Kurzzusammenfassung

[2.2]Paracyclophan ist eine gängige cyclische Verbindung, die sich durch π–π Wechselwirkungen und eine verbogene sowie gespannte Struktur auszeichnet. Neben der daraus resultierenden transannularen Wechselwirkung besitzt die Verbindung eine Chiralitätsebene wenn mindestens ein Substituent vorhanden ist. Aufgrund dieser besonderen Eigenschaften ist [2.2]Paracyclophan synthetisch anspruchsvoll und bisher nur wenig erforscht.

Die Fortschritte, welche bei der selektiven Funktionalisierung und chiralen Auflösung von [2.2]Paracyclophan erzielt wurden, haben dieser Verbindung eine Sonderrolle in verschiedensten Anwendungsbereichen eingeräumt. Aufgrund seiner planar-chiralen Eigenschaften findet das Molekül sowohl Verwendung in der asymmetrischen Synthese, als auch in Materialwissenschaften wie zum Beispiel bei energiebezogener Forschung für Photovoltaik, Polymeren oder Parylen-Beschichtungen. Der Fokus liegt hierbei auf der Untersuchung der planaren Chiralität und der für [2.2]Paracyclophan typischen, transannularen elektronischen Kommunikation der sich überlappenden π-Systeme.

Das Ziel dieser Arbeit ist es, neue Synthesemethoden zu entwickeln um den Zugang zu enantiomerenreinen [2.2]Paracyclophanderivaten zu erleichtern und diese in der asymmetrischen Katalyse und den Materialwissenschaften einzusetzen. Außerdem soll das sterisch anspruchsvolle und rigide Gerüst genutzt werden, um sowohl die chirale Kooperativität als auch die Wechselwirkung zwischen zwei Metallzentren zu untersuchen.

Es wurde eine neue Methode zur Enantiomerentrennung mittels kinetischer Auflösung gefunden, welche den Zugang zu einer Reihe an wichtigen [2.2]Paracyclophanbausteinen ermöglicht. Dieses Konzept, welches auf der asymmetrischen Hydrierung beruht, wurde auf mehrfach funktionalisierte Derivate angewendet, sodass neben der kinetischen Auflösung auch eine Desymmetrisierung von *meso*-Verbindungen ermöglicht werden konnte.

Während der synthetischen Problemstellungen wurde eine wenig erforschte Reaktion, die photo-ARBUZOV Reaktion beobachtet. Diese wurde unter dem Aspekt der Mehrfachsubstitution und Dominoreaktion zur Darstellung von Phosphonsäureestern neu beleuchtet.

Auf [2.2]Paracyclophan basierende Alkohole mit zentral chiralem Element, welche unter anderem aus der kinetischen Auflösung erhalten werden konnten, wurden in der chemischen Gasphasenabscheidung verwendet. In der templatbasierten Selbstassemblierung dieser Alkohole wurden Flüssigkristalle genutzt, um Polymerfasern zu erhalten. Hierbei wurde ein Chiralitätstransfer aus der molekularen Ebene in die Nanometer und Mikrometerskala beobachtet.

Des Weiteren wurde die Cyclopropanierung von α-Alkyl-α-diazo-Verbindungen mit einem auf [2.2]Paracyclophan basierendem Rhodium Tetracarboxylat-Katalysator untersucht. Anhand dieser Reaktion wurde ebenfalls eine chirale Kooperativität betrachtet. Hierzu wurde der Carboxylatligand des Katalysators um ein zusätzliches, zentral chirales Element erweitert.

Abschließend wurde die Rigidität, regioselektive Funktionalisierung und transannulare elektronische Kommunikation von [2.2]Paracyclophan für das Design von heterobimetallischen Gold/Ruthenium Komplexen verwendet. Die kooperativen Effekte zwischen den beiden Metallzentren wurden aufgrund ihrer Anwendung als Photoredoxkatalysator mittels photophysikalischer und elektrochemischer Messungen untersucht

Abstract

[2.2]Paracyclophane is a prevalent π-stacked carbocyclic scaffold with a "bent and battered" structure. This results not only in a transannular communication but also in a chiral plane within the molecule if at least one substituent is present. These unique properties make this structure synthetically challenging but also scarcely investigated.

Advances made in both selective functionalization and chiral resolution of [2.2]paracyclophane have made it an important scaffold for a variety of different applications. The inherent planar chirality led to its use not only as catalyst or ligand in asymmetric synthesis, but it has also found its place in material science in e.g., energy materials for photovoltaics, polymers, or parylene coatings. This research focuses on the investigation of the planar chirality and the transannular communication of the two π–systems, characteristic to [2.2]paracyclophane.

This thesis deals with the development of new synthetic methodologies to facilitate access to enantiomerically pure [2.2]paracyclophane derivatives and their application in asymmetric synthesis and material science. Furthermore, the sterically demanding and rigid scaffold was used to investigate chiral cooperative effects and cooperative effects between two metal centers.

A new method for enantio-separation based on the kinetic resolution was developed, which allows the facile access to [2.2]paracyclophane-based building blocks. This concept, which uses asymmetric hydrogenation, was extended to multiply-substituted derivatives, such that beyond kinetic resolution, the desymmetrization of *meso*-compounds was possible.

During synthetic efforts, the scarcely investigated photo-ARBUZOV reaction was observed. Under the aspect of multiple and domino reactions, this phosphorylation method was revisited and reassessed.

In a chemical vapor deposition process, [2.2]paracyclophanyl alcohols containing an additional central chiral element were evaluated. These can be obtained by the previously established kinetic resolution method and were used for the liquid crystal templated self-assembly of nanofibers. A chirality transfer from the molecular to the nanometer scale and even to a mesoscale was observed.

Furthermore, the cyclopropanation of α-alkyl-α-diazo compounds with a [2.2]paracyclophane-based rhodium tetracarboxylate complex was investigated. Based on this, the aspect of chiral cooperativity was examined by incorporating an additional, central chiral element into the carboxylate ligands of the catalyst.

Finally, the rigidity, regioselective functionalization, and transannular communication of [2.2]paracyclophane were exploited in the design of heterobimetallic gold/ruthenium complexes. Cooperative effects of these metal complexes were studied under the aspect of their potential application as photoredox catalysts by photophysical and electrochemical measurements.

1   Introduction

One of the most important and notorious structures in organic chemistry is benzene. It has the simplest and most fundamental structure of aromatic compounds and was first discovered in 1825 by MICHAEL FARADAY.[1] The peculiar reactivity that benzene exhibits, puzzled chemists for a long time and led them to propose various structures to explain this behavior (**Figure 1**). The symmetrical ring of six carbon atoms with alternating single and double bonds that was proposed by KEKULÉ in 1865 ultimately put an end to, at least the discussion about the geometric form. The electronic structure, on the other hand, is still subject to research.[2]
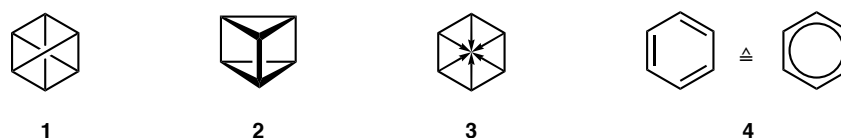

Figure 1. Historic structures of benzene as proposed by CLAUS (**1**), LADENBURG (**2**), ARMSTRONG (**3**), and KEKULÉ (**4**).

The investigation of cyclohexane, the saturated aliphatic analog of benzene, played a central role in the development of organic stereochemistry. Cycloalkanes are classified as small (C_3 - C_4), common (C_5 - C_7), medium (C_8 - C_{12}), and large ($C_{n>12}$) ring systems. The first three classes of cycloalkanes are of considerable interest to chemists due to their inherent ring-strain (BAEYER-, PITZER-, PRELOG strain).[2a, 3]

Conjugated, unsaturated ring systems were also thoroughly studied throughout the years, especially in the context of non-benzenoid aromaticity and the research of annulenes. This class was crucial in the development of the HÜCKEL molecular orbital theory, which led to a whole myriad of new fields of study: non- and anti-HÜCKEL-aromatic compounds, methanoannulenes (**5**), fluxional hydrocarbons (**6**), cyclic benzene isomers (**7**), polycyclic aromatic hydrocarbons (PAHs, **8**), and ultimately fullerenes (**9**, **Figure 2**).[2b]
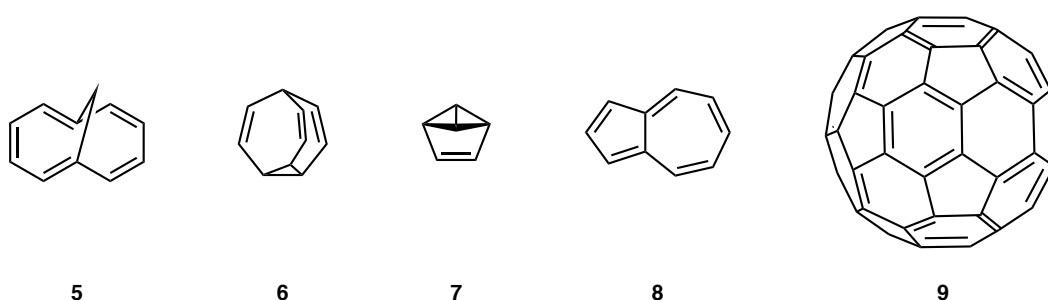

Figure 2. Examples of well-studied ring systems: 1,6-methano[10]annulene (**5**), bullvalene (**6**), benzvalene (**7**), azulene (**8**), and C60-fullerene (**9**).

The previously shown structures infer the current progression to put two- and three-dimensional structures to greater use and employ them in larger molecules such as molecular bands or host-guest molecules.[2a, 4]

The theories and hypotheses that resulted from the study of cyclic compounds and ring systems not only led to the development of new fields of research but contributed substantially to other areas in chemistry, as well.

1.1 [2.2]Cyclophanes

Some of the most noteworthy and intriguing structures belong to the class of cyclophanes. These aromatic compounds are a **cycl**ic arrangement of at least one aromatic core (**ph**enyl) bridged by alk**ane**diyl-chains, hence the acronym **cyclophane** (**Figure 3**). The number of methylene units forming the bridge is given in brackets, while the substitution pattern is given in parentheses. More commonly, the prefixes *ortho-*, *meta-*, and *para-* are used.
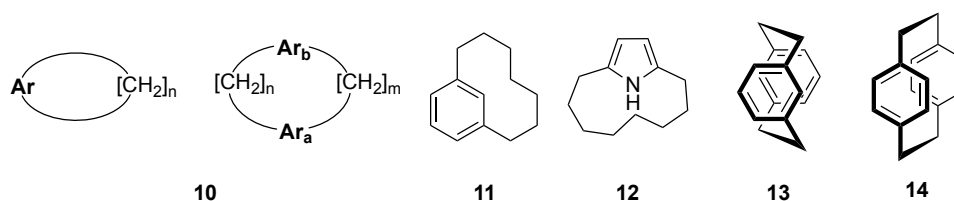

Figure 3. General structures (**10**) and examples of (hetero-)cyclophanes: [7]metacyclophane (**11**), [8](2,5)pyrrolophane (**12**), [2.2]metacyclophane (**13**), and [2.2]paracyclophane (**14**).

Of all cyclophanes, the [2.2]phanes are by far the most interesting compounds and are at the center of cyclophane chemistry. In his first publication about paracyclophanes, CRAM *et al.* stated the peculiar properties that would arise from such systems – namely electronic interactions between the face-to-face aligned aromatic rings whereby the substitution reactions on one aromatic ring are influenced *via* transannular electronic effects by the second aromatic ring. Furthermore, the possibility of intramolecular charge-transfer-complexes and the effects of ring, steric and transannular strain on the molecular structure were highlighted.[5] The investigation of the unique structural and chemical properties that arise in such compounds makes them an exciting field of study. Historically, the first synthesis of a cyclophane was achieved by PELLEGRIN in 1899 *via* WURTZ coupling of 1,3-bis(bromomethyl)benzene to obtain [2.2]metacyclophane (**13**).[6] Apart from this compound, there are five other [2.2]cyclophane isomers, all of which are known and can be synthesized with the exception being [2.2]orthoparacyclophane (**18**). All other isomers apart from **15** show the unique properties that were predicted by CRAM *et al.* – a characteristic deformation of the benzene rings, transannular electronic and steric interactions as well as the necessity of particular synthetic strategies to obtain these compounds.[2a, 7]
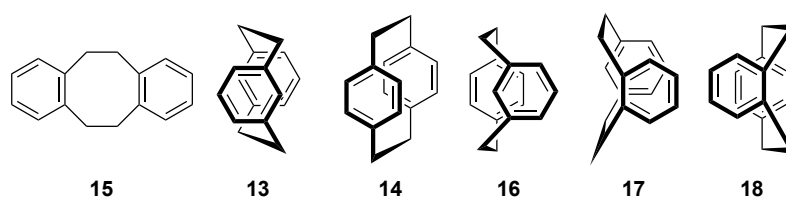

Figure 4. Isomers of [2.2]cyclophane: [2.2]*ortho-* (**15**), [2.2]*meta-* (**13**), [2.2]*para-* (**14**), [2.2]*metapara-* (**16**), [2.2]*orthometa-* (**17**), and [2.2]*orthopara*cyclophan (**18**).
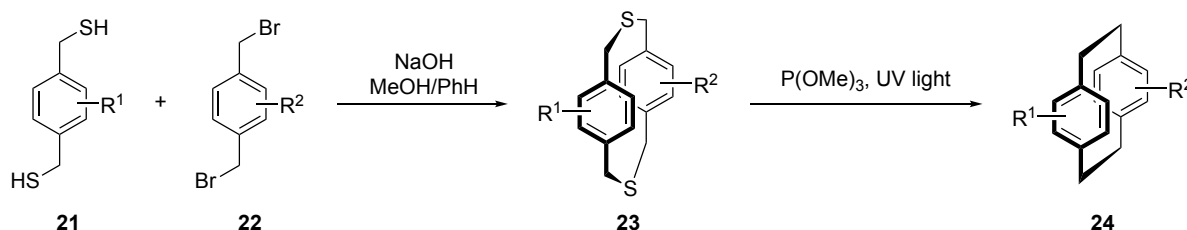
1.1.1 [2.2]Paracyclophane

[2.2]Paracyclophane (PCP, **14**) was first reported by BROWN and FARTHING in 1948 as one of the products obtained from the low-pressure pyrolysis of *p*-xylene and was later synthesized by intramolecular WURTZ reaction.[5, 8] This synthesis route suffers in terms of practicability and yield. The current method to produce [2.2]paracyclophane on an industrial scale is based on the 1,6-HOFMANN elimination of ammonium bromide **19** as described by WINBERG *et al*. in 1960 (**Scheme 1**).[9] By the addition of silver(I) oxide to the ammonium salt **19**, the corresponding ammonium hydroxide intermediate is generated *in situ*. Upon heating, *p*-xylylene (**20**) is formed as reactive species that dimerizes to [2.2]paracyclophane (**14**). By the addition of phenothiazine (PTZ) as a polymerization inhibitor, a yield of 17% was achieved.
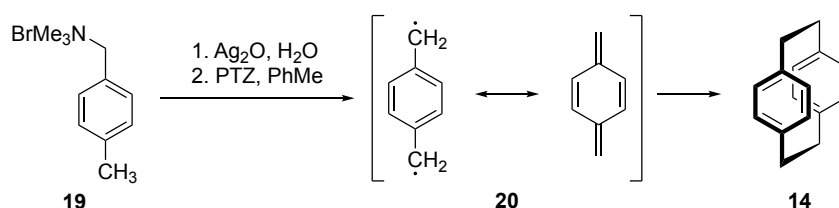
Scheme 1. Synthesis of [2.2]paracyclophane (**14**) *via* 1,6-HOFMANN elimination. PTZ = phenothiazine.

A more general approach, which also allows the synthesis of **14** with functionalized ethylene bridges, disparately substituted decks, and the incorporation of heterocycles such as pyridine into the scaffold, was developed in 1969.[10] In this synthesis route, larger sulfur-containing dithia[3.3]paracyclophanes **23** are synthesized from the corresponding dithiols **21** and dibromides **22** (**Scheme 2**). Even under high dilution, the competing formation of oligomers leads to moderate yields of **23**. Subsequent ring contraction by photolytic sulfur extrusion or sulfone pyrolysis is necessary to form the [2.2]paracyclophane derivatives **24**. Alternative methods and more functional group tolerant methods have been reported and make use of modified conditions for STEVENS[11] or PUMMERER[12] rearrangements.

Scheme 2. General access to unsymmetrically substituted [2.2]paracyclophanes **24** *via* photolytic sulfur extrusion.

The short ethylene chains bridging two benzene rings, each in *para*-position, result in a rigid and highly strained ring system. The consequences of the proximity of the benzene rings to one another are twofold: interaction of the π-electrons of the two decks is observed and secondly, deformation of the benzene rings occurs (**Figure 5**, left). With 3.09 Å, the gap between the two

decks is shorter than the separation of two graphite layers (3.35 Å).[13] The resulting steric strain forces the aromatic rings into a boat form, accompanied by a twist out of the eclipsed state, and to further compensate the transannular steric and electronic interactions, the CH_2–CH_2 bond length of the bridges is considerably larger than usual. The small separation of the decks in [2.2]paracyclophane not only leads to a distorted geometric structure, but also to an overlap of the π-electrons such that a single, over both rings extended π-system, is formed. The bending of the decks causes a rise in energy of the HOMO (highest occupied molecular orbital) as well as a lowering of the LUMO (lowest unoccupied molecular orbital), which is a consequence of the torsion of the π-bonds. A reduced aromatic character is a result that leads to increased reactivity of [2.2]paracyclophane towards electrophilic substitution reactions. A substituent that is introduced to one of the benzene rings influences further substitution reactions. The effect is not only towards the already substituted deck but is also significant on the second ring. In the case of an electron-withdrawing substituent e.g., further functionalization *via* electrophilic aromatic substitution is disfavored on both rings.[2a, 7, 13a] Temperature-dependent X-ray analysis has shown that [2.2]paracyclophane, even though a highly strained and rigid scaffold, exhibits a concertina movement in which the benzene rings draw closer together and push apart (**Figure 5**, middle) as well as a twisting vibration where the decks rotate in opposite directions to one another (**Figure 5**, right).[2a, 4b, 14]
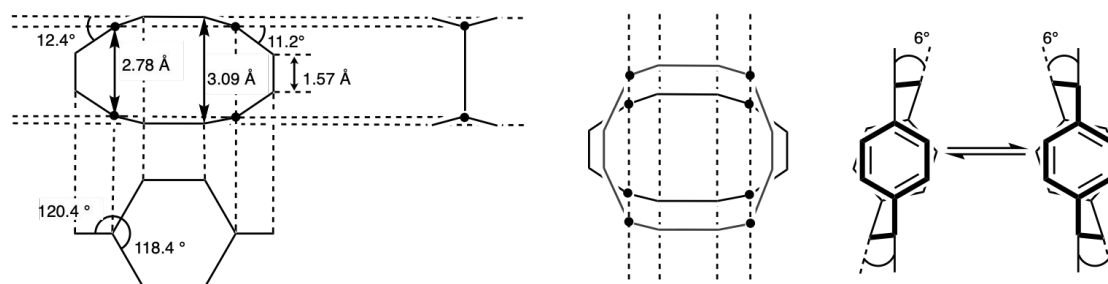

Figure 5. Geometry (left), concertina movement (middle) and twisting vibration (right) of [2.2]paracyclophane.

At room temperature, [2.2]paracyclophane belongs to the D_{2h} point group and thus features a C_2-axis as well as a σ_h- plane. Even though [2.2]paracyclophane shows a concertina and twisting movement, it cannot rotate freely alongside the bridges, which allows the symmetry to be broken by introducing a substituent either to one of the bridges or to one of the benzene rings. The former introduces a central chiral element, whereas the latter renders the molecule planar chiral. To determine the planar chirality, the substituted benzene ring is set as the plane of chirality, and the first atom closest to the substituent, but outside the plane of chirality is set as a pilot atom (1, **Figure 6**). In the case of multiple substitutions, the substituent with the highest priority according to Cahn-Ingold-Prelog rules is preferred. The stereodescriptor (R_p) or (S_p) is determined by the sense of rotation, viewed from the pilot atom.[15]
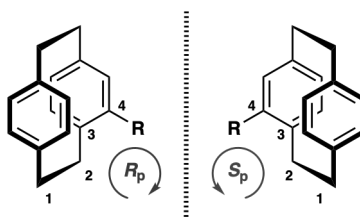
Figure 6. Planar chirality of monosubstituted [2.2]paracyclophane.

Apart from few examples that resort to a *de-novo* synthesis to access functionalized derivatives of [2.2]paracyclophane, the electrophilic aromatic substitution of the parent compound is the most convenient and most common entry point to functionalized derivatives. By controlling the stoichiometry, reaction temperature, and time, monofunctionalization is possible in a highly selective manner. That way, the corresponding formyl, bromo, and nitro compound, as well as a variety of FRIEDEL-CRAFTS acylation (FCA) products, can be obtained. These basic structures allow further functionalization by well-established synthetic procedures and the separation into their enantiomers, either by (semi-)preparative chiral HPLC or chiral derivatization.[16]

More challenging is the synthesis of difunctionalized [2.2]paracyclophane derivatives with a defined substitution pattern. The distribution of regioisomers in the electrophilic aromatic substitution of monofunctionalized [2.2]paracyclophane was studied by CRAM and REICH.[7, 17] Their experimental findings were not the distribution of products that was expected from the assumed transannular resonance effect. Upon double bromination and acylation, the pseudo-*ortho* and pseudo-*para* isomers are the main products that were obtained. The canonical structures **25** with an electron-donating, and the structures **26** with an electron-withdrawing substituent in place, pseudo-*meta*/pseudo-*geminal* and pseudo-*ortho*/pseudo-*para*, respectively are the major products that were expected (**Figure 7**). Instead of looking at the transannular resonance structure, the intraannular resonance structures **27** give a good explanation for the experimental results. A correlation between the most basic positions on the substituted ring and the observed regioselectivity explains the transannular directing effect, which was described in detail by CRAM *et al*.
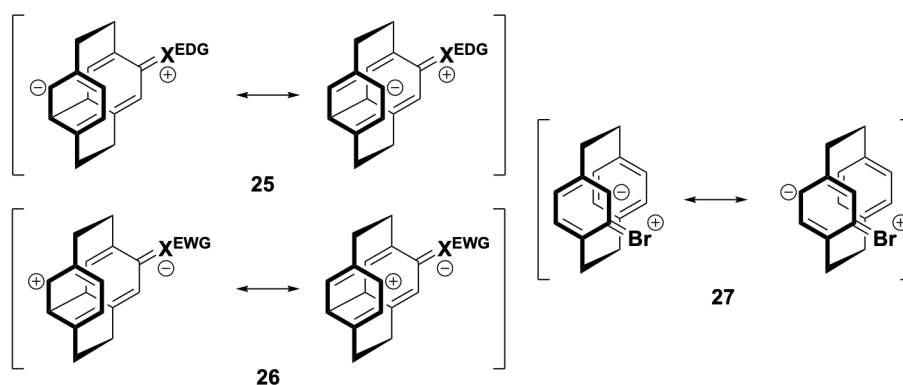

Figure 7. Interannular resonance structures for S$_E$Ar reactions of [2.2]paracyclophane bearing an electron-donating (EDG, **25**) or an electron-withdrawing (EWG, **26**) group. Intraannular resonance structure of 4-bromo[2.2]paracyclophane (**27**).

This unique directing effect is especially useful in the bromination of [2.2]paracyclophane deriv-atives with a basic oxygen (carboxy, methoxy, acetyl, nitro, etc.) or nitrogen (pyridyl, oxazolyl, etc.) substituent. Thermodynamically unfavored, but kinetically preferred, high selectivity for the pseudo-*geminal* isomer is observed.[18]

The pseudo-*geminal*/pseudo-*meta* and the pseudo-*para*/pseudo-*ortho* isomers can easily be in-terconverted. Upon heating [2.2]paracyclophane above 200 °C, the high ring strain causes the ethyl bridges to be cleaved homolytically forming a diradical intermediate (**29**, **Scheme 3**), which can rotate freely. For monosubstituted derivatives, this only leads to racemization. But in this way, disubstituted [2.2]paracyclophanes such as the easily accessible pseudo-*para* dibromide (**28**) can be isomerized to the pseudo-*ortho* derivative **30**. This reaction leads to a 1:1 mixture of both isomers, whereas the steric repulsion of the substituents in pseudo-*geminal* derivatives leads to much higher isomerization ratios.[18-19]
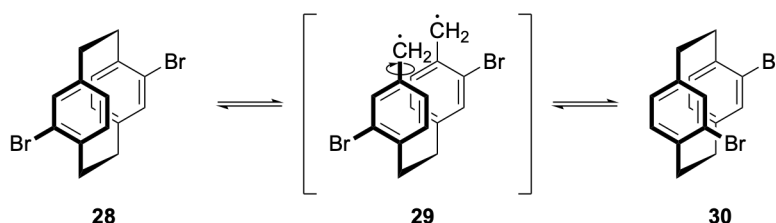
Scheme 3. Thermal isomerization of 4,16-dibromo[2.2]paracyclophane (**28**).

1.1.2 Application of [2.2]Paracyclophane

The considerable advances in the selective functionalization and chiral resolution of [2.2]paracy-clophane have gained this compound a unique position in a multitude of applications. It has been widely used for its planar chiral property in asymmetric synthesis[16b-d] but also for energy mate-rials, π-stacked polymers,[20] parylene coatings,[16b, 21] and various applications in material science with a special focus on the investigation of planar chirality and through-space conjugation.[4b] Here, only the aspect of asymmetric catalysis and parylene coatings by chemical vapor deposition (CVD) polymerization will be considered in detail.

Asymmetric Synthesis based on [2.2]Paracyclophane

Enantioselective synthesis does not rely exclusively on central chirality (**31**, **Figure 8**). Axial chiral ligand systems where e.g., binaphthyl is used as backbone (**32**) [22] or the incorporation of planar chiral elements based on ferrocene (**33**) are well established. Since the success of planar chiral ferrocene-based systems, especially the JosiPhos family, the element of planar chirality has taken a crucial role in the development of modern ligand systems.[23] Compared to these ligand sys-tems, however, the [2.2]paracyclophane scaffold was overlooked for a long time and had not been used as a chiral ligand until the early 1990s. The synthesis of enantiomerically pure PhanePhos (**34**) by PYE and ROSSEN has sparked an ever-increasing interest in [2.2]paracyclo-phane-based ligand systems.[24] Its potential in stereoselective synthesis is exceptional due to its

configurational stability up to 200 °C, stability towards acids and bases, easy functionalization, and the diversity of chiral structures that are accessible by changing the substitution pattern.[16a, 16c, 16d]
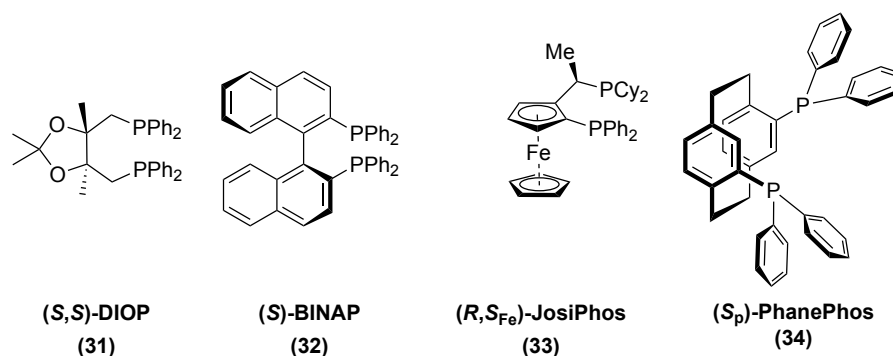

Figure 8. Selected central (**31**), axial (**32**), and planar chiral (**33** and **34**) ligand systems.

Currently, the prevailing ligand system based on [2.2]paracyclophane are disubstituted derivatives. Only few monosubstituted derivatives were successfully employed with a highly enantioselective reaction outcome and have therefore gained little attention. However, promising results were achieved by the incorporation of an additional central chiral stereocenter. This type of cooperative chirality and the role of the planar chiral [2.2]paracyclophane scaffold is yet to be investigated in detail.[16c, 16d]

CVD Polymerization of [2.2]Paracyclophane

Chemical vapor deposition (CVD) enables the coating of nearly any surface with a polymer. In this solvent-free method, gas-phase monomers spontaneously polymerize at interfaces to form thin, macromolecular films. Since CVD is a solvent-free method, it also enables the synthesis of insoluble polymers, highly crosslinked organic frameworks and minimizes unwanted side-reactions that may occur in solution as well as co-polymerization of monomers. This makes this process ideal for substrates that swell, dissolve, or degrade in solution. For some substrates and polymers, CVD polymerization is the only fabrication option available which has made it a leading research topic in biotechnology, optoelectronics, photonics, nanotechnology, and microfluidics.[21b, 25]

The process itself was described by GORHAM in 1966 to prepare non-functionalized poly-*p*-xylylenes (**36**).[26] By sublimation of [2.2]paracyclophane or functionalized derivatives thereof (**24**), the compound is transferred into the gas-phase and a pyrolysis zone (**Scheme 4**).[21b] Under high temperature, the ethylene bridges are cleaved homolytically and nearly quantitatively without forming any side products. The corresponding quinodimethanes **35** are generated and spontaneously polymerize in the cooler deposition chamber. The individual control of the polymerization parameters including pyrolysis temperature, pressure, carrier gas flow, and substrate temperature allows the use of a wide range of functionalized [2.2]paracyclophanes to be deposited on almost any surface. Not only does this allow post-CVD surface engineering but also for

sequential deposition of different precursors, random co-polymers, gradients and microstructuring.[4b, 21b]
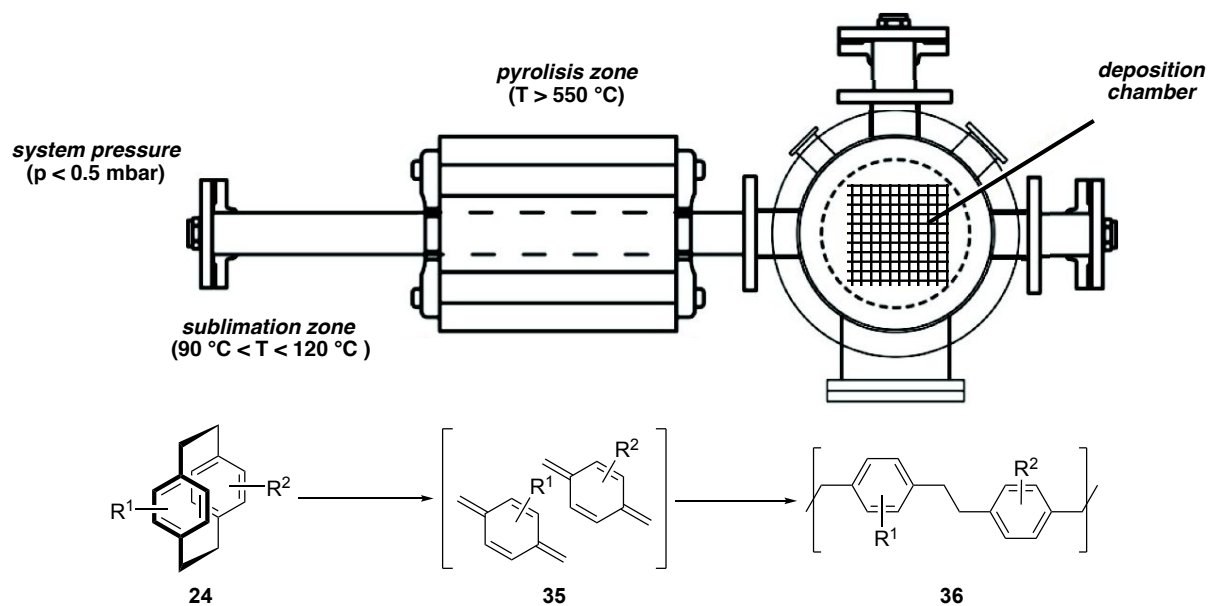
Scheme 4. Schematic setup of an apparatus used for CVD polymerization to prepare parylene coatings. Adapted with permission from H. Y. Chen, Langmuir 2010. Copyright (2011) American Chemical Society.[21b]

The low process temperatures and absence of solvent in the CVD polymerization process gives excellent control over the thickness and chemical composition of the polymer that is deposited. The ability to precisely control the properties of the coating has opened the path for surface patterning and the fabrication of 1D and 2D structures.[21, 27]

1.2   Photoredox Catalysis

Over the past decades, photochemical reactions have emerged as an exceptional tool in synthetic organic chemistry with the potential to construct molecular complexity under very mild conditions.[28] All light-driven reactions involve electronically excited states that result from the absorption of photons. The highly reactive and transient intermediate that is generated alters the properties of the compound drastically and enables unusual reaction pathways, unattainable through thermal reaction control.[29] Classical photochemistry uses ultraviolet (UV) light for the direct excitation of organic compounds to generate these intermediates. The perception of the discipline as inconvenient with the need for a special reaction setup without general application has precluded photochemical reactions from their wide-spread use.[30] However, the seminal works by MacMillan, Yoon, and Stephenson in 2008 were milestones in popularizing photocatalysis as a means to generate the intended product in high yield and with excellent selectivity.[31] The great advantage of using lower energy visible instead of high energy UV light allows a much simpler reaction setup using light bulbs, compact fluorescent lamps, or LEDs. In many cases the reactions have a higher selectivity, are more predictable, and easier to control than UV light-driven reactions.[30]

Nevertheless, most organic molecules do not interact with the wavelengths of visible light which makes its use in photochemical synthesis especially challenging.[32] The development of organic and transition metal photocatalysts, as well as a variety of photosensitizers, has pathed the way for practical synthesis strategies involving radical ions, diradicals, and electronically excited compounds.[33] The generic activation modes by which a photocatalyst (PC) drives the selective reaction of a substrate have increased drastically over the years (**Scheme 5**). The most common are (i) energy transfer, (ii) atom transfer, and (iii) electron transfer.[33] In this thesis, only electron transfer will be discussed.
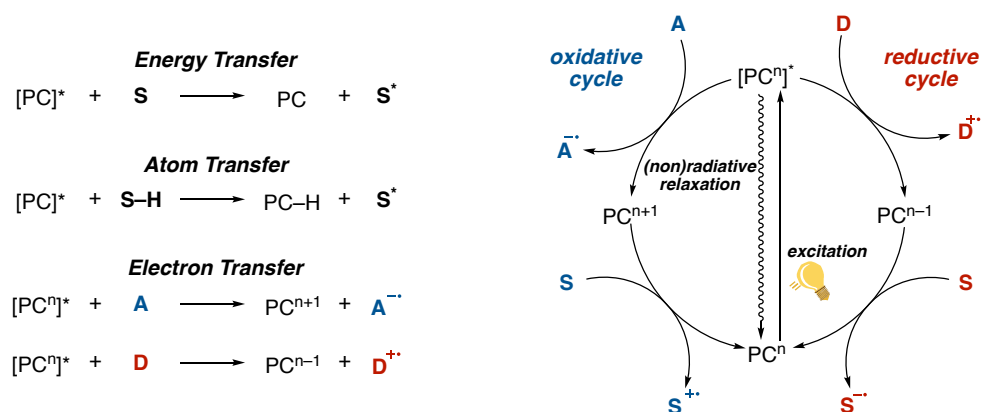

Scheme 5. Generic activation modes of a photocatalyst (left), and electron transfer process (right). A – acceptor, D – donor, S – substrate, PC – photocatalyst (ground state), PC* – photocatalyst (excited state).

In the electronically excited state, molecules exhibit profoundly different reduction and oxidation properties compared to their ground state. In photoredox catalysis, an additional light-absorbing compound is used to initiate or modulate the redox process.[34] Upon excitation, the catalyst can either remove (oxidative cycle) from or donate (reductive cycle) an electron to organic or organometallic substrates by a single electron transfer (SET) process which gives access to highly reactive radical species under mild reaction conditions. A variety of organic dyes such as eosin Y, 9,10-dicyanoanthracene, or triphenylpyrylium salts as well as a large array of redox-active metal complexes absorb light in the visible region and allow a SET to occur from the excited state.[29, 35] An absorption in the region of higher energy visible light (400-475 nm) is considered desirable to make use of the maximum potential energy without the disadvantage of undesired side reactions that come with the direct excitation of organic molecules.[36] Ruthenium and iridium-based polypyridyl complexes proved most versatile and efficient. Other approaches using organic molecules, heterogeneous semiconductors, or various metal oxides and sulfides, are equally capable in photoredox catalysis and have their place in organic synthesis.[37] The principles of photoredox catalysis, however, will be discussed of the prototypical complex tris(bipyridine)ruthenium(II) (**37**).

Upon irradiation, an electron from the filled t_{2g} orbital of the ruthenium center is lifted into the empty π^* orbital of the 2,2'-bipyridine (bpy) ligand, creating an electron-hole at the metal center

in the form of a single occupied t_{2g} orbital. The dipolar excited state **37*** created in this transition, called metal to ligand charge transfer (MLCT), can act as both, reducing and oxidizing agent and provides access to redox-neutral processes (**Scheme 6**).[38]
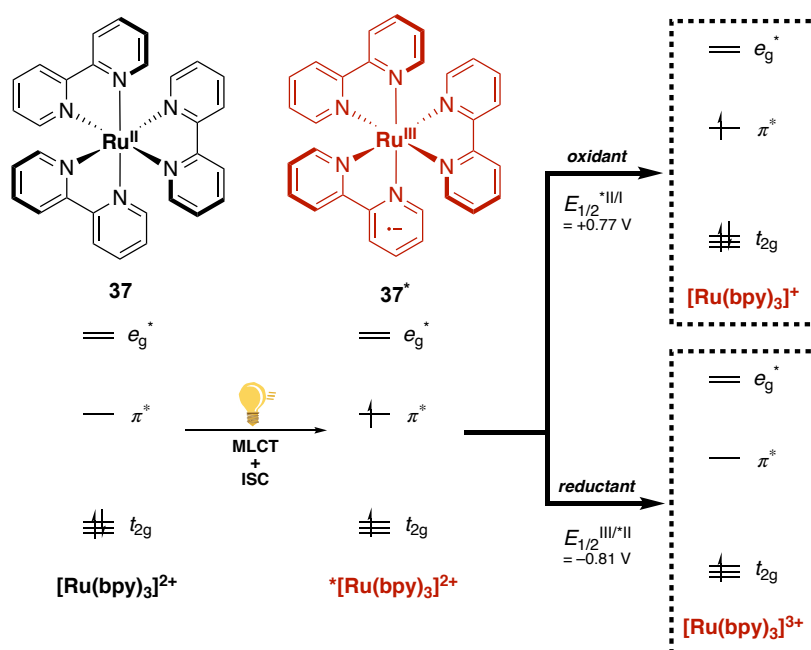
Scheme 6. Metal to ligand charge transfer (MLCT) in $[Ru(bpy)_3]^{2+}$ (**37**) to its excited state **37***. bpy = 2,2'-bipyridine. (*) indicates either the excited state or an anti-bonding orbital.

The reactivity and kinetic features that govern molecular photophysical processes can be represented by a state diagram, also referred to as the JABLONSKI diagram (**Figure 9**, left).[37c] Metal to ligand charge transfer promoted by light ($\lambda_{max}([Ru(bpy)_3]Cl_2)$ = 452 nm) occurs from the singlet ground state ($^1A_1$) of the photocatalyst into one of numerous excited singlet states [*PC ^{1}MLCT$_n$]. Initial relaxation by internal conversion (ic) into the lowest spin-allowed singlet states [*PC ^{1}MLCT$_1$] occurs. Rapid inter-system crossing (isc) into the triplet state manifold takes place, followed by internal conversion to the long-lived first triplet excited state [*PC ^{3}MLCT$_1$]. Other deactivation pathways such as fluorescence and internal conversion from [*PC ^{1}MLCT$_1$] only play a minor role.[36, 38] The resulting triplet excited state is long-lived (1100 ns) and capable to participate in single-electron transfer processes. The redox behavior of the metal center in polypyridyl ligands can be described as oxidation of the metal and reduction of the ligands, which allows an adjustment of the ground state redox potentials by different metal-ligand combinations.[36, 39]
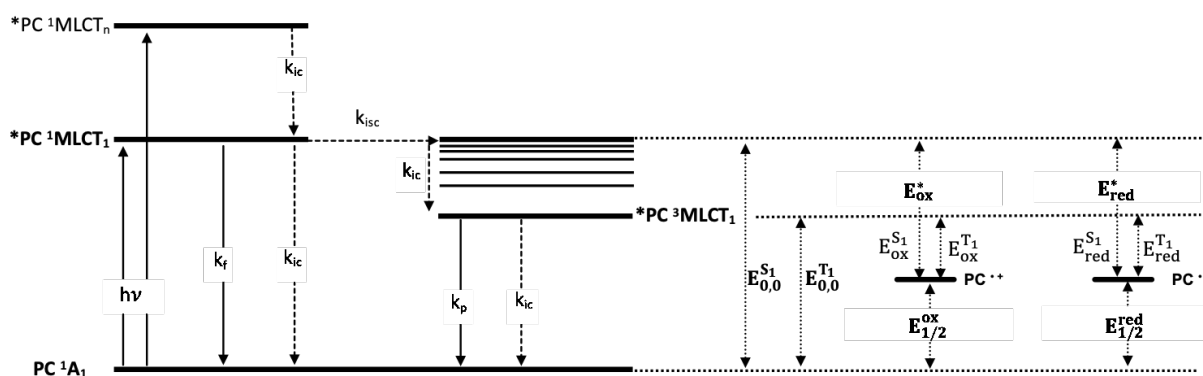
Figure 9. Simplified JABLONSKI diagram (left) and correlation to ground state and excited state (*) potentials (right). ic – internal conversion, isc – intersystem crossing, f – fluorescence, p – phosphorescence.

In its excited state, the overall energy content of the photocatalyst is higher than in the ground state, which also makes it both a stronger oxidant and reductant than it is in the ground state. In contrast to the ground state redox potentials, the excited state potentials cannot be measured easily and are therefore calculated from cyclovoltammetry and spectroscopic data.[40] An approximative value is obtained from a method developed by REHM and WELLER using the maximum emission of the catalyst (**Equation 1**).[41]

$$E_{red}^* = E_{1/2}^{red} + E_{0,0} + \omega_r$$

$$E_{ox}^* = E_{1/2}^{ox} - E_{0,0} + \omega_r$$

Equation 1. REHM and WELLER'S theory for the approximation of the excited state reduction potentials. E^* = excited-state potential. $E_{0,0}$ = zero-zero transition energy. $E_{1/2}$ = ground state potential. ω_r = coulombic term.

The zero-zero transition energies ($E_{0,0}$) and the ground state potential ($E_{1/2}$) relate to the excited state potentials (E^*). The COULOMB term ω_r, which accounts for electrostatic interactions that arise from charge separation and is generally omitted due to its overall small contribution (< 0.1 eV).[37c]

2   Objective

[2.2]Paracyclophane is a prevalent π-stacked carbocyclic scaffold with a "bent and battered" structure with peculiar properties. The research of this thesis focuses on the investigation of the planar chiral properties and the transannular communication of the two π–systems, characteristic to [2.2]paracyclophane (**Figure 10**).
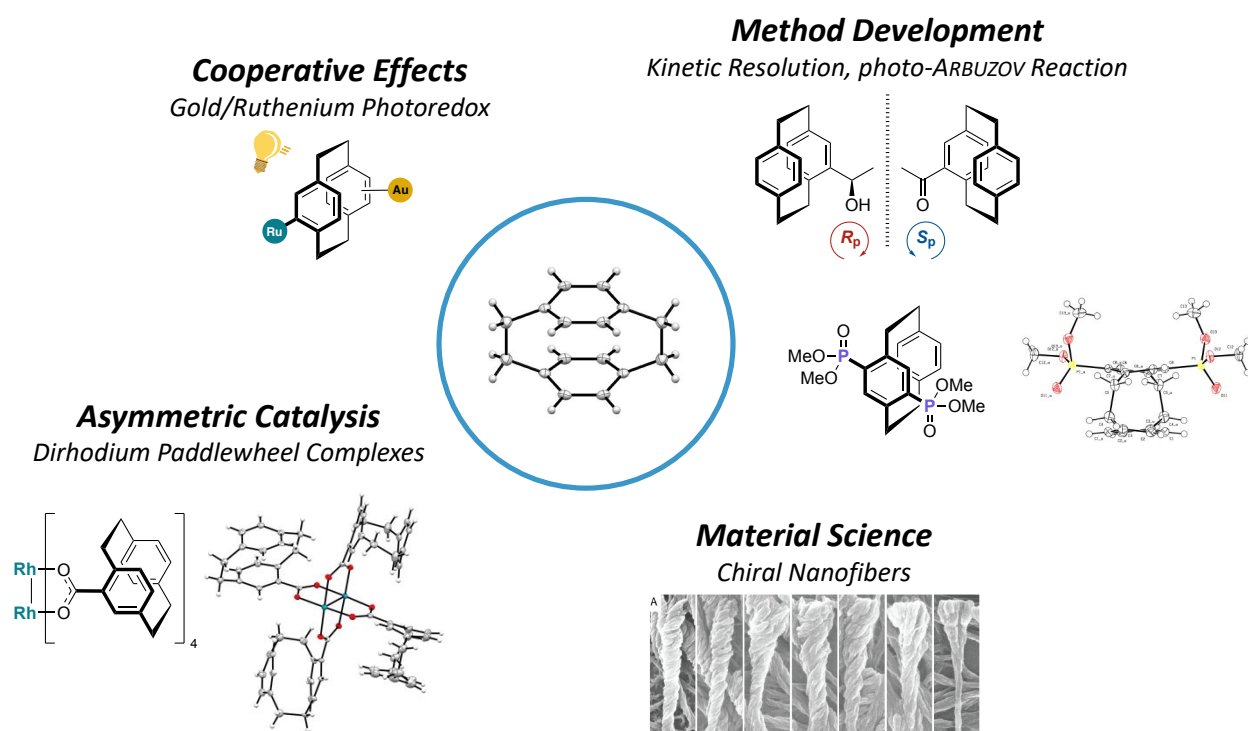

Figure 10. Projects of this thesis for the investigation of the planar chirality and the transannular communication in [2.2]paracyclophane.

In the first part of this thesis, a reliable and facile method to access enantiomerically pure [2.2]paracyclophane derivatives on a multi-gram scale was developed. These derivatives could then be used in the synthesis of chiral catalysts and ligands as well as chiral precursors for material applications. The photo-ARBUZOV reaction of aromatic halides, which was observed during the *de-novo* synthesis of *para*-disubstituted [2.2]paracyclophane, was revisited and reassessed under the aspects of multiple and domino reactions.

In the second part, chiral [2.2]paracyclophanyl alcohols, which can be obtained by the previously established method for enantio-separation, were employed in the liquid crystal templated self-assembly of nanofibers. The aim here was to study the chirality transfer from the molecular to the nanometer and mesoscale.

Rhodium tetracarboxylate complexes based on [2.2]paracyclophane were investigated in the third part of this thesis. These were tested in cyclopropanation reactions while taking a closer look at chiral cooperativity by incorporating an additional, central chiral element into the carboxylate ligand of the catalyst.

In the last chapter, the rigid [2.2]paracyclophane scaffold was used to install Au(I) and Ru(II) centers in well-defined and fixed distances to one another. Photophysical and electrochemical measurements of these metal complexes were then taken to analyze M–M interactions and the influence of transannular and through-space communication.