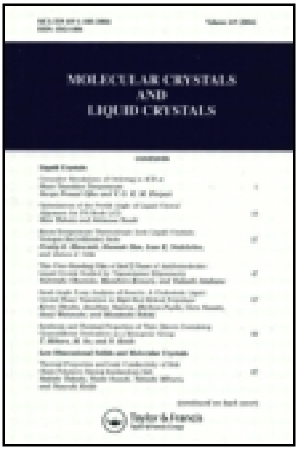

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Molecular Recognition of the Dichiral Liquid Crystals Containing Fluorines

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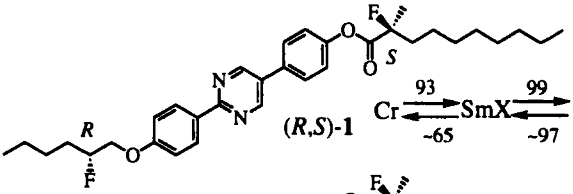
Novel dichiral liquid crystal compound 2-[4-((*R*)-2-fluorohexyloxy)phenyl]-5-[4-((*S*)-2-fluoro-2-methyldecanoyloxy)phenyl]-pyrimidine *((R,S)*-**1***)* exhibits new optically isotropic phase (IsoX) with an endothermic transition enthalpy on cooling. In contrast, (*S,S*)-**1** did not show the unusual transition. However, a 1:1 mixture of *(S,S)*-**1** and *(R,R)*-**1** exhibited IsoX phase. These results suggest that the appearance of IsoX phase is attributed to a chirality-dependent molecular recognition.

Keywords: dichiral ferroelectric liquid crystals; new optically isotropic phase; endothermic transition; molecular recognition; molecular aggregation

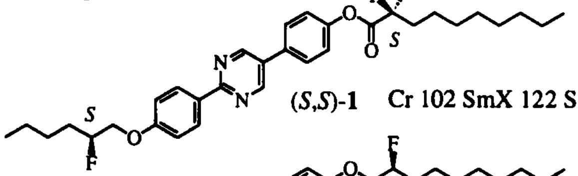
INTRODUCTION

In order to explore ferroelectric liquid crystals (FLC) that exhibit large spontaneous polarization (Ps) and short response time, we designed and synthesized various kinds of optically active compounds useful for chiral dopants.[1, 2] Of the compounds we prepared, we have found 2-[4-((*S*)-2-fluorohexyloxy)phenyl]-5-[4-((*S*)-2-fluoro-2-methyldecanoyloxy)phenyl]-pyrimidine ((*S*,*S*)-**1**) exhibits large Ps, but its diastereomer, 2-[4-((*R*)-2-fluorohexyloxy)phenyl]-5-[4-((*S*)-2-fluoro-2-methyldecanoyloxy)phenyl]-

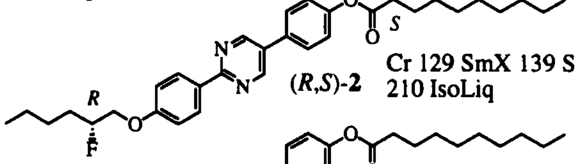


(*R*,*S*)-1

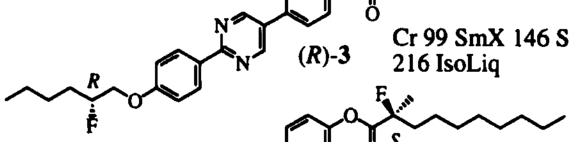
$$\begin{tikzcd}
\mathrm{Cr} \arrow[r, shift left, "93"] & \mathrm{SmX} \arrow[l, shift left, "\sim 65"] \arrow[r, shift left, "99"] & \mathrm{IsoX} \arrow[l, shift left, "\sim 97"] \arrow[r, "131"] & \mathrm{IsoLiq} \arrow[dl, shift left, "116"] \\
 & & \mathrm{SmC^*} \arrow[u, "113"] \arrow[ur, shift left, "117"] &
\end{tikzcd}$$



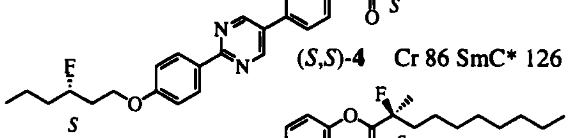
(*S*,*S*)-1 Cr 102 SmX 122 SmC* 128 IsoLiq



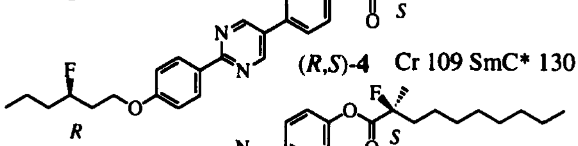
(*R*,*S*)-2 Cr 129 SmX 139 SmC* 191 SmA 210 IsoLiq



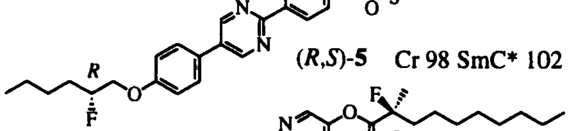
(*R*)-3 Cr 99 SmX 146 SmC* 209 SmA 216 IsoLiq



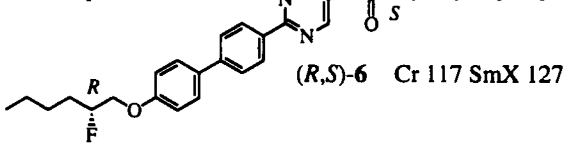
(*S*,*S*)-4 Cr 86 SmC* 126 IsoLiq



(*R*,*S*)-4 Cr 109 SmC* 130 IsoLiq



(*R*,*S*)-5 Cr 98 SmC* 102 SmA 136 IsoLiq



(*R*,*S*)-6 Cr 117 SmX 127 IsoLiq

pyrimidine ((*R*,*S*)-**1**), undergoes an endothermic transition upon cooling from a chiral smectic C (SmC*) phase to an optically isotropic (IsoX) phase.[3] In order to study the structural factors affecting the trantion to IsoX phase, we designed compounds **2**-**6**. Herein we report their synthesis and properties as well as the miscibility of the stereoisomers of (*R*,*S*)-**1**.

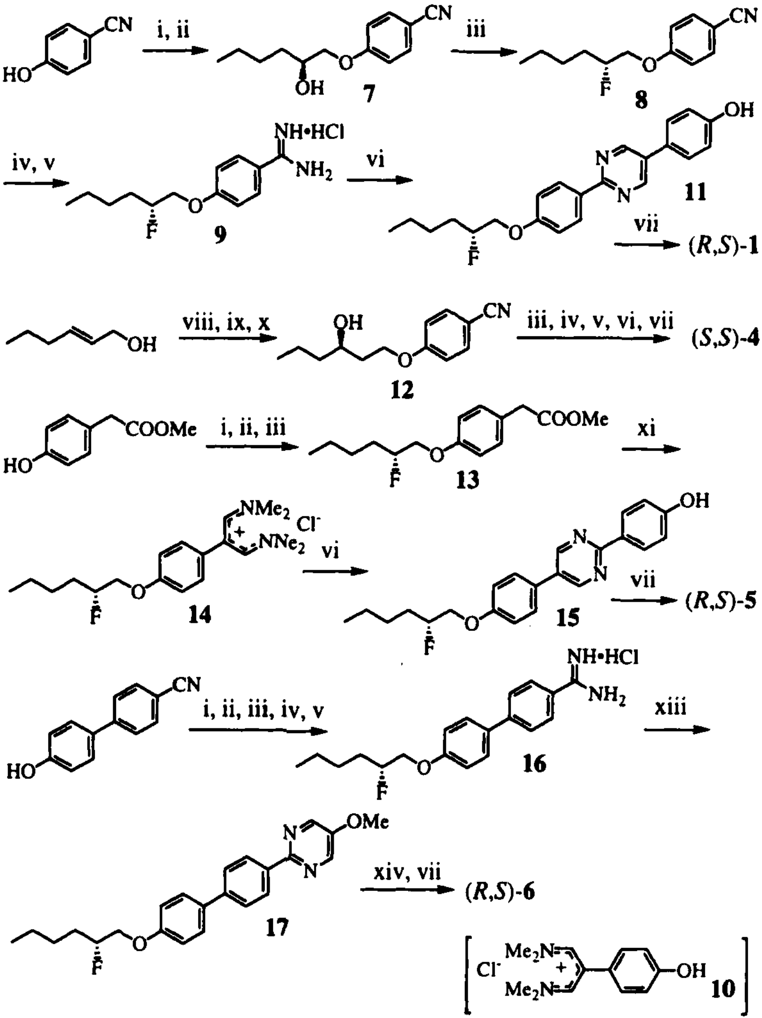
SYNTHESIS

Syntheses of optically active fluorohexyloxy type compounds (*R*,*S*)-**1**, (*S*,*S*)-**4**, (*R*,*S*)-**5**, and (*R*,*S*)-**6** were carried out according to the route shown in Scheme 1. (*R*)-4-(2-Fluorohexyloxy)benzonitrile (**8**) was prepared by the fluorination of (*S*)-4-(2-hydoxyhexyloxy)benzonitrile (**7**) obtained through the reaction of 4-hydroxybenzonitrile with (*R*)-epichlorohydrin followed by the reaction with *n*-$Pr_2CuMgBr$. Reaction of **8** with HCl and ethanol and subsequently with NH_3 afforded amidine **9**. Pyrimidine ring formation[4] of **9** with vinamidinium salt **10** gave **11** which was allowed to react with (*R*)-2-fluoro-2-methyldecanoic acid using dicyclohexylcarbodiimide to give (*R*,*S*)-**1**. In a similar manner, (*S*,*S*)-**1**, (*S*,*R*)-**1**, (*R*,*R*)-**1**, (*R*,*S*)-**2** and (*R*)-**3** were obtained.

(3-Fluorohexyloxy)phenylpyrimidine (*S*,*S*)-**4** was synthesized, starting with (*S*)-4-(3-hydoxyhexyloxy)benzonitrile (**12**) in lieu of **7**. Benzonitrile **12** was easily prepared from 2-hexen-1-ol in 3 steps.

5-[4-(2-Fluorohexyloxy)phenyl]pyrimidine (*R*,*S*)-**5** was synthesized from **13** which was prepared from methyl 4-hydroxyphenylacetate in 3 steps. Acetate **13** was allowed to react with $POCl_3$ and *N*,*N*-dimethylformamide to give vinamidinium salt **14**. Reaction of **14** with 4-hydroxybenzamidine followed by esterification with (*R*)-2-fluoro-2-methyldecanoic acid afforded (*R*,*S*)-**5**.

Amidine **16** prepared from 4-cyano-4'-hydroxybiphenyl in 5 steps was allowed to react with $MeOC(=CHNMe_2)CHO$ to give methoxypyrimidine **16**. Demethylation followed by esterification afforded (*R*,*S*)-**6**.



i: (R)-epichlorohydrin, *t*-BuOK; ii: *n*-$Pr_2CuMgBr$; iii: Et_2NSF_3; iv: HCl, EtOH; v: NH_3; vi: **10**, MeONa; vii: (R)-HOCOCHFMe-*n*-C_8H_{17}, dicyclohexylcarbodiimide; viii: Sharpless oxidation; ix: Red-Al; x: HOC_6H_4CN, $(=NCOOEt)_2$, PPh_3; xi: $POCl_3$, *N,N*-dimethylformamide; xii: $HOC_6H_4C(=NH)NH_2$•HCl, MeONa; xiii: $MeOC(=CHNMe_2)CHO$, MeONa; xiv: NaOH, Δ

SCHEME 1

PROPERTIES

Of the compounds prepared, (*R*,*S*)-**1** and (*S*,*R*)-**1** exhibited IsoX phase with endothermic transition enthalpy on cooling. However, diastereomers (*S*,*S*)-**1** and (*R*,*R*)-**1**, demethyleted analogue (*R*,*S*)-**2**, monochiral compound (*R*)-**3**, regioisomers (*S*,*S*)-**4** and (*R*,*S*)-**4** containing a chiral 3-fluorohexyloxy group, and (*R*,*S*)-**5** and (*R*,*S*)-**6** having different core aromatics, did not show IsoX phase. Whether IsoX phase appears or not is affected by not only the configurations of the two chiral centers but also the structures of the substituents on the chiral carbons, the positions of the chiral centers, and the structures of the core aromatics.

Next, miscibility studies of the stereoisomers, (*R*,*S*)-**1**, (*S*,*R*)-**1**, (*S*,*S*)-**1**, and (*R*,*R*)-**1**, were performed. Figure 1 shows the phase diagram between enantiomers (*R*,*S*)-**1** and (*S*,*R*)-**1** on cooling. All the mixtures exhibited IsoX phase and showed the same phase transition regardless of the ratio of (*R*,*S*)-**1** to (*S*,*R*)-**1**. Figure 2 shows the phase diagram between diastereomers (*R*,*S*)-**1** and (*R*,*R*)-**1**. Although the isotropic liquid to SmC* phase transition temperatures for (*R*,*S*)-**1** continues into that for (*R*,*R*)-**1**, there is a clear discontinuity in the SmC* to IsoX phase transition. Figure 3 shows the phase diagram between enantiomers (*R*,*R*)-**1** and (*S*,*S*)-**1**. Although both did not exhibit IsoX phase in a pure state, the mixture between 3:2 to 2:3 did show IsoX phase. Thus, a 1:1 ratio of (*R*)-2-fluoroalkoxy and (*S*)-2-fluoro-2-methylalkanoyloxy group (and/or (*S*)-2-fluoroalkoxy and (*R*)-2-fluoro-2-methylalkanoyloxy group) appears to be particularly requisite to the emergence of IsoX phase. These observations suggest that the appearance of IsoX phase should be attributed to a chirality-dependent molecular recognition.

We propose a model structure corresponding to IsoX phase in Figure 4. In SmC* phase, liquid crystal molecules rotate around a molecular long axis. Upon the SmC* to IsoX phase transition, the anisotropy of molecular motion is reduced to induce rotation around a short axis by forming a molecular aggregation via a stereospecific intermolecular interaction in each layer. Although this model can explain the appearance and properties of IsoX phase,

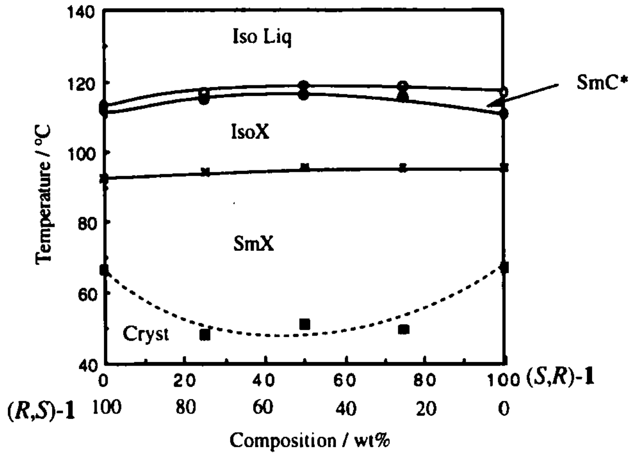


FIGURE 1 Phase diagram between (*R*,*S*)-**1** and (*S*,*R*)-**1**. The transition temperatures were determined by DSC upon cooling.

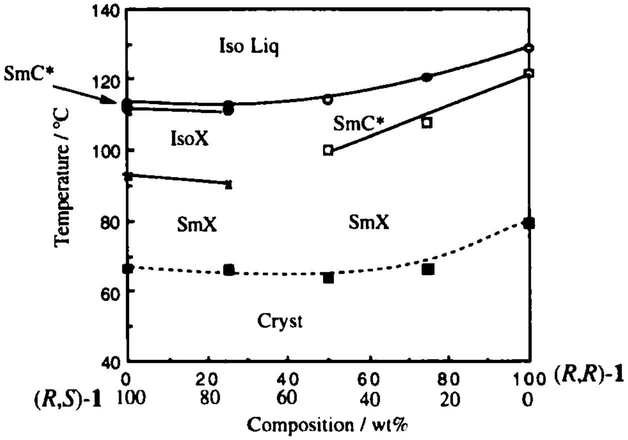


FIGURE 2 Phase diagram between (*R*,*S*)-**1** and (*R*,*R*)-**1**. The transition temperatures were determined by DSC upon cooling.

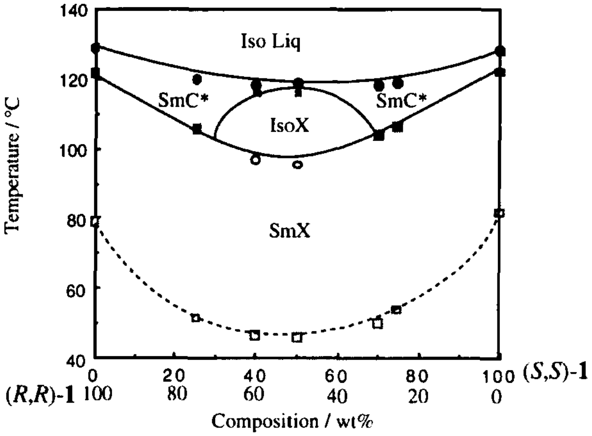


FIGURE 3 Phase diagram between (*R*,*R*)-**1** and (*S*,*S*)-**1**. The transition temperatures were determined by DSC upon cooling.

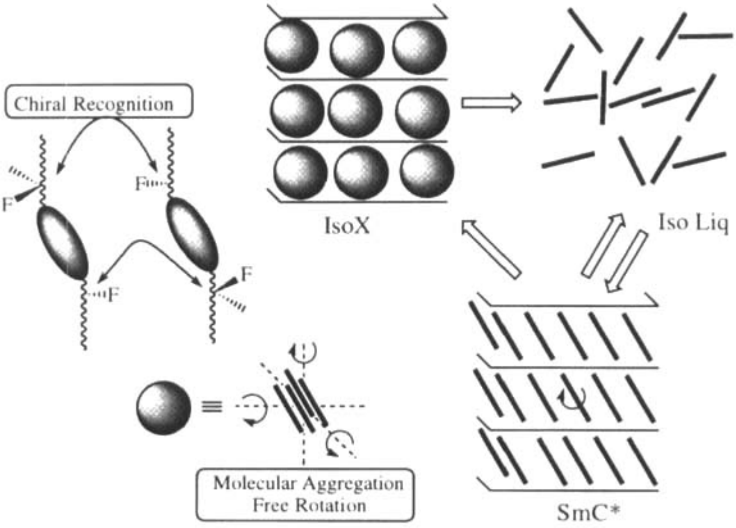


FIGURE 4 A possible model for the emergence of IsoX phase.

the possibility of cubic phase[5,6] or plastic crystal[7] cannot be ruled out. The structure analysis of IsoX phase is in progress in our Laboratories.

In summary, we have synthesized dichiral liquid crystal compounds containing two fluorines and demonstrated 2-[4-((*R*)-2-fluorohexyloxy)-phenyl]-5-[4-((*S*)-2-fluoro-2-methyldecanoyloxy)phenyl]pyrimidine, its (*S*,*R*)-isomer, and a 1:1 mixture of (*R*,*R*)- and (*S*,*S*)-isomers exhibit new optically isotropic phase (IsoX) with an endothermic transition enthalpy on cooling. These observations led us to propose a new stereospecific intermolecular interaction.

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