Supramolecular Chirality

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Orthogonal Action of Noncovalent Interactions for Photoresponsive Chiral Columnar Assemblies**

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Chiral supramolecular aggregation to give helical architectures appears to be a valuable strategy to attain functional materials under structural control.[1,2] An attractive aspect regarding helically structured materials is the possibility of implementing dynamic responses to external stimuli, including the amplification of chirality,[3] photodriven supramolecular chirality,[4] and ion sensing.[5]

Liquid crystals have been shown as useful materials for the creation and stabilization of dynamic helical architectures based on noncovalent interactions. Indeed, the exploitation of the selectivity and directionality of hydrogen bonds and π stacking within columnar mesophases is particularly useful for this purpose, since it allows the spontaneous assembly of mesogens to give well-defined helical architectures within two-dimensional mesomorphic arrangements.[6] The key issue is the design of the appropriate molecular building blocks that give rise to such mesomorphic arrangements.

In this respect, supramolecular macrocycles[7] have received growing interest because of the possibility of achieving functional complex structures, such as tubular aggregates in solvents[8] or self-organized columnar mesomorphic arrangements.[9] Some of these assemblies have been reported to adopt chiral helical architectures originating from chiral building blocks.[5a,10] Since the first report on "rosette" systems,[11] many examples of these supramolecular macrocycles have been described based on the use of self-complementary species, such as melamine and cyanuric acid derivatives.[12]

Herein, we combine the two systems mentioned above, namely columnar liquid crystals and supramolecular macrocycles, to attain helical supramolecular architectures implemented with dynamic functionality. Previous results of our research showed that nonmesogenic carboxylic acids endowed with a rigid V shape (**A** in Figure 1a) formed H-bonded complexes with a melamine derivative (**T** in Figure 1a) in a 3:1 proportion. These complexes self-organized into helical columnar mesomorphic systems, the chirality of which was controlled by chiral building blocks and/or circularly polarized light (CPL).[13]

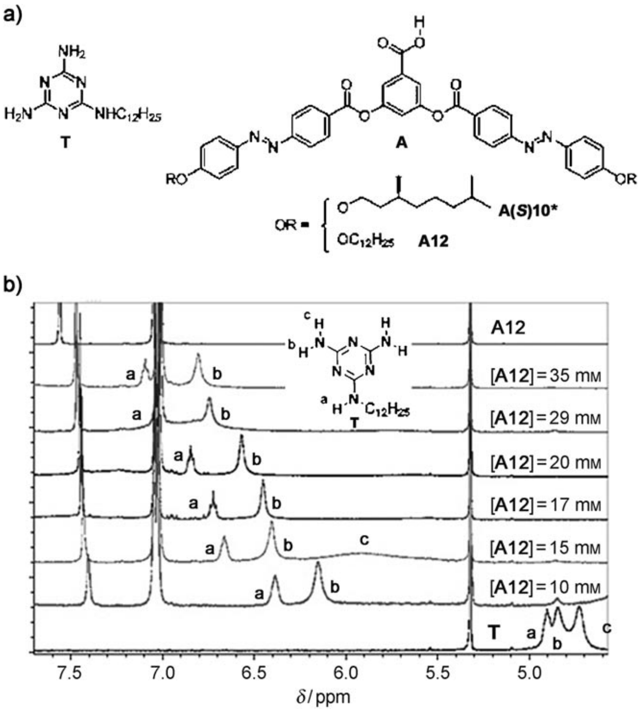

Figure 1. a) Chemical structures of the melamine derivative **T** and V-shaped acids **A12** and **A(S)10***, used to build the supramolecular complexes. b) ^{1}H NMR spectra obtained for different concentrations of the acid **A12**, while maintaining constant the concentration of **T** (9.2 mM in CD_2Cl_2). Peaks a–c represent the three types of NH proton (H-bonded or non-H-bonded) that can be distinguished in the spectra.

In the present study, our attention is focused on the versatility shown by these two supramolecular units to build functional columnar systems, and on how we can make use of it to attain novel dynamic helical architectures based on supramolecular macrocycles through an easy preparation process. The idea is based on the ability of melamine derivatives to self-associate into rosettes, which in turn can self-organize into columnar systems. The challenge of our melamine/V-shaped acid binary system is to achieve control of the competition between the establishment of two different

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H-bonding interactions, that is, melamine–melamine or melamine–acid.

The strategy pursued is the formation of complexes of the V-shaped acids and the melamine in a 1:1 ratio, which should lead the rigid acid counterpart to play the role of the bulky peripheral group that favors the formation of rosettes versus ribbonlike supramolecular structures.[14] Moreover, by taking advantage of the strong lateral self-interactions between V-shaped rigid mesogens,[15] these rosettes can yield twisted columnar assemblies with a tubular shape, the chirality of which can be controlled by chiral building blocks and/or CPL. Furthermore, ion–dipole interactions can be established along the helical architecture, which should open new possibilities for these systems.

Complexes between **T** and **A** in a 1:1 ratio were prepared from CH_2Cl_2 solution by slowly removing the solvent under mechanical stirring. The equilibrium established in solution between these compounds and their supramolecular associations was studied by ^1H NMR spectroscopy. Titration experiments in CD_2Cl_2 showed that all NH proton signals of the melamine derivative **T** are shifted downfield upon increasing the proportion of the V-shaped acid in the solution (Figure 1 b). The so-called continuous variation method yielded Job's plots with a maximum at $\chi_A = 0.5$ for these NH protons, a finding that clearly indicates a 1:1 stoichiometry for the **T**–**A** association in this solvent. Accordingly, a significant binding constant of 335 L mol^{-1} was calculated by nonlinear regression analysis (see the Supporting Information).[16]

On removing the solvent, the materials prepared (**T-A(*S*)10*** and **T-A12**) appeared homogeneous to the eye and showed textures consistent with columnar mesomorphism by polarized optical microscopy (POM; see the Supporting Information). The transition temperatures and associated enthalpy values as well as mesophase lattice parameters are presented in Table 1.

According to these results, columnar mesomorphic materials consisting of **T-A** complexes in a 1:1 ratio were obtained from nonmesogenic supramolecular units. Nevertheless, the intriguing question about these results concerns the structure of the supramolecular entity responsible for the formation of the columnar mesomorphic arrangement. In line with the stoichiometry found in the NMR experiments, the complex consisting of a molecule of melamine **T**, H-bonded to a molecule of acid **A** (Figure 2 a), was taken as the simplest building block in the mesomorphic organization.

Table 1: Phase transition temperatures (*T*) and enthalpies (Δ*H*) for the complexes.[a] Lattice parameters were measured in the mesophase by X-ray diffraction at room temperature.

Compound	Thermal properties				Lattice parameters [Å]
	Phase	*T* [°C]	Δ*H* [kJ mol^{-1}]	Phase	
T-A(*S*)10*	I	98.2	3.1	Col$_h$	*a* = 74.5
T-A12	I	114.7	3.2	Col$_h$	*a* = 79.4 *h* = 3.35
T-A(*S*)10*-LiTf	I	151.9	7.9	Col$_h$	*a* = 70.7 *h* = 3.5
T-A12-LiTf	I	147.1	10.1	Col$_h$	*a* = 97.6 *h* = 3.35

[a] Transition temperatures are given for the cooling process at 10°C min^{-1} scans. I = isotropic liquid, Col$_h$ = hexagonal columnar mesophase, LiTf = lithium triflate.

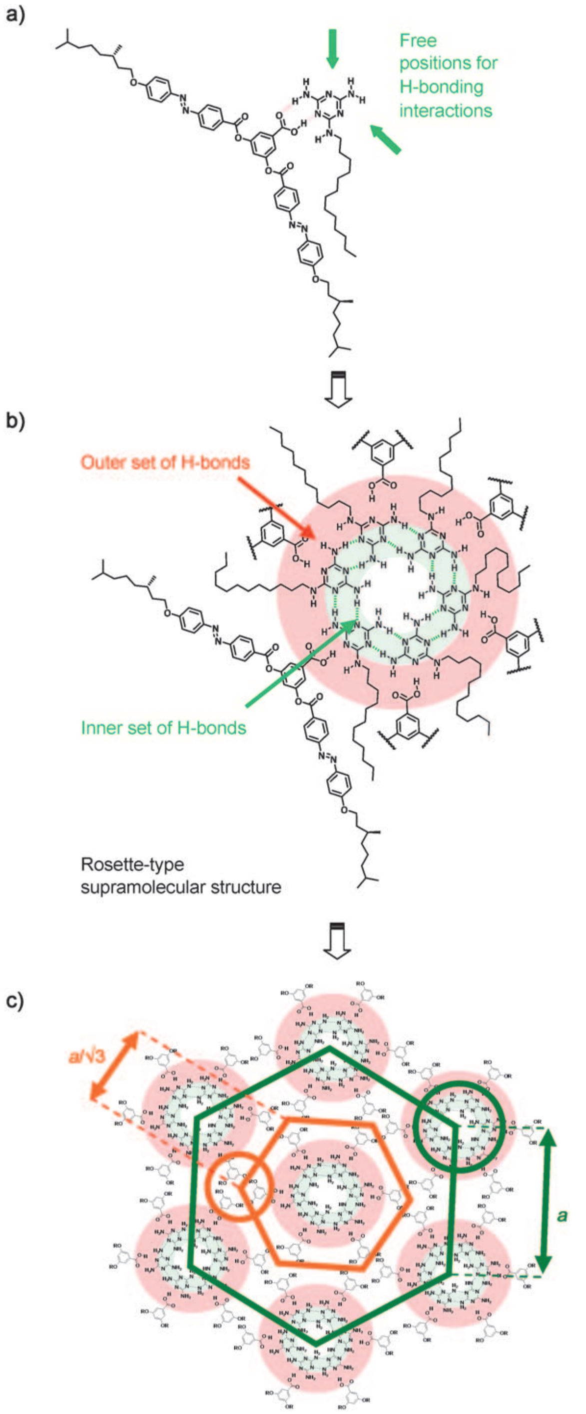

Figure 2. Hierarchical self-assembly process proposed for the formation of the mesophase in these systems. a) Structure of the **T-A** [1:1] complex. b) Rosette structure of the macrocycle formed by six **T-A** [1:1] complexes. The two types of H bond, that is, melamine–melamine and melamine–acid, are shown in different colors. c) Hexagonal two-dimensional packing (green hexagon) in the mesophase. Each node of the lattice is formed by a rosette. Three acids of contiguous rosettes coincide in the corners of a hexagonal sublattice (orange hexagon). -OR represents the azobenzene arms of the V-shaped acids.

The values of the lattice parameters, estimated from XRD studies, can be used to deduce the number Z of these [1:1] complexes per two-dimensional unit cell in the $\mathrm{Col_h}$ mesophase on the basis of the packing density (see the Supporting Information). For both **T-A12** and **T-A(*S*)10***, reasonable density values of about $0.8\,\mathrm{g\,cm^{-3}}$ were obtained on the assumption that there are six **T-A** [1:1] complexes per unit cell ($Z=6$).

The value $Z=6$ means that, for both materials, there are six melamine derivatives and six V-shaped acids in each node of the hexagonal lattice. In analogy to other similar structures described in the literature,[9b] it can be proposed that these **T-A** [1:1] complexes are able to self-associate through the free H-bonding sites remaining in their corresponding melamine component (Figure 2a). These interactions generate rosette-like supramolecular structures (Figure 2b), each of which contains six melamine molecules and six V-shaped acid molecules assembled in such a way that two sets of H-bonding interactions are formed.[17] In this organization, an inner set of melamine–melamine interactions is surrounded by a set of melamine–acid H-bonding interactions. In the proposed structure, the resulting columns consist of a central core containing the stacked hexameric melamine macrocycles, each surrounded by six V-shaped acids, organized in a hexagonal lattice (Figure 2c).

Additionally, it can be seen in the X-ray patterns (Figure 3a,b) that the reflection (11) is unusually strong. The most intense ring is usually the fundamental reflection (10). This difference can be interpreted as being the result of a combination of two effects: 1) there is a hole in the center of the rosette, the diameter of which is estimated to be between 4 and 5 Å; and 2) there is a strong modulation of the electronic density with a period $\sqrt{3}$ times shorter than the (10) spacing. The latter is consistent with the existence of a hexagonal sublattice within the hexagonal lattice. From Figure 2c it is apparent that the electronic density distribution deduced from the X-ray patterns corresponds to groups of three acids located at the corners of the hexagon defined by the sublattice, with a sublattice constant of $a/\sqrt{3}$.

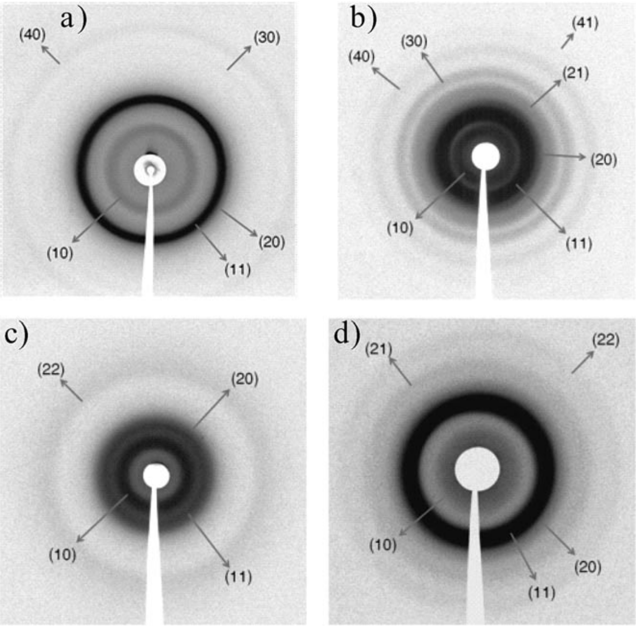

Figure 3. Small-angle X-ray scattering (SAXS) patterns of the mesophase of the complexes **T-A(S)10*** (a), **T-A12** (b), **T-A(S)10*-LiTf** (c), and **T-A12-LiTf** (d) at room temperature after cooling from the isotropic liquid.

In line with this model, it can be proposed that the assembly process that leads to the formation of the columnar mesophase is hierarchical in nature, and involves the formation of H-bonded acid–melamine [1:1] complexes that self-associate into rosettes. These rosettes stack to give well-organized columnar mesophases, in which the interior of the columns has electron-rich and electron-poor atoms that make the assembly susceptible to hosting small ions, stabilized by ion–dipole interactions. Indeed, the incorporation of lithium triflate (LiTf) in the ratio **T**/**A**/LiTf 1:1:1/6 causes changes in the mesomorphic behavior. POM observations showed textures (see the Supporting Information) similar to those observed for the material without LiTf. However, the I–$\mathrm{Col_h}$ temperatures and their corresponding enthalpy values are higher than those of the corresponding salt-free systems (Table 1), a finding that indicates stabilization of the columnar architecture. The existence of ion–dipole interactions that reinforce the π stacking of the rosette complexes could account for this behavior.

Experimental confirmation of this proposal was provided by the X-ray diffraction pattern of **T-A(*S*)10*-LiTf**. The pattern showed an additional large-angle scattering halo (see the Supporting Information), which corresponds to a distance of 3.5 Å (Table 1) and which is assigned to a regular stacking of the disks. The fact that the hexagonal lattice constant, a, decreases after the incorporation of the salt may probably be related to some tilt of the melamine hexamers, a change that would reduce the cross section of the column. The density deduced for this LiTf-containing material, assuming $Z=6$, is $0.9\,\mathrm{g\,cm^{-3}}$. Thus, the columnar arrangement is the same as in the salt-free material, although the packing is slightly denser. In addition, the innermost ring, that is, the (10) reflection (Figure 3c), is more intense than that of the salt-free complex. This result is consistent with a density increase in the core of the columns as a consequence of the tilt of the rosettes (the same mass is accommodated in a narrower cross section).

In contrast, the supramolecular organization of the columnar mesophase is probably different in **T-A12-LiTf**, as deduced from the noticeable increase in the hexagonal lattice constant ($a=97.6$ Å). The outermost halo is still observed and corresponds to the same value of 3.35 Å. However, the lattice parameter a of 97.6 Å is not consistent with the rosette model proposed above. In fact, the Z value deduced for this material is 10. A possible structural model to account for this situation is a ribbonlike supramolecular structure of H-bonded melamines (each of which is complexed to one acid molecule), which may combine regular stacking between melamine units and a significantly larger lattice parameter. This ribbonlike unit would adopt a helical arrangement, which accommodates the ions.

As for the salt-free complexes, the X-ray pattern in Figure 3d shows a very weak maximum for the (10) reflection, thus suggesting a low electronic density at the nodes of the two-dimensional hexagonal lattice, and a strong (11) maximum, which can be accounted for by the disposition of the acid counterparts in the outer part of the column. The formation of a continuous ribbonlike structure in this complex upon the incorporation of LiTf is supported by the fact that it forms gels in dichloromethane (see the Supporting Information).

In both salt-free and salt-containing supramolecular organizations, efficient columnar assembly arises from π interactions between the stacked melamine units self-associated either in rosettes (**T-A12**, **T-A(*S*)10***, and **T-A(*S*)10*-LiTf**) or in helical ribbons (**T-A12-LiTf**). In this situation, the surrounding V-shaped molecules can be tilted with respect to the plane perpendicular to the column axis, to avoid steric hindrance between their long rodlike arms and to optimize space filling. This disposition favors an inherent helical arrangement along the column. For the chiral complexes **T-A(*S*)10*** and **T-A(*S*)10*-LiTf**, this kind of stacking generates respective systems that show superstructural chirality, as revealed by CD (Figure 4a and b, solid lines)[18] and vibrational CD (VCD; see the Supporting Information) spectra, which suggest the formation of a helical stacking that strongly involves the V-shaped acids. For the complexes with nonchiral acids, the two helical senses should coexist in the same proportion, thus yielding CD-silent materials (Figure 4c and d, solid lines).

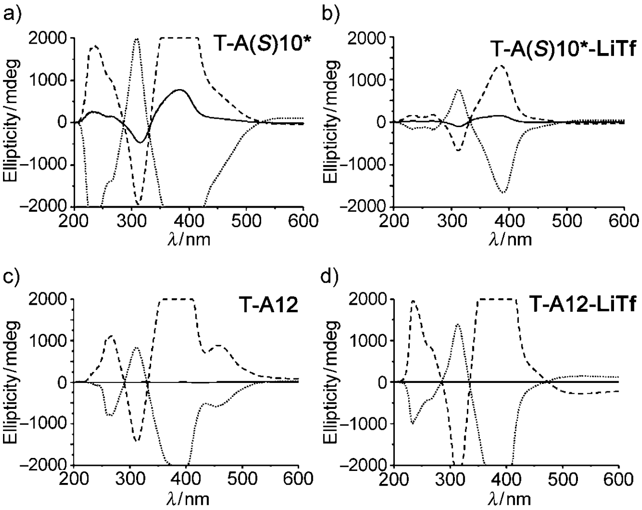

Figure 4. CD spectra of cast films of **T-A12**, **T-A12-LiTf**, **T-A(*S*)10***, and **T-A(*S*)10*-LiTf** recorded at room temperature as fresh samples (——), and after irradiation with a 488 nm Ar$^+$ laser with left-handed CPL (•••••) and right-handed CPL (-----). The ellipticity measured strongly depended on the cell thickness, which was smaller for the complex **T-A(*S*)10*-LiTf**.

Subsequent experiments on the photomodulation and photoinduction of supramolecular chirality were based on this proposed helical model. Accordingly, illumination of the chiral system **T-A(*S*)10*** with CPL led to either an increased CD signal or the opposite sign depending on the handedness of the CPL used (Figure 4a,b). Similar behavior was found for the architecture adopted by **T-A(*S*)10*-LiTf**. The sign of the induced CD, which corresponds to absorption bands in the UV/Vis spectra (see the Supporting Information), is dependent on the CPL sign, and this indicates the possibility of external modulation of the supramolecular chirality. Furthermore, the original CD spectra of both systems can be recovered by heating at 90 °C for 5 seconds. This means that it is not necessary to destroy the columnar organization (see Table 1) to erase the chiral information recorded by irradiation.

Finally, it was possible to transfer the chirality of CPL to the achiral systems. Both systems, the rosette-type association, **T-A12**, and the proposed helical ribbonlike H-bonded organization, **T-A12-LiTf**, show intense CD bands (Figure 4c and d) upon irradiation with CPL, thus indicating the induction of chirality into the supramolecular systems. On irradiation with light of the opposite handedness, the CD shows the opposite sign, which indicates that the supramolecular chirality of the mesophase can be inverted by the external chiral radiation. The chiral photoresponse achieved upon illumination is stable for long periods of time.

In summary, we have demonstrated the hierarchical self-assembly of simple nonmesogenic building blocks into hexagonal columnar mesophases. During the hierarchical process, the orthogonal action of different noncovalent interactions takes place. Indeed, two types of H-bonding interaction, melamine–melamine and melamine–acid, operate in the plane of the macrocycle to form a rosettelike stacking unit, whereas π–π interactions are mainly active in the direction perpendicular to the rosette plane. These interactions account for the formation of the columns that organize within the Col$_h$ mesophase. Furthermore, it is shown that these columns can accommodate the ions of a salt such as lithium triflate after small architectural modifications, which involve the formation of columns with long-range stacking order.

Our interpretation of the observed structural changes relies on the influence of the smallest Li$^+$ ions. Ion–dipole interactions between the N atoms of the triazine ring and Li$^+$ are proposed to occur, and these allow the incorporation of Li$^+$ ions most likely sandwiched between rosettes. For the chiral complex **T-A(*S*)10***, which does not show a regular stacking distance, the inclusion of Li$^+$ cations in the proposed way compels the rosettes to get closer along the column. Complex **T-A12**, which shows a regular stacking distance, also accommodates the Li$^+$ cations without disrupting the columnar mesomorphic order.

With regard to our proposal for the formation of inherent helical structures along the column, it is shown that this self-assembly process leads to functional materials, from simple building blocks, which are capable of showing dynamic supramolecular chirality and working as chirooptical switches. In fact, during the light-induced reorientation process of azobenzene groups, it is possible to tune the supramolecular chirality at will by using CPL of different handedness.

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