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Compact CPL emitters based on a [2.2]paracyclophane scaffold: recent developments and future perspectives†

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Due to their unique three-dimensional framework and intriguing electronic properties, [2.2]paracyclophanes (pCps) have been employed over the years as building blocks in materials science for the development of organic light-emitting diodes and non-linear optical systems. In addition, depending on their substitution patterns, [2.2]paracyclophanes can display planar chirality and are nowadays considered as useful scaffolds for the development of original circularly poliarized luminescence (CPL) emitters. This perspective gives an overview on the synthesis and characterization of different families of compact luminescent compounds derived from planar chiral [2.2]paracyclophanes. The chiroptical properties of these small molecules are described, with a particular focus on their ability to emit circularly polarized luminescence in solution. Some future prospects on the design and potential applications of CPL emitters derived from pCps are finally presented.

Introduction

Circularly polarized luminescence (CPL) is a fascinating property of chiral molecules that corresponds to the ability of differently emitting right-handed and left-handed circularly polarized light.[1,2] This phenomenon has attracted considerable attention for the development of chiral materials for smarter displays and photonic technologies, thanks to the higher resolution and lower loss of energy provided by circularly polarized emitters.[3–8] Among various chiral luminophores, organic CPL active compounds[9] are currently actively investigated due to their advantageous characteristics, which include tuneable emission profiles, high luminescence efficiencies, as well as ease of manufacturing and testing. The design of chiral organic molecules exhibiting high CPL efficiency is therefore an important objective in the photonics field.

Originally discovered in a serendipitous fashion by vapor phase pyrolysis of *p*-xylene,[10] [2.2]paracyclophane (pCp) and its derivatives have rapidly gained popularity amongst chemists due to their unique three-dimensional architecture.[11] These compounds incorporate two distorted benzene rings covalently fixed in a stacked geometry by two ethylene bridges at their *para* positions. The conformational stiffness and proximity of the two π systems favours transannular through-space and through-bond interactions that confer on pCps intriguing electronic properties.[12,13] These molecules show a unique reactivity[14–20] and an unusual spectroscopic behaviour.[21,22] The absorption spectrum of commercially available pCp is characterized by a low-intensity band with a maximum around 302 nm which is rarely observed for more common benzene derivatives. Non-substituted pCp also displays a broad emission band with a maximum at 356 nm. [2.2]Paracyclophanes have been successfully exploited in material science for the development of organic light-emitting diodes (OLEDs) and nonlinear optical materials.[23–26] Differently functionalized pCps have also been employed as starting materials to produce through-space conjugated polymers and functionalized surfaces using chemical vapor deposition (CVD) methods.[27]

Another fascinating feature of [2.2]paracyclophanes is their planar chirality.[28] Since their rigid structure precludes any rotational motion of their aromatic rings, all mono-substituted pCps are optically active compounds. Different planar chiral molecules can be rapidly generated by increasing the number of substituents on the pCp core.[29] Chiral pCps are characterized by high configurational stability (up to 200 °C), they can be stored for long periods of time and are generally easy to handle. These compounds also show chemical stability towards light and

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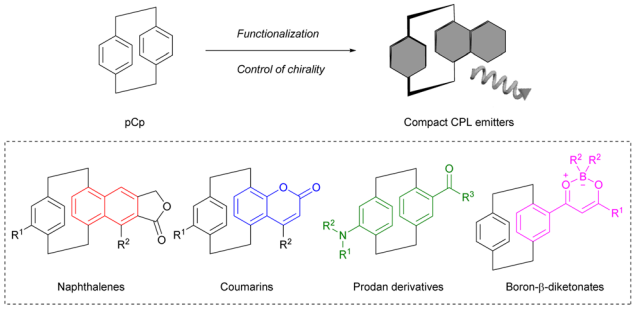


Scheme 1 Different families of compact CPL emitters based on the pCp scaffold.

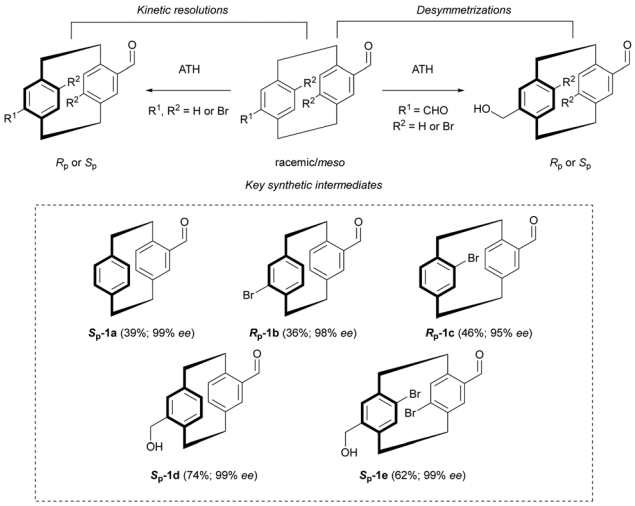
oxidants, as well as a good tolerance to the action of acids and bases. Thanks to their advantageous physico-chemical properties, pCps have gradually emerged as powerful ligands or catalysts in stereoselective synthesis and asymmetric catalysis.[30–33] Enantiopure paracyclophanes are also increasingly employed as building blocks to access new families of optically active luminescent compounds. Various dyes showing strong electronic circular dichroism (ECD) and CPL have been reported in the literature. As attested by recent reviews,[34,35] most of the CPL active pCp-based chromophores developed so far present "branched" π-extended structures or complex three-dimensional shapes.[35–40] In this short account of results obtained in our laboratories,‡ we will give an overview on the synthesis and (chir)optical properties of more compact planar chiral dyes (Scheme 1).

Different families of small organic luminophores derived from [2.2]paracyclophanes will be described: naphthalenes, coumarins, PRODAN derivatives and boron-β-diketonates. We will present practical methods to control the planar chirality of these three-dimensional analogues of well-known "flat" aromatic dyes. The spectroscopic properties of the optically active luminophores will be described, with an emphasis on their chiroptical behaviours. The potential use of pCps as building blocks for the development of innovative CPL emitters will be discussed. Finally, prospects on the design and possible applications of compact CPL emitters derived from pCps will be outlined.

Control of planar chirality

The synthesis of functionalized planar chiral [2.2]paracyclophanes, including CPL active dyes, generally relies on the preparation and derivatization of optically active key intermediates. To obtain such compounds, different strategies have been reported in the literature over the years. Although quite expensive, chiral HPLC on semi-preparative or preparative scales is frequently employed in paracyclophane chemistry as a useful way to access a variety of enantiopure products.[41–49] To-date, this technique remains a method of choice for the late-stage separation of complex

‡ Synthesis and spectroscopic characterization through unpolarized absorption and emission spectroscopies of different families of compact pCp-based luminophores have been performed at the Laboratoire de Chimie et de Biochimie Pharmacologiques et Toxicologiques (Université Paris Cité). Investigation of the chiroptical properties of all enantiopure pCp-based compact dyes has been realized at the Institut des Sciences Chimiques de Rennes (Univ Rennes).



Scheme 2 Access to optically active pCp key intermediates through kinetic resolution and desymmetrization reactions.

pCp molecules. Chemical processes constitute a valuable alternative to access optically active pCps in an efficient, more economical fashion.

Among the different possibilities,[50–56] the kinetic resolutions and desymmetrization reactions of racemic/*meso* pCp-based aldehydes developed by us present several advantages, including easy implementation, good repeatability, and cost-effective scalability.[57–59] These procedures, which involve asymmetric transfer hydrogenations (ATH) promoted by commercially available Noyori's catalysts,[60–62] readily afford enantioenriched pCps decorated with various reactive groups (Scheme 2). As highlighted in the next sections of this perspective, such compounds have been successfully engaged in a variety of late-stage derivatisation processes and can be considered as key precursors for the preparation of several compact pCp-based luminescent compounds.

Compact pCp-based organic luminophores

As mentioned above, the [2.2]paracyclophane scaffold has been broadly employed in recent years as a valuable building block to develop original organic luminophores due to its unique three-dimensional geometry and unusual spectroscopic properties. Up to now, the photophysical characteristics of pCp-based dyes have mainly been tuned by introducing "branched" π-extended motifs onto their aromatic rings.[35–40] A less frequently exploited strategy to modulate the spectroscopic behaviour of luminophores derived from [2.2]paracyclophane consists in chemically modifying the benzene rings of the pCp scaffold to access functionalized polycondensed aromatic hydrocarbons or heterocycles.[63] This approach can deliver dyes with more compact structures and improved solubility. The ability to control the chirality of these objects is a key aspect to access compounds with advantageous chiroptical behaviours.

pCp-based naphthalene luminophores

Naphthalenes constitute a well-known class of organic luminophores widely used in biochemistry and related fields as

convenient biological labels or fluorescent sensors.[64–66] These compounds have also been successfully employed over the years as building blocks to develop light-harvesting systems and materials for light-emitting diodes.[67] In this field, the preparation of naphthalene-based CPL emitters may foster innovation and promote the emergence of new technologies.

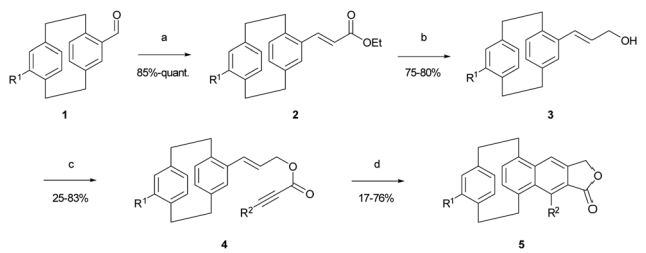
Recently, we have employed an intramolecular dehydrogenative Diels–Alder reactions as key step to construct functionalized naphthalenes motifs onto one of the two benzene rings of [2.2]paracyclophane (Scheme 3).[68]

The precursors of these compounds (**4**, Scheme 3) have been obtained starting from aldehydes intermediates (**1**, Scheme 3) in only three synthetic steps. The structure of the pCp-based naphthalenes could be decorated with a variety of functional groups, including aromatic and aliphatic moieties, electron-rich or electron-poor motifs, and halogen atoms.

A photophysical study revealed that the pCp-based luminophores display red-shifted absorption and emission bands in comparison with analogous "flat" naphthalene derivatives (Table 1). The "out-of-plane" ring of pCps can therefore be considered as a non-conventional electron-donating substituent and highlights the influence of through-space conjugation.[69] Interestingly, amine-containing pCp-based naphthalenes display intriguing solvatochromic properties.[68]

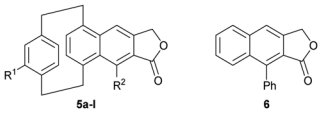
Starting from enantiopure aldehydes R_p-**1a** and S_p-**1a**, optically active pCp-based naphthalenes S_p-**5a** and R_p-**5a** have been prepared in good overall yields (~37% over 4 steps). These luminophores exhibit interesting ECD and CPL activities. The ECD spectra of the enantiomeric pair recorded in CH_2Cl_2 display mirror-image relationships (Fig. 1). Two main ECD-active bands of moderate strength can be observed, the first at 250 nm ($\Delta\varepsilon$ = +12 M^{-1} cm^{-1} for S_p-**5a**) and the second at 300 nm ($\Delta\varepsilon$ = −16 M^{-1} cm^{-1} for S_p-**5a**). Naphthalenes S_p-**5a** and R_p-**5a** also possess reliable mirror-image CPL signatures in CH_2Cl_2 (Fig. 1). An absorption dissymmetry factor (g_{abs}) of 6.6 × 10^{-4} at 350 nm and a luminescence dissymmetry factor (g_{lum}) of 6.7 × 10^{-4} at 450 nm (Table 3) have been calculated for these compounds, which sets them in the typical range for CPL-active pCp derivatives.[70,71]

Interestingly, in addition to the classical Stokes shift often used to describe the structural and electronic reorganization of a fluorophore excited-state prior to the emission process, the



Scheme 3 Synthesis of pCp-based naphthalenes. Reaction conditions: (a) triethyl phosphonoacetate (1.5 equiv.), DBU, Ar, rt, 4 h; (b) DIBAL-H (4 equiv.), Et_2O, Ar, −78 °C to rt, 4 h; (c) propiolic acid derivative (1.05 equiv.), DCC (1 M in CH_2Cl_2, 1.5 equiv.), DMAP (0.01 equiv.), CH_2Cl_2, Ar, rt, 4 h; (d) μw, $PhNO_2$, 180 °C, 30 min.

Table 1 Spectroscopic properties of pCp-based naphthalenes and analogue **6**



Entry	Compound	R^1, R^2	λ_{max}^{abs} [c] (nm)	λ_{max}^{em} (nm)	θ [d] (%)
1[a]	**5a**	H, Ph	376	440	62
2[a]	**5b**	Br, Ph	371	430	17
3[a]	**5c**	NHBn, Ph	365	555	6
4[a]	**5d**	H, Me	373	420	39
5[a]	**5e**	H, CH_2OH	373	415	16
6[a]	**5f**	H, *p*-Cl-Ph	375	440	41
7[a]	**5g**	H, *p*-OTf-Ph	378	445	43
8[a]	**5h**	H, *p*-OMe-Ph	378	443	41
9[a]	**5i**	H, *p*-NMe_2-Ph	400	510	23
10[a]	**5k**	H, *p*-NHBn-Ph	385	485	30
11[b]	**5l**	H, *p*-OH-Ph	374	454	16
12[a]	**6**	—	345	380	22

[a] 10^{-5} M solutions of the dyes in CH_2Cl_2. [b] 10^{-5} M solutions of the dye in DMSO. [c] Absorption maximum of the most red-shifted band (putative cyclophane band). [d] Relative fluorescence quantum yields (θ) were determined using anthracene and 9,10-diphenylanthracene as standards.

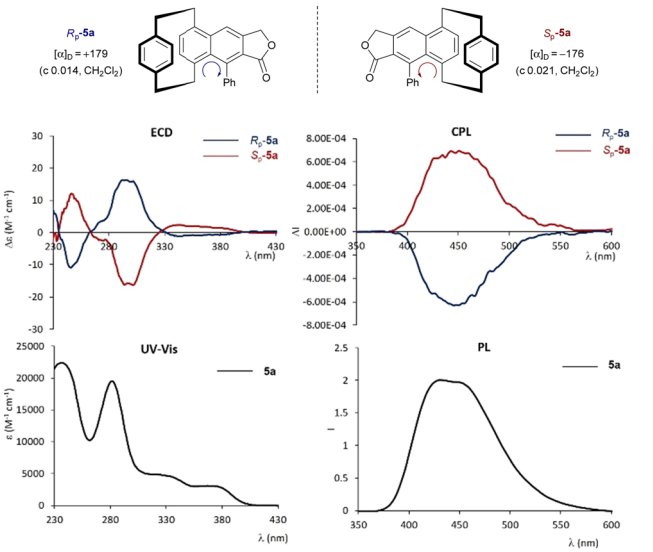


Fig. 1 Chiroptical properties of pCp-based naphthalenes S_p-**5a** and R_p-**5a**. UV-Vis, PL, ECD and CPL spectra were recorded in CH_2Cl_2 (10^{-5} M solutions, λ_{ex} = 365 nm).

g_{abs}/g_{lum} ratio for a chiral emitter appears as a complementary value to discuss the impact of that reorganization on the chirality of the ground- *vs.* excited states. Here, the g_{lum}/g_{abs} ratio of 1 reveals that no structural/electronic reorganization occurred during the excitation/emission processes.

pCp-based coumarins

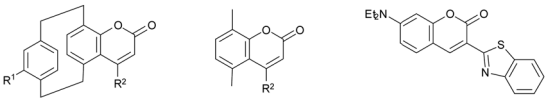
Coumarins have been extensively studied over the years because of their promising pharmacological properties.[72] These compounds also possess impressive luminescent behaviours and

have found several applications in a variety of research fields ranging from optoelectronics to cellular imaging.[73–78] Chiral light-emitting analogues of these compounds can constitute ideal candidates for developing innovative optical brighteners. We have successfully prepared a series of [2.2]paracyclophanepyranones starting from differently substituted 4-formyl[2.2]paracyclophanes. This new class of pCp-based luminophores incorporating coumarin moieties can indeed be obtained in a straightforward manner through a three-step synthetic procedure which involves a gold-catalysed intramolecular cyclization as the key step (Scheme 4).[79]

The influence of the pCp motif and its "*phane*" interactions on the spectroscopic properties of coumarins **10a–o** has been studied by unpolarized UV-vis absorption and fluorescence emission spectroscopy. As a general trend, the 3D coumarins showed red-shifted absorption and emission bands when compared to paracyclophane-deprived model compounds (**11a, b**, Table 2). The extension of the π-conjugation between the pCp and coumarin motifs in the novel luminophores is clearly responsible for this behaviour. It is worth mentioning that the UV-vis absorption profiles of the pCp-based coumarins are significantly blue-shifted in comparison with commercially available flat dyes which display a substantial intramolecular charge transfer (coumarin **6**, Table 2).

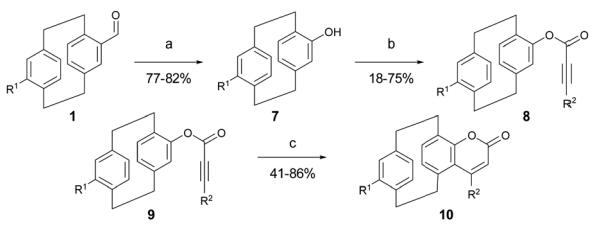
The introduction of different functional groups on the "out-of-plane" deck of the pCp core significantly influences the luminescence of the [2.2]paracyclophanepyranones. For example, halogen-containing derivatives show blue-shifted emission bands in comparison with their non-substituted analogues (Table 2, entries 5 and 6 *vs.* entries 1 and 2). On the contrary, for compounds incorporating electron-donating amino groups, strong bathochromic shifts of the emission maxima are observed (Table 2, entry 13 *vs.* entry 1). These results clearly demonstrate that the photophysical properties of this series of compounds can easily be tuned simply by playing with the nature and the relative position of their substituents. Note that all coumarins **10a–o** showed a good photostability,[79] as well as extremely large Stokes shifts (up to 43 478 cm^{-1} for compound **10m**) compared to their "flat" analogues. Low fluorescence quantum yields were however observed for these molecules ($0.1\% < \theta < 5\%$). When optically active aldehydes R_p-**1a** and S_p-**1a** (Scheme 2) are employed as synthetic precursors, enantiopure planar chiral coumarins can be obtained in an analogous manner as previously described for the pCp-based naphthalene derivatives. The two enantiomers of coumarin **10b** have been prepared as a proof of concept. The chiroptical behaviour of these dyes has been investigated by ECD and CPL spectroscopies. An interesting mirror-image Cotton effect can be observed when ECD spectra are recorded in CH_2Cl_2 (10^{-5} M solutions, Fig. 2). Coumarin S_p-**10b** displays a quite intense positive response at 240 nm ($\Delta\varepsilon = +64\ M^{-1}\ cm^{-1}$), as well as a more moderate negative one at 320 nm ($\Delta\varepsilon = -23\ M^{-1}\ cm^{-1}$). As expected, opposite signals are detected for compound R_p-**10b** (Fig. 2). The CPL spectra of R_p-**10b** and S_p-**10b** also display clear mirror image signals in CH_2Cl_2 (10^{-5} M solutions, λ_{ex} = 330 nm). The pCp-based coumarin dyes show higher absorption and luminescence dissymmetry factors ($g_{abs} \sim 6.2 \times 10^{-3}$ at 360 nm; $g_{lum} \sim 4 \times 10^{-3}$ at 440 nm, see Table 3) in comparison with pCp-based naphthalenes. Such values are quite remarkable especially if one considers the very compact structure of these purely organic luminophores, as compared to former π-extended systems.[35–40] Here again, the g_{lum}/g_{abs} ratio of 0.7 highlights rather weak reorganization upon excitation/emission.

Table 2 Spectroscopic properties of pCp-based coumarins and flat analogues



Entry	Compound	R^1, R^2	λ_{max}^{abs} (nm)	λ_{max}^{em} [d] (nm)
1[a]	**10a**	H, Ph	265, 300, 330	460
2[a]	**10b**	H, Me	301, 319	435
3[a]	**10c**	H, i-Pr	300, 320	432
4[a]	**10d**	H, H	304, 320	445
5[a]	**10e**	Br, Ph	307, 325	450
6[a]	**10f**	Br, Me	306, 320	425
7[a]	**10g**	H, *p*-MePh	315	455
8[a]	**10h**	H, *p*-OMePh	300, 330	455
9[a]	**10i**	H, *p*-ClPh,	288, 310, 335	465
10[a]	**10j**	H, *p*-OTfPh,	280, 330	470
11[a]	**10k**	H, *p*-CF_3Ph	270, 335	475
12[a]	**10l**	NHBoc, Ph	317	450
13[a]	**10m**	NH_2, Ph	300, 330	560
14[a]	**10n**	H, *p*-NHBocPh	317	450
15[a]	**10o**	H, *p*-NH_2Ph	330	470
16[b]	**11a**	—, Ph	294	418
17[b]	**11b**	—, Me	286	413
18[c]	Coumarin **6**	—	455	498

[a] 10^{-4} M solutions in DCE. [b] 10^{-5} M solutions in DCE. [c] 10^{-5} M solution in CH_2Cl_2. [d] No significant effects were observed on the emission spectra while changing the excitation wavelength or the concentration of the samples.



Scheme 4 Synthesis of pCp-based coumarins. Reaction conditions: (a) H_2O_2 (1.4 equiv.), H_2SO_4 (1.4 equiv.), CH_2Cl_2/MeOH, rt, overnight; (b) Propiolic acid derivative (1 equiv.), DCC (1 M in CH_2Cl_2, 1.5 equiv.), DMAP (0.015 equiv.), CH_2Cl_2, Ar, rt, 2–4 h; (c) $AuCl_3$ (0.08 equiv.), $AgSbF_6$ (0.16 equiv.), μw, DCE, Ar, 80 °C, 7 min.

pCp-based PRODAN derivatives

PRODAN, is a well-known push–pull charge-transfer chromophore which displays a naphthalene central core functionalized with a dimethylamino group and a propionyl moiety at its C-2 and C-6 positions (Fig. 3).[80] This dye exhibits a strong solvatochromic behaviour due to important changes in its dipole moment upon electronic excitation.[81] Consequently, PRODAN has been extensively used in chemical biology as a probe to

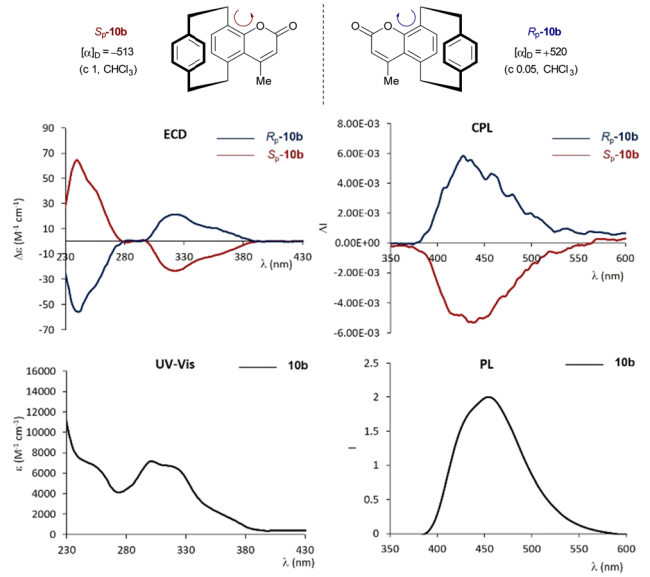


Fig. 2 Chiroptical properties of pCp-based coumarins S_p-**10b** and R_p-**10b**. UV-Vis, PL, ECD and CPL spectra were recorded in CH_2Cl_2 (10^{-5} M solutions, λ_{ex} = 320 nm).

Table 3 Comparison of absorption and emission dissymmetry factors of selected enantiopure pCp systems

Entry	g_{abs}/λ_{abs} (nm)	g_{lum}/λ_{lum} (nm)	g_{lum}/g_{abs}
S_p-**5a**	$-2.6 \times 10^{-3}/305$ $+6.6 \times 10^{-4}/350$	$+6.7 \times 10^{-4}/450$	1.02[a]
S_p-10b	$+8.4 \times 10^{-3}/240$ $-6.2 \times 10^{-3}/360$	$-4.3 \times 10^{-3}/440$	+0.7[a]
S_p-**15**	$+1.3 \times 10^{-3}/350$ $-1.7 \times 10^{-3}/380$	$+4 \times 10^{-3}/486$	−2.9
S_p-**21a**	$-2 \times 10^{-3}/335$ $6 \times 10^{-4}/380$ $\sim 10^{-4}/\sim 480$[b]	$-7 \times 10^{-4}/550$	n.d.[b]
S_p-**21b**	$-2 \times 10^{-3}/330$ $9 \times 10^{-4}/380$ $\sim 10^{-4}/\sim 480$[b]	$-8 \times 10^{-4}/550$	n.d.[b]

[a] The lowest absorption energy values have been considered. [b] Values are too low to be determined accurately.

study protein and DNA interactions,[82–87] lipid bilayers and cellular membranes.[88–92] The development of chiral CPL-emitting analogues of this compound could widen the range of applications of such environmentally sensitive dyes.

Planar chiral PRODAN derivatives in which the naphthalene core of the parent molecule has been replaced with the pCp scaffold have recently been synthesized and spectroscopically characterized in our laboratory.[93]

Notably, a *pseudo-para* disubstituted analogue was obtained in five steps starting from enantiopure intermediates R_p-**1d** and S_p-**1d** (Scheme 5). The propionyl group was introduced first, *via* a Grignard addition and subsequent double oxidation reaction. The dimethylamino motif was then obtained through the conversion of key oxime **13** to the corresponding aniline **14**, followed by dimethylation under standard conditions.

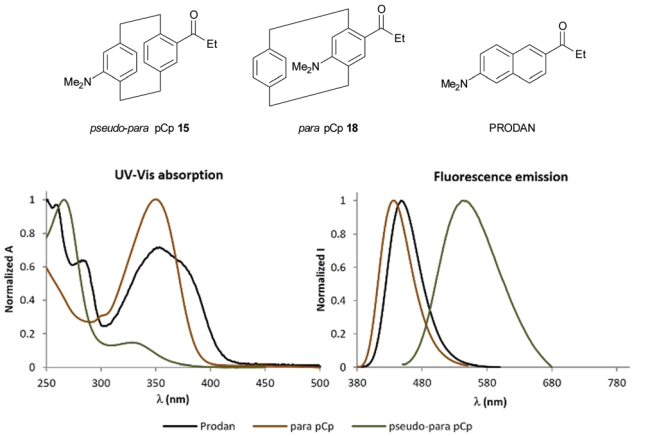
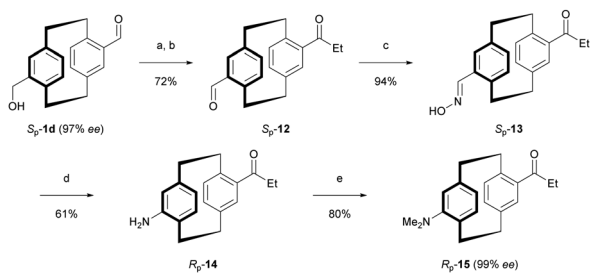


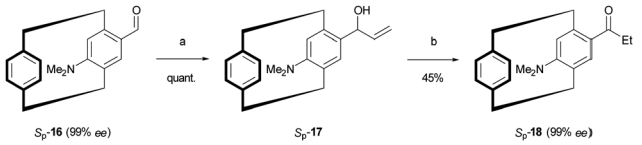
Fig. 3 Absorption and emission spectra of PRODAN (λ_{abs} = 350 nm; λ_{em} = 446 nm), *pseudo-para* disubstituted pCp **15** (λ_{abs} = 328 nm; λ_{em} = 542 nm); and *para* disubstituted pCp **18** (λ_{abs} = 350 nm; λ_{em} = 437 nm). 10^{-5} M solutions of the dyes in CH_2Cl_2 were employed to perform the analyses. All compounds were excited at 350 nm to record fluorescence emission.

Optically active *para* disubstituted analogues of PRODAN based on the pCp core have been prepared as well starting from key intermediate **16** (Scheme 6). Note that this compound can be obtained in its enantiopure form from aldehydes R_p-**1a** and S_p-**1a** in 3 steps.[20] After the addition of a vinyl Grignard reagent leading to alcohol **17**, an isomerization reaction afforded both enantiomers of product **18** in good overall yields (Scheme 6).

A photophysical study was again conducted to evaluate the impact of the pCp core and its "*phane*" interactions on the spectroscopic properties of compound **15** and **18** compared to "classical" PRODAN. When dissolved in dichloromethane, the *pseudo-para* disubstituted pCp-based dye **15** showed a blue-shifted absorption spectrum, as well as a red-shifted emission band (Fig. 3). As a result, an extremely large Stokes shift (46 730 cm^{-1}) was observed for this compound. Theoretical calculations highlighted that such an extreme value can arise from the large geometrical relaxation of the strongly dipolar excited state of the molecule.[93]



Scheme 5 Representative synthesis of an enantiopure *pseudo-para* disubstituted pCp-based analogue of Prodan (R_p-**15**). Both enantiomers were prepared following this strategy. Reaction conditions: (a) EtMgBr (2.4 equiv.) THF, 0 °C to rt, 16 h; (b) DMP (2.5 equiv.), CH_2Cl_2, rt, overnight; (c) $H_2NOH{\cdot}HCl$ (1.25 equiv.), NaOH (1.25 equiv.), EtOH, 30 min, 80 °C; (d) Koser's reagent (1.4 equiv.), DMSO, rt for 30 min then 80 °C for 1 h, then NaOH (1.5 equiv.), 80 °C, 1.5 h; (e) MeI (7.5 equiv.), K_2CO_3 (5.8 equiv.), DMF, rt, 24 h. Both R_p and S_p products were obtained following this strategy.



Scheme 6 Representative synthesis of an enantiopure *para* disubstituted pCp-based analogue of Prodan (S_p-**18**). Both enantiomers were prepared following this strategy. Reaction conditions: (a) vinyl magnesium bromide (1.0 M in THF), THF, 0 °C to rt, 4 h; (b) $(PPh_3)_3RuCl_2$ (0.05 equiv.), *n*-BuLi (1.6 M in hexane, 0.1 equiv.) dry THF, reflux overnight.

On the contrary, the *para* disubstituted pCp analogue **18** displayed absorption and emission profiles close to those of PRODAN (Fig. 3). The pCp-based dyes showed low luminescence quantum yields in dichloromethane (<0.1% and ~1% for **15** and **18** respectively). The lower fluorescence quantum yields as compared to the parent PRODAN were supposed to originate from the increased flexibility of the dyes, which may favour non-radiative decay.[94]

The solvatochromic behaviour of pCp derivatives **15** and **18** was investigated and compared with that of commercially available PRODAN. As expected, increasing solvent polarity resulted in clear bathochromic shifts of the emission bands for both pCp-based PRODAN analogues. The *para* disubstituted compound **18** showed a slightly less pronounced solvatochromism in comparison with the parent compound (Table 4). For the *pseudo-para* disubstituted derivative **15** a strongly red-shifted emission band was observed in dichloromethane compared to toluene (Table 4). An improved solvatochromic behaviour is therefore displayed by pCp **15** in comparison with both **18** and PRODAN. The *pseudo-para* di substituted compound however suffered from fluorescence quenching in polar solvents, such as acetonitrile (MeCN) and ethanol. Interestingly, PRODAN analogue **15** exhibited enhanced luminescence at the solid state (Fig. 4). An absolute fluorescence quantum yield of 9% was measured in this case. The observed aggregation-induced emission enhancement was supposed to originate from the stiffening occurring at the solid state.

These effects could indeed decrease the vibrational motion of the molecule and therefore reduce the efficiency of non-radiative decay routes.

Optically active compounds **15** and **18** were found to display quite different chiroptical properties. Indeed, while several

Table 4 Solvatochromic properties of pCp-based chromophores **15** and **18** *vs.* PRODAN

Solvent	λ^{em}_{max} PRODAN[a] (nm)	λ^{em}_{max} pCp **15**[b] (nm)	λ^{em}_{max} pCp **18**[b] (nm)
Toluene	416	486	424
1,4-Dioxane	422	506	425
CH_2Cl_2	446	542	437
MeCN	455	—	440
EtOH	485	—	458

[a] Fluorescence emissions of PRODAN in different solvents have been described before, see ref. 95. [b] 10^{-5} M solutions of the pCp dyes were used to perform the analyses (λ_{ex} = 350 nm for both compounds **15** and **18**).

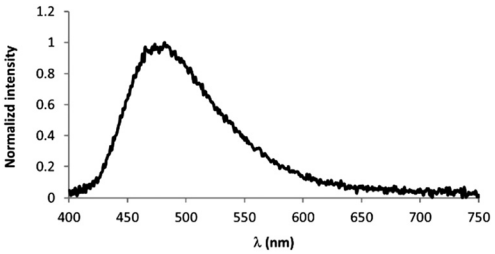


Fig. 4 Emission spectra of *pseudo-para* disubstituted pCp **15** at the solid state (λ_{ex} = 360 nm, λ_{em} = 480 nm).

ECD-active bands of moderate strength with mirror-image relationships were observed for the *para* disubstituted derivative R_p-**18** and S_p-**18** in CH_2Cl_2,[93] this molecule was found to be CPL inactive. pCps R_p-**15** and S_p-**15** also displayed clear ECD signals in CH_2Cl_2 with bands of moderate strength at 250 ($\Delta\varepsilon$ = −18 M^{-1} cm^{-1}), 272 ($\Delta\varepsilon$ = +15 M^{-1} cm^{-1}), 304 ($\Delta\varepsilon$ = −5 M^{-1} cm^{-1}), 334 ($\Delta\varepsilon$ = +2 M^{-1} cm^{-1}), and 365 nm ($\Delta\varepsilon$ = −1 M^{-1} cm^{-1}) (Fig. 5). However, contrary to pCps R_p-**18** and S_p-**18**, compounds R_p-**15** and S_p-**15** were found to possess clear CPL activity in toluene (Fig. 5). Fluorescence dissymmetry factors g_{lum} of ~4 × 10^{-3} were obtained for these planar chiral PRODAN analogues (λ_{exc} = 350 nm, λ_{em} = 486 nm, Table 3). The g_{lum}/g_{abs} ratio is negative and different from 1, which highlights strong reorganization of the excited state prior to the emission process, most probably through charge reorganization due to strong charge transfers.[93] It is worth mentioning that mirror-imaged spectra were recorded in CD_2Cl_2 through vibrational circular dichroism spectroscopy (VCD) for optically active pCps R_p-**15** and S_p-**15**, and clear fingerprints were detected between 1025 and 1625 cm^{-1} (Fig. 5). Note that the C=O stretching mode observed

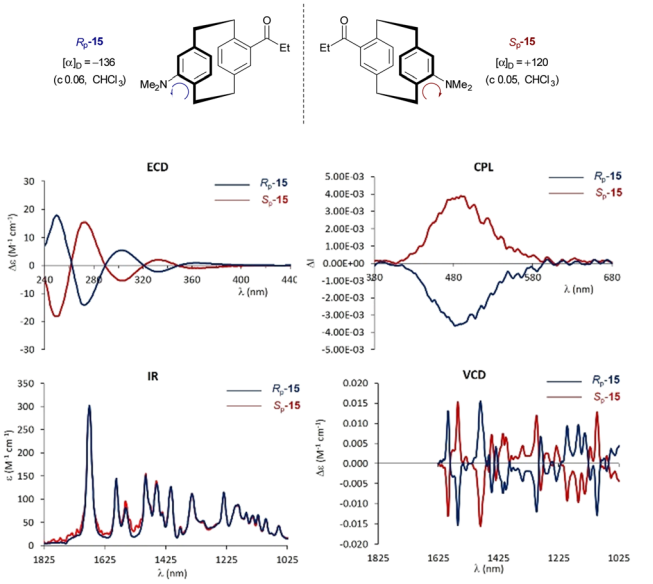
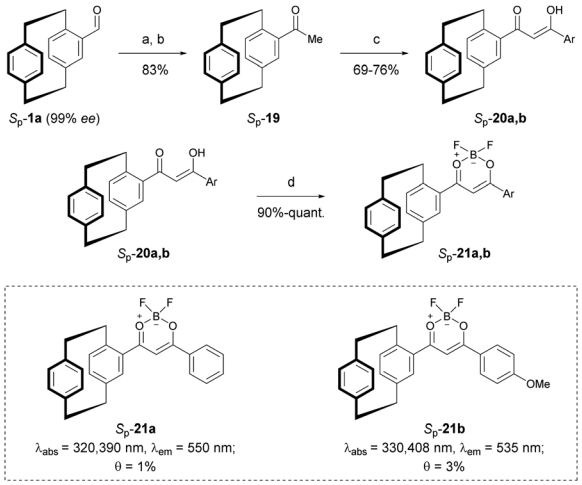


Fig. 5 Chiroptical properties of pCp-based PRODAN analogues R_p-**15** and S_p-**15**. ECD spectra were recorded in toluene (10^{-3} M solutions). CPL spectra were recorded in toluene (10^{-5} M solutions). IR and VCD spectra were recorded in CD_2Cl_2 (10^{-1} M solutions, 200 microns pathlength).



Scheme 7 Representative synthesis of an enantiopure pCp-based boron-β-diketonate (S_p-**18**). Both enantiomers were prepared following this strategy. Reaction conditions: (a) MeMgBr (1.3 equiv.), THF, 0 °C to rt, 1.5 h; (b) DMP (1.5 equiv.), CH_2Cl_2, rt, 2 h; (c) $ArCO_2Me$ (2 equiv.), NaH (5 equiv.), THF, 75 °C, 24 h; (d) $BF_3{\cdot}Et_2O$ (1.9 equiv.), toluene, rt or 120 °C, 18 h. Spectroscopic data were recorded in CH_2Cl_2 (10^{-6} M solutions). Relative fluorescence quantum yields were determined using anthracene as the reference (θ = 2.6% in cyclohexane).

in the IR spectra was too strong to enable VCD measurements due to saturation. When compounds R_p-**18** and S_p-**18** were analysed under the same conditions, less resolved VCD signals of low intensity were detected. This set of spectroscopic data may therefore reveal useful in future endeavours to distinguish between different pCp regioisomers. These results show that the (chir)optical properties of the pCp-based PRODAN analogues are significantly influenced by through-space interactions. The spectroscopic behaviour of these dyes can indeed be strongly modulated by changing the relative position of the substituents onto the two aromatic rings of the pCp core. To observe promising CPL activity in these donor-acceptor derivatives, within this series, it appears important to decorate both decks of [2.2]paracyclophane, and maintain a *pseudo-para* relationship between the electron-donating and electron-withdrawing groups on the molecule.

pCp-based boron-β-diketonates

Boron diketonates constitute another class of compact organic compounds that have been widely employed in optoelectronics for the development of photoresponsive materials, OLEDs, organic field-effect transistors (OFETs), or sensory and biological imaging materials.[96–101] The design of original chiral versions of these luminophores is expected to prompt significant innovation in this field.

Racemic [2.2]paracyclophane-based boron-β-diketonates have been described in the literature and showed promising aggregation induced emission and solvatochromic properties.[102,103] More recently, enantiopure analogues of these dyes have been synthesized by our group in four steps starting from optically active aldehydes R_p-**1a** and S_p-**1a** (Scheme 7). In fact, two enantiopure boron-difluoride derivatives were isolated, incorporating either a

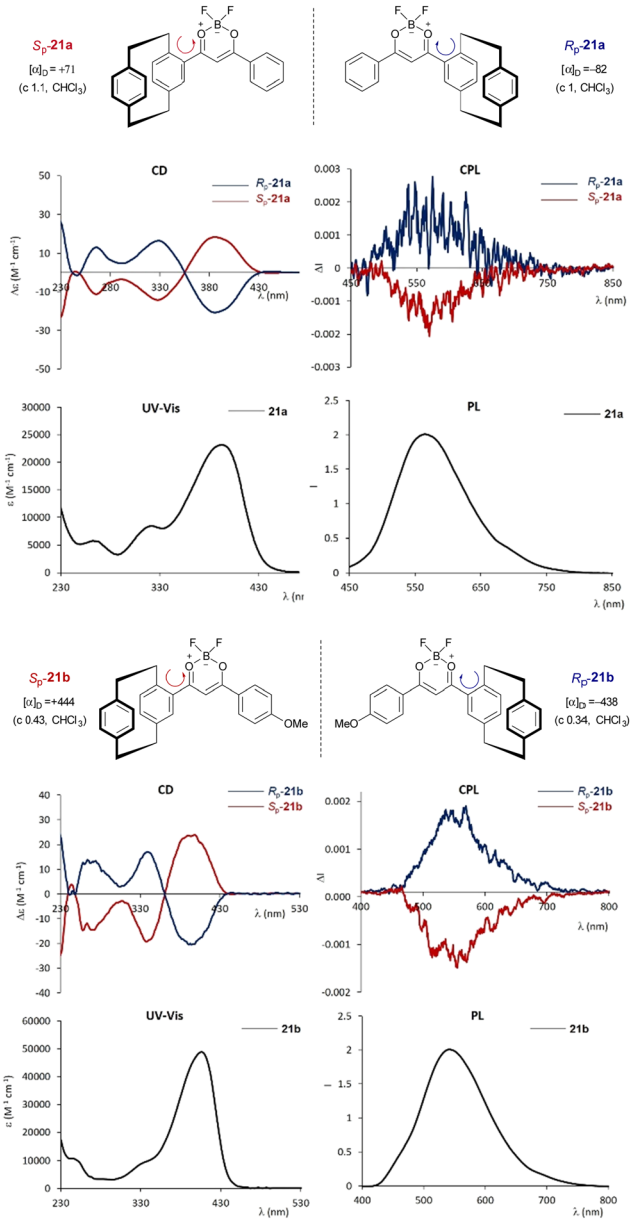


Fig. 6 Chiroptical properties of pCp based β-diketonates R_p-**21a, b** and S_p-**21a, b**. UV-Vis and ECD spectra were recorded in CH_2Cl_2 (10^{-4} M solutions). PL and CPL spectra were recorded in CH_2Cl_2 (10^{-5} M solutions, λ_{ex} = 360 nm).

phenyl or a 4-methoxyphenyl group on their β-diketonates moieties (compounds **21a** and **21b**, respectively). The main spectroscopic characteristics of these dyes are reported in Scheme 7. Note that the more electron-rich derivative **21b** shows a slightly reduced Stokes shift and a higher fluorescence quantum yield compared to **21a**. The chiroptical properties of these compounds have been studied in dichloromethane.

As previously observed for the other families of compact pCp-based planar chiral dyes, boron-β-diketonates displayed clear ECD signatures with several mirror-image signals of moderate intensity. The pCp-based boron-β-diketonates dyes also exhibited mirror-image CPL bands, with luminescence

dissymmetry factors g_{lum} around 7.8×10^{-4} at their maximum emission (Fig. 6 and Table 3). Absorption dissymmetry factors $g_{abs} \sim 2 \times 10^{-3}$ at 330 nm and ~6-9 $\times 10^{-4}$ at 380 nm were determined for R_p-**21a, b** and S_p-**21a, b**, respectively. Note that the low-energy g_{abs} values are too low to be determined accurately. Nevertheless, they are of same sign but much lower than the g_{lum} suggesting strong electronic reorganization of the excited state prior to the emissive process through intramolecular charge transfer (ICT) as illustrated by important solvatochromism associated with a strong conformational change (see ref. 102). Overall, these results pave the way for the design of new planar chiral CPL emitters with finely tuned photophysical properties.

Conclusion

Different families of compact planar chiral luminophores based on a [2.2]paracyclophane scaffold have been prepared in our laboratory starting from key aldehydes intermediates. These include naphthalene and coumarin derivatives, pCp-based PRODAN as well as boron-β-diketonates analogues. Spectroscopic characterization of these compounds revealed interesting photophysical behaviours. As a general trend, the absorption and emission profiles of the [2.2]paracyclophane dyes can be easily tuned simply by playing with the nature of the substituents on the pCp core as well as the relative position in the 3D space of electron-donating and electron-withdrawing groups. Compared to planar fluorophores, the pCp scaffold offers a wider range of substitution patterns to adjust their optical properties. For each family of luminophores, different examples of enantiopure compounds have been synthesized. The latter displayed appealing chiroptical behaviours both in circular dichroism and circularly polarized luminescence. Absorption dissymmetry factors up to 8×10^{-3} and luminescence dissymmetry factors up to 5×10^{-3} have indeed been obtained. These values are quite remarkable considering the compact structure of these dyes. However, apart from naphthalene derivatives, the pCp-based luminophores isolated so far display rather low fluorescence quantum yields ($0.1\% < \theta < 2\%$). This behaviour is supposed to arise from stronger vibrational motions of the molecules compared to the pCp-deprived parent compounds (*i.e.*, commercially available coumarins or PRODAN, and more classical aromatic boron-β-diketonate dyes). The lack of stiffness could indeed favour non-radiative decay pathways. Further research efforts are required in this field to rigidify the structure of compact planar chiral emitters, and thus drive the development of more performant CPL active small organic luminophores based on the [2.2]paracyclophane scaffold.

Conflicts of interest

There are no conflicts to declare.

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