): δ −0.6 (broad).

¹³C{¹H} NMR (100 MHz, CDCl₃, 298 K): δ 173.58 (broad, 2C, C² and C¹⁵), 159.53 (d, ¹JC = 257 Hz, 2C, C⁴ and C¹³), 154.97 (2C, C²′ and C²″), 140.60 (2C, C⁶′ and C⁶″), 136.60 (2C, C⁴′ and C⁴″), 133.40 (2C, C⁶a and C¹⁰a), 130.27 (C⁸a), 129.06 (C¹⁶c), 127.74 (2C, C⁸ and C⁹), 127.01 (d, ¹JC = 3 Hz, 2C, C⁶a and C¹⁶c), 126.54 (2C, C⁷ and C¹⁰), 125.18 (2C, C¹ and C¹⁶), 124.46 (2C, C⁶ and C¹¹), 123.96 (2C, C¹⁰b and C¹⁰d), 121.78 (d, ²JC = 17 Hz, 2C, C⁴a and C¹²a), 120.98 (d, ³JC = 8 Hz, 2C, C⁸

XXIV
and C\textsuperscript{12}), 119.27 (2C, C\textsuperscript{5′} and C\textsuperscript{5″}), 118.29 (2C, C\textsuperscript{3′} and C\textsuperscript{3″}), 112.30 (d, \(^2\)J\textsubscript{CF} = 17 Hz, 2C, C\textsuperscript{3} and C\textsuperscript{14}), 12.30 (broad, 2C, −CH\textsubscript{3}), 5.98 (broad, 2C, −CH\textsubscript{3}).

\(^{19}\)F NMR (377 MHz, CDCl\textsubscript{3}, 298 K): −119.5 (d, \(^3\)J\textsubscript{HF} = 8.8 Hz).

HRMS-ESI\textsuperscript{+}: (m/z) calcd. for C\textsubscript{40}H\textsubscript{30}N\textsubscript{2}F\textsubscript{2}B\textsubscript{2}Na ([M+Na]\textsuperscript{+}) 621.24609, found 621.2472.

Reference

## §2 Crystallographic Data

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<td>4688.9(2)</td>
<td>2152.6(3)</td>
<td>2619.9(2)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>ρ(_{Calculated})</td>
<td>1.316</td>
<td>1.344</td>
<td>1.376</td>
</tr>
<tr>
<td>Absorption coefficient (mm(^{-1}))</td>
<td>0.452</td>
<td>0.081</td>
<td>0.085</td>
</tr>
<tr>
<td>F(000)</td>
<td>1904</td>
<td>912</td>
<td>1136</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.288 (\times) 0.140 (\times) 0.068</td>
<td>0.24 (\times) 0.14 (\times) 0.12</td>
<td>0.32 (\times) 0.28 (\times) 0.26</td>
</tr>
<tr>
<td>θ range for data</td>
<td>2.936 to 27.000</td>
<td>2.68 to 26.99</td>
<td>2.73 to 27.00</td>
</tr>
<tr>
<td>collection (°)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Limiting indices</td>
<td>(-16 \leq h \leq 16)</td>
<td>(-10 \leq h \leq 7)</td>
<td>(-8 \leq h \leq 9)</td>
</tr>
<tr>
<td></td>
<td>(-24 \leq k \leq 24)</td>
<td>(-38 \leq k \leq 38)</td>
<td>(-23 \leq k \leq 23)</td>
</tr>
<tr>
<td></td>
<td>(-25 \leq l \leq 25)</td>
<td>(-11 \leq l \leq 11)</td>
<td>(-26 \leq l \leq 27)</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>68974</td>
<td>16034</td>
<td>20632</td>
</tr>
<tr>
<td>Reflections unique</td>
<td>20444 (R_{int} = 0.0623)</td>
<td>4703 (R_{int} = 0.0871)</td>
<td>10979 (R_{int} = 0.0407)</td>
</tr>
<tr>
<td>Completeness</td>
<td>99.8% (θ = 25.242^\circ)</td>
<td>99.9% (θ = 26.99^\circ)</td>
<td>95.8% (θ = 27.00^\circ)</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Max. transmission</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Min. transmission</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on (F^2)</td>
<td>Full-matrix least-squares on (F^2)</td>
<td>Full-matrix least-squares on (F^2)</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>20444 / 0 / 1099</td>
<td>4703 / 0 / 308</td>
<td>10979 / 0 / 757</td>
</tr>
<tr>
<td>Goodness-of-fit on (F^2)</td>
<td>1.056</td>
<td>0.714</td>
<td>1.011</td>
</tr>
<tr>
<td>Final (R) indices ((I &gt; 2\sigma(I)))</td>
<td>(R_1 = 0.0667)</td>
<td>(R_1 = 0.0423)</td>
<td>(R_1 = 0.0663)</td>
</tr>
<tr>
<td></td>
<td>(wR_2 = 0.1762)</td>
<td>(wR_2 = 0.0599)</td>
<td>(wR_2 = 0.2150)</td>
</tr>
<tr>
<td>(R) indices (all data)</td>
<td>(R_1 = 0.1070)</td>
<td>(R_1 = 0.1255)</td>
<td>(R_1 = 0.1348)</td>
</tr>
<tr>
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<td>(wR_2 = 0.1940)</td>
<td>(wR_2 = 0.0715)</td>
<td>(wR_2 = 0.2348)</td>
</tr>
<tr>
<td>Absolute structure parameter</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>0.0030(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Largest diff. peak (eÅ(^{-3}))</td>
<td>1.462</td>
<td>0.194</td>
<td>0.543</td>
</tr>
<tr>
<td>Largest diff. hole (eÅ(^{-3}))</td>
<td>-1.356</td>
<td>-0.185</td>
<td>-0.300</td>
</tr>
<tr>
<td></td>
<td>11d</td>
<td>M.R.R-15b</td>
<td>P.R.R-15b</td>
</tr>
<tr>
<td>----------------------</td>
<td>----------</td>
<td>-----------</td>
<td>-----------</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C(<em>{36})H(</em>{20})F(_2)N(_2)</td>
<td>C(<em>{40})H(</em>{30})ClNO(_2)PtS</td>
<td>C(<em>{41})H(</em>{31})ClNO(_2)</td>
</tr>
<tr>
<td>Formula weight</td>
<td>518.54</td>
<td>819.25</td>
<td>938.62</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>140(2)</td>
<td>140(2)</td>
<td>120(2)</td>
</tr>
<tr>
<td>Wavelength (Å)</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
<td>Monoclinic</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
<td>P(_2_1)</td>
<td>P(_2_1)(_2_1)(_2_1)</td>
</tr>
<tr>
<td>a (Å)</td>
<td>9.0687(6)</td>
<td>7.7976(2)</td>
<td>13.2528(2)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>9.7590(7)</td>
<td>13.3596(4)</td>
<td>14.7365(2)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>15.6480(10)</td>
<td>15.2470(4)</td>
<td>18.3823(3)</td>
</tr>
<tr>
<td>α (°)</td>
<td>107.216(7)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β (°)</td>
<td>90.903(6)</td>
<td>93.639(2)</td>
<td>90</td>
</tr>
<tr>
<td>γ (°)</td>
<td>113.683(7)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Volume (Å(^3))</td>
<td>1196.98(16)</td>
<td>1585.12(8)</td>
<td>3590.06(9)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>(\rho_{\text{calculated}}) (g·cm(^{-3}))</td>
<td>1.439</td>
<td>1.716</td>
<td>1.737</td>
</tr>
<tr>
<td>Absorption coefficient (mm(^{-1}))</td>
<td>0.095</td>
<td>4.615</td>
<td>4.303</td>
</tr>
<tr>
<td>(F(000))</td>
<td>536</td>
<td>808</td>
<td>1848</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.249 × 0.212 × 0.168</td>
<td>0.23 × 0.19 × 0.12</td>
<td>0.24 × 0.21 × 0.18</td>
</tr>
<tr>
<td>(\theta) range for data collection (°)</td>
<td>3.020 to 26.999</td>
<td>2.62 to 26.99</td>
<td>2.61 to 27.00</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>(-11 \leq h \leq 11)</td>
<td>(-9 \leq h \leq 9)</td>
<td>(-16 \leq h \leq 16)</td>
</tr>
<tr>
<td></td>
<td>(-11 \leq k \leq 12)</td>
<td>(-17 \leq k \leq 17)</td>
<td>(-18 \leq k \leq 18)</td>
</tr>
<tr>
<td></td>
<td>(-19 \leq l \leq 19)</td>
<td>(-19 \leq l \leq 19)</td>
<td>(-23 \leq l \leq 23)</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>9472</td>
<td>21943</td>
<td>50658</td>
</tr>
<tr>
<td>Reflections unique</td>
<td>5221 (R_{int} = 0.0459)</td>
<td>6871 (R_{int} = 0.0913)</td>
<td>7834 (R_{int} = 0.0379)</td>
</tr>
<tr>
<td>Completenss</td>
<td>99.8% ((\theta = 25.242°))</td>
<td>99.9% ((\theta = 26.99°))</td>
<td>99.9% ((\theta = 27.00°))</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>None</td>
<td>Analytical</td>
<td>None</td>
</tr>
<tr>
<td>Max. transmission</td>
<td>0.65230</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Min. transmission</td>
<td>0.45772</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on (F^2)</td>
<td>Full-matrix least-squares on (F^2)</td>
<td>Full-matrix least-squares on (F^2)</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>5221 / 0 / 361</td>
<td>6871 / 1 / 415</td>
<td>7834 / 0 / 451</td>
</tr>
<tr>
<td>Goodness-of-fit on (F^2)</td>
<td>0.991</td>
<td>0.927</td>
<td>1.098</td>
</tr>
<tr>
<td>Final (R) indices ((I &gt; 2\sigma))</td>
<td>(R_1 = 0.0616)</td>
<td>(R_1 = 0.0418)</td>
<td>(R_1 = 0.0270)</td>
</tr>
<tr>
<td></td>
<td>(wR_2 = 0.1373)</td>
<td>(wR_2 = 0.0790)</td>
<td>(wR_2 = 0.0719)</td>
</tr>
<tr>
<td>(R) indices (all data)</td>
<td>(R_1 = 0.1101)</td>
<td>(R_1 = 0.0641)</td>
<td>(R_1 = 0.0310)</td>
</tr>
<tr>
<td></td>
<td>(wR_2 = 0.1736)</td>
<td>(wR_2 = 0.0826)</td>
<td>(wR_2 = 0.0729)</td>
</tr>
<tr>
<td>Absolute structure parameter</td>
<td>−0.017(8)</td>
<td>−0.017(6)</td>
<td></td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Largest diff. peak (eÅ(^3))</td>
<td>0.257</td>
<td>1.787</td>
<td>1.516</td>
</tr>
<tr>
<td>Largest diff. hole (eÅ(^3))</td>
<td>−0.254</td>
<td>−0.568</td>
<td>−1.296</td>
</tr>
<tr>
<td></td>
<td>8b</td>
<td>P,R,R-15c</td>
<td>8c</td>
</tr>
<tr>
<td>------------------</td>
<td>---------------------------</td>
<td>----------------------------</td>
<td>----------------------------</td>
</tr>
<tr>
<td><strong>Empirical formula</strong></td>
<td>C$<em>7$H$</em>{54}$N$_2$O$_6$Pt$_2$</td>
<td>C$<em>{37}$H$</em>{33}$Cl$_2$N$_2$O$_6$Pt$_2$S$_2$</td>
<td>C$<em>{30}$H$</em>{26}$N$_2$O$_4$Pt$_2$</td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>1457.37</td>
<td>1169.20</td>
<td>868.71</td>
</tr>
<tr>
<td><strong>Temperature (K)</strong></td>
<td>120(2)</td>
<td>120(2)</td>
<td>120(2)</td>
</tr>
<tr>
<td><strong>Wavelength (Å)</strong></td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71069</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>Triclinic</td>
<td>Orthorhombic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P-1</td>
<td>$P_{21}2_12_1$</td>
<td>$C_2/c$</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>7.55400(10)</td>
<td>17.2805(2)</td>
<td>11.8533(2)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>17.9390(4)</td>
<td>17.2812(2)</td>
<td>9.92050(10)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>21.6527(6)</td>
<td>12.5128(2)</td>
<td>22.5187(4)</td>
</tr>
<tr>
<td>$\alpha$ (°)</td>
<td>66.669(2)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>$\beta$ (°)</td>
<td>87.131(2)</td>
<td>90</td>
<td>103.333(2)</td>
</tr>
<tr>
<td>$\gamma$ (°)</td>
<td>86.992(2)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td><strong>Volume (Å$^3$)</strong></td>
<td>2689.18(10)</td>
<td>3736.67(9)</td>
<td>2576.62(7)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>2</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td><strong>ρ$_{\text{calc}}$ (g·cm$^{-3}$)</strong></td>
<td>1.800</td>
<td>2.078</td>
<td>2.240</td>
</tr>
<tr>
<td><strong>Absorption coefficient (mm$^{-1}$)</strong></td>
<td>5.260</td>
<td>7.986</td>
<td>10.888</td>
</tr>
<tr>
<td>$F(000)$</td>
<td>1432</td>
<td>2232</td>
<td>1632</td>
</tr>
<tr>
<td><strong>Crystal size (mm)</strong></td>
<td>0.028 x 0.072 x 0.065</td>
<td>0.147 x 0.061 x 0.047</td>
<td>0.234 x 0.189 x 0.131</td>
</tr>
<tr>
<td><strong>θ range for data collection (°)</strong></td>
<td>3.79 to 27.00</td>
<td>2.64 to 26.99</td>
<td>2.71 to 27.00</td>
</tr>
<tr>
<td><strong>Limiting indices</strong></td>
<td>$-9 \leq h \leq 9$</td>
<td>$-18 \leq h \leq 22$</td>
<td>$-15 \leq h \leq 15$</td>
</tr>
<tr>
<td></td>
<td>$-22 \leq k \leq 22$</td>
<td>$-22 \leq k \leq 22$</td>
<td>$-12 \leq k \leq 12$</td>
</tr>
<tr>
<td></td>
<td>$-27 \leq l \leq 27$</td>
<td>$-15 \leq l \leq 14$</td>
<td>$-28 \leq l \leq 28$</td>
</tr>
<tr>
<td><strong>Reflections collected</strong></td>
<td>38377</td>
<td>28455</td>
<td>18028</td>
</tr>
<tr>
<td><strong>Reflections unique</strong></td>
<td>11638 ($R_{\text{int}} = 0.0658$)</td>
<td>8115 ($R_{\text{int}} = 0.0610$)</td>
<td>2815 ($R_{\text{int}} = 0.0330$)</td>
</tr>
<tr>
<td><strong>Completeness</strong></td>
<td>99.1% ($\theta = 27.00^\circ$)</td>
<td>99.9% ($\theta = 26.99^\circ$)</td>
<td>100.0% ($\theta = 27.00^\circ$)</td>
</tr>
<tr>
<td><strong>Absorption correction</strong></td>
<td>Analytical</td>
<td>Analytical</td>
<td>Analytical</td>
</tr>
<tr>
<td><strong>Max. transmission</strong></td>
<td>0.76261</td>
<td>0.73384</td>
<td>0.33631</td>
</tr>
<tr>
<td><strong>Min. transmission</strong></td>
<td>0.46734</td>
<td>0.52497</td>
<td>0.15490</td>
</tr>
<tr>
<td><strong>Refinement method</strong></td>
<td>Full-matrix least-squares on $F^2$</td>
<td>Full-matrix least-squares on $F^2$</td>
<td>Full-matrix least-squares on $F^2$</td>
</tr>
<tr>
<td><strong>Data / restraints / parameters</strong></td>
<td>11638 / 0 / 727</td>
<td>8115 / 0 / 445</td>
<td>2815 / 0 / 173</td>
</tr>
<tr>
<td><strong>Goodness-of-fit on $F^2$</strong></td>
<td>1.139</td>
<td>0.796</td>
<td>1.046</td>
</tr>
<tr>
<td><strong>Final $R$ indices ($I &gt; 2\sigma$)</strong></td>
<td>$R_1 = 0.0524$</td>
<td>$R_1 = 0.0312$</td>
<td>$R_1 = 0.0232$</td>
</tr>
<tr>
<td></td>
<td>$wR_2 = 0.1165$</td>
<td>$wR_2 = 0.0397$</td>
<td>$wR_2 = 0.0586$</td>
</tr>
<tr>
<td><strong>$R$ indices (all data)</strong></td>
<td>$R_1 = 0.0819$</td>
<td>$R_1 = 0.0509$</td>
<td>$R_1 = 0.0307$</td>
</tr>
<tr>
<td></td>
<td>$wR_2 = 0.1222$</td>
<td>$wR_2 = 0.0415$</td>
<td>$wR_2 = 0.0603$</td>
</tr>
<tr>
<td><strong>Absolute structure parameter</strong></td>
<td>-0.018(5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Extinction coefficient</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Largest diff. peak (eÅ$^{-3}$)</strong></td>
<td>9.811</td>
<td>1.813</td>
<td>1.258</td>
</tr>
<tr>
<td><strong>Largest diff. hole (eÅ$^{-3}$)</strong></td>
<td>-1.439</td>
<td>-1.021</td>
<td>-0.652</td>
</tr>
<tr>
<td>14d</td>
<td>8d</td>
<td>9e</td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>----</td>
<td>----</td>
<td></td>
</tr>
<tr>
<td>Empirical formula</td>
<td>$\text{C}<em>{86}\text{H}</em>{75}\text{N}_4\text{O}_8\text{Pt}_4\text{S}_4$</td>
<td>$\text{C}<em>{68}\text{H}</em>{48}\text{N}_2\text{O}_6\text{Pt}_2$</td>
<td>$\text{C}<em>{12}\text{H}</em>{12}\text{BN}$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>2520.15</td>
<td>1128.98</td>
<td>181.04</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>140(2)</td>
<td>100(2)</td>
<td>150(2)</td>
</tr>
<tr>
<td>Wavelength (Å)</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$\text{C}_2/c$</td>
<td>$P\text{2}_1\text{1}$</td>
<td>$I\text{2}/a$</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>28.2143(4)</td>
<td>10.2150(3)</td>
<td>11.3267(3)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>20.5539(3)</td>
<td>19.3332(4)</td>
<td>9.2997(2)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>15.3083(2)</td>
<td>10.4408(3)</td>
<td>19.5545(5)</td>
</tr>
<tr>
<td>$\alpha$ (°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>$\beta$ (°)</td>
<td>90.7020(10)</td>
<td>112.871(6)</td>
<td>94.891(2)</td>
</tr>
<tr>
<td>$\gamma$ (°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Volume (Å$^3$)</td>
<td>8876.8(2)</td>
<td>1899.83(9)</td>
<td>2052.27(9)</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>$\rho_{\text{calculated}}$ (g·cm$^{-3}$)</td>
<td>1.886</td>
<td>1.974</td>
<td>1.172</td>
</tr>
<tr>
<td>Absorption coefficient (mm$^{-1}$)</td>
<td>6.705</td>
<td>7.412</td>
<td>0.067</td>
</tr>
<tr>
<td>$F(000)$</td>
<td>4848</td>
<td>1088</td>
<td>768</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.22 × 0.18 × 0.11</td>
<td>0.154 × 0.086 × 0.040</td>
<td>0.374 × 0.290 × 0.231</td>
</tr>
<tr>
<td>θ range for data collection (°)</td>
<td>2.66 to 27.00</td>
<td>2.59 to 27.00</td>
<td>3.43 to 27.00</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>$-36 \leq h \leq 36$</td>
<td>$-13 \leq h \leq 13$</td>
<td>$-14 \leq h \leq 14$</td>
</tr>
<tr>
<td></td>
<td>$-26 \leq k \leq 26$</td>
<td>$-23 \leq k \leq 24$</td>
<td>$-11 \leq k \leq 11$</td>
</tr>
<tr>
<td></td>
<td>$-19 \leq l \leq 19$</td>
<td>$-13 \leq l \leq 13$</td>
<td>$-24 \leq l \leq 24$</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>62599</td>
<td>16481</td>
<td>8867</td>
</tr>
<tr>
<td>Reflections unique</td>
<td>9696 ($R_{\text{int}} = 0.1204$)</td>
<td>7790 ($R_{\text{int}} = 0.0658$)</td>
<td>2236 ($R_{\text{int}} = 0.0279$)</td>
</tr>
<tr>
<td>Completeness</td>
<td>99.9% (θ = 27.00°)</td>
<td>99.8% (θ = 27.00°)</td>
<td>99.9% (θ = 27.00°)</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Analytical</td>
<td>Analytical</td>
<td>None</td>
</tr>
<tr>
<td>Max. transmission</td>
<td>0.47712</td>
<td>0.77915</td>
<td>—</td>
</tr>
<tr>
<td>Min. transmission</td>
<td>0.24794</td>
<td>0.41561</td>
<td>—</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on $F^2$</td>
<td>Full-matrix least-squares on $F^2$</td>
<td>Full-matrix least-squares on $F^2$</td>
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<tr>
<td>Data / restraints / parameters</td>
<td>9696 / 0 / 517</td>
<td>7790 / 13 / 512</td>
<td>2236 / 0 / 12</td>
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<tr>
<td>Goodness-of-fit on $F^2$</td>
<td>1.128</td>
<td>0.922</td>
<td>1.020</td>
</tr>
<tr>
<td>Final $R$ indices ($I &gt; 2\sigma(I)$)</td>
<td>$R_1 = 0.0545$</td>
<td>$R_1 = 0.0450$</td>
<td>$R_1 = 0.0397$</td>
</tr>
<tr>
<td></td>
<td>$wR_2 = 0.1603$</td>
<td>$wR_2 = 0.0923$</td>
<td>$wR_2 = 0.0925$</td>
</tr>
<tr>
<td>$R$ indices (all data)</td>
<td>$R_1 = 0.0740$</td>
<td>$R_1 = 0.0672$</td>
<td>$R_1 = 0.0527$</td>
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<tr>
<td></td>
<td>$wR_2 = 0.1645$</td>
<td>$wR_2 = 0.1057$</td>
<td>$wR_2 = 0.1019$</td>
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<tr>
<td>Absolute structure parameter</td>
<td>0.211(14)</td>
<td>—</td>
<td>0.0004(4)</td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>—</td>
<td>—</td>
<td>0.212</td>
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<tr>
<td>Largest diff. peak (eÅ$^{-3}$)</td>
<td>4.468</td>
<td>2.028</td>
<td>—</td>
</tr>
<tr>
<td>Largest diff. hole (eÅ$^{-3}$)</td>
<td>−1.453</td>
<td>−1.004</td>
<td>−0.149</td>
</tr>
<tr>
<td>Property</td>
<td>Value</td>
<td></td>
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</tr>
<tr>
<td>--------------------------------</td>
<td>--------------------------------------------</td>
<td></td>
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<tr>
<td>Empirical formula</td>
<td>C₈₀H₆₀Br₄F₄N₄</td>
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<td></td>
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<tr>
<td>Formula weight</td>
<td>1196.56</td>
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<td></td>
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<tr>
<td>Temperature (K)</td>
<td>140(2)</td>
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<td>Wavelength (Å)</td>
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<td>Space group</td>
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<tr>
<td>a (Å)</td>
<td>10.9416(5)</td>
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<tr>
<td>b (Å)</td>
<td>15.9229(7)</td>
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<tr>
<td>c (Å)</td>
<td>18.7015(9)</td>
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<tr>
<td>α (°)</td>
<td>77.829(4)</td>
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<tr>
<td>β (°)</td>
<td>89.171(4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ (°)</td>
<td>73.008(4)</td>
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<tr>
<td>Volume (Å³)</td>
<td>3042.1(3)</td>
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</tr>
<tr>
<td>Z</td>
<td>2</td>
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<tr>
<td>ρ_calculated (g·cm⁻³)</td>
<td>1.306</td>
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<tr>
<td>Absorption coefficient (mm⁻¹)</td>
<td>0.083</td>
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<td>F(000)</td>
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<td>Crystal size (mm)</td>
<td>0.252 × 0.122 × 0.094</td>
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<td></td>
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<tr>
<td>θ range for data collection (°)</td>
<td>3.063 to 27.000</td>
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<td></td>
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<tr>
<td>Limiting indices</td>
<td>-13 ≤ h ≤ 13</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-20 ≤ k ≤ 20</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>-23 ≤ l ≤ 23</td>
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<td>43793</td>
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<tr>
<td>Reflections unique</td>
<td>13246 (R_int = 0.0669)</td>
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<td>Completenss</td>
<td>99.8% (θ = 25.242°)</td>
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<tr>
<td>Absorption correction</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Max. transmission</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Min. transmission</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix</td>
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<td></td>
<td>least-squares on F²</td>
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<td>Data / restraints / parameters</td>
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<tr>
<td></td>
<td>wR₂ = 0.1336</td>
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</tr>
<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.1210</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>wR₂ = 0.1554</td>
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</tr>
<tr>
<td>Absolute structure parameter</td>
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<td></td>
</tr>
<tr>
<td>Extinction coefficient</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Largest diff. peak (eÅ⁻³)</td>
<td>0.283</td>
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<td></td>
</tr>
<tr>
<td>Largest diff. hole (eÅ⁻³)</td>
<td>-0.268</td>
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</tr>
</tbody>
</table>
§3 Luminescence measurements

These measurements have been performed by Prof. Gareth Williams (Durham university, England).

Absorption spectra were measured on a Biotek Instruments XS spectrometer, using quartz cuvettes of 1 cm path length. Steady-state luminescence spectra were measured using a Jobin Yvon FluoroMax-2 spectrofluorimeter, fitted with a red-sensitive Hamamatsu R928 photomultiplier tube. The spectral $\lambda_{\text{max}}$ values in Table 1 are those obtained after correction for the wavelength dependence of the detector and emission monochromator. Samples for emission measurements at room temperature were contained within quartz cuvettes of 1 cm path length modified with appropriate glassware to allow connection to a high-vacuum line. Degassing was achieved via a minimum of three freeze-pump-thaw cycles whilst connected to the vacuum manifold; final vapour pressure at 77 K was $< 5 \times 10^{-2}$ mbar, as monitored using a Pirani gauge. Luminescence quantum yields were determined using quinine sulfate in $\text{H}_2\text{SO}_4(\text{aq})$ as the standard for the proligands ($\Phi_{\text{lum}} = 0.548^i$), and $[\text{Ru(bpy)}_3\text{Cl}_2$ in degassed aqueous solution for the complexes ($\Phi_{\text{lum}} = 0.042^ii$). The estimated uncertainty in $\Phi_{\text{lum}}$ is ± 20% or better.

The fluorescence lifetimes of the proligands were measured by time-correlated single-photon counting, following excitation at 374.0 nm with an EPL-375 pulsed-diode laser. The emitted light was detected at 90° using a Peltier-cooled R928 PMT after passage through a monochromator. The estimated uncertainty in the quoted lifetimes is ± 10% or better. The phosphorescence lifetimes of the proligands and of the Pt-helicenes were determined following excitation with a microsecond flashlamp, using the same detector operating in multichannel scaling mode. The bimolecular rate constants for quenching by molecular oxygen, $k_Q$, were determined from the lifetimes in degassed and air-equilibrated solution, taking the concentration of oxygen in CH$_2$Cl$_2$ at 0.21 atm O$_2$ to be 2.2 mM dm$^{-3}$.iii Luminescence data at 77 K were acquired in a glass of diethyl ether / isopentane / ethanol (2:2:1 v/v), abbreviated EPA below, using 4 mm diameter quartz tubes within a home-built quartz Dewar.

---

**Compound 9c**

Absorption $\lambda_{\text{max}} / \text{nm} (\varepsilon / \text{M}^{-1} \text{cm}^{-1})$: 256 (49300), 288 (18200), 342 (18100), 375 (15600), 391 (14300).

Fluorescence at 298 K: $\lambda_{\text{max}} = 427 \text{ nm}$  $\Phi = 0.49$  $\tau = 3.2 \text{ ns}$

Emission at 77 K: $\lambda_{\text{max}} / \text{nm} = 397, 415, 443, 474 \text{sh}$  — fluorescence: $\tau = 3.9 \text{ ns}$

556, 604, 654  — phosphorescence: $\tau = 620 \text{ ms}$
Absorption $\lambda_{\text{max}}$ / nm ($\varepsilon$ / M$^{-1}$ cm$^{-1}$): 237 (46000), 263 (26400), 295 (33100), 307 (30400), 344 (10300), 359 (9740), 377 (6910), 398 (5250).

Fluorescence at 298 K: $\lambda_{\text{max}}$ / nm = 404, 425, 450sh  $\Phi = 0.21$  $\tau = 4.1$ ns

Emission at 77 K: $\lambda_{\text{max}}$ / nm = 396, 417, 443, 471 – fluorescence: $\tau = 7.2$ ns  543, 581, 626 – phosphorescence: $\tau = 1.1$ s
**Absorption** $\lambda_{\text{max}}$ / nm ($\varepsilon$ / M$^{-1}$ cm$^{-1}$): 232 (53900), 265 (46700), 324 (25500), 352sh (15800), 374sh (10500), 404 (2190), 429 (1440).

**Fluorescence at 298 K:** $\lambda_{\text{max}}$ / nm = 435, 458, $\Phi$ = 0.069, $\tau$ = 5.3 ns

**Emission at 77 K:** $\lambda_{\text{max}}$ / nm = 427, 454, 484, 516 – fluorescence: $\tau$ = 7.3 ns

546, 593, 643 – phosphorescence: $\tau$ = 1.2 s
Absorption $\lambda_{\text{max}}$ / nm ($\varepsilon$ / M$^{-1}$ cm$^{-1}$): 269 (60200), 337 (31200), 377sh (12400), 415 (4020), 440 (3000).

Fluorescence at 298 K: $\lambda_{\text{max}}$ / nm = 443, 471, 502, 541 $\Phi = 0.074$ $\tau = 5.5$ ns

Emission at 77 K: $\lambda_{\text{max}}$ / nm = 437, 464, 496, 532 – fluorescence: $\tau = 7.3$ ns

554, 599, 657 – phosphorescence: $\tau = 1.1$ s
**Compound 8d**

Absorption $\lambda_{\text{max}}$ / nm ($\varepsilon / \text{M}^{-1} \text{cm}^{-1}$): 242 (72400), 297 (57000), 368sh (20800), 426 (9250), 446 (8380), 479 (6850).

Fluorescence at 298 K: $\lambda_{\text{max}}$ / nm = 639, 663 $\Phi = 0.066$ $\tau = 27 \mu\text{s}$

Emission at 77 K: $\lambda_{\text{max}}$ / nm = 615, 665, 738sh $\tau = 61 \mu\text{s}$
§4 HPLC separations

These separations have been performed by Nicolas Vanthuyne and coworkers (ISM2, Marseille).

Analytical chiral HPLC separation for compound 9a

- The sample is dissolved in EtOH, injected on the chiral column, and detected with an UV detector at 254 nm and circular dichroïsm at 254 nm. The flow-rate is 1 mL/min.

<table>
<thead>
<tr>
<th>Column</th>
<th>Mobile Phase</th>
<th>t1</th>
<th>k1</th>
<th>t2</th>
<th>k2</th>
<th>α</th>
<th>Rs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chiralcel</td>
<td>Heptane / EtOH (97/3)</td>
<td>5.63</td>
<td>0.88</td>
<td>5.99</td>
<td>1</td>
<td>1.13</td>
<td>1.11</td>
</tr>
</tbody>
</table>

![Chiralcel OD-3 Heptane / EtOH (97/3) graph]

<table>
<thead>
<tr>
<th>UV Results</th>
<th>Area</th>
<th>Area %</th>
<th>Capacity Factor</th>
<th>Relative RT</th>
<th>Resolution (USP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Retention Time</td>
<td>5.63</td>
<td>19084522</td>
<td>48.45</td>
<td>0.88</td>
<td>0.00</td>
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<tr>
<td></td>
<td>5.99</td>
<td>20307880</td>
<td>51.55</td>
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</tr>
<tr>
<td>Totals</td>
<td></td>
<td>39392402</td>
<td>100.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Semi-preparative separation for compound 9a:

• Sample preparation: About 90 mg of compound SCS772 are dissolved in 18 mL of EtOH/Hexane (1/1).
  • Chromatographic conditions: Chiralcel OD-H (250 x 10 mm), hexane / EtOH (97/3) as mobile phase, flow-rate = 5 mL/min, UV detection at 220 nm.
  • Injections (stacked): 100 times 180 µL, every 8 minutes.
  • Collection: five fractions are collected between 8.4 and 11 minutes. One fraction with impurities is also collected.

Three of these fractions are purified in the same chromatographic conditions.

• Injections (stacked): 140 times 50 µL, every 1.6 minutes and 220 times 75 µL, every 2.5 minutes.

• Collection: the first eluted enantiomer is collected between 8.7 and 9.1 minutes, the second one between 9.5 and 11 minutes.
  • First fraction: 16.3 mg of the first eluted ( (+, CD 254nm)-enantiomer) with ee > 98%
  • Second fraction: 16 mg of the second eluted ( (-, CD 254nm)-enantiomer) with ee > 96%

• Chromatograms of the collected fractions:
Chiralcel OD-3
Heptane / EtOH
(97/3)

<table>
<thead>
<tr>
<th>UV Results</th>
<th>Retention Time</th>
<th>Area</th>
<th>Area %</th>
<th>Capacity factor</th>
<th>Relative RT</th>
<th>Resolution (USP)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5.61</td>
<td>6944297</td>
<td>100.00</td>
<td>0.57</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Totals |

6944297 | 100.00
Chiralcel OD-3
Heptane / EtOH

<table>
<thead>
<tr>
<th>UV Results</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Retention Time</td>
<td>Area</td>
<td>Area %</td>
<td>Capacity factor</td>
<td>Relative RT</td>
</tr>
<tr>
<td>5.63</td>
<td>5.96</td>
<td>377583</td>
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<td>0.88</td>
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<td>18886937</td>
<td>98.04</td>
<td>0.99</td>
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<tr>
<td>Totals</td>
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<td>19264520</td>
<td>100.00</td>
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</tr>
</tbody>
</table>
Analytical chiral HPLC separation for compound 9b

- The sample is dissolved in chloroform, injected on the chiral column, and detected with an UV detector at 254 nm and circular dichroïsm at 254 nm. The flow-rate is 1 mL/min.

<table>
<thead>
<tr>
<th>Column</th>
<th>Mobile Phase</th>
<th>t1</th>
<th>k1</th>
<th>t2</th>
<th>k2</th>
<th>α</th>
<th>Rs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chiralpak IF</td>
<td>Heptane / 2-PrOH / chloroform (90/5/5)</td>
<td>5.59 (-)</td>
<td>0.86</td>
<td>6.57 (+)</td>
<td>1.19</td>
<td>1.38</td>
<td>2.58</td>
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</table>

### Results

<table>
<thead>
<tr>
<th>Retention Time</th>
<th>Area</th>
<th>Area %</th>
<th>Capacity factor</th>
<th>Relative RT</th>
<th>Resolution (USP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.59</td>
<td>40489090</td>
<td>50.18</td>
<td>0.86</td>
<td>1.00</td>
<td>0.00</td>
</tr>
<tr>
<td>6.57</td>
<td>40200728</td>
<td>49.82</td>
<td>1.19</td>
<td>1.38</td>
<td>2.58</td>
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</tbody>
</table>
Semi-preparative separation for compound 9b:

- Sample preparation: About 51 mg of compound SCS73 are dissolved in 24 mL of chloroform.
- Chromatographic conditions: Chiralpak IF (250 x 10 mm), hexane / 2-PrOH / chloroform (90/5/5) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.
- Injections (stacked): 265 times 90 µL, every 2.8 minutes.
- Collection: the first eluted enantiomer is collected between 5.2 and 6 minutes, the second one between 6.6 and 7.6 minutes.
- First fraction: 27 mg of the first eluted ((-,CD 254nm)-enantiomer) with ee > 97%
- Second fraction: 24 mg of the second eluted ((+,CD 254nm)-enantiomer) with ee > 98%

- Chromatograms of the collected fractions:
Chiralpak IF
Heptane / 2-PrOH /
chloroform (90/5/5)

<table>
<thead>
<tr>
<th>Retention Time</th>
<th>Area</th>
<th>Area %</th>
<th>Capacity factor</th>
<th>Relative RT</th>
<th>Resolution (USP)</th>
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</thead>
<tbody>
<tr>
<td>5.57</td>
<td>223429</td>
<td>0.88</td>
<td>0.86</td>
<td>1.00</td>
<td>0.00</td>
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<tr>
<td>6.69</td>
<td>25187055</td>
<td>99.12</td>
<td>1.23</td>
<td>1.44</td>
<td>2.73</td>
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</table>
Analytical chiral HPLC separation for compound 9c

• The sample is dissolved in ethanol, injected on the chiral columns, and detected with an UV detector at 254 nm and CD 254 nm. The flow-rate is 1 mL/min.

<table>
<thead>
<tr>
<th>Column</th>
<th>Mobile Phase</th>
<th>t1</th>
<th>k1</th>
<th>t2</th>
<th>k2</th>
<th>α</th>
<th>Rs</th>
</tr>
</thead>
<tbody>
<tr>
<td>(S,S)-Ulmo</td>
<td>Heptane / 2-PrOH (95/5)</td>
<td>8.13 (+)</td>
<td>1.71</td>
<td>9.27 (-)</td>
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<td>1.22</td>
<td>2.02</td>
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<tr>
<td>Chiralpak IB</td>
<td>Heptane / 2-PrOH (95/5)</td>
<td>6.59 (+)</td>
<td>1.20</td>
<td>7.12 (-)</td>
<td>1.37</td>
<td>1.14</td>
<td>1.26</td>
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</tbody>
</table>

(S,S)-Ulmo
Heptane / 2-PrOH (95/5)

UV Results

<table>
<thead>
<tr>
<th>Retention Time</th>
<th>Area</th>
<th>Area %</th>
<th>Capacity factor</th>
<th>Relative RT</th>
<th>Resolution (USP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.13</td>
<td>14455860</td>
<td>49.22</td>
<td>1.71</td>
<td>0.00</td>
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</tr>
<tr>
<td>9.27</td>
<td>14914025</td>
<td>50.78</td>
<td>2.09</td>
<td>1.22</td>
<td>2.02</td>
</tr>
</tbody>
</table>
Semi-preparative separation for compound 9c:

- Sample preparation: About 120 mg of compound 9c are dissolved in 14 mL of dichloromethane.
- Chromatographic conditions: (S,S)-Ulmo (250 x 10 mm), hexane / 2-PrOH (95/5) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.
- Injections: 700 times 20 µL, every 2 minutes.
- Collection: the first eluted enantiomer is collected between 6.6 and 7.1 minutes, the second one between 7.6 and 8.1 minutes.
- First fraction: 50 mg of the first eluted ([+, CD 254nm]-enantiomer) with ee > 96%
- Second fraction: 50 mg of the second eluted ([-, CD 254 nm]-enantiomer) with ee > 96%

- Chromatograms of the collected fractions:
(S,S)-Ulmo
Heptane / 2-PrOH (95/5)

<table>
<thead>
<tr>
<th>UV Results</th>
<th>Retention Time</th>
<th>Area</th>
<th>Area %</th>
<th>Capacity factor</th>
<th>Relative RT</th>
<th>Resolution (USP)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8.14</td>
<td>429064</td>
<td>1.49</td>
<td>1.71</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>9.23</td>
<td>28441261</td>
<td>98.51</td>
<td>2.08</td>
<td>0.00</td>
<td>1.92</td>
</tr>
</tbody>
</table>

XLVII
First-order kinetic of enantiomerization for compound 9c:

About 1 mg of a (-, CD 254nm) enriched sample of 9c is heated in about 15 mL of ethanol at 78°C. 20 μL are taken and then injected every 10 minutes on (S,S)-Ulmo (Heptane / 2-ProH (95/5), 1 mL/min, UV 254 nm). Thus, the decrease of the percentage of the (-, CD 254nm) enantiomer is monitored.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>% enantiomer (-, CD254)</th>
<th>ln ((%t-50%)/(%t=0)-50%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>98.24</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>94.94</td>
<td>-0.070860286</td>
</tr>
<tr>
<td>20</td>
<td>91.95</td>
<td>-0.13971012</td>
</tr>
<tr>
<td>30</td>
<td>89</td>
<td>-0.212626906</td>
</tr>
<tr>
<td>40</td>
<td>86.26</td>
<td>-0.285473347</td>
</tr>
<tr>
<td>50</td>
<td>83.71</td>
<td>-0.358394023</td>
</tr>
<tr>
<td>60</td>
<td>81.34</td>
<td>-0.431293315</td>
</tr>
<tr>
<td>70</td>
<td>79.14</td>
<td>-0.504076752</td>
</tr>
<tr>
<td>80</td>
<td>77.11</td>
<td>-0.576285889</td>
</tr>
<tr>
<td>90</td>
<td>75.19</td>
<td>-0.649741462</td>
</tr>
<tr>
<td>100</td>
<td>73.45</td>
<td>-0.721318058</td>
</tr>
</tbody>
</table>

\[ y = -0.00723687x + 0.00277280 \]
\[ R^2 = 0.99996364 \]

\[ k_{\text{enantiomerisation}} = 6.0307.10^{-5} \text{ s}^{-1} (78°C, \text{ethanol}) \]
\[ \Delta G^\circ = 114.9 \text{ kJ.mol}^{-1} (78°C, \text{ethanol}) \]
Analytical chiral HPLC separation for compound SCS774

- The sample is dissolved in EtOH, injected on the chiral column, and detected with an UV detector at 220 nm and circular dichroïsm at 254 nm. The flow-rate is 1 mL/min.

<table>
<thead>
<tr>
<th>Column</th>
<th>Mobile Phase</th>
<th>t1</th>
<th>k1</th>
<th>t2</th>
<th>k2</th>
<th>α</th>
<th>Rs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lux-Cellulose-2</td>
<td>Heptane / EtOH (95/5)</td>
<td>5.28</td>
<td>0.79</td>
<td>5.70</td>
<td>0.93</td>
<td>1.18</td>
<td>2.07</td>
</tr>
</tbody>
</table>
Lux Cellulose-2
Heptane / EtOH

**Signal:** DAD1 B, Sig=220.4 Ref=off

<table>
<thead>
<tr>
<th>RT [min]</th>
<th>Area</th>
<th>Area%</th>
<th>Capacity Factor</th>
<th>Enantioselectivity</th>
<th>Resolution (USP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.28</td>
<td>1108</td>
<td>51.14</td>
<td>0.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.70</td>
<td>1058</td>
<td>48.86</td>
<td>0.93</td>
<td>1.18</td>
<td>2.07</td>
</tr>
<tr>
<td>Sum</td>
<td>2167</td>
<td>100.00</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Semi-preparative separation for compound 9d:

- Sample preparation: About 55 mg of compound 9d are dissolved in 53 mL of EtOH/Hexane (1/1).

- Chromatographic conditions: Lux-Cellulose-2 (250 x 10 mm), hexane / EtOH (95/5) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.

- Injections (stacked): 240 times 220 µL, every 2.4 minutes.

- Collection: the first eluted enantiomer is collected between 7.1 and 7.7 minutes, the second one between 8.1 and 8.9 minutes.

- First fraction: 26 mg of the first eluted ((−, CD 254nm)-enantiomer) with ee > 99%

- Second fraction: 28 mg of the second eluted ((+, CD 254nm)-enantiomer) with ee > 97%

- Chromatograms of the collected fractions:
**Signal:** DAD1 B, Sig=220.4 Ref=off

<table>
<thead>
<tr>
<th>RT [min]</th>
<th>Area</th>
<th>Area%</th>
<th>Capacity Factor</th>
<th>Enantioselectivity</th>
<th>Resolution (USP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.29</td>
<td>89</td>
<td>1.37</td>
<td>0.79</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.70</td>
<td>6450</td>
<td>98.63</td>
<td>0.93</td>
<td>1.18</td>
<td>1.87</td>
</tr>
<tr>
<td>Sum</td>
<td>6548</td>
<td>100.00</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Analytical chiral HPLC separation for compound 14d

- The sample is dissolved in ethanol / chloroform (8/2), injected on the chiral column, and detected with an UV detector at 254 nm and polarimeter. The flow-rate is 1 ml/min.

Chiralpak IA
Hexane/ ethanol / chloroform
85/5/10

<table>
<thead>
<tr>
<th>Retention Time</th>
<th>Area</th>
<th>Area %</th>
<th>Capacity factor</th>
<th>Relative RT</th>
<th>Resolution (USP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.81</td>
<td>33320424</td>
<td>50.02</td>
<td>4.27</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>18.19</td>
<td>33294068</td>
<td>49.98</td>
<td>5.06</td>
<td>1.18</td>
<td>2.43</td>
</tr>
</tbody>
</table>
Semi-preparative separation for compound 14d:

- Sample preparation: About 20 mg of compound 14d are dissolved in 15 mL of a mixture hexane/chloroform/ethanol (6/3/1).
- Chromatographic conditions: Chiralpak IA (250 x 10 mm), thermostated at 30°C, hexane/ethanol/chloroform (85/5/10) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.
- Injection (stacked injections): 100 times 150 μL, every 6 minutes.
- Collection: the first eluted enantiomer is collected between 0.2 and 2 minutes and the second one between 3 and 6 minutes.
  - First fraction: 10 mg of the first eluted ((-)polarimeter-enantiomer) with ee = 98%
  - Second fraction: 10 mg of the second eluted ((+)polarimeter-enantiomer) with ee = 95%

- Chromatograms of the collected enantiomers:
Chiralpak IA
Hexane/ethanol/chloroform
85/5/10

<table>
<thead>
<tr>
<th>Retention Time</th>
<th>Area</th>
<th>Area %</th>
<th>Capacity factor</th>
<th>Relative RT</th>
<th>Resolution (USP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.71</td>
<td>835482</td>
<td>2.32</td>
<td>4.57</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>18.31</td>
<td>35231428</td>
<td>97.68</td>
<td>5.10</td>
<td>0.00</td>
<td>1.44</td>
</tr>
</tbody>
</table>
Analytical chiral HPLC separation for compound 8d

- The sample is dissolved in chloroform, injected on the chiral column, and detected with an UV detector at 254 nm and polarimeter. The flow-rate is 1 mL/min.

<table>
<thead>
<tr>
<th>Column</th>
<th>Mobile Phase</th>
<th>t1</th>
<th>k1</th>
<th>t2</th>
<th>k2</th>
<th>α</th>
<th>Rs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chiralpak IF</td>
<td>Heptane / Ethanol/Chloroform</td>
<td>4.01(−)</td>
<td>0.34</td>
<td>4.85(+)</td>
<td>0.62</td>
<td>1.82</td>
<td>2.41</td>
</tr>
<tr>
<td></td>
<td>(50/10/40)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Semi-preparative separation for compound 8d:

- Sample preparation: About 54 mg of compound 8d are dissolved in 20 mL of chloroform.
- Chromatographic conditions: Chiralpak IF (250 x 10 mm), hexane/Ethanol/Chloroform (50/10/40) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.
  - Injections: 134 times 150 μL, every 2 minutes.
  - Collection: the first eluted enantiomer is collected between 3.4 and 4 minutes, the second one between 4.4 and 5.1 minutes.
  - First fraction: 22 mg of the first eluted ((-, polarimeter)-enantiomer) with ee >99.5 %
  - Second fraction: 23mg of the second eluted ((+, polarimeter)-enantiomer) with ee >99.5 %

- Chromatograms of the collected fractions:

<table>
<thead>
<tr>
<th>Retention Time</th>
<th>Area</th>
<th>Area %</th>
<th>Capacity factor</th>
<th>Relative RT</th>
<th>Resolution (USP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.08</td>
<td>8603103</td>
<td>100.00</td>
<td>0.36</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>
§5 VCD and ROA

The measurements were performed partly in our lab and partly by Dr. Juan Casado (Malaga University, Spain).

**Vibrational Circular Dichroism (VCD) and Infrared (IR)** spectra were recorded in a PMA50 optical bench coupled to a Vertex70 spectrometer, both supplied by Bruker ©. In the PMA50, the infrared radiation (3800-600 cm\(^{-1}\) range) is focused by a BaF\(_2\) lens toward a ZnSe photo-elastic modulator (PEM, 50 kHz frequency). The circularly polarized beam is then driven to the sample and finally collected by a D313/QMTC detector. A calibration of the PEM at a fixed wavenumber had been used before recording any VCD spectrum, to ensure a proper chiroptical signal within a spectral region of 600 cm\(^{-1}\) around the tuning wavenumber. Typically, calibrations at 1450 cm\(^{-1}\) allowed us to
obtain a spectrum over the most meaningful region for conjugated organic systems. Every VCD spectrum was the result of averaging a minimum of 36000 scans, recorded at a spectral resolution of 4 cm\(^{-1}\). In order to ensure the absence of linear dichroism interference, caused by preferential orientations within the gels, (Chirality 2009, 21, S153-S162) spectra on different aliquots of these compounds were recorded at different angles without observing appreciable deviations. As a proof of the quality of the recorded data, spectra from pure enantiomeric samples result in mirror images. The samples in dichloromethane at 0.03 M concentration were prepared for vibrational spectra measurements. After thermal treatment, the samples were placed, at room temperature, in a demountable cell A145 (Bruker, Germany) supplied with KBr windows. For the monoFe complex a 0.5 mm Teflon spacer was used to obtain the optimal IR signal for VCD. Netherless, for the bisFe complex 0.2 mm Teflon spacer was required at the same concentration.

**Raman and ROA** spectra were measured using a ChiralRAMAN© spectrometer\(^1\) supplied by BioTools. The samples in dichloromethane at 0.003 M concentration were prepared for ROA measurements Raman and ROA spectra with a resolution better than 4 cm\(^{-1}\) were simultaneously recorded using a quartz cell of 4 mm optical path length. Visible fluorescence from traces of impurities, which can give large backgrounds in Raman spectra, was quenched by leaving the samples to equilibrate in the laser beam before ROA data was acquired. The experimental conditions were as follows: 532 nm laser wavelength, 30 mW laser power at the sample and 12 hours of routine acquisition time.
Appendices
Appendices

1. Optical rotation

The optical rotation is the characteristic property of chiral molecules because of the circular birefringence. When planar polarized light passes through a chiral sample, the plane of polarization will rotate, thus we call this sample having optical activity. From the observer’s view, when optical analyzer rotates clockwise, this sample is dextrorotatory, while anti-clockwise, the sample is levorotatory.

![Optical Rotation Diagram](image)

Usually, sodium light (589.3 nm) is used to measure the optical rotation, and the specific rotation \([\alpha]_D\) is defined as:

\[
[\alpha]_D = \frac{\alpha_{\text{measured}}}{c \times l} \times 100
\]

In this equation, \(\alpha_{\text{measured}}\) is the optical rotation directly observed, \(c\) is the mass of solute in gram in 100 mL solvent, and \(l\) is the length of sample well in decimeter. The unit of specific rotation is \text{deg·cm}^3\cdot\text{dm}^{-1}\cdot\text{g}^{-1}.

And molar rotation \([\phi]_D\) is defined as:

\[
[\phi]_D = \frac{[\alpha]_D \times M_r}{100}
\]

In this equation, \(M_r\) is the molar mass of the chiral molecule. The unit of molar rotation is \text{deg·cm}^2\cdot\text{dmol}^{-1}.

2. Circular dichroism spectroscopy

For chiral sample, the molar absorptivity of the two circularly polarized lights, the left-handed circularly polarized light and the right-handed circularly polarized light are different, thus \(\varepsilon_L \neq \varepsilon_R\). This phenomenon is called circular dichroism (CD), and the difference between \(\varepsilon_L\) and \(\varepsilon_R\) is:

\[
\Delta \varepsilon = \varepsilon_L - \varepsilon_R
\]
Δε is changed according to the wavelength \( \lambda \). Taking Δε as vertical coordinate and wavelength \( \lambda \) as horizontal coordinate, we can obtain the CD spectrum. When the wavelength is in the UV-visible region, and the absorption is mainly caused by the electronic charge-transfer transitions, we called it electronic circular dichroism or ECD. While the wavelength is in the infrared region, and the absorption is mainly caused by the vibrations, we called it vibrational circular dichroism or VCD.

In VCD spectroscopy, \( g \) factor is used for studying the strength of the VCD signal.

\[
g = \frac{\Delta \varepsilon}{\varepsilon}
\]

In this equation \( \Delta \varepsilon \) is the molar circular dichroism value of VCD in a chosen wavelength, and \( \varepsilon \) is the absorptivity of the same wavelength from corresponding IR spectrum.

3. Raman spectroscopy and Raman optical activity

Raman optical activity ROA spectroscopy is a spectroscopic technique to the vibrational spectral range, and is a complementary technique to VCD. For some chiral substance, we can find the system is favored to generate more one circularly polarized light than the other one. ROA spectroscopy studies the difference between the intensity of two circularly polarized Raman scattered light.

In ROA spectroscopy, the intensity \( \Delta I \) is the difference between the right-handed polarized scattered light and left-handed polarized scattered light.
\[ \Delta I = I_R - I_L \]

4. Circularly polarized luminescence

The phenomenon of circularly polarized luminescence (CPL) is caused by the ability of a chiral compound in generating different left-handed and right-handed polarized lights from a chiral system. The intensity of left-handed polarized emission \( I_L \) and the right-handed polarized emission \( I_R \) may differ, which causes the CPL signal.

The dissymmetry factor \( g_{\text{lum}} \) is used to quantify the CPL, which equals twice of the difference between \( I_L \) and \( I_R \) and the sum of \( I_L \) and \( I_R \). The maximum values are -2 and +2.

\[
g_{\text{lum}} = 2 \frac{I_L - I_R}{I_L + I_R}
\]
Résumé français
Résumé français

Hélicènes hétéroatomiques et organométalliques : synthèse et propriétés chiroptiques

§1 Motivation et but du travail

Les \([n]\)hélicènes sont des systèmes \(\pi\)-conjugués non-planaires composés de \(n\) cycles aromatiques ortho-fusionnés. En raison de leur chiralité hélicoïdale inhérente, ils présentent des propriétés chiroptiques intenses (pouvoir rotatoire, dichroïsme circulaire, luminescence polarisée circulairement).

Grâce à leurs propriétés chiroptiques et structurelles, on peut utiliser les hélicènes dans beaucoup de domaines, comme par exemple, en catalyse, dans les diodes électroluminescentes, les moteurs moléculaires, commutateurs chiroptiques, etc. Récemment, beaucoup de travaux ont été consacrés aux recherches sur les hélicènes.

Mes travaux de thèse portent sur la synthèse d'hélicènes organométralliques et hétéroatomiques, et se divisent suivant trois axes majeurs.

Le premier sujet est l'étude des hélicènes avec un centre métallique rédox. Nous avons introduit un motif chimique contenant un atome de fer sur l'hélicène connecté par une liaison \(\text{C}≡\text{C}\). Dans ce sujet, nous voulons étudier les propriétés chiroptiques avec le changement d'état rédox du centre métallique. Pour cela, nous avons utilisé des techniques spectroscopiques chiroptiques comme le dichroïsme circulaire vibrationnel, le spectre d'activité optique Raman qui opèrent dans la région infrarouge.

Le deuxième sujet est l'étude d'hélicènes avec un centre rédox et un centre photochrome. Nous avons introduit l'hélicène sur un bloc chimique contenant du ruthénium connecté par liaison une \(\text{C}≡\text{C}\), puis introduit le motif photochrome DTE (dithiényléthène) sur le ruthénium. La molécule contient donc trois parties : un centre chiral, un centre rédox et un centre photochrome. Dans ce sujet, nous voulons étudier l'activité d'interrupteur chiroptique provoquée par un stimulus rédox et/ou par la lumière.

Le troisième sujet est l'étude de platinahélicènes et borahélicènes qui sont issus de l'incorporation d'un ou deux platinacycles ou cycles azaboroles dans le squelette de l'hélicène. Dans ce sujet, nous voulons examiner les propriétés optiques et chiroptiques, et étudier l'influence du nombre de cycles et du nombre d'hétérocycles. Ces produits ont également révélé des propriétés d'émission et de la luminescence polarisée circulairement.

§2 Complexes de fer à base d’hélicène comme interrupteurs chiroptiques rédox

Le bloc à base de fer \((η^2\text{-dppe})(η^5\text{-C}_5\text{Me}_3)\text{Fe}≡\text{C}≡\text{C}−\) est un bon candidat pour des interrupteurs provoqués par stimulus rédox; il présente une bonne interaction avec ses ligands \(\pi\)-conjugués, une bonne réversibilité et une bistabilité dans le processus de commutation. Ce bloc a deux états : état
neutre avec un centre métallique Fe$^{II}$, et état radical cationique avec un centre métallique Fe$^{III}$. Il peut changer son état de l’un à l’autre en gagnant ou en perdant un électron.

Schéma 1 Les deux états rédox pour le bloc ($\eta^2$-dppe)($\eta^5$-C$_5$Me$_5$)Fe–C≡C$^\text{−}$.

Si on introduit un chromophore chiral connectant ce bloc de fer, on peut obtenir un interrupteur chiroptique rédox. Les hélicènes ont de bonnes propriétés chiroptiques, et nous avons préparé trois molécules d’hélicène à base de fer : 1a, 1b et 1c (à l’état neutre Figure 1). Pour 1a, il y a une unité de [4]hélicène connectant un bloc fer avec une liaison C≡C. Pour 1b, c’est une unité de [6]hélicène avec un bloc fer et pour 1c une unité de [6]hélicène avec deux blocs fer aux deux bouts de l’hélicène.

Figure 1 Les trois complexes d’hélicène à base du bloc de fer 1a, 1b and 1c.

Pour synthétiser les complexes à l’état neutre, nous avons préparé les ligands de type hélicène fonctionnalisés par un ou deux groupes éthynyles (2a, 2b et 2c) que nous avons fait réagir avec le bloc de fer ($\eta^2$-dppe)($\eta^5$-C$_5$Me$_5$)FeCl (Schéma 2). Pour les ligands 2b et 2c, la présence du [6]hélicène conduit à deux énantiomères $P$ et $M$. On obtient ainsi les complexes racémiques rac-1b et rac-1c à partir des ligands racémiques rac-2b ou rac-2c, et les complexes énantiopurs $P$- / $M$-1b, et $P$- / $M$-1c à partir des ligands énantiopurs $P$- / $M$-2b, et $P$- / $M$-2c.

La figure 2 présente la synthèse pour les trois complexes en l'état neutre 1a, 1b et 1c.

Schéma 2 Schéma synthétique pour les trois complexes en l'état neutre 1a, 1b et 1c.


Nous avons ensuite étudié les propriétés électrochimiques de ces trois complexes par
voltammétrie cyclique (Figure 2). Les trois complexes possèdent une bonne réversibilité entre l’état neutre et l’état cationique, et pour 1c, on obtient deux vagues d’oxydation très proches.

Figure 2 les voltamogrammes cycliques pour 1a, 1b and 1c à la vitesse de balayage de 0.2 V·s⁻¹.


Les trois complexes ont été étudiés par diverses spectroscopies (UV-vis, dichroïsme circulaire électronique, spectroscopie infrarouge, dichroïsme circulaire vibrationnel, spectroscopie Raman et activité optique Raman) et par polarimétrie.

Tout d’abord, nous avons étudié les propriétés d’interrupteur rédox en spectroscopie UV-vis. Les expériences ont été menées dans une cellule électrochimique (OTTLE), que l’on peut utiliser pour changer le potentiel tout en enregistrant le spectre. Quand on augmente le potentiel à 0.4 V (vs. fil de platine) les trois complexes 1a, 1b et 1c sont oxydés à l’état cationique [1a]+, [1b]+ et [1c]⁻²⁺ respectivement (Figure 3a le spectre d’évolution pour [1c]⁻²⁺) et on observe des changements dans les spectres UV-vis. Par exemple, on observe que les bandes entre 350 et 550 nm diminuent durant le processus d’oxydation, et en même temps une nouvelle bande est générée à environ 760 nm sur une gamme s’étendant jusqu’à 900 nm. Ce processus est réversible quand on inverse le potentiel à −0.4 V. Par ailleurs, le même processus d’oxydation apparaît par oxydation chimique avec de l’iode (Figure 3b).
LXIX

Figure 3 (a) Le processus d’oxydation électrique de 1c; (b) le processus d’oxydation chimique de 1c observé par spectroscopie UV-visible.

Ensuite, nous avons étudié cette propriété d’interrupteur pour 1b et 1c (Figure 4) en dichroïsme circulaire électronique. Comme dans le spectre UV-vis, on observe aussi l’apparition de la bande à environ 760 nm avec un signe positif pour les énantiomères P à l’état radical cationique.

Figure 4 Oxydation de 1c par iode observée par dichroïsme circulaire électronique.

Le pouvoir rotatoire change aussi entre l’état neutre et l’état radical cationique. Pour P-1c, le pouvoir rotatoire molaire est modifié de $+7.97 \times 10^4$ à $+8990$ par oxydation à la longueur d’onde de 589 nm. Plus intéressant, le pouvoir rotatoire molaire change de signe à la longueur d’onde de 1.54 μm (domaine des télécommunications).

Nous avons également étudié les propriétés optiques et chiroptiques de 1b et 1c dans la région vibrationnelle, et examiné la modification de l’état neutre à l’état radical cation (Figure 5). Ceci est l’un des rares exemples d’hélicènes étudiés par VCD, et aussi le premier exemple d’hélicènes étudiés par modulation chiroptique rédox. Dans le spectre infrarouge, on trouve la vibration de la liaison C=C à environ 2050 cm$^{-1}$, et dans le spectre VCD, le signal correspondant est positif pour les énantiomères $P$ et négatif pour les énantiomères $M$ des deux complexes. Après oxydation à l’iode, le nombre d’onde de cette vibration se déplace vers le rouge à environ 1952 cm$^{-1}$. Plus important est le facteur
dissymétrie $g (\Delta \varepsilon/\varepsilon)$ qui augmente significativement. Pour $[1c]^{-2+,2}\Gamma$, cette valeur augmente de $10^{-4}$ à $10^{-2}$, ce qui est très rare.

**Figure 5** (a) Les spectres VCD (haut) et les spectres IR (bas) pour $P-1c$ (rouge solide) et $M-1c$ (bleu pointillé); (b) Les spectres VCD (haut) et les spectres IR (bas) pour $P-[1c]^{-2+,2}\Gamma$ (rouge solide) et $M-[1c]^{-2+,2}\Gamma$ (bleu pointillé).

De même, nous avons utilisé la spectroscopie Raman et l'activité optique Raman (ROA) pour étudier la région infrarouge (**Figure 6**) dans le domaine de résonance (à 532 nm). Ceci est aussi l’un des rares exemples d’hélicène étudié par spectroscopie ROA. Dans les spectres, on trouve clairement la bande correspondant à la liaison C≡C, et aussi la bande D (environ 1300 cm$^{-1}$) et bande G (environ 1300 cm$^{-1}$) analogues aux molécules de type graphènes. On observe aussi la modulations des spectres par oxydation. Le plus évident est la bande de la liaison C=C qui se déplace vers le rouge, ainsi que la bande D et la bande G qui s’élargissent.
(a) Les spectres ROA (haut) et les spectres Raman (bas) pour $P$-$1c$ (rouge solide) et $M$-$1c$ (bleu pointillé); (b) Les spectres ROA (haut) et les spectres Raman (bas) pour $P$-$[1c]^{2+},2I^-$ (rouge solide) et $M$-$[1c]^{2+},2I^-$ (bleu pointillé).

En conclusion, nous avons synthétisé trois complexes d’hélicène $1a$, $1b$ et $1c$ possédant un ou deux blocs de fer. Nous avons étudié les propriétés optiques et chiroptiques par spectroscopie UV-vis, dichroïsme circulaire électronique, infrarouge, dichroïsme circulaire vibrationnel, Raman, activité optique Raman, ainsi que par polarimétrie. Les complexes $1b$ et $1c$ ont manifesté une bonne réponse à l’oxydation à l’état radical cation, et présenté de bonnes propriétés d’interrupteur chiroptique en spectroscopie de dichroïsme circulaire électronique.

§3 Complexe de ruthénium à base d’hélicène et de DTE comme interrupteur provoqué par rédox et/ou lumière

Dans ce sujet, nous avons synthétisé un complexe de ruthénium à base d’hélicène et de DTE ($4o$), en deux étapes à partir d’un [6]hélicène $2b$, d’un dérivé de type DTE $5o$, et d’un complexe de ruthénium $\text{Ru(dppe)}_2\text{ClO}_2$ (Schéma 4). Les complexes racémiques, et énantiopurs $P$ et $M$ ont été synthétisés à partir respectivement des ligands racémiques et énantiopurs.

Cette molécule possède trois parties : le centre chiral – l’hélicène qui a bonnes propriétés chiroptiques, le centre rédox – le ruthénium qui a bonne réversibilité rédox et une bonne interaction avec ses ligands, le centre de photochrome – le DTE qui a bonne réponse et réversibilité à l’irradiation lumineuse.
2b \((\text{rac-}, P\text{-} \text{or} \ M)\)

6 \((\text{rac-}, P\text{-} \text{or} \ M)\)

6 + 5o

4o \((\text{rac-}, P\text{-} \text{or} \ M)\)

Schéma 4 Synthèse de 4o.

Ce complexe possède une propriété d’interrupteur selon deux façons : l’interrupteur provoqué par stimulus rédox ou l’interrupteur provoqué par la lumière. Si on module le potentiel entre −0.4 et +0.6 V, l’état de ce complexe alterne entre l’état neutre 4o et l’état cationique \([4o]^+\). De même, si on module la longueur d’onde de l’irradiation entre 365 et 650 nm, l’état alterne entre la forme ouverte 4o et la forme fermée 4c. Plus intéressant, quand on étudie la propriété d’interrupteur provoquée par stimulus rédox pour l’état neutre fermé 4c, l’état radical cationique \([4c]^+\) est instable et se transforme directement en \([4o]^+\). Au contraire, l’état ouvert radical cationique \([4o]^+\) est stable et peut être de nouveau réduit à l’état \([4o]\).

Schéma 5 La propriété d’interrupteur provoqué par stimulus rédox et par irradiation de 4.

Pour la propriété d’interrupteur de 4o, nous avons étudié les spectres UV-vis et de dichroïsme.
circulaire électronique, et nous avons observé des modifications des spectre de 4o par irradiation à 365 nm (Figure 7) pour générer 4c, ou par oxydation pour générer [4o]⁺ (Figure 8). Par exemple, nous avons observé une bande à 679 nm pour l’état neutre fermé due à la présence du chromophore DTE avec un Δε = +3 L·mol⁻¹·cm⁻¹ (dans le dichlorométhane, à la concentration 5 10⁻⁵ M). Nous avons également observé une bonne réversibilité pour ces deux processus par réduction via un potentiel bas (−0.4 V) ou par irradiation à 650 nm.

Figure 7 Les spectres de ECD pour P-4o (jaune solide), M-4o (jaune pointillé), P-4c (vert solide) et M-4c (vert pointillé).

Figure 8 Les spectres de ECD pour P-4o (jaune solide), M-4o (jaune pointillé), P-[4o]⁺ (brun solide) et M-[4o]⁺ (brun pointillé).

Nous avons également étudié la modifications des spectres UV-vis et de dichroïsme circulaire électronique (Figure 9) lors de l’oxydation de la forme neutre fermée au cours de laquelle nous avons observé la transformation spontanée de la forme oxydée fermée [4c]⁻ en la forme ouverte [4o]⁺.
Figure 9 Les spectres de ECD pour processus d’oxydation de 4c, P-4c (vert solide), M-4c (vert pointillé), P-[4o]+ (brun solide) et M-[4o]+ (brun pointillé)

Grâce à ses propriétés uniques d’interrupteur moléculaire, cette molécule peut être traitée comme une fonction logique optique. En effet, si on fixe la longueur de l’onde à 679 nm, quand il y a de l’absorption, on définit le signal sortant comme “1”, et quand il n’y a pas d’absorption, on définit le signal sortant comme “0”. Par conséquent, cette molécule manifeste la fonction logique “NOR”.

Figure 10 (a) Symbole de la porte logique “NOR”; (b) table de la fonction logique “NOR”.

En conclusion, nous avons synthétisé un complexe de ruthénium se comportant comme un interrupteur chiroptique provoqué par deux stimuli différents. La propriété d’interrupteur a été étudiée par les spectroscopies UV-vis et dichroïsme circulaire électronique. Ainsi, cette molécule peut être traitée comme la fonction logique optique “NOR”.

§4 Platinahélicènes et borahélicènes

Les hélicènes possédant des ions métalliques ou des hétéroatomes incorporés dans leur squelette π-conjugué sont d’un grand intérêt en raison de l’interaction directe entre l’hélicène et le métal ou l’hétérocycle. Ceci conduit à une riche diversité structurelle et à de nouvelles propriétés photophysiques comme la phosphorescence à température ambiante ou la fluorescence avec un rendement quantique élevé. Dans ce contexte, nous avons synthétisé huit molécules dont quatre platinahélicènes 8a-8d et quatre borahélicènes 9a-9d (Figure 11). Les platinahélicènes ont été synthétisés par la réaction d’ortho-platination à partir des ligands hélicéniques avec un ou deux

Comparé aux complexes de fer ou de ruthénium précédents, les chromophore de type platinacycle ou cycle azaborole sont ici insérés dans le squelette héliénique, ce qui modifie l’interaction entre le chromophore et l’héliène.

Figure 11 Les huit produits synthétisé dans ce sujet.

Schéma 6 Schéma de synthèse de 8b.

Schéma 7 Schéma de synthèse de 9b.
Après avoir obtenu les huit molécules énantiopures, nous avons étudié leurs propriétés optiques et chiroptiques par spectroscopies UV-vis et de dichroïsme circulaire électronique (ECD), ainsi que leur pouvoir rotatoire. Dans le cas du pouvoir rotatoire molaire, on observe que les valeurs augmentent rapidement avec le nombre de cycles fusionnés. En outre, les valeurs obtenues pour les platinahélicènes sont plus élevées que celles des borahélicènes.

**Tableau 1** Les valeurs de pouvoirs rotatoires molaires $[\phi]_{D}^{23}$ (°·cm$^{-2}$·dmol$^{-1}$).  

<table>
<thead>
<tr>
<th></th>
<th>$P$-$8a$</th>
<th>$P$-$8b$</th>
<th>$P$-$8c$</th>
<th>$P$-$8d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P$-$8a$</td>
<td>$+8170$</td>
<td>$+2.25\times10^{4}$</td>
<td>$+8950$</td>
<td>$+3.55\times10^{4}$</td>
</tr>
<tr>
<td>$P$-$9a$</td>
<td>$+5060$</td>
<td>$+1.40\times10^{4}$</td>
<td>$+5210$</td>
<td>$+3.21\times10^{4}$</td>
</tr>
</tbody>
</table>

Dans les spectres ECD (**Figure 12** et **Figure 13**), nous avons observé une bande négative intense à des longueurs d’onde courtes et une bande positive intense à des longueurs d’onde plus longues pour tous les produits de configuration $P$ (excepté pour les dérivés $P$-$8c$ et $P$-$9c$). Ces deux bandes sont très caractéristiques des hélicènes. Les bandes ECD se déplacent vers le rouge quand le nombre de cycles fusionnés augmente parce que le système $\pi$-conjugué est plus étendu.

**Figure 12** Les spectres de ECD pour $P$-$8a$ (jaune), $P$-$8b$ (orange), $P$-$8c$ (rose) et $P$-$8d$ (rouge).
Figure 13 Les spectres de ECD pour $P$-$9a$ (bleu clair), $P$-$9b$ (bleu foncé) $P$-$9c$ (vert clair) et $P$-$9d$ (vert foncé).

Nous avons également étudié les propriétés de luminescence (Figure 14 et Figure 15). Les quatre platinahélicènes sont phosphorescents à température ambiante, et les quatre borahélicènes sont fluorescents. Notamment, le complexe bis-boré $9c$ manifeste une forte fluorescence avec un rendement quantique de 49%. En outre, nous avons examiné la luminescence polarisée circulairement (CPL). Pour les platinahélicènes, les énantiomères $P$ possèdent un signal positif et les énantiomères $M$ un signal négatif. Dans le cas des borahélicènes, les résultats sont différents. $P$-$9d$ présente un signal positif, mais au contraire, $P$-$9a$, $9b$ et $9c$ manifestent les signaux négatifs. La valeur $g_{\text{lum}}$ est utilisée pour évaluer la qualité du signal de CPL, et $8a$ manifeste le plus grand $|g_{\text{lum}}| = 0.011-0.013$.

Figure 14 Les spectres de CPL (haut) et les spectres de luminescence (bas) pour $8a$ ($\lambda_{\text{ex}} = 452$ nm), $8b$ ($\lambda_{\text{ex}} = 452$ nm) et $8c$ ($\lambda_{\text{ex}} = 459 - 469$ nm).
En conclusion, nous avons synthétisé quatre nouveaux platinahélicènes et quatre borahélicènes. Les propriétés optiques et chiroptiques ont été caractérisées par spectroscopies UV-vis et dichroïsme circulaire électronique, par polarimétrie, et par émission non polarisée et polarisée circulairement. Nous avons constaté que les chromophores de type platinacycle ou cycle azaborole, bien qu’ils ne soient pas des éléments stéréogènes, donnent accès à des propriétés de luminescence polarisée circulairement (valeur de facteurs de dissymétrie $g_{\text{lum}}$ jusqu’à $10^{-2}$).

Reference


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Heteroatomic and Organometallic Helicenes: Synthesis and Chiroptical Properties

Résumé

Mes travaux de thèse se sont portés sur la synthèse d'hélicènes organométalliques et hétéroatomiques, et se divisent suivant trois axes majeurs. Le premier sujet est l’étude des hélicènes avec un centre métallique rédox. Nous avons introduit un motif chimique contenant un atome de fer sur l’hélicène connecté par une liaison C≡C. Dans ce sujet, nous avons étudié les propriétés chiroptiques avec le changement d'état rédox du centre métallique. Pour cela, nous avons utilisé des techniques spectroscopiques chiroptiques comme le dichroïsme circulaire vibrationnel, le spectre d’activité optique Raman qui opèrent dans la région infrarouge.


Summary

My PhD work has focused on the synthesis of organometallic and heteroatomic helicenes and is separated into three subjects. The first subject is the study of helicene with one redox metal center. We have introduced a building block containing an iron atom on the helicene connected by a C≡C bond. In this subject, we have studied the chiroptical properties with the change of the redox state of the metal center. Besides, we have used the techniques of chiroptical spectroscopies such as the vibrational circular dichroism, the Raman optical activity which occur in the infrared region. The second subject is the study of helicenes with one redox center and one photochromic center. We have introduced the helicene on the ruthenium building block, and then introduced a photochromic unit DTE (dithienylethene) on the ruthenium through C≡C bonds. This molecule contains three parts: one chiral center, one redox center and one photochromic center. In this subject, we have studied the redox- and/or light-triggered chiroptical switching activity. The third subject is the study on the platinahelicenes and borahelicenes which show one or two platinacycles or azaborole cycles incorporated in the helicene skeleton. In this subject, we have studied the optical and chiroptical properties, and also studied the influence of the number of cycles and number of the heterocycles. These compounds are also studied in the emission properties and circularly polarized luminescence.

Key words

chirality, heterohelicenes, organometallic helicenes, metallahelicenes, chiroptical properties, switching properties.