ELSEVIER

Journal of Fluorine Chemistry 110 (2001) 37–42

JOURNAL OF FLUORINE CHEMISTRY

www.elsevier.com/locate/jfluchem

Synthesis and mesomorphic properties of mesogens containing (4-polyfluoroalkoxy-2,3,5,6-tetrafluorophenyl)ethynyl groups

Kan Wang, Baoquan Chen, Yonggang Yang, Hengfeng Li, Kegang Liu, Jianxun Wen*

Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, PR China

Received 25 January 2001; accepted 18 April 2001

Abstract

Due to the activation of fluorine atoms in aromatic rings by four other fluorine atoms and a 4-ethynyl bond, polyfluoroalkoxy chains can be introduced into aromatic rings by direct nucleophilic substitution reaction using potassium carbonate as base to prepare 4-polyfluoroalkoxy-2,3,5,6-tetrafluorophenylacetylenes. Seven compounds containing (4-polyfluoroalkoxy-2,3,5,6-tetrafluorophenyl)ethynyl groups have been prepared by catalytic reaction using bis(triphenylphosphine)palladium dichloride and copper(I) iodide as catalysts. Mesomorphic properties of target compounds were investigated by optical polarizing microscopy and differential scanning calorimetry (DSC). Mesophases were devalued by highly fluorinated alkoxy terminal chains compared with similar compounds whose terminal chains were not highly fluorinated. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Mesogens; Highly fluorinated alkoxy tolane

1. Introduction

Fluorinated mesogens have been paid close attention in the past decade due to their unique properties, such as low viscosity, low conductivity and high chemical and thermal stability. Laterally, fluorinated mesogens have been widely studied, from their synthesis to their physical properties. The 2,3,5,6-tetrafluorotolanes, which were reported firstly by our group, possess high birefringence, low viscosity, low conductivity and high photochemical stability [1–7], and are valuable as components of mixtures for some electro-optical applications, such as super twisted nematic (STN) and thin film transistor (TFT) liquid crystals displays (LCD). At the same time, mesogens containing highly fluorinated alkyl terminal chains are advantageous to the formation of smectic C phases [8,9] and are valuable as potential important components of mixtures for ferroelectric liquid crystals display (FLCD). In order to meet the higher quality requirements for materials and observe the relationship between structures and properties, the synthesis of mesogens containing a group that combines the two units mentioned above was desired. The structures of the groups are shown in Scheme 1.

Various methods have been developed to synthesize fluoroalkyl aryl ethers [10]. Direct aromatic nucleophilic fluoroalkoxylation was used in some reactions, which can be carried out for activated aryl and heteroaryl halides [11–13]. Polyfluorosubstituents and triple bonds were considered as activating substituents in aromatic rings. So direct aromatic nucleophilic fluoroalkoxylation can be carried out under weakly basic conditions, such as with potassium carbonate. Strong bases, such as sodium hydride or potassium hydroxide are so strong that they can attack other fluorine atoms and produce by-products.

In this paper, we describe a convenient method to prepare seven novel compounds containing (4-polyfluoroalkoxy-2,3,5,6-tetrafluorophenyl)ethynyl groups and discuss the mesomorphic properties of these compounds. The synthesis of the target compounds is outlined in Scheme 2.

2. Results and discussion

Although it is difficult to obtain 1*H*,1*H*-perfluoroalkoxybenzene by the direct etherification of the 1*H*,1*H*-perfluoroalkanol, due to the activation of fluorine atoms in aromatic ring by the other four fluorine atoms and 4-ethynyl bond, but the fluoroalkoxylation can easily be carried out using potassium carbonate as base.

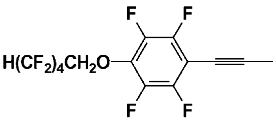
The transition behaviors of target compounds were summarized in Table 1.

It was reported by our group that the compounds containing the structures in Scheme 3 are not mesogens [16]. There

---

* Corresponding author. Tel.: +86-21-6416-3300.
E-mail address: wenjianxun@pub.sioc.ac.cn (J. Wen).

PII: S0022-1139(01)00403-1



Scheme 1.

is a widely known conclusion that mesogens containing highly fluorinated alkyl terminal chains are advantageous to the formation of mesophases, especially of a tilted smectic phases. So at first, we wanted to obtain the ferroelectric phases by introducing both the highly fluorinated alkyl terminal chain and chiral center into the 2,3,5,6-tetrafluorotolane mesomorphic cores; compound **g** was synthesized based on this idea. But **g** did not exhibit mesophases. It was considered that the short mesomorphic cores that include only two aromatic rings, give it poor mesomorphic properties. For this reason, four chiral three-ring compounds (**c**, **d**, **e**, **f**) were prepared. The observed results prove that all these four compounds are mesogens, but only **c** exhibits a narrow chiral smectic C phase (7.6°C), the other three compounds do not exhibit ferroelectric phases. Compounds **c** and **f** exhibit a narrow blue phase (BP) between the cholesteric phase and the isotropic liquid. For illustrating the influence of highly fluorinated alkyl terminal chains, phase transition temperatures of compounds **c′** and **d′** [17] were compared with **c** and **d**. The structures of **c′** and **d′** are seen in Scheme 4 and their phase transition properties are listed in Table 1. It is clear that the range of mesophases were depressed by highly fluorinated alkyl chains, but that the smectic phase become stable.

Compounds **a** and **b** have two highly fluorinated alkyl chains at both terminal sides, so they are strongly hydrophobic molecules. When they were compared with corresponding compounds (**a′** and **b′**, their structures are in Scheme 5 and their phase transition properties are listed in Table 1 [18]), which contain no fluorosubstituent on the tolane side, it can be concluded that their mesormorphic properties have been damaged by their second highly fluorinated alkyl chain, and especially **b** does not exhibit a mesomorphic state at all. It seems that the second highly fluorinated alkyl chains in 2,3,5,6-tetrafluorotolanes are disadvantageous to the formation of mesophases in the structures. This is considered to be caused by the effects of self-assembly. These compounds can be divided into two blocks, a fluorophilic block and a fluorophobic block [19]. There are almost no fluorophobic blocks in compounds **a** and **b**, so it is difficult for them to arrange in an ordered way, on the other side; the suitable layer arrangements can be formed easily in compounds **a′** and **b′**.

In conclusion, 4-polyfluoroalkoxy-2,3,5,6-tetrafluorotolanes exhibit less good mesomorphic properties than corresponding 4-alkoxy-2,3,5,6-tetrafluorotolanes or 4-alkoxytolanes. Higher quality mesogens were not obtained in these structures. It is considered that highly fluorinated alkyl terminal chains are advantageous to the formation of smectic phases, not nematic phases, but a 2,3,5,6-tetrafluorophenyl is advantageous to the formation of a nematic phase and can depress smectic phases. A combination of these two contradictory characters damages all mesophases.

3. Experimental details

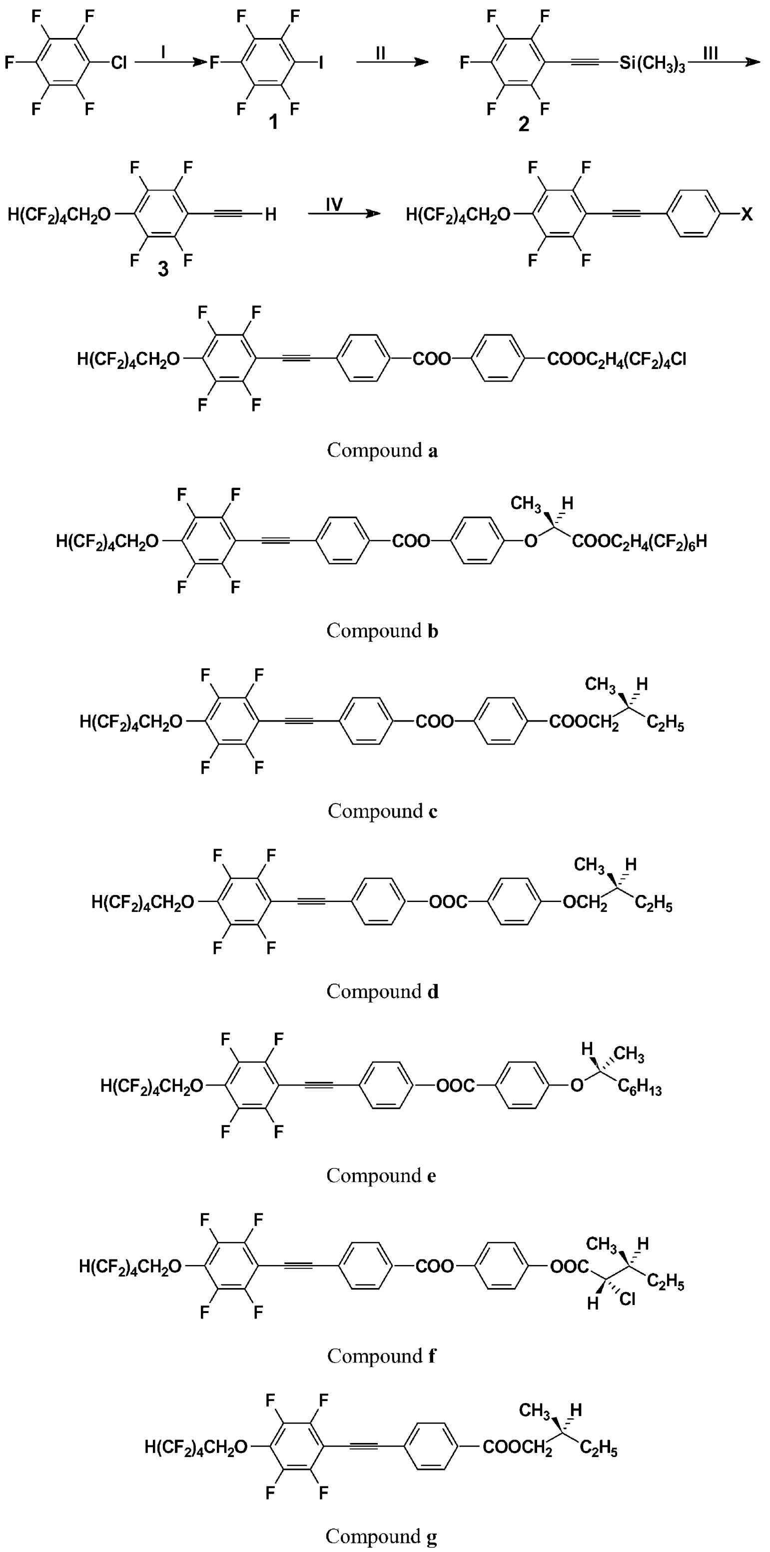
3.1. General techniques

The structures of the final products and intermediates were elucidated by a variety of spectral methods. IR spectra were recorded on a PE-983G spectrophotometer, using KBr pellets of solids or films of liquids. ^{1}H NMR spectra with tetramethylsilane (TMS) as internal standard and ^{19}F NMR spectra with trifluoroacetic acid (TFA) as external standard were recorded on a Bruker 300 spectrometer (300 MHz), a Varian EM360L spectrometer (60 MHz) or a FX-90Q spectrometer (90 MHz). For ^{19}F NMR spectra high field was positive. MS spectra were measured with a Finnigan-4021 spectrometer using electrical ionization. The phase transition temperatures of the target compounds were measured visually by optical microscopy using a polarizing microscope (Olympus PM-6) fitted with a heating stage

Table 1
The phase transition temperatures of the target compounds on heating and subsequent cooling[a]

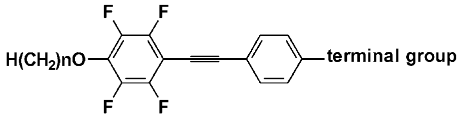
Compounds	Transition temperatures (°C)
a	Cr 122.29 SmA 162.76 I 159.47 SmA 96.71 Recr
b	Cr 110.68 I 89.00 Recr
c	Cr 126.7 SmC* 134.3 SmA 159.1 Ch 163.2 (BP) I (BP) 161.5 Ch 156.9 SmA 132.0 SmC* 103.6 Recr
d	Cr 96.0 SmA 121.7 Ch 133.7 I 132.2 Ch 120.3 SmA 65.7 Recr
e	Cr 65.6 I 56.7 SmA 42.5 Recr
f	Cr 119.9 SmA 135.7 Ch 148.8 (BP) I (BP) 147.2 Ch 127.5 SmA 102.8 Recr
g	Cr 80.6 I 63.7 Recr
a′	Cr 130.36 SmA 222.20 I 220.08 SmA 112.02 Recr
b′	Cr 84.7 SmB 87.4 SmA 157.5 I 154.6 SmA 85.8 SmB 68.4 CrE
c′	Cr 89.5 SmC* 90.0 SmA 124.7 Ch 153.1 I 152.9 Ch 124.2 SmA 89.7 SmC* 70.6 Recr
d′	Cr 93.8 Ch 141.1 I 139.9 Ch 53.4 Recr

[a] Cr: crystal; CrE: crystal E phase; SmA: smectic A phase; SmC: smectic C phase; Ch: cholesteric phase; SmC*: chiral smectic C phase; I: isotropic liquid; N: nematic phase; BP: blue phase; Recr: recrystallization.



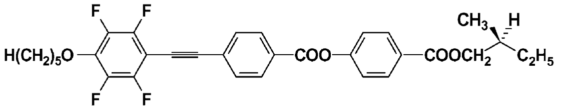
Conditions and reagents: (I) 1. Mg/THF, 2. I_2/THF; (II) $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, H-≡-$SiMe_3$, Et_3N; (III) $H(CF_2)_4CH_2OH$, K_2CO_3, DMF; (IV) 4-I-C_6H_4-X, $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, Et_3N.

Scheme 2. Synthesis route.

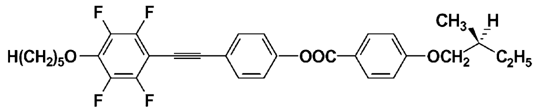


Terminal group =CN, alkyl, alkoxy, Cl, Br, NO_2, etc.

Scheme 3.



Compound **c'**



Compound **d'**

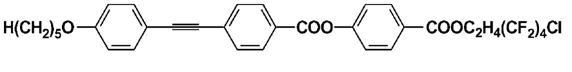
Scheme 4.

(METTER FP-80) and a control unit (FP-82), and by differential scanning calorimetry (DSC, Shimadzu DSC-50 calorimeter with a data system, heating and cooling rate 5°C min^{-1}). The transition temperatures reported in this paper were the peak values of the transition on DSC traces. Phase identification was made by comparing the observed texture with those in the literature [14,15].

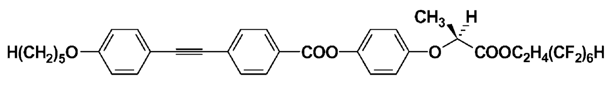
3.2. Synthesis route

The synthesis of the target compounds is outlined in Scheme 2. The preparation of intermediate **2** was reported previously [16]. References to the preparation of the reagents noted 4-I-C_6H_4-X in Scheme 2 used to synthesis target compounds **a**–**g** are given in [18,20–22].

Pentafluorochlorobenzene was reacted with magnesium filings in anhydrous tetrahydrofuran solution at −10°C, then iodine was added into the obtained Grignard reagent to get pentafluoroiodobenzene (compound **1**). Compound **1** was coupled with trimethylsilylacetylene using bis(triphenylphosphine)palladium dichloride and copper(I) iodide as catalyst in anhydrous triethylamine solution; the product was trimethylsilylethynyl-2,3,4,5,6-pentafluorobenzene (compound **2**). The fluorosubstituent on the *para*-position of compound **2** was substituted by a 2,2,3,3,4,4,5,5-octafluoropentoxy group under basic conditions, at the same time, the trimethylsilyl protected group was removed and 4-(2,2,3,3,4,4,5,5-octofluoropentoxy)-2,3,5,6-tetrafluorophenylacetylene (compound **3**) was obtained. Target compounds were prepared by cross-coupling reaction between compound **3** and corresponding reagents (4-I-C_6H_4-X) using bis(triphenylphosphine)palladium dichloride and copper(I) iodide as catalyst.



Compound **a'**



Compound **b'**

Scheme 5.

3.2.1. Preparation of 4-(2,2,3,3,4,4,5,5-octafluoropentoxy)-2,3,5,6-tetrafluorophenylacetylene (compound 3)

Trimethylsilylethynyl-2,3,4,5,6-pentafluorobenzene (compound **2**) (2.00 g, 7.58 mmol), potassium carbonate (1.27 g, 9.20 mmol), 2,2,3,3,4,4,5,5-octafluoropentanol (2.54 g, 10.95 mmol) and anhydrous *N,N*-dimethylformamide (30 ml) were added into a 100 ml flask, then stirred at room temperature. ^{19}F NMR monitored the reaction solution until the reagent 2 was disappeared. Diethyl ether (50 ml) and water (20 ml) were added into the flask, the solution was extracted with diethyl ether. The ether extracts were washed neutral with brine and dried over anhydrous magnesium sulfate. Solvent was removed in vacuo and the residue was purified by column chromatography on silica gel using petroleum ether (bp 60–90°C) as the eluent to give compound **3** as a colorless liquid 1.92 g, yield 63%. ^1H NMR ($CDCl_3$/TMS, 90 MHz) δH (ppm): 3.46 (s, 1H, ≡C–H), 4.62 (t, 2H, $J = 13$ Hz, CF_2CH_2O), 5.95 (tt, 1H, $J_1 = 52$ Hz, $J_2 = 6$ Hz, CF_2H). ^{19}F NMR ($CDCl_3$/TFA, 56.4 MHz) δF (ppm): 44.4 (t, 2F, $J = 13$ Hz, CF_2CH_2), 48.7 (m, 2F, CF_2), 53.6 (m, 2F, CF_2), 59.5–61.7 (m, 4F, CF_2H and Ar_F), 79.5 (d, 2F, $J = 24$ Hz, Ar_F).

3.2.2. Synthesis of target compounds

*3.2.2.1. Preparation of 4-(6-chloro-3,3,4,4,5,5,6,6-octafluorohexoxycarbonyl)phenyl 4-[4-(2,2,3,3,4,4,5,5-octafluoropentoxy-2,3,5,6-tetrafluorophenyl)ethynyl]benzoate (**a**). Typical procedure*: Compound **3** (250 mg, 0.496 mmol), 4-(6-chloro-3,3,4,4,5,5,6,6-octofluorohexoxycarbonyl)phenyl 4-iodobenzoate (192 mg, 0.40 mmol), bis(triphenylphosphine)palladium dichloride (30 mg), copper(I) iodide (50 mg), triphenylphosphine (80 mg), anhydrous triethylamine (15 ml) were added into a 25 ml flask. The resulting mixture was stirred at 60°C for 48 h under a nitrogen atmosphere. After the reaction was completed, the precipitate formed was filtered off and washed with water, then dried over anhydrous magnesium sulfate. The solvent was removed in vacuo and the residue was purified by column chromatography on silica gel using petroleum ether (bp 60–90°C) ethyl acetate (12:1) as the eluent. This gave pale yellow crystals, which were recrystallized from methanol to yield white flaky crystals of compound (**a**) 408 mg, yield 90%. MS (*m/z*, %): 906 (M^+, 0.11), 507 (*p*-H(CF$_2$)$_4$CH$_2$O–C$_6$F$_4$≡C$_6$H$_4$–CO$^+$, 100.00), 691 ((*M*–H(CF$_2$)$_4$CH$_2$)$^+$, 0.51), 292 (O–C$_6$F$_4$≡C$_6$H$_4$–CO$^+$, 5.66). Anal. for C$_{33}$H$_{15}$ClF$_{20}$O$_5$ calc. C 43.71, H 1.67, F 41.90%, found C 43.78, H 1.78, F 41.99%. ^{1}H NMR (CDCl$_3$/TMS, 90 MHz) δ_H (ppm): 2.70 (m, 2H, CH$_2$CF$_2$), 4.50–5.20 (m, 4H, OCH$_2$), 6.20 (tt, 1H, $J_1 = 52$ Hz, $J_2 = 6$ Hz, CF$_2$H), 7.45 (d, 2H, $J = 9$ Hz, Ar$_H$), 7.83 (d, 2H, $J = 9$ Hz, Ar$_H$), 8.10–8.40 (m, 4H, Ar$_H$). ^{19}F NMR (CDCl$_3$/TFA, 56.4 MHz) δ_F (ppm): −9.4 (m, 2F, CF$_2$Cl), 36.2 (m, 2F, CF$_2$), 42.4 (m, 2F, CF$_2$), 43.5 (m, 2F, CF$_2$), 45.5 (m, 2F, CF$_2$), 47.7 (m, 2F, CF$_2$), 53.4 (m, 2F, CF$_2$), 58.4–60.7 (m, 4F, CF$_2$H and Ar$_F$), 78.7 (m, 2F, Ar$_F$). IR (KBr, υ_{max}, cm^{-1}): 1739, 1603, 1490, 1443, 1406, 1346, 1260, 1168, 1133, 1067, 992, 764, 700, 544, 504.

*3.2.2.2. (S)-4-[1-(3′,3′,4′,4′,5′,5′,6′,6′,7′,7′,8′,8′-dodecafluorooctoxycarbonyl)ethoxy]phenyl 4-[4-(2,2,3,3,4,4,5,5-octafluoropentoxy-2,3,5,6-tetrafluorophenyl)ethynyl]-benzoate (**b**).* [α_D^{24}] = −1.837° (*C* = 5.743 mg/1.2 ml). MS (*m/z*, %): 1016 (*M*$^+$, 0.82), 507 (*p*-H(CF$_2$)$_4$CH$_2$O–C$_6$F$_4$≡C$_6$H$_4$–CO$^+$, 100.00), 643 ((*M*–COOC$_2$H$_4$(CF$_2$)$_6$H)$^+$, 2.97). Anal. for C$_{37}$H$_{20}$F$_{24}$O$_6$ cacl. C 43.72, H 1.98, F 44.85%, found C 43.68, H 2.03, F 45.00%. ^{1}H NMR (CDCl$_3$/TMS, 90 MHz) δ_H (ppm): 1.78 (d, 3H, $J = 6.8$ Hz, CH$_3$), 2.62 (m, 2H, CH$_2$CF$_2$), 4.55–5.05 (m, 5H, 2OCH$_2$ and OCH), 5.50–6.90 (m, 2H, 2CF$_2$H), 7.05 (d, 2H, $J = 9$ Hz, Ar$_H$), 7.30 (d, 2H, $J = 9$ Hz, Ar$_H$), 7.83 (d, 2H, $J = 9$ Hz, Ar$_H$), 8.33 (d, 2H, $J = 9$ Hz, Ar$_H$). ^{19}F NMR (CDCl$_3$/TFA, 56.4 MHz) δ_F (ppm): 36.8 (m, 2F, CF$_2$), 44.0–49.0 (m, 10F, 5CF$_2$), 53.0 (m, 2F, CF$_2$), 59.0–61.5 (m, 6F, 2CF$_2$H and Ar$_F$), 79.0 (m, 2F, Ar$_F$). IR (KBr, υ_{max}, cm^{-1}): 1753, 1727, 1605, 1491, 1406, 1444, 1272, 1250, 1202, 1140, 1078, 990, 860, 765, 693, 541.

*3.2.2.3. (S)-(2-methyl-butoxycarbonyl)phenyl 4-[4-(2,2,3,3,4,4,5,5-octafluoropentoxy-2,3,5,6-tetrafluorophenyl)-ethynyl]benzoate (**c**).* [α_D^{24}] = 1.450° (*C* = 3.57 mg/1.2 ml). MS (*m/z*, %): 714 (*M*$^+$), 507 (*p*-H(CF$_2$)$_4$CH$_2$O–C$_6$F$_4$≡C$_6$H$_4$–CO$^+$, 100.00). Anal. for C$_{32}$H$_{22}$F$_{12}$O$_5$ calc. C 53.79, H 3.07, F 31.90%, found C 53.66, H 2.63, F 32.00%. ^{1}H NMR (CDCl$_3$/TMS, 90 MHz) δ_H (ppm): 0.95–1.04 (m, 6H, 2CH$_3$), 1.25–1.57 (m, 2H, CH$_2$), 1.85–1.89 (m, 1H, *CH), 4.18 (d, 2H, $J = 7$ Hz, OCH$_2$), 4.72 (t, 2H, $J = 12$ Hz, OCH$_2$CF$_2$), 6.09 (tt, 1H, $J_1 = 52$ Hz, $J_2 = 6$ Hz, CF$_2$H), 7.31 (d, 2H, $J = 9$ Hz, Ar$_H$), 7.71 (d, 2H, $J = 9$ Hz, Ar$_H$), 8.14 (d, 2H, $J = 9$ Hz, Ar$_H$), 8.21 (d, 2H, $J = 9$ Hz, Ar$_H$). ^{19}F NMR (CDCl$_3$/TFA, 56.4 MHz) δ_F (ppm): 43.9 (t, 2F, $J = 12$ Hz, CH$_2$CF$_2$), 48.2 (m, 2F, CF$_2$), 52.9 (t, 2F, $J = 52$ Hz, CF$_2$), 59.1 (m, 2F, Ar$_F$), 60.1 (d, 2F, $J = 52$ Hz, CF$_2$H), 79.2 (m, 2F, Ar$_F$). IR (KBr, υ_{max}, cm^{-1}): 1730, 1708, 1492, 1269, 1206, 1170, 1132, 991, 768.

*3.2.2.4. [4-(2,2,3,3,4,4,5,5-octafluoropentoxy-2,3,5,6-tetrafluorophenyl)ethynyl]phenyl (S)-4-(2-methylbutoxy)-benzoate (**d**).* [α_D^{24}] = 1.626° (*C* = 2.14 mg/1.2 ml). MS (*m/z*, %): 686 (*M*$^+$), 191 (*p*-C$_2$H$_5$CH(CH$_3$)CH$_2$O–C$_6$H$_4$–CO$^+$, 100.00), 121 (O–C$_6$H$_4$–CO$^+$, 82.81). Anal. for C$_{31}$H$_{22}$F$_{12}$O$_4$ calc. C 54.24, H 3.23, F 33.21%, found C 54.35, H 2.93, F 33.30%. ^{1}H NMR (CDCl$_3$/TMS, 90 MHz) δ_H (ppm): 0.90–2.08 (m, 9H, R$_H$), 3.90 (d, 2H, $J = 6$ Hz, OCH$_2$), 4.72 (t, 2H, $J = 12$ Hz, OCH$_2$CF$_2$), 6.05 (tt, 1H, $J_1 = 60$ Hz, $J_2 = 6$ Hz, CF$_2$H), 6.95 (d, 2H, $J = 9$ Hz, Ar$_H$), 7.24 (d, 2H, $J = 9$ Hz, Ar$_H$), 7.64 (d, 2H, $J = 9$ Hz, Ar$_H$), 8.14 (d, 2H, $J = 9$ Hz, Ar$_H$). ^{19}F NMR (CDCl$_3$/TFA, 56.4 MHz) δ_F (ppm): 43.9 (t, 2F, $J = 12$ Hz, CH$_2$CF$_2$), 48.2 (m, 2F, CF$_2$), 52.9 (t, 2F, $J = 52$ Hz, CF$_2$), 59.1 (m, 2F, Ar$_F$), 60.1 (d, 2F, $J = 52$ Hz, CF$_2$H), 79.2 (m, 2F, Ar$_F$). IR (KBr, υ_{max}, cm^{-1}): 1731, 1605, 1516, 1493, 1264, 1203, 1170, 991, 536.

*3.2.2.5. [4-(2,2,3,3,4,4,5,5-octafluoropentoxy-2,3,5,6-tetrafluorophenyl)ethynyl]phenyl (R)-(4-oct-2-oxy)-benzoate (**e**).* [α_D^{24}] = −0.12° (*C* = 5.45 mg/1.2 ml). MS (*m/z*, %): 729 ((*M*$^+$ + 1), 0.15), 121 (O–C$_6$H$_4$–CO$^+$, 100.00), 233 (4-C$_6$H$_{13}$CH(CH$_3$)O–C$_6$H$_4$–CO$^+$, 59.42). Anal. for C$_{34}$H$_{28}$F$_{12}$O$_4$ calc. C 56.05, H 3.87, F 31.29%, found C 56.15, H 3.71, F 31.20%. ^{1}H NMR (CDCl$_3$/TMS, 90 MHz) δ_H (ppm): 0.82–1.82 (m, 16H, R$_H$), 4.52 (t, 1H, $J = 7$ Hz, OCH), 4.77 (t, 2H, $J = 12$ Hz, OCH$_2$CF$_2$), 6.15 (tt, 1H, $J_1 = 60$ Hz, $J_2 = 6$ Hz, CF$_2$H), 7.03 (d, 2H, $J = 9$ Hz, Ar$_H$), 7.30 (d, 2H, $J = 9$ Hz, Ar$_H$), 7.70 (d, 2H, $J = 9$ Hz, Ar$_H$), 8.18 (d, 2H, $J = 8$ Hz, Ar$_H$). ^{19}F NMR (CDCl$_3$/TFA, 56.4 MHz) δ_F (ppm): 44.0 (t, 2F, $J = 12$ Hz, CH$_2$CF$_2$), 48.2 (m, 2F, CF$_2$), 53.0 (t, 2F, $J = 52$ Hz, CF$_2$), 59.7 (m, 2F, Ar$_F$), 60.2 (dt, 2F, $J_1 = 52$ Hz, $J_2 = 5.2$ Hz, CF$_2$H), 79.2 (m, 2F, Ar$_F$). IR (KBr, υ_{max}, cm^{-1}): 2925, 2857, 1683, 1604, 1528, 1496, 1433, 1295, 1257, 1204, 1132, 1003, 894, 861, 838, 777, 723, 553.

*3.2.2.6. (1S,2S)-(1-chloro-2-methyl-butylcarbonyloxy)phenyl 4-[4-(2,2,3,3,4,4,5,5-octafluoropentoxy-2,3,5,6-tetrafluorophenyl)ethynyl]benzoate (**f**).* [α_D^{24}] = 1.45° (*C* = 3.57 mg/1.2 ml). MS (*m/z*, %): 507 (H(CF$_2$)$_4$CH$_2$O–C$_6$F$_4$≡C$_6$H$_4$–CO$^+$), 109 (100.00), 135 (7.11). Anal. for C$_{32}$H$_{21}$ClF$_{12}$O$_5$ calc. C 51.32, H 2.83, F 31.95%, found C 51.46, H 2.60, F 31.54%. ^{1}H NMR (CDCl$_3$/TMS, 90 MHz) δ_H (ppm): 0.90–2.60 (m, 9H, R$_H$), 4.37 (t, 1H, $J = 7$ Hz, OCH), 4.73 (t, 2H, $J = 13$ Hz, OCH$_2$CF$_2$), 6.06 (tt, 1H, $J_1 = 52$ Hz, $J_2 = 6$ Hz, CF$_2$H), 7.15–7.45 (m, 4H, Ar$_H$), 7.72 (d, 2H, $J = 9$ Hz, Ar$_H$), 8.23 (d, 2H, $J = 9$ Hz, Ar$_H$). ^{19}F NMR (CDCl$_3$/TFA, 56.4 MHz) δ_F (ppm): 43.9 (t, 2F, $J = 13$ Hz, CH$_2$CF$_2$), 48.2 (m, 2F, CF$_2$), 53.0 (t, 2F, $J = 52$ Hz, CF$_2$), 59.1 (m, 2F, Ar$_F$), 60.1 (dt, 2F, $J_1 = 52$ Hz, $J_2 = 5.2$ Hz, CF$_2$H), 79.2 (m, 2F, Ar$_F$). IR (KBr, υ_{max}, cm^{-1}): 2971, 1726, 1605, 1493, 1446, 1406, 1273, 1178, 1080, 1019, 990, 860, 767, 694, 524.

*3.2.2.7. (S)-2-methyl-butyl 4-[4-(2,2,3,3,4,4,5,5-octafluoropentoxy-2,3,5,6-tetrafluorophenyl)ethynyl]benzoate (**g**).* [α_D^{24}] = 0.27° (*C* = 11.79 mg/1.2 ml). MS (*m/z*, %): 594 (*M*$^+$, 14.80), 507 (H(CF$_2$)$_4$CH$_2$O–C$_6$F$_4$≡C$_6$H$_4$–CO$^+$, 100.00). Anal. for C$_{25}$H$_{18}$F$_{12}$O$_3$ calc. C 50.52, H 3.05, F 38.35%, found C 50.73, H 2.79, F 38.57%. ^{1}H NMR (CDCl$_3$/TMS, 90 MHz) δ_H (ppm): 0.95–1.04 (m, 6H,

$2CH_3$), 1.25–1.57 (m, 2H, CH_2), 1.85–1.89 (m, 1H, $^*CH$), 4.18 (d, 2H, $J = 7$ Hz, OCH_2), 4.70 (t, 2H, $J = 13$ Hz, OCH_2CF_2), 6.06 (tt, 1H, $J_1 = 60$ Hz, $J_2 = 6$ Hz, CF_2H), 7.61 (d, 2H, $J = 9$ Hz, Ar_H), 8.03 (d, 2H, $J = 9$ Hz, Ar_H). ^{19}F NMR ($CDCl_3$/TFA, 56.4 MHz) δ_F (ppm): 44.0 (t, 2F, $J = 12$ Hz, CH_2CF_2), 48.2 (m, 2F, CF_2), 53.0 (t, 2F, $J = 52$ Hz, CF_2), 59.7 (m, 2F, Ar_F), 60.2 (dt, 2F, $J_1 = 52$ Hz, $J_2 = 5.2$ Hz, CF_2H), 79.2 (m, 2F, Ar_F). IR (KBr, υ_{max}, cm^{-1}): 2969, 1707, 1606, 1493, 1446, 1408, 1391, 1279, 1248, 1180, 1132, 1060, 1022, 990, 897, 864, 817, 775, 698, 626, 531.

Acknowledgements

The authors gratefully acknowledge the National Natural Science Foundation of China for financial support (no. 29974038).

References

[1] Y. Xu, Q. Chen, J. Wen, Liq. Crys. 15 (6) (1993) 915–918.
[2] Y. Xu, Q. Chen, J. Wen, Mol. Cryst. Liq. Cryst. 241 (1994) 243–248.
[3] J. Wen, M. Tian, Q. Chen, J. Fluorine Chem. 68 (1994) 117–120.
[4] J. Wen, M. Tian, Q. Chen, Liq. Cryst. 16 (3) (1994) 445–451.
[5] J. Wen, M. Tian, H. Yu, Z. Guo, Q. Chen, J. Mater. Chem. 4 (2) (1994) 327–330.
[6] J. Wen, H. Yin, M. Tian, Q. Chen, Liq. Cryst. 19 (4) (1995) 511–517.
[7] X. Chen, J. Wen, Liq. Cryst. 26 (10) (1999) 1563–1565.
[8] E.P. Janulis, J.C. Novack, G.A. Papapolymerou, M. Tristani-Kendra, W.A. Huffman, Ferroelectrics 85 (1988) 375–384.
[9] A.V. Ivashchenko, E.I. Kovshev, V.T. Lazareva, E.K. Prudnikova, V.V. Titov, T.I. Zverkova, M.I. Barnik, L.M. Yagupolski, Mol. Cryst. Liq. Cryst. 67 (14) (1981) 235–240.
[10] D. Prescher, T. Thiele, R. Ruhmann, J. Fluorine Chem. 79 (2) (1996) 145–148.
[11] J.P. Idoux, J.T. Gupton, C.K. McCurry, A.D. Crews, C.D. Jurss, C. Colon, R.C. Rampi, J. Org. Chem. 48 (21) (1983) 3771–3773.
[12] J.T. Gupton, J.P. Idoux, G. DeCrescenzo, C. Colon, Synth. Commun. 14 (7) (1984) 621–629.
[13] J.T. Gupton, J. Coury, M. Moebus, J.P. Idoux, Synth. Commun. 15 (5) (1985) 431–441.
[14] D. Demus, L. Richter, Textures of Liquid Crystals, Verlag Chemie, Weinheim, Germany, 1978.
[15] G.W. Gray, J.W. Goodby, Smectic Liquid Crystals: Textures and Structures, Heyden and Son, Philadelphia, PA, 1984.
[16] Y. Zhang, J. Wen, J. Fluorine Chem. 49 (1990) 293–300.
[17] J. Wen, Y. Xu, M. Tian, Q. Chen, Ferroelectrics 148 (1993) 129–138.
[18] K. Wang, Y. Yang, J. Wen, Chinese Liq. Cryst. Displays, in press (in Chinese).
[19] P. Kromm, M. Cotrait, H.T. Nguyen, Liq. Cryst. 21 (1) (1996) 95–102.
[20] H. Li, Y. Yang, J. Wen, Chinese J. Chem. 18 (6) (2000) 900–909.
[21] Y. Yang, B. Chen, J. Wen, Liq. Cryst. 26 (6) (1999) 893–896.
[22] Y. Xu, W. Wang, Q. Chen, J. Wen, Liq. Cryst. 21 (1) (1996) 65–71.