

Supramolecular Tools for the Stabilisation of Blue-Phase Liquid Crystals

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Received: 29.06.2022

Accepted after revision: 19.09.2022

DOI: 10.1055/s-0042-1757971; Art ID: OM-2022-06-0014-SR

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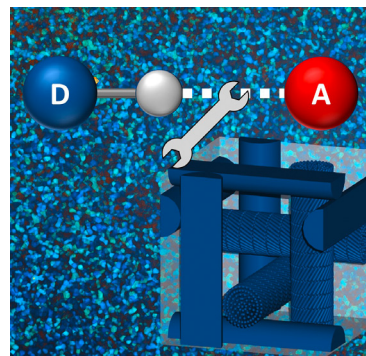
Abstract Blue phases (BPs), a unique manifestation of chirality in the liquid crystalline state, have gained considerable attention due to the unusual combination of properties such as sub-millisecond response times to electrical fields and Bragg reflection of circularly polarised light. Initially they were regarded as promising materials for the development of the next-level display technologies. However, in recent years, they have gained increasing attention as responsive photonic materials with sensing or optoelectronics properties (photonic mirrors and filters). A major limitation so far has been their narrow temperature range in which they usually exist. The aim of the present review is to summarise the recent efforts made to stabilise BPs by employing specific non-covalent bonds and the principles of supramolecular chemistry.

- 1 Introduction
- 2 Stabilisation of Blue Phases by Supramolecular Methods
 - 2.1 Doping Approach
 - 2.2 Design Approach
- 3 Conclusions and Outlook

Key words: liquid crystals, blue phases, supramolecular materials, hydrogen bonds, chirality, photonic crystals

1. Introduction

Chiral mesophases such as the chiral nematic (N^{*}) or the blue phases (BPs) are regarded as promising materials for the development of photonic materials, due to their periodic nanostructures.¹ For example, the exoskeleton of the jewelled beetle, *Chrysina gloriosa*, is made of helicoidally stacked chitin nanofibrils.² These structures selectively reflect circularly polarised light and cause the characteristic metallic green appearance of the beetle.



Chiral-nematic structures represent one-dimensional photonic crystals, because of their periodically changing refractive indices along the director axis.³ The reflected wavelength depends on the pitch (P) of the helical structure, the refractive index contrast (n_{avg}) of the compound and the angle of the incident light ($\sin(\theta)$), and can be described by a deviation of the Bragg law.⁴ Thereby, the helical pitch corresponds to the repeating distance of a full 360° turn of the liquid crystalline molecules. Materials appear structurally coloured when half of the pitch ($P/2$) of the chiral structure is in the region of the wavelength of visible light (see Figure 1). Due to the helical photonic structure, the reflected light is

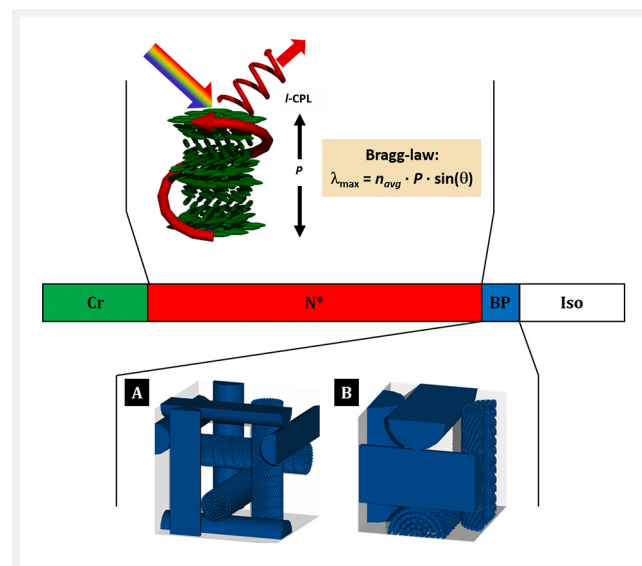


Figure 1 Schematic of a usual phase sequence of a blue-phase liquid crystal. Phase sequence: crystalline phase (Cr), chiral nematic phase (N^{*}), blue phase (BP), and isotropic liquid (Iso). Helix of a chiral nematic liquid crystal with reflection of circularly polarised light and equation of Bragg's law. A body-centered cubic unit cell of BP I (A) and a simple cubic unit cell of BP II (B).

Biosketches



Felix Kraus studied chemistry at the University of Würzburg, where he prepared his Bachelor's thesis on the synthesis and characterisation of dithienopyrroles as acceptor materials for organic electronics under the supervision of Prof. Dr. Frank Würthner. For his Master's thesis he continued his work on dye chemistry concerning hydroxy-substituted perylene bisimides in the same group. In October 2019 he joined the Giese's group and started his current work on stabilisation of blue-phase liquid crystals.



Michael Giese studied Chemistry at the RWTH Aachen University, where he worked on anion- π interactions in the group of Prof. Markus Albrecht. After receiving his PhD in 2011, he moved to the University of British Columbia to work together with Prof. Mark MacLachlan on supramolecular materials based on cellulose nanocrystals. In 2014 he started his independent work as a junior professor at the University of Duisburg-Essen funded by the Professor-Werdemann Foundation. After two years as a deputy professor, he got promoted to a Heisenberg professorship at the University of Duisburg-Essen. His research interests are in the field of supramolecular functional materials including liquid crystals, polymers, gels and functional assemblies. Since 2021, he is head of the Co-Creation Lab Product Innovations, a 3D printing lab supporting scientists to develop their ideas and prototype for starting their own business.

circularly polarised with a handedness determined by the chirality, and a maximum of 50% of the incident light will be reflected. The remaining 50% light with opposite handedness transmits through the film without loss of intensity.

In 1888, Reinitzer observed the unusual melting behaviour of cholesteryl benzoate, the first example of a chiral nematic phase.⁵ However, it was Lehmann who comprehensively investigated this mesophase and coined the term "liquid crystal" (LC).⁶ They also observed the first BP, which was initially considered as a transition phenomenon in the transition from the isotropic to the chiral nematic phase. But only in 1973, these mesophases were recognised as distinct liquid crystalline phases by Coates and Gray and named as "blue phase," which relates back to the first observations of Reinitzer observing a blue-coloured reflection of the mesophase.⁷ Three kinds of BPs are known: BP I, BP II and BP III. While BP III represents a disordered, amorphous structure,⁸ BP I has a body-centered cubic symmetry (Figure 1A) and BP II a simple cubic symmetry (Figure 1B).⁹ Both, BP I and BP II have a periodic nanostructure built by double-twisted cylinders (DTCs). Since it is impossible to fill the three-dimensional space continuously by the DTCs, line defects occur, the so-called disclination lines.

Due to this unique structures, BP possess interesting properties like sub-millisecond response times to electrical fields, Bragg reflection of circularly polarised light and, due to their cubic unit cell, optical isotropy.¹⁰ Therefore, these materials are candidates for the usage in applications such as displays¹¹, photonic sensors or switchable diffraction gratings (Figure 2).¹² With respect to photonic applications, BP I

and BP II represent three-dimensional photonic crystals, whereby the maximum of the reflected wavelength λ is described by:⁹

$$\lambda = 2nd \cos \theta = \frac{2nd \cos \theta}{\sqrt{h^2 + k^2 + l^2}}$$

where n represents the average refractive index contrast, d is the lattice constant of the BP, θ is the angle between the incident light and the crystallographic direction, and h , k , and l are the Miller indices of the crystal orientation planes.

BPs are accessible by doping nematic host materials with chiral dopants with high helical twisting powers (HTPs).¹³ However, a limitation with respect to applications is the narrow temperature range of only a few K, in which this specific mesophase usually appears. Therefore, in the last few decades, a lot of efforts have been made into the stabilisation of BP for making them appealing for application in optoelectronics or photonic sensing. To stabilise the structural features of BPs, and thereby widening the temperature range, different approaches have been followed like the introduction of polymers^{11c} and nanoparticles (NPs),¹⁴ or by doping with low-molecular weight additives.¹⁵ Polymer stabilisation was first reported by Kikuchi et al. who could achieve a BP temperature range of more than 60 °C.¹⁶ This most prominent method to stabilise BPs is based on the accumulation of polymeric material in the disclination areas of the three-dimensional structure (Figure 3A). Since the existence of defects requires sufficient energy, which is usually provided as thermal energy, BP vanishes at lower temperatures due to a lack of energy. As soon as the disclination lines are filled by a

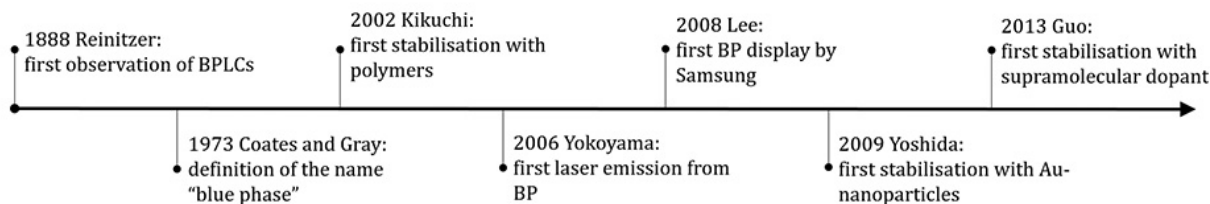


Figure 2 Milestones in BP research.

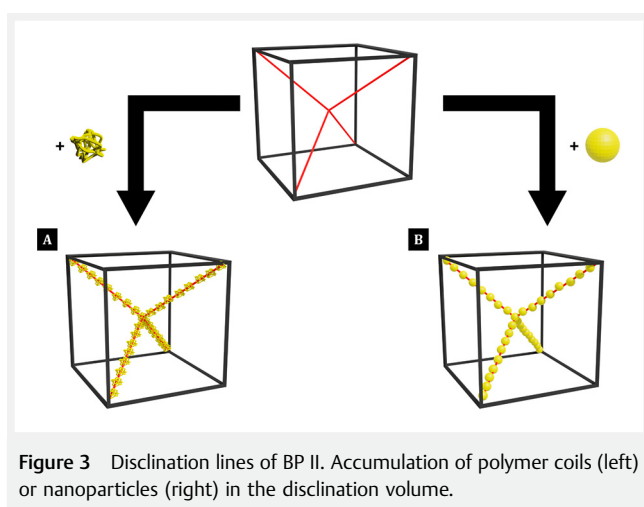


Figure 3 Disclination lines of BP II. Accumulation of polymer coils (left) or nanoparticles (right) in the disclination volume.

polymer, the energy requirement for the maintenance of the defects is lower and the BP can exist over a broader temperature range.

Another common method is to dope BP liquid crystals (BPLCs) with NPs, which also accumulate in the disclination lines (Figure 3B), and stabilise the BP structure by similar effects mentioned above.¹⁷ Additionally, some NPs can positively influence the switching voltage of BPs.¹⁸ For example, the LaF₃-NPs utilised by Zhu et al. as dopants lowered the on-state voltage of polymer-stabilised BPLCs to about 59% by increasing the anchoring energy of the mesogen molecules due to their large dipole moments.

A comprehensive overview on polymer and NP stabilisation of BPs was given in a recent review by Rahman et al.^{17b}

In addition, a series of unconventional approaches have been reported. For example, Zhao et al. doped their BPLC composites with aminoalkyl-substituted graphene oxide flakes and successfully broadened the temperature range of the BP to 6.4 °C.¹⁹ Furthermore, Lin et al. confined their BPLC in micrometer-scale two-dimensional honeycomb microwells and showed that this leads to an increase in BP stability.²⁰ In addition to the broadening of the BP temperature range to $\Delta T = 7.1$ °C, the reflectivity and the thermal stability of the reflection peak wavelength have also been improved.

These examples show that a variety of methods have been employed to stabilise BPs and broaden the temperature range of the chiral mesophase. In all cases, a balance of attractive and repulsive intermolecular forces between the liquid crystalline system and the stabilising additives is crucial for efficient stabilisation. Therefore, the transfer of supramolecular principles and the specific targeting of non-covalent bonds are a promising approach for superior BPLC materials. Here, especially the employment of hydrogen bonding (H-bonding) and halogen bonding (X-bonding) appears promising, since these non-covalent interactions are highly directional and easy to tune in their strength. Furthermore, they provide a facile synthetic access to a variety of new supramolecular mesogens, which can be tuned by simple replacement of the donor or acceptor moiety. However, while a series of BPLCs are reported which were constructed or stabilised by hydrogen bonding, to the best of our knowledge, efficient stabilisation of BPs via halogen bonding has not been reported so far. Therefore, the aim of the present review is to summarise the recent efforts made to stabilise BPs by employing hydrogen bonds and the principles of supramolecular chemistry.

2. Stabilisation of Blue Phases by Supramolecular Methods

As pointed out in the Introduction section, the main disadvantage of BPLCs is the narrow temperature range in which the BP occurs. However, since the formation of the liquid crystalline state is the result of a balanced interplay of attractive and repulsive intermolecular forces, supramolecular chemistry, as the chemistry of the non-covalent bond, appears to be the perfect tool to address this challenge. Within the past three decades, supramolecular chemistry has evolved to an effective approach towards functional materials.²¹ With respect to liquid crystals, especially hydrogen²² and halogen bonds²³ have proven to be ideal supramolecular forces to induce and stabilise mesophases. A number of studies employed hydrogen bonds for the stabilisation of BPLCs. However, at the moment, the studies report mostly

individual examples, and the empirical results raise a lot of questions with respect to a comprehensive understanding of structure–property relationships. In general, there are two different approaches to utilise hydrogen bonding in the stabilisation of BPs found in the literature. The more common method adds hydrogen-bonded assemblies (HBAs) as a dopant to a BPLC mixture (doping approach), while the second approach uses hydrogen bonding for the formation of self-assembled mesogens (design approach) with BPs. More specifically, in the doping approach, the materials are based on conventional, mostly commercially available nematic host LCs, which are doped with H-bonded additives to broaden the BP temperature range. In this case, the hydrogen-bonded assemblies may be liquid crystalline, but they do not have to be liquid crystalline. In contrast to this, the design approach employs hydrogen bonding to construct new supramolecular mesogens forming BPs. Here, no separate host material is needed to facilitate liquid crystallinity.

2.1. Doping Approach

The doping approach usually starts from a commercially available nematic LC host system. A chiral dopant is added to induce chiral mesophases. The hydrogen-bonded assemblies are added to stabilise the BPs by, e.g., introducing a bent-shaped structure, adding structural flexibility to adopt the chiral structure and improve the compatibility of the host and dopant system. In some examples, the HBAs bear chiral entities to increase the HTP and thereby broaden the temperature and concentration ranges of the BPs.

The first example using a HBA as an additive for BPLCs was reported by Guo et al.²⁴ The LC mixtures consisted of an achiral mesogenic host (**8CB**) and a chiral dopant (**ISO(C₆OBA**)₂), and for stabilisation via polymerisation mono- and di-functional monomers together with a photoinitiator. In their studies, they screened the influence of two different HBAs (Figure 4), one terminated with a chiral branched alkyl chain (**CB15 acid**...**ISIN**) and another with an alkoxy chain (**DOBA**...**ISIN**), as additives in LCs on the stability of BPs. By varying the content of HBAs, they could successfully broaden the BP temperature range up to $\Delta T = 13^\circ\text{C}$ in the cooling cycle for a mixture containing 8 wt% HBA **CB15 acid**...**ISIN**. They explained their observations by an increase in HTP and viscosity. The HBAs, as isosorbide derivatives, can act as additional chiral dopants to increase the HTP and thereby the chiral force in the whole system. This helps to stabilise the BP over a wider temperature range. Additionally, due to their size and shape, the HBAs have a high steric demand, which increases the viscosity of the material. This in turn leads to a stronger supercooling effect and a longer persistence of the BP.

Later, the approach was extended to bent- and T-shaped HBAs as dopants for cholesteric LCs. These molecular shapes

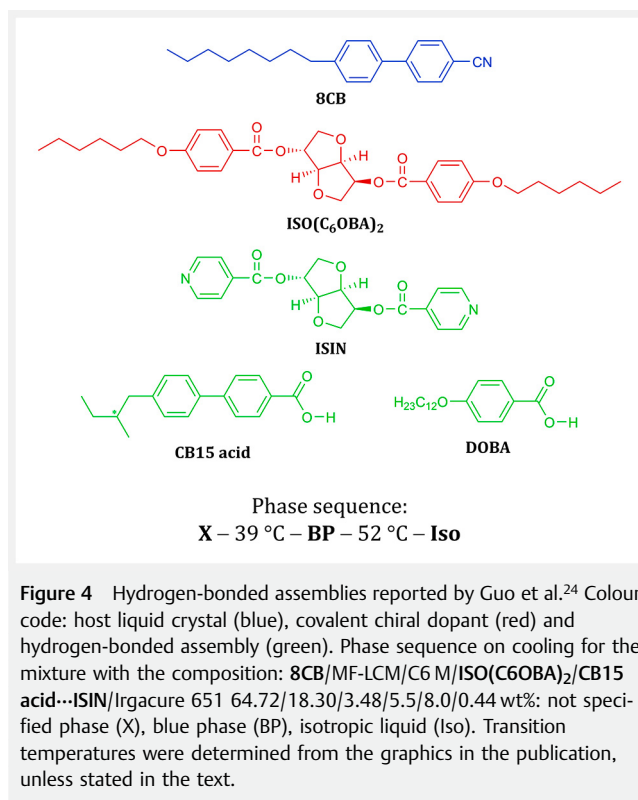
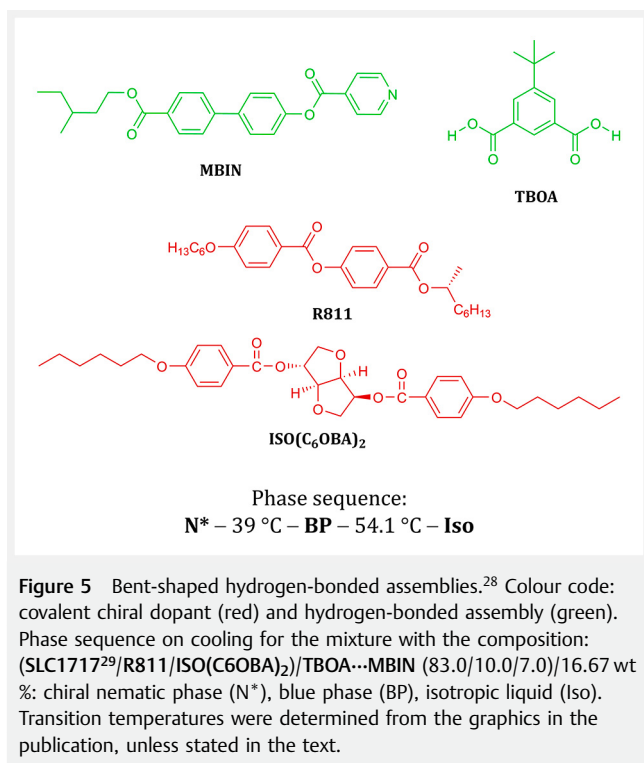


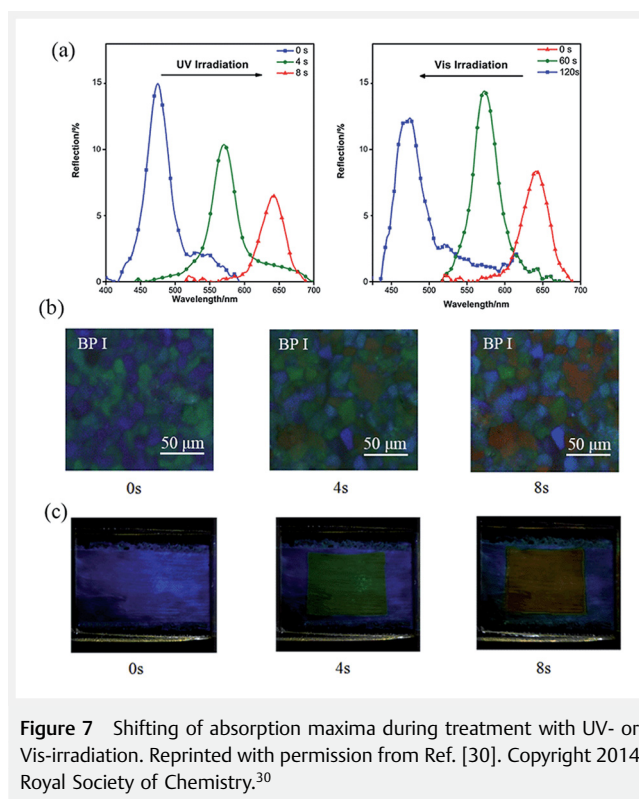
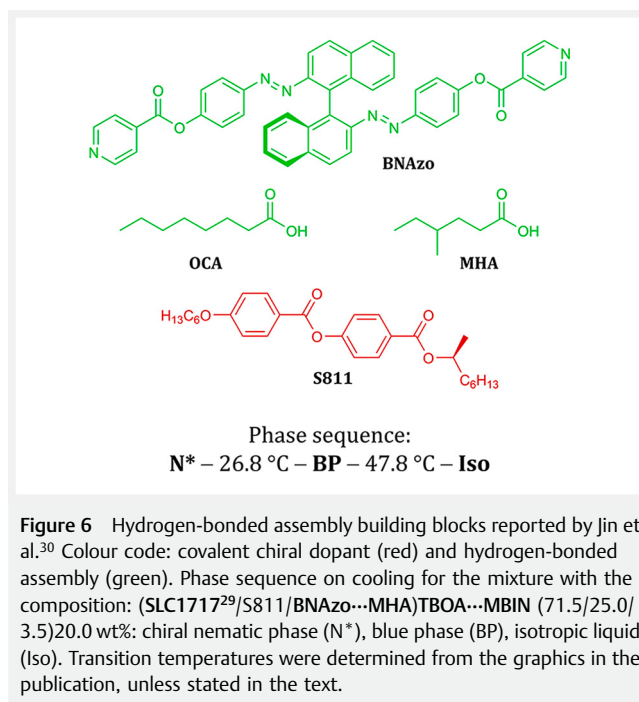
Figure 4 Hydrogen-bonded assemblies reported by Guo et al.²⁴ Colour code: host liquid crystal (blue), covalent chiral dopant (red) and hydrogen-bonded assembly (green). Phase sequence on cooling for the mixture with the composition: **8CB**/MF-LCM/C6 M/**ISO(C₆OBA**)₂/**CB15 acid**...**ISIN**/Irgacure 651 64.72/18.30/3.48/5.5/8.0/0.44 wt%: not specified phase (X), blue phase (BP), isotropic liquid (Iso). Transition temperatures were determined from the graphics in the publication, unless stated in the text.

are discussed to be beneficial for the stabilisation of chiral mesophases. The reason for the stabilisation of BPs is not yet fully understood. However, the addition of bent- or T-shaped HBAs is known to increase the HTP of a chiral dopant present in the same mixture and dopants with high HTP values are known to be beneficial for the formation of BPs.²⁵ Another factor which is discussed is the biaxiality of these additives, which seems to contribute to the stabilisation of the DTCs of BPs.²⁶ Additionally, the bent-shaped structure can decrease the free energy for the disclinations by introduction of elasticity to the surfaces of the DTCs. To understand this effect, different possible factors have to be considered.²⁷ One is the reduction of interfacial tension due to higher elastic constants. The other aspect is the reduction of the disclination line radius caused by a reorientation of the molecules in the defect volume induced by the bent core additive. In 2003, Shi et al. employed **SLC1717** as a host system (83 wt %) doped with 10 wt% chiral dopant **R811** and 7 wt% chiral dopant **ISO(C₆OBA**)₂.²⁸ The BP temperature range could be successfully increased to $\Delta T = 15.1^\circ\text{C}$ for the mixture containing **TBOA**...**MBIN** (Figure 5). Additionally, the BP–N* transition temperature was brought closer to room temperature (39 °C). The major difference with the previously reported systems was the non-linear structure of the HBAs. According to the authors, the combination of chirality and biaxiality was the main reason for the stabilisation of BP. In addition, tertiary butyl and other branched end groups at



the central core and the edges are beneficial for the BP temperature range since they force a competition between attractive π - π interactions and steric repulsion and thereby promote the double-twisted arrangement. As compared to conventional covalently bound bent- and T-shaped molecules, the HBAs are more flexible and can therefore adapt more efficiently to its environment resulting in an increased miscibility. In addition, the flexibility of the assemblies leads to weaker intermolecular interactions leading to lower BP-N* transition temperatures.

In an attempt to generate optically tunable BPLCs, Jin et al. doped H-bonded chiral azobenzene switches in their LC system: SLC1717, S811 and TBOA...MBIN from the previous study of Guo's group.^{28,30} The dopants (Figure 6) are based on a binaphthyl core BNAzo connected to two peripheral pyridyl units via an azo-benzene-containing linker group. Together with either octanoic OCA or 4-methyl hexanoic carboxylic acid MHA, the corresponding HBAs were obtained as dopants. With this further development of the earlier system, the BP temperature ranges were also increased by the doping of the LCs up to $\Delta T = 21$ °C for the HBA BNAzo...MHA with the branched terminal chain. This effect was explained by an increase in HTP leading to a wider BP temperature range. Additionally, they could show that irradiation of BNAzo...OCA with UV light (365 nm, 10 mW·cm⁻¹) induced photo-isomerisation of the azo moiety and results in an increase of the lattice constant of the DTC, yielding a bathochromic shift in the reflection maxi-



mum from 473 to 642 nm (Figure 7). The irradiation of the sample with visible light (450 nm, 15 mW·cm⁻²) caused the reversion of the *trans*-*cis* isomerisation and therefore the

reflection wavelength shifts back to 473 nm. It should be noted that all these processes occurred in a stable BP I and no phase transitions could be observed during the experiment. Like mentioned above, the increased stability of the BP was explained by an increased HTP in the system by substituting the isosorbide-based dopant, **ISO(C₆OBA)₂**, from the system of Shi et al. with the binaphthol-based dopant (**BNazo**). This indicates that the HTP value of the employed chiral dopant is crucial for the stability of the BP. The exact role of the H-bond in this system was not identified by the authors but an increase in the size of the chiral dopant leading to an improved HTP by the attachment of the carboxylic acids appears reasonable.

Another series of supramolecular azobenzene switches (Figure 8) was reported by Wang et al.³¹ In contrast to the previously reported system (see **BNazo**, Figure 6),³⁰ the photo-switch is now introduced via **DAIC** in a peripheral position. The HBAs are composed of two pyridine-containing azo compounds H-bonded to an isophthalic acid (**IPA**) or a 4-bromoisophthalic acid (**BIPA**) core. This gives them a bent-core shape resembling the non-switchable bent-core dopants (Figure 5) from the same group.²⁸ Like in the previous study, a mixture of **SLC1717** and **S811** was used as a host system. Although the BPs generated by doping of the bent-core HBAs are not as stable as the ones reported before, the optical switching properties were different. In contrast to the earlier reports from Guo's group,³⁰ the new systems exhibited a hypsochromic shift of the reflected wavelength induced by *trans*-*cis* isomerisation via irradiation with UV light (365 nm, 10 mW·cm⁻¹). This effect is due to the back-

folding of the peripheral H-bond acceptors towards the core moiety of the HBAs and thereby reducing the lattice parameter due to the reduced length of the assembly in the direction of the long axis. This explanation is in concert with the one for the **BNazo** system, meaning an expansion of the assemblies leads to a bathochromic shift, while a contraction leads to a hypsochromic shift due to the changes in lattice constant. Regarding the stability of the BP, the widest temperature range of $\Delta T = 16.7^\circ\text{C}$ was achieved by doping of the host LC with 3% of brominated HBA **BIPA**...**DAIC**. In contrast to the non-brominated derivative, there was no constant trend towards lower BP transition temperatures with higher contents of additives but an increase with higher concentrations. According to the authors, the presence of bromine in the HBAs decreases their compatibility with the host LC system and therefore the BP transition temperature increases with higher amounts of the dopant. This in turn increases the total chirality of the LC system. Also, the reduction of free energy around the defect lines due to the biaxiality of the HBAs and the better compatibility induced by the H-bonds were mentioned as reasons for the increased BP temperature range. The reports summarised so far indicate that the introduction of bent-shaped HBAs is beneficial for the stabilisation of BPs and that the assemblies increase the HTP yielding a broader temperature and concentration range of the BPs.^{24,28,30,31} In this context, the structural flexibility and reversibility of hydrogen bonds are discussed to be beneficial since they more effectively adopt the double-twisted structure of the BPs as compared to rigid covalent-bonded analogues.

In a study of He et al., chiral H-bonded molecules and their covalent bonded analogues were synthesised (Figure 9) and employed as additives in chiral nematic LC systems, composed of 75 wt% of nematic LC host **SLC4** and 25 wt% of chiral dopant **S811**.³² The additives were synthesised in different sizes, with 3, 4 or 5 hydrocarbon cycles in their mesogenic core. Also, the terminal alkyl chain as well as the fluorination pattern was varied. In general, longer alkyl chains and a higher number of rings led to broader temperature range of the mesophases, chiral nematic and chiral smectic A, with enantiotropic phase behaviour and higher clearing temperatures in the pure compounds, which was attributed to the increased length-to-width ratio. When used as additives in the host LC, it was shown that the HBAs, even though possessing lower HTPs compared to the covalent molecules, can induce wider BP temperature ranges. The broadest BP temperature range was about $\Delta T = 20^\circ\text{C}$ for the system doped with the HBA **S8HBA**...**PyS8PBA** (Figure 9) bearing chiral terminal groups on both ends, the H-bonding acceptor and the donor unit. As explanation, the authors stated that the reversible and flexible H-bond can more easily respond to structural changes in surroundings to assume lower energy positions during self-assembly than the covalent analogues and therefore lowering the disclination line volume

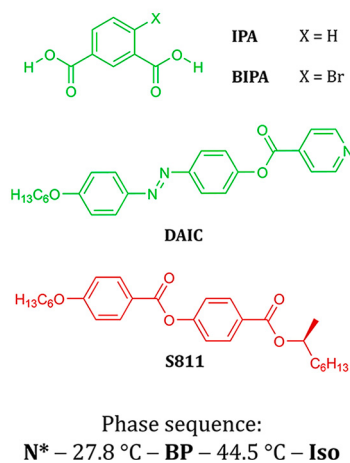
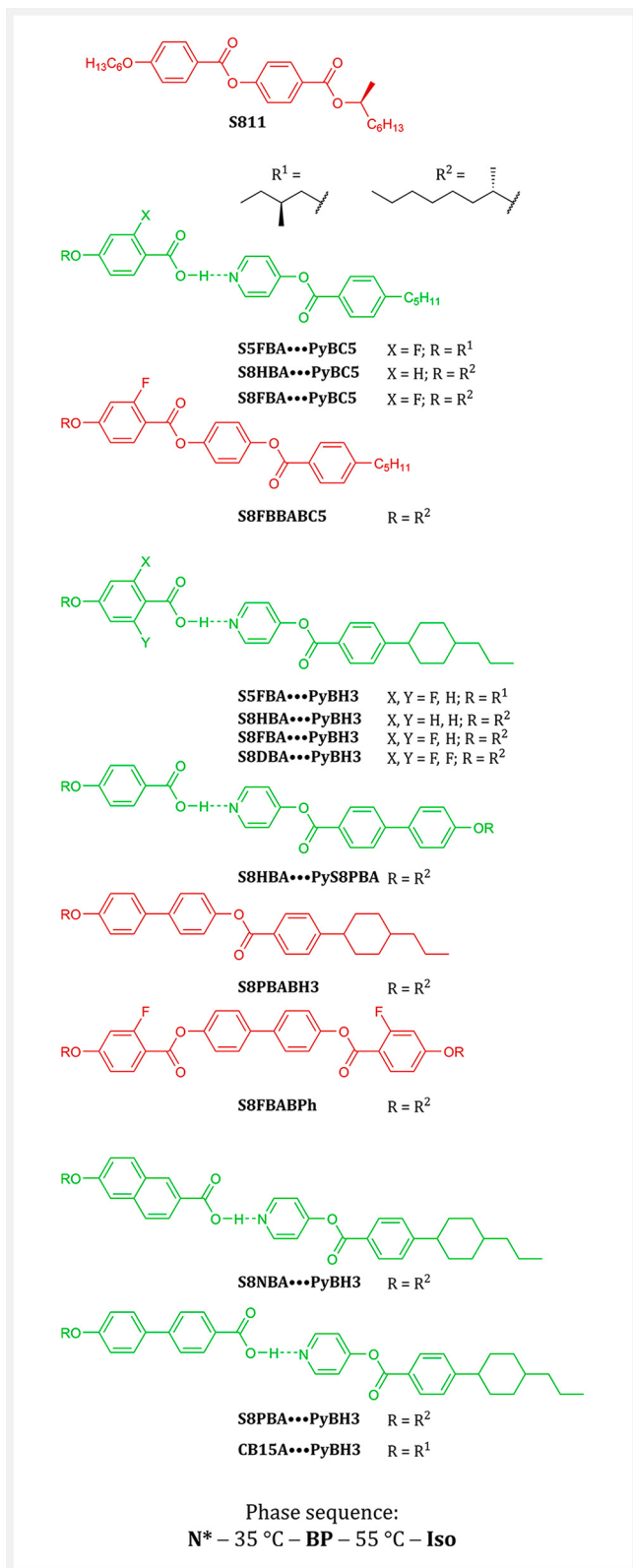


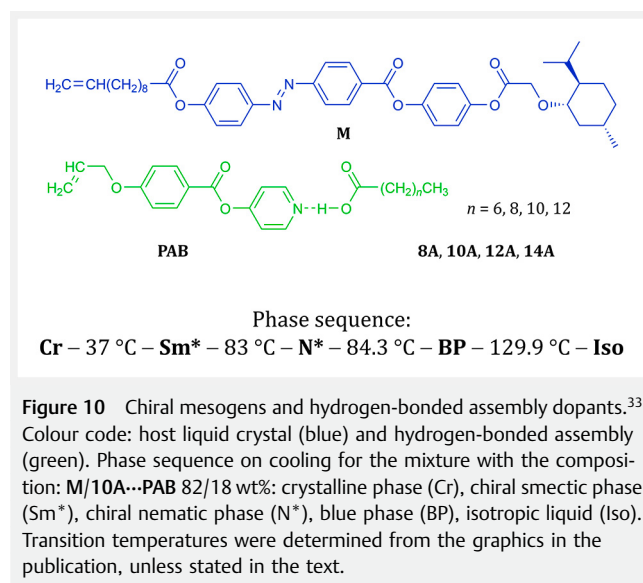
Figure 8 Bent-shaped azo-benzene switches.³¹ Colour code: covalent chiral dopant (red) and hydrogen-bonded assembly (green). Phase sequence on cooling for the mixture with the composition: (**SLC1717**²⁹/**S811**)**BIPA**...**DAIC** (67/33)3.0 wt%: chiral nematic phase (N*), blue phase (BP), isotropic liquid (Iso). Transition temperatures were determined from the graphics in the publication, unless stated in the text.



◀ **Figure 9** First generation of hydrogen-bonded assemblies reported by He et al.³² Colour code: covalent chiral dopant (red) and hydrogen-bonded assembly (green). Phase sequence on cooling for the mixture with the composition: (SLC4²⁹/S811)/S8HBA...PyS8PBA (75/25)/35 wt %: chiral nematic phase (N*), blue phase (BP), isotropic liquid (Iso). Transition temperatures were determined from the graphics in the publication, unless stated in the text.

and the corresponding free energy, which is in line with previous studies. Interestingly, the authors found that the HBA, having a lower HTP value than the covalent analogue stabilises the BP more efficiently. This contradicts previous statements claiming higher twisting power to be beneficial for BP stability.

This contradiction seems to support the findings by Li et al., where a chiral mesogen **M** was doped with an achiral supramolecular assembly (**A**...**PAB**, Figure 10) to increase the BP temperature range.³³ The HBAs are assembled from a pyridine-containing molecule **PAB** as a hydrogen-bond acceptor (H-acceptor) and a carboxylic acid (**8A**, **10A**, **12A** or **14A**) as a hydrogen-bond donor (H-donor), which were varied with respect to their alkyl chain length. While doping the individual HB donors or acceptors to the LC mixture had only a minor effect on the mesogenic behavior of the system, doping with the HBA led to a significant increase in the BP temperature range as shown in Figure 8. Although the HBAs possess neither chirality nor any LC phases, the effect on the BP of the LC after doping was evident. Interestingly, the LC system showed only a chiral smectic and a cholesteric phase before doping with the achiral HBAs. However, after the addition of the HBAs, BPs were induced, whereby the temperature range of the BP depended on the chain length of the used carboxylic acids as well as their concentrations (Figure 11). The best results were obtained for **10A**...**PAB** with a dopant amount of 18 wt%, giving rise to a BP temper-



ature range of $\Delta T = 45.6^\circ\text{C}$. According to the authors, the presence of the H-bond promotes an intramolecular twist in the neighbouring mesogen molecules. At the position of the H-bond, the diameter of the mesogen is reduced, which leaves something like a notch. The turning of the neighbouring molecules allows them to come closer to the HBA and slide into this notch. This means the neighbours of the HBA turn in opposite senses around the H-bond to practically squeeze it between them (Figure 12). Taking this into account, the proposed stabilisation mechanism is in fact in line with the examples given above, reasoning the increase in twisting power in the system to be the crucial factor for stabilising BPs over a wider temperature range.

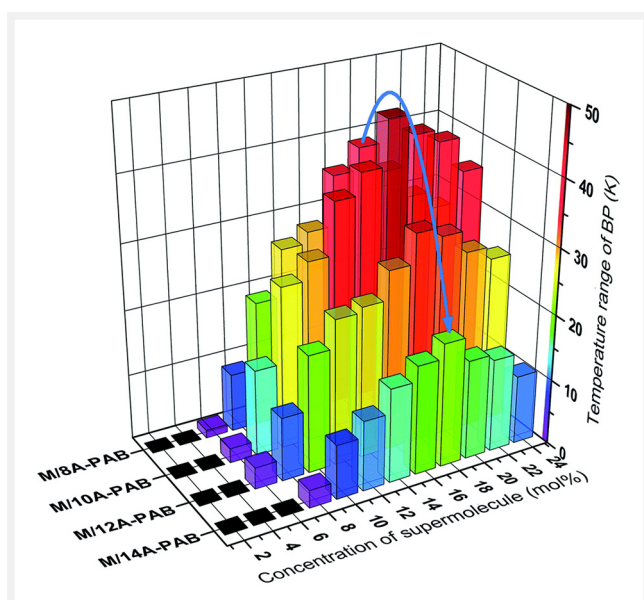


Figure 11 Summary of BP temperature ranges compared to different additives at different concentrations. Reprinted with permission from Ref. [33]. Copyright 2014 Royal Society of Chemistry.³³

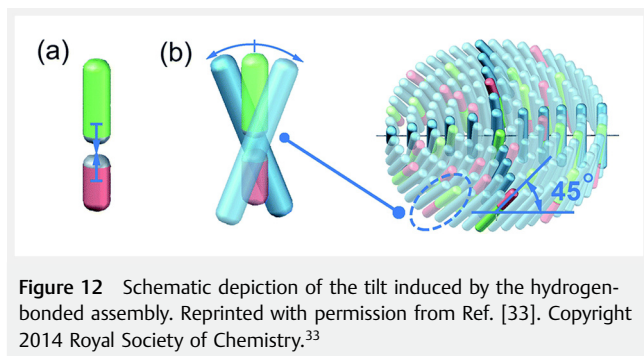
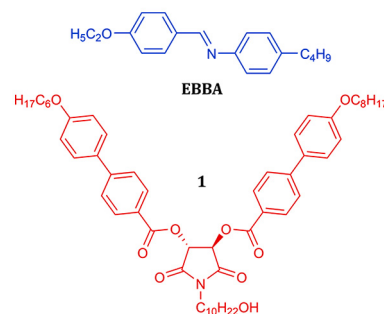


Figure 12 Schematic depiction of the tilt induced by the hydrogen-bonded assembly. Reprinted with permission from Ref. [33]. Copyright 2014 Royal Society of Chemistry.³³

In an approach of Kishikawa et al., the chiral succinimide derivative **1** bearing a hydroxyl group at the edge of its terminal alkyl chain was synthesised (Figure 13).³⁴ This compound was used as an additive in the commercially available



Phase sequence:
BP – 50.3 °C – N* – 52.3 °C – Iso

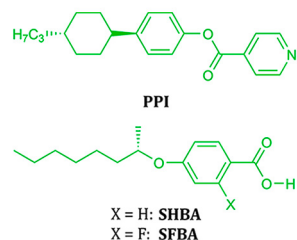
Figure 13 Succinimide derivative reported by Kishikawa et al.³⁴ Colour code: host liquid crystal (blue) and covalent chiral dopant (red). Phase sequence on cooling for the mixture with the composition: EBBA/1/1,8-octanediol 94.5/5.0/0.5 mol%: blue phase (BP), metastable chiral nematic phase (N*), isotropic liquid (Iso). Transition temperatures were determined from the graphics in the publication, unless stated in the text.

LC N-(4-ethoxybenzylidene)-4-*n*-butylaniline (EBBA), to increase the BP temperature range to $\Delta T = 9.5^\circ\text{C}$ upon heating and $\Delta T = 22.7^\circ\text{C}$ upon cooling. Furthermore, the addition of alkane diols to the already doped mixture led to an extension of the BP temperature range up to $\Delta T = 35^\circ\text{C}$ in the cooling cycle. The BP was remarkably stable at room temperature since the lower transition temperature was below 20°C . Also the impact of the length of the diols was investigated during this study. The best results were achieved for octane diol while the results for the two longer additives (decane diol slightly and dodecane diol considerably) were inferior. Furthermore, the increase of amount of diol additive was not favourable; the increase from 0.5 mol% to 1.0 mol% reduced the temperature range of the BP to $\Delta T = 6.5^\circ\text{C}$ on heating. For comparison, a succinimide derivative without hydroxyl group at the terminal alkyl chain was synthesised and tested as an additive together with octane diol. In this case, the BP temperature range was much narrower, $\Delta T = 3.9^\circ\text{C}$ on heating and $\Delta T = 13.3^\circ\text{C}$ on cooling, which confirms the relevance of the lateral hydroxyl group. The proposed mechanism for the stabilisation of the BP was the arrangement of the bent-shaped succinimide molecules around the DTCs with their terminal alkyl chains filling the disclination lines. The diols in the mixture form reversible hydrogen-bonded networks throughout the disclination areas between the hydroxyl groups of the succinimide molecules and thereby stabilise the BP structure. However, an explanation why some of the diols have a positive effect and others do not was not provided by the authors.

2.2. Design Approach

The second approach is to design the BP-forming mesogens with H-bonds. Here the host and the dopant are obtained via self-assembly of hydrogen-bonded building blocks.

He et al. obtained their LC diad (Figure 14) by H-bonding of an achiral pyridine-bearing molecule **PPI** and a chiral carboxylic acid **SHBA/SFBA**.³⁵ Additionally, excess acid formed homo-dimers in the mixture. Careful variation of the molar ratios of the two components, H-donor and H-acceptor, led to a BP with a temperature range of $\Delta T = 23.0^\circ\text{C}$ at a molar ratio of about 2 : 1 (H-donor:H-acceptor) for a fluorinated derivative (**SFBA**) of the acid. Since the excess carboxylic acid forms homo-dimers, it can be seen as a chiral H-bonded dopant for the LC and therefore can contribute to the extension of the BP temperature range. However, the acid does not show mesogenic behaviour and too much additional acid suppresses the formation of mesophases. Part of their explanation for the widened BP was the flexibility of the H-bonds which facilitates the formation of the double-twisted structure. Also, the presence of the fluorine substituents was expected to have a positive effect on the BP stability

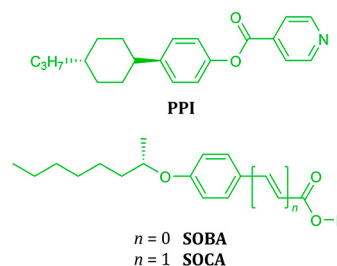


Phase sequence:
Cr – 47 °C – **Sm*** – 63 °C – **N*** – 70 °C – **BP** – 93 °C – **Iso**

Figure 14 Second generation of hydrogen-bonded assemblies reported by He et al.³⁵ Colour code: hydrogen-bonded assembly (green). Phase sequence on cooling for the mixture with the composition: **SFBA/PPI** 2/1 molar ratio: crystalline phase (Cr), chiral smectic phase (**Sm***), chiral nematic phase (**N***), blue phase (BP), isotropic liquid (Iso). Transition temperatures were determined from the graphics in the publication, unless stated in the text.

since it can form weak H-bonds with aliphatic protons to further stabilise the BP structure. In addition, the electron-withdrawing character of the fluorine might assist in the packing of the aromatic rings by reducing the electron density of the π -system.

Later, another derivative (**SOCA**---**PPI**, Figure 15) based on cinnamic acid was reported by He et al. to be H-bonded with the previously mentioned achiral H-acceptor bearing a pyridine.³⁶ Although the BP temperature ranges were not as wide as in the previously reported systems, only $\Delta T = 10^\circ\text{C}$ for the 2 : 1 complex, BPs could also be observed in the heat-



Phase sequence:
Cr – 70 °C – **Sm*** – 96 °C – **N*** – 104 °C – **BP** – 114 °C – **Iso**

Figure 15 Third generation of hydrogen-bonded assemblies reported by He et al.³⁶ Colour code: hydrogen-bonded assembly (green). Phase sequence on cooling for the mixture with the composition: **SOCA/PPI** 2/1 molar ratio: crystalline phase (Cr), chiral smectic phase (**Sm***), chiral nematic phase (**N***), blue phase (BP), isotropic liquid (Iso). Transition temperatures were determined from the graphics in the publication, unless stated in the text.

ing cycle, which was not the case before. In this report, the stability of the BP was attributed again to the chirality induction of the homo-dimer dopant and the flexibility of H-bonds. Additionally, according to DFT calculations, the cinnamic acid-derived compounds possessed a greater H-bond distance and inter-plane bending. Therefore, the enhanced flexibility, induced by the longer H-bond and the additional double bond, of the newer molecules as well as the stronger bent-shape character can explain the enantiotropic behaviour of the BP. These two examples demonstrate that the flexibility provided by H-bonds does not only positively influence the compatibility but also interactions in the host system.

Huang et al. reported Schiff base derivatives (Figure 16) exhibiting mesogenic behaviour including BP.³⁷ This example stands out, since the mesogens are not built by hydrogen bonds rather than covalent ones. However, in one series of molecules they possess hydroxyl groups forming intramolecular H-bonds leading to the formation of the BP. These compounds do not possess large BP temperature ranges; however, they nicely demonstrate the influence of intramolecular H-bonding inside of the mesogens on the existence of BP. Two series of molecules were synthesised, one bearing the branched chiral alkyl chain near the salicylaldehyde core (**OH II**) and one with the chiral centre far from the core (**OH I**). In the first series, a compound possessing a hydroxyl group exhibits a BP temperature range of $\Delta T = 3.6^\circ\text{C}$, while the structurally related derivative **H I**, missing the hydroxyl group, exhibits no BP. Also, the increase in terminal chain length caused the BP to disappear, so only compounds of the first series with $n = 6$ and 7 exhibited BPs. For the ones with longer alkyl chains, the BP did not appear. In contrast, all molecules of the second series did possess BPs, so no con-

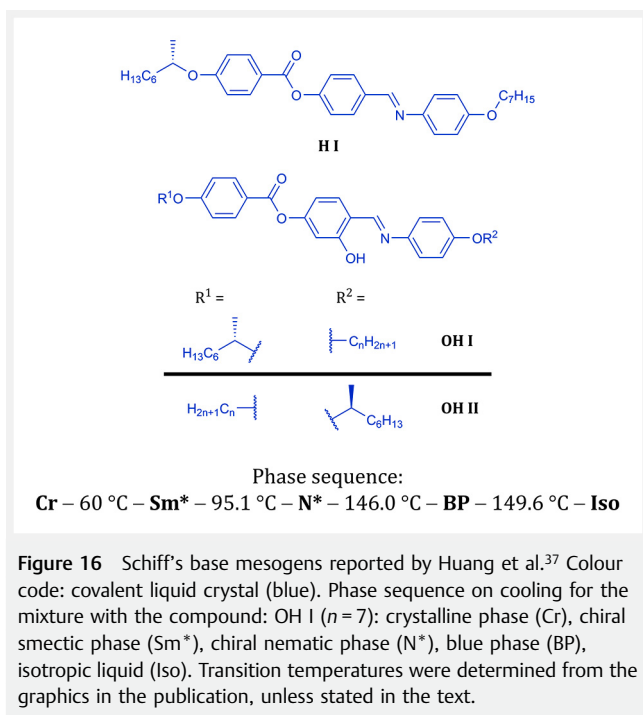


Figure 16 Schiff's base mesogens reported by Huang et al.³⁷ Colour code: covalent liquid crystal (blue). Phase sequence on cooling for the mixture with the compound: OH I ($n = 7$): crystalline phase (Cr), chiral smectic phase (Sm*), chiral nematic phase (N*), blue phase (BP), isotropic liquid (Iso). Transition temperatures were determined from the graphics in the publication, unless stated in the text.

clusions could be drawn regarding the influences on the BP formation. The observation in the first series, the disappearance of BP by removing the H-bonding moiety, was explained by the enhanced rigidity and polarity induced by the H-bonds. This statement is in clear contrast to the reasons claimed by other groups for the stabilisation of BPs, which usually claim the flexibility of the HBA structure as a reason for the stabilisation. Possibly, this is due to the fact that in this example discrete molecules are employed, whereas in the other cases, HABs are utilised. But still, rigidity contradicts flexibility.

A comparative study was published by Wei et al. in which they investigated the different effects of H-bonded mesogens and compared their properties with the covalently bonded counterparts (Figure 17).³⁸ A library of different molecules was synthesised including chiral and achiral as well as fluorinated and non-fluorinated carboxylic acids as H-donors together with chiral and achiral pyridine-bearing molecules as H-acceptors. Interestingly, only in HBAs containing chiral H-donors BPs could be observed, while the system bearing only a chiral centre at the H-acceptor did not form BPs. In addition to the different combinations of donors and acceptors, also variations in the molar ratio were investigated by increasing the amount of H-donor in the mixture. The results showed that the BP temperature range increases with higher contents of acid up to a molar ratio of 3 : 1. After that, the BP temperature range decreases rapidly. Herein, the chiral acid homo-dimers acted again as a chiral dopant for the LC mixture to increase the HTP. Also lateral fluoro-substitution is believed to have a positive effect on

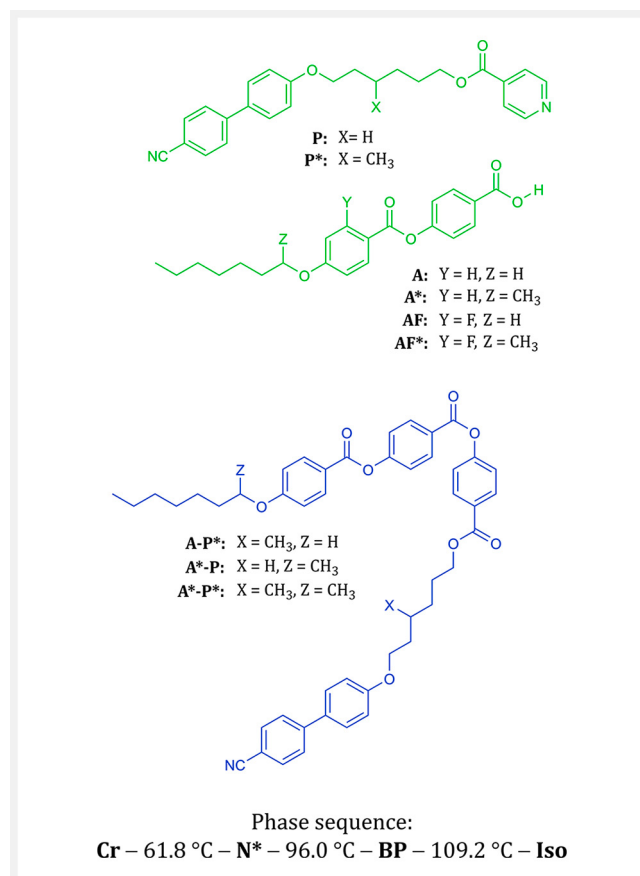


Figure 17 Hydrogen-bonded assemblies and covalent analogues reported by Wei et al.³⁸ Colour code: covalent liquid crystal (blue) hydrogen-bonded assembly (green). Phase sequence on cooling for the mixture with the composition: AF*/P* 3/1 molar ratio: crystalline phase (Cr), chiral nematic phase (N*), blue phase (BP), isotropic liquid (Iso). Transition temperatures were determined from the graphics in the publication, unless stated in the text.

the BP temperature range. Therefore, the highest BP temperature range of $\Delta T = 13.2$ °C was observed for **AF*...P***, a complex between a fluorinated chiral H-donor and a chiral H-acceptor in a molar ratio of 3 : 1, respectively. An additional explanation for these results was the favourable bent angles in the complexes showing BP, which should be between 132.1° and 152.9°. Accordingly, the absence of BP in some of the compounds was explained by unfavourable bent angles. A conclusive explanation on the role of the H-bond was not provided.

To investigate the influence of the position of the H-bond in their bent-core supramolecular systems, Han et al. expanded the library of compounds started by Wei et al.^{38,39} They observed a loss of LC behaviour in the HBAs (Figure 18) having their H-bond far from the bent core. The covalently bound analogues did not show liquid crystalline behaviour. Consequently, the authors focused on derivatives with H-

bonds close to the core of the molecular structure. The variation of the terminal alkyl chain at the H-acceptor showed that the elongation of the chain led to an increase in the BP temperature range. Again the molar ratio played an important role in inducing the BP. While none of the HBAs exhibited BP behaviour with a molar ratio of 1 : 1, a slight excess of H-donor induced the BP, which is attributed to the already mentioned effect of the formation of the homo-dimers of the acid molecules. Another interesting observation was the effect of alkyl chain length on the range of molar ratios in which BP is present. The lowest range was found for the HBAs with alkyl chains of the same length on H-acceptor and H-donor (55–70 mol% $A_{II}F^*$ in $P_{III}C_7$), while alkyl chains of different lengths were more beneficial for the molar ratio range. This means the shorter or longer chain derivatives could take up more of the acid homo-dimers (55–75 mol% $A_{II}F^*$ in $P_{III}C_5$ and 55–80 mol% $A_{II}F^*$ in $P_{III}C_9$) before the BP disappeared. In contrast, the BP temperature range increased with increasing length of the H-acceptor alkyl chain. The best results were obtained for the supramolecular complex $P_{III}C_9 \cdots A_{II}F^*$ with a molar ratio of 7 : 3 (H-donor : H-acceptor) using the H-acceptor with the longest (C_9) chain. This system exhibited a temperature range for the BP of $\Delta T = 12^\circ\text{C}$. In this study also, the fluorination effect was identified to be beneficial for the BP stability, which supports previous examples of fluorinated compounds. The importance of the position of the H-bond in the HBA is nicely demonstrated by the loss of liquid crystallinity in the system possessing the inappropriately positioned H-bond. However, a comprehensive understanding on the structure–property relationship is still pending.

Han et al. reported deeper insights into the effects of substitution in HBAs by adding more aromatic rings to the molecular structure of the mesogens previously reported by Lin and co-workers.^{38–40} These molecules were structurally related to the previously reported ones but the terminal alkyl chain of the H-acceptor was extended by a cyano bisphenyl unit (see Figure 18). Additionally, a H-donor extended by one benzoic acid unit was tested. Exclusively the HBA $P_{III}C_9 \cdots A_{II}F^*$ (Figure 19) exhibited BP for a 1 : 1 ratio of H-donor and H-acceptor. In addition, additional H-donor to the supramolecular mesogens yielded a decrease in the BP temperature range, which was attributed to the poor miscibility of the supramolecular LC and the acid homo-dimers. The BP temperature range of $\Delta T = 13.7^\circ\text{C}$ was explained by the appropriate HTP value and a large biaxial parameter, as this parameter promotes the twisted arrangement of the mesogens in the system.²⁷ However, fluorination was not beneficial in this case, which is in contrast to the previous reported findings where the introduction stabilised the BP.

A modular approach for the investigation of BPs in supramolecular LCs was reported by Giese and co-workers.⁴¹ In this study, the HBAs were constructed using a H-donating core and a H-accepting side-unit (Figure 20). As a H-bond-

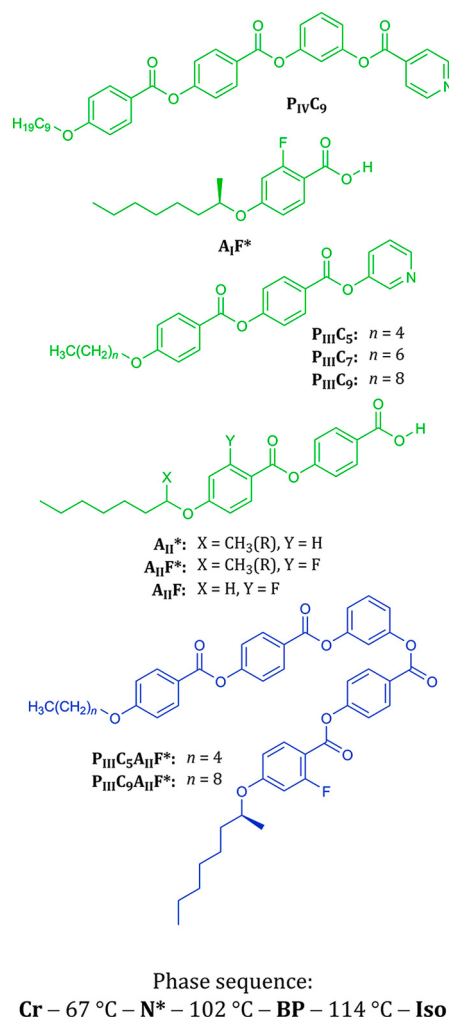


Figure 18 Hydrogen-bonded assemblies and covalent analogues reported by Han et al.³⁹ Colour code: covalent liquid crystal (blue) and hydrogen-bonded assembly (green). Phase sequence on cooling for the mixture with the composition: $P_{III}C_9/A_{II}F^*$ 3/7 molar ratio: crystalline phase (Cr), chiral nematic phase (N*), blue phase (BP), isotropic liquid (Iso). Transition temperatures were determined from the graphics in the publication, unless stated in the text.

donating core, phloroglucinol (**PHG**) or fluoro-phloroglucinol (**F-PHG**) was used and combined with pyridyl-bearing stilbenes (**St**) and azo derivatives (**Ap**) as H-bond acceptors. Different combinations of acceptors were tested in this study; however, the total ratio of core to side-unit was 1 : 3 in order to preserve the mesogenic behaviour. To induce chirality in the system, the H-bond-accepting moieties were partially substituted by their respective chiral equivalents. For example, the stilbene bearing a terminal octyl chain was exchanged with a stilbene equipped with a citronellyl rest. During a screening it became evident that a substitu-

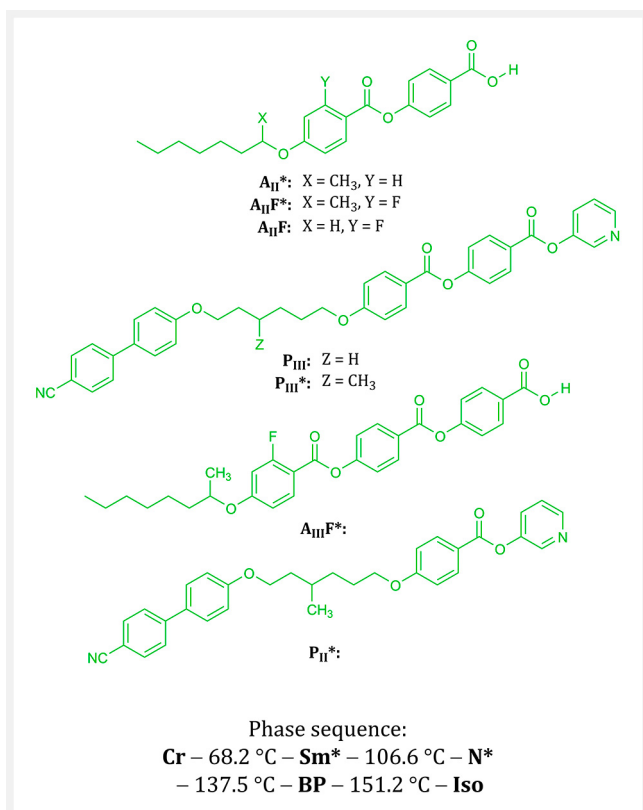


Figure 19 Hydrogen-bonded assemblies reported by Han et al.⁴⁰ Bottom: colour code: hydrogen-bonded assembly (green). Phase sequence on cooling for the mixture with the composition: **P_{III}*/A_{II}*** 1/1 molar ratio: crystalline phase (Cr), chiral smectic phase (Sm*), chiral nematic phase (N*), blue phase (BP), isotropic liquid (Iso). Transition temperatures were determined from the graphics in the publication, unless stated in the text.

tion of 50% of achiral side chains with chiral ones produced the best results. For the complex **PHG**⋯(**St_{1.5}/St_{1.5}***), only a broad chiral nematic phase was found, whereas for the **PHG**⋯(**Ap_{1.5}/Ap_{1.5}***) assembly, a BP I from 75 to 67 °C ($\Delta T = 8$ °C) could be observed. The introduction of fluorine into the core unit led to a stabilisation of the mesophases in previous studies, so the same was done here. However, the effects were of opposite nature. By changing **PHG**⋯(**St_{1.5}/St_{1.5}***) to **F-PHG**⋯(**St_{1.5}/St_{1.5}***), the temperature range of the cholesteric phase dropped from $\Delta T = 87$ °C to $\Delta T = 81$ °C. In the case of **PHG**⋯(**Ap_{1.5}/Ap_{1.5}***), the BP temperature range was lowered by only 6 °C. Still the trends remained the same. As the stilbazole-based assemblies exhibited wider mesophases, combinatorial studies have been conducted by combining **St** with **Ap*** as well as **Ap** with **St***. The assembly **PHG**⋯(**St_{1.5}/Ap_{1.5}***) showed three mesophases, namely, a chiral nematic, a twist grain boundary, and a chiral smectic A; however, no BP was observed. In contrast, the **PHG**⋯(**Ap_{1.5}/St_{1.5}***) with a chiral moiety on the stilbazole instead of the azopyridine showed a BP tempera-

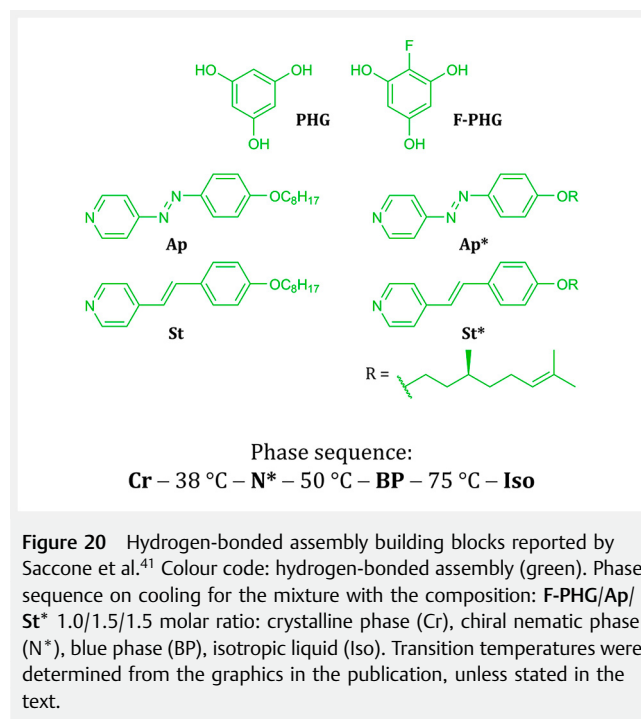


Figure 20 Hydrogen-bonded assembly building blocks reported by Saccone et al.⁴¹ Colour code: hydrogen-bonded assembly (green). Phase sequence on cooling for the mixture with the composition: **F-PHG/Ap/St*** 1.0/1.5/1.5 molar ratio: crystalline phase (Cr), chiral nematic phase (N*), blue phase (BP), isotropic liquid (Iso). Transition temperatures were determined from the graphics in the publication, unless stated in the text.

ture range of $\Delta T = 10$ °C. Also for this composition, the core units were exchanged for their fluorinated counterparts. The resulting assembly **F-PHG**⋯(**St_{1.5}/Ap_{1.5}***) showed only a cholesteric phase from 108 °C to 44 °C, while **F-PHG**⋯(**Ap_{1.5}/St_{1.5}***) was most interesting. The latter exhibited a very stable BP I in a temperature range of $\Delta T = 25$ °C between 75 °C and 50 °C. These findings clearly indicate that the presence of the achiral **Ap** is mandatory to facilitate good chirality transfer. Also the presence of fluorine is beneficial due to non-classical H-bonding (C–F⋯H–C) between the core and the side chain, as well as a more efficient packing due to reduced electron density in the core. This is another example supporting the positive influence of fluorine on the BP stability standing against the negative examples. To shed light on the structural features of the BP I and chiral nematic phase, a solid-state ¹⁹F-NMR study was conducted.^{41,42} In principle, these experiments could confirm the three-dimensional structure of the BP I by comparing the recorded with calculated spectra. The order parameter pseudo exponent β was found to be 0.333 for the BP I and 0.168 for the cholesteric phase, which correlate well with their phase symmetries.

The same system was reinvestigated recently to get more insight into the structure–property relationship.⁴³ As the assemblies employing achiral **Ap** in the host system exhibit BP while the ones based on **St** do not, HTP values have been determined in the respective host LCs. It was shown that both chiral acceptors possess higher HTPs in the **Ap**-based system. Furthermore, computer-assisted modelling was performed to investigate the intermolecular interactions in the

host systems. Here, the attractive forces between the **St** molecules were found to be stronger leading to higher ordered arrangements. From there, it can be rationalised that the presence of achiral **Ap** weakens the interactions in the host material facilitating an improved chiral transfer from the chiral dopants. These findings nicely demonstrate the importance of not only the nature of the chiral dopant, but also the ability of the host system to receive the provided chiral information in the formation of BP.

3. Conclusions and Outlook

The liquid crystalline state is a result of a balanced interplay of attraction and repulsion of the molecular entities, which is controlled by a sophisticated orchestration of intermolecular forces. Therefore, a supramolecular view on liquid crystalline materials can shed light into the structure–property relationship and support the stabilisation of unusual mesophases such as the discussed BPs. In this context, hydrogen bonding appears to be a promising tool for stabilisation of BPs. Although a number of studies clearly demonstrated a positive impact of hydrogen bonding on the stability of BPs, the underlying principle remains obscure and, in some cases, controversial observations were made. For example, most authors explain the hydrogen bonding effect by an increase in the flexibility of the structure; in other cases rigidification by intramolecular hydrogen bonding was mentioned as beneficial for the stabilisation of BPs. Another controversially discussed effect is the fluorination effect which in most cases appears beneficial with respect to the liquid crystalline behaviour and the temperature range of BPLCs; however, there are examples observing the opposite effect. In addition, longer alkyl chains, fluorination and bent-shape of the molecules seem to be beneficial. However, today there are some contradictions in the explanations of the stabilising effects, which demonstrates that further comprehensive studies are crucial for the understanding of these materials and the development of new BP materials for applications in photonic sensing, display technology or optoelectronics.

Funding Information

We thank the DFG for generous funding (GI-882/3-1).

Conflict of Interest

The authors declare no conflict of interest.

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