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Extended Enantiopture ortho-Phenylene Ethylene (o-OPE)-based Helical Systems as Scaffolds for Supramolecular Architectures. A Study of Chiroptical Response and its Connection to the CISS effect

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A novel synthetic strategy based on a bifunctional stapled chiral nucleus from which segments of different lengths can be added to both ends of o-phenylene ethynlenes (o-OPEs) has been developed to obtain a new type of foldamers and a novel chiral Pd₄L₄ metalacycle. For the first time, an enantiopure fully-conjugated helical foldamer based on having 14 phenyl rings and 13 alkynes is reported. The folded structure has four complete loops and is able to host three Ag(I) cations in their cavity with high binding constants. The complete photophysical and chiroptical (ECD, CPL and VCD) characterization of these foldamers has shown that these molecules show intense chiroptical responses with dissymmetry ratios in the range of 10⁵. Theoretical modeling of these systems reveals the origin of these remarkable responses and points out to a potential connection with the Chiral Induced Spin Selectivity (CISS) effect. The magnetic dipole moment is proposed as a key physical variable connecting the chiroptical properties and CISS-based spin filtering properties observed in chiral compounds.

Introduction

Helical structures are widely spread motifs in biomolecules and many efforts have been carried out to imitate such geometry using abiotic components. Thus for example, [n]-helicenes have attracted the attention of chemists for almost a century. Particularly appealing is the fact that they present a conjugated system arranged in a helical geometry, which is preserved beyond [6]-helicenes. Their chiroptical properties, derived from their intrinsic chirality, such as Optical Rotatory Dispersion (ORD), Electronic Circular Dichroism (ECD), Vibrational Circular Dichroism (VCD), Raman Optical Activity (ROA) and more recently, Circularly Polarized Luminescence (CPL)⁴,⁵ are in fact remarkable, and have been extensively studied. Moreover, the helical geometry is also relevant in other fields. It has been suggested that conductive helical arrangements are of importance in the context of the Chiral Induced Spin Selectivity (CISS) effect⁶ once they can be prepared as enantiopure entities. The CISS effect is based on the phenomenon of electron spin polarization in electron transfer, electron transport and bond polarization processes in chiral molecules. Although initial experiments were based on biomacromolecules,⁷ it is worth noting that it has also been observed in fully conjugated [7]-helicene and in other helicene-like molecules.⁸ Consequently, fully conjugated helical molecules have been theoretically suggested as interesting candidates for spintronics, quantum sensing and quantum information applications.⁹⁻¹¹ Moreover, the remarkable geometry of [6]-helicenes have also been used in the context of chiral metallosupramolecular architectures¹²,¹³ as bidentate donors with an angle between the binding sites close to 0°.¹⁴ These systems have emerged as an unique research field owing to their electronic, optical and sensing capabilities. However, the main drawback in [n]-helicene chemistry is the challenging synthesis of members with increasing turns, even in their racemic form. In fact, the longest member of the series, [16]-helicene, composed by two and a half turns, represents an isolated example (Figure 1, top).¹⁵

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Although longer related helicene-like molecules (two and a half turns) have been described, easy access to fully conjugated helical systems continues being a synthetic challenge. Therefore, easy-to-prepare extended and conjugated helical systems would be highly desirable to search for important applications, like those mentioned above. Within this context, foldamers based on conjugated subunits constitute a privileged scaffold for a number of different reasons: i) they can be easily prepared by iterative protocols using simple conjugated monomers with different geometry, ii) the functionality present in such monomers can cooperatively act to strengthen their properties or even create new ones, and iii) they can also interact dynamically with the environment. In fact, many aromatic foldamers can be switched between different states by different stimuli such as the presence of light, changes in temperature, or water binding, and redox processes. Moreover, foldamers are able to generate chirality in a dynamic way even using achiral monomers/repeating units. Therefore, the control of the P/M helicity yields systems able to act as chiroptical probes or even CPL emitters.

In recent years, we have been working on conjugated helical structures based on o-OPEs as an alternative to [n]-helicenes exhibiting, in many cases, better chiroptical responses. Our approach relies on widening the inner cavity present in [n]-helicenes, which translates into an enhancement in the magnetic moment of optical transitions and the corresponding chiroptical response, especially at the longest wavelength. Thus, we have developed two strategies to obtain enantiopure folded fully conjugated helical systems: the first based on the use of chiral sulfoxides and, secondly, the use of chiral staples, demonstrating that enantiopure P/M helices can be also prepared by an efficiently chirality transfer from a chiral staple to the o-OPE core, including even double staples to avoid racemization processes. However, those later systems could be synthesized with only one turn and a half. All the above approaches provide structures with remarkable chiroptical responses in ECD, CPL and VCD. It is worth noting that the response of ECD in terms of molar circular dichroism has been for some time correlated with the magnitude of the Chiral-Induced Spin Selectivity (CISS) effect. Actually, this phenomenon has been recently discovered, offering a promising change of paradigm the discrimination and filtering of spin states. The spin of the electron, \( S = \frac{1}{2} \), yields two quantum states characterized by its projection on a given axis, \( m_s = \pm \frac{1}{2} \). The two states are degenerate in the absence of either internal or external magnetic fields and, consequently, any electron current under such circumstances will consist of a half-half mixture of both states. The separation of the spin states of the electrons is a milestone of the greatest importance for the development of spintronics. Although spin states of neutral particles can be selected passing through an in-homogenous magnetic field, charged particles, like the electron, suffer the Lorentz force arising from the interaction of the electric charge with the magnetic field, preventing Zeeman’s effect-based technique to be used for separating electron spin states. Although more complex...
architectures can be used, the (preferential) selection of the spin state of electrons travelling through chiral structures is highly appealing. The chemically relevant fact is that now it is the scattering of electrons through the molecular (helical) structure which induces the filtering of the electron spin states. Namely, depending on the helicity of the molecular structure, it preferentially allows the passage of one of the two spin states over the other, because helicity couples the spin of the electron with its own linear momentum, resulting in the selective transmission of the electrons with the preferred spin state. This opens the way to great opportunities for “chemical control” in the selection and discrimination of the spin state of electric currents. The key concept resides in the achievement of precise chemical control on the factors affecting molecular helical structure, i.e. length, diameter, pitch, chemical composition, chemical environment, either the solvent selection or its deposition on selected surfaces, including nanoparticles, etc. The absence of external electromagnetic fields avoids any interference with the spins in “ uncontrollable” ways. The implications of the CISS effect for the control of electronic spin state have already been documented. Nevertheless, a longstanding goal, not fully resolved at the current stage, is to know beforehand which molecules are best for CISS spin-filtering. Within this context, a remarkable effort has been made by Waldeck et al., who showed conclusive experimental evidence for the direct correlation between CISS induced spin-filtering power and the magnitude of features of the molecule electronic circular dichroism (ECD) spectrum. A direct correlation of the dissymmetry of the electron-transfer rate for photoelectrons produced by circularly polarized light was found with both sign and intensity of the ECD signal of electron acceptor chiral molecules. This suggests that the larger the ECD signal intensity the better the CISS spin-filtering a molecule can perform. The sign determines which spin is preferentially filtered. Although the relationship between both phenomena seems plausible, it is not clear which factors are relevant for such connection. One conceivable hypothesis is that the CISS effect may be associated with a transient magnetic moment in chiral molecules. Indeed, the intrinsic magnetic nature of the CISS effect suggests that induced magnetic transition moments (m) could be relevant to characterize the magnetic molecular response associated with the dynamic spin-polarized electron transport through a molecule. The optimal design of structures in which such relationship could be validated is, therefore, essential.

Here we report on a versatile scaffold to explore new helical architectures using simple derivatizations. Chiral stapled nucleus (S,S,P)-1 can be used as a chiral seed for the synthesis of highly extended enantiopure conjugated helical systems (S,S,P)-2-(S,S,P)-6 (Figure 1, bottom) containing one up to four complete turns. In the presence of Ag(I) we have obtained the most extended enantiopure systems with a well-defined structure described up to date. This situation is optimal to gain insight onto the importance of the length of helical systems, of the magnitude of the magnetic dipole transition moment (m) associated to the less energetic transition, and their potential use as predictor of CISS capabilities for an organic architecture. We must emphasize that a comprehensive theoretical model coupling optical dichroism with the CISS effect is still missing, but the work reported here may be a step forward in this direction.

Moreover, the usefulness of (S,S,P)-1 is also demonstrated with the preparation of ligand (S,S,P)-7. This compound increases the toolbox of supramolecular research area showing that simple helical foldamers can be also used as building block for the Pd(II)-directed self-assembly of a chiral Pd₇L₂ metallacycle, thus expanding the scarce number of examples of chiral metallosupramolecular architectures reported to date.

Results and discussion

Synthesis

The main of our approach is the synthesis of a chiral core able to be further functionalized. Taking into account our previous successful route to enantiopure stapled α-OPES based on an ethenification reaction of a simple α-OPE and a chiral bis-tosylate derivative, we decided to adapt this strategy to access to compound (S,S,P)-1. Hence, this compound could be easily prepared following the route described in Scheme 1. (S,S,P)-1 presents two aromatic bromides suitable for symmetric extension of the conjugated system using different Sonogashira reactions. Enantiomeric (R,R,M)-1 was also prepared resulting in the expected and opposite chiroptical properties (see figures S118 and S134). For simplicity, from now on the discussion is restricted to the (S,S,P)-1 enantiomer. A simple coupling reaction affords enantiopure compounds (S,S,P)-2 to (S,S,P)-6 with increasing number of alkynes, enabling the study of systems from three alkynes/one turn, (S,S,P)-1, to thirteen alkynes/turn, (S,S,P)-6, reaching in the latter case four complete turns, which has no precedent in the literature. The coupling reaction of the chiral nucleus (S,S,P)-1 with pyridine-containing dialkyne 19 yielded (S,S,P)-7. These reactions demonstrate that (S,S,P)-1 is in fact a versatile chiral building block that enables the access to a variety of structures in a straightforward and modular way.

![Scheme 1. Synthesis of helical systems (S,S,P)-2-(S,S,P)-6 and ligand (S,S,P)-7. Reagents and conditions: a) Ac₂O (1.4 eq.), DMAP (2 eq.), CH₂Cl₂, rt, 5 min, 100%; b) Pd(CH₂CN)₂Cl₂ (0.03 eq.), CuIBu, PhBF₃ (0.06 eq.), Cu₂(CN)₂, NH, CH₂Cl₂, rt, 24h, 70%; c) K₂CO₃ (7 eq.), THF, reflux, 30min, 88%; d) Cs₂CO₃, CH₃CN, reflux, 24h, 56%; e) Pd(CH₂CN)₂Cl₂, CuI, PhBF₃, I₂, NH/THF, 60 °C, 24h; f) Pd(CH₂CN)₂Cl₂, CuI, PhBF₃, I₂, NH/THF, 60 °C, 24h, 81%. Yields of step e for each derivative are described in the ESI.](image-url)

Photophysics of compounds (S,S,P)-1 to (S,S,P)-7.

Compound (S,S,P)-1 was fully characterized by NMR and mass spectrometry (see ESI) but also by means of optical and
chiroptical techniques. The absorption spectrum in CH$_2$Cl$_2$ exhibits two main bands centered at 305 nm and 290 nm with a smooth shoulder around 350 nm (Figure 2a). On the other hand, emission spectrum presents one band at 410 nm (Figure S110) with a fluorescence quantum yield of 4.6% (Table S1).

Circular dichroism of (S,S,P)-1 (CH$_2$Cl$_2$) showed a positive Cotton effect at the longest wavelength, $\Delta \varepsilon = +47 \, \text{M}^{-1} \cdot \text{cm}^{-1}$, which is characteristic of $P$ helicity (Figure 2b). We note that molar circular dichroism ($\Delta \varepsilon$) depends on the intensity of absorption (that is, on electric transition dipole moment) and its magnitude cannot be always correlated with the intrinsic chirality of the sample. In that situation, dimensionless $g_{abs}$ value, $\Delta \varepsilon/c$, is more representative and easy to compare with theoretical values. Nevertheless, extracting reliable experimental $g_{abs}$ values from ECD bands is tricky since calculations predict energetically close transitions with opposite sign, such that observed $g_{abs}$ value results from the algebraic sum of $g$-values for the individual transitions. Being interested in the first electronic transition, the best estimate can be obtained from the tail of the CD band. In that case, the experimental $g_{abs}$ value ($+1 \times 10^{-2}$) is comparable to previously described values for related systems.$^{52-53}$

The origin of this helical chirality could be clarified using Density Functional Theory (DFT) calculations. After a Molecular Mechanics (MM) conformational search, all structures within 5 kcal/mol have been optimized with both $P$ and $M$ helicities at the B3LYP/6-31G** level in CH$_2$Cl$_2$, treated with the Polarizable Continuum Model (PCM). Only three conformers, corresponding to the relative spatial orientations of the bromine atoms (out-out, out-in and in-in), have been obtained with non-negligible populations (Figure 2c and Table S10). They all present $P$ helicity and, considering the calculated energy, are nearly equally populated. As a consequence, the $P$ epimer dominates the conformational equilibrium and makes possible a definite assignment of the (S,S,P)-1 absolute configuration in solution. This conclusion was strengthened by the similarity between the averaged simulated ECD and absorption spectra of the above mentioned $P$ conformers (M06/6-31G** level) and the experimental ones (Figure 2a,b). The calculated $g_{abs}$ value for the longest wavelength transition is in reasonable agreement with the experimental one. Fortunately we could also obtain the single-crystal X-ray diffraction structure of (S,S,P)-1, which confirms its helical geometry with $P$ preference in the solid state (Figure 2c). This helical arrangement generates a dihedral angle between the central aromatic rings close to 40°. The outer aromatic rings adopt a parallel orientation, although displaced, with a distance between their main planes of 3.5 Å and a distance between centroids of 3.8 Å, suggesting the establishment of $\pi$-stacking interactions between them. Being dynamic systems, foldamers are affected by the environment and, consequently, their properties are usually solvent dependent. In this case, we only observed a single set of signals in NMR, showing that any conformational equilibrium takes place faster than the NMR timescale. Absorbance and fluorescence of (S,S,P)-1 were analyzed in different solvents, including apolar, polar and protic ones. Although no significant differences were observed in emission spectra, a slightly increment of the shoulder in the absorbance spectra appeared in some solvents (Figure S109). Fluorescence lifetimes were also measured at the emission maximum using an excitation source of 325 nm. In all tested solvents, decays were fitted to a

![Figure 2. Comparison of the calculated (dashed orange, purple and green) and experimental (black) absorption and b) ECD spectra of (S,S,P)-1 in CH$_2$Cl$_2$ (2.5×10$^{-3}$ M); c) X-ray structure of (S,S,P)-1 and calculated structures of the in/in, in/out and out/out conformers. Calculated spectra are 20 nm blue-shifted and their intensity divided by a factor of two.](image-url)
bienexponential function where the shortest fluorescence lifetimes were around 0.5 ns in most cases, except in CH₂Cl₂ in which it presented the considerably lower value of 0.2 ns. However, we observed higher differences for the longest fluorescence lifetimes, which varied between 0.7 ns in CH₂Cl₂ to 4.1 ns in toluene (See Table S2 for more details). In view of these results we recorded the Time-Resolved Emission Spectra (TRES) of compound (S,S,P)-1 in CH₂Cl₂ covering all the emission range, between 340 and 600 nm. This global analysis also afforded a biexponential decay showing, along the whole spectra, an exclusive contribution of the shortest lifetime species, being the presence of the largest almost negligible (See Figure S106).

Regarding chiroptical properties and according to the above mentioned data, minor changes in ECD of (S,S,P)-1 were obtained. We noticed that the chiroptical response of (S,S,P)-1 is maximized in MeOH with an experimental $g_{abs}$ value of $+1.3 \times 10^{-2}$. Since (S,S,P)-1 is fluorescent and chiral, CPL is a valuable tool to extract information of the dynamic system. Although the fluorescence was weak, reliable dissymmetry factors of the emission, $g_{lum}$ values defined as $2(I(|l)_h)/(I(|l)_h)$, could be measured (CH₂Cl₂: $g_{lum} = +1.1 \times 10^{-2}$, MeOH: $g_{lum} = +1.0 \times 10^{-2}$, MeCN: $g_{lum} = +1.0 \times 10^{-2}$, n-hexane: $g_{lum} = +0.9 \times 10^{-2}$). These results suggest that the P helicity is preserved in the excited state. Consequently, the similarity of $g_{abs}$ and $g_{lum}$ values also reveals that the structure is highly preserved in the excited state despite the apparent conformational flexibility. Analogous studies were carried out with compounds (S,S)-2 to (S,S)-7 (Figure 3). Again, chiroptical properties, especially ECD and CPL, were highly informative and solvent dependent. The compound presenting five alkynes, (S,S,P)-2, showed remarkable molar circular dichroism in MeCN ($\Delta \varepsilon = +41$ M⁻¹cm⁻¹, $g_{abs} = +1.0 \times 10^{-2}$), being compatible with a relatively ordered structure. Again, we found a correlation between the polarity of the solvent and the $g_{abs}$ value for the longest wavelength transition, with similar values in MeOH ($\Delta \varepsilon = +36$ M⁻¹cm⁻¹, $g_{abs} = +1.4 \times 10^{-2}$) to those obtained in MeCN, being weaker in CH₂Cl₂ ($\Delta \varepsilon = +20$ M⁻¹cm⁻¹, $g_{abs} = +0.8 \times 10^{-2}$) and hexane ($\Delta \varepsilon = +20$ M⁻¹cm⁻¹, $g_{abs} = +1 \times 10^{-2}$). If we assume $g_{abs}$ values as the representative parameter of the system helicity, polar solvents are apparently favoring the folding process. Although this is a well-known effect for m-OPEs, this is the first time it is clearly observed for o-OPEs.

Theoretical calculations support the prevalence of the fully folded conformations both considering CH₂Cl₂ and acetonitrile in the polarizable continuum model using the integral equation formalism variant (iepcm) (see ESI), showing again a clear preference for the P conformation. The rotational barrier for the unfolding process was theoretically estimated by turning one arm of the folded structure in $10^6$ steps (Figure S156), achieving a maximum at 8.1 kcal mol⁻¹. Therefore, the partially disordered situation favored by less polar solvents might explain the observed differences (See Figure S119, in the ESI).

Figure 3. Experimental (solid line) and calculated (dashed line) ECD spectra of (a) (S,S,P)-2 and (S,S,P)-3 and (b) (S,S,P)-4- (S,S,P)-7 in MeCN (calculated spectra are 20 nm shifted) and c) CPL spectra of (S,S,P)-2, (S,S,P)-7 in MeOH.

Compound (S,S,P)-2 is also fluorescent, with quantum yield values varying from 19% to 29% depending on the solvent (see
Table S3 in the ESI). Fluorescence lifetime at the emission maximum showed again two values around 4 and 2 ns in all solvents. Interestingly, time-resolved fluorescence allows the deconvolution of the emission spectra, providing the ratio of the different emitting species by using the areas of the species-associated emission spectra (SAEMS). In the four solvents we could detect two main contributions coming from two different species with around 4.6 and 2.6 ns, which cannot interconvert in that timescale. Although relative proportion depends on solvent nature (see Figure S107), two limit situations are present in hexane and MeOH, in which the corresponding populations are reversed. The coexistence of fully folded and partially folded structures in the excited state may be a reasonable explanation, being fully folded structures maximized in MeOH.

Since the chiroptical properties of the above mentioned species are expected to be different, CPL is once again a valuable tool to extract information of the dynamic system. Representative solvents as MeOH, MeCN, CH₂Cl₂ and hexane were evaluated using this technique, obtaining remarkable high $g_{\text{lum}}$ values (MeOH: +1.3 × 10⁻², MeCN: +1.3 × 10⁻², CH₂Cl₂: +0.88 × 10⁻², hexane: +1 × 10⁻²). Once more, a correlation with the polarity of the solvent was observed, being the fully folded conformations with higher $g_{\text{lum}}$ values preferred in MeOH or MeCN. Positive sign of CPL is correlated with positive sign of the ECD signal for the longest wavelength transition, being $P$ helicity preserved in excited state.⁴ Similarity of $g_{\text{abs}}$ and $g_{\text{lum}}$ values also reveals that geometrical structure of the ground state is preserved in excited state. In fact, the optimized structure for the first excited state starting from the lowest-energy fully folded ground state structure resulted in a nearly superimposable helix in both ground and excited states, showing differences only in the Bond Length Alteration (BLA) of the C–C=C–C groups (see Figure 4f and Table S12).

Similar conclusions were extracted for (S,S,P)-3–(S,S,P)-5 and (S,S,P)-7. Molar circular dichroism and $g_{\text{abs}}$ values remain high, specially in MeCN ((S,S,P)-3: $\Delta \varepsilon = +21$ M⁻¹cm⁻¹, $g_{\text{abs}}= +0.9 \times 10^{-2}$; (S,S,P)-4: $\Delta \varepsilon = +18$ M⁻¹cm⁻¹, $g_{\text{abs}}= +0.5 \times 10^{-2}$; (S,S,P)-5: $\Delta \varepsilon = +47$ M⁻¹cm⁻¹, $g_{\text{abs}}= +0.9 \times 10^{-2}$; (S,S,P)-7: $\Delta \varepsilon = +19$ M⁻¹cm⁻¹, $g_{\text{abs}}= +0.8 \times 10^{-2}$), compared to CH₂Cl₂ ((S,S,P)-3: $\Delta \varepsilon = +6$ M⁻¹cm⁻¹, $g_{\text{abs}}= +0.3 \times 10^{-2}$; (S,S,P)-4: $\Delta \varepsilon = +8$ M⁻¹cm⁻¹, $g_{\text{abs}}= +0.3 \times 10^{-2}$; (S,S,P)-5: $\Delta \varepsilon = +13$ M⁻¹cm⁻¹, $g_{\text{abs}}= +0.3 \times 10^{-2}$; (S,S,P)-7: $\Delta \varepsilon = +19$ M⁻¹cm⁻¹, $g_{\text{abs}}= +0.3 \times 10^{-2}$), although exceptions can be also observed (See ESI). These higher $g_{\text{abs}}$ in MeCN suggest a relatively ordered structure in more polar solvents, in accordance with the stability of the helical structure. Nevertheless, the increasing number of potential conformations did not allow a complete modeling of the conformational space as in previous cases. Even so, it seems reasonable to assume that in absence of solvophobic interactions many more disordered structures in solution could be present. For compound (S,S,P)-6, we found some solubility issues in hexane and MeOH and reliable CD spectra could be obtained only in CH₂Cl₂ ($\Delta \varepsilon = +13$ M⁻¹cm⁻¹, $g_{\text{abs}}= +0.3 \times 10^{-2}$) and MeCN ($\Delta \varepsilon = +15$ M⁻¹cm⁻¹, $g_{\text{abs}}= +0.3 \times 10^{-2}$).

Fluorescence lifetimes and quantum yields for such longer oligomers (S,S,P)-3–(S,S,P)-7 were evaluated in MeOH, MeCN, CH₂Cl₂ and hexane are summarized in Table S4. Quantum yields depend on both solvent and number of alkynes present in the molecule, but no sensible relationships could be obtained in any of the cases. However, it is remarkable that, except for compound (S,S,P)-3, the intensity-averaged lifetime of longer oligomers is always lower in hexane (around 3 ns) than in MeOH and CH₂CN (around 4 ns), showing again a higher contribution of the shortest lifetime species in apolar solvents, in accordance with the results obtained for TRES of the first member of the series (S,S,P)-2.

All helical systems were also very efficient CPL emitters, specially in MeOH ((S,S,P)-3, $g_{\text{lum}} = +1.3 \times 10^{-2}$; (S,S,P)-4, $g_{\text{lum}} = +1.1 \times 10^{-2}$; (S,S,P)-5, $g_{\text{lum}} = +1.3 \times 10^{-2}$; (S,S,P)-6, $g_{\text{lum}} = +1.3 \times 10^{-2}$; (S,S,P)-7, $g_{\text{lum}} = +0.54 \times 10^{-2}$). Modeling CPL properties has been be carried out for compound (S,S,P)-2 in the most stable folded conformer. However, the analysis of larger systems is computationally too demanding. Despite this limitation, the structures were optimized by DFT calculations (Figure 4b-e). Although, the similarity between $g_{\text{abs}}$ and $g_{\text{lum}}$ values, which is also observed in experimental trends, is expected, $g_{\text{lum}}$ value is controlled by the $S_1 \rightarrow S_0$ transition, which cannot be assumed identical with the $S_2 \rightarrow S_0$ transition because the structural changes in the excited state may affect the ground state transition parameters.

Figure 4. Optimized DFT (B3LYP/6-31G***) structures of: a) (S,S,P)-2; b) (S,S,P)-3; c) (S,S,P)-4; d) (S,S,P)-5; e) (S,S,P)-6. Color coding: C, gray; O, red. H atoms have been left out for clarity. The optimized structure for the first excited state starting from the lowest-energy fully folded ground state structure resulted in a nearly superimposable helix in both excited and ground states, showing differences only in the Bond Length Alteration (BLA) of the C–C=C–C groups (see Figure 4f and Table S12).
(S,S,P)-1-(S,S,P)-7 Ag(I) complexes

Stapled o-OPEs present a perfect arrangement for coordination of Ag(I) cations (AgBF₄) using carboxylate interactions. In this case, we restricted our study to CH₂Cl₂ owing to the incompatibility of such interaction and polar coordinating solvents.

The first member of the series, (S,S,P)-1, presents evident structural changes after Ag(I) addition as we observed an increased resolution and downfield shielding of the aromatic protons (Figure S49). Regarding to the ¹³C NMR spectra, alkyne carbons, which were initially located within 1 ppm around 92 ppm, evolve to three different signals at 89, 92 and 94 ppm by coordination with Ag(I) cation (Figure S50). The coordination process was also followed by ECD spectroscopy (Figure S126). In this particular case, we observed a decrease in the chiroptical response. This fact is in agreement with previous results in related o-OPEs with three alkynes owing to a planarization of the helical structure. ECD titration experiments resulted in a relatively strong single binding event, $K_{S,Ag} = 32480 \pm 2\% \text{ M}^{-1}$. Theoretical calculations (M06/6-31G* plus LANL2DZ (valence + ECP) for silver in CH₂Cl₂) showed that the minimum energy structure corresponds to a distorted trigonal bipyramidal geometry (Figure 6b) in which the bromine atoms participate in the coordination to the Ag(I) cation.

Compound (S,S,P)-2 is expected to behave as a ligand for only one Ag(I) cation taking into account the previous studies of related o-OPE systems. The binding process can be again properly followed by ¹H NMR spectroscopy. NMR titrations showed that the original signals of ortho hydrogen atoms of the inner phenyl rings experience the characteristic deshielding (i.e. from 6.45 ppm to 6.64 ppm, Figure 6a) attributed to Ag(I) coordination. In addition, significant changes in the chemical shift of alkyne carbons were observed in the ¹³C NMR spectrum (Figure S52). The ECD response at the longest wavelength is intense ($\Delta \varepsilon = +85 \text{ M}^{-1}\text{cm}^{-1}$, $g_{abs} = +2.5 \times 10^{2}$) in agreement with a well-defined helical structure upon formation of the complex (Figure 6). It is worth noting that such dissymmetry ratio is huge compared with usual values for organic molecules at the longest wavelength. The corresponding ECD titration showed a high binding constant $K_{S,Ag} = 3.67 \times 10^{5} \pm 5\% \text{ M}^{-1}$. As expected, the DFT-based conformational analysis (see ESI) of complex (S,S,P)-2:Ag is in agreement with experimental findings, showing a stabilization of the fully folded structure. Calculated ECD is also in good agreement with the experimental one, thus confirming the folding process with Ag(I) (Figure 5a and 6c). In this case, the distorted trigonal bipyramidal geometry is generated by coordination with five alkyne.

Ag-alkyne bond distances are predicted to lay within 2.51–2.69 Å, with the Ag–C (alkyne) distances ranging from 2.57 to 2.76 Å. Distance between the terminal aromatic rings of the side arms and those on the corners on the central core of the helix, which display a quite displaced parallel arrangement, is ca. 3.5–3.6 Å, which suggests some extent of π-interactions between them.

On the other hand, the increase to seven potential binding sites for Ag(I) cations in compound (S,S,P)-3 did not result in a significant increase of the chiroptical properties ($\Delta \varepsilon = +21 \text{ M}^{-1}\text{cm}^{-1}$, $g_{abs} = +1 \times 10^{2}$). In principle, a single Ag(I) cation does not need all the alkynes in the binding event, making the remaining ones useless to stabilize a second Ag(I) cation. In this situation the presence of loosely or non-bound side arms can result in a more disordered structure compared to (S,S,P)-2, even in the presence of Ag(I). Unfortunately, the complex conformational space makes difficult performing any theoretical prediction. As a consequence of the previous assumption, ECD titrations showed that the compound is only bound to one Ag(I) cation with a binding constant $K_{S,Ag} = 3.7 \times 10^{6} \pm 15\% \text{ M}^{-1}$. Minimum energy calculated structures showed that Ag(I) is interacting with five alkynes. Only two alkynes remain free to bind a new cation. Our previous studies indicated that two alkynes are unable to provide an efficient coordination to another Ag(I) cation. Different spatial arrangement for these two additional...
unbounded side chains and even in-cavity Ag(I) displacements could explain the weaker ECD response.

The presence of two additional alkynes in (S,S,P)-4 should be in principle beneficial for the coordination process. Nevertheless, the ECD response remains weak and similar to the previous case ($\Delta\varepsilon = +24$ M$^{-1}$ cm$^{-1}$, $g_{obs} = +0.6 \times 10^{-2}$). This fact suggest that at the concentrations used for the ECD experiments there is only a relevant binding constant, although subsequent Ag(I) coordination processes can take place with a modest binding constant. Accordingly, in the titration experiments a higher overall binding constant, $K_{4Ag2} = 2.4\times10^{14} \pm 12\%$ M$^{-2}$, was obtained (see Figures S129 to S131). It is worth noting that the corresponding NMR studies were carried out at much higher concentrations. Under such experimental conditions more than two equivalents of Ag(I) cation are required to fully resolve the signals, suggesting the existence of a symmetric dimetallated structure.

Compound (S,S,P)-5, presenting eleven alkynes, is able to accept two Ag(I) cations, thus yielding a longer helical structure. The first evidence came from the ECD spectra, showing a remarkable molar circular dichroism ($\Delta\varepsilon$) at the longest wavelength ($\Delta\varepsilon = +85$ M$^{-1}$ cm$^{-1}$, $g_{obs} = +1.7 \times 10^{-2}$) in presence of an excess of Ag(I). ECD titrations also showed strong coordination of two Ag(I) cations ($K_{4Ag2} = 18\times10^{8} \pm 16\%$ M$^{-2}$). This is the first example of a pure and well-defined o-OPE system presenting an enantiopure helical structure with three and a half turns. This fact shows that the chiral nucleus can be useful with the aid of Ag(I) cations in the preparation of long and conjugated helical systems. Although different situations are possible, DFT calculations showed that the energetically favored case is that in which the Ag(I) cations are separated by a distance of approximately 5.2 Å (Figure 6f).

The best chiroptical response was observed for compound (S,S,P)-6, which showed an even higher molar circular dichroism ($\Delta\varepsilon = +130$ M$^{-1}$ cm$^{-1}$, $g_{obs} = +2.2 \times 10^{-2}$). Again, this result strongly suggests a fully folded helical structure. ECD titrations also showed three strong binding events with three Ag(I) cations ($K_{6Ag3} = 2.7\times10^{12} \pm 19\%$ M$^{-3}$). As it can be seen in Figure 6g, DFT calculations predict a highly symmetric structure with four complete loops. The interatomic distances between consecutive Ag(I) cations are 4.4 and 4.5 Å. Interestingly, on the basis of the Ag–alkyne distances, calculations predict that the metal centers are coordinated to five alkynes. As a result, there are two alkynes that coordinate simultaneously to two Ag(I) centers, which results in longer Ag–alkyne distances (2.74–2.89 Å) in comparison with those involving the triple bonds coordinated just to one metal center (Ag-alkyne distances: 2.44–2.65 Å).

### VCD studies

The existence of the helical structures was also confirmed by VCD spectroscopy, particularly evident when considering longer oligomers (see SI). Concerning IR measurements, the presence of the Ag(I) complex results in a band shift and broadening of the feature observed at 1500 cm$^{-1}$ and in the appearance of a band at 1315 cm$^{-1}$ (Figure 7). In VCD an intensification of the triplet signal at 1445, 1482 and 1493 cm$^{-1}$ ($\pm$28 cm$^{-1}$) is also characteristic of the presence of interacting Ag(I) cation, particularly considering (S,S,P)-4 to 6 compounds. This hints at the possibility of designing good silver switches based on IR range measurements. This $\pm$28 cm$^{-1}$ triplet show similar intensity in short and long chains in absence of silver, suggesting that the central portion of the backbone rigidified by the staple is the one responsible for this signal in all compounds.

To better understand the origin of the spectroscopic changes upon silver addition, we examined two representative cases with the aid of DFT calculations: the shortest oligomer (S,S,P)-2...
and a longer case, (S,S,P)-5. For the first case, we considered the possible conformers and compared the calculated spectra for the most stable structures in the absence or presence of silver. The details of this analysis are given in the ESI (conformers characteristics and spectra). Due to the staple, the structure of the short oligomer is rigid enough to present a VCD signal typical of the ordered OPE structures already observed.\textsuperscript{50,61} In particular, configuration of the staple dictates the prevalent helicity sense and the most stable conformer presents already the correct shape to host a silver ion, however, also partially unfolded structures of (S,S,P)-2 maintain the spectroscopic pattern. In the presence of Ag(I), the calculated spectrum reproduces the wavenumber shift of the two higher energy components of the previously cited triplet (\( r_\gamma^+ \)) and the 1315 cm\(^{-1}\) feature intensification (Figure 7). Also the IR spectra differences are correctly predicted.

In the case of the longer oligomer, Ag(I) cations give rise to the enhancement of the triplet at 1450-1500 cm\(^{-1}\). The phenomenon can be attributed to normal modes delocalized along the whole molecule, consisting of in-plane bending of the phenyl CH bonds. Structures with various Ag contents have been optimized: one central Ag ion, two Ag ions symmetrically or non-symmetrically disposed and three Ag ions (see Figure S150 for the optimized structures and Figure S151 for the corresponding calculated spectra). Overall, there is a good correspondence between calculated and experimental data. In fact, compound (S,S,P)-5 revealed to be quite efficient in incorporating silver ions and has sufficient length to show an enhancement of VCD signals when it is guided to form a regular helix by the presence of silver. In conclusion, in the presence of silver, the longer backbone assumes an ordered structure able to show intensification of the triplet; the increase in intensity is more regular considering VCD, while ECD shows a non-

Figure 7. Comparison of theoretical and experimental a) IR and b) VCD spectra of compound (S,S,P)-2 in CHCl\(_3\) as solvent.

Chiroptical properties and CISS effect for compounds (S,S,P)-2 to (S,S,P)-6 and their corresponding Ag(I)-complexes

In this vein, compounds denoted as (S,S,P)-2-6, appear as ideal for examining the influence of the number of turns of helical molecules on their chiroptical properties and its eventual connection to the CISS effect-based spin selection power. The chiroptical properties are customarily quantified by the dissymmetry factor, \( g_{\text{abs}} \), of the electronic transitions. The latter quantity is expressed in terms of the extinction coefficients for left- and right-polarized, \( e_r \) incident exciting light and reads as, \( g_{\text{abs}} = 2(e_r - e_l)(e_r + e_l) = 4(|\mu| |m| \cos(\theta) |(|m|^2 + |\mu|^2)| = 4R/D, \) where \( R \) and \( D \) are the rotational and dipole strengths respectively for the corresponding \( S_D \rightarrow S_S \) transition. This equation expresses the dissymmetry factor in terms of the electric dipole transition moment, \( \mu \), and the magnetic dipole transition moment, \( m \), and the angle subtended by these two vectors, \( \theta \). Since the magnetic dipole transition moment is normally much smaller than the corresponding electric one, one can expand \( (|\mu|^2 + |m|^2) \approx 4|m| |\mu| \cos(\theta) \). On the other hand, the CISS effect translates into an additional component of the magnetic moment associated with a Rashba-like term: \( m_{\text{CISS}} = \alpha \langle E, (\sigma \times \mu) \rangle \), being \( \alpha \) a coupling constant, \( E \) the molecular electric field, \( \sigma \) the Pauli matrix vector and \( \mu \) the linear momentum of the electron involved in the transport. This additional term has to be included in the optical response, generating, in principle, a direct connection between ECD and the CISS effect Namely, as noted above, an electron moving along the electric field in a chiral structure defined by the fixed nuclei and not by an external field, will experience in its rest frame a magnetic field, which will interact equally as above with the electron magnetic moment. Hence, the electron magnetic moment appears to be directly connected to the CISS effect. Given the nature of the optical activity response, one could hypothesize the transition magnetic vector \( m \) as a descriptor for enhanced chiroptical properties, which could explain the observed relationship between the chiroptical properties and enhanced CISS spin selectivity power.\textsuperscript{75} Despite the fact that \( g_{\text{abs}} \) values can be high when \( |m| \) and \( |\mu| \) are similar in magnitude and aligned as possible, that fact does not guarantee the absolute value of \( |m| \) to be high. That is, compounds can present high \( g_{\text{abs}} \) values simply by diminishing \( |\mu| \). We hypothesize that conductive helical structures, which supposedly are ideal candidates for relevant CISS effect, must show a high \( |m| \), higher than \( 1 \times 10^{-20} \) cgs units,\textsuperscript{76} for transitions capturing the helical structure of the involved molecular orbitals. Moreover, CISS effect is directional and must be analyzed in the direction of electron transport, which is difficult using scalar quantities like \( g_{\text{abs}} \) or rotational strength \( R = (|\mu| |m| \cos(\theta)) \). The lower energy transitions are of special relevance since the most accessible orbitals for electron transport at low voltages are involved.

We have analyzed the relevant chiroptical parameters, such as electric and magnetic dipole transition moments \( |m| \) and \( |\mu| \), dipole (D) and rotational strengths (R), angle between electric dipole transition moment and magnetic dipole transition moment, obtained by TD-DFT calculations (M06/6-31G***) of molecules (S,S,P)-2 to (S,S,P)-6 and their corresponding Ag(I) complexes. It is important to note that the studied systems are quite large and cannot be fully modelled at high level of theory. Consequently, only tendencies and not precise values can be
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provided by the calculations. It is worth noting that theoretical calculations overestimate the predicted $\gamma_{abs}$ values.\textsuperscript{77} In this case, we use CHCl$_3$ as solvent for a better comparison with the parent compounds and Ag(I) complexes derived.

Inspection of the data of Table 1, shows that the magnetic dipole transition moment for the $S_0\rightarrow S_1$ transition increases monotonically with the number of windings for the whole set of helical molecules ($S,S,P$)-2 to ($S,S,P$)-6. This is in agreement with the naïve view that holds that increasing helicity of the compound should translate into an increase of the magnetic moment. It had been suggested that when the magnetic dipole transition moment stands for the power absorbed from the exciting light magnetic field in a conductive helix, a linear relationship between the transition magnetic dipole moment and the number of loops $n$ exists.\textsuperscript{78}

Table 1. Electric and magnetic dipole transition moments $\mu$ and $m$, dipole (D) and rotational strengths (R), angle between electric dipole transition moment and magnetic dipole transition moment E-M and dissymmetry ratio $\gamma_{abs}$ obtained by TD-DFT calculations (m06/6-31g**) for the first electronic transition. Units for electric and magnetic dipole transition moments are esu·cm. For D and R are esu·cm$^2$.

| Compound ($S,S,P$)-2 | $\mu$ | $m$ | D (10$^{-26}$) | Length | R (10$^{-26}$) | E-M | $\gamma_{abs}$ |
|----------------------|------|-----|---------------|--------|---------------|-----|-------------|
| (S,S,P)-2            | 204  | 3.74| 41568         | 645    | 32            | 0.06|             |
| (S,S,P)-3            | 382  | 3.97| 146279        | 1407   | 22            | 0.03|             |
| (S,S,P)-4            | 426  | 4.19| 181829        | 1606   | 26            | 0.03|             |
| (S,S,P)-5            | 442  | 4.20| 195208        | 1727   | 22            | 0.03|             |
| (S,S,P)-6            | 524  | 4.42| 275017        | 2237   | 15            | 0.03|             |

In that case, the classical electromagnetic power dissipated by light absorption of intensity $E_0^2$ and wavelength $\lambda$ by the magnetic field alone in a helix of conductivity $\sigma$, cross section $a$, radius $r$, pitch length $d$, and pitch angle $\Phi$, is dictated by $P = ad(E_0^2 \sin \Phi/4\lambda)^3(d^2 + 4\pi^2 \sigma^2)^{-1}$. Such linear relationship is nicely paralleled by the plot in Figure 8 of the magnetic dipole transition moment $|m|$ versus $n$. The number of alkynes displayed on the x-axis, is related to the number of loops $n$ through the $n = N/3$. This is in agreement with a seminal paper about the CISS effect by Zacharias et al.\textsuperscript{79} in which the spin polarization increases as a function of the number of turns in helical polyamide molecules adsorbed on a gold surface, a result that runs in parallel with the observed dependence of the transition magnetic moment.

As suggested above we speculate that the magnetic transition vector or its projection in the electron transport direction of a selected transition could be the missing link between the CISS effect and chirooptical properties. This can be supported by the interpretation of the CISS effect as an additional contribution to molecular magnetic response that is triggered in the presence of electron transport through a chiral (helical) structure. A simple theoretical explanation of this dependence of the spin polarization with molecular length in helices can be given in terms of a scattering model including both coherent and incoherent contributions to electron transport.\textsuperscript{80} All these assumptions, although promising, require further theoretical inquiries.

Metallosupramolecular complex ($S,S,P$)-7

Finally, we have checked the coordination capabilities of homochiral ligand ($S,S,P$)-7 towards Ag(I) and Pd(II) cations. Despite the presence of five alkynes, this ligand has two additional pyridine rings that can coordinate to non-carbophilic...
metal centres as Pd(II). The meta substitution of these pyridine rings results in an almost parallel orientation of the binding sites (with an angle between them close to 0°). This geometry allows the assembly of well-defined metallosupramolecular entities with metal centres with coordination sites in a 180° orientation, resulting on either linear Ag(I) complexes or on square planar Pd(II) complexes with two additional ligands in trans positions. In the case of the Ag(I) cations, two different binding sites are possible, the alkynes and the pyridines. ECD spectroscopy was highly informative to discriminate between the two alternatives. As in the case of related compound (S,S,P)-3, intensification of the ECD signal at the longest wavelength ($\Delta\varepsilon = +41 M^{-1} cm^{-1}$, $\delta_{abs} = +0.45 \times 10^{-3}$) is observed upon addition of a Ag(I) salt to a solution 2.5×10^{-5} M of (S,S,P)-7, compatible with an increase of the helicity of the system (Figure S121). Moreover, titration experiments also showed that this increase was related with the coordination of the ligand to one Ag(I) cation (K$_{2,Ag} = 8.21 \times 10^{2} \pm 13 \% \ M^{-1}$) (Figure S132). Therefore, the interaction of Ag(I) cations with the alkynes seems to be the most favorable interaction for the first added equivalent. Nevertheless, in the presence of an excess of Ag(I) cation the ECD signals drastically decreases suggesting the formation of insoluble material in CH$_2$Cl$_2$. probably by subsequent coordination of the cation with the available pyridine groups. All these results allow us to conclude that carbophilic metals cannot easily direct the self-assembly of metallosupramolecular structures for our systems.

On the other hand, addition of a solution of trans-PdCl$_2$(MeCN)$_2$ (10 mM) to solutions of (S,S,P)-7 in CD$_2$Cl$_2$ or DMSO-d$_6$ (10 mM) resulted in the appearance of new signals in the corresponding 'H NMR spectra. This fact indicates the presence of new species in solution and suggests the formation of a metalacycle as a result of the coordination of the pyridine rings to the Pd(II) centers (see ESI, Figures S92-102). The DOSY NMR spectrum in DMSO-d$_6$ of this mixture (Figure S103) agrees with the presence of two species as two diffusion coefficients are observed for the 'H signals. Thus, the new set of signals that appeared after Pd(II) addition shows a lower diffusion coefficient, supporting the coordination of the (S,S,P)-7 to the metal center and the self-assembly of the larger metalacycle. By increasing the amount of added Pd(II) complex, this new set of signals became the main one in the mixture, being practically the only one present when 1.1 equiv. of trans-PdCl$_2$(MeCN)$_2$ were added (Figures S93 and S98). In this case, the DOSY NMR spectrum confirms that all signals correspond to a single species that diffuses as a whole, as expected, as only one diffusion coefficient is observed (Figures S65 and S70).

The clear solution obtained in DMSO-d$_6$ was monitored over time by 'H NMR spectroscopy, showing no significant changes in the spectrum over 6 days (see ESI, Figure S102). In CD$_2$Cl$_2$, the evolution of the system was more complicated since a precipitate was formed soon after the addition of the metal when a final concentration of 5 mM was used. After filtration, the 'H NMR spectrum of the remaining solution showed two sets of signals, one corresponding to the free ligand and the other one to the newly formed species, postulated as the (S,S,P)-7-Pd$_2$ complex. However, the ratio between species was not maintained over time, as a decrease of the proportion of the coordination complex was observed. 'H NMR monitoring. Better results were obtained when the concentration was lowered to 2.5 mM, as no precipitation was observed. In this case, the set of signals attributed to the coordinated species was present almost exclusively after 24 h and good stability was observed over time (Figure S96).

Comparison of the 'H NMR of (S,S,P)-7 before and after the addition of Pd(II) both in DMSO-d$_6$ and CD$_2$Cl$_2$ shows a downfield shift ($\Delta \delta_{Ha} = 0.23 \text{ ppm}$; $\Delta \delta_{Hb} = 0.32 \text{ ppm}$ in CD$_2$Cl$_2$ and $\Delta \delta_{Ha} = 0.22 \text{ ppm}$; $\Delta \delta_{Hb} = 0.23 \text{ ppm}$ in DMSO-d$_6$) of the H atoms of the pyridine ring in positions 2 and 6 (Figure 9a). This is the expected behavior for the coordination of the pyridine ring to the Pd(II) center. To lend further support to the fact that the observed shift corresponds to the binding event, 3-(phenylethynyl)pyridine was prepared as a model ligand. The similarities between the chemical shift for the signals of the pyridine nuclei and their variation in the two complexes ($\Delta \delta_{Ha} = 0.23 \text{ ppm}$; $\Delta \delta_{Hb} = 0.25 \text{ ppm}$ in CD$_2$Cl$_2$ and $\Delta \delta_{Ha} = 0.23 \text{ ppm}$; $\Delta \delta_{Hb} = 0.19 \text{ ppm}$ in DMSO-d$_6$, see Figures S93 and S104) support the same coordination pattern in both cases.

Dilution experiments down to 0.5 mM both in CD$_2$Cl$_2$ or DMSO-d$_6$ show that the self-assembled complex is the only species at 2.5 mM in CD$_2$Cl$_2$ and in the 2.5-2.5 mM range in DMSO-d$_6$, and the major one down to 1 mM in both solvents. This fact strongly suggests that the more entropically favored complex is being obtained. At 0.5 mM in CD$_2$Cl$_2$, the complex is still the major species in solution, although the free ligand is clearly observed. On the contrary, a considerable amount of the bare (S,S,P)-7 ligand is observed in DMSO-d$_6$ at the same concentration. This is not surprising taking into account the
The self-assembly of a \( \{(S,S,P)\}-\text{Pd}\), which leads to a higher self-assembly concentration.\(^{33}\) The self-assembly of a \( \{(S,S,P)\}-\text{Pd}\) complex was further demonstrated by MALDI mass spectrometry of an evaporated sample of the complex. The high-resolution mass spectrum shows a signal at \( m/z = 2193.3 \), whose exact mass and isotopic distribution (Figure 9b) nicely match to those calculated for the \( [\text{M} - \text{Cl}]^+ \) ion, resulting from the loss of one chloride ligand by one of the Pd centers. Chiroptical properties were not particularly informative owing to just a moderate distortion of the electronic states after coordination. Therefore, very similar UV-Vis and almost identical ECD spectra to those of the free ligand were obtained (Figures 9c and S122). To confirm that we were really observing the signal associated with the complex, the \(^1\)H NMR spectra of the sample was carried out before and after the UV-CD measurements, performed at the NMR concentration (Figures S123-S124). Finally, the structures of the metallosupramolecular complex \( \{(S,S,P)\}-\text{Pd}\), and its \( \{(R,R,M)\}-\text{Pd} \), enantiomer were investigated by means of DFT calculations at the \( \omega B97XD/def2SVP \) level of theory both in DMSO and \( \text{CD}_2\text{Cl}_2 \) (Figure 10 and Tables S25-28). The optimized structures gave structural arrangements which were in good agreement with the experimental data. They showed the coordination of the pyridine rings to the Pd(II) metal centers and the generation of a chiral cavity defined by the helical cores.

**Conclusions**

In this work, we have synthesized a new family of enantiopure helical foldamers with increasing number of turns. Moreover, in the presence of Ag(I) cation well defined structures containing up to three ions and four turns are formed. As a consequence of such helical structure intense chiroptical properties associated to electron transitions both from the ground (ECD) and excited state (CPL) have been observed. The versatility of this approach has been further validated preparing an enantiopure metallacyclic structure upon coordination with Pd(II), thus enriching this chemistry with a new class of chiral ligands. We have observed that \( g_{abs} \) does not monotonically depend on the number of turns, in contrast to the trend observed in the \( B_0 \) band in helicenes.\(^3\) While magnetic dipole transition moment seems non progressive with increasing number of rings in helicenes, we have found a linear dependence of this vector in these helical foldamers. This fact can also be related with the potential use of these systems as spin filters, being the magnetic dipole transition moment a potential predictor for CISS-based spin filtering capabilities of these Ag(I)-complexes.

**Author Contributions**

A.M.O.: formal analysis, investigation, validation.

P.R.: formal analysis, investigation, validation.

S.R.: formal analysis, investigation.

L.A.C.: conceptualization, formal analysis, writing-original draft.

V.B.: investigation, formal analysis, writing-original draft.

J.M.P.: investigation, formal analysis.

A.J.M.: formal analysis, methodology, writing-original draft.

G.M.: methodology, formal analysis.

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G.L.: conceptualization, formal analysis, writing-original draft.

D.M.: funding acquisition, methodology, supervision, project administration, writing-original draft, writing—review.

J.M.C.: conceptualization, funding acquisition, methodology, project administration, supervision, writing-original draft, writing—review & editing.

**Conflicts of interest**

“There are no conflicts to declare”.

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