Room Temperature Nematic Photoswitchable Liquid Crystals — Molecular Modularisation of Functional Elements

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The successful design of photochromic self-assembly systems requires understanding (on both the molecular and sub-molecular scales) of diverse and often competing structure-property relationships. Such molecular systems are promising as components for photonically switchable components in opto-electronic devices. Molecular modularisation can be an efficient approach to obtain such materials. The design, synthesis and the photochromic and mesomorphic properties of stable photochromic systems which exhibit nematic LC phase behaviour at room temperature are reported.

Introduction

The combination of liquid-crystallinity and photochromic behaviour in molecular systems promises to be very useful in optical technological devices.

However to fulfil this potential, photochromic liquid crystals have not only to be stable in both forms of the photochromic systems, but they have to exhibit liquid crystalline phase behaviour (preferably the nematic phase) at ambient or near-ambient temperatures. Furthermore, the structure-property relationships of such a system should be fully understood, or at least some clear rules of how to obtain certain properties should be developed.[1] A further important feature is to be able to decouple the absorption behaviour of the photochromic systems from that of the molecular groups responsible for the formation of mesomorphic behaviour. This is important to avoid competing absorption of the mesogens in the UV region, and potentially unwanted anisotropic FRET (Fluorescence Resonance Energy Transfer) effects in the liquid crystal phase.[2] At the current stage of knowledge in this field, these effects, which influence the self-assembly properties of the molecular system, are both difficult to assess and control.

In order to achieve these goals, molecules **I** and **II** were synthesised and investigated (Figure 1). They contain as a photochromic core the 1,2-bis(2-methylbenzo[*b*]thiophen-3-yl)hexafluorocyclopentene group (Figure 2), which has been investigated in great detail and has been employed for mesomorphic photochromes.[3] Compared to many other photochromic systems, substituted diarylethenes are thermally very robust; both forms are stable even at high temperatures and photonic switching at elevated temperatures is possible. This not only allows the study of photochromic behaviour, but also the effects of photochromism on mesomorphic assembly.

The photochromic core of **II** is symmetrically functionalised in the 6- and 6′-positions with phenol units, which are connected by a C_4 spacer, a tetramethyldisiloxane group and a further C_4 spacer to a mesogenic group.[4,5] This group is a rod-like (calamitic) mesogen, which is connected by its long axis to the spacer and so to the photochromic unit. This approach to some degree decouples the soft assembly behaviour and the photochromic properties of the system.

The use of laterally connected mesogens has been successfully used in the investigation of organic/inorganic hybrids (silsesquioxanes), dendrimers (carbosilazanes) and LC ferrocenes, where the liquid-crystalline phase behaviour and the properties have been found to be broadly independent of the "encapsulated core". Indeed, in such systems some molecular modes, associated with the rotation around the long axis of the molecules, are faster than in the corresponding low molecular mass systems.[5] The selected approach is essentially modular. The mesogenic group is designed in such manner that attachment to the photochromic system does not alter the phase structure, so as to ensure a nematic phase close to room temperature and (ideally), the absence of crystallisation. Photochromic behaviour and liquid-crystalline properties can then be addressed selectively. Furthermore, the delocalised π-electron system, which is responsible for the mesomorphic behaviour, has to be interrupted in order to avoid an overlap with the absorption maximum of the photochromic group at the wavelength of irradiation.[5b−5e] (In structurally related mesogenic systems, LC phase behaviour is generally due to shape anisotropy and van der Waals interactions of π-electrons).

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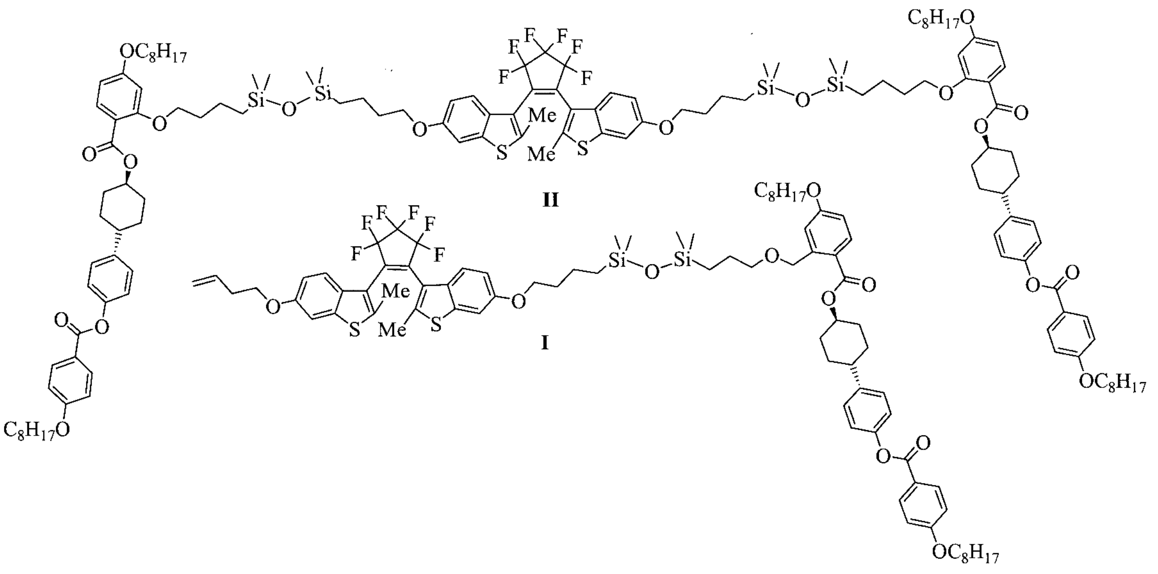


Figure 1. Molecular structures of the photochromic liquid crystals **I** and **II**

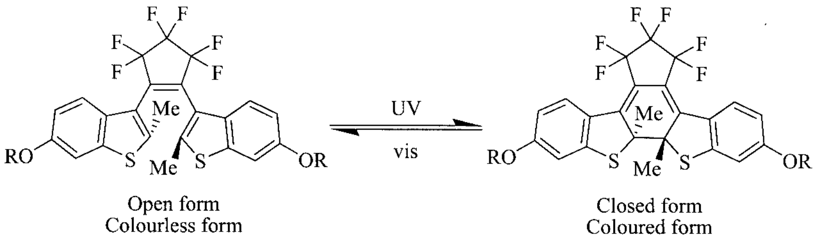


Figure 2. Photochromic interconversion in **I** and **II**

In order to achieve this, an alicyclic group was incorporated, interrupting the electron conjugation in the mesogen.

Results and Discussion

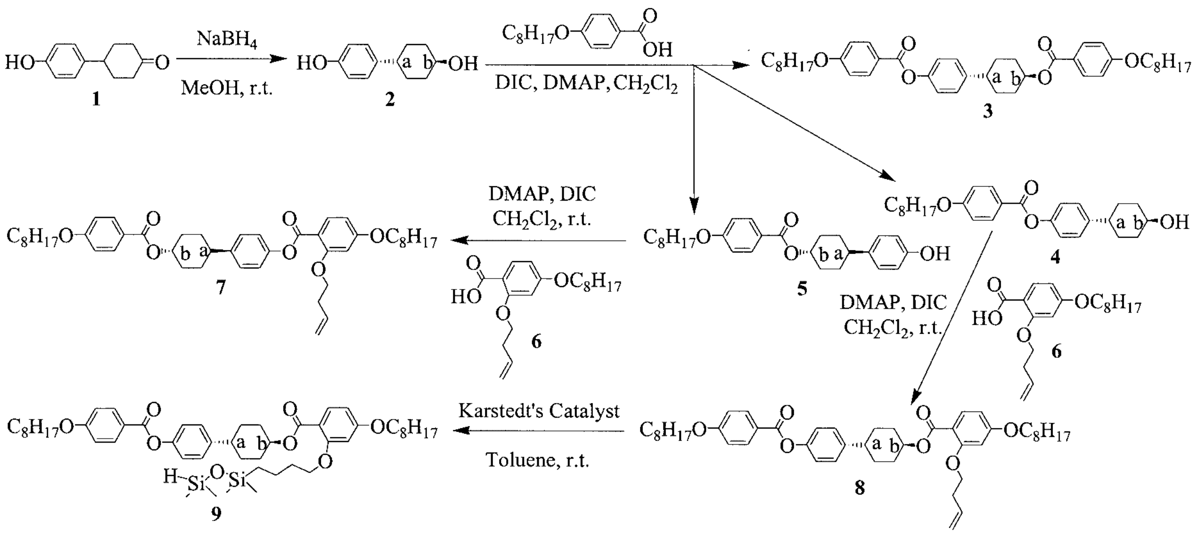
Synthesis

The reduction of 4-(4-hydroxyphenyl)cyclohexanone (**1**) with sodium borohydride in methanol at room temperature gave selectively *trans*-4-(4-hydroxy-cyclohexyl)phenol (**2**) after recrystallisation from ethanol.[6] The alcohol **2** was obtained in 77 % yield, despite the poor solubility of the substrate **1** in the solvent used. When **2** was treated with 4-octyloxybenzoic acid in dichloromethane in the presence of diisopropylcarbodiimide and DMAP, we surprisingly observed the formation of **3** (8 %) and **5** (22 %) in addition to the expected product **4**, obtained in 44 % yield. Subsequent esterification, carried out in the same manner as for compounds **4** and **5**, but with 4-octyloxy-2-(pent-4-en-1-yloxy)benzoic acid (**6**), gave **7** and **8** in 35 % and 22 % yield respectively.[7] The ester **8** was converted to **9** by hydrosilylation with 1,1,3,3,5,5-hexamethyltrisiloxane and Karstedt's catalyst in 77 % yield. As the compound **7** did not exhibit any liquid-crystalline behaviour, no further reactions were performed on it.

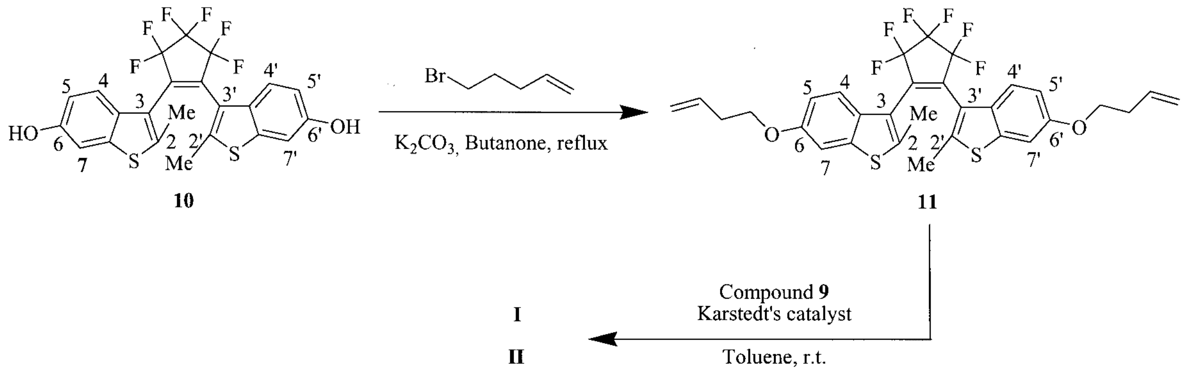
The synthesis of photochromic liquid crystals **I** and **II** (Scheme 2) required the preparation of a photochromic compound **11**, which was obtained in 84 % yield from **10**[1g,8] by treatment with 4-bromobut-1-ene in the presence of potassium carbonate and butanone at reflux. Hydrosilylation of **11** with **9** at room temperature results in the formation of the glassy nematic compounds **I** and **II**. The use of high dilution and one equivalent of the mesogenic group **9** gave the monosubstituted compound **I** in 49 % yield, whereas use of two equivalents of **9** afforded the disubstituted compound **II** in 71 % yield.

Photochromic Properties

The diarylethenes **I** and **II** underwent a reversible photochromic reaction in cyclohexane by alternate exposure to light at wavelengths of 313 nm (UV) and 546 nm (visible), with retention of the isosbestic points. The colour of the solutions of all the compounds was found to change from colourless to red (520 nm). The photochromic behaviour of the new compounds was compared with that obtained for the unsubstituted parent compound, 1,2-bis(2-methyl-1-benzothiophen-3-yl)hexafluorocyclopentene.[9]



Scheme 1. Synthesis of the mesogenic unit **9**



Scheme 2. Convergent synthesis of target compounds **I** and **II**

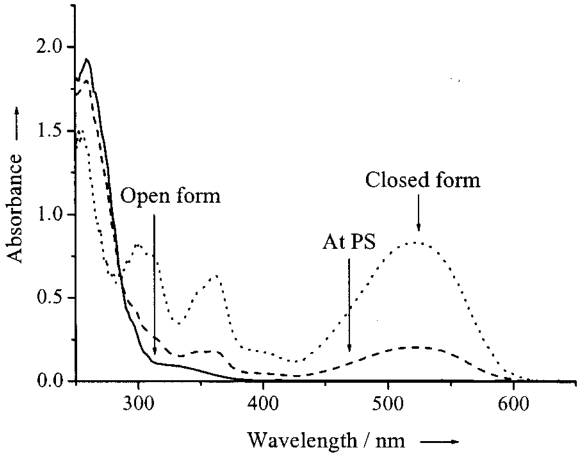


Figure 3. Absorption spectra of a cyclohexane solution (3.33×10^{-5} mol L^{-1}) of the open-ring isomer **I**, the closed-ring isomer **Ia** and the photostastionary state under 313 nm radiation.

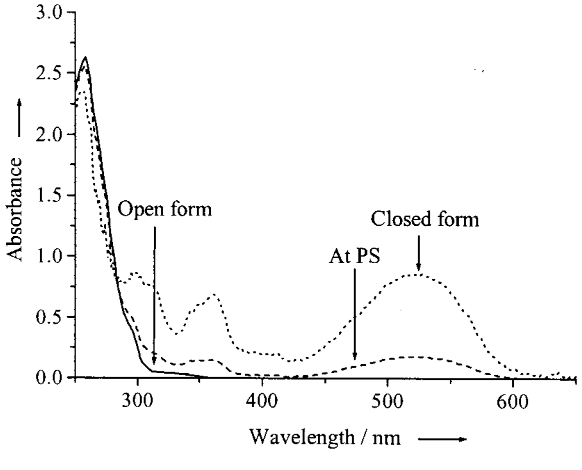


Figure 4. Absorption spectra of a cyclohexane solution (3.33×10^{-5} mol L^{-1}) of the open-ring isomer **II**, closed-ring isomer **IIa** and in the photostastionary state under 313 nm radiation.

Figures 3 and 4 show the spectral changes of compounds **I** and **II** between the open- and the closed-ring isomers and the system in photostationary state under 313 nm radiation. The absorption spectra of the closed forms were calculated from the absorption spectra obtained at the photostationary state (PS) by using Equation (1),[10] which describes the absorbance for a mixture of two compounds at a given wavelength.

$$[A]_{PS} = [A]_{OF}\,(1 - Cv) + [A]_{CF}\,(Cv) \qquad (1)$$

where $[A]_{PS}$: absorption obtained at the PS state, $[A]_{OF}$: absorption of the open form, $[A]_{CF}$: absorption of the closed form, and Cv: the degree of conversion from open- to closed-ring isomers. $[A]_{PS}$ and $[A]_{OF}$ can be determined by UV spectroscopy and Cv can be calculated using HPLC data, by integration of the peaks for the open and the closed forms.

As can be seen in Figures 3 and 4, the UV/Visible absorption spectra of compounds **I** and **II** are similar for both the open and closed forms. Because the mesogenic groups are connected to the photochromic core by an alkyl spacer and absorb only below 305 nm (Figure 5), no differences are observed between the absorption spectrum for the monomer and that for the dimer above 305 nm.

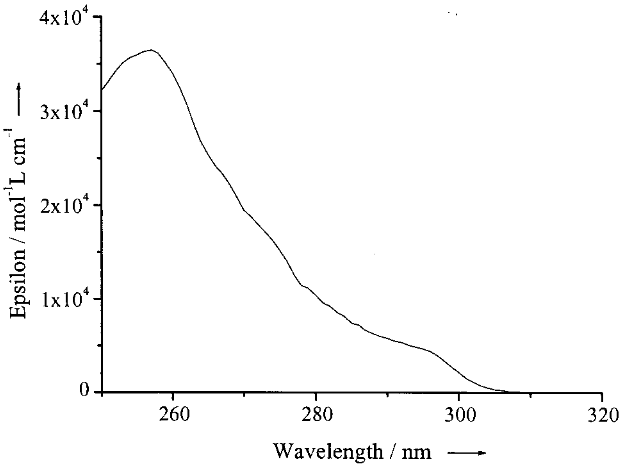


Figure 5. Absorption spectrum of **8** in cyclohexane

The absorption maximum of compounds **Ia** and **IIa** is identical to that obtained for the parent molecule (520 nm). However the ε value at this wavelength for compounds **Ia** and **IIa** (between 23500 and 24000 $mol^{-1}\ L\ cm^{-1}$) is at least 2.5 times higher than for the parent molecule **Ref** (9100 $mol^{-1}\ L\ cm^{-1}$). The absorption maxima and ε values of the open- and closed-ring isomers are summarised in Table 1 (the values for **Ref** and **Refa** are taken from the literature[9]).

Table 1. Absorption maxima and ε values of the open forms **I**, **II** and **Ref** and the closed forms **Ia**, **IIa** and **Refa**

Compound	λ_{max}/nm (ε/mol^{-1} L cm^{-1})
I	258 (57600)
II	258 (79000)
Ref	258 (21000), 290 (6900), 299 (7400)
Ia	258 (46500), 310 (23000), 360 (20200), 520 (24000)
IIa	258 (67000), 310 (22500), 360 (20000), 520 (23600)
Refa	517 (9100)

Quantum Yield and Conversion Measurements

The quantum yields for the cyclisation and photocycloreversion reactions of **I** and **II** were measured in cyclohexane. **Ref** was used as reference. $\Phi_{OF\rightarrow CF}$ was calculated from the slope of the graph of absorbance (followed at the maximum wavelength of the closed-ring isomer) versus time at the beginning of the photochromic process, by comparing the values of the rate constant for the photocyclisation reaction of the reference compound with that for the molecule studied.[11] The conversions of compounds **I** and **II** under 313 nm radiation were determined by HPLC. The two forms can be easily separated by HPLC (Merck-Hitachi) on a silica column, eluting with a 96:4 cyclohexane/ethyl acetate mixture. The results are summarised in Table 2 (the values for **Ref** are taken from the literature[9]).

Table 2. Quantum yield and conversion of cyclisation under 313 nm radiation and quantum yield of cycloreversion under 546 nm radiation

Compound	Cyclisation[a] (313 nm) $\Phi_{OF\rightarrow CF}$	Conversion	Cycloreversion[b] (546 nm) $\Phi_{CF\rightarrow OF}$
I	0.18	0.24	0.44
II	0.19	0.24	0.46
Ref	0.35	0.43	0.35

[a] All photochromic reactions were performed in cyclohexane solution. [a] For all compounds the conversion of the cycloreversion reaction was 100 %.

The quantum yields of photocyclisation and photoreversion and the values of the conversions obtained at the photostationary state (PS) are very similar for both **I** and **II** (Table 2).

The lower quantum yield of photocyclisation for compounds **I** and **II**, as compared to the unsubstituted photochromic compound **Ref**, is clearly not influenced by the number of mesogenic groups attached to the central photochromic core. Similarly, a reduction in the quantum yield of photocyclisation has been previously reported for dibenzothienylethene derivatives having methoxy groups or cholesterol derivatives at the 6,6′-positions.[8]

The quantum yield of photoreversion for **I** and **II** is slightly larger than for the reference compound **Ref**, and the conversions obtained at the photostationary state for **I** and **II** were lower than measured for **Ref** (Table 2).

Liquid-Crystalline Properties

The results of investigations into the mesomorphic properties of the liquid crystalline intermediates using differential scanning calorimetry (DSC) and optical polarising microscopy are summarised in Table 3 (the values for **Ref 1**, **Ref 2** and **Ref 3** are taken from the literature[5b]).

Table 3. Transition temperatures as determined by DSC

Compound	Thermal transition temperatures/°C[a]
3	Cr 87.4 SmC 106.6 SmA 156.2 N 255.3 Iso
7	Cr 64.6 Iso
8	Cr 84.3 N 138.7 Iso
9	Cr 45.9 N 83.6 Iso
Ref 1	Cr 140.4 SmA 213.7 N 300 Iso
Ref 2	Cr 99.4 N 173.2 Iso
Ref 3	Cr 67.1 (SmA, 51.3) N 123.8 Iso

[a] Cr: crystalline, SmC: smectic C, SmA: smectic A, N: nematic, Iso: Isotropic liquid; ( ) denotes a monotropic transition

The liquid crystalline behaviour of **I** and **II** and their photostationary states $\mathbf{I_{PS}}$ and $\mathbf{II_{PS}}$ are given in Table 4.

Table 4. Transition temperatures as determined by DSC

Compound	Thermal transition temperatures/°C[a]
I	T_g −10.4 N 14.2 Iso
II	T_g 2.6 N 54.3 Iso
$\mathbf{I_{PS}}$	T_g −1.9 N 14.3 Iso
$\mathbf{II_{PS}}$	T_g 7.4 N 51.3 Iso

[a] T_g: glass transition, N: nematic, Iso: Isotropic liquid

For a discussion of the mesomorphic behaviour, comparison with the fully aromatic mesogens is instructive (Figure 6).[5b,5c] The linear molecule **Ref 1** has a clearing point of 300 °C, but the introduction of a lateral alkyl group (**Ref 2**) reduces the phase stability to 173 °C and results in the loss of all of the more highly ordered LC phases. The introduction of a siloxane group (**Ref 3**) reduces the clearing point to 123.8 °C, at which point a more highly ordered LC phase (SmC) reappears as a thermodynamically non-stable phase. Overall, the temperature at which the phases are stable is reduced by about 175 °C, and the melting temperature is reduced by about 70 °C.

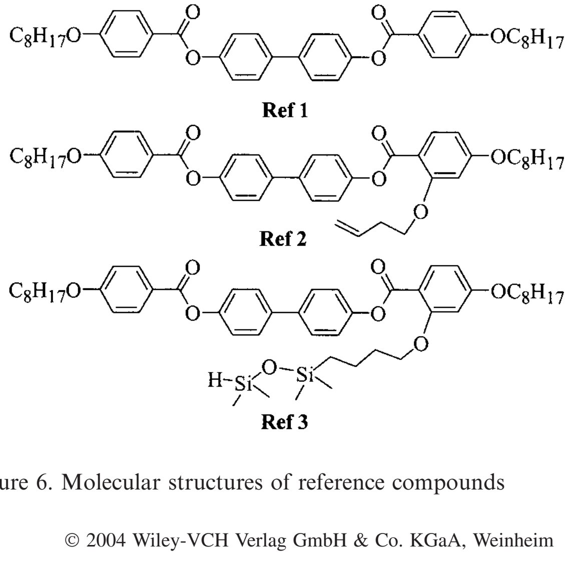


Figure 6. Molecular structures of reference compounds

The clearing point of compound **3** is 255.3 °C; at lower temperatures it shows a rich polymorphism of lamellar LC phases (SmC: molecules in layers, tilted with respect to the layer normal; SmA: layered structure, mesogens on average orthogonal to the layer normal). The introduction of a lateral alkyl group (**8**) lowers the transition temperature to 138.7 °C and the higher ordered LC phases are lost. Coupling to the tetramethyldisiloxane group (**9**) results in a further decrease in the transition temperature to 83.6 °C, which is approximately 55 °C lower than in **8**. The overall reduction in phase stability from **3** to **9** is about 170 °C and the reduction of the melting point (melting to glass transition temperature) is 40 °C. The liquid crystal phase range is lower than in the fully aromatic system. Overall, the lower transition temperatures are due to the lower transition temperatures of the materials containing the alicyclic group, reflecting the smaller conjugated π-system. The observed smaller reductions in the crystallisation temperatures are in line with the known tendency of alicyclic compounds to form crystals, in contrast to aromatic groups.

The importance of detailed molecular engineering in the design of these systems is highlighted when compounds **7** and **8** (which only differ in the position of the central cyclohexyl groups) are compared. **7** does not show any LC behaviour and melts at 64.6 °C to an isotropic liquid, because the conjugated π-electron system in **7** is close to the lateral connecting group. In **8**, the cyclohexyl ring separates the π-electron system from the connecting group, leading to a better electronic interaction between adjacent molecules and mesomorphic behaviour.

The fusion of one or two molecules of **9** to the photochromic core leads to the target materials **I** and **II**. In the case of **I**, which contains one mesogenic and one photochromic group, a nematic phase was observed, which clears at 14.2 °C and vitrifies at −10.4 °C. This results in a liquid crystal phase range of 24 °C at a temperature about 70 °C lower than is required for **9**. However, the overall impact on the mesomorphic behaviour is smaller than for **9** and **7**, because both the transition and vitrification temperatures have been modulated. Indeed, under photostationary conditions, the systems clear at the same temperature (14.3 °C), but the glass transition temperature is higher, which can be attributed to a decrease in flexibility of the photochromic core caused by the electrocyclisation. This is an indication of a good decoupling of LC properties and mesomorphic behaviour, enabling them to be addressed independently.

For the disubstituted system **II**, the adverse effect of the photochromic core on the mesomorphic behaviour is smaller; it clears from the nematic state at 54.3 °C, which is about 30 °C lower than in **9**. However, the system has a glass transition temperature of 2.6 °C, leading to a nematic phase range of more than 50 °C, spanning the ambient temperature range. The disubstituted system **II** at PS clears at a similar temperature (51.3 °C), whereas the glass transition temperature is slightly (4.8 °C) higher at 7.4 °C, reflecting the increased stiffness of the photochromic core, in line with the results for **I** and structurally related systems.[1g,8]

Conclusions

The use of a stable photochromic and functionalised diarylethene unit in conjunction with a mesomorphic group which does not absorb at the same wavelengths as the photochrome is the basis of this system. Crucial to suppressing the crystalline state and decoupling the electronic and mesomorphic properties is the nature of the linkage; in this work we have reported spacers containing both methylene and siloxane units.

In conclusion, the identification of the structural elements that are responsible for the LC properties and a convergent synthesis based on the modularisation of functional elements is an efficient method by which to investigate the structure-property relationships of photoswitchable room-temperature nematic liquid crystals. This approach can now be extended to related materials.

Experimental Section

General Remarks: Melting points (°C) were measured in capillary tubes on a Gallenkamp apparatus and are uncorrected. Transition temperatures were measured using a Mettler FP52 heating stage and FP5 control unit in conjunction with an Olympus BH2 polarizing microscope and were confirmed using differential scanning calorimetry (Perkin−Elmer DSC 7 with an indium standard). ^{1}H and ^{13}C NMR spectra were recorded on a JEOL Lambda 400 spectrometer (at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR), using tetramethylsilane as an internal standard. UV/Visible spectra were recorded on a Cary50−diode array spectrophotometer. Elemental analyses of products were carried out using a Fisons EA 1108 CHN analyzer. All reactions were monitored by thin-layer chromatography carried out on 0.2 nm Merck silica gel plates (60F-254). Column chromatography was performed on silica gel (Fluorochem 35−70u 60A). The purity of all final compounds was checked (and found to be > 99.5 %) by HPLC analysis using a Merck-Hitachi system fitted with a Rainin Dynamax Microsorb 5μm silica column (25 cm long, 4.6 mm internal diameter). The identification of previously reported compounds was made by comparision of their ^{1}H NMR spectra and melting points with the literature data.

Chemicals: Solvents (purchased from Fisher Chemicals) were dried over molecular sieves and used without further purification. Octyloxybenzoic acid and 4-octyloxy-2-(pent-4-en-1-yloxy)benzoic acid were synthesised according to the literature procedure.[7]

Photochemical Measurements: Absorption spectra were performed in spectrometric grade cyclohexane at 25 °C (±0.2 °C). The cell (optical pathlength 10 mm) was placed in a thermostatted copper block inside the sample chamber of a Cary 50-diode array spectrophotometer. An Oriel 250 W high pressure Hg/Xe lamp was used for irradiation. Mercury lines of 313 and 546 nm were isolated by passing through a monochromator (Oriel).

***trans*-4-(4-Hydroxycyclohexyl)phenol (2):** 4-(4-Hydroxyphenyl)cyclohexanone (**1**) (10 g, 52 mmol) was dissolved in methanol (300 mL). $NaBH_4$ (2.13 g, 58 mmol) was added at room temperature in small portions over 2 hours. After stirring overnight, the mixture was cooled in an ice-water bath, and then quenched with aqueous HCl (10 %). The solution was extracted several times with ethyl acetate. The resulting organic phase was washed with water, dried over magnesium sulfate, and then concentrated under reduced pressure. The residue was recrystallised from cold ethanol to give pure white crystals of **2** (8.7 g, 87 %). M.p.: 213−215 °C (ref.[6] 213−215 °C). ^{1}H NMR ([D$_6$]DMSO, 400 MHz): δ = 1.20−1.45 (m, 4 H, CH_2), 1.69 (d, J = 12.4 Hz, 2 H, CH_2), 1.86 (d, J = 12.4 Hz, 2 H, CH_2), 2.29 (m, 1 H, H_a), 3.41 (m, 1 H, H_b), 4.54 (s, 1 H, OH), 6.64 (d, J = 8.6 Hz, 2 H, ArH), 6.96 (d, J = 8.6 Hz, 2 H, ArH), 9.12 (s, 1 H, ArOH) ppm.

Compounds 3, 4 and 5: Dry CH_2Cl_2 (400 mL) was added to a mixture of **2** (10 g, 52 mmol) and 4-octyloxybenzoic acid (13.02 g, 52 mmol), followed by DMAP (0.66 g, 5.2 mmol) and diisopropylcarbodiimide (6.35 g, 52 mmol). After stirring overnight, the solvent was distilled off and the residue purified by column chromatography on silica gel (eluent: CH_2Cl_2) to give pure **3**, **4**, and **5** as white solids.

Compound 3: Yield: 8 %. Transition temperatures (°C): Cr 87.4 SmC 106.6 SmA 156.2 N 255.3 Iso. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.82 (m, 6 H, CH_3), 1.10−2.17 (m, 32 H, CH_2), 2.55 (m, 1 H, H_a), 3.96 (m, 4 H, OCH_2), 4.94 (m, 1 H, H_b), 6.84 (m, 2 H, ArH), 6.90 (m, 2 H, ArH), 7.07 (m, 2 H, ArH), 7.20 (m, 2 H, ArH), 7.94 (m, 2 H, ArH), 8.07 (m, 2 H, ArH) ppm. $C_{42}H_{56}O_6$ (656.89): calcd. C 76.79, H 8.59; found C 76.70, H 8.64.

Compound 4: Yield: 44 %. M.p.: 148−149 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.88 (m, 3 H, CH_3), 1.10−1.82 (m, 16 H, CH_2), 1.93 (2 H, d, J = 12.8 Hz, CH_2), 2.11 (2 H, d, J = 11.7 Hz, CH_2), 2.51 (m, 1 H, Ha), 3.68 (m, 1 H, Hb), 4.02 (t, J = 6.6 Hz, 2 H, OCH_2), 6.95 (m, 2 H, ArH), 7.11 (m, 2 H, ArH), 7.25 (m, 2 H, ArH), 8.13 (m, 2 H, ArH) ppm. $C_{27}H_{36}O_4$ (424.57): calcd. C 76.38, H 8.55; found C 76.25, H 8.62.

Compound 5: Yield: 22 %. M.p.: 105.9 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.88 (m, 3 H, CH_3), 1.10−1.90 (m, 21 H, CH_2), 2.53 (m, 1 H, H_a), 4.02 (t, J = 6.4 Hz, 2 H, OCH_2), 4.11 (m, 1 H, H_b), 6.93 (m, 2 H, ArH), 7.10 (m, 2 H, ArH), 7.25 (m, 2 H, ArH), 8.12 (m, 2 H, ArH) ppm. $C_{27}H_{36}O_4$ (424.57): calcd. C 76.38, H 8.55; found C 76.20, H 8.64.

Compound 7: Dry CH_2Cl_2 (60 mL) was added to a mixture of **5** (3.50 g, 8.24 mmol) and 4-octyloxy-2-(pent-4-enyloxy)benzoic acid **6** (2.75 g, 8.24 mmol), followed by DMAP (0.1 g, 0.83 mmol) and diisopropylcarbodiimide (1.0 g, 8.24 mmol). After stirring overnight, the solvent was distilled off and then the resulting products were purified by column chromatography on silica gel (eluent: CH_2Cl_2) to give pure **7** as white solid (3.28 g, 35 %). M.p.: 64.6 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.88 (m, 6 H, CH_3), 1.10−2.25 (m, 34 H, CH_2), 2.62 (m, 1 H, H_a), 4.02 (m, 6 H, OCH_2), 4.97 (m, 2 H, $CH_2{=}CH$), 5.30 (m, 1 H, H_b), 5.80 (m, 1 H, $CH{=}CH_2$), 6.47 (m, 2 H, ArH), 6.96 (d, J = 8.6 Hz, 2 H, ArH), 7.12 (d, J = 8.6 Hz, 2 H, ArH), 7.28 (m, 2 H, ArH), 7.87 (d, J = 8.6 Hz, 1 H, ArH), 8.12 (d, J = 8.6 Hz, 2 H, ArH) ppm. $C_{46}H_{62}O_7$ (726.98): calcd. C 76.00, H 8.60; found C 75.89, H 8.68.

Compound 8: Dry CH_2Cl_2 (100 mL) was added to a mixture of **4** (5.23 g, 12 mmol) and **6** (2.75 g, 12 mmol), followed by DMAP (0.17 g, 1.4 mmol) and diisopropylcarbodiimide (1.46 g, 12 mmol). After stirring overnight, the solvent was distilled off and the residue purified by column chromatography on silica gel (eluent: CH_2Cl_2) to give pure **8** as a white solid (1.91 g, 22 %). Transition temperatures (°C): Cr 84.3 N 138.7 Iso. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.88 (m, 6 H, CH_3), 1.10−2.33 (m, 34 H, CH_2), 2.57 (m, 1 H, H_a), 4.01 (m, 6 H, OCH_2), 5.01 (m, 3 H, $CH_2{=}CH$ + H_b); 5.87 (m, 1 H, $CH{=}CH_2$), 6.45 (m, 2 H, ArH), 6.96 (d, J = 8.6 Hz, 2 H, ArH), 7.12 (d, J = 8.6 Hz, 2 H, ArH), 7.25 (m, 2 H, ArH); 7.82 (d, J =

8.6 Hz, 1 H, ArH), 8.12 (d, *J* = 8.6 Hz, 2 H, ArH) ppm. $C_{46}H_{62}O_7$ (726.98): calcd. C 76.00, H 8.60; found C 76.08, H 8.54.

Compound 9: 1,1,3,3,5,5-Hexamethyltrisiloxane (3.26 g, 24.8 mmol) was added to a solution of **8** (1.8 g, 2.48 mmol) in anhydrous toluene (200 mL). Dry air was bubbled through the solution for 2 min and a solution of Karstedt's catalyst (5 % Pt solution in xylene, 32 μL) was added. After stirring the solution at room temperature overnight with the exclusion of moisture, the solvent and the excess of 1,1,3,3,5,5-hexamethyltrisiloxane were distilled off. The crude product was purified by column chromatography on silica gel (eluant: pentane/dichloromethane, 80:20) to give pure **9** as a white solid (1.64 g, 77 %). Transition temperature (°C): Cryst 45.9 N 83.6 Iso. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.01 (s, 6 H, $SiCH_3$), 0.08 (d, *J* = 2.8 Hz, 6 H, $SiCH_3$), 0.53 (m, 2 H, $SiCH_2$), 0.81 (m, 6 H, CH_3), 1.10−1.80 (m, 32 H, CH_2), 1.93 (m, 2 H, CH_2), 2.18 (m, 2 H, CH_2), 2.51 (m, 1 H, H_a), 3.96 (m, 6 H, OCH_2), 4.60 (m, 1 H, SiH), 4.94 (m, 1 H, H_b); 6.40 (m, 2 H, ArH), 6.89 (d, *J* = 8.6 Hz, 2 H, ArH),), 7.06 (d, *J* = 8.6 Hz, 2 H, ArH), 7.19 (m, 2 H, ArH); 7.76 (d, *J* = 8.6 Hz, 1 H, ArH), 8.07 (d, *J* = 8.6 Hz, 2 H, ArH) ppm. $C_{50}H_{76}O_8Si_2$ (861.30): calcd. C 69.72, H 8.89; found C69.80, H 8.86.

Compound 11: K_2CO_3 (0.20 g, 1.41 mmol) and 4-bromobut-1-ene (0.42 g, 3.10 mmol) were added to a solution of **10**[1g,8] (0.72 g, 1.41 mmol) in dry butanone (14 mL). The resulting mixture was refluxed for 24 h and then allowed to cool to room temperature. The reaction mixture was filtered and the butanone was distilled off under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: CH_2Cl_2) to give pure **11** as a glassy material (0.74 g, 84 %) as a mixture of parallel and antiparallel conformers (p:ap, 36:64). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.05 (s, 3.84 H, ap CH_3), 2.33 (s, 2.16 H, p CH_3), 2.47 (m, 4 H, CH_2), 3.88 (s, 2.16 H, p OCH_3), 3.95 (s, 3.84 H, ap OCH_3), 5.07 (m, 4 H, $CH_2{=}CH$), 5.81 (m, 1 H, $CH{=}CH_2$), 6.70 (dd, *J* = 8.9 and 2.2 Hz, 0.72 H, p H-5), 6.90 (dd, *J* = 8.8 and 2.2 Hz, 1.28 H, ap H-5), 6.97 (d, *J* = 2.2 Hz, 0.72 H, p H-7), 7.06 (d, *J* = 2.2 Hz, 1.28 H, ap H-7), 7.31 (d, *J* = 8.9 Hz, 0.72 H, p H-4), 7.44 (d, *J* = 8.9 Hz, 1.28 H, ap H-4) ppm. $C_{31}H_{26}F_6O_2S_2$ (608.66): calcd. C 61.17, H 4.31; found C 61.35, H 4.25.

Compounds I and II: Dry air was bubbled through a solution of **11** (0.2 g, 0.33 mmol) in anhydrous toluene (5 mL) for 2 min. A solution of Karstedt's catalyst (5 % Pt solution in xylene, 5 μL) was added, the solution stirred at room temperature for 5 min, and a solution of **9** (0.56 g, 0.66 mmol) in anhydrous toluene (5 mL) added. After stirring overnight, the toluene was distilled off under vacuum. The crude product was purified by column chromatography on silica gel (eluant: pentane/dichloromethane, 80:20) to give pure **I** and **II**.

Monomer (I): Yield: 7 %, as a mixture of parallel and antiparallel conformers (p:ap, 33:67). Transition temperatures (°C): T_g −10.4 N 14.2 Iso. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.01 (s, 12 H, $SiCH_3$), 0.51 (m, 4 H, $SiCH_2$), 0.83 (m, 6 H, CH_3),1.10−1.85 (m, 32 H, CH_2), 1.92 (m, 2 H, CH_2), 2.05 (s, 4 H, ap CH_3), 2.18 (m, 2 H, CH_2), 2.34 (s, 2 H, p CH_3), 2.51 (m, 1 H, H_a), 3.96 (m, 10 H, OCH_2), 4.96 (m, 3 H, $CH_2{=}CH$ + H_b); 5.85 (m, 1 H, $CH{=}CH_2$), 6.40 (m, 2 H,, ArH); 6.70 (dd, *J* = 8.9 and 2.2 Hz, 0.67 H, p H-5), 6.89 (m, 3.33 H, 2 × ArH + 1.33 ap H-5), 6.97 (d, *J* = 2.2, 0.67 H, p H-7), 7.06 (m, 3.33 H, 2 ArH + 1.33 ap H-7), 7.19 (m, 2 H, ArH), 7.31 (d, *J* = 8.9 Hz, 0.67 H, p H-4), 7.44 (d, *J* = 8.9 Hz, 1.33 H, ap H-4), 7.77 (d, *J* = 8.6 Hz, 1 H, ArH), 8.07 (d, *J* = 8.6 Hz, 2 H, ArH) ppm. UV/Vis (cyclohexane): λ_{max} (ε) = 258 (57600). $C_{81}H_{102}F_6O_9S_2Si_2$ (1469.96): calcd. C 66.18, H 6.99; found C 66.25, H 6.92.

Dimer (II): Yield: 71 %, as a mixture of parallel and antiparallel conformers (p:ap, 33:67). Transition temperatures (°C): T_g 2.6 N 54.3 Iso. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.01 (s, 24 H, $SiCH_3$), 0.51 (m, 8 H, $SiCH_2$), 0.82 (m, 12 H, CH_3), 1.10−1.85 (m, 64 H, CH_2), 1.91 (m, 4 H, CH_2), 2.05 (s, 3.98 H, ap CH_3), 2.18 (m, 4 H, CH_2), 2.34 (s, 2.02 H, p CH_3), 2.51 (m, 1 H, H_a), 3.91 (m, 16 H, OCH_2), 4.96 (m, 1 H, H_b); 6.40 (m, 4 H, ArH), 6.73 (dd, *J* = 8.9 and 2.2 Hz, 0.67 H, p H-5), 6.89 (m, 5.33 H, 4 × ArH + 1.33 ap H-5), 6.97 (0.67 H, d, *J* = 2.2 Hz, p H-7), 7.06 (5.33 H, m, 4 ArH + 1.33 ap H-7), 7.19 (m, 4 H, ArH), 7.31 (0.67 H, d, *J* = 8.9 Hz, p H-4), 7.44 (1.33 H, d, *J* = 8.9 Hz, ap H-4), 7.77 (d, *J* = 8.6 Hz, 2 H, ArH), 8.07 (d, *J* = 8.6 Hz, 4 H, ArH) ppm. UV/Vis (cyclohexane): λ_{max} (ε) = 258 (79000). $C_{131}H_{176}F_6O_{18}S_2Si_4$ (2331.27): calcd. C 67.49, H 7.70; found C 67.40, H 7.72.

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