DOI: 10.1002/cjoc.201300286

Fluorocarbon and Hydrocarbon Benzodioxocycloalkane (C_8—C_{10}) End Groups: Effects on Mesomorphism

Wanwan Cao,[a] Peilian Liu,[a] Hongren Chen,[a] Yaohang Zhu,[a] Rihao Chen,[a] Qifang Zhou,[a] and Zhuo Zeng*[,a,b]

[a] *College of Chemistry & Environment South China Normal University, Guangzhou, Guangdong 510006, China*
[b] *Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*

A new class of benzodioxocycloalkane-based (C_8—C_{10}) liquid crystals were prepared. The impact of ring (C_8—C_{10}) as end group was investigated. The 8—9 membered ring derivatives, **3a**—**3b**, exhibited the nematic phases (N). The mesomorphic behaviors were weakened with increasing the size of the ring. For the fluorinated medium ring (C_8—C_{10}) **3d**—**3f**, it was found only the fluorinated ten membered ring **3f** showed the LC phases behaviours. Modification of the ring size with different length alkyl groups and variation of the alkyl to polyfluoroalkyl markedly influenced the properties of these compounds.

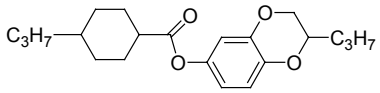
Keywords fluorine, heterocycles, liquid crystals, mesophases, phase transitions

Introduction

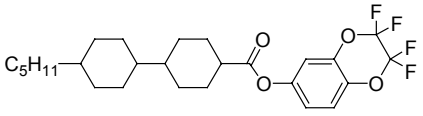
The interest in the development of new liquid crystal materials continues at a very high level,[1-8] particularly for stable mesophases with broad mesomorphic ranges[9,10] and low viscosities.[11-14] One of the special interest is liquid crystal compound having alkyl or fluorine-substituted benzodioxane ring, because it offers significant advantages over currently used liquid crystal materials.[15]

Low dense, chemically stable benzodioxane ring with a variety of liquid crystal building blocks makes it a promising candidate in the development of new liquid crystal materials.[16] There are reports of many benzodioxane derivatives as liquid crystal materials. Some of these reported[15, 17] liquid crystal moleculars are shown in Scheme 1.

Scheme 1 Structure of some known benzodioxane-based liquid crystals



Merck Broad Nematic range liquid crystal



Chisso large dielectric constant liquid crystal

Studies involving the use of bulky cyclic end groups[18] have revealed that smectic A phases can be suppressed while twist grain boundary phases are formed due to the weakening of interlayer interactions through steric effects. Other studies using fluorinated end groups[19-23] have shown that mesophase stability is increased with the terminal fluorine environment. It shows that steric effects or polarity at layer interface are more important in controlling mesophase sequence. Modification of the ring size from benzodioxane (C_8) to (C_{10}) as end groups markedly influences the properties of the benzodioxane-based liquid crystals.

In this work, we report a series of benzodioxocycloalkane-based (C_8—C_{10}) liquid crystals in an effort to establish the impact of the ring steric effects or polyfluoroalkyl substituent on the liquid crystal physicochemistry properties.

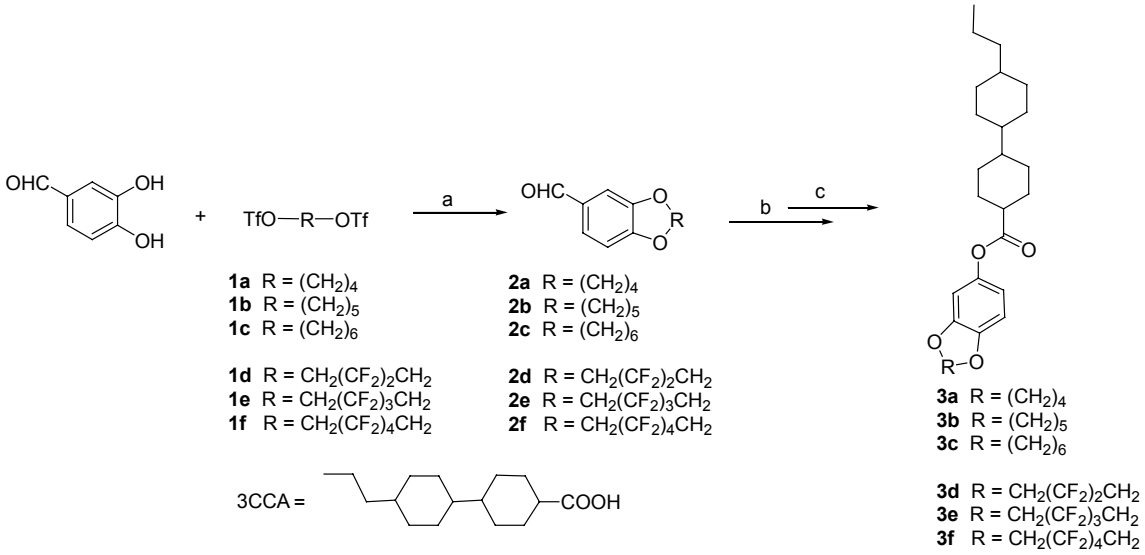
Results and Discussion

Synthesis

Synthetic routes to target compounds benzodioxocycloalkane-based liquid crystals, **3a**—**3f** are depicted in Scheme 2. In the previous report, macrocyclic benzodioxocycloalkanes were prepared by using catechol with *α*-*ω*-dibromoalkane to form *o*-(*ω*-bromoalkoxy)phenols as intermediate, the intermediate further intramolecularly cyclized to give the macrocyclic benzodioxocycloalkane in low yield.

* E-mail: zhuoz@scnu.edu.cn
Received April 3, 2013; accepted June 27, 2013; published online July 19, 2013.
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cjoc.201300286 or from the author.

Scheme 2 Synthesis of benzodioxocycloalkane-based liquid crystals



The combination of trifluoromethanesulfonic fluoroalkylenediyl esters and benzylamine gave the fluorinated piperidine and azepine in high yield as our previous report.[24] The straightforward approach encouraged us to employ trifluoromethanesulfonic acid long chain alkyl or fluoroalkyldiyl esters and catechol to synthesize macrocyclic benzodioxocycloalkane and its fluorinated derivatives.

The trifluoromethanesulfonic alkylenediyl and fluoroalkyldily esters **1a**—**1f**, were reacted with 3,4-dihydroxybenzaldehyde in the presence of K_2CO_3 in CH_3CN to give **2a**—**2f**, respectively. The oxidation of benzaldehydes, **2a**—**2f**, to phenols can be attained by Dakin or Baeyer-Villiger reaction. When the fluorinated aldehydes, **2d**—**2f** were reacted with H_2O_2 and H_3BO_3 under the Dakin reaction condition, in an effort to obtain the corresponding phenol, approximately six products were observed by TLC. Treated the **2d**—**2f** with *m*-chloroperoxybenzoic acid followed by base hydrolysis under the Baeyer-Villiger reaction condition gave the corresponding phenol at the 80% yield, which was used further without purification. Then *trans*-4'-propyl-(1,1'-bicyclohexyl)-4-carboxylic acid (3CCA) was esterified with the corresponding phenol using dicyclohexylcarbodiimide (DCC) and *N*,*N*-dimethylaminopyridine (DMAP) in dichloromethane to give **3d**—**3f** in 82% yield. This is the first example of the 3CCA derivatives with macrocyclic benzodioxocycloalkane as end group, some of which display good liquid crystal properties.

Thermal stability

Thermal stabilities, which range from 250 to 300 ℃ and depend on the size of macrocyclic ring, were determined by thermal gravimetric analysis (TGA). The TGA traces of **3a**—**3f** are given in the Supporting Information. In general, the new compounds with large macrocyclic ring as end group are thermally less stable, *e.g.*, comparing the analogous 8, 9, 10 membered fluorinated ring derivatives, **3d** (C_8), **3e** (C_9) and **3f** (C_{10}) have T_d values of 285, 271 and 272 ℃, respectively. There exists strong strain in the larger 9, 10 membered ring, which is the fundamental factor to influence thermal stability.

The fluorinated derivatives also exhibited higher melting point, *e.g.*, **3d** (C_{8F}), m.p. 125.4 ℃ and **3a** (C_8), m.p. 86.3 ℃. The introduction of a polyfluoroalkyl group increases the van der Waals interactions which contribute to the higher melting point of these compounds.

Liquid crystalline properties

The new compounds were investigated for their potential liquid crystalline properties by a combination of hot stage polarizing optical microscopy and differential scanning calorimetry (DSC). The transition temperatures are presented in Table 1. The assignment of the mesophases was made based on their optical texture.

Table 1 Transition temperatures (℃) of new compounds

Compd	Phase behavior T^a/℃			
3a	Cr→N	86.3	N→Iso	106.0
3b	Cr→N	78.1	N→Iso	108.1
3c	Cr→Iso	78.8		
3d	Cr→Iso	125.4		
3e	Cr→Iso	121.7		
3f	Cr→SmA	104.6	SmA→Iso	119.9

[a] Cr=Crystalline state; N=Nematic phase; SmA=Smectic A phase; Iso=Isotropic liquid state.

CHINESE JOURNAL OF CHEMISTRY

As shown in Table 1, the three new compounds **3a**, **3b** and **3f** with macrocyclic ring as end group display good liquid crystal properties. Two factors which affect the mesomorphic behaviour include: (1) the size of the macrocyclic ring; (2) the polyfluoroalkyl substituent group.

The nematic phase was evidenced based on its marbled or threaded texture. An example of such a texture can be seen in Figures 1 and 2. Compounds **3a** and **3b**, which use 8 and 9 membered hydrocarbon ring as terminal group, showed a nematic phase. This transition also could be evaluated from the DSC trace (see Supporting Information), two endothermic peaks at 86.3 and 106.0, 78.1 and 108.1 ℃ were observed for **3a** and **3b**, respectively. Investigations of DSC and POM showed that **3c** melted into isotropic liquid at 78.8 ℃ directly and no texture of liquid crystal was observed. It shows that the mesomorphic behaviour is dominated by the size of the macrocyclic benzodioxocycloalkane ring from **3a**—**3c**. As the terminal benzodioxocycloalkane size increases from eight to ten membered ring, the range of mesomorphic phases narrows rapidly.

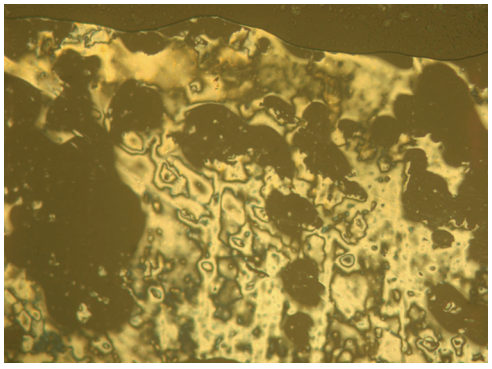


Figure 1 POM texture for compound **3a** at 88 ℃.

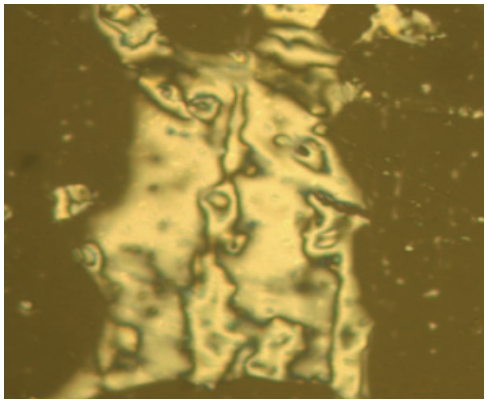


Figure 2 POM texture for compound **3b** at 90 ℃.

The introduction of a polyfluoroalkyl group affects the steric conformation of the macrocycle which attracts us to investigate the relationship between the fluorinated macrocyclic ring and liquid crystal properties. Compared with **3a**—**3c**, the fluorinated macrocyclic derivatives **3d**—**3f** (C_8—C_{10}) display a different mesomorphic behaviour. Closer examination of **3d**—**3e** by polarized optical microscopy (POM) revealed that they are not liquid crystals. No typical texture of the LC could be observed when **3d**—**3e** were heated to the melting point, there was no texture change upon further heating, and these compounds did not show mesophase behavior. These are in agreement with the observation by DSC, they only have one endothermic peak in the heating cycle (see Supporting Information).

Interestingly, focal-conic fan of SmA phase can be seen in **3f** (C_{10}). In order to ascertain the structures of the smectic observed, variable-temperature X-ray diffraction (VTXRD) experiments were carried out on **3f**. The diffraction patterns were recorded by heating the sample into the isotropic phase from the crystal. A representative and typical diffraction pattern obtained for compound **3f** at 115 ℃ is shown in Figure 3. A sharp scattering at 5.22° corresponding to the d spacing of 16.89 Å given in the small angle region. One diffuse scattering at 15.26° corresponding to the d spacing of 5.80 Å was also obtained. These results indicate the formation of a smectic phase at 115 ℃. The optical polarizing micrograph (Figure 4) reveals focal-conic fan for **3f** at this temperature range. Both results are consistent with a smectic A structure. This arises from the fact that the benzodioxocycloalkane has weakly associated layers, whereby the steric nature of the end group prevents strong interactions between the layers in stark

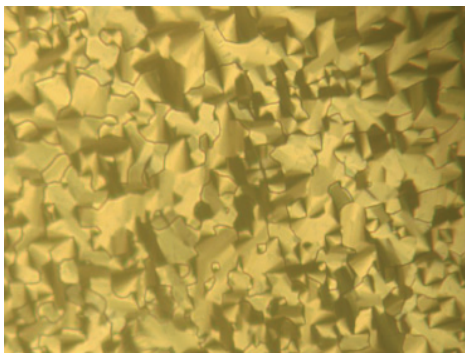


Figure 3 POM texture for compound **3f** at 110 ℃.

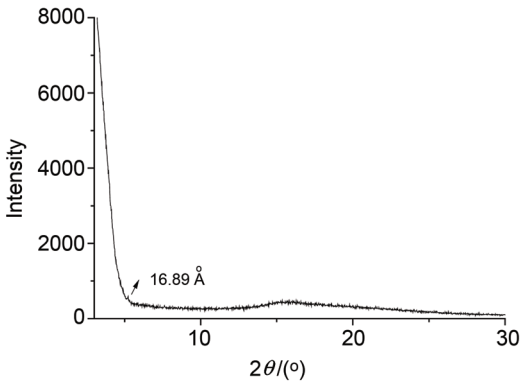


Figure 4 XRD diffraction pattern for **3f** recorded at 115 ℃.

contrast to the strongly associated layers of the fluorinated benzodioxocycloalkane, hence the formation of a SmA phase in the phase diagram as the polar interactions begins to dominate at the interface.

Conclusions

We have synthesized and characterized novel liquid crystals containing benzodioxocycloalkane as the terminal heterocycle. The C_8—C_9 membered **3a**—**3b**, displayed good liquid crystals properties. The properties of these liquid crystals can be adjusted by varying the size of ring. It is shown that the nature of a bulky end group can have a strong effect on the behaviour of a classical mesogen. The compound, which bear the ten membered benzodioxocycloalkane as terminal heterocycle, does not show liquid crystal properties. Its fluorinated derivative **3f** shows the SmA phases behaviours. It was also found that terminal fluorinated heterocycle configurations have a great impact on liquid crystal properties. Further research should provide broad insight into the development of the novel liquid crystals.

Experimental

All the reagents were of analytical grade, purchased from commercial sources and used as received. ^{1}H and ^{19}F and spectra were recorded on a 400 MHz nuclear magnetic resonance spectrometer operating at 400, 376 MHz respectively. Chemical shifts were reported relative to Me_4Si for ^{1}H, and CCl_3F for ^{19}F. The solvent was $CDCl_3$ unless otherwise specified. Thermogravimetric analysis (TGA) measurements were performed at a heating rate of 10 ℃•min^{-1} with a Netzsch STA409PC (Germany) instrument. The DSC curves were recorded on a differential scanning calorimeter at a scan rate of 10 ℃/min. Optical micrographs were observed with a polarizing optical microscope (POM) (*Nikon* LINKAM-THMSE600); Variable-temperature X-ray diffraction (XRD) experiments were performed on a Bruker D8 Advance X-ray diffractometer (using Cu Kα1 radiation of a wavelength of 1.54 Å) with temperature controller. Elemental analyses were performed on an EXETER CE-440 Elemental Analyzer.

General procedure for the preparation of trifluoromethanesulfonic acid alkyldily and fluoroalkyldily esters 1a—1f

All the above mentioned compounds were synthesized by the same method. The synthetic method will be described taking the example of compound **1a**.

1,4-Butanediol (1 mmol), pyridine (2.3 mmol), and dichloromethylene (20 mL) were stirred at room temperature under a nitrogen atmosphere. After 20 min, trifluoromethanesulfonic anhydride (2.5 mmol) was slowly added (over 1 h) by using an addition funnel. The mixture was stirred for 24 h, washed with water (10 mL×3) and then 10% sodium bicarbonate (10 mL×2), and dried over anhydrous sodium sulfate. The solvent was removed under a vacuum to give trifluoromethanesulfonic acid 1,4-butanedily ester **1a**, which was used without further purification.

General procedure for the preparation of 2a—2f

All the above mentioned compounds were synthesized by the same method. The synthetic method will be described taking the example of compound **2a**.

A mixture of 3,4-dihydroxy-benzaldehyde (0.345 g, 2.5 mmol), potassium carbonate (3.453 g, 25 mmol) was refluxed in acetonitrile (20 mL) at 373 K for 45 min, then a solution of trifluoromethanesulfonic acid 1,4-butanedily ester **1a**, in acetonitrile (5 mL) was added. The mixture was heated under reflux for 12 h. After cooling to room temperature, the inorganic salts were removed by filtration. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford a white solid 2,3,4,5-tetrahydro-1,6-benzodioxocine-8-carbaldehyde (**2a**).

2,3,4,5-Tetrahydro-1,6-benzodioxocine-8-carbaldehyde (2a)[25] 72% yield; white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.78 (s, 1H), 7.46—7.47 (m, 2H), 6.99 (s, 1H), 4.37 (d, J=12.0 Hz, 4H), 1.88 (d, J=4.0 Hz, 4H).

3,4,5,6-Tetrahydro-2*H*-1,7-benzodioxonin-9-carbaldehyde (2b) 72.5% yield; colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.82 (s, 1H), 7.57—7.37 (m, 2H), 7.01 (dd, J=26.8, 8.3 Hz, 1H), 4.49 (t, J=4.9 Hz, 2H), 4.19 (t, J=4.5 Hz, 2H), 2.01—1.65 (m, 6H). MS (ESI) m/z: 207.3 $[M+H]^+$. Anal. calcd for $C_{12}H_{14}O_3$: C 69.21, H 7.74, found: C 69.17, H 7.76.

2,3,4,5,6,7-Hexahydro-1,8-benzodioxecin-10-carbaldehyde (2c) 72% yield; White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.82 (s, 1H), 7.57—7.37 (m, 2H), 7.01 (dd, J=26.8, 8.3 Hz, 1H), 4.49 (t, J=4.9 Hz, 2H), 4.19 (t, J=4.5 Hz, 2H), 2.01—1.65 (m, 6H). MS (ESI) m/z: 220.3 (M^+). Anal. calcd for $C_{13}H_{16}O_3$: C 70.89, H 7.32; found C 70.35, H 7.36.

3,3,4,4-Tetrafluoro-2,3,4,5-tetrahydro-1,6-benzodioxocine-8-carbaldehyde (2d)[26] 75% yield; white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.87 (s, 1H), 7.61—7.58 (m, 2H), 7.20—7.15 (m, 1H), 4.67—4.61 (m, 2H), 4.48—4.42 (m, 2H); ^{19}F NMR ($CDCl_3$) δ: −123.03—−123.27 (m, 2F), −123.49—−123.68 (m, 2F).

3,3,4,4,5,5-Tetrafluoro-3,4,5,6-tetrahydro-2*H*-1,7-benzodioxonin-9-carbaldehyde (2e) 73% yield; white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.91—9.88 (m, 1H), 7.71—7.56 (m, 2H), 7.24—7.21 (m, 1H), 4.83—4.65 (m, 2H), 4.59—4.52 (m, 2H); ^{19}F NMR ($CDCl_3$) δ: −116.70—−117.08 (m, 2F), −117.18—−117.63 (m, 2F), −125.58 (s, 2F); MS (ESI) m/z: 354.6 (M^+). Anal. calcd for $C_{12}H_8F_6O_3$•$2H_2O$: C 41.39, H 2.89; found C 41.18, H 2.56.

3,3,4,4,5,5,6,6-Octafluoro-2,3,4,5,6,7-hexahydro-1,8-benzodioxecin-10-carbaldehyde (2f) 70% yield; white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.88 (s, 1H), 7.61 (dd, J=8.2, 1.9 Hz, 1H), 7.55 (d, J=1.8 Hz, 1H),

7.16 (d, J=8.2 Hz, 1H), 4.60 (d, J=12.0 Hz, 4H); ^{19}F NMR ($CDCl_3$) δ: −114.68 (s, 4F), −119.85 (d, J=86.1 Hz, 4F); MS (ESI) m/z: 420.6 (M^+). Anal. calcd for $C_{13}H_8F_8O_3$•H_2O: C 40.85, H,2.64; found C 41.10, H 2.21.

General procedure for the preparation of 3a—3f

All the above mentioned compounds were synthesized by the same method. The synthetic method will be described taking the example of compound **3a**.

2,3,4,5-Tetrahydro-1,6-benzodioxocine-8-carbaldehyde **2a** (1 mmol) and *m*-CPBA (1.8 mmol) were refluxed in $CHCl_3$ for 20 h. Most of the $CHCl_3$ was removed by distillation under reduced pressure and the residue was dissolved in ethyl acetate (75 mL). The solution was washed with aq. $NaHCO_3$ until effervescence ceased, then with brine, and dried over anhydrous sodium sulfate. Removal of the solvent left crude formate. The crude formate was dissolved in a little MeOH and hydrolyzed with a slight excess of 10% KOH at room temperature. After completion of the reaction, the reaction mixture was acidified with dilute HCl and extracted with ethyl acetate (100 mL×2). The combined organic layers were washed with water, brine. Removal of the solvent gave curde phenol, which was used further without purification. 3CCA, DCC, DMAP were taken in $CHCl_3$ at room temperature. After 10 min the crude phenol was added. The reation mixture was stirred and heated at reflux for 12 h. After cooling, the organic solvent was removed under reduced pressure. After the solvent was removed, the crude product was purified by silica gel column chromatography (DCM∶Hexane=1∶2) to give **3a**.

(*trans*,*trans*)-4-Propyl-[1,1'-bicyclohexyl]-4-carboxylic acid 2,3,4,5-tetrahydro-1,6-benzodioxocine-8-yl ester (3a) 85% yield; white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.94 (d, J=8.6 Hz, 1H), 6.67 (d, J=2.6 Hz, 1H), 6.62 (dd, J=8.7, 2.6 Hz, 1H), 4.38—4.36 (m, 2H), 4.27—4.24 (m, 2H), 2.44—2.38 (m, 1H), 2.12 (d, J=12.1 Hz, 2H), 1.95—1.80 (m, 6H), 1.79—1.66 (m, 4H), 1.53—1.44 (m, 2H), 1.33—1.25 (m, 2H), 1.19—0.91 (m, 9H), 0.90—0.78 (m, 5H). MS (ESI) m/z: 414.66 (M^+). Anal. calcd for $C_{26}H_{38}O_4$: C 75.32, H 9.24; found C 75.11, H 9.33.

(*trans*,*trans*)-4-Propyl-[1,1'-bicyclohexyl]-4-carboxylic acid 3,4,5,6-tetrahydro-2*H*-1,7-benzodioxonin-9-yl ester (3b) 86% yield; white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.97 (d, J=8.6 Hz, 1H), 6.71 (d, J=2.8 Hz, 1H), 6.65 (dd, J=8.7, 2.8 Hz, 1H), 4.24 (dd, J=37.3, 5.1 Hz, 4H), 2.42 (tt, J=12.1, 3.5 Hz, 1H), 2.12 (d, J=10.9 Hz, 2H), 1.83 (s, 7H), 1.79—1.68 (m, 4H), 1.51 (dd, J=25.2, 12.6 Hz, 2H), 1.37—1.23 (m, 3H), 1.18—0.92 (m, 9H), 0.91—0.75 (m, 5H). MS (ESI) m/z: 467.5 $[M+K]^+$. Anal. calcd for $C_{27}H_{40}O_4$: C 75.66, H 9.41; found C 75.21, H 9.33.

(*trans*,*trans*)-4-Propyl-[1,1'-bicyclohexyl]-4-carboxylic acid 2,3,4,5,6,7-hexahydro-1,8-benzodioxecin-10-yl ester (3c) 85% yield; white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.02 (d, J=8.6 Hz, 1H), 6.76 (s, 1H), 6.70 (d, J=8.6 Hz, 1H), 4.19—4.06 (m, 4H), 2.46—2.38 (m, 1H), 2.13 (d, J=12.4 Hz, 2H), 1.90—1.44 (m, 15H), 1.44—1.20 (m, 3H), 1.20—0.91 (m, 9H), 0.86 (dd, J=14.7, 7.8 Hz, 5H). MS (ESI) m/z: 884 ($2M^+$). Anal. calcd for $C_{28}H_{42}O_4$: C 75.98, H 9.56; found C 75.66, H 9.60.

(*trans*,*trans*)-4-Propyl-[1,1'-bicyclohexyl]-4-carboxylic acid 3,3,4,4-tetrafluoro-2,3,4,5-tetrahydro-1,6-benzodioxocine-8-yl ester (3d) 83.5% yield; white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.05 (d, J=8.8 Hz, 1H), 6.80 (d, J=2.6 Hz, 1H), 6.74 (dd, J=8.8, 2.6 Hz, 1H), 4.59—4.40 (m, 4H), 2.45—2.39 (m, 1H), 2.12 (d, J=12.4 Hz, 2H), 1.89—1.67 (m, 6H), 1.56—1.44 (m, 2H), 1.33—1.25 (m, 2H), 1.19—0.91 (m, 9H), 0.91—0.78 (m, 5H); ^{19}F NMR ($CDCl_3$) δ: −123.49—−123.73 (m, 2F), −123.75—−123.91 (m, 2F). MS (ESI) m/z: 525.7 $[M+K]^+$. Anal. calcd for $C_{26}H_{34}F_4O_4$: C 64.18, H 7.04; found C 63.90, H 6.95.

(*trans*,*trans*)-4-Propyl-[1,1'-bicyclohexyl]-4-carboxylic acid 3,3,4,4,5,5-tetrafluoro-3,4,5,6-tetrahydro-2*H*-1,7-benzodioxonin-9-yl ester (3e) 85% yield; white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.10 (d, J=8.7 Hz, 1H), 6.86 (d, J=2.2 Hz, 1H), 6.79 (dd, J=8.7, 2.4 Hz, 1H), 4.63—4.50 (m, 4H), 2.52—2.36 (m, 1H), 2.12 (d, J=12.3 Hz, 2H), 1.91—1.65 (m, 6H), 1.50 (dd, J=22.7, 10.2 Hz, 2H), 1.33—1.26 (m, 2H), 1.19—0.91 (m, 9H), 0.91—0.78 (m, 5H); ^{19}F NMR ($CDCl_3$) δ: −117.20 (d, J=83.8 Hz, 4F), −125.73 (s, 2F). MS (ESI) m/z: 536.5 (M^+). Anal. calcd for $C_{27}H_{34}F_6O_4$: C 60.44, H 6.39; found C 60.12, H 6.41.

(*trans*,*trans*)-4-Propyl-[1,1'-bicyclohexyl]-4-carboxylic acid 3,3,4,4,5,5,6,6-octafluoro-2,3,4,5,6,7-hexahydro-1,8-benzodioxecin-10-yl ester (3f) 82.5% yield; white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.15 (d, J=8.7 Hz, 1H), 6.91 (d, J=1.9 Hz, 1H), 6.85 (dd, J=8.7, 2.0 Hz, 1H), 4.68—4.55 (m, 4H), 2.49 (dd, J=16.8, 7.7 Hz, 1H), 2.17 (d, J=12.1 Hz, 2H), 1.98—1.71 (m, 6H), 1.61—1.48 (m, 2H), 1.38—1.31 (m, 2H), 1.24—0.97 (m, 9H), 0.97—0.83 (m, 5H); ^{19}F NMR ($CDCl_3$) δ: −115.68 (d, J=74.7 Hz, 4F), −118.85 (d, J=139.6 Hz, 4F). MS (ESI) m/z: 586.6 (M^+). Anal. calcd for $C_{28}H_{34}F_8O_4$•H_2O: C 55.33, H 6.00; found C 55.55, H 6.00.

Acknowledgement

The authors gratefully acknowledge the support of the National Natural Science Foundation of China (No. 21272080), Department of Science and Technology, Guangdong Province (Nos. 2010A020507001-76, 5300410, FIPL-05-003), and the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry.

References

[1] Yasuda, T.; Shimizu, T.; Liu, F.; Ungar, G.; Kato, T. *J. Am. Chem. Soc.* **2011**, *133*, 13437.

[2] Minch, B. A.; Xia, W.; Donley, C. L.; Hernandez, R. M.; Carter, C.; Carducci, M. D.; Dawson, A.; O'Brien, D. F.; Armstrong, N. R. *Chem. Mater*. **2005**, *17*, 1618.
[3] Jimenez, J.; Laguna, A.; Gascon, E.; Sanz, J. A.; Serrano, J. L.; Barbera, J.; Oriol, L. *Chem. Eur. J.* **2012**, *18*, 16801.
[4] Alexej, B.; Miroslav, K.; Vera, H.; Ute, D.; Frank, G. *Beilstein J. Org. Chem*. **2013**, *9*, 425.
[5] Yang, J.; Ye, D. Y. *Chin. Chem. Lett.* **2012**, *23*, 367.
[6] Liu, L. J.; Li, G.; Zhou, E. L.; Lam, J. W. Y.; Tang, B. Z. *Chin. J. Chem.* **2011**, *29*, 631.
[7] Yu, Z. Q.; Zhu, C. Z.; Zhang, Z.; Liu, J. H.; Lam, J. W. Y.; Tang, B. Z. *Chin. Chem. Lett*. **2011**, *22*, 1355.
[8] Sun, J.; Hu, J. S.; Chao, C. Y.; Guo, Z. X.; Qi, Y. *Acta Chim. Sinica* **2010**, *68*, 1003 (in Chinses).
[9] Andersch, J.; Diele, S.; Tschierske, C. *J. Mater. Chem*. **1996**, *6*, 1465.
[10] Aguilera, C.; Saez, P.; Morel, M.; Gallegos, P. *Liq. Cryst.* **2007**, *34*, 1233.
[11] Dabrowski, R.; Dziaduszek, J.; Ziolek, A.; Szczucinski, L.; Stolarz, Z.; Sasnouski, G.; Bezborodov, V.; Lapanik, W.; Gauza, S.; Wu, S. T. *Opto-Electron. Rev*. **2007**, *15*, 47.
[12] Dabrowski, R.; Dziaduszek, J.; Stolarz, Z.; Kedzierski, J. *J. Opt. Technol.* **2005**, *72*, 662.
[13] Kirsch, P.; Huber, F.; Lenges, M.; Taugerbeck, A. *J. Fluorine Chem.* **2001**, *112*, 69.
[14] Peng, Z.; Liu, Y.; Cao, Z.; Mu, Q.; Yao, L.; Hu, L.; Yang, C.; Wu, R.; Xuan, L. *Liq. Cryst.* **2013**, *40*, 91.
[15] Fuss, P.; Hittich, R. *DE 3335244*, **1985** [*Chem. Abstr*. **1985**, *103*, 169970].
[16] Takiguchi, T.; Iwaki, T.; Tokano, G.; Nakamura, S.; Yamada, Y.; Nakazawa, I. *JP 07070108*, **1995** [*Chem. Abstr*. **1995**, *123*, 70521].
[17] Sasata, Y.; Miyazawa, K.; Murashiro, K.; Kubo, Y. *JP 2003081967*, **2003** [*Chem. Abstr*. **2003**, *138*, 262775].
[18] Cowling, S. J.; Hall, A. W.; Goodby, J. W. *Liq. Cryst*. **2005**, *32*, 1483.
[19] Cowling, S. J.; Hall, A. W.; Goodby, J. W.; Wang, Y.; Gleeson, H. F. *J. Mater. Chem*. **2006**, *16*, 2181.
[20] Fafara, A.; Gestblom, B.; Wrobel, S.; Dabrowski, R.; Drzewinski, W.; Kilian, D.; Haase, W. *Ferroelectrics* **1998**, *212*, 79.
[21] Drzewinski, W.; Czuprynski, K.; Dabrowski, R.; Neubert, M. *Mol. Cryst. Liq. Cryst*. **1999**, *328*, 401.
[22] Drzewinski, W.; Dabrowski, R.; Czuprynski, K. *Pol. J. Chem*. **2002**, *76*, 273.
[23] Tao, J. Q.; Zhong, J. W.; Liu, P. L.; Daniels, S.; Zeng, Z. *J. Fluorine Chem*. **2012**, *144*, 73.
[24] Zeng, Z.; Shreeve, J. M. *J. Fluorine Chem*. **2009**, *130*, 727.
[25] Li, D. D.; Fang, F.; Li, J. R.; Du, Q. R.; Sun, J.; Gong, H. B.; Zhu, H. L. *Bioorg. Med. Chem. Lett*. **2012**, *22*, 5870.
[26] Zeng, Z.; Zhong, J. W.; Wang, H.; Wang, J.; Cao, W. W. *Acta Cryst.* **2010**, *E66*, o1137.

(Lu, Y.)

