



**Order parameters and time evolution of mesophases in the lyotropic chromonic liquid crystal Sunset Yellow FCF by DNMR**

Journal:	<i>Soft Matter</i>
Manuscript ID	SM-ART-06-2018-001221.R1
Article Type:	Paper
Date Submitted by the Author:	24-Jul-2018
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Journal Name

ARTICLE

## Order parameters and time evolution of mesophases in the lyotropic chromonic liquid crystal Sunset Yellow FCF by DNMR

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Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Uniaxial order parameters of the nematic and columnar mesophases in the lyotropic chromonic liquid crystal Sunset Yellow FCF have been determined from deuteron nuclear magnetic resonance, where random confinement of the system by the dispersion of Aerosil nanoparticles have been performed to help obtaining the angular dependent spectra. The long-time evolution study of the order parameters shows that the system requires tens of hours to stabilize after a deep change in temperature, in contrast with the very fast assembly process of the aggregates. Finally, the degree of order of the water molecules, forced by the uniaxial environment, have been determined.

### 1. Introduction

Lyotropic liquid crystals (LLC)<sup>1-3</sup> are usually formed by amphiphilic molecules in water solutions. As their concentration increases, the molecules form supramolecular aggregates, such as spherical and cylindrical micelles, bilayers, etc.<sup>3,4</sup> An interesting and relatively new class of lyotropic liquid crystals is the so-called lyotropic chromonic liquid crystals (LCLCs). The LCLC forming molecules are usually of an aromatic (rather than aliphatic) type, with a relatively rigid disc-like core and ionisable groups at the periphery. While in water, the molecules tend to stack face-to-face, forming a polydisperse system of rod-like cylindrical aggregates. The average length of the aggregate increases with concentration and decreases with temperature. Within a certain range of concentration and temperatures, the aggregates form liquid crystalline phase with a long-range orientational order of the aggregates.<sup>5-11</sup>

The mechanisms controlling aggregation in LCLCs remain poorly understood. Recent experimental works initiated the first steps in this direction,<sup>12-36</sup> these studies may have also been inspired by the potential medical applications of LCLCs.<sup>37,38</sup> It appears that the main forces behind the structure of each aggregate are weak non-

covalent attractive interactions of the cores and repulsive electrostatic interactions of the polar groups ionized by the presence of water. Inter-aggregate interactions are expected to be controlled by the excluded volume effects, electrostatic and hydration forces.<sup>24,27</sup>

Depending on temperature and concentration, LCLCs exhibit three different phases: isotropic (I), nematic (N) and columnar (C), with broad regions of phase coexistence. The diameter of the aggregates varies in the range from 1 nm to 3 nm, depending on the number of molecules within the cross-section of the aggregate<sup>11,23</sup> and the separation between adjacent molecules inside the aggregates is about 0.34 nm. The structure is thus similar to that of the double-strand  $\beta$ -DNA molecules, with the important difference that the length of chromonic aggregates is not fixed covalently. The length of aggregates is the most difficult feature to characterize; first of all, it is strongly polydisperse, second, it is expected to vary strongly with concentration and temperature. In the LCLC formed by the dye Sunset Yellow (SSY),<sup>14</sup> it was noticed that the average length that appears in the X-ray experiment might not be necessarily the true length characterizing the extension of aggregates in space; it was suggested that some aggregates might form branched structures with stalking faults such as molecular lateral shifts or Y-junctions, among other possibilities.<sup>19</sup> An independent evidence of the presence of these stalking faults is probably brought about by dynamic light scattering experiments.<sup>39</sup>

Lyotropic liquid crystals formed by amphiphilic micelles, are among the most promising potential candidates for exhibiting a nematic phase with a biaxial orientational order,<sup>40-43</sup> although some authors consider this biaxial orientation as merely transient.<sup>44,45</sup> Furthermore, some liquid crystals formed by discotic molecules show columnar arrangements with the biaxial cross-section.<sup>46-48</sup> In

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principle, one can expect a similar effect of non-circular cross-sectional shape in chromonic aggregates.

*A key problem regarding the LCLC systems is their transient nature. Molecular aggregation is a process with a characteristic rate that depends not only on temperature and concentration, but also on the age of the system since preparation.<sup>11</sup> An interesting review and discussion of kinetic experiments to study the assembly and disassembly processes of the aggregates, by means of absorption and circular dichroism measurements, among others, and a comparison of the results with theoretical models have been presented by Collings et al.<sup>11</sup> Nevertheless, additional studies of the time evolution of LCLC systems would be very helpful in establishing a better understanding of these systems. Among these, long-time evolution studies should be included, as only experiments of the order of milliseconds have been performed to date.<sup>11</sup>*

The goals of the present work include: checking the existence of biaxial phases in an LCLC, determining the order parameters of the uniaxial and, if biaxial phases are present, studying the time evolution of these order parameters and evaluating the degree of order of the water molecules induced by the ordered aggregates. We have thus performed a systematic investigation of the following systems: partially deuterated SSY-d<sub>4</sub> in H<sub>2</sub>O (dS-h) and non-deuterated SSY in D<sub>2</sub>O (S-d), using deuteron nuclear magnetic resonance (DNMR). Both systems have been characterized as a function of concentration and temperature. Furthermore, the dS-h system has been studied as a function of time, with temperature and concentration kept constant. This is the first time that a LCLC system is monitored to analyse its time evolution.

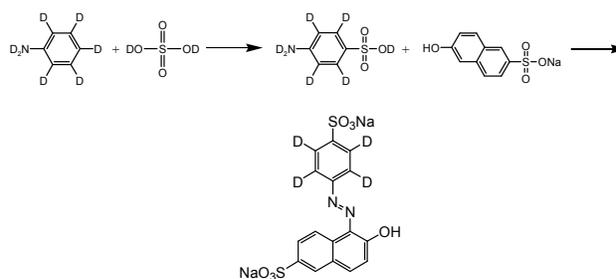
DNMR is a very powerful technique determining static properties, such as molecular orientations and conformations, as well as molecular dynamics, self-diffusion or viscoelastic properties, in a totally or partially deuterated systems.<sup>49</sup> This technique is especially useful for determining the existence of oriented phases, such as nematic and columnar mesophases. When a magnetic pulse is applied to a system of spins placed in a strong static magnetic field, nuclear spins are perturbed producing a particular spectrum in the frequency domain. In the isotropic phase, due to the fast reorientation of the molecules, DNMR spectra show a single absorption peak, centred at the Larmor frequency. For samples in a uniaxial phase, we may have different spectra, depending on the angles the C-D bonds form with the magnetic field. When the distribution of C-D bonds is such that all the possible angles are present (from 0° to 90°), we have the so-called “powder pattern”. This powder pattern is a summation over all the possible contributions of the different orientations, each of them with the C-D bonds forming just one angle with respect to the magnetic field. If this is the case, the peak present in the isotropic phase splits into two, creating a doublet separated in frequency by an amount proportional to the uniaxial order parameter and to a function of the angle between the mesophase director and the static magnetic field. This splitting takes its largest value (full splitting) for the nematic director parallel to the magnetic field and it comes to half

this value (half splitting) for the director perpendicular to the magnetic field.<sup>47-50</sup> When the mesophase is biaxial, the difference between axes perpendicular to the director affects the half splitting, creating two different doublets.<sup>47</sup> To properly study the mesophases, it is important to obtain contributions from all the possible angles between the C-D bonds and the magnetic field, which corresponds to the powder pattern. It has been an intrinsic difficulty for doing so with LCLCs, because the magnetic field is strong enough to reorient the director whenever the direction of the field changes. In order to overcome this problem, we have dispersed hydrophilic aerosil particles in the mixtures. These particles create a random network which has been successfully employed in the study of thermotropic liquid crystalline materials.<sup>51-57</sup> Aerosil particles are silica spheres of 7nm diameter and surface area of 300m<sup>2</sup>/g with hydroxyl groups covering their surface. If the density exceeds the gelation threshold, the spheres form a network that freezes the overall orientation of the director even when the magnetic field is applied.

The studies discussed below reveal several new results as compared to some previous experimental studies where dLCLC + H<sub>2</sub>O<sup>58-60</sup> and LCLC + D<sub>2</sub>O<sup>61,62</sup> systems were analyzed by means of DNMR.

The paper is organized as follows. In section 2, we describe the synthesis of the partially deuterated SSY. In section 3, the sample preparation and the experimental techniques are detailed. Section 4 presents and discusses the experimental results. Finally, the main conclusions are summarized in section 5.

## 2. Synthesis of partially deuterated Sunset Yellow FCF (SSY-d<sub>4</sub>)



**Scheme 1** Synthesis procedure of SSY-d<sub>4</sub>.

The chemicals were purchased from Aldrich chemical company and used without further purification.

Deuterated sulfuric acid (0.010 mol) was added to deuterated aniline (0.034 mol) with stirring. The reaction was heated to 180 °C, stirred for 5 hours, and allowed to cool down to 50°C and poured carefully with stirring into 20 ml of ice cold heavy water (D<sub>2</sub>O). The precipitated deuterated sulfanilic acid is collected on a Buchner funnel, washed with heavy water and drained. The crude product is dissolved in the minimum volume of boiling heavy water. Upon cooling the deuterated sulfanilic acid separates in colorless crystals.

The precipitate is filtered and dried between sheets of filter paper. The yield of deuterated sulfanilic acid is 47%.

The deuterated sulfanilic acid (4.77 mmol) was dissolved in a sodium carbonate solution in D<sub>2</sub>O (41.42 mmol per 20 mL) and cooled to 5 °C (and kept) using an ice bath. A cooled solution of sodium nitrate in heavy water was added slowly (8.83 mmol per 2 mL). The reaction mixture thus far was added drop wise into a cooled diluted DCI solution in ice cold heavy water (2mL conc. DCI in 20mL D<sub>2</sub>O). After the addition, the cooled mixture was added to a cooled solution of hydroxy naphthylene sulfonic acid hydrate (3.99 mmol) in 4mL of 10% NaOD in D<sub>2</sub>O. The reaction was stirred for 1 hour over an ice bath. After the reaction and formation of the dye, the mixture is heated to dissolve all the solid, sodium chloride is added and then left to cool at room temperature for 2 days. The precipitate that formed was filtered with a Buchner funnel, by gentle suction, and washed with cold D<sub>2</sub>O. To remove salt, the solid was recrystallized in 30mL of a D<sub>2</sub>O/ethanol mixture thrice. The final product was dried in an oven under vacuum. The product is a bright red orange solid at 35% yield.

<sup>1</sup>H NMR (D<sub>2</sub>O): δ = 6.211 (d, J = 9.6, 1H), 7.220 (d, J = 9.8, 1H), 7.528 (s, 1H), 7.581 (d, J = 8.0, 1H), 7.917 (d, J = 8.4, 1H).

<sup>13</sup>C NMR (D<sub>2</sub>O): δ = 116.430, 121.729, 125.537, 125.826, 125.902, 126.721, 128.694, 133.944, 139.574, 140.121, 142.177, 142.716, 178.012.

### 3. Experimental details

#### 3.1 Sample preparation

Non deuterated Sunset Yellow FCF was purchased from Sigma Aldrich, with a purity of 95.7%. A further purification procedure was made as follows. SSY was dissolved in water and later, ethanol was added to cause precipitation. The precipitate was then filtered from the solvent with impurities and dried in a vacuum oven.<sup>19</sup> The procedure was repeated twice.

Samples with different concentrations of both systems (SSY-d<sub>4</sub> + H<sub>2</sub>O and SSY + D<sub>2</sub>O) were prepared. The solvent was first poured into a NMR tube with diameter of 5 mm (the tube is previously cut to a length of ~2 cm), then, the chromonic material was added, until reaching the desired concentration. The NMR tubes were sealed with epoxy to prevent water loss and then the solution was mechanically mixed by rotation of the tube. The weight of the samples was monitored for over one month, and indicated that no water was lost during that time. Studied concentrations were, in weight percentage of solute, 30%, 34%, 37% and 40% for the SSY-d<sub>4</sub> + H<sub>2</sub>O (dS-h) system and 34% and 37% for the SSY + D<sub>2</sub>O (S-d) system.

The orientation of the LCLC solutions with 30% and 40% concentrations was stabilized by adding aerosil particles. Aerosil was added to distilled water and the solution was well mixed by stirring. Afterwards, the solvent (H<sub>2</sub>O+aerosil) was poured into the

NMR tube and the SSY-d<sub>4</sub> was added as in the non-confined samples.

#### 3.2 DNMR measurements

The DNMR experiments were conducted in a 400 MHz high resolution superconducting wide bore magnet, with a generated magnetic field of about 9.4T. This corresponds to a Larmor frequency,  $\nu_L$ , of 61.4 MHz for deuterons. Control of temperature is achieved by means of a PT-100 thermometer placed next to the coil where the sample is. The electronic components, the probe and the instrumental controlling software were purchased from Tecmag.

To characterize the DNMR spectra of the systems studied here, we first provide a brief review of DNMR in discotic liquid crystalline materials.<sup>47,63</sup> In such systems, and considering an aligned sample of single domains, each deuterium exhibits a doublet whose spacing depends on the orientation of the nematic director with respect to the magnetic field. In the principal coordinate system of the average quadrupole tensor, this spacing is given by

$$\Delta\nu = \frac{3}{2} \frac{e^2 q Q}{h} \left[ \frac{1}{2} (3 \cos^2 \theta - 1) + \frac{\eta}{2} \sin^2 \theta \cos 2\varphi \right] S_{CD} \quad (1)$$

where  $e^2 q Q/h$  is the deuteron principal quadrupole interaction constant,  $\eta$  is the biaxial quadrupole interaction parameter, the angles  $\vartheta$ ,  $\varphi$ , are the polar coordinates of the liquid crystalline phase director with respect to the magnetic field, which takes the direction of the Z axis and  $S_{CD}$  is a weighted average of the order parameter for the C-D bonds of the molecule:

$$S_{CD} = D_{00}^2(\alpha\beta\gamma)C_{00} + f(\eta, C_{m0}, \alpha\beta\gamma) \quad (2)$$

Here,  $D_{00}^2(\alpha\beta\gamma)$  is the 00 component of the Wigner rotation matrix,  $C_{m0}$  ( $-2 < m < 2$ ) are the order parameters of the C-D bonds (the 00 term being the uniaxial order parameter) and  $f$  is a function depending on the biaxiality of the phase and the Euler angles,  $\alpha\beta\gamma$ ,  $\beta$  corresponding to the angle between the C-D bonds and the static magnetic field. In our case,  $\beta = \pi/2$  and, therefore,  $D_{00}^2(\alpha\beta\gamma) = 1/2$ .

We direct the z axis of the system along the phase director. When the sample is a distribution of domains the spectrum is a powder pattern because of superposition of doublets. The outer peaks are those corresponding to the z axis of the system ( $\vartheta=0$ ),  $\Delta\nu_z$ , the inner peaks are those of the x axis ( $\vartheta=\pi/2$ ,  $\varphi=0$ ),

$$\Delta\nu_x = \frac{(1-\eta)\Delta\nu_z}{2} \quad (3)$$

and those in the middle correspond to the y axis ( $\vartheta=\pi/2$ ,  $\varphi=\pi/2$ ),

$$\Delta\nu_y = \frac{(1+\eta)\Delta\nu_z}{2} \quad (4)$$

If there is no biaxiality, both  $x$  and  $y$  axes are equivalent and their peaks coincide, and their splitting values are just half of that corresponding to the  $z$  axis.

We have to consider another type of distribution, when the principal  $z$  axis of the liquid crystalline system is perpendicular to the magnetic field, and the  $x$  and  $y$  directions are more or less equally distributed in the perpendicular directions. This happens in mesophases of samples with negative anisotropic magnetic susceptibility and small (or non-existent) biaxiality in a strong magnetic field. In such a case,  $\vartheta = \pi/2$ , while all possible values of  $\varphi$  are equally probable. The spectrum in this particular situation shows just the peaks corresponding to the  $x$  and  $y$  axes, with

$$\Delta\nu_x \cong \Delta\nu_y = \frac{\Delta\nu_z}{2} \quad (5)$$

To obtain different orientations, samples are manually rotated in the magnetic field to any desired angle.

#### 4. Results and discussion

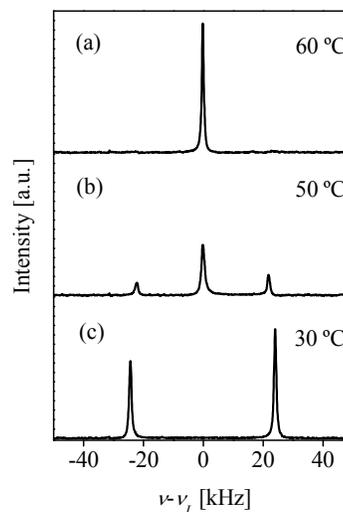
In the present work, we have been able to improve some previous studies of similar chromonic systems by DNMR measurements.<sup>58-62</sup> Firstly, we have observed both mesophases, nematic and columnar, as well as the coexistence regions, N+I and N+C. In addition, determination of the alignment of the samples at different orientations of the aggregates with respect to the magnetic field has been possible by the dispersion of aerosil particles into the system. This has helped, as discussed below, the understanding of whether biaxiality exists in these mesophases. Also, we monitored the evolution of the dS-h system over time, maintaining constant temperature and concentration. It was found that rapid temperature variations induce changes in the frequency splitting which translates into changes in the orientational order parameter with time, as it reaches the equilibrium state. Finally, we were able to estimate the degree of order of the water molecules in the system.

##### 4.1 Phase recognition in the SSY-d<sub>4</sub> + H<sub>2</sub>O (dS-h) system

To determine the phase diagram of the dS-h system, DNMR measurements of several samples (30%, 34% and 37%) were collected as a function of temperature, in both heating and cooling runs. Starting at room temperature, samples were heated up inside the magnet up to the isotropic phase when possible, but never exceeding 90°C, to prevent evaporation and NMR tube breaking. Afterwards, the samples were cooled back to room temperature. As both heating and cooling runs produced essentially identical results, heating runs are discussed hereafter.

DNMR spectra for sample with 30% concentration are shown in Fig. 1. The observed phase sequence is the following:

N - 41°C - N+I - 55°C - I

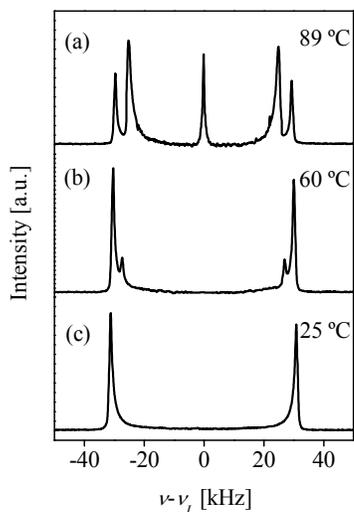


**Fig. 1** DNMR spectra for the sample with concentration 30%. (a) Isotropic phase at 60°C. (b) Isotropic and nematic phase coexistence at 50°C. (c) Nematic phase at 30°C.

From Fig. 1a, the I phase is represented by a single absorption frequency peak. The N phase, represented by a frequency splitting due to the nematic orientational order parameter, is shown in Fig. 1c. In between them, in Fig. 1b, coexistence of I and N phases can be seen. The value of the frequency splitting ranges between ~50 kHz at around 30°C and ~43 kHz in the N+I coexistence region. Spectra for the sample of concentration 34% (shown as Supplementary Information) are qualitatively identical to those for the 30%, except that they occur at a different transition temperatures:

N - 70°C - N+I - 83°C - I

In contrast, the results for samples with 37% concentration are presented in Fig. 2. Given the presence of two doublets of varying intensity as the temperature is changed, initially the data can be interpreted as (a) evidence of a columnar mesophase and a biphasic N+C region (at higher temperatures); or (b) evidence of the presence of a biaxial phase.



**Fig. 2** DNMR spectra for the sample with concentration of 37%. (a) Isotropic, nematic and columnar coexistence at 89°C. (b) Nematic and columnar coexistence at 60°C. (c) Columnar phase at 25°C.

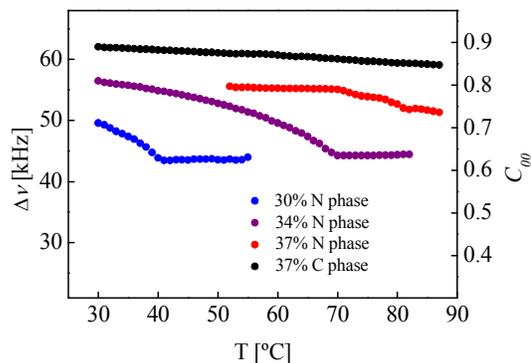
It can be seen from Fig. 2a and 2b that the relative intensities of both peaks interchange, the inner splitting intensity decreases with decreasing temperature. The interchange in the peaks' intensities can be explained as a fundamental behaviour of a compound experiencing a first order phase transition. As temperature increases, the percentage of molecules in the nematic phase (area under the inner absorption peak) with respect to those in the columnar phase also increases. At the lowest temperatures, only the columnar phase is present, as shown in Fig. 2c. This suggests that a N+C coexistence is more likely than a biaxial phase.

In both N and C phases the aggregation proceeds through stacking of the disc-like molecules on top of each other. As proposed by Park et al.,<sup>19</sup> these aggregates are more complex than simple rods, at least in the nematic phase, and the entire aggregate is longer than would be if formed by just a number of molecules  $n \sim 10$ , as concluded from x-ray measurements. X-rays can detect only small parts of the entire aggregates, with  $n \sim 10$ , but cannot take into account the entire aggregates as these are uncorrelated from the point of view of x-rays. This may suggest that there is no significant difference in the length of the entire aggregates in either mesophase, nematic or columnar; the difference between mesophases may just be due to the concentration. In diluted systems, the entire aggregates are more diffusive and parts of them (small aggregates) are mobile, giving the nematic phase its characteristics. When the concentration is increased, the mobility of the small aggregates is sufficiently reduced that the mesophase changes, becoming columnar. Therefore, the difference between N and C phases could be due to aggregates' mobility caused by a more reduced space because the entire aggregates are closer to

each other. In what follows, we assume that there exists an N+C phase coexistence in the 37% concentration sample. We can estimate the phase sequence for this concentration as:

C -50°C – N+C

We could not observe the higher temperature phase transitions by DNMR, as they occur over 90°C.



**Fig. 3** Frequency splitting (left Y axis) and uniaxial order parameter (right Y axis) vs. temperature for samples with concentrations of 30% (N phase), 34% (N phase) and 37% (N and C phases).

In Fig. 3 we plot the temperature dependence of the frequency splittings of the different doublets for the three studied concentrations. The splitting decreases when temperature increases, which is expected, as the orientational order (and therefore the splitting, as shown in Eq. 1) of the mesophases decreases while heating the samples. When the N+I coexistence region is reached in the 30% and 34% samples, the nematic splitting (and thus the order parameter) remains nearly constant (below 45 kHz in both cases). For the highest concentration sample studied (37%), the difference in absolute splitting values between N and C mesophases is at least 5 kHz. As the temperature rises and the system approaches the isotropic phase, the N and C splittings decrease in value, but the former decreases faster, which can be understood due to the columnar phase greater viscosity, which makes it more difficult to change its orientational order as compared to the nematic one.

#### 4.2 Aerosil network in the d5-h system. Uniaxial order parameters of the mesophases

Since the static magnetic field prevents an arbitrary orientation of the sample, by reorienting the molecules back to their original position, it is thus not possible to perform angular dependence studies of the frequency splitting in bulk samples, which are fundamental for a complete DNMR characterization. In order to overcome this difficulty, we have confined SSY by using a dispersion of hydrophilic aerosil particles. The presence of hydroxyl groups in the surface of the aerosil particles could lead to ionic interactions between them and the chromonic system, which could ultimately

disturb the behavior of the system with respect to the bulk sample. This issue must be considered when analyzing the results.

The magnetic field does not affect the director structure as long as the magnetic coherence length is bigger than the mean void size of the aerosil network. The magnetic coherence length can be expressed as

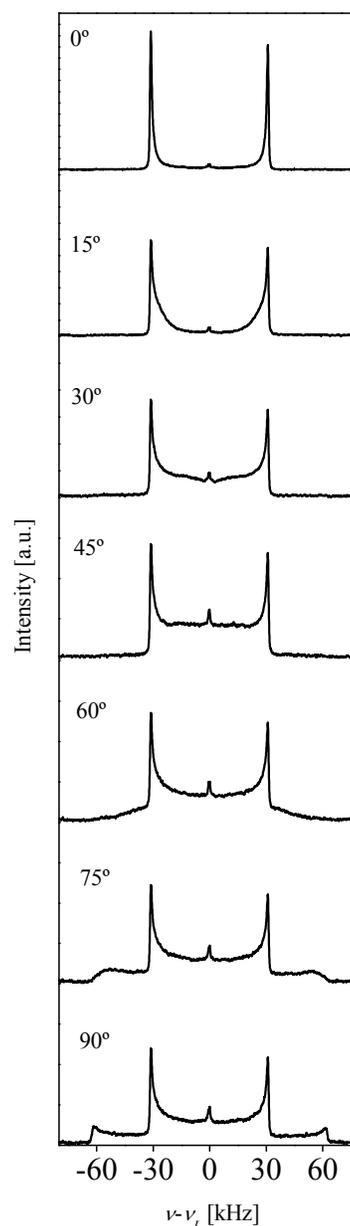
$$\xi_M = \sqrt{\frac{\mu_0 K}{B_0^2 |\Delta\chi|}} \quad (6)$$

where  $K$  is the average Frank elastic constant. The mean void size, meanwhile, can be calculated as

$$l_0 = \frac{2}{s\rho_s} \quad (7)$$

where  $S$  is the surface area of the nanoparticles and  $\rho_s$  the aerosil density (mass of aerosil per volume of LC system). Taking values for  $K$  and  $\Delta\chi$  from reference [28], we obtain  $\xi_M \sim 100\text{nm}$ . We have prepared an aerosil network with  $\rho_s = 0.1 \text{ g/cm}^3$ , for which the mean void size equals 67nm, which is less than the magnetic coherence length.

The selected sample for the aerosil dispersion has been one of 40% of concentration of SSY, corresponding, in weight, to 10% aerosil, 36% SSY- $d_4$  and 54%  $\text{H}_2\text{O}$ . The sample was placed in the magnet and cooled from 90°C down to 30°C and a study of the angular dependence was performed; these results are shown in Fig. 4. The frequency splitting and consequently the order parameter of the C phase shows no change resulting from the addition of the nanoparticles at an angle of 0°, which shows that the Aerosil network do not disturb the chromonic system. The spectra were obtained every 15°. At 0°, the spectrum is similar to those obtained in every bulk sample studied before. In this case the splitting measured corresponds to a half splitting, when contrasted to the full splitting present in the 90° spectrum. This means that the measured bulk samples aligned spectra (as well as the confined samples at 0 degrees) correspond to a molecular distribution when the principal  $z$  axis of the liquid crystalline system lies in a plane perpendicular to the magnetic field ( $\vartheta = \pi/2$ ), as explained in section 3.2. These results confirm the negative magnetic susceptibility anisotropy of SSY.<sup>28</sup>



**Fig. 4** Angular dependence DNMR spectra for the confined sample with 10% Aerosil, 36% SSY- $d_4$  and 54%  $\text{H}_2\text{O}$  at 30°C.

Assuming negative magnetic susceptibility and, consequently, alignment of molecular discs perpendicularly to the magnetic field,

the angular dependence of the line shape should match that of Fig. 3 with  $\eta=0$  in a previous work by Zalar et al.<sup>64</sup> From the point of view of deuteron NMR, the distribution of molecules around the circumference of channels (with channel symmetry axes oriented along the magnetic field) is analogous to the distribution of molecular director in the plane perpendicular to the magnetic field, both cases result in a half-splitting at the  $0^\circ$  orientation. On reorienting the sample the splitting of the inner singularity should remain fixed whereas the other singularity exhibits a strong angular dependence, but this is not the case in our experiment. On the other hand, the outer singularities at  $90^\circ$  are quite pronounced and similar to what is predicted in the work by Zalar et al.<sup>64</sup> These results mean that the sample is only partially stabilized by Aerosil; on reorientation, one part of the molecules is instantaneously realigned perpendicularly to the field due to the negative diamagnetic anisotropy, whereas the other part of the sample exhibits the cylindrical pattern anticipated for completely stabilized structure.

The presence of one single doublet at the half splitting in the spectrum at  $90^\circ$ , allows us to definitely rule out the possibility of existence of a biaxial phase and, therefore, both N and C mesophases are uniaxial,  $\eta=0$  and the only order parameter different from zero is  $C_{00}$ . From Eqs. 1 and 2, we have

$$\Delta\nu = \frac{3}{4} \frac{e^2 q Q}{h} \left[ \frac{1}{2} (3 \cos^2 \theta - 1) \right] C_{00} \quad (8)$$

Therefore, we can obtain the uniaxial order parameter of the C-D bonds from the half-splitting values ( $\Delta\nu_{half}$ ) of the aligned samples discussed in the previous sub-section, in which  $\theta=\pi/2$ :

$$C_{00} = \frac{8}{3} \left( \frac{e^2 q Q}{h} \right)^{-1} \Delta\nu_{half} \quad (9)$$

with the deuteron principal quadrupole interaction constant for aromatic deuterons given by,<sup>47</sup>

$$\frac{e^2 q Q}{h} = 186 \text{ kHz} \quad (10)$$

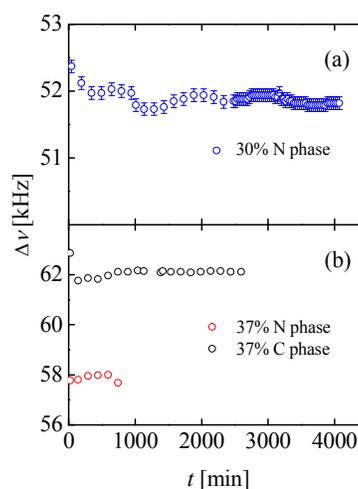
The uniaxial order parameter dependence with temperature for the samples with concentrations of 30%, 34% and 37% are plotted in Fig. 3. From the figure, the order parameter in the nematic phases ranges from 0.6 to 0.8 while it nears 0.9 in the columnar phase, an indication of its higher degree of order.

In comparison, previous works on LCLC + D<sub>2</sub>O systems<sup>58-60</sup> only measured samples aligned at a single, fixed angle with respect to the magnetic field, and thus would be unable to provide a complete picture. Also, such works suggested an order parameter value near 1; given the results here and those from Nastishin et al,<sup>15</sup> such a "near 1" value would seem to be an overestimate.

### 4.3 Time evolution of the dS-h system

It is important to study whether the transient nature of the system plays a significant role in its properties or it does not. Specifically, the orientational order parameter of the mesophases and, therefore, the frequency splittings in the DNMR spectra, might depend not only on temperature and concentration, but also on time. This transient nature arises from the kinetics of the assembly and disassembly processes of the aggregates<sup>11</sup> and also in the inherent fluidity of the system. Such studies, in which temperature is kept constant and concentration is changed, indicate that the assembly process in some chromonic systems and, in particular, the SSY system, can be modelled asisodesmic, where the change in free energy when adding or subtracting one molecule from an aggregate does not depend on the size of the aggregate.<sup>11</sup> Diffusion DNMR measurements in the isotropic phase for the SSY + D<sub>2</sub>O system have also been performed.<sup>65</sup> In these experiments,<sup>11,65</sup> it is shown that the assembly process in SSY takes less than 1ms, under the studied conditions.

Here, we deal with a different kind of kinetic experiments. On the one hand, we maintain the concentration constant and track the system after a significant change of the temperature. Also, we are far from the orders of magnitude of the assembly process, as we evaluate the overall long-time (tens of hours) evolution of the system, by means of the frequency splitting in the mesophases, which is proportional to the order parameter (Eqs. 1, 8 and 9). Thus, molecules may continuously assemble and disassemble from the aggregates as the system evolves with time during our experiments.



**Fig. 5** Frequency splitting vs. time for samples with concentrations of (a) 30% (N phase) and (b) 37% (N and C phase) at 27°C, after rapid change of temperature. With time, the nematic phase disappears in the sample of 37%. Error bars have been added in (a).

This effect may be different depending on how this change of temperature is. In the studied case, after the sample has been prepared, it has been taken to 80°C and allowed to cool down

in the magnet. Fig. 5 shows the evolution of the frequency splitting vs time for two samples, with concentrations 30% and 37%, at 27°C. It can be observed how the splitting value in the N phase for the 30% sample (Fig. 5a) takes some time to stabilize ( $\sim 1200$  minutes = 20 hours). It must be noted that there exists a continuous oscillation of the splitting value, with an amplitude around 0.2 kHz, which corresponds to  $\sim 0.4\%$  of the average value, but this is within the experimental error and the possible marginal stability of the temperature controller.

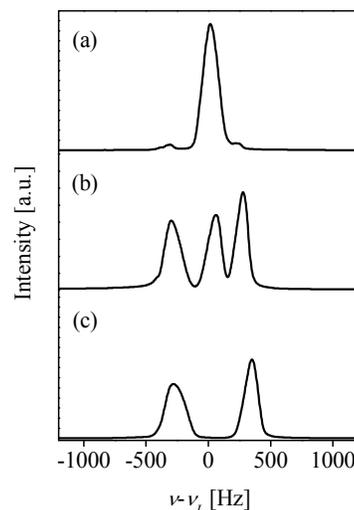
Regarding the 37% sample (Fig. 5b), where both N and C phases appear initially, after some time in which both splittings oscillate, the inner peak (N phase) disappears and, simultaneously, the average value of the splitting of the outer peak (columnar phase) increases. It looks like we are in a point of the phase diagram close to the limit separating the C phase and the N+C coexistence regions. It takes approximately 900 minutes ( $\sim 15$  hours) for the frequency splitting to finally stabilize to some fixed value, within the experimental error.

As mentioned above, in our particular system molecules assemble in rod-like aggregates (of about 10 molecules) and these aggregates connect through "stalking faults" to form the actual entire aggregates responsible for the uniaxial character of the phase. In the present kinetic experiments, it is the interaction between these entire aggregates which ultimately affects the change in the value of the order parameter. The complex structure of the aggregates, together with their great length, relative to individual molecules, makes the relaxation process to the equilibrium state much slower ( $\sim 10$ -20 hours) than the assembly process of the small rod-like aggregates ( $\sim 1$ ms). From these results, we believe that the system should wait this time ( $\sim 10$ -20 hours) remain stable before any static property is measured.

#### 4.4 Water ordering in the SSY + D<sub>2</sub>O (S-d) system

An alternative way to understand the properties of SSY by means of DNMR measurements is by dissolving the non-deuterated liquid crystal in D<sub>2</sub>O.<sup>61,62</sup> Two such samples (S-d) were prepared ( $x=34\%$  and 37%). For both samples, a splitting can be observed at low temperatures and a central peak, indicative of the isotropic phase, at higher T. By increasing temperature, the intensity of the central peak increases while the doublet decreases. At higher temperatures, the splitting completely disappears. This behavior, shown in Fig. 6, corresponds to what happens when analyzing the dS-h systems, with the only difference being the values of the splitting. There are two important things we must observe: first, there is no evidence of the double splitting typical of the N+C phase coexistence and, second, all the water seems to be in an ordered state when the system is in any of the mesophases. The fact that no double splitting when N and C coexist can be observed is due to the width of the peaks in the DNMR spectra. The frequency splitting difference between the N and the C phase as shown in figure 4 (for  $x=37\%$ ) is less than 10 kHz ( $\sim 20\%$  with respect to the value for the N phase). For the S-d system, as the frequency splitting is  $\sim 1$  kHz, the

difference between both peaks should be  $\sim 100$  Hz (splitting difference  $\sim 200$  Hz), which is of the order of the width of the peaks.



**Fig. 6** DNMR spectra for the sample with 37% SSY and 63% D<sub>2</sub>O. (a) Isotropic phase (with small bumps indicating a very low percentage of the sample in the nematic phase). (b) Isotropic and nematic coexistence. (c) Nematic phase.

To picture the S-d system, one may imagine that the water should be in some way "affected" by the order of the SSY molecules in the mesophases, N or C. As shown in Fig. 6c, there is no central peak, characteristic of the isotropic phase, which means that all the water presents uniaxial order, even if the order parameter is extremely small. Taking into account Eq. 6 and a quadrupolar frequency of about 200 kHz for D<sub>2</sub>O,<sup>66</sup> the order parameter for the water molecules is estimated to be between  $10^{-2}$  and  $10^{-3}$ .

## Conclusions

In this work we presented an experimental study of the lyotropic chromonic liquid crystal Sunset Yellow FCF (SSY) dissolved in water for some different concentrations by means of DNMR measurements. More precisely, two different systems were studied: partially deuterated SSY (synthesized for the first time) + H<sub>2</sub>O and non-deuterated SSY + D<sub>2</sub>O. This study not only confirms previous observations but provides additional important understanding of the system.

In particular, we were able to accurately obtain for the first time the uniaxial order parameters of the mesophases in the SSY by means of DNMR measurements. In order to study the angular dependence of the system, random confinement of the system was introduced by dispersing aerosil nanoparticles. These nanoparticles form a network confining the SSY, which allowed the determination of the DNMR angular dependence for the chromonic liquid crystal system. The values of the order parameters indicate a high degree of order

of both mesophases and agree with the values obtained by light absorption experiments on other similar chromonic systems.<sup>15</sup>

This work is also the first one in which a long-time evolution study has been performed on any chromonic system, showing that when the system is driven to some set point temperature, it takes several hours to stabilize and, afterwards, the order parameters remain constant. Thus, when dealing with the study of these systems, two kinds of transient phenomena are present, the isodesmic assembly process of molecules to form the aggregates and the process in which these molecular assemblies interact with each other to provide the uniaxial character of the mesophases. As both processes are well separated in the time domain, we can assume that the continuous molecular assembly processes during the variation of temperature or concentration of the system, do not play any role in the orientation of the aggregates in the mesophases, which is driven by the interactions between aggregates alone. Such interactions are responsible of the long time required to equilibrate the system after a big change in the temperature, at least.

Finally, we have found how all the water is affected by orientation of the chromonic molecules and no isotropic clusters of water are present in the uniaxial phases. This water ordering forced by the SSY molecules is, nevertheless, extremely small.

### Conflicts of interest

There are no conflicts to declare.

### Acknowledgements

This work was supported by the grant NSF DMR-1729509 and by the MICINN Project No. MAT2015-66208-C3-2-P (MINECO-FEDER). The authors also thank the recognition from the Generalitat de Catalunya of GRPFM as Consolidated Research Group (2017-SGR-335). Any opinions, findings, and conclusions or recommendations expressed in this article are those of the authors and do not necessarily reflect the views of the National Science Foundation.

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