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Synthesis and Structural Studies of Polyphilic Mesogens with Central or Terminal Perfluoroalkyl Chains

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Benzyl 4-iodoperfluorobutanoate was synthesized by partial pyrolysis of perfluoroglutaryl chloride in the presence of potassium iodide followed by esterification. This compound gives access to mesogenic molecules with alkyl chain, perfluoroalkyl central bridge, and biphenyl moieties. Segregation of these chemical fragments depends on the molecular design. The molecule with a central alkyl chain forms smectic A layers (123−145 °C) with interdigitation of aliphatic and aromatic parts. In contrast, the smectic E phase is observed between 60 and 87 °C when the perfluoroalkyl chain is in the center of the molecule. In this case, X-ray diffraction data are consistent with the presence of three sublayers differing in their chemical nature.

1. Introduction

The macroscopic properties of molecular materials are closely related to the type of symmetry and organization existing in the condensed phase considered. In this respect, any pertinent factor permitting one to predict, to some extent the type of structures that will be encountered with a given molecule is of utmost interest.

The amphiphilic character, initially defined by Hartley[1] for explaining the organization properties of soaps, is now considered to be relevant even for thermotropic liquid crystals.[2] Lyotropic mesogens have two parts, one hydrophilic and one hydrophobic, and their segregation induces the formation of cylinders, lamellae, etc. On the basis of structural similarities between lyotropic and thermotropic liquid crystals, Skoulios and co-workers[3] recognized that the very existence of smectic phases was also related to amphiphilicity. The majority of smectogens have a polarizable rigid core bearing one or several flexible side chains. They can be considered as amphiphilic molecules as soon as the two different chemical fragments segregate in the smectic layers.

As a generalization of this concept, polyphilic compounds[4] are made up of a sequence of (more than two) fragments differing by their chemical nature. In the mesomorphic state, unlike fragments have a tendency to form segregated sublayers.

Perfluoroalkyl chains have been widely used in the design of polyphilic materials[5−10] but always as end groups. Starting from benzyl 4-iodoperfluorobutanoate, we have initiated the synthesis of new polyphilic compounds incorporating a perfluoroalkyl section in the middle of the molecule.

Three typical molecules of different chemical architecture (compounds **9**, **13**, and **15**, Figure 1) were synthesized. The X-ray study of their mesophase organization was used to characterize the polyphilic behavior of these materials. We found that the diblock biphenyl/perfluoroalkyl molecule, **15**, and the triblock one, **9**, with a central perfluoroalkyl chain and the alkyl and biphenyl moieties at the extremities form smectic layers composed of well-defined sublayers, exactly as expected from polyphilic compounds. In contrast, compound **13** with the alkyl chain in the middle of the sequence is only partially segregated, the alkyl and biphenyl fragments being interdigitated.

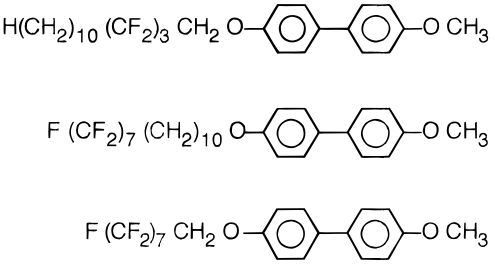

Figure 1. The three polyphilic compounds investigated.

2. Synthesis

Perfluoroalkyl iodides permit the formation of stable C−C bonds by the Ullman reaction[11] or by free-radical addition to olefines followed by dehalogenation.[12,13] These reactions are commonly used in the design of highly fluorinated molecular materials.[14−17] Symmetric α,ω-diiodoperfluoroalkanes are available by several routes[18−20] and their use in the design of mesomorphic polymers was reported.[21] However, to our knowledge there is no efficient procedure for the synthesis of a perfluoroalkyl chain bearing two different reactive groups in the α and ω positions.

When reacting perfluoroglutaryl chloride with potassium iodide at 200−400 °C (Scheme 1), McLoughlin noticed the formation of some amount of 4-iodoperfluorobutyryl chloride,[20] the latter was isolated in the form of the free acid.

When an excess of potassium iodide is used, both steps can be regarded as first order. If the same reactivity is assumed for the two acid chloride groups, the amounts n_1, n_2, n_3 of the three compounds can be written as a function of the quantity

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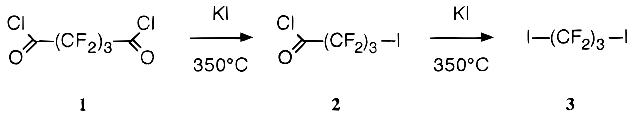
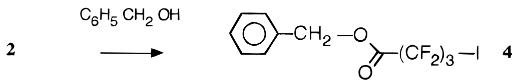
SCHEME 1



SCHEME 2



of starting material, n_0 and the degree of conversion ξ:

$$n_1 = n_0(1 - \xi)^2 \tag{1}$$

$$n_2 = 2n_0\xi(1 - \xi) \tag{2}$$

$$n_3 = n_0\xi^2 \tag{3}$$

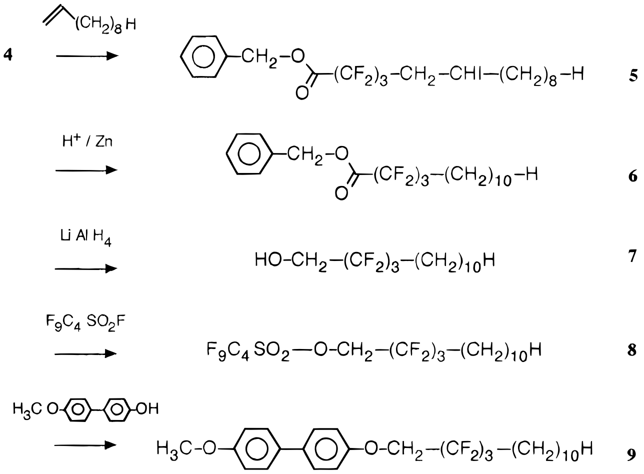
The theoretical amount of **2** passes through the maximum $n_2 = {}^1/_2 n_0$ when $\xi = 0.5$. In the original work,[20] relatively high yields (50−60%) of **3** were obtained when using high temperatures and long reaction times. In our experiments,[22] all precautions were taken to stop the progression of the reaction at the optimum time.

The starting material (hexafluoroglutaryl chloride) was vaporized at 220 °C with a nitrogen flow and passed at 350 °C through a glass tube packed with finely ground potassium iodide. The reaction time was determined by the flow of nitrogen. The products were trapped at −78 °C. The degree of conversion, ξ, was estimated by the relative intensities of the 1793 cm^{-1} (C=O stretching) and 1128 cm^{-1} (CF stretching) infrared bands; it was optimized close to the $\xi = 0.5$ theoretical maximum by changing the reaction time.

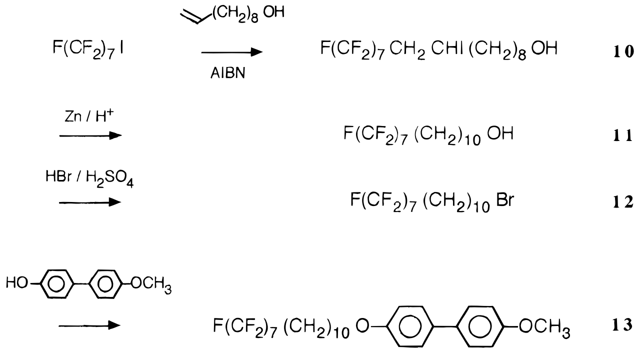
Compound **2** is highly sensitive to moisture, is undetectable by thin-layer or gas chromatography, and can hardly be distinguished from a mixture of compounds **1** and **3**. Due to these difficulties, we decided to form a versatile derivative of **2** which may be purified and characterized. For this purpose, the benzyl moiety has the double advantage of being easily removable[23] and light absorbing in the 254 nm region.

The products **1** + **2** + **3** were immediately treated with benzyl alcohol in toluene in the presence of pyridine, and benzyl 4-iodoperfluorobutanoate **4** was isolated by liquid chromatography (Scheme 2). Compound **4** was characterized by NMR, IR, GC-MS, and elemental analysis. The overall yield did not exceed 16% but was reproducible when all the above precautions were taken. In our opinion, this result is perfectible: Ankudinov et al.[24] obtained good yields by reacting 4-(carboxymethyl)-perfluorobutyryl chloride with sodium or potassium iodide at 200 °C; the electrochemical reduction of perfluoroglutaryl chloride is also an alternative way to a mixture of compounds **2** and **3**.[25] Regardless of the method chosen, the key step in each is to achieve a single substitution onto a bifunctional molecule.

SCHEME 3



SCHEME 4



SCHEME 5

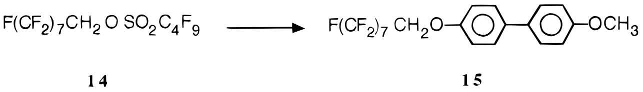


TABLE 1: Transition Temperatures (°C) of Compounds 9, 13, and 15 Detected by DSC[a]

compd	K	M		S_E		S_A		I
9	●		60 (28.0)	●	87 (14.4)			●
13		●	123 (40.8)			●	145 (9.4)	●
15	●		72 (14.4)	●	138 (7.8)	●	168 (10.4)	●

[a] The transition enthalpies (kJ/mol) are indicated in parentheses.

Compound **9** was synthesized in five steps starting from benzyl 4-iodo-perfluorobutanoate, **4** (Scheme 3). The homolytic cleavage of the carbon−iodine bond was induced by the thermal decomposition of AIBN[12,13] hence initiating the 1,2 addition of **4** on 1-decene. The iodine atom in the α position of the perfluoroalkyl fragment in compound **5** was removed by Zn/H^+ reduction[13] and benzyl 2,2,3,3,4,4-hexafluorotetradecanoate, **6**, was obtained. The latter was reduced to 2,2,3,3,4,4-hexafluoro-1-tetradecanol, **7**, with the aid of lithium aluminum hydride. The nonaflate activation[26] of **7** proved to be efficient for initiating the S_N2 reaction despite the inductive effect of vicinal fluorine atoms. In these conditions, **8** reacted with a phenate in dimethylformamide (DMF) giving rise to the polyphilic compound **9**.

Polyphilic compound **13** with the perfluoroalkyl chain at the extremity was prepared in four steps using standard procedures[5] (Scheme 4): The semifluorinated alcohol **11** was obtained by 1,2 addition of perfluoroalkyl iodide on 9-decen-1-ol followed by reduction; it was then converted to the bromide **12** and reacted with 4-methoxy-4′-hydroxybiphenyl giving **13**. Compound **15** was prepared similarly from 1*H*,1*H*-perfluorooctanol through nonaflate activation (Scheme 5).

3. Mesomorphic Properties

Investigation of the polymorphism of compound **15** has been reported;[27] this material forms smectic E and A phases (Table 1). The mesomorphic properties of compounds **9** and **13** have been investigated by differential scanning calorimetry (DSC),

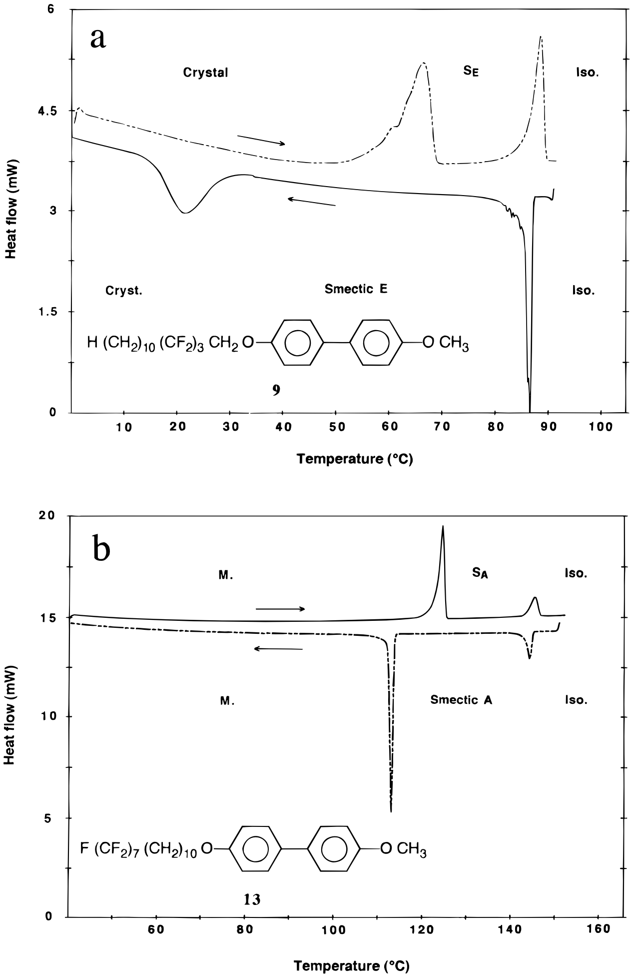


Figure 2. DSC thermogram (±5 °C/ min) of compounds **9** (a) and **13** (b).

Figure 3. The *lancet* texture of compound **9** in the S_E phase, 80 °C, crossed polarizers, full width = 1 mm.

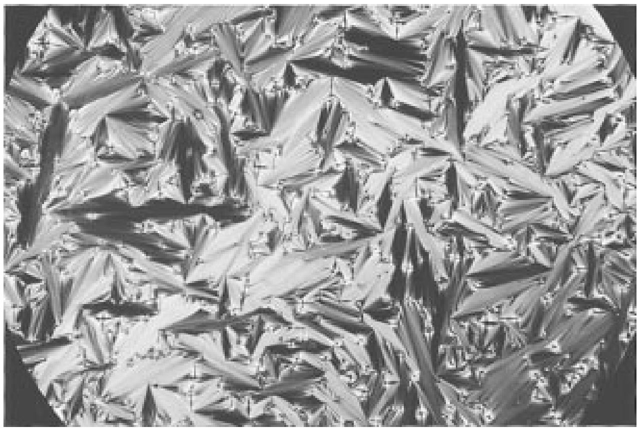


Figure 4. The *focal conics* texture of compound **13** in the S_A phase, 130 °C, same conditions as in Figure 3.

optical microscopy, and X-ray diffraction. DSC thermograms were recorded at ±5 °C per minute using a Perkin-Elmer DSC 7 apparatus; the transition temperatures and enthalpies are collected in Table 1. On heating, the polymorphism of **9** was evidenced by a broad endotherm between 57 and 70 °C and a well-defined transition at 87 °C (Figure 2a). On cooling, this transition was detected by an exotherm at 86 °C. The phase existing below this temperature was then overcooled to 15−20 °C, the temperature at which the compound slowly recrystallizes. Optical microscopy was carried out using a Leitz Orthoplan polarizing microscope equipped with a Mettler FP52 hot stage. On cooling from the isotropic phase, the growth of birefringent lancets like domains is observed below 87 °C (Figure 3). This texture characterizes a smectic E phase growing directly from the isotropic liquid.[28] The “lancet texture” was stable down to room temperature whereupon the recrystallization takes place. The transitions occurring between 57 and 70 °C correspond to crystal−crystal transitions and have not been investigated in details.

The DSC thermogram of compound **13** (Figure 2b) shows two sharp peaks at 123 and 145 °C with a few degrees of supercooling for the latter. On cooling from the isotropic phase, the birefringence of **13** was detected at 145 °C by the growth of *bâtonnets*;[29] on further cooling, the characteristic *focal conics* texture can be recognized (Figure 4). The mesophase was identified as smectic A since homeotropic domains were also present in some portions of the specimens. The smectic A phase can be overcooled to about 114 °C. On further cooling, a transition to an ordered smectic mesophase M exhibiting paramorphotic focal conic textures was observed. At room temperature, the X-ray diffraction figure of the latter phase displays several maxima in the vicinity of $q = 1.2{-}1.5$ Å^{-1} which cannot be indexed in the hexagonal or orthorhombic systems hence excluding the identification as smectic B or E phase. The structure of the “M” phase will not be discussed here.

4. X-ray Diffraction Experiments.

4.1 Methods. Due to its biaxial symmetry, the smectic E phase cannot form single domains on application of a magnetic field or by surface treatements. X-ray spacings and intensities were determined from powder samples for all compounds, using the Cu Kα radiation. Relative intensities of 00*l* reflections were estimated by scanning the films obtained with a Debye−Scherrer camera and analyzed using the classical formula:[30]

$$I(q_{00l}) \propto \frac{1}{q_{00l}^2} |F(q_{00l})|^2 \exp(-\sigma^2 q_{00l}^2) \tag{4}$$

$1/q_{00l}^2$ is the relevant Lorentz correction factor at small diffraction angles, $F(q_{00l})$ is the structure factor, and σ is the Debye−Waller coefficient that accounts for positional fluctuations. For liquid crystals, similar expressions have been established.[31] In the case of rodlike mesogens, the electronic density is supposed to be uniform within the layers and equal to zero in the interlayer gaps. In the limit case of infinitely thin interfaces, all $|F(q_{00l})|^2$ are equal to unity. This approach cannot explain the nonmono-

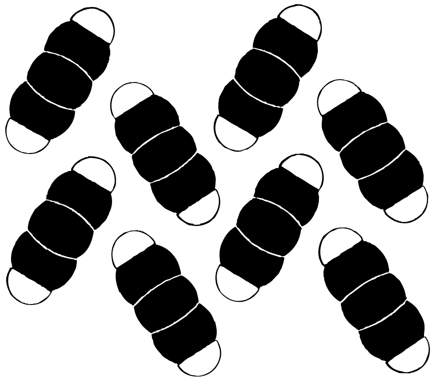


Figure 5. Herringbone packing of biaryl cores. Drawn from the data of ref 37.

tonic decay of the intensities $I(q_{00l})$ observed in our case: due to the presence of heavy fluorine atoms in one part of the molecules, the electronic density can no longer be considered as uniform in the layers. We calculated ^{1}D structure factors along the layer normal by considering for each molecular fragment the number of electrons and the dimensions given by molecular models and by geometrical considerations. To reduce the number of adjustable parameters, the width of the interlayer gap, z, was taken equal to the value previously determined for compound **15**[27] ($z = 1.1$ Å).

4.2. Structure of the Smectic E Layers of Compound 15. The geometrical analysis and form factor calculations have demonstrated that the S_E phase of this material is composed of well-segregated sublayers as expected from the amphiphilic constitution of the molecule.[27] Recent structural investigations of polyfluoroalkyl-(4-phenylbenzylidene) imines have demonstrated that the same conclusions are also valid for other perfluoroalkyl/biphenyl amphiphiles.[32] In the biphenyl sublayer, the long axis of the rigid stems are parallel to the layer normal; in the layer plane, the elliptic shapes of the aromatic rings form a rectangular arrangement with the $p2gg$ ^{2}D symmetry. This herringbone packing which is schematically represented in Figure 5 is a quite frequent situation for parasubstituted biphenyls, as a matter of fact, the a and b parameters recorded in the smectic E phase of fluorinated[27,32] and nonfluorinated[33,34] smectic E materials are all very close to those reported for poly paraphenylenes in their monoclinic form.[35−37] Perfluoroalkyl chains, in a liquidlike conformation are located on either side of the crystalline sublayer.

4.3. Structure of the Smectic E Layers of Compound 9. Diffraction diagrams of the smectic E phase were recorded at 72 °C (Figure 6a, Table 2). They contain three $00l$ reflections at small angles corresponding to an interlayer distance of $c = 34.5$ Å. At larger angles three $hk0$ reflections were indexed with a ^{2}D rectangular unit cell of parameters $a = 7.9$ Å and $b = 5.6$ Å. A broad scattering signal with a maximum at $q = 4\pi \sin(\theta)/\lambda = 1.20$ Å^{-1} was recorded (Figure 6a) hence indicating that a liquidlike order with an average molecular distance of $r = 1.15 \times 2\pi/q = 6.0$ Å is also present within the layers. (For estimation of this distance, we consider that the local order is close to a hexagonal packing: $r = (2/\sqrt{3})(2\pi/q)$.) The rectangular cell ($a = 7.9$, $b = 5.6$ Å) is almost identical to that of unsubstituted biphenyl ($a = 8.12$, $b = 5.63$ Å), hence indicating that the packing is again of the herringbone type (Figure 5). In this structure, the area available per each biphenyl core in the ab plane is 22.1 Å.^{2} The perfluoroalkyl fragments, with a typical cross section of 27−31 Å^2, must be alternated on either side of the aromatic sublayer (Figure 7). However, in this arrangement, a surface of 44.2 Å^2 is available in the ab plane for each perfluoroalkyl and alkyl chain. They have to take disordered conformations which can be related to the presence of a halo in the diffraction figure. According to this model, the biphenyl units and their oxymethylene groups are overlapped by a length of about 12.8 Å. Hence, the volume available for each side chain (perfluoroalkyl + alkyl) is 480 Å^3. A typical volume of 410 Å^3, slightly inferior than the previous value, is found from the molar volumes of alkanes[38] and perfluoroalkanes[39] at room temperature. Thus, as already encountered with compound **15**,[27] the smectic E phase is characterized by the coexistence of crystallized biphenyl cores and liquidlike flexible chains. Such an arrangement is schematically represented in Figure 7.

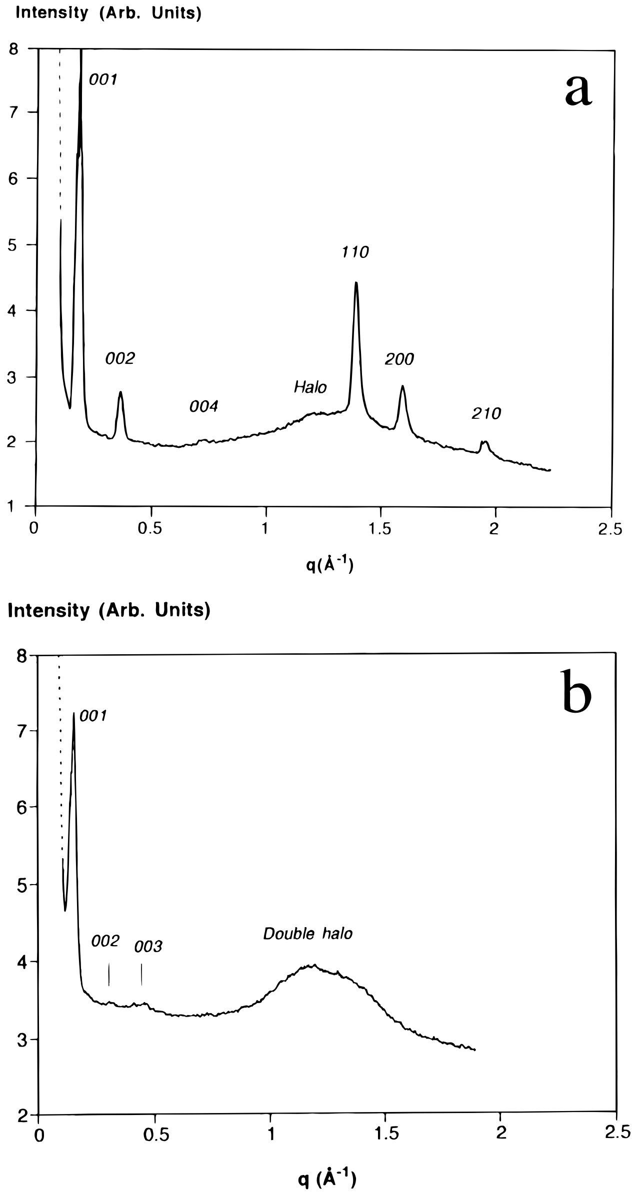


Figure 6. X-ray diffraction patterns of a: mesogen **9**, S_E phase at 72 °C; (b) mesogen **13**, S_A phase, 134 °C (densitometric profile of the photographic film).

TABLE 2: Experimental Values of the Intensities of the 00*l* Reflections in the S_E Phase of 9 and the Calculated Values from the Model of Figure 7

	001	002	003	004
expt	100	6.5		0.6
calc	100	5	0.05	0.3

This model should be tested by considering the relative intensities of the X-ray reflections. The three different molec-

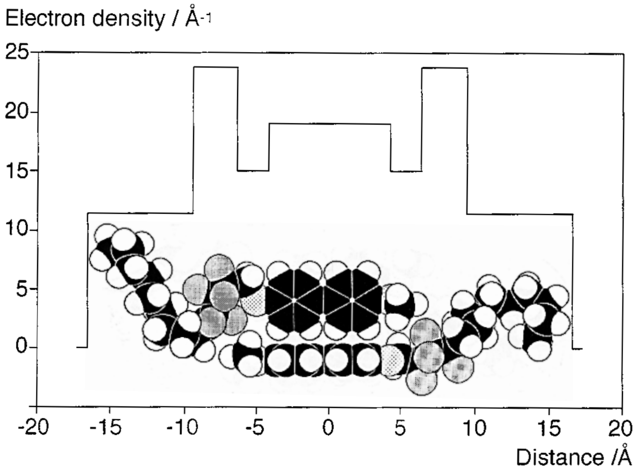


Figure 7. Model for the repartition of molecular cores and chains in the smectic E layer of compound **9**. The corresponding mean electron density profile perpendicular to the layers taken to calculate the X-ray intensities is shown.

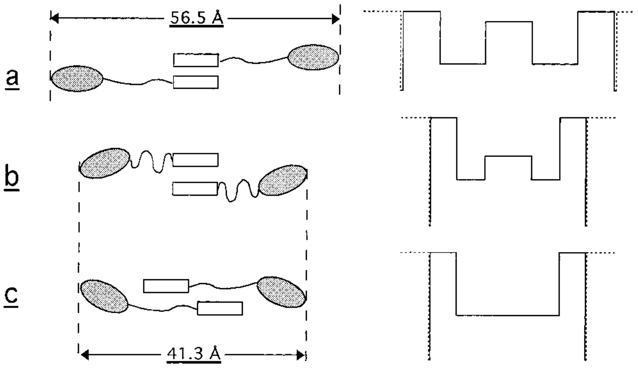


Figure 8. Structural hypothetic models for the S_A phase of compound **13** with corresponding electron density profiles: (a) with stretched chains and interdigitated cores, (b) with disordered alkyl chains and interdigitated cores, (c) with overlap of the alkyl and aryl parts.

ular fragments are characterized by their electronic density distribution along a direction perpendicular to the smectic layer. We used the density profile shown in Figure 7 to calculate the 00*l* reflections intensities. Formula 1 was applied with σ as adjustable parameter. The results of the best fit are collected in Table 2. The value $\sigma = 1.3$ Å indicates well-defined surfaces between consecutive layers. The above analysis affords the picture of a smectic layer made up of well-segregated sublayers as expected from the polyphilic constitution of the molecule.

4.4. Structure of the Smectic A Layers of Compound 13. Compound **13** was investigated in its smectic A phase at 134 °C. At small angles, three 00*l* reflections were recorded corresponding to an interlayer distance of 41.3 Å. At larger angles, a double halo is detected, indicating that two different characteric distances may be recognized in the *in-plane* arrangement of the molecules. In the smectic A phase, the interlayer distance is 41.3 Å, which is significantly larger than the end-to-end molecular length in the fully extended conformation (34.5 Å); a bimolecular packing with a partial overlap of the molecules should therefore be postulated.

Let us first assume that we are still dealing with a fully segregated arrangement, with interdigitation of the biaryl cores. The picture of Figure 8a, with stretched perfluoroalkyl and alkyl moieties, leads to an interlayer distance of 56.5 Å which is greater than observed. On the other hand, the model does not satisfy the close packing principle since it leaves a lot of empty space in the region of the side chains.

TABLE 3: Experimental and Calculated Values of the Intensities of the 00*l* Reflections in the S_A Phase of 13

	001	002	003	004
expt	100	1.3	1.7	
calc	100	1.4	1.6	

To optimize the packing, it may be hypothesized that the perfluoroalkyl and alkyl fragments adopt a disordered conformation (Figure 8b), consistent with the presence of a double halo in the diffraction figure. In that model, the length covered by the overlapped biphenyl rings with their oxymethylene groups is 12.5 Å, as noted previously. Hence, each alkyl/perfluoroalkyl side chain should be curled up as to be accommodated into a total distance of 14.4 Å. In such a conformation, these fragments will occupy approximately the same volume as in the liquid state. If we perform the calculation as above, we expect a molecular volume of 565 Å^3 for the $F(CF_2)_7\,(CH_2)_{10}-$ fragment which corresponds to a cross section of 39 Å^2. This area does not match the cross section of 44 Å^2 which is characteristic of overlapped biphenyl rings, on the other hand, the herringbone ordering of biphenyl stems would likely induce the appearance of the smectic B or smectic E phase at lower temperature, which is not observed. This model is also unsatisfactory from the standpoint of structure factor analysis: in the situation of Figure 8b, the electron density profile displays two maxima corresponding to the perfluoroalkyl chains at the layer boundaries and one secondary maximum related to the biphenyl rings in the middle of the layer. Such distribution would magnify the second harmonic rather than any other, in contradiction with experimental data (Table 3).

Alternatively, the interlayer distance which is only 20% larger than the molecular length may be interpreted by the formation of a more completely interdigitated arrangement. In Figure 8c, the alkyl and biphenyl fragments, which have approximately the same length, are covering each other whereas the perfluoroalkyl chains form separated sublayers on either side of the hydrocarbon region. Such an arrangement has been already encountered in the crystal phase of certain polyphilic compounds;[9] the mixture of the alkyl and aryl moieties in the center of the layer may also explain the absence of the herringbone arrangement. In that case, the double diffraction halo can be interpreted as follows: the first peak at $2\pi/q = 5.4$ Å is due to the perfluoroalkyl chains in a disordered conformation, and the second one at $2\pi/q = 4.8$ Å is to be attributed to the random distribution in the alkyl/aryl sublayer with an average intermolecular distance of $r = 1.15 \times 2\pi/q = 5.54$ Å. (The local order was considered to be close to a hexagonal packing: $r = (2/\sqrt{3})(2\pi/q)$.) (Figure 9). In the model of Figure 8c, the electron density modulation has the shape of a square signal: Electron-poor hydrocarbons cover one-half of the layer period whereas the perfluoroalkyl chains with a higher electron density fill the remaining space. In our structure factor calculations, the length of the overlap, a and the Debye−Waller coefficient, σ, were used as adjustable parameters; the results of the best fit are summarized in Table 3. Such a distribution enhances the third harmonic intensity as observed experimentally. The value of $a = 23$ Å indicates that the biphenyl and alkyl fragments are completely overlapped. The value $\sigma = 3.4$ Å gives an estimate of the thermal fluctuations amplitude. This value is larger than in the smectic E phase of compound **9** and **15**, also consistent with more disordered and less segregated molecules.

5. Conclusion

In compounds **15** and **9**, the geometrical characteristics of the whole arrangement in the S_E phase are influenced by the

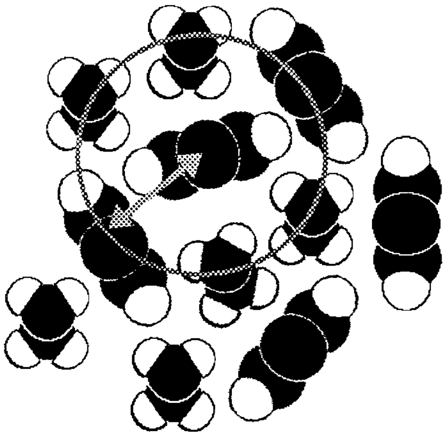


Figure 9. Random repartition of interdigitated alkyl and biphenyl groups in the hydrocarbon sublayer giving rise to the diffuse reflection at $2\pi/q = 4.8$ Å.

herringbone packing of biphenyl cores close to the crystal structure of unsubstituted biphenyl. The flexible chains in a liquidlike conformation are located up and down alternatively. As a comparison, polyphilic compounds with perfluoroalkyl side chains at both extremities were not shown to form herringbone structures,[40] but in this case, the bulkiness of terminal groups prevents the biphenyls from approaching each other. In compounds **9** and **15**, the perfluoroakyl fragment, nearly globular in shape, located on a single side of the aromatic core, limits the molecular motions across the layer, favoring a well-segregated arrangement. Despite important disparities in cross sections the various fragments may be accommodated in the same area thanks to the flexibility of the side chains. Molecular modeling of compound **15** using the esff force-field simulation demonstrates that the perfluoroalkyl-methyloxy chain in its *all-trans* conformation forms an angle of about 30° with respect to the biphenyl axis. In the mesophase, additional gauche bonds distributed along the flexible chains enable them to deviate even more from the layers normal direction. In compound **9**, the alkyl fragment with a basic cross section of 20−22 Å^2 is able to swell itself as to fill the 44 Å^2 available; most likely such a swelling would be unrealizable if both extremities were fasten in a predetermined position as in **13.** Compound **13**, with the alkyl chain in the middle, displays a quite different behavior. In that case, the molecular fragments are only partially segregated. As a consequence, the herringbone packing is not observed, and the thin alkyl fragment freely permeates the biaryl region. Compound **13** may be regarded as an amphiphilic molecule in which only two segregating parts are recognized: the perfluoroalkyl chain on one side; the full hydrocarbon part (alkyl + aryl) on the other side.

6. Experimental Section

Hexafluoroglutaryl Dichloride (1). In a 25 mL Claisen flask bearing a 5 cm long Vigreux column, 4 g of hexafluoroglutaric acid (16.7 mmol) (Fluorochem), 123 mg of potassium chloride (1.6 mmol), and 6.7 mL of oxalyl dichloride (78 mmol) (Fluka) were stirred together at 30 °C with the help of an ultrasonic stage. After 2 h, the mixture was carefully fractionated. The excess of oxalyl chloride distillates at 63−64 °C. Hexafluoroglutaryl dichloride was collected in the fraction boiling at 111 °C (yield: 78%). IR (KBr, cm^{-1}): 1805.5 [C=O], 1190 [C−F].

Benzyl 4-Iodo-2,2,3,3,4,4-hexafluorobutanoate (4). The reaction tube of length 80 mm and diameter 20 mm fitted with an electrical heating belt (38 × 24 mm) was packed with 45 g of finely ground potassium iodide, and heated at 350 °C for 2 h under a stream of nitrogen. 3.62 g (13 mmol) of hexafluoroglutaryl dichloride (1) was vaporized at 220 °C from a 50 mL two-necked flask and driven by the nitrogen flow into the reaction tube. The reaction began at the contact with potassium iodide which turned to a pink coloration. The temperature and the flow of nitrogen (140 mL/h) were monitored throughout the process. The vapors that issued from the reaction tube were trapped at −78 °C. After consumption of the starting material, potassium iodide turned colorless and the process was stopped. The reaction mixture was immediately diluted with 5 mL of toluene and added dropwise at 0 °C to 13 mmol of freshly distillated benzyl alcohol. Two drops of pyridine were added as a catalyst. The reaction occurred immediately. The product was purified by liquid chromatography on silica [63−200 μm] with a cyclohexanes−ether (98:2) mixture as eluent and collected as a liquid. The purity was checked by gas chromatography (GC-MS). (Yield: 17% (relative to perfluoroglutaryl chloride).) Anal. Found: C, 32.18; H, 1.76; I, 30.89. Calcd: C, 32.06; H, 1.71; I, 30.80. IR (KBr, cm^{-1}): 1778.9 [C=O], 1190.1, 1145.0 [C−F], 770 [δ C−H arom *out-of-plane*]. MS (electron impact, *m*/*z*): 412 [M]$^+$, 277, 227, 177, 127 [M − $(CF_2)_nCO_2CH_2C_6H_5$]$^+$, 91 [C_7H_7]$^+$. NMR ^{1}H ($CDCl_3$, TMS, 300 MHz, δ ppm): 7.43 (s, 5H, cycle), 5.4 (s, 2H, CH_2). NMR ^{13}C ($CDCl_3$, 75 MHz, δ ppm): 158.45 (t, J = 29.9 Hz, CF_2COOR), 133.23 (s, arom), 129.11 (s, arom), 128.73 (s, arom), 128.48 (s, arom), 108.45 (m, J = 265.5 Hz, J = 31.75 Hz, $CF_2CF_2CF_2COOR$), 106.94 (m, J = 267.95 Hz, J = 33.6 Hz, CF_2CF_2COOR), 93.39 (m, J = 319.8, J = 41.5, ICF_2CF_2-CF_2), 69.75 (s $COCH_2$). NMR ^{19}F ($CDCl_3$, 235 MHz, δ ppm): −59.5 (m, 2F, I CF_2), −114.7 (m, 2F, $CF_2CF_2CF_2$), −117.7 (t, J = 11.2 Hz, 2F, CF_2COOR).

Benzyl 2,2,3,3,4,4-Hexafluoro-6-iodo-1-tetradecanoate (5). In a 50 mL three-necked flask fitted with a reflux condenser and a nitrogen inlet, 344 mg (835 μmol) of benzyl 4-iodoperfluorobutanoate (**4**), 5 mL of heptane, and 142 mg (1 mmol) of 1-decene (Aldrich) were heated at 90 °C with stirring. AIBN (α,α'-azobisisobutyronitrile, Fluka) was added by small portions every 15 min, whereupon the pinkish solution turned colorless. After three AIBN additions and the 1.5 h reaction at 90 °C, the solvent was evaporated and the crude product was purified by liquid chromatography on silica (eluant: 2% ether in cyclohexane). Compound **5** was obtained as a pale yellow liquid (yield: 74%). The product rapidly decomposes and must be used without delay in the next step. Anal. Found: C, 47.51; H, 5.27. Calcd: C, 45.67; H, 4.92. IR (KBr cm^{-1}): 2926.3 [C−H asym], 2855.8 [C−H sym], 1780 [C=O], 1179.6, 1178.3 [C−F], 1138.5 [CF]. MS (electron impact, *m*/*z*): 425 [M − I]$^+$, 91 [C_7H_7]$^+$. NMR ^{1}H ($CDCl_3$, TMS, 300 MHz, δ ppm): 7.40 (s, 5H, cycle), 5.37 (s, 2H, $CH_2-C_6H_5$), 4.30 (m, 1H, CHI), 2.82 (m, 2H, $CHI-CH_2-CF_2$), 1.78 (m, 2H, CH_2-CH_2-CHI), 1.44 (alkyl), 0.89 (t, CH_3). NMR ^{13}C ($CDCl_3$, 75 MHz, δ ppm): 159.01 [t, J = 29.9 Hz, CF_2-COO], 133.42 [s, arom], 129.11 [s, arom], 128.77 [s, arom], 128.56 [s, arom], 117.78 [m, J = 256.3 Hz, J = 31.1 Hz, $CH_2-CF_2-CF_2$], 110.39 [m, $CF_2-CF_2-CF_2$], 108.22 [m, CF_2-CF_2-COO], 69.63 [s, $CH_2-C_6H_5$], 41.64 [t, J = 21 Hz, $CH_2-CF_2-CF_2$], 40.32 [s, CH_2-CHI], 31.95 [s, $H_3C-CH_2-CH_2$], 29.69−28.53 [CH_2], 22.71 [s, H_3C-CH_2], 21.16 [s, CHI], 14.11 [s, CH_3].

Benzyl 2,2,3,3,4,4-Hexafluoro-1-tetradecanoate (6). In a 250 mL two-necked flask fitted with a gas inlet and a reflux condenser, 988 mg (1.85 mmol) of benzyl 2,2,3,3,4,4-hexafluoro-6-iodotetradecanoate (**5**) was diluted in a mixture of 20 mL isooctane and 15 mL acetic acid. This solution was heated at

100 °C in an oil bath. 1.21 g (18 mmol) of zinc powder was added with vigorous stirring. Gaseous HCl was admitted into the solution, and the reaction began. After consumption of the Zn powder (3 h), the mixture was cooled to room temperature and filtered, and the precipitate was washed with water and dried over magnesium sulfate. The liquid phase was concentrated under vacuum and benzyl 2,2,3,3,4,4-hexafluorotetradecanoate was obtained as a liquid after Kugelrohr distillation (yield: 80%). Anal. Found: C, 59.15; H, 6.62. Calcd: C, 58.80; H, 6.35. IR (KBr cm^{-1}): 2926.2 [C−H asym], 2856.5 [C−H sym], 1781.2 [C═O], 1178, 1138 [C−F]. MS (electron impact, *m/z*): 426 $[M]^+$ 293, 133, 91 $[C_7H_7]^+$. NMR ^1H ($CDCl_3$, TMS, 300 MHz, δ ppm): 7.4 (s, 5H, C_6H_5), 5.36 (s, 2H, $CH_2-C_6H_5$), 2.05 (m, 2H, CH_2-CF_2), 1.57 (m, 2H, $CH_2-CH_2-CF_2$), 1.46−1.29 (alkyl.), 0.92 (t, CH_3). NMR ^{13}C ($CDCl_3$, 75 MHz, δ ppm): 159.34 [t, $J = 29.9$ Hz, CF_2-*C*OO], 133.52 [s, arom], 129.02 [s, arom], 128.74 [s, arom], 128.49 [s, arom], 118.39 [m, $J = 252.6$ Hz, $J = 30.5$ Hz, $CH_2-CF_2-CF_2$], 110.87 [m, $J = 265$ Hz, $J = 34.5$ Hz, $CF_2-CF_2-CF_2$], 108.38 [m, $J = 265$ Hz, $J = 31.1$ Hz, CF_2-CF_2-COO], 69.49 [s, $CH_2-C_6H_5$], 30.77 [t, $J = 23.2$ Hz, $CH_2-CF_2-CF_2$], 31.9 [s, $H_3C-CH_2-CH_2$], 29.7−29.1 [CH_2], 22.68 [s, H_3C-CH_2], 20.07 [s, $CH_2-CH_2-CF_2$], 14.10 [s, CH_3].

2,2,3,3,4,4-Hexafluoro-1-tetradecanol (7). 60 mg (1.6 mmol) of $LiAlH_4$ was stirred with 30 mL of anhydrous ether in a 250 mL three-necked flask fitted with a nitrogen inlet and reflux condenser. 498 mg (1.16 mmol) of benzyl 2,2,3,3,4,4-hexafluoro-1-tetradecanoate (**6**), diluted in 3 mL of ether, was added after 15 min using a separatory funnel. The mixture was refluxed for 15 min and cooled to room temperature. 36 mL water were added carefully, and the mixture was poured into 30 mL of 10% (w/w) aqueous sulfuric acid. The ether phase was separated and dried over magnesium sulfate. After evaporation of the solvent, the excess of benzyl alcohol was removed by azeotropic evaporation with 2 mL of water (yield: 64%). NMR ^1H ($CDCl_3$, TMS, 300 MHz, δ ppm): 4.02 (t, 2H, $J = 14.7$ Hz, CF_2-CH_2-OH), 3.07 (s, 1H, CH_2OH, 2.04 (m, 2H, CH_2-CF_2), 1.58 (m, 2H, $J = 7.35$ Hz, $CH_2-CH_2-CF_2$), 1.28 (s, 7H, CH_2), 0.89 (t, 3H, $J = 6.6$ Hz, CH_3).

2,2,3,3,4,4-Hexafluoro-1-tetradecyl Nonafluorobutylsulfonate (8). 355 μL (2 mmol) of perfluorobutane sulfonyl fluoride (Fluorochem) was dissolved in 20 mL of dichloromethane previously dried over neutral aluminum oxide (Merck 90, activity I) and cooled to −40 °C under nitrogen in a 250 mL three necked flask. 581 mg (1.8 mmol) of 2,2,3,3,4,4-hexafluoro-1-tetradecanol and 277 μL (2 mmol) of triethylamine dissolved in 5 mL CH_2Cl_2 were added at −40 °C after 15 min. The mixture was kept at this temperature for 45 min after the end of addition. The reaction mixture was heated to 10 °C and washed with 20 mL of HCl (5% in H_2O), 20 mL of NaOH (5% in H_2O) and 80 mL of water. The organic phase was separated, dried over $MgSO_4$, and evaporated (yield 93%). MS (electron impact, *m/z*): 533 $[M - (CH_2)_4CH_3]^+$, 219 $[C_4F_9]^+$. NMR ^1H ($CDCl_3$, TMS, 300 MHz, δ ppm): 4.81 (t, 2H, $J = 12.8$ Hz, CF_2-CH_2-OS), 2.04 (m, 2H, CH_2-CF_2), 1.58 (m, 2H, $J = 12.8$ Hz, $CH_2-CH_2-CF_2$), 1.27 (CH_2), 0.87 (t, 3H, $J = 6.6$ Hz, CH_3). NMR ^{13}C ($CDCl_3$, 75 MHz, δ ppm): 118.67, 110.8, 109.72 (CF_2), 69.43 (t, $J = 25$ Hz, CF_2-CH_2-O), 30.65 (t, $J = 22$ Hz, $C_9H_{19}-CH_2-CF_2$), 31.8 (s, $H_3C-CH_2-CH_2$), 29.5−29.1 (CH_2), 22.65 (s, H_3C-CH_2), 20.01 (s, $CH_2-CH_2-CF_2$), 13.92 (s, CH_3).

4-Methoxy-4′-(2,2,3,3,4,4-hexafluoro-1-tetradecyloxy)diphenyl (9). In a 50 mL two-necked flask fitted with a reflux condenser, 143 mg (718 μmol) of 4′-methoxy-4-hydroxybiphenyl (prepared according to ref 41), 198 mg (1.43 mmol) of K_2CO_3, and 5 mL of dry DMF were stirred under nitrogen. 434 mg (718 μmol) of 2,2,3,3,4,4-hexafluoro-1-tetradecyl nonafluorobutane-sulfonate were added, and the mixture was heated at 90 °C for 2.5 h. The reaction mixture was poured into 20 mL of a saturated NaCl aqueous solution, and the organic layer was extracted using 40 mL of CH_2Cl_2. The organic layer was washed with 400 mL water, dried over $MgSO_4$, and purified by liquid chromatography on Kieselgel 60 (Merck) with a mixture of cyclohexane/ethyl acetate (90:10) as eluent. The product was recrystallized from acetonitrile (mp: 88.5 °C, yield: 27%). IR (KBr cm^{-1}): 2918.7 [C−H asym], 2850.5 [C−H sym], 1610.1 [arom C═C], 1275.9 [C−O], 1252.7, 1187.7, 1150.5 [C−F], 808.6 [δ C−H *out-of-plane*]. MS (electron impact, *m/z*): 504 $[M]^+$, 489 $[M\text{-}CH_3]^+$, 199 $[CH_3O-(C_6H_4)_2-O]^+$. Anal. Found: C: 64.58, H: 6.51. Calcd: C, 64.27; H, 6.78. NMR ^1H ($CDCl_3$, TMS, 300 MHz, δ ppm): 7.52 (2H), 7.50 (2H), 7.03 (2H), 6.99 (2H) (aa′bb′ patterns, $J = 8.82$ Hz arom), 4.50 (t, 2H, $J = 14.7$ Hz, CF_2-CH_2-O), 3.86 (s, 3H, $O-CH_3$), 2.12 (m, 2H, $CH_2-CH_2-CF_2$), 1.64 (m, 2H, $J = 6.99$ Hz, $CH_2-CH_2-CF_2$), 1.31 (CH_2), 0.93 (t, 3H, $J = 6.63$ Hz, CH_2-CH_3). NMR ^{13}C ($CDCl_3$, 75 MHz, δ ppm): 158.93 (s, $C-O-CH_3$), 156.88 (s, $C-O-CH_2$), 135.11 and 133.01 (s, C_6H_4-C), 127.86, 127.80, 115.25 and 114.18 (s, arom *C*H), 65.63 (t, $J = 25.6$ Hz, CF_2-CH_2-O), 55.27 (s, OCH_3), 31.00 (t, $J = 22.6$ Hz, $C_9H_{19}-CH_2-CF_2$), 31.88 (s, $H_3C-CH_2-CH_2$), 29.52−29.16 (CH_2), 22.67 (s, H_3C-CH_2), 20.17 (s, $CH_2-CH_2-CF_2$), 14.08 (s, CH_3).

9-Iodo-11,11,12,12,13,13,14,14,15,15,16,16,17,17,17-pentadecafluoroheptadecan-1-ol (10). 887 mg (5.67 mmol) of 9-decen-1-ol and 2.5 g (5.04 mmol) of perfluoroheptyl iodide were stirred under reflux in 5 mL of dry heptane. Azobisisobutyronitrile was added every 5 min by portions of about 20 mg during 30 min. The reaction mixture was kept one hour under reflux for 1 h after AIBN addition, and the solvent was evaporated. The oily residue was crystallized from methyl ethyl ketone at −15 °C. Recrystallization from acetone (−15 °C) afforded 1.77 g (54%) of **10** mp 28.9 °C. Anal. Found: C, 31.31; H, 2.55. Calcd: C, 31.31; H, 3.09. IR (KBr cm^{-1}): 3393.2 (OH), 2931.2 (C−H asym), 2931.2 (C−H sym), 1240.0, 1209.9, 1149.3 (C−F). NMR ^1H (CCl_4, TMS, 90 MHz, δ ppm): 1.27−1.43 (br. CH_2), 1.55 (s, O*H*), 1.75 (br., OCH_2CH_2), 1.1−2 (integral: 15 H), 2.6, 3.1 (m, 2H, CH_2CHI), 3.53 (t, $J = 5.7$ Hz, 2H, OCH_2), 4.3 (qt., $J = 6.5$ Hz, 1H, C*H*I).

11,11,12,12,13,13,14,14,15,15,16,16,17,17,17-Pentadecafluoroheptadecan-1-ol (11). 2.3 g of 9-iodo-11,11,12,12,13,13,14,14,15,15,16,16,17,17,17-pentadecafluoroheptadecan-1-ol (**10**) were dissolved in a mixture of *n*-propanol (30 mL) and isooctane (50 mL) and heated at 100 °C. 0.5 g of Zn powder was added, and HCl gas was injected into the mixture until complete dissolution of the metal. Then, the reaction mixture was filtered through paper and evaporated. 20 mL of water was added, and the product crystallized. The solid was collected onto a glass filter, thoroughly washed with water, and dried over P_2O_5 in vacuum. The product was recrystallized three times in 20 mL of acetonitrile (yield: 58%). Anal. Found: N, 0.00; C, 38.84; H, 3.49. Calcd: N, 0.00; C, 38.79; H, 4.02. IR (KBr cm^{-1}): 3422.1 [O−H], 2934.3 [C−H asym], 2855.2 [C−H sym], 1240.9, 1210.3, 1168.1, 1148.1 [C−F]. MS (electron impact, *m/z*): 55 $[C_4F_7]^+$, 57 $[C_4H_9]^+$, 69 $[CF_3]^+$, 83 $[C_6H_{11}]^+$, 97 $[C_7H_{15}]^+$, 119 $[C_2F_5]^+$, 131 $[C_3F_5]^+$, 169 $[C_3F_7]^+$, 181 $[C_4F_7]^+$, 391 $[C_7F_{14}]^+$ and $[C_3F_5]^+$, 424, 438, 452, 466, 480 $[M-C_nH_{2n} + H_2O]^+$, 508 $[M-H_2O]^+$. NMR ^{13}C ($CDCl_3$, 75 MHz, δ ppm): 62.90 (CH_2OH), 32.63 (CH_2CH_2OH), 30.86

(t, $J = 22$ Hz, CF_2CH_2), 29.46, 29.35, 29.27, 29.17, 29.06 (CH_2), 25.56 ($CH_2CH_2CH_2OH$), 19.93 ($CF_2CH_2CH_2$). NMR ^{1}H ($CDCl_3$, TMS, 300 MHz, δ ppm): 1.32 (br., 12H, CH_2), 1.53−1.68 (m, 5H, $CH_2CH_2CF_2$ + CH_2CH_2OH + OH), 2.07 (m, 2H, CH_2-CF_2), 3.66 (t, $J = 6.61$ Hz, CH_2OH).

1-Bromo-11,11,12,12,13,13,14,14,15,15,16,16,17,17,17-Pentadecafluoroheptadecane (12). 560 mg (1.06 mmol) of 11,11,12,12,13,13,14,14,15,15,16,16,17,17,17-pentadecafluoroheptadecan-1-ol (11) were placed in the bottom of a 25 mL Pyrex tube and carefully melted with the aid of an oil bath. A mixture of 1 g sulfuric acid and 3 g fuming hydrobromic acid (37% in water) and a piece of carborundum were added. The tube was fitted with a reflux condenser and heated at 130 °C for 2 h. After cooling, 10 mL of water and 10 mL CH_2Cl_2 were added with stirring. The organic layer was separated and dried over $MgSO_4$. The solvent was then evaporated and the product purified by liquid chromatography on silica with a mixture of cyclohexane/dichloromethane (90:10) as eluent (yield: 80%; mp = 38−39 °C). IR (KBr cm^{-1}): 2920.8, 2853.5, 1471.1, 1371.7, 1325.1, 1241.0, 1215.9, 1204.4, 1168.2, 1150.0, 1131.2, 1096.0, 1048.0, 1030.8, 1002.1, 978.1, 948.1, 777.9, 722.6, 699.5, 657.3, 570.6, 542.3, 532.0, 477.7. MS (electron impact, *m/z*): 467 $[M-C_3H_6Br]^+$, 453 $[M-C_4H_8Br]^+$, 439 $[M-C_5H_{10}Br]^+$, 425 $[M-C_6H_{12}]^+$, 181 $[C_4F_7]^+$, 163−165 $[C_6H_{12}Br]^+$, 149−151 $[C_5H_{10}Br]^+$, 135−137 $[C_4H_8Br]^+$, 121−123 $[C_3H_6Br]^+$, 119 $[C_2F_5]^+$, 107−109 $[C_2H_4Br]^+$, 69 $[CF_3]^+$ and $[C_5H_9]^+$, 57 $[C_4H_9]^+$, 55 $[C_4H_7]^+$. Anal. Found: C, 35.00; H, 3.56. Calcd: C, 34.65; H, 3.42. NMR ^{1}H ($CDCl_3$, TMS, 300 MHz, δ ppm): 1.31 (br., 12H, CH_2), 1.61 (m, 2H, $CH_2CH_2CF_2$), 1.87 (m, 2H, CH_2CH_2Br), 2.06 (m, 2H, CH_2CF_2), 3.42 (t, $J = 6.79$ Hz, CH_2Br). NMR ^{13}C ($CDCl_3$, 75 MHz, δ ppm): 19.93 (br., $CH_2CH_2CF_2$), 27.98 ($CH_2CH_2CH_2Br$), 28.56, 28.92, 29.02, 29.09, 29.17 (CH_2), 30.73 (t, $J = 22.2$ Hz, CH_2CF_2), 32.65 (CH_2-CH_2Br), 32.81 (CH_2Br). NMR ^{19}F ($CDCl_3$, 235 MHz, δ ppm): −81.3 (t, $J = 9.6$ Hz, CF_3), −114.9 (m, CF_2CH_2), −122.3, −122.6, −123.3, −124.0, −125.3 (CF_2), −126.7 (CF_3CF_2).

4-(11,11,12,12,13,13,14,14,15,15,16,16,17,17,17-Pentadecafluoroheptadecyl oxy)-4′-methoxybiphenyl (13). 45 mg (320 μmol) K_2CO_3, 38 mg (190 μmol) of 4′-methoxy-biphenyl-4-ol,[41] and 8 mL DMF were placed in a 50 mL two-necked flask fitted with reflux condenser, nitrogen inlet, and calcium chloride tube. The mixture was heated at 90 °C with strirring. After complete dissolution, 112 mg (190 μmol) of 1-bromo-11,11,12,12,13,13,14,14,15,15,16,16,17,17,17-pentadecafluoro heptadecane (**12**) were added. After 2 h of reaction, the mixture was cooled, and the jelly-like solid was separated from the solvent by filtration and dried over P_2O_5. The product was purified by liquid chromatography on silica at 50 °C (cyclohexane 85%: ethyl acetate 15%) and recrystallization from cyclohexane (yield: 67%). IR (KBr cm^{-1}): 2935.9 [C−H asym], 2852.1 [C−H sym], 1608.3 [arom C═C], 1274.5 [C−O], 1247.6, 1217.9, 1145.5 [C−F], 824.8 [δ C-H *out-of-plane*]. MS (electron impact, *m/z*): 708 $[M]^+$. Anal. Found: C, 50.82; H, 4.33. Calcd: C, 50.86; H, 4.41. NMR ^{1}H ($CDCl_3$, TMS, 300 MHz, δ ppm): 7.49 (2H), 7.47 (2H), 6.97 (2H), 6.95 (2H) (aa′bb′ patterns, $J = 8.8$ Hz arom), 4.01 (t, 2H, $J = 6.6$ Hz, CH_2-CH_2-O), 3.85 (s, 3H, $O-CH_3$), 2.06 (m, 2H, $CH_2-CH_2-CF_2$), 1.81 (m, 2H, $J = 6.6$ Hz, CH_2-CH_2-O), 1.61−1.34 (CH_2). NMR ^{13}C ($CDCl_3$, 75 MHz, δ ppm): 158.65 (s, $C-O-CH_3$), 158.24 (s, $C-O-CH_2$), 135.53 and 132.27 (s, C_6H_4-C), 127.8, 114.73 and 114.13 (s, arom CH), 68.04 ($CH_2-O-C_6H_4$), 55.33 ($CH_3-O-C_6H_4$), 30.87 (t, $J = 23.2$ Hz, CF_2-CH_2), 29.42−20.08 (CH_2).

2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Pentadecafluorooctyl Nonafluorobutanesulfonate (14). A solution of 2.15 mL (12 mmol) of nonafluorobutanesulfonyl fluoride (fluorochem) in 60 mL of dry dichloromethane was cooled to −40 °C under nitrogen. A solution of 4.4 g (11.5 mmol) of 1*H*,1*H*-perfluorooctanol (Aldrich) in 2 mL of triethylamine was added with the help of a separatory funnel. The reaction mixture was brought back to −15 °C. The white precipitate was collected and recrystallized from dichloromethane (yield: 49%; mp = 46 °C). NMR ^{1}H ($CDCl_3$, TMS, 300 MHz, δ ppm): 4.86 (t, $J = 12.6$ Hz, CF_2CH_2). IR (KBr cm^{-1}): 1202.7, 1144.8 [C−F], 1042.7 [C═O], 1010.1 [S═O]. MS (electron impact, *m/z*): 683 $[M]^+$, 463 $[M-C_4F_9]^+$, 447 $[M\text{-}OC_4F_9]^+$, 219 $[C_4F_9]^+$, 169 $[C_3F_7]^+$, 131 $[C_3F_5]^+$, 119 $[C_2F_5]^+$, 69 $[CF_3]^+$. Anal. Found: C, 20.76; H, 0.30; S, 5.04. Calcd: C, 21.12; H, 0.29; S, 4.69.

4-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Pentadecafluorooctyloxy)-4′-methoxybiphenyl (15). 404 mg (2.34 mmol) of potassium carbonate, 234 mg (1.17 mmol) of 4′-methoxy-biphenyl-4-ol,[41] and 10 mL of DMF were stirred at 90 °C under nitrogen. 800 mg (1.7 mmol) of 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl nonafluorobutanesulfonate (compound **14**) was added. After 2.5 h at 90 °C, the reaction mixture was cooled and poured into 10 mL of water. The precipitate was collected onto a glass filter, thoroughly washed with water, and dried over P_2O_5 under vacuum. The solid was purified by liquid chromatography at 50 °C on silica (eluent: cyclohenane + ethyl acetate 85:15) and recrystallization from cyclohexane (yield: 74%; mp = 168 °C). IR (KBr cm^{-1}): 1610.3, 1505.8 [arom C═C], 1243.6 [C−O], 1209.3, 1149.8 [C−F], 820.9 [δ C−H *out-of-plane*]. MS (electron impact, *m/z*): 582 $[M]^+$,567 $[M\text{-}CH_3]^+$, 199 $[CH_3O(C_6H_4)_2O]^+$, 313, 363, 413, 463 $[CH_3O(C_6H_4)_2OCH_2\text{-}(CF_2)_n]^+$. Anal. Found: C, 43.17; H, 2.09. Calcd: C, 43.31; H, 2.24. NMR ^{1}H ($CDCl_3$, TMS, 300 MHz, δ ppm): 7.52 (d, $J = 9$ Hz, 2H, arom), 7.49 (d, $J = 8.8$ Hz, 2H, arom), 7.01 (d, $J = 8.8$ Hz, 2H, $J = 9$ Hz, arom), 6.98 (d, $J = 9$ Hz, 2H, arom), 4.51 (t, $J = 13.2$ Hz, OCH_2CF_2), 3.86 (s, 3H, H_3CO). NMR ^{13}C ($CDCl_3$, 75 MHz, δ ppm): 158.87 (s, $C-O-CH_3$), 156.41 (s, $C-O-CH_2$), 135.36 and 132.8 (s, C_6H_4-C), 127.8, 127.7, 115.12 and 114.1 (s, arom CH), 65.37 (t, $J = 29.9$ Hz, $CH_2-O-C_6H_4$), 55.19 ($CH_3-O-C_6H_4$).

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References and Notes

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