CHEMISTRY
A European Journal

Accepted Article

Authors: Juan M. Cuerva, Sandra Resa, Delia Miguel, Santiago Guisán-Ceinos, Giuseppe Mazzeo, Duane Choquesillo-Lazarte, Sergio Abbate, Luis Crovetto, Diego J. Cárdenas, M. Carmen Carreño, María Ribagorda, Giovanna Longhi, Antonio J. Mota, and Luis Álvarez de Cenfuegos

FULL PAPER

Sulfoxide-Induced Homochiral Folding of *o*-OPEs by Ag^I Templating: Structure and Chiroptical Properties

Sandra Resa,[a] Delia Miguel,[b] Santiago Guisán-Ceinos,[c] Giuseppe Mazzeo,[d] Duane Choquesillo-Lazarte,[e] Sergio Abbate,[d] Luis Crovetto,[b] Diego J. Cárdenas,[c] M. Carmen Carreño,[c] María Ribagorda,[c] Giovanna Longhi,[d] Antonio J. Mota,[f] Luis Álvarez de Cienfuegos,*[a] and Juan M. Cuerva,*[a]

Dedication ((optional))

Abstract: A new family of homochiral silver complexes based on carbophilic interactions with *ortho*-phenyleneethynylene (*o*-OPE) scaffolds containing up to two silver atoms is described. These compounds represent a unique class of complexes with chirality at the metal. Chiral induction is based on the inclusion of chiral sulfoxides which allow an efficient transfer of chirality to the helically folded *o*-OPE, leading to CPL and VCD active compounds. In the presence of Ag^I cation carbophilic interactions dominate, promoting helical structures with a defined helicity. This is one of the very scarce examples of the use of such interactions in the attractive field of abiotic foldamers. The switching event has been extensively studied using different chiroptical techniques including CD, CPL and VCD, also representing one of the few CPL switches described in literature.

Introduction

Synthesis of new enantiopure abiotic helical nanostructures is an intense research field owing to the expected properties derived from their intrinsic dissymmetry.[1] For example, designing homochiral helical systems with a precise size and shape as potential nanopores is a challenging task although they could lead to important applications. Structures able to include in their core very different species depending on the specific functionalisation of the cavity are known.[2] Notable examples correspond to the inclusion of 1-D water chains,[3] different anions[4] and cations,[5] and chiral organic molecules.[6] Moreover, the corresponding chirality is a useful feature in different fields, such as chiral materials and asymmetric catalysis. Among the corresponding chiroptical properties, the ability of organic monomolecular emitters to produce efficient chiral emission (circularly polarized luminescence, CPL) [7-9] has been less explored, despite its huge interest for advanced optoelectronic applications.[10] CPL switches[11] capable of modulating their emission in the presence of external stimuli, are especially appealing. To this end, such systems must be flexible enough to accommodate different *P/M* helicities in a reversible manner. Moreover, from a structural point of view, helical structures presenting a conductive backbone have been suggested as spin filters based on chiral-induced spin selectivity (CISS) effect. [12]

Within this context, the study of oligomeric structures able to adopt well-defined secondary conformations is a research field of growing interest. In particular, all-conjugated aryl-ethynyloligomers have been extensively used as hosts of different species.[13] For instance, *meta*[14] and *ortho*-phenyleneethynylenes (*o*-OPEs) [15] are able to reversibly fold into helical arrangements[16-18] even in a chiral way when chiral side chains[19] or chiral subunits exist in the backbone,[20] or in the presence of chiral guests.[21]

We recently showed that folded *o*-OPE-based nanopores can be filled with Ag^I cations through carbophilic interactions with the alkynes,[22] to give a new class of metallofoldamers (Figure 1, acyclic non-chiral organic emitters).[23] We also synthesized helical stapled *o*-OPEs[24] with an enantiopure 2,3-dihydroxybutanediether moiety, which showed excellent CPL responses (Figure 1, cyclic chiral enantiopure organic emitters).[25]

These homochiral helically folded structures suffer a change in the CPL emission in the presence of Ag^I, exemplifying the first case of CPL active small organic molecular emitters whose response can be modulated by carbophilic interactions in a reversible manner. These results showed the potential of OPEs as efficient and versatile CPL emitters. Nevertheless, enantiopure OPE foldamers having CPL emission have not been reported up to date. To this end a chiral inducer must be placed in the OPE. In this sense, sulfoxides are very efficient chiral inducers and have been widely used in asymmetric

[a] S. Resa, L. Álvarez de Cienfuegos, J. M. Cuerva
Department of Organic Chemistry
University of Granada, UGR
C. U. Fuentenueva, 18071 Granada, Spain
E-mail: jmcuerva@ugr.es, lac@ugr.es

[b] D. Miguel, L. Crovetto,[b]
Department of Physical Chemistry
University of Granada, UGR
Cartuja Campus, 18071 Granada, Spain

[c] S. Guisán-Ceinos, D. J. Cárdenas, M. C. Carreño, M. Ribagorda,c
Department of Organic Chemistry t
Universidad Autónoma de Madrid
Cantoblanco, 28049 Madrid, *Spain*

[d] G. Mazzeo, S. Abbate, G. Longhi
Dipartimento di Medicina e Traslazionale
Università di Brescia
Viale Europa 11, 25123 Brescia, Italy

[e] D. Choquesillo-Lazarte
Laboratorio de Estudios Cristalográficos
Instituto Andaluz de Ciencias de la Tierra, CSIC-UGR
Armilla, Granada, Spain.

[f] A. J. Mota
Department of Inorganic Chemistry
University of Granada, UGR
C. U. Fuentenueva, 18071 Granada, Spain

Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate))

synthesis. [26] This group has already been used to control, in a very efficient manner, the conformation and configuration of sulfinyl containing azobenzene photoswitches.[27] In that case, a *p*-tolylsulfoxide situated in an aromatic ring adopted a fixed conformation both in *E* and *Z* isomers of azobenzenes being able to transfer the central chirality to the azobenzene core.[27]
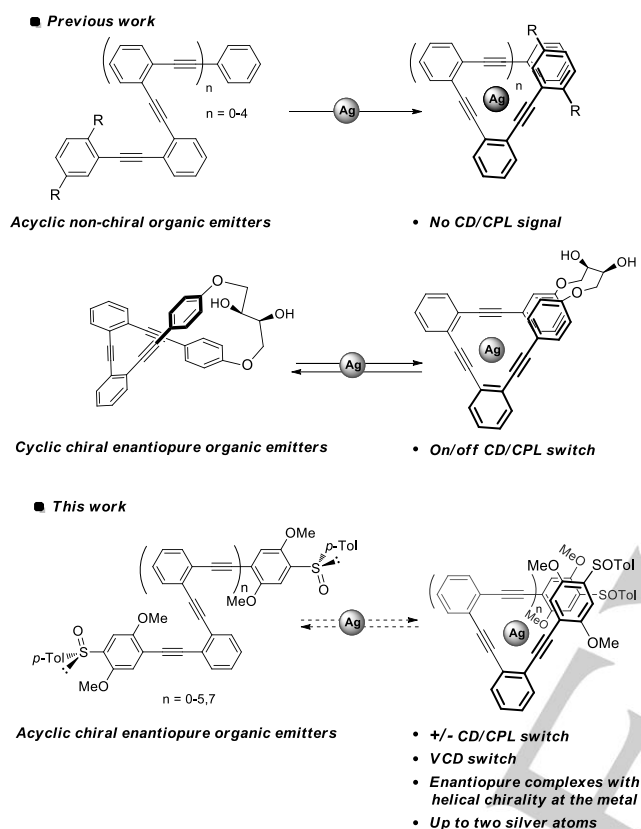

Figure 1. Working hypothesis.

On this basis, we expected an effective transfer of chirality from the stereogenic sulfur of chiral sulfoxides to a helically folded *o*-OPE. Herein, we present the synthesis of enantiopure sulfinyl substituted *o*-OPE foldamers and metallofoldamers and a study of the structural and chiroptical properties of the resulting systems (Figure 1, acyclic chiral enantiopure organic emitters). We could evidence that they behave as a new class of very scarce CPL active switches, based in this case on Ag[I] carbophilic interactions. Moreover, the synthetized complexes were able to include more than one silver atom in their structure depending on the length of the oligomer. This fact would generate simple molecules that, in principle, could have two conductive pathways: an axial one due to the presence of Ag[I] cations and a helical one due to the organic foldamer. The switching event could be followed by NMR, ECD, fluorescence, less common CPL spectroscopy and also by X-ray crystallography. Remarkably, the switching process could be

also observed in the vibrational wavelengths range,[29] using vibrational circular dichroism (VCD).[30]

Results and Discussion

The known compound (*S*)-1-bromo-2,5-dimethoxyphenyl-4-(*p*-tolylsulfinyl)benzene(*S*)-**A**,[27-28] was chosen as the homochiral starting material due to its availability and its known ability to freeze a sulfoxide conformation thanks to the vicinal disposition of methoxy and sulfinyl groups at the aryl ring. Sonogashira reaction between (*S*)-**A** and trimethylsilylacetylene, using catalytic amounts of Pd(CH₃CN)₂Cl₂, *t*Bu₃P•HBF₄ and CuI (3 mol %) in *i*-Pr₂NH/THF (1:1) as solvent, was followed by a desilylation to give *p*-tolylsulfinyl aryl substituted acetylene derivative (*S*)-**I** in 75 % isolated yield (Scheme 1). This intermediate was then used in the synthesis of acetylene derivative (*S*,*S*)-**1** and series of *o*-OPEs (*S*,*S*)-**2** to (*S*,*S*)-**8**, with up to eight *o*-phenyleneethynylene units (Scheme 1).[31-32]
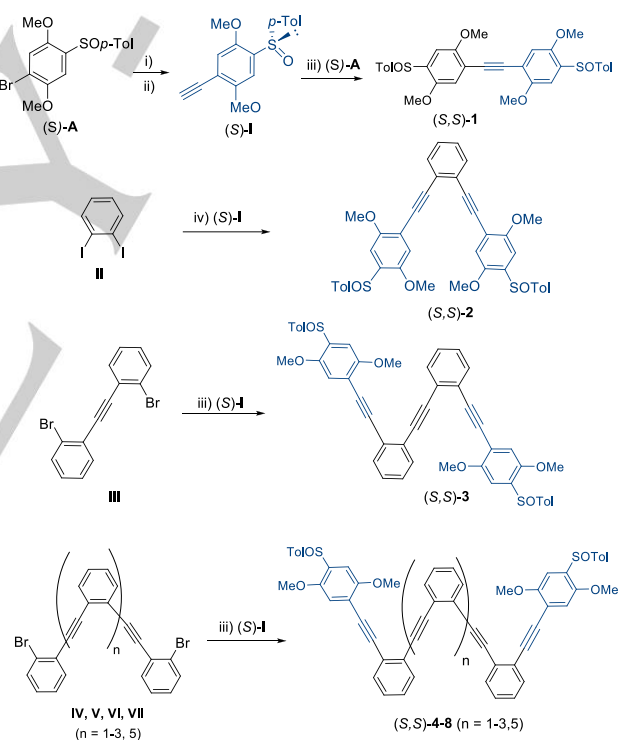
Scheme 1. Synthesis of (*S*,*S*)-**1** to (*S*,*S*)-**8**. Reaction conditions: i) Pd(CH₃CN)₂Cl₂ (0.03 equiv), *t*Bu₃P•HBF₄ (0.06 eq), CuI (0.03 equiv), trimethylsilyl acetylene (2 equiv) in *i*-Pr₂NH/THF, RT. ii) Bu₄NF, THF. iii) Pd(CH₃CN)₂Cl₂ (0.03 equiv), *t*Bu₃P•HBF₄ (0.06 equiv), CuI (0.03 equiv), **III-VII** (1 equiv), *(S)*-**I** (2 equiv) in *i*-Pr₂NH/THF, 60 ºC. iv) Pd(PPh₃)₂Cl₂ (0.05 equiv), CuI (0.1 equiv), diiodobenzene (1 equiv),*(S)*-**I** (2 equiv) in Et₃N/THF.

Photophysical characterization of (*S*,*S*)-1 to (*S*,*S*)-8. To evaluate the changes associated with folding in the OPEs containing the enantiopure (*S*)-sulfoxides, we recorded the electronic spectra of compounds (*S*,*S*)-**1** to (*S*,*S*)-**8** in CH₃CN

(common helicogenic solvent, Figure S1) and CH_2Cl_2 (non-helicogenic solvent, Figure S2). Such solvents were selected based on the previous behavior described for *o*- and *m*-OPEs.[33]

Compound (*S,S*)-**1** was studied as a model, owing to the presence of two sulfoxides as the sole chiral elements without any potential interference of emerging helical structures. CD spectra of (*S,S*)-**1** to (*S,S*)-**8** in CH_2Cl_2 are shown in Figure 2. Two main absorption bands appeared in the UV-vis, one in the region around 260-280 nm, where the sulfoxide absorbs, and a band at 330-380 nm ($\pi \rightarrow \pi*$ transition) owing to the aromatic (phenylene-ethynylene) chromophore. The CD spectra of (*S,S*)-**1-8** also showed a common positive band at λ = 260-270 nm corresponding to the (*S*)-configured sulfoxides slightly red shifted in the more conjugated (*S,S*)-**3-8**. Slight differences could also be observed in the other bands for compounds (*S,S*)-**1** and (*S,S*)-**2** when compared with (*S,S*)-**3-8**. Derivatives (*S,S*)-**1** and (*S,S*)-**2** present a peak with a negative Cotton effect, which was assigned to the aromatic groups, at λ = 330 nm and 370 nm respectively. The appearance of this band suggested that the sulfoxide is inducing a chiral perturbation in the aromatic system. Higher oligomers, (*S,S*)-**3** to (*S,S*)-**8**, where folded conformations are possible, showed two negative bands at ca. 320 nm and ca. 360 nm, also corresponding to the aromatic absorptions. The intensity of these chiral peaks increases with the number of phenyleneethynylene units ($\Delta\varepsilon$ = -25 to -55), being the largest for compound (*S,S*)-**8** ($\Delta\varepsilon$ = -55). Thus, the increasing number of phenyleneethynylene units seemed to produce a significant folding of these systems giving a chiroptical response that could be due to the presence of helically chiral foldamers, even in a non-helicogenic solvent. We used dimensionless dissymmetry factor g_{abs} for comparison between the different structures, showing that their values do not increase linearly with the number of alkynes (See Figure S3). This fact may reflect a conformational disorder in solution, which increases with the number of alkynes. Moreover, g_{abs} values are relatively low (0.5-1 x 10^{-3}) in comparison to the usually high dissymmetric factor found in helical structures, thus supporting such conformational disorder in solution. In CH_3CN, the recorded CD and UV-spectra were very similar to those obtained in CH_2Cl_2 (See Figures S1-S4), also suggesting that for these structures either the solvophobic promoted folding is minimum or that they present an intrinsic tendency to fold in solution independently of the nature of the solvent.

To obtain more information on these highly flexible systems we carried out (TD)-DFT-based theoretical calculations.[32] Despite the increasingly complex conformational space of these structures, we could obtain some representative minima, which could explain the experimental data. For the simplest compound (*S,S*)-**1**, calculations gave two minimum energy conformations,[34] corresponding to the *anti* and *syn* disposition of the tolyl groups: (*S,S*)-**1** *anti* and (*S,S*)-**1** *syn*, shown in Figure 3. The *syn* conformer is slightly favored (−0.6 Kcal·mol⁻¹) over the *anti*. They also present opposite theoretical CD spectra (Figure 2b). Comparison of experimental and calculated CDs of (S,S)-**1** at the longest wavelength suggests that the most stable

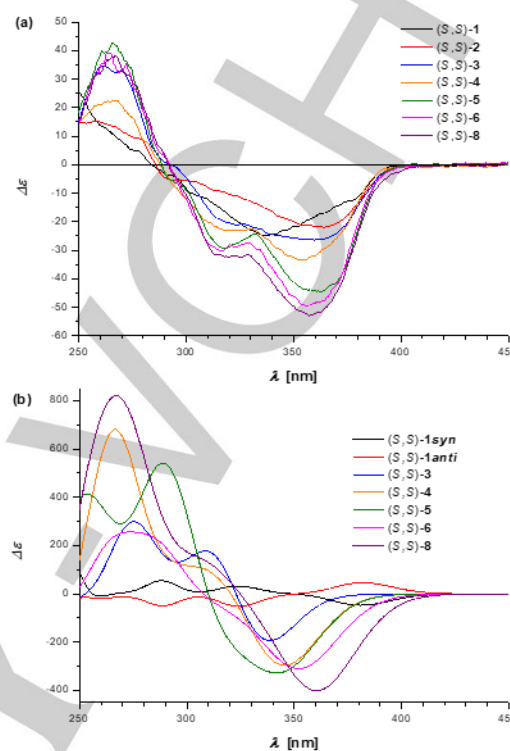syn conformation shown in Figure 3, may predominate in solution.

Figure 2. (a) Experimental CD spectra of compounds (*S,S*)-**1** to (*S,S*)-**8**. (b) Calculated CD spectra of compounds of (*S,S*)-**1** *anti*, (*S,S*)-**1** *syn*, (*S,S*)-**3** with two CH_2Cl_2 molecules, (*S,S*)-**4** with two CH_2Cl_2 molecules, (*S,S*)-**5** with two CH_2Cl_2 molecules, (*S,S*)-**6**, and (*S,S*)-**8**. Spectra of compounds (*S,S*)-**3**-(*S,S*)-**8** have been offset 70 nm.

Calculations of compound (*S,S*)-**2** gave a series of different conformations, which are very close in energy and easily interconvertible. Consequently many relative minima conformations must coexist in solution. This conformational flexibility was experimentally confirmed in the corresponding Time Resolved Emission Spectroscopy (TRES) experiments (details can be found below). Moreover, the calculated CD signal of (*S,S*)-**2** was highly dependent on the particular conformation, with no apparent relationship with the emerging helicity. Therefore, the structure in solution for (*S,S*)-**2** is uncertain.

For higher oligomers the study is much more complex owing to the presence of unfolded, partially folded and folded conformers with different *P* or *M* helicities. Moreover, the *p*-tolyl groups of the chiral sulfoxides can adopt different spatial dispositions: (a) *open conformation:* the *p*-tolyl groups pointing outside the helical structure: or (b) *compact conformation*: the *p*-tolyl groups placing along the axis of the helix. In any case, experimental CD showed a peak with a negative Cotton effect at the longest wavelength. Theoretical calculations, setting CH_2Cl_2 as solvent,[32] revealed small differences in energy between the different conformations, thus suggesting that both *P/M* helical epimers can coexist in solution. Nevertheless, (*S,S,M*) configuration with

a *compact conformation* of the *p*-tolylsulfinyl group is slightly favored, with the exception of (*S*,*S*,*M*)-**6**, in which *open* conformation is the only possible one (See Figure 3). [32] This preference for the (*S*,*S*,*M*) folded conformations qualitatively matches with the experimental negative bands appearing at 340-370 nm.[35-36]
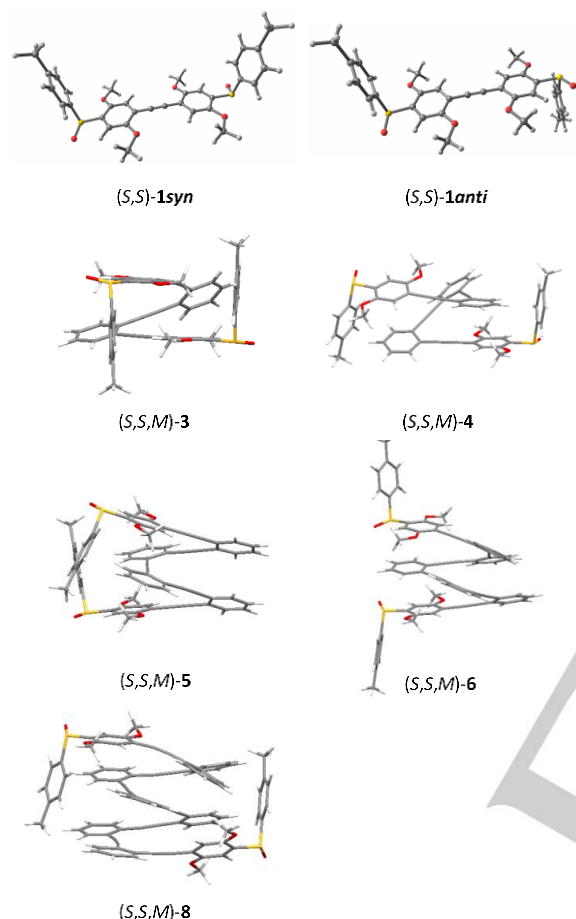

Figure 3. Side and top views of representative more stable calculated conformers of compounds (*S*,*S*)-**1**, (*S*,*S*)-**3** to (*S*,*S*)-**8**. Solvent molecules (CH₂Cl₂) have been removed for clarity (see SI).

The fluorescent properties of (*S*,*S*)-**1** to (*S*,*S*)-**8** in different organic solvents, including CH_2Cl_2 and CH_3CN, were also evaluated (see Figure S8). All of them were fluorescent with quantum yields highly dependent on the solvent but ranging from 0.56 for (*S*,*S*)-**1** to 0.20 for (*S*,*S*)-**8** in CH_2Cl_2. Besides, the photochemical stability of these compounds was highly dependent on the number of alkynes. *o*-OPEs with up to three alkynes,(*S*,*S*)-**1** to (*S*,*S*)-**3**, were stable. However, beyond that number they become unstable after intense irradiation. [32] In those cases, the proximity of two alkynes in the folded structure could facilitate a photochemically induced [2+2] cycloaddition, [37] being this the origin of this lack of stability. The resulting cyclobutadienes[38] could not be isolated due to their instability.

[39] Recently, Itami *et al.* reported a similar behavior for related cyclophenyleneethynylenes. [40]

Time Resolved Emission Spectroscopy (TRES) is a useful technique to gather information about the fluorescent species involved in the emission process as long as their interconversion occurs in a time scale similar or higher than the emission lifetime. [32] Within this limitation, we observed only one lifetime (τ_1 = 1.37 ns, CH_2Cl_2) for (*S*,*S*)-**1**, which suggested that all the conformations are equilibrated at room temperature. For (*S*,*S*)-**2** and (*S*,*S*)-**3** the emission spectra in CH_2Cl_2 and CH_3CN presented three different time resolved emissions (τ_1, τ_2 and τ_3), which are very similar in shape, suggesting a dynamic interconversion between them (Figures S9 y S10). These results are in agreement with the expected complex conformational behavior predicted by calculations. Compound (*S*,*S*)-**3** is able to fold in solution creating helical *P/M* epimers and also unfolded conformations thus justifying the three different time-resolved emissions with different shapes (Figure S10), which could be related with three structurally different excited states (roughly unfolded, *P*-folded and *M*-folded states). These states also represent the average emission of fast conformational equilibria.

Binding properties of (*S*,*S*)-1 to (*S*,*S*)-8 with Agᴵ cation. As we described previously, Agᴵ cation is able to selectively bind to the alkynes presented in *o*-OPE systems, thus promoting a folding process through carbophilic interactions. In structures (*S*,*S*)-**1**-**8**, the enantiopure sulfoxides and methoxy groups of the *o*-OPE structures offer additional coordination sites. Taking this variable into consideration, we studied the effect of the presence of Agᴵ cation in the structure and the chiroptical properties of *o*-OPEs (*S*,*S*)-**1**-**8**. The products were dissolved in a 9:1 mixture of CH_2Cl_2:acetone in the presence of $AgBF_4$, having a non-coordinating counteranion. The resulting absorbance spectra are shown in Figure S5 and the CD spectra are depicted in Figure 4. For (*S*,*S*)-**1** no significant changes in the CD spectrum could be observed after Agᴵ addition. This result points out that the chiroptical response of (*S*,*S*)-**1** is not affected upon Agᴵ addition. Nevertheless, the change in the chemical shift of the ¹³C NMR alkyne signal suggested that the metal binds to the alkyne.[32] On the other hand, dramatic changes can be clearly observed in the CD spectra (both in shape and sign) upon Agᴵ addition to compounds (*S*,*S*)-**2** to (*S*,*S*)-**8** (Figure 4a). The appearance of a positive Cotton effect at ca. 390 nm indicated a change in the helicity after coordination with Agᴵ cation. Taking into account this CD band at the highest λ, we could deduce a preferred opposite *P* helicity after coordination with Agᴵ cation. Molar circular dichroism values ($\Delta\varepsilon$) at 390 nm monotonically increased from (*S*,*S*)-**2** ($\Delta\varepsilon$ = +26) to a maximum for (*S*,*S*)-**6** ($\Delta\varepsilon$ = +144), which could be related with an increase in the magnetic dipole transition moment owing to the created helicity.

Titration experiments using CD variations revealed an initial binding event with increasing binding constants: $K_{(S,S)-2}$ = 79.5 ± 4% M⁻¹, $K_{(S,S)-3}$ = 4.91x10³ ± 3% M⁻¹, $K_{(S,S)-4}$ = 9.56x10⁴ ± 4%M⁻¹, $K_{(S,S)-5}$ = 2.80x10⁵ ± 10.6% M⁻¹ and $K_{(S,S)-6}$ = 1.19x10⁶ ± 25% M⁻¹. [41] Accordingly with this finding, a trend of the binding constant with the number of alkynes can be observed (See Figure S19). Despite the minor variations in the CD signals of model

compound (*S*,*S*)-**1** a binding constant value of $K_{(S,S)\text{-}1}$ = 4.09x10^4 ± 40% M^{-1} could be estimated, which is unusually high compared to those obtained in the other related systems. On the other hand, compound (*S*,*S*)-**3** showed a very intense chiroptical response in the presence of an excess of Ag^I cation, ($\Delta\varepsilon$ = +125 at 390 nm after addition of 215 equiv of Ag^I). In this case the CD titration experiments also showed the presence of two additional different binding constants, 2.06x10^2 ± 15% M^{-1}, and 1.26x10^3 ± 6% M^{-1}, assigned to (*S*,*S*)-**3**:**Ag$_3$** complex.
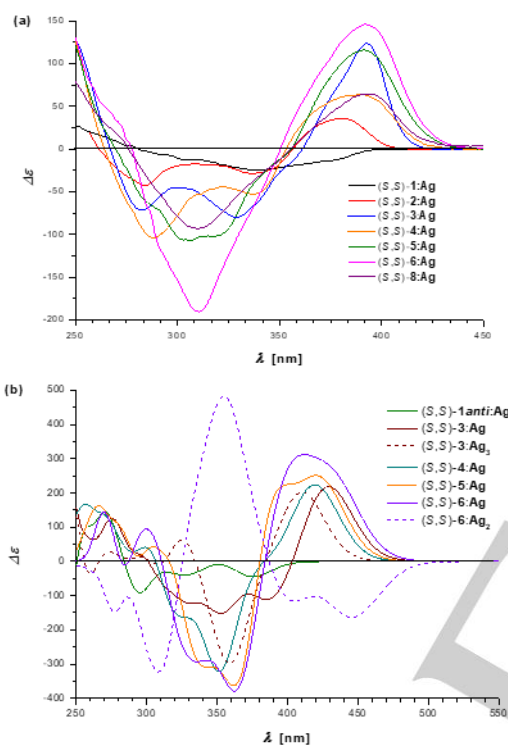

Figure 4. Experimental CD spectra of compounds (*S*,*S*)-**1** to (*S*,*S*)-**8** in presence (a) of an excess of Ag^I and (b) calculated CDs of compounds of (*S*,*S*)-**1***anti*:Ag, (*S*,*S*)-**3**:**Ag**, (*S*,*S*)-**3**:**Ag$_3$**, (*S*,*S*)-**4**:**Ag**, (*S*,*S*)-**5**:**Ag**, (*S*,*S*)-**6**:**Ag** and (*S*,*S*)-**6**:**Ag$_2$**.

Compounds (*S*,*S*)-**5**, and (*S*,*S*)-**6** present seven and eight potential binding sites (five/six alkynes and two of the four OMe groups), respectively. In principle, under this situation just one Ag^I cation is unable to simultaneously bind to all of them, and a second Ag^I cation may take part in the interaction. However, electrostatic repulsions could result in an unfavorable bimetallic coordination. The titration experiments of such compounds only showed a second binding event for (*S*,*S*)-**6** with a modest associated binding constant ($K_{2(S,S)\text{-}6}$= 60.3 ± 16% M^{-1}), suggesting that the second coordination event was not very favorable despite the number of available binding sites. It is worth noting that this second binding event is related with a decrease in the CD signal. [42]
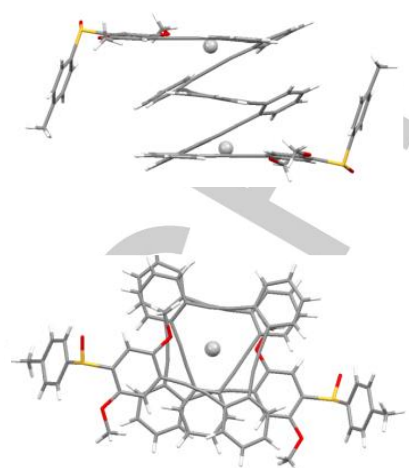

Figure 5. Side and top views of X-Ray structure of (*S*,*S*)-**8**:**Ag$_2$**. Solvent molecules have been removed for clarity.

o-OPE (*S*, *S*)-**8**, with ten potential binding sites (eight alkynes and two of the four OMe groups) becomes insoluble in the presence of an excess Ag^I. We were able to roughly obtain the corresponding CD spectra and an estimation of constant for the first binding event ($K_{(S,S)\text{-}8}$= 8.6x10^5± 41%M^{-1}). Fortunately, a suitable crystal for X-ray diffraction analysis was obtained for (*S*,*S*)-**8**:**Ag$_2$** complex. As it can be seen in Figure 5, o-OPE (*S*,*S*)-**8** is able to accomodate two Ag^I cations in a chiral helical environment with a Ag^I-Ag^I distance about 5.98 Å. In this situation, the number of binding sites seems to be optimal. Moreover, in the X-ray structure (Figure 5) a *compact conformation*, with the *p*-tolylsulfinyl groups situated along the axis of the helix is clearly observed. In such disposition, the electrostatic repulsions between the SO and the vicinal OMe groups are minimized. Interestingly, the configuration of the helix in the solid state is *M,* which is the opposite to that suggested by CD in solution. This finding, together with the decreasing intensity of the CD signal during the second binding event for (*S*,*S*)-**6**, strongly suggested that the helicity for mono and bimetallic structures is not the same.

Accordingly with CD spectra, significant changes were also evident in ^{1}H and ^{13}C NMR chemical shifts. A representative example is shown in Figure 6 for compound (*S*,*S*)-**5**. As it can be seen, the shielding of the ^{1}H-NMR signals corresponding to the aromatic hydrogens in both 1,4-dimethoxyaryl groups (see arrows in Figure 6) as well as the shielding of one of the OMe signals strongly suggested the existence of folded structures. ^{13}C NMR spectra showed variations in the chemical shifts of the acetylenic carbons due to the coordination to Ag^I. Accordingly, the NMR signals of ligands (*S*,*S*)-**3** and (*S*,*S*)-**6** are quite complex in the presence of less than 3 equiv of Ag^I. Probably, at such concentrations (0.01 M) the signals were due to a mixture of mono-and polymetallic complexes.
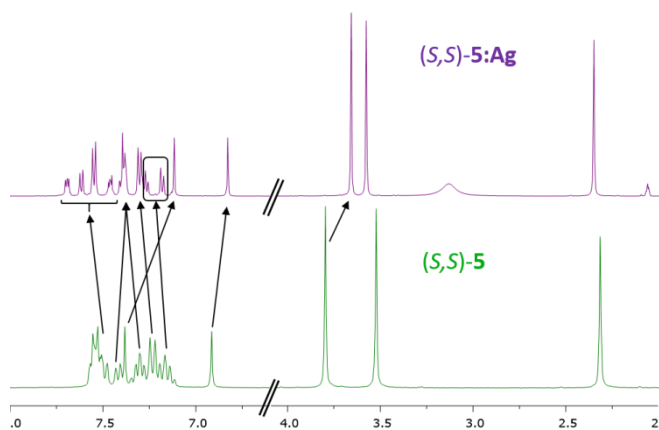
Figure 6. Representative ^{1}H-NMR spectra of compounds (S,S,M)-**5** and (S,S,P)-**5**:**Ag**.

CPL and VCD studies. Owing to the problems encountered in the photochemical stability of compounds (S,S)-**4** to (S,S)-**8**, reliable CPL studies were not satisfactory, so we limited our study to compounds (S,S)-**1** to (S,S)-**3**. Before complexation with Ag^I cation, o-OPEs(S,S)-**1** and (S,S)-**2** were shown to be modest CPL active compounds. After Ag^I addition, their corresponding g_{lum} factor increased from roughly 3×10^{-4} to 6×10^{-4}.
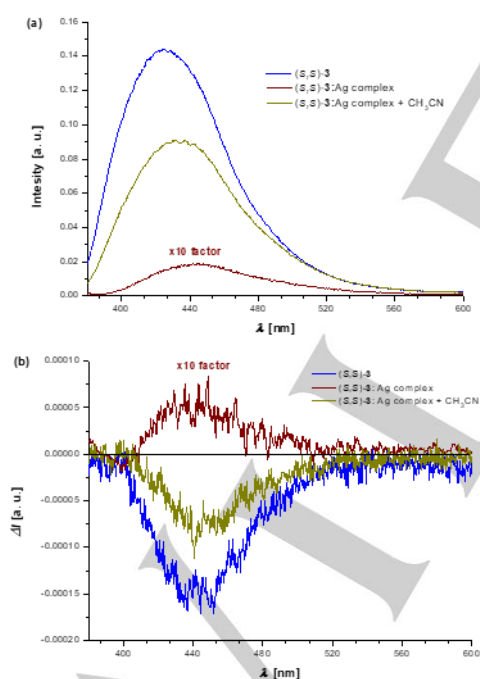

Figure 7. (a) Fluorescence and (b) CPL spectra of compound (S,S)-**3** in CH$_2$Cl$_2$ solutions in absence of Ag^I (blue line), in the presence of an excess of Ag^I (burgundy line, signal has been multiplied by 10 to show it in the graph) and after CH$_3$CN addition (green line)

Compound (S,S)-**3** was also a CPL active derivative with a better g_{lum} value around 1×10^{-3}. This value is similar to the g_{abs} previously obtained for that compound (see SI), showing that chirality is retained in the excited state.[43] Remarkably, in the presence of an excess of Ag^I cation[44] the CPL signal of (S,S)-**3** is inverted (Figure 7b), with a g_{lum} value of 5×10^{-3}. This is a significant value for a small organic-based monomolecular emitter, even though the fluorescence is quenched by Ag. Moreover, the initial signal can be recovered by addition of CH$_3$CN and therefore this homochiral o-OPE can be considered a new class of CPL switch based on a folding process with interesting g_{lum} values.
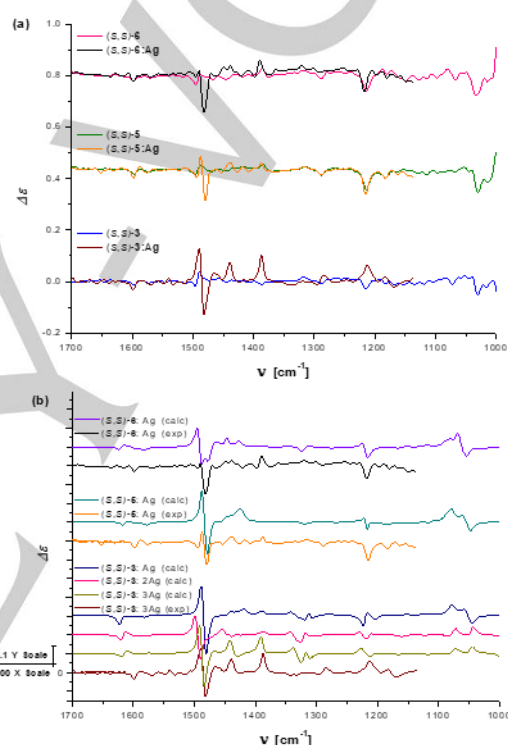

Figure 8. (a) Experimental VCD spectra of compounds (S,S)-**3**, (S,S)-**5** and (S,S)-**6** in absence and presence of Ag^I salt. (b) Comparison of experimental and calculated spectra of Ag^I complexes of compounds (S,S)-**3**, (S,S)-**5** and (S,S)-**6**. In all graphs an offset was employed in Y-axis scales.

On the other hand, VCD is very useful for conformational analysis, due to the fact that vibrational chiroptical response can reflect local differences and may be heavily dependent on hindered torsions.[45] Therefore, VCD gives relevant structural information about the sample in solution, which in many cases cannot be inferred by other spectroscopic techniques. [46]

In the representative studied cases (S,S)-**3**, (S,S)-**5**, and (S,S)-**6**,[47] the corresponding VCD spectra should be sensitive to the *open* and *compact* spatial disposition of the p-tolyl moieties of the sulfoxides. This fact was relevant to understand the behavior of the ligands in solution. It is also worth noting the observed inversion of some signals in the presence of Ag^I, which could be

explained considering a significant change in the spatial disposition of such p-tolyl groups before and after Ag^I addition. In particular, in the presence of Ag^I a shift and intensification of the band at about 1490 cm^{-1} due to C=C ring stretching vibration (shift from 1492 to 1485 cm^{-1}) was observed in the absorption spectra (for representative examples see Figure S7). In VCD spectra, all samples without Ag^I present a weak doublet at 1494-1487 cm^{-1} (Figure 8a). Upon salt addition, all cases showed a change in this region, presenting an opposite intense doublet 1489-1482 cm^{-1}. However, the higher energy component at 1489 cm^{-1} loses intensity for longer oligomers. Especially relevant was the case of compound (S,S)-**3**, which in the presence of Ag presented additional VCD bands, quite intense and opposite in sign to the bands observed without Ag^I (see bands at ca 1386 cm^{-1} and 1212 cm^{-1}). Interestingly, the sign inversion of the latter bands was not observed in the other cases. These results were pointing out the different disposition of the p-tolyl groups in (S,S)-**3**:**Ag$_3$** complex compared to the other ones. These experimental results represent one of the very scarce examples of VCD switches reported up to date. [48]

Theoretical studies of o-OPE: Ag^I complexes To better understand all these observations, we carried out theoretical calculations for the Ag^I complexes of o-OPE ligands (S,S)-**1** to (S,S)-**8**. For (S,S)-**1,** theoretical calculations revealed that the more favorable situation corresponded to silver coordinated between the alkyne and the OMe (Figure 9), where both -OMe groups are oriented to the Ag$^+$ ion, leading to a highly stabilizing interaction. The system in such a disposition was adopting an anti-conformation. The calculated CD for (S,S)-**1**anti:**Ag** is in fact very similar in shape and sign to that obtained for uncomplexed (S,S)-**1**syn. Therefore, theoretical calculations supported the experimental observation that after Ag^I coordination the CD sign and shape of (S,S)-**1** is retained despite the fact that the syn/anti conformation of the sulfoxides is reversed.

Compound (S,S)-**2** was able to coordinate to Ag^I through different binding groups adopting different conformations of both sulfinyl groups. Nevertheless, as in the case of this compound without silver, none of all the calculated structures yielded any simulated VCD and ECD able to fit reasonably well with the experimental ones. This complex is probably too flexible and different structures are equilibrated in the time scale of the experimental measurement.

Theoretical calculations for ligand (S,S)-**3** showed a preference for the coordination of Ag^I cation with the three alkynes in a helical environment, as it was previously observed.[22], [25] Such arrangement forces the coordination with a OMe group, and the configuration of the helix is inverted from (S,S,M) in the absence of Ag^I to the (S,S,P)-**3**:**Ag** complex. This inversion is energetically favored by 10.4 kcal mol^{-1}, and is in agreement with the observed inversion of the Cotton effect in the experimental CD spectra (see Figure 4). Under this new disposition, the sulfoxides offer a perfect environment for accepting new Ag^I cations (up to two). This extra binding event using the sulfoxides arms create a much more rigid structure. The simulated CD for such bi and trimetallic complexes is also in

agreement with the observed chiroptical response of (S,S)-**3** in the presence of an excess of Ag^I. Moreover, experimental and theoretical VCD is in this case in agreement with such spatial disposition of the sulfoxides, confirming the sign and shape of the observed bands. As it can be also seen in Figure 8b, mononuclear silver complex (navy blue line) does not invert the sign of the signal at 1211 cm^{-1} as trinuclear complex does (burgundy line). Bi- (pink line) and trimetallic (dark yellow line) ones show the suitable set of signals with the right signs, strongly supporting the existence of such complexes in solution. Simulation of VCD of free (S,S)-**3** is more difficult taking into account its conformational freedom. Nevertheless simulated VCD of representative conformations of (S,S)-**3** showed a reasonable fitting with the experimental one. [32]
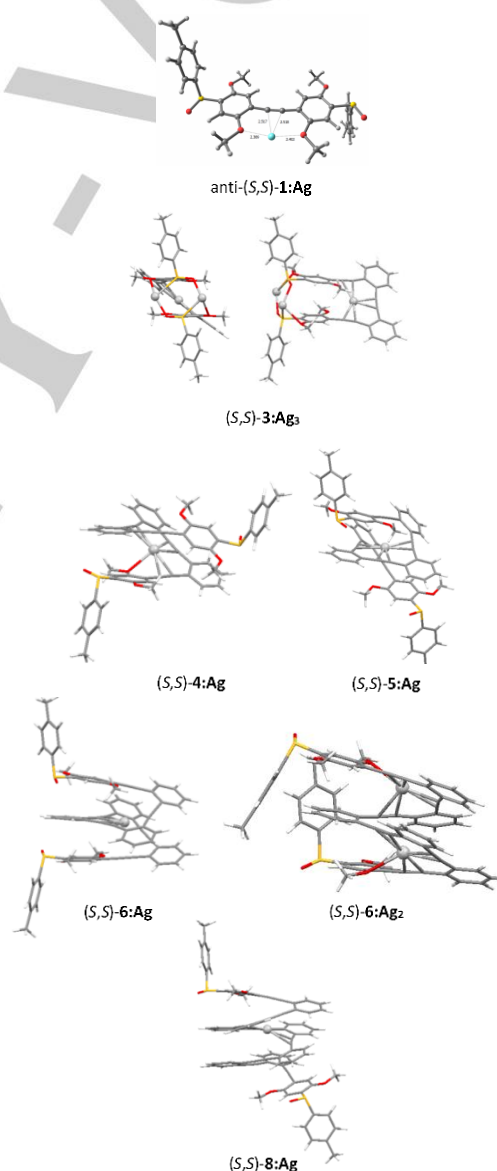

Figure 9. Side views of representative calculated structures for Ag^I complexes (S,S)-**1**:**Ag** to (S,S)-**8**:**Ag**.

The good matching between calculated and experimental VCD for (*S*,*S*)-**5**:Ag confirmed the monometallic nature of this complex and the spatial *open* disposition of the sulfoxide side groups. A more complex situation resulted for *o*-OPE (*S*,*S*)-**6**, which is able to accept two Ag[I] cations. Theoretical calculations showed that for the bimetallic complex, the most favorable structure adopted a *M* helicity resembling the X-ray structure of (*S*,*S*)-**8**:Ag₂ (Figure 5). As a consequence of the *M* helicity, the calculated CD sign of the last peak is negative, which is in agreement with the observed decrease of the CD signal in the presence of an excess of Ag[I]. On the other hand, The simulation of monometallic (*S*,*S*)-**6**:Ag was more complex. The best fit was obtained for the structure in Figure 9, in which the Ag[I] is placed in the middle of the helix and the *p*-tolyl substituents are pointing out in the opposite directions to thus calculated/observed for (*S*,*S*)-**6**:Ag2 and (*S*,*S*)-**8**:Ag2. Calculated ECD and VCD for the monometallic complex is in reasonable agreement with the experimental ones, thus supporting such structure for (*S*,*S*)-**6**:Ag. The small discrepancies observed in the VCD are probably due to the presence of minor amounts of (*S*,*S*)-**6**:Ag₂ in the sample. Accordingly, the calculated VCD of (*S*,*S*)-**6**:Ag₂ is not in accordance with the experimental one but could explain the distortions.

Finally, we could find that ligand (*S*,*S*)-**8** is able to accept the first Ag[I] cation adopting a type-*P* minimum energy conformation with an *open* disposition of the sulfoxide groups, placing the metal in the middle of the helical structure. The complex (*S*,*S*)-**8**:Ag₂ is insoluble and its structure in solution was not calculated.

Conclusions

In summary, we have described the synthesis of a novel family of chiral enantiopure acyclic *o*-OPEs incorporating two sulfinyl groups using Sonogashira coupling between (*S*)-1-ethynyl-2,5-dimethoxy-4-(*p*-tolylsulfinyl)benzene and different halo substituted *o*-phenyleneethynylene moieties as the key step. The study of chiroptical properties evidenced an efficient transfer of chirality from the sterogenic sulfur to the aromatic helically folded system. Upon Ag[I] complexation, the chiroptical responses of these sulfinyl bearing *o*-OPEs underwent changes, being the most significant the helix inversion. The initial *o*-OPEs could be recovered by CH₃CN addition to liberate the Ag[I], showing that these compounds behave like reversible enantiopure silver sensors. Additionally, this switching event could be followed by CD, CPL and VCD. The *o*-OPEs were able to include up to two silver atoms, depending on the length of the oligomer. The resulting metal complexes are a unique class of chiral bimetallic compounds with chirality at the metal, [49] resembling a somehow hybrid conjugated polymer-inorganic coaxial wire, which may be relevant for the chiral-induced spin selectivity effect (CISS effect).

Acknowledgements

[1]   a) L. Zhang, T. Wang, Z. Shen, M. Liu, *Adv. Mater.* **2016**, *28*, 1044-1059; b) L. Zhang, L. Qin, X. Wang, H. Cao, M. Liu, *Adv. Mat.* **2014**, *26*, 6959-6964; c) L. Zhang, T. Wang, Z. Shen, M. Liu, *Adv. Mater.* **2016**, *28*, 1044-1059; d) E. Yashima, N. Ousaka, D. Taura, K. Shimomura, T. Ikai, K. Maeda, *Chem. Rev.* **2016**, *116*, 13752-13990.

[2]   a) K. Maeda, L. Hong, T. Nishihara, Y. Nakanishi, Y. Miyauchi, R. Kitaura, N. Ousaka, E. Yashima, H. Ito, K. Itami, *J. Am. Chem. Soc.* **2016**, *138*, 11001-11008; b) J. S. Kim, H.-G. Jeon, K.-S. Jeong, *Chem. Commun.* **2016**, *52*, 3406-3409; c) M. Obana, T. Fukino, T. Hikima, T. Aida, *J. Am. Chem. Soc.* **2016**, *138*, 9246-9250; d) X. Wei, G. Zhang, Y. Shen, Y. Zhong, R. Liu, N. Yang, F. Y. Al-mkhaizim, M. A. Kline, L. He, M. Li, Z.-L. Lu, Z. Shao, B. Gong, *J. Am. Chem. Soc.* **2016**, *138*, 2749-2754; e) G. W. Collie, R. Bailly, K. Pulka-Ziach, C. M. Lombardo, L. Mauran, N. Taib-Maamar, J. Dessolin, C. D. Mackereth, G. Guichard, *J. Am. Chem. Soc.* **2017**, *139*, 6128-6137.

[3]   a) H.-G. Jeon, J. Y. Jung, P. Kang, M.-G. Choi,K.-S. Jeong, *J. Am. Chem. Soc.* **2016**, *138*, 92-95; b) H. Zhao, S. Sheng, Y. Hong, H. Zeng, *J. Am. Chem. Soc.* **2014**, *136*, 14270-14276; c) J. Kim, H.-G. Jeon, P. Kang, K.-S. Jeong, *Chem. Commun.* **2017**, *53*, 6508-6511.

[4]   a) C. J. Massena, N. B. Wageling, D. A. Decato, E. M. Rodriguez, A. M. Rose, O. B. Berryman, *Angew. Chem. Int. Ed.* **2016**, *55*, 12392-12402; *Angew. Chemie* **2016**, *128*, 12586-12590; b) H.-G. Jeon, H. B. Jang, P. Kang, Y. R. Choi, J. Kim, J. H. Lee, M.-G. Choi, K.-S Jeong, *Org. Lett.* **2016**, *18*, 4404-4407; c) V. R. Naidu, M. C. Kim, J.-M. Suk, H.-J. Kim, M. Lee, E. Sim, K.-S. Jeong, *Org. Lett.* **2008**, *10*, 5373-5376; d) Y. Haketa, Y. Bando, K. Takaishi, M. Uchiyama, A. Muranaka, M. Naito, H. Shibaguchi, T. Kawai, H. Maeda, *Angew. Chem. Int. Ed.* **2012**, *51*, 7967-7971; *Angew. Chemie* **2012**, *124*, 8091-8095; e) Y. Hua, Y. Liu, C.-H. Chen, A. H. Flood, *J. Am. Chem. Soc.* **2013**, *135*, 14401-14412.

[5]   a) J. Shen, C. Ren, H. Zeng, *J. Am. Chem. Soc.* **2017**, *139*, 5387-5396; b) M. Horeau, G. Lautrette, B. Wicher, V. Blot, J. Lebreton, M. Pipelier, D. Dubreuil, Y. Ferrand, I. Huc, *Angew. Chem. Int. Ed.* **2017**, *56*, 6823-6827; *Angew. Chemie* **2017**, *129*, 6927-6931; c) P. Mateus, B. Wicher, Y. Ferrand, I. Huc, *Chem. Commun.* **2017**, *53*, 9300-9303.

[6]   a) J.—L. Hou, X.-B. Shao, G.-J. Chen, Y.-X. Zhou, X.-K. Jiang, Z.-T. Li, *J. Am. Chem. Soc.* **2004**, *126*, 12386-12394; b) T. Nishinaga, A. Tanatani, K. Oh, J. S. Moore, *J. Am. Chem. Soc.* **2002**, *124*, 5934-5935; c) G. Lautrette, B. Wicher, B. Ñauffmann, Y. Ferrand, I. Huc, I. *J. Am. Chem. Soc.* **2016**, *138*, 10314-10322; d) N. Chandramouli, Y. Ferrand, G. Lautrette, B. Auffmann, C. D. Mackereth, M. Laguerre, D. Dubreuil, I. Huc, *Nat. Chem.* **2015**, *7*, 334-341.

[7]   a) E. M. Sanchez-Carnerero, A. R. Agarrabeitia, F. Moreno, B. L. Maroto, G. Muller, M. J. Ortiz, S. de la Moya, S. *Chem. Eur. J.* **2015**, *21*, 13488-13500; b) E. Castiglioni, S. Abbate, F. Lebon, G. Longhi, *Methods Appl. Fluoresc.* **2014**, *2*, 024006; c) N. Berova, L. Di Bari, G. Pescitelli, *Chem. Soc. Rev.* **2007**, *36*, 914-931; d) J. Kumar, T. Nakashima, T. Kawai, *J. Phys. Chem. Lett.* **2015**, *6*, 3445-3452; e) G. Longhi, E. Castiglioni, J. Koshoubu, G. Mazzeo, S. Abbate,*Chirality* **2016**, *28*, 696-707.

[8]   For selected recent references: a) C. Shen, M. Srebro-Hooper. M. Jean, N. Vanthuyne, L. Toupet, J. A. G. Wilians, A. R. Torres, A. J. Riives, G. Muller, J. Autschbach, J. Crassous, J. *Chem. Eur. J.* **2017**, *23*, 407-418; b) J. F. Kögel, S. Kusada, R. Sakamoto, T. Iwashima, M. Tsuchiya,

R. Toyoda, R. Matsuoka, T. Tsukamoto, J. Yuasa, Y. Kitagawa, T. Kawai, H. Nishihara, *Angew. Chem. Int. Ed.* **2016**, *55*, 1377-1381; *Angew. Chemie* **2016**, *128*, 1399-1403; c) S. Feuillastre, M. Pauton, L. Gao, A. Desmarchelier, A. J. Riives, D. Prim, D. Tondelier, B. Geffroy, G. Muller, G. Clavier, G. Pieters, *J. Am. Chem. Soc.* **2016**, *138*, 3990-3993; d) J.-B. Xiong, H.-T. Feng, J.-P. Sun, W.-Z. Xie, D. Yang, M. Liu, Y.-S. Zheng, *J. Am. Chem. Soc.* **2016**, *138*, 11469-11472; e) N. Hellou, M. Srebro-Hooper, L. Favereau, F. Zinna, E. Caytan, L. Toupet, V. Dorcet, M. Jean, N. Vanthuyne, J. A. G. Williams, L. Di Bari, J. Autschbach, J. Crassous, *Angew. Chem. Int. Ed.* **2017**, *56*, 8236-8239; *Angew. Chemie* **2017**,*129*, 8348-8351; f) T. R. Schulte, J. J. Holstein, L. Krause, R. Michel, D. Stalke, E. Sakuda, K. Umakoxhi, G. Longhi, S. Abbate, G. H. Clever, *J. Am. Chem. Soc.* **2017**, *139*, 6863-6866; g) M. Gon, Y. Morisaki, Y. Chujo*, Chem. Commun.* **2017**, 8304-8307.

[9]   J.-C. G. Bünzli, C. Piguet, *Chem. Soc. Rev.* **2005**, *34*, 1048-1077.

[10]   Circularly polarized LEDS has been reported: a) E. Peeters, P. T. Christiaans, R. A. J. Janssen, H. F. M. Schoo, H. P. J. M. Dekkers, E. W. Meijer, *J. Am. Chem. Soc.* **1997**, *119*, 9909-9910; b) A. Satrijo, S. C. J. Meskers, T. M. Swager, *J. Am. Chem. Soc.* **2006**, *128*, 9030-9031; c) J. Liu, H. Su, L. Meng, Y. Zhao, C. Deng, J. C. ng, P. Lu, M. Faisal, J. W. Y. Lam, X. Huang, H. Wu, K. S. Wong, B. Z. Tang, *Chem. Sci.* **2012**, *3*, 2737-2747; d) B. A. San Jose, J. Yan, K. Akagi, *Angew. Chem. Int. Ed.* **2014**, *53*, 10641-10644; *Angew. Chemie* **2014***, 126*, 10817-10820; e) A. T. Frawley, R. Pal, D. Parker, *Chem. Commun.* **2016**, *52*, 13349-13352; f) F. Zinna, U. Giovanella, L. Di Bari, *Adv. Mater.* **2015**, *27*, 1719-1795; g) . R. Brandt, X. Wang, Y. Yang, A. J. Campbell, M. J. Fuchter, *J. Am. Chem. Soc.* **2016**, *138*, 9743-9746.

[11]   a) H. Maeda, Y. Bando, K. Shimomura, I. Yamada, M. Naito, K. Nobusawa, H. Tsumatori, T. Kawai, *J. Am. Chem. Soc.* **2011**, *133*, 9266-9269; b) H. Maeda, Y. Bando, *Pure Appl. Chem.* **2013**, *85*, 1919-2004; c) N. Saleh, B. Moore, M. Srebro, N. Vanthuyne, L. Toupet, J. A. G. Williams, C. Roussel, K. K. Deol, G. Muller, J. Autschbach, J. Crassous, *J. Chem. Eur. J.* **2015**, *21*, 1673-1681; d) Y. Hashimoto, T. Nakashima, D Shimizu, T. Kawai, *Chem. Commun.* **2016**, *52*, 5171-5174; e) H. Isla, M. Srbo-Hooper, M. Jean, N. Vanthuyne, T. Roisnel, J. L. Lunkley, G. Muller, J. A. G. Willians, J. Autschbach, J. Crassous, *Chem. Commun.* **2016**, *35*, 5932-5935.

[12]   a) P. C. Mondal, C. Fontanesi, D. H. Waldeck, R. Naaman, *Acc. Chem. Res.* **2016**, *49*, 2560-2568; b) V. Kiran, S. P. Mathew, S. P. Cohen, I. H. Delgado, J. Lacour, R. Naaman, *Adv. Matter.* **2016**, *28*, 1957-1962; c) R. Naaman, D. H. Waldeck, *Annu. Rev. Phys. Chem.* **2015**, *66*, 263-281.

[13]   C. L. Vonnegut, B. W. Tresca, D. W. Johnson, M. M. Haley, *Chem. Asian J.* **2015**, *10*, 522-535.

[14]   a) R. B. Prince, J. G. Saven, P. G. Wolynes, J. S. Moore, *J. Am. Chem. Soc.* **1999**, *121*, 3114-3121; b) S. Lahiri, J. L. Thompson, J. S. Moore, *J. Am. Chem. Soc.* **2000**, *122*, 11315-11319; c) S. Y.-L. Leung, A. Y.-Y. Tam, C.-H Tao, H. S. Chow, V. W.-W. Yam, *J. Am. Chem. Soc.* **2012**, *134*, 1047-1056.

[15]   a) T. V. Jones, M. M. Slutsky, R. Laos, T. F. A. de Greef, G. N. Tew, *J. Am. Chem. Soc.* **2005**, *127*, 17235-17240; b) M. M. Slutsky, T. V. Jones, G. N. Tew, *J. Org. Chem.* **2007**, *72*, 342-347; c) M.-X. Zhu, W. Lu, N. Zhu, C.-M. Che, *Chem., Eur. J.* **2008**, *14*, 9736-9746; d) Y.-T. Shen, N. Zhu, X.-M. Zhang, K. Deng, W. Feng, Q. Yan, S. Lei, D. Zhao, Q.-D. Zeng, C. Wang, *Chem. Eur. J.* **2011***, 17*, 7061-7068.

[16]   B.-B. Ni, Q. Yan, Y. Ma, D. Zhao, *Coor. Chem. Rev.* **2010**, *254*, 954-971.

[17]   K. Matsuda, M. T. Stone, J. S. Moore, *J. Am. Chem. Soc.* **2002**, *124*, 11836-11837.

[18]   R. F. Kelly, B. Rybtchinski, M. T. Stone, J. S. Moore, M. R. Wasielewski, *J. Am. Chem. Soc.* **2007**, *129*, 4114-4115.

[19]   a) L. Brunsveld, E. W. Meijer, R. B. Prince, J. S. Moore, *J. Am. Chem. Soc.* **2001**, *123*, 7978-7984; b) M. A. B. Block, S. Hetch, *Macromolecules* **2008**, *41*, 3219-3227; c) T. V. Jones, R. A. Blatchly, G. N. Tew, *Org. Lett.* **2003**, *5*, 3297-3299; d) M. Banno, T. Yamaguchi, K.

Nagai, C. Kaiser, S. Hecht, E. Yashida, *J. Am. Chem. Soc.* **2012**, *134*, 8718-8728.

[20]   a) M. S. Gin, T. Yokozawa, R. B. Prince, J. S. Moore, *J. Am. Chem. Soc.* **1999**, *121*, 2643-2644; b) M. T. Stone, J. M. Fox, J. S. Moore, *Org. Lett.* **2004**, *6*, 3317-3320; c) N. Saito, R. Terakawa, M. Shigeno, R. Amemiya, M. Yamaguchi, *J. Org. Chem.* **2011**, *76*, 4841.4858.

[21]   a) A. Tanatani, M. J. Mio, J. S. Moore, *J. Am. Chem. Soc.* **2001**, *123*, 1792-1793; b) A. Tanatani, T. S. Hughes, J. S. Moore,*Angew. Chem. Int. Ed.* **2002**, *41*, 325-328; *Angew. Chemie* **2002**, *114*, 335-338.

[22]   A. Martín-Lasanta, L. Álvarez de Cienfuegos, A. Johnson, D. Miguel, A. J. Mota, A. Orte, M. J. Ruedas-Rama, M. Ribagorda, D. J. Cárdenas, M. C. Carreño, A. M. Echavarren, Cuerva, *Chem. Sci.* **2014**, *5*, 4582-4591.

[23]   *Metallofoldamers. Supramolecular Architectures from Helicates to Biomimetics*; G. Maayan, M. Albrecht, Eds; Wiley-VCH: Weinheim, Germany, **2013**.

[24]   N. Fuentes, A. Martin-Lasanta, L. Alvarez de Cienfuegos, R. Robles, D. Choquesillo-Lazarte, J. M. Garcia-Ruiz, L. Martinez-Fernandez, I. Corral, M. Ribagorda, A. J. Mota, D. J. Cardenas, M. C. Carreño, J. M. Cuerva, *Angew. Chem. Int. Ed.* **2012**, *51*, 13036-13040; *Angew. Chemie* **2012**, *124*, 13213-13217.

[25]   S. P. Morcillo, D. Miguel, L. Álvarez de Cienfuegos, J. Justicia, S. Abbate, E. Castiglioni, C. Bour, M. Ribagorda, D. J. Cárdenas, J. M. Paredes, L. Crovetto, D. Choquesillo-Lazarte, A. J. Mota, M. C. Carreño, G. Longhi, J. M. Cuerva, *Chem. Sci.* **2016**, *7*, 5663-5670.

[26]   a) M. C. Carreño, I. García, M. Ribagorda, E. Merino, I. Nuñez, S. Pieraccini, G. P. Spada, *J. Am. Chem. Soc.* **2007**, *129*, 7089-7100; b) M. C. Carreño, I. García, M. Ribagorda, E. Merino, S. Pieraccini, G. P. Spada, *Org. Lett.* **2005**, *7*, 2869-3406.

[27]   a) G. Hernandez-Torres, M. C. Carreño, A. Urbano, F. Colobert, *Chem., Eur. J.* **2011**, *17*, 1283-1293; b) A. M. Del Hoyo, A. Urbano, M. C. Carreño, *Org. Lett.* **2016**, *18*, 20-23. b) I. Nuñez, E. Merino, M. Lecea, S. Pieraccini, G. P. Spada, C. Rosini, G. Mazzeo, M. Ribagorda, M. C. Carreño, *Chem. Eur. J.* **2013**, *19*, 3397.

[28]   [28]   Model compounds lacking of sulfoxide group and presenting *S*-(+)-citronellyl ether instead of methyl ether groups were also prepared for comparison. Nevertheless, no significant chiral folding could be observed, pointing out the relevance of homochiral sulfoxides as chiral inducers.

[29]   a) H. Sato, T. Yajima, A. Yamagishi, *Chirality* **2015**, *27*, 659-666; b) B. Nieto-Ortega, V. J. Nebot, J. F. Miravet, B. Escuder, J. T. López Navarrete, J. Casado, F. J. Ramirez, *J. Phys. Chem. Lett.* **2012**, *3*, 2120-2124; c) J. Li, M. Du, Z. Zhao, H. Liu, *Macromolecules* **2016**, *49*, 445-454; d) S. Domingos, H. J. Sanders, F. Hartl, W. J. Buma, S. Woutersen, *Angew. Chem. Int. Ed.* **2014**, *53*, 14042-14045; *Angew. Chemie* **2014**, *126*, 14266-14269; e) G. Mazzeo, S. Abbate, G. Longhi, E. Castiglioni, S. E. Boiadjiev, D. A. Lightner *J. Phys. Chem. B* **2016**, *120*, 2380-2387.

[30]   C. Shen, G. Loas, M. Srebo-Hooper, N. Vanthuyne, L. Toupet, O. Cador, F. Paul, J. T. López Navarrete, F. J. Ramirez, B. Nieto-Ortega, J. Casado, J. Autschbach, M. Vallet, J. Crassous, *Angew. Chem. Int. Ed.* **2016**, *55*, 8062-8066; *Angew. Chemie* **2016**, *128*, 8194-8198.

[31]   Enantiomer (*R,R*)-**3** was also synthesized to illustrate the versatility of the sulfinyl group to induce opposite chiroptical responses. See Supporting Information.

[32]   See supporting information for details.

[33]   D. J. Hill, J. S. Moore, *Proc. Nat. Acad. Sci.* **2002**, *99*, 5053-5057.

[34]   Any other possible competing conformations are higher in energy so we have considered them as negligible in the conformational equilibrium although some among them are thermally accessible at a given moment.

[35]   a) Y. Nakai, T. Mori, Y. Inoue, *J. Phys. Chem. A* **2013**, *117*, 83−89; b) F. Furche, R. Ahlrichs, C. Wachsmann, E. Weber, A. Sobanski, F. Vögtle, S. Grimme, *J. Am. Chem. Soc.* **2000**, *122*, 1717-1724.

[36]   Consequently, enantiomer (*R,R*)-**3** showed exactly the opposite chiroptical response than the (*S,S*)-**3**.

[37] G. Maier, C. Lautz, *Eur. J. Org. Chem.* **1998**, 769-776.

[38] T. Bally, S. Masamune, *Tetrahedron* **1980**, *36*, 343-370.

[39] V. R. Sandel, H. H. Freedman, *J. Am. Chem. Soc.* **1968**, *90*, 2059-2069.

[40] K. Matsui, M. Fushimi, Y. Sagawa, K. Itami, *Org. Lett.* **2016**, *18*, 5352-5355.

[41] The fitting was carried out with DynaFit program (v. 4.06019). See also: a) F. Ulatowski, K. Dabrowa, T. Balakier, J. Jurczak, *J. Org. Chem.* **2016**, *81*, 1746-1756; b) D. B. Hibbert, P. Thordarson,*Chem. Commun.* **2016**, *52*, 12792-12805.

[42] Ligands (*S*, *S*)-**5** and (*S*, *S*)-**6** suffer from some photodegradation (See Figure S11). Nevertheless control experiments showed that the observed changes in the corresponding CD spectra are due to real interactions with Ag^I cation.

[43] Homochiral sulfoxides suffer from racemisation under intense irradiation. During the CPL acquisition we observed some degradation of the chiroptical signal: C. Aurisicchio, E. Baciocchi, M. F. Generi, O. Lanzalunga, *Org. Lett.* **2007**, *9*, 1939-1942.

[44] It has been recently reported that the coordination of chiral aryl sulfoxides to metals avoids the epimerization/racemization process: R. S. Kathayat, L. Yang, T. Sattasathuchana, L. Zopp, K. K. Baldridge, A. Linden, N. S. Finney, *J. Am. Chem. Soc.* **2016**, *138*, 15889-15995.

[45] a) V. Setnicka, M. Urbanova, P. Bour, V. Kral, K. Volka, *J. Phys. Chem. A* **2001**, *105*, 8931−8938; b) S. Abbate, L. F. Burgi, E. Castiglioni, F. Lebon, G. Longhi, F. Toscano, S. Caccamese, *Chirality* **2009**, *21*, 436−441; c) M. Passarello, S. Abbate, G. Longhi, S. Lepri, R. Ruzziconi, V. P. Nicu, *J. Phys. Chem. A* **2014**, *118*, 4339−4350.

[46] a) L. A. Nafie, "*Vibrational Optical Activity, Principles and applications*", John Wiley&Sons Ltd. **2011**, NY; b) P. L. Polavarapu, "*Chiroptical Spectroscopy, Fundamentals and Applications*", CRC Press, Taylor and Francis Group, **2017**, BocaRaton, FL; c) T. L. Buffeteau, L. Ducasse, L. Poniman, N. Delsuc, I. Huc, *Chem. Commun.* **2006**, *25*, 2714-2714; d) M. Losada, H. Tran, Y. Xu, *Phys. Chem. Chem. Phys.* **2007**, 9, 3127-3135; e) G. Longhi, S. Abbate, R. Gangemi, E. Giorgio, C. Rosini, *J. Phys. Chem. A* **2007**, 110, 4958-4968.

[47] Compound (*S*,*S*)-**8** was also studied but the insolubility of the complex resulted in spectra with overall minor intensities. See Supporting Information.

[48] C. H. Pollok, T. Riesebeck, C. Merten, *Angew. Chem. Int. Ed.* **2017**, *56*, 1925-1928; *Angew. Chemie* **2017**, *129*, 1952-1955.

[49] J. Crassous*, Chem. Commun.* **2012**, *48*, 9684-9692.

WILEY-VCH

Entry for the Table of Contents

Layout 1:

FULL PAPER

A new family of homochiral silver complexes based on carbophilic interactions with *ortho*-phenyleneethynylene (*o*-OPE) scaffolds containing up to two silver atoms is described
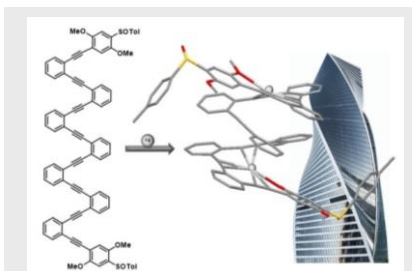
S. Resa, D. Miguel, S. Guisán-Ceinos, G. Mazzeo, D. Choquesillo-Lazarte, S. Abbate, L. Crovetto, D. J. Cárdenas, M. C. Carreño, M. Ribagorda, G. Longhi, A. J. Mota, L. Álvarez de Cienfuegos,[*] and J. M. Cuerva,[*]

Page No. – Page No.

Sulfoxide-Induced Homochiral Folding of *o*-OPEs by Ag^I Templating: Structure and Chiroptical Properties