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Preliminary communication

Mesogens containing *p*-polyfluoro-*m*-nitrobenzoate and 2,3-difluorotolane groups

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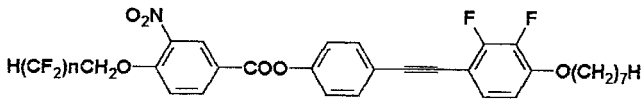
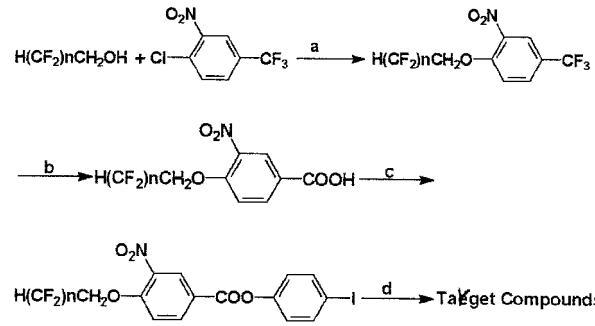
A series of 4-(4-*n*-heptoxy-2,3-difluorophenylethynyl)phenyl 3-nitro-4-polyfluoroalkoxybenzoate liquid crystals was synthesized and their phase transition behaviours were studied by optical polarizing microscopy and DSC. The results show that the mesogens containing long polyfluoroalkoxy chain tend to exhibit the smectic A phase.

Owing to their excellent properties in ferroelectric liquid crystalline display (FLCD) devices, chiral smectic C phase (SmC*) mesogens have been intensely studied in recent years. Generally, the structure of these compounds comprises one or more chiral centres. Liquid crystal compounds containing highly fluorinated alkyl or alkoxy chains as terminal groups tend to form smectic C phases with an increased temperature range [1–3]; however cholesteryl *p*-polyfluoroalkoxy-*m*-nitrobenzoate [4], exhibits only the cholesteric and smectic A phases. We therefore wish to introduce the *p*-polyfluoroalkoxy-*m*-nitrobenzoate moiety into other structures to obtain novel mesogens, possibly with the smectic C phase. The work of Gray *et al.* [5–7] has shown that the inclusion of a lateral difluorinated phenyl ring into a mesogenic core can produce liquid crystals with negative dielectric anisotropy and biaxiality, leading to the suppression of the more ordered smectic phases and the formation of tilted smectic phases. In this work, we prepared a series of 4-(4-*n*-heptoxy-2,3-difluorophenylethynyl)phenyl 3-nitro-4-polyfluoroalkoxybenzoate liquid crystals, shown in the structure below. Their preparation paths are outlined in the scheme.



The mesomorphic properties of new compounds were studied by thermal optical polarizing microscopy using a polarizing microscope (Olympus PM-6) fitted with a heating stage (Mettler FP-80) and a temperature control unit (FP-82); and by differential scanning calorimetry



Conditions and Reagents: a: K_2CO_3, DMF; b: fuming H_2SO_4; c: *p*-I-C_6H_4-COOH, DCC, DMAP, CH_2Cl_2; d: 4-*n*-heptoxy-2,3-difluorophenylacetylene, $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, Et_3N.

Scheme.

(DSC, Shimadzu-50 calorimeter with a data system, heating and cooling rate 5°C min^{-1}). Phase identification was made by comparing the observed textures with those reported in the literatures [8, 9]. Their transition temperatures are summarized below (°C).

$n = 2$, Cr 95.28 SmA 131.78 N 137.75 I 135.27 N 128.82 SmA 74.66 Recr.

$n = 4$, Cr 95.11 SmA 139.93 I 136.91 SmA 59.85 Recr.

From the observation of the mesomorphic properties of these compounds, some interesting results have been obtained. First, the melting and clearing points remain almost same with increasing length of fluorocarbon chain. Second, the compound with $n = 2$ shows both enantiotropic nematic and smectic A phases, while the compound with $n = 4$ exhibits only an enantiotropic smectic A phase. In these cases, therefore, the introduction of fluorine atoms suppresses the nematic phase

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and increases the thermal stability and temperature range of the smectic phase [10, 11]. This is ascribed to the strong attractive interaction between polyfluoroalkoxy chains. With a short polyfluoroalkoxy chain, the lateral attractive interaction is weaker than that between terminal chains, which favours the formation of the nematic phase. With increasing length of polyfluoroalkoxy chain, the lateral attractive interaction increases, favouring the stacking of molecules in layers and the formation of the smectic phase. Third, these compounds exhibit the smectic A phase more readily than cholesteryl *p*-polyfluoroalkoxy-*m*-nitrobenzoate [4], which contains the same polyfluoroalkoxy chain. This shows that the cholesteryl group is less advantageous than the aromatic rings systems to the formation of the smectic phase. Fourth, although the polyfluoroalkoxy and 2,3-difluorophenyl moieties, which both are advantageous to the formation of a tilted smectic phase, are introduced into one mesogen, no smcectic C phase was observed. On the other hand, other similar mesogens containing the 2,2,3,3,4,4,5,5-octa fluoroalkoxy terminal chain but no *m*-nitro group exhibit a broad smectic C phase [12]. This is because (1) the *o*-nitro group is so large that it increases the breadth of the molecule; (2) the dipole moment of the *m*-nitro group is opposite to the total dipole moment of the whole molecular. Thus the *m*-nitro group is disadvantageous to the formation of the smectic C phase.

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Appendix

The following are results of identification analyses on the target compounds.

4-(4-*n*-heptoxy-2,3-difluorophenylethynyl)phenyl 3-nitro-4,2,2,3,3-tetrafluoropropoxybenzoate ($n = 2$). MS (*m*/*z*): 623 (M^+, 39.41), 280 (*p*-$H(CF_2)_2CH_2O$-*m*-NO_2−$C_6H_3CO^+$, 100.00), 525 ($(MH(CH_2)_7)^+$, 16.25), 133 (20.06). Anal. for $C_{31}H_{27}F_6O_6N$ calc. C 59.71, H 4.37, N 2.25, F 18.28; found C 59.29, H 4.18, N 2.15, F 18.46%. ^{1}H NMR ($CDCl_3$/TMS, 90 MHz) δH (ppm): 0.90–1.20 (m, 3H, CH_3), 1.20–1.80 (m, 8H, RH), 4.17 (t, 2H, $J = 6$ Hz, OCH_2), 4.70 (t, 2H, $J = 14$ Hz, OCH_2CF_2), 6.30 (tt, 1H, $J_1 = 52$ Hz, $J_2 = 6$ Hz, CF_2H), 6.60–7.10 (m, 2H, ArH), 7.10–7.50 (m, 3H, ArH), 7.70 (d, 2H, $J = 9$ Hz, ArH), 8.48 (d, 1H, $J = 9$ Hz, ArH), 8.80 (s, 1H, ArH). ^{19}F NMR ($CDCl_3$/TFA, 56.4 MHz) δF (ppm): 49.0 (m, 2F, CF_2), 55.5 (m, 1H, ArF), 64.1 (d, 2F, $J = 56$ Hz, HCF_2), 80.5 (m, 1F, ArF). IR (KBr, ν_{max}, cm^{-1}): 2949, 1739, 1615, 1514, 1533, 1474, 1280, 1238, 1204, 1167, 1104, 1082, 876, 810, 753, 533.

4-(4-*n*-heptoxy-2,3-difluorophenylethynyl)phenyl 3-nitro-4,2,2,3,3,4,4,5,5-octa fluoropentoxybenzoate ($n = 4$). MS (*m*/*z*): 723 (M^+, 30.27), 380 (*p*-$H(CF_2)_4CH_2O$-*m*-NO_2−$C_6H_3CO^+$, 100.00), 625 ($(MH(CH_2)_7)^+$, 17.97), 246 (15.66). Anal. for $C_{33}H_{27}F_{10}O_6N$ calc C 54.78, H 3.76, N 1.94, F 26.28; found C 54.70, H 3.79, N 1.95, F 26.39%. ^{1}H NMR ($CDCl_3$/TMS, 90 MHz) δH (ppm): 0.90–1.20 (m, 3H, CH_3), 1.20–1.80 (m, 8H, RH), 4.20 (t, 2H, $J = 86$ Hz, OCH_2), 4.83 (t, 2H, $J = 14$ Hz, OCH_2CF_2), 6.30 (tt, 1H, $J_1 = 52$ Hz, $J_2 = 6$ Hz, CF_2H), 6.60–7.10 (m, 2H, ArH), 7.10–7.50 (m, 3H, ArH), 7.72 (d, 2H, $J = 9$ Hz, ArH), 8.48 (d, 1H, $J = 9$ Hz, ArH), 8.77 (s, 1H, ArH). ^{19}F NMR ($CDCl_3$/TFA, 56.4 MHz) δF (ppm): 41.6 (m, 2F, CF_2), 47.8 (m, 2F, CF_2), 52.5 (m, 2F, CF_2), 55.5 (m, 1H, ArF), 59.8 (d, 2F, $J = 56$ Hz, HCF_2), 80.5 (m, 1F, ArF). IR (KBr, ν_{max}, cm^{-1}): 2929, 2856, 1739, 1622, 1534, 1517, 1474, 1294, 1244, 1202, 1171, 1134, 1085, 808, 754, 534.

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