Chemical communications

COMMUNICATION

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The spontaneous formation of a chiral phase via molecular recognition in a system consisting of achiral components is reported. Specifically, the liquid crystalline behaviour of two molecular complexes assembled by hydrogen bonding between a stilbazole-based template and alkoxybenzoic acids has been characterised. The complexes exhibit the heliconical twist-bend nematic phase (N TB) over a broad temperature range despite the hydrogen-bond acceptor not being liquid crystalline and the donor exhibiting the conventional achiral nematic phase.

The recent discovery of the twist-bend nematic phase, N TB, nearly 30 years after its prediction, first by Meyer [2] and later independently by Dozov [3] has generated considerable research interest. In the N TB phase a conical helix is formed, in which the director is tilted with respect to the helical axis. The helices may be either left- or right-handed and equal amounts of both are expected to form. The helical pitch length in the N TB phase is strikingly small, typically around just 10 nm, which corresponds to 3-4 molecular distances. A particularly fascinating feature of the N TB phase is the observation of spontaneous chirality in a fluid system composed of effectively achiral molecules. This breaking of mirror symmetry in a fluid is of fundamental importance in chemistry, physics and biology and believed to play a central role in the origin of biological homochirality.

The primary structural requirement for the observation of the N TB phase is widely believed to be molecular curvature. This is in accord with Maier-Saupe theory for V-shaped particles, for which the N TB-nematic (N) transition temperature is found to be particularly sensitive to the bend angle, and shows that the N TB phase is formed only for a narrow range of molecular curvatures [5]. This molecular curvature is most often realised using dimers which consist of two mesogenic groups linked through a flexible spacer having an odd number of atoms [6]. Such molecules have, on average, a bent molecular shape in which the two mesogenic groups are inclined at some angle with respect to each other (see, for recent examples, [7]). If the N TB phase is preceded by a conventional nematic phase with uniform director structure, this has an anomalously low bend elastic constant which may be exploited in new applications [8]. It should be noted, however, that the N TB phase need not be preceded by a conventional nematic phase, and direct N TB-isotropic phase transitions have been observed [9].

Hydrogen bonding has recently emerged as an alternative approach in the design of new twist-bend nematogens. Specifically, the N TB phase exhibited by 4-[6-(4′-cyanobiphenyl-4-yl)hexyloxy]benzoic acid (CB6OBA) has been attributed to the formation of hydrogen-bonded complexes between pairs of acids yielding bent supramolecular complexes [10]. However, there is no element of molecular recognition in the CB6OBA system because the complexes consist of two identical molecules. Here for the first time we show that the N TB phase can be induced in mixtures containing unlike hydrogen bond donors and acceptors and report the thermal behaviour of equimolar complexes between the hydrogen bond acceptor, 4-[(E)-2-(4-[(6-[(4′-methoxy[1,1′-biphenyl]-4-yl)]oxy]phenyl)ethenyl]pyridine (1OB6OS) and the hydrogen bond donor, alkoxybenzoic acid (nOBA) with different lengths of terminal alkoxy chain, n (Fig. 1).

The spontaneous chirality through mixing achiral components: A twist-bend nematic phase driven by hydrogen-bonding between unlike components

Fig. 1. Molecular structure of the hydrogen-bonded complex 1OB6OS:nOBA.
These particular complexes were chosen for study because the overall odd-membered hexyloxy spacer has been shown to impart a sufficiently bent molecular shape to promote the N$_{TB}$ phase in conventional liquid crystal dimers$^{[13]}$, and the hydrogen bond between pyridyl-based fragments and benzoic acids is strong enough to promote liquid crystalline complexes$^{[12]}$. The synthesis of 10B6OS and characterisation methods are described in detail in the ESI. The equimolar binary mixtures of 10B6OS and 4OBA or 5OBA were prepared by co-dissolving pre-weighed amounts of each compound in dichloromethane and allowing the solvent to evaporate slowly at room temperature. The mixtures were further dried in a vacuum oven at 50 °C for 16 h. The phase properties of the 10B6OS:nOBA complexes and their components are listed in Table 1, and their DSC traces obtained on cooling from the isotropic phase and subsequent reheating are shown in Fig. S1 and S2.

<table>
<thead>
<tr>
<th>Phase sequence</th>
<th>10B6OS:4OBA</th>
<th>10B6OS:5OBA</th>
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<tbody>
<tr>
<td>4OBA</td>
<td>Cr 146.8 (17.9) N 158.9 (2.4) I</td>
<td>Cr 142.8 (93.0) I</td>
</tr>
<tr>
<td>5OBA</td>
<td>Cr 126.1 (20.3) N 152.3 (1.9) I</td>
<td>Cr 121.9 (46.7) [SmX 86.2 (7.2) N$_s$ 109.4($0$) $^+$ N166.4 (2.4)]</td>
</tr>
<tr>
<td>10B6OS:4OBA</td>
<td>Cr 112.0 (39.3) [SmX 85.4 (4.1) SmA 93.5 (0.2) N$_s$ 98.0($0$)] N 157.7 (2.1) I</td>
<td></td>
</tr>
</tbody>
</table>

* from microscopy; $^+$ extracted from cooling DSC scan.

The complexes show several LC phases and over a broad temperature range even though 10B6OS is not liquid crystalline and nOBA, with $n = 4$ or 5, exhibits only a short temperature range nematic phase$^{[13]}$. On cooling from the isotropic phase, the 10B6OS:4OBA complex exhibits two nematic phases distinguished by their optical textures: in cells with planar anchoring the upper temperature nematic phase shows a perfectly uniform texture, and at the transition to the lower temperature phase, a stripe texture develops characteristic of the twist-bend nematic phase (Fig. 2). The formation of the N$_{TB}$ phase was accompanied by the cessation of the optical flickering due to director fluctuations observed in the nematic phase. The N–N$_{TB}$ transition was detected using DSC as a small jump in the heat capacity (Fig. S2). This is in accord with the general observation that, as the temperature range of the preceding nematic phase increases, the N–N$_{TB}$ transition tends towards becoming second order in nature, i.e., $\Delta H \approx 0$.$^{[19]}$ In thin cells, in which sample crystallisation is suppressed, a reversible N$_s$–smectic X (SmX) transition is detected (Fig. 2). Unfortunately, the monotropic nature of this phase precluded its study using X-ray diffraction, but given the large enthalpy change associated with the transition (Fig. S1), it is assumed to be a highly ordered smectic phase. For the 10B6OS:5OBA complex the temperature range of the N$_{TB}$ phase narrows to ~5 K, insufficient for the stripe texture to develop. Below the N$_{TB}$ phase, SmA and SmX phases are observed.

The N and N$_{TB}$ phases have similar X-ray diffraction patterns with broad signals indicative of a liquid-like arrangement of the molecules. For 10B6OS:5OBA weak, broad signals in the low angle region correspond to spacings of about 39 Å and 13 Å while the estimated all-trans molecular length of the hydrogen-bonded complex is 39.4 Å. In the wide angle region both nematic phases show a broad signal corresponding to about 4.5 Å that is related to the molecular distance along the direction perpendicular to the director. The X-ray patterns indicate that the signals in the low angle region for both nematic phases correspond to the first and third harmonics in the crystal pattern (Fig. 3). The absence of the second harmonic in the nematic phases’ patterns implies an unusual electron density profile along the director in the local aggregates (cybotactic groups). The reverse Fourier transform of the X-ray pattern gives an electron density profile with three maxima per repeating period. Assuming a head-to-tail molecular arrangement, the electron density maxima can be ascribed to the regions in which the aromatic fragments of neighbouring complexes overlap (Fig. 3). On decreasing the temperature for the 10B6OS:5OBA complex, the signal corresponding to the full molecular length sharpens showing that the smectic A phase locks to a monolayer structure with layer spacing ~ 40 Å, close to the molecular length of the complex.

The temperature dependent Fourier transform infrared (FT-IR) spectra for the 10B6OS:4OBA complex show in the high frequency region (Fig. 4) the intense C-H stretching signals are superimposed on a broad band at $\nu \sim 2900$ cm$^{-1}$, associated with the fundamental vibration of hydrogen-bonded hydroxyl groups, referred to as the Fermi A-type band$^{[14]}$. The observation of the A-type band and the absence of contributions arising from free hydroxyl groups at $\nu > 3500$ cm$^{-1}$ indicates strong hydrogen bonding. This view is further supported by the presence of Fermi B-type (~2700-2400 cm$^{-1}$) and C-type (~1900 cm$^{-1}$) bands$^{[14]}$. The inset in Fig. 4 compares the high frequency region of the FT-IR spectrum for the...
**1OB60S:4OBA** complex to that of pure **4OBA**. The absence of two well-defined maxima in the B-type region characteristic of benzoic acids[14], together with the shift of the band to lower frequencies, and the marked increase in the intensity in the C-type band also supports the formation of a hydrogen-bonded complex between the unlike components. The shift in the carbonyl stretching band from 1690 to 1700 cm\(^{-1}\) on cooling (Fig. 4) further confirms the formation of the **1OB60S:4OBA** complex[10b].

The geometric parameters, electronic properties, and hydrogen bond dissociation energies of the **1OB60S:4OBA** complex were determined using quantum mechanical density functional theory (DFT) calculations (see the ESI for details). Geometric optimisation was performed with the spacer in the all-trans conformation. It is known, however, that for dimers containing the hexyloxy spacer the gauche state of the O-C-C-C dihedral is more stable than the trans state[11] due to favourable interactions between the oxygen atom and the CH\(_2\) group. Thus geometric optimisation was also performed with the spacer containing this gauche state. The space filling models and electrostatic potential isosurfaces for the ground state and all-trans conformations of the **1OB60S:4OBA** complex are shown in Fig. 5. The ground state of the complex was found to contain the gauche linkage although the difference in energy between the two states is small, 0.8 kJ mol\(^{-1}\), and this is likely to be substantially different in an ordered liquid crystal phase in which the more linear all-trans conformation will be favoured[15]. Both conformations show a bent geometry consistent with the observation of the NTB phase, and also possess a lateral dipole moment which may assist in the packing of these bent structures.

The hydrogen bond dissociation energy of the complex was estimated by comparing the energy of the all-trans conformation of the **1OB60S:4OBA** complex with that of the system in which the hydrogen bond length had been increased to 5 Å. Similar calculations were performed for the acid dimer, see Table S1 in the ESI, which lists the calculated hydrogen bond lengths and dissociation energies of the two systems. The hydrogen bond length is shorter in the **4OBA** dimer (1.672 Å) than in the **1OB60S:4OBA** complex (1.759 Å) and the dissociation energy higher (86.50 and 61.41 kJ mol\(^{-1}\), respectively). However, it should be remembered that the **4OBA** dimer contains two hydrogen bonds such that the bond dissociation energy per hydrogen bond is 43.25 kJ mol\(^{-1}\), and considerably smaller than that seen for the hydrogen bond in the **1OB60S:4OBA** complex. This is consistent with the interpretation of the FT-IR spectra. Although the single **4OBA** dimer is enthalpically favourable over a single **1OB60S:4OBA** complex, in the equimolar mixture of **1OB60S** and **4OBA**, the **1OB60S:4OBA** complex is both enthalpically and entropically favoured. The hydrogen bond in the **1OB60S:4OBA** complex is relatively weak but sufficient to stabilize the molecular complex.
In summary, hydrogen-bonded complexes of achiral 1OB6OS and nOBA show twist-bend nematic behaviour providing an example of how molecular recognition can induce spontaneous chirality in a condensed phase. Molecular curvature is widely thought to be the critical structural parameter in promoting the N_{TB} phase simply as a result of the crystalline behaviour even on supercooling the isotropic phase. This is normally curvature is widely thought to be the critical structural example of how molecular recognition can induce hydrogen bonding but how this is related to shape is unclear. Increases in the N_{TB}-N transition temperatures have been observed for similarly shaped conventional covalent complexes, which by itself does not show liquid crystalline behaviour even on supercooling the isotropic phase. We also note that for 1OB6OS an additional driving force was considered to be the formation of laterally hydrogen-bonded chains which may stabilize the helical arrangement found within the twist-bend nematic phase and the dynamic nature of the hydrogen bond. These intriguing possibilities are now the subject of further study.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgments

The work was supported by the National Science Centre (Poland) under the grant no. 2016/22/A/ST5/00319. RW gratefully acknowledges the Carnegie Trust for the Universities of Scotland for funding the award of a PhD scholarship.

Notes and references