

An ω -functionalized perfluoroalkyl chain: synthesis and use in liquid crystal design

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A multiblock polyphilic compound incorporating a perfluoroalkyl spacer and associating groups at both extremities exhibits smectic A and smectic C mesophases.

Perfluoroalkyl iodides permit the formation of stable C–C bonds by the Ullman reaction¹ or by free-radical addition to alkenes followed by dehalogenation.² They have been widely used in the design of highly fluorinated mesomorphic materials.^{3,4} In the course of our research into polyphilic mesogens,⁵ the need arose for new molecular architectures incorporating a central perfluoroalkyl bridge. Symmetric α,ω -diiodoperfluoroalkanes are available by several routes^{6,7} but, 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.

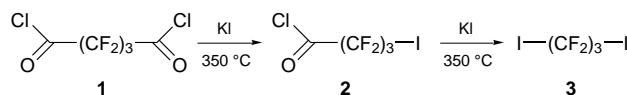
When reacting perfluoroglutaryl chloride with potassium iodide at 200–400 °C, McLoughlin noticed the formation of some 4-iodoperfluorobutyryl chloride,⁷ which was isolated in the form of the free acid (Scheme 1).

In this original work,⁷ relatively high yields (50–60%) of **3** were obtained when using high temperatures and long reaction times. In our experiments, all precautions were taken: (i) to stop the progression of the reaction at the optimum time; (ii) to avoid the hydrolysis of **2** into the corresponding acid; and (iii) to form a versatile derivative of **2** which may be easily purified and characterized.

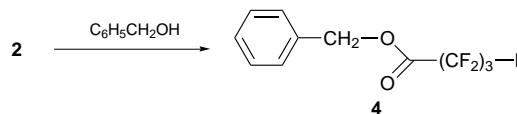
The starting material (hexafluoroglutaryl chloride), obtained from hexafluoroglutaric acid and oxalyl chloride, was vaporized at 220 °C with a nitrogen flow and passed at 350 °C through a glass tube packed with finely ground potassium iodide. The reaction time was determined by the flow of nitrogen. The products were trapped at –78 °C. The degree of conversion estimated by the relative intensities of the 1793 cm^{–1} (C=O stretch) and 1128 cm^{–1} (CF stretch) IR bands; was taken as a criterion for optimizing the reaction time. The products **1**, **2** and **3** were immediately treated with benzyl alcohol in toluene in the presence of pyridine and benzyl-4-iodoperfluorobutanoate **4** was isolated by liquid chromatography with an overall yield of 16% (Scheme 2).‡

Bifunctional spacer units are useful in the chemistry of covalently grafted surfaces, artificial membranes, liquid crystalline polymers, etc. Compound **4** allows the preparation of new mesomorphic materials as will be exemplified below.

Polyphilic compounds are made up of a sequence of molecular fragments differing in their chemical nature. In the



Scheme 1

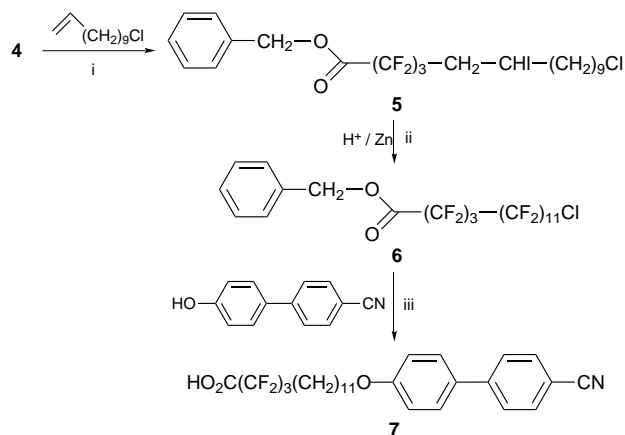


Scheme 2

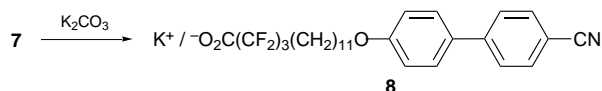
mesomorphic state, unlike fragments have a tendency to segregate, hence leading to the formation of smectic layers.^{4,5,8–10} Perfluoroalkyl chains have been widely used in the design of such materials, but always as end-groups. Starting from benzyl 4-iodoperfluorobutanoate, we have initiated the synthesis of new polyphilic compounds incorporating a perfluoroalkyl spacer in the central part of the molecule. Compound **7** was synthesized in three steps starting from **4** (Scheme 3).

Compound **4** was treated with 1-chloroundec-10-ene in the presence of azoisobutyronitrile (AIBN) to give benzyl 15-chloro-2,2,3,3,4,4-hexafluoro-6-iodopentadecanoate **5** which was in turn reduced to benzyl 15-chloro-2,2,3,3,4,4-hexafluoropentadecanoate **6** using Zn/HCl. Compound **6** was reacted with 4-cyano-4'-hydroxybiphenyl in the presence of K₂CO₃ in DMF to give the polyphilic compound **7**.† Compound **7** melts at 124.5 °C and is not mesomorphic. The pK_a value of **7** is <2. The potassium salt **8** was prepared by treatment with an aqueous solution of K₂CO₃ (Scheme 4).

The mesomorphic properties of **8** have been investigated by differential scanning calorimetry, optical microscopy and X-ray diffraction. On cooling from the isotropic phase, birefringence was detected at 186 °C by the growth of *bâtonnets*¹¹ which gradually merge to form the well known focal conic texture. This mesophase was identified as smectic A since homeotropic domains were also evident in the same temperature range. The focal conic texture is stable down to 135 °C, the temperature at which the focal domains become divided into subdomains showing different interference colours (broken fan texture^{12,13}). At the same temperature, the *schlieren* texture appears in the previously homeotropic domains. These texture changes are



Scheme 3 Reagents and conditions: i, AIBN, heptane, 90 °C, 4 h, 81%; ii, isoocetane + acetic acid, 110 °C, 2 h, 72%; iii, K₂CO₃, DMF, 90 °C, 3 h, then HCl, 68%



Scheme 4

characteristic of the smectic A \rightarrow smectic C transition.¹³ This second fluid mesophase is monotropic, it may be observed for a few minutes in the 135–110 °C range, whereupon crystallization rapidly occurs.

The DSC trace shows, on heating, two endotherms at 135 and 190 °C with enthalpies of 8.9 and 4.3 kJ mol⁻¹ respectively, corresponding to the K \rightarrow S_A and S_A \rightarrow I transitions. On cooling the reverse transitions take place at 186 and 123 °C.

Thus, whilst **7** is isotropic in the 135–190 °C range, the appearance of lamellar order in **8** may be related to the segregation of the ionic head from all other hydrophobic moieties.

X-Ray diffraction experiments were carried out on unoriented samples using Cu-K α radiation. Attempts to investigate **8** in the smectic C phase failed due to its metastable character. The X-ray diffraction pattern recorded at 150 °C in the smectic A phase of **8** is presented in Fig. 1.

At large angles, a broad diffuse ring with a maximum at $2\pi/q = 4.9 \text{ \AA}$ ($q = 4\pi \sin\theta/\lambda$) confirms the identification as smectic A and gives an estimate of the average intermolecular distance (ca. 5.7 Å). At narrow angles, the diagram shows three 00l reflections corresponding to an interlayer distance of 42.2 Å. The distance is intermediate between once and twice the molecular length (32 Å); a partially bilayered packing of the smectic A_d type¹⁴ may therefore be proposed. A similar observation was reported for other rodlike mesogens with ionic head-groups.¹⁵ In Na⁺ and K⁺ long-chain carboxylates, a lipidic sublayer thickness 1.3 times greater than the alkyl chain length was interpreted by the formation of a double layer with strongly disordered alkyl chains.¹⁶ In our case, the rigid cyanobiphenyl cores cannot be accommodated in any conformation, however, these fragments usually tend to optimize their packing by partial interdigitation. As already mentioned for polyphilic mesogens with cyanobiphenyl cores, the appearance of the smectic A_d and C phases can be related to the close packing of lengthwise dimers associated through the cyano groups.⁹

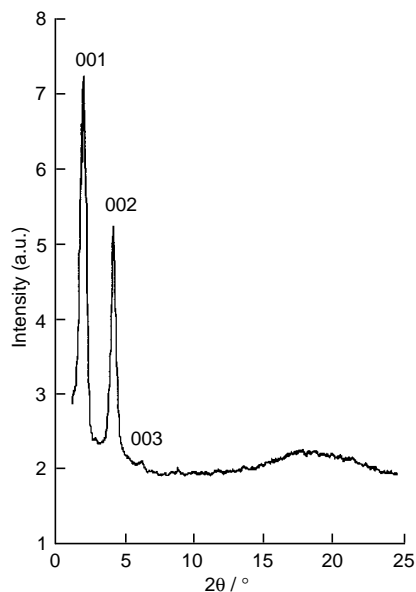


Fig. 1 X-Ray (Debye-Scherrer) diffraction diagram of compound **8** recorded at 150 °C (densitometric profile of the photographic film)

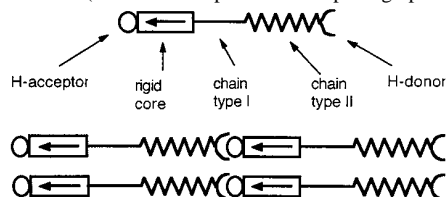


Fig. 2 Polar rows of molecules expected from polyphilic compounds bearing hydrogen-bond donor and acceptor groups at the extremities

The potentialities of hydrogen-bond associated systems in the design of new mesomorphic architectures have been evidenced by several authors.¹⁷ The synthetic scheme described in this paper permits the grafting of hydrogen-bond donor and acceptor groups at each molecular end of a polyphilic compound. It is noteworthy that polar rows of molecules may be formed in the liquid phases of such materials (Fig. 2).

J. Simon is thanked for helpful and stimulating discussions, D. Lelièvre for her help in X-ray measurements.

Footnotes

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‡ Selected analytical data: **4**: MS (EI, m/z): 412 [M]⁺, 277 [M - CO₂CH₂C₆H₅]⁺, 227 [M - CF₂CO₂CH₂C₆H₅]⁺, 177 [M - (CF₂)₂CO₂CH₂C₆H₅]⁺, 127 [M - (CF₂)₃CO₂CH₂C₆H₅]⁺, 91 [M - I(CF₂)₃CO₂]⁺. IR (KBr, cm⁻¹): 1778.9 (C=O), 1190.1, 1145.0 (C-F), 770 (C-H arom., out of plane). ¹H NMR (CDCl₃, Me₄Si, 300 MHz, δ) 7.43 (s, 5 H, C₆H₅), 5.4 (s, 2 H, CH₂). ¹³C NMR (CDCl₃, 75 MHz, δ) 158.45 (t, J 29.9 Hz, CF₂COOR), 133.23 (s, arom.), 129.11 (s, arom.), 128.73 (s, arom.), 128.48 (s, arom.), 108.45 (m, J 265.5, 31.75 Hz, CF₂CF₂CF₂COOR), 106.94 (m, J 267.95, 33.6 Hz, CF₂CF₂COOR), 93.39 (m, J 319.8, 41.5 Hz, ICF₂CF₂CF₂), 69.75 (s, COCH₂). **7**: MS (CI, m/z): 561 [M + NH₄]⁺, 543 [M]⁺. Anal. Found: C, 61.29; H, 5.87; N, 2.61. Calc. C, 61.87; H, 5.74; N, 2.57. IR (KBr, cm⁻¹): 3649 (OH), 2921.5 (C-H asym.), 2850.3 (C-H sym.), 2246.1 (CN), 1781.8 (C=O), 1603.7 (C=C), 1178.1, 1142.5 (C-F), 827.0 (C-H, out of plane). ¹H NMR ([²H₆]acetone, 300 MHz, δ) 8.19 (s, 1 H, COOH), 7.79 (4 H, arom.), 7.67 (2 H, J 9.18 Hz, arom.), 7.05 (2 H, J 9.18 Hz, arom.), 4.03 (t, 2 H, J 6.6 Hz, OCH₂), 2.13 (m, 2 H, CH₂CF₂), 1.78 (qnt, 2 H, J 6.6 Hz, CH₂CH₂CF₂), 1.2 (m, alkyl). ¹³C NMR ([²H₆]acetone, 75 MHz, δ) 160.86 (s, arom.), 160.75 (t, J 28.7 Hz, CF₂COOH), 145.87 (s, arom.), 133.46 (s, arom.), 131.80 (s, arom.), 129.17 (s, arom.), 127.86 (s, arom.), 119.61 [m, J 251.4, 31 Hz, (CH₂)₁₁CF₂CF₂CF₂], 119.51 (s, CN), 115.94 (s, arom.), 112.06 (m, J 263 Hz, CF₂CF₂CF₂COOH), 110.84 (s, arom.), 109.57 (m, J 263, 32 Hz, CF₂CF₂COOH), 68.72 (s, OCH₂), 31.43 [t, J 22 Hz, CH₂(CF₂)₃], 29.8 (CH₂), 26.76 [s, OCH₂CH₂CH₂(CH₂)₈], 20.94 [s, (CH₂)₉CH₂CH₂(CF₂)₃].

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Received, 3rd January 1997; Com. 7/00085E