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3,4-Difluoropyrrole-, 3,3,4,4-tetrafluoropyrrolidine-based tolan liquid crystals

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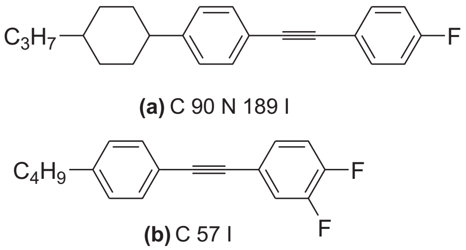
ABSTRACT

A series of new 3,4-difluoropyrrole-, 3,3,4,4-tetrafluoropyrrolidine-based tolan liquid crystals resulted from palladium-free Sonogashira coupling reactions of 1-(4-iodophenyl)-3,4-difluoropyrrole, 1-(4-iodophenyl)-3,3,4,4-tetrafluoropyrrolidine with terminal phenyl acetylenes. These new compounds exhibit typical nematic and smectic phases, good thermal stabilities, and high clearing points in comparison to the liquid crystal phase of 3,4-difluorobenzene-based tolan. These encouraging results lead us to believe this class of compounds could be used as new liquid crystalline materials. It is possible that the fluorinated *N*-heterocycles, 3,4-difluoropyrrole and 3,3,4,4-tetrafluoropyrrolidine, could replace the expensive 2,3-difluorobenzene, 3,4-difluorobenzene, and 3,4,5-trifluorobenzene components in the tolan core structure to form promising liquid crystalline materials.

1. Introduction

The super twisted nematic liquid crystal display (STN-LCD) product was widely used in cell phones, PDAs, and vehicles that carry intellectualization alphanumeric display terminals.[1–4] However, their display performances in the area as contrast and response rates were insufficient for new electronic product requirements.[5] Liquid crystalline materials need to have large birefringence (Δn) values, which are essential for liquid crystal displays with a high response speed. These materials must be also free from interference fringes.[6] It has been shown that the response speed can be accelerated with an increase in the birefringence (Δn) value and a decrease in the viscosity (η) of liquid crystal materials.[7–9] Tolan-type liquid crystal compounds with the strong conjugation between the benzene rings and an acetylenic bond within the liquid crystal have some advantages. These include large thresholds, low viscosity, broader nematic phase ranges, and lower melting points.[10–12] One can modify the liquid crystal birefringence and clearing points to improve the response speed of a liquid crystal material.[12] Interest in modern high-performance display materials continues to grow and a large number of tolan-type liquid crystals have been reported.[13] There are reports of many 4-fluorobenzene and 3,4-difluorobenzene derivatives as STN and TFT liquid crystal materials.[1,13–16] Some of these reported liquid crystal molecules are shown in Scheme 1. The tolan molecules with a fluorine atom as a substituent on the benzene ring have large birefringence values and low viscosities.



Low viscosity and large birefringence value tolan LCD

Scheme 1. Fluorinated tolan liquid crystals.

Among these fluorinated tolan molecules, compound (a) has a relatively high clearing point. However, it has inferior compatibility with other liquid crystal compounds when deposited. Hence, this drawback makes it impossible to take advantage of this feature. Compound (b) has no liquid crystal phase and hence when it is used as a component of liquid crystal composition, it adversely reduces

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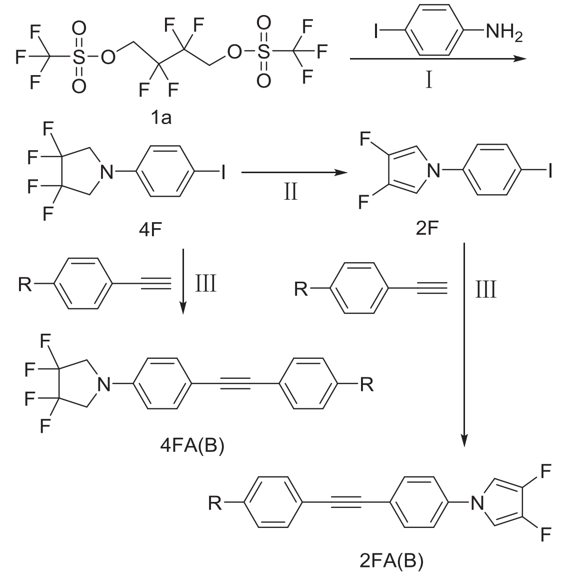
nematic–isotropic (N–I) phase transitions of the composition. It is possible that by replacing fluorobenzene or difluorobenzene in the liquid crystals by fluorinated heterocycles could either improve their solubility, increase their compatibility with other liquid crystalline compounds or increase the liquid crystal phase range for these compounds.

We have a continuing interest in fluorinated *N*-heterocycles for new building blocks in high-performance liquid crystal materials.[17–19] New fluorinated liquid crystals (FLCs) bearing fluorinated *N*-heterocycles will prove to be highly valuable because of their advantageous applications. The advantages of 3,3,4,4-tetrafluoro pyrrolidine and its dehydrofluorinated derivative, 3,4-difluoro pyrrole, that make them attractive candidates for further investigation include: (a) they have a large dielectric constant, which gives the liquid crystal the appropriate dipole moment; (b) linking 3,4-difluoropyrrole with phenyl acetylene compounds will expand the tolan conjugation system; (c) stronger electron withdrawing properties relative to fluorobenzene and difluorobenzene-based tolan liquid crystal giving novel characteristics. Therefore, in this work, we report the synthesis, characterization, and properties of some new 3,4-difluoropyrrole-, 3,3,4,4-tetrafluoropyrrolidine-based tolan liquid crystals.

2. Results and discussions

2.1. Synthesis

3,4-Difluoropyrrole-, 3,3,4,4-tetrafluoropyrrolidine-based tolan liquid crystals, **4FA1**,**4FA2**, **4FB1**–**4FB3**, **2FA1**–**2FA6**, **2FB1**–**2FB3**, and **2FC1**–**2FC3** were synthesized as shown in Schemes 2 and 3. Details of the synthesis and characterization of the materials are given in Supplementary data.



4FA1-4FA2: R=OCH$_3$, OC$_2$H$_5$; 4FB1-4FB3: R=C$_2$H$_5$, n-C$_3$H$_7$, n-C$_5$H$_{11}$;
2FA1-2FA2: R=OCH$_3$, OC$_2$H$_5$; 2FB1-2FB3: R=C$_2$H$_5$, n-C$_3$H$_7$, n-C$_5$H$_{11}$.
Reagents and conditions: I) (Et)$_3$N, CH$_3$CH$_2$OH, reflux, 24h.
II) t-BuONa, DMSO, N$_2$, 100 ^{0}C, 12h. III) CuI, PPh$_3$, PEG-600,
H$_2$O, K$_2$CO$_3$, 120 ^{0}C, 24h.

Scheme 2. Synthesis of the fluorinated *N*-heterocycles tolan-type liquid crystals.

Three synthetic routes for preparation tolan-type liquid crystals have been described previously. These include the Fristch–Buttenberg–Wiechell rearrangement,[20] the 1,2-dibromo-1,2-diarylethane dehydrobromination reaction,[21] and the Sonogashira coupling reaction.[22] We choose to use the Sonogashira coupling reaction, which has been extensively used in recent years and is based on the aryl iodides and terminal acetylenes.[23] The aryl iodide **4F**, 3,3,4,4-tetrafluoro-1-(4-iodophenyl)pyrrolidine, was obtained by the trifluoromethanesulfonic alkyl esters **1a** reacted with 4-iodobenzenamine in the presence of Et$_3$N in CH$_3$CH$_2$OH. Dehydrofluorination of **4F** with excess *t*-BuONa in DMSO at 90 °C for 12 h generated the 3,4-difluoro-1-(4-iodophenyl)pyrrole, **2F**, in high yields. The Sonogashira reaction procedure is sensitive to oxygen; traces of oxygen can lead to self-coupling, and utilizes an expensive palladium catalyst or a variety of homogenous palladium catalyst, which raises the cost.[24] An efficient palladium-free Sonogashira reaction procedure has been developed.[25] Reaction of aryl iodides **4F** and **2F** with phenyl acetylene in the water with CuI catalyst combining polyethylene glycol as phase transfer catalyst, we synthesized a series new 3,4-difluoropyrrole-, 3,3,4,4-tetrafluoropyrrolidine-based tolan liquid crystals **4FA1**,**4FA2**, **2FA1**,**2FA2**, **4FB1**–**4FB3**, and **2FB1**–**2FB3** were obtained in 90% yield. This synthetic route is of palladium-free, producing high yield, thus making the industrialization of these tolan-type liquid crystals possible (Scheme 2). This method appears to be an untried, but should be a straight forward single step route to these fluorinated *N*-heterocycles tolan-type liquid crystalline materials.

Tolan liquid crystals with a longer alkoxy substituent display good compatibility properties and can be used as effective components to form liquid crystals that have a large birefringence. The 3,4-difluoropyrrole-based tolan liquid crystals with C3–C6 alkoxy and ester group chains as substituent, **2FA3**–**2FA6** and **2FC1**–**2FC3** are shown in Scheme 3.

Demethylation of **4FA1** with BBr$_3$ in dichloromethane at 0 °C for 4 h yielded the 4-(2-(4-(3,3,4,4-tetrafluoropyrrolidin-1-yl)phenyl)ethynyl)phenol, **4FOH**.[26] The dehydrofluorination **4FOH** with excess *t*-BuONa gave the intermediate 4-(2-(4-(3,4-difluoro-1*H*-pyrrol-1-yl)phenyl)ethynyl)phenol, **2FOH**. Alkylation of **2FOH** with alkyl bromide in DMF as solvent at 90 °C for 12 h gives longer alkoxy substituent tolan liquid crystals, **2FA3**–**2FA6**. When **2FOH** is reacted with a slight molar excess of acrylic acid, *trans*-4′-propyl-(1,1′-cyclohexyl)-4-carboxylic acid (3CA) or *trans*-4′-propyl-(1,1′-bicyclohexyl)-4-carboxylic acid (3CCA), the resulting compounds are an alkyl ester substituted 3,4-difluoropyrrole-based tolan liquid crystals, **2FC1**–**2FC3**.

2.2. Liquid crystalline properties

The phase transitions and thermodynamic data of compounds were investigated by differential scan calorimetry (DSC), thermal gravimetric analysis (TGA), polarizing optical microscope (POM), and variable-temperature X-ray diffraction (VTXRD). Three series of 3,4-difluoropyrrole-, 3,3,4,4-tetrafluoropyrrolidine-based tolan liquid crystal molecules, which differ in structure especially at the terminal position will be investigated. Substituents such as alkoxyl, alkyl, and ester groups in the *para* positions of arylacetylene unit were used (Schemes 4–6). There is evidence that these compounds exhibit diverse thermal behavior. In the following, detailed accounts of all the series of mesophase behaviors are presented and compared with homologous tolan compounds bearing different substituents.

The transition temperatures and mesophase behaviors for the series A liquid crystals are given in Table 1. All the compounds were found to exhibit mesomorphic behavior. Their enthalpy values are in the range of 0.28–16.74 J/g by the differential scan calorimetry (DSC) thermograms.

A mosaic texture of a smectic B (SmB) phase was observed from polarizing optical microscope (POM) for 3,3,4,4-tetrafluoropyrrolidine-based tolan compounds **4FA1**, **4FA2** at 198.0 °C, and 190.0 °C upon sample cooling. They exhibited a narrow phase

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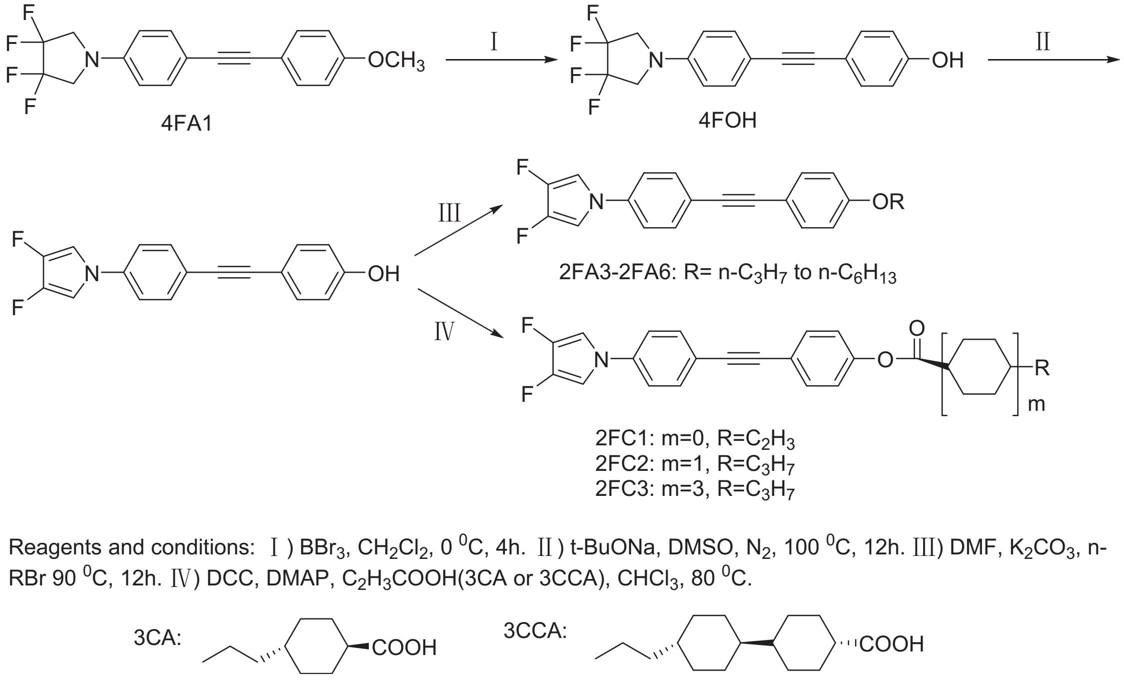
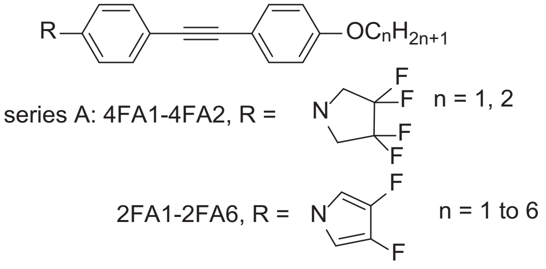
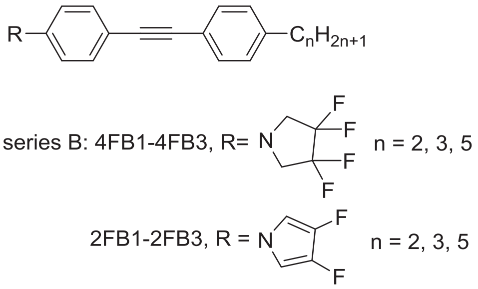


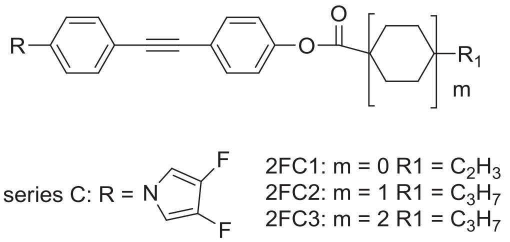
Scheme 3. Synthesis of the fluorinated *N*-heterocycles tolan-type liquid crystals with alkoxy and ester group as substituents.



Scheme 4. Fluorinated *N*-heterocycles tolan-type liquid crystals with an alkoxy as substituent (series A).



Scheme 5. Fluorinated *N*-heterocycles tolan-type liquid crystals with an alkyl as a substituent (series B).



Scheme 6. Fluorinated *N*-heterocycles tolan-type liquid crystals with an ester as a substituent (series C).

Table 1
Thermal and mesophase behavior of the series A compounds

Compd	*n*	Phase behavior/°C [Δ*H*]/J/g			
4FA1	1	Cr 199.3 [7.51]	SmB 209.0		Iso[b]
4FA2	2	Cr 193.2 [16.14]	SmB 200.0		Iso[b]
2FA1	1	Cr 152.5 [6.38]	SmF 171.0 [14.76][a]	N 190.0	Iso[b]
2FA2	2	Cr 166.2 [3.43]	SmF 182.5 [7.94][a]	N 207.0	Iso[b]
2FA3	3	Cr 157.3 [1.90]	SmF 188.7 [5.78][a]	N197.0	Iso[b]
2FA4	4	Cr 146.9 [0.28]	SmF 179.3 [1.22][a]		Iso[b]
2FA5	5	Cr 187.0 [8.06]	SmF 196.0		Iso[b]
2FA6	6	Cr 179.8 [5.80]	SmF 183.4 [2.19][a]		Iso[b]

Abbreviation: Cr=crystalline solid, N=nematic phase, SmB=smectic B, SmF=smectic F, Iso=isotropic liquid state.

[a] Transition temperature and enthalpy change (in square brackets) was determined by DSC (peak temperature, first heating scan, 5 K/min^{-1}).

[b] Transition temperatures were determined by POM.

transformation range, e.g., **4FA1** (Cr 199.3 °C SmB 209.0 °C), **4FA2** (Cr 193.2 °C SmB 200.0 °C). The 3,3,4,4-tetrafluoropyrrolidine ring distorts the N1-envelope conformation. In addition the shorter methoxyl, ethoxyl substituents in the molecules decrease the mesophase range.

Replacing the distorted conformation 3,3,4,4-tetrafluoropyrrolidine ring with aromatic 3,4-difluoropyrrole to give compounds, **2FA1**–**2FA6**, which result an increase in the mesophase range, e.g., **4FA1** (Cr 199.3 °C SmB 209.0 °C), **2FA1** (Cr 152.0 °C SmF 171.0 °C).

The compounds, **2FA1**–**2FA6**, were observed from polarizing optical microscope (POM) as a mosaic texture of a smectic F (SmF) phase (Fig. 1a). Upon further heating of these compounds, the schlieren texture of a nematic phase (Fig. 1b) was observed for **2FA1**–**2FA3** with C1–C3 alkoxy substituents as the end groups, e.g., **2FA1** (Cr 152.5 °C SmF 171.0 °C N 190.0 °C), **2FA2** (Cr 166.2 °C SmF 182.5 °C N 207.0 °C), **2FA3** (Cr 157.3 °C SmF 188.7 °C N 197.0 °C). In order to ascertain the structures of the two different mesophases observed, variable-temperature X-ray diffraction (VTXRD) experiments were carried out on **2FA1**. The diffraction patterns were recorded by heating the sample into the isotropic phase from the crystal. A representative and typical diffraction pattern obtained for

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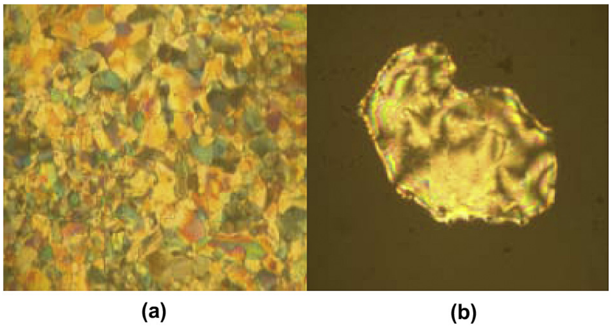

Fig. 1. Optical texture of (a) smectic F phase for **2FA1** upon cooling to 167 °C and (b) nematic phase for **2FA1** upon cooling to 186 °C.

compound **2FA1** at 167.0 °C is shown in Fig. 2A. The diffuse character of the wide angle peak at 6.51 Å indicates a liquid like in-plane order. In the small angle region two sharp reflections were seen with spacing of (d) 19.57 and 9.73Å. These reflections are in the ratio 1:2 or 2:4 indicating a lamellar ordering in the mesophase. Smectic F shows a diffuse outer ring accompanied by a strong inner diffraction as observed in previous reports.[27] The smectic F (SmF) phase for **2FA1** was judged by variable-temperature X-ray diffraction (VTXRD) experiments and the polarizing photomicrographs. When **2FA1** was heated further to 186.0 °C, there is no diffraction peak at the small angles, indicating that it does not form a layered structure. There is only one diffuse peak, around $2\theta=20°$, which reflects remote disorder of the molecule arrangement in the horizontal direction (Fig. 2B). The nematic phase was characterized at 186.0 °C for **2FA1** by the XRD and POM experiments. With the increase in alkoxy chain length, the nematic phase thermal stability decreases and the smectic phase thermal stability increases. When longer alkoxy substituents (C4, C5, C6) were employed, the **2FA4**–**2FA6** only show the smectic F (SmF) phase and the nematic phase disappears.

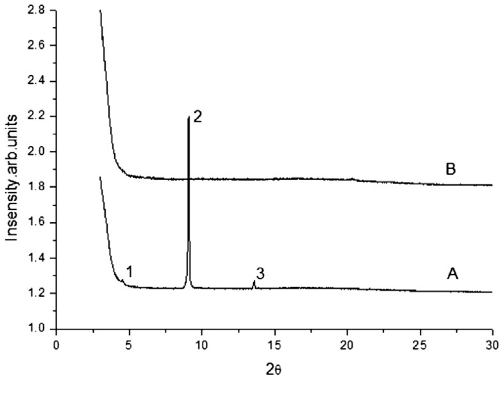

Fig. 2. Variable-temperature X-ray diffraction (VTXRD) obtained in (A) the SmF phase of **2FA1** at 167.0 °C and (B) the nematic phase of **2FA1** at 186.0 °C.

Thermal stabilities for **4FA1**, **2FA1** were determined by thermal gravimetric analysis (TGA). Data show that the decomposition temperatures were higher than the clearing point for these compounds. **4FA1**, **2FA2** had a T_d at 270.2 °C, 275.2 °C, respectively.

Modifying the substituent in the *para*-position of arylacetylene unit influences the liquid crystal state. Changing the substituent of series A from alkoxy to alkyl forms the series B liquid crystals, **4FB1**–**4FB3**, **2FB1**–**2FB3**. These compounds form the smectic G, **4FB1**–**4FB3**, and smectic E phase, **2FB1**–**2FB3** (Table 2). Compound **4FB1** displayed a mosaic texture of SmG at 180 °C upon cooling (Fig. 3a). A mosaic texture of a smectic E (SmE) phase was observed for compound **2FB1** at 168 °C upon cooling. In order to ascertain the structures of the mesophases observed, variable-temperature X-ray diffraction (VTXRD) experiments were carried out on **2FB1**. In the small angle region, two sharp reflections were seen with spacing of (d) 10.23 and 20.60 Å. These reflections are in the ratio 1:2 or 2:4 indicating a lamellar ordering in the mesophase, three sharp reflections were seen with spacing of (d) 6.78, 4.51, 4.04 Å in the wide angle region. The liquid crystal state for SmE, SmG, SmI shows several sharp outer diffraction peaks as previously reported.[27] The smectic E (SmE) phase for **2FB1** was determined by the polarizing photomicrographs (Fig. 3b) and variable-temperature X-ray diffraction (VTXRD) experiments (Fig. 4).

Table 2
Thermal and mesophase behavior of the series B compounds

Compd	n	Phase behavior/°C [ΔH]/J/g		
4FB1	2	Cr 173.5 [9.56]	SmG 182.0	Iso[b]
4FB2	3	Cr 176.8 [5.75]	SmG 186.0	Iso[b]
4FB3	5	Cr 157.4 [9.15]	SmG 165.3	Iso[b]
2FB1	2	Cr 137.1 [2.07]	SmE 164.2	Iso[a]
2FB2	3	Cr 159.3 [13.01]	SmE 167.0	Iso[b]
2FB3	5	Cr 149.6 [4.76]	SmE160.0	Iso[b]

Abbreviation: Cr=crystalline solid, SmE=smectic E, SmG=smectic G, Iso=isotropic liquid state.

[a] Transition temperature and enthalpy change (in square brackets) was determined by DSC (peak temperature, first heating scan, 5 K/min^{-1}).

[b] Transition temperatures were determined by POM.

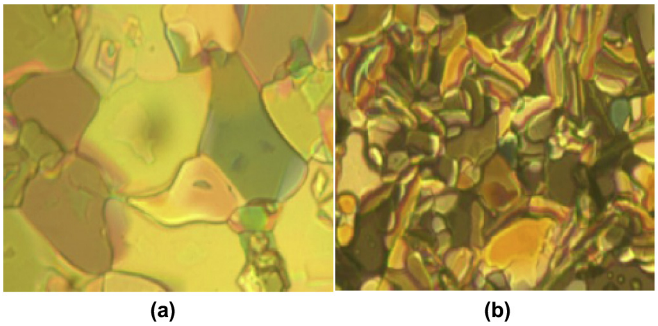

Fig. 3. Optical texture of (a) smectic G phase for **4FB1** upon cooling to 180 °C and (b) smectic E phase for **2FB1** upon cooling to 168 °C.

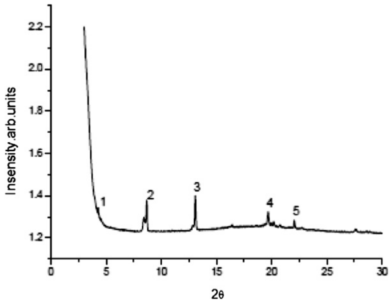

Fig. 4. Variable-temperature X-ray diffraction (VTXRD) of smectic E (SmE) phase of **2FB1** upon cooling to 160.0 °C.

A comparison of the series B liquid crystals with the analogous series A, shows an increase the amount of order from SmB to SmE, e.g., **4FA2** (Cr 193.2 °C SmB 200.0 °C), **4FB1** (Cr 176.8 °C SmG 186.0 °C), **2FA2** (Cr 152.5 °C SmF 171.0 °C N 190.0 °C), and **2FB1** (Cr 137.1 °C SmE 164.2 °C), respectively.

The decomposition temperatures were higher than the clearing point for these compounds, e.g., **4FB1**, **2FB2** had a T_d at 259.3 °C, 269.2 °C, respectively.

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The series C compounds (Scheme 6), **2FC1**–**2FC3**, with the ester as the terminal group were synthesized by combination the **2FOH** with the liquid crystal building block (acrylic acid, 3CA, 3CCA) giving high yields (Table 3). The **2FC1** with acrylic ester as the terminal group displayed a typical schlieren texture of the nematic phase (Fig. 5), **2FC1** (Cr 183.3 °C N 220.0 °C). Variable-temperature X-ray diffraction (VTXRD) experiments were carried out on **2FC1**, only a wide diffraction peak was observed at 180.0 °C in the small angle region, which indicates that no lamellar ordering exists in the mesophase (Fig. 6). Though the use of a combination the polarizing photomicrographs of compound **2FC1** and variable-temperature X-ray diffraction (VTXRD) experiments, the nematic (N) phase for **2FC1** was identified.

Table 3
Thermal and mesophase behavior of the series C compounds

Compd	Phase behavior/°C [Δ*H*]/J/g		
2FC1	Cr 183.3 [8.14]	N 220.0	Iso[a]
2FC2	Cr 160.3 [9.42]	Sm A 208.0	Iso[a]
2FC3	Cr 172.1 [3.71]	Sm A 180.0	Iso[a]

Abbreviation: Cr=crystalline solid, SmA=smectic A, Iso=isotropic liquid state.

[a] Transition temperature was determined by POM, DSC and enthalpy change (in square brackets) was determined by DSC (peak temperature, first heating scan, 5 K/min^{-1}).

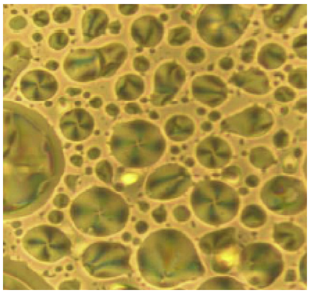

Fig. 5. Optical texture of nematic phase for **2FC1** upon cooling to 200.0 °C.

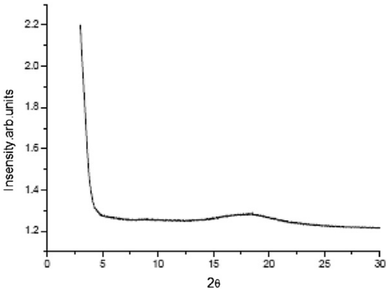

Fig. 6. Variable-temperature X-ray diffraction (VTXRD) of nematic phase of **2FC1** upon cooling to 180 °C.

The ester bond is a polar moiety, when the terminal ester chain is long enough, it will facilitate lamellar stacking and generate a smectic phase. The compounds **2FC2**–**2FC3**, with *trans*-4′-propyl-(1,1′-mono or bicyclohexyl)-4-carboxylic (3CA, 3CCA) ester as the terminal group, were observed to form smectic A. A typical focal conic texture of a SmA phase was identified for compound **2FC2** with 3CA as ending group between 160.3 and 208.0 °C (Fig. 7). Replacement of the 3CA with the longer 3CCA liquid crystal building block resulted in a change in the mesophase behavior. A fan-shaped texture of a SmA phase for compound **2FC3** was observed. Data show that the decomposition temperatures were higher than the clearing point for the compound **2FC2** had a T_d at 288.7 °C.

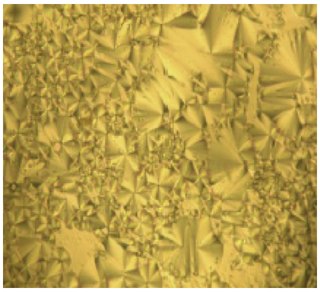

Fig. 7. Optical texture of smectic A phase for **2FC2** upon cooling to 177.0 °C.

2.3. Discussion

2.3.1. Evaluation of the influence of the alkyl, alkoxy, and ester chain. The terminal alkyl, alkoxy, and ester chains have an influence on the mesophase of these new compounds. Increasing the length of the carbon chain of the terminal alkoxy group increases the polarization and thus the lateral attraction between molecules. When the lateral attraction is greater than the terminal attraction, the smectic phase forms preferentially. Compounds with short or medium carbon chain lengths as the alkoxy substituent (OCH_3 to OC_6H_{13}), **2FA1**–**2FA6**, always show a smectic phase and a nematic phase, e.g., **2FA1** (Cr 152.5 °C SmF 171.0 °C N 190.0 °C), **2FA2** (Cr 166.2 °C SmF 182.5 °C N 207.0 °C), **2FA3** (Cr 157.3 °C SmF 188.7 °C N 197.0 °C), **2FA4** (Cr 146.9 °C SmF 179.3 °C), **2FA5** (Cr 187.0 °C SmF 196.0 °C), **2FA6** (Cr 179.8 °C SmF 183.4 °C).

Compounds, **4FB1**–**4FB3** and **2FB1**–**2FB3**, with nonpolar alkyl terminal groups only show a smectic phase. The compound, **2FC1**, with an unsaturated acrylic ester as ending group shows the nematic phase with the highest clearing point. The terminal unsaturated acrylic ester group for **2FC1** incorporates the conjugation effect into the molecule. This effect increases the polarizability anisotropy and rigidity of the molecule, hence influencing the mesophase behavior and the clearing point. The introduction the cyclohexyl group at the 4-positions for liquid crystal molecules can increase the order parameter by increasing the linearity of the entire structure. It can be seen the **2FC2**–**2FC3** with mono or bicyclohexyl group show the smectic A phase.

2.3.2. Influence of the terminal fluorinated heterocycle. The melting points and clearing points of the new liquid crystals with a fluorinated pyrrolidine as core structure are higher than those with fluorinated pyrrole structure with the same terminal substituent, e.g., **4FA1** (Cr 199.3 °C SmB 209.0 °C), **2FA1** (Cr 152.0 °C SmF 171.0 °C N 190.0 °C), **4FB1** (Cr 176.8 °C SmG 186.0 °C), **2FB1** (Cr 137.1 °C SmE 164.2 °C). The liquid crystal compounds having the expensive 2,3-difluorobenzene, 3,4-difluorobenzene, and 3,4,5-trifluorobenzene structures already have been disclosed to have a high dielectric aniostropy and intermediate viscosity.[1,13–16] Our introduction of a convenient and easy synthetic route into fluorinated 3,4-difluoropyrrole as the core structure of liquid crystal molecules should open the door to more investigation. The fluorinated core structure will increase the symmetrical characteristic and van der Waals interactions within the molecules, which should enhance the liquid crystal properties. The 3,3,4,4-tetrafluoropyrrolidine ring adopts a distorted N1-envelope conformation, which greatly impacts the mesophase behavior. It also exhibits a narrow phase transformation range. Comparatively, compounds **2FA1**–**2FA6**, **2FB1**–**2FB3**, **2FC1**–**2FC3**, having a five-membered fluorinated pyrrole, increase the mesophase range remarkably. The results indicate that having a symmetrical 3,4-difluoropyrrole as the core structure building block elongates

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the structure and impacts the liquid crystal properties significantly.

3. Conclusion

A series of new 3,4-difluoropyrrole-, 3,3,4,4-tetrafluoro pyrrolidine-based tolan liquid crystals were synthesized by a palladium-free Sonogashira coupling reaction at high yields. The new fluorinated compounds **4FA1**,**4FA2**, **2FA1**–**2FA6**, **4FB1**–**4FB3**, **2FB1**–**2FB3**, **2FC1**–**2FC3** are the first examples of tolan-based liquid crystal with fluorinated *N*-heterocycles as the core structure. They have displayed good liquid crystalline properties. Their melting points, decomposition temperatures, clearing points, and mesomorphism type were determined. The properties of these liquid crystals can be adjusted by using different *N*-heterocycles, alkyl, alkoxy, and ester substituents as the ending groups. The mesophase behavior can be affected by altering the *N*-heterocycle core structure. Compounds **4FA1**,**4FA2**, **4FB1**–**4FB3** with the terminal 3,3,4,4-tetrafluoropyrrolidine ring adopted a distorted N1-envelope conformation showing an oblique molecular axis smectic B and G phase. Comparatively, compounds **2FA1**–**2FA6**, **2FB1**–**2FB3**, and **2FC2**–**2FC3** with a 3,4-difluoropyrrole as terminal group exhibit vertical molecular axis smectic F, E, A phase, respectively. It can be seen that with the acrylic ester substituent on the terminal acetylenes, compound **2FC1** exhibits a nematic phase. The 3,4-difluoropyrrole can replace the expensive 2,3-difluoro benzene, 3,4-difluorobenzene, and 3,4,5-trifluorobenzene in the LCs to form promising new liquid crystalline materials. These new *N*-heterocycles liquid crystals exhibit high clearing points and thermal stabilities, meeting one of the criteria for high-performance liquid crystals.

4. Experimental section

4.1. General considerations

All the reagents used were analytical reagents purchased from commercial sources and used as received. ^1H and ^{19}F were recorded on a 400 MHz nuclear magnetic resonance spectrometer operating at 400 and 376 MHz, respectively. Chemical shifts were reported relative to Me_4Si for ^1H, and CCl_3F for ^{19}F. The solvent was $CDCl_3$ unless otherwise specified. Thermal gravimetric analysis (TGA) measurements were performed at a heating rate of 10 °C/min with a Netzsch STA409PC (Germany) instrument. The DSC was recorded at a scan rate of 2 °C/min on a Netzsch DSC200PC apparatus. Optical micrographs were observed with a polarizing optical microscope (POM) (Nikon LINKAM-THMSE600) equipped with a heating plate (HCS601). 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.

4.2. General procedure for the preparation of 3,4-difluoro pyrrole-, 3,3,4,4-tetrafluoropyrrolidine-based tolan

CuI (0.05 mmol, 9.5 mg), PPh_3 (0.1 mmol, 26.2 mg), and H_2O (2.4g) were added to a 10 ml round-bottomed flask. The mixture was stirred for 10 min at room temperature. Compounds **4F** (1 mmol, 344.9 mg) or **2F** (1 mmol, 302.9 mg) and phenyl acetylene (1.2 mmol) were added to this solution. The resulting mixture was stirred in oil bath, heated to 120 °C under nitrogen for 24 h. The crude product was added to 50 mL dichloromethane and then washed with water (3×30 mL), and dried over anhydrous sodium sulfate. The solvent was removed under vacuum, and the residue was purified by chromatography on silica gel to give the target product.

4.3. General procedure for the preparation of 3,4-difluoro pyrrole-based longer alkoxy substituent tolan

2FOH (1 mmol, 295.3 mg), alkyl bromide (1.2 mmol), K_2CO_3 (10 mmol, 1380.0 mg), and DMF (15 ml) were placed in a Pyrex glass tube, sealed, heated at 90 °C for 12 h, and then allowed to cool to room temperature. The crude product was added to 50 mL dichloromethane and then washed with water (3×30 mL), and dried over anhydrous sodium sulfate. The solvent was removed under vacuum, and the residue was purified by chromatography on silica gel to give the target product.

4.4. General procedure for the preparation of alkyl ester substituted 3,4-difluoropyrrole-based tolan

2FOH (1 mmol, 295.3 mg), alkyl acid (1.2 mmol), 4-dimethylamiopryidine (0.1 mmol, 12.2 mg), and *N*,*N*′-dicyclohexycarbodiimide (1 mmol, 206.3 mg) were placed in a Pyrex glass tube, sealed, heated at 90 °C for 12 h, and then cooled to room temperature. The crude product was added to 50 mL dichloromethane and then washed with water (3×30 mL), and dried over anhydrous sodium sulfate. The solvent was removed under vacuum, and the residue was purified by chromatography on silica gel to give the target product.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.04.077.

References and notes

1. Pauluth, D.; Tarumi, K. *J. Mater. Chem.* **2004**, *14*, 1219–1227.
2. Leenhout, F.; Schadt, M.; Fromm, H. *J. Appl. Phys. Lett.* **1987**, *50*, 1468–1470.
3. Takatoha, K.; Harimaa, A.; Kanamea, Y.; Shinoharaa, K.; Akimotoa, M. *Liq. Cryst.* **2012**, *39*, 715–720.
4. Kwok, H. S. *J. Appl. Phys.* **1996**, *80*, 3687–3693.
5. Li, J.; Lee, E. S.; Vithana, H. P.; Bos, J. *Jpn. J. Appl. Phys.* **1996**, *35*, 1446–1448.
6. Peer, K.; Eike, P. *Adv. Mater.* **1998**, *10*, 602–606.
7. Dubtsov, A. V.; Pasechnik, S. V.; Shmeliova, D. V.; Tsvetkov, V. A.; Chigrinov, V. G. *Appl. Phys. Lett.* **2009**, *94*, 181910/1–181910/3.
8. Berghausen, J.; Zipfel, J.; Lindner, P.; Richtering, W. *Europhys. Lett.* **1998**, *43*, 683–689.
9. Bartmann, E. *Adv. Mater.* **1996**, *8*, 570–573.
10. Simpson, S. H.; Richardson, R. M.; Hannaa, S. *J. Chem. Phys.* **2007**, *127*, 104901/1–104901/14.
11. Wu, S. T. *Phys. Rev. A* **1986**, *30*, 1270–1274.
12. Wu, S. T.; Margerum, J. D.; Meng, B. H.; Dalton, L. R.; Hsu, C. S.; Lung, S. H. *Appl. Phys. Lett.* **1992**, *61*, 630–633.
13. Wu, S. T.; Hsu, C. S.; Chen, Y. N.; Wang, S. F. *Appl. Phys. Lett.* **1992**, *61*, 2275–2277.
14. Michael, H. *Chem. Soc. Rev.* **2007**, *36*, 2070–2095.
15. Demus, D.; Goto, Y.; Sawada, S.; Nakagawa, E.; Saito, H.; Tarao, R. *Mol. Cryst. Liq. Cryst.* **1995**, *260*, 1–21.
16. Goto, Y.; Ogawa, T. EP 0276067, 1988.
17. Goossens, K.; Lava, K.; Nockemann, P.; Van Hecke, K.; Van Meervelt, L.; Driesen, K.; Gorller-Walrand, C.; Binnemans, K.; Cardinaels, T. *Chem.—Eur. J.* **2009**, *15*, 656–674.
18. Sasada, Y.; Miyazawa, K. *Liq. Cryst.* **2003**, *30*, 1371–1375.
19. Tao, J.; Zhong, J.; Liu, P.; Daniels, S.; Zeng, Z. *J. Fluorine Chem.* **2012**, *144*, 73–75.

20. (a) Rezaei, H.; Yamanoi, S.; Chemla, F.; Normant, J. F. *Org. Lett.* **2000**, *2*, 419–421; (b) Luu, T.; Morisaki, Y.; Cunningham, N.; Tykwinski, R. R. *J. Org. Chem.* **2007**, *72*, 9622–9629.
21. (a) James, A.; Alan, J. P. *Aust. J. Chem.* **1983**, *36*, 1705–1717; (b) James, A. *Aust. J. Chem.* **1986**, *39*, 677–686.
22. (a) Miyaura, N.; Yamada, K.; Suzuki, A. *Tetrahedron Lett.* **1979**, *20*, 3437–3440; (b) Miyaura, N.; Suzuki, A. *J. Chem. Soc., Chem. Commun.* **1979**, 866–867; (c) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *16*, 4467–4470; (d) Heck, J. P.; Nolley, J. *J. Org. Chem.* **1972**, *37*, 2320–2322.
23. (a) Li, P.; Wang, L.; Zhang, L.; Wang, G. W. *Adv. Synth. Catal.* **2012**, *354*, 1307–1318; (b) Chinchilla, R.; Najera, C. *Chem. Soc. Rev.* **2011**, *40*, 5084–5121; (c) Dudnik, A.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2010**, *49*, 2096–2098.
24. (a) Martin, R.; Buchwald, S. L. *Acc. Chem. Res.* **2008**, *41*, 1461–1473; (b) Fu, G. C. *Acc. Chem. Res.* **2008**, *41*, 1555–1564; (c) Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Angew. Chem., Int. Ed.* **2007**, *46*, 2768–2813; (d) Christmann, U.; Vilar, R. *Angew. Chem., Int. Ed.* **2005**, *44*, 366–374; (e) Nicolaou, K. C.; Bulger, P. G.; Sarlah, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 4442–4489; (f) Nicolaou, K. C.; Bulger, P. G.; Sarlah, D. *Angew. Chem., Int. Ed.* **2002**, *41*, 4176–4211.
25. (a) Monnier, F.; Turtaut, F.; Duroure, L.; Taillefer, M. *Org. Lett.* **2008**, *10*, 3203–3206; (b) Chen, G.; Xie, J.; Weng, J.; Zhu, X.; Zheng, Z.; Cai, J.; Wang, Y. *Synth. Commun.* **2007**, *41*, 3123–3133.
26. (a) Mcomie, J. F. W.; Watts, M. L.; West, D. E. *Tetrahedron* **1968**, *24*, 2289–2292; (b) Cai, Y. S.; Guo, Y. W.; Krohn, K. *Nat. Prod. Rep.* **2010**, *27*, 1840–1870.
27. Krigbaum, W.; Watanabe, R.; Ishikawa, J. T. *Macromolecules* **1983**, *16*, 1271–1279.

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