



**HAL**  
open science

## [2.2]Paracyclophanes: From Selective Functionalization to Optical Properties

Shiqi Wu, Simon Felder, Jules Brom, Fabrice Pointillart, Olivier Maury,  
Laurent Micouin, Erica Benedetti

► **To cite this version:**

Shiqi Wu, Simon Felder, Jules Brom, Fabrice Pointillart, Olivier Maury, et al.. [2.2]Paracyclophanes: From Selective Functionalization to Optical Properties. *Advanced Optical Materials*, 2024, 12 (21), pp.2400934. 10.1002/adom.202400934 . hal-04614001

**HAL Id: hal-04614001**

**<https://hal.science/hal-04614001v1>**

Submitted on 2 Jul 2024

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

## **[2.2]Paracyclophanes: from selective functionalization to optical properties**

*Shiqi Wu, Simon Felder, Jules Brom, Fabrice Pointillart, Olivier Maury, Laurent Micouin and Erica Benedetti\**

S. Wu, S. Felder, J. Brom, L. Micouin, and E. Benedetti

Université Paris Cité, CNRS, Laboratoire de Chimie et de Biochimie Pharmacologiques et Toxicologiques, F-75006 Paris, France.

E-mail: [erica.benedetti@u-paris.fr](mailto:erica.benedetti@u-paris.fr);

F. Pointillart

Univ Rennes CNRS, ISCR (Institut des Sciences Chimiques de Rennes), UMR 6226, 35000 Rennes, France

O. Maury

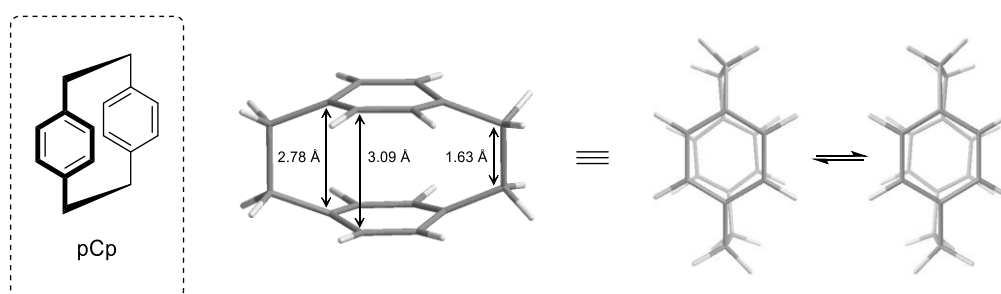
Univ Lyon, CNRS, ENS de Lyon, Laboratoire de Chimie UMR 5182, 46 allée d'Italie, 69364 Lyon, France

Keywords: [2.2]Paracyclophanes, regioselective functionalization, planar chirality, circularly polarized luminescence, thermally activated delayed fluorescence, lanthanide complexes

Since their discovery, [2.2]paracyclophane (pCp) and its derivatives have fascinated the scientific community due to their original molecular architecture and unusual electronic behavior. Over the years, significant efforts have been devoted to the development of substituted pCps for a variety of applications in different fields, ranging from organic synthesis and asymmetric catalysis to polymer chemistry and material science. This review describes a series of useful approaches that allow chemists to selectively decorate pCps, control the planar chirality that these molecules can display as soon as they are functionalized, and tune their photophysical behaviors. For each of these aspects of paracyclophane chemistry, selected examples of major advances are presented, and possible directions for future research are outlined. The application of pCp as central core for the development of uncommon three-dimensional luminophores is finally highlighted. Emphasis is placed on the potential use of planar chiral luminescent paracyclophanes as antennas or ligands for the design of multifunctional lanthanide complexes, a quite underdeveloped but highly promising area for future research endeavors.

## 1. Introduction

[2.2]Paracyclophane (pCp) is the smallest member of the [n.n]cyclophane family.<sup>[1]</sup> This original molecule was serendipitously discovered in 1949 by Brown and Farthing as a by-product formed during the gas-phase pyrolysis of *para*-xylene.<sup>[2]</sup> [2.2]Paracyclophane is constituted of two phenyl rings stacked in a face-to-face geometry and linked together by two ethylene bridges at their *para* positions (**Figure 1**). As observed in 1972 by X-ray crystallographic analysis,<sup>[3]</sup> the two aromatic “decks” of pCp adopt an unusual boat-shaped conformation (**Figure 1**). Further crystallographic and computational studies allowed chemists to gain additional insight into the structural features and molecular dynamics of unsubstituted pCp. While at low temperature the molecule can adopt two distinct distorted geometries with a  $D_2$  symmetry, at room temperature the rapid interconversion between the conformers globally affords an achiral  $D_{2h}$  strained structure (**Figure 1**).<sup>[4]</sup>



**Figure 1.** Structure of unsubstituted [2.2]paracyclophane

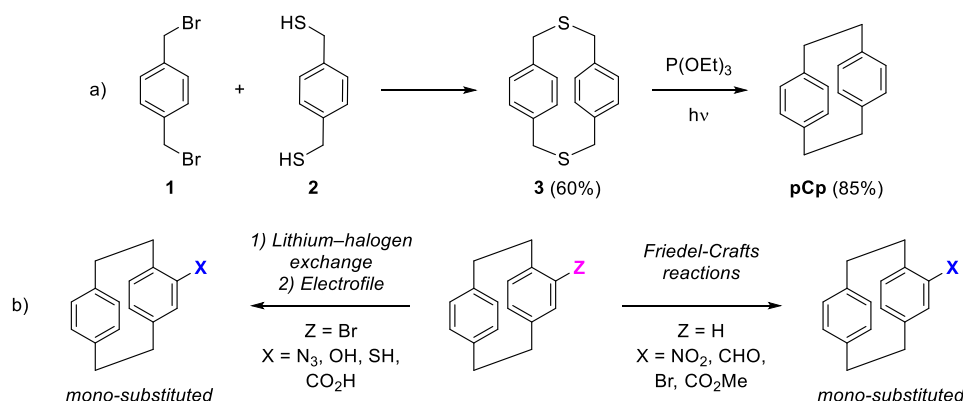
The conformational stiffness of pCp favors through-space and through bond electronic interactions which significantly influence the reactivity of the aromatic units of the molecule. Consequently, even if an array of transformations can be employed to decorate the pCp core, including for example Friedel-Crafts reactions, Diels-Alder cyclizations, hydrogenations or ionic additions,<sup>[5]</sup> this molecule has frequently proved to be unreactive in a variety of other classical chemical processes, thus posing ongoing challenges in synthetic organic chemistry. Because of its unusual features, pCp has rapidly fascinated the scientific community. As a result, the synthesis and functionalization of this compound, as well as its physicochemical properties and its applications in different research fields have been extensively investigated over the years.

This review gives an overview of different methods, developed during the last twenty years, which reveal useful to selectively functionalize [2.2]paracyclophanes, control their planar chirality, and tune their spectroscopic behaviours. The versatility of pCps in different

domains will be finally highlighted with a particular focus on the potential use of these molecules as building blocks to access original luminescent compounds.

## 2. Functionalization of the pCp core

Since the first report on pCp, different synthetic strategies have been developed to prepare this compound in a more efficient fashion,<sup>[6]</sup> the highest yielding one being the method described by Brink in 1975.<sup>[7]</sup> This approach relies on a coupling between 1,4-bis(bromomethyl)benzene **1** and 1,4-bis(mercaptomethyl)benzene **2** leading to dithia[3.3]paracyclophane **3** (**Scheme 1a**). Intermediate **3** is then submitted to a photodesulphurisation that generates the expected product in 51% overall yield. As of today, a variety of pCp derivatives have been synthesized using this process.<sup>[8]</sup>



**Scheme 1.** Synthesis and mono-functionalization of pCp

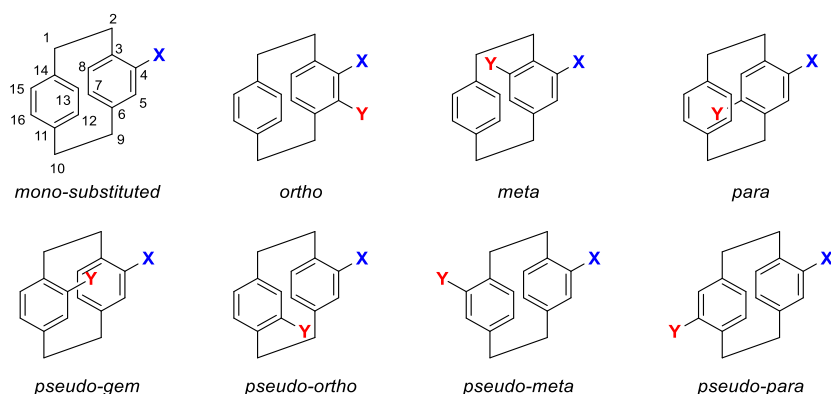
[2.2]Paracyclophanes are generally stable to the action of acids, bases, oxidants, and light. They also exhibit good thermal stability up to 200 °C. Beyond this temperature, an homolytic cleavage of the ethylene bridges is observed, leading to the opening of the pCp core.<sup>[9]</sup> This behaviour has successfully been exploited in material science to access different polymers by chemical vapor deposition (CVD).<sup>[10]</sup> Unsubstituted pCp is indeed typically used as key precursor for the preparation of parylene,<sup>[11]</sup> an aromatic polymer used to coat optical elements, electronic devices or other equipment and protect them against moisture, corrosion or chemical attack. Consequently, this building block is commercially available at low cost due to its wide industrial applications.

Since their parent compound is a cheap and readily available starting material, differently substituted [2.2]paracyclophanes are nowadays preferentially prepared via the

derivatization of the unsubstituted molecule rather than through the direct synthesis of functionalized pCp frameworks.

The two aromatic rings of [2.2]paracyclophane possess eight possible modification sites. Monofunctionalization of the pCp core is usually achieved by electrophilic aromatic substitution, and different groups can easily be installed in one step (e.g., Br, NO<sub>2</sub>, CHO, COMe). Alternatively, starting from bromine-substituted pCp, a halogen-lithium exchange followed by quenching with different electrophiles can be used as an efficient method to decorate the molecule with important functions, such as amino or hydroxyl groups, azides, thiols, carboxylic acids and phosphines (**Scheme 1b**).<sup>[12]</sup> Note that, in addition to these techniques, direct C-H activation of the pCp core has recently been described.<sup>[13]</sup>

Starting from mono-substituted pCps, various disubstituted derivatives can be prepared. These compounds are usually described based on their substitution patterns. *Ortho*-, *meta*- and *para*-disubstituted pCps are obtained when the two functional groups (X and Y, Figure 2) are located on the same “deck”. In addition, *pseudo-gem*-, *pseudo-ortho*-, *pseudo-meta* or *pseudo-para* compounds can be formed when two substituents are employed to decorate both aromatic rings of the pCp core (**Figure 2**).



**Figure 2.** Numeration, substitution patterns and nomenclature of pCps

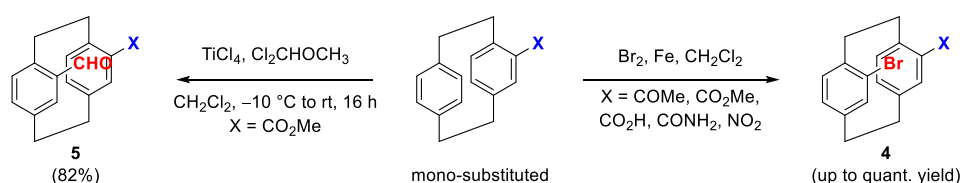
Tri- and tetra-substituted pCps are usually prepared starting from di-substituted precursors by successive electrophilic substitution reactions.<sup>[14]</sup> [2.2]Paracyclophanes bearing more than four substituents on their aromatic rings are highly strained systems, and have rarely been described in the literature.<sup>[15]</sup>

Various strategies have been developed over the years to selectively functionalize [2.2]paracyclophanes at different positions. In the next sections, selected examples of practical methods allowing to decorate both “decks” or only one aromatic ring of pCps at specific

positions will be detailed. Emphasis will be placed on the obtention of compounds incorporating halogen atoms, amines or aldehyde groups since these derivatives can reveal particularly useful as synthetic intermediates to rapidly access more structurally complex pCps.

## 2.1. Selective decoration of both decks

The introduction of a first substituent on one aryl moiety of pCp modifies the electron-density distribution of the system and, in some cases, can deactivate or, on the contrary, activate specific positions on the other aromatic ring. This unique property of [2.2]paracyclophane reactivity, known as "*transannular directive effect*", has been extensively exploited to prepare di-substituted compounds.<sup>[16]</sup> The most well-known example of such behaviour is the regioselective *pseudo-gem* functionalization of pCp derivatives incorporating electron-withdrawing groups. For example, bromination reactions or Rieche formylation occur smoothly starting from esters or other electron-deficient pCps to deliver the desired product in excellent yields (Scheme 2). Despite these advantageous methods, the development of procedures allowing to selectively functionalize mono-substituted pCps at their *pseudo-ortho*, *pseudo-meta* or *pseudo-para* positions is still highly desirable.



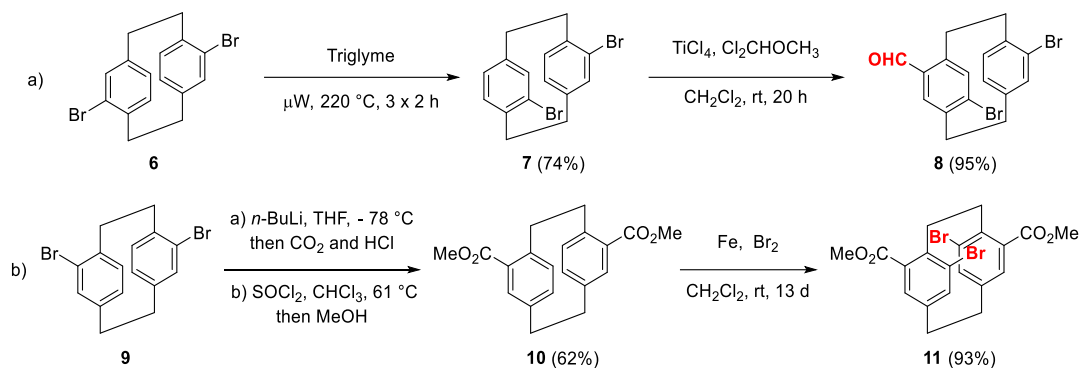
**Scheme 2.** Selected examples of *pseudo-gem* functionalization of pCps

*Pseudo-para*- and *pseudo-meta* di-bromo[2.2]paracyclophanes are usually obtained as major products while performing the bromination of unsubstituted pCp under harsh conditions.<sup>[17]</sup> These di-substituted derivatives are nowadays commercially available and can be easily converted into a variety of poly-substituted compounds.

*Pseudo-para*-di-bromo[2.2]paracyclophane **6** is known to smoothly undergo a thermal isomerization in triglyme at 220 °C to afford *pseudo-ortho*-di-bromo derivative **7** in an efficient way. The process proceeds through the homolytic cleavage of one ethylene bridge of **6**, followed by rotation of the resulting diradical intermediate, and subsequent ring closure.<sup>[18]</sup> Recently, product **7** was selectively functionalized at its *para* position through a Rieche formylation to afford tri-substituted pCp **8** (Scheme 3a).<sup>[19a]</sup> *Pseudo-meta* di-

bromo[2.2]paracyclophanes **9** reacts in a similar manner.<sup>[19b]</sup> Tetra-substituted products can also be obtained using similar approaches.<sup>[14,19]</sup>

Diester **10**, readily obtained from **9**, can be functionalized in a selective fashion tacking advantage, once again, of the "*transannular directive effect*" of pCps. For instance, tetra-substituted bromine containing product **11** has been isolated in high yields using this strategy (**Scheme 3b**).<sup>[20]</sup>



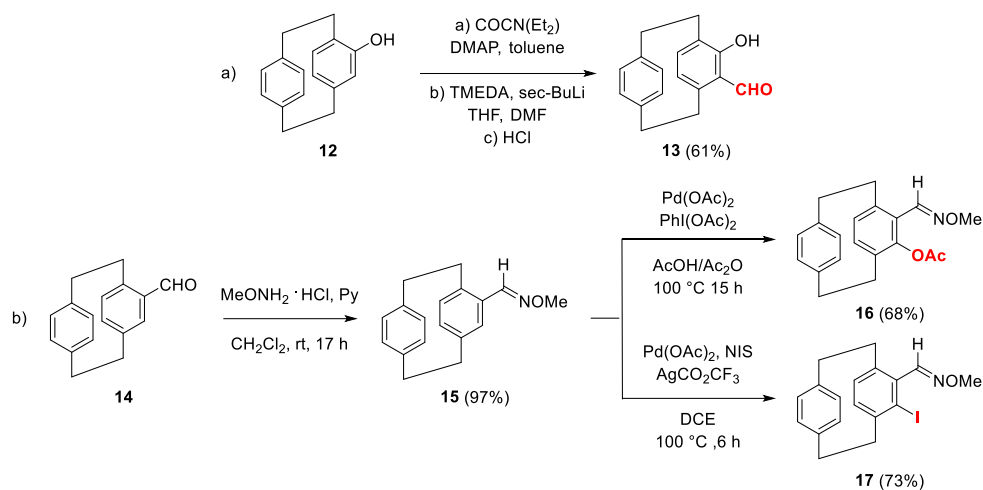
**Scheme 3.** Examples of selective functionalization leading to tri- or tetra-substituted pCps

Other diesters derived from pCp behave analogously under similar reactions conditions.<sup>[14]</sup> Selective *ortho* and *para* di-functionalization of different *pseudo-meta* di-substituted pCps have finally been described.<sup>[19]</sup>

## 2.2. Selective decoration of only one deck

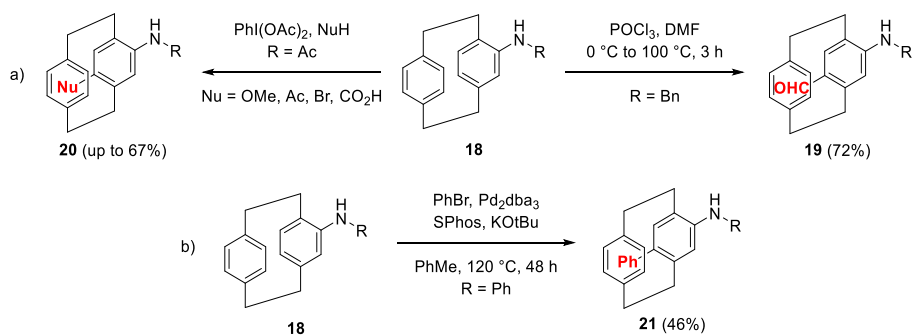
Functionalization of only one aromatic ring of the pCp core can be achieved following different useful strategies. *Ortho*-disubstituted [2.2]paracyclophanes are prepared in a selective manner through directed metalation processes, for example starting from 4-hydroxy[2.2]paracyclophane **12** (**Scheme 4a**).<sup>[21]</sup>

Various metal-catalysed C-H activation processes realised in the presence of different directing groups can also be employed to selectively decorate mono-substituted pCps at their *ortho* position (**Scheme 4b**). Halogenation reactions also occur at the *ortho* position starting from oximes derived from pCp such as compound **15** (**Scheme 4b**).<sup>[22]</sup>



**Scheme 4.** Examples of selective *ortho*-functionalization of mono-substituted pCps

Selective *para*-functionalization of only one aromatic ring of pCps is usually achieved starting from mono-substituted compounds incorporating electron-donating groups or mild electron-withdrawing functions. For example, amine-containing [2.2]paracyclophanes can easily undergo formylation using Vilsmeier-Haack conditions to generate product **19** (**Scheme 5a**).<sup>[23]</sup> This type of compounds incorporates two different reactive groups that can be engaged in orthogonal derivatization processes leading to structurally more complex pCp derivatives in a straightforward way. Other reactions with various nucleophiles have been described to afford products **20** in good yields starting from amides (**Scheme 5a**).<sup>[24]</sup> 4-Methoxy[2.2]paracyclophane can be submitted to similar transformations.<sup>[25]</sup> Anilines derived from pCp have finally been described to undergo C-H activation reactions at their *para* position capable of generating new carbon-carbon bonds (**Scheme 5b**).<sup>[26]</sup>



**Scheme 5.** Examples of selective *para*-functionalization of anilines derived from pCp

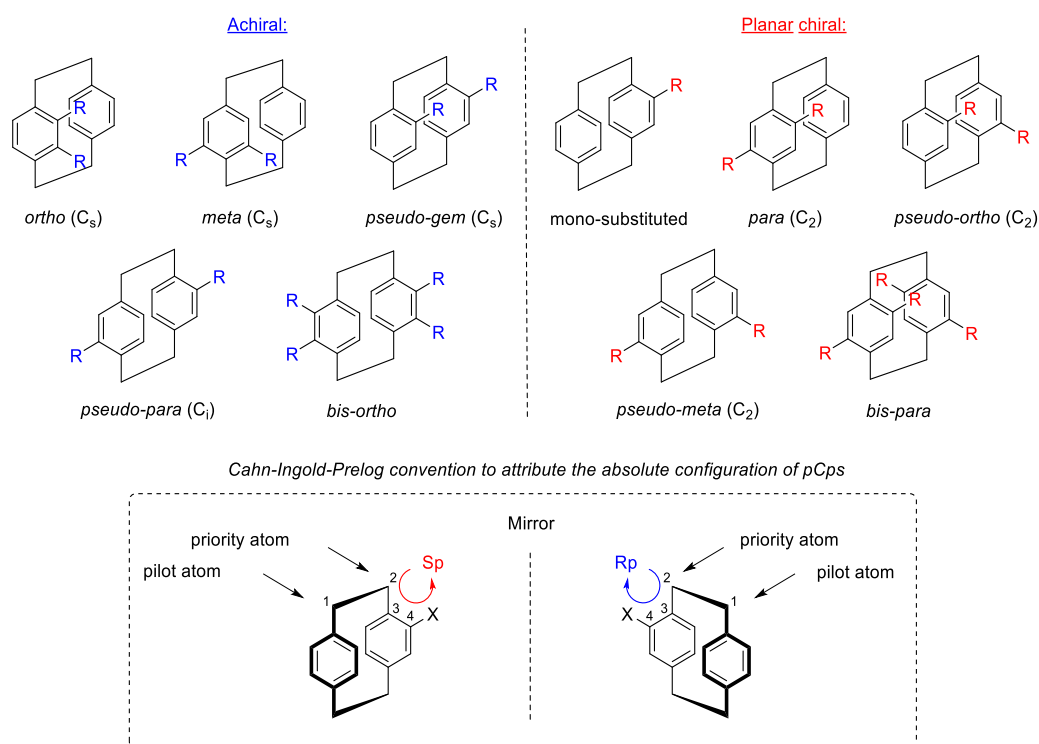
As described hereabove, most of the strategies reported in the literature up to now enable the preparation of useful synthetic intermediates derived from pCp bearing various functional



groups at their *ortho* and *para* positions. On the contrary, the development of new reactions leading to the selective functionalization of mono-substituted compounds at their *meta* position still appears difficult to achieve. Further efforts will be required in the future to address this not trivial synthetic problem.

### 3. Control of Planar Chirality

Substituted [2.2]paracyclophanes can exhibit planar chirality since their rigid strained structure prevents the rotation of the aryl moieties around their axes. Interestingly, while any mono-substituted pCp is chiral, optically active disubstituted derivatives may or may not be obtained depending on the nature and relative position of their substituents (**Figure 3**).<sup>[12]</sup> Indeed, in the presence of two identical functions on the molecules, *ortho*, *meta*, *pseudo-gem* and *pseudo-para* compounds will always be achiral substrates, while *para*, *pseudo-ortho*, and *pseudo-meta* derivatives will never be superimposable on their mirror images and therefore show planar chirality. A similar behaviour is observed for tetra-substituted derivatives.



**Figure 3:** Achiral and planar chiral pCps

To attribute the absolute configuration of enantiopure pCps, specific rules were proposed by Cahn, Ingold and Prelog in 1966 (*CIP conventions*).<sup>[27]</sup> According to these rules, the aromatic ring of the pCp core functionalized with the highest priority atoms (or groups) is

considered to be the chiral plane. The carbon of the ethylene bridge close to the substituent on the chiral plane is called "*priority atom*", while the second carbon of the same bridge, the one outside the chiral plane, is called "*pilot atom*" (**Figure 3**). Substituted [2.2]paracyclophanes should be drawn with the less substituted aromatic ring on the front and the chiral plane on the back. Starting from the "*pilot atom*", the carbons of pCp are numbered according to "*CIP conventions*". Therefore, from the "*priority atom*", if the numbering describes a clockwise circle, the absolute configuration  $R_p$  will be assigned. Conversely, in the case where the order of precedence describes an anti-clockwise circle, the paracyclophane will have a  $S_p$  configuration (Figure 3).<sup>[28]</sup> Nowadays, the  $R_p$  and  $S_p$  descriptors (p for identifying planar chirality) are commonly used in cyclophane chemistry.

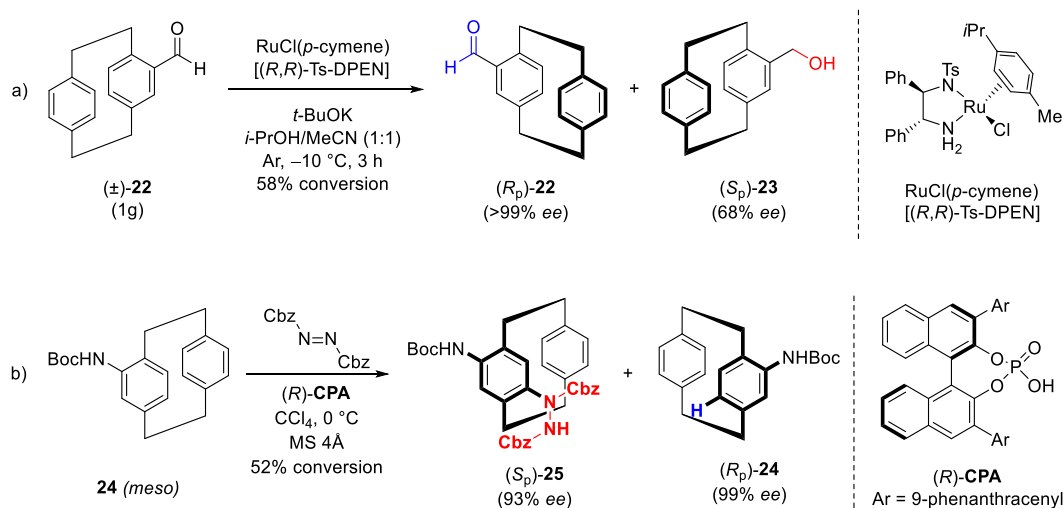
The first evidence of this intriguing property of pCps was observed in 1955 by Gram and Allinger.<sup>[29]</sup> At first, nearly all studies focusing on chiral pCps involved the synthesis of mono-substituted compounds and the determination of their absolute configuration. Starting from the early 1990s onward, chiral paracyclophanes have emerged as powerful ligands in asymmetric catalysis,<sup>[30]</sup> and several poly-substituted compounds have been prepared. Today, optically active pCps are also increasingly employed as central motifs for the development of circularly polarized light-emitting materials.<sup>[31]</sup> However, chirality-controlled synthesis of poly-substituted paracyclophanes frequently reveals difficult to achieve. The lack of procedures providing access to enantiopure pCps on synthetically useful scales significantly limits the application of these molecules in many research fields. The development of new synthetic approaches able to widen the chemical space and range of applications of these chiral compounds therefore constitute a major goal for current and future research in cyclophane chemistry.

Generally, access to complex enantiopure pCps is achieved via the preparation and functionalization of optically active key intermediates. To obtain such versatile substrates, different approaches have been reported in the literature over the years. High performance liquid chromatography (HPLC) on chiral stationary phases has been extensively applied to access a variety of enantiopure pCp derivatives (including acids,<sup>[32]</sup> anilines,<sup>[33]</sup> imines or hydrazones,<sup>[34]</sup> and sulfur-containing derivatives<sup>[35]</sup>), and today remains a method of choice for the late-stage separation of complex paracyclophanes.<sup>[36]</sup> This approach however relies on the use of expensive equipment and large quantities of solvents. Efficient classical chemical resolution procedures involving the formation of diastereoisomeric products have also been described in the literature, notably for the preparation of enantioenriched carboxylic acids,<sup>[37]</sup> aromatic halides,<sup>[38]</sup> anilines,<sup>[39]</sup> aldehydes and ketones,<sup>[40]</sup> phenols and thiols<sup>[41]</sup> or phosphine

oxides.<sup>[42]</sup> Despite being able to afford products with high optical purity, these strategies usually involve several steps and can be quite time-consuming. More recently kinetic resolutions and desymmetrization procedures have emerged as valuable alternatives to previously described methods to access optically active pCps. Selected examples of these useful approaches are described in the next sections.

### 3.1. Chemical kinetic resolutions

Kinetic resolutions (KR) are convenient processes in which racemates are submitted to an asymmetric transformation in the presence of a chiral catalyst. The two enantiomers of the initial mixture react with different reaction rates so that theoretically, at 50% of conversion, one enantiomer will be recovered as the starting material while the other will be isolated as the reaction product. This strategy has gained in popularity in cyclophane chemistry during the last few years and several useful reactions leading to enantioenriched planar chiral derivatives have been described. These include, for example access, to optically active aromatic halides,<sup>[43]</sup> amines,<sup>[44]</sup> imines and *N*-sulfonylimines.<sup>[45]</sup> Enantioenriched pCp-based aldehydes and ketones have successfully been prepared through different asymmetric reduction approaches.



**Scheme 6.** Selected examples of kinetic resolutions of racemic pCps

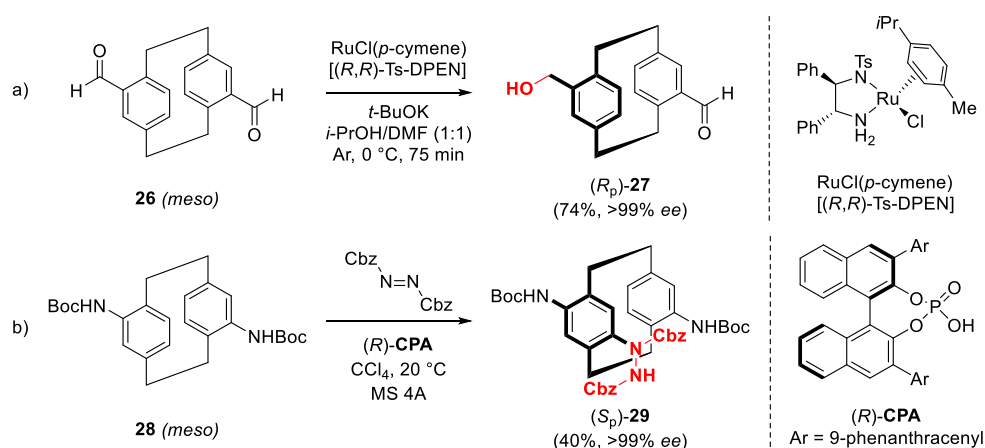
Aldehydes were found capable of undergoing asymmetric transfer hydrogenation processes (ATH) in the presence of commercially available Noyori's catalysts ( $\text{RuCl}(p\text{-cymene})[(R,R)\text{-Ts-DPEN}]$ , **Scheme 6a**),<sup>[46]</sup> while ketones could be reduced in the presence of a chiral Corey-Bakshi-Shibata oxazaborolidine catalyst [ $(S)$ -CBS] and boranes<sup>[47]</sup> or using a ruthenium-based catalyst [ $(S)$ -RUCY<sup>®</sup>-XylBINAP] under high hydrogen pressure.<sup>[48]</sup> More

recently, amides derived from pCp have been successfully resolved through a chiral phosphoric acid (CPA)-catalysed asymmetric amination reaction (**Scheme 6b**).<sup>[49]</sup>

All these reactions are particularly convenient for preparing various enantiopure key intermediates on multigram scale useful scales. The optically active products have successfully been engaged in a variety of derivatization reactions. Such approaches may therefore inspire the development of new practical transformations in the near future.

### 3.2. Desymmetrizations

The main limitation of the kinetic resolution methods presented here above, unrelated to how efficient they are, is their maximum theoretical yield of 50% for enantiopure products. On the contrary, desymmetrization of *meso* derivatives can theoretically provide enantiopure compounds in up to 100% yield. Despite such clear advantage, this technique, which relies on the differentiation of the prochiral sites of achiral molecules, has rarely been applied to [2.2]paracyclophanes. Among the few examples reported so far, asymmetric transfer hydrogenation appears particularly attractive tools to prepare enantiopure pCp derivatives *via* the desymmetrization of centrosymmetric *meso* dialdehydes (**Scheme 7a**).<sup>[50]</sup> This transformation was found to be particularly efficient up to a multi-gram scale. A similar approach also proved successful for ketones derived from pCps. Finally, asymmetric amination reaction revealed useful to desymmetrize centrosymmetric di-amido pCps (**Scheme 7b**).<sup>[49]</sup>



**Scheme 7.** Examples of desymmetrizations of centrosymmetric pCps

While very promising, this type of approach is rare and therefore needs to be explored further in the future to try and expand the substrate scope and access other optically active pCps in a rapid and efficient way. Of course, one key point is also to be able to prepare in an efficient manner *meso* starting materials.

#### 4. Tuning the photophysical behaviors of pCps

Along with their planar chirality, [2.2]paracyclophanes possess interesting photophysical properties which arise from through-space and through-bond conjugation between their two aromatic rings.<sup>[51]</sup> Commercially available pCp indeed displays an unusual UV-visible spectrum, with absorption maxima at 225, 244, 286 and 302 nm.<sup>[52]</sup> Its most red-shifted absorption band, called “*cyclophane band*”, is displaced into a wavelength region rarely observed for more common benzene derivatives. Unsubstituted pCp also shows a characteristic fluorescence emission spectrum with a broad band at 356 nm.<sup>[53]</sup> As a result, [2.2]paracyclophane has been frequently employed as central core for the development of different three-dimensional organic luminophores over the years.

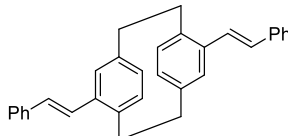
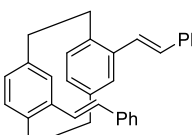
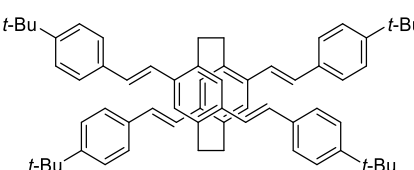
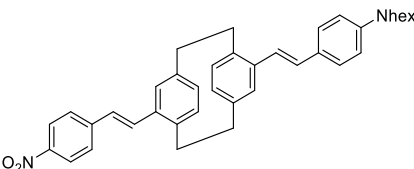
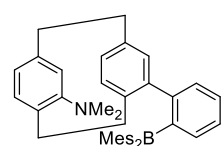
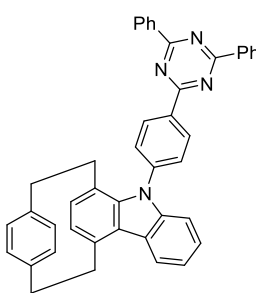
In seminal works, various excimer mimics have been described. Generally, excimers are short-lived (hetero) dimeric molecules whose association occurs in the excited state and can only be detected by fluorescence spectroscopy.<sup>[54]</sup> The pCp-based analogues, on the contrary, are stable at the ground state and constitute ideal model compounds to examine. Several examples of stilbene dimers, such as compounds **30** and **31** (**Table 1, entries 1 and 2**), have been prepared and fully characterized.<sup>[55]</sup> More conjugated derivatives and tetra-substituted pCps have also been reported (**Table 1, entry 3**).<sup>[55]</sup> As a general trend, important bathochromic shifts of the absorption and emission bands were observed for these luminophores in comparison with similar pCp-deprived molecules.

Example of di- or tetra-substituted pCps incorporating electron-donating and electron-withdrawing groups have also been prepared with the aim of studying through-space charge transfer delocalization.<sup>[56]</sup> This type of luminescent molecules, such as compound **33** (**Table 1, entry 4**), displayed interesting solvatochromic behaviours, as their emission maxima changed significantly depending on the polarity of their surroundings. Such pCps may reveal useful in the future to access innovative probes, indicators, or chromogenic reagents.

In addition to these examples, [2.2]paracyclophanes showing reversible colour changes of their solid-state photoluminescence induced by external mechanical stimuli (mechanochromic luminescence) have been described (for example pCp **34**, **Table 1, entry 5**).<sup>[57]</sup> These compounds have great application potentials in advanced optoelectronic devices, pressure sensors, security technologies, and wearable electronics.

Recently, pCp derivatives displaying thermally activated delayed fluorescence (TADF) have been developed, including carbazole derivative **35** (**Table 1, entry 6**).<sup>[58]</sup>

**Table 1.** Selected examples of luminophores based on a pCp scaffold.

Entry	Compound	medium	$\lambda_{\text{abs}}$ (nm)	$\lambda_{\text{em}}$ (nm)	$\Phi$
1	<b>30</b> 	hexane	307	412	-
2	<b>31</b> 	hexane	264 325	401	-
3	<b>32</b> 	hexane	330 390	450	-
4	<b>33</b> 	hexane	372	505	0.27
		DMF	384	590	0.01
5	<b>34</b> 	pristine powder	365	496	0.58
		grinded powder	365	505	0.73
6	<b>35</b> 	toluene	375	470	0.55

TADF is an interesting behaviour, which allows to harvest excited triplet state electrons to generate fluorescence of the singlet excited state through thermally activated back energy transfer.<sup>[59]</sup> TADF organic materials that promise high efficiencies without the use of heavy metals are today increasingly employed for the development of improved organic light emitting diodes (OLEDs).<sup>[60]</sup> A sky blue OLED utilizing compound **35** has successfully been developed. This new device demonstrated an external quantum efficiency notably higher than that of a

reference OLED relying on an analogous, yet pCp-lacking, TADF emitter.<sup>[58]</sup> Preformat pCp dyes, exhibiting this property, may hence pave the path for novel applications in material science in the future.

#### 4.1. Planar chiral luminescent compounds

By combining the planar chirality of pCps with their interesting photophysical properties, original emitters of circularly polarized luminescence (CPL) have finally been developed. For example, helicene derivatives incorporating a pCp central core have been synthesized and characterized.<sup>[61]</sup> Optically active second-ordered structures based on a pCp scaffold have also been reported, including V-, N-, M-, triangle-, propeller-, and X-shaped molecules.<sup>[62]</sup> These structurally-complex [2.2]paracyclophane derivatives were found to display large molar extinction coefficients ( $\epsilon$ ), good photoluminescence and quantum efficiencies ( $\Phi$ ), and excellent absorption or luminescence dissymmetry factors ( $g_{\text{abs}}$  and  $g_{\text{lum}}$ ).<sup>[63]</sup> Such CPL emitters have great potential in practical applications including, for example, the development of 3D optical displays, information storage, advanced security materials and innovative chiroptical sensors.

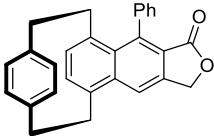
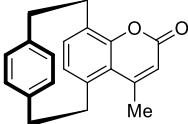
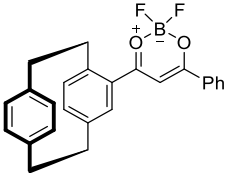
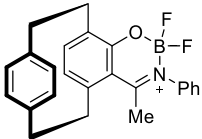
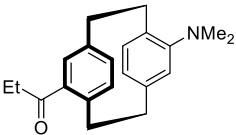
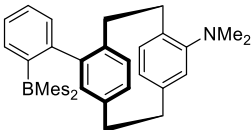
An alternative, scarcely exploited, strategy to modulate the spectroscopic characteristics of chiral pCp-based luminophores consists in expanding the aromatic rings of the [2.2]paracyclophane scaffold to access functionalized polycondensed (hetero)aromatic hydrocarbons. This approach should lead to optically active dyes with more compact structures and improved solubility, both important properties for in solution applications, such as catalytic processes or supramolecular recognition events.

Different families of planar chiral three-dimensional luminophores derived from [2.2]paracyclophane were successfully prepared starting from enantiopure aldehydes obtained through the kinetic resolution and desymmetrization approaches described above. These include pCp-based naphthalenes,<sup>[64]</sup> coumarins,<sup>[65]</sup> or boron diketone<sup>[66]</sup> such as ( $S_p$ )-**36**, ( $S_p$ )-**37** and ( $S_p$ )-**38**. These compact compounds displayed promising chiroptical properties, including luminescence dissymmetry factors ( $g_{\text{lum}}$  values) up to  $4.3 \times 10^{-3}$  in dichloromethane (**Table 2, entries 1-3**). Planar chiral boron difluoride showing aggregation-amplified CPL in solution and at the solid state have also been reported in the literature, as exemplified by pCp ( $S_p$ )-**39** (**Table 2, entry 4**).<sup>[67]</sup>

Planar chiral solvatochromic dyes based on a pCp scaffold have been described. These include, for example, Prodan<sup>[68]</sup> analogues in which the central naphthalene core has been replaced with a pCp motif functionalized with a dimethylamino group and a propionyl moiety

at the *para* or *pseudo-para* positions (**Table 2, entry 5**).<sup>[69]</sup> The photophysical properties of these molecules were found to be strongly influenced by the relative disposition of their substituents. Notably, the *pseudo-para* di-substituted derivative **40** displayed luminescence in the blue region of the electromagnetic spectrum at the solid state and a remarkable CPL activity in toluene ( $g_{\text{lum}}$  values up to  $4 \times 10^{-3}$ ).

**Table 2.** Selected examples of compact CPL emitters based on a pCp scaffold.

Entry	Compound	Solvent	$g_{\text{abs}}$ ( $\lambda_{\text{abs}}$ )	$g_{\text{lum}}$ ( $\lambda_{\text{lum}}$ )	$\Phi$
1	(S <sub>p</sub> )- <b>36</b> 	CH <sub>2</sub> Cl <sub>2</sub>	+ 6.6 × 10 <sup>-4</sup> (350 nm)	+ 6.2 × 10 <sup>-4</sup> (450 nm)	0.62
2	(S <sub>p</sub> )- <b>37</b> 	CH <sub>2</sub> Cl <sub>2</sub>	- 6.2 × 10 <sup>-3</sup> (360 nm)	- 4.3 × 10 <sup>-3</sup> (440 nm)	0.05
3	(S <sub>p</sub> )- <b>38</b> 	CH <sub>2</sub> Cl <sub>2</sub>	+ 6 × 10 <sup>-4</sup> (380 nm)	- 7 × 10 <sup>-4</sup> (550 nm)	0.01
4	(S <sub>p</sub> )- <b>39</b> 	CH <sub>2</sub> Cl <sub>2</sub>	-	+ 4.5 × 10 <sup>-3</sup> (543 nm)	0.39
		THF/H <sub>2</sub> O (9:1)	-	+ 6.2 × 10 <sup>-3</sup> (563 nm)	0.64
5	(S <sub>p</sub> )- <b>40</b> 	toluene	- 1.7 × 10 <sup>-3</sup> (380 nm)	+ 4 × 10 <sup>-3</sup> (486 nm)	0.01
6	(S <sub>p</sub> )- <b>41</b> 	cyclohexane	-	+ 1.7 × 10 <sup>-2</sup> (461 nm)	0.93
		THF	-	- 9.1 × 10 <sup>-3</sup> (538 nm)	0.10

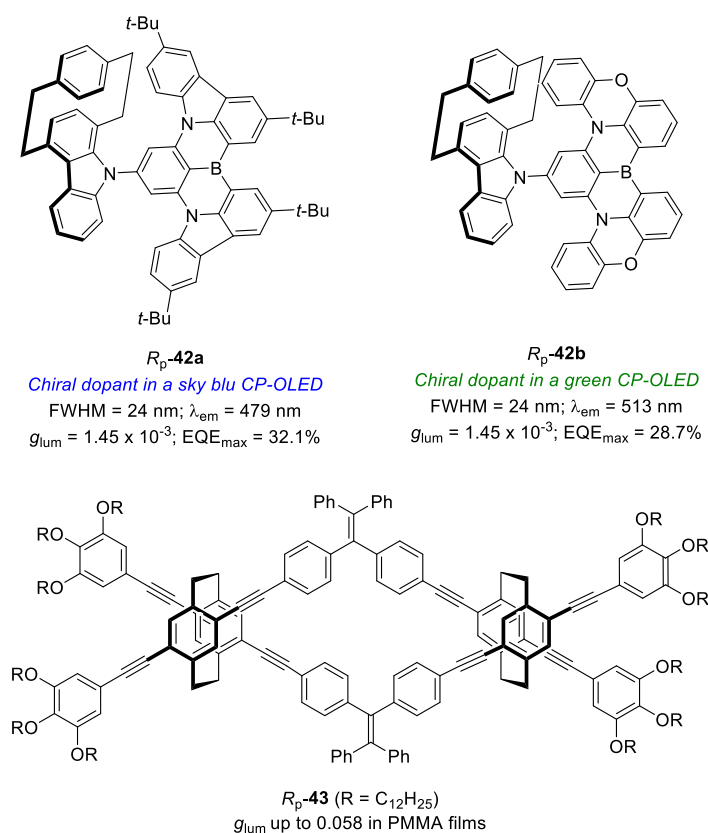
Finally, enantiopure 2-(dimesitylboryl)phenyl-substituted [2.2]paracyclophanes have been synthesized. These promising three-dimensional luminophores not only possess a clear solvatochromic behaviour, but they also display intense CPL and high quantum yields.<sup>[70]</sup>



Within this last family of molecules, the same enantiomer of a *pseudo-meta*-substituted derivative [(*S<sub>p</sub>*)-**41**] was found to show CPL sign inversion when switching from nonpolar solvent to a more polar medium (cyclohexane vs THF, **Table 2, entry 6**).<sup>[70]</sup>

All these compact pCps may prove useful in the future as building blocks for the development of CPL-active materials. However, in many cases, the fluorescence quantum yields of the PCP-based luminophores have been found to be quite low, leaving room for improvement. Rigidification of the structures of pCps may play a key role to access chiral dyes with improved properties.<sup>[71]</sup>

Notably, pCp-based compounds with a rigid helical scaffold<sup>[72]</sup> or those incorporating boron/nitrogen frameworks<sup>[73]</sup> (**42a** and **42b**, Figure 4) have been successfully employed to develop CPL-based organic light-emitting diodes (CP-OLEDs) showing narrow full width at half maximum (FWHM), high EQE<sub>max</sub> values and encouraging luminescence dissymmetry factors (*g<sub>lum</sub>*).



**Figure 4:** Examples of planar chiral pCps used for the design of CP-OLEDs

Additionally, double helices based on planar chiral [2.2]paracyclophanes and tetraphenylethylene (**R<sub>p</sub>-43**, Figure 4) were found to exhibit tunable CPL activity driven by self-assembly. In particular, remarkable *g<sub>lum</sub>* values (up to 0.058), accompanied by a high

fluorescence quantum yield (51%), were observed for poly(methyl methacrylate) films doped with these compounds. The formation of diverse nanostructures such as nanofiber sheets, nanospheres, and higher ordered nanorods could be observed by transmission electron microscopy, confirming the possibility to fabricate advanced molecular CPL materials with tunable and amplified  $glum$  values.<sup>[74]</sup> These findings are expected to inspire additional research in this captivating domain.

## 5. Towards the development of multimodal pCp-based lanthanide complexes

Lanthanides ions (Ln) are currently widely studied in the field of molecular magnetism since they can be considered as excellent candidates to construct single-molecule magnets (SMMs) for high-density data storage and quantum calculation.<sup>[75]</sup> Lanthanide complexes indeed combine large magnetic moment and strong magnetic anisotropy due to the large orbital contribution to the magnetic moment and spin-orbit coupling. One of the main challenges in this field is to combine the SMM behavior of Ln complexes with other chemical, optical, or physical properties such as ferroelectricity, redox activity/conductivity, luminescence, nonlinear optics, and chirality/chiroptical activity. In particular, the effective combination of chirality and magnetism in a single crystalline material can lead to fascinating cross-effects, such as Circularly Polarized Luminescence (CPL)<sup>[76]</sup> and magneto-chiral dichroism (MChD),<sup>[77]</sup> which may play a fundamental role in various technological applications. At this point it could be useful to remind that MChD is an enantioselective and polarization independent light-matter interaction displayed by magnetized chiral materials. In this context, the development of original chiral luminescent ligands capable of modulating the magnetic anisotropy of Ln(III) single-ion magnets could lead not only to exceptional SMMs but also to multifunctionality, with multiple co-existing or strongly interacting physical and chemical properties. Indeed, some of us demonstrated that the association of a lanthanide center [Yb(III) and Dy(III)] with chiral  $\beta$ -diketonate (stereogenic center),<sup>[78]</sup> binaphthyl- (axial chirality)<sup>[79]</sup> or helicene-(helicoidal chirality)<sup>[80]</sup> based ligands allowed the observation of such MChD phenomenon from an oriented single crystal as well as CPL in solid-state. Deep investigations of the molecular materials have been carried out to evaluate the relative role of both magnetic anisotropy and the chirality for the observation of strong MChD and CPL behavior. In such research area, the planar chirality was not yet investigated highlighting the suitable and needed approach to use pCp ligands for designing new CPL/MChD active lanthanide materials and for determining the role of the type of chirality into the origin of these properties.<sup>[81]</sup>

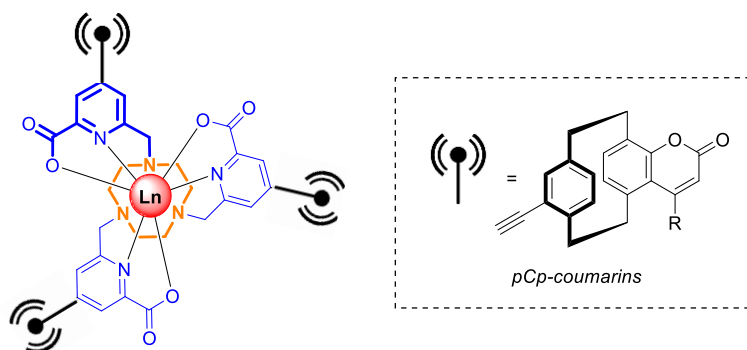
As described in the previous section of this article, pCps have been successfully employed as building blocks to access new families of optically active luminophores, and various dyes showing strong electronic circular dichroism (ECD) and circularly polarized luminescence (CPL).<sup>[61-70]</sup> In addition, thanks to their advantageous physicochemical characteristics, enantiopure paracyclophanes have efficaciously played the role of ligands or catalysts in asymmetric synthesis.<sup>[82]</sup> However, although several transition metal complexes featuring pCps have been described over the years,<sup>[28]</sup> these molecules have rarely been employed as ligands in lanthanide chemistry. Access to unique Ln complexes with multiple properties could therefore significantly extend the range of potential applications of pCps.

### 5.1. Luminescent pCp-based lanthanide compounds

In the literature, only few studies deal with the preparation of lanthanide complexes incorporating [2.2]paracyclophanes. In these rare examples, racemic  $\beta$ -diketonates ligands bearing a pCp moiety have been successfully employed to develop electroluminescent europium complexes.<sup>[83]</sup>

Substituted pCps have also been used as antennas for the sensibilization of different lanthanide ions. In particular, pCp-based coumarins incorporating a triple bond at their *pseudo-para* position could be covalently linked to picolinate-based Ln ligands (**Table 3**).

**Table 3:** Examples of lanthanide complexes incorporating pCp-based antennas

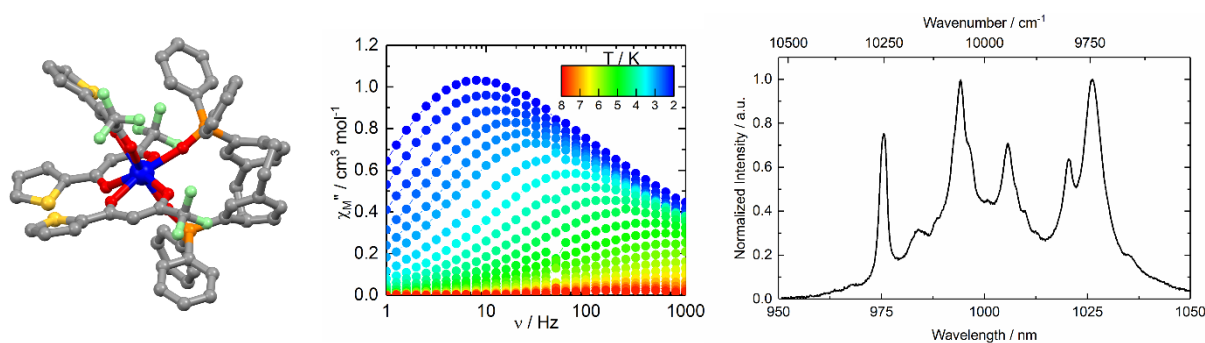


Entry	Ln	$\lambda_{\text{abs}}$ (nm) <sup>a</sup>	$\epsilon$ (L·mol <sup>-1</sup> ·cm <sup>-1</sup> )	$\lambda_{\text{em}}$ (nm) <sup>a</sup>	$\tau_{\text{obs}}$ ( $\mu$ s) <sup>a</sup>	$\Phi^b$	$\Phi_{\Delta}^c$
1	Yb	332	48500	980	9.48	<0.01	0.00
2	Gd	332	61000	422	-	<0.01	0.45

<sup>a</sup>) 10<sup>-5</sup> M solutions in CH<sub>2</sub>Cl<sub>2</sub>; <sup>b</sup>) Fluorescence quantum yield; <sup>c</sup>) singlet oxygen quantum yield

The spectroscopic characterization of the obtained antennas revealed that after excitation, the pCp derivatives can undergo a rapid inter-system crossing from their singlet excited-state to populate a triplet excited state localized at  $19500\text{ cm}^{-1}$ . The pCp-based antennas were therefore found able to sensitize the luminescence of Yb(III) ( $\lambda_{\text{ex}} = 332\text{ nm}$ ;  $\lambda_{\text{em}} = 980\text{ nm}$ , **Table 3, entry 1**) ions or to efficiently produce singlet oxygen when associated to a non-emissive Gd(III) ion ( $\Phi_{\Delta}$ , **Table 3, entry 2**).<sup>[84]</sup> These results opens the way to the design of new lanthanide containing probes for bioimaging applications using confocal two-photon microscopy<sup>[85]</sup> or for the recently promising CPL-microscopy under enantiomerically pure form.<sup>[86]</sup> Alternatively, modified Gd(III) complexes should be envisaged for theranostic applications combining Magnetic Resonance Imaging with PhotoDynamic Therapy.<sup>[87]</sup>

More recently, racemic pCp-based phosphine oxide ligands<sup>[42a,88]</sup> could be employed to generate a crystal field and an electronic distribution around the lanthanide suitable for the observation of slow magnetic relaxation in cases of Yb(III) and Dy(III) complexes (**Figure 5**).<sup>[89]</sup> The synthesized complexes also presented characteristic luminescence in the green or in the near-infrared region of the electromagnetic spectrum leading to luminescence field induced SMMs Magneto-structural correlation between both emission and magnetic properties was carried out. Studies of analogous enantiopure complexes are underway to fully characterize and investigate their physical properties especially CPL.



**Figure 5:** Example of a Ln(III) complex incorporating pCp-based ligand (left side) and their slow magnetic relaxation behaviour (middle) and NIR emission (right side)

Whether still in their infancy, these promising investigations pave the way for the design of performant multifunctional magneto luminescent SMM based on pCps. To do so, the development of the enantiopure version of the pCp-based ligand involved in lanthanide materials is in progress in our laboratories to design chiral SMMs or ferromagnets having an opened hysteresis loop to use MChD to readout the magnetic state of chiral materials by means

of unpolarized light. Novel polarized-free optical data readout technologies might result from such a breakthrough.

## 6. Conclusions

[2.2]Paracyclophanes have attracted increasing attention over the years due to their original geometry, unique electronic properties and unusual reactivity. In this review, different approaches have been highlighted that allow chemists to selectively functionalize the aromatic rings of pCps, control their planar chirality and modulate their photophysical properties. Nowadays, functionalized pCps find interesting applications in different fields of research, ranging from organic synthesis and asymmetric catalysis to polymer chemistry and material science. Among many other possibilities, the use of pCps as central motifs to access innovative organic and organometallic luminophores appears particularly promising. However, many synthetic challenges remain to be tackled in this field to further broaden the scope of decorated pCps potentially accessible. The development of methods allowing the selective functionalization of the ethylene bridges, or the *meta* and *pseudo-meta* positions of these molecules should be particularly considered in future endeavors. Access to enantiopure compounds through efficient and scalable catalytic asymmetric approaches also needs to be fostered and generalized.

In recent years, significant advancements have been made in the development of OLEDs and CPL OLEDs utilizing luminophores derived from pCps. However, it's crucial to emphasize that additional research is essential to delve deeper into this field. The possibility of using enantiopure pCps as central core for the development of novel CPL emitters undoubtedly deserves to be further explored with the aim of accessing compounds with improved properties both in solution and at the solid state.

Within the domain of lanthanide chemistry, the ability of luminescent planar chiral pCps to act as ligands or antennas for Ln sensitization should also be more deeply studied. These investigations, today largely unexplored, may indeed pave the way for the design and development of innovative multifunctional metallic complexes for diverse applications in both material science and the biomedical field. [2.2]Paracyclophanes therefore clearly still offer numerous possibilities for the pursuit of original research in the years to come.

## Acknowledgements

The authors gratefully thank the *Agence Nationale de la Recherche* (ANR PhotoChiraPhane), CNRS, *IdEx Université Paris Cité*, and the *Ministère de l'Enseignement Supérieur et de la Recherche* for financial support.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

## References

- [1] D. J. Cram, H. Steinberg, *J. Am. Chem. Soc.* **1951**, *73*, 5691–5704
- [2] C. J. Brown, A. C. Farthing, *Nature* **1949**, *164*, 915–916.
- [3] H. Hope, J. Bernstein, K. N. Trueblood, *Acta Cryst. B.* **1972**, *28*, 1733–1743.
- [4] a) S. E. Walden, D. T. Glatzhofer, *J. Phys. Chem. A* **1997**, *101*, 8233–8241; b) D. Henseler, G. Hohlneicher, *J. Phys. Chem. A* **1998**, *102*, 10828–10833; c) S. Grimme, C. Mück-Lichtenfeld, *Isr. J. Chem.* **2012**, *52*, 180–192.
- [5] a) A. A. Aly, H. Hopf, L. Ernst, *Eur. J. Org. Chem.* **2000**, *2000*, 3021–3029; b) L. Minuti, A. Marrocchi, I. Tesei, E. Gacs-Baitz, *Tetrahedron Lett.* **2005**, *46*, 8789–8792; c) A. A. Aly, S. Ehrhardt, H. Hopf, I. Dix, P. G. Jones, *Eur. J. Org. Chem.* **2006**, *2006*, 335–350.
- [6] a) D. J. Cram, H. Steinberg, *J. Am. Chem. Soc.* **1951**, *73*, 5691–5704; b) H. E. Winberg, F. S. Fawcett, W. E. Mochel, C. W. Theobald, *J. Am. Chem. Soc.* **1960**, *82*, 1428–1435.
- [7] M. Brink, *Synthesis* **1975**, *12*, 807–808.
- [8] a) T. Otsubo, V. Boekelheide, *Tetrahedron Lett.* **1975**, *45*, 3881–3884; b) A. Iwama, T. Toyoda, M. Yoshida, T. Otsubo, Y. Sakata, S. Misumi, *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2988–2994; c) M. Montanari, A. Bugana, A. K. Sharma, D. Pasini, *Org. Biomol. Chem.* **2011**, *9*, 5018–5020.
- [9] W. Sander, *Modern Cyclophane Chemistry* (Eds. R. Gleiter, H. Hopf), Wiley-VCH, Weinheim, Germany, **2004**, p. 211–228.
- [10] a) J. Lahann, D. Klee, H. Höcker, *Macromol. Rapid Comm.* **1998**, *19*, 441–444; b) H. Nandivada, H.-Y. Chen, L. Bondarenko, J. Lahann, *Angew. Chem. Int. Ed.* **2006**, *45*, 3360–3363; c) H. Pu, Y. Wang, Z. Yang, *Materials Lett.* **2007**, *61*, 2718–2722; d) Z. Hassan, D. Varadharajan, C. Zippel, S. Begum, J. Lahann, S. Bräse, *Adv. Mater.* **2022**, *34*, 2201761.
- [11] D. Klee, N. Weiss, J. Lahann, *Modern Cyclophane Chemistry* (Eds. R. Gleiter, H. Hopf), Wiley-VCH, Weinheim, Germany, **2004**, p. 463–484.
- [12] Z. Hassan, E. Spuling, D. M. Knoll, S. Bräse, *Angew. Chem. Int. Ed.* **2020**, *59*, 2156–2170.

- [13] J. Pu, L. Chen, R.-R. Wu, P. Ye, H.-L. Li, S. Wang, Z.-Y. Xu, S.-J. Lou, D.-Q. Xu, *Chem. Commun.* **2023**, 59, 9348–9351.
- [14] M.-L. Delcourt, S. Felder, S. Turcaud, C. H. Pollok, C. Merten, L. Micouin, E. Benedetti, *J. Org. Chem.* **2019**, 84, 5369–5382.
- [15] S. H. Eltamany, H. Hopf, *Tetrahedron Lett.* **1980**, 21, 4901–4904.
- [16] K. P. Javasundera, D. N. M. Kusmus, L. Deuilhé, L. Etheridge, Z. Farrow, D. J. Lun, G. Kaur, G. J. Rowlands, *Org. Biomol. Chem.* **2016**, 14, 10848–10860.
- [17] H. J. Reich, D. J. Cram, *J. Am. Chem. Soc.* **1969**, 91, 3527–3533.
- [18] D. C. Braddock, S. M. Ahmad, G. T. Douglas, *Tetrahedron Lett.* **2004**, 45, 6583–6585.
- [19] a) B. Dominguez, A. Zanotti-Gerosa, W. Hems, *Org. Lett.* **2004**, 6, 1927–1930; b) F. Biliz, M. Cakici, *Eur. J. Org. Chem.* **2021**, 2021, 4828–4834.
- [20] N. V. Vorontsova, E. V. Vorontsov, E. V. Sergeeva, V. I. Rozenberg, *Tetrahedron Lett.* **2006**, 47, 2357–2360.
- [21] V. Rozenberg, T. y. Danilova, E. Sergeeva, E. Vorontsov, Z. Starikova, A. Korlyukov and H. Hopf, *Eur. J. Org. Chem.* **2002**, 468–477.
- [22] a) P. Lennartz, G. Raabe, C. Bolm, *Adv. Synth. Catal.* **2012**, 354, 3237–3249; b) J. J. P. Kramer, C. Yildiz, M. Nieger, S. Bräse, *Eur. J. Org. Chem.* **2014**, 2014, 1287–1295.
- [23] S. Felder, L. Micouin, E. Benedetti, *Eur. J. Org. Chem.* **2021**, 4015–4018.
- [24] P. Schaal, H. Baars, G. Raabe, I. Atodiresei, C. Bolm, *Adv. Synth. Catal.* **2013**, 355, 2506–2512.
- [25] B. Wang, J. W. Graskemper, L. Qin, S. G. Di Magno, *Angew. Chem. Int. Ed.* **2010**, 49, 4079–4083.
- [26] C. Zippel, E. Spuling, Z. Hassan, M. Polamo, M. Nieger, S. Bräse, *Chem. Eur. J.* **2020**, 26, 13771–13775.
- [27] R. S. Cahn, C. Ingold, V. Prelog, *Angew. Chem. Int. Ed.* **1966**, 5, 385–415.
- [28] S. E. Gibson, J. D. Knight, *Org. Biomol. Chem.* **2003**, 1, 1256–1269.
- [29] D. J. Cram, N. L. Allinger, *J. Am. Chem. Soc.* **1955**, 77, 6289–6294.
- [30] a) J. F. Schneider, R. Fröhlich, J. Paradies, *Isr. J. Chem.* **2012**, 52, 76–91. b) S. Bräse, S. Dahmen, S. Höfener, F. Lauterwasser, M. Kreis, R. E. Ziegert, *Synlett* **2004**, 15, 2647–2669.
- [31] a) Y. Morisaki, Y. Chujo, *Bull. Chem. Soc. Jpn.* **2019**, 92, 265–274. b) K. J. Weiland, A. Gallego, M. Mayor, *Eur. J. Org. Chem.* **2019**, 2019, 3073–3085.
- [32] M. Lämmerhofer, P. Imming, W. Lindner, *Chromatographia.* **2004**, 60, S13–S17.
- [33] G. Meyer-Eppler, R. Sure, A. Schneider, G. Schnakenburg, S. Grimme, A. Lützen, *J. Org. Chem.* **2014**, 79, 6679–6687.

- [34] D. S. Masterson, T. L. Hobbs, D. T. Glatzhofer, *J. Mol. Cat. A* **1999**, *145*, 75–81.
- [35] D. Deschamps, J-F. Lohier, C. J. Richards, A-C. Gaumont, S. Perrio, *J. Org. Chem.* **2021**, *86*, 507–514.
- [36] a) M. Hasegawa, K. Kobayakawa, Y. Nojima, Y. Mazaki, *Org. Biomol. Chem.* **2019**, *17*, 8822–8826; b) C. Mézière, M. Allain, C. Oliveras-Gonzalez, T. Cauchy, N. Vanthuyne, L. G. Sarbu, L. M. Birsa, F. Pop, N. Avarvari, *Chirality*. **2018**, *30*, 568–575; c) T. Furo, T. Mori, T. Wada, Y. Inoue, *J. Am. Chem. Soc.* **2005**, *127*, 8242–8243.
- [37] a) V. Rozenberg, N. Dubrovina, E. Sergeeva, D. Antonov, Y. Belokon', *Tetrahedron Asymm.* **1998**, *9*, 653–656; b) B. Dominguez, A. Zanotti-Gerosa, W. Hems, *Org. Lett.* **2004**, *6*, 1927–1930; c) B. Jiang, X.-L. Zhao, X.-Y. Xu, *Tetrahedron Asymm.* **2005**, *16*, 1071–1074.
- [38] a) H. J. Reich, K. E. Yelm, *J. Org. Chem.* **1991**, *56*, 5672–5679; b) R. Parmar, M. P. Coles, P. B. Hitchcock, G. J. Rowlands, *Synthesis* **2010**; 2010, 4177–4187; c) Y. Morisaki, R. Hifumi, L. Lin, K. Inoshita, Y. Chujo, *Chem. Lett.* **2012**, *41*, 990–992.
- [39] A. Cipiciani, F. Fringuelli, V. Mancini, O. Piermatti, F. Pizzo, R. Ruzziconi, *J. Org. Chem.* **1997**, *62*, 3744–3747.
- [40] a) D. Y. Antonov, Y. N. Belokon, N. S. Ikonnikov, S. A. Orlova, A. P. Pisarevsky, N. I. Raevski, V. I. Rozenberg, E. V. Sergeeva, Y. T. Struchkov, V. I. Tararov, E. V. Vorontsov, *J. Chem. Soc., Perkin. Trans. I* **1995**, 1873–1879; b) V. Rozenberg, T. Danilova, E. Sergeeva, E. Vorontsov, Z. Starikova, K. Lysenko, Y. Belokon', *Eur. J. Org. Chem.* **2000**, 2000, 3295–3303; c) E. V. Sergeeva, I. A. Shuklov, D. Y. Antonov, N. V. Vorontsova, E. V. Vorontsov, Z. A. Starikova, M. M. Il'in, V. I. Rozenberg, *Tetrahedron Asymm.* **2010**, *21*, 1004–1010; d) N. V. Vorontsova, G. S. Bystrova, D. Y. Antonov, A. V. Vologzhanina, I. A. Godovikov, M. M. Il'in, *Tetrahedron Asymm.* **2010**, *21*, 731–738; e) C. J. Friedmann, S. Ay, S. Bräse, *J. Org. Chem.* **2010**, *75*, 4612–4614; f) M. Cakici, S. Bräse, *Eur. J. Org. Chem.* **2012**, 2012, 6132–6135; g) D. Y. Antonov, V. I. Rozenberg, T. I. Danilova, Z. A. Starikova, H. Hopf, *Eur. J. Org. Chem.* **2008**, 2008, 1038–1048; h) L. Minuti, A. Taticchi, A. Marrocchi, *Tetrahedron Asymm.* **2000**, *11*, 4221–4225.
- [41] a) N. V. Vorontsova, R. P. Zhuravsky, E. V. Sergeeva, E. V. Vorontsov, Z. A. Starikova, V. I. Rozenberg, *Russ. Chem. Bull.* **2007**, *56*, 2225–2231; b) B. Jiang, X.-L. Zhao, *Tetrahedron Asymm.* **2004**, *15*, 1141–1143; c) Y. Morisaki, R. Sawada, M. Gon, Y. Chujo, *Chem. Asian J.* **2016**, *11*, 2524–2527; d) R. Zhuravsky, Z. Starikova, E. Vorontsov, V. I. Rozenberg, *Tetrahedron Asymm.* **2008**, *19*, 216–222; e) Y. Morisaki, M. Gon, T. Sasamori, N. Tokitoh, Y. Chujo, *J. Am. Chem. Soc.* **2014**, *136*, 3350–3353; f) R. Sawada, M. Gon, J. Nakamura, Y.



- Morisaki, Y. Chujo, *Chirality* **2018**, 30, 1109–1114; g) A. Vincent, D. Deschamps, T. Martzel, J.-F. Lohier, C. J. Richards, A.-C. Gaumont, S. Perrio, *J. Org. Chem.* **2016**, 81, 3961–3966.
- [42] a) P. J. Pye, K. Rossen, R. A. Reamer, N. N. Tsou, R. P. Volante, P. J. Reider, *J. Am. Chem. Soc.* **1997**, 119, 6207–6208; b) M. N. Cheemala, M. Gayral, J. M. Brown, K. Rossen, P. Knochel, *Synthesis* **2007**, 24, 3877–3885; c) T.-Z. Zhang, L.-X. Dai, X.-L. Hou, *Tetrahedron Asymm.* **2007**, 18, 251–259.
- [43] a) K. Rossen, P. J. Pye, A. Maliakal, R. P. Volante, *J. Org. Chem.* **1997**, 62, 6462–6463; b) M. Kreis, C. J. Friedmann, S. Bräse, *Chem. Eur. J.* **2005**, 11, 7387–7394.
- [44] N. Dendele, F. Bisaro, A.-C. Gaumont, S. Perrio, Richards CJ, *Chem. Commun.* **2012**, 48, 1991–1993.
- [45] a) Y. Zhao, H. Wang, B. Wu, Y.-G. Zhou, *Org. Chem. Front.* **2019**, 6, 3956–3960; b) Y. Zhao, X.-Q. Wang, Y.-J. Yu, Y.-G. Zhou, *J. Org. Chem.* **2021**, 86, 1262–1272.
- [46] M.-L. Delcourt, S. Felder, S. Turcaud, C. H. Pollok, C. Merten, L. Micouin, E. Benedetti, *J. Org. Chem.* **2019**, 84, 5369–5382.
- [47] P. Dorizon, C. Martin, J.-C. Daran, J.-C. Fiaud, H. B. Kagan, *Tetrahedron Asymm.* **2001**, 12, 2625–2630.
- [48] C. Zippel, Z. Hassan, A. Q. Parsa, J. Hohmann, S. Bräse, *Adv. Synth. Catal.* **2021**, 363, 2861–2865.
- [49] S. Yu, H. Bao, D. Zhang, X. Yang *Nature Comm.* **2023**, 14, 5239.
- [50] M.-L. Delcourt, S. Felder, E. Benedetti, L. Micouin, *ACS Catal.* **2018**, 8, 6612–6616.x
- [51] P. Rademacher, *Modern Cyclophane Chemistry* (Eds.: R. Gleiter, H. Hopf), Wiley-VCH, Weinheim, **2004**, pp. 275–310
- [52] D. J. Cram, N. L. Allinger, H. Steinberg, *J. Am. Chem. Soc.* **1954**, 76, 6132–6141.
- [53] R. N. Nurmukhametov, A. V. Shapovalov, A. M. Sergeev, *J. Appl. Spectrosc.* **2014**, 81, 49–56.
- [54] T. Förster, *Angew. Chem. Int. Ed.* **1969**, 8, 333–343.
- [55] a) G. C. Bazan, W. J. Oldham, R. J. Lachicotte, S. Tretiak, V. Chernyak, S. Mukamel, *J. Am. Chem. Soc.* **1998**, 120, 9188–9204; b) G. P. Bartholomew, G. C. Bazan, *Acc. Chem. Res.* **2001**, 34, 30–39; c) W. J. Oldham, Y. J.; Miao, R. J. Lachicotte, G. C. Bazan, *J. Am. Chem. Soc.* **1998**, 120, 419–420; c) G. C. Bazan, W. J. Oldham, R. J. Lachicotte, S. Tretiak, V. Chernyak, S. Mukamel, *J. Am. Chem. Soc.* **1998**, 120, 9188–9204.
- [56] J. Zyss, I. Ledoux, S. Volkov, V. Chernyak, S. Mukamel, G. P. Bartholomew, G. C. Bazan, *J. Am. Soc. Chem.* **2000**, 122, 11956–11962.
- [57] M.-Y. Zhang, Q. Peng, C.-H. Zhao, *J. Mater. Chem. C* **2021**, 9, 1740–1745.

- [58] a) E. Spuling, N. Sharma, I. D. W. Samuel, E. Zysman-Colman, S. Bräse, *Chem. Commun.* **2018**, *54*, 9278–9281; b) N. Sharma, E. Spuling, C. M. Mattern, W. Li, O. Fuhr, Y. Tsuchiya, C. Adachi, S. Bräse, I. D. W. Samuel, E. Zysman-Colman, *Chem. Sci.* **2019**, *10*, 6689–6696.
- [59] Z. Yang, Z. Mao, Z. Xie, Y. Zhang, S. Liu, J. Zhao, J. Xu, Z. Chi, M. P. Aldred, *Chem. Soc. Rev.* **2017**, *46*, 915–1016.
- [60] a) M. Y. Wong, E. Zysman-Colman, *Adv. Mater.* **2017**, *29*, 1605444; b) Y. Liu, C. Li, Z. Ren, S. Yan, M. R. Bryce, *Nat. Rev. Mater.* **2018**, *3*, 18020.
- [61] A. Yanagawa, M. Tsuchiya, R. Inoue, Y. Morisaki, *J. Mater. Chem. C* **2023**, *11*, 986–993.
- [62] a) Y. Morisaki, M. Gon, T. Sasamori, N. Tokitoh, Y. Chujo, *J. Am. Chem. Soc.* **2014**, *136*, 3350–3353; b) Y. Morisaki, K. Inoshita, Y. Chujo, *Chem. Eur. J.* **2014**, *20*, 8386–8390; c) Y. Morisaki, R. Hifumi, L. Lin, K. Inoshita, Y. Chujo, *Polym. Chem.* **2012**, *3*, 2727–2730; d) M. Gon, Y. Morisaki, Y. Chujo, *J. Mater. Chem. C* **2015**, *3*, 521–529; e) M. Gon, H. Kozuka, Y. Morisaki, Y. Chujo, *Asian J. Org. Chem.* **2016**, *5*, 353–359; f) M. Gon, Y. Morisaki, Y. Chujo, *Eur. J. Org. Chem.* **2015**, 7756–7762; g) M. Gon, Y. Morisaki, R. Sawada, Y. Chujo, *Chem. Eur. J.* **2016**, *22*, 2291–2298; h) A. Morisaki, R. Inoue, Y. Morisaki, *Chem. Eur. J.* **2023**, *29*, e202203533.
- [63] X. Li, Y. Xie, Z. Li, *Adv. Photonics Res.* **2021**, *2*, 2000136.
- [64] E. Benedetti, M.-L. Delcourt, B. Gatin-Fraudet, S. Turcaud, L. Micouin, *RSC Adv.* **2017**, *7*, 50472–50476.
- [65] M.-L. Delcourt, C. Reynaud, S. Turcaud, L. Favereau, J. Crassous, L. Micouin, E. Benedetti, *J. Org. Chem.* **2019**, *84*, 888–899.
- [66] S. Felder, M.-L. Delcourt, D. Contant, R. Rodríguez, L. Favereau, J. Crassous, L. Micouin, E. Benedetti, *J. Mater. Chem. C* **2023**, *11*, 2053–2062.
- [67] K. Li, H. Ji, Z. Yang, W. Duan, Y. Ma, H. Liu, H. Wang, S. Gong, *J. Org. Chem.* **2021**, *86*, 16707–16715.
- [68] a) C. Reichardt, *Chem. Rev.* **1994**, *94*, 2319–2358; b) B. E. Cohen, T. B. McAnaney, E. S. Park, Y. N. Jan, S. G. Boxer, L. Y. Jan, *Science* **2002**, *296*, 1700–1703.
- [69] S. Felder, M.-L. Delcourt, M. H. E. Bousquet, D. Jacquemin, R. Rodríguez, L. Favereau, J. Crassous, L. Micouin, E. Benedetti, *J. Org. Chem.* **2022**, *87*, 147–158.

- [70] a) M.-Y. Zhang, Z.-Y. Li, B. Lu, Y. Wang, Y.-D. Ma, C.-H. Zhao, *Org. Lett.* **2018**, *20*, 6868–6871 ; b) M.-Y. Zhang, X. Liang, D.-N. Ni, D.-H. Liu, Q. Peng, C.-H. Zhao, *Org. Lett.* **2021**, *23*, 2–7.
- [71] a) K. Matsumura, R. Inoue, Y. Morisaki, *Adv. Funct. Mater.* **2023**, 2310566 ; b) M. Hasegawa, W. Xiao, Y. Ishida, K. Asahi, H. Nishikawa, R. Ohno, D. Hayauchi, M. Hasegawa, Y. Mazaki, *Adv. Funct. Mater.* **2024**, 2315215.
- [72] Z. Lian, J. He, L. Liu, Y. Fan, X. Chen, H. Jiang, *Nature Commun.* **2023**, *14*, 2752.
- [73] X.-J. Liao, D. Pu, L. Yuan, J. Tong, S. Xing, Z.-L. Tu, J.-L. Zuo, W.-H. Zheng, Y.-X. Zheng, *Angew. Chem.Int. Ed.* **2023**, *62*, e2022170.
- [74] J. He, Y. Fan, Z. Lian, S. Guo, Y. Wang, H. Jiang, *Adv. Optical Mater.* **2023**, 2302221.
- [75] F.-S. Guo, B. M. Day, Y.-C. Chen, M.-L. Tong, A. Mansikkamäki, R. A. Layfield, *Science* **2018**, *362*, 1400–1403.
- [76] a) J. P. Riehl, F. S. Richardson, *Chem. Rev.* **1986**, *86*, 1–16; b) R. Carr, N. H. Evans, D. Parker, *Chem. Soc. Rev.* **2012**, *41*, 7673–7686.
- [77] G. L. J. A. Rikken, E. Raupach, *Nature* **1997**, *390*, 493–494.
- [78] B. Lefeuvre, C. A. Mattei, J. Flores Gonzalez, F. Gendron, V. Dorcet, F. Riobé, C. Lalli, B. Le Guennic, O. Cador, O. Maury, S. Guy, A. Bensalah-Ledoux, B. Baguenard, F. Pointillart, *Chem. Eur. J.* **2021**, *27*, 7362-7366.
- [79] C. A. Mattei, V. Montigaud, B. Lefeuvre, V. Dorcet, G. Argouarch, O. Cador, B. Le Guennic, O. Maury, C. Lalli, Y. Guyot, S. Guy, C. Gindre, A. Bensalah-Ledoux, F. Riobé, B. Baguenard, F. Pointillart, *J. Mater. Chem.*, **2023**, *11*, 7299 -7310.
- [80] a) M. Atzori, K. Dhbaibi, H. Douib, M. Grasser, V. Dorcet, I. Breslavetz, K. Paillot, O. Cador, G. L. J. A. Rikken, B. Le Guennic, J. Crassous, F. Pointillart, C. Train, *J. Am. Chem. Soc.*, **2021**, *143*, 2671-2675; b) K. Dhbaibi, M. Grasser, H. Douib, V. Dorcet, O. Cador, N. Vanthuyne, F. Riobé, O. Maury, S. Guy, A. Bensalah-Ledoux, B. Baguenard, G. L. J. A. Rikken, C. Train, B. Le Guennic, M. Atzori, F. Pointillart, J. Crassous, *Angew. Chem. Int. Ed.* **2023**, e202215558; c) M. Sara Raju, K. Dhbaibi, M. Grasser, V. Dorcet, I. Breslavetz, K. Paillot, N. Vanthuyne, O. Cador, G. L. J. A. Rikken, B. Le Guennic, J. Crassous, F. Pointillart, C. Train, M. Atzori, *Inorg. Chem.* **2023**, *62*, 17583-17587.
- [81] F. Pointillart, M. Atzori, C. Train, *Inorg. Chem. Front.* **2024**, *11*, 1313-1321.
- [82] Z. Hassan, E. Spuling, D. M. Knoll, J. Lahann, S. Bräse, *Chem. Soc. Rev.* **2018**, *47*, 6947–6963.
- [83] R. Grykien, B. Luszczynska, I. Glowacki, L. Puntus, I. Pekareva, K. Lyssenko, F. Kajzar, I. Rau, C. A. Lazar, *Opt. Mater.* **2016**, *57*, 114–119.

- [84] S. Wu, L. A. Galan, M. Roux, F. Riobe, B. Le Guennic, Y. Guyot, T. Le Bahers, L. Micouin, O. Maury, E. Benedetti, *Inorg. Chem.* **2021**, *60*, 16194–16203.
- [85] N. Hamon, A. Roux, M. Beyler, J.-C. Mulatier, C. Andraud, C. Nguyen, M. Maynadier, N. Bettache, A. Duperray, A. Grichine, S. Brasselet, M. Gary-Bobo, O. Maury, R. Tripier, *J. Am. Chem. Soc.* **2020**, *142*, 10184–10197.
- [86] D. F. De Rosa, P. Stachelek, D. J. Black, R. Pal, *Nature Commun.* **2023**, *14*, 1537.
- [87] L. Abad Galán, N. Hamon, C. Nguyen, E. Molnár, J. Kiss, J. Mendy, K. Hadj-Kaddour, M. Onofre, G. Trencsényi, C. Monnereau, M. Beyler, G. Tircsó, M. Gary-Bobo, O. Maury, R. Tripier, *Inorg. Chem. Front.* **2021**, *8*, 2213–2224.
- [88] G. Meyer-Eppler, E. Vogelsang, C. Benkhäuser, A. Schneider, G. Schnakenburg, A. Lützen, *Eur. J. Org. Chem.* **2013**, *2013*, 4523–4532.
- [89] H. Flichot, A. Sickinger, J. Brom, B. Lefeuvre, V. Dorcet, T. Guizouarn, O. Cador, B. Le Guennic, L. Micouin, O. Maury, E. Benedetti, F. Pointillart, *Manuscript submitted*.

## Author biographies and photographs



**Shiqi Wu** completed his undergraduate studies at Dalian University of Technology, earning a degree in Chemical Engineering in 2018. That same year, he was awarded a CSC fellowship and commenced his doctoral studies under the supervision of Dr. E. Benedetti and Dr. L. Micouin at *Université Paris Cité*. His research focused on the synthesis of luminescent [2.2]paracyclophane derivatives and the characterization of their photophysical properties. He successfully obtained his PhD in organic chemistry in July 2022.



**Simon Felder** completed his master's degree in molecular chemistry at Université Paris Cité in 2018. That same year, he began his doctoral studies under the guidance of Dr. E. Benedetti and Dr. L. Micouin at Université Paris Cité, concentrating on the control of planar chirality and selective functionalization of [2.2]paracyclophanes. He successfully defended his PhD thesis in organic chemistry in February 2022. Currently, he holds a postdoctoral research position at UNC Chapel Hill (USA) in the group of Prof. Kevin Weeks.



**Jules Brom** pursued his undergraduate studies at Université Paris-Saclay and obtained his master's degree and a magister in physics and molecular chemistry in 2020. Following an internship under the supervision of Dr. A. Guérinot at ESPCI Paris, he joined the research group of Dr. E. Benedetti and Dr. L. Micouin at Université Paris Cité to pursue his doctoral studies focused on the synthesis and application of [2.2]paracyclophanes. He successfully completed his PhD in organic chemistry in October 2023.



**Fabrice Pointillart** obtained his PhD in physics and chemistry of materials from Pierre et Marie Curie University in 2005, supervised by Prof. Cyrille Train and Prof. Michel Verdaguer. After his postdoctoral research at the University of Florence with Prof. Roberta Sessoli, he joined the University of Rennes in 2007, as a CNRS researcher. He has been awarded the CNRS Bronze Medal (2014) and Young researcher Coordination Chemistry Division (2017). His current interests are focused on multifunctional molecular materials based on lanthanides combining magnetic and (chir)optical properties for the observation of single molecule magnet behaviour, magneto-chiral dichroism and circularly polarized luminescence.



**Olivier Maury** graduated from *École Nationale Supérieure de Chimie de Paris* in 1993 and completed his Ph.D. in 1997 under the supervision of M. Ephritikhine (CEA Saclay). After a postdoctoral stay with J.-M. Basset (CPE-Lyon), he got a CNRS position as Chargé de Recherche in 1999 at the University of Rennes in the group of H. Le Bozec. In 2004 he moved to ENS de Lyon where he founded his own group. His current research interests concern the design of lanthanides containing molecular materials and NIR chromophores with optimized spectroscopic properties (luminescence, transient absorption, chiroptics and nonlinear optics).



**Laurent Micouin** earned his engineering diploma from the *Ecole Nationale Supérieure de Chimie de Paris* in 1990. In 1995, he completed his PhD under the supervision of Prof. J.-C. Quirion at the laboratory of Prof. H.-P. Husson (Paris Descartes University). Following a postdoctoral position in Marburg (Germany) as a Humboldt Fellow under the guidance of Prof. P. Knochel, he secured a permanent position at CNRS in 1996. Since October 2005, he has held the position of *Directeur de Recherche* at *Université Paris Cité*. His primary research interests center on methodological advancements, particularly in organoaluminum chemistry, asymmetric catalysis, and diversity-oriented synthesis.



**Erica Benedetti** completed her doctoral studies at the University of Insubria, in collaboration with Sorbonne University, under the supervision of Profs. A. Penoni and L. Fensterbank. She obtained her PhD in 2011. In 2012, she joined the research group of Prof. K. M. Brummond at the University of Pittsburgh as a postdoctoral fellow. After a postdoctoral stay at ESPCI ParisTech in the group of Prof. J. Cossy, in 2014, she became a CNRS researcher at *Université Paris Cité*. Her current research focuses on the synthesis and functionalization of planar chiral [2.2]paracyclophanes. In recognition of her achievements, she was awarded the CNRS Bronze Medal in 2022 and the Thieme Chemistry Journals Award in 2024.

[2.2]Paracyclophanes (pCps) constitute a fascinating class of molecules that can find a variety of applications in different fields, ranging from synthetic organic chemistry to material science. This review gives an overview of valuable methods providing a straightforward access to compact pCp-based luminophores with intriguing properties through key modifications of their aromatic rings. The use of these compounds as building blocks for the development of original OLEDs is discussed, alongside potential new avenues for this field.

Shiqi Wu, Simon Felder, Jules Brom, F. Pointillart, O. Maury, Laurent Micouin\* and Erica Benedetti\*

### [2.2]Paracyclophanes: from selective functionalization to optical properties

