# Ionic Liquid Crystals Derived from 4-Alkoxypyridines

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### Liquid Crystalline properties of pyridinium salts.

Liquid crystalline behaviors of these pyridinium salts ($[C_nPyOC_n][X]$, X=$Br^-$, $PF_6^-$ and $BF_4^-$; $[C_nPyOH]Cl)$ were studied by polarized optical microscopy (POM), differential scanning calorimetry (DSC) and powder x-ray diffraction (PXRD); in all cases SmA mesophase are assigned. To avoid the influence of $H_2O$ on the thermal behavior, the hydrated samples were heated at 100 ℃ for one hour on the sample holder, in which the cover of the cell lid was punched with holes to allow the evaporation of water during thermal treatment.. The layer distances of these compounds at different phases and temperatures are given in Table 2. The neutral compounds, $[C_nPyO]$ and $[PyOC_n]$, are nonmesomorphic.

POM of $[C_nPyOC_n][Br]$ shows that upon melting, the fluid exhibits focal-conic texture and homeotropic domain, the latter is caused by a molecular vector orthogonal to the substrate but parallel to the light source, a typical behavior for SmA mesophase. DSC thermogram for the compound of n = 18 shows that the phase transition from crystal to mesophase appears at 86.9 ℃ with an enthalpy of 73.7 kJ $mol^{-1}$, and the transition to isotropic liquid appears at 132.9 ℃ with an enthalpy of 1.7 kJ $mol^{-1}$. The small value of enthalpy upon clearing is consistent with the presence of mesophase. The compounds of n = 16, 14, 12 and 10 have melting temperatures at 78.5, 76.9, 69.6 and 62.8 ℃ and clearing temperatures at 133.3, 135.5, 120.2 and 69.3 ℃ respectively. Increasing the chain length from 12 to 18, there is a small but gradual increase on the melting and clearing temperatures. These bromide salts have a temperature range $\Delta T$ of about 55 ℃, except for n = 10, which has a $\Delta T$ value of 6.5 ℃. PXRD was utilized to characterize the mesophase structures. Since single crystal structural data of $[C_{16}PyOC_{16}][Br]$ is available, results of this compound will be discussed first. A set of three equally spaced peaks at small angle region corresponding to (001), (002) and (003) reflections are observed, suggesting a well-defined lamellar structure with a layer distance of 33.2 Å, consistent with that from single crystal. If the temperature is raised to mesophase at 90 ℃, the layer spacing increases slightly to 34.4 Å and shows a faint halo at medium angle. Upon further heating to 100 then 110 ℃, the distance decreases to 33.8 then 32.9 Å. The slight increase of layer distance from crystal to mesophase presumably is caused by the alignment of the molecular rod perpendicular to the layer plane and by the thermal motion of the chain at mesophase; the former tends to elongate the layer spacing, while the later tends to shorten the layer spacing. These results are consistent with a SmA mesophase. Similar arguments apply to the other members in this series.

Except for the nonmesomorphic compound of n = 10, the fan and homeotropic textures are observed for $[C_nPyOC_n][PF_6]$ under POM, again suggesting a SmA mesophase (Figure 1 for n = 16).

For these ILCs of pyridinium salts, different anions affect the temperature range of mesophase, when the anion is bromide, the melting temperature is higher than other anions ($PF_6^-$, $BF_4^-$), and the clearing temperature also has similar condition. For these three different anions, the bromide salts have the widest temperature range of mesophase. Because the strength of H-bonding between bromide anion and cation is stronger than the other anions. The similar phenomenon was also observed for imidazolium salts. Compared with the other pyridinium salts, our compounds have the larger range in mesophase, because they have the oxygen atom and long carbon chains to make crystal structure having the better packing fashion.

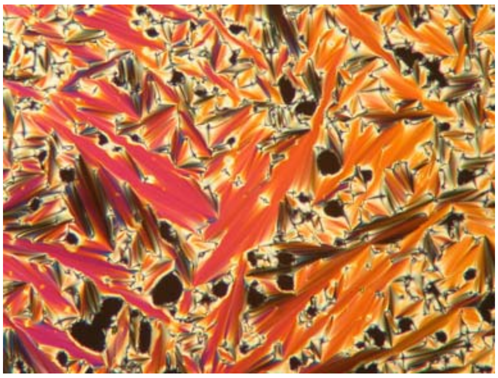

**Figure 1.** The texture of $[C_{16}PyOC_{16}][PF_6]$ at mesophase (99 ℃) upon heating

| Compound | *n* | *d*-Spacing / Å (T / ℃) | |
|---|---|---|---|
| | | Solid state | Mesophase |
| $[C_nPyOC_n][Br]$ | 18 | 37.1 (RT) | 37.1 (100) |
| | 16 | 33.2 (RT) | 33.8 (100) |
| | 14 | 29.7 (RT) | 29.9 (100) |
| | 12 | 26.9 (RT) | 27.1 (100) |
| | 10 | 23.3 (RT) | 22.8 (100) |
| $[C_nPyOC_n][PF_6]$ | 18 | 26.2 (RT) | 31.2 (100) |
| | 16 | 23.9 (RT) | 28.8 (100) |
| | 14 | 21.3 (RT) | 25.8 (85) |
| $[C_nPyOC_n][BF_4]$ | 18 | 29.2 (RT) | 32.2 (90) |
| | 16 | 25.6 (RT) | 29.7 (90) |
| | 14 | 23.1 (RT) | 26.9 (90) |
| | 12 | 20.5 (RT) | 24.3 (70) |
| $[C_nPyOH][Cl]$ | 18 | 31.8 (RT) | 34.1 (90) |
| | 16 | 29.5 (RT) | 31.7 (90) |

**Table 2.** The *d*-spacings of $[C_nPyOC_n][Br]$, $[C_nPyOC_n][PF_6]$, $[C_nPyOC_n][BF_4]$ and $[C_nPyOH][Cl]$ from powder X-ray diffraction. (RT = room temperature