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Induction of a cholesteric phase via self-assembly in supramolecular networks built of non-mesomorphic molecular components

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Supramolecular hydrogen-bonded networks have been prepared by self-assembly of a chiral bifunctional H-bond acceptor and achiral trifunctional H-bond donors. A stilbazole dimer, (*R*)-1,2-bis{4-[2-(4-pyridyl)ethenyl]phenoxy}propane (**1**) has been synthesized for use as a chiral component for cholesteric networks. Compound **1** has been complexed with trifunctional H-bond donors, *p*,*q*-bis{2-[2-(4-carboxyphenoxy)ethoxy]ethoxy}benzoic acids (**2–6**) [*p*,*q* = 2,4 (**2**); 2,5 (**3**); 2,6 (**4**); 3,4 (**5**); 3,5 (**6**)], maintaining the 1 : 1 donor/acceptor group stoichiometry. With the exception of the complex from **1** and **6**, these H-bonded complexes exhibit cholesteric phases and glass transition behaviour, while all individual components are non-mesomorphic. For example, the H-bonded complex consisting of **1** and **2** shows a cholesteric phase from 75 to 184°C on heating. These results suggest that supramolecular liquid crystalline networks with macroscopic helical structures have been formed by intermolecular hydrogen bonds between non-mesomorphic smaller molecules. The solid state films obtained by cooling the samples from their mesophases exhibit cholesteric colours associated with selective reflection. The cholesteric structure is preserved in the glassy state of the networks.

1. Introduction

Cholesteric liquid crystals have attracted attention because of their unique optical properties such as selective reflection of light, thermochromism, and circular dichroism [1–3]. Generally, cholesteric aromatic liquid crystal compounds are prepared by introducing optically active groups into nematogens.

We have already reported that supramolecular liquid crystalline complexes which show a variety of mesophases are prepared through intermolecular hydrogen bonding [4–10]. The H-bonded complexes of a chiral benzoic acid and achiral stilbazoles [9], or of achiral benzoic acids and chiral stilbazoles [10], exhibit chiral mesophases including cholesteric phases. The cholesteric phases of the complexes change to smectic or crystalline phases with decreasing temperature, so that the cholesteric structures cannot be retained in the solid states. Lehn and co-workers have obtained hexagonal columnar liquid crystals which have helix superstructures formed by triple hydrogen bonding of complementary pairs [11]. Ionic interactions have also been used for the construction of liquid crystalline complexes which show chiral mesophases [12]. Recently, liquid crystalline networks have been prepared by supramolecular self-assembly of non-mesomorphic molecules [13, 14] or of a functionalized polymer and a small molecule by us [15]. We show liquid crystalline phases and reversible phase transitions between mesophases and isotropic phases because the networks have been formed by non-covalent interaction, i.e. intermolecular hydrogen bonds between multifunctional H-bond donors and acceptors. Moreover, most of the networks exhibit glass transition behaviour due to the formation of polymeric random structures [13–15].

In the present paper, we report our approach to supramolecular construction of chiral networks. An

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optically active stilbazole dimer (**1**) has been prepared for use as a bifunctional H-bond acceptor to complex with various trifunctional H-bond donors (**2–6**) having three benzoic acid units (figure 1).

2. Experimental

2.1. *Materials*

(*S*)-(-)-1,2-Ditosyloxypropane and methyl 3,5-dihydroxybenzoate were commercial products used without further purification. Ethyl 2,4-, 2,5-, and 2,6-dihydroxybenzoates were synthesized from the corresponding dihydroxybenzoic acid by esterification with ethanol using concentrated sulphuric acid.

2.2. *Synthesis of chiral bifunctional H-bond acceptor* ***1***

The synthesis of chiral bifunctional H-bond acceptor **1** is shown in scheme 1. A mixture of *trans*-4-hydroxy-4′-stilbazole [6, 16] (0·51 g, 2·6 mmol), (*S*)-(-)-1,2-ditosyloxypropane (0·5 g, 1·3 mmol), Cs_2CO_3 (1·70 g, 5·2 mmol), and DMF (20 ml) was stirred at room temperature under nitrogen atmosphere for three days. The reaction mixture was extracted with chloroform. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The crude product was purified by column chromatography on a silica gel, using chloroform/methanol (30/1) as eluent, and recrystallized from a mixture of chloroform and hexane to afford pale yellow cyrstals. Yield 0·13 g (23·0%). $[\alpha]_D^{25} + 15{\cdot}0°$ (*c* 1%, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 27°C, ppm), δ 8·55 (d, 4 ArH, *ortho* to N), 7·49, 7·48 (d, 4 ArH, *meta* to –O–), 7·34 (d, 4 ArH, *meta* to N), 7·26, 6·89 (d, 4 H, –CH=CH–), 6·98, 6·94 (d, 4 ArH, *ortho* to –O–), 4·82 (m, 1 H, –C*H*(CH_3)CH_2–), 4·22, 4·08 (m, 2 H, –CH(CH_3)CH_2–), 1·48 (d, 3 H, –CH(CH_3)CH_2–).

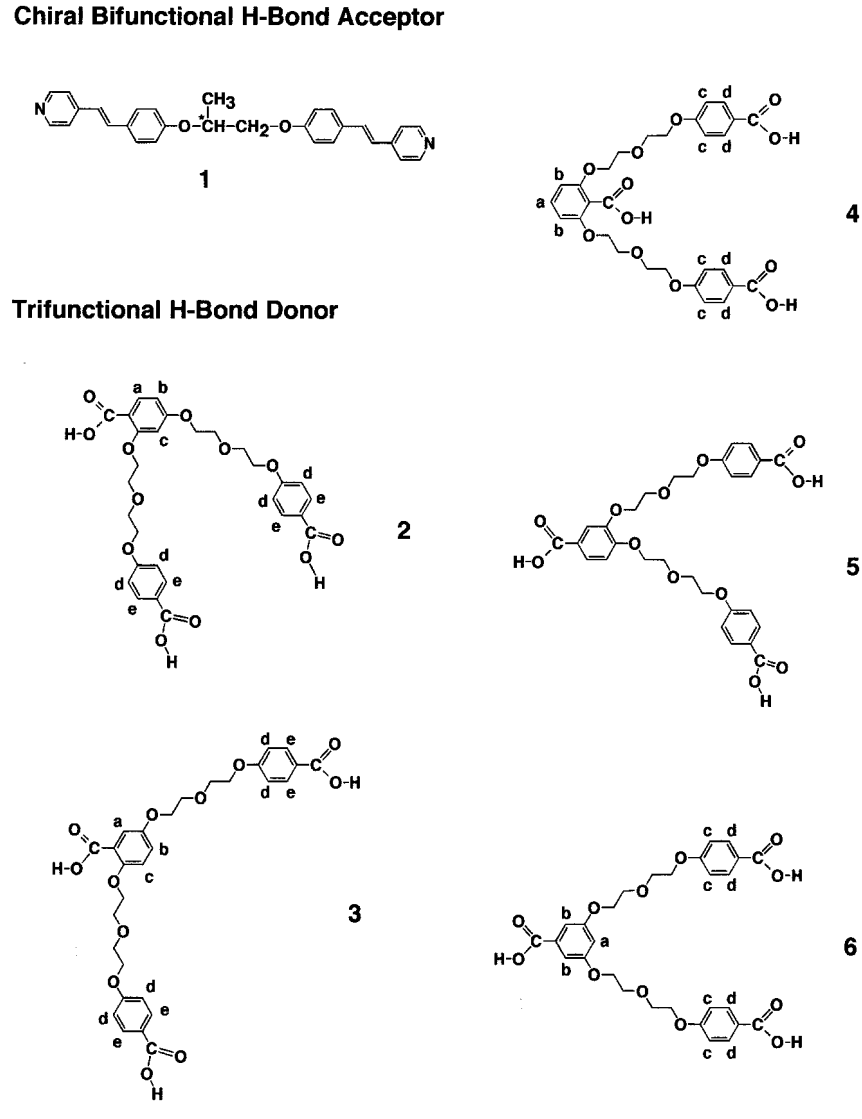
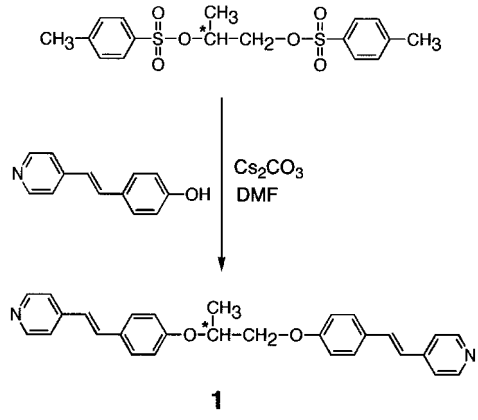


Figure 1. Bifunctional H-bond acceptor (**1**) and trifunctional H-bond donors (**2–6**).



Scheme 1.

2.3. *Syntheses of trifunctional H-bond donors* ***2–6***

The syntheses of the tosylate having a benzoic acid moiety and trifunctional H-bond donor **5** were described in a previous paper [13]. Trifunctional H-bond donors **2–4** and **6** were synthesized by a similar procedure, as shown in scheme 2. A DMF solution containing the tosylate (2 equiv.), the corresponding dihydroxybenzoic acid methyl or ethyl ester (1 equiv.), and Cs_2CO_3 (3 equiv.) was stirred at 25°C under a nitrogen atmosphere for two days. After reaction, DMF was removed and the remaining mixture was extracted with chloroform. The crude product was purified by chromatography on a silica gel column using hexane/EtOAc (2/1) as eluent. The resulting solid was hydrolysed by NaOH in DMSO and then acidified with dilute aqueous HCl to precipitate the triacid. The crude product was recrystallized from a mixture of DMF and water.

Compound ***2***

Yield 71·2% (based on ethyl 2,4-dihydroxybenzoate). ^{1}H NMR (DMSO-d$_6$, 27°C, ppm) δ 7·88 (d, 4 ArH, H-e), 7·68 (d, 1 ArH, H-a), 7·02 (d, 4 ArH, H-d), 6·66 (s, 1 ArH, H-c), 6·58 (d, 1 ArH, H-b), 4·19 (m, 8 H, $-CH_2CH_2OAr$), 3·89–3·81 (m, 8 H, $-CH_2CH_2OAr$).

Compound ***3***

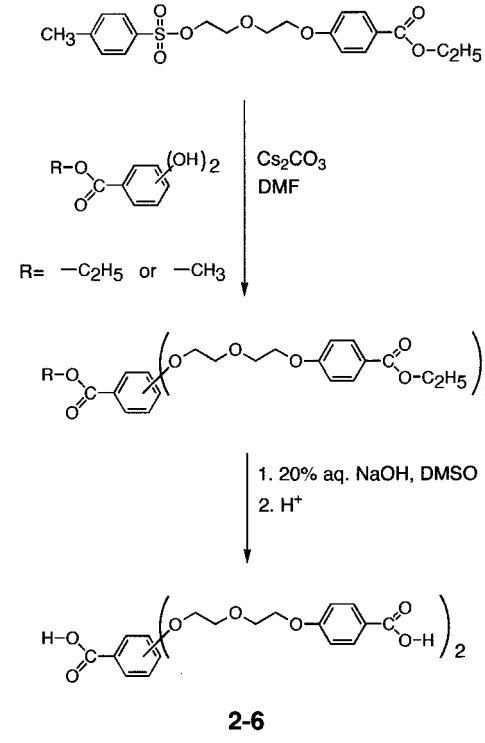
Yield 60·6% (based on ethyl 2,5-dihydroxybenzoate). ^{1}H NMR (DMSO-d$_6$, 27°C, ppm) δ 7·86 (d, 4 ArH, H-e), 7·16 (s, 1 ArH, H-a), 7·05 (m, 2 ArH, H-b, H-c), 7·01 (d, 4 ArH, H-d), 4·19–4·06 (m, 8 H, $-CH_2CH_2OAr$), 3·85–3·77 (m, 8 H, $-CH_2CH_2OAr$).

Compound ***4***

Yield 61·9% (based on ethyl 2,6-dihydroxybenzoate). ^{1}H NMR (DMSO-d$_6$, 27°C, ppm) δ 7·87 (d, 4 ArH, H-d), 7·25 (t, 1 ArH, H-a), 7·01 (d, 4 ArH, H-c), 6·69 (d, 2 ArH, H-b), 4·17–4·10 (m, 8 H, $-CH_2CH_2OAr$), 3·83–3·74 (m, 8 H, $-CH_2CH_2OAr$).

Compound ***6***

Yield 75·3% (based on methyl 3,5-dihydroxybenzoate). ^{1}H NMR (DMSO-d$_6$, 27°C, ppm) δ 7·86 (d, 4 ArH, H-d), 7·05 (s, 2 ArH, H-b), 7·02 (d, 4 ArH, H-c), 6·76 (s, 1 ArH, H-a), 4·18 (m, 8 H, $-CH_2CH_2OAr$), 3·79 (m, 8 H, $-CH_2CH_2OAr$).



2-6

Scheme 2.

2.4. *Preparation of hydrogen-bonde d complexes*

Hydrogen-bonded complexes were prepared by the evaporation technique described in previous papers [4–10, 13–17]. The pyridine solution containing stoichiometric amount of H-bond donor and acceptor moieties was evaporated under reduced pressure. The resulting solid was dried *in vacuo* for 24 h.

2.5. *Characterization*

^{1}H NMR spectra were obtained by using a JEOL GX JNM270 FT NMR spectrometer. DSC measurements were performed with a Mettler DSC 30. Heating the cooling rates were 10°C in all cases; transition temperatures 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. The circular dichroism (CD) spectrum was obtained with a Jasco model J-500A.

3. Results and discussion

The chiral H-bond acceptor **1** has two stilbazole units connected through an optically active spacer. The melting

point of **1** is 196°C and no mesomorphic behaviour is seen for this compound. Compound **1** was complexed with trifunctional H-bond donors **2–6**. These molecules are benzoic acids having two benzoic acid moieties linked through flexible oxyethylene spacers. Benzoic acids **2–6** are the positional isomers. All of the trifunctional H-bond donors treated in this study are non-mesomorphic; their melting points are given in table 1. Compound **4** has no melting point and decomposes at 224°C.

Hydrogen-bonded 1 : 1 complexes were prepared from H-bond acceptor **1** and H-bond donors **2–6**, maintaining the stoichiometry of pyridine and carboxylic acid moieties. It has already been established [4–6, 9, 10, 13–17] that intermolecular hydrogen bonds are formed between benzoic acid units and pyridyl moieties, resulting in the generation of supramolecular mesogenic cores. The formation of supramolecular structure is expected for the mixture of **1** and **2**, as shown in figure 2. In a previous study [13], trifunctional H-bond donor **5** was complexed with bipyridines to obtain supramolecular H-bonded networks. These H-bonded complexes based on **5** exhibited nematic phases. For example, the H-bonded networks derived from **5** and *trans*-1,2-bis(4-pyridyl)ethylene showed a nematic phase from 184 to 202°C on heating. The dynamic nature of the H bonds contributed to the induction of liquid crystallinity for the network. Furthermore, reversible phase transitions between nematic and isotropic phases were observed for the H-bonded networks due to the thermo-reversible association and dissociation of H bonds.

Table 1. Thermal properties of multifunctional H-bond donors. Transition temperatures (°C); Cr = crystalline, I = isotropic.

H-bond donors	Phase transitions
2	Cr 226 I
3	Cr 203 I
4	Cr 224 decomp.
5	Cr 237 I
6	Cr 203 I

Thermal properties of the complexes containing the chiral component are listed in table 2. All complexes exhibit cholesteric phases and glass transitions with the exception of complex **1/6**. Complexes **1/2**, **1/3**, and **1/5** show enantiotropic cholesteric phases, while **1/4** exhibits monotropic behaviour. Focal-conic fan textures, characteristic of cholesteric phases with relatively short helical pitches, have been observed for the complexes under the polarizing microscope. Cholesteric phases are induced for the complexes whereas H-bond donors have no simple rod-like structures. It is noteworthy that complex **1/6** shows direct transition between crystalline and isotropic phases. The lack of liquid crystallinity in **1/6**

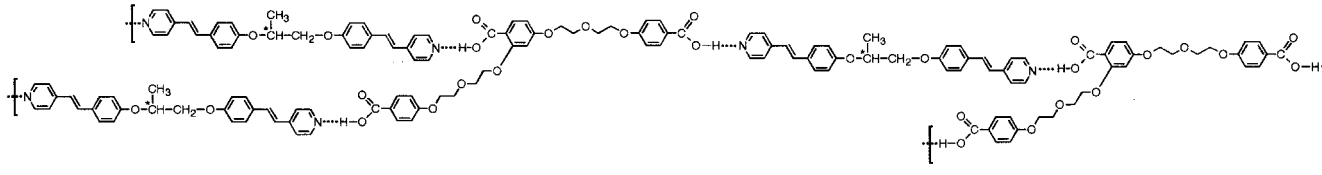


Figure 2. Supramolecular structure built through intermolecular hydrogen bonds between compounds **1** and **2**.

Table 2. Thermal properties of H-bonded complexes built from trifunctional H-bond donors (**2–6**) and the chiral bifunctional H-bond acceptor (**1**). Transition temperatures (°C) and enthalpies of respective transitions (J g^{-1}, in parentheses). T_g = glass transition; T_c = cold crystallization; T_m = melting; $T_{ch\text{-}i}$, $T_{i\text{-}ch}$ = cholesteric → isotropic, isotropic → cholesteric; $T_{i\text{-}cr}$ = isotropic → crystalline.

H-bonded complex	Phase transition behaviour						
	T_g	T_c	T_m	$T_{ch\text{-}i}$	$T_{i\text{-}ch}$	$T_{i\text{-}cr}$	T_g
1/2	75	—	—	184 (9·5)	176 (6·7)	—	71
1/3	68	—	—	180 (10·9)	174 (7·8)	—	62
1/4	82	153	187 (21·9)	—	165 (6·4)	—	81
1/5	83	147	193 (33·0)	210 (8·3)	202 (14·3)	—	77
1/6	—	—	201 (38·6)	—	—	182 (39·7)	—

is attributed to the stabilization of the crystalline phase derived from the symmetrical structure of **6**.

Figure 3 shows DSC thermograms of H-bonded complexes measured on 1st cooling and 2nd heating. In the DSC thermograms of **1/2** (figure 3-A) and **1/3** (figure 3-B), glass transitions and mesophase–isotropic phase transitions are observed on both heating and cooling scans. Cholesteric phases are seen for these complexes. For example, an isotropic phase of H-bonded complex **1/2** changes into a cholesteric phase at 176°C and a glassy phase is subsequently formed at 87°C on cooling. The cholesteric texture is preserved at room temperature. Similarly, the H-bonded complexes of **1/4** and **1/5** exhibit glass transitions on cooling, while cold crystallization occurs on heating for complexes **1/4** and **1/5**. In the subsequent heating, complex **1/4** shows the direct transition from crystalline to isotropic phases at 187°C (figure 3-C), whereas **1/5** exhibits crystalline–nematic and nematic–isotropic transitions at 193 and 210°C, respectively (figure 3-D). In the DSC curve of **1/6** (figure 3-E) the larger peaks corresponding

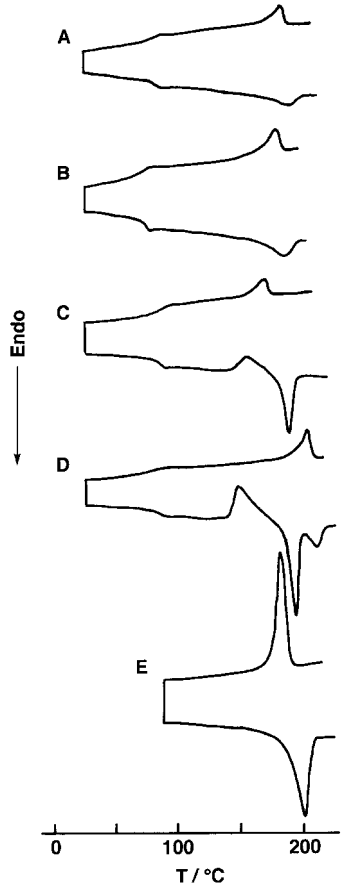


Figure 3. DSC thermograms for H-bonded complexes: (A) **1/2**; (B) **1/3**; (C) **1/4**; (D) **1/5**; (E) **1/6**; on first cooling and second heating scans.

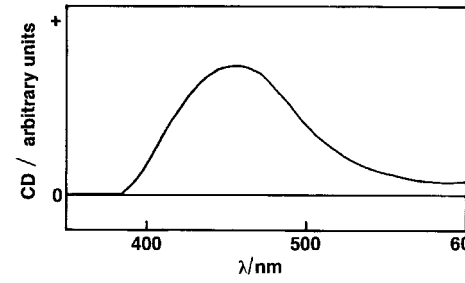


Figure 4. CD spectrum of the solid state film obtained by cooling the H-bonded complex **1/2** from a cholesteric phase.

to crystalline–isotropic phase transitions are observed at 201 and 182°C on heating and cooling scans, respectively.

The Grandjean texture was seen when the sample of complex **1/2** was placed on glass plates, heated into the cholesteric range, and sheared [18]. The macroscopic helical structure of the cholesteric phase can be retained in the solid state even by slow cooling, which suggests the glassy state of complex **1/2**, is significantly stable. The resulting film exhibits the same colour as that of the mesophase. This film gives a CD spectrum with a peak around at 460 nm, as shown in figure 4. This result confirms that the twisted structure of the cholesteric phase can be preserved in the solid state. Ths sign of the CD effect is positive, indicating that the sense of the cholesteric helix is left-handed. Conventional cholesteric LC networks have been prepared by slightly cross-linked low molecular weight cholesteric materials [19–22]. FTIR measurements have confirmed that intermolecular hydrogen bonds between carboxylic acid and pyridyl moieties are dominantly formed for the H-bonded complexes [13, 17]. It is interesting that helical structures have been induced for the network complexes even though a high density of non-covalent cross-linking is formed. The helical pitch of the supramolecular networks might possibly be changed by external stimuli and molecular recognition because the networks are built through non-covalent intermolecular interactions.

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