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Minireview

Functionalized Cyclophanes | *Very Important Paper* |

VIP

Beyond Simple Substitution Patterns – Symmetrically Tetrasubstituted [2.2]Paracyclophanes as 3D Functional Materials

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Abstract: [2.2]Paracyclophane is the prototypical layered hydrocarbon and has been essential for investigations of through-space electronic interactions. Over the last years more examples of tetrasubstituted derivatives have been reported. This mini-review discusses the synthetic approaches towards various substitution patterns and provides a survey over different approaches used to achieve and derivatize symmetric tetrasubstitution. The first two sections of this work present homo-tetrasubstituted derivatives, while the third section gives insight into symmetrically hetero-tetrasubstituted analogues. These approaches are briefly discussed, the resulting structures are presented in detail, and their specific properties resulting from the incorporation of [2.2]paracyclophane are elucidated.

1. Introduction

In 1949, *Farthing* and *Brown* isolated [2.2]paracyclophane (PC, **1**) as by-product from low-pressure pyrolysis of *para*-xylene.[1] This prototypical layered molecule was for the first time successfully synthesized through an intramolecular macrocyclization only two years later by *Cram* and *Steinberg*, who also demonstrated the transannular electronic communication of the benzene rings by means of UV/Vis spectroscopy.[2] *Cram* and *Reich* were further able to elucidate the chemistry of PC, where they found remarkable transannular effects and unique behavior, for example in thermal isomerization of substituted isomers and in directing effects, which can dominate the direction of the electrophilic aromatic substitution on PC derivatives.[3–5] Nowadays, the focus has shifted away from the chemical modification of PC and its application in asymmetric catalysis, and materials chemistry is now in the foreground.[6–8] The extraordinary configuration of the molecule displays a face-to-face arrangement of a two slightly-bent aromatic rings, with short inter-ring distances between 2.83 and 3.09 Å. It allows an effective transannular charge transfer between the benzene rings, leading to unique applications of PC derivatives in optoelectronics, non-linear optics, chemical vapor deposition or photoluminescent conjugated polymers.[2,7,9] Until recently, most of these materials were based on mono- or disubstituted PCs due to their well-known chemistry.[10] Higher substituted PCs were barely isolated,[11,12] although the formation of symmetrical tetrasubstituted PCs was reported by the elimination of sulfur for appropriately substituted 2,11-dithia[3.3]paracyclophanes in low yields.[13,14] Nowadays, dedicated chemists achieve the efficient synthesis and modification of symmetrical tetrasubstituted CPs, which have led to the design of a variety of complex

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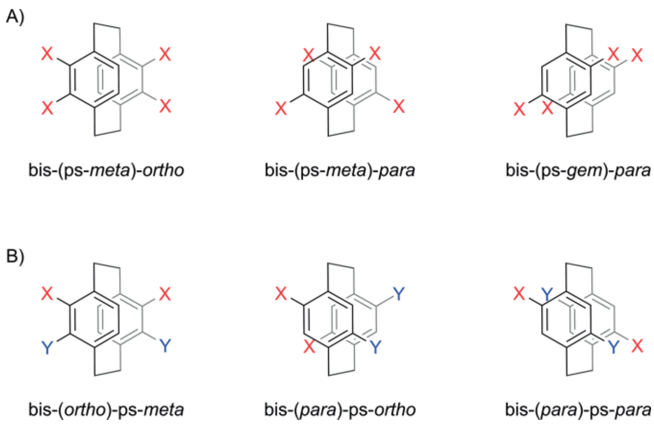
Marcel Mayor received his PhD in 1995 from the University of Bern under the supervision of Rolf Scheffold and Lorenz Walder. After working with Jean-Marie Lehn at the University Louis Pasteur in Strasbourg (France) and at the Collège de France in Paris (France), he founded his own research group in the Institute of Nanotechnology (INT) at the Karlsruhe Institute of Technology (KIT, Germany) in 1998. In 2004 he became Professor of Chemistry at the Department of Chemistry of the University of Basel (Switzerland), and in 2011 he became adjunct Professor of Chemistry of School of Chemistry of the Sun Yat-Sen University in Guangzhou (China). His current research interests are supramolecular chemistry, molecular electronics, nanoscale architectures, functional and hybrid materials.

and interesting molecules based on these building blocks, with promising applications.

In this minireview we provide an overview over tetrasubstituted PC scaffolds (Scheme 1). We will discuss the different synthetic strategies, as well describing the most remarkable optical and electronic properties. Here, we will show that tetrasubstituted PCs can be easily achieved in a statistical approach. We will further present advances made towards chiral resolution of planar chiral tetrasubstituted PCs. We will demonstrate that symmetrically tetrasubstituted PCs serve as key building blocks that are used to investigate transannular charge transfer and optoelectronical properties. Furthermore, we will present examples, where chiroptical effects are introduced through helically chiral tetrasubstituted PCs.



Scheme 1. Overview of some symmetric fourfold homo-substituted (A) and hetero-substituted (B) PC patterns discussed in this mini-review. The nomenclature used is based on the suggestion of *Hopf* and co-workers,[7] labelling the spatial relation between substituents attached to opposed phenyl rings with the prefix "ps" for "pseudo".

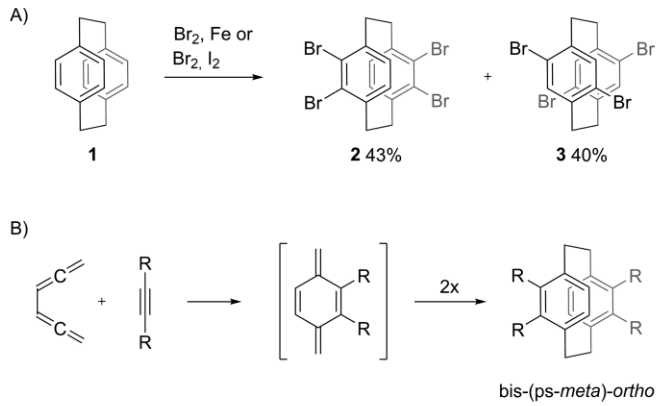
The review is organized by the molecules structures and not from a chronological perspective. It is divided in 3 sections. The first two describe molecules whose design and structure are based on tetrasubstituted PCs with identical substituents in positions 4, 5, 12, 13 and 4, 7, 12, 15 (bis(ps-*meta*)-*ortho* and bis(ps-*meta*)-*para* isomers respectively), and the third one focuses on tetrasubstituted PCs derivatives with unequal substituents. While there are different nomenclatures found in literature, we rely on the one introduced by Hopf and co-workers.[7]

2. Bis(ps-*meta*)-*ortho*-homo-tetrasubstituted [2.2]paracyclophanes

In 1969 *Cram* and *Reich* reported on the reaction of PC with an excess of bromine, which leads to two main tetrabrominated products, compound **2** and **3**.[5] They were able to isolate both compounds by means of column chromatography and further derivatize both compounds (see Scheme 2, A).

In 1992, *de Meijere* and co-workers demonstrated that the treatment of PC with liquid bromine and catalytic amounts of iodine over seven days at room temperature leads to two structural isomers of homo-symmetrically tetrasubstituted PC.[15]

The isomers could be separated on the basis of their different solubility in dichloromethane. The isomers **2** and **3** are often used as precursors of functionalized homo-tetrasubstituted PCs with either a bis(ps-*meta*)-*ortho* or a bis(ps-*meta*)-*para* substitution pattern, respectively. This chapter will discuss the bis(ps-*meta*)-*ortho* arrangement, the discussion of the bis-(ps-*meta*)-*para* configuration is given in the next chapter. An alternative synthetic approach has been reported for bis-(ps-*meta*)-*ortho* homo-tertasubstituted PCs,[16] which can be obtained directly by a one-step *Diels-Alder* cyclization using acetylene precursors decorated with electron withdrawing groups (Scheme 2, B). A variety of symmetrically functionalized PC derivatives was obtained by this strategy, and some of the exposed electron withdrawing groups could be further modified.[16]

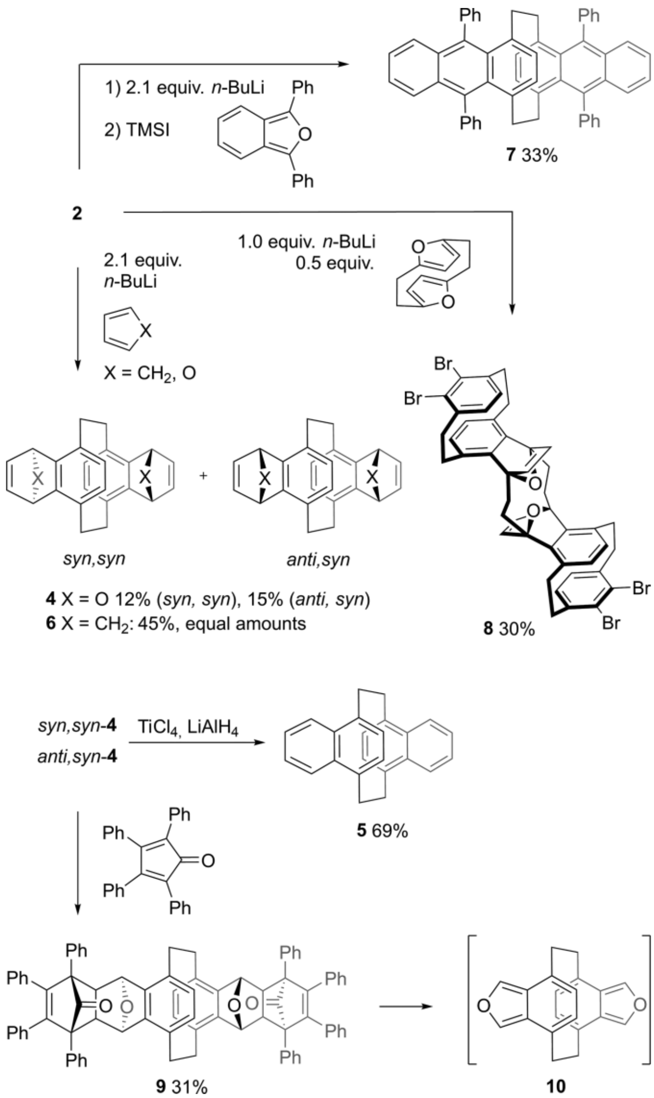


Scheme 2. A) Synthesis of bromine precursors of bis(ps-*meta*)-*ortho* and bis(ps-*meta*)-*para* homo-tetrasubstituted PCs, **2** and **3**, respectively. Yields reported from *de Meijere* and co-workers.[15] B) Alternative approach to bis-(ps-*meta*)-*ortho* PCs obtained by direct *Diels-Alder* cyclization (R = electron withdrawing e.g. CO_2CH_3, $CO_2C_2H_5$, CO_2H, CN, CF_3).

In 1992, *de Meijere* and co-workers, isolated compounds **2** and **3** on large scale by exploiting their different solubility. The authors report on one derivative obtained from **2**, where they achieved a fourfold *Heck* coupling with styrene. The obtained chromophore shows intense blue-green fluorescence when exposed to daylight. Following up on their seminal work on homo-tetrasubstituted PC, *de Meijere* and co-workers developed a strategy, where **2** was employed as an aryne equivalent.[17] Both *Cram* and *Reich*,[5] as well as *de Meijere* and co-workers found, that **2** can be used as a bis-aryne equivalent upon treatment with two equivalents of *n*-butyllithium (*n*BuLi).

When the aryne is generated in the presence of furan *syn,syn*-**4** and *anti,syn*-**4** are obtained in 12 and 15 % yield, respectively, while the *anti,anti*-isomer was not observed (Scheme 3). Further reductive deoxygenation with low-valent titanium leads to **5.** The authors successfully applied the same strategy to the reaction of the bis aryne with cyclopentadiene. The ratio of regioisomers for the synthesis of *syn,syn*-**6** and *anti,syn*-**6** is the same as for **4**. When reacting **2** with 2,5-diphenylisobenzofuran, **7** could be obtained in higher yields, but could only be deoxygenated with in situ generated trimethylsilyl iodide.

Interestingly, after treating **2** with one equivalent of *n*BuLi and trapping of the intermediate with a half-equivalent of [2.2]furanophane, stair-like molecule **8** could be obtained,



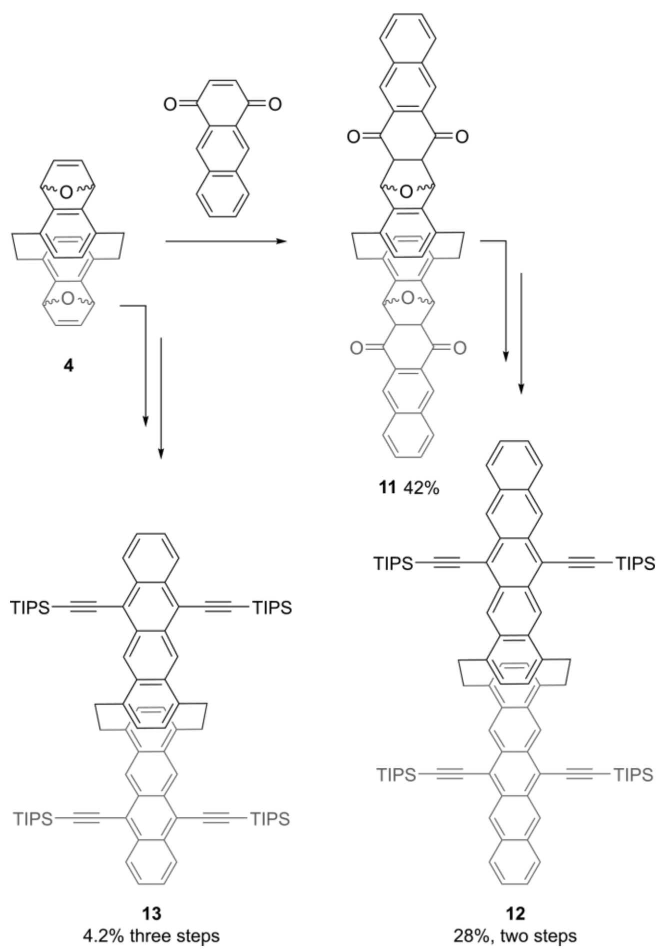
Scheme 3. Scope of the reactivity of **2** under aryne-forming conditions.[5,17,18] Only one stereoisomer of **9** is shown.

where the deoxygenation was unsuccessful, due to steric hindrance of the cyclic ethers. When *syn,syn*-**4** and *anti,syn*-**4** where refluxed with tetraphenylcyclopentadienone in benzene, the *Diels-Alder* adduct **9** was obtained as a mixture of four stereoisomers.[18]

Further heating of **9** led to a retro-*Diels-Alder* reaction, to give reactive intermediate **10**, which could not be isolated but only be confirmed through mass spectrometry. Trapping of **10** with *p*-benzoquinone led to the twofold *Diels-Alder* addition product in an undetermined mixture of regioisomers.

Based on the mixture of regioisomers of **4**, Bettinger and coworkers reported on a covalently coupled pentacene dimer.[19]

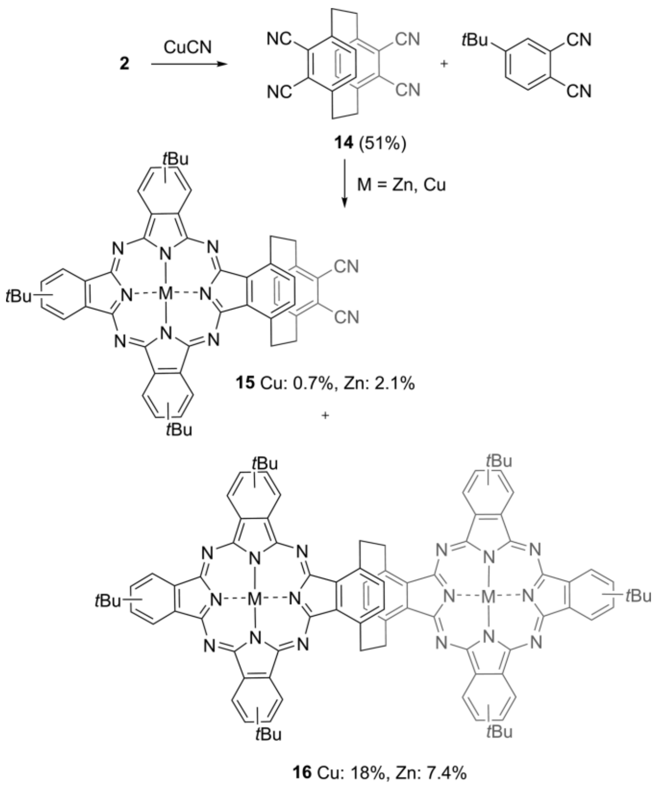
Diels-Alder addition of **4** and anthraquinone gives tetraketone **11**, which could be deoxygenated and reacted with lithium triisopropylsilylacetylide (Scheme 4). Subsequent reduction leads to pentaceneophane **12**. Comparison of the absorption spectra of **12** with the one obtained from 6,13-bis(triisopropylsilylethynyl)pentacene revealed a red shift of the p-band of 20 nm, which the authors attribute to through-space coupling of the pentacene units of **12**. In a similar approach *Bettinger* and co-workers furthered the understanding of through-space coupled *anti*-[2.2](1,4)acenophanes by following the same strategy to form tetracenophane **13**.[20] The regioisomeric mixture of **4** is reacted under *Diels-Alder* conditions with 1,4-naphtaquinone in the presence of 3,6-di(2-pyridyl)-1,2,4,5-tetrazine, followed by basic deoxygenation and addition of lithium triisopropylsilylacetylide. The investigation of the absorption spectra reveals a general red shift of the spectrum of **13** when compared with its non-phane analogue. The through-space coupling of the tetracene dimers is more pronounced than the coupling of the pentacene dimers reported above, the red shift of the tetraceneophane of 26 nm is larger, compared to the red shift of **12**.



Scheme 4. Synthesis of pentacenophane **12** and tetracenophane **13**. *Diels-Alder* reaction of **4** followed by basic dehydration and addition of lithium triisopropylsilylacetylide gives pentaceneophane **12**.[19] Compound **13** was achieved following a similar pathway.[20]

In 2007, *Kobayashi* and co-workers reported on a phthalocyanine dimer (Scheme 5), which is coupled through a central PC building block, also derived from compound **2**.[21]

The authors found that cyanation of **2** proceeds in good yields and were subsequently able to generate both the mono- and dimeric phthalocyanines **15** and **16** in one step under typical conditions for phthalocyanine synthesis. The tetranitrile precursor **14** can also be obtained by the *Diels-Alder* based strategy

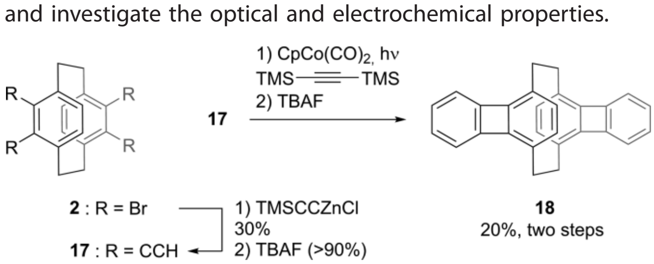


Scheme 5. Synthesis of phthalocyanine-monomer **15** and -dimer **16**.[21]

(see Scheme 2 B) from 1,2,4,5-hexatetraene and dicyanoacetylene.[16] Optical investigations of Zn-**15** and Zn-**16** and comparison with non-PC-substituted zinc-tetra-(tertbutyl)-phthalocyanine revealed a significant redshift of the absorption bands. Both absorption bands are split when compared to the non-PC containing analogue, hinting to substantial electronic communication through the PC-building block.

The electronic communication was further confirmed through DFT calculations, where it was shown that the electronic coupling of one phthalocyanine subunit through the PC is a substantial factor for the shape of the absorption spectrum and the splitting of the absorption band.

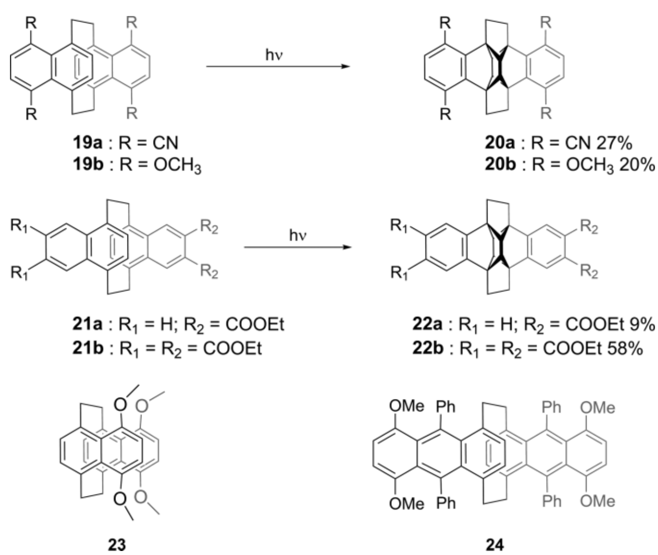
In 2004, *Jin* and co-workers reported on the synthesis of *anti*-[2.2](1,4)biphenyleneophane.[22] In an elegant synthetic sequence (Scheme 6), they were able to prepare biphenylene **18** and investigate the optical and electrochemical properties.



Scheme 6. Synthesis of *anti*-[2.2](1,4)biphenyleneophane **18**.[22]

The authors successfully grew single crystals suitable for X-ray analysis of **18** and found the inner benzene rings to be bent in a boat-like conformation, while the outer rings were unaffected by the strain of the cyclophane. The C=C and C–C bonds of the benzene ring in the PC subunit differ by length in 0.062 Å while the carbon-carbon bonds of the outer benzene rings differ in length by 0.045 Å. The PC thus resembles more the electronic structure of cyclohexatriene, while the outer benzene rings are of aromatic nature. When the authors investigated the absorption spectra and compared them with the one of biphenylene, they found a considerable red shift, which they assign to phane-contributions to the delocalization of the frontier orbitals. Two irreversible single-electron oxidations separated by 180 mV were observed during the electrochemical investigation of **18**, documenting the electrostatic repulsion between both biphenylene subunits.

Another interesting class of molecules was reported in 1997 by *Gleiter* and co-workers, forming dibenzoequinenes based on bis(ps-*meta*)-*ortho*-homo tetrasubstituted PCs (Scheme 7).[23] Some of the starting materials were not prepared from the tetrabromo compound **2** but by reaction of 1,2,4,5-hexatetraene with suitable internal acetylenes, as reported by *Hopf* and co-workers.[16] While the synthesis of such building blocks is only briefly mentioned in this minireview (Scheme 2 B), it remains an important access to symmetrically substituted PCs. Subsequent modifications provided the desired substitution pattern after the synthesis of the PC core of the respective molecules.



Scheme 7. Scope of the substitution pattern of substituted dibenzoequinene,[23] and tetramethoxy PC derivatives **23** and **24** by *Neugebauer* and co-workers which were compared with **19b**.[24]

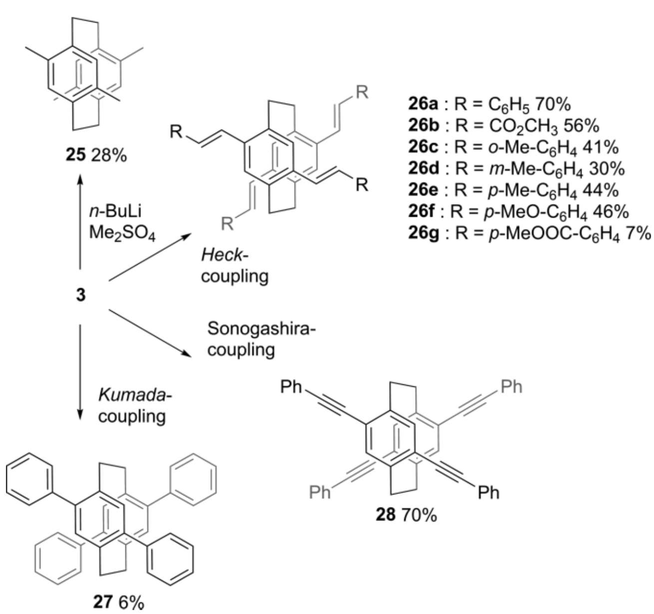
In order to achieve the asymmetrically substituted derivative **21a**, a [3.3]selenophane was generated, from which selene was released by UV-irradiation. The four [2.2]naphthalenophanes were then irradiated in benzene at a wavelength of 350 nm yielding the corresponding dibenzoequinenes in yields from 9–58 %. The solid-state structure of **20a** showed considerable deviations from the optimized angle of 90° for the four membered rings (92.7–83.4°). The average bond length of the four membered rings was 1.579 Å, which is longer than the average bond length of cyclobutane compounds (1.554 Å). These differences in bond lengths and angles are accounted for by the ethano bridges over the four membered rings, which also introduce strong folding in the five-membered rings.

Neugebauer and co-workers utilized bis(ps-meta)-ortho CP derivatives to investigate the transannular delocalization in radical cations.[24] To achieve this, they synthesized and studied three species of PCs, **19b**, **23** and **24** by means of EPR and ENDOR spectroscopy. *Syn*-[2.2]naphthalenophane **23** was obtained as a by-product following the synthesis of **19b**. The synthesis of *anti*-[2.2]anthracenophane **24** was performed similarly to the synthesis of **7**. To compare the electronic delocalization of the series of cyclophanes, they were oxidized and were subjected to EPR and ENDOR spectroscopy. The naphthalenophanes showed a high degree of electronic conjugation through the PC building block, which was determined through the small splitting of the aromatic hydrogen atoms directly on the PC in the ENDOR spectrum. The ENDOR spectrum for **24** showed that electron transfer between the two electrophores is slow on the EPR time-scale, while there is still substantial spin population within the PC.

3. Bis(ps-*meta*)-*para*-homo-tetrasubstituted [2.2]paracyclophanes

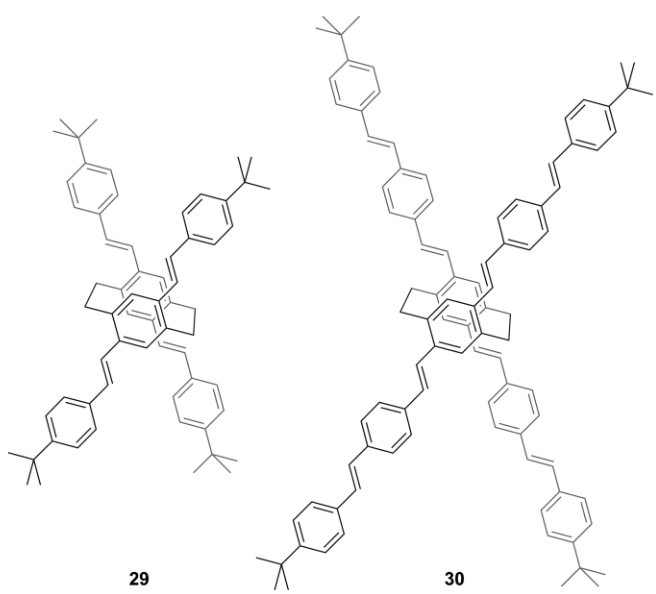
The substitution pattern discussed above is achiral since **2** has an inversion center. Also obtained in the synthesis of **2** is bis(ps-*meta*)-*para* tetrabrominated PC, **3,** which is planar chiral. The compound described here can either be obtained by subjecting the crude to chromatography,[5] or by exploiting the difference in solubility of **2** and **3** in dichloromethane.[15]

Cram and *Reich* initially were able to prove the substitution pattern of **3** by reacting it with *n*BuLi and dimethyl sulfate, yielding compound **25** (Scheme 8).[5] *De Meijere* and co-workers addressed **3** with transition metal catalyzed cross-coupling conditions and provided a series of tetraolefin-substituted PC derivatives **26** through fourfold palladium catalyzed *Heck* reactions with **3**.[15] Depending on the styrene derivative employed, yields up to 70 % were obtained. The scope of palladium catalyzed coupling reactions was complemented by engaging **3** in a *Sonogashira*-coupling protocol with phenylacetylene giving **28** in good yields. Nickel catalyzed transformation of **3** with phenylmagensium bromide gave **27** in low yields. When the absorption spectra of the star-shaped molecules were compared with their linear oligophenylvinyl (OPV) and oligophenylethynyl (OPE) analogues, a bathochromic shift of the PC-based molecules was found for all cases. The synthetic accessibility and its easy engagement in cross coupling reactions made **3** a popular parent structure for model compounds investigating through space cross-conjugation.



Scheme 8. Synthesis and derivatization of **3** by lithiation and trapping, as well as Pd-catalyzed coupling chemistry.[5,15]

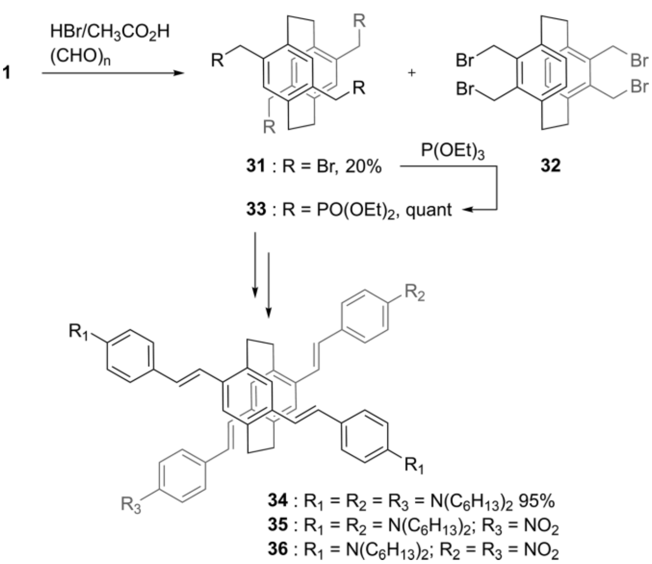
An example of such model compounds for the study of PC mediated through-space conjugation are the PC connected OPV structures **29** and **30** (Scheme 9). The compounds were synthesized by *Bazan* and co-workers employing a fourfold *Heck* reaction[25] comparable with the approach of *de Meijere* and co-workers. The compounds were isolated in low yields, which was rationalized by limited solubility of the intermediates in the reaction. Comparison of the absorption spectra of **29** and **30** revealed similar absorption properties. The authors further concluded that excitations were delocalized across the entire molecules, which they describe as strong mixing of the "phane" and the antenna (chromophore) states within the respective molecule. This was contrasting symmetrically disubstituted distyryl-PCs, where the absorption of the molecules occurs via the stilbene fragments, and therefore the absorption spectra are similar to those of the constitutional monomers.[26]



Scheme 9. Symmetrically tetrasubstituted OPV based chromophores by *Bazan* and co-workers.[25]

Shortly after, *Bazan* and *Bartholomew* published on donor-acceptor tetrasubstituted PC based chromophores.[27] Based on the previous experience of the group concerning the poor solubility and general challenges in the handling of tetrasubstituted PCs, they designed a more selective pathway involving the

Horner-Emmons coupling precursor **33** (Scheme 10). The initial synthesis proceeded through a sonication driven bromomethylation of **1**, from which both **31** and **32** were obtained. After separation of the two regioisomers, **31** was converted to **33** in excellent yields. Subsequent *Horner-Emmons* reactions give chromophores **34**, **35**, and **36**. Compounds **35** and **36** were obtained by reaction of **33** with one or two equivalents of 4-dihexylaminobenzaldehyde and subsequent isolation of the desired precursor, enabling the formation of the target compounds upon treatment with 4-nitrobenzaldehyde.



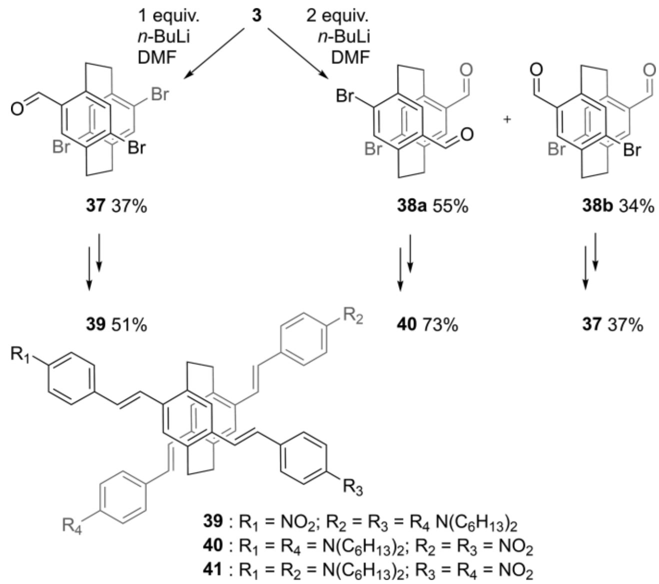
Scheme 10. Bromomethylation of **1** followed by preparation of the *Horner-Emmons* precursor **33** and synthesis of the tetraamine **34**. Asymmetric chromophores **35** and **36**, which are obtained in a statistical approach from **33**.[27]

This strategy to tetrasubstituted PCs with different styrene substituents based on **33** faced severe limitations and thus, the authors developed an alternative synthetic access to this class of model compounds. The fourfold substituted push-pull CP chromophores **39**, **40** and **41** were assembled using this site-selective strategy (Scheme 11). The approach is based on the transformation of bromines of **3** into aldehydes by a bromine lithium exchange followed by addition of *N*,*N*-dimethylformamide (DMF).

The extent of lithiation of the tetrabromide **3** was controlled by the equivalents of the reagent. Upon addition of two equivalents of *n*BuLi, exclusively the two regioisomers **38a** and **38b** with a formyl group attached at each phenyl ring of the CP were obtained after treatment with DMF.

Monoformyl-compound **37** first was subjected to *Heck* coupling conditions with *para*-dihexylaminostyrene and after isolation of the intermediate, exposed to *Horner-Emmons* conditions using 4-nitrophenylmethanephosphonate to yield the asymmetric chromophore **39**. The two diformylated regioisomers **38a** and **38b** were first isolated by high-performance liquid chromatography (HPLC) before the same strategy as applied for **37** provided the push-pull target PC structures **40** and **41**.

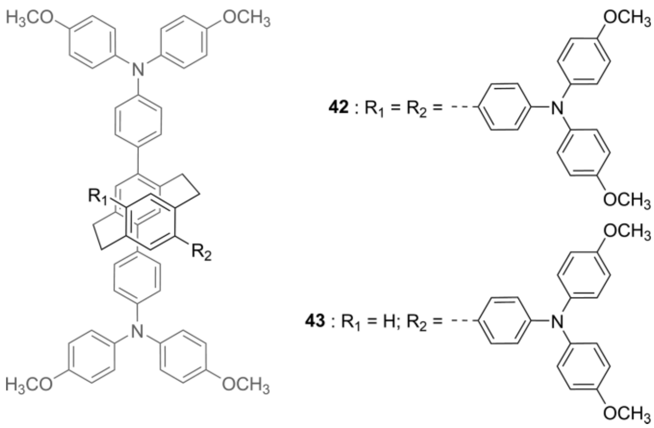
Investigation of the optical properties of compounds **35**, **36** and **39** revealed that the relaxation of the internal conversion



Scheme 11. Synthetic access to donor acceptor tetrasubstituted PCs.[27]

from S_2 to S_1 was not complete, and emission from S_2 was observed. For **34**, **40**, and **41** delocalization through the entire molecule was observed. *Bazan* and co-workers further elaborated on the charge delocalization throughout similarly tetrasubstituted charged PCs where the molecules were either tetraammonium salts or tetrasulfonate salts of X-shaped styryl chromophores.[28] The molecules were prepared from their common intermediate **33**. The authors reported that the through-space state, created by electron exchange across the PC core, is susceptible to solvent polarity. The solvatochromic behavior of such molecules is dominated by the charge transfer component of the distyrylbenzene chromophore. Notably, based on elongated OPV structures of **34** efficient materials for two-photon absorption (TPA) applications were synthesized also from precursor **33**.[29] These materials have a TPA cross section which has about twice the size of the individual monomer, and the excited states are further fully delocalized throughout the entire molecule. Comparison of linear absorption and TPA revealed that the trough-space conjugation affected one- or two-electron absorption differently. Absorption spectroscopy for the X-shaped molecules reveals a characteristic *Davydov* splitting of the monomer band into two components. In contrast TPA gives no such splitting as the contributions of each monomer of the X-shaped molecules are additive.

The electron delocalization through a homo-tetrasubstituted PC was also employed for the assembly of an efficient hole-transporting material in a perovskite based solar cell by *Son* and co-workers (Scheme 12).[30,31] The hole transporting material **42** was fabricated through a tetrafold *Suzuki* reaction starting from **3**. It was incorporated into the hole transporting layer of a perovskite solar cell, were the rigid geometry of **42** allowed for 3D directional transport pathways, resulting in increased charge carrier mobility. The device achieved a solar cell efficiency of 17.9 %, whereas the efficiency of the solar cell, where **43** was employed as hole transporting material was 16.4 % The higher efficiency for the device made with **42** was attributed to its greater capacity for efficient charge transfer from the perovskite layer to the hole transporting material.



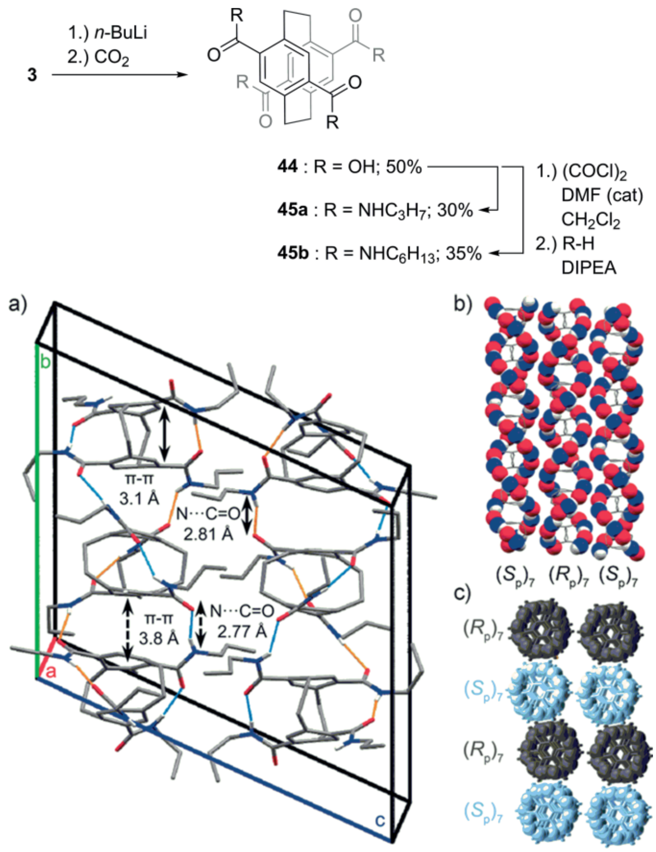
Scheme 12. Hole transporting materials **42** and **43**.[30,31]

A fascinating approach to incorporate racemic homo tetra-substituted PC into chiral functional materials was presented by *Castellano* and co-workers in 2016.[32] They synthesized bis-(ps-*meta*)-*para* substituted tetraamide **45** in which the amides allow for efficient intra- and intermolecular hydrogen bonding. The molecules form well-defined 1D columns, in which the racemic molecules are separated such that the monomers in a particular column have the same chirality (Scheme 13).

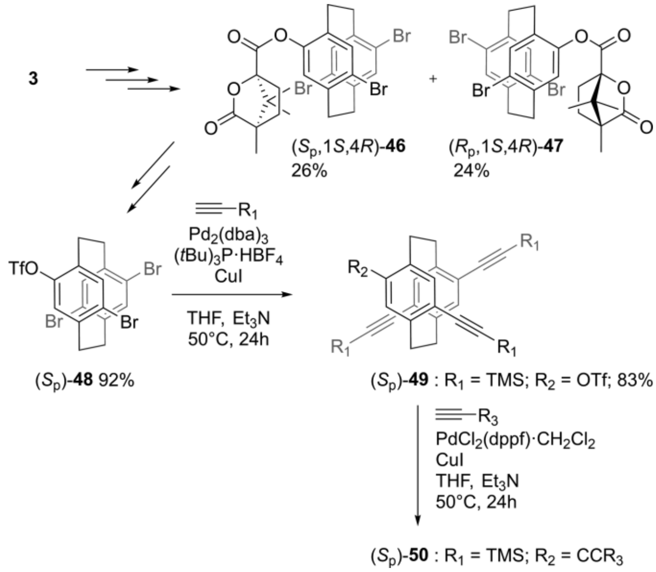
Analysis of the crystal data revealed intramolecular aryl-aryl distances of 3.1 Å, and intermolecular distances of 3.8 Å. The intra- and intermolecular H-bonding distances were 2.81 Å and 2.77 Å, respectively. A pronounced shift of the amide-proton by 0.6 ppm upon increasing the concentration enabled to observe the association behavior by ^{1}H-NMR experiments. The supramolecular growth of the arrangement was analyzed by DOSY-NMR. As macroscopic feature, the increased viscosity of the solution already at mM concentrations upon altering the solvent to apolar media is described.

As already discussed in the introduction, compound **3** is chiral and it is obtained as a racemic mixture in all reported syntheses.[5,15] An elegant method making gram scale quantities of a fourfold substituted pure PC enantiomer available was reported by *Chujo* and co-workers.[33] The synthetic strategy (Scheme 14) is based on the conversion of one of the four bromines into a hydroxyl group, which is subsequently engaged in the ester formation with (–)-(1*S*,4*R*)-camphanoyl chloride (Cam-Cl) yielding the pair of diastereomers (S_p,1*S*,4*R*)-**46a** and (R_p,1*S*,4*R*)-**46b**, which were separated by flash column chromatography and further purified by recrystallization giving both with a diastereomeric ratio better than 99.5 %. The absolute configuration of the diastereomers was determined by single crystal analysis.

Hydrolysis of the diastereomer (S_p,1*S*,4*R*)-**46a** followed by treatment with trifluoromethanesulfonic anhydride provided the enantiopure PC derivative (S_p)-**47** with three bromine and one triflate substituents. Optimized reaction conditions enabled to address the bromines selectively over the triflate in a *Sonogashira–Hagihara* cross-coupling reaction, providing the trialkyne PC (S_p)-**48** in very good yields. The selectivity of the



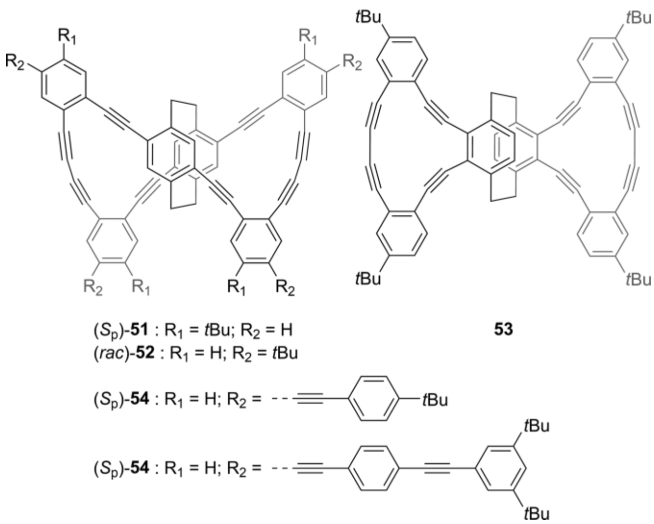
Scheme 13. Synthesis of tetraamide **45** and crystal structure (R = propyl), reprinted from *Castellano* and co-workers.[32] a) Unit cell containing each enantiomorphic asymmetric unit, b) side view of extended PC stacks, c) packing diagram showing different stacks from a top down view. Reproduced with permission from ref.[32]. Copyright 2016 WILEY.



Scheme 14. Synthetic strategy for the chiral resolution of bis(ps-*meta*)-*para* tetrasubstituted PC.[33]

catalytic system allowed *Morisaki* and co-workers to introduce asymmetric tetrasubstituted X-shaped compounds based on tetraalkyne substituted PC derivatives.[34]

The protocol further lead to the first enantioselective synthesis of the trimethylsilyl (TMS)-protected tetraalkyne (S_p)-**50**. Further modification of **50** resulted in the chiral propeller shaped molecule (S_p)-**51** (Scheme 15).[33] The similar PC scaffold **52** was already reported by *Hopf* and co-workers, albeit not enantioselectively.[35] Electron delocalization was investigated by absorption spectroscopy and delocalization through the central PC unit was mainly found for the propeller shaped **52**, while model compounds like e.g. the constitutional isomer **53** did not display comparable extents of delocalization.



Scheme 15. Propeller shaped molecules (S_p)-**51** by *Chujo* and co-workers[33] and (*rac*)-**52** by Hopf and co-workers.[35] Constitutional isomer **53** which was used by *Hopf* and co-workers to elucidate cross conjugation properties. Compounds **54** and **55**, which were used to investigate chiroptical properties of extended propellers by *Chujo* and co-workers.[36]

Chujo and co-workers investigated the chiroptical properties of compound **51**. They found intense signals in the electronic circular dicroism (ECD) spectra for both enantiomers, which they attributed to the fixed and rigid geometry of **51**.

A qualitatively similar chiroptical behavior was observed for a derivative of the described compound where the outer benzene rings were replaced by naphthalenes.[36] When the optical properties of **52** were compared with the ones observed for compounds **54** and **55**, *Chujo* and co-workers observed intense chiroptical properties for all investigated species.[37] The key parameters describing the chiroptical properties are the dissymmetry factor of absorbance ($g_{abs} = 2(\Delta\varepsilon/\varepsilon)$) and the circular polarized luminescence (CPL) dissymmetry factor ($g_{lum} = 2(I_{left} - I_{right})/(I_{left} + I_{right})$). For g_{abs} the extinction coefficient of the molecule is compared with the circular dichroism due to electronic transitions (ECD), and for g_{lum} the polarized luminescence intensities of left and right CPL (I_{left} and I_{right} respectively) are compared. For both enantiomers of **52** the values for g_{abs} and g_{lum} were exceptionally high at $1.0 \pm 0.1 \times 10^{-2}$, and the minor differences in the respective values were interpreted as indication of only small structural changes between ground and excited states. This hypothesis was further supported by the absence of temperature- or solvent-induced change in the UV, ECD and CPL spectra. The peripheral oligophenylethylene (OPE) decorated derivatives **54** and **55** have localized excited states on their OPE arms, while molecule **52** has its excited state localized on the central cyclophane. Of particular interest was the comparison of the chiroptical properties of the propeller shaped molecules with their precursors with a not yet fixed propeller structure. Considerable larger molar ellipticities and CPL dissymmetry factors were observed for the propellers. These intense chiroptical properties are discussed as emerging from the rigid propeller shaped secondary structure of the molecules, which was maintained in the excited state. The g_{abs} and g_{lum} for **54** and **55** were in the same range as for **52**.

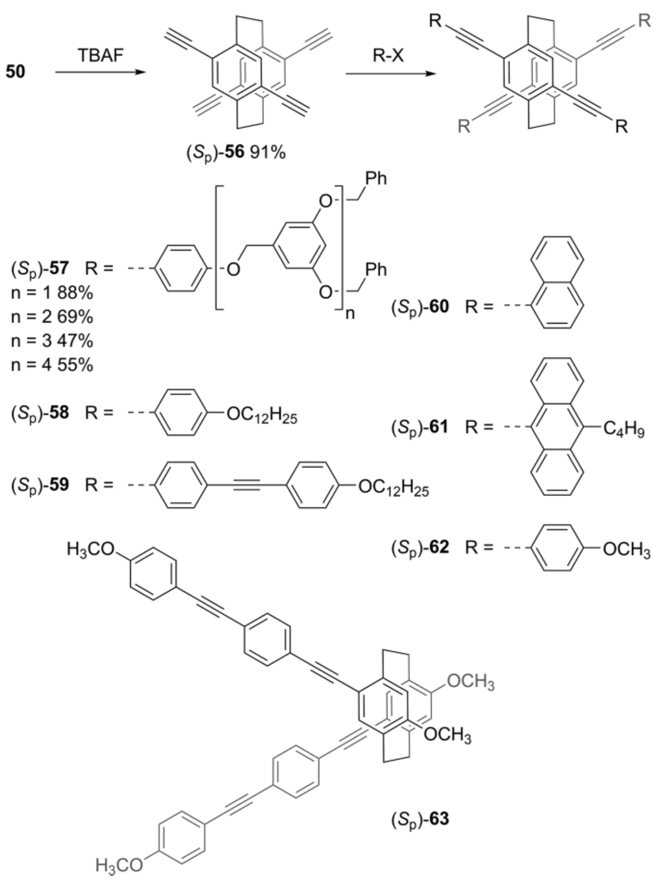
To further explore the potential of X-shaped conjugated structures with a central PC subunit, the same group attached dendrons via *Sonogshira*-type chemistry at the four alkynes of the enantiopure tetraalkyne **56**.[38]

The authors present the series of dendrimers **57**. The aromatic branches act as light harvesting antennas and inhibit aggregation induced quenching of the excited state. The series of dendrimers have strong CPL both in solution and in thin films, as evidenced by their high g_{abs} and g_{lum} values around 10^{-3}, recorded for the four members of **57** in solution, as well as in thin films.

Chujo and co-workers further reported optically active PC compounds to study the influence of aggregation on emission properties.[39] They prepared enantiopure samples of compound **26a** (R = phenyl) from **47**, together with an analogue comprising an extended peripheral π-system. For both model compounds g_{abs} and g_{lum} values of ca. 10^{-3} were recorded, which are of comparable dimensions as the ones observed for the series of dendrimers **57**. Interestingly, the chiroptical features of these compounds displayed temperature dependence with decreasing polarized luminescence with increased temperature. The same authors further elaborated on aggregation studies of X-shaped molecules **58** and **59** exposing mesogenic substituents of various dimension.[40] The chiroptical properties of these model compounds were investigated in solution as well as in thin films obtained by drop-casting and spin coating. Different aggregates were observed depending on the film preparation. In particular, the dissymmetry factors changed their sign depending on the film deposition technique. Simulation of the stacking behavior of the molecules in each deposition technique supported the observed behavior. Transmission electron microscopy even displayed fiber formation for the enantiopure CP **59**. Annealing of the films of **58** and **59** triggered their transformation into the thermodynamically most stable aggregates.

The series of CP model compounds reported by *Chujo* and co-workers was further complemented by the enantiopure tetra-aryl decorated X-shaped structures **28**, **60** and **61**.[41] Intense chiroptical effects were found (characteristic g_{abs} and g_{lum} values are ca. 10^{-3}) for these compounds emerging from the rigid confirmation of the X-shaped center of the molecule. Interestingly, the chirality of the central CP subunit was not communicated to the peripheral anthracene units of **61**, as it displayed substantial *Cotton* effects only in the region where the core of the molecule contributed to the ECD-spectrum.

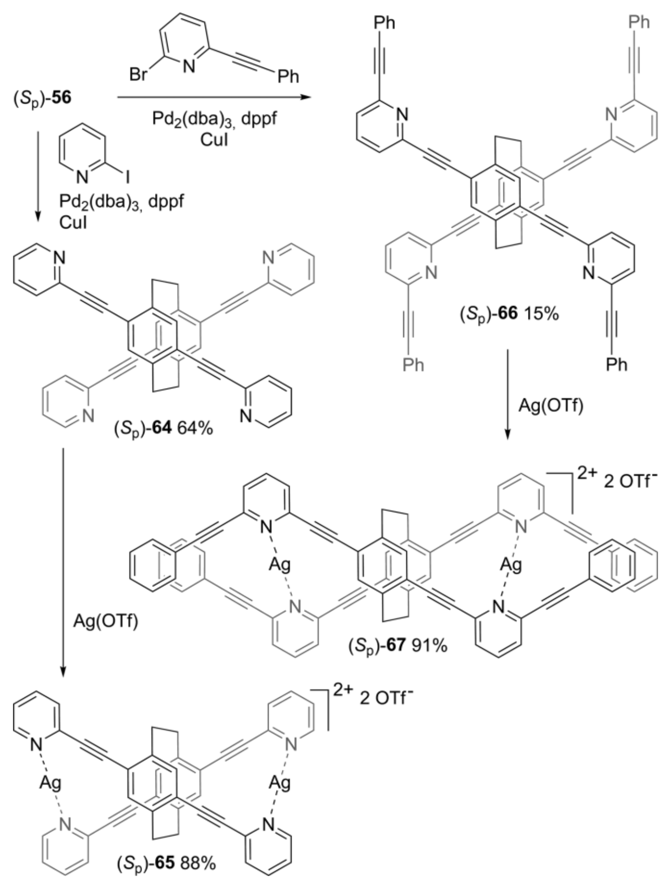
Another recent example of an X-shaped PC derivative synthesized as pure enantiomer is **62** (Scheme 16), acting as model compound for two terminally methoxy functionalized OPE rods with stacked central phenyl units. The chiroptical properties of X-shaped **62** were compared with its V-shaped structural isomer **63** (Scheme 16), with stacking terminal phenyl subunits.[42] Also **63** was synthesized as pure enantiomer and the access of pure enantiomers of the PC building block will be discussed in the following chapter 4 (**80** in Scheme 19). Comparison of the CPL features of the X- and V-shaped model compounds **62** and **63** displayed opposite CPL signs with respect to the chirality of their CP subunit. The authors thus identified the spatial orientation of both OPE rods as more important for their chiroptical properties than their absolute configuration.[42]



Scheme 16. Synthesis of the series of chiral CP comprising dendrimers **57**[38] and the X-shaped molecules **58** and **59** for aggregation studies,[39] the extended model compounds **60** and **61**, which were analyzed as CPL emitters,[40] and the V-shaped model compound **63**.[42]

Morisaki and *Chujo* recently summarized their attempts to control optical features of model compounds with CP controlled intramolecular π-stacking.[43]

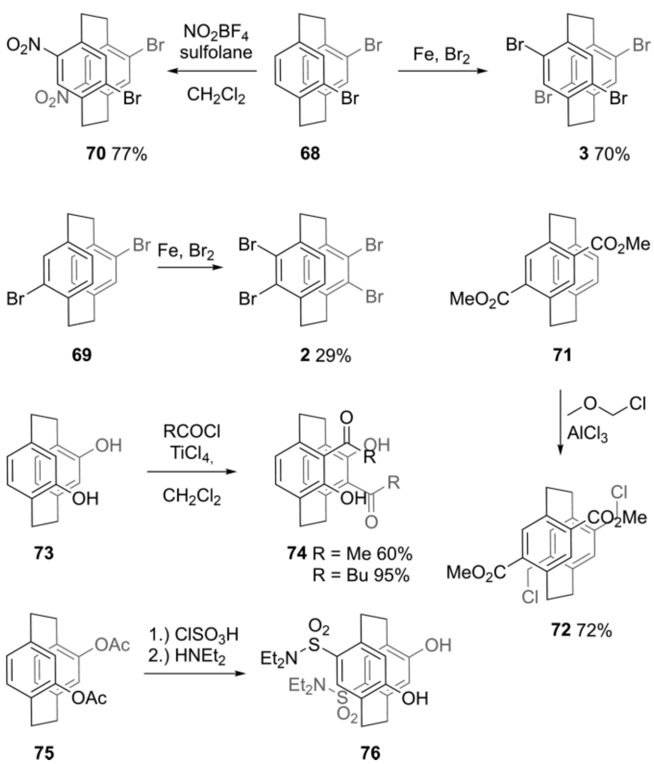
An appealing approach to vary chiroptical properties is the introduction of binding sites at the periphery of **56** giving access to higher order structure through metal coordination.[44] For the purpose enantiopure **56** was decorated with pyridiyl-substituents providing the X-shaped multidentate ligands **64** and **66**. The synthesis is shown in Scheme 17. The intramolecular coordination of silver ions by pyridine nitrogens rigidifies the secondary structure of both dinuclear complexes **65** and **67**. The change of the degree of freedom in vicinity of the pyridyl groups is low for the silver ion coordination of **64** giving **65**. Consequently, the chiroptical properties are qualitatively hardly affected. While the maximum absorption is red-shifted, the intensity of the *Cotton* effects in the ECD spectrum remains almost the same upon coordination. The situation is different for the extended structure **66**, which is more rigidified upon coordination of silver-cations yielding in **67**. While the absorption spectrum is only slightly affected by the transition from **66** to **67**, the *Cotton* effects in the ECD spectra are tripled in intensity. Interestingly, the coordination of silver quenches the circular polarized luminescence for **67** selectively. The authors suggest two competing second order structures as potential explanation with the silver ions not exclusively coordinating to the pyridyl nitrogens but also interacting with the π-system of the molecule.



Scheme 17. Synthesis of the tetra-pyridyl ligands **64** and **66**, together with their dinuclear Ag(I)-coordination compounds **65** and **67**.[44]

4. Symmetrically Tetrasubstituted PCs with Heterosubstituents: PC Design through Regioselective Electrophilic Aromatic Substitution

In the preceding chapter, we have seen the amazing potential of synthetic strategies providing precise control over more than one type of substituents. Until 2008, the number of symmetrically tetrasubstituted PC derivatives mainly relied on synthetic approaches displayed before, also commonly employed was the *Hoffmann* 1,6-elimination to synthesize the parent hydrocarbon, as well as symmetrically higher substituted analogues. *Hopf* and co-workers elucidated in a seminal publication the double electrophilic substitution of suitable disubstituted PCs.[7] Until this point, only isolated examples of regioselective disubstitution were known, which are summarized in Scheme 18.

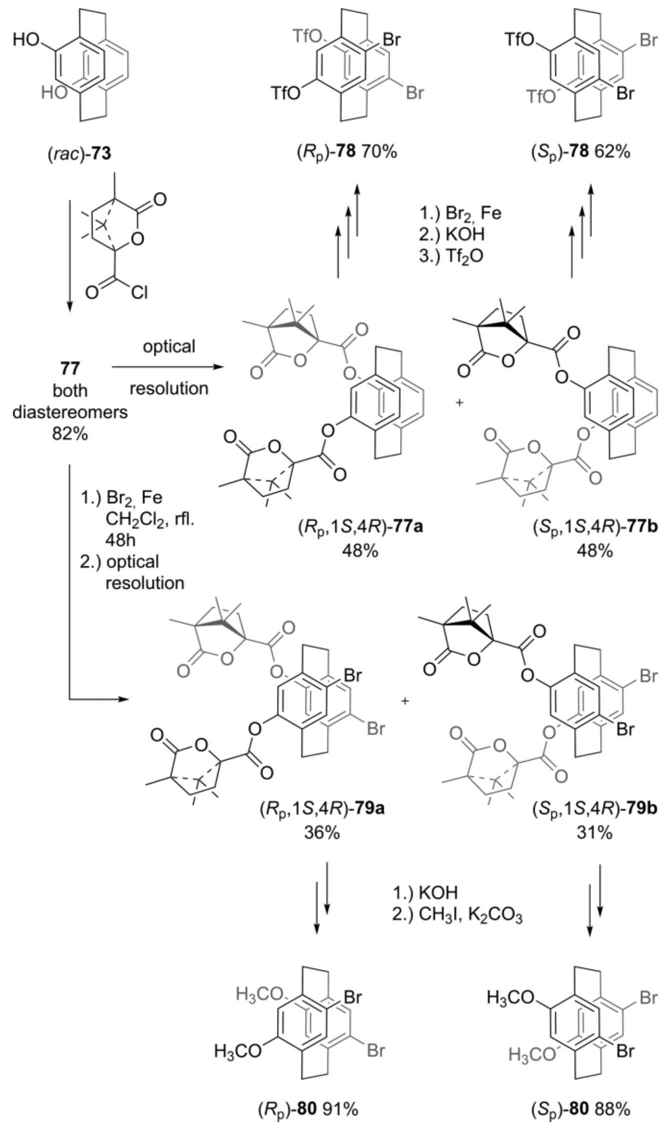


Scheme 18. Overview over the double electrophilic substitution prior to the work of *Hopf* and co-workers. The reactions to form **2** and **3** were elucidated by *Cram* and *Reich*.[5] Compounds **70**, **74**, and **76** were elucidated by *Braddock* and co-workers.[45] Compound **72** was prepared by *Gray* and *Boekelheide*.[46]

In their synthesis of a hydrogen-bonding chiral organocatalyst, *Braddock* and co-workers found that the dinitration of **68** proceeds *para* selectively, as did the chorosulfination of diacetate **75**. The diacylation of diol **73** proceeded in the *ortho* position regioselectively.[45] *Gray* and *Boekelheide* found the chloromethylation of diester **71** to proceed pseudo-*gem* regioselectively, when they elaborated on the synthesis of [2.2.2.2](1,2,4,5)cyclophane.[46]

An interesting access to planar chiral [2.2]paracyclophanes, based on the twofold electrophilic substitution of purified samples of the diester **77**,[47] was reported by *Chujo* and co-workers in 2016 (Scheme 19). With a very similar approach as already applied by the authors before,[33] the diol **73**[48] was treated with camphanoyl chloride to yield the pair of diastereomers (R_p,1*S*,4*R*)-**77a** and (S_p,1*S*,4*R*)-**77b** which were separated by chromatography on silica gel. Each diastereomer was obtained in 48 % yield with a diastereomeric excess larger than 99.5 %.

Having the isolated diastereomers in hand, the authors further converted them into the symmetrically tetrasubstituted

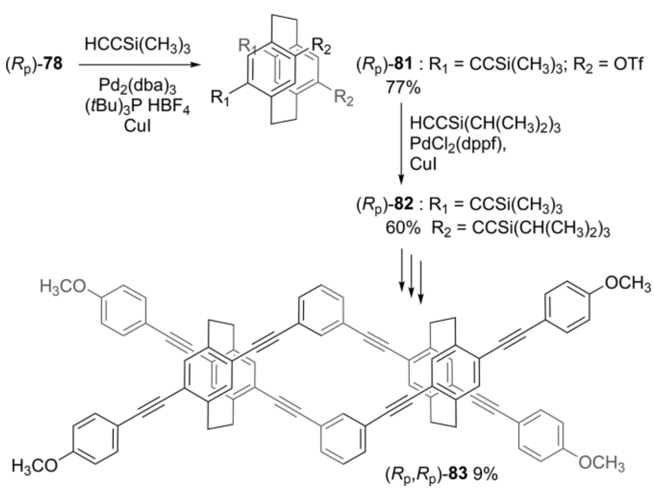


Scheme 19. Optical resolution and transformation of diastereomers **77**[47] and **79**.[42]

enantiomers (R_p)-**78** and (S_p)-**78**. The diesters (R_p,1*S*,4*R*)-**77a** and (S_p,1*S*,4*R*)-**77b** were regioselectively dibrominated, and after saponification, both phenolic OH-groups were converted to triflates providing the enantiopure building blocks (R_p)-**78** and (S_p)-**78**.

A variation of the optical resolution procedure giving access to the enantiopure building blocks (R_p)-**80** and (S_p)-**80** has been reported recently by the same group.[42] The pairs of diastereomers **77** was first doubly brominated and subsequently separated by crystallization and silica gel chromatography, making both diastereomers (R_p,1*S*,4*R*)-**79a** and (S_p,1*S*,4*R*)-**79b** available in gram scale. Removal of the chiral auxiliary followed by methylation of the liberated phenol groups provided both enantiomers (R_p)-**80** and (S_p)-**80** in excellent yields. Subsequent substitution of the bromine via Sonogashira cross-coupling reactions gave the enantiopure samples of the V-shaped model compound **63**.

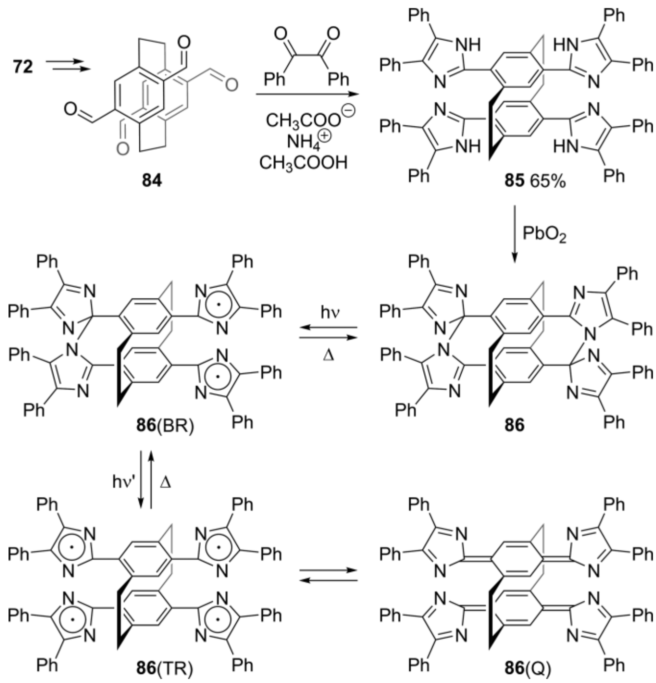
Careful selection of the catalytic system enabled to address exclusively the bromide substituents of (R_p)-**78** in a *Sonogashira–Hagihara* cross-coupling reaction with TMS acetylene, providing the enantiopure di-TMS-alkyne decorated CP (R_p)-**81** in good yields (Scheme 20). In a second *Sonogashira–Hagihara* reaction the conditions were optimized to substitute the triflates with triisopropylsilylacetylene. Thus (R_p)-**81** was converted into the CP derivative (R_p)-**82**, exposing two pairs of differently protected alkyne groups. Selective deprotection of the TMS protecting group of (R_p)-**82** gave the building block required for the assembly of the helical structure (R_p,R_p)-**83**, with a handedness emerging from the planar chiral CP subunit.



Scheme 20. Synthesis of the planar chiral building block **82**, enabling the assembly of the one-handed helix **83**.[47]

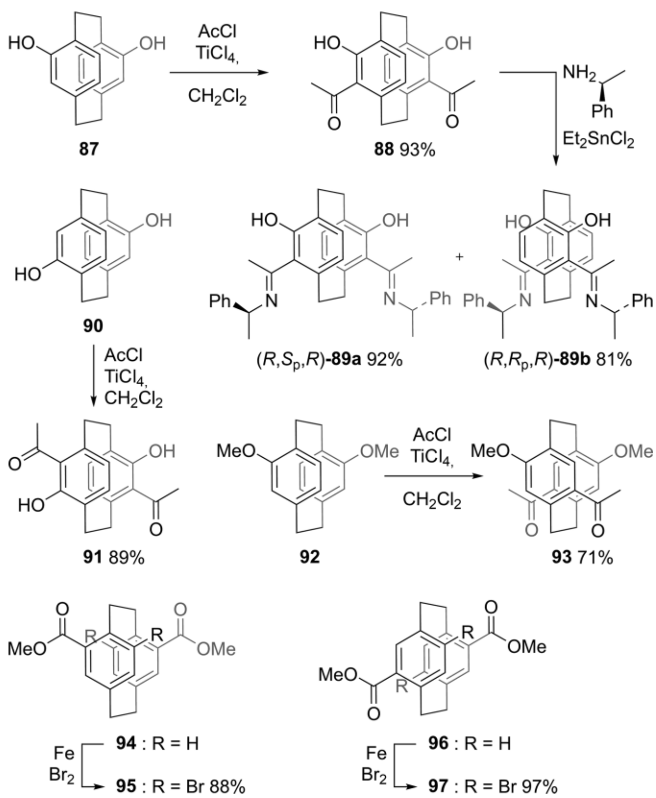
Investigation of **83** by UV/Vis spectroscopy displayed π-conjugation throughout the entire molecule and ECD of enantiopure samples showed intense chiroptical properties with comparable values (g_{abs} and g_{lum}) as found for the chiral dendrimers **57**. The same group reported the isolation of the bis(*para*)-ps-*ortho* regioisomers of **78**, which were isolated by column chromatography.[49]

Abe and co-workers reported the synthesis of the PC bridged bis(imidazole dimer) **86**, with a central tetrasubstituted PC subunit (Scheme 21).[50] The structure displayed interesting photochromic properties with promising potential as multiphoton gated optical materials: Upon absorption of the first photon by **86**, the short-lived biradical species **86**(BR) is formed, which transforms back to **86** within a few ms. Upon absorption of a second photon by **86**(BR) however, the tetraradical **86**(TR) is formed which undergoes quickly a photochromic reaction to the long-liver quinoid form **86**(Q). Interestingly, the transformation could be performed by incoherent continuous-wave irradiation, pointing at the high efficiency of the processes involved in the transformation. The synthesis of **86** used the symmetrically tetrasubstituted PC **72** as starting point, which was converted into the PC-tetracarbaldehyde **84** in a few steps. Treatment with benzil and ammonium acetate in acetic acid provided the fourfold (4,5-diphenyl-1H-imidazol-2-yl)substituted PC **85**, which was oxidized with lead dioxide to **86**.



Scheme 21. Synthesis of the PC-bridged tetraimidazole model compound **86** and its two-photon-gated photochemical transformation.[50]

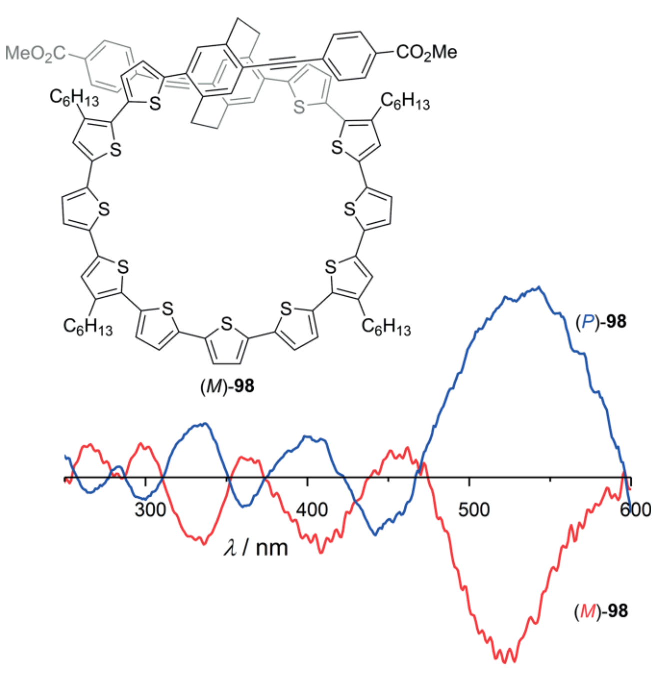
Hopf and co-workers elaborated on the regioselective double electrophilic substitution of symmetrically disubstituted PCs[7] and their findings are summarized in Scheme 22. Both diols **87**



Scheme 22. Scope of the double regioselective electrophilic substitution on symmetrically disubstituted PCs by *Hopf* and co-workers.[7]

and **90** were acylated regioselectively in the *ortho* position with acetyl chloride giving the diketones **88** and **91**. The racemic diketone **88** was converted into the pair of diastereomeric bisimines (R,S_p,R)-**89a** and (R,R_p,R)-**89b**, which were separated by conventional column chromatography. The catalytic activity and selectivity of both diastereoisomers **89** in the asymmetric additions of diethylzinc to benzaldehyde was investigated. The reaction proceeded with an enantiomeric excess (*ee*) of 76 % with (R,S_p,R)-**89a** as catalyst, and an *ee* of 36 % using (R,R_p,R)-**89b**. Interestingly, the addition of benzoyl chloride to **87** gave a mixture of products. Next, Hopf and co-workers investigated the double electrophilic substitution of acetyl chloride on PC methyether **92**. The double *para*-acylated compound **93** was formed in reasonable yields as the major product of the reaction. They further elaborated on the double electrophilic substitution of the PC di-methyl esters **94** and **96**. For both compounds, exclusively pseudo-*gem* dibromination was found, providing the symmetric fourfold decorated PCs **95** and **97** in very good yields. With respect to compound **97** the authors concluded with the visionary statement: "We believe this compound to be a prominent precursor of a wide range of novel [2.2]paracyclophane derivatives obtainable by further chemical transformations of its bromine atoms and/or of its ester groups."

Very recently, we were able to make a first contribution verifying the expressed belief of *Hopf* and co-workers. The fourfold substituted PC **97** was the ideal building block to introduce a step into a macrocyclic oligothiophene. The introduction of a PC-subunit into the framework of the macrocycle results in a helical chiral architecture. While for that purpose a twofold functionalized PC like **69** would be enough,[51] only a fourfold substituted PC like **97** enables the decoration with bulky substituents slowing down the racemization process to a level enabling the isolation of the helical chiral enantiomers. As first model compound the macrocycle **98** exposing two *para*-(methoxycarbony)phenylethynyl substituents (Scheme 23) stabilizing both enantiomers to a level, enabling their isolation was assembled.[52]



Scheme 23. *Top*: Helically chiral macrocycle **98**, assembled from the diester **97**. For clarity exclusively one enantiomer ((*M*)-**98**) is displayed. *Bottom*: ECD spectra of both enantiomers (*M*)-**98** (red) and (*P*)-**98** (blue).[52]

The synthesis of **98** was based on **97**, the two bromine substituents allowed the integration into the macrocycle by *Suzuki* cross-coupling reactions, while the two methyl ester substituents were reduced to aldehydes and subsequently converted to alkynes by a *Corey-Fuchs* reaction sequence. The two enantiomers were separated by high-performance chromatography on a chiral stationary phase and displayed weak *Cotton* effects pointing at the high flexibility of the helical chiral structure. The structure racemizes at room temperature with a half-life time of a few minutes. The racemization process requires the penetration of one *para*-(methoxycarbony)phenylethynyl substituent through the macrocycle and was confirmed by modeling using semiempirical calculations.

5. Conclusion

Symmetrically tetrasubstituted [2.2]paracyclophanes are compounds of great value in many fields of chemical materials research. The first substitution pattern, based on achiral bis(ps-*meta*)-*ortho* homotetrasubstitution has provided layered aromatic compounds, which are important building blocks in the investigation of transannular communication. The most prominent approach to advanced structures in this class is the double aryne forming reaction, which is then reacted with suitable electrophiles. The second class of materials, with the largest number of synthetic approaches, is based on bis(ps-*meta*)-*para*-homotetrasubstituion. These materials were incorporated into functional devices and were also used to understand transannular chromophore interactions. Bis(ps-*meta*)-*para*-homotetrasubstitution gives access to planar chiral molecules, enantioselective syntheses of such structures, and the corresponding chiroptical studies of compounds in X-, propeller- and helix-shapes were described herein. The third class of materials relies on regioselective double electrophilic aromatic heterosubstitution, and only few such examples are known. These materials however also provide access to a new synthetic route to symmetrically substituted PCs, and a first example of functional materials based on such compounds is described.

Overall, this minireview highlights the current synthetic routes and functional materials based on symmetrically tetrasubstituted PCs, an appealing family of aromatic compounds with unique properties based on the special 3D geometry of PC. Even 70 years after the discovery of the parent hydrocarbon, PC based materials are a promising class of organic compounds with excellent structural and optical features.

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Keywords: [2.2]Paracyclophanes · Layered compounds · π-Stacking · Cross-conjugation · Chirality

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