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PAPER

Insight into the supramolecular organization of columnar assemblies with phototunable chirality†

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New supramolecular associations with photoaddressable azobenzene units have been synthesized in order to better understand the structure of these complexes and their mesophases. The complexes are formed by a melamine core and three V-shaped acids and they exhibit columnar mesomorphism. The acids consist of two different arms, one derived from azobenzene and the other derived from phenyl benzoate. This design has allowed decreasing T_g values and also avoiding the tendency to crystallize, favouring regular and reproducible structures, together with the possibility of photoresponse. The mesomorphic properties of the complexes have been studied by POM, DSC and X-ray diffraction, showing $\mathrm{Col_h}$ or $\mathrm{Col_r}$ mesophases. CD activity of these materials in the mesophase (that reveals chiral structures) has been controlled by irradiation with CPL. XRD and AFM studies have been carried out to check the molecular organization in the films before and after CPL exposure, which confirmed that the mesophase retains its structure after switching the corresponding supramolecular chirality.

Introduction

In recent years, a great deal of attention has been focused on the incorporation of chirality into self-organized materials, ranging from bulk materials to solvent-assisted aggregates.[1–3] The chiral properties of self-organized materials not only rely on the molecular structure but also on the supramolecular interactions between building blocks.[4,5] Accordingly, a challenge in this area is the design of appropriate building blocks that can self-assemble into helical architectures with a given handedness. Helical handedness often comes from the chiral information encoded in the constituent molecules (*i.e.* chiral building blocks).[6–12] Other origins for chirality have been observed in self-organized systems. These include spontaneous resolution into chiral domains due to particular molecular structures and phases[13–18] and the induction of chirality through the interaction of appropriately designed achiral building blocks with external chiral sources, such as light,[19–21] chiral templates,[22,23] solvents,[24,25] *etc.* Very recently, chiral selection has been reported for porphyrin aggregates, a process determined by rotational and magnetic forces during the nucleation step.[26]

Particularly, the efficient transfer of chirality to the supramolecular architecture of self-organized bulk materials has been demonstrated for columnar liquid crystals.[27] Columnar mesophases allow the construction of functional materials with well-defined 1D organizations.[28–31] In this respect, the structural control of mesogens that provide columnar assemblies, and of the resulting columnar mesomorphic order, has proven to be a valuable tool to construct self-organized chiral materials with well-defined 1D helical architectures.[27] In this type of system, supramolecular chirality has also been reported to be generated from different origins such as chiral mesogens,[32–34] spontaneous resolution[35] or light-induced chirality.[36,37] Moreover, the use of the supramolecular chemistry strategy for the design of columnar LCs brings additional features to these systems such as dynamic responses and further possibilities for molecular design.[38,39]

Triazine derivatives, such as diamino-1,3,5-triazine[40–42] and triamino-1,3,5-triazine,[43–48] constitute a valuable class of supramolecular synthons for the design of liquid crystals with well-defined mesomorphic organizations. In previous papers we described the remarkable self-organizing ability of propeller-like H-bonded complexes built from 2-alkylamino-4,6-diamino-1,3,5-triazine to give columnar mesophases.[36,49] This ability was ascribed to the synergistic action of the π-stacking tendency of the melamine-derived core and the strong lateral interactions between V-shaped molecules. This ability is general for this type of complex, regardless of the chemical composition of the acid, and this allowed functionality to be imparted to these systems by tuning the molecular structure of the acid. Thus, transfer of

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molecular chirality to the columnar organization,[49] luminescent properties[50] and photoresponsive features established by the ability of azobenzene-derived systems to follow the helicity of circularly polarized light[36] has been verified in these materials.

In this paper we present a study of these systems with particular emphasis on their columnar organization and whether it is affected by the dynamic process involved in response to CPL. For this purpose, we designed the new complexes represented in Chart 1. The novelty of the complexes lies in the chemical structure of the V-shaped acid, which combines two different arms – one derived from phenyl benzoate and the other arm containing the azobenzene photoactive group. These complexes show good processing features and are good film-forming materials. The incorporation of asymmetric V-shaped acid structures allowed us to decrease the contents of photoactive units to 50% with respect to the previously described materials in a controlled manner. Furthermore, a general study was carried out on the structure of the mesophase shown by these complexes and the switching and chirality induction behaviour. The films prepared from these complexes were studied by X-ray diffraction (XRD) and atomic force microscopy (AFM) before and after irradiation in order to determine whether the columnar organization of the complexes is affected upon the CPL irradiation process.

Results and discussion

Synthesis

The supramolecular complexes **T–AR–ER′** were prepared by slow evaporation of a dichloromethane solution of the two supramolecular synthons, triazine and V-shaped acid, in a 1 : 3 ratio, respectively. The mixture was then heated to the isotropic state, and the sample was used for subsequent experiments. The melamine derivative 2,4-diamino-6-dodecylamino-1,3,5-triazine, **T**, was synthesized by reaction of *n*-dodecylamine with 2,4-diamino-6-chloro-1,3,5-triazine.[51] The synthetic pathway followed to prepare the V-shaped acids is outlined in Scheme 1. Acid **1** was prepared by azoic coupling of ethyl 4-aminobenzoate and phenol followed by Williamson etherification of the hydroxy group and hydrolysis of the ethyl ester, as described previously.[36,37] The phenyl benzoate arm, acid **5**, was synthesized by esterification of benzyl 4-hydroxybenzoate with the corresponding 4-alkoxybenzoic acid using DCC/DMAP in dichloromethane, and subsequent cleavage of the benzyl ester by hydrogenation.[49] The V-shaped acid, **7**, was synthesized in two steps. First, the central ring, **3**,[52] was reacted with acid **1**, *via* the acid chloride **2**,[36,37] in a 1 : 1 molar ratio. The intermediate **4** was separated by flash chromatography. The phenol intermediate **4** was then coupled with acid **5** by the Steglich reaction. Cleavage of the TIPS group of compound **6** was carried out with tetra-*n*-butylammonium fluoride (TBAF) in THF and this afforded the final acids, **7**, after acidification with acetic acid. All of the products were fully characterized by ^{1}H-NMR, IR and their purity was confirmed by elemental analysis (see ESI†).

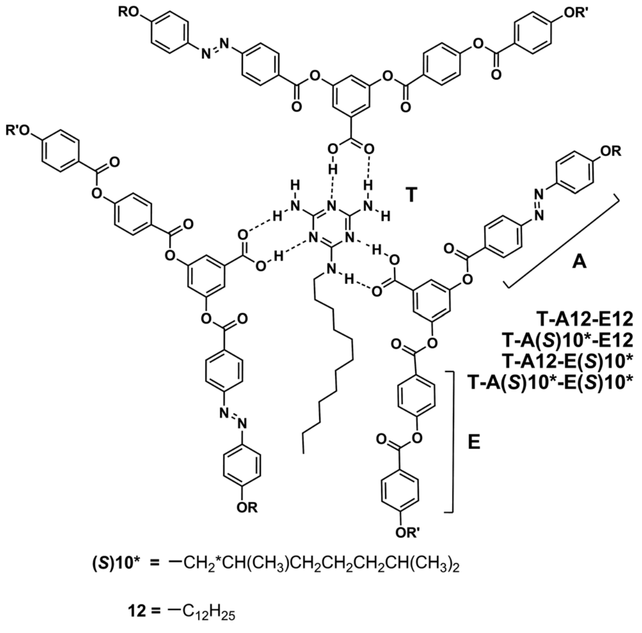
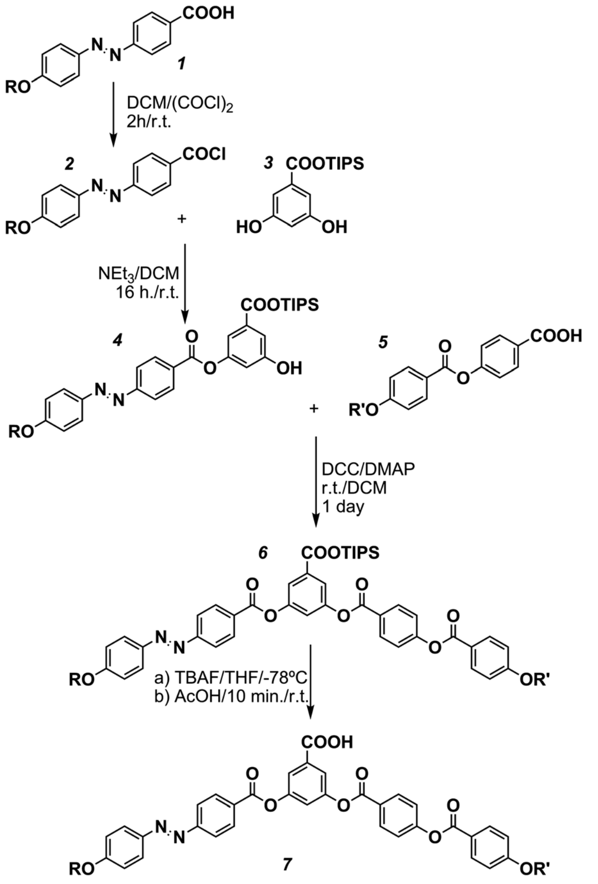


Chart 1



Scheme 1

Characterization of the complexes

The supramolecular associations were studied in deuterated chloroform solution by ^{1}H-NMR spectroscopy, which evidenced the formation of supramolecular species given the significant changes observed in the chemical shifts of some protons in both supramolecular synthons, as previously described for analogous complexes. Furthermore, DOSY experiments indicated that a fast exchange between associated and isolated species occurs in solution, since only one apparent diffusion coefficient was observed (see ESI†). The formation of the complexes **T–AR–ER′** [1 : 3] was also confirmed by solid state ^{13}C-CPMAS NMR spectroscopy (Fig. 1). It is especially significant that the peak corresponding to the carbonyl group of the non-complexed acid (174 ppm) is broadened and shifted in the spectrum of the mixture. Furthermore, the signals for some carbon atoms, of both the acid and the melamine synthons, are significantly shifted upon complexation. The upfield shift of the signals for the carbon atoms within the *N*-alkyl tail of the melamine is worth noting, and must be due to the strong influence that the aromatic rings of the acid partners have on the carbon atoms of the tail.

Mesomorphic properties

All of the supramolecular complexes prepared from the melamine derivative, **T**, and the V-shaped acids, **AR–ER′**, combining azo and ester arms, appear as uniform materials by optical microscopy and show textures, between crossed polarizers, that reveal liquid crystalline behaviour over broad temperature ranges. Only the complex **T–A(*S*)10*–E(*S*)10*** had to be annealed for 1 hour, at a temperature a few degrees below the clearing point measured by DSC, in order to allow the mesophase to develop a texture that was visible through the crossed-polarizers. None of the acids used to form these complexes are liquid crystalline (see ESI†). The melamine derivative (**T**) shows metastable SmA mesomorphic behaviour on cooling from the isotropic liquid; C 103 °C (SmA 38 °C) I.[51]

All of the complexes showed textures between crossed-polarizers that are indicative of columnar mesophases (Fig. 2). The type of two-dimensional arrangement was further confirmed by X-ray diffraction (see below). Transition temperatures and enthalpy values, determined by differential scanning calorimetry, are gathered in Table 1. Thermograms recorded at a cooling rate of 10 °C min^{-1} (see ESI†) showed a single peak in the cooling process and this corresponds to the transition from the isotropic liquid to the mesophase. It was found that the cooling rate was crucial for the appearance of the mesophases, since a rapid cooling rate led to the segregation of the supramolecular synthons and prevented the formation of the mesogenic complex.[49] However, once formed, the mesophase was stable at room temperature for all the complexes studied.

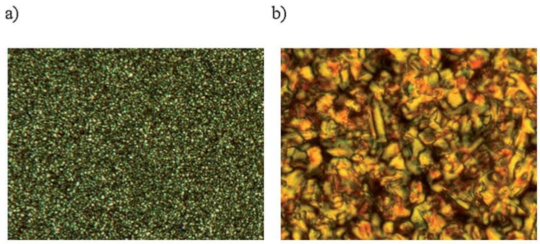


Fig. 2 POM pictures taken at room temperature for associations (a) **T–A12–E(*S*)10***, Col$_h$, and (b) **T–A(*S*)10*–E12**, Col$_r$.

Table 1 Thermal and thermodynamic properties of the complexes[a]

Complex	Transition temperatures, °C (enthalpy values, kJ mol^{-1})
T–A12–E12	I 108 (6.1) Col$_r$
T–A(*S*)10*–E12	I 103 (8.5) Col$_r$
T–A12–E(*S*)10*	I 92 (2.9) Col$_h$
T–A(*S*)10*–E(*S*)10*	I 85 (4.3) Col$_h$

[a] I: isotropic liquid; Col$_r$: rectangular columnar mesophase; Col$_h$: hexagonal columnar mesophase.

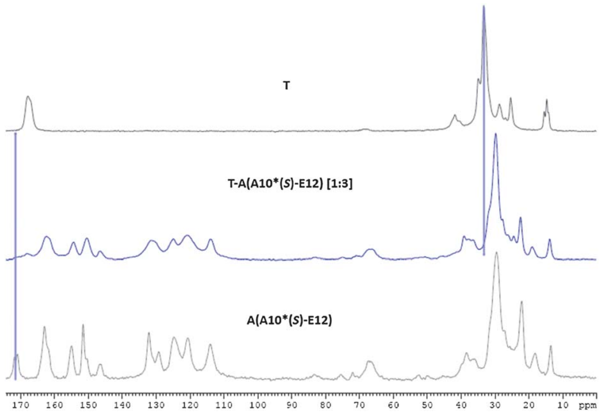


Fig. 1 ^{13}C-CPMAS spectra of **T**, **T–A(*S*)10*–E12**, and **A(*S*)10*–E12**. Vertical lines indicate the chemical shifts of the C atoms of the carbonyl group of the acid and those of the alkyl tail of the melamine core.

To confirm the nature and structural details of each mesophase, powder X-ray diffraction experiments were carried out on all materials at room temperature. Measurements were performed on samples that were previously treated in the capillary, *i.e.* the material was heated to the isotropic liquid and then cooled down to room temperature at a rate of 10 °C min^{-1}. X-ray diffractograms were, in general, rich in reflections, as shown in Fig. 3. The structural parameters of the mesophase for each complex are given in Table 2. The type of columnar mesophase was confirmed as Col$_h$ for complexes **T–A12–E(*S*)10*** and **T–A(*S*)10*–E(*S*)10***. In contrast, the complexes that have the same arm **E12** [**T–A12–E12** and **T–A(*S*)10*–E12**] show a Col$_r$ mesophase. It is difficult to establish the reason for this behaviour. What can be deduced is that there is a relationship between the number of chiral tails and the mesophase symmetry, which also depends on the position of the chiral tail. Indeed, the achiral complex **T–A12–E12** shows rectangular columnar behaviour,

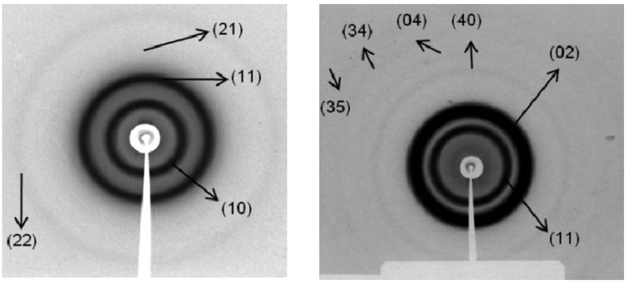


Fig. 3 SAXS patterns of *left*: the Col$_h$ mesophase of the complex **T–A12–E(*S*)10***, and *right* the Col$_r$ mesophase of complex **T–A(*S*)10*–E12** (the reflection 31 was too weak to be seen in the digitalized pattern).

Table 2 Lattice parameters for the associations measured by powder X-ray diffraction at room temperature

Complex	Phase	Parameters (Å)	d_{obs} (Å)	d_{calc} (Å)	*hk*
T–A12–E12	$\mathrm{Col_r}$	$a = 94$; $b = 72$	57.2	57.2	11
			47.0	47.0	20
			36.0	36.0	02
			28.6	28.6	22
				28.7	31
			23.5	23.5	40
			19.5	19.7	42
T–A(*S*)10*–E12	$\mathrm{Col_r}$	$a = 80$; $b = 68$	51.7	51.8	11
			33.9	34.0	02
			24.7	24.8	31
			19.7	20.0	40
			16.8	17.0	04
			14.0	14.3	34
			11.8	12.1	35
T–A12–E(*S*)10*	$\mathrm{Col_h}$	$a = 68.4$	59.2	59.2	10
			34.4	34.2	11
			23.0	22.4	21
			17.1	17.1	22
T–A(*S*)10*–E(*S*)10*	$\mathrm{Col_h}$	$a = 65.4$	56.9	56.6	10
			33.5	32.7	11
			20.6	21.4	21

whereas the complex with two chiral tails **T–A(*S*)10*–E(*S*)10*** forms a hexagonal arrangement.

Examination of the WAXS patterns showed that a high-angle halo was absent in all of the materials, apart from the diffuse maximum corresponding to the disordered aliphatic tails. This means that the correlations along the column in the mesophase are only short-range and there is no regular stacking distance. Nevertheless, on the basis of our previous studies,[36,49] the stacking distance in the complexes can be estimated as 3.3–4.0 Å, and this allowed us to estimate the density of the materials. It was found from these estimations that, as in previous studies, the number of molecules per unit cell, *Z*, is 2 for the hexagonal mesophases and 4 for the rectangular mesophases. This situation is consistent with the findings for previous complexes of this type.[36,49,50] The differences in the rectangular lattice constants between the non-chiral complex **T–A12–E12** and the chiral complex **T–A(*S*)10*–E12** might well be due to the existence of molecular tilting in the latter. Indeed, if the 1 : 3 complex tilts as a whole with respect to the column axis, the cross-section of the column must decrease as the cosine of the tilt angle. The consequence of the tilt is a larger value for the mean stacking distance, with an estimated value that evolves from about 3.5 Å for **T–A12–E12** to about 4 Å for the chiral counterparts. The hexagonal lattice constant of **T–A12–E(*S*)10*** and **T–A(*S*)10*–E(*S*)10*** is in agreement with the parameter found for the previously described complexes derived from all-azo V-shaped acids, and is consistent with an estimated value for the mean stacking distance close to 3.3 Å.[34]

Chiroptical properties

The optical activity of the mesophase was studied for all of the chiral complexes by Circular Dichroism (CD) experiments on thin films (*ca.* 300 nm to 1μm thickness measured by profilometry) prepared by casting a dichloromethane solution of the corresponding complex onto an amorphous quartz plate and subsequent thermal treatment as for X-ray experiments. For every complex, six CD spectra were recorded at six different orientations measured by rotating the sample cells by 60° around the light beam. The spectra were almost identical for all orientations of the sample, and this rules out the prevalence in the observed signals of possible linear dichroism effects due to the macroscopic orientation.[53] The supramolecular chirality of the mesophase was expected to originate from a helical disposition of the chromophores along the column. Indeed, all of the complexes bearing chiral tails gave spectra with bands corresponding to circular dichroism (Fig. 4), which can be accounted for by the transmission of the molecular chirality to the supramolecular organization of the mesophase. It was found that the presence of a single chiral tail in the V-shaped acid [*i.e.* **T–A12–E(*S*)10*** and **T–A(*S*)10*–E12**] is sufficient to induce CD-active columnar organizations, and this occurs regardless of the chemical nature of the rigid arm in which the chiral tail is located, either the azobenzene (**A**) group or the phenyl benzoate (**E**) group. In addition, the transmission of the molecular chirality to the supramolecular organization occurs regardless of the type of two-dimensional organization of the columnar mesophase (hexagonal or rectangular), indicating that the supramolecular chirality appears because of the intrinsic chirality of the complex, and does not depend on the arrangement of the columns.

It is worth noting the differences observed in the spectrum profiles of the different complexes. These differences are ascribed to the presence of two different chromophores, phenyl benzoate (**E**) and azobenzene (**A**) groups, with either chiral or achiral tails, randomly stacked along the columns.[50] The absorption maxima of these two units are around 280 nm and 360 nm, respectively. The CD spectra can show bands corresponding to the helical disposition of either identical chromophores or different chromophores, and this must increase the complexity of the corresponding CD curves. In any case, the optical activity of all the materials was maintained over time. The material **T–A12–E12** was not CD active under the same experimental conditions.

Chiral switching and chiral induction with CPL

The presence of azobenzene units in the V-shaped acids confers on the complexes the ability to respond to light as an external

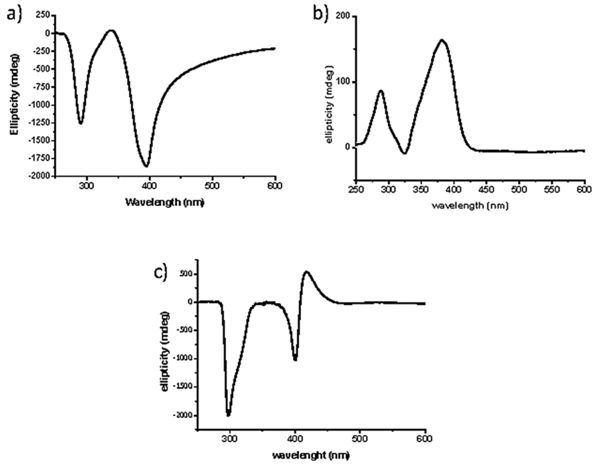


Fig. 4 CD spectra recorded at r.t. for thin films of (a) **T–A(*S*)10*–E12**, (b) **T–A12–E(*S*)10*** and (c) **T–A(*S*)10*–E(*S*)10***.

stimulus. Indeed, the photoinduced *E*/*Z* isomerisation of azobenzene is a well documented phenomenon, which proceeds reversibly upon irradiation with UV and visible light. The isomerization of azobenzene units proceeds with a large structural change that affects the dipole moment and geometry and gives rise to the Weigert effect,[54] responsible for the photo-orientation of azobenzene materials.[55] This effect can trigger macroscopic effects such as induction of linear birefringence and dichroism[56] or photomechanical responses[57] in azopolymers. Additionally, liquid crystals are especially interesting for these effects due to the intrinsic anisotropic organization of azobenzene groups.[58]

When light used is circularly polarized (CPL), chiral photoinduction has been described for azobenzene-containing liquid crystals.[56,59,60] In general, the transfer of the angular momentum from CPL to the liquid crystalline medium by means of the asymmetric photoisomerization of azobenzene groups is proposed.

In the particular case of columnar liquid crystals we previously described the possibility of inducing chirality into the columnar organizations for H-bonded complexes containing V-shaped acids consisting of two azobenzene arms.[36] The complexes reported herein contain only one azobenzene group per V-shaped acid.

Thin films of all the three chiral complexes were irradiated at room temperature with CPL (488 nm, Ar+ laser line, 20 mW cm^{-2}) and the chirality of the material followed the handedness of the light, either increasing the intensity of their natural CD signal or displaying the opposite sign (Fig. 5). Likewise, irradiation of the achiral material **T–A12–A12** with CPL gives rise to materials that show optical activity by CD spectroscopy, with signs corresponding to the handedness of the light used (Fig. 6), showing that the chirality of light is transmitted to the CD silent materials. Chiral photoswitching occurs in a reproducible manner for all the complexes, which give rise to CD signals of opposite sign for left and right-CPL irradiation. Furthermore, heating the materials at 80 °C for a relatively short time (20–60 s) led to the original situation (see ESI†), showing that it is not necessary to reach the isotropic state and destroy the columnar organization to eliminate the photoinduced effect.

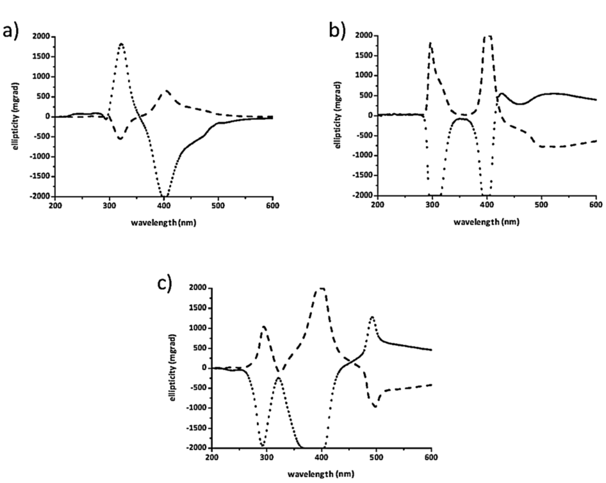


Fig. 5 CD spectra recorded for thin films of (a) **T–A(*S*)10*–E12**, (b) **T–A(*S*)10*–E(*S*)10*** after irradiation for 30 min; (c) **T–A12–E(*S*)10*** after irradiation for 60 min. Dotted line: after left-CPL irradiation; dashed line: after right-CPL irradiation.

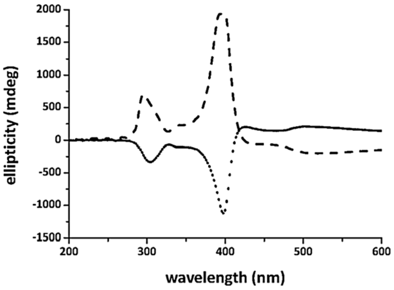


Fig. 6 CD spectra recorded at r.t. for a thin film of **T–A12–E12** irradiated for 30 min with left-CPL (dotted line) and with right-CPL (dashed line).

The transfer of chiral information from light to the materials was studied in all cases after 30 minutes irradiation in order to ensure that each material reached a photostationary situation (see ESI†). However, it was considered of interest to determine the time needed to achieve transmission of chiral information and thus examine the ability of the material to respond to the stimulus. The experiment was carried out on the achiral material **T–A12–E12** and it was observed that after only 30 seconds irradiation the material was optically active, as shown by the CD spectra (Fig. 7). Nevertheless, irradiation for 30 minutes gave rise to a signal that did not increase upon longer irradiation times.

An additional band at around 490 nm, which does not correspond to an absorption band in the UV spectra (see ESI†), was observed for films of **T–A12–E(*S*)10*** upon irradiation for 1 hour (Fig. 5c). Under these conditions, the intensity of the CD curves did not increase except the band at 490 nm. This type of band has been detected previously and reported as a Bragg band reflection in nematic azobenzene polymers[61,62] or nematic azodendrimers.[63] However, this band was not seen for smectic azobenzene polymers.[64] The origin of this band is unclear[59] but it could correspond to a higher order supramolecular organization, as in chiral nematic liquid crystals[65] or chiral nematic columnar liquid crystals,[66] with a periodic pitch approximately equivalent to the wavelength of the incident light. Nevertheless, it was not possible to demonstrate such type of organization in the present case.

Structural study of the films

The chirality induction and switching phenomena described above are based on columnar systems and it is proposed that

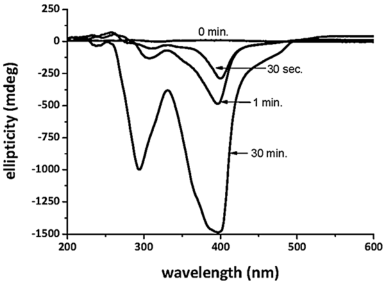


Fig. 7 CD spectra recorded at r.t. for a thin film of **T–A12–E12** before irradiation (solid line) and irradiated for 30 seconds, 1 min and 30 min (the film is different from that used for experiment in Fig. 6).

these are related to the changes in the handedness of the helical organization along the column. One of the objectives of the present study was to gain a deeper insight into the supramolecular organization in the thin films before and after the irradiation experiments. The surface of the film and the mesomorphic organization within the film were investigated by AFM and X-ray diffraction techniques, respectively.

AFM images were taken for cast films on amorphous quartz plates at room temperature, after thermal treatment, in tapping mode (Nanoscope IIIa, Veeco). The pictures on the left refer to topography, while the ones on the right show the amplitude signal (Fig. 8). The latter images are shown to emphasize steep changes in height. The AFM images recorded for the three complexes **T–A12–E12**, **T–A12–E(*S*)10*** and **T–A(*S*)10*–E(*S*)10*** show line patterns in which the gaps between lines are within the range of the cell parameters (*i.e.* intercolumnar distance) measured by X-ray diffraction (Table 2). The topographic relief observed can thus be related to either columns lying on the surface of the plate or, most probably, columns tilted with respect to the plate. Both situations can explain the observed AFM images. On comparing the surface images of all three complexes, it is worth noting the different organization of line-domains, which seems to be related to the chirality of the system. For the achiral complex, **T–A12–E12**, the columns seem to orient in large domains. In contrast, smaller domains with different orientations in the organization of the columns are seen when all tails in the complex are chiral, **T–A(*S*)10*–E(*S*)10***. In the case of **T–A12–E(*S*)10***, there are some zones that could be interpreted as being homeotropic regions in which columns lie probably perpendicular to the quartz plate.

AFM observations after CPL irradiation proved that the surface morphology of the thin films is not altered. AFM images of a thin film of **T–A12–E(*S*)10*** on a quartz plate are shown in Fig. 9 before CPL irradiation (Fig. 9a) and after 1 hour irradiation (Fig. 9b). It can be seen that the line pattern visualized on the surface is similar for both samples.

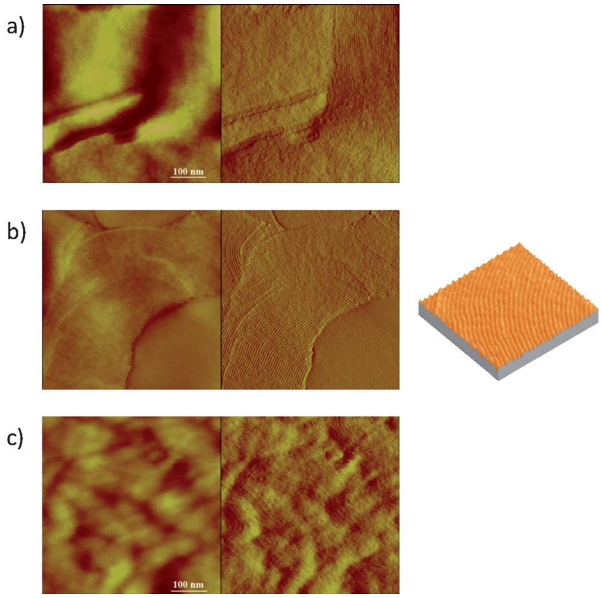


Fig. 8 AFM images of (a) **T–A12–E12**, (b) **T–A12–E(*S*)10***, and its 3D visualization; the homeotropic region is visible in the bottom right corner, and (c) **T–A(*S*)10*–E(*S*)10***. These films were deposited on a quartz plate.

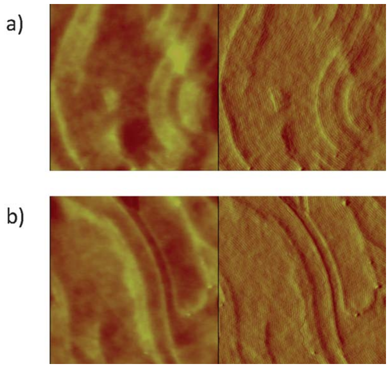


Fig. 9 AFM images of different zones of thin films of complex **T–A12–E(*S*)10*** deposited on quartz, before irradiation (a) and after 60 min irradiation (b).

Further information about the supramolecular organization within the film was obtained by X-ray diffraction experiments. X-ray diffractograms for thin films of the complexes **T–A12–E(*S*)10*** and **T–A(*S*)10*–E12** are shown in Fig. 10. These samples were chosen as representative examples of $\mathrm{Col_h}$ and $\mathrm{Col_r}$ organizations, respectively. The diffractograms are compared with the patterns registered for powder samples in capillaries, from which lattice parameters were measured (Table 2). As deduced by the coincidence of the two most intense maxima, it is clear that in

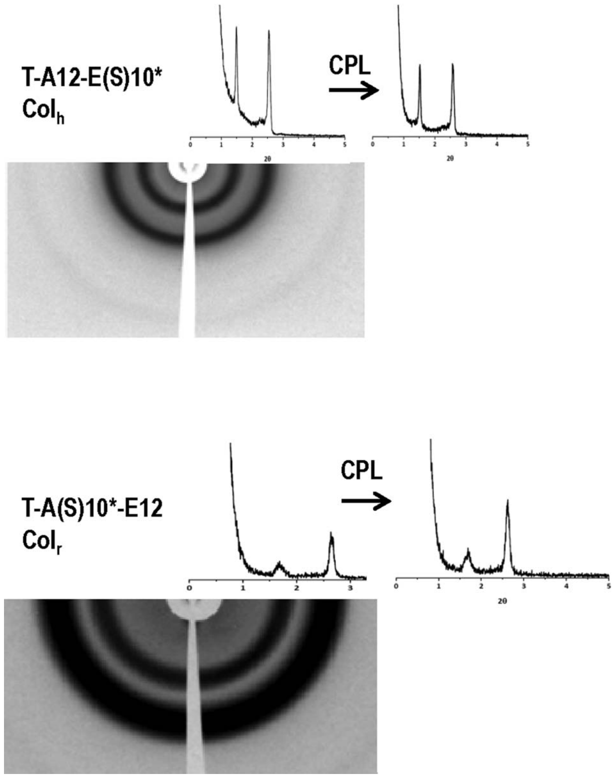


Fig. 10 XRD diffractograms (transmission and reflection) taken at room temperature before CPL irradiation and after irradiation of **T–A12–E(*S*)10*** and **T–A(*S*)10*–E12**.

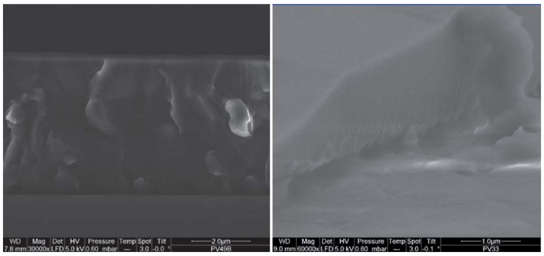


Fig. 11 SEM images (both on a quartz plate) of a cut region of **T–A12–E12** film (left), and (right) a cut of a film **T–A12–E(*S*)10***.

all situations, *i.e.* powder samples and thin films before and after CPL irradiation, the columnar mesomorphic organization remains mainly unaltered.

As for additional information on the structure of the mesophase, sections of freeze-fractured films were imaged using environmental scanning microscopy. A regular organization was not deduced from the images taken from the achiral material (Fig. 11, left). In contrast, for the chiral complex **T–A12–E(*S*)10*** a fibre-like structure was detected, which could correspond to the flat region observed by AFM and could be interpreted as columns with homeotropic alignment, *i.e.* perpendicular to the substrate.

Conclusions

Rectangular and hexagonal columnar mesophases have been obtained from supramolecular assemblies consisting of H-bonded synthons (a melamine derivative and three V-shaped acid molecules) that self-organize into columns. When stereogenic centres are present in the V-shaped molecules, chiral transfer into the columns occurs. The presence of photoaddressable azobenzene units in the arms of the acids makes it possible to induce chirality in chiral and non-chiral mesophases by CPL irradiation. It is deduced that decreasing the concentration of azobenzene groups in the columnar architecture to 50%, with respect to previous studies, did not hamper the photoresponse of the materials and not only photocontrol but also photoinduction of supramolecular chirality was achieved. In addition, the induced chiral information is stable for a long time. The presence of ester bonds in the arms of the V-shaped acids makes these materials easier to process and more difficult to crystallize. A structural study of these compounds (CD, XRD in powder and film and AFM) reveals that after irradiation there are no changes in the mesophase structures, meaning that changes in chirality after CPL irradiation may be due to a small change in the disposition of the tilted arms of the V-shaped acids attached to the melamine centres rather than to modifications of the corresponding supramolecular organizations.

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