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F. G. Tournilhac[a]; L. Bosio[a]; J. Simon[a]; L. M. Blinov[b]; S. V. Yablonsky[b]
[a] ESPCI, Paris, Cedex 05, France [b] Institute of Crystallography, Russian Academy of Science, Moscow, Russia

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Synthesis of polyphilic compounds
Evidence for ferroelectricity in a non-chiral mesophase

by F. G. TOURNILHAC*, L. BOSIO and J. SIMON
ESPCI, 10 rue Vauquelin, 75231 Paris Cedex 05, France

L. M. BLINOV and S. V. YABLONSKY
Institute of Crystallography, Russian Academy of Science,
Leninsky Prospect 59, 117333, Moscow, Russia

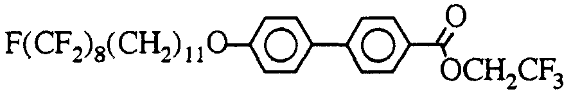
The synthesis and properties of new mesomorphic ferroelectrics composed of nonchiral polyphilic molecules are described. Polyphilic molecular units are made up of a sequence of chemical fragments differing by their chemical nature. The segregation between unlike species is used to favour a polar packing. Ferroelectricity is demonstrated by the measurement of an acoustically induced piezoelectric response and the determination of repolarization currents. It is the first time that a ferroelectric repolarizable mesophase is obtained with non-chiral molecular units. The mechanism of ferroelectricity is therefore different from that found in conventional chiral smectic C.

1. Introduction

The normal tendency of rod-like molecules having a strong dipole moment along their long axes is to form head to tail dimers. When attempting to build a *longitudinal* ferroelectric mesophase in which the polar axis is parallel to the director, it is therefore necessary to overcome this antiparallel coupling by another type of interaction.

Self assembly is one of the possible ways to induce novel supramolecular structures. In this way, the amphiphilic character is one of the parameters permitting us to predict the type of organization for both thermotropic and lyotropic mesogens [1]. Amphiphilic molecules consist of two fragments differing by their chemical nature, for example, hydrophilic/hydrophobic, stiff/flexible, aliphatic/polyaromatic, polar or polarizable/non-polar or non-polarizable.

In the condensed state, fragments of the same chemical nature locate in homogeneous microdomains inducing various types of organization: cylinders, lamellae, vesicles, etc. In polyphilic molecules, three or more chemically different fragments can also segregate resulting in the formation of smectic mesophases; furthermore, a judicious sequence may induce a polar order in the layers provided that all intermolecular affinities are satisfied [2–4]. The polyphilic compounds **I** and **II** have been synthesized from a biphenyl rigid core, an alkyl chain and two perfluorinated ends. Compounds **I** and **II** differ from each other by the direction of their longitudinal dipoles, since the ether and ester linkages have been exchanged



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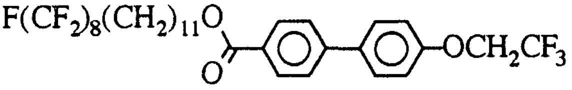

II

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* Author for correspondence.

2. Synthesis

The polyphilic mesogens **I** and **II** were obtained in seven steps starting from commercially available products. Semifluorinated long chain synthons could be prepared by 1,2 addition of perfluoroalkyl iodide R_FI ($R_FI = n\text{-}C_mF_{2m+1}I$) on an ω-alkene followed by reduction [5]

$$R_FI + CH_2{=}CH{-}(CH_2)_{n-2}{-}OH \xrightarrow{\text{AIBN}} R_F{-}CH_2{-}CHI{-}(CH_2)_{n-2}{-}OH,$$

$$R_F{-}CH_2{-}CHI{-}(CH_2)_{n-2}{-}OH \xrightarrow{\text{Zn/H}^+} R_F{-}(CH_2)_n{-}OH.$$

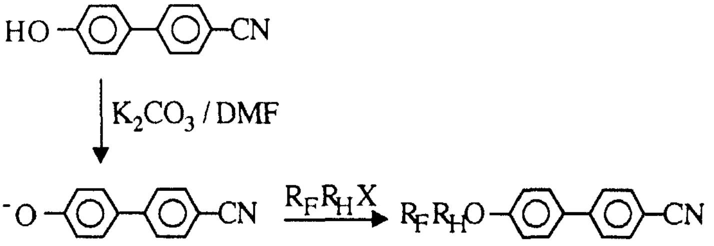
For $n \geqslant 4$, $R_F(CH_2)_nOH$ behaves like a normal primary alcohol and can be interacted with HBr:

$$R_F{-}R_H{-}OH \xrightarrow{\text{HBr/H}_2\text{SO}_4} R_F{-}R_H{-}Br.$$

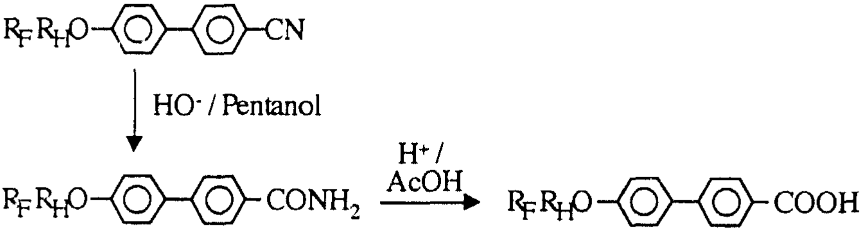
For short alkyl spacers ($n < 4$), perfluoroalkyl sulphonate activation is preferred [6]:

$$R_F{-}CH_2{-}OH \xrightarrow{C_4F_9SO_2F} R_F{-}CH_2{-}O{-}SO_2{-}C_4F_9.$$

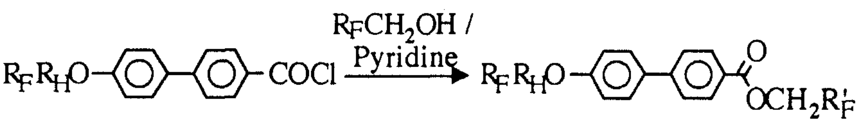
Both compounds can be reacted with the 4-cyano-4′-hydroxybiphenyl in a basic medium



The long chain cyano-derivative was hydrolysed to the amide with NaOH in pentanol and transformed into the corresponding acid with HCl/AcOH. Ultrasonication is necessary in the first step to overcome the water-repellent effect of the perfluorinated chain.



The acid derivative is finally transformed into the corresponding acid chloride using $SOCl_2$/toluene and reacted with the desired alcohol to give the products **I** and **II**



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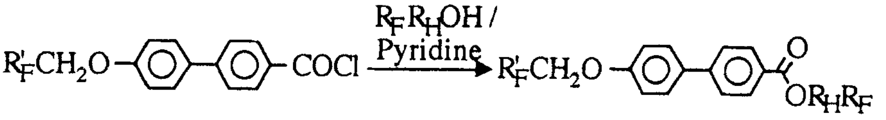


II

3. Mesomorphic properties

On cooling from the isotropic phase, compounds **I**, **II** and their mixtures all show a smectic A mesophase as indicated by the appearance of focal-conic and homeotropic textures. This mesophase is monotropic for compound **II**. In all cases, the lamellar spacing is found by X-ray diffraction to be equal to the length of the molecule (42 Å). The transition temperatures detected by DSC are reported in the table.

Transition temperatures observed by DSC for the compounds **I**, **II** and the mixture 70 wt% **I**, 30 wt% **II** (**M70**). Monotropic phases are indicated in parentheses.

Compound	C		S_X or $S_{X'}$		S_A		I
I	●	95°C	(●	92°C)	●	113°C	●
II	●	109°C	(●	88°C	●	95°C)	●
M70			●	82°C	●	105°C	●

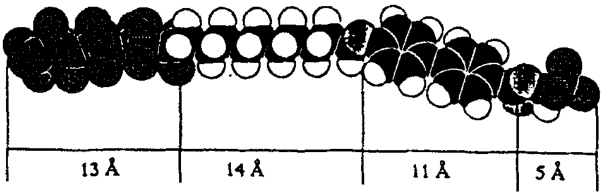
At lower temperatures, an ordered smectic mesophase is observed. For the pure compounds, the low-temperature mesophase (abbreviated smectic X) is monotropic. Its appearance is detected by a striation of the focal conics and a milky aspect in the homeotropic texture. For the mixture **M70** (70 wt% **I**: 30 wt% **II**), both homeotropic and focal-conic textures similar to those of the smectic A phase could be observed in the ordered mesophase (noted smectic X′); this indicates a uniaxial character. The birefringence decreases dramatically at the transition from the smectic A to the smectic X′ phase. Smectic X′ is enantiotropic and stable down to room temperature. X-ray diffraction shows three narrow reflections with Bragg spacings in the ratio 1:2:3 indicating a lamellar organization (interlayer distance: 33 Å); at wide angles, a slightly diffuse ring with a maximum at about 4·5 Å and two rather sharp lines with comparable intensities at 4·8 Å and 4·4 Å are detected.

The interlayer spacing is therefore smaller than the length of the molecule and a tilted arrangement must be postulated. In the plane of the layers, all directions of tilting must be equiprobable to account for the uniaxial character. 4·8 and 4·4 Å can be related to the typical average distances between two perfluorinated chains [7–10] and between two hydrocarbon chains respectively. If we assume a segregated and quasihexagonal packing of these moieties, this would correspond to a cross section of 27 Å^2 for the perfluorinated chains and 22 Å^2 for the hydrocarbon chains. In order to match the area occupied by each part in the layer plane, the perfluorinated and hydrocarbon fragments must be differently tilted [3, 11] resulting in a *zig-zag* conformation (see figure 1).

The tilt angle θ of each part can be calculated

$$l_F \cos\theta_F + l_H \cos\theta_H + l_\phi \cos\theta_\phi = d,$$

$$\sigma_F/\cos\theta_F = \sigma_H/\cos\theta_H = \sigma_\phi/\cos\theta_\phi,$$



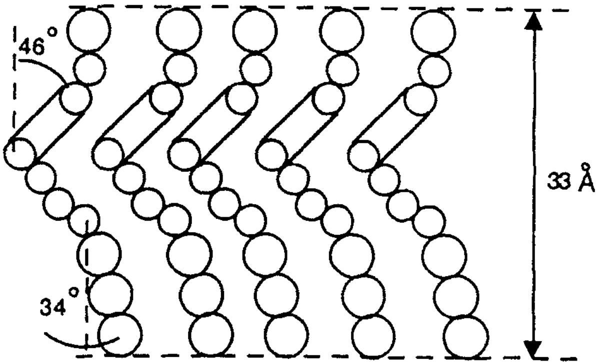


Figure 1. (*a*) Molecular model of the polyphilic compound **I**. The dimensions of the various fragments are indicated. (*b*) Structure proposal for the ordered smectic mesophase formed by the mixture **M70**. The various fragments are differently tilted, according to their different cross sections.

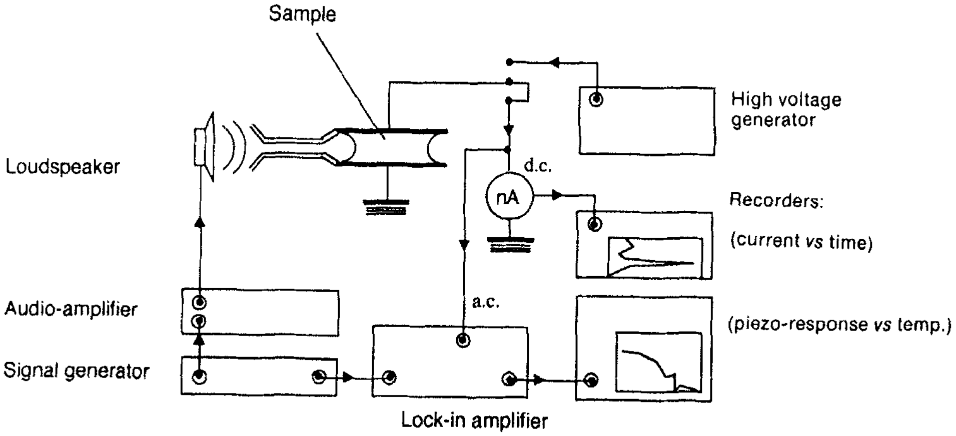


Figure 2. Experimental set up for the determination of the piezoelectric response and repolarization current of mesomorphic material.

where l_F, l_H, l_ϕ, σ_F, σ_H, σ_ϕ are the lengths and cross sections of the perfluorinated, alkyl and biphenyl fragments, respectively. With this model, tilt angles of 34° for the perfluoroalkyl chains and 46° for the biphenyl and alkyl chains are found (the approximation $\sigma_H = \sigma_\phi$ has been used). The large value found for the biphenyl group, which represents the main contribution to the dielectric anisotropy is consistent with the weak birefringence (the birefringence would be zero at the angle $\arccos(1/\sqrt{3}) = 54{\cdot}7°$).

4. Ferroelectric properties

A high piezoelectric response is one of the characteristic properties of a ferroelectric. The equipment necessary to measure the piezoelectric response is schematically represented in figure 2, and a full description can be found in [12, 13]. A drop of a substance was placed into a flat capillary formed by two glasses covered with SnO_2 optically transparent electrodes. Piezoelectricity is induced by a mechanical distortion of the material due to the AC air flow generated by a loudspeaker. The cell is placed in a thermostat and the optical texture of the substance can be observed with a polarizing microscope. Alternatively a change of the overall dipole orientation in the material generates a current (repolarization current) in the external circuit; integration of the repolarization currents allows one to calculate the spontaneous polarization.

With the mixture **M70**, the amplitude of the piezoelectric signal is three orders of magnitude higher than the response obtained with non-ferroelectric substances; it is within the range of the signals generated by S_C^* reference materials with spontaneous polarizations ranging from 3 to 100 nC cm^{-2}. On heating, the piezovoltage associated with the mixture **M70** decreases. Around 75°C, the application of a DC pulse across the sample results in a high piezo-response which rapidly decreases to a non-zero value. The magnitude of the remnant signal increases with the duration of the pulse. At 75°C, the characteristic repolarization time is around 5 s. The plot of the piezo-response against the poling voltage shows a hysteresis loop typical of a ferroelectric (see figure 3).

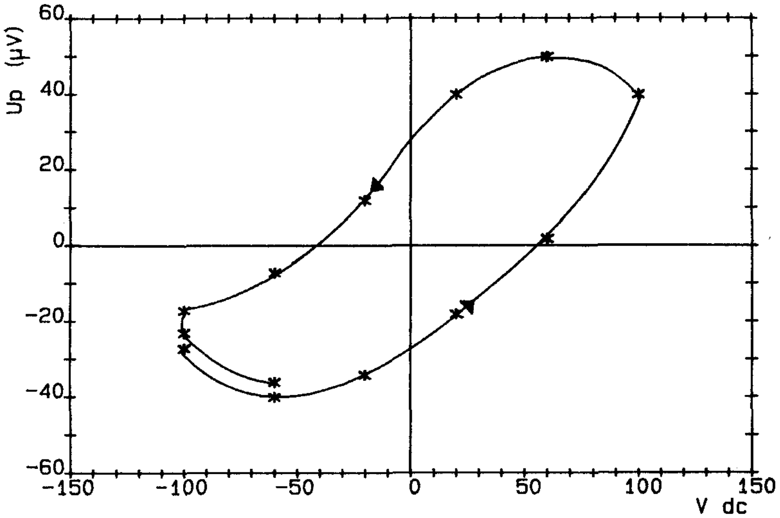


Figure 3. Hysteresis loop for the piezoelectric signal obtained at 75°C for the X′ phase of the mixture **M70**. Each point of the loop is taken after application of a 10 s poling pulse of the corresponding voltage and 1 min relaxation of the signal.

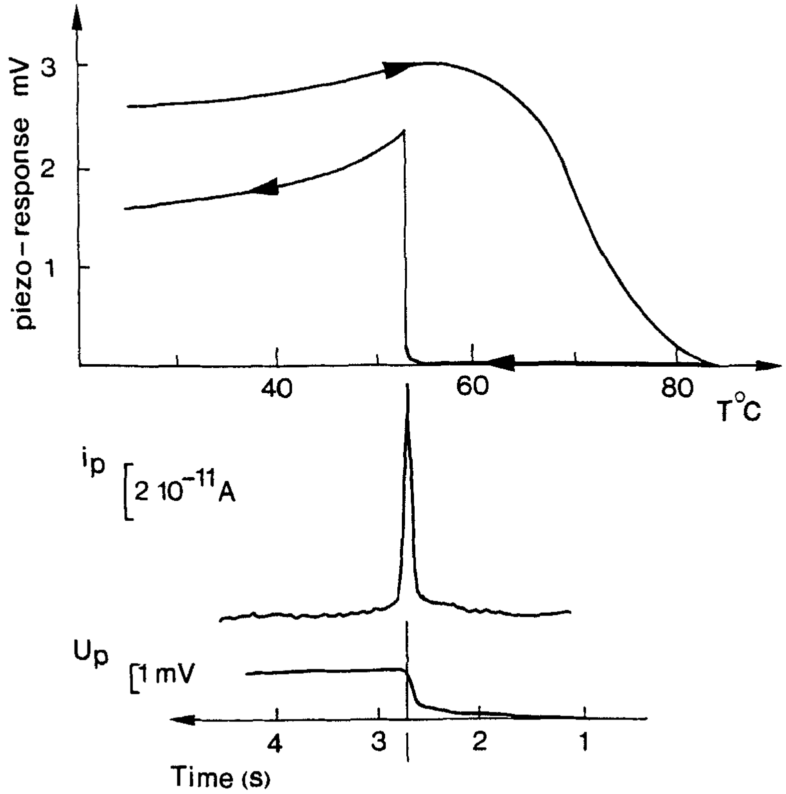


Figure 4. The temperature behaviour of the piezoelectric response during heating of the spontaneously polarized mixture **M70** and the subsequent cooling cycle. The spontaneous transition to the polar state occurs in the smectic X′ phase at $T = 53°C$. The associated jump of the piezo-response $U_p(t)$ and the corresponding pulse of the repolarization current $i(t)$ flowing through the electrometric amplifier (fast feedback mode) are shown below the first curve.

However, for this field-induced effect, it was not possible to determine the repolarization current which overlapped with the current due to the drift of ionic impurities.

When entering into the smectic A phase, the piezo-response vanishes. On cooling, the piezo-response reappears, not at the transition to the smectic X′ (75°C), but *in* the smectic X′ stability domain around 50°C. This spontaneous repolarization occurs even without any field ever having been applied. The appearance of the polar state is detected by sharp steps (from one to five) of the piezoelectric voltage accompanied by narrow peaks of the repolarization current (see figure 4). No change in the optical texture of the X′ phase can be detected after the spontaneous transitions. The sign of the current pulses correlates with the sign of the corresponding piezovoltage steps. The spontaneous polarization P_S at the transition can be calculated by integrating the area under the $i(t)$ curve knowing the area of the material drop. For mixture **M70**, the observed P_S values are in the range 1–1·5 nC/cm^2 (for U_p signals 2–3 mV). At room temperature, spontaneously repolarized samples show a stable piezoelectric response.

Other characteristic properties of ferroelectric materials have been determined. Firstly, optical second harmonic generation [14] (1·06 μm) has been observed for unoriented samples of **M70**, and secondly the dielectric constant ε of homeotropically oriented samples shows a sharp maximum at the transition $S_{X'}$–S_A; this is indicative of a ferroelectric transition [15].

5. Experimental

2,2,2-trifluoroethyl perfluorobutyl sulphonate. Using the procedure of Hansen [6], 18·4 g (60·9 mmol) of perfluorobutyl sulphonyl fluoride were dissolved in 300 ml of dichloromethane previously dried over neutral aluminium oxide (Merck 90, activity I) and cooled down to −50°C under nitrogen in a 1 l three necked flask. Then 8·1 g (80·0 mmol) of freshly distilled triethylamine and 8·1 g (81·0 mmol) of 2,2,2,-trifluoroethanol (Aldrich) were added slowly at −40°C. The mixture was then heated to 0°C. The reaction mixture was washed with 200 ml of HCl solution (5 per cent), 200 ml of 5 per cent NaOH and twice with 200 ml of water. The organic phase was dried over Na_2CO_3, the solvent was removed, and the product distilled (60°C at 500 Pa). Yield = 52 per cent. IR (neat): 1433, 1355, 1290, 1244, 1203, 1145, 1035, 964, 792, 737, 700 cm^{-1}. ^1H NMR ($CDCl_3$, TMS): 4·82 (triplet, $J = 12{\cdot}6$ Hz).

10-iodo,12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,19-heptadecafluorononadecan-1-ol. 3·4 g (20 mmol) of 10-undecenol (Aldrich) and 10·9 g (20 mmol) of perfluorooctyl iodide were stirred under reflux in 15 ml of dry heptane under nitrogen. Azo-*bis*-isobutyronitrile (Merck) was added every 5 min in portions of approx. 20 mg during 30 min. The reaction mixture was kept 1 h under reflux after completion of the addition and the solvent was evaporated. The residue was filtered on silica (Merck 63–200 mm) with dichloromethane and ether as eluents. The product was recrystallized from acetonitrile. Yield = 73 per cent, mp = 46°C (other transition at 36°C). Elemental analysis, calculated: C = 31·86, H = 3·10, I = 17·72 per cent. Found: C = 31·88, H = 2·97, I = 17·71 per cent ^1H NMR (CCL_4, TMS): 1·33–1·73 (broad, 16 H, CH_2), 2·55 (broad, 1 H, OH), 2·5–3·1 (multiplet, 2 H, OCH_2), 4·28 (quintuplet, 1 H, CHI).

12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,19-heptadecafluorononadecan-1-ol. 4·5 g (628 μmol) of the precursor iodo-compound were dissolved in a mixture of 100 ml of *n*-propanol and 175 ml of *iso*-octane and heated at 100°C. 2 g of zinc powder were added with stirring. HCl gas was then injected into the mixture. After dissolution of the metal (several hours), the reaction mixture was filtered through paper and evaporated. Shaking with water gave a white solid which was collected on a sinter, thoroughly washed with water and dried under vacuum; it was then redissolved in hot acetonitrile, filtered and recrystallized. Yield = 83 per cent, mp = 82°C. IR (KBr): 3384, 2921, 2853, 1471, 1372, 1334, 1206, 1152, 1118, 1053, 704, 658, 561, 530 cm^{-1}. Elemental analysis, calculated: C = 38·66, H = 3·93, OH = 2·88 per cent. Found: C = 38·94, H = 3·90, OH = 2·91 per cent. ^1H NMR ($CDCl_3$, TMS): 1·27 (broad, > 20 H, $CH_2 + OH$), 3·61 (triplet, $J = 6$ Hz, 2 H, CH_2OH). ^{13}C NMR ($CDCl_3$, TMS): 20·14 (broad, $C^{10}H_2$), 25·76 (C^3H_2), 29·12 (CH_2), 29·20 (CH_2), 29·42 (CH_2), 29·55 (CH_2), 29·71 (CH_2), 30·64 (triplet, $C^{11}H_2$), 32·84 (C^2H_2), 63·04 (C^1H_2), 106·5–122·58 (multiplet, CF_2 and CF_3).

1-bromo-12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,19-heptadecafluorononadecane. 14 g of concentrated sulphuric acid were poured into 42 g (244 mmol) of hydrobromic acid (47 per cent). 8·2 g (13·9 mmol) of the precursor polyfluorinated alcohol were added and the mixture was heated at 130–140°C for 3 h without stirring. After cooling, the mixture was poured into 100 ml of cold water. The aqueous phase was extracted with dichloromethane and washed with sulphuric acid, twice with water, once with a sodium thiosulphate solution and again with water. After filtration on silica, the solvent was evaporated. The melting point of the yellowish solid obtained was insensitive to further purification. Yield: 86 per cent, mp = 38°C. IR (KBr): 2922, 2853, 1472, 1372, 1334, 1248, 1213, 1148, 1116, 1050, 950, 722, 704, 656, 561, 531 cm^{-1}. Analysis, calculated: C = 34·93, H = 3·39 per cent. Found: C = 34·89, H = 3·18 per cent. ^1H NMR (CCl_4, TMS): 1·33 (broad, 20 H, CH_2), 3·33 (triplet, $J = 6{\cdot}5$ Hz, 2 H, CH_2Br).

4-cyano-4′-(12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,19-heptadecafluorononadecyloxy)biphenyl. 52 mg (266 μmol) of 4-cyano-4′-hydroxybiphenyl (TCI), 360 mg (2·6 mmol) of K_2CO_3 and 15 ml of dry DMF were stirred under nitrogen. 175 mg (268 μmol) of the precursor bromo-compound were added and the mixture heated at 120°C for 8 h. The mixture was cooled slowly, allowing the product to crystallize. After addition of 20 ml of water, the solid was collected on a glass filter, washed and dried under vacuum. It was purified by chromatography on silica (Merck: Kieselgel-60, 63–200 μm) with a mixture CH_2Cl_2 + petroleum ether (1 : 1) as eluent. Yield: 81 per cent, mp = 142°C. Analysis, calculated: C = 50·07, H = 3·95, N = 1·82 per cent. Found: C = 50·07, H = 3·84, N = 1·77 per cent. IR (KBr): 2923, 2853, 2228, 1606, 1496, 1474, 1245, 1205, 1180, 1149, 1110, 1050, 826, 657, 531 cm^{-1}. ^1H NMR ($CDCl_3$, TMS): 1·3 (broad, CH_2), 1·8 (multiplet, CH_2), (integration 1–2·4 ppm = 20 H), 4·00 (triplet, $J = 6$ Hz, 2 H, OCH_2), 6·97 (doublet, $J = 9$ Hz, 2 H, $C^{3',5'}H$), 7·51 (doublet, $J = 9$ Hz, 2 H, $C^{2',6'}H$), 7·67 (singlet, 4 H, $C^{2,3,5,6}H$). UV (CH_2Cl_2): 297 nm (log ε = 4·36).

4-cyano-4′-(2,2,2-trifluoroethoxy)biphenyl was obtained similarly except that the product did not crystallize in the reaction mixture. It was precipitated by water addition and separated by centrifugation. Yield: 72 per cent, mp = 121°C. Analysis, calculated: C = 64·98, H = 3·63, N = 5·05 per cent. Found: C = 64·91, H = 3·50, N = 4·88 per cent. IR (KBr): 1605, 1495, 1291, 1242, 1172, 1160, 1075, 980, 865, 822 cm^{-1}. ^1H NMR ($CDCl_3$, TMS): 4·42 (quadruplet, $J = 8$ Hz, 2 H, CHCF), 7·06 (doublet, $J = 9$ Hz, 2 H, $C^{3',5'}H$), 7·57 (doublet, $J = 9$ Hz, 2 H, $C^{2',6'}H$), 7·65 (singlet, 2 H, $C^{2,6}H$), 7·72 (singlet, 2 H, $C^{3,5}H$). ^{19}F NMR ($CDCl_3$): −11·06.

4-(4′-(12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,19-heptadecafluorononadecyloxy)phenyl)benzamide. 1·5 mg (1·95 mmol) of the precursor cyano- compound in 10 ml of pentanol were treated with 8·5 ml of 30 per cent aqueous KOH and 250 μl of H_2O_2 (130 vols). The reaction vessel was sonicated at 110–120°C. After 2 h, a white precipitate appeared. The disappearance of the CN band (2225 cm^{-1}) was checked by IR spectroscopy. After dilution with water, the solid was collected on a glass filter, washed with ethanol and continuously extracted with acetic acid from which it was recrystallized. Yield = 92 per cent, mp = 224°C (other transitions at 164 and 179°C). Analysis, calculated: C = 47·95, H = 4·02, N = 1·75 per cent. Found: C = 48·28, H = 4·10, N = 1·65 per cent. IR (KBr): 3426, 2921, 2853, 1653, 1559, 1529, 1500, 1472, 1403, 1333, 1291, 1246, 1205, 1150, 1052, 830, 773, 723, 705, 659, 560, 532 cm^{-1}.

4-(4′-(2,2,2-trifluoroethoxy)phenyl)benzamide was obtained similarly. Yield: 83 per cent, mp = 261°C. IR (KBr): 3396, 3182, 1648, 1618, 1560, 1500, 1408, 1251, 1184, 1073, 977, 830 cm^{-1}.

4-(4′-(12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,19-heptadecafluorononadecyloxy)phenyl)benzoic acid. The amide (1·44 g; 1·83 mmol) was dissolved in 150 ml acetic acid and heated at 100°C with stirring. Then 20 ml of 36% aqueous HCl diluted with 100 ml of acetic acid were added dropwise during 15 h; the addition was temporarily stopped in the case of the formation of a skin at the surface. The shift of the infrared carbonyl band from 1654 to 1680 cm^{-1} was checked during the reaction. After 24 h, the mixture was cooled and poured into 250 ml of cold water. The precipitate was collected and dried. It was then continuously extracted using toluene and recrystallized.

Yield = 88 per cent, mp = 260°C (other transition at 180°C). IR (KBr): 2923, 2853, 1679, 1604, 1430, 1248, 1202, 1151, 1052, 832, 776, 656 cm^{-1}.

4-(4'-(2,2,2-trifluoroethoxy)phenyl)benzoic acid was obtained similarly. Yield: 97 per cent, mp = 283°C (other transition at 260°C). IR (KBr): 1676, 1605, 1526, 1500, 1290, 1243, 1190, 1163, 1086, 976, 868, 832, 776, 726 cm^{-1}.

2,2,2-trifluoroethyl 4-(4'-(12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,19-hepta-decafluorononadcyloxy)phenyl)benzoate (*Compound I*). The carboxylic acid (1·26 g; 1·60 mmol) was kept at 50°C for 3 h in 6 ml of $SOCl_2$ under nitrogen. The thionyl chloride was evaporated under vacuum; the evaporation was completed by addition of toluene (5 ml) followed by evaporation to dryness. More toluene (5 ml) was added, followed by 250 μl of pyridine and 1 g of 2,2,2-trifluoroethanol. The mixture was kept overnight at 50°C, and the solvent then evaporated. The crude product was purified by 12 bars chromatography (stationary phase: Merck Kieselgel 15–40 μm, eluent: cyclohexane, fluorocarbon 113, chloroform (1 : 1 : 1)). Yield: 70 per cent. Analysis, calculated: C = 47·02, H = 3·71 per cent. Found: C = 47·25, H = 3·67 per cent. IR (KBr): 2923, 2855, 2367, 1728, 1604, 1499, 1384, 1246, 1202, 1149, 832, 768, 657, 452, 443, 419, 404 cm^{-1}. ^{1}H NMR ($CDCl_3$, TMS): 1·3 (broad, 20 H, CH_2) 4·00 (triplet, $J = 6$ Hz, 2 H, OCH_2), 4·7 (quadruplet, $J = 8$ Hz, 2 H, CH_2CF_3), 7·0 (doublet, $J = 9$ Hz, 2 H, $C^{3',5'}H$), 7·6 (doublet, $J = 9$ Hz, $C^{2',6'}H$), 7·7 (singlet, 4 H, $C^{2,6}H$), 8·3 (doublet, $J = 9$ Hz, 2 H, $C^{3,5}H$). UV (CH_2Cl_2): 300 nm.

12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,19-heptadecafluorononadecyl 4-(4'-(2,2,2-ethoxyphenyl)benzoate (*Compound II*) was obtained similarly. Analysis, calculated: C = 47·02, H = 3·71 per cent. Found: C = 47·20, H = 3·32 per cent. IR (KBr): 2933, 1704, 1606, 1294, 1203, 1149, 1051, 829, 774, 658 cm^{-1}. ^{1}H NMR ($CDCl_3$, TMS): 1·3 (broad, 20 H, CH_2) 4·3 (triplet, $J = 6$ Hz, 2 H, OCH_2), 4·4 (quadruplet, $J = 8$ Hz, 2 H, CH_2CF_3), 7·0 (doublet, $J = 9$ Hz, 2 H, $C^{3',5'}H$), 7·6 (doublet, $J = 9$ Hz, 2 H, $C^{2',6'}H$), 7·6 (singlet, 4 H, $C^{2,6}H$), 8·3 (doublet, $J = 9$ Hz, 2 H, $C^{3,5}H$). UV (CH_2Cl_2): 284 nm.

6. Conclusions

The smectic X' phase of a mixture of polyphilic compounds shows ferroelectric properties. This mesophase very probably consists of polar domains which can spontaneously realign. The direction of the macroscopic polarization can be switched by an external field with hysteresis loops typical of ferroelectrics. The polyphilicity was used as a strategy for obtaining novel mesomorphic ferroelectrics without the need of chirality as in chiral smectic C. However, the part played by the polyphilic character in the ferroelectricity mechanism needs further studies to be established.

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