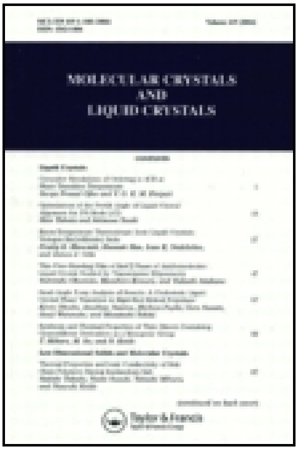

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Photoinduction and Control of the Supramolecular Chirality in Liquid Crystalline Azomaterials

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Photoinduction and Control of the Supramolecular Chirality in Liquid Crystalline Azomaterials

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Liquid crystals (LC) containing azobenzene moieties are materials of interest in different optical technologies. Applications of azomaterials derived from the capability of reversible isomerization between the E- and Z-configurations. Among the different applications reported so far, photoinduction or chirality deserves to be studied in details as can provide, e.g., new chiroptical switches and molecular rotors based on achiral compounds. Here, we review our recent work on the formation, manipulation and control of the chiral supramolecular organization of LC azomaterials using circular polarized light as the chiral stimulus.

Keywords: aggregates; azobenzene; hydrogen bonds; liquid crystals; supramolecular chirality

1. INTRODUCTION

Nature offers many beautiful examples of the biological systems in which the chirality of the molecular level is transferred to a supramolecular and macromolecular level. Research on artificial chiral architectures that mimic the nature is a subject of increasing interest. Actually, the challenge of controlling chirality at different hierarchical levels is particularly significant in molecular self-assembly, protein folding, design of memory systems, sensors and nanostructured

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materials [1–3]. In this context, circularly polarized light (CPL) is a chiral electromagnetic radiation that has been shown to be able to induce and control molecular chirality [4]. In addition, CPL is able to tune supramolecular chiral organizations by means of the control of the molecular chirality. This control can be transferred from molecular to supramolecular chirality through different types of noncovalent interaction, such as π-stacking, hydrogen bonding and solvophobic and ionic interactions.

The incorporation of azobenzene units into liquid crystal materials allows the modulation of optical properties, such as birefringence and dichroism, controlled through E/Z isomerization upon irradiation [5–8]. In addition, the relatively large geometrical change in the azobenzene units due to isomerization influences the surroundings, especially in liquid crystalline systems. Actually, the liquid crystalline ordering facilitates the transfer of the processes occurring at the molecular level into macroscopic phenomena [9–11]. The irradiation with a chiral radiation of azobenzene units included into a liquid crystalline organization gives rise to very interesting results related to the control of supramolecular chirality, and, moreover, the photoinduction of chiral organizations. For instance, enantiomeric excess values in two chiral domains in a Bx phase of bent-core molecules have been obtained using CPL [12]. Moreover, Nikolova *et al.* detected the photoinduction of a large circular birefringence and circular dichroism (CD) in films of a side-chain azobenzene liquid crystalline polyester by illumination with CPL [13]. Natansohn *et al.* reported the photoinduction of a chiral supramolecular structure by illumination of a smectic azopolymer with CPL [14] and also they detected a circular Bragg reflection in a glassy nematic film after irradiation with CPL [15]. Galstian and co-workers reported the photoinduced macroscopic chirality in a non-chiral azo-dye-doped polymer film and the non-resonant optical breakdown of the chiral symmetry in inherent non-chiral nematics [16,17]. More recently, photoinduced supramolecular chirality by irradiation with CPL was attained in main-chain polymeric liquid crystalline systems doped with azobenzene-containing W-shaped molecules [18].

Herein, we present the possibility of transferring the chirality of circularly polarized light to the supramolecular architecture of two types of liquid crystalline organization based on azo-containing mesogens. On one hand, side-chain azopolymers are shown to adopt a chiral organization upon irradiation with CPL, mediated by azo-aggregation processes. On the other hand, the helical stack of propeller-like complexes is biased towards a prevailing sense by irradiation with CPL, through hydrogen-bonding and π-stacking interactions.

2. EXPERIMENTAL

The chemical structure of the liquid crystalline azopolymers investigated (coded as **PC2**, **PC6**, **PC10** and **P100**) is shown in Figure 1. The columnar propeller-like liquid crystals used were **T-A14**, **T-A(*S*)10*** and **T-A(*R*)10*** (Fig. 2). The detailed synthesis and properties of these materials where described elsewhere [19–21]. The molecular weight, polydispersity and thermal properties of azopolymers are collected in Table 1. The characterization data of propeller-like columnar liquid crystals are gathered in Table 2. Molecular weights and polydispersities were measured by GPC using a Waters 600E HPLC (Waters Styragel columns HR2 and HR4) with a UV Waters 991 photodiode array detector. THF was used as the eluant and standard samples of polystyrene were employed. Thermal stability was measured by thermogravimetry using a TA Instruments STD 2960 apparatus at 10°C · min^{-1} under a nitrogen atmosphere. Thermal transitions were measured using a DSC-MDSC TA Instruments 2910 calorimeter at 10°C · min^{-1} under a nitrogen atmosphere. Tg value was measured as the midpoint in the heat capacity increase and the other transitions were taken as the maximum of the transition peak. Mesomorphism was studied using an Olympus BH-2 polarizing optical microscope (POM) equipped with a Linkam THMS-600 hot stage and Linkam TMS91 temperature controller. UV-vis spectra were registered using a Unicam UV4-200 or simultaneously with the circular dichroism (CD) spectrum using a Jasco J-810 Spectropolarimeter. The films deposited onto fused silica slides were placed in a rotating holder around the light beam and CD spectra were registered every 60 degrees. Films (thickness about 300 nm) were prepared by casting

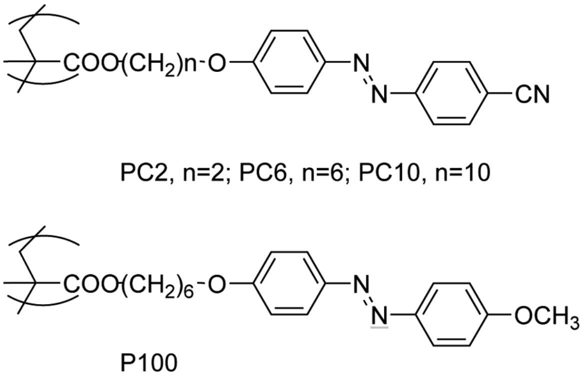

FIGURE 1 Structures of the studied azopolymers.

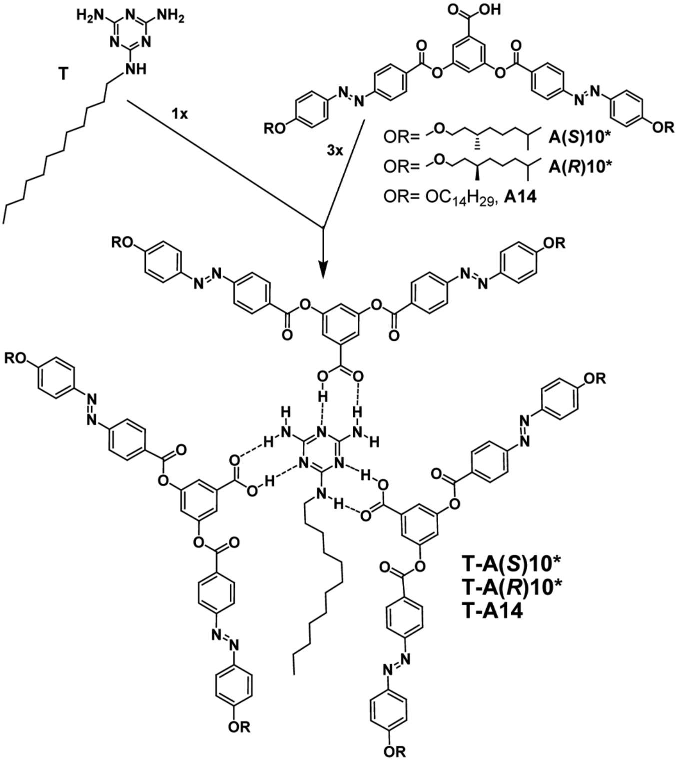

FIGURE 2 Synthesis of hydrogen-bonded complexes that incorporate azobenzene groups in each of the arms of the V-shaped acid.

TABLE 1 Molecular Weight, Thermal Stability, Thermal Transition and Mesomorphism of Azopolymers Determined by GPC, DSC, POM and X-ray Diffraction

Polymer	Mn	Mw/Mn	T_{dec}/°C[a]	T_{DGT}/°C[a]	Thermal transitions/°C[b]
PC2	10225	3.1	260	345/398	g 105 N 158 I
PC6	41000	2.1	270	343/409	g 56 S_A 163 I
PC10	5400	1.7	280	356/422	g 28 S_A 131 I
P100	25400	2.1	275	326	g 64 S 89 N 126 I

[a] T_{dec}: Onset of decomposition detected on the thermogravimetric curve; T_{DTG}: Temperature of maximum decomposition detected on the derivative thermogravimetric analysis.

[b] Measured by DSC on the second heating scan.g, glass; S_A, smectic A; S, smectic; N, nematic; I, isotropic.

TABLE 2 Phase Transition Temperatures and Enthalpies of the Complexes[a]

Association	Phase	T/°C	ΔH[kJ/mol]	Phase	T/°C	Phase
T-A(*S*)10*	I	123	6.8	Col_h	51	g
T-A(*R*)10*	I	123	6.8	Col_h	51	g
T-A14*	I	134	6.1	Col_r		

[a] Transition temperatures are given for the cooling process. I = isotropic liquid, Col_h = hexagonal columnar mesophase, Col_r = rectangular columnar mesophase, g = glass.

solutions of the polymer in chloroform onto clean, fused silica slides. These films were dried under vacuum at 30°C during 24 h. After, the films were then heated above the clearing temperature for 5 min and annealed for 15 min at a reduced temperature ($T_{annealing}/T_i$) of around 0.7. The samples were then placed onto a metal block at 25°C for 30 min. This process gave rise to a polydomain phase. Annealed films of azomaterials were irradiated for 30 min with *left*- or *right*-circularly polarized light (*l*-CPL or *r*-CPL, respectively) from the 488 nm line of an Ar^+ laser (power $20\,mW \cdot cm^{-2}$). UV-vis and CD spectra of the illuminated film on clean, fused silica slides were recorded after keeping the samples in darkness at room temperature for at least 30 min.

3. RESULTS AND DISCUSSION

A. Azopolymers

The molecular weight, polydispersity and thermal properties of the synthesized polymers are collected in Table 1. These materials have good thermal stability and weight loss was not observed at temperatures below 250°C. The mesomorphic properties of the synthesized polymers were determined by DSC, POM and X-ray diffraction. Some discrepancies are observed in comparison to the data previously reported for **PC2**, which was occasionally described as smectic [22], probably due to the poorly defined sanded texture of the mesomorphic phase. However, the X-ray diffraction pattern of the mesophase of this polymer is unambiguously assigned to a nematic phase [23]. An increase in the spacer length in the side chain results in smectogenic materials such as **PC6** and **PC10** and a decrease in the Tg. **P100** exhibited a glass transition temperature at 64°C, a short range of smectic phase and a broad nematic range up to approx. 130°C, as previously reported by several groups [24–26].

The annealed thin films of **PC2**, **PC6**, **PC10** and **P100** were irradiated with *l*- or *r*-CPL from the 488 nm line of an Ar^+ laser (power

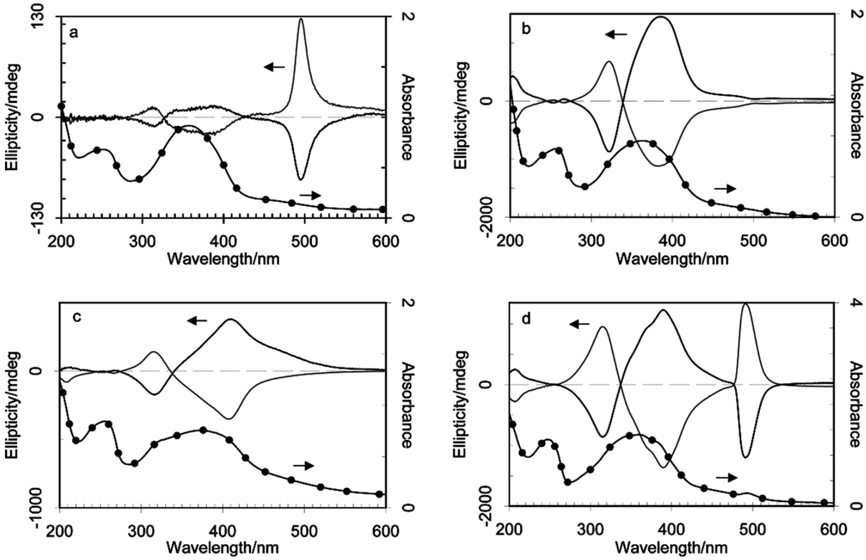

FIGURE 3 CD spectra of films irradiated with *r*-CPL (black lines) or *l*-CPL (grey lines) from 488 nm line of Ar^+ laser ($20\,mW \cdot cm^{-2}$) for 30 min and UV-vis (—●—) spectra of films irradiated with *r*-CPL for 30 min: a) **PC2;** b) **PC6;** c) **PC10**, and d) **P100**. Adapted from [20] and [21].

$20\,mW/cm^2$) for 30 min. The polymers both in film and solution were totally CD-silent prior to irradiation. However, all the azopolymers exhibited photoinduced CD signals after irradiation. The contribution of linear dichroism to the CD spectra is negligible as can be deduced from the comparison of several CD spectra that were recorded at different film positions rotated around the light beam. CD and UV-vis spectra of illuminated films are shown in Fig. 3. The CD spectra of the irradiated polymers exhibit an exciton couplet corresponding to the $\pi - \pi^*$ absorption band of the azobenzene and centered between 330 and 340 nm, that is blue-shifted in comparison to the $\pi - \pi^*$ absorption band of the UV-vis spectra corresponding to isolated azobenzene groups [20,21]. These exciton couplets are due to the splitting of an H-band as a consequence of a chiral interaction between adjacent chromophores [27–29]. The Cotton effect at 390 nm can be due to the superposition of the band of the exciton couplet centered around 330–340 nm, the induced Cotton effects of the isolated azobenzene units and J-aggregates [30]. The exciton couplet associated to chiral H-aggregates was presented in the CD spectra of all irradiated azopolymers. However, different CD spectra were observed when the glassy mesophase is smectic or nematic. First, the CD spectra of smectic **PC6** and **PC10** exhibit a weak exciton couplet centered around 260 nm which corresponds to the $\pi - \pi^*$ transition moment along the short axes. The signal is slightly red-shifted, i.e., a J-shift, in comparison to the maximum of the UV-vis band [27]. On the other hand, the CD spectra of nematic irradiated polymers, **PC2** and **P100**, only show the main exciton couplet but exhibit a signal around 490 nm. This signal is not an absorption band of the azobenzene groups; in fact this band is associated with a selective reflection [15] due to a photoinduced helical organization of the azobenzene chromophores similar to a chiral nematic mesophase [31,32]. CD spectra having similar absorption but reverse signs were obtained by irradiating the annealed films of the polymers with *l*- or *r*-CPL. This observation confirms a chiral switching facility. According to the obtained results the photoinduced chiral supramolecular order of smectic polymers is limited to chiral H-aggregates of azobenzene units. However, the irradiation of glassy nematic azopolymers gives rise to a long-range helical superstructure. Moreover, the optical behavior of the ideal helices indicated that the irradiation with *l*-CPL produced a left-handed helix and *r*-CPL illumination induces a right-handed helix. The CD spectra of the irradiated **PC6** and **P100**, which exhibit a Tg around 60°C, display higher ellipticity values than the CD spectra of irradiated **PC2** (Tg, 105°C) and **PC10** (Tg, 28°C). Probably, a high Tg prevent molecular motions required to get the chiral supramolecular organization but a material with a low Tg, around room temperature, is unable to record and freeze a photoinduced suprastructure. Indeed, storage of irradiated **PC2**, **PC6** and **P100** films at 30°C for two months in the dark did not lead to a modification in the photoinduced supramolecular structure. However, the CD signals of irradiated **PC10** disappeared after similar storage as a consequence of the relaxation of the supramolecular structure around the Tg. As an example, the CD spectra of irradiated **PC10** after 30 min and 30 h at 30°C in the dark are shown in Figure 4c.

In order to study the thermal stability of the photoinduced supramolecular structures, the irradiated films of **PC2**, **PC6** and **P100** were successively heated at different temperatures for 5 min and then quenched to room temperature. The CD spectra of the films were measured after each treatment and these are shown in Figure 4. It should be pointed out that the quenching below Tg allows the "freezing-in" of the supramolecular structure formed by annealing [33]. Thermal annealing of irradiated **PC6** (Fig. 4b) with *r*- or *l*-CPL at a temperature close to the Tg (56°C) gave a slight red shift in the maximum of the positive band and only a very slight decrease in the ellipticity

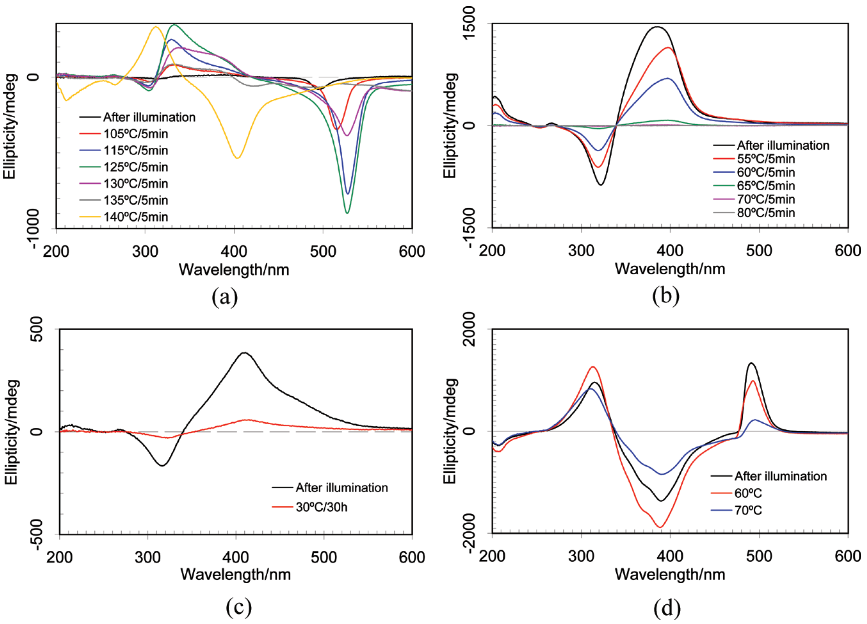

FIGURE 4 CD spectra of irradiated a) **PC2;** b) **PC6;** c) **PC10**, and d) **P100** with *r*-CPL from 488 nm line of an Ar^+ laser (20 mW · cm^{-2}) for 30 min after annealing for 5 min at the indicates temperatures. Adapted from [20] and [21].

values of the negative band. Nevertheless, annealing at temperatures above the Tg produced a significant and continuous decrease in the ellipticity values. When the annealing temperature was 70°C the peaks in the CD spectrum completely disappeared, which evidenced that the photoinduced supramolecular structure can be thermally erased above Tg. The CD signals of irradiated **P100** are stable by annealing at temperatures up to around Tg. Thermal annealing of irradiated **P100** at a temperature close to the Tg (64°C) causes an increase in the ellipticity values of the CD bands corresponding to the transition bands of *E*-azobenzene chromophores. However, a decrease in the ellipticity values of the selective reflection is detected by annealing at temperatures below the Tg; in fact the ellipticity values gradually decrease up to 75°C. At this temperature, which is slightly above the Tg, the photoinduced helical structure and chiral aggregates disappear.

Nevertheless, **PC2** showed an unexpected behaviour (Fig. 4a). Annealing of the sample at temperatures up to 100°C, close to Tg, did not modify the CD spectrum. However, annealing from 100°C up to 125°C, in the nematic phase, gave rise to an increase in the CD signal intensities, a fact that indicates the development of a photoinduced supramolecular structure (Fig. 4a). Moreover, a blue shift of the cross-over (from 328 nm to 312 nm) corresponding to the exciton couplet was detected and this could be associated with an increase in the level of aggregation or different packing within the aggregates. Furthermore, a bathochromic shift was observed in the selective reflection as the temperature was increased. This result seems to indicate a modification of the pitch of a long-range helical order similar to that exhibited by a chiral nematic phase [34]. On using annealing temperatures above 125°C the trend changes (Fig. 4a). The use of a temperature up to 135°C led to a decrease in the selective reflection and Cotton effect bands. In this case the selective reflection corresponding to the long-range helical order disappeared at 135°C. However, the signals corresponding to the chiral H-aggregates (exciton couplet) could still be observed. An unexpected modification of the CD signal was detected by annealing the sample at 140°C. The sign of the CD signals associated with H-aggregation changed and might be related with the type of the aggregates as it has been recently calculated by Painelli and co-workers [28]. This thermally induced new structure is stable up to isotropization temperature. Moreover, when the thermal stability of an irradiated film of **PC2** with *l*-CPL was evaluated, the modification of the CD responses with different annealing temperatures was similar but had opposite signs. The origin of the supramolecular structure developed by annealing at high temperature is currently under investigation.

The change in the macroscopic optical properties was investigated by irradiation of the nematic polymer **P100** in a wedge cell with an aligning layer for planar orientation. The irradiated region of the wegde cell exhibits a photoinduced iridescent green reflection, which is observed with the naked eye [20]. This selective reflection corresponds to the photoinduced band detected in the UV-vis and CD spectrum around 490 nm.

This photoinduced supramolecular chirality could begin at the molecular level with an asymmetric photoisomerization of enantiomeric conformers of azobenzenes (either *E* or *Z*-isomers) [18]. The asymmetric photoisomerization can trigger an enrichment of one chiral conformation, which acts as chiral dopant for the nematic phase and transfer its chirality to an arrangement of azobenzene groups, first to produce locally formed exciton couplings having a preferential sense and eventually inducing a long-range supramolecular organization in a similar way that a chiral nematic phase.

B. Propeller-like columnar liquid crystals

In a recent publication [19] we described supramolecular complexes in which non-mesogenic V-shaped acids showed mesogenic ability when forming a tetrameric complex around a melamine derivative. This unusual mesogenic core, interpreted as a propeller-like structure, promoted the appearance of well defined columnar mesophases by combining the π-stacking tendency of the melamine and the lateral interaction between V-shaped molecules. The proposed model was compatible with the existence of supramolecular chirality arising from an inherent helical stacking of propeller-like supramolecules.

Chiral complexes (**T-A(*S*)10***and **T-A(*R*)10***) organized into a hexagonal columnar mesophase, and the achiral complex (**T-A14**) showed a rectangular columnar mesophase. Both mesophases were initially characterized by texture observations and further confirmed by x-ray measurements. The formation of the tetrameric complex was studied by IR and NMR spectroscopy, and ^{13}C NMR on solid samples that was particularly revealing and helped to confirm the complex stoichiometry. The mesophase order achieved on cooling from the isotropic liquid was stable at room temperature for long periods of time in all cases.

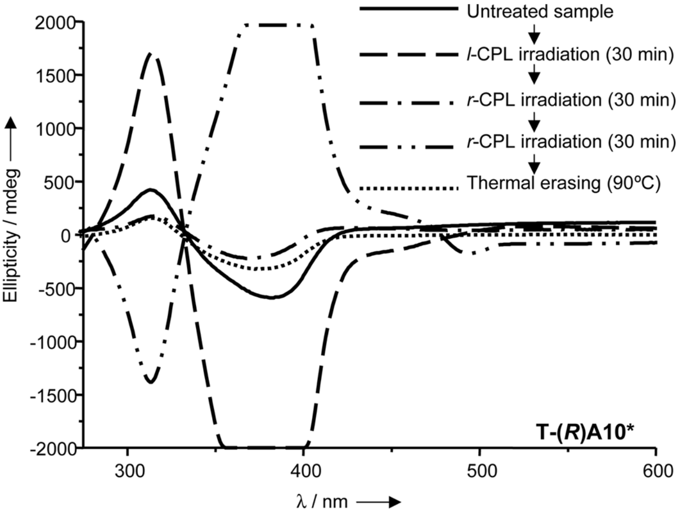

FIGURE 5 CD spectra corresponding to successive irradiation of cast film of complex **T-(*R*)A10*** with *l*-CPL and *r*-CPL at room temperature. The irradiation times are given with respect to the previous irradiation step. Adapted from [19].

We assessed the optical activity of the mesophases of the chiral complexes by circular dichroism. These materials did not show any CD signal indicative of optical activity in the isotropic liquid. However, on cooling to room temperature, a strong signal appeared and this was identified as an exciton splitting (solid line in Fig. 5). This optical activity was interpreted, as the consequence of must come from a chiral environment that corresponds to the mesophase arrangement, as confirmed by X-ray studies at room temperature. Moreover, the handedness of this helical arrangement was biased towards a given chiral sense that is determined by the configuration of the estereogenic centre. Thus, the CD spectrum of the complex formed by the enantiomeric acid presents an opposite sign, indicating opposite helical handedness.

The corresponding experiments aimed at controlling and tuning the chirality of the mesophases were undertaken. This was carried out by irradiating the columnar-ordered material with CPL. The CD spectra corresponding to different irradiation processes in the same chiral material **T-(*R*)A10*** are shown in Figure 5. The sample was irradiated with *l*-CPL for 30 min at room temperature. The resulting CD spectrum shows the same shape as the original one but with a considerable higher intensity. This means that an amplification of the chirality occurs and this is likely to arise from an increase in the population of azobenzene chromophores absorbing light within a helical disposition. Subsequent irradiation with the orthogonal CPL (i.e. right-handed) for 30 min gave rise to a decrease in the CD intensity, which became very close to the original one. This observation can be interpreted in terms of the chiral information achieved by the supramolecular organization during the first irradiation being erased and returning to the initial situation. Irradiation with *r*-CPL for additional 30 minutes afforded an induced optical activity of similar magnitude to that observed after irradiation with *l*-CPL, but with the opposite sign. Finally, the chiral information attained in any irradiation process could be thermally erased by heating at 90°C for few seconds. It was not necessary to heat the material above the clearing point. These experiments demonstrated that it is possible to control and tune the supramolecular chirality of a columnar mesophase, as if the proposed helical stacking could wind and unwind following the handedness of the incident CPL through the photoisomerization process of the azobenzene groups.

The next challenge was to assess whether the chiral information of CPL could be transferred to the columnar arrangement of achiral mesogens. We therefore performed irradiation experiments in the $\mathrm{Col}_{\mathrm{r}}$ mesophase of the achiral complex **T-A14**. This complex did not show

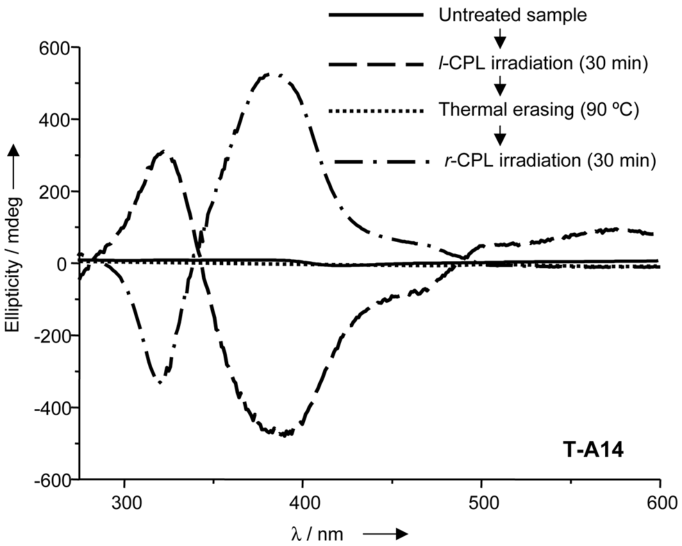

FIGURE 6 CD spectra corresponding to a *l*-CPL irradiation/thermal erasing/*r*-CPL irradiation cycle for a cast film of complex **T-A14**. The irradiation times are given with respect to the previous irradiation step. Adapted from [19].

optical activity in the ‘as prepared’ cast film (Fig. 6). Irradiation with *l*-CPL for 30 min gave rise to the induction of strong signals in the CD spectrum of the film. Furthermore, the resulting CD spectrum had the same shape as that observed for the original optical activity shown by the $\mathrm{Col_h}$ mesophase of the chiral complexes. This could mean that the proposed helical stacking was similar in both materials regardless of the lattice type (hexagonal or rectangular) in which the columns are organized. As observed in the experiments with chiral complexes, the induced optical activity could be completely erased by heating the material up to 90°C. Furthermore, the CD spectrum with the opposite sign was obtained when the film was irradiated with the orthogonal CPL (*r*-CPL).

4. CONCLUSION

Here, we present the possibility of controlling of the supramolecular chirality of two different types of liquid crystalline azomaterials by a chiral radiation. First, we demostrated that the irradiation of thin films of azopolymers gives rise to the development of supramolecular chirality based on chiral H-aggregates. Moreover, the selective reflection of visible light observed on the nematic polymers seems to demonstrate that the irradiation of this glassy nematic azopolymer induces a helix as a consequence of the chiral arrangement of the azobenzene units. In addition, the chirality of the irradiated polymers can be switched in a reversible manner by illumination with orthognal CPL. Secondly, chirality transfer from the molecule to the mesophase occurs in columnar mesophases of tetrameric complexes of melamine derivative and nonmesomorphic chiral V-shaped acids through hydrogen-bonds. The irradiation with CPL enables a control of the chirality of these columnar mesophase through the azobenzene units. Furthermore, achiral columnar systems can be biased towards a chiral supramolecular organization by ilumination with the corresponding CPL.

The manipulation by illumination of intermolecular noncovalent interactions allows the control of the supramolecular chirality of azomaterials, in particular, the photoinduction of supramolecular structures with CPL of opposite handedness, a phenomenon that imparts on these materials the basic requirement for a supramolecular switch: the bistability.

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