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Stapled helical *o*-OPE foldamers as new Circularly Polarized Luminescence emitters based on carbophilic interactions with Ag(I)-sensitivity[§]

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ortho-Oligo(phenylene)ethynylenes (*o*-OPEs) stapled with enantiopure 2,3-dihydroxybutane diethers feature highly intense circular dichroism (CD) spectra and excellent circular polarized luminescence (CPL) responses (g_{lum} values up to 1.1 x 10^{-2}), which are consistent with homochiral helically folded structures. In the presence of Ag(I), a change in the CPL emission is observed, representing the first example of CPL active small organic molecular emitters, which can be modulated by carbophilic interactions in a reversible manner.

Introduction

Homochiral organic structures capable to produce efficient CPL responses are of huge interest, due to their promising applications as new luminescent materials such as optical devices and biosensors.[1] Different enantioenriched molecules, such as helicenes,[2,3] lanthanide complexes,[4] and helical polymers,[5] have been reported to exhibit high CPL in solution, as aggregates, or in the solid state, due to their self-organized structures. Up to now, the few reported CPL active organic molecules showed small dissymmetry factors (g_{lum}) in solution, with very few exceptions such as super-organized cholesteric crystals.[6] Unfortunately, supramolecular organization has a negative influence on the emission efficiency. The synthetic accessibility and great versatility of simple chiral organic molecules make them attractive circular polarized luminescence probe candidates. New and efficient applications require the development of simple structures able to maintain chiral environments in the excited state while maintaining a reasonable fluorescence quantum yield (Φ). Within this context some [n]-helicene-type compounds have shown high g_{lum} values (10^{-2}–10^{-3}) although their quantum yields are usually low.[7] A possible solution to improve intrinsic CPL characteristics of [n]-helicenes could be the construction of rigid helical structures with large magnetic transition dipole moments (rotational strengths), in which the self-quenching process were decreased. Control of CPL emission by external factors in simple molecular emitters is even less common, although it can be viewed as a potential probe for them. To the best of our knowledge only anions (halides, acetate and *L*-phenylalanine anion), ammonium salts, light, Zn(II) cation and acids/bases, have been used as external modulators of CPL emission.[8]

We recently reported that fluorescent *ortho*-oligo(phenylene)ethynylenes (*o*-OPEs) can be stapled into helical conformations, even in a chiral way.[9] This structural restriction provided new chiroptical properties to the system. Moreover, the inner cavity was able to selectively bind Ag(I) cation, giving rise to a new class of Ag(I)-based metalofoldamers.[10] As an extension of this previous work , we now report a new easy-to-tune class of molecular CPL active compounds **1**-**4** (Figure 1) showing excellent g_{lum} (up to 1.1 x 10^{-2}) values. The structures, based on *o*-OPEs, are easily accessible and show, as a significant feature, a CPL emission which is modulated in the presence of Ag(I) cation. Modulation of chiroptical emission in solution by a carbophilic metal is unprecedented in literature. The only related example, described by Crassous,[8] is based on heliceneterpyridine:Zn(II) interactions. Remarkably, silver could be later removed by

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ARTICLE   JournalName

simple addition of MeCN, being the CPL response of the *o*-OPEs recovered. This result provides a unique class of CPL-active silver sensitive molecular switches.

Results and discussion

Racemic *para,para-(p,p-)*, *meta,meta-* (*m,m-*) and *para,meta-(p,m-)*substituted *o*-OPEs **1-3**, containing a 2,3-butanediol fragment, were prepared starting from adequately positioned (*p-* or *m-*) allyl aryl ethers **A** (Figure 1), by a Ru-catalyzed alkene metathesis and dihydroxylation of the resulting butene fragments (Figure 1a, representative synthesis of *m,m-***2**). Preparative chiral HPLC resolution (see ESI) allowed the isolation of both enantiomers of *p,p-***1**, *m,m-***2** and *p,m-***3** (Figure 1b, only one enantiomer is represented). In addition to the stereogenic diols present on each enantiomer, a new element of chirality (helicity) has been stereoselectively produced by the stapling process, thus generating interesting chiroptical properties. Chemical resolution of diols *rac-m,m-***2** was achieved through the formation and separation of the corresponding (1´*S*,4´*R*)-camphanoyl esters **4a** and **4b** (Figure 1c), bearing different helicities in each case.
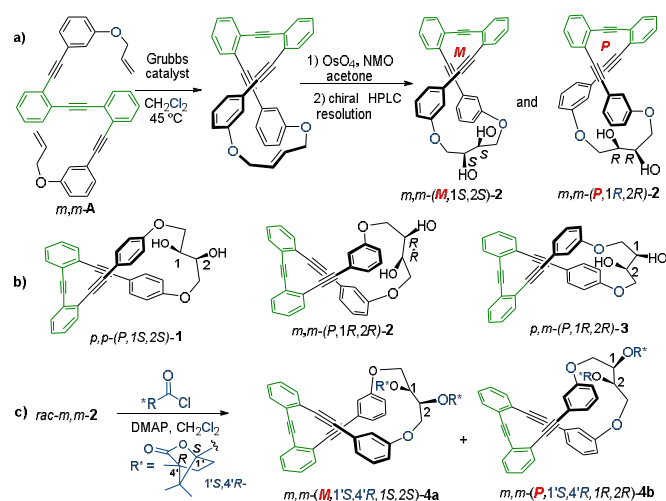
Fig.1. Representative synthetic route (a) to enantiopure diol *m,m-*(*M*,1*S*,2*S*)-**2** and *m,m-*(*P*,1*R*,2*R*) **2**. (b) Structure of *p,p-***1**, *m,m-***2** and *p,m-***3** enantiomer(c) Synthesis of diastereomeric (1´*S*,4´*R*)-camphanoyl esters **4a** and **4b**.

The absolute (1´*S*,4´*R*,*M*,1*S*,2*S*) configuration of *m,m-***4a** was established unequivocally by X-ray diffraction, taking into account the known (1´*S*,4´*R*) configuration of the camphanoyl moieties (Figure 2).
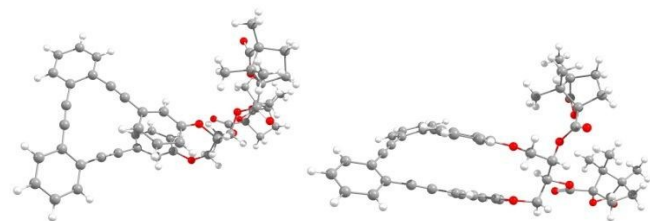

Fig.2. X-Ray structure of (1´*S*,4´*R*,*M*,1*S*,2*S*)-**4a**: top view (left) and side view (right).

Transesterification of **4a** afforded free diol *m,m-*(*M*,1*S*,2*S*)-**2**, identical to one of the enantiomers of *m,m-***2** previously obtained by HPLC resolution. The (*P*,1*R*,2*R*) absolute configuration could thus be assigned to the corresponding enantiomer of *m,m-***2** and the (1´*S*,4´*R*,*P*,1*R*,2*R*) to **4b**. The CD spectra of both diastereoisomers **4a** and **4b** in CH$_2$Cl$_2$[11] are depicted in Figure 3a. Compounds *m,m-***4a** and *m,m-***4b** behaved as pseudoenantiomers, showing that the configuration of the camphanoyl moiety does not affect significantly their chiroptical response. The relationship between the absolute configuration of simple [n]-helicenes and the sign of the first intense band[12] at the longest wavelength of the CD spectra had been pointed out.[13] With these precedents and on the basis of TD-DFT calculations on the geometry obtained by optimization of the X-ray structure for compound **4a** (see ESI), we may correlate the negative Cotton effect at λ =345 nm (Figure 3a) with its *M* helical configuration.

The corresponding CD spectra of compounds **1-3** are shown in Figure 3b (one enantiomer). Since alcohols absorb at λ<200 nm, the CD bands observed in compounds **1-3** at λ>240 nm must be due to the presence of new elements of chirality with a defined absolute configuration. While the band at ca. 260 nm is attributed to the conjugated triple bonds transitions, the Cotton effects at 280-300 nm and 340-370 nm evidence a transfer of chirality from the stereogenic centers to the aromatic fragments, thus suggesting a helical chiral structure in solution. CD signals are also maintained in different solvents and at different temperatures, suggesting that the helical structure is preserved in any case (See ESI). The high Δε values, especially for compounds **1** and **4**, are also consistent with the presence of such helical chirality and suggest a significant contribution of the helical aromatic framework to these chiral absorptions.

The helix sense can be established as follows: the presence of Cotton effect of the same sign for the 340-370 nm band in *m,m-***4a** and *p,p-***1** (λ=360 nm, Figure 3a-b) suggested the same *M* absolute configuration for both structures. The positive Cotton effect appearing at λ=345 nm for *m,m-***4b** confirms the *P* absolute configuration previously assigned for this camphanoyl diastereoisomer. In turn, the positive bands at ca. 350 nm observed for *m,m-***2** and *p,m-***3** assigned the *P* absolute configuration to their helices, whereas the negative one supported the *M* configuration for their enantiomers (see ESI). The induced helicity can be correlated with the relative regiochemistry of the substituents of the aryl rings involved in the staple, as we had previously observed.[9] Comparison of CD spectra of compounds **1-4** evidences significantly lower intensities of enantiopure *m,m-***2** and *p,m-***3**.
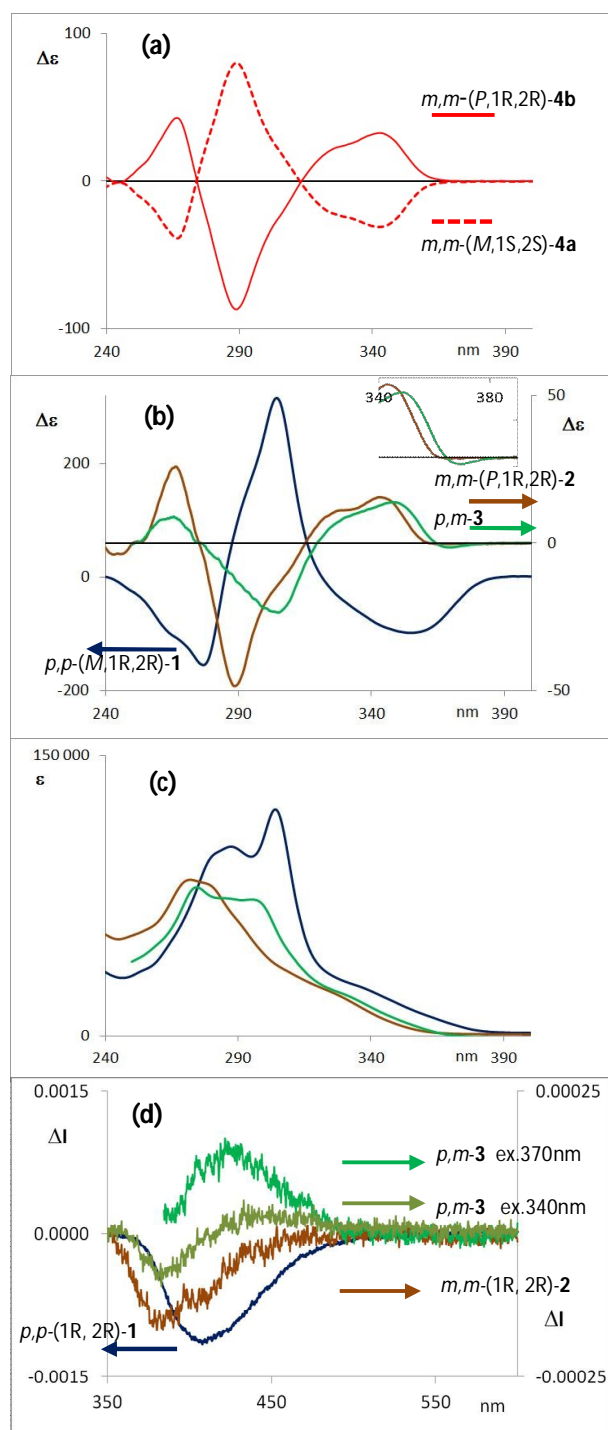
Fig.3. (a) CD spectra of diastereoisomers **4a** (1′S,4′R,M,1S,2S) and **4b** (1′S,4′R,P,1R,2R). (b) CD spectra of one enantiomer of each compound **1-3** (configuration 1R,2R for compounds **1** and **2**). (c) Absorption spectra of compounds **1-3**. (d) CPL spectra of compounds **1**, **2** and **3,** same enantiomer as for CD spectra presented above. Two excitation wavelengths are given for CPL spectra of **3**.

The dissymmetry value g_{abs} of **1** in CH_2Cl_2 (0.96 x 10^{-2}) was one order of magnitude higher than those obtained for **2** (1.9 x 10^{-3}) and **3** (1.5 x 10^{-3}). The weaker chiroptical responses for **2** and **3** could be a consequence of the presence of two opposite helicities and/or the possible existence of a variety of quite distorted structures. To provide support to all these experimental evidences, and the stereoselectivity generated upon the methatesis/dihydroxylation stapling process, DFT calculations were conducted to determine the energy of the different diastereoisomers (see ESI for details). Molecular mechanics (MM) conformational search was performed for molecules **1**, **2** and **3**. Conformers within 5 kcal/mol were all optimized at B3LYP/6-31g* level. Populated conformers were also optimized within the framework of polarizable continuum model approximation (PCM), checking that all structures correspond to minima and evaluating the Gibbs free energy; the LANL2DZ pseudopotential was used for Ag(I). Thus, the p,p-(P,1S,2S)-**1** diastereoisomer is energetically favored by about 2 kcal mol^{-1} with respect to the M helical epimer (M,1S,2S). Thus, the calculated energies supported that p,p-substitution in the final aromatic ring of stapled OPE **1** favors the P helical configuration in the case of S,S configured diols and M for R,R diols. The calculated CD spectrum (Figure 4 top) was in agreement with the helicity previously assigned on the basis of the experimental CD. Taking into account these findings, we could assign the p,p-(M,1R,2R)-**1** absolute configuration to the enantiomer whose CD and CPL are included in Figure 3 and p,p-(P,1S,2S)-**1** absolute configuration to its enantiomer. For diols **2** and **3**, however, the situation is more complex because the calculated energies for P and M diastereoisomersare very close (see ESI for details), suggesting that both helical epimers could coexist in solution. This situation could be at the origin of the lower intensity of the chiroptical responses observed in both m,m-**2** and p,m-**3** derivatives. In spite of this, the calculated energies definitely supported that m,m substitution in **2,** considering all the possible conformer populations, slightly favors a P helix for R,R configured diols and M for S,S diols (see ESI for details), which is in agreement with the X-ray structure of **4a**.
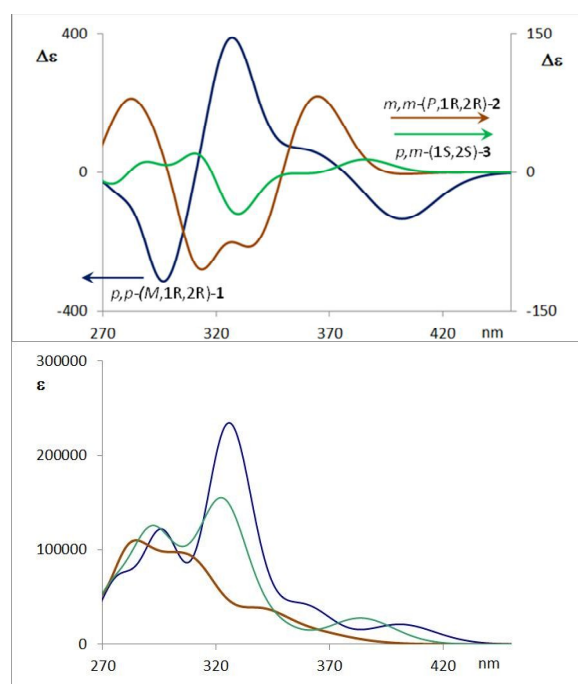
Fig.4. Average calculated CD (top) and Absorption spectra (bottom) for the main conformers for *p,p*-**1** (blue),*m,m*-**2** (brown),and *m,p*-**3** (green) in CH_2Cl_2(average on energy). The calculated spectra are at about 30 nm higher wavelengths than observed.

Table 1. Quantum yields and lifetimes of compounds**1**-**3**

SOLVENT	*p,p*-1			*m,m*-2			*p,m*-3		
	Φ	$\tau_1 \pm SD$ (ns)	$\tau_2 \pm SD$ (ns)	*Φ*	$\tau_1 \pm SD$ (ns)	$\tau_2 \pm SD$ (ns)	*Φ*	$\tau_1 \pm SD$ (ns)	$\tau_2 \pm SD$ (ns)
Dichloromethane	0.069	4.86±0.02	1.15±0.02	0.181	4.16±0.06	1.08±0.01	0.520	4.54±0.02	1.08±0.02
Acetonitrile	0.065	5.64±0.02	1.90±0.04	0.144	4.73±0.04	1.47±0.03	0.356	5.27±0.03	1.58±0.05
Acetone	0.056	5.14±0.02	1.52±0.04	0.029	3.76±0.05	1.14±0.03	0.531	4.74±0.04	1.17±0.03
THF	0.089	7.13±0.04	2.29±0.02	0.016	6.49±0.05	1.88±0.02	0.097	6.33±0.04	1.8±0.02
Diethyl ether	0.037	6.84±0.05	3.43±0.03	0.023	5.88±0.06	1.38±0.02	0.100	4.17±0.02	0.85±0.02
Ethyl acetate	0.068	8.41±0.10	4.14±0.02	0.011	5.82±0.08	1.49±0.04	0.117	4.85±0.03	1.24±0.03
Methanol	0.057	6.13±0.07	1.54±0.03	0.032	5.82±0.05	1.90±0.03	0.091	5.60±0.04	1.78±0.03
Hexane	0.136	4.60±0.08	1.03±0.01	0.014	2.96±0.02	1.23±0.01	0.055	3.36±0.04	1.11±0.02
Toluene	0.236	4.17±0.02	0.70±0.02	0.024	3.32±0.05	0.94±0.01	0.175	3.91±0.03	0.72±0.02

Moreover, the chemical correlation of *m,m*-(*M*,1*S*,2*S*)-**2** resulting from transesterification of *m,m*-(1´*S*,4´*R*,*M*,1*S*,2*S*)-**4a** allows its unequivocal assignment. The CD spectrum shown in Figure 3b corresponds to the *m,m*-(*P*,1*R*,2*R*)-**2** enantiomer. The presence of only one set of signals in the corresponding ^{1}H-NMR spectrum of *m,m*-**2** at room temperature suggests a low *P/M* epimerization barrier. Moreover, low temperature NMR experiments for diols **1-3** down to −80 °C only show a broadening of the signals (see ESI), suggesting that a rapid equilibrium between the *P* and *M* helical structures might occur at room temperature. These data also support that the epimerization barriers are low. Therefore the chiroptical responses emerge from the differences in energy of these dynamic structures.

The configurational assignment of *p,m*-**3** is less clear since the spectroscopic behavior strongly suggested a rapid interconversion between both helical conformers. Besides NMR experiments, some other experimental observations support such dynamic situation. While **1** shows only one CD band at 360 nm (Figure 3b), diol **3** presents a sequence of oppositely signed bands centered at 350 and 370 nm respectively (a weaker negative band at lower energy and a stronger positive band at higher energy, Figure 3b inset). Such a pattern suggests the coexistence of both epimeric *P* and *M* helices in solution. In fact, good correspondence with experiment can be obtained considering the calculated weight of all the energetically accessible conformations and the corresponding calculated CD spectra (Figure 4b and ESI). Moreover, the ratio between the intensity of these two bands in the CD spectra of *p,m*-**3** is modified in different solvents, supporting the idea of a *P/M* epimerization process (Figure S13, ESI). On the other hand, the unique helical configuration formed in *o*-OPEs **4**, and observed also in the crystal structure,

must be due to the presence of bulky camphanoyl groups. Such groups make the structure more rigid, hindering any interconversion between *M* and *P* helimers and stabilizing one over the other.

Concerning fluorescence properties, the three diols **1-3** are fluorescent with quantum yields and lifetimes highly dependent on structure and solvent (Table 1). The experimental protocol for their measure is described in ESI.

CPL spectra of enantiopure *p,p*-**1**, *m,m*-**2** and *p,m*-**3** are represented in Figure 3d. As expected, all the CPL spectra show an intense band at 370-450 nm for samples excited at 340 nm. Remarkably, the g_{lum} value for compound **1** is 0.011 (λ = 390 nm), which is one of the highest values ever reported for an organic-based monomolecular emitter.[1] The conformational equilibrium of these compounds in the excited state is less clear than in the ground state. In this case, Time Resolved Emission Spectroscopy (TRES) allowed the complete deconvolution of the total emission spectrum by recovering the species-associated emission spectra (SAEMS) for each one of the decay times (see ESI). In all cases, we could confirm the presence of two main emissive species, generated by some degree of structural relaxation in the excited state. For compound **1**, the species with the larger decay time (τ_1 = 4.86 ns) is dominating the equilibrium. The second one (τ_2 = 1.15 ns) could derive from some minor structural changes before the emission maintaining the original helicity, owing to the excellent g_{lum} value. For compound **2**, only one component is significantly present with the shorter lifetime (τ_2 = 1.08 ns), which also suggests that in this case structural relaxation takes place. Possibly, the presence of several quite distorted geometries for compound **2** is responsible for the short life time relaxation, and also for the fact that, on average, helicity is inverted as suggested by the observed inversion in the CPL

sign. The camphanoyl esters **4a** and **4b** derived from diol **2**, show a related profile, and mainly one emitting specie is present in the excited state (**4a**, τ_2 = 0.86 ns, **4b**, τ_2 = 0.84 ns). In compound **3**, two slightly wavelength biased emissive species are present. This fact, combined with the observed bisignated signal in CD (Figure 3b inset) and the dependence on the excitation wavelength in CPL, suggests that they may derive from *P* and *M* epimers already present before excitation.

Essentially, a control of this dynamic situation observed for diols **1**-**3** would allow an efficient and reversible modulation of the intrinsic chiroptical properties of the system. Bearing this idea in mind, we next studied the binding ability of these helical *o*-OPEs. Remarkably, compounds **1**-**4** are able to accommodate Ag(I) in their inner cavities via carbophilic interactions similarly as we had previously described for related *o*-OPEs.[10] The coordination behavior of compounds **1**-**4** with Ag(I) have been studied by NMR, CD and CPL spectroscopy. Significant changes in ¹H and ¹³C NMR signals are produced after addition of AgBF₄, demonstrating that coordination occurs in all cases (Figure 5 and ESI).
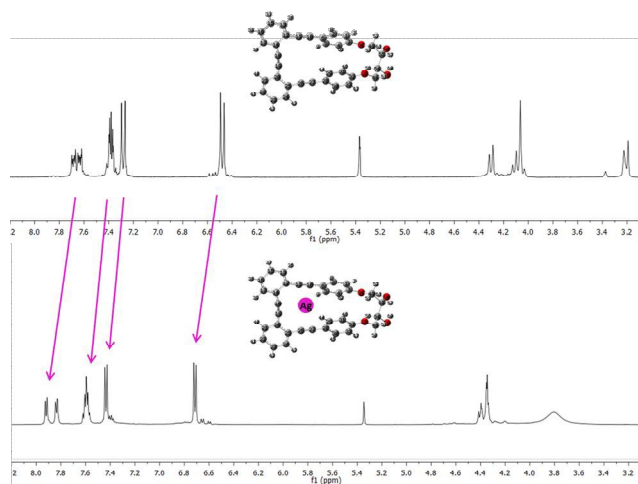
Fig.5. Representative example: Spectrum of pure *p,p*-**1** (top) and after saturation with Ag(I) (bottom) in a   9:1 CD₂Cl₂:Actone-d_6 mixture.

CD spectroscopy evidences very remarkable changes of the signal intensities upon Ag(I) addition to compounds **1**-**3** (Figure 6, top). This might be a consequence of a change from the helical structure to a more planar trigonal arrangement, forced by the alkyne interaction with Ag(I). A similar structural behavior had been previously observed by us in X-ray structures of closely related complexes.[10] DFT calculations (Figure 6, middle and ESI) of the Ag(I)-complexed structures **1**-**3** confirm this lack of helicity. The titration curves allow to obtain the corresponding binding constants of the corresponding complexes *o*-OPEs:Ag(I) with the following values: (**1**) $K_{1:Ag}$ = 12211 ± 635 M⁻¹, (**2**) $K_{2:Ag}$ = 4805 ± 161 M⁻¹, (**3**) $K_{3:Ag}$ = 35926 ± 1064 M⁻¹, (**4a**) $K_{4a:Ag}$ = 1099 ± 42 M⁻¹, (**4b**) $K_{4b:Ag}$ = 466 ± 11 M⁻¹. Although all three diols interact with Ag(I) cation, the more symmetric derivative **1** shows the best geometry for Ag(I) accommodation. Moreover, the almost

planar geometry of **1**:Ag(I) complex ensures a very weak chiroptical response, as can be seen in the CD spectra (Figure 6 top). The **1**:Ag(I) complex signal (light blue line) is almost one order of magnitude less intense than the one of pure **1** (blue line). Moreover, the original CD signals can be easily recovered by simple addition of a stoichiometric amount of CH₃CN to the solution containing the Ag(I) complexes (Figure 6 top, blue dashed line).
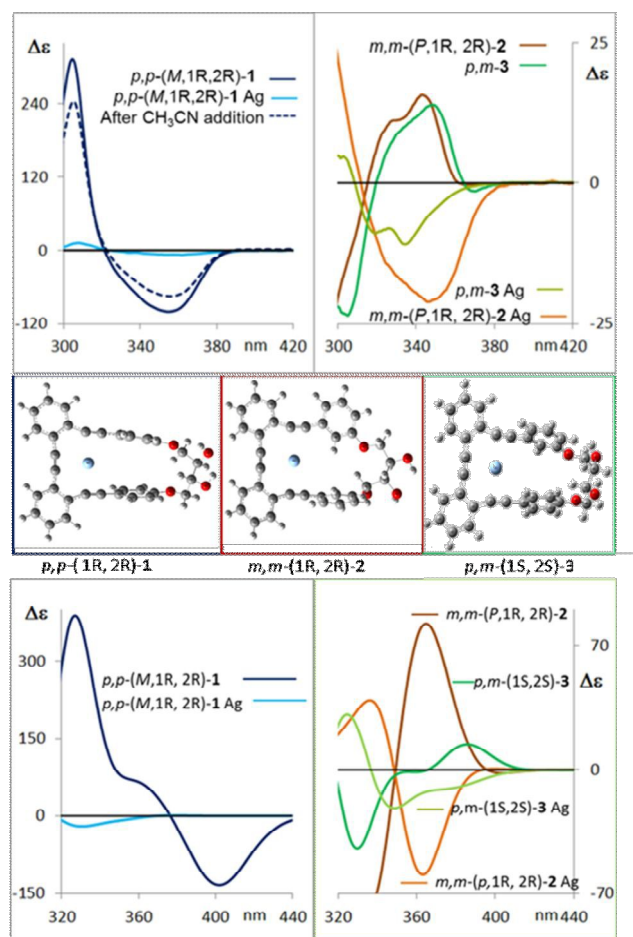
Fig.6 Top left: Measured CD spectra of compounds *p,p*-**1** (blue), *p,p*-**1** saturated with Ag(I) (light blue) and recovery of CD signal of *p,p*-**1**-after CH₃CN addition to the Ag(I) complex solution (dashed dark blue line). Top right: Measured CD spectra of pure compounds *m,m*-**2** (dark brown) and *p,m*-**3** (dark green), and when saturation with Ag(I) is observed (light brown and green). Middle: Calculated structures of the most populated conformer of silver complexes of diols **1**-**3**. Bottom: Comparison of average calculated CD spectra over main conformers for diols and Ag(I) complexes of *p,p*-**1**(blue),*m,m*-**2** (brown),and *m,p*-**3** (green) in CH₂Cl₂. The calculated spectra are at about 30 nm higher wavelengths than observed.

Fluorescence and CPL studies of the Ag(I) complexes also confirm the above observations (see ESI). In the presence of Ag(I), the CPL signal almost disappears for compound **1**, supporting the formation of a planar structure in the excited state, which switched off the chiral helical component and therefore silences the CD or CPL response due to helicity (Figure 7). For compounds **2** and **3** the signals are also significantly changed, suggesting a change in the geometry of

ARTICLE

JournalName

the excited state. Interestingly, the CPL signals can be recovered adding a stoichiometric amount of CH_3CN to the solution containing the Ag(I) complexes (Figure 7), thus making these systems the first CPL switches based on carbophilic interactions. The neat modification of the CD and CPL signals of these helical structures when interacting with Ag(I) opens the possibility to use them as Ag(I)-sensitive chiroluminescent products.

Finally, the photostability of compounds **1**-**4** was also studied (See ESI), suggesting that partial degradation of samples under irradiation during CPL acquisition could be the responsible of incomplete recovery of CPL signal intensity (Figures S3, S4 and S19).
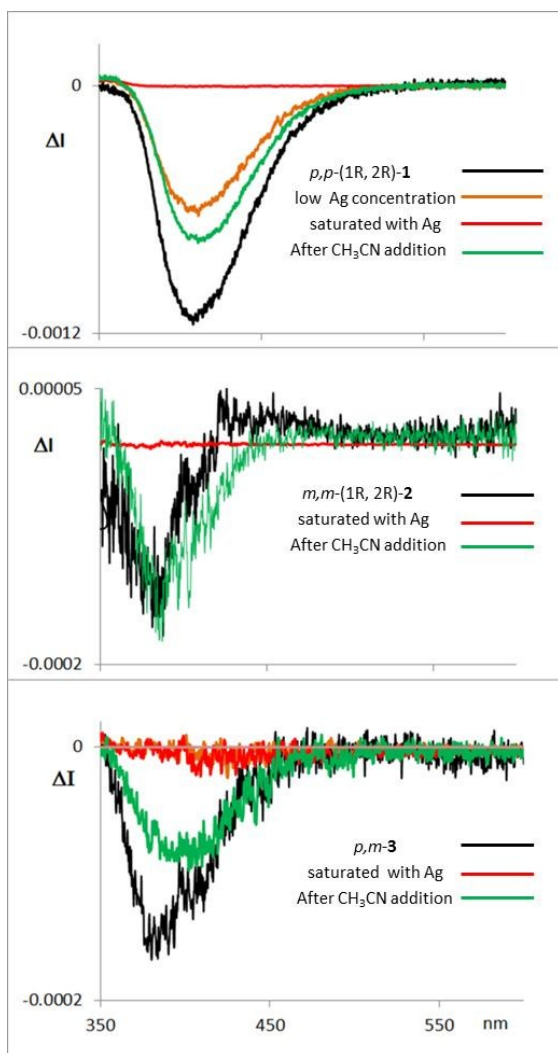
Fig.7 CPL spectra of compounds **1**, **2** and **3**, same enantiomer as for CD and CPL spectra presented above in Fig. 3d. Compounds were measured in CH_2Cl_2, with addition of $AgBF_4$ until saturation, and with further addition of CH_3CN thereafter.

Conclusions

In summary, new enantiopure *o*-OPE derivatives **1**-**4** have been synthesized and their chiroptical properties have also been studied. All investigated structures show excellent CD and CPL

responses as well as reasonable quantum yields. In particular, *o*-OPE *p,p*-**1** featured a g_{lum} = 0.011, which is one of the highest values described up to now for a small organic compound. These stapled compounds represent a promising new class of CPL emitters with great structural versatility and easy access, opening the possibility to develop new CPL emitters with improved and novel applications. It is also worth noting that these stapled OPEs combine a defined helical structure with a flexible inner core, which makes them useful in dynamic chiral photoresponses. This fact has been exemplified in the interaction with Ag(I), which acts as a reversible silencer of their chiral CD or CPL responses.

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Notes and references

§ We dedicate this work to Ettore Castiglioni who, with his high experience in the field of chiroptical spectroscopies, gave important contributions also to the development of CPL instrumentation.

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