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Chiral Photoinduction

Light-Driven Supramolecular Chirality in Propeller-Like Hydrogen-Bonded Complexes That Show Columnar Mesomorphism**

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Nature offers many beautiful examples of biological systems whose unique functionalities arise from a well-defined helical organization as the expression of supramolecular chirality.[1] Research on artificial helical architectures[2] that can endow a material with unique properties has found that columnar liquid crystals[3] are an excellent synthetic building block.[4,5] These systems allow helical organizations to be built with amplified supramolecular chirality through different types of noncovalent interactions, such as π stacking, hydrogen bonding, and solvophobic and ionic interactions, which permit molecular chirality to be transferred to the supramolecular organization in the mesophase.[6] However, the transfer of chirality by an external stimulus such as light remains unexplored in these systems.

In a recent publication,[7a] we described supramolecular complexes in which nonmesogenic V-shaped acids show an ability to form mesogenic phases upon formation of a tetrameric complex around a melamine derivative.[7] This unusual mesogenic core, which was interpreted as a propeller-like structure, promotes the appearance of well-defined rectangular columnar mesophases by combining the π-stacking tendency of the melamine derivative and the lateral interaction between V-shaped molecules. Moreover, on the basis of X-ray diffraction and circular dichroism (CD) measurements on chiral complexes, we proposed a model that is compatible with the existence of supramolecular chirality arising from an inherent helical stacking of propeller-like supramolecules. Given the helical stacking of these hydrogen-bonded complexes, our next challenge is to control and induce a supramolecular chiral response of the supramolecular organization by using light as an external stimulus.

The isomerization of azobenzene upon irradiation with light is a well-documented phenomenon and the possibilities that this reaction offers for the control of self-assembly in liquid crystals have been recognized.[8] The use of circularly polarized light (CPL) as the irradiation source has led to enantiomeric excess values in two chiral domains in the Bx phase of bent-core molecules.[9] Moreover, supramolecular chirality photoinduced by CPL has been reported in azopolymers[10] and in main-chain polymeric liquid-crystal systems doped with azobenzene-containing W-shaped molecules.[11] However, attempts to induce supramolecular chirality in columnar mesophases formed by azobenzene-containing mesogens have not been described to date. We demonstrate herein the possibility of controlling the supramolecular chirality of a helical stack of propeller-like complexes using an external chiral stimulus such as CPL. This control must involve not only the modification of an existing chirality, which is transferred from the molecular chirality, but also the induction of supramolecular chirality within the columnar mesophase consisting of achiral mesogens.

Hydrogen-bonded complexes that incorporate azobenzene groups in each of the arms of the V-shaped acids were prepared following an approach developed in our previous work (see Scheme 1 and the Supporting Information). The presence of the photoaddressable azobenzene group should allow CPL to be used as the external stimulus to induce or switch the supramolecular chirality of the columnar liquid crystalline organization.

The formation of the tetrameric complex was studied by IR and NMR spectroscopy (see the Supporting Information). Assuming that there must be fast exchange between the complex and its components in solution, strong evidence of hydrogen-bonding interactions between the triazine and acid molecules was found in the solution ^{1}H and ^{13}C NMR spectra of the complexes.

The ^{13}C NMR spectra of solid samples were particularly revealing and helped to confirm the complex stoichiometry. The ^{13}C cross polarization (CP) magic-angle spinning (MAS) NMR spectra of several mixtures of melamine **T** and the acid **A(*S*)10*** in different proportions are shown in Figure 1. It is especially significant that the peak corresponding to the carbonyl group of the acid itself (**A(*S*)10***) does not appear in the spectrum of the mixture **T-A(*S*)10*** (1:3), thus indicating that all the acid present must be complexed to the melamine derivative. In order to provide further evidence to support this conclusion, we compared the ^{13}C NMR spectrum of the complex **T-A(*S*)10*** (1:3) with the spectra of mixtures containing an excess of acid, a situation that ensures the presence of some acid that is not complexed with **T** (**T:A(*S*)10*** proportions of 1:3.5 and 1:4). It is evident from Figure 1 that as soon as free acid is present the original

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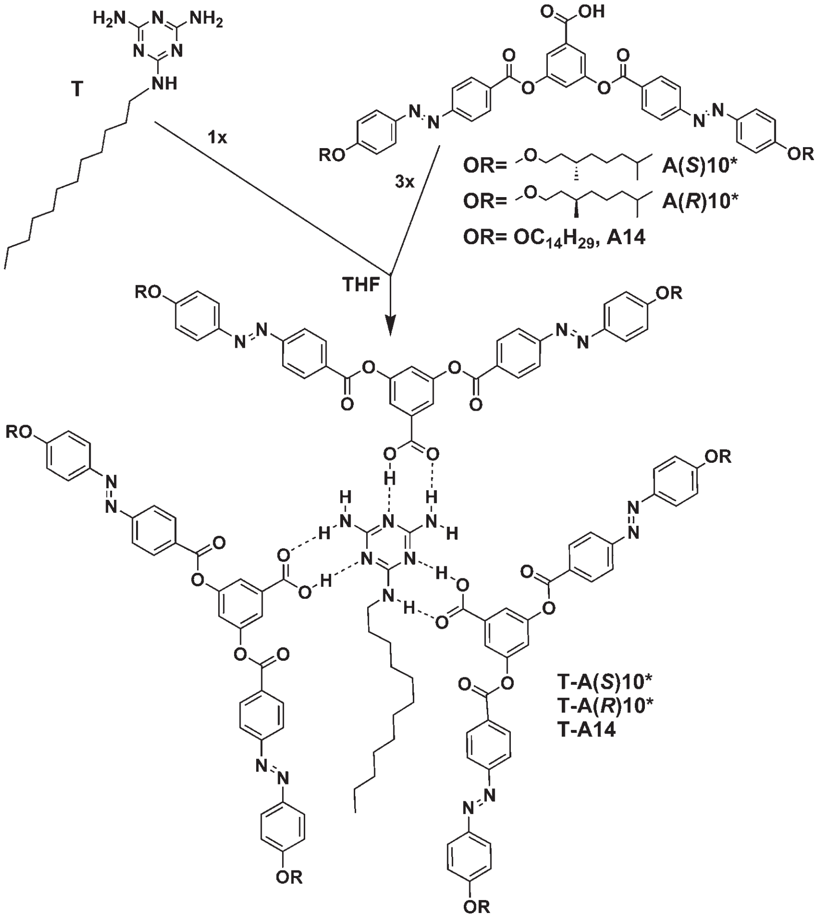

Scheme 1. Synthesis of hydrogen-bonded complexes that incorporate azobenzene groups in each of the arms of the V-shaped acid.

carbonyl carbon peak of the acid is visible in the spectrum. Furthermore, the signals for some carbon atoms of both the acid and the melamine units are significantly shifted upon complexation. The upfield shift of the signals for the carbon atoms within the *N*-alkyl tail of **T** upon complexation is worthy of note. This shift is also visible in solution experiments (see the Supporting Information), and must be associated with the strong influence that the aromatic rings of the acid units have on the carbon atoms of the tail. These NMR experiments in the solid state support the idea that a mixture of one part of **T** and three parts of the V-shaped acid provides mostly the tetrameric hydrogen-bonded complex **T-A(S)10*** (1:3), which is stable in the solid state at room temperature.

The thermal behavior of the materials was studied by the commonly used techniques polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). The melamine derivative **T** is mesomorphic over a very small temperature range. It shows a smectic A mesophase on cooling from the isotropic liquid to a temperature (38 °C) below the melting point of the crystal (103 °C).[7a] The acids used to prepare the complexes are *not* mesogenic (melting points: 191 °C for **A(S)10*** and **A(R)10***; 170 °C for **A14**). In contrast, both chiral and achiral complexes show textures that indicate mesomorphic behavior, which could be suggestive of columnar arrangements (see the photomicrographs in the Supporting Information). DSC revealed only one peak in the cooling process, which corresponds to the transition from the isotropic liquid to the mesophase. Additionally, a glass transition was detected at 51 °C for the chiral complexes (see the thermograms in the Supporting Information). The thermal data are collected in Table 1.

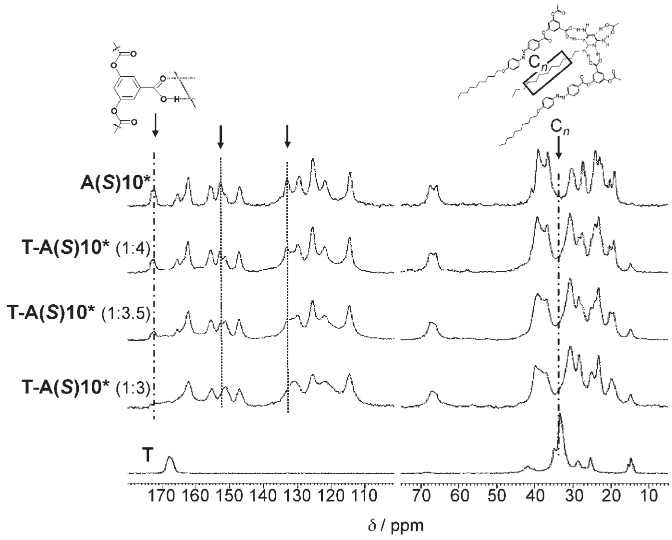

Figure 1. ^{13}C CPMAS NMR spectra of **T**, **A(S)10***, and mixtures of **T** and **A(S)10*** with different proportions of acid. Arrows indicate the most meaningful shift differences indicating the presence or absence of free acid.

Table 1: Phase transition temperatures (T) and enthalpies (ΔH) of the complexes.[a]

Compound	Thermal properties					
	Phase	T [°C]	ΔH [kJ mol^{-1}]	Phase	T [°C]	Phase
T-A(S)10*	I	123	6.8	$\mathrm{Col_h}$	51	g
T-A(R)10*	I	123	6.8	$\mathrm{Col_h}$	51	g
T-A14	I	134	6.1	$\mathrm{Col_r}$		

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

The most outstanding result concerning the thermal behavior found in the complexes is in the fact that the combination of nonmesogenic molecular components leads to mesogenic complexes that show mesomorphism over broad temperature ranges. Moreover, the mesophase order achieved on cooling from the isotropic liquid is stable at room temperature for long periods of time in all cases, as determined by POM and DSC.

Confirmation of the nature of both types of mesophase (see Table 1) was achieved by X-ray diffraction experiments at room temperature, which also confirmed the stability of the mesophase order at this temperature. The X-ray patterns of one of the enantiomers of the chiral complex **T-A(*S*)10*** are shown in Figure 2 a. The small-angle X-ray scattering (SAXS) pattern shows a number of maxima that are consistent with a hexagonal lattice. The lattice parameter of the hexagonal columnar (Col$_h$) phase was calculated from these maxima. The wide-angle X-ray scattering (WAXS) pattern (see the Supporting Information) shows two diffuse maxima. The inner maximum corresponds to the "molten" aliphatic chains and is usually observed in liquid-crystalline systems, whereas the outer maximum corresponds to the average stacking distance, for which a value of 3.3 Å was calculated. This distance allowed us to estimate the density of the material. In the hexagonal mesophase, the number of tetrameric complexes per unit cell (Z) is 2, which is not usual in such a mesophase.

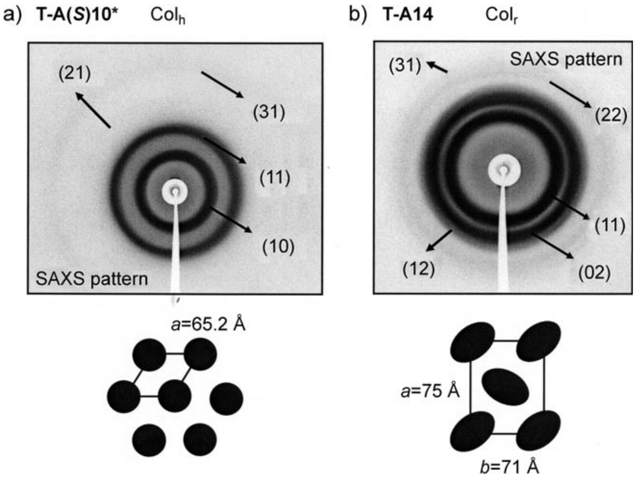

Figure 2. SAXS patterns with indexing of a) the Col$_h$ mesophase of complex **T-A(*S*)10***, where *a* is the lattice parameter of the hexagonal arrangement of the chiral complex, and b) the Col$_r$ mesophase of complex **T-A14**, where *a* and *b* are the lattice parameters of the rectangular arrangement of the achiral complex. Both patterns were recorded at room temperature after cooling from the isotropic liquid.

The X-ray patterns of complex **T-A14**, whose mesophase was proposed to be rectangular columnar (Col$_r$) by POM, are shown in Figure 2 b and in the Supporting Information. The lattice parameters *a* and *b* of the rectangular arrangement were calculated from the diffraction maxima observed in the SAXS pattern. Classically, a Col$_r$ phase has two columns per unit cell, one of which is in the center and the other in the corner of the unit cell. However, in this case, an unusual value of $Z = 4$, that is, four tetrameric complexes per unit cell, was calculated from density estimations.[12] These unusual Z values ($Z = 2$ for the hexagonal mesophase and $Z = 4$ for the rectangular one) are consistent with a bidimensional arrangement in which two columns must be located at each node of the unit cell. Further information on how two columns can be accommodated in each node is therefore required. Despite this fact, on the basis of the inherent helical arrangement proposed for this type of complex in our previous study[7a] we could envisage a supercoiled structure consisting of a double helix.[13]

On the basis of the helical stacking proposed for these complexes, we assessed the optical activity of the mesophases of the chiral complexes by CD.[14] These materials do not show any CD signal indicative of optical activity in the isotropic liquid. However, a strong signal, which was identified as an exciton splitting, appeared on cooling to room temperature (solid line in Figure 3). This optical activity must come from a chiral environment that corresponds to the mesophase arrangement, as confirmed by X-ray studies at room temperature. The appearance of an exciton coupling at the maximum absorption wavelength of the chromophore (azobenzene group) can be assigned to a helical disposition of at least two chromophores,[15] which is consistent with a helical stacking. Moreover, the handedness of this helical arrangement is biased towards a given chiral sense that is determined by the configuration of the stereogenic center. Thus, the CD spectrum of the complex formed by the enantiomeric acid presents an opposite sign (see the Supporting Information), which indicates an opposite helical handedness.

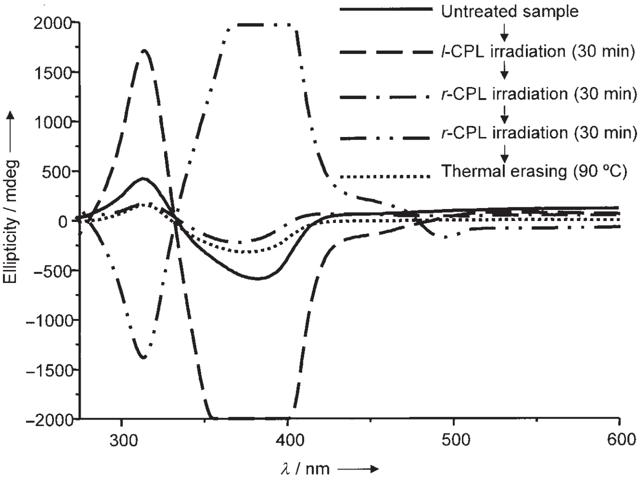

Figure 3. CD spectra corresponding to successive irradiation of a cast film of complex **T-(*R*)A10*** with *l*-CPL and *r*-CPL at room temperature. The irradiation times are given with respect to the previous irradiation step.

In an effort to fulfill our objective, we undertook experiments aimed at controlling and tuning the chirality of the mesophase by irradiating the columnar-ordered material with CPL. The CD spectra corresponding to different irradiation processes of the same chiral material (**T-(*R*)A10***) are shown in Figure 3. The sample was irradiated with left-handed CPL (*l*-CPL) for 30 min at room temperature. The resulting CD spectrum has the same shape as the original one but with a considerably 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 (i.e., right-handed) CPL for

30 min caused a decrease in the CD intensity almost 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 an additional 30 min 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 a few seconds. It was not necessary to heat the material above the clearing point. These experiments demonstrate that it is possible to control and tune the supramolecular chirality of a columnar mesophase as if the proposed helical stacking were able to wind and unwind following the handedness of the incident CPL through the photoisomerization of the azobenzene groups.

The next challenge was to assess whether the chiral information in the CPL could be transferred to the columnar arrangement of achiral mesogens. We therefore performed irradiation experiments with the $\mathrm{Col_r}$ mesophase of the achiral complex **T-A14**. This complex clearly does not show optical activity in the "as-prepared" cast film (Figure 4). Irradiation with *l*-CPL for 30 min at room temperature induced strong signals in the CD spectrum of the film. Furthermore, the resulting CD spectrum has the same shape as that observed for the $\mathrm{Col_h}$ mesophase of the chiral complexes. This could mean that the proposed helical stacking is 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 to 90 °C, and the CD spectrum with the opposite sign was obtained when the film was irradiated with the orthogonal CPL (*r*-CPL).

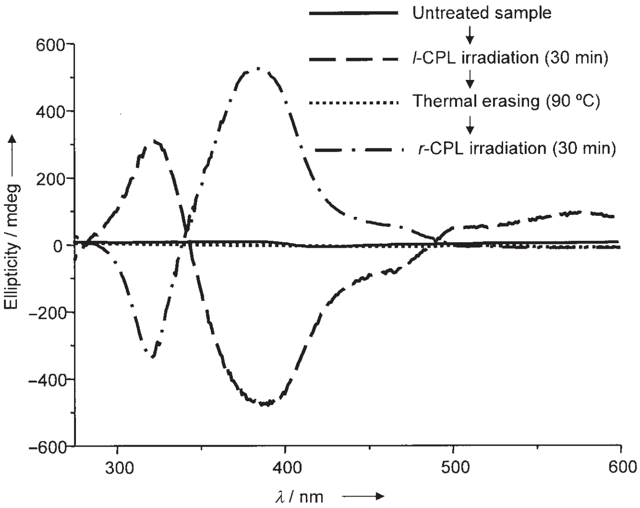

Figure 4. CD spectra corresponding to a *l*-CPL irradiation/thermal erasing/*r*-CPL irradiation cycle for a cast film of complex **T-A14**. The irradiation times are given with respect to the previous irradiation step.

In summary, chiral columnar mesophases have been obtained from hydrogen-bonded tetrameric complexes of a melamine derivative and nonmesomorphic V-shaped acids. Chirality transfer from the molecule to the mesophase occurs when stereogenic centers are present in the acid counterparts. Furthermore, the chiral information of CPL is transferred to the columnar organization through photochromic azobenzene groups. This process enables reversible switching of the supramolecular chirality of the columnar arrangement upon illumination with CPL of the opposite handedness. Furthermore, achiral columnar systems can be biased towards a chiral supramolecular organization by illumination with the corresponding CPL. The chiral photoresponse achieved upon illumination is stable for long periods of time. The results described herein make these systems promising as supramolecular chiroptical switches[16,17] for optical information storage. Control of the chiroptical response of materials with irradiation time is the subject of current research. Further work should be devoted to gaining a deeper understanding of the relationship between the chemical composition of the mesogenic entities and the chiral photoinduction.

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