Chiral Nematic Glasses from Novel Hydrogen-Bonded Mesogens

V. Ajay Mallia, P. K. Sudhadevi Antharjanam, and Suresh Das*
Photochemistry Research Unit, Regional Research Laboratory (CSIR), Trivandrum 695 019, India

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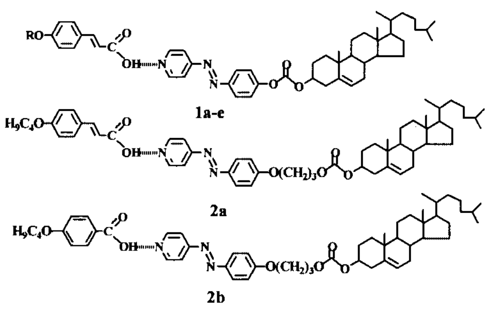
A novel class of liquid crystals capable of forming chiral nematic glasses has been obtained via intermolecular hydrogen bonding between cholesterol linked azopyridyl derivatives and substituted aromatic acids.

Glassy liquid crystals (GLCs) constitute a state of matter wherein the long-range molecular order of liquid crystals is frozen into a solid state.[1–3] The combination of optical properties of liquid crystals and mechanical properties of solids make these materials uniquely suited for a variety of optical and optoelectronic applications.[4] Recent studies by Tamaoki et al., have shown that N* GLCs can be used to develop full color rewritable recording devices that can operate in the thermal and photon mode.[5–7] Non-covalent interactions, such as hydrogen bonding between molecular species have been advantageously used in recent years to develop a large variety of liquid crystals.[8–11] Formation of N* GLCs from hydrogen-bonded polymeric materials have been reported.[12] However N* GLCs of low molecular weight intermolecular hydrogen-bonded liquid crystals have not been reported.

Here we report that low molecular weight N* GLCs can be generated using hydrogen-bonding interactions between suitable donor and acceptor molecules. Self organization through intermolecular hydrogen bonding between cholesterol derivatives such as cholest-5-en-3β-yl 4-(pyridin-4-ylazo)phenyl carbonate (CPPC), cholest-5-en-3β-yl 3-(4-(pyridin-4-ylazo)phenyl)propyl carbonate (CPPPC) and carboxylic acids such as 4-*n*-alkyloxycinnamic acids (n-CA), 4-*n*-butyloxybenzoic acid (4-BA) resulted in the formation of materials showing N* and smectic A (S_A) phases. GLCs showing the characteristic iridescent colors could be obtained by freezing the N* phases of some of these materials.

The cholesterol derivatives CPPC and CPPPC were prepared using procedures reported for the synthesis of related compounds.[13] The hydrogen-bonded complexes (Figure 1) were synthesized by thorough mixing of equimolar quantities of the hydrogen bond donor and acceptor above their melting point followed by slow cooling. The formation of the intermolecular hydrogen-bonded complexes could be confirmed by IR spectroscopy. The O–H bands observed around 3000 cm^{-1} for the weakly hydrogen-bonded dimer in pure acid were replaced by O–H bands around 2500 and 1920 cm^{-1} in the complexes, indicating strong intermolecular hydrogen-bonding.[14,15] The phase transitions of the complexes were characterized using a polarizing optical microscope (POM) and differential scanning calorimetry (DSC).[16] The supramolecular assembly **1a** melts at 175.7 °C to form a mesophase (ΔH = 19.9 kJmol^{-1}, ΔS = 44.4 Jmol^{-1}K^{-1}) and becomes isotropic at 197.7 °C (ΔH = 1.1 kJ mol^{-1}, ΔS = 2.3 Jmol^{-1} K^{-1}). The Grandjean texture observed by POM for **1a** suggests the formation of an N* phase.[17] This is also consistent with the observation of selective reflection of visible light. Similar observations were made for **1b**. On the other hand, **1c**, **1d** and **2a**, **b**, show S_A phases at lower temperatures, as confirmed by POM which showed focal conic textures with homeotropic areas. At higher temperatures these assemblies showed the characteristic fingerprint as well as single wavelength reflecting Grandjean textures of N* LC phases. These complexes also exhibited a twist grain boundary (TGB) phase, which was confirmed from the Vermis texture (Figure 2).[18] On slow heating (0.2 °C min^{-1}) the filament structure of the TGB phase grows slowly into the homeotropic regions of the S_A phase and subsequently turns into an N* phase with fan-shaped structure. Oily streaks were also seen upon subjecting the preparation to mechanical stress. The phase transition temperatures and the thermodynamic parameters of the hydrogen bonded supramolecular complexes are summarized in Table 1. The hydrogen-bonded complex **1e** does not show an N* phase. It melts to a S_A LC phase at 156.3 °C (ΔH = 24.9 kJ mol^{-1}, ΔS = 75.7 Jmol^{-1} K^{-1}), which becomes isotropic at 173.9 °C (ΔH = 0.7 kJ mol^{-1}, ΔS = 1.5 Jmol^{-1} K^{-1}).



1a, R = C_4H_9 **1d**, R = $C_{10}H_{21}$
1b, R = C_6H_{13} **1e**, R = $C_{12}H_{25}$
1c, R = C_8H_{17}

Figure 1.

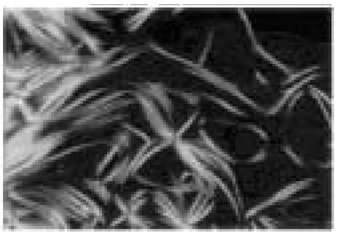


Figure 2. Twist grain boundary phase observed in **1d**.

Confirmation of the formation of unique hydrogen-bonded materials was obtained by studying the binary phase diagram of the mixtures of CPPC and 4-CA.[19] The binary mixtures containing 10–90 mol% of CPPC exhibit mainly N* phases (Figure 3). The presence of a melting maximum as well as an isotropization maximum for the mixture containing 50 mol% of

Table 1. Phase transition temperatures and thermodynamic parameters of **1a–e**, **2a**, **b**, CPPC and CPPPC

	Phase transition temperature in °C[a]	$\Delta H_{K\text{-}LC}$ kJ mol^{-1} ($\Delta S_{K\text{-}LC}$ JK^{-1}mol^{-1})	$\Delta H_{LC\text{-}I}$ kJ mol^{-1} ($\Delta S_{LC\text{-}I}$ JK^{-1}mol^{-1})
1a	K 175.7 N* 197.7 I	19.9 (44.4)	1.1 (2.3)
1b	K 168.3 N* 194.8 I	26.4 (59.8)	1.8 (3.9)
1c	K 162.1 S 164.3 TGB 164.7 N* 189.4 I	26.5 (60.6)	0.7 (1.5)
1d	K 161.2 S 177.6 TGB 178.1 N* 188.2 I	31.6 (72.8)	0.9 (1.9)
1e	K 156.3 S 174.3 I	24.9 (75.7)	0.7 (1.5)
2a	K 144.0 S 155.8 TGB 157.5 N* 179.9 I	30.3 (72.6)	4.7 (10.4)
2b	K 142.0 S 150.2 TGB 152.3 N* 170.7 I	24.4 (58.7)	4.4 (10.0)
CPPC	K 198.0 I	-	-
CPPPC	K 125.3 I	-	-

[a] K= crystalline, N* = chiral nematic, S = smectic A, TGB = twist grain boundary phase and I = isotropic phase.

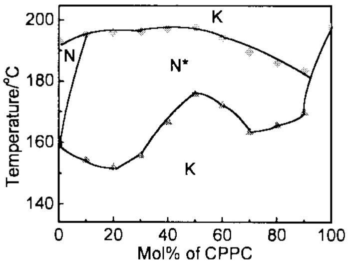


Figure 3. Binary phase diagram obtained for 4-CA and CPPC.

CPPC strongly supports the formation of a well-defined 1:1 stoichiometric compound. Additional support is provided by the presence of two eutectic points at 20 and 70 mol% of CPPC.

On slow cooling (5 °C min^{-1}), the complex **1a** exhibits an N* phase from 191 °C, which crystallizes at 75.7 °C. Rapid cooling to 0 °C of thin films of the N* phase of **1a** obtained in the heating and cooling cycle resulted in the formation of glassy materials showing the characteristic iridescent colors of chiral nematics. The N* GLCs formed in this manner are stable over long periods (more than eight months). The Grandjean texture of N* could be observed by POM in these glasses (Figure 4). Stable glasses could also be obtained by rapid cooling of the N* phases of **1b**, **2a** and **2b**. The fixed colors are extremely stable at room temperature and can be erased by heating the glasses above 100 °C. The glasses obtained by rapid cooling of the N* phases of **1c** and **1d** were however unstable and undergo slow crystallization. In conclusion, the present study shows that low molecular weight N* GLCs can be conveniently generated via intermolecular hydrogen bonding between suitable donor and acceptor molecules.

Figure 4. Grandjean texture observed in N* GLC of **1a**.

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