Amplification of chirality in liquid crystals

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The amplification of molecular chirality by liquid crystalline systems is widely applied in investigations towards enantioselective solvent–solute interactions, chiral supramolecular assemblies, smart materials, and the development of liquid crystal displays. Here we present an overview of recent achievements in the development of new chiral dopant systems for the generation of cholesteric liquid crystalline phases. Based on a distinction between shape-persistent and bistable dopants, several dopant classes will be discussed.

Introduction

Liquid crystals (LCs) form a unique state of matter. Between the solid (crystalline) and liquid (isotropic) phases some compounds display a distinctly different, intermediate state, also referred to as the *fourth state of matter*, or the mesophase. As such, these materials display properties common to both solids and liquids. Due to anisotropic weak intermolecular interactions, the molecules,[1] or mesogens, in such a liquid crystalline assembly possess to some extent either positional or orientational order, but with a much lower degree of organization than in a crystalline solid. Because of this combination of dynamic behaviour and high degree of organization, liquid crystals tend to be sensitive to various stimuli, such as temperature, electric and magnetic fields and non-mesogenic molecules dissolved in the liquid crystalline matrix. Together with their self-assembling behaviour, it makes them extremely interesting for both chemistry and physics. Due to their unique properties these materials have found widespread applications in liquid crystal displays (LCDs). Although a rich variety of molecules are known that are prone to form liquid crystalline phases, showing large differences in the degree and kind of orientation, they all have a strongly anisotropic shape in common. Especially elongated rod-like (calamitic) and disc-like (discotic) molecules are known to possess a liquid crystalline state. This strong shape anisotropy is reflected in a strong anisotropy in the organization of the macroscopic liquid crystalline phase and its physical properties.

Liquid crystalline systems can be classified in many ways.[2] Apart from the distinction between calamitic and discotic, one

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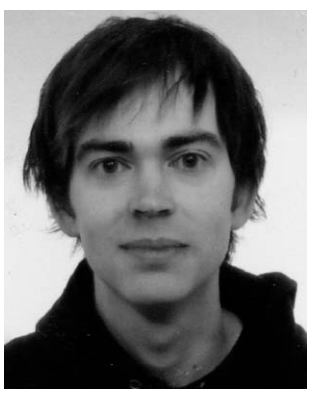

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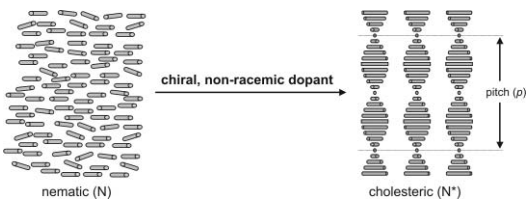
Ben L. Feringa received his PhD degree from the University of Groningen in 1978 with Professor Hans Wynberg. He was a research scientist with Royal Dutch Shell, both at the Shell Research Center in Amsterdam and at the Shell Biosciences Laboratories in Sittingbourne, UK, from 1978 to 1984. He joined the University of Groningen in 1984 as a lecturer, was appointed Professor at the same University in 1988 and in 2003 was appointed as the distinguished Jacobus van't Hoff Professor in Molecular Sciences. He was the recipient of several international awards. In 2004 he was elected foreign honorary member of the American Academy of Arts and Sciences and in 2006 became member of the Royal Netherlands Academy of Sciences. He has recently received the Spinoza award from the Netherlands Organization of Scientific Research and the Prelog Medal of the ETH Zurich. Professor Feringa is the scientific Editor of the RSC journal Organic & Biomolecular Chemistry.

can discriminate between amphiphilic or non-amphiphilic, metal containing or non-metal containing and low molecular weight or polymeric liquid crystals. Moreover, most LC materials described above show thermotropic behaviour, meaning that they are solvent-free systems, that are liquid crystalline in a limited temperature range. Below this range a thermotropic liquid crystalline substance will form a crystalline phase and above this temperature an isotropic liquid phase exists. However, there are many solvent–solute systems, where the aggregation of the solutes results in liquid crystallinity (lyotropic behaviour). The research covered in this review will focus on calamitic, thermotropic liquid crystals that are of low molecular weight, non-metal containing and non-amphiphilic. These liquid crystals can be divided into several types of sub-phases that differ in the degree of orientational ordering. Three important sub-phases are smectic (Sm), nematic (N) and cholesteric (N*) (or chiral nematic). The simplest liquid crystalline phase possible is the nematic phase (N), as it has only a slight orientational order of the individual mesogens. The molecules can translate freely and can rotate around their long axis, leading to a much lower viscosity than observed for smectic phases. The cholesteric (or chiral nematic, N*) liquid crystalline phase is essentially a nematic phase with an additional helical change in orientation of the director (Scheme 1).



Scheme 1 Schematic representation of nematic to cholesteric phase transition and definition of the cholesteric pitch.

Whereas the director in an ordinary nematic liquid crystal has a constant direction, in a cholesteric phase it changes direction in a helical fashion throughout the sample, perpendicular to the helix axis. The orientation of the director describes a helical propagation along the cholesteric helix axis that is non-superimposable on its mirror image, making it chiral. The resulting supramolecular chirality is indicated by the sign and magnitude of the cholesteric pitch (p), which is the distance in the material across which the director rotates a full 360° (Scheme 1). The name of the cholesteric phase originates from the cholesterol derivatives for which this phenomenon was first observed[3,4] but in principle any chiral nematic phase is referred to as cholesteric.

Doped liquid crystals, obtained by dissolving a chiral guest (the dopant) in a nematic host, have many interesting properties.[2,5] The nature of the induced cholesteric phase is highly dependent on the properties of the chiral dopant; this is reflected both in the sign as well as the magnitude of the cholesteric pitch. The efficiency of the dopant to induce a helical organization in a liquid crystalline matrix is expressed in the helical twisting power (β). This parameter, intrinsic to every chiral compound and different for every host–guest combination, reflects the amount of dopant needed to reach a cholesteric phase with a certain pitch. The pitch then is inversely proportional to the concentration (c), the helical twisting power and the enantiomeric excess (ee) of the dopant (eqn 1).

$$p = (\beta \mathrm{ee} \cdot c)^{-1} \quad (1)$$

Compared to cholesteric LCs made up of chiral mesogens, doped liquid crystals offer some major advantages. Most importantly, the pitch of the material is easily tuned by changing the host–guest ratio or the nature of the guest. Chiral guests can be synthesized separately, after which the nematic host and the chiral guest can self assemble to form a cholesteric liquid crystalline phase. Moreover, the molecular chirality of the guest is amplified in the supramolecular helix structure.

Cholesteric liquid crystals show selective reflection of light (colour) when the length of their helical pitch is of the same order of magnitude as the wavelength of visible light. As the pitch, which determines the colour of the cholesteric phase, is dependent on the properties of the chiral dopant, the colour of a doped LC can be influenced by changing the concentration, enantiomeric excess or helical twisting power of the dopant. This offers the possibility of generating many different colours with a single dopant, something which is not possible with a dye. Change in colour can also be achieved using a dopant in which the helical twisting powers can be modulated, allowing selective colour change of a single film, which might find future application in light-controllable liquid crystal colour displays.[6]

Dopants

Over the last 25 years, chiral doped liquid crystal research has emerged into two major directions. The first focuses on the development of shape persistent dopants, mainly aiming at reaching high helical twisting powers and investigation of the interactions between chiral dopants and LC host molecules.[7] In the second field the focus lies on the development of switchable dopants, which can change shape in reaction to an external stimulus, usually light or heat.[6,8] In this area the emphasis lies more on future application, for instance in liquid crystal displays.

Shape persistent dopants

Typical commercially available chiral compounds have rather low helical twisting powers, mostly due to shape, size, polarisation, or conformational incompatibility with the LC host. Therefore, specially designed molecules have been tested for their interaction with liquid crystalline hosts (Fig. 1). Based on their structure, these dopants can roughly be divided into four classes.

Mesogenic functionalisation

The most straightforward way of designing a suitable chiral dopant is to functionalise a chiral molecule with a liquid crystal resembling (mesogenic[9]) group, in order to enhance the solubility and its interactions with the LC host. This approach is mostly applied to molecules owing their chirality to the presence of a stereogenic centre. A representative example is (*R*)-octan-2-ol **1**, which has an extremely low helical twisting power of 0.8 μm^{-1} in LC host MBBA (*p*-methoxybenzylidene-*p*-butylaniline) (*vide supra*), probably due to its lack of structural similarity.[10] Functionalisation with a group resembling MBBA improved the helical twisting power to 19.4 μm^{-1} (Fig. 2).

A similar approach was applied in the development of imine-based dopants.[11] Where (*R*)-phenylethylamine **3** has an

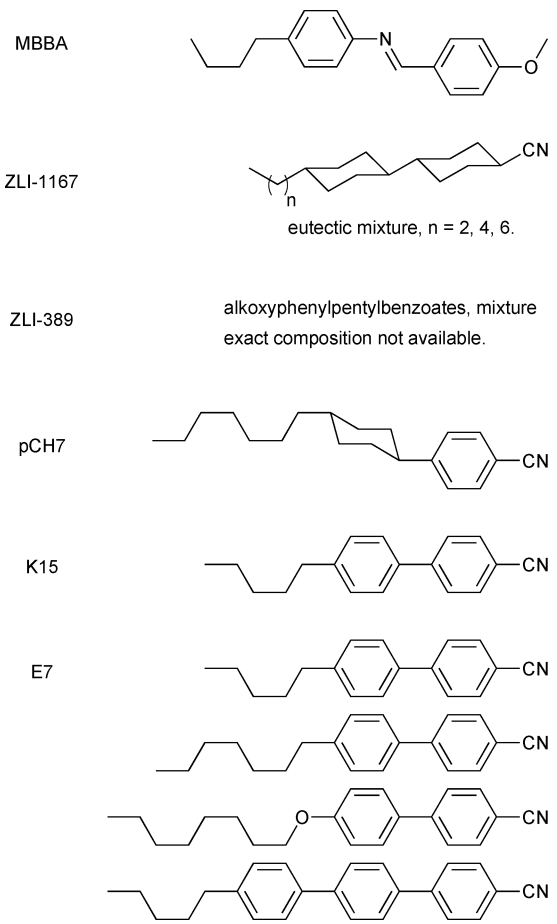


Fig. 1 Some common calamitic liquid crystalline hosts.

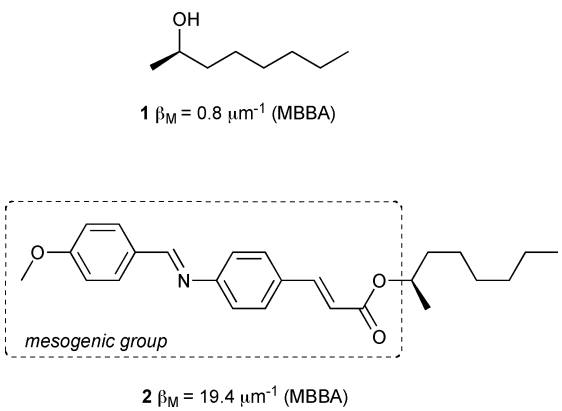


Fig. 2 Functionalisation of a chiral alcohol with a mesogenic group.

immeasurably small helical twisting power, functionalisation with a mesogenic group afforded dopants with helical twisting powers ranging from 17.1 μm^{-1} in phenyl benzoate LC host **5** to 43.2 μm^{-1} in biphenyl LC host K15 (Fig. 3).

The same principle holds for mesogenic amide functionalisation of chiral amines, as the helical twisting powers in cyanobicyclohexyl LC host ZLI-1695 are vastly improved by attaching an alkylbicyclohexyl group to the amine moiety (Fig. 4).[12,13] Interestingly, in the same paper an anthraquinone functionalisation of chiral amines is described that produces even higher cholesteric induction, although the structural similarity between

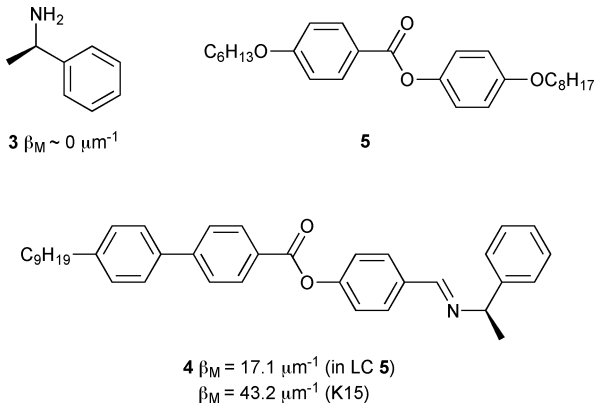


Fig. 3 Functionalisation of a chiral amine with a mesogenic group.

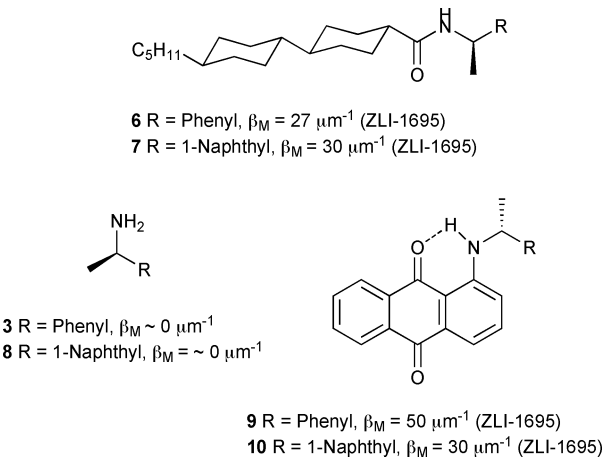
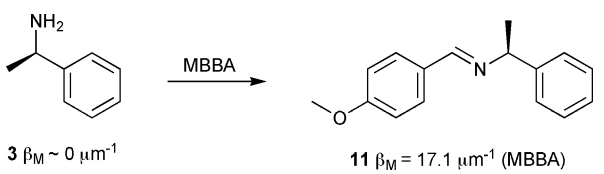


Fig. 4 Mesogenic functionalisation of chiral amines with bicyclohexyl and anthraquinone moieties.

the anthraquinone and the mesogenic host is not that obvious. In this class of compounds an intramolecular hydrogen bond between the amine and the anthraquinone carbonyl reduces the number of different chiral conformers. It seems that this conformational 'locking' is partly responsible for the high helical twisting powers, as the possible conformers all have different helical twisting powers and apparently the ones with a high β value are in excess.[12]

Overall, the mesogenic functionalisation method has not been particularly successful, as only a few dopants with reasonably high helical twisting powers have been reported.[11–14] However, due to the ease of mesogenic functionalisation, some interesting analytical techniques based on this principle have been developed. Rinaldi and coworkers found that amine **3** when dissolved in MBBA undergoes a transimination with the LC host, yielding **11** with a helical twisting power of 17.1 μm^{-1} (Scheme 2).[15] Because of this much higher helical twisting power, a cholesteric phase with a small pitch is easily generated upon doping MBBA with a small amount



Scheme 2 Transimination of LC material MBBA with chiral amine **3**.

of **3**. As a result of the large supramolecular chirality in this system, liquid crystal induced circular dichroism (LC-ICD) is readily observed, where the sign of the CD is dependent on the absolute configuration of **3**. This technique was later extended to absolute configuration determinations for other amines and amino alcohols, although in these cases no helical twisting powers were reported.[16]

A related approach was taken in 2001 by Feringa and van Delden, who reported the mesogenic functionalisation of simple chiral amines and alcohols, leading to LC dopants with β_M ranging from 21.1 to 36.7 μm^{-1} in biphenyl dopant E7 (Scheme 3).[14,17] These high helical twisting powers allowed the generation of coloured LC films. As the colour of these films is dependent on the enantiomeric excess of the dopants, this method allowed the evaluation of the enantiomeric excess of simple chiral compounds by inspection of the colour after mesogenic derivatisation and doping in a nematic LC. Based on this principle and using a pre-functionalised reaction substrate, a colour test for enantiomeric excess determination of enantioselective reactions was developed (Scheme 4).[18]

Chiral coordination complexes

Coordination complexes owing their chirality either to a chiral ligand or a chiral metal centre can be highly effective dopants for induction of cholesteric mesophases. Helical twisting powers up to 180 μm^{-1} were found for C_2-symmetric ruthenium diketonate complexes **19–21** with $\Delta\Lambda$ chirality at the metal centre, with the cholesteric induction being largely dependent on the ligands and the mesogenic host employed (Fig. 5).[19,20] The observation that

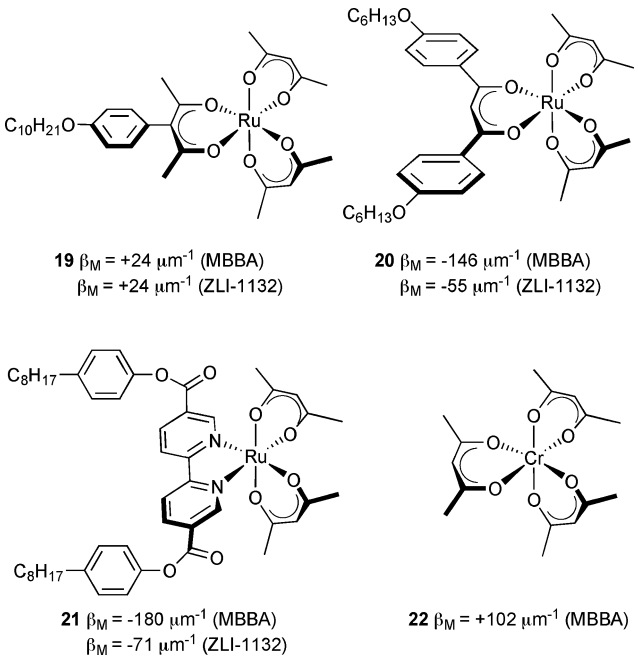
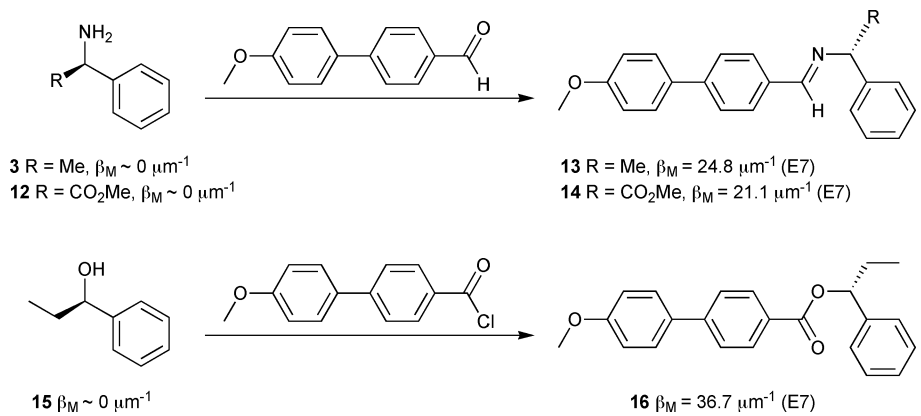
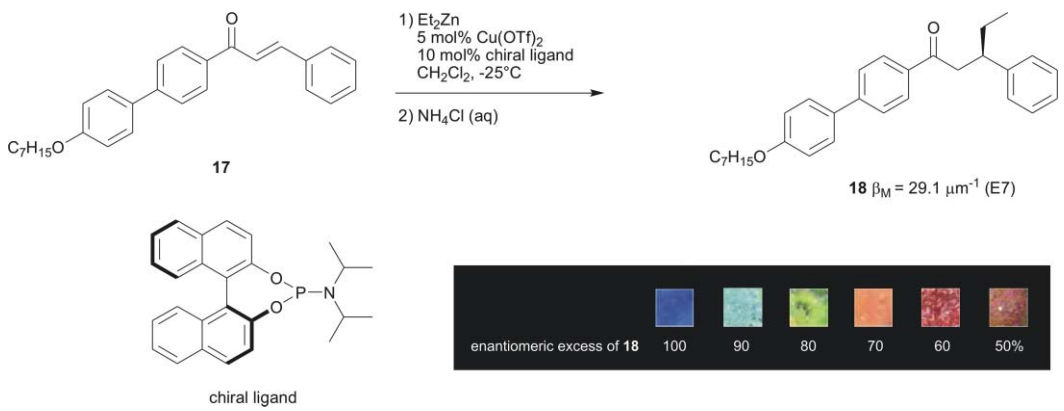


Fig. 5 Chiral coordination complexes with high helical twisting powers.



Scheme 3 Mesogenic functionalisation of chiral amines and alcohols for LC-based colour test.



Scheme 4 Conjugate addition to mesogenically functionalised chalcone **17**. Due to the high helical twisting power of **18**, the ee of these reaction products could be determined directly by an LC based colour test.

chiral chromium diketonate complex **22** also has an enormous helical twisting power (β_M = 102 μm^{-1} in MBBA) shows that mesogenic functionalisation as described in the previous section is not essential for this type of dopant, although mesogenic ligands can have a distinct effect on the cholesteric behaviour and the solubility of the complex.[21,22] The sign of the cholesteric induction for the ruthenium complexes inversed going from complex **19** to complex **20**, while the configuration of the metal centre remained the same.

The interaction of a chiral dopant with an LC host can also be improved by metal coordination, as was shown for chiral tripyridylamine-based ligands **23** and **24** (Fig. 6). Without a metal present, β_M values do not exceed 2.2 μm^{-1} (**24** in MBBA), whereas complexation to Cu(I) or Cu(II) yielded dopants with greatly enhanced helical twisting powers, up to 98 μm^{-1} for **23**·$Cu^{II}(ClO_4)(PF_6)$. This effect was attributed to a reduced conformational flexibility of the ligand and a propeller-like shape of the coordination complex.[23]

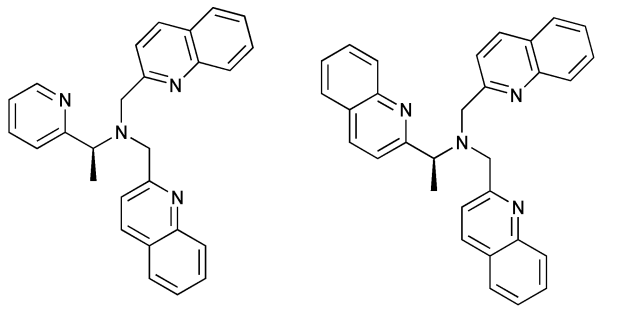


Fig. 6 Enhancement of helical twisting power by metal coordination. LC host = MBBA.

Vic-diols and related compounds

The combination of reasonable backbone rigidity and strategic placement of aryl substituents is generally assumed to afford efficient cholesteric induction.[7] 1,2-Diol-based compounds like TADDOLs and 4,5-diaryl-1,3-dioxolanes possess both these requirements and consequently constitute one of the most effective dopant classes known today (Fig. 7).

TADDOLs, originally designed as chiral auxiliaries and ligands for asymmetric synthesis, are tartaric acid derivatives with four aryl substituents in a propeller type conformation.[24] In addition to the 1,3-dioxolane structure they also possess a 1,4-diol moiety which participates in intramolecular hydrogen bonding, thereby

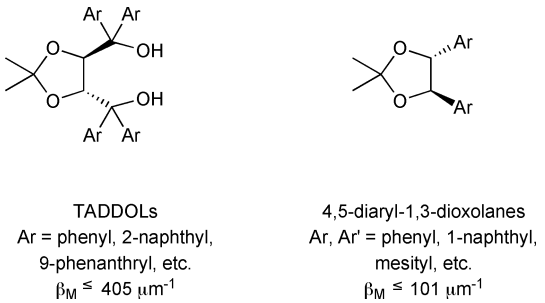


Fig. 7 General structures of TADDOL and 4,5-diaryl-1,3-dioxolanes.

providing the structures with a fair amount of rigidity. Where the original TADDOL **25** with four phenyl substituents already shows an impressive β_M of 100 μm^{-1} in both LC hosts ZLI-1695 and K15, replacement of the phenyls by 9-phenanthryl groups improves this to 310 μm^{-1} and 405 μm^{-1}, respectively (TADDOL **29**).[25–27]

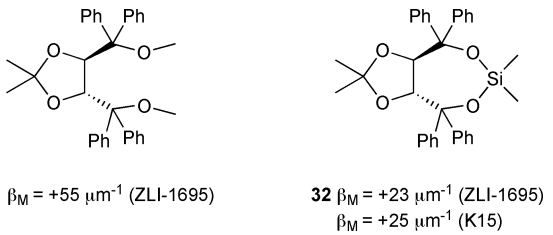


Fig. 8 Influence of bridging substituents on the helical twisting power of tetraphenyl-TADDOL.

All in all, six TADDOLs with helical twisting powers ≥100 μm^{-1} were described, differing in aryl and dioxolane bridge substituents (Table 1). The importance of the intramolecular hydrogen bonding of the 1,4-diol moiety was demonstrated by methylation of the hydroxyl groups, which reduced the helical twisting power from 100 μm^{-1} (**25**) to 55 μm^{-1} (**31**) (ZLI-1695). Similarly, replacement of the 1,4-diol by a silane bridge lowered β_M to 23 μm^{-1} (**32**, Fig. 8).

An interesting correlation between backbone shape, aryl configuration and cholesteric induction can be observed for 4,5-diaryl-1,3-dioxolanes **33** and related *trans*-1,2-diphenyloxirane **41**.[28,29] For 4,5-diaryl-1,3-dioxolanes, two conformations are conceivable, of which the quasi-gauche conformation **33a** is preferred due to steric interactions of the aryl substituents with the methyl groups on the dioxolane bridge in the staggered form **33b** (Fig. 9). In this quasi-gauche conformation the aryls have to adopt an arrangement nearly perpendicular to the plane of the dioxolane ring, with a resulting helicity of which the sign depends on the configuration of the molecule. Many 4,5-diaryl-1,3-dioxolanes show high helical twisting powers in E7, with the highest β_M obtained for dopants with large aryl substituents (Table 2). The

Table 1 Influence of substituents on the helical twisting power of TADDOL

TADDOL	Ar	β_M/μm^{-1} (ZLI-1695)	β_M/μm^{-1} (K15)
25	Phenyl	+100	+100
26	1-Naphthyl	+225	+230
27	2-Naphthyl	+180	+250
28	6-Hydroxy-2-naphthyl	+200	+340
29	9-Phenanthryl	+310	+405
30	4′-Biphenyl	+130	+185

Table 2 Influence of dioxolane substitution on helical twisting power

	Dioxolane	Ar	Ar′	β_M/μm^{-1} (MBBA)	β_M/μm^{-1} (K15)
	34	Phenyl	Phenyl	−5.4	−17.8
	35	1-Naphthyl	1-Naphthyl	−48.7	−58.3
	36	2-Naphthyl	2-Naphthyl	−23.1	−36.1
	37	1-Naphthyl	2-Naphthyl	−20.9	−26.2
	38	Mesityl	Mesityl	−59.5	−101
	39	4-Tolyl	4-Tolyl	−18.2	−22.3
	40	4′-Biphenyl	4′-Biphenyl	−28.5	−58

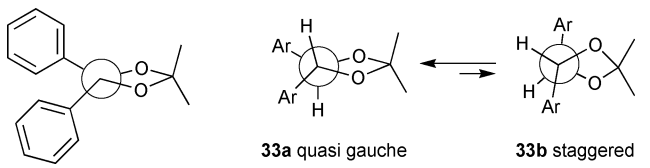


Fig. 9 Conformational equilibrium of 4,5-diaryl-1,3-dioxolanes.

steric bulk on the aryls is believed to force them into this helical conformation, thus producing an overall configuration of the molecule that is ideal for dopant–LC interactions.

Interestingly, where 4,5-diaryl-1,3-dioxolanes display large cholesteric induction in E7, helical twisting powers in MBBA are always lower (Table 2). As the length of the aromatic unit of dioxolane **34** is similar to the biphenyl part of E7, but approximately 2 Å shorter than MBBA, π-stacking interactions between these two moieties seem responsible for the magnitude of the cholesteric induction. This conclusion is supported by the finding that chiral diaryloxiranes, with an aromatic array similar to MBBA in length, have higher helical twisting powers in MBBA than in E7 (Fig. 10). Based on these findings a model for the interaction between dopant and mesogen molecules was proposed

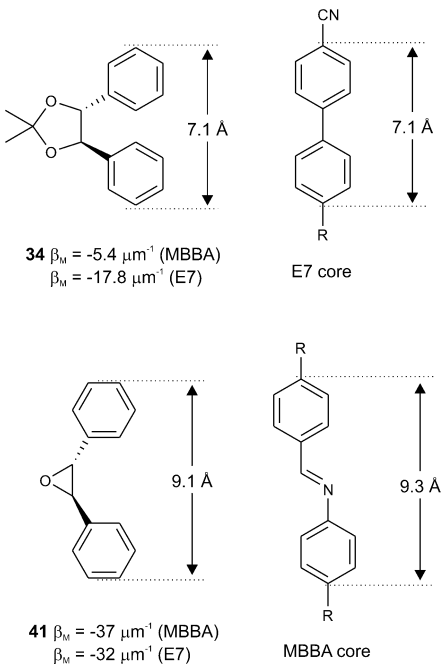


Fig. 10 Comparison of aryl–aryl distances in dopants **34** and **41**, and LC cores of E7 and MBBA. The distances were obtained by computational modelling.

(Fig. 11). It comprises an aromatic helical cleft on the dopant, capable of interactions with the mesogen, and thereby inducing a preferred helicity in this mesogen. This preferred chirality in the mesogen is then transferred *via* neighbouring mesogens to the bulk LC phase.[7] Although a possible mechanism, it was never confirmed experimentally.

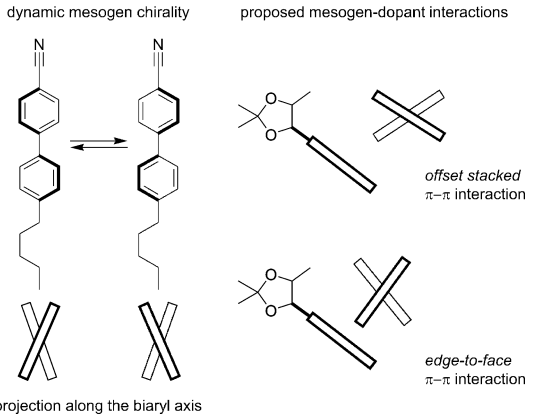


Fig. 11 Models for the interactions between 4,5-diaryl-1,3-dioxolanes and biphenyl mesogens. The twisted biaryl core of the mesogen is situated in the aromatic cleft of the dioxolane.

Atropisomer-based dopants

By far the most extensively studied class of chiral dopants consists of inherently chiral molecules, like binaphthyls, biphenyls and helicenes. These compounds are generally characterized by the absence of stereogenic centres; instead they possess a chiral plane or axis. As a result of their synthetic accessibility and generally high helical twisting powers, they are widely applied in liquid crystal research.

Optically pure 1,1′-binaphthyl compounds can exist in two conformations, either cisoid or transoid, as the dihedral angle (θ) between the two naphthalene rings is dependent on the substituents at the 2 and 2′ positions (Fig. 12). When these substituents are either covalently linked or capable of intramolecular hydrogen bonding, the cisoid conformation is preferred, whereas the presence of large, unlinked substituents leads to a more favourable transoid conformation. The helical twisting power of 1,1′-binaphthyl compounds is largely dependent on the dihedral angle.[30–32]

Especially cisoid compounds exhibit large cholesteric induction, whereas transoid dopants are usually somewhat less efficient. The lowest helical twisting powers are obtained for compounds with a dihedral angle close to 90°, often found for 1,1′-binaphthyls

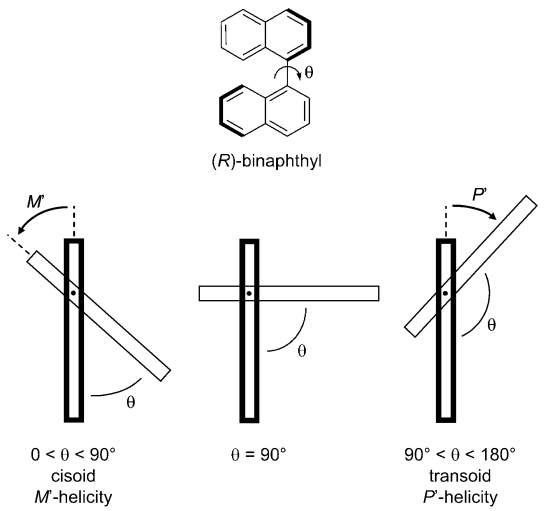


Fig. 12 (*R*)-Binaphthyl and associated conformers.

with small, unlinked substituents at the 2,2′ positions. In addition to these features, the sign of the induced cholesteric helix is also dependent on the dihedral angle. For 1,1′-binaphthyls with the same absolute configuration, a cisoid dopant will provide a cholesteric helicity opposite to that obtained using the transoid type. This is explained by the opposite pseudo helicities of these two conformations, as defined in Fig. 12.[33] An *S*-cisoid dopant will have pseudo-*P* helicity, leading to *P* cholesterics, whereas an *S*-transoid dopant has pseudo-*M* helicity and will induce an *M* cholesteric helix. These effects are clearly observed in 1,1′-binaphthyl-2,2′-diol (BINOL) derivatives (Fig. 13). The β_M of +32 μm^{-1} (K15) for (*S*)-BINOL **42** is the result of intramolecular hydrogen bonding between the two hydroxyl moieties, leading to a cisoid conformation.[30] Bridged BINOL derivatives have even higher helical twisting powers, up to +85 μm^{-1} (K15) for (*S*)-**45**.[34] However, methylation of both hydroxyl substituents reduces the helical twisting power to +1.5 μm^{-1} ((*S*)-**43**, K15), indicating a dihedral angle close to 90°, or an equal population of cisoid and transoid conformation due to the high flexibility of the structure of **43**. Substitution of the hydroxyl group by large isopropoxy substituents enhances the steric hindrance which results in a more effective cholesteric induction (**44**, $\beta_M = -8.2$ μm^{-1}, K15), but reversal of sign, indicative of a transoid conformation.[35]

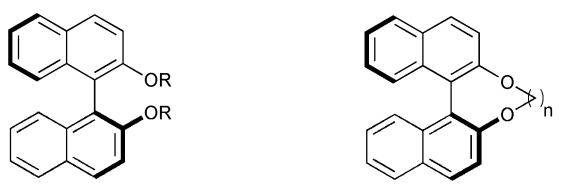
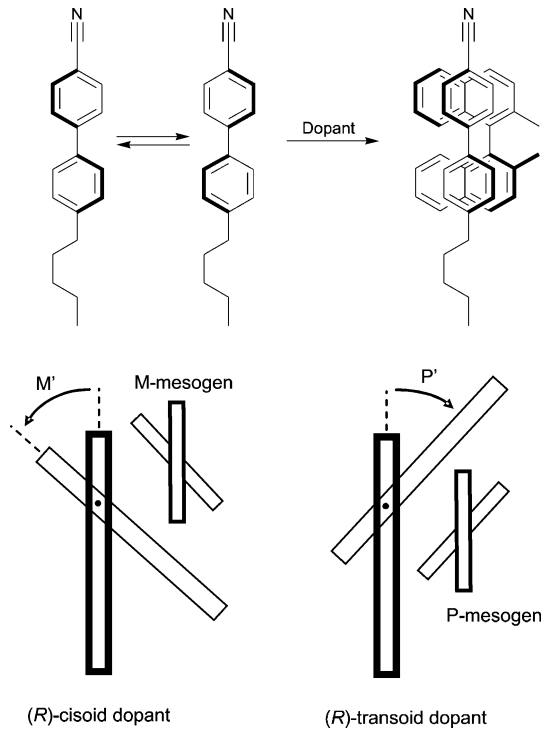


Fig. 13 Helical twisting powers of BINOL derivatives depending on their substitution pattern.

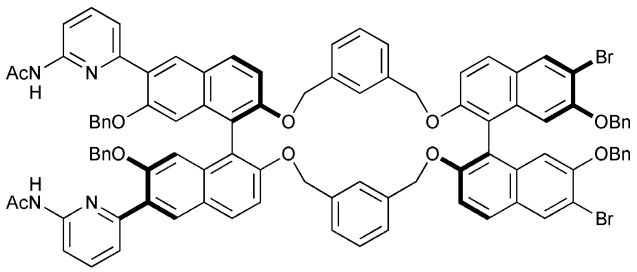
Using linear dichroism (LD) the orientation of dopants **43** and **46** in nematic LC ZLI-1167 was determined, and it was found that the twofold symmetry axes of these molecules are aligned perpendicular to the nematic director.[30,34] Similar to the 1,2-diols described above, dopants **42** and **45**–**47** perform better in biphenyl hosts E7 and K15 than in imine-based MBBA. Based on these two observations a model for the interaction of binaphthyl dopants and biphenyl LC hosts was proposed (Scheme 5). In this model the dopant and a mesogen are associated through π-interactions, with their individual biaryl axes in parallel alignment. Through a mechanism similar to that described for the chiral dioxolane-based dopants (*vide supra*), the chirality is then transferred to the bulk mesophase.



Scheme 5 Proposed model for the transfer of chirality from the binaphthyl dopant to the mesogens.

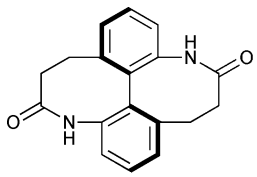
In general, the magnitude and sign of cholesteric induction in biphenyl mesogens by BINOL-based dopants is in accordance with the model described above.[36–38] Depending on the substitution around the naphthalene rings, open chain dopants usually possess helical twisting powers up to 50 μm^{-1}, whereas in their bridged analogues these values can go up to 130 μm^{-1}. Structurally similar 4,4′-biphenanthryls and helicenes show comparable behaviour.[39] An interesting exception is BINOL dimer **48**, reported by Diederich and Spada *et al.*, which has remarkably high helical twisting powers, both in E7 ($\beta_M = -242.3$ μm^{-1}) and MBBA ($\beta_M = -239.5$ μm^{-1}) (Fig. 14).[38] As these values are much higher than can be expected from simply adding two BINOL monomers with similar substitution patterns, the cholesteric induction is thought to proceed *via* a different, yet unknown, mechanism.

Chiral biphenyls do not fit the model with great uniformity, despite the structural similarity to binaphthyls (Fig. 15).[40,41] Especially 4,4′-substituted biphenyls tend to induce cholesteric LC phases with helicities opposite to those predicted by the model.[30] This behaviour could be the result of a different dopant orientation with respect to the nematic director, which was supported by calculations on the dopant order parameter.[42]

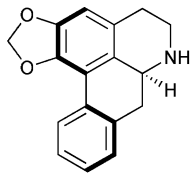


48 β_M = -239.5 μm^{-1} (MBBA)
β_M = -242.3 μm^{-1} (E7)

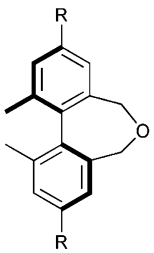
Fig. 14 A BINOL dimer with a high helical twisting power.



49 β_M = +58 μm^{-1} (E7)



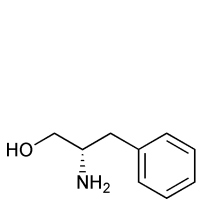
50 β_M = +24 μm^{-1} (E7)



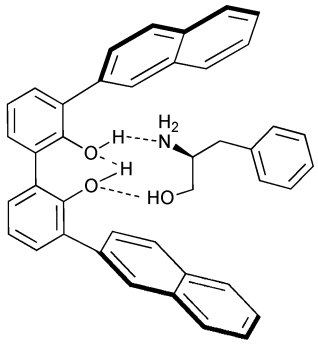
51 R = H, β_M ~ 0 μm^{-1} (E7)
52 R = OMe, β_M = -11.4 μm^{-1} (E7)
53 R = Br, β_M = -19.3 μm^{-1} (K15)
54 R = NO_2, β_M = -20.3 μm^{-1} (K15)

Fig. 15 Some chiral biphenyl derivatives and associated helical twisting powers.

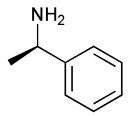
The ability of chiral biphenyls to induce cholesteric order was also applied by Eelkema and Feringa in an approach to amplify the chirality of simple chiral amines and aminoalcohols. Dynamically chiral biphenol and biphenyl phosphoric acid receptors **56** and **57** were allowed to bind to chiral amines through hydrogen bonding. This binding event then induced a chiral conformation in the biphenyl receptor, which in turn induced a nematic to cholesteric phase transition in a calamitic LC (E7)



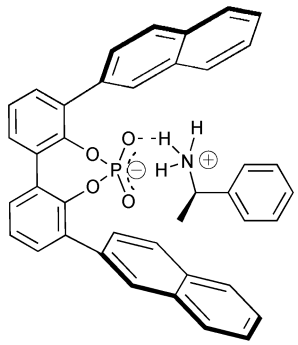
55 infinite pitch (E7)



56•55 p 12 μm (E7)



3 infinite pitch (E7)



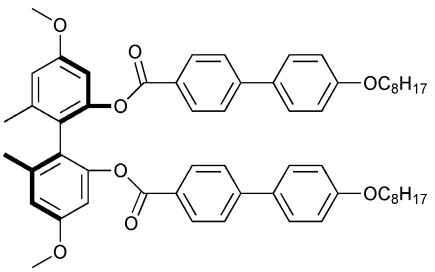
57•3 p 10 μm (E7)

Fig. 17 Dynamically chiral biphenyl-based receptors for the amplification of cholesteric induction.

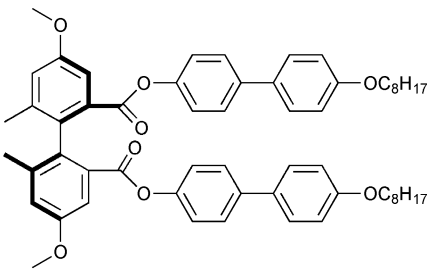
(Fig. 17). As these chiral amines have immeasurably low helical twisting powers by themselves, their chirality is amplified by the presence of the biphenyl receptor.[43,44]

A study on chiral heptalene derivatives revealed a comparable dependence of the helical twisting power on the conformation and orientation of the dopant.[45] Heptalenes are intrinsically dissymmetric molecules with a highly twisted C_2 or nearly C_2 symmetric structure, without the presence of stereogenic centres.[46] The propeller like structure has the intriguing feature that, for any given conformation, the heptalene skeleton has opposite helicities in the *x* and *y* directions (Fig. 18). Heptalenes of the same absolute configuration were found to show opposite helical twisting powers depending on the substituents around the rings (Fig. 18).[45] The cholesteric induction by derivative *P*-**58** is reflected in a moderate +23 μm^{-1} (E7) whereas *P*-**59** shows a β_M of −27 μm^{-1} (Fig. 19).

P-**58** is oriented with its *x*-axis parallel to the nematic director, as was determined by linear dichroism. *P*-**59** has its *y*-axis parallel



60 β_M = -39 μm^{-1} (ROTN 3010)



61 β_M = -50 μm^{-1} (ROTN 3010)

Fig. 16 Mesogenic functionalisation of chiral biphenyls.[49]

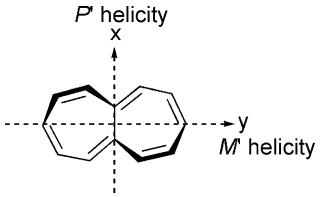
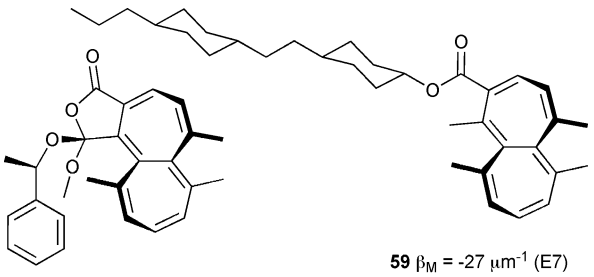


Fig. 18 Heptalene general structure and double helicity; the *x*-axis helicity is used in the absolute configuration description of the molecules.



58 β_M = + 23 μm^{-1} (E7)

59 β_M = -27 μm^{-1} (E7)

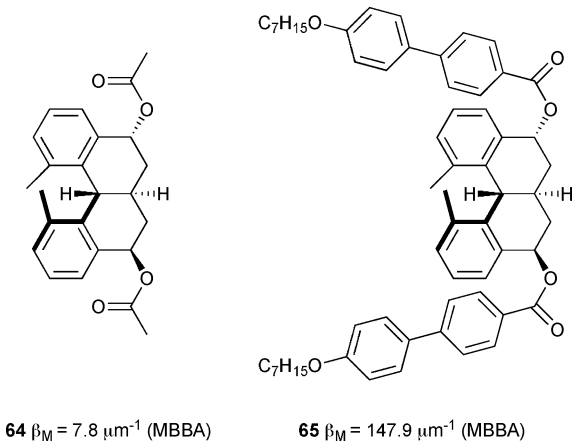
Fig. 19 Opposite helical twisting powers of functionalised heptalenes depending on the substitution pattern.

to the director, showing that the sign of the cholesteric induction is governed by the axis helicity in agreement with the model described above.

The concept of mesogenic functionalisation has also been applied to chiral biphenyl and binaphthyl derivatives, with effects similar to those observed for molecules with central chirality. Moderate cholesteric induction was reported with mesogenically functionalised biphenyls, with a pronounced influence on the way in which the mesogenic group is tethered to the biphenyl unit (Fig. 16).[42,47–49] Mesogenic functionalisation of BINOL proved quite fruitful, providing a β_M of around 200 μm^{-1} for **62** (Fig. 20).[50]

Akagi and coworkers reported a Ziegler–Natta type acetylene polymerisation in a cholesteric film doped with BINOL derivative **63**, yielding helical polyacetylene.[51–53] In this system, the asymmetric nature of the polymerisation is dictated by the cholesteric helicity and not directly by any chiral ligand on the catalyst. No helical twisting power was reported for this dopant, although by comparison to other systems,[36,53] it is not expected to be higher than 100 μm^{-1}, and probably considerably lower. It is not entirely clear why such a complicated molecule has to be applied, when much simpler and more efficient dopants are readily available (*vide supra*).

Results comparable to the BINOL mesogenic functionalisation were obtained for helicene-based hexahydrobenzo-



64 β_M = 7.8 μm^{-1} (MBBA)

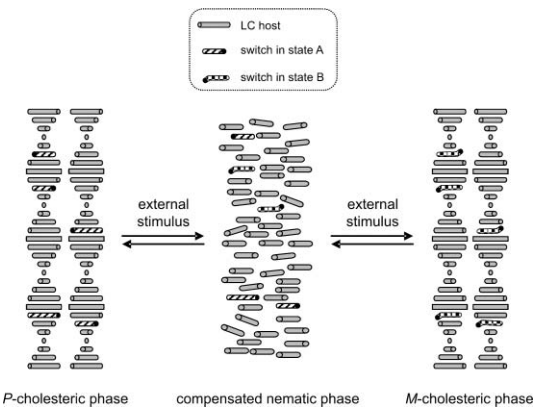
65 β_M = 147.9 μm^{-1} (MBBA)

Fig. 21 Mesogenic functionalisation of helicene derivatives.

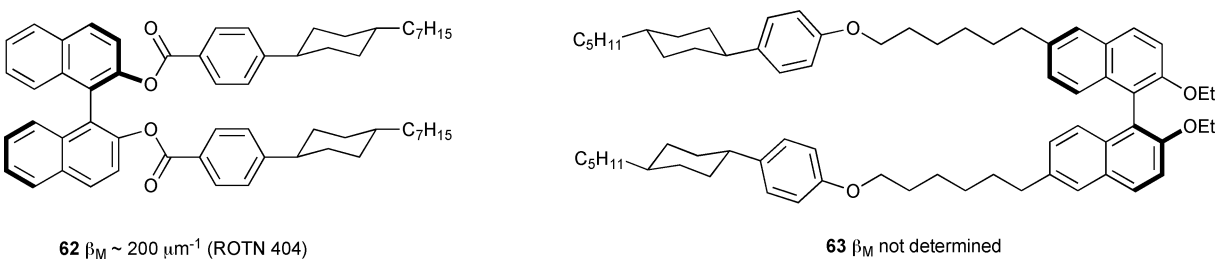
[*c*]phenanthrenes (Fig. 21).[54] Without mesogenic groups, helical twisting powers remained low, whereas the incorporation of 4′-alkylbiphenyl groups improved the cholesteric induction to an impressive 147.9 μm^{-1} (MBBA).

Bistable dopants for photocontrol of liquid crystalline phases

The incorporation of bistable ('switchable') moieties in liquid crystal dopants offers the possibility of controlling the supramolecular chirality of cholesteric liquid crystalline phases using external stimuli (Scheme 6).[8] Furthermore, as the helical pitch and sign of helicity are a direct result of the state of the dopant incorporated, the macroscopic properties of the cholesteric LC can be applied



Scheme 6 Schematic representation of the switching of the chirality of a doped cholesteric liquid crystal.



62 β_M ~ 200 μm^{-1} (ROTN 404)

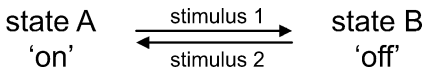
63 β_M not determined

Fig. 20 Mesogenic functionalisation of chiral BINOL derivatives.[50]

for non-destructive read-out of the switch state (*vide infra*), and amplification of its chirality. Especially photochemical switching of cholesteric phases might lead to materials with potential applications in all-optical devices, enhanced speed of data processing and the possibility of controlling the selective reflection and transmission of light.

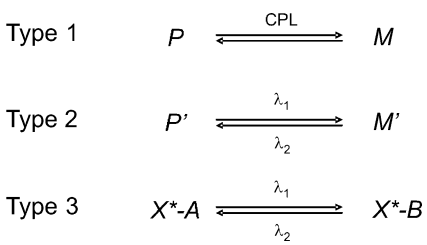
Switches

In recent years, much attention has been paid to the development of molecular machinery, for use in the bottom-up approach in nanotechnology.[55] An essential part in this nanotechnology toolbox is a simple switch that can differentiate between two states, and as such provides the molecular equivalent of the electronic on and off *switch* (Scheme 7).



Scheme 7 Schematic representation of a bistable switch.

For this purpose many different molecular systems have been developed, including catenanes, rotaxanes, azobenzenes, overcrowded alkenes, fulgides, diarylethenes, and spiropyrans.[56] Some of these systems are chiral and as such can, in theory, be applied as bistable dopants for switching between different cholesteric states. Although in principle a variety of external stimuli, such as pH, solvent, pressure, magnetic or electric fields, heat, light and chemical reactions can be applied to achieve switching,[57] generally only heat and light are used for switching in liquid crystal systems, due to their non-destructive nature. Especially light offers enormous advantages over other stimuli, as it can be used at selected wavelengths, distinct polarisations and intensities. Furthermore it offers the possibility of using lasers and masks, for accurate irradiation of defined areas. As a result of these features, practically all switches designed for use in an LC matrix are optical switches, *i.e.* they experience a change in certain properties upon irradiation with a specific wavelength of light. Three different chiral optical switches can be distinguished (Scheme 8).

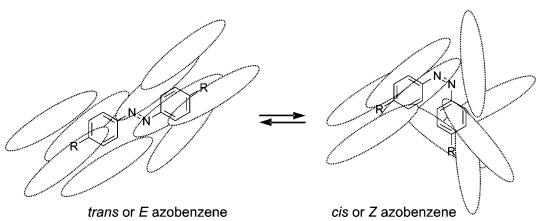


Scheme 8 Schematic representation of different types of chiral switches. *P* and *M* represent molecular helicities, *X** represents a chiral auxiliary unit in the molecule.

In Type 1 the switching takes place between enantiomers, in which case irradiation with unpolarised light leads to racemisation of the switch, due to the equal absorption of light as a result of the enantiomeric relationship of the two states. Therefore, circular polarised light is needed to switch selectively from one state to the other. Type 2 describes switching of pseudoenantiomers, where the chiral properties of the switch are inversed upon switching, but the two states do not have an enantiomeric relationship. Irradiation with unpolarised light can then lead to selective interconversion between the usually diastereomeric states. In Type 3 switches, comprising a switching unit and a chiral auxiliary unit, the chirality of the system does not change so dramatically, for instance, because the switching moiety is situated more remotely from the chiral unit in the molecule. However, switching does result in conformational change and as a result, influences the chiral properties of the entire molecule.

Type 3 switchable dopants

Azobenzene-based switchable dopants. Azobenzenes can undergo a reversible *trans–cis* (or *E–Z*) isomerisation upon irradiation with UV–VIS light, resulting in large conformational and polarisation changes in the molecule. The *trans* form has a rod-like structure and as such can stabilise calamitic liquid crystals, whereas the *cis* form is bent and generally destabilises the LC superstructure by generating disorder in the aligned systems (Scheme 9). This principle has been applied in photochemical orientation of nematic films,[8] pitch change in cholesterics[8,58] and phase transitions from nematic to isotropic states.[59] The first dopant ever to effect a change in cholesteric pitch upon irradiation was an achiral dopant containing an azobenzene core.[60] Even today the azobenzene moiety is the most frequently applied photoactive bistable group in liquid crystal research. It is easily synthesised and generally shows good compatibility with the LC phase, especially in the *trans* form. Moreover, due to the large difference in structure the helical twisting powers of *trans* and *cis* isomers are usually quite different, which allows efficient switching of the cholesteric pitch.



Scheme 9 Destabilisation of liquid crystalline order by *trans* to *cis* isomerisation of an azobenzene dopant.

Similar to the shape persistent dopants described in the previous section, the helical twisting powers of chiral azobenzene-based dopants are largely dependent on the nature of the chiral group in the molecule. In general, azobenzenes with an atropisomeric moiety show much more efficient chiral induction than azobenzenes possessing central chirality (Fig. 22). For the latter type of compounds, the highest helical twisting powers reported are around 15 μm^{-1},[62] whereas binaphthyl-based azobenzenes can have β_M-values over 200 μm^{-1}.[63–66] The *trans* isomers normally show more efficient cholesteric induction than the *cis* form, in accordance with the model presented in Scheme 9. However, when substituted at the 2,2′- and 3,3′-positions, the *cis* isomers possess a more rod-like character and the structural modification is associated with higher helical twisting powers (**69**, Scheme 10).[67]

As the helical twisting powers of these azobenzenes are generally low, selective colour reflection of the LC film with these photobistable dopants as guests and manipulation of the colour by optical switching is practically impossible. However, high compatibility with calamitic mesogens made the use of chiral

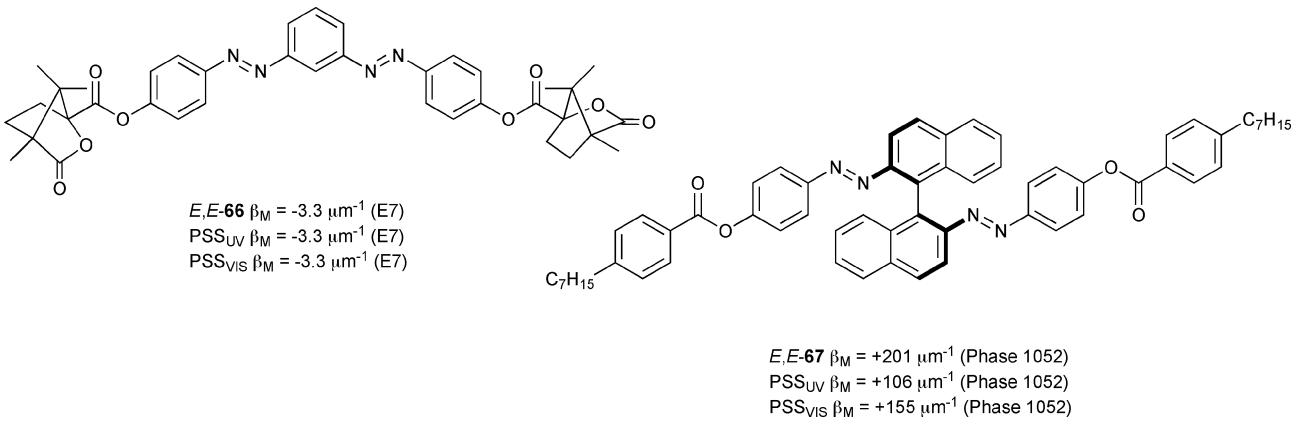
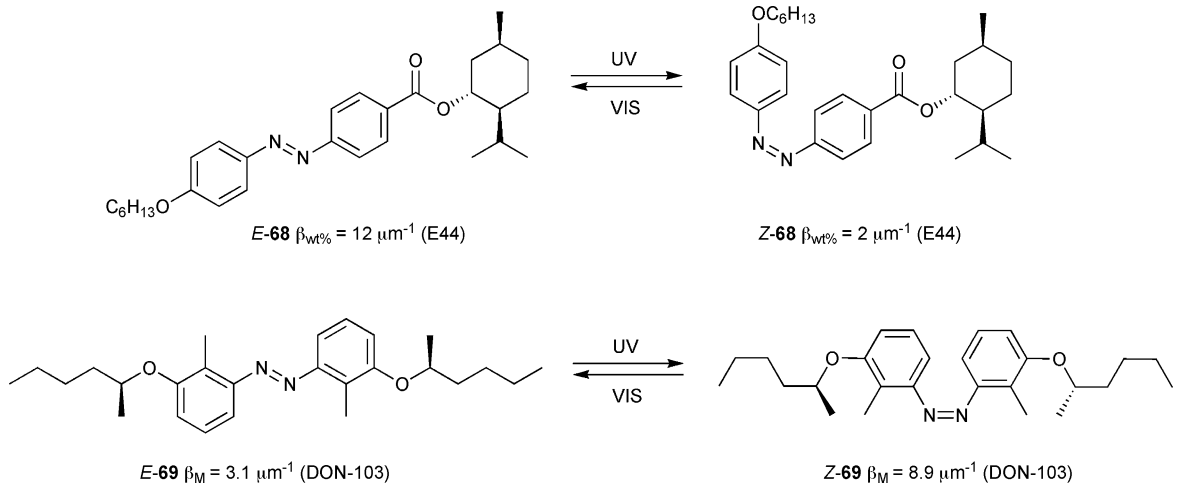


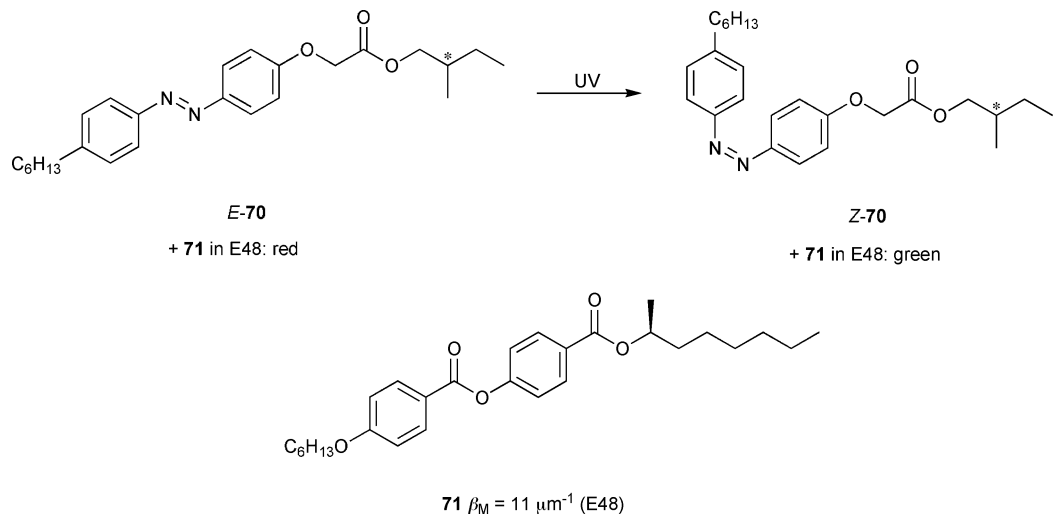
Fig. 22 Azobenzene-based dopants and associated helical twisting powers.



Scheme 10 4,4′- *vs.* 3,3′-Disubstituted chiral azobenzenes as bistable dopants.[68]

non-photo addressable co-dopants of enhanced compatibility and helical twisting power feasible, resulting in efficient switching of coloured cholesteric films (Scheme 11).[8,62c,62e,69]

The helical twisting power of azobenzene switches was considerably enhanced by incorporation of axially chiral binaphthyl moieties. Especially binaphthyldiamine-based switches **67** (Fig. 22),



Scheme 11 Photochemical modulation of the colour of a liquid crystalline film using a chiral co-dopant. The exact helical twisting power of **70** is unknown, but too low to generate a reflective LC film in E48 on its own. Chiral co-dopant **71** has a moderate helical twisting power but a high compatibility with the LC host, allowing doping of high concentrations leading to coloured LC films.[61,69a]

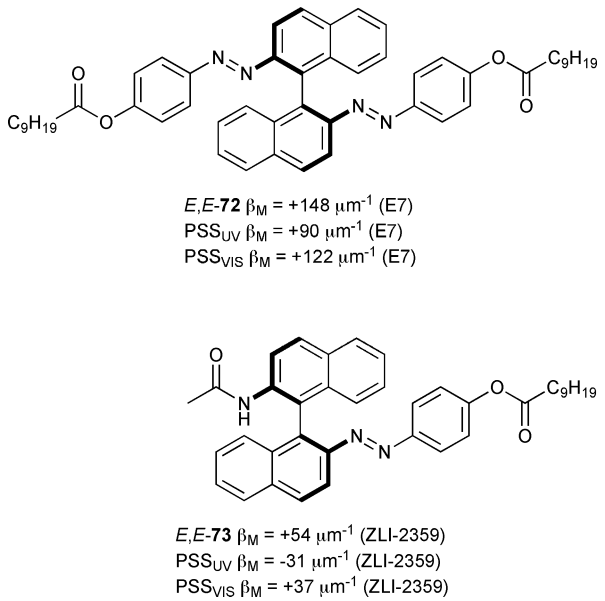
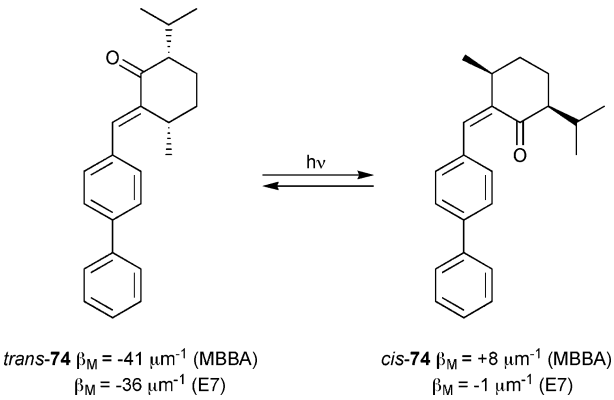


Fig. 23 Binaphthalene-based azobenzene switches showing efficient cholesteric induction.

72 and **73** (Fig. 23), developed by Gottarelli and Spada *et al.*, constitute a powerful system for optical switching of the cholesteric pitch, as the high helical twisting powers allow for colour generation and switching without added chiral co-dopants.[64] Furthermore, UV irradiation of an LC film doped with switch **73** ($\beta_M = +37\ \mu m^{-1}$, PSS_{VIS}, in ZLI-2359) leads to a cholesteric phase of opposite helicity ($\beta_M = -31\ \mu m^{-1}$, PSS_{UV}), a phenomenon that is rarely observed to such a degree for Type 3 switches.[70,71]

Olefin-based switchable dopants. The same *trans–cis* isomerisation is also used for switching of chiral cyclohexane derivatives with an exocyclic olefinic double bond.[72] Menthone derivatives

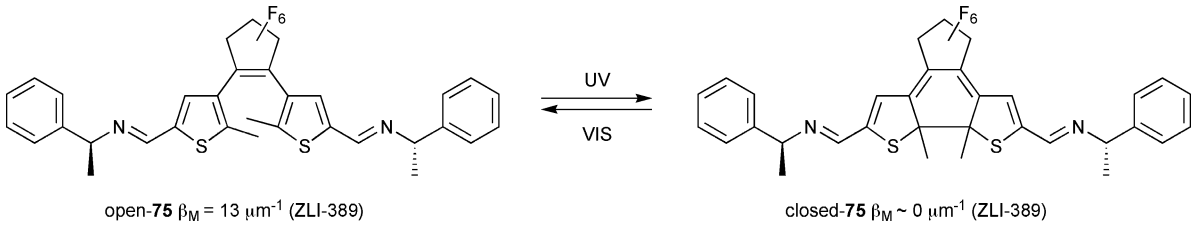


Scheme 12 Menthone based switchable dopants.

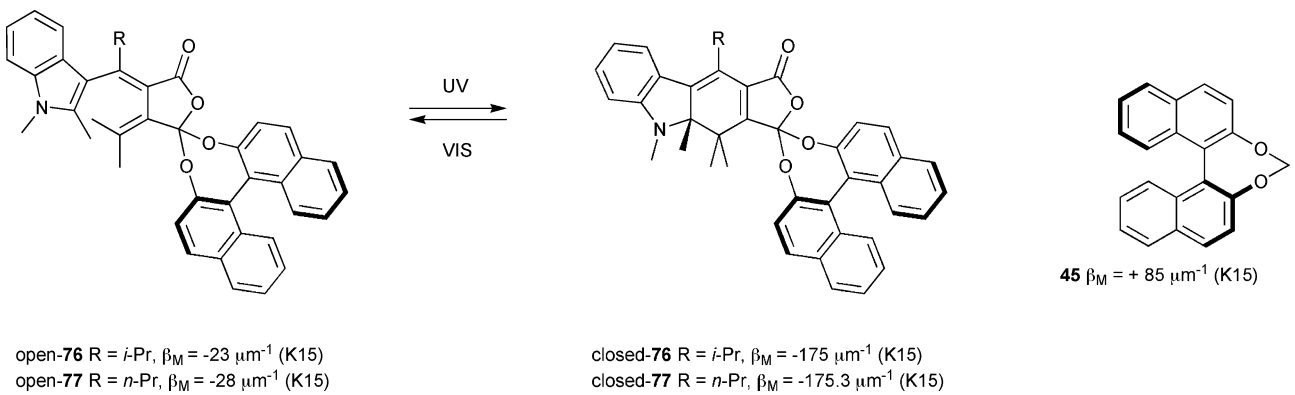
showing high helical twisting powers and efficient cholesteric pitch switching were reported,[73] and later these compounds were also used for light induced colour change of cholesteric copolymers (Scheme 12).[74]

Diarylethenes. Photochromic diarylethenes undergo a reversible 6π electron cyclisation upon irradiation, leading to distinct changes in structure and electronic configuration of the molecule.[75] This switching unit has been applied for reversible cholesteric to nematic transitions and manipulation of the cholesteric pitch.[76,77] The cholesteric to nematic transitions were made possible because in all described cases either the closed or the open form of the switch has an extremely low helical twisting power (Scheme 13). Overall, cholesteric induction by this type of switch is not very efficient.

Fulgides. A similar reversible 6π electron cyclisation is used for switching fulgides.[78] The incorporation of a chiral binaphthol moiety in the switch resulted in a bistable system with an enormous difference in helical twisting power between the open and closed forms of the switch (Scheme 14).[79] The open form of



Scheme 13 Diarylethene-based switchable dopants.



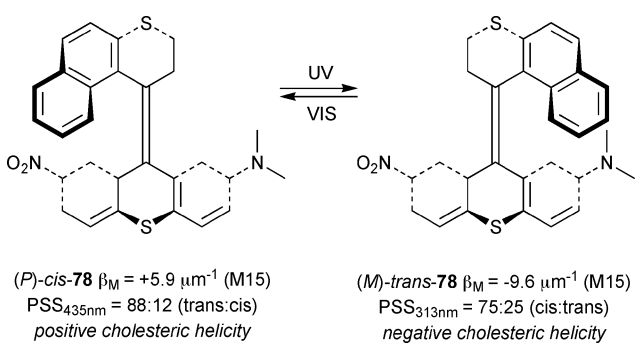
Scheme 14 Fulgide-based switchable dopants.

chiral fulgide **77** has a β_M of $-28.0\ \mu m^{-1}$ in K15, whereas ring closure leads to an impressive β_M of $-175.3\ \mu m^{-1}$. This allows photoswitching between cholesteric phases with a long and a short pitch, respectively, using very small amounts of dopant. However, it does not result in a change in sign of the cholesteric helicity. This shortcoming was circumvented by addition of non-switchable chiral dopant **45** showing opposite helical twisting power ($+85\ \mu m^{-1}$), resulting in reversible switching between a positive and negative cholesteric phase.[79b]

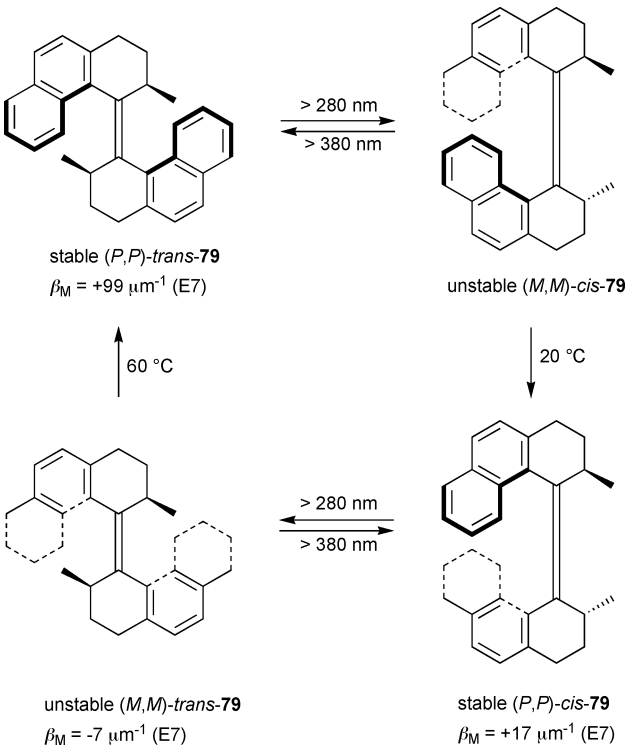
Type 2 switchable dopants

Overcrowded alkenes. As a result of the pseudoenantiomeric relationship[80] between the two switch states, Type 2 switches are much more likely to show inversion of the cholesteric helix sign upon switching than Type 3 switches. This principle was first shown for the overcrowded alkene-based switches developed by Feringa *et al*.[81,82]

The inherently dissymmetric alkene *cis*-**78** has a *P* chirality, which, upon irradiation with UV light, is converted to its *M*-*trans* isomer (Scheme 15). The pseudoenantiomeric relationship of these two isomers is clearly reflected in their CD spectra. Doping of LC host M15 with *P*-*cis*-**78** transformed this nematic phase to a cholesteric phase with positive helicity ($\beta_{M,cis} = +5.9\ \mu m^{-1}$).[83] Irradiation with UV light then led to a photostationary state consisting of 75% *M*-*trans*-**78** and 25% *P*-*cis*-**78** and an overall negative cholesteric helicity. The *M*-*trans* switch has a helical twisting power of $-9.6\ \mu m^{-1}$. Subsequent irradiation with 465 nm light led to a photostationary state made up of 88% *P*-*cis* and 12% *M*-*trans*, and consequently a positive helical pitch. Similar results were obtained in other liquid crystalline hosts and with structural variants of switch **78**.[84–86] Overall, helical twisting powers of these types of switches are not very high, but cholesteric helix inversion takes place quite efficiently and with nearly equal magnitude as a result of the pseudoenantiomeric relationship of the switch states. Light-driven unidirectional molecular motors were also used as chiral guests in LC host materials. For the first generation of the overcrowded alkene-based molecular motors,[87] the behaviour mentioned above is inversed compared to the switches; the β_M of the stable *P*,*P*-*trans* form of **79** is $+99\ \mu m^{-1}$ (E7), but generation of a cholesteric helix with an opposite sign of similar pitch is impossible, as only the *M*,*M*-*trans* form possesses a minor negative helical twisting power ($\beta_M = -7\ \mu m^{-1}$, E7) (Scheme 16).[85,88] As a result of the high helical twisting power of the *P*,*P*-*trans* form, coloured liquid crystalline films are easily generated using this dopant. Photochemical and thermal isomerisation of the motor leads to irreversible colour change in the LC film.

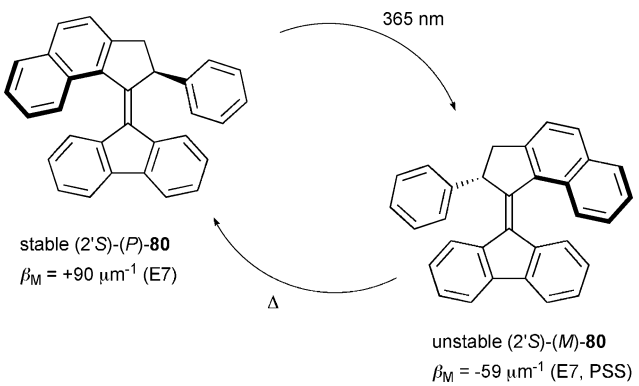


Scheme 15 Overcrowded alkene-based molecular switch **78** and its influence on a liquid crystalline host.



Scheme 16 Unidirectional rotation of molecular motor **79** in a liquid crystalline host, and associated helical twisting powers.

A major breakthrough in this area was achieved with the introduction of fluorene-derived molecular motors. Possibly due to the structural compatibility of the fluorene group with the LC host's biphenyl core, motor **80** was found to possess very large helical twisting powers for both stable and unstable forms (Scheme 17). Moreover, these two forms induce cholesteric phases of opposite signs, making it possible to switch efficiently between cholesteric helicities. As the thermal isomerisation step (from unstable to stable form) occurs readily at room temperature, these motors were found to be able to induce fully reversible colour change of a liquid crystalline film across the entire visible spectrum.[89]



Scheme 17 Unidirectional rotation of molecular motor **80** in a liquid crystalline host, and associated helical twisting powers. For the unstable form, the helical twisting power of the photostationary state (PSS) is described, as the composition of the PSS could not be determined.

Moreover, switching of this molecular motor in a liquid crystalline environment induced an unprecedented rotational reorganisation of the LC film, which was applied in the light-driven rotation of microscale glass rods.[90]

Type 1 switchable dopants

Bistable switches with an enantiomeric relationship between the switch states can be interconverted using circularly polarised light. Furthermore, irradiation of a racemic Type 1 switch with circularly polarised light (CPL) of one handedness can lead to partial photoresolution. As the two enantiomers absorb left- or right-handed CPL differently, one enantiomer is excited preferentially, leading to racemisation. The other enantiomer is affected less and will accumulate until an equilibrium or photostationary state is reached. The enantiomeric excess of this photostationary state at a certain wavelength of irradiation depends on the Kuhn anisotropy factor g_λ, defined as the ratio of the circular dichroism ($\Delta\varepsilon$) and the extinction coefficient (ε) (eqn 2).

$$ee_{PSS} = g_\lambda/2 = \Delta\varepsilon/2\varepsilon \quad (2)$$

As g-values normally do not exceed 0.01, CPL photoresolution seldom leads to enantiomeric excesses over 0.5%.[91] Such ee values can be difficult to determine using conventional methods. However, as the conversion from nematic to cholesteric is essentially thresholdless, these ee values are theoretically high enough to trigger a nematic to cholesteric transition. The ee can then be determined from the cholesteric pitch *via* eqn 2. Likewise, using this system, the helicity of a cholesteric phase can be controlled using only the chiral information in the circularly polarised light. Finally, a cholesteric to nematic transition can be caused by irradiation with unpolarised or linearly polarised light, leading to racemisation of the chiral switch.

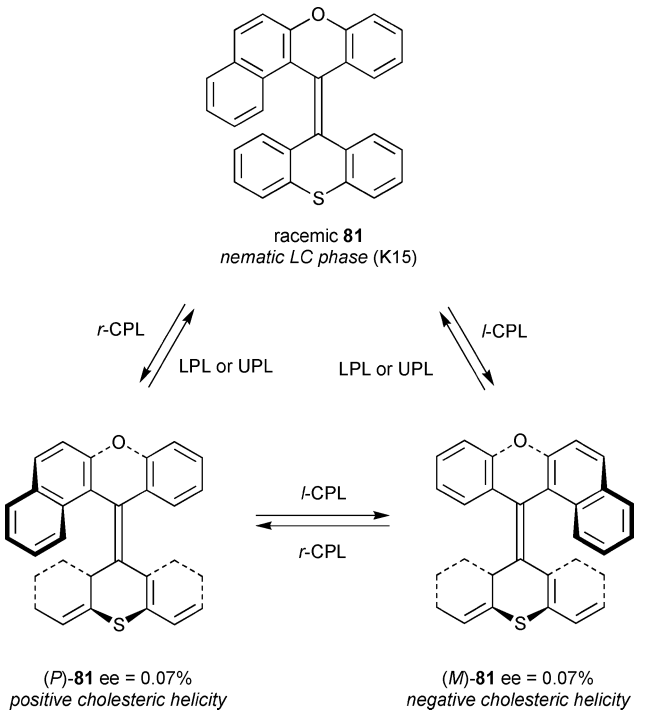
Overcrowded alkenes

The concept described above was first proven using inherently dissymmetric overcrowded alkene **81** (Scheme 18).[82,92] In this way, a 3-stage LC switching system comprising nematic, positive cholesteric and negative cholesteric LC phases was developed. Irradiation of this racemic Type 1 switch with l-CPL (313 nm) led to *M*-**81** with 0.07% ee. When this irradiation was carried out in a nematic LC host[83] (20 wt% **81** in M15) a cholesteric phase was generated, which disappeared again upon irradiation with linearly polarised light. Irradiation with r-CPL resulted in a cholesteric phase of opposite handedness.

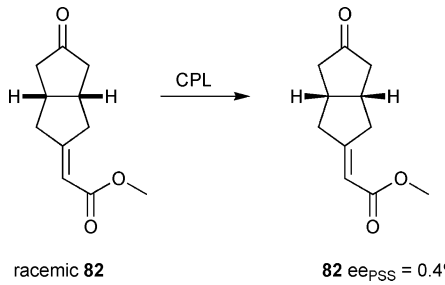
Due to the rather low helical twisting power of *M*-**81** ($\beta_M = -0.1\ \mu m^{-1}$ in M15) and low anisotropy factor ($g_{314} = -0.0064$ in *n*-hexane) these effects were small and only very large cholesteric pitches could be addressed. However, it did show the potential of this system for amplification of chirality, from the handedness of circularly polarised light *via* a chiral molecular switch to a macroscopic nematic to cholesteric phase transition.

Axially chiral bicyclic ketones

Schuster and Suarez showed reversible photoswitching of a racemic bistable compound using CPL.[93] Racemic axially chiral bicyclic ketone **82** was irradiated with l-CPL, leading to partial photoresolution (Scheme 19). Irradiation of more than 6.7 h



Scheme 18 CPL-induced deracemisation of overcrowded alkene-based switch **81** in a liquid crystalline environment resulting in 3-stage LC switching. LPL = linearly polarised light, UPL = unpolarised light.



Scheme 19 CPL-induced deracemisation of axially chiral bicyclic ketone **82**.

resulted in a photostationary state with 0.4% ee. This value was in good agreement with the ee value predicted by the anisotropy factor ($g_{305} = 0.0105$ at 305 nm), but the enantiomeric enrichment was not sufficient to cause a nematic–cholesteric phase transition, probably due to a low helical twisting power.

Several of these bicyclic ketones were especially designed as photochemical triggers for the control of liquid crystalline phases.[94] Due to the rigid bicyclic core and the ketone chromophore, these structures generally possess large g-values. Unfortunately, both the helical twisting power and solubility in nematic LC hosts are often low (Fig. 24). Finally, the incorporation of a mesogenic unit in the switch resulted in a system capable of reversible nematic–cholesteric phase transition using circularly polarised light (Scheme 20).[95] Switch **83** contains a mesogenic moiety resembling the LC host ZLI-1167 resulting in a helical twisting power of 15 μm^{-1}, a high g-value ($g_{300} = 0.016$) and good solubility. CPL irradiation ($\lambda > 295$ nm) of a nematic mixture containing 13 mol% rac-**83** resulted in a cholesteric phase with a pitch of 190 μm. This was more than twice as long as the pitch

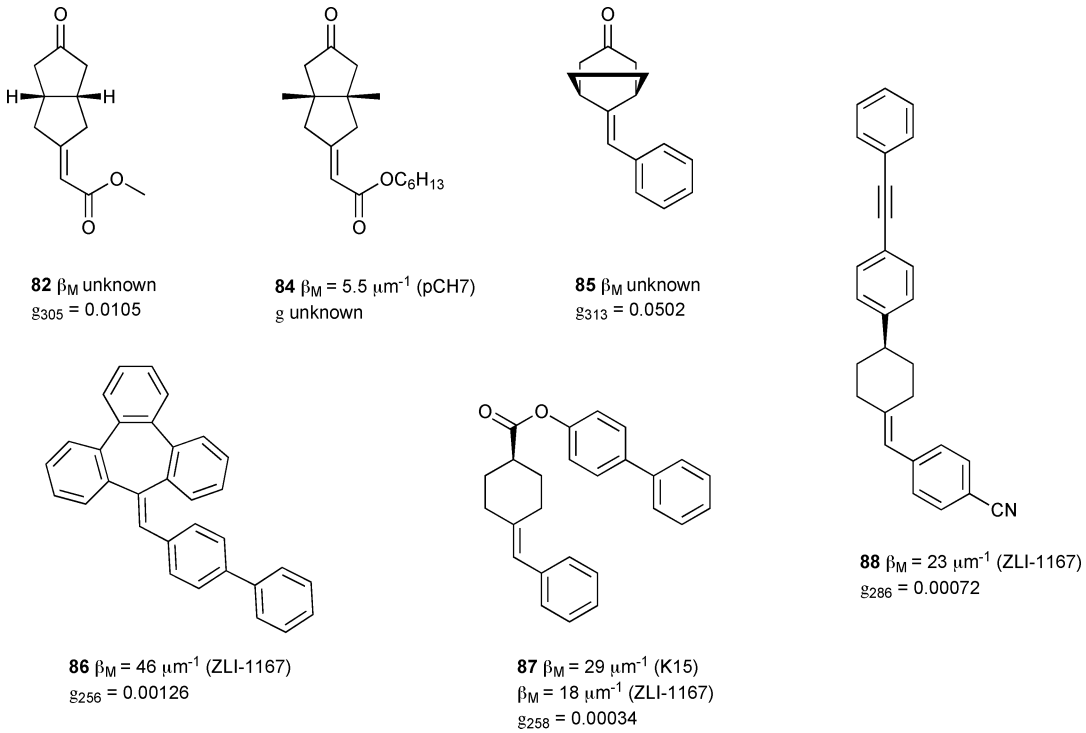
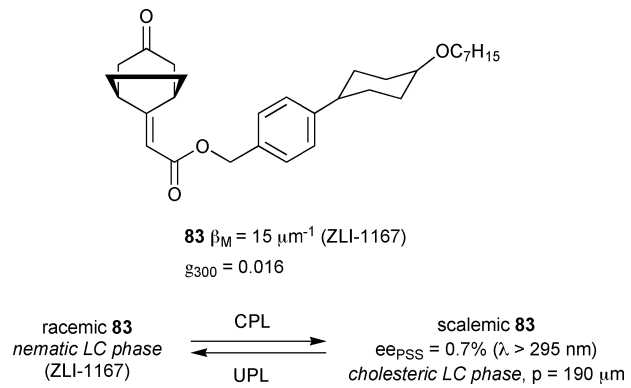


Fig. 24 A selection of chiral dopants developed by Schuster and coworkers.[93–95]



Scheme 20 Nematic to cholesteric phase transition by CPL irradiation of an axially chiral bicyclic ketone.

obtained when a photoresolved sample at the photostationary state was doped in the mesogenic host, probably due to scattering of the CPL by the liquid crystalline mixture.

Conclusions

The amplification of molecular chirality by liquid crystalline systems manifests itself in chiral surface structures, helical supramolecular assemblies and several physical properties, such as optical rotation, circular dichroism and selective light reflection. For the efficient generation of cholesteric liquid crystals several low molecular weight dopant systems with varying helical twisting powers have been developed. Among the most successful dopant classes today are TADDOLs, dioxolanes, binaphthol-based systems and chiral coordination complexes with helical twisting powers up to 400 μm^{-1}. These dopants allow the generation of sub-micrometre pitch cholesterics using millimolar quantities of chiral dopant. Although some trends in the relation between molecular structure and helical twisting power can be observed, no general rules for the design of efficient dopants have been established. The incorporation of bistable moieties in chiral dopants has led to the development of several classes of switchable chiral dopants, which allow the manipulation of sign and pitch of a cholesteric phase using an external stimulus, in particular with light. On one hand, amplification of the switch state in the chiral organisation of the LC superstructure can be applied in methods for non-destructive read out. On the other hand, manipulation of the cholesteric pitch allows controlled colour change of liquid crystalline films. Moreover, racemic bistable dopants can be deracemised using circularly polarised light, inducing a transition from the nematic to the cholesteric phase. The development of more efficient chiral switches with high helical twisting powers of opposite sign for both switch states remains a formidable challenge to be addressed but also offers exciting opportunities for the application of these systems in smart materials and nano- or information technology.

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