

## Induction of a liquid-crystalline phase for supramolecular network obtained by self-assembly of nonmesogenic trifunctional H-bond donor and acceptor molecules

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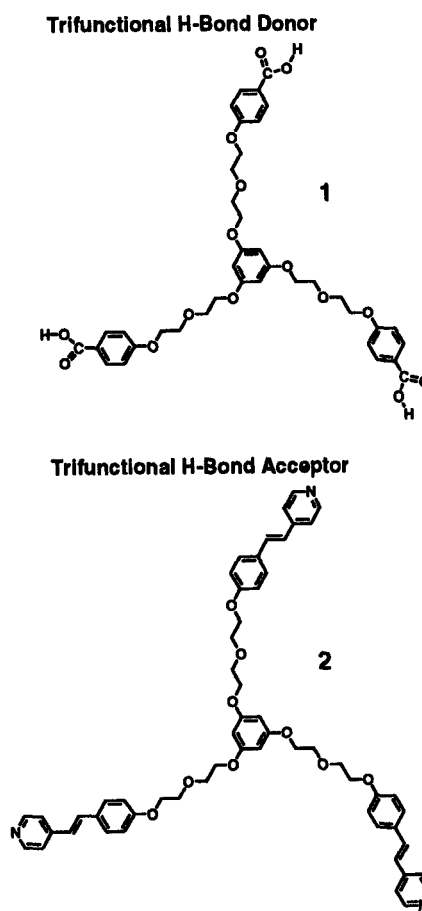
A supramolecular network has been prepared by self-assembly of trifunctional molecules of H-bond donor and acceptor through the formation of intermolecular hydrogen bonds. As a trifunctional H-bond donor, 1,3,5-tris(2-(2-(4-carboxyphenoxy)ethoxy)ethoxy)benzene (1) having three carboxylic acid moieties was selected. 1,3,5-Tris(2-(2-(4-(2-(4-pyridyl)ethenyl)phenoxy)ethoxy)ethoxy)benzene (2) containing three pyridyl units was synthesized for the use as a trifunctional H-bond acceptor. The network shows a smectic A phase from 144 to 162 °C, though each of the single components is nonmesogenic.

### 1. INTRODUCTION

Hydrogen bonding is one of powerful tools for construction of self-assembled and well-defined molecular architecture [1-5]. We have reported supramolecular liquid-crystalline complexes built through intermolecular hydrogen bonds between independent and dissimilar molecules [6-16]. The single hydrogen bond between carboxylic acid and pyridine [6-13], and the double hydrogen bonds between carboxylic acid and 2-aminopyridine [14,15] have been used for preparation of supramolecular liquid-crystals. Furthermore, we have reported liquid-crystalline miscible polymer blends through intermolecular hydrogen bonds between phenol and pyridine units [16].

On the other hand, solid-state molecular networks have been obtained by hydrogen bonds [17-21]. For example, Lauher and co-workers prepared H-bonded networks from dicarboxylic acid urea derivatives [21].

We have obtained supramolecular hydrogen-bonded networks [12,13] which exhibit mesomorphic properties by careful design of the molecular structure of H-bond donors and acceptors. In a previous paper, we reported [13] that supramolecular H-



bonded networks formed by self-assembly of trifunctional H-bond donors and bifunctional H-bond acceptors showed nematic and smectic phases. We concluded that the mesophases have been induced due to the dynamic nature of the interaction and the types of mesophases could be controlled by the conformation of the individual multifunctional components for liquid-crystalline networks because dynamic hydrogen bonds fix the position of the mesogenic core even in the molten state.

In the present study, we have prepared a hydrogen-bonded network by the complexation of trifunctional H-bond donor and acceptor, as shown in Chart 1, and examined its thermal properties.

## 2. EXPERIMENTAL

### 2.1 Syntheses of trifunctional H-bond donor 1 and acceptor 2

A preparation of trifunctional H-bond donor 1, which has three benzoic acid moieties in its periphery, was described in a previous paper [13].

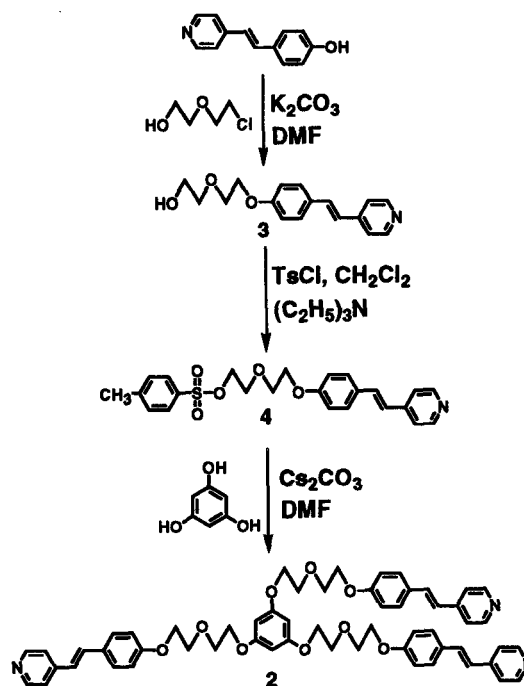
Trifunctional H-bond acceptor 2 was synthesized according to Scheme 1.  $^1\text{H}$  NMR for 2 ( $\text{CDCl}_3$ , 27 °C, ppm)  $\delta$  8.55, 7.38 (pyridyl), 7.47, 6.93 (phenyl), 7.28, 6.89 (-CH=CH-), 6.12 (1,3,5-substituted benzene), 4.18, 4.09, 3.92 (oxyethylene).

### 2.2 Preparation of H-bonded complex

Hydrogen-bonded complex was prepared by the evaporation technique described in previous papers [1,6]. The pyridine solution containing equimolar amount of H-bond donor and acceptor moieties was evaporated under reduced pressure. The resulting solid was dried in vacuo at 60 °C for 24 h.

### 2.3 Characterization

$^1\text{H}$  NMR spectrum was obtained by using JEOL GX JNM270 FT NMR spectrometer. DSC measurements were performed with Mettler DSC 30. Heating and cooling rate were 10 °C/min. Transition temperatures



Scheme 1

were taken at the maximum of transition peaks. A polarizing microscope Olympus BH2 equipped with a Mettler FP82HT hot stage was used for visual observation.

## 3. RESULTS AND DISCUSSION

Trifunctional H-bond acceptor 2 has the same structural feature as 1, but contains three stilbazole moieties instead of benzoic acids. These trifunctional compounds 1 and 2 are nonmesogenic and their melting points are 175 and 101 °C, respectively.

Hydrogen-bonded complex 1/2 was prepared from an equimolar amounts of 1 and 2. It was expected that intermolecular hydrogen bonds between carboxylic acids of 1 and pyridyl moieties of 2 were formed by complexation, resulting in a supramolecular H-bonded network. Thermal properties of complex 1/2 are shown in Table 1. The complex exhibits enantiotropic smectic A phase. We previously reported that H-bonded complexes obtained from 1 and

Table 1 Thermal properties of H-bonded complex 1/2

Phase transition behavior <sup>a</sup>							
heating				cooling			
K	144	S <sub>A</sub>	162	I	I	157	S <sub>A</sub>
	(21.7)		(11.9)		(12.9)		(16.2)

<sup>a</sup>Transition temperatures (°C) and enthalpies of transitions (J/g, in parentheses). K: crystalline, S<sub>A</sub>: smectic A, I: isotropic.

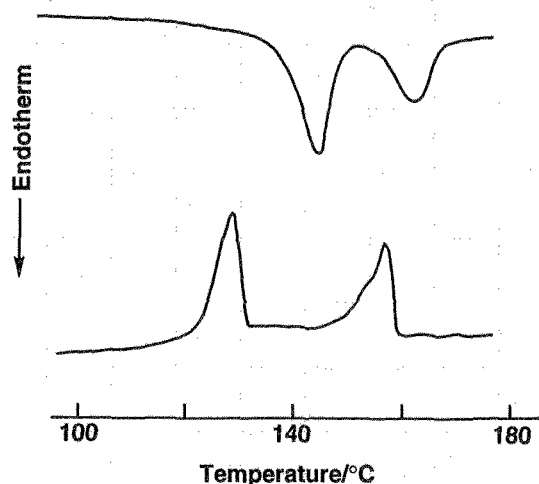


Figure 1. DSC thermograms of H-bonded complex 1/2.

bifunctional H-bond acceptors [13]. These complexes showed only monotropic smectic A phase. It is of interest that enantiotropic mesophase is induced for complex 1/2. This behavior is considered to be due to a preferred conformation of 1 and flexibility of compound 2 based on oxyethylene spacers.

Figure 1 shows DSC thermograms of complex 1/2. On heating scan, two peaks corresponding to crystal—smectic A (K→S<sub>A</sub>) and smectic A— isotropic (S<sub>A</sub>→I) transitions are clearly seen at 144 and 162 °C, respectively. Two peaks due to I→S<sub>A</sub> and S<sub>A</sub>→K transitions are observed on cooling. A focal-conic fan texture characteristic of

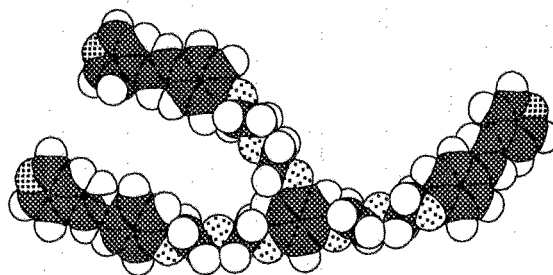


Figure 2. Molecular modeling of 2.

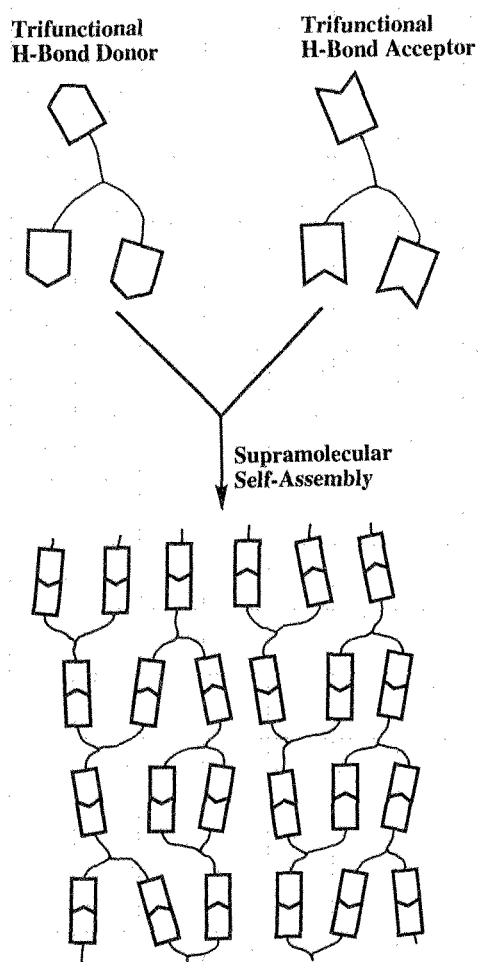


Figure 3. Schematic illustration of smectic network formed by supramolecular self-assembly of 1 and 2.

smectic A phase is seen between the two peaks under a cross-polarizing microscope.

In a previous paper [13], we have concluded that trifunctional H-bond donor **1** adopted linear conformation that induced calamitic behavior with bipyridine compounds [22]. We have also performed molecular modeling for trifunctional acceptor **2**. The result is depicted in Figure 2. If one of the spacer of **2** lies parallel to the others, the stilbazole moieties are able to align and the free volume can decrease. This molecular model is consistent with the result that complex **1/2** exhibits a smectic A phase. A schematic illustration for the formation of smectic network through supramolecular self-assembly of **1** and **2** is shown in Figure 3. The induction of mesomorphic properties in this self-assembled network is attributed to the dynamic nature of its hydrogen bonds.

In this study, supramolecular liquid-crystalline network could be obtained by the combination of trifunctional H-bond donor and acceptor. Furthermore, we consider it is possible to prepare supramolecular liquid-crystalline networks by the combination of four- or more-functional (eventually, poly-functional) H-bond donor and acceptor.

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