Molecular Self-Organization of Liquid Crystals through the Formation of Hydrogen-Bonded Networks among a Mesogenic Diol and Imidazoles

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A new class of liquid-crystalline materials consisting of a mesogenic diol and imidazoles exhibits stable smectic liquid-crystalline phases by self-organization through the formation of *hetero*-intermolecular hydrogen-bonded networks.

It is known that molecular self-assembly can be achieved by non-covalent interactions such as hydrogen bonds. The use of hydrogen bonding is one of the central principles that directs the design and control of functional molecular systems. Liquid crystal is one of the important molecular aggregates which has potential for dynamic functional materials.

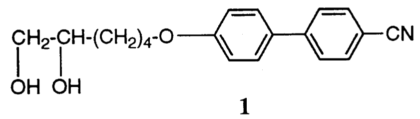
A few systems involving *homo*-intermolecular hydrogen bonds which function among *identical* molecules have been reported to exhibit liquid-crystalline states.[1-7] Sugars,[1,2] diols,[3-6] and polyols[7] exhibit mesomorphism due to the formation of hydrogen bonding among hydroxyl groups.

Supramolecular liquid-crystalline system which is a new class of mesogenic materials has been designed and prepared by the formation of H-bonded mesogenic cores with well-defined structures.[8-14] Molecular recognition and self-organization derived from *hetero*-intermolecular hydrogen bond between *different* and *independent* molecules in neat state may bridge supramolecular chemistry and materials chemistry.

In the case of liquid-crystalline diols and polyols,[1-7] mesomorphism has been achieved by the formation of networks of *homo*-intermolecular hydrogen bonds among hydroxyl groups in the neat or water-saturated states. In nature, the cooperation of different functional groups through *hetero*-intermolecular non-covalent bonds plays an important role in chemical and biological processes in high efficiency.

We report here a new class of liquid-crystalline self-organized system obtained through the formation of *hetero*-intermolecular H-bonded networks between amphiphilic diols and imidazoles. 4-Cyano-4'-(5,6-bis(hydroxy)hexyloxy)-biphenyl (**1**)[4,15] incorporating a diol moiety at the extremity at its one end group was selected for the hydrogen bonding molecule. Amphiphilic compound **1** is crystalline solid at room temperature and exhibits only a nematic phase from 99 to 125 °C on heating and from 124 to 45 °C on cooling. Mesogenic compound **2**, 4-cyano-4'-(6-(hydroxy)hexyloxy)biphenyl[16] has one hydroxyl group at the terminal position.

Nematogenic compound **1** with a diol moiety complexed with heterocyclic molecules, imidazole (**3**) and 2-methylimidazole (**4**),[17,18] has been found to form self-organized smectic structures over wide temperature ranges, while no smectic behavior is observed for the complexes based on monohydroxyl mesogen **2**. Table 1 gives thermal behavior of the complexes of **1** and **2** with **3** and **4**. Figure 1 shows DSC thermogram of the 1:2 complex (molar ratio) of **1** and **3** on the 2nd heating. Interestingly, the smectic phase is seen even below 0 °C and preserved as a glassy state on cooling. On the heating, the glass transition to the subsequent smectic phase is observed at -23 °C. On polarizing microscopy observation, the liquid-crystalline complexes tend to show homeotropic molecular alignment due to the interaction of the hydrogen bonding moieties and the glass surfaces.



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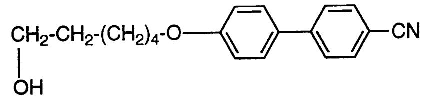

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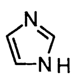

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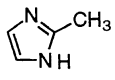

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Table 1. Thermal behavior of complexes of dihydroxyl and monohydroxyl compounds and imidazoles[a]

Complex	Molar ratio	Phase behavior / °C													
		Heating							Cooling						
1/3	1:1	G	-24	S_A	69	N	86	I	I	84	N	67	S_A	-29	G
1/3	1:2	G	-23	S_A	60	N	74	I	I	73	N	60	S_A	-27	G
1/4	1:1	G	-17	S_A	49	N	66	I	I	64	N	48	S_A	-22	G
2/3	1:1					K	77	I	I	70	N	41	K		
2/4	1:1			K	94	N	103	I	I	101	N	73	K		

[a] K: crystalline, G: glassy, S_A: smectic A, N: nematic, I: isotropic. On 1st cooling and 2nd heating.

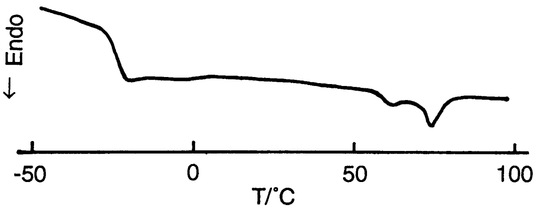

Figure 1. DSC thermogram of the 1:2 complex of **1** and **3** on heating.

Infrared spectra were obtained for **1** and complex of **1** and **3**. The broad OH absorption was seen at 3440 cm^{-1} for the single component of **1**. For the complex, a new shoulder band appeared at 3340 cm^{-1}, which indicates the formation of stronger hydrogen bond between the hydroxyl group and the nitrogen of the imidazole.

The formation of random networks of hydrogen bonds between the diol moiety and the imidazoles may result in the molecular self-organized materials, as shown in Figure 2. Heterocyclic compounds, imidazoles, which are nonmesogenic molecules, function in the liquid-crystalline materials as a part of the hydrogen-bonded network which may have potential for functional materials such as anisotropic catalytic system.

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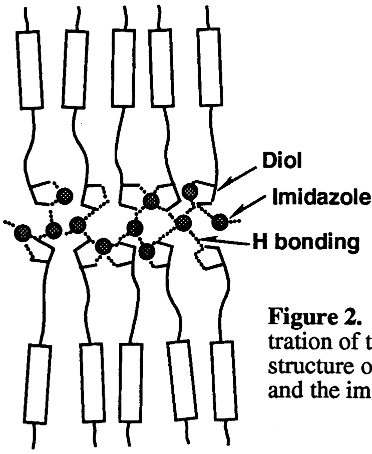

Figure 2. Schematic illustration of the self-organized structure of the mesogenic diol and the imidazoles.

References and Notes

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15 Compound **1** was prepared by hydrolysis of 4-cyano-4'-(4-(2,2-dimethyl-1,3-dioxolane-4-yl)butyloxy)biphenyl, which was obtained by Mitsunobu etherification for 4-(2,2-dimethyl-1,3-dioxolane-4-yl)-1-butanol and 4-cyano-4'-(hydroxy)biphenyl. O. Mitsunobu, *Synthesis*, **1981**, 1.
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17 Imidazole (**3**) and 2-methylimidazole (**4**) are white crystalline solid at room temperature and simply melt to isotropic liquid at 90 and 143 °C, respectively.
18 The complexes were prepared by evaporation of the requisite amount of the mixture in methanol.