Effect of Alkali Metal Ion on the Ionic Conductivity of a Novel Liquid Crystal Containing a Dibenzo-18-Crown-6 Unit

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A novel liquid crystal containing a dibenzo-18-crown-6 unit was prepared. The ionic conductivity was increased 1.5 orders of magnitude by the addition of an equimolar amount of K^+. However neither Na^+ nor Li^+ yielded suitable samples corresponding to the ion-size matching of the crown ether unit.

Since the discovery of crown ether,[1] a large number of crown ether compounds and their derivatives have been prepared and studied in various fields due to their superior metal ion recognition properties. However application to ordered structures was quite limited.[2,3] Percec et al. showed large increase of ionic conductivity [from 10^{-12} to $10^{-7.5}$ S cm^{-1}] at the phase transition from the crystalline to the liquid crystalline phases using a benzo-15-crown-5 (B15C5) derivative.[2] In addition Nakamura et al. demonstrated that Li^+ passes through the center of 15-crown-5 (15C5) in the crystal of $Li_{0.6}(15C5)[Ni(dmit)_2]_2\cdot(H_2O)$ and the ionic conductivity was 2×10^{-8} S cm^{-1} at 60 °C.[3]

In the framework of our recent studies on metal ion recognition[4] and development of new liquid crystals and related compounds,[5] molecular recognition of ionic species in a well ordered structure became an attractive research area. We have been interested in the application of liquid crystals as a matrix for functional materials or devices. Here we report the synthesis of a novel liquid crystal containing a dibenzo-18-crown-6 (DB18C6) unit and the effect of alkali metal ions on the compound's ionic conductivity and thermal properties.

A new liquid crystalline (LC) compound **1** was prepared starting from DB18C6. DB18C6 was formylated,[6] reduced, and then esterified[2] with 3,4,5-tris(*p*-dodecyloxybenzyloxy)benzoic acid, which was kindly supplied by Canon Inc., to give **1** in 31% total yield as a white solid. The product, a mixture of two regioisomers (the ratio was not determined), gave satisfactory analytical and spectroscopic (IR, ^1H NMR) data.[7] All 1:1 mixtures of **1** and Li^+, Na^+, or K^+ for the DSC and the ionic conductivity measurements were prepared as follows: a $CHCl_3$ solution of **1** and an EtOH solution of each metal perchlorate were mixed at rt for several hours and then the mixture was concentrated.

The thermal properties of **1** and its 1:1 mixtures with alkali metal ions were determined using a Mac Science DSC-3100 differential scanning calorimeter. The ionic conductivities of **1** and **1**+K were determined using a pair of electrodes (ITO, 0.32 cm^2 in area and 2 μm in thickness) with a set of impedance analyzer (Schlumberger SI 1260), an amplifier (Keithley 428) and a temperature controller (Mettler FP 80).

As seen in Figure 1a, **1** has a narrow and unstable LC phase, at 112–117 °C and again at 125–145 °C during the cooling and heating processes, respectively. Although the characterization of the LC phase was difficult due to these facts, a discotic columnar phase was suggested for **1** as indicated by polarizing microscope observations using the cells with and without rubbing surface treatment.

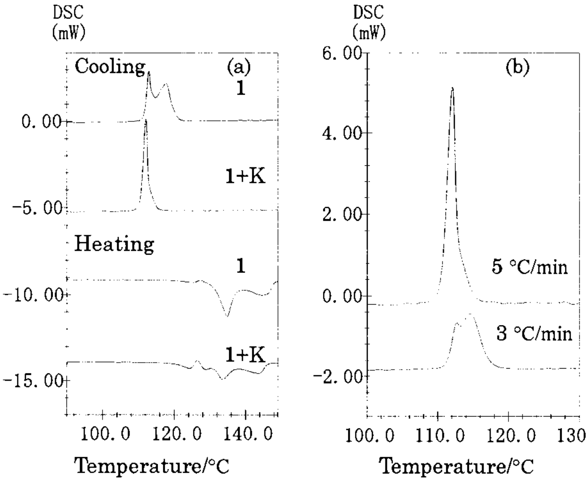

Figure 1. (a) DSC traces of **1** and **1**+K. They are from the first cooling and the second heating processes at 5 °C/min. (b) Cooling rate dependence of the DSC trace of **1**+K.

The DSC charts for **1**+Li and **1**+Na (not shown) indicated a minimal and very unstable LC phase with a drastic decrease of the heat of transition (Table 1). They appeared heterogeneous in the conductivity measurement cells. In fact the cells were not completely filled, preventing the experiments from

Table 1. DSC data and the total heat of transition of **1** and its 1:1 mixtures with alkali metal ions[a]

Samples	Transition Temperature /°C		Total heat of transition[b]
	1st cooling	2nd heating	/ J g^{-1}
1	I • 118 • M • 113 • Cr	Cr • 125 • M • 135 • M • 145 • I	38.3
1 + Li	I • 105 • M • 102 • M • 98 • M • 96 • Cr	Cr • 95 • M • 102 • M • 112 • M • 117 • I	4.8
1 + Na	I • 103 • Cr	Cr • 109 • M • 121 • M • 137 • I	7.3
1 + K	I • 111 • Cr	Cr • 124 • M • 129 • M • 134 • M • 144 • I	32.1

[a] Heating and cooling rates; 5 °C / min. I, M, and Cr stand for the isotropic, mesomorphic and crystalline phases, respectively.
[b] Total heat of transition is the sum of the heats of transition at all transitions on the 2nd heating process.

being performed. On the other hand, **1** + K showed a similar heating DSC chart to that of **1** with ~20% smaller heat of transition. Therefore **1** + K was expected to form a similar LC phase to that of **1**. Only a single exothermal peak was observed on the cooling scan at the rate of 5 °C/min. However a narrower LC phase was observed at a slower cooling rate (Figure 1b), the DSC chart became similar to that of **1** with a further smaller heat of phase transition. Good host–guest interaction between the crown ether unit in **1** and K^+ was expected in both solid and LC states; among the three alkali metal ions, only K^+ was complexed by the DB18C6 unit and the LC property of **1** was preserved to some extent. The effect of the cooling rate on the DSC chart was also interpreted by the interaction between the crown unit and K^+. Reorganization of the complex was likely to be retarded from the isotropic to the LC phase transition. The expected structure was schematically illustrated in Figure 2.

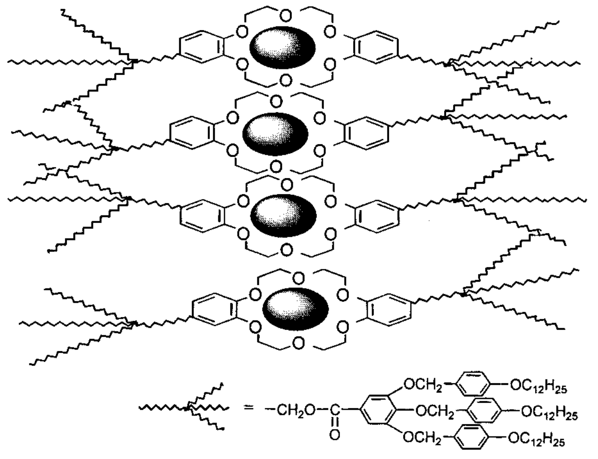

Figure 2. Schematic figure of the 1:1 mixture of **1** and **K^+ (1+K)**.

According to the literature,[1] the UV–Vis spectrum was measured in order to detect the interaction difference between alkali metal ions. However, little difference was observed for the UV–Vis and the NMR spectra of all mixtures [8×10^{-4} mol dm^{-3} in $CHCl_3$–MeOH (3:1); Shimadzu UV-265]. The difference for K^+ and for Li^+ or Na^+ seems much less in solution than that observed by DSC measurements mentioned above. From these results, the effect of the DB18C6 unit on K^+ recognition seems to be larger in the solid or LC phase than for in the liquid phase.

The ionic conductivity of **1** and **1** + K was measured and the results shown in Figure 3. As mentioned previously, the samples of **1** + Li and **1** + Na were not suitable for the measurements. It is clear that the ionic conductivity was increased about 1.5 orders of magnitude by the addition of K^+ throughout the range presently under investigation. The temperature dependence of **1** + K [from 10^{-10} to 10^{-7} S cm^{-1}] was as much as that of **1** both in the solid and the LC phases (Figure 3). We expected lower ionic conductivity in the isotropic phase than in the LC phase considering K^+ recognition by a DB18C6 unit and the discotic columnar phase. A completely disordered isotropic phase should be less favorable for ionic conductivity than an ordered LC phase. The magnitude of the ionic conductivity was similar to that reported by Percec et al.[2] for the cooling process but less for the heating one. Obviously, further study, especially the effect of size fitting of the crown unit, on the electronic properties of **1** is necessary.

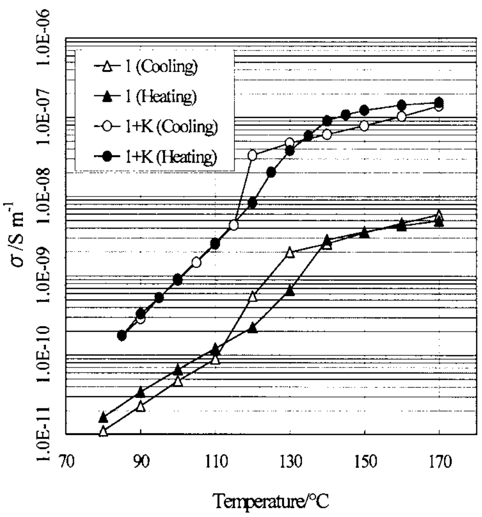

Figure 3. Ionic conductivities of **1** (▲, △) and **1**+K (●, ○). Filled and open symbols represent the data in the heating and the cooling processes, respectively.

In summary a novel liquid crystal was synthesized using a DB18C6 unit as its core. The liquid crystalline phase was well preserved by the addition of equimolar amount of K^+ while Li^+ and Na^+ mostly disordered, which is a good example of size fit recognition by a crown ether moiety in an ordered structure. The addition of K^+ increased the ionic conductivity of the parent compound ~1.5 orders of magnitude. It is worth noting that the higher ionic conductivity of **1**+K was achieved with maintenance of the original ordered structure of **1**, not only in the solid, but also in the LC phase.

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References and Note

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7 Found: C, 75.98; H, 9.18%. Calcd for $C_{150}H_{216}O_{22}$: C, 76.05; H, 9.28%. ^1H NMR ($CDCl_3$) δ 7.36 (s, 4H), 7.31 (d, *J* = 8.5 Hz, 8H), 7.23 (d, *J* = 8.5 Hz, 4H), 6.98–6.94 (m, 6H), 6.87 (d, *J* = 8.8 Hz, 4H), 6.74 (d, *J* = 8.5 Hz, 4H), 5.23 (s, 4H), 5.01 (s, 8H), 4.98 (s, 4H), 4.19 (s, 4H), 4.02 (s, 8H),3.98–3.88 (m, 12H), 1.81–1.73 (m, 12H), 1.27 (bs, 108H), 0.88 (t, *J* = 7.0 Hz, 18H). IR (KBr) 2923, 2853, 1709, 1614, 1588, 1516, 1249, 1174, 1124 cm^{-1}.