Antiferroelectric Switchable Mesophases of Nonchiral Bent-Core Liquid Crystals Containing Fluorinated Central Cores

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A new series of liquid-crystalline bent-core molecules comprising a central 3,4′-disubstituted biphenyl unit (biphenyl 3,4′-bis-4-[4-dodecyl(oxy)benzoyloxy]benzoates) at which one, two, or even three H atoms in various positions were replaced by F atoms has been synthesized. The biphenyl cores were built up by orthometalation, followed by palladium-catalyzed cross-coupling reactions. The compounds were characterized by polarizing microscopy, DSC, X-ray scattering, and electro-optical investigations. Most compounds exhibit broad regions of antiferroelectrical switchable SmCP$_A$ phases, but also rectangular columnar mesophases have been observed for some representatives. Extremely large values of the spontaneous polarization (up to 2300 nC cm^{-2}) have been found for some representatives. Additionally, for some smectic compounds a third peak was detected in the polarization current curve beside the two peaks corresponding to the antiferroelectric switching process. The coexistence of ferroelectric and antiferroelectric domains is discussed as one possible explanation, but requires further investigations.

Introduction

Materials with a macroscopic polar order have a variety of useful properties, such as piezo- and pyro-electricity and second-order nonlinear optical activity.[1,2] Ferroelectric and antiferroelectric liquid-crystalline materials are of special interest because such polar materials can be switched with external electric fields.[3,4] This makes them useful for electro-optic devices, for information storage, and as switchable NLO materials.[5] At first, smectic phases with tilted arrangements of nonracemic chiral molecules have been used for this purpose (SmC* and SmC$_A$* phases), but more recently it was shown by Niori et al. that bent-core mesogenic compounds (banana-shaped molecules) can provide easy access to polar order in liquid-crystalline systems without molecular chirality.[6] The liquidlike smectic layers of such bent-core molecules have a polar structure provided by the dense packing of the bent aromatic cores. To escape from a macroscopic polar order, the bent direction in adjacent layers is antiparallel so that the layer polarization alternates from layer to layer, which leads to a macroscopic apolar (antiferroelectric) structure.[7] The resulting smectic phase is biaxial whereby one optical axis is in most cases additionally tilted relative to the layer normal (see Figure 1).[7] These mesophases can be described as SmAP$_A$[8] or SmCP$_A$,[7] nontilted (SmA), respectively tilted (SmC) smectic phases with a polar order of the molecules (P) within the layers, and an antiferroelectric correlation between adjacent layers (A). When an electric field is applied, the molecules can be switched into a ferroelectric, that is, macroscopically polar structure (SmAP$_F$ or SmCP$_F$).[7] Large second-order NLO effects have been reported for such bent-core molecules in this non-centrosymmetric SmCP$_F$ structure.[5,9] More recently, a macroscopically polar (ferroelectric) structure was also reported for the ground state of some bent-core molecules (SmC$_S$P$_F$).[10–12] In such tilted (ferroelectric or antiferroelectric) SmCP phases the symmetry is reduced in comparison to conventional

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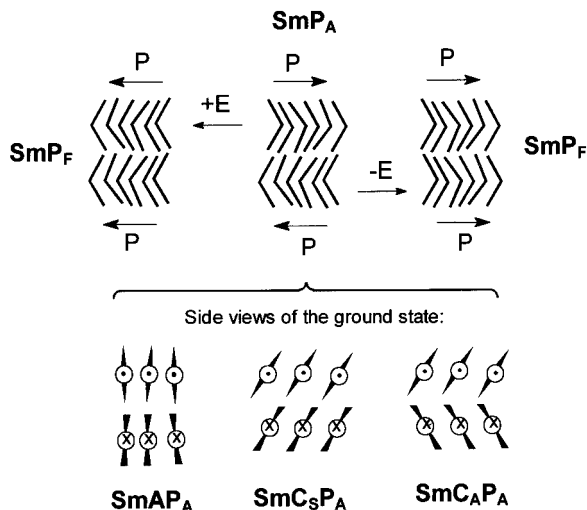
Figure 1. Organization of bent-core molecules in the antiferroelectrical switchable mesophases. Owing to the bent-core, each molecule possesses a dipole moment in the molecular plane and perpendicular to the long axis of the molecules. The molecules are arranged in layers whereby the polar direction changes from layer to layer (antiferroelectric order, SmP_A). By application of an external electrical field ($\pm E$), the molecules can be switched into macroscopically polar states with uniform polar direction (ferroelectric, SmP_F). The side views show the possible organizations of such molecules in the ground state (SmP_A). The molecules can be nontilted with respect to the layer normal ($SmAP_A$) or tilted ($SmCP_A$) either with synclinic (SmC_SP_A) or with anticlinic interlayer correlation (SmC_AP_A).

SmC phases, which gives rise to an inherent handedness. It is geometrical in nature and does not result from a molecular chirality.[7,13,14] Additionally, in these SmCP phases the molecules in adjacent layers can have a synclinic (molecules in adjacent layers are tilted in the same direction) or an anticlinic (molecules in adjacent layers are tilted in opposite directions) interlayer correlation, leading to further modifications of the phase structure (e.g., SmC_SP_A, SmC_AP_A).[7] Depending on the molecular structure, the history of the sample, and other specific boundary conditions, one of them can be predominating in the samples or they can coexist side-by-side.[15-17]

Though, since the time of its discovery, numerous bent-core molecules have been synthesized by several groups, an understanding of the fundamental relationship between chemical structure and properties of such materials is still at a very initial state.[18-20] Therefore, systematic structural variations are necessary to obtain

a deeper understanding of the structure–property relations in this special class of mesogens, which could lead to new materials with interesting properties.

The substitution of hydrogen by fluorine has become a widespread principle in drug design, materials chemistry, and the molecular design of liquid crystals. In liquid crystals the effect of the substitution of H atoms by F atoms strongly depends on the number and position of the fluorine atoms within the mesogenic molecules. Replacement of several CH_2 groups of terminal alkyl chains by CF_2 groups can lead to polyphilic molecules and in many cases gives rise to the induction or stabilization of positionally ordered mesophases due to the segregation of the incompatible fluorinated and hydrogenated segments.[21-23] The effect of the replacement of H atoms at aromatic molecular parts by fluorine is quite distinct from that at aliphatic chains. The highest electronegativity of all elements is responsible for a high polarization of the C–F bond and induces strong local dipole moments. Additionally, the electron density of aromatic systems is reduced, and therefore, in contrast to the case of fluorinated and nonfluorinated aliphatic chains that repel each other, attractive forces can arise between fluorinated (electron-acceptor) and nonfluorinated (electron-donor) aromatic segments.[24] Additionally, the rather small size of the fluorine atoms leads to a minimal steric effect of such substituents in comparison to all other substituents. For these reasons fluoro substitution strongly influences the properties of liquid crystals, such as dielectric properties, melting points, phase transition temperatures, mesophase morphology, and viscosity.[25,26] Replacement of H by F may also be an important tool for the molecular design in the newly arising class of bent-core molecules. Here,

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semifluorinated terminal alkyl chains have been used to stabilize their smectic phases.[27,28] Also, the introduction of fluorine substituents at the aromatic rings of the bent-core molecule has been done, but only in peripheral positions.[29] Here, they influence the clearing and melting points but they could also lead to a special packing of the molecules that could give rise to interesting new mesophases such as the so-called B_7 phase with a helical supramolecular structure.[18,30] However, to date, no bent-core mesogens with fluorine substituents positioned at the aromatic rings in the central region of the rigid cores have been prepared.
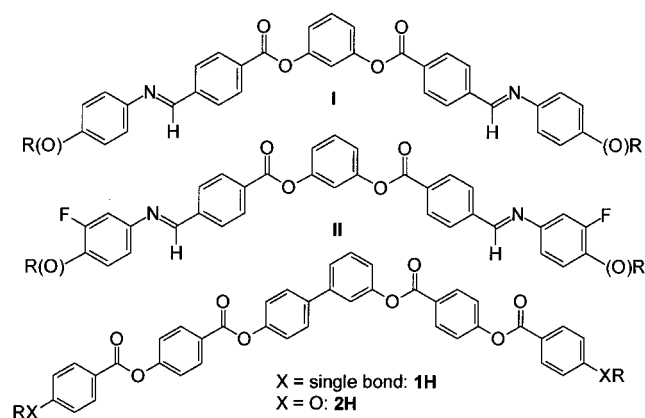
Compounds such as **1H** and **2H**, incorporating a 3,4′-disubstitued biphenyl core, have recently been reported as examples of bent-core molecules showing especially broad regions of antiferroelectrical switchable SmCP$_A$ phases.[27,31] Additionally, in contrast to most other bent-core molecules, which represent resorcinol bisbenzoates incorporating at least one Schiff-base unit,[18] such molecules, incorporating exclusively ester linking units, have the advantage of an increased chemical and photochemical stability. Therefore, we have chosen such molecules to study the influence of fluorine substituents on the mesomorphic properties and have synthesized new compounds of this type in which one, two, or even three H atoms in various positions at the central 3,4′-disubstituted biphenyl unit were replaced by F atoms (see Figure 2). Two series of compounds **1** and **2** have been synthesized, which differ in the connection of the
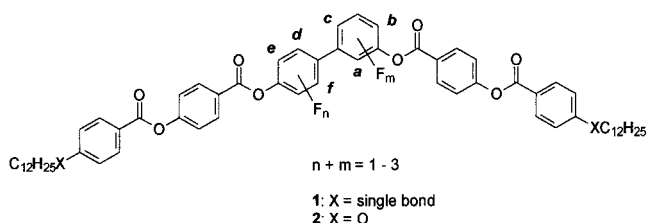
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Figure 2. Structures of the compounds under investigation. The notation of the compounds is based on the connection of the alkyl chains to the aromatic core (X = single bond: **1**; X = O: **2**) and on the position(s) of the F substituent(s) according to the shown assignment of the positions.

Scheme 1. Synthesis of Compounds 1/2a, 1/2ad, and 1/2ae
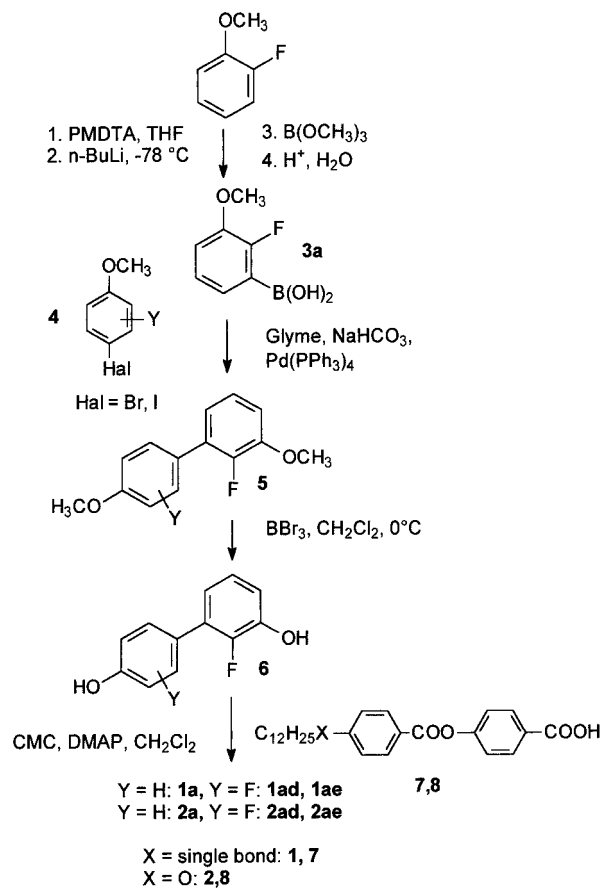
dodecyl chains with the aromatic core (single bond or O). Further notation of the compounds is based on the position(s) of the F substituent(s) according to the assignment shown in Figure 2.

Synthesis

The synthetic routes to these new compounds are essentially based on ortho-metalation reactions of appropriately substituted fluorobenzene derivatives, followed by Suzuki cross-coupling reactions.[32] As a representative example, the synthesis of compounds **1/2a**, **1/2ad**, and **1/2ae** is shown in Scheme 1. Here, 2-fluoroanisole was the starting material. It has two nonequivalent acidic protons at the aromatic core, one in the ortho position to the fluorine atom and one ortho to the methoxy group, which both can be exploited to introduce

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appropriate functional units. To obtain the correct substitution pattern, the two acidic protons have to be distinguished. This was possible by using deprotonation conditions described by Schlosser.[33] Accordingly, the 2-fluoroanisole was ortho-lithiated with *n*-BuLi in the presence of *N,N,N,N,N′,N′*-pentamethyldiethylene triamine (PMDTA) in THF at −78 °C. Thereby, the chelating polyamine directs the metalation selectively into the ortho position beside the more electronegative fluorine substituent. At −78 °C B(OCH$_3$)$_3$ was added, followed by acidic hydrolysis to generate the boronic acid **3a**. The boronic acid was purified by crystallization from toluene and afterward coupled with appropriately substituted bromo- and iodofluoromethoxybenzenes **4** under standard conditions (Pd(PPh$_3$)$_4$, 1,2-dimethoxyethane, NaHCO$_3$ solution, reflux)[32] to give the fluorine-substituted 3,4′-dimethoxybiphenyls **5**. The methoxy groups were cleaved with BBr$_3$[34] and the resulting divalent phenols **6** were washed with water and purified by crystallization from toluene. The final compounds were obtained by esterification of these divalent phenols **6** with 2.2 equiv of 4-(4-dodecylbenzoyloxy)benzoic acid **7**[27] or 4-(4-dodecyloxybenzoyloxy)benzoic acid **8**[27] with *N*-cyclohexyl-*N′*-[2-(*N*-methylmorpholino)-ethyl]carbodiimide-4-toluenesulfonate (CMC) as the condensation agent and DMAP as the acylation catalyst.[35] The crude products were purified by preparative thin-layer chromatography by means of a Chromatotron (Harrison research) and then crystallized from ethyl acetate. Most compounds **1** and **2** were obtained in quite similar ways, as summarized in Scheme 2. Some haloanisoles **4** were commercially available (3- and 4-bromoanisole and 4-bromo-2-fluoroanisole); others were prepared by bromination of 2,3-difluoroanisole with bromine in CHCl$_3$ (compound **4de**)[26c] or by iodation of 3-fluorophenol with NaOCl/NaI,[36] followed by etherification with methyliodide (compound **4d**, see Scheme 2).[37]

A slightly different way was used to realize the substitution pattern of the molecules **1b** and **2b**. As shown in Scheme 3, 4-bromo-1-fluorobenzene was first coupled with 4-methoxybenzene boronic acid. The resulting 4-fluoro-4′-methoxybiphenyl[38] was ortho-lithiated as described above to produce the boronic acid **10**. Oxidation of the boronic acid **10** with H$_2$O$_2$ provided the phenol **11**.[39] The methoxy group of **11** was cleaved and the resulting divalent phenol **6b** was used for esterification to provide the compounds **1b** and **2b**. As a representative example, the synthesis of **2ad** is described in detail in the Experimental Section. The synthesis and analytical data of all other compounds are reported in the Supporting Information.

Experimental Section

2-Fluoro-3-methoxybenzeneboronic Acid 3a. *n*-Butyllithium (34.0 mL of a 1.6 M solution, 55.0 mmol) was slowly added with stirring to a solution of 2-fluoromethoxybenzene (7.9 g, 50.0 mmol) and PMDTA (10.4 mL, 50 mmol) in THF (60 mL). The solution was kept for 2 h at −78 °C. Trimethylborate (16.8 mL, 150 mmol) was slowly added at −78 °C and the mixture was allowed to come to room temperature overnight. After acidification with hydrochloric acid (50 mL, 1 M), the layers were separated and the aqueous layer was extracted with diethyl ether (3× 50 mL). The combined organic layers

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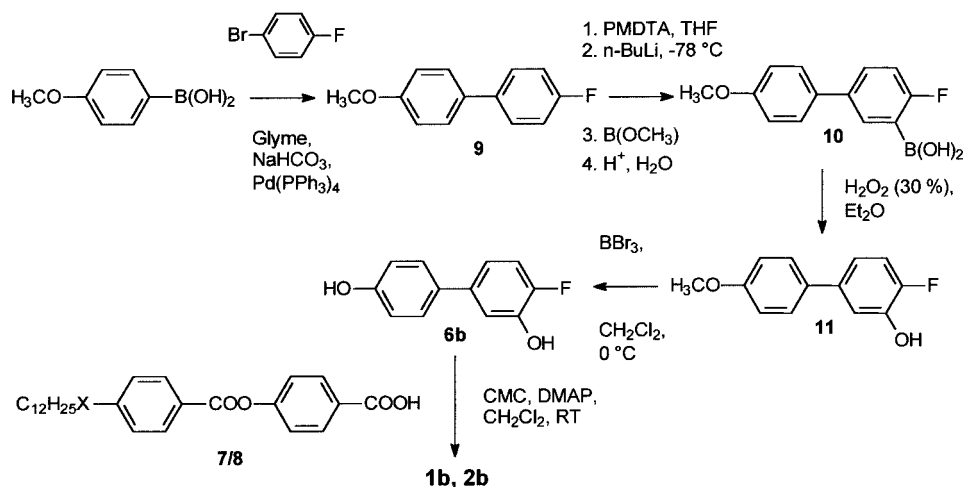
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Scheme 2. Overview over the Synthetic Pathway to the Bent-Core Mesogens with Fluorinated Biphenyl Cores[a]
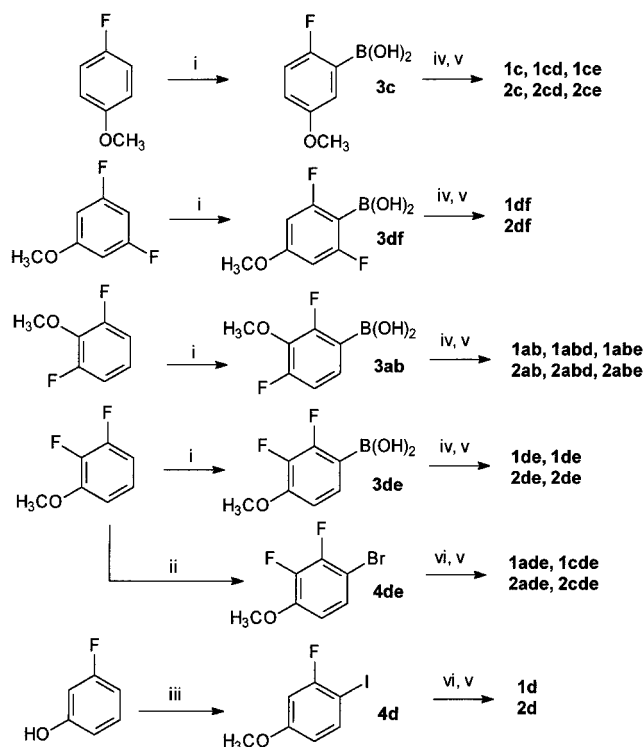
[a] Reagents and conditions: (i) 1. BuLi, PMDTA, THF, −78 °C; 2. B(OMe)$_3$, −78 °C; 3. H$_2$O, HCl. (ii) Br$_2$, CHCl$_3$, 62 °C. (iii) 1. NaOCl, NaOH, NaI, H$_2$O, MeOH, 0 °C; 2. MeI, K$_2$CO$_3$, MeCN, reflux. (iv) **4**, Pd[PPh$_3$]$_4$, NaHCO$_3$, H$_2$O, glyme. (v) 1. BBr$_3$, CH$_2$Cl$_2$, 20 °C; 2. **7** or **8**, CMC, DMAP, CH$_2$Cl$_2$, 20 °C. (vi) **3**, Pd[PPh$_3$]$_4$, NaHCO$_3$, H$_2$O, glyme.

were dried over Na$_2$SO$_4$ and evaporated. The resulting solid was crystallized from toluene. Yield: 5.7 g (67%). mp 205−206 °C (toluene). δ_H (CDCl$_3$; 200 MHz): 7.40−7.33 (m, 1H, Ar−H), 7.14−7.08 (m, 2H, Ar−H), 5.14 (d, *J* 6.5, 2H, OH), 3.88 (s, 3H, OCH$_3$). *m/z* (70 eV): 170 (100), 155 (30), 127 (26), 107 (28).

3-Fluoro-4-iodomethoxybenzene 4d. One equivalent each of sodium iodide (30.0 g, 0.20 mol) and sodium hydroxide (8.0 g, 0.20 mol) were added to a solution of 3-fluorophenol (22.4 g, 0.20 mol) in methanol (550 mL). Aqueous sodium hypochlorite (360 mL, 4%) was added dropwise at 0 °C. The solution was stirred for 2 h at 0 °C and then treated with aqueous sodium thiosulfate (70 mL, 30%). The mixture was adjusted to pH 7 using 10% hydrochloric acid. The aqueous phase was extracted with ether (3× 300 mL) and the combined organic layers were washed with brine, dried, and evaporated. The residue was crystallized from hexane. Yield: 34.2 g of 3-fluoro-4-iodophenol (71%). mp 90−93 °C (hexane). δ_H (CDCl$_3$; 400 MHz): 7.52 (dd, *J* 8.8, 7.2, 1H, Ar−H), 6.60 (dd, *J* 9.1, 2.7, 1H, Ar−H), 6.44 (dd, *J* 8.7, 2.7, 1H, Ar−H), 5.04 (s, OH). δ_F (CDCl$_3$; 188 MHz): −92.68. *m/z* (70 eV): 238 (100), 127 (19), 111 (24), 83 (50), 57 (33). A mixture of 3-fluoro-4-iodophenol (11.6 g, 48.7 mmol), potassium carbonate (27.6 g, 200 mmol), and iodomethane (16.0 g, 112 mmol) in acetonitrile (450 mL) is kept under reflux for 8 h. The solid was filtered off and washed with diethyl ether (2× 50 mL). The solvent was distilled off via a Vigreux column. The resulting product is purified by distillation in vacuo. Yield: 9.3 g (76%). bp 40−42 °C (0.02 mbar). δ_H (CDCl$_3$; 400 MHz): 7.59 (dd, *J* 8.6, 7.4, 1H, Ar−H), 6.63 (dd, *J* 9.9, 2.8, 1H, Ar−H), 6.50 (dd, *J* 8.8, 2.7, 1H, Ar−H), 3.77 (s, 3H, OCH$_3$). *m/z* (70 eV): 252 (100), 237 (24), 209 (13), 110 (11).

2,2′-Difluoro-3,4′-dimethoxybiphenyl 5ad. 3a (1.8 g, 10.7 mmol) was added to a solution of **4d** (2.6 g, 10.7 mmol) in a mixture of 1,2-dimethoxyethane (20 mL) and saturated aque-

Scheme 3. Synthesis of Compounds 1/2b

Results and Discussion

A. Mesomorphic Properties. The mesomorphic properties of the obtained compounds were investigated by polarized light optical microscopy on a hot stage (Mettler FP 82 HAT) and by differential scanning calorimetry (DSC-7, Perkin-Elmer, heating and cooling scans 10 °C/min). The transition temperatures and the corresponding enthalpy values of all synthesized compounds are summarized in Table 1. All monofluorinated molecules show highly fluid mesophases with textures as typical for the $SmCP_A$ phases (see for example Figure 3) of the parent compounds **1H** and **2H** without the fluorine substituent. The same texture was found for many of the difluorinated molecules and some trifluorinated molecules. This phase assignment was confirmed by X-ray scattering. The X-ray diffraction diagrams (Guinier-film method) of compounds **1c** and **1ad** were recorded as representative examples. In the small-angle region they show two reflections, corresponding to a layer structure with $d = 3.95$ nm (**1c**) and $d = 3.92$ nm (**1ad**) in addition to a diffuse wide-angle scattering corresponding to the mean distance between the fluid alkyl chains (0.45 nm), as characteristic for fluid smectic phases. The layer periods in these smectic phases are very close to that of the parent compound **1H** ($d = 3.96$ nm). In all cases the period of the smectic phases is significantly smaller than the molecular length ($L = 5.7$ nm in the most stretched conformation with all trans conformation of the alkyl chains, according to CPK models), which is in accordance with a tilted arrangement of the molecules within the layers. This phase assignment was additionally confirmed by the switching behavior (see below).

As obvious from Table 1, the replacement of one aromatic H atom by F leads to a slight decrease of the mesophase stability of the $SmCP_A$ phases, whereby the isotropization temperature strongly depends on the position of the F atom. The smallest reduction of the mesophase stability in comparison to compound **1/2H** is found for compounds **1c** and **2c** ($\Delta T = 5-6$ °C), which have the F atom in the center of the biphenyl system, whereas in the case of compounds **1b** and **2b**, with the F atom neighboring the ester group, the mesophase destabilizing effect is especially strong ($\Delta T = 21-23$ °C). Also, the transition enthalpies are especially low (ΔH

ous $NaHCO_3$ solution (10 mL). $Pd(PPh_3)_4$ (0.6 g, 5 mol %) was then added. The mixture was refluxed for 6 h. The organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (3× 50 mL), and the combined organic layers were washed with brine and dried over Na_2SO_4. After evaporation of the solvent, the crude product was purified by column chromatography ($CHCl_3$) and crystallized from methanol. Yield: 1.9 g (71%). mp 63−65 °C δ_H ($CDCl_3$; 400 MHz): 7.28 (dd, J 8.6, 8.6, 1H, Ar−H), 7.09 (ddd, J 8.2, 8.2, 1.4, 1H, Ar−H), 6.98−6.89 (m, 2H, Ar−H), 6.76 (dd, J 8.4, 2.5, 1H, Ar−H), 6.71 (dd, J 11.7, 2.5, 1H, Ar−H), 3.90 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3). δ_C ($CDCl_3$; 100 MHz): 162.87, 160.97, 160.75, 157.93, 152.26, 148.12, 147.91, 147.32, 131.91, 131.86, 131.76, 124.37, 124.13, 123.65, 123.54, 122.85, 115.57, 115.25, 112.65, 112.62, 110.04, 109.98, 102.04, 101.52, 56.33, 55.58. δ_F ($CDCl_3$; 188 MHz): −112.60 (m), −137.79 (m). m/z (70 eV): 250 (100), 235 (20), 207 (24), 164 (10).
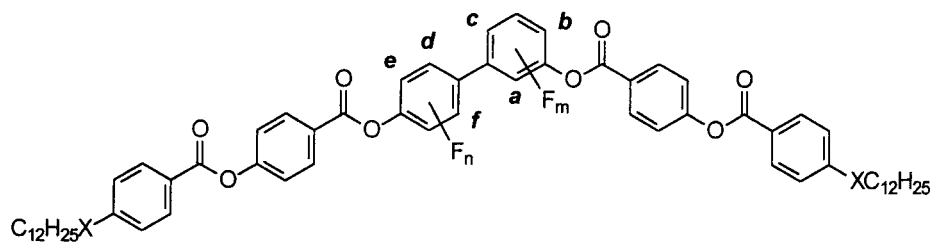
2,2′-Difluorobiphenyl-3,4′-diol 6ad. 5ad (1.5 g, 6.0 mmol) was dissolved in dry CH_2Cl_2 (15 mL). At 0 °C BBr_3 (2.6 mL, 27.6 mmol) was added via a syringe. The mixture was then stirred at room temperature for 24 h. Water was slowly added and the resulting solid was separated and crystallized from toluene. Yield: 1.3 g (97%). mp 171−172 °C (toluene). δ_H (acetone-d_6; 200 MHz): 8.91 (s, OH), 8.61 (s, OH), 7.24 (dd, J 8.6, 8.6, 1H, Ar−H), 7.09−6.94 (m, 2H, Ar−H), 6.85−6.74 (m, 2H, Ar−H), 6.69 (dd, J 11.7, 2.3, 1H, Ar−H). m/z (70 eV): 222 (100), 146 (10).

2,2′-Difluorobiphenyl 3,4′-Bis-4-(4-dodecyloxybenzoyl-oxy)benzoate 2ad. A suspension of **6ad** (0.2 g, 0.90 mmol), 4-(4-dodecyloxybenzoyloxy)benzoic acid **8** (0.86 g, 2.00 mmol), CMC (0.89 g, 2.10 mmol), and DMAP (60 mg, 0.44 mmol) in dry CH_2Cl_2 (20 mL) was stirred at 20 °C for 48 h. When the reaction was completed (TLC), the mixture was washed with water (50 mL). The aqueous phase was extracted with CH_2Cl_2 and the combined organic layers were dried over Na_2SO_4. After evaporation of the solvent, the product was purified by chromatography ($CHCl_3$) and then crystallized from ethyl acetate. Yield: 183 mg (41%). Transitions (°C): Cr 81 $SmCP_A$ 136 Iso. (Found: C, 73.73; H, 6.73%; $C_{64}H_{72}F_2O_{10}$ requires C, 73.97; H, 6.98%.) δ_H ($CDCl_3$; 400 MHz): 8.29 (d, J 8.6, 2H, Ar−H), 8.27 (d, J 8.8, 2H, Ar−H), 8.14 (d, J 8.8, 4H, Ar−H), 7.49 (dd, J 8.4, 8.0, 1H, Ar−H), 7.38 (d, J 8.8, 2H, Ar−H), 7.37 (d, J 8.6, 2H, Ar−H), 7.34−7.25 (m, 3H, Ar−H), 7.13 (d, J 9.6, 2H, Ar−H), 6.97 (d, J 8.4, 4H, Ar−H), 4.04 (t, J 6.5, 4H, OCH_2), 1.81 (q, J 7.4, 4H, CH_2), 1.46 (q, J 7.6, 4H, Ar−H), 1.37−1.26 (m, 32H, CH_2), 0.87 (t, J 6.8, 6H, CH_3). δ_C ($CDCl_3$; 100 MHz): 164.44, 164.15, 164.03, 163.65, 161.20, 158.69, 155.81, 153.07, 151.94, 151.84, 150.56, 139.03, 138.90, 132.54, 132.17, 132.00, 128.93, 126.49, 126.18, 124.62, 124.49, 124.17, 124.13, 123.83, 122.29, 122.25, 121.08, 121.04, 120.59, 120.44, 117.75, 117.72, 114.52, 110.41, 110.16, 31.82, 29.55, 29.53, 29.48, 29.45, 29.25, 29.24, 28.99, 25.87, 22.56, 13.96. δ_F ($CDCl_3$; 188 MHz): −111.69 (m), −130.18 (m).

Table 1. Phase Transition Temperatures (*T*/°C) and Corresponding Enthalpy Values (Δ*H*/kJ mol⁻¹, Lower Lines in Italics) of the Fluorinated Compounds 1 and 2 in Comparison to the Parent Nonfluorinated Compounds 1H and 2H[a]

Position of F	Comp.	X = single bond T/°C ΔH/kJmol⁻¹	Comp.	X = O T/°C ΔH/kJmol⁻¹
-	1H	Cr 78 SmCP$_A$ 156 Iso *6.3 20.7*	2H	Cr 106 SmCP$_A$ 159 Iso *19.3 23.2*
a	1a	Cr 95 SmCP$_A$ 148 Iso *7.6 24.7*	2a	Cr 120 SmCP$_A$ 148 Iso *32.4 24.7*
b	1b	Cr 99 SmCP$_A$ 135 Iso *25.0 15.6*	2b	Cr 110 SmCP$_A$ 136 Iso *48.9 14.4*
c	1c	Cr 110 SmCP$_A$ 151 Iso *23.6 25.6*	2c	Cr 115 SmCP$_A$ 153 Iso *22.1 25.2*
d	1d	Cr 111 SmCP$_A$ 148 Iso *18.1 24.7*	2d	Cr 103 SmCP$_A$ 146 Iso *23.2 24.2*
e	1e	Cr 75 SmCP$_A$ 143 Iso *10.6 20.6*	2e	Cr 88 SmCP$_A$ 137 Iso *15.3 18.9*
a, d	1ad	Cr 104 SmCP$_A$ 135 Iso *11.8 25.9*	2ad	Cr 81 SmCP$_A$ 136 Iso *26.1 25.1*
a, e	1ae	Cr 104 SmCP$_A$ 134 Iso *8.3 22.4*	2ae	Cr 80 SmCP$_A$ 135 Iso *25.3 26.1*
c, d	1cd	Cr 104 SmCP$_A$ 133 Iso *32.0 23.1*	2cd	Cr 114 Col$_r$ 134 Iso *22.2 21.3*
c, e	1ce	Cr 83 SmCP$_{(A)}$ 129 Iso *19.4 21.6*	2ce	Cr 74 Col$_r$ 141 Iso *59.8 21.6*
d, f	1df	Cr 90 SmCP$_{(A)}$ 134 Iso *17.9 25.0*	2df	Cr 85 SmCP$_{(A)}$ 129 Iso *24.7 19.5*
a, b	1ab	Cr 135 (M 114) Iso *46.9*	2ab	Cr 140 (M 106) Iso *50.3*
a, b, d	1abd	Cr 121 (SmCP$_A$ 117) Iso *36.7*	2abd	Cr 114 (Col$_r$ 108) Iso *50.1 13.8*
a, b, e	1abe	Cr 119 (SmCP$_A$ 99) Iso *41.0*	2abe	Cr 126 (Col$_r$ 104) Iso *49.8*
d, e	1de	Cr 81 SmCP$_A$ 118 Col$_r$ 121 Iso *12.7 17.0[b]*	2de	Cr 98 Col$_r$ 135 Iso *25.0 17.7*
a, d, e	1ade	Cr 95 SmCP$_A$ 121 Iso *25.0 19.0*	2ade	Cr 103 Col$_r$ 120 Iso *15.6 14.5*
c, d, e	1cde	Cr 128 (Col$_r$ 121) Iso *49.7*	2cde	Cr 100 Col$_r$ 129 Iso *39.2 51.2*

[a] Abbreviations: SmCP$_A$ = antiferroelectric polar smectic C phase (see Figure 1); SmCP$_{(A)}$ = polar smectic phases characterized by the occurrence of three distinct peaks in a half period of the switching current curve; Col$_r$ = rectangular columnar phase (see Figure 4d). Values in parentheses refer to monotropic (metastable) mesophases. [b] Total of the SmCP$_A$−Col$_r$ and Col$_r$−Iso transition.

= ca. 15 kJ mol⁻¹) for compounds **1b** and **2b**. The transition enthalpies of all other SmCP$_A$ isotropic transitions are in the range between 19 and 25 kJ mol⁻¹.

The stability of the SmCP$_A$ phases is further reduced by increasing the number of F atoms. Again, the mesophase destabilization is especially strong if one of the F atoms is placed beside the ester group (position b). Such compounds (**1ab** and **1abe**) are only monotropic. In the case of compounds **1ab** and **2ab** the crystallization is so fast that it was not possible to certainly

determine the mesophase type (which are therefore designated as M in Table 1).

Additionally, for many of the alkoxy-substituted compounds with two or three fluoro substituents, the SmCP$_A$ phases are replaced by columnar phases. The textures of these columnar phases are very characteristic and typical for a special type of rectangular columnar phases (Col$_r$, B$_1$ phases,[18] see for example Figure 4a,b). Such phases have also been found for the shorter homologues of **1H** and **2H**[27] as well as for other
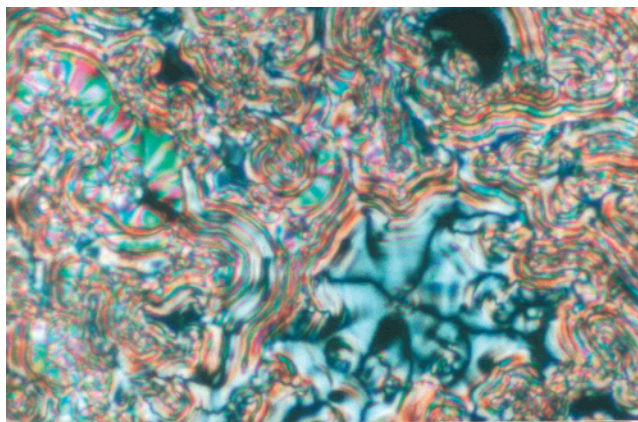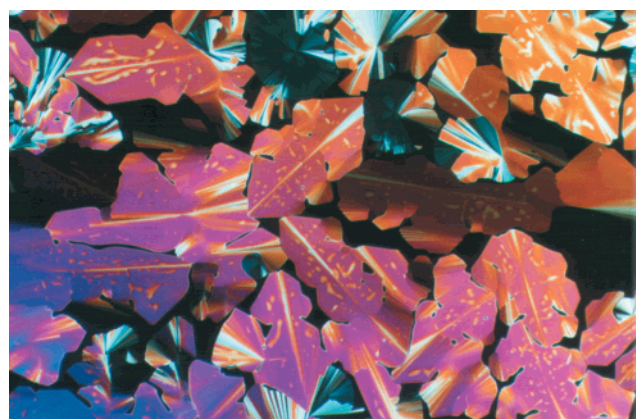
Figure 3. Optical photomicrograph (crossed polarizers) of the SmCP$_A$ phase of compound **1cd** as obtained by cooling from the isotropic liquid at 123 °C.

bent-core molecules.[40] These columnar phases have recently been investigated by means of X-ray scattering with aligned samples and it was shown that they are built up of ribbons of parallel aligned and nontilted bent-core molecules as shown in Figure 4d.[27,40] The bending direction of molecules in neighboring ribbons is anti-parallel. In this way the dipoles can cancel out from ribbon to ribbon, and the system can efficiently escape from a macroscopic polar order. The powder-like pattern

(Guinier) of the mesophase of **1cde**, as a representative example, is characterized by a diffuse scattering in the wide-angle region ($d = 0.45$ nm, corresponding to the fluid alkyl chains) and two sharp reflections in the small-angle region at $d_1 = 3.62$ (02) and $d_2 = 2.51$ (11). The lattice constants, calculated on the basis of a rectangular cell, amount to $a = 5.22$ nm and $c = 5.02$ nm. These parameters are in good agreement with the values obtained for the Col$_r$ phases occurring in the homologous series of compounds **1H** and **2H**. Also in line with the observations made in the series of compounds **1H** and **2H**[27] is the preferred occurrence of the columnar mesophases in the series of alkoxy-substituted compounds, whereas they are more disfavored in the alkyl-substituted series. Additionally, the tendency to form these Col$_r$ phases increases with a rising number of F atoms, but also the substitution pattern has a significant influence on the mesophase type. Especially alkoxy-substituted compounds **2** with a 2,3-substitution pattern (substituents in the positions d and e as in compounds **2cde**, **2ade**, and **2de**) and di- and trifluorinated compounds with F atoms in position c (compounds **2cd**, **2ce**, and **2cde**) have a strong tendency toward formation of columnar phases. If both substitution patterns, which prefer the formation of Col$_r$ phases, are combined in one molecule, that is, if the 2,3-substitution pattern (positions d and e) is combined with the fluoro substitution in position c, then even the alkyl-substi-
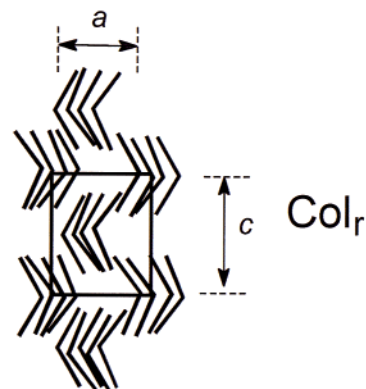

a)

c)
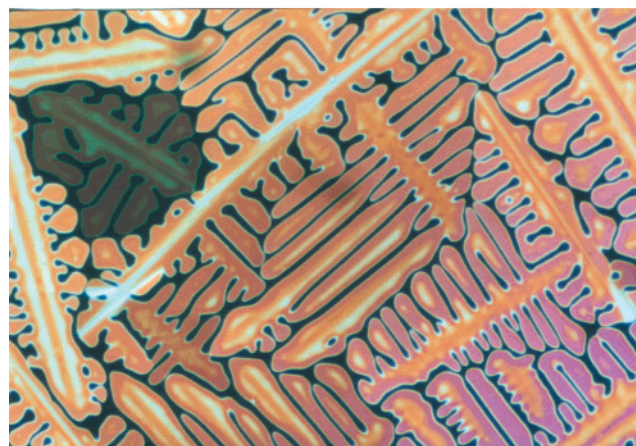
b)

d)

Figure 4. Optical photomicrographs (crossed polarizers) of the Col$_r$ phases as obtained by cooling from the isotropic liquid: (a) compound **2ce** at 136 °C; (b) compound **2de** at 135 °C; (c) compound **2abd** at 105 °C; and (d) model of the organization of the bent-core molecules in the Col$_r$ phases.

tuted compound (compound **1cde**) shows a (monotropic) columnar mesophase. It seems that the dipole moments have a significant impact on the formation of these columnar phases. In the molecules with a 2,3-disubstitution pattern the dipole moments of the two F atoms are fixed with respect to each other, so that they should efficiently enhance each other. In the compounds with the F atoms in position c the fluorine dipole moment gives always a component in the same direction as the molecular bent. It is known that in 2,2′-difluorobiphenyl the *syn*-rotamer is energetically favored over the *anti*-rotamer by 0.8 kJ mol^{-1}.[41] Therefore, in these molecules the F dipole should not be canceled by adoption of an antiperiplanar alignment with the F dipole(s) at the neighboring phenyl rings (in positions c and d). Hence, it seems that an increased dipole moment within the aromatic core region, especially if it is directed in the same direction as the bent of the aromatic core, favors the formation of columnar phases and disfavors the fluid smectic SmCP$_A$ phase. This makes some sense because the special ribbonlike arrangement within the columnar phases should allow a better compensation of the local dipole moments.

Compound **1de** shows two different liquid-crystalline phases. Upon cooling from the isotropic liquid state, at first the typical texture of the Col$_r$ phase occurs, and upon further cooling, the transition of this Col$_r$ phase into the SmCP$_A$ phase takes place. Additionally, in the temperature region of the Col$_r$ phase of this compound not only the typical textures, as shown in Figure 4a,b occur, but also the region with a gray spherulitic texture can be seen (Figure 4c). Because this texture is always accompanied by the typical texture of the Col$_r$ phase, the question remains open if it indicates the occurrence of another (columnar) mesophase or if it is a special variant of the texture of the Col$_r$ phase.

B. Electro-optical Investigation. Electro-optical investigations were performed in 4- and 6-μm polyimide-coated and 5-μm noncoated ITO cells ($A = 1$ cm^2). The cells were filled in the isotropic state by means of capillary forces. The switching process was studied after slow cooling (1 K min^{-1}) the sample from the isotropic phase to the mesophase without an external field. At a temperature of about 10 K below the clearing point, a triangular voltage ($f = 7-9$ Hz) was applied. At lower voltage (<80 V) only one switching current peak could be detected. At higher triangular voltage (80−120 V) a second peak became visible and grew sharper with rising voltage (see Figure 5a). The appearance of two sharp peaks during a half-period indicate an antiferroelectric switching process and confirms the SmCP$_A$ structure of the smectic mesophases.[4] The spontaneous polarization determined by integration of the switching current peaks amounts to between 700 and 2300 nC cm^{-2} ($\pm10\%$). These values are higher than those of the nonsubstituted parent compounds (400−700 nC cm^{-2}).[27] The highest value (2300 nC cm^{-2}) was found for compound **1c** with the F substituent at the 1,3-disubstituted benzene ring, positioned neighboring to the attached phenyl ring. This is the highest value of a
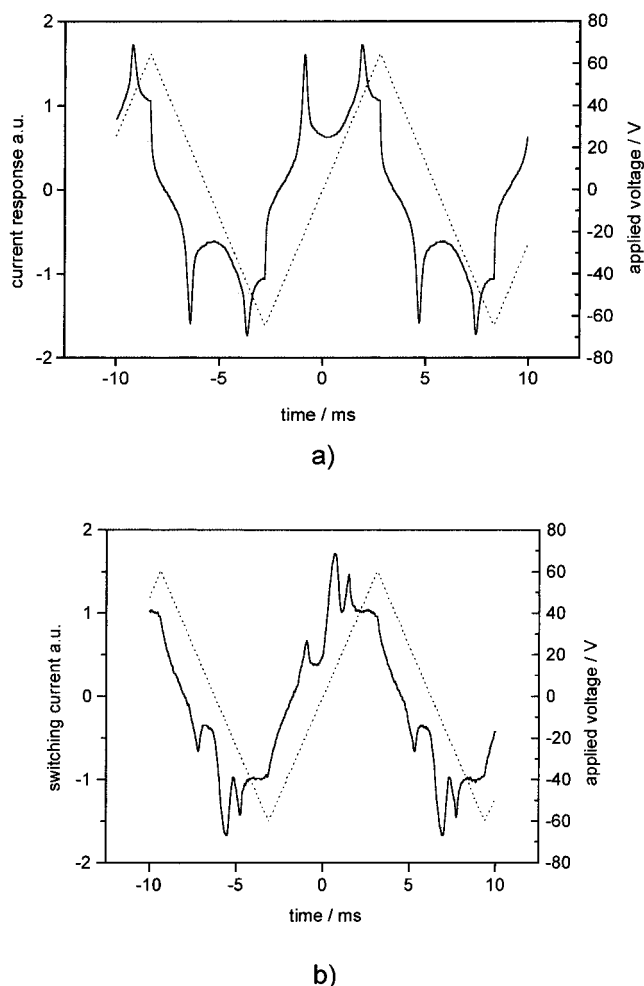
(40) Watanabe, J.; Niori, T.; Sekine, T.; Takezoe, H. *Jpn. J. Appl. Phys.* **1998**, *37*, L139.
(41) Aldridge, B.; De Luca, G.; Edgar, M.; Edgar, S. J.; Emsley, J. W.; Furby, M. I. C.; Webster, M. *Liq. Cryst.* **1998**, *24*, 569.

a)

b)

Figure 5. Switching current response (a) in the SmCP$_A$ phase of compound **2ad** obtained by applying a triangular voltage (Vpp = 130 V, f = 9 Hz, T = 125 °C) and (b) in the SmCP$_{(A)}$ phase of **1df** (Vpp = 120 V, f = 9 Hz, T = 116 °C).

spontaneous polarization ever observed for an achiral bent-core molecule. The isomeric compounds **1a** and **1b** with the fluorine atoms in other positions (neighboring the carboxyl groups) have significantly lower values of the spontaneous polarization (700 respectively 900 nC cm^{-2}). Interestingly, also the type of terminal chain has a large impact. Hence, the spontaneous polarization of the alkoxy-substituted compound **2c** amounts only to 1300 nC cm^{-2}, which is nearly a half of the value of **1c** with the alkyl chains directly attached to the aromatic core. In contrast, the alkoxy-substituted compounds **2a** (1000 nC cm^{-2}) and **2b** (1200 nC cm^{-2}) have higher values than the alkyl-substituted analogues. This shows that the situation is quite complex and cannot be explained solely on the basis of the molecular dipole moments.

Whereas compounds **1** and **2**, which have F atoms exclusively at the 1,3-substituted benzene ring, show a typical antiferroelectric switching behavior characterized by the occurrence of two polarization current peaks, the situation becomes more complex for compounds with F atoms at the 1,4-substituted phenyl ring of the biphenyl unit. In the case of compound **2e** a small additional peak can be reproducibly found between the two polarization current peaks corresponding to the antiferroelectric switching process. This third peak

Table 2. Values of the Spontaneous Polarization (P_S/nC cm^{-2}) of Selected Compounds Measured $\approx$10 °C below the Clearing Temperature

compd	P_S/nC cm^{-2}	compd	P_S/nC cm^{-2}
1a	700	**2a**	1000
1b	900	**2b**	1200
1c	2300	**2c**	1300
1d	1400	**2d**	1000
1ad	1100	**2ad**	1200
1ae	1200	**2ae**	1000
1df	1100	**2df**	1100

becomes very strong for compounds **1ce**, **1df**, and **2df** (see for example Figure 5b). It appears independent of the switching frequency above a certain voltage, grows sharper with increasing voltage, and disappears together with the two other peaks at the transition to the isotropic state. A possible explanation could be that regions with antiferroelectric and regions with ferroelectric SmCP phases are coexisting under the experimental conditions. It should be mentioned that only the two polarization current peaks corresponding to the antiferroelectric switching process were used for the calculation of the spontaneous polarization given in Table 2.

The switching process was additionally observed between crossed polarizers. In the cases of samples **2e**, **1df**, and **1ce** well-developed focal conic domains could easily be obtained by applying a voltage of 20 V during cooling (0.5 K min^{-1}) from the isotropic liquid state. Figure 6b shows a well-developed focal conic texture obtained as described above with compound **1ce** after removal of the electric field. By application of an electric field, the birefringence increases and some orthogonal extinction brushes rotate clockwise respectively anticlockwise with reversal of the polarization of the applied field as shown in parts a and c of Figure 6. Brushes of different domains rotate in the same direction or in the opposite direction. This type of switching behavior is indicative of regions with supramolecular homogeneous chiral antiferroelectric SmC$_A$P$_A$ structure with opposite handedness. However, most of the extinction crosses do not rotate by changing the polarization of the electric field, which is characteristic for the supramolecular racemic SmC$_S$P$_A$ arrangement.[7] So in the SmCP$_A$ phases of the compounds under discussion the homogeneous chiral and the racemic ground state are coexisting under our experimental conditions. In this respect the fluorosubstituted compounds are different from the parent compounds **1H** and **2H** for which the homochiral ground state is predominating.[27]

As mentioned above, some of the fluorinated compounds show three peaks in the polarization current curve, which points to an additional ferroelectric switching process (compounds **1df** and **1ce**). Surprisingly, however, also these compounds show essentially the same switching behavior between crossed polarizers as **2e** with only two peaks. None of these compounds show domains with a bistable switching as required for a ferroelectric switching process of homogeneous chiral
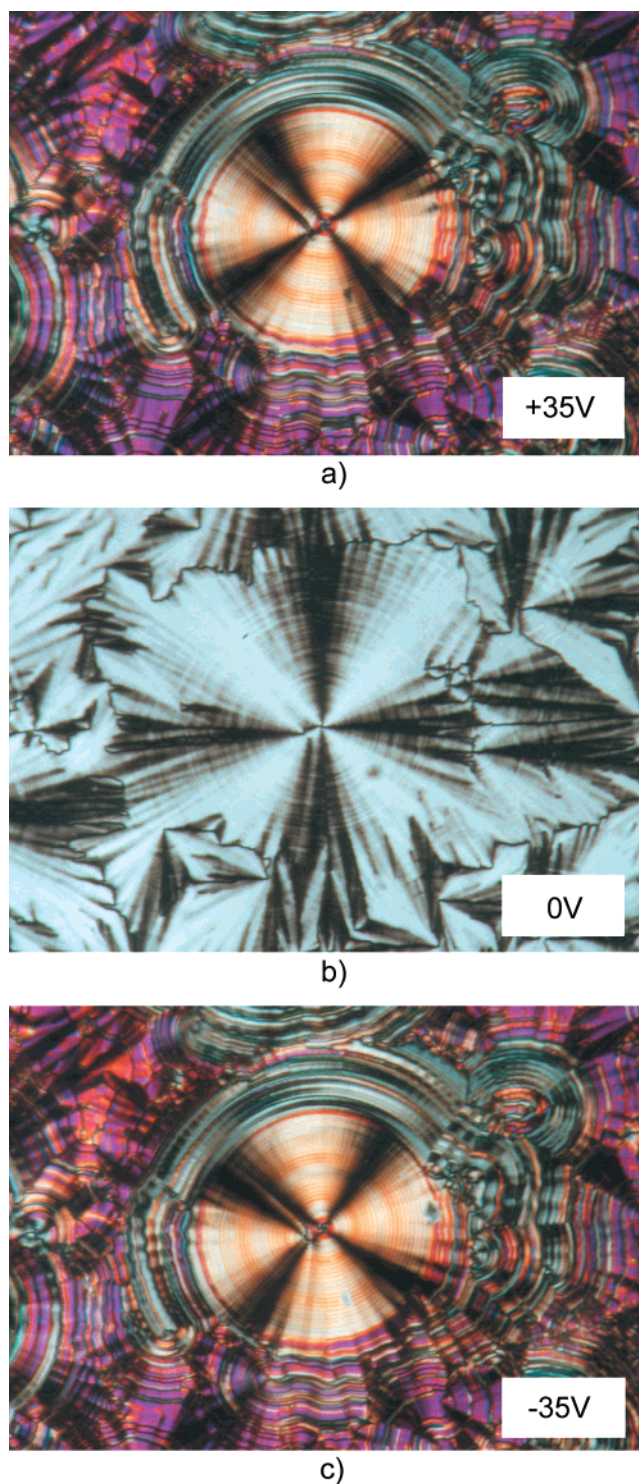
(42) (a) Salfetnikova, J.; Zhuchkova, T.; Dantlgraber, G.; Tschierske, C.; Kresse, H. *Liq. Cryst.* **2002**, *29*, 155. (b) Kresse, H.; Salfetnikova, J.; Tschierske, C.; Dantlgraber, G.; Zhuchkova, T. *Liq. Cryst.* **2001**, *28*, 1575.

Figure 6. Rotation of an extinction cross in the mesophase of compound **1ce** upon application of an electric field (polyimide-coated ITO cell, sample thickness 6 μm, $T = 125$ °C). The brightness of each image was separately scaled, which means that in reality the birefringence of (b) is significantly lower than those of (a) and (c).

SmC$_S$P$_F$ domains. Probably the ferroelectric domains have the racemic SmC$_A$P$_F$ structure. These domains should not rotate by reversal of the electric field and, hence, some of the nonrotating domains could represent such SmC$_A$P$_F$ domains.[10] However, this could not be unambiguously proven, so the occurrence of the third peak in the polarization current curve requires ad-

ditional detailed investigations, which will be reported in separate papers.[42]

Supporting Information Available: Experimental procedures, elemental analyses data, and ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra of all reported compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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