Chirality induction in confined chromonics: A case study

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ABSTRACT

Chromonic liquid crystals are a sub-category of lyotropic liquid crystalline materials whose self-assembling mechanisms in complex supramolecular structures are still not fully understood. Chirality can be induced in chromonics using chiral aminoacids with alternating results. Understanding the key factors that lead to maximize this phenomenon is important for the design of novel materials able to self-assemble in chiral macroscopic structures with tailored optical properties, as selective reflection.

In this work, we present a comparative study involving a not commercial chromonic, a synthesized metal containing chromonic compound $[(Bpy-OH)_2Ag][CH_3COO]H_2O$, and two model chromonics that behave in different manner with respect to chiral induction. Spherical confinement provides a quick way to qualitatively evaluate the elasticity properties in new materials. Also, optical textures of the metal compound, after doping the material with a chiral moiety, show that its chiral phase is more similar to one of the two model chromonics. This observation points to a role played by the flexibility of the molecular structure that it's reflected into the resistance of the columnar aggregates to undergo a twist. This last observation can be useful when selecting the most suitable building blocks in designing new materials.

1. Introduction

Liquid crystals (LCs) are soft materials that usually possess an orientational order and in some cases a positional one. They can either be thermotropic or lyotropic. LC molecules are called mesogens and the phases they form are named mesophases [1–4]. Few examples of new calamitic liquid-crystalline materials with flexible hydrophilic chains, have been reported exhibiting both, thermotropic and lyotropic behavior [5]. Thermotropic mesogens, in general, have the common structural feature to be anisotropic in shape (rod-like or disk-like), giving rise to anisotropic physical properties (optical, electrical, and magnetic properties). The different mesophases are observed as a function of the temperature. Lyotropic chromonic liquid crystals (LCLCs) are usually referred to as the lyotropic counterparts of the thermotropic discotics. Lyotropic chromonic mesophases are displayed by numerous drugs, dyes and nucleic acids when dispersed in a solvent: molecules stack mainly by π-π interactions and form cylinders which in turn give rise to mesophases [6]. In this case the different mesophases are

observed as a function of both mesogens concentration in a solvent and temperature. The mechanism of self-assembly is known as isodesmic, i.e. no critical micelle concentration is reported as for common lyotropics. Two main chromonic phases have been clearly identified, the nematic (N) and hexagonal (M) phases. The N phase consists of nematic arrays of columns with no positional ordering; the M phase is a hexagonal columnar phase that appears at higher concentrations.

Almost universally, thermotropic discotic liquid crystals adopt a homeotropic alignment at the solid-to-liquid crystal interface and a planar orientation at the air-to-liquid crystal interface [7]. As a result, columnar phases that align in a homeotropic manner when sandwiched between glass slides or between ITO electrodes, align in a planar fashion in thin 'open-to-the-air' films. On the contrary the alignment of the lyotropic counterparts is not straightforward.

Sunset Yellow (SSY) and di-sodium cromoglycate (DSCG) are two commercially available chromonic liquid crystals (Fig. 1). SSY is a dye used in food industry. At room temperature, SSY presents itself as a red powder, which can be easily solubilized in water and displays a N phase

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at concentration above 28 % wt in water [8].

Information on the supramolecular assembly and stacking energy between the molecules in this compound has been inferred by statistical mechanics [9], absorption measurements studies and X-ray diffraction [10]. The powder diffraction X-ray analysis performed on SSY at various concentrations from the isotropic, to the N and M phases, allowed to suggest a head-to tail dimer stacks organization of SSY molecules. In fact, in Ref. [11], the authors observed off-axis diffuse X-ray reflections in all three phases (isotropic, N and M) hence excluding inter column correlations within the mesophases. A stacking model of molecules organized in a "head-to-tail" fashion, alternating rotated by π radians about the column axis, and producing a helical structure characterized by a short pitch, has been proposed. Confirmation of a preference for head-to-tail stacking and antiparallel dipole order in dilute solutions to form stacked aggregates is reported in [12].

SSY is well studied and its elastic constants [13] and its alignment in planar geometries [14] are well known. When confined in a planar cell, SSY tends to align in homeotropic configuration, like thermotropic discotic materials, and depending on polymer/surface treatment used, the final homeotropic configuration can be reached just after filling the cell or by stripes formation. In fact, for example, stripes can be observed when SSY 30 % wt is confined among two glasses covered with a hydrophobic polymer as, for example, polydimethylsiloxane (PDMS) (Fig. 2b). The stripes, whose dimension is related to the cell thickness, evolve toward homeotropic anchoring as checked either by conoscopy measurements and pressing the cell.

Similar examples are reported in literature for SSY confined in cylindrical capillaries covered with parylene [15] and in cells made of glasses covered with APTES, (3-aminopropyl)triethoxysilane [16]. In all the references the stripes are metastable and in time they evolve towards homeotropic alignment.

Regarding the anti-asthmatic drug and chromonic liquid crystal DSCG (Fig. 1b), its white powder is highly hygroscopic. Cox *et al.* reported back in 1971 [17] on a systematic crystallographic study of DSCG powder at different humidity conditions and compared their observations with the crystallographic data of DSCG single crystal. In 1974, Hamodrakas *et al.* reported the X Ray single crystal molecular structure of DSCG heptahydrate, showing the non-coplanarity of the chromone (benzopyrone) rings and the occurrence of water-filled 'channels' in the crystal lattice [18]. The core of the molecule is supposed to have a certain degree of flexibility as hypothesized in Ref. [19].

Several models have been proposed for DSCG assembly: stack, [20,21], chimney-like [22] and threadlike assemblies [23]. The reference [19] confirmed the stacked model thanks to measurements of nematic and hexagonal aligned phases. Concerning the number of molecules in the columns, some authors [21] deduce that this value is between 1 and 2 and others consider just one molecules for columns [19]. The former result could explain the larger flexibility of DSCG with respect to SSY and [(Bpy-OH)$_2$Ag][CH$_3$COO]H$_2$O whose columns are formed just by one flat molecule.

Consequently, together with the single plane rectangular frame, commonly used to represent DSCG columnar assembly, another possible view could be the two twisted brick frames linked by a spring, this latter
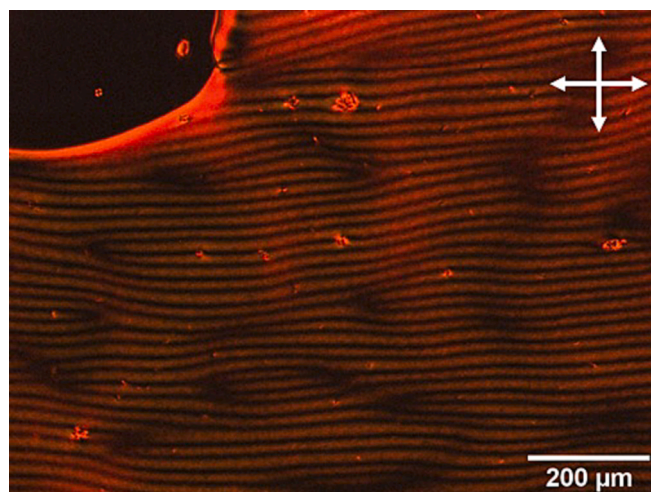

Fig. 2. SSY confined between two rubbed PDMS covered glasses.

representing the flexibility of the alkoxy linker chain, as shown in Fig. 3.

The physical properties of this compound are well known [13] and its behavior in a planar cell is different from the one of SSY. Indeed, DSCG is easily aligned in a planar configuration but hardly aligned homeotropically. Few examples of homeotropic alignment have been reported and were observed only when the nematic phase was confined between two glasses covered with materials with a very low surface energy [14,24]. This difficulty most probably arises indeed from the non-coplanarity of the two chromone moieties as depicted in Fig. 3a.

Together with full organic LCLC molecules, also metal complexes have shown their advantages in supramolecular ordering [25,26]. Metal complexes have a broad range of oxidation states and coordination geometries offering new opportunities for the design of original LCLC mesophases, rendering them advantageous over their organic counterparts [11,27,28]. Indeed, metal complexes may offer different functionalities, modulated by the type of coordinated ligand, as well as intriguing spectroscopic, catalytic and redox properties. Several metal complexes displaying chromonic-like behavior have been reported so far [29–31].

In particular, coordinating Ag(I) with suitable hydrophilic functionalized bipyridine ligands, an unconventional LCLC of chemical formula [(Bpy-OH)$_2$Ag][CH$_3$COO]H$_2$O (where Bpy-OH stands for 4,4′-bis (hydroxymethyl)-2,2′-bipyridine), was recently reported [31]. This complex, herein named AgC, spontaneously self-assembles in water into LCLC phases, characterized by a phase diagram showing that at room temperature the complex has a N region at a concentration ranging from 15 % to 50 % wt, with a transition directly to the isotropic phase when the temperature is increased.

Although this complex seems achiral, the twisting of the two surrounding bipy ligands in a strong distorted square planar geometry, as observed by single crystal X-ray crystal structure analysis [31], induces a geometric chirality around the metal centre (Fig. 4). Hence, a racemic mixture of the two geometrical isomers is obtained and, as expected, the
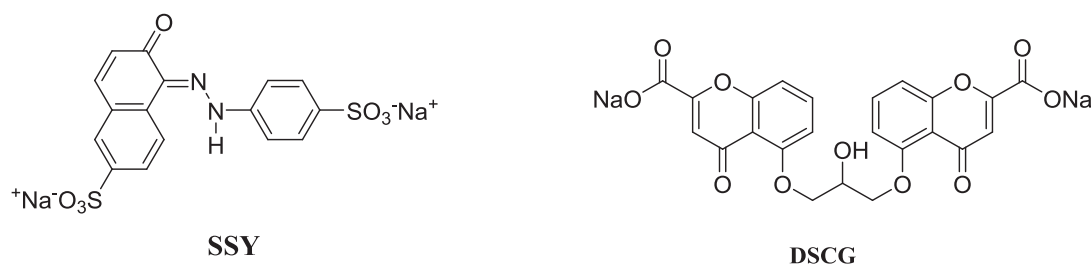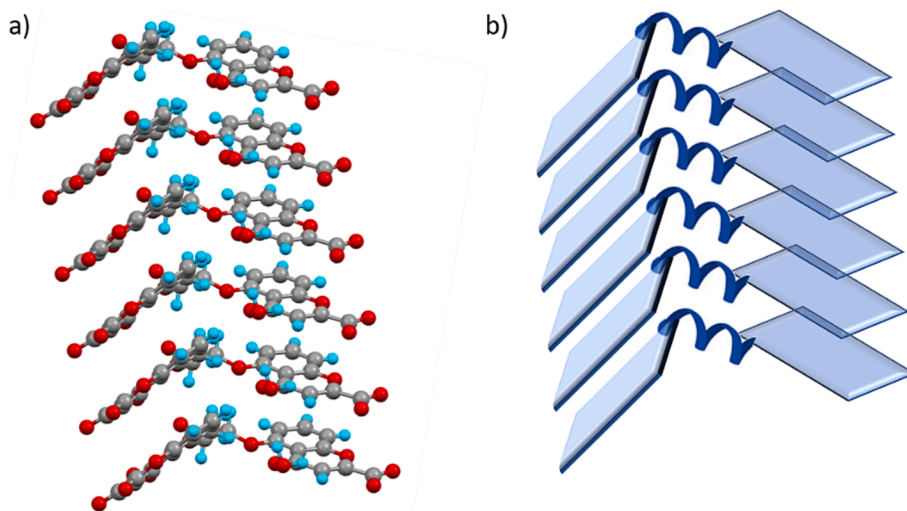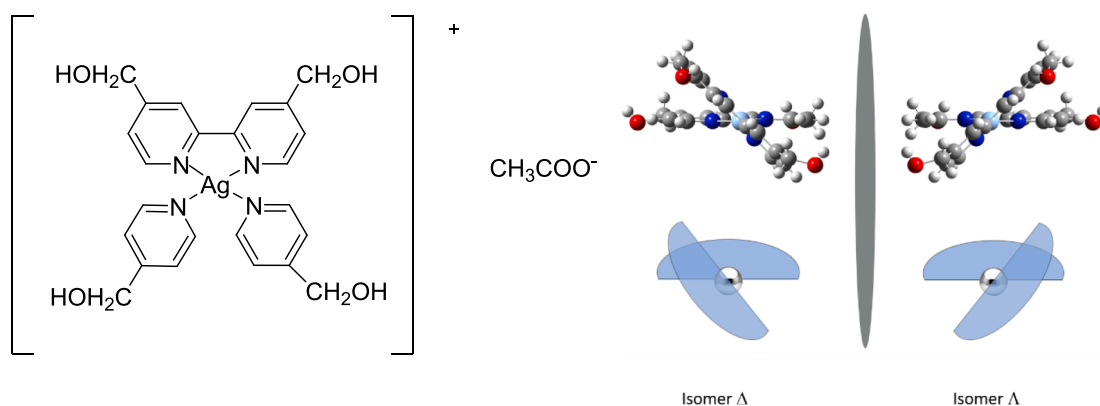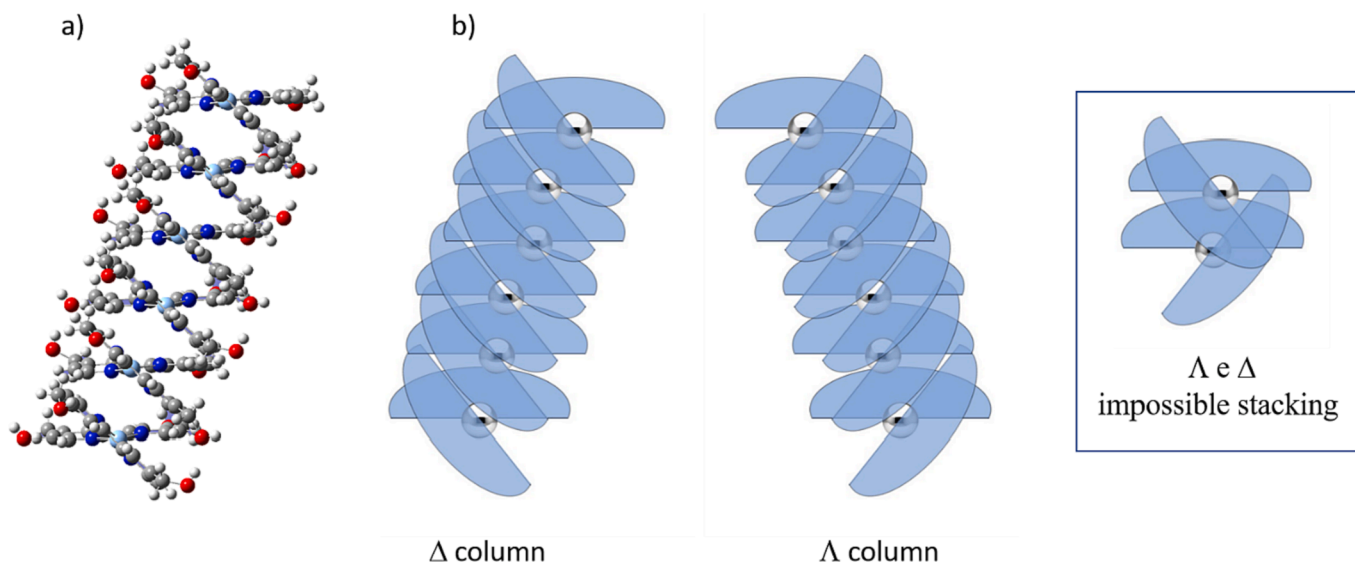

SSY

DSCG

Fig. 1. Molecular structure of SSY (left) and DSCG (right).

Fig. 3. (a) Crystal packing of six DSCG molecules along the a axis of the crystal cell, from the published reported structure of disodium glycosylate heptahydrate [18]. (b) Proposed representation of the columnar assembly of DSCG in the mesophase.

Fig. 4. Optical isomers of [(Bpy-OH)$_2$Ag][CH$_3$COO]H$_2$O complex (AgC).

Fig. 5. (a) Column of six AgC molecules extracted from its reported crystal structure along the c axis [30,31], (b) proposed model stack of chiral columns in the mesophase. In inset, a scheme showing the impossibility of efficient stacking between the two geometric chiral isomers.

circular dichroism (CD) spectrum of the pure complex dissolved in methanol does not show any specific dichroic signal (Fig. S1).

Noteworthy, the AgC nematic phase (20 % wt in water), once sandwiched between two hydrophobic polymer covered glasses as Cytop [31], tends initially to align in a planar texture, but this configuration is metastable. After a while, stripes develop and the LCLC final homeotropic configuration is obtained. In the mesophase, AgC molecules probably self-assemble to form a racemic mixture of homochiral columns, since the peculiar geometry around the metal centre precludes the possibility of two geometric isomers to efficiently stack (Fig. 5).

Here, we present our investigation on the possibility to obtain reflection symmetry breaking in the nematic phase of newly synthesized chromonic material, AgC, when confined in a spherical geometry as well as on the possibility to induce chirality using suitable dopants. We compare the results to what is observed for SSY and DSCG in the same conditions [32,33]. The aim is to understand the role of chiral moieties in the formation of the chiral phase as well as to identify a common feature that could play a fundamental role in chirality amplification from the molecular to the macroscale. Measurements point to a role played by the molecular flexibility.

These results are important in the perspective of building new chromonic materials in which chirality can be amplified and tuned and that can be used for applications in the field of optics and photonics.

2. Results and discussion

Spherical confinement is obtained by mixing a chromonic with an immiscible matrix and the resulting blend is mechanically stirred to induce the final emulsion. Spherical confinement, indeed, is a method that allows to detect chirality even when usual methods such as Cano wedge or homeotropic cells are not allowing the observation of chiral features [34,35]. Among the matrices, we concentrated on polydimethylsiloxane (PDMS) since it produces an homeotropic alignment at the microspheres interface and this boundary condition is more suitable to detect chirality [32].

In Fig. 6 microspheres containing pure SSY in PDMS matrix are reported showing either a radial twisted texture or a distortion, predominantly located in the inner part of the sphere. We have clearly observed chiral textures doping SSY with *trans*-hydroxy-L-proline (Trans-Hyp) (molar ratio SSY:Trans-Hyp is 1:3) as shown in Fig. 6b. In fact, a periodic structure similar to the Frank-Pryce texture, usually observed in chiral thermotropic nematic, is obtained. This texture is related to a radial distribution of the helical axes.

When AgC complex is confined in an emulsion, the textures observed are very intriguing. For small microspheres the typical radial texture with a Maltese cross is observed (Fig. 7a). In the radial structure a point defect is located at the center of the microsphere and the director field is untwisted. For larger droplets, the textures observed (Fig. 7b, 7c) could be ascribed to a nematic configuration, the axial one, usually metastable. In TLCs, this texture has been observed by, for example, by Lavrentovich [36,37], changing the boundary conditions by increasing

the temperature or sometimes this configuration has been induced by applying an electric or a magnetic field [38,39]. Hence, the axial texture existence depends on several factors like elasticity, boundary conditions and external fields.

In alternative the texture can be considered a signature of cholesteric features, the so-called Toron texture in Ref. [40], that appears in TLC under confinement with homeotropic boundary conditions.

Ponting out that LCLCs have a different elastic energy with respect to TLCs [41], in our system this texture could be an axial one, stabilized thanks to the elastic constants relative values and boundary conditions given by PDMS matrix, or a Toron-like texture.

In our measurements, an equatorial circular defect line near the surface of the droplet, is observed in the same conditions in SSY in 12 % of cases, in AgC the number of microspheres showing it increases until 27 % and finally is not observed in DSCG samples (Fig. 7b). The defect is clearly seen when the symmetric axis of the structure is in the observation plane (Fig. 7c).

In any case, the measurements confirmed that the spherical confinement is effective in enhancing the spontaneous twist of the AgC complex mesophase. When the sample is doped with Trans-Hyp (molar ratio AgC:Trans-Hyp 1:7), immediately after their preparation, the microspheres display axial/toron-like textures (Fig. 8) in 41.7 % of microspheres.

However, after few days upon slow evaporation of the solvent or to a relaxation process, a layer-like texture (Fig. 9a,b) and a Frank-Pryce like texture (Fig. 9c,d) are observed. The first is linked to the bipolar distribution of the helical axes presenting a double twist defect line near the surface.

The evaporation is slow in emulsions, and this allows the director realignment giving rise to these cholesteric textures. Other chiral amino acids (for example L-Lysine and L-alanine) are not effective in inducing chirality in AgC complex as also reported for SSY, while the same dopant, Trans-Hyp, is effective in inducing a chiral pitch in both chromonics.

On the contrary, the behavior of DSCG is different than the one observed for SSY and AgC, since in this case different aminoacids are able to torque its mesophases [42,43], giving rise to very well defined Frank-Pryce textures [33,44].

This could be related to the higher flexibility of the molecular structure of DSCG with respect to SSY or AgC. The flexibility of the alkoxy-linker chains probably allows an easier twisting of the two chromone rings to accommodate the amino acid molecules in the supramolecular edifice such as to induce a chiral pitch into the resulting assembly.

To understand the effect of the presence of a chiral dopant on the ordering of the supramolecular columnar structures, thin films of AgC complex on polymeric surfaces following a slow drying process have been prepared. Observing the sample during the drying procedure using a polarized optical microscope (POM), it was possible to note that the AgC doped with Trans-Hyp (Fig. 10) shows typical fingerprint textures that are the signature of the cholesteric phase confirming, hence, the
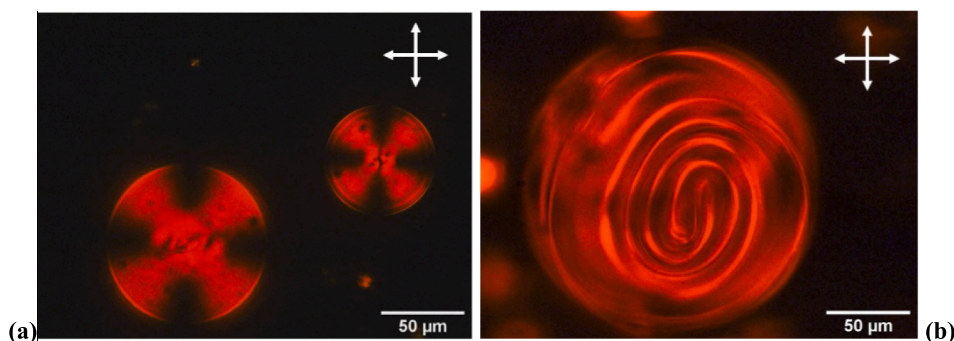

Fig. 6. Optical textures observed in microspheres containing (a) pure SSY and (b) SSY doped with Trans-Hyp.
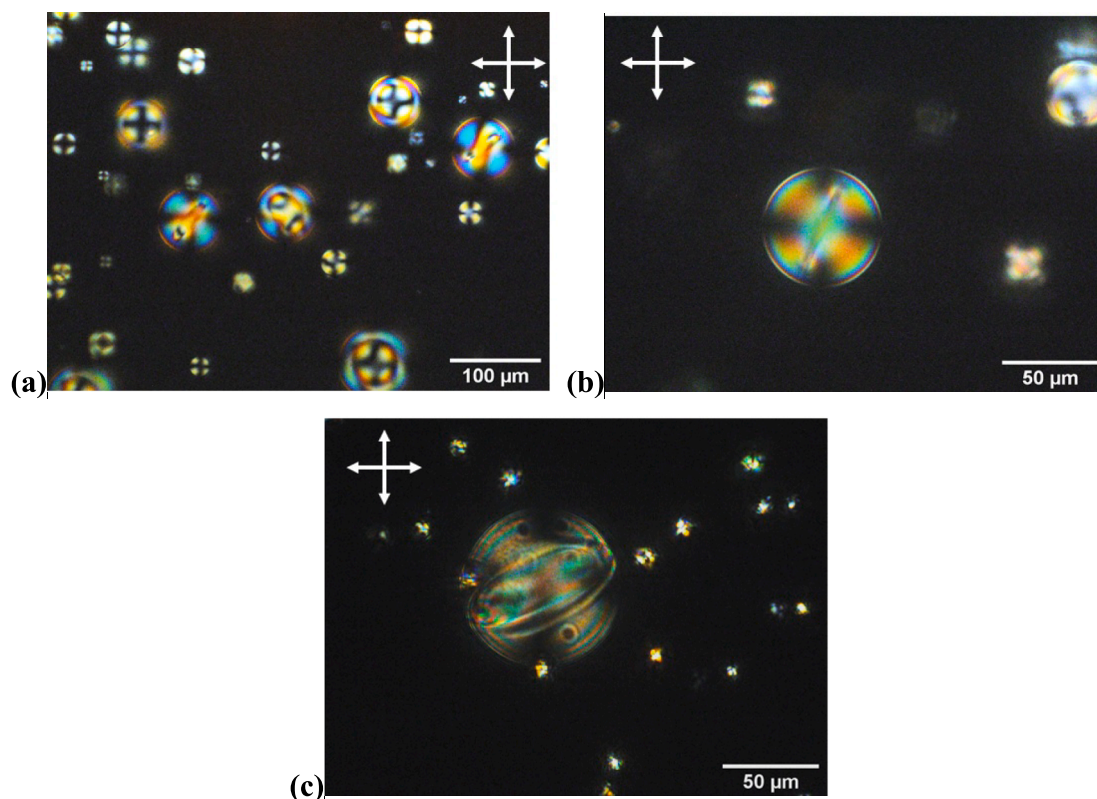
Fig. 7. Microspheres in PDMS showing (a) Maltese crosses and (b, c) axial/Toron-like textures.
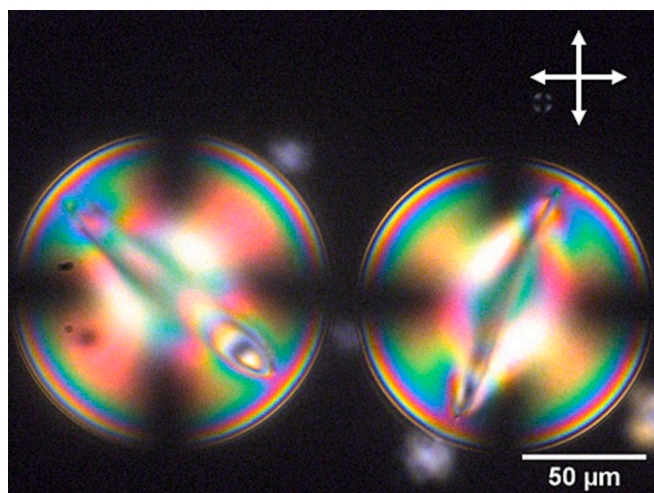

Fig. 8. Microspheres in PDMS of AgC complex doped with Trans-Hyp.

results observed in curved geometries. The corresponding image for the pure AgC, is reported in Fig. S2.

The AgC complex (alone and doped with Trans-Hyp) has been examined by POM at the end of the drying process. Both samples showed crystalline domains, being the ones observed in the case of AgC doped with Trans-Hyp larger than the ones observed in the pure sample (Fig. S3a and S3b). The X-Ray diffraction pattern of AgC complex film on PDMS substrates is comparable with the calculated pattern based on the single crystal data of AgC [31] (Fig. S4a). For the Trans-Hyp doped sample, the X-Ray powder pattern clearly is the superimposition of both the crystalline AgC and Trans-Hyp reflections (Fig. S4b) indicating that the large observed crystallites in POM can be reconducted to the crystallization of Trans-Hyp expelled from the mesophase upon drying. The

chiral dopant expulsion was also observed for SSY and DSCG.

Finally, to test the effectiveness of Trans-Hyp in inducing chirality, in all chromonics, considering the same chromonic/Trans-Hyp ratio was used. In fact, the Helical Twisting Power (HTP) reported in the Materials section and in literature is related to the DSCG matrix. Evaluating this parameter for SSY and AgC is very difficult due to the low torsion capability of Trans-Hyp for these compounds. The 1:3 M ratio was selected to satisfy both dopant solubility limit and the existence of the nematic phase for the three compounds. For this ratio, SSY displayed cholesteric features, as already reported above. The pitch of *ca.*14 micron was measured from POM images using Image J (NIH, USA). In the case of AgC complex, the microspheres were characterized by Toron-like and intermediate layer-like textures but no layer like textures, as observed with 1:7 M ratio, were detected.

As expected, the Trans-Hyp doped DSCG microspheres at this molar ratio still presented periodic cholesteric features with well defined Frank Pryce textures whose measured pitch was *ca.* 11 μm. These results, reported in Fig. 11 suggest that, when the chromonic/Trans-Hyp ratio is 1:3, the dopant confirms its ability in inducing the chiral phase being more effective in DSCG than in SSY and AgC complex. This difference could be correlated to the flexibility of DSCG around the alkoxy-linker chain that might proceed to a rotation to accommodate favorable interactions with the amino-acid, hence inducing an helicoidal structure that reflects the chirality of the Trans-Hyp dopant. For SSY, the structural flexibility is highly reduced, the molecules having to stick with their planar geometry. However, the introduction of the Trans-Hyp dopant must in a certain extent provoke a rotation of the molecule within the columns, hence inducing a screw axis leading to the cholesteric phase. On the other hand, the AgC complex with the highest structural rigidity can only respond to the insertion of the dopant by weak distortions of the tetrahedral coordination around the metal centre, and for that reason AgC is the least susceptible to respond to the induction of chirality by the amino acid.
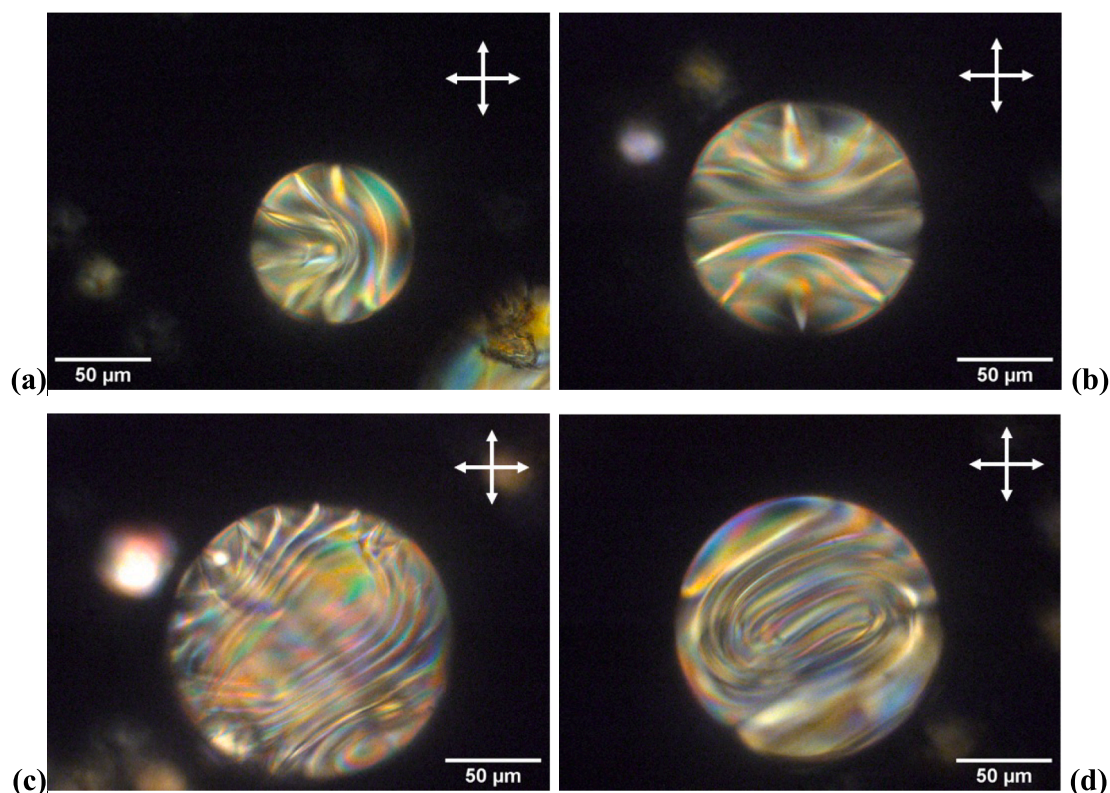
Fig. 9. Microspheres in PDMS of AgC complex doped with Trans-Hyp after slow evaporation of solvent. Layer-like (a,b) and Frank Pryce-like textures (c,d).
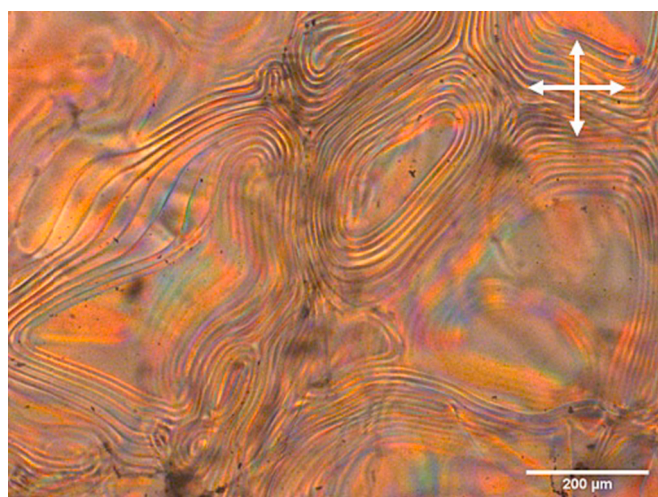
Fig. 10. Fingerprint textures observed in a Trans-Hyp doped AgC complex thin film.

3. Conclusions

In this work three chromonic liquid crystals: the commercial Sunset Yellow and di-sodium cromoglycate, as well as the synthesized complex, [(Bpy-OH)$_2$Ag][CH$_3$COO]H$_2$O have been compared with respect to chirality amplification in curved geometries. In particular, peculiar textures have been observed in microspheres containing the pure AgC complex. Similar configurations have been observed in SSY but never in DSCG confined in the same matrix. This confinement, hence, provides qualitative information on the elastic properties of the chromonic material.

When the mentioned chromonic liquid crystals are doped by using a suitable aminoacid, induced chirality effects are observed. While for SSY and DSCG chirality has already been obtained using the chiral amino acid Trans-Hyp, it is the first time that chirality amplification is obtained for this noncommercial chromonic. This is revealed by the fact that the observed textures are similar to those obtained in thermotropic chiral liquid crystals. As show by POM investigations the effect of chirality induction becomes more evident with time, probably related to the evaporation process. Previous investigations, based on X-Ray diffraction and optical microscopy, have shown that Trans-Hyp is expelled from the nematic phase of DSCG and SSY during water evaporation and the same effect is observed for the novel AgC material. This leads to infer that, also in this case, the aminoacid molecules do not intercalate during the AgC self-assembly into columnar aggregates, but, rather interact through physical bonds with the external surface of columns causing their twist, also explaining the expulsion from the mesophase.

However, chirality induction is less efficient in SSY and AgC with respect to what observed when DSCG is doped with the same amino acids. This suggests that a key parameter for designing new materials in which chirality can be easily amplified, is the molecular flexibility.

The development of new materials with a high flexibility in the molecular core could be useful to amplify chirality at the macroscale, paving way for several applications in the field of optics, photonics and sensing.

4. Materials and methods

The commercial chromonic liquid crystals SSY and DSCG were purchased from Sigma Aldrich and used without further purification.

The [(Bpy-OH)$_2$Ag][CH$_3$COO]H$_2$O complex is prepared as reported in literature [31]. For all complex, chirality was induced by doping with an appropriate amount of Trans-Hyp. Trans-Hyp was purchased from Sigma-Aldrich (Steinheim, Germany). The helical twisting power of Trans-Hyp in DSCG is 11.6 (10^5 nm mol%).

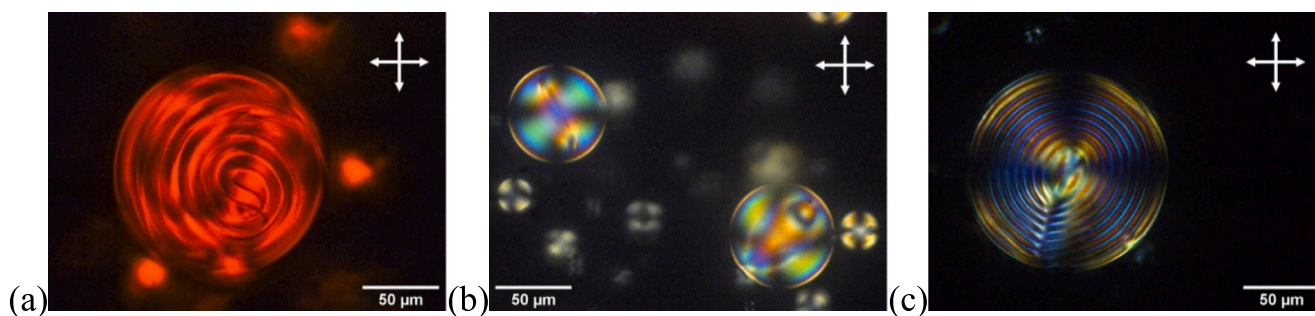Polydimethylsiloxane (PDMS) is polymeric organosilicon compound

Fig. 11. SSY doped with Trans-Hyp (a), [(Bpy-OH)$_2$Ag][CH$_3$COO]H$_2$O doped with Trans-Hyp (b) and DSCG doped with Trans-Hyp textures (c).
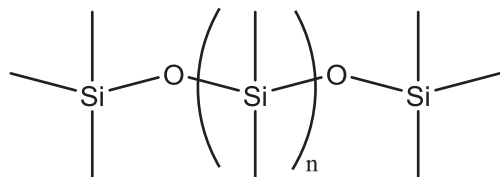

Fig. 12. Molecular structure of PDMS.

(Sylgard kit 184). PDMS is liquid, optically clear and has high viscosity. It is composed of two compounds: the material and the hardener. The structure is shown in Fig. 12. PDMS is used both as an oil, without the hardener, to act as the immiscible matrix in the emulsion and as a thin film for XRD, mixed with the hardener in a 10:1 proportion.

The compounds have been confined in spherical geometry using PDMS which provides homeotropic anchoring at the interface. The microspheres textures have been analyzed using a polarized microscope Leica DMRX (Germany) (POM). The images have been acquired using either a 20X or a 40X objective.

X- Ray diffraction pattern of thin films of [(Bpy-OH)$_2$Ag][CH$_3$COO] H$_2$O complex were acquired by using a D8 Discover (Bruker), λ = 1.5418 Å with two different geometries, Bragg Brentano and Asymmetric Geometry, at 40 kV and 40 mA, with a step size of 0.01° (2θ).

CD spectrum was recorded in methanol at room temperature on a JASCO J815 spectropolarimeter, using 0.5 mm cell, and concentration of $1.54 \cdot 10^{-3}$M.

4.1. Preparation of solutions

The solutions were prepared as follows: powder and ultrapure water were mixed in appropriate proportions to obtain a solution containing SSY in water (30 % wt) or [(Bpy-OH)$_2$Ag][CH$_3$COO]H$_2$O in water (20 % wt). The percentage were chosen in order to have the chromonic in their nematic phase. The sample was prepared 24 h prior to its use, ensuring the effective formation of the N phase.

For the preparation of the chiral solution, a solution of Trans-Hyp was initially prepared as follows: chiral dopant powder and ultrapure water were mixed in appropriate proportions to obtain solutions containing Trans-Hyp 26 wt%, Trans-Hyp 14 wt% and Trans-Hyp 11 wt%. Subsequently, the chromonic powder and dopant solution were mixed in appropriate proportions to obtain solutions containing SSY 30 wt%, AgC 20 wt% and DSCG 13 wt%.

4.2. Preparation of films

[(Bpy-OH)$_2$Ag][CH$_3$COO]H$_2$O complex thin films were prepared as in the following. Initially, glasses were thoroughly washed to remove dust and oily residues, then, they were dried with a jet of hot air. A thin polymeric layer of PDMS with cross linker was deposited by spin-coating on the glasses and, to eliminate any solvents residue, they were placed in an oven at 130 °C for 30 min. Once the substrates were ready, 5 µl of chromonic solution (pure and Trans-Hyp doped) was deposited on each of them. Samples were kept at 4 °C and at controlled humidity for one week, then, they were brought back to room temperature and analyzed.

CRediT authorship contribution statement

Lorenza Spina: Writing – review & editing, Investigation, Data curation. **Eugenia Giorno:** Writing – review & editing, Data curation, Investigation. **Federica Ciuchi:** Supervision, Conceptualization, Writing – review & editing, Writing – original draft, Conceptualization. **Iolinda Aiello:** Writing – review & editing, Writing – original draft, Supervision, Investigation. **Alessandra Crispini:** Writing – review & editing, Writing – original draft, Investigation. **Nicolas Godbert:** Writing – review & editing, Writing – original draft, Supervision, Investigation. **Sandra Belviso:** Writing – review & editing, Investigation. **Maria Penelope De Santo:** Conceptualization, Supervision, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2024.124035.

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