



# Article Chromonic Ionic Liquid Crystals Forming Nematic and Hexagonal Columnar Phases

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Abstract: We designed an ionic salt by combining a  $\pi$ -conjugated anion and a cholinium cation. It formed homogeneous mixtures with water in various weight ratios. The obtained mixtures showed chromonic liquid-crystalline behavior in a wider concentration range as compared to analogous compounds with inorganic cations. Although only an exhibition of nematic phases was previously reported by Kasianova et al. for analogous compounds with an inorganic cation in 2010, the ionic salt with a cholinium cation showed not only nematic phases but also hexagonal columnar phases. The formation of hexagonal columnar phases is attributed to its ability to form mesophases even in a high concentration range, which enables the cylindrical aggregates of the  $\pi$ -conjugated anions to form dense packing. By examining the states of the water molecules, we revealed that the ability of the cholinium cation to form a hydrated ionic liquid state strongly contributes to the widening of the concentration range forming chromonic liquid-crystalline behavior.

Keywords: chromonic liquid crystal; ionic liquid; nematic; hexagonal columnar phase



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## 1. Introduction

Chromonic liquid crystals are a class of lyotropic liquid crystals. A unique point of chromonic liquid crystals is that they have molecular structures composed of a polycyclic aromatic core having several ionic and/or hydrophilic groups at its periphery [1–8]. It has been generally understood that the aromatic core plays a key role for the formation of self-assembled cylindrical aggregates through  $\pi$ - $\pi$  interactions and/or other interactions. The hydrophilic groups are important for solubility into water. To date, there have been many reports of ionic compounds exhibiting chromonic liquid-crystalline (LC) behavior. Most of them are composed of  $\pi$ -conjugated mesogens with anionic groups and inorganic cations [1–6] while, in some case, chromonic liquid crystals composed of  $\pi$ -conjugated cations and inorganic anions have been also reported [7,8].

On the other hand, in the several decades of studies, there have been a growing interest on the use of organic cations for creating functional ionic compounds, such as ionic liquids [9–11], ionic liquid crystals [12–15], ionic plastic crystals [16–18], and ionic crystals [19]. In the course of studies on ionic liquids, it has been revealed that there is a potential that a slight difference of the organic cation structures results in the large difference of physicochemical properties and functions. For example, imidazolium cations are recognized as one of the most suitable cations for designing ionic liquids dissolving cellulose [20,21]. On the other hands, the use of cholinium cation has attracted an increasing attention for yielding hydrated ionic liquids for dissolving some bio-functional polymers [22]. For example, Fujita and Ohno reported that hydrated ionic liquids have a great potential as liquid media for enzyme storage [23–25]. One of the important characteristics of hydrated ionic liquids is that they maintain liquid states even in quite high concentration conditions. This characteristic leads us to envision that the employment of suitable organic cations would be one of an advanced strategy for controlling the chromonic LC behavior of  $\pi$ -conjugated compounds with anionic groups. As an anion with  $\pi$ -conjugated structure, we have employed 4,4-(5,5-dioxidodibenzo[b, d]thiene-3,7-diyl)dibenzenesulphonic acid (**pQpdS**) anion. It is an anion whose Cs salt was reported to exhibit chromonic LC behavior at a water content of 85 wt% by Kasianova et al. in 2010 [26]. As an organic cation, a cholinium (Ch) cation has been selected. By combining these cation and anion, we have synthesized an organic salt, **pQpdS-Ch** (Figure 1). Its chromonic LC behavior in water has been examined using polarized optical microscopy (POM) observation, differential scanning calorimetry (DSC), and X-ray diffraction (XRD) measurements.



Figure 1. Molecular structure of pQpdS-Ch.

#### 2. Materials and Methods

The synthesis scheme of **pQpdS-H** is shown in Scheme 1. To an aqueous solution of choline hydroxide, an equimolar amount of 4,4-(5,5-dioxidodibenzo[b,d]thiene-3,7-diyl)dibenzenesulphonic acid (**pQpdS-H**) was added. The solution was stirred until the white solid of **pQpdS-H** dissolved into the solution. Evaporation of water yielded a **pQpdS-Ch** as a white solid.



Scheme 1. Synthesis of pQpdS-Ch.

<sup>1</sup>H NMR (400MHz, D<sub>2</sub>O):  $\delta$  = 7.78 (s, 2H), 7.64 (d, *J* = 8.4 Hz, 4H), 7.41–7.35 (m, 8H), 3.92–3.89 (m, 4H), 3.37–3.35 (m, 4H), 3.05 (s, 18H).

#### 3. Results and Discussion

Mixtures of **pQpdS-Ch** and  $H_2O$  in 100–X:X weight ratios (X = 90, 80, 70, 60, and 50) were prepared by adding two components into Eppendorf tubes. In order to increase the homogeneity of the mixtures, the tubes were vibrated and centrifugation was performed.

We could obtain the homogeneous mixtures when  $90 \ge X \ge 50$  while it was not obtained when  $X \leq 40$ . Small amounts of the homogeneous mixtures were put on a slide glass and covered with a cover glass. Polarizing optical microscope (POM) observation was carried out for them while cooling from isotropic phases observed at around 80 °C. The obtained textures are shown in Figure 2. It has been found that the samples with X  $\geq$  90 shows no birefringence in the temperature range, indicating that mesomorphic behavior is not induced when  $X \ge 90$ . On the other hand, the mixture with X = 80 shows a schlieren texture, which is a characteristic of nematic phases. This behavior is similar to that reported by Kasianova et al. for **pQpdS** with Cs cation [26]. A notable difference has been observed when  $X \leq 70$ . These mixtures show focal conic fan-textures, which are indicative of the formation of columnar LC phases. The thermotropic phase transition behavior of the mixtures is summarized in a bar graph (Figure 3). The formation of the nematic phases results from the cylinder aggregation of the pQpdS anions and the subsequent axial alignment of the cylinders. That of the columnar phases can be attributed to the formation of the positional order of the cylinders as the decrease of the inter-cylinder distance.



**Figure 2.** Polarized optical microscopic images of the mixtures of **pQpdS-Ch** and H<sub>2</sub>O in the 100–X:X weight ratios. (a) X = 90 at 25 °C, (b) X = 80 at 10 °C, (c) X = 70 at 25 °C, (d) X = 60 at 25 °C, and (e) X = 50 at 25 °C.



**Figure 3.** Bar graph of the thermotropic phase transition behavior of the mixtures of **pQpdS-Ch** and H<sub>2</sub>O in the 100–X:X weight ratios on cooling.

In order to confirm the formation of columnar phases, we have performed XRD measurements for the mixtures at 30 °C. For avoiding the evaporation of water from the sample, the LC samples were put on an aluminium pan and rapidly covered by a polymer film (DURA SEAL, DIVERSIFIED BIOTECH). A XRD pattern observed for the mixture (X = 60) is shown in Figure 4. An intense peak and two weak peaks were found in the small angle region. The *d*-values estimated from the peak position  $\theta$  values are 32.7, 18.7, and 16.0 Å, respectively. These peaks can be indexed as (100), (110), and (200) reflections of a hexagonal structure, which lead us to identify the columnar phase as a hexagonal columnar (Col<sub>h</sub>) phase. The intercolumnar distances in the Col<sub>h</sub> LC phase can be calculated to be 37.8 Å from the *d*-values. The formation of Col<sub>h</sub> phases for bent shaped chromonic liquid crystals has been also reported by Wang et al. in 2018 [27], which supports our characterization.



Figure 4. X-ray diffraction (XRD) pattern of  $pQpdS-Ch/H_2O$  (X = 60) weight ratio at 30 °C.

POM observation for macroscopically aligned samples is a useful strategy for deducing the molecular assembled structures in LC states. In order to employ this strategy for the present materials, we sandwiched a small amount of a  $pQpdS-Ch/H_2O$ (X = 60) mixture between a cover glass and a slide glass and then added a mechanical shearing to the cover glass. It is a technique to align the column axis to the shearing direction [28]. As expected, the sheared sample show a homogeneous texture under POM observation, which is indicative of the formation of 1D-aligned columnar phases. The aligned samples were observed under POM with a 530 nm retardation plate inserted in the optical path at 45 degrees. The shearing direction is set parallel and perpendicular to the slow axis direction of the retardation plate. It has been found that, when these two directions are parallel, the texture is observed in a yellow (Figure 5a). It turns into in a blue as the rotation of the sample through 90 degrees (Figure 5b). These results mean that the slow axis of the Col<sub>h</sub> liquid crystals is perpendicular to the column axis, namely the **pQpdS-Ch**/ $H_2O$  (X = 60) mixture has a negative birefringence. It is consistent with the results obtained for analogous compound with the Cs cation in a nematic phase that was reported by Kasianova et al. [26].



**Figure 5.** Polarized optical microscopic images of the mixtures of  $pQpdS-Ch/H_2O$  (X = 60) in the Col<sub>h</sub> phase after shearing. (a) The shearing direction is parallel to the slow axis of the retardation plate. (b) The shearing direction is perpendicular to the slow axis of the retardation plate.

In order to further confirm the molecular assembled structure of the **pQpdS**-**Ch**/H<sub>2</sub>O mixtures in the Col<sub>h</sub> phase, we have performed polarized IR measurements. A 1D-aligned sample of the **pQpdS-Ch**/H<sub>2</sub>O (X = 70) mixture was prepared by the same method. IR absorbance was measured with setting the angle of the polarizer ( $\theta_p$ ) in the range from 0 to 180 degrees. The Col<sub>h</sub> LC sample was set in such a way that its column axis was parallel to  $\theta_p = 0$  degree. While the S=O stretching vibration ( $\nu_{S=O}$ ) of the **pQpdS** molecules was observed at 1301 cm<sup>-1</sup> independent of the  $\theta_p$  angles, the peak strength of  $\nu_{S=O}$  clearly depended on the  $\theta_p$  angles. For example, the absorbance of  $\nu_{S=O}$  was 0.20 when  $\theta_p = 0$  degree, which increases as the increase of  $\theta_p$  (Figure 6a). For further clarify  $\theta_p$ -dependence of the  $\nu_{S=O}$  absorbance, we have constructed a polar plot (Figure 6b). It indicates that the sulfonyl groups of the **pQpdS** molecules are oriented perpendicular to the 1D column axis.



**Figure 6.** (a)  $\theta_p$ -dependence of IR spectra of the **pQpdS-Ch**/H<sub>2</sub>O (X = 70) mixture in the Col<sub>h</sub> phase. (b) A polar plot of the absorbance of the S=O stretching vibration ( $\nu_{S=O}$ ) observed at 1301 cm<sup>-1</sup>.

The phase transition behavior of these mixtures has been further examined using DSC measurements. The DSC measurements were performed in the temperature range from 0 to 80 °C at the heating/cooling rate of 10 °C min<sup>-1</sup>. The obtained DSC charts on cooling and heating are shown in Figure 7a,b, respectively. In the cooling process, an exothermic peak is found for each sample when  $X \leq 80$ . These peaks can be attributed to the enthalpy change at the phase transition from an isotropic phase to an LC phase. It can be seen that the peak position shifts to higher temperature region as the decrease of X, which is consistent with the isotropization temperatures observed by POM observation. The thermal stabilization

of the mesophases upon the decrease of X can be explained by the increase of the packing density of the cylinder aggregates. Another notable trend is that the peak area increases as the decrease of X. For example, the peak area of the phase transition from the Col<sub>h</sub> to Iso phases is 0.83 mJ/mg for the **pQpdS-Ch**/H<sub>2</sub>O (X = 70) mixture while it increases to 2.16 mJ/mg for **pQpdS-Ch**/H<sub>2</sub>O (X = 50). These enthalpy changes can be mainly ascribed to the cleavage of the dipole–dipole interaction between the sulfonyl groups. Rough calculation is described in the Supplemental Information.



Figure 7. DSC thermograms of the pQpdS-Ch/H<sub>2</sub>O mixtures: (a) on cooling and (b) on heating.

It is considered that the water molecules in the mixtures exist as bound water and/or free water. With an aim to investigate the states of water in the mixtures, we have performed DSC measurements in lower temperature region. The DSC measurements were carried out from room temperature to -80 °C. A peak corresponding to crystallization of free water was found at a temperature lower than 0 °C. By estimating the amount of free water in the mixtures from the peak area, the molar ratios of bound water and free water in the mixtures (X = 50–90) were investigated and summarized in Table 1. It has been found that 15–25 water molecules strongly interact with a **pQpdS-Ch** molecule and then exist as bound water. These results are consistent with the number of hydration water molecules reported for cholinium-based hydrated ionic liquids [29]. We assume that the cylindrical aggregates formed by the **pQpdS** anions are surrounded by sheath of hydrated ionic liquids that produce liquidity and prevent crystallization even in the water poor condition (70  $\ge X \ge 50$ ).

Water Content X	Exothermic Peak Area (mJ/mg)	Component Ratios in Weight			<b>Component Ratios in Mole</b>		
		pQpdS-Ch	Free Water	Bound Water	pQpdS-Ch	Free Water	Bound Water
90	256	10	77	13	1	313	55
80	228	20	38	12	1	139	24
70	184	30	55	15	1	75	20
60	135	40	40	20	1	41	20
50	106	50	32	18	1	26	15

Table 1. Weight ratios and molar ratios of pQpdS-Ch, free water, and bound water.

Based on the results of POM observation, DSC, and XRD measurements, here we discuss the molecular assembled structure of the  $pQpdS-Ch/H_2O$  mixtures. For assuming the molecular assembled structures, an important characteristic of pQpdS-Ch is that it has a strong dipole moment at the sulfonyl group, which can be calculated

to be 5.2 D by DFT calculation (Figure S1) (see supplementary materials). Therefore, it is expected that it forms a dimer in the dissolved state as well as in the assembled states in water. The size of the **pQpdS-Ch** anion is about 20 Å. Based on these results, here we imagine a molecular assembled structure of the **pQpdS-Ch**/H<sub>2</sub>O (X = 60) mixture in the Col<sub>h</sub> phase. The number of bound water per the dimer of the **pQpdS-Ch** molecules calculated from the endothermic peaks in the DSC charts is  $20 \times 2 = 40$ . The inter columnar distance is calculated to be 37.8 Å as explained in the above paragraph. Considering these data and the component weight ratio, the molecular assembled structures of the **pQpdS-Ch**/H<sub>2</sub>O (X = 60) mixture in the Col<sub>h</sub> phase is drawn as shown in Figure 8.



**Figure 8.** A schematic image of the molecular assembled structure of the **pQpdS-Ch**/H<sub>2</sub>O (X = 60) mixture in the Col<sub>h</sub> phase.

In order to further confirm the effects of the cation species, we have also prepared analogous compounds with other inorganic cations, such as Li, Na, and K cations. **pQpdS-Y** (Y = Li, Na, and K) were prepared according to the same procedure used for **pQpdS-Ch**. They were obtained as white or slightly yellowish white compounds (Figure S2). The mixtures of these compounds and water were prepared with varying the component ratios and their phase transition behavior was examined by POM observation.

It has been found that the exhibition of N phases was observed for the **pQpdS-Li**/H<sub>2</sub>O mixtures when the water content value is  $90 \ge X \ge 85$  and that of Col<sub>h</sub> phases was observed when X = 80 (Figure 9). The water content dependence of the mesophase pattern is similar to that of the **pQpdS-Ch**/H<sub>2</sub>O mixtures. These results indicate that the formation of Col<sub>h</sub> is a phenomena that is observed not solely for **pQpdS-X** with organic cations but also for **pQpdS-X** with inorganic.



**Figure 9.** Polarized optical microscopic images of the **pQpdS-Li**/H<sub>2</sub>O mixtures in the 100–X:X weight ratios. (a) X = 95 at 25 °C, (b) X = 90 at 20 °C, (c) X = 85 at 25 °C, (d) X = 80 at 50 °C, and (e) X = 70 at 25 °C.

On the other hand, we have found that the **pQpdS-Na**/H<sub>2</sub>O mixtures forms only N phases when  $95 \ge X \ge 80$  (Figure 10) and those with  $70 \ge X$  form crystalline states. Comparing the water content range forming mesophases for the **pQpdS-X**/H<sub>2</sub>O mixtures (Figures 3 and 11), it can be seen that the employment of the cholinium cation provides chromonic liquid crystals showing LC behavior in the widest water content range. It is attributed to the higher solubility of **pQpdS-Ch** into water that results from its lower crystallinity than those with inorganic cations. Namely, the employment of the cholinium cation increases the conformational degrees of freedom, which contributes to the inhibition of the crystallization. The melting point of **pQpdS-Ch** is higher than 100 °C (Figure S3) that is the important temperature of the definition of ionic liquids. However, considering the recent studies on ionic liquids where hydrated organic salts are called hydrated ionic liquids [23–25,30], we expect that **pQpdS-Ch**/H<sub>2</sub>O mixture can be regarded as hydrated ionic liquids exhibiting chromonic LC behavior.

In the course of studies on ionic liquids, they have been used in a wide range of fields, including electrochemistry, analysis, catalysis, and solvents. Focusing on hydrated ionic liquids, they have been expected as potential solvent for biomolecules [23,31]. On the other hand, chromonic liquid crystals have been investigated as sensors [32] and optical materials [33]. We believe that the present material design will attract attention in a wide field of research ranging from biotechnology to material chemistry.



**Figure 10.** Polarized optical microscopic images of the **pQpdS-Na**/H<sub>2</sub>O mixtures in the 100–X:X weight ratios. (a) X = 95 at 25 °C, (b) X = 90 at 25 °C, (c) X = 85 at 25 °C, and (d) X = 80 at 25 °C.



**Figure 11.** Bar graphs of the thermotropic phase transition behavior of; (**a**) the **pQpdS-Li**/H<sub>2</sub>O mixtures on cooling; (**b**) the **pQpdS-Na**/H<sub>2</sub>O mixtures on cooling.

### 4. Conclusions

We have succeeded in preparing a new class of an organic salt **pQpdS-Ch** showing chromonic liquid-crystalline (LC) behavior. This compound is composed of a rod-shaped aromatic anion with a strong dipole moment and cholinium cations. Both of two components owes their specific tasks. The former plays a key role for the formation of cylindrical aggregates via dipole–dipole interactions. The latter plays an important role for the formation of hydrated states. Moreover, since the hydrated cholinium cations, it results in the inhibition of the crystallization of the cylindrical aggregates. This effect enables to form chromonic LC mesophases even in a wider concentration range than a series of analogous compounds with inorganic cations, which leads to the exhibition of chromonic hexagonal columnar phases.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/cryst12111548/s1, Figure S1: A schematic image of the molecular assembled structure. Figure S2: Pictures of the synthesized compounds; Figure S3: TG/DTA result.

**Author Contributions:** T.I., M.K. and K.S. conceived and designed the experiments; T.I., M.K. and K.S. performed the experiments and analyzed the data; T.I., M.K. and K.S. wrote the paper. All authors have read and agreed to the published version of the manuscript.

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