Preparation and properties of lateral monofluoro-substituted benzoxazole-based mesogenic compounds

Kun Hu\textsuperscript{a,b}, Pei Chen\textsuperscript{a,b,*}, Qiang Weng\textsuperscript{a,b}, Dingqian Shi\textsuperscript{a,b}, Ran Chen\textsuperscript{a,b}, Xinbing Chen\textsuperscript{a,b,*} and Zhongwei An\textsuperscript{a,b}

\textsuperscript{a}Key Laboratory of Applied Surface and Colloid Chemistry of Ministry of Education, Shaanxi Normal University, Xi’an, P R China; \textsuperscript{b}School of Materials Science and Engineering, Shaanxi Normal University, Xi’an, P R China

(Received 25 May 2015; accepted 1 July 2015)

A series of 2-(3′-fluoro-4′-alkoxy-1′,1′-biphenyl-4-yl)-benzoxazole liquid crystals (coded as nPF(3)PBx) were prepared, where a lateral fluorine substituent, as well as methyl, chlorine and nitro terminal groups, was introduced into the molecules to investigate the effects of different polar substituents on the liquid crystal properties. The mesomorphic and photophysical properties were investigated. The results show that compounds nPF(3)PBx have enantiotropic mesophases; meanwhile, they exhibit UV–vis absorption bands with maxima at 323–326 nm and photoluminescence emission peaks at 389–395 nm, respectively. It is noted that nPF(3)PBx with terminal polar groups or electron-withdrawing groups (NO\textsubscript{2}, Cl) display higher clearing temperatures and wider mesophase range than those of the corresponding homologues with terminal non-polar groups or electron-donating groups (CH\textsubscript{3}, H). Meanwhile, compared with two lateral fluorine-substituted analogues containing 3,5-difluorophenyl unit, lateral monofluoro-substituted nPF(3)PBx display enhanced mesophase range both in heating and cooling except for terminal methyl-substituted compounds, as well as show obvious red-shifted UV–vis absorption bands and photoluminescence emission, which are attributed to the enhanced dipole–dipole interaction caused by increased dipole moment.

Keywords: lateral fluorine; benzoxazole-based liquid crystals; mesophase; photophysical property

1. Introduction

To improve mesomorphic properties of the classical mesogenic compounds, altering the molecular polarity and geometry of the mesogenic core structures is generally regarded as an effective method.\textsuperscript{[1]} Benzoxazole derivatives have been developed as one kind of mesogenic heterocyclic compounds, including benzoxazole-based mesogenic\textsuperscript{[2–7]} and metallomesogenic\textsuperscript{[8–10]} materials. Since fluorine is a relatively small atom with a large electronegativity, fluorine atom has been widely introduced into the mesogenic core structure to alter the molecular polarity, and furthermore, to modify mesophase morphology and the physical properties of liquid crystalline materials.\textsuperscript{[11–13]}

Recently, we prepared a series of two lateral fluorine-substituted mesogenic benzoxazole compounds,\textsuperscript{[14]} 2-(3′,5′-difluoro-4′-alkoxy-1′,1′-biphenyl-4-yl)-benzoxazole derivatives (compounds \textsuperscript{I} in Figure 1), whereas the compounds display a narrow mesophase range, which is attributed to the enhanced molecular width resulting from the two lateral fluorines located at both sides of the molecule and to the reduced molecular polarity caused by anti-parallel dipole ordering of two lateral fluorines compared with the benzoxazole group. It is known that dipole–dipole interaction among molecules is one of the key factors for the formation of the mesophase, and the interaction can be enhanced via increasing the molecular polarity. Therefore, to further investigate the effects of different polar substituents on the liquid crystal properties, a series of new 2-(3′-fluoro-4′-alkoxy-1′,1′-biphenyl-4-yl)-benzoxazole liquid crystals (coded as nPF(3)PBx, Figure 1) were prepared with lateral monofluorine substituents incorporated into the molecule, where the compounds can be sub-divided into nPF(3)PBH, nPF(3)PBM, nPF(3)PBC and nPF(3)PBN according to the different terminal substituents of H, CH\textsubscript{3}, Cl and NO\textsubscript{2}, respectively. Based on the calculated dipole moments by density functional theory,\textsuperscript{[15]} it is demonstrated that compounds nPF(3)PBx have much larger dipole moments than the corresponding two lateral fluorine-substituted analogues (Table 1); hence, an enlarged mesophase range is expected for the present lateral monofluoro-substituted compounds nPF(3)PBx because of their enhanced dipole–dipole interactions among molecules.

2. Results and discussion

2.1. Synthesis and characterisation

A series of nPF(3)PBx were prepared via four-step reactions, as shown in Figure 2, where nPF(3)PB and the corresponding Schiff base intermediates nPF(3)PSx with carbon atoms in the alkoxy chain

\textsuperscript{*}Corresponding authors. Email: chenxinbing@snnu.edu.cn (X. Chen), chenpei@snnu.edu.cn (P. Chen)

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from 4 to 10 were obtained in purities greater than 98% (high-performance liquid chromatography (HPLC) or gas chromatography (GC)).

Infrared (IR), proton nuclear magnetic resonance (1H-NMR), gas chromatography with electron impact-mass spectrometry (GC/EI-MS) and elemental analysis (EA) were employed to confirm the structures of nPF(3)PBx and nPF(3)PSx. Here, 8PF(3)PBM is chosen as an example to analyse. For IR spectrum, the peaks at 1606, 1571 and 1496 cm\(^{-1}\) are attributed to vibrations of the aromatic ring skeleton, and the strong peak at 1057 cm\(^{-1}\) is attributed to vibration of C–F bond. It is noted that the absorption band of C=N in the benzoxazole moiety overlaps with the vibrations of the aromatic ring skeleton, and a similar phenomenon is found with compounds nPF(3)PBH, nPF(3)PBM and nPF(3)PBC. In the 1H-NMR spectrum, the protons of phenyl rings in both benzoxazole and biphenyl groups overlap with each other to some extent, but the quantities of the aromatic protons are consistent with 8PF(3)PBM molecules. The terminal methyl protons in benzoxazole moiety appear at 2.49 ppm. The protons in the CH\(_2\) group adjacent to the oxygen atom are assigned at 4.10 ppm, and the protons in the alkoxyl group appear at 0.80–2.00 ppm. For the GC/EI-MS spectrum, the peak of the positively charged molecular ion appears at \(m/z\) 431.27 with a relative intensity of 12%, which is consistent with the theoretical value (431.54) of 8PF(3)PBM. Elemental analysis of 8PF(3)PBM (C 77.92, H 6.71 and N 3.22) is in accordance with the calculated data (C 77.93, H 7.01 and N 3.25). All the results demonstrate that the obtained compounds have the proposed structures for nPF(3)PSx and nPF(3)PBx.

### Table 1. Dipole moments calculated by density functional theory for kinds of benzoxazole-based liquid crystals.

|                  | nPF(3)PBx Dipole moment (Debye) | Compounds I Dipole moment (Debye) |
|------------------|---------------------------------|-----------------------------------|
| Compounds I      | 1.5893                          | 0.5022                            |
|                  | 1.1697                          | 0.5043                            |
|                  | 4.0684                          | 2.7270                            |
|                  | 7.5744                          | 6.2031                            |

Figure 2. Synthesis of nPF(3)PSx and nPF(3)PBx.
2.2. Mesomorphic properties

Differential scanning calorimetry (DSC) and polarising optical microscopy (POM) are employed to determine the mesomorphic properties of nPF(3)PBx and nPF(3)PSx, where the peak values of the transition on the DSC curves are used to represent the phase transition temperatures, and liquid crystal phases are identified via comparing the observed textures with those reported in the literature. It is noted that phase transition temperatures and mesophase textures are determined only by POM for chloro-substituted compounds (nPF(3)PBC and nPF(3)PSC) to avoid serious corrosion of the silver-coated cell during DSC measurement.

The phase transition temperatures, the associate enthalpy changes and mesophase textures of nPF(3)PSx and nPF(3)PBx are summarised in Tables 2 and 3, respectively. The Schiff base derivatives with non-terminal groups (nPF(3)PSSH and nPF(3)PSM) show enantiotropic mesophases, whereas the compounds with polar terminal groups (nPF(3)PSC and nPF(3)PSN) display no mesophase at all, except for 10PF(3)PSC, as shown in Table 2. The compounds nPF(3)PSx display multiple mesophases including smectic C (typical focal conic texture) and nematic phases (Schlieren texture), which are confirmed via observing under POM, where 4PF(3)PSH and 6PF(3)PSM are chosen as examples in Figure 1 in supplementary information.

A series of nPF(3)PBx with alkoxy chain lengths of 4–10 carbons exhibit enantiotropic smectic/nematic mesophases (Table 3), where small nematic–isotropic enthalpy changes can be interpreted in terms of the bent nature of these benzoxazole-based molecules, which enhanced their molecular biaxiality and hence reduced the entropy change at the transition.[16–18] The liquid crystal phases are assigned from the typical marble textures, focal conic textures and Schlieren textures during heating and cooling for 7PF(3)PBM, 8PF(3)PBM, 6PF(3)PBC and 4PF(3)PBN, respectively, as shown in Figure 3. It is found that nPF(3)PBH and nPF(3)PBC exhibit only smectic mesophase, nPF(3)PBN show smectic mesophase for a long terminal alkoxy chain (n > 8) and nematic mesophase for a short terminal chain (n ≤ 8), whereas nPF(3)PBM display multiple mesophases (smectic C and nematic) during heating and cooling.

Compared with two lateral fluoro-substituted analogues (compounds I in Figure 1),[14] lateral monofluoro-substituted compounds nPF(3)PBx have approximately the same type of mesophases for the

| Compounds | Heating process | Cooling process |
|-----------|----------------|----------------|
| 4PF(3)PSH | Cr 132.8 (37.76) SmC 143.6 (1.68) N 150.8 (0.84) I | I 152.8 (~0.47) N 141.4 (~2.06) SmC 100.5 (~30.93) Cr |
| 5PF(3)PSH | Cr 132.8 (36.24) SmC 147.2 (2.31) N 149.6 (0.52) I | I 147.9 (~0.19) N 145.3 (~2.04) SmC 95.3 (~29.88) Cr |
| 6PF(3)PSH | Cr 117.1 (30.02) SmC 152.0 (1.12) N 154.1 (0.07) I | I 151.1 (~0.12) N 149.9 (~1.86) SmC 93.9 (~26.70) Cr |
| 7PF(3)PSH | Cr 129.6 (62.02) SmC 151.9 (6.10) I | I 149.7 (~6.51) SmC 96.3 (~60.37) Cr |
| 8PF(3)PSH | Cr 114.9 (21.73) SmC 155.4 (2.50) I | I 153.5 (~2.55) SmC 94.3 (~21.40) Cr |
| 10PF(3)PSH | Cr 115.3 (41.47) SmC 155.7 (4.74) I | I 153.5 (~4.82) SmC 90.4 (~42.21) Cr |
| 4PF(3)PSM | Cr 111.5 (20.08) Cr 116.4 (4.03) SmC 124.8 (0.74) I | I 113.6 (~4.26) SmC 76.6 (~17.18) Cr |
| 5PF(3)PSM | Cr 111.7 (22.54) SmC 117.2 (4.01) I | I 115.1 (~4.03) SmC 80.6 (~18.34) Cr |
| 6PF(3)PSM | Cr 98.6 (24.50) SmC 121.7 (4.98) I | I 119.7 (~5.09) SmC 65.5 (~19.41) Cr |
| 7PF(3)PSM | Cr 100.1 (20.08) SmC 123.0 (3.89) I | I 120.8 (~3.92) SmC 67.7 (~15.77) Cr |
| 8PF(3)PSM | Cr 96.8 (22.75) SmC 125.1 (4.78) I | I 123.3 (~4.75) SmC 67.1 (~19.50) Cr |
| 10PF(3)PSM | Cr 96.2 (25.14) SmC 126.6 (4.35) I | I 124.4 (~4.44) SmC 68.6 (~2.62) Cr, 66.7 (6.02) Cr |
| 4PF(3)PSC | Cr 130.0 (~130.8 I | – |
| 5PF(3)PSC | Cr 122.0 (~122.6 I | – |
| 6PF(3)PSC | Cr 120.0 (~120.7 I | – |
| 7PF(3)PSC | Cr 119.0 (~120.3 I | – |
| 8PF(3)PSC | Cr 118.0 (~119.1 I | – |
| 10PF(3)PSC | Cr 113.7 SmC 120.0 I | I 119.4 SmC 95.0 Cr |
| 4PF(3)PSN | Cr 170.0 (~170.4 I | – |
| 5PF(3)PSN | Cr 164.8 ~165.3 I | – |
| 6PF(3)PSN | Cr 161.4 ~162.1 I | – |
| 7PF(3)PSN | Cr 160.4 ~161.0 I | – |
| 8PF(3)PSN | Cr 160.0 ~160.6 I | – |
| 10PF(3)PSN | Cr 158.9 ~159.5 I | – |
same terminal groups; however, nPF(3)PBx with non-polar terminal groups (nPF(3)PBH and nPF(3)PBM) show obviously higher melting and clearing points, and nPF(3)PBx with polar terminal groups (nPF(3)PBC and nPF(3)PBN) display much higher clearing points (see Table 1 in supplementary information), which are attributed to their bigger length–width ratio and larger dipole–dipole interaction resulting from the enhanced dipole moments (Table 1). Moreover, it is noted that lateral monofluoro-substituted compounds nPF(3)PBx (except for nPF(3)PBM) exhibit much wider mesophase range (during heating or cooling) than the corresponding two lateral fluorine-substituted analogues because of the above same reason, which indicate that the lateral monofluorosubstituent appears to be much more effective to increase mesophase stability than the two lateral fluorines lying at both sides of the molecule.

### 2.3. Thermal stability

Thermogravimetric analysis (TGA) is used to measure the thermal stability of nPF(3)PBx. TGA curves of nPF(3)PBx are recorded at 30–600°C under a nitrogen atmosphere (Figure 4), where 8PF(3)PBB, 8PF(3)PBM and 8PF(3)PBC show the onset of decomposition at 280, 282 and 288°C, respectively, and almost completely decompose until 360°C. Whereas 8PF(3)PNB start to decompose at 295°C, and only 60 wt% decompose even up to 600°C. The results suggest that the decomposition temperatures increase with increasing polarity of the molecules, and a series of nPF(3)PBx are stable up to their clearing points.

#### 2.4. The effects of alkoxy chain and terminal substituents on liquid crystalline properties

The effects of alkoxy chain on liquid crystalline properties are investigated, where the dependence of transition temperatures during heating on the number of methylenic units (n) in the alkoxy chain is shown in Figure 5. It is obvious that the length of the alkoxy chain plays an important role on both the mesophase type and the mesomorphic temperature range. It is noted that compounds nPF(3)PBN start to display smectic C mesophase from nematic mesophase when the length of the terminal alkoxy chain increases above 8 carbon atoms, which is due to the enhanced interaction between the terminal chains. On the other hand, the elongation of the terminal alkoxy chain generally produces an increase in the mesomorphic temperature ranges 39–52°C and 51–71°C for nPF(3)PBH, 76–94°C and 111–124°C for nPF(3)PBM,
133–163°C and 166–192°C for nPF(3)PBC, and 94–103°C and 110–123°C for nPF(3)PBN, respectively.

The effects of terminal substituents on the mesophase ranges during heating are drawn in Figure 6.

Compared with unsubstituted homologues nPF(3)PBH, methyl, chloro and nitro terminal-substituted compounds (nPF(3)PBM, nPF(3)PBC and nPF(3)PBN) exhibit much wider mesophase ranges,
indicating that terminal substituents are useful to enhance the mesophase stability. It is noted that compounds nPF(3)PBx with chloro substituent exhibit widest mesophase ranges among the corresponding homologues, where the terminal substituents enhance the mesophase ranges in the order Cl > NO$_2$ > CH$_3$ > H, which is not completely consistent with the polarity of these groups (NO$_2$ > Cl > CH$_3$ > H). These indicate that calamitic mesogenic compounds substituted with polar terminal groups generally lead to wider mesophase range, but too high dipole moment will hamper to increase the mesophase stability.

2.5. Photophysical properties

Compounds with π-conjugated fused rings generally have good photophysical properties such as intense luminescence.[19,20] Here, UV–vis and fluorescence spectra are used to characterise the photophysical properties of nPF(3)PBx, respectively, where the spectra are recorded in methylene chloride, as shown in Figures 7 and 8. From Figure 7, it is found that 7PF(3)PBx exhibit broad absorption bands with maxima at 323–326 nm, which is attributed to the electronic transition originating from the π-molecular orbitals. It is noted that, compared with unsubstituted homologues

Figure 4. (colour online) TGA curves of compounds 8PF(3)PBx.

Figure 6. (colour online) The effects of terminal substituents on the mesophase ranges of nPF(3)PBx during heating.

Figure 5. (colour online) Transition behaviour of the compounds nPF(3)PBH (a), nPF(3)PBM (b), nPF(3)PBC (c) and nPF(3)PBN (d) series: dependence of the transition temperatures on the number (n) of methylene units of the alkoxy chain.
7PF(3)PBH, methyl, chloro and nitro terminal-substituted compounds (7PF(3)PBM, 7PF(3)PBC and 7PF(3)PBN) exhibit slightly red-shifted absorption bands, which is due to the impact of substituents on electronic properties resulted from $\sigma$–$\pi$, $p$–$\pi$ and $\pi$–$\pi$ conjugation, respectively.

Nitro terminal-substituted compound 7F(3)PBN shows a very weak emission (Figure 8), which is a common phenomenon in nitro-substituted fluorophores. Except for 7PF(3)PBN, the other compounds exhibit intense photoluminescence emission bands at 389 nm (7PF(3)PBH), 390 nm (7PF(3)PBM) and 395 nm (7PF(3)PBC), respectively. It is noted that, compared with above UV–vis absorption spectra, the terminal substituents have same effects on photoluminescence emission, where methyl, chloro and nitro substituents enhance the photoluminescence emission because of $\sigma$–$\pi$, $p$–$\pi$ and $\pi$–$\pi$ conjugation, respectively.

Besides, compared with the photophysical properties of the two lateral fluorine-substituted analogues (compounds I in Figure 1),[14] compounds nPF(3)PBx show obviously red-shifted UV–vis absorption bands by 2–10 nm and red-shifted photoluminescence emission by 7–10 nm (see Table 2 in supplementary information), respectively, which suggest that $\pi$–$\pi$ interaction between molecules is reinforced by the enhanced dipole–dipole interaction caused by increased dipole moments.

### 3. Conclusions

A series of nPF(3)PBx were prepared and their properties investigated. They show enantiotropic mesophases with the mesophase ranges of 39–163°C and 51–192°C during heating and cooling. Moreover, they exhibit UV–vis absorption bands with maxima at 323–326 nm and photoluminescence emission peaks at 389–395 nm, respectively. Compared with two lateral fluorine-substituted analogues (compounds I in Figure 1), it is found that lateral monofluoro-substituted nPF(3)PBx display enhanced mesophase ranges both in heating and cooling except for terminal methyl-substituted compounds, which are attributed to the enhanced dipole–dipole interactions caused by increased dipole moments. Meanwhile, compounds nPF(3)PBx show obviously red-shifted UV–vis absorption bands and photoluminescence emission than two lateral fluorine-substituted analogues, which suggest that $\pi$–$\pi$ interaction between molecules is reinforced by the enhanced dipole–dipole interaction caused by increased dipole moment. These results indicate that the quantity and position of fluorine atom in molecule play important roles in mesomorphic and photophysical properties.

### 4. Experimental

#### 4.1. Materials

2-Fluoro-4-bromophenol, 4-formylphenylboronic acid, 2-aminophenol, tetrabutyl ammonium bromide, tetra-kis(triphenylphosphine)palladium, 2-amino-4-nitrophenol, 2-amino-4-chlorophenol, 2-amino-4-methylphenol and 2,3-dichloro-5,6-dicyano-benzoquinone (DDQ) were purchased from Aladdin reagent Co. (Shanghai, China) and used as received. The other reagents were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China) and anhydrous potassium carbonate was dried at 150°C in vacuum prior to use. Chloroform was dehydrated using pre-dried 4 Å molecular sieves.

#### 4.2. Characterisation and measurements

IR spectra ( Nicolet Avatar360E spectrometer, Thermo Electron Corporation, Madison, WI, USA), 1H-NMR spectra (Bruker AV 300, Bruker Corporation,
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Karlsruhe, Germany), mass spectra (GC/EI-MS Thermo DSQ II, Thermo Finnigan, CA, USA) and Elemental analysis (Elementar Vario EL III instrument, Elementar Analysensysteme GmbH, Hanau, Germany) were employed to confirm the structures of the intermediates and final products. The phase transition temperatures were measured by DSC (Shimatsu DSC-60, Shimadzu Corporation, Kyoto, Japan) in nitrogen at a heating and cooling rate of 5°C min⁻¹, and TGA was carried out with a TA Q50 (TA Instruments, USA) in nitrogen (flow rate: 100 cm³ min⁻¹) at a heating rate of 10°C min⁻¹. UV–vis absorption spectra (Hitachi U-3900UV spectrometer 345, Hitachi High-Technologies Corporation, Tokyo, Japan) and emission spectra (Hitachi F-7000 spectrometer, Hitachi High-Technologies Corporation, Tokyo, Japan) were used to investigate the photophysical properties of the products.

4.3. Synthesis

As an example, the preparation procedure of 2-(3'-fluoro-4'-octyloxy-1,1'-biphenyl-4-yl)-5-methyl benzoazole (8PF(3)PBM) is described below.

4.3.1. Synthesis of 3-fluoro-4-octyloxy-(1,1'-biphenyl-4-yl)-5-methyl benzoaldehyde

To a 100 mL, three-neck, round-bottom flask equipped with an overhead stirrer and condenser, 1.91 g of 3-fluoro-4-bromophenol (10.0 mmol), 2.11 mL of n-octyl bromide (12.0 mmol), 2.76 g of anhydrous potassium carbonate (20.0 mmol), 0.16 g of KI and 40 mL of N,N-dimethylformamide were added. Then the reaction system was stirred at 80°C for 3 h. After the mixture was cooled to room temperature, the system was washed with nitrogen for 3 h. After the mixture was cooled to room temperature, it was filtrated through Celite. The solid was washed with 15 mL of ethanol for several times to give purity above 98%, suitable for HPLC or GC, yellow crystals, yield 91%; mp 97°C.

1H-NMR (300 MHz, CDCl₃, TMS): δ (ppm) 8.71 (s, 1H), 7.97 (d, J = 8.1 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H), 7.42–7.34 (m, 2H), 7.14–7.01 (m, 4H), 6.93 (d, J = 8.4 Hz, 1H), 4.11 (t, J = 6.6 Hz, 2H), 2.33 (s, 3H), 1.88–1.83 (m, 2H), 1.49–1.30 (m, 10H), 0.89 (t, J = 6.6 Hz, 3H). IR (KBr, pellet, cm⁻¹): 3428, 3031, 2955, 2920, 2853, 1623, 1601, 1580, 1558, 1533, 1506, 1473, 1403, 1382, 1314, 1288, 1268, 1241, 1220, 1192, 1178, 1133, 1038, 995, 874, 839, 810, 529, 516. EI-MS m/z (rel. int.): 433.21 (M⁺, 54), 320.19 (100), 188.61 (15), 134.14 (35).

The other Schiff base compounds (nPF(3)PSx) were prepared using a similar procedure, and their spectroscopic data are listed in supplementary information.

4.3.2. Synthesis of 2-(((3'-fluoro-4'-octyloxy-1,1'-biphenyl-4-yl)methylene)amino)-4-methylphenol (8PF(3)PSM)

To a 100 mL, three-neck, round-bottom flask equipped with an overhead stirrer and condenser, 0.72 g of 3-fluoro-4-octyloxy-(1,1'-biphenyl-4-yl)carboxaldehyde (2.2 mmol), 0.33 g of 2-amino-4-methylphenol (2.64 mmol) and 25 mL of ethanol were added. The reaction system was stirred at reflux for 6 h. After the mixture was cooled to room temperature, it was filtrated through Celite. The solid was washed with 15 mL of ethanol for several times to give purity above 98%, suitable for HPLC or GC, yellow crystals, yield 91%; mp 97°C.

1H-NMR (300 MHz, CDCl₃, TMS): δ (ppm) 8.1: 3428, 3031, 2955, 2920, 2853, 1623, 1601, 1580, 1558, 1533, 1506, 1473, 1403, 1382, 1314, 1288, 1268, 1241, 1220, 1192, 1178, 1133, 1038, 995, 874, 839, 810, 529, 516. EI-MS m/z (rel. int.): 433.21 (M⁺, 54), 320.19 (100), 188.61 (15), 134.14 (35).

The other Schiff base compounds (nPF(3)PSx) were prepared using a similar procedure, and their spectroscopic data are listed in supplementary information.

4.3.3. Synthesis of 2-((3'-fluoro-4'-octyloxy-1,1'-biphenyl-4-yl)-5-methylbenzoazole (8PF(3)PBM)

To a 100 mL round-bottom flask equipped with an overhead stirrer and condenser, 0.46 g of 8PF(3)PSM (1.07 mmol), 0.30 g of DDQ (1.32 mmol) and 50 mL of anhydrous chloroform. The reaction system was stirred at reflux for 6 h. After completion of the reaction, the mixture was diluted with water and extracted with chloroform for three times. The combined organic phase was dried over MgSO₄. After removal of the solvent in vacuo, the residue was purified through recrystallisation from ethanol to give purity greater than 98% for HPLC or GC measurements. Pale white crystals were obtained with yield 75% and mp 105°C.

1H-NMR (300 MHz, CDCl₃, TMS): δ (ppm) 8.29 (d, J = 8.1 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H), 7.57 (s, 1H), 7.47–7.35 (m, 3H), 7.18 (q, 3J = 8.1 Hz, 2J = 0.9 Hz, 1H), 7.07 (t, J = 8.4 Hz, 1H), 4.10 (t, J = 6.6 Hz, 2H), 2.49 (s, 3H), 1.87 (m, 2H), 1.49, 1.30 (m, 10H), 0.89 (t, J = 6.6 Hz, 3H). IR (KBr, pellet, cm⁻¹): 3428, 3031, 2955, 2920, 2853, 1623, 1601, 1580, 1558, 1533, 1506, 1473, 1403, 1382, 1314, 1288, 1268, 1241, 1220, 1192, 1178, 1133, 1038, 995, 874, 839, 810, 529, 516. EI-MS m/z (rel. int.): 433.21 (M⁺, 54), 320.19 (100), 188.61 (15), 134.14 (35).

The other Schiff base compounds (nPF(3)PSx) were prepared using a similar procedure, and their spectroscopic data are listed in supplementary information.
The other lateral monofluoro substituted compounds (nPF(3)PBx) were prepared using a similar procedure, and their spectroscopic data are listed in supplementary information.

Acknowledgement
The authors are grateful to Professor Wenliang Wang at Shaanxi Normal University for theoretical calculations at Shaanxi Normal University.

Disclosure statement
No potential conflict of interest was reported by the authors.

Funding
The authors acknowledge the financial support by the Shaanxi Natural Science Foundation [grant number 2014JMH17270]; the Key Technologies R&D Program of Xian [grant number CXY1430(2)]; the Key Technologies R&D Program of Shaanxi Province [grant number 2014K10-06]; Program for Key Science & Technology Innovation Team of Shaanxi Province [grant number 2012KCT-21]; Program for Changjiang Scholars and Innovative Research Team in University [grant number IRT_14R33]; the Fundamental Research Funds for the Central Universities [grant number GK2015030308], [grant number GK201501007], [grant number GK201501002].

Supplemental data
Supplemental data for this article can be accessed here.

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