

## Luminescent Ionic Liquid Crystals Based on Tripodal Pyridinium Salts

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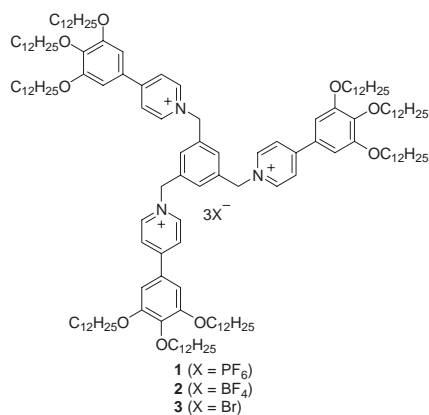
Three-fold symmetrical pyridinium salts tethering tridodecyloxyphenyl substituents form liquid-crystalline columnar and micellar cubic phases and exhibit photoluminescent properties in liquid-crystalline states.

Liquid crystals are functional materials that combine dynamic nature with anisotropic structures.<sup>1,2</sup> Ionic liquid crystals<sup>3</sup> have attracted much attention because of their potential usability as ion-conductive<sup>4</sup> and redox-active<sup>5</sup> materials. Recently, we have reported on nanostructured ion-conductive liquid crystals based on imidazolium<sup>4a–4c</sup> and ammonium<sup>4d</sup> salts. For further functionalization of these ionic liquid crystals, the introduction of luminescent moieties is an important approach. There has been a growing interest in luminescent organic salts constituted of  $\pi$ -conjugated ionic units<sup>6,7</sup> as a new class of chemosensory materials for biomolecules such as DNA, RNA, and proteins via electrostatic interactions. Despite their great potential applications, only a few examples of luminescent ionic liquid crystals have been reported to date.<sup>7</sup>

Herein we report on new luminescent tripodal ionic liquid crystals based on pyridinium salts. The three-fold symmetrical shape of these molecules would be of advantage to chemoselective molecular and anion recognition.<sup>8</sup>

Pyridinium salts **1–3** (Figure 1) were prepared via the quaternization reaction of 4-(3,4,5-tridodecyloxyphenyl)pyridine with 1,3,5-tris(bromomethyl)benzene, followed by the counterion exchange.<sup>9</sup> The liquid-crystalline (LC) properties of **1–3** are summarized in Table 1. Compounds **1** and **2** exhibit rectangular columnar (Col<sub>r</sub>) and hexagonal columnar (Col<sub>h</sub>) phases, respectively, over wide temperature ranges including room temperature. Compound **3** with Br anions forms a micellar cubic (Cub) phase at a higher temperature range above a Col<sub>h</sub> phase.

X-ray diffraction (XRD) measurements were performed for

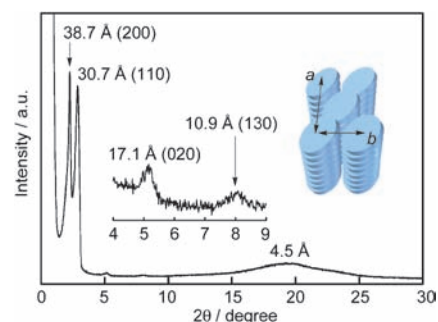


**Figure 1.** Molecular structures of liquid-crystalline pyridinium salts **1–3**.

**Table 1.** Liquid-crystalline properties of **1–3**

Compound	Phase-transition behavior <sup>a</sup>	Lattice parameter <sup>b</sup>
<b>1</b> (X = PF <sub>6</sub> )	Cr 13 Cr' 24 Col <sub>r</sub> 245° Iso (6) (7)	$a = 77.4 \text{ \AA}$ , $b = 33.4 \text{ \AA}$
<b>2</b> (X = BF <sub>4</sub> )	Cr –3 Col <sub>h</sub> 160 Iso (24) (5)	$a = 40.5 \text{ \AA}$
<b>3</b> (X = Br)	Cr 77 Col <sub>h</sub> 179 Cub 245° Iso (20) (4)	$a = 40.6 \text{ \AA}$ (Col <sub>h</sub> ) $a = 80.5 \text{ \AA}$ (Cub)

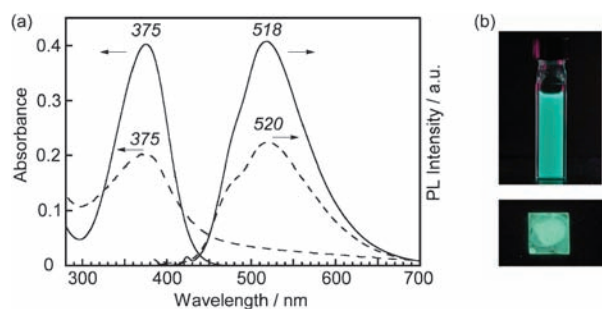
<sup>a</sup>Transition temperatures (°C) and enthalpies (kJ mol<sup>-1</sup>, in parentheses) determined by DSC on the second heating at 10 °C min<sup>-1</sup>. Cr: crystalline; Col<sub>r</sub>: rectangular columnar; Col<sub>h</sub>: hexagonal columnar; Cub: micellar cubic; Iso: isotropic. <sup>b</sup>Measured in the Col phases at 140 °C for **1–3** and the Cub phase at 215 °C for **3**. <sup>c</sup>The isotropization temperatures (°C) were determined by polarized optical microscopy.



**Figure 2.** X-ray diffraction pattern of **1** in the Col<sub>r</sub> phase at 140 °C. The inset shows schematic representation of the proposed structure of the liquid-crystalline state.

compounds **1–3**. As shown in Figure 2, the XRD pattern of **1** taken at 140 °C shows two intense peaks at 38.7 and 30.7 Å and two weak peaks at 17.1 and 10.9 Å, which can be assigned to the (200), (110), (020), and (130) reflections of the Col<sub>r</sub> phase, respectively. In addition, a diffuse halo around 4.5 Å due to the molten aliphatic moieties is observed, whereas no distinct peaks corresponding to the stacking periodicity could be detected in the wide-angle region. These results suggest that the molecules have a high degree of conformational flexibility in the LC states. The lattice parameters of the Col<sub>r</sub> phase for **1** are calculated to be  $a = 77.4 \text{ \AA}$  and  $b = 33.4 \text{ \AA}$  from the XRD data (Table 1).

On the other hand, the XRD patterns of **2** and **3** in the Col<sub>h</sub> phases clearly show three reflection peaks in the small-angle region with the reciprocal  $d$ -spacing ratio of  $1:\sqrt{3}:2$ , characteristic of Col<sub>h</sub> structures.<sup>9</sup> As the temperature rises, columnar assemblies of **3** reorganize into micellar assemblies by increasing the volume fraction of the aliphatic moieties. The XRD pattern of **3** in the Cub phase at 215 °C gives three peaks at 40.4 (200), 35.9 (210), and 32.7 Å (211), suggesting that this phase has  $Pm\bar{3}n$  space group. In the Cub phase, each micelle is assumed to contain approximately 16 clustered molecules on average.<sup>10</sup>



**Figure 3.** (a) UV-vis absorption and photoluminescence spectra of **1** in a dichloromethane solution (solid line) and in a thin film (dashed line). The excitation wavelength is 375 nm. (b) Photographs of **1** in a dichloromethane solution (upper) and in an LC thin film (lower).

It is noteworthy that different LC structures were observed depending on the counter anions. This structural difference in the Col and Cub phases can be explained in terms of the difference in the anion size. As the anion size decreases, the ionic pyridinium cores should be packed more closely through electrostatic interactions. Therefore, the molecules preferably form the Cub structures rather than the Col structures. The nanosegregation between ionic and nonionic moieties is crucial for thermotropic ionic liquid crystals based on ammonium, pyridinium, and imidazolium salts.<sup>3–5</sup>

Compound **1** exhibits intense green photoluminescence (PL) emission both in solution and in the LC state. The UV-vis absorption and PL spectra of **1** in the Col<sub>r</sub> phase shows the peaks at 375 and 520 nm, respectively (Figure 3), whose positions are very similar to those in the solution. When the temperature is increased from room temperature to 200 °C, the PL emission peak is blue-shifted by ca. 20 nm. In addition, the PL spectra of **2** and **3** are essentially identical to that of **1**,<sup>9</sup> suggesting that the light-emission occurs from  $\pi$ -conjugated cationic 3,4,5-trialkoxyphenylpyridinium units and is almost independent of the kind of counter anions. These results indicate that  $\pi$ -conjugated cationic arms are electronically isolated from each other even in the condensed LC state, because of their mutual electrostatic repulsion. This PL behavior is markedly different from that of usual  $\pi$ -conjugated molecules, in which the PL properties are significantly suppressed by the molecular aggregation.<sup>11</sup> The PL quantum yields of **1–3** are 3–6% in solutions.

In conclusion, we have prepared tripodal pyridinium-based ionic liquid crystals that show thermotropic Col or Cub phases in wide temperature ranges. These LC materials emit green light under photoirradiation. We expect that these luminescent ionic liquid crystals are a promising candidate as new chemosensory materials for anionic molecules.

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- 9 Supporting Information is also available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.
- 10 The average number of molecules ( $\mu$ ) in a micelle was estimated according to the following equation:  $\mu = (N_A a^3 \rho) / 8M$ , where  $N_A$  is Avogadro's number,  $\rho$  is the density (assumed to be  $1 \text{ g cm}^{-3}$ ), and  $M$  is the molecular weight of the compound.
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