Modulation of the Absorption, Fluorescence, and Liquid-Crystal Properties of Functionalised Diarylethene Derivatives

Michel Frigoli and Georg H. Mehl*[a]

Abstract: Systematic variation of the molecular symmetry in a photochromic system based on a 1,2-bis(2-methylbenzo[*b*]thiophen-3-yl)hexafluorocyclopentene group, connected by decyl spacers to two cyanobiphenyl groups as mesogens, allows for a systematic investigation of the correlations between molecular shape and symmetry, electronic effects, photochromic conversion and liquid-crystalline properties.

Keywords: fluorescence · liquid crystals · molecular switches · photochromism

Introduction

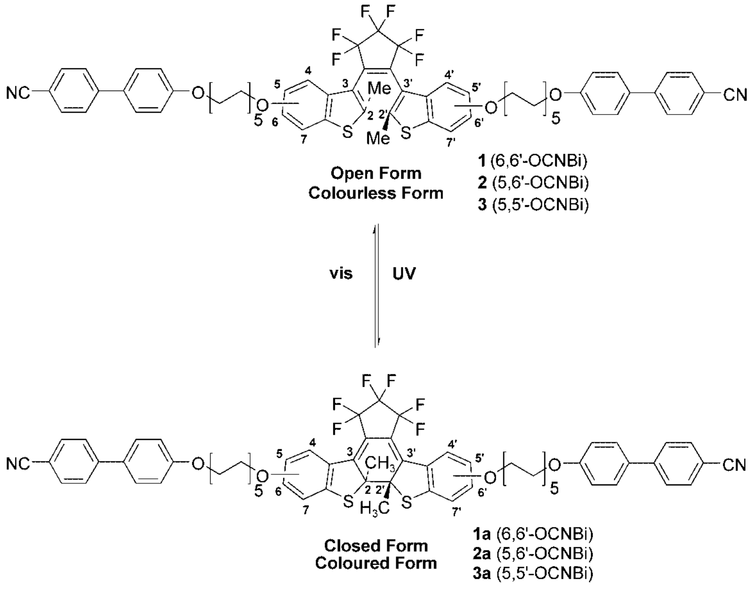

Figure 1. Photochromic liquid crystal systems.

The concept of switching molecular or supramolecular systems reversibly from one state to another by using light, in which the states have significantly different properties, is widespread in biological systems and has been in the focus of materials research for many years.[1,2] Such synthetic systems are promising as high-density data-storage systems, sensors, photonic switches and molecular logic gates. The concept of optically addressable molecules promises miniaturisation to the molecular scale and potentially of optical computing on that level. In the area of liquid crystal (LC) research, concerned with information transmission, the power of light modulation was recognised early on, and systems based on azo groups, spyropyranes, spirooxazines or, more recently, fulgides have been investigated for data storage or for the alignment of LCs on surfaces (command surfaces).[2g,3–5] However, relaxation phenomena, the colouring of both states and thermal stability have been the main concerns in such systems. Thus, progress in research on functionalised diarylethenes, some of which are thermally very stable and which can be mixed into LC systems or can be functionalised to be liquid-crystalline, is very interesting. For such materials the correlation between molecular structure, electronic properties and mesomorphic behaviour remains to be investigated.

Our approach for this investigation is modular, making use of a photochromic core, a 1,2-bis(2-methylbenzo[*b*]thiophen-3-yl)hexafluorocyclopentene system which is connected to two cyanobiphenyl groups as mesogens via spacers of ten methylene groups, as shown in Figure 1. The position of the ether linking group to the mesogens was varied from 6,6′-substitution in **1**, 5,6′-functionalisation in **2** to a 5,5′-substitution of the methylbenzothiopene cores in **3**. This allows for a systematic investigation of the influence of molecular shape and electronic properties on the absorption behaviour

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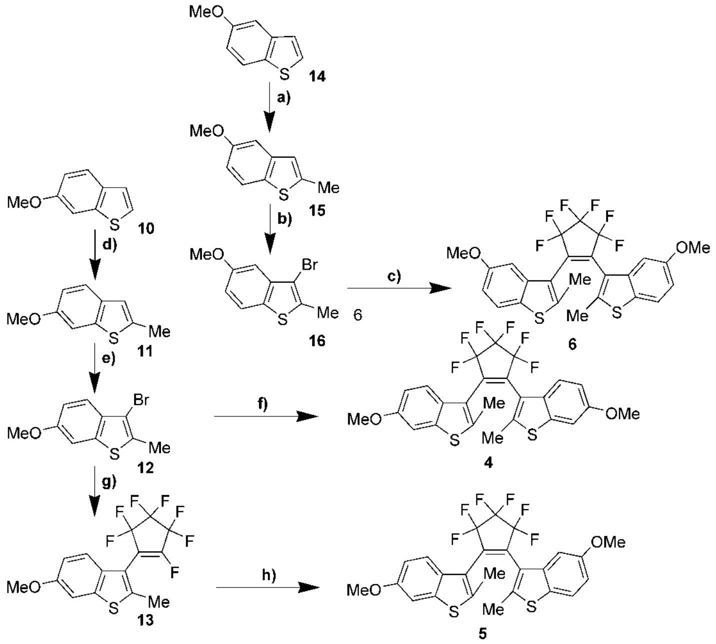
and the photochromic properties, as well as the correlation of these properties with the mesomorphic behaviour of the systems.

Results and Discussion

Synthesis: The preparation of photochromic liquid crystal systems **1**–**3** requires the synthesis of photochromic compounds which are suitably functionalised. The synthetic pathway to these new compounds is outlined in Schemes 1 and 2.

The arylhexafluorocyclopentenes are usually obtained by a reaction involving nucleophilic attack of an aryllithium on octafluorocyclopentene, followed by elimination of fluoro groups.[2b] Direct substitution of 1,2-bis(2-methylbenzo[*b*]thiopen-3-yl)hexafluorocyclopentene allows only the 6-position of the photochromic core to be targeted.[6] Thus, in order to obtain **4**–**6**, the starting material must be substituted by a methoxyl group.



Scheme 1. Reagents and conditions: a) *n*BuLi, MeI, THF, 92 %; b) Br_2, $CHCl_3$, 45 %; c) *n*BuLi, 0.5 equiv octafluorocyclopentene, THF, 62 %; d) *n*BuLi, MeI, THF, 97 %; e) Br_2, $CHCl_3$, 82 %; f) *n*BuLi, 0.5 equiv octafluorocyclopentene, THF, 68 %; g) *n*BuLi, 3 equiv octafluorocyclopentene, THF, 68 %; h) lithiated derivative of **16**, THF, 65 %.

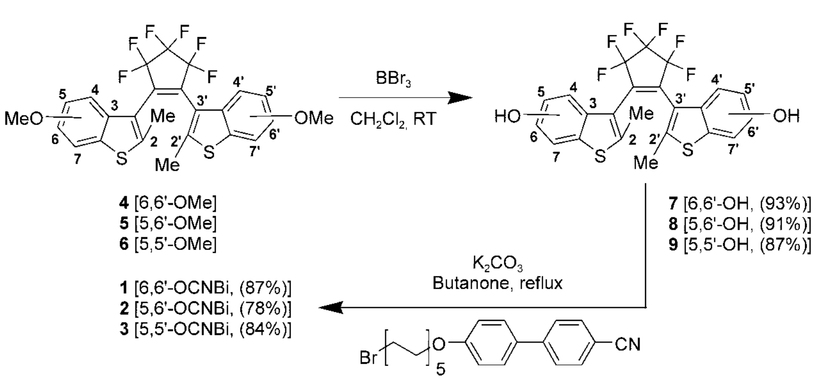
6-Methoxybenzothiophene (**10**) and 5-methoxybenzothiophene (**14**) were prepared according to procedures described in the literature.[7] The symmetrical photochromes **4** and **6** were obtained in three steps from the corresponding methoxybenzothiophenes **10** and **14**, which were methylated in the 2-position by using *n*BuLi at −40 °C followed by addition of methyliodide at −78 °C to afford **11** and **15** in yields of 92 and 96 %. Bromination at the 3-position of **11** and **15** with bromine in $CHCl_3$ at room temperature gave **12** and **16** in 82 and 47 % yield, respectively.

The formation of a not yet identified byproduct in the bromination of **15** is responsible for the moderate yield. Treatment of **12** and **16** in THF with *n*BuLi at −78 °C followed by the addition at the same temperature of a semi-equivalent amount of octafluorocyclopentene yielded photochromes **4** and **6** (62 and 68 %, respectively). In this reaction, the product of monocondensation, which is useful for the investigation of asymmetric photochromes, can be obtained selectively by using an excess of octafluorocyclopentene.

Compound **13** is obtained in 82 % yield from **12** by using *n*BuLi at −78 °C followed by addition of three equivalents of octafluorocyclopentene. Condensation of the lithiated derivative of **16** with **13** at −78 °C afforded **5** in 56 % yield.

The synthesis of the photochromic liquid crystal systems is achieved in two steps from **4**–**6** (Scheme 2). Deprotection of the methoxyl group with boron tribromide in CH_2Cl_2 at room temperature resulted in **7**–**9** in yields higher than 80 %. An etherification reaction between **7**–**9** and mesogenic groups in butanone at reflux with K_2CO_3 afforded the targeted molecules **1**–**3** in good yield.

Photochromic properties: All synthesised diarylethenes underwent reversible photochromic reactions in cyclohexane with alternating light at wavelengths of 313 (UV) and 546 nm (visible) with retention of isosbestic points. The colour of the solutions changed from colourless for all compounds to red (**1a**, **4a**), red-purple (**2a**, **5a**) or purple (**3a**, **6a**). The photochromic behaviour of the new compounds was compared with that of the unsubstituted parent compound 1,2-bis(2-methyl-1-benzothiophen-3-yl)hexafluorocyclopentene, denoted **Ref.**[8]



Scheme 2. Synthesis of the photochromic liquid-crystalline systems **1**–**3**.

The effect of the position of methoxyl groups on the benzothiophene part of the photoactive core on the absorption properties was examined. Figures 2 and 3 show absorption spectra of the open-ring isomers **4**, **5**, and **6** and the corresponding closed-ring isomers **4a**, **5a**, and **6a**. The absorption spectra of the closed forms were calculated from the ab-

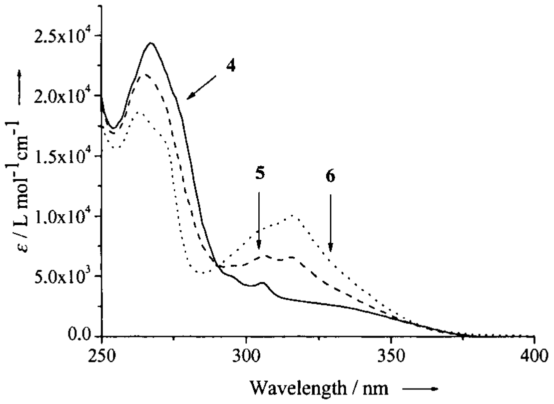


Figure 2. Absorption spectra of the open-ring isomers **4**–**6** in cyclohexane.

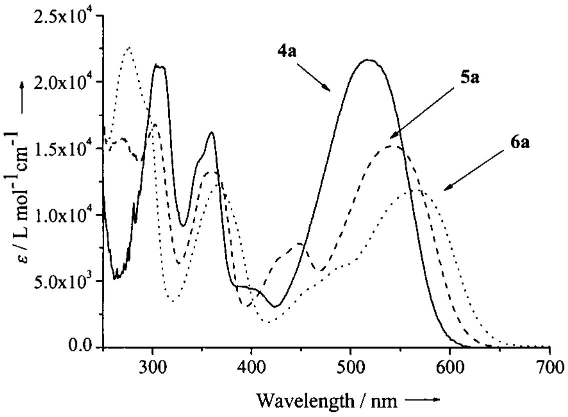


Figure 3. Absorption spectra of the closed-ring isomers **4a**–**6a** in cyclohexane.

sorption spectra obtained at the photostationary state (PS) by using Equation (1) for the absorbance of a mixture of two compounds at any wavelength.[9]

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

In Equation (1) $[\mathrm{A}]_{\mathrm{PS}}$ is the absorption obtained at the PS state, $[\mathrm{A}]_{\mathrm{OF}}$ the absorption of the open form, $[\mathrm{A}]_{\mathrm{CF}}$ the absorption of the closed form, and Cv the conversion from open- to closed-ring isomer; $[\mathrm{A}]_{\mathrm{PS}}$ and $[\mathrm{A}]_{\mathrm{OF}}$ can be determined by UV spectroscopy, and Cv can be calculated from HPLC data by integration of the peaks for the open and closed forms.

Variation of the position of the methoxyl groups leads to changes in the absorption coefficient ε at the absorption maximum of the open forms in the far and near UV without modifying much the position of the absorption maximum in the UV spectrum (Figure 2). At the irradiation wavelength (313 nm), the ε value of compound **6** (5,5′-OMe) is approximately three times higher than those of **4** (6,6′-OMe) and **Ref.**[8] The ε value of compound **5** (5,6′-OMe) lies between those obtained for **4** and **6**. Structurally related dithienylethene derivatives with methoxyl groups at the reaction centres were reported to exhibit a decrease in the absorption coefficient.[10]

The absorption maxima and absorption coefficients of the closed forms depend on the positions of the methoxyl groups. As can be seen from the spectra, **6a** absorbs at the highest wavelength (569 nm) with the lowest ε value (11300 L mol^{-1}cm^{-1}), while **4a** absorbs at the lowest wavelength (520 nm) with the highest ε value (20400 L mol^{-1}cm^{-1}). The absorption maximum and ε value of **5** (542 nm, 15000 L mol^{-1}cm^{-1}) are intermediate between those of **4** and **6**. In this series, the ε values decrease with shifting of the absorption maxima to longer wavelengths. This suggests that, in line with classical concepts of the relative positions of maxima in the absorption spectra, the energy difference between the ground state and the first excited state for **4a** is higher than for the other systems. This could be due to electronic or steric effects (the dipoles of the perfluoro and ether groups point in different directions in **4a**). In the absence of reported systematic MO calculations on substituted benzothiophene-based diarylethene systems, any explanation must be very tentative. However, Pariser–Parr–Pople molecular orbital calculations for linear azo dyes, in which the substitution pattern was varied systematically, allowed us to relate the values of the extinction coefficients to the inverse mean absorption wavelength $1/\lambda$.[11] A similar effect might occur for the closed forms of the substituted diarylethenes.

Differences are noticeable between the absorption spectra of the open- and closed-ring isomers of compounds **1** and **4** (Figure 4). The presence of two cyanobiphenyl groups in **1** leads to a significant increase in the absorption coefficient ε of the open-ring isomer compared with parent molecule **4**. At the irradiation wavelength (313 nm), the ε value of **4** is approximately eight times higher than that of **1**. Indeed, the absorption spectrum of **1** corresponds roughly to the sum of the spectra of the photochromic core and the cyanobiphenyl groups; the alkyl spacer that connects these two entities is a nonconjugating junction. Compounds **1a** and **4a** have the same absorption properties in the wavelength interval between 332 and 650 nm at which cyanobiphenyl groups do not absorb. The electronic effects induced by methoxyl or decanoxyl groups on the photochromic core are broadly the same. The absorption coefficient of the closed-ring isomer

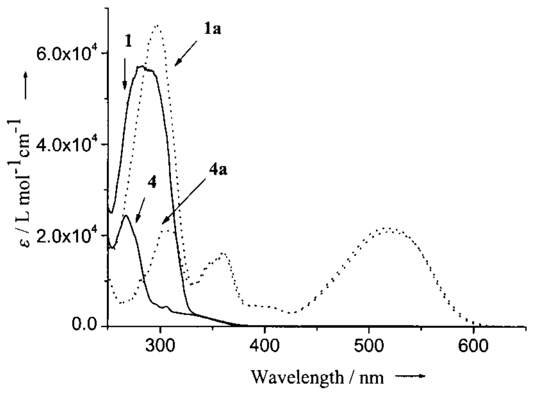


Figure 4. Absorption spectra of open-ring isomers **1** and **4** and closed-ring isomers **1a** and **4a**.

4a is approximately seven times higher than that of the open-ring isomer **4**. This explains in part the low conversion obtained for **4** (see Table 3) at the photostationary state with irradiation at 313 nm. At low concentration, the percentage conversion from the open-ring to the closed-ring isomers at the photostationary state is defined by Equation (2) in which ε_{OF} and ε_{CF} are the absorption coefficients of the open- and closed-ring isomers at the irradiation wavelengths.

Table 1. Absorption maxima and coefficients of the open-ring isomers **1**–**6**.[a]

	λ_{max} [nm] (ε [mol^{-1}Lcm^{-1}])		λ_{max} [nm] (ε [mol^{-1}Lcm^{-1}])
1	280 (57000)	**4**	267 (23800), 305 (4500)
2	292 (63000)	**5**	265 (21300), 306 (6600), 316 (6600)
3	292 (58000)	**6**	262 (15000), 307 (8400), 316 (9000)
		Ref	258 (21000), 290 (6900), 299 (7400)

[a] All absorption spectra were recorded in cyclohexane.

$$\text{Conversion} = \varepsilon_{OF}\Phi_{OF\rightarrow CF}/(\varepsilon_{OF}\Phi_{OF\rightarrow CF} + \varepsilon_{CF}\Phi_{CF\rightarrow OF}) \qquad (2)$$

The ε_{OF} and ε_{CF} can be determined by UV spectroscopy, and $\Phi_{OF\rightarrow CF}$ calculated from the slope of absorbance (monitored at the maximum wavelength of the closed-ring isomer) versus time at the beginning of the photochromic process when the photoreversion reaction can be neglected, by comparing the values of rate constant of photocyclisation reaction of the reference compound and of the molecule studied.[12] When the ratio of the quantum yields $\varepsilon_{OF}\Phi_{OF\rightarrow CF}/\varepsilon_{CF}\Phi_{CF\rightarrow OF}$ is low, conversion is weak. Similar observations are valid for the pairs **2** and **5** and **3** and **6**.

Absorption maxima and coefficients of the open- and closed-ring isomers are summarised in Tables 1 and 2.

Table 2. Absorption maxima and coefficients calculated for the closed-ring isomers **1a**–**6a**.

	λ_{max} [nm] (ε [mol^{-1}Lcm^{-1}])
1a	294 (66000), 360 (15600), 520 (20400)
2a	292 (72000), 365 (13200), 542 (15300)
3a	292 (69000), 368 (11000), 569 (10500)
4a	310 (21000), 360 (15000), 520 (21300)
5a	268 (15300), 301 (16200), 366 (12900), 542 (15000)
6a	278 (22500), 366 (11600), 569 (11300)
Ref[a]	517 (9100)

[a] Taken from ref. [8].

Quantum yield and conversion measurements: The quantum yield of cyclisation and photocycloreversion of **1**–**6** were measured in cyclohexane; **Ref** was used as reference. The conversions of **1**–**6** on irradiation with 313 nm light were determined by HPLC. The two forms can be easily separated (see Experimental Section for conditions). The results are summarised in Table 3.

A decrease in the quantum yield of photocyclisation for all the compounds **1**–**6** was observed. This is not influenced by the position of the methoxyl groups on the benzothiophene part of the photochromic core, when the results for these materials are compared with the value obtained for the unsubstituted photochromic compound **Ref** (0.35). The quantum yields of photocyclisation for **4**–**6** were found to be in the range of 0.14–0.23. For structurally related dithienylethene derivatives in which the methoxyl groups are at the reaction centers a reduction in the quantum yield of photocyclisation has been reported, too.[10]

Table 3. Quantum yield and conversion of cyclisation with 313 nm light and quantum yield of cycloreversion with 546 nm light.

Compounds	Cyclisation[a]		Cycloreversion[b]
	$\Phi_{OF\rightarrow CF}$	Conversion	$\Phi_{CF\rightarrow OF}$
1	0.19	0.56	0.41
2	0.12	0.63	0.19
3	0.05	0.64	0.16
4	0.20	0.22	0.48
5	0.14	0.48	0.21
6	0.23	0.68	0.17
Ref[c]	0.35	0.43	0.35

[a] All photochromic reactions were performed in cyclohexane solution. [b] For all compounds the conversion of the cycloreversion reaction was 1. [c] Taken from ref. [8].

The quantum yield of the photoreversion with irradiation at 546 nm depends on the relative positions of the methoxyl groups in the molecule. When the two methoxyl groups are in 6,6′-positions (**4**), the quantum yield of photoreversion increases slightly relative to **Ref**. By contrast, when the two methoxyl groups are in the 5,6′- (**5**) or 5,5′-positions (**6**), the quantum yield for photoreversion decreases to 40% for **5** and 52% for **6**.

Compounds **1** (0.19) and **2** (0.12) have quantum yields for cyclisation similar to that of parent compounds **4** (0.20) and **5** (0.14). The quantum yield of **3** (0.05) is 4.6 times lower than that of parent molecule **6** (0.23). By contrast, no dissimilarity of the values of the quantum yields of cycloreversion is observed for each group of molecules.

The conversions obtained at the photostationary state were also dependent on the position of the methoxyl groups in the molecule. Compound **6** (5,5′-OMe) has the highest conversion (0.68), while **4** (6,6′-OMe) has the lowest (0.22). An intermediate value (0.48) was obtained for **5** (5,6′-OMe), which is very close to that obtained for **Ref** (0.43). For **1**, **2** and **3**, conversions were in the range of 0.56–0.64. The conversions of **1** (0.56) and **2** (0.63) are higher than those of the parent molecules **4** (0.22) and **5** (0.48). This increase is directly correlated with the absorption properties of the open and closed forms at the wavelength of irradiation in accordance with Equation (2). Indeed, at 313 nm, the ratio between the absorption coefficient of the closed-ring isomer **4a** and that of the open-ring isomer **4** is 7:1, and this ratio is 2:1 for **5**. In contrast, for **1** and **2**, the absorption coefficients of the two forms are roughly the same, and this leads to an enhanced conversion compared to the parent compounds. Indeed, in the systems **1**–**3**, active participation of the cyanobiphenyl groups (donors) in the photochromism takes place, as can be deduced from the results of fluorescence studies given in Table 4; in other words, the photochromic process is assisted by a fluoresecence resonance energy transfer (FRET) or Förster-type effect.

Table 4. Relative fluorescence and emission quantum yield (Φ_{em}) for the open forms **1**–**3** and for the systems at the PS state.

Compound	Fluorescence wavelength [nm]	Fluorescence intensity[a]	Φ_{em}[b]
1	338	530	0.019
$\mathbf{1_{PS}}$	338	340	9.2×10^{-3}
2	338	405	0.011
$\mathbf{2_{PS}}$	338	300	7.5×10^{-3}
3	338	390	0.011
$\mathbf{3_{PS}}$	338	300	9.1×10^{-3}

[a] At 313 nm; arbitrary units: 3.33×0^{-5} mol L^{-1} solutions of compounds in cyclohexane. [b] At 313 nm; all compound are referenced to 4-cyano-4'-butyloxybiphenyl ($\Phi_{em}=0.74$).[13].

All compounds **1**–**3** exhibit fluorescence properties which are attributed to the presence of cyanobiphenyl groups. This is supported by the observation that parent compounds **4**–**6** display only very weak fluorescence properties with a fluorescence maximum wavelength of 440 nm when exited at 313 nm. Furthermore, the fluorescence spectra of all compounds **4**–**6** are similar to that obtained for the cyanobiphenyl group, with a fluorescence maximum at a wavelength of 338 nm.

Even though **1**–**3** have two cyanobiphenyl groups which are strong fluorophores ($\Phi_{em}=0.74$), the quantum yields of fluorescence observed are generally low. This indicates that an energy transfer from the cyanobiphenyl groups to the open forms takes place when the molecules are exited at 313 nm. This phenomenon is also observed when the molecules are exited in the region in which the cyanobiphenyl groups absorb. At the photostationary state, the systems display a lower intensity of emission fluorescence than is obtained for the corresponding open forms (Figure 5). This indicates that the closed forms can also act as acceptors. These conclusions are in line with earlier results for a diheteroarylethene (acceptor) coupled via an alkyl spacer to Lucifer Yellow (donor).[14]

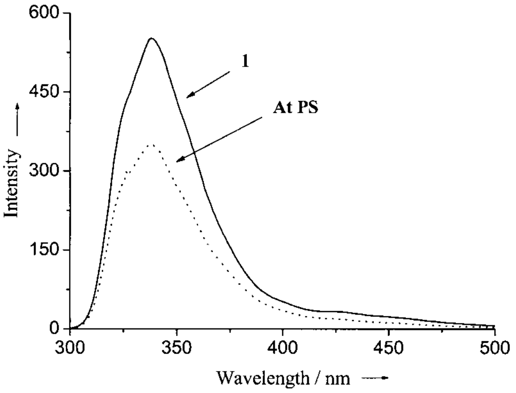


Figure 5. Emission fluorescence spectra of open-ring isomer **1** and at PS state

Liquid-crystalline properties: The results of the investigation of the mesomorphic properties of the open-ring isomers **1**–**3** and at the photostationary state (irradiation wavelength 313 nm) $\mathbf{1_{PS}}$–$\mathbf{3_{PS}}$ by DSC and optical polarizing microscopy are summarised in Table 5.

Table 5. Transition temperatures [°C] by DSC.

	Thermal transition[a]		Thermal transition[a]
1	Cr 33.3 SmC 74.5 N 78.5 Iso	$\mathbf{1_{PS}}$[b]	Tg 26.5 SmX 54.6 N 75.9 Iso
2	Cr 45.4 SmC 79.5 N 92.1 Iso	$\mathbf{2_{PS}}$	Tg 31.8 SmC 92.6 Iso
3	Cr 141.3 (N 88.8) Iso	$\mathbf{3_{PS}}$	Cr 121.9 (SmX 63.5) Iso

[a] Cr: crystalline, SmX: as yet unidentified smectic, SmC: smectic C, N: nematic. [b] Taken from ref. [5f].

The liquid-crystalline properties of the materials in this series are modulated both by the substitution pattern of the photochromic core and the conversion from the colourless open forms to the deeply coloured closed forms.

The liquid-crystalline phase behaviour for all of these systems **1**–**3** and $\mathbf{1_{PS}}$–$\mathbf{3_{PS}}$ is broadly similar in terms of the type of phase structures and the range of the isotropisation transition temperatures, if viewed in the context of the structure of the mesogens. There are significant differences with regard to the thermodynamic stability of phases and the occurrence of some LC phases and the range of the mesomorphic state.

For **1**–**3**, the highest stable phase is a nematic phase. For **1** and **2** this phase is thermodynamically stable; for **3**, it is only observable on cooling (monotropic LC behaviour). The material with the most linear molecular structure of this series, that is, **2**, has the highest isotropisation temperature of 92.1 °C, followed by that of the "V-shaped" compound **1** of 72.1 °C. Compound **3**, in which the central perfluorinated cyclopentene ring points in the same direction as the connections of the ether linkages to the mesogens, shows a monotropic transition at 88.8 °C. In addition, compounds **1** and **2** exhibit an SmC phase (tilted lamellar structure) at 74.5 °C for **1** and at 79.5 °C for **2**.

Irradiation with UV light (313 nm) modifies these properties significantly. Under PS conditions the stability of the nematic phase for **1** is reduced by 2.6 °C for $\mathbf{1_{PS}}$ to 75.9 °C; more importantly, at lower temperatures a smectic phase of unidentified structure (SmX) at 54.6 °C is found, and the material vitrifies at 26.5 °C. For $\mathbf{2_{PS}}$ the nematic phase is lost altogether, and the mesomorphic state is enhanced by 0.5 °C; the material melts from an SmC phase to the isotropic liquid at 92.6 °C. Additionally the crystalline low-temperature state is replaced by a glassy state with a transition T_g at 31.8 °C. For $\mathbf{3_{PS}}$ the melting point is reduced (to 121.9 °C) relative to **3**, and the monotropic nematic phase of **3** is replaced by a highly ordered, but unidentified, smectic phase (SmX) at 63.5 °C, which represents a reduction by 25.3 °C compared to the open form.

Detailed comparisons of these three systems are not possible. Due to different conversion rates at the PS state they are at different positions in their binary phase diagrams of open and closed forms. Nevertheless, we note that the system with the most linear molecular shape of the series, that is, **2**, is the least affected by the modulation in molecular rigidity in the central core on going from the open to the closed form; indeed, a small enhancement of the mesomorphic state occurs, and the presence of the more rigid closed systems promotes the formation of a higher ordered LC phase. For **1** and **3** the reduction in flexibility due to ring closure reduces the mesomorphic stability, and for **3**, in which all functionalities of the central aromatic core unit (perfluorinated group, connections to the mesogens) are crowded on one side of the long axis of the central photochromic core, this results in a dramatic reduction of the stability of the mesomorphic state and the self-assembly behaviour.

The combination of diarylethene-based photochromic groups with cyanobiphenyl moieties as mesogens allows for the investigation of molecular switches, in which the colour, absorption behaviour, liquid-crystalline properties and fluorescence behaviour can be systematically modulated. They can be considered as molecular logic gates (depending on the addressing scheme several logical functions can be considered (e.g., YES, NO functions), and more complex operations are conceivable. This is particularly interesting as the miscibility of these systems with commercial LC mixtures (e.g., E7) points towards an avenue for optical computing using LC technology.[2b,c]

Experimental Section

Materials: THF was dried by distillation from Na/benzophenone. The other solvents (Fisher Chemicals) were used without further purification other than drying over molecular sieves. Melting points, measured in capillary tubes on a Gallenkamp apparatus, are uncorrected. Transition temperatures were measured by differential scanning calorimetry (Perkin–Elmer 7 series DSC with an indium standard). The phase type and structure was confirmed by optical polarising microscopy using a Mettler FP52 heating stage and FP5 control unit in conjunction with an Olympus BH2 polarizing microscope (the coloured molecules were annealed in the dark state, and the light of the microscope was switched on for only very short periods of time, as decolouration takes place with the broadband-emitting tungsten bulb of the miscroscope). ^{1}H and ^{13}C NMR spectra were recorded on a JEOL Lambda 400 spectrometer (400 and 100 MHz for ^{1}H and ^{13}C, respectively) with tetramethysilane as internal standard. Chemical shifts are given in parts per million and coupling constants in hertz. UV/Vis spectra were recorded on a Cary 50-diode array spectrophotometer. Elemental analyses were carried out with a Fisons EA 1108 CHN analyzer. All reactions were monitored by thin-layer chromatography on 0.2 nm Merck silica gel plates (60F-254). Column chromatography was performed on silica gel (Fluorochem 35-70u 60A). The purities of all final compounds were checked by GLC analysis on a Chrompack 9001 capillary gas chromatograph fitted with a WCOT fused silica column (CP-Sil5 CB 0.12 m, 10 m long, 0.25 mm internal diameter) with nitrogen as carrier gas and by HPLC analysis on a Merck-Hitachi system fitted with a Rainin Dynamax Microsorb 5 μm silica column (25 cm long, 4.6 mm internal diameter) and were found to be >99.5%. Previously reported compounds were identified by comparison of ^{1}H NMR spectra and melting points with literature data.

Photochemical measurements: Absorption spectra were performed in cyclohexane solutions of spectrometric grade (Fisher Chemicals) at 25 ± 0.2. The analysis cell (optical path lengh 10 nm) was placed in a thermostated copper block inside the sample chamber of a Cary 50-diode array spectrophotometer. An Oriel 200 W high-pressure Hg/Xe lamp was used for irradiation. Mercury lines of 313 and 546 nm were isolated by passage through a monochromater (Oriel).

Fluorescence measurements: Emission spectra were measured in cyclohexane solutions of spectrometric grade (Fisher Chemicals) at 25 ± 0.2 °C by using a Shimadzu RF-1501 spectrofluorophotometer.

Conversion measurements: The open- and the closed-ring isomers were easily separated by HPLC using a Merck-Hitachi system fitted with a Rainin Dynamax Microsorb 5 μm silica column (25 cm long, 4.6 mm internal diameter) with hexane as eluent for **4**–**6** and hexane/ethyl acetate (94:6) for **1**–**3**.

6-Methoxy-2-methylbenzo[*b*]thiophene (11): 6-Methoxy-benzo[*b*]thiophene (**10**; 20.20 g, 0.12 mol) diluted in anhydrous THF (450 mL) was introduced into a three-necked round-bottomed flask under nitrogen. The mixture was cooled to −60 °C, and a solution of *n*BuLi (2.5 M, 64 mL, 0.14 mol) in hexane was added dropwise. The resulting mixture was stirred for 90 min at −40 °C and then cooled to −78 °C. Methyl iodide (52 g, 0.36 mol) was added. The mixture was allowed to return to room temperature, then hydrolysed with water (250 mL). The water/THF mixture was extracted three times with Et_2O (300 mL). The resulting organic phase was washed several times with saturated aqueous NaCl solution, dried over magnesium sulfate and then concentrated under reduced pressure. The solid collected was recrystallised from methanol to give a white solid (21.25 g, 97%). M.p. 88–89 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=2.50$ (s, 3H; CH_3), 3.80 (s, 3H; OCH_3), 6.83 (s, 1H; H-3), 6.90 (dd, $J=8.6$, 2.4 Hz, 1H; H-5), 7.21 (d, $J=2.5$ Hz, 1H; H-7), 7.49 ppm (d, $J=8.6$ Hz, 1H; H-4); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta=16.1$ (q), 56.4 (q), 104.8 (d), 113.9 (d), 121.6 (d), 123.3 (d), 134.3 (s), 137.9 (s), 140.9 (s), 156.6 ppm (s); elemental analysis calcd (%) for $C_{10}H_{10}OS$ (178.25): C 65.82, H 4.91; found: C 65.90, H 4.84.

3-Bromo-6-methoxy-2-methylbenzo[*b*]thiophene (12): A mixture of **11** (20.63 g, 0.13 mol) and $CHCl_3$ (250 mL) was cooled in an ice-water bath. A solution consisting of Br_2 (20.08 g, 0.14 mol) and $CHCl_3$ (90 mL) was added dropwise. After the addition was completed, the mixture was stirred for 30 min at room temperature and then hydrolysed with saturated aqueous $Na_2S_2O_6$ solution (300 mL). The aqueous phase was extracted twice with $CHCl_3$ (300 mL). The combined organic phases were washed several times with water, dried over magnesium sulfate and then concentrated under reduced pressure. The resulting solid was recrystallised from methanol to give a white solid (28.50 g, 82%). M.p. 80–81 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=2.50$ (s, 3H; CH_3), 3.86 (s, 3H; OCH_3), 6.90 (dd, $J=8.8$, 2.4 Hz, 1H; H-5), 7.21 (d, $J=2.4$ Hz, 1H; H-7), 7.57 ppm (d, $J=8.8$ Hz, 1H; H-4); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta=15.3$ (q), 55.6 (q), 104.9 (d), 105.8 (s), 114.4 (s), 114.5 (d), 123.1 (d), 132.4 (s), 138.2 (s), 157.8 ppm (s); elemental analysis calcd (%) for $C_{10}H_9BrOS$ (257.15): C 46.71, H 3.53; found: C 46.93, H 3.60.

1-[6-Methoxy-2-methylbenzo[*b*]thiophen-3-yl]heptafluorocyclopentene (13): A solution of *n*BuLi (2.5 M, 11.90 mL, 0.034 mol) in hexane was added dropwise to a stirred solution of **12** (7.61 g, 0.03 mol) in anhydrous THF (120 mL) at −78 °C under nitrogen. The resulting mixture was stirred for 30 min at −78 °C, then octafluorocyclopentene (20 g, 0.09 mol) was added in a single portion. After the addition was completed, the mixture was allowed to return to room temperature, then hydrolysed with water (120 mL). The THF/water mixture was extracted three times with Et_2O (150 mL). The resulting organic phase was washed several times with saturated aqueous NaCl solution, dried over magnesium sulfate and then concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with pentane/CH_2Cl_2 (100:0 to 80:20) to give slightly yellow crystals (8.12 g, 68%). M.p. 41–42 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=2.48$ (s, 3H; CH_3), 3.86 (s, 3H; OCH_3), 7.03 (dd, $J=8.8$, 2.4 Hz, 1H; H-5), 7.27 (d, $J=2.4$ Hz, 1H; H-7), 7.41 ppm (d, $J=8.8$ Hz, 1H; H-4); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta=14.4$ (q), 55.6 (q), 104.9 (d), 113.9 (s), 114.8 (d), 122.2 (d), 132.0 (d), 139.7 (s), 141.3 (s), 157.6 ppm (s); elemental analysis calcd (%) for $C_{15}H_{15}F_7OS$ (370.29): C 48.65, H 2.45; found: C 48.45, H 2.59.

5-Methoxy-2-methylbenzo[*b*]thiophene (15): This compound was prepared from **14** according the same procedure as described for the synthesis of the **11**. White solid (92% yield). M.p. 97–98 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=2.56$ (s, 3H; CH_3), 3.84 (s, 3H; OCH_3), 6.89 (m, 2H; H-3, H-5), 7.12 (d, $J=2.5$ Hz, 1H; H-4), 7.59 ppm (d, $J=8.6$, 1H; H-6); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta=16.3$ (q), 55.6 (q), 105.2 (d), 113.2 (d), 121.5 (d), 122.7 (d), 132.0 (s), 141.5 (s), 142.3 (s), 157.4 ppm (s); elemental analysis calcd (%) for $C_{10}H_{10}OS$ (178.25): C 65.82, H 4.91; found: C 65.95, H 4.81.

3-Bromo-5-methoxy-2-methylbenzo[*b*]thiophene (16). This compound was prepared from **15** according to the same procedure as described for the synthesis of **12**. Oily product (45% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=2.50$ (s, 3H; CH_3), 3.86 (s, 3H; OCH_3), 6.92 (dd, $J=8.7$, 2.5 Hz, 1H; H-6), 7.12 (d, $J=2.5$ Hz, 1H; H-4), 7.53 ppm (d, $J=8.7$ Hz, 1H; H-6); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta=15.7$ (q), 55.6 (q), 104.9 (d), 106.3 (s), 115.0 (d), 123.0 (d), 129.3 (d), 136.5 (s), 139.5(s), 158.2 ppm (s);

elemental analysis calcd (%) for $C_{10}H_9BrOS$ (257.15): C 46.71, H 3.53; found: C 46.78, H 3.41.

1,2-Bis(6-methoxy-2-methyl-benzo[*b*]thiophen-3-yl)hexafluorocyclopentene (4): A solution of *n*BuLi in hexane (2.5 M, 17.9 mL, 0.044 mol) was added dropwise to a stirred solution of **12** (10 g, 0.039 mol) in anhydrous THF (150 mL) at −78 °C under nitrogen atmosphere. The resulting mixture was stirred for 30 min at −78 °C, then octafluorocyclopentene (4.12 g, 0.019 mol) was added in a single portion. After the addition was completed, the mixture was allowed to return to room temperature, then hydrolysed with water (150 mL). The THF/water mixture was extracted three times with Et_2O (150 mL). The resulting organic phase was washed several times with saturated aqueous NaCl solution, dried over magnesium sulfate and then concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with pentane/CH_2Cl_2 (100:0 to 70:30). The resulting solid was recrystallised from methanol to give a white solid (6.22 g, 62 %). M.p. 128–129 °C; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 2.13$ (s, 3.84 H; ap CH_3), 2.42 (s, 2.16 H; p CH_3), 3.77 (s, 2.16 H; p OCH_3), 3.84 (s, 3.84 H; ap OCH_3), 6.79 (dd, $J = 8.9$, 2.2 Hz, 0.72 H; p H-5), 6.98 (dd, $J = 8.8$, 2.2 Hz, 1.28 H; ap H-5), 7.07 (d, $J = 2.2$ Hz, 0.72 H; p H-7), 7.16 (d, $J = 2.2$ Hz, 1.28 H; ap H-7), 7.39 (d, $J = 8.9$ Hz, 0.72 H; p H-4), 7.52 ppm (d, $J = 8.9$ Hz, 1.28 H; ap H-4); parallel (p) conformer/antiparallel (ap) conformer = 36:64; UV/Vis (cyclohexane): λ_{max} (ε) = 267 (23 800), 305 nm (4500); elemental analysis calcd (%) for $C_{25}H_{18}F_6O_2S_2$ (528.53): C 56.81, H 3.43; found: C 56.88, H 3.53.

1-(5-Methoxy-2-methyl-benzo[*b*]thiophen-3-yl)-2-(6′-methoxy-2′-methylbenzo[*b*]thiophen-3′-yl)hexafluorocyclopentene (5): A solution of *n*BuLi (2.5 M, 7.2 mL, 0.018 mol) in hexane was added dropwise to a stirred solution of **16** (4.78 g, 0.018 mol) in anhydrous THF (100 mL) at −78 °C under nitrogen. The resulting mixture was stirred for 30 min at −78 °C, then a solution of **13** (7 g, 0.018 mol) in of anhydrous THF (40 mL) was added slowly. After the addition was completed, the mixture was allowed to return to room temperature, then hydrolysed with water (140 mL). The THF/water mixture was extracted three times with Et_2O (150 mL). The resulting organic phase was washed several times with saturated aqueous NaCl solution, dried over magnesium sulfate and then concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with pentane/CH_2Cl_2 of increasing polarity (100:0 to 70:30). The resulting solid was recrystallised from methanol to give a white solid (5.42 g, 57 %). M.p. 118–119 °C; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 2.18$ (s, 3.72 H;ap 2-CH_3, ap 2′-CH_3), 2.40 (s, 1.14 H; p 2-CH_3 or p 2′-CH_3), 2.56 (s, 1.14 H;p 2-CH_3 or p 2′-CH_3), 3.72 (s, 1.14 H;p 5-OCH_3 or p 6′-OCH_3), 3.78 (s, 1.14 H;p 5-OCH_3 or p 6′-OCH_3), 3.84 (s, 1.86 H; ap 5-OCH_3 or ap 6′-OCH_3), 3.87 (s, 1.86 H; ap 5-OCH_3 or ap 6′-OCH_3), 6.79–7.20 (m, 4 H), 7.41–7.60 ppm (m, 2 H); parallel conformer/antiparallel conformer = 38:62; UV/Vis (cyclohexane): λ_{max} (ε) = 265 (21 300), 306 (6600), 316 nm (6600); elemental analysis calcd (%) for $C_{25}H_{18}F_6O_2S_2$ (528.53): C 56.81, H 3.43; found: C 56.89, H 3.48.

1,2-Bis(5-methoxy-2-methylbenzo[*b*]thiophen-3-yl)hexafluorocyclopentene (6): This compound was prepared from **16** according the same procedure as described for the synthesis of **4**. White solid (69 % yield); M.p. 182–183 °C; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 2.10$ (s, 3.32 H; ap CH_3), 2.38 (s, 2.82 H; p CH_3), 3.60 (s, 2.82 H; p OCH_3), 3.79 (s, 3.32 H; ap OCH_3), 6.78 (dd, $J = 8.8$, 2.4 Hz, 0.92 H; p H-6), 6.78 (dd, $J = 8.8$, 2.4 Hz, 1.08 H; ap H-6), 6.92 (d, $J = 1.6$ Hz, 0.92 H; p H-4), 7.06 (d, $J = 1.6$ Hz, 1.08 H; ap H-4), 7.41 (d, $J = 8.8$ Hz, 0.92 H; p H-7), 7.49 ppm (d, $J = 8.8$ Hz, 1.08 H; ap H-7); parallel conformer/antiparallel conformer = 45:55; UV/Vis (cyclohexane): λ_{max} (ε) = 262 (21 000), 307 (8400), 316 nm (9000); elemental analysis calcd (%) for $C_{25}H_{18}F_6O_2S_2$ (528.53): C 56.81, H 3.43; found: C 56.78, H 3.51.

1,2-Bis(6-hydroxy-2-methylbenzo[*b*]thiophen-3-yl)-hexafluorocyclopentene (7): Compound (**4**) (5.60 g, 0.01 mol) and dried CH_2Cl_2 (100 mL) were introduced into a three-necked round-bottomed flask under nitrogen. The resulting mixture was cooled in an ice-water bath, then BBr_3 (4.91 mL; 0.05 mol) was added dropwise. The solution was warmed to room temperature and stirred for 6 h. Then, the mixture was cooled in an ice-water bath, and 10 % aqueous HCl solution (100 mL) was added slowly. The chlorinated phase was separated from the aqueous phase, and the latter was extracted several times with ethyl acetate. The combined organic phases were washed with water, dried over magnesium sulfate and then concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with CH_2Cl_2/Et_2O (100:0 to 90:10) to give a white solid (93 % yield). M.p. 236–237 °C; ^1H NMR ([D_6]acetone, 400 MHz): $\delta = 2.16$ (s, 3.18 H; ap CH_3), 2.39 (s, 2.82 H; p CH_3), 6.73 (dd, $J = 8.6$, 2.2, 0.94 H; p H-5), 6.91 (dd, $J = 8.6$, 2.2 Hz, 1.06 H; ap H-5), 7.12 (d, $J = 2.2$ Hz, 0.94 H; p H-7), 7.20 (d, $J = 2.2$ Hz, 1.06 H; ap H-7), 7.34 (d, $J = 8.6$ Hz, 0.94 H; p H-4), 7.38 (d, $J = 8.6$ Hz, 1.06 H; ap H-4), 9.66 (s, 0.47 H; p OH), 9.76 ppm (s, 0.53 H; ap OH); parallel conformer/antiparallel conformer = 47:53; elemental analysis calcd (%) for $C_{23}H_{14}F_6O_2S_2$ (500.48): C 55.20, H 2.82; found: C 55.25, H 2.72.

1-(5-Hydroxy-2-methylbenzo[*b*]thiophen-3-yl)-2-(6′-hydroxy-2′-methylbenzo-[*b*]-thiophen-3′-yl)hexafluorocyclopentene (8): This compound was prepared from **5** according to the same procedure as described for the synthesis of **4**. White solid (91 % yield). M.p. 227–228 °C; ^1H NMR ([D_6]acetone, 400 MHz): $\delta = 2.20$ (s, 1.67 H; ap 2-CH_3 or ap 2′-CH_3), 2.21 (s, 1.67 H; ap 2-CH_3 or ap 2′-CH_3), 2.42 (s, 1.33 H; p 2-CH_3 or p 2′-CH_3), 2.52 (s, 1.33 H; p 2-CH_3 or p 2′-CH_3), 6.73–6.75 (m, 0.87 H; p H-6 and p H-5′), 6.85 (dd, $J = 8.6$, 2.2 Hz, 1.13 H; ap H-6), 6.93 (dd, $J = 8.6$, 2.2 Hz, 1.13 H; ap H-5′), 6.98 (sl, 1 H; p H-4 and ap H-4), 7.13 (d, $J = 2.2$ Hz, 0.46 H; p H-7′), 7.20 (d, $J = 2.2$ Hz, 0.54 H; ap H-7′), 7.35–7.41 (m, 1 H; p and ap H-4′), 7.58 (d, $J = 8.6$ Hz, 0.46 H; p H-7), 7.66 (d, $J = 8.8$ Hz, 0.54 H; ap H-7), 9.51 (s, 0.23 H; p 5-OH), 9.65 (s, 0.50 H; ap 5-OH and p 6′-OH), 9.65 ppm (s, 0.37 H; ap 6′-OH); parallel conformer/antiparallel conformer = 44:56; elemental analysis calcd (%) for $C_{23}H_{14}F_6O_2S_2$ (500.48): C 55.20, H 2.82; found: C 55.35, H 2.90.

1,2-Bis(5-hydroxy-2-methylbenzo[*b*]thiophen-3-yl)hexafluorocyclopentene (9): This compound was prepared from **6** according to the same procedure as described for the synthesis of the **4**. White solid (87 % yield). M.p. 250–251 °C; ^1H NMR ([D_6]acetone, 400 MHz): $\delta = 2.23$ (s, 4.44 H; ap CH_3), 2.48 (s, 1.56 H; p CH_3), 6.75 (dd, $J = 8.6$, 2.2 Hz, 0.52 H; p H-6), 6.85 (dd, $J = 8.8$, 2.4 Hz, 1.48 H; ap H-6), 6.93 (d, $J = 2.2$ Hz, 0.52 H; p H-4), 6.97 (d, $J = 2.4$ Hz, 1.48 H; ap H-4), 7.57 (d, $J = 8.6$ Hz, 0.52 H; p H-7), 7.64 (d, $J = 8.8$ Hz, 1.48 H; ap H-7), 9.38 (s, 0.26 H; p OH), 9.64 (s, 0.74 H; ap OH); parallel conformer/antiparallel conformer = 26:74; elemental analysis calcd (%) for $C_{23}H_{14}F_6O_2S_2$ (500.48): C 55.20, H 2.82; found: C 55.26, H 2.86.

Compound 1: A mixture of **4** (0.15 g, 0.30 mmol), 4′-(6-bromohexyloxy)-biphenyl-4-carbonitrile (0.26 g, 0.72 mmol), K_2CO_3 (0.10 g, 0.72 mmol) and dry butanone (20 mL) was refluxed for 24 h, then allowed to return to room temperature. The reaction mixture was filtered, and the butanone distilled off under reduced pressure. The crude product was purified by column chromatography on silica gel with CH_2Cl_2 to give a white solid (0.26 g, 87 % yield). Transition *T*/°C: Cr 40.1 SmC 74.5 N 78.5 Iso liq; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 1.25$–1.48 (m, 24 H), 1.80–1.86 (m, 8 H), 2.13 (s, 3.92 H; ap CH_3), 2.43 (s, 2.08 H; p CH_3), 3.98–4.93 (m, 8 H; OCH_2), 6.80 (dd, $J = 8.6$, 2.2 Hz, 0.70 H; p H-5), 6.96–7.06 (m, 5.30 H; 4H-arom + ap H-5), 7.05 (d, $J = 2.2$ Hz, 0.70 H; p H-7), 7.15 (d, $J = 2.2$ Hz, 1.30 H; ap H-7), 7.39 (d, $J = 8.6$ Hz, p 0.70 H; H-4), 7.52 (m, 5.30 H; 4H-arom + ap H-4), 7.60–7.70 ppm (m, 8 H; 8H-arom); parallel conformer/antiparallel conformer = 35:65; UV/Vis (cyclohexane): λ_{max} (ε) = 280 nm (57 000); elemental analysis calcd (%) for $C_{69}H_{68}F_6N_2O_4S_2$ (1167.41): C 70.99, H 5.87, N 2.40; found: C 70.94, H 5.89, N 2.45.

Compound 2: This compound was prepared from **8** according to the same procedure as described for synthesis of **1**. White solid (78 % yield); Transition *T*/°C: Cr 45.4 SmA 79.5 N 92.1 Iso liq; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 1.30$–1.48 (m, 24 H), 1.68–1.83 (m, 8 H), 2.15 (s, 3.90 H; ap 2-CH_3, ap 2′-CH_3), 2.37 (s, 1.05 H; p 2-CH_3 or p 2′-CH_3), 2.49 (s, 1.05 H; p 2-CH_3 or p 2′-CH_3), 3.81–4.00 (m, 8 H; OCH_2), 6.79–7.20 (m, 8 H), 7.41–7.68 ppm (m, 10 H); parallel conformer/antiparallel conformer = 35:65; UV/Vis (cyclohexane): λ_{max} (ε) = 292 nm (63 000); elemental analysis calcd (%) for $C_{69}H_{68}F_6N_2O_4S_2$ (1167.41): C 70.99, H 5.87, N 2.40; found: C 71.10, H 5.78, N 2.44.

Compound 3: This compound was prepared from **9** according to the same procedure as described for synthesis of **1**. White solid (84 % yield); Transition *T*/°C: Cr 141.3 (N 88.8) Iso liq; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 1.29$–1.53 (m, 24 H), 1.68–1.81 (m, 8 H), 2.15 (s, 3.35 H; ap CH_3), 2.41 (s, 2.65 H; p CH_3), 3.81–3.98 (m, 8 H; OCH_2), 6.80 (dd, $J = 8.6$, 2.2 Hz, 0.88 H; p H-6), 6.93–697 (m, 6 H; 4H-arom + ap H-6 + p H-4), 7.05 (d, $J = 1.6$ Hz, 1.12 H; ap H-4), 7.43 (d, $J = 8.6$ Hz, 0.88 H; p H-7), 7.47–7.52 (m, 5.12 H; 4H-arom + ap H-7), 7.59–7.67 ppm (m, 8 H; 8H-arom); parallel conformer/antiparallel conformer = 44:56; UV/Vis (cyclohexane): λ_{max}

$(\varepsilon) = 292$ nm (58000); elemental analysis calcd (%) for $C_{69}H_{68}F_6N_2O_4S_2$ (1167.41): C 70.99, H 5.87, N 2.40; found: C 71.07, H 5.82, N 2.47.

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