Four ring achiral ferroelectric liquid crystals of 1,2,4-oxadiazoles: synthesis and characterisation

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ABSTRACT
A novel series of four-ring achiral ferroelectric liquid crystals containing 1,2,4-oxadiazole cores with unsymmetrical substitutions at C-3 and C-5 positions are synthesised and characterised. A fluoro substituted biphenyl moiety is prepared by Suzuki coupling reaction and is directly attached to the oxadiazole core at the C-5 position for the first time in the literature. An octyl benzoate is attached to the oxadiazole core at the C-3 position of it. All the compounds exhibit polar smectic (B$_2$) mesophases with ferroelectric switching along with the orthogonal smectic-A mesophases. These compounds possess high mesomorphic thermal ranges of polar smectic phases and are towards the ambient temperatures. The influence of a more electronegative fluorine substituent on the electron rich biphenyl moiety (at the C-5 position) of the oxadiazole core is analysed for the prevalence and abundance of polar smectic (ferroelectric) mesophases.

1. Introduction
The functional materials of the recent origin [1–4] evince their applications in addressing the societal technical issues. Due to rich electro-optic (EO) response, the liquid crystalline (LC) materials have been exploited for various technical [5,6] and biological [7,8] applications. The various classes of LC materials include calamitic [9], discotic [10], sanidic and phosmidic [11], bent [12] (banana), supramolecular hydrogen bonded [13,14] (HB), organometallic [15] etc. represent the shape imparted performance materials in EO devices. Owing to the device savvy nature of ferroelectric (FE) phase structures, LC research initially is directed to involve the chiral ingredients to realise [16] FE phase structures. As chiral synthesis has a natural rustication of yield economy imbroglio, LC researchers switched over to design new LC systems with bent cores which are achiral but capable of exhibiting [12,17,18] polar smectic phase structures.
Although non-zero spontaneous polarisation ($P_s$) is realised in bent core LCs (BLCs), realisation of their FE phase structure (polar smectic) abundance in the vicinity of ambient temperatures remains a challenging task. An overview of the literature \cite{17, 18} in the field of design of BLCs seems to hint for a tailoring approach involving proper selection of central and lateral moieties, flexible end chains and or polar end groups etc.

The researchers have put considerable efforts to realise the structure–property relationships in achiral bent/banana shape molecules with different central cores viz., resorcinol \cite{19}, 2,7-naphthalenediol \cite{20}, isophthalaldehyde \cite{21}, 3-amino-benzoic acid \cite{22}, isopthalic acid \cite{23}, oxadiazole \cite{24–27}, oxazole biphenol \cite{28} etc., and different rod-like side fragments (mesogenic/non-mesogenic) covalently bonded with the central core. The effect of the number of aromatic rings \cite{29} in the molecular frame on the realisation of polar smectic (FE) phase structures in these achiral systems is reported. The achiral compounds \cite{30, 31} with less number (three or four) of aromatic rings in the molecular skeleton have been synthesised by various authors in anticipation of the FE phase structures at ambient temperatures. However, the attempts were not fruitful. Also, the five membered heterocyclic oxadiazoles are reported as multifunctional materials due to their wide spectrum of biological \cite{32–34} and technical applications \cite{35–38} such as organic light emitting diodes (OLEDs), electroluminescence and LCs. The oxadiazoles contain two nitrogens and oxygen in its ring structure. Depending on the relative positions of the three atoms (N, N and O) in its structure, four different isomers \cite{24} are possible. The 2,4-substituted 1,3,5-oxadiazole derivatives are reported \cite{25} with the conventional smectic phases. The 2,5-substituted 1,3,4-oxadiazole derivatives are reported \cite{39} with the nematic phase. The 3,5-substituted 1,2,4-oxadiazole derivatives are of great interest \cite{40, 41} at the momentum due to their biaxial nematic phase structure and the FE like switching in external electrical stimuli due to cybotactic cluster formation.

An extensive survey and the implications involved with respect to the number of aromatic rings, nature of substitutions and length of the flexible end chain in realising polar smectic phase structures in achiral bent core systems is presented \cite{37} in our earlier report. The literature reveals that the non-symmetric (about the central core) molecular frames favour the polar smectic mesomorphism. A novel series of achiral non-symmetric LCs with the 1,2,4-oxadiazole central core exhibiting the polar smectic phase structures with wide thermal ranges are synthesised \cite{37} and reported. In our other reports on LCs formed through HB, the more electronegative fluoro substituent is found to influence \cite{42, 43} the melting and clearing temperatures as well as the mesomorphic thermal ranges appreciably. By keeping in mind, the low clearing and melting temperatures due to the fluoro substituent and a wide thermal range of polar smectic mesophases in non-symmetric 1,2,4-oxadiazole derivatives, a humble attempt is presently made to synthesise and study the influence of a lateral fluoro substituent (on biphenyl fragment of the 1,2,4-oxadiazole) on mesomorphism. The lateral fluoro group on the biphenyl moiety is assumed to enhance the non-symmetric nature of the molecular frame due to higher C–F bond length than the corresponding C–H bond length in unsubstituted compounds. The biphenyl moiety with the fluoro substituent is prepared by Suzuki coupling reaction and is attached to the oxadiazole core at the C-5 position of it.

2. Experimental methods
The required chemicals for the synthesis viz., 4-cyanobenzoic acid, 1-octanol, 4-bromo-2-fluoro phenol, 1-bromooalkanes (octyl, decyl, dodecyl, pentadecyl and hexadecyl) are procured from Sigma-Aldrich and are used without further purification. Catalysts like Pd(dpdpf)$_2$Cl$_2$ and Pd(pph$_3$)$_2$Cl$_2$ are procured from Hindustan Platinum, India. AR grade solvents like dimethylformamide (DMF), 1,4-dioxane, 1,2-dimethoxy ethane, acetonitrile and ethanol are procured from Spectrochem. The intermediate products and the final products during the synthesis are purified by column chromatography. The intermediate products are characterised by TLC. All the final products are characterised by $^1$H NMR, $^{13}$C NMR, FTIR spectroscopy techniques and elemental analysis. The optical textures exhibited by the mesophases are characterised using a polarising optical microscope (POM) equipped with a hot stage. The phase transition temperatures and the enthalpy changes across the transitions are determined using a Shimadzu (DSC-60 model) differential scanning calorimeter (DSC). The spontaneous polarisation of the ferroelectric mesophases in these compounds is determined by the field reversal \cite{44, 45} method.

3. Results and discussion
3.1. Synthesis and characterisation
The central core of the present series of compounds viz., 1,2,4-oxadiazole is prepared via dehydrative cyclisation of amidoxamine as per the procedure reported \cite{37, 46} earlier. The 4-cyano benzoic acid was esterified with octanal-1-ol to yield the octyl 4-cyanobenzoate. It is then converted into amidoxime by treating it with hydroxylamine hydrochloride followed by sodium hydroxide. The dehydrative cyclisation of amidoxime is carried out by treating it with 4-bromobenzoyl chloride. An off white solid of
octyl 4-(4-bromophenyl)-1, 2, 4-oxadiazol-3-yl) benzoate (1) is obtained.

The 4-bromo-2-fluoro-phenol (2) is alkylated by Williamson’s process with the corresponding 1-bromoalkane to give the alkylated bromofluoro compounds (3a–3e). To get a biphenyl moiety through Suzuki coupling, either of the bromo compounds viz., 1 or (3a–3e), is converted into the corresponding boronic esters, and then treated with the other bromo compound. In the present case, the alkylated bromofluoro compounds (3a–3e) are converted into the respective boronic esters (4a–4e) by treating it with Pin$_2$B$_2$ in presence of Palladium catalyst for convenience. The boronic esters are reacted with the 1,2,4-oxadiazole derivative (1) under Suzuki coupling \cite{47,48} conditions, yielded the final products (5a–5e), C$_8$Ox.FBP.C$_n$. The compounds are purified by recrystallisation. The synthetic route for the preparation of this series of compounds is presented in the following scheme 1. The $^1$H and $^{13}$C NMR spectra of important intermediates and the products are given in supplementary information file.

**General procedure for synthesis of 4-bromo-1-alkyloxy-2-fluorobenzene (3a–3e):**

To a stirred solution of 4-bromo-2-fluoro-phenol 6 (10.4 mmol) in dry acetonitrile (20 mL), K$_2$CO$_3$ (15.6 mmol) and the respective n-alkyl bromide (11.5 mmol) are added and the reaction mixture is refluxed at 80°C for 8 h. After completing the reaction, the solvent is distilled off and the residue is extracted with EtOAc. The extractant is washed with water followed by brine. The products obtained (3a–3e) are colourless oils. They are dried over anhydrous sodium sulphate.

4-bromo-1-octyloxy-2-fluorobenzene (3a): Yield is about 90.0%. $^1$H NMR: $\delta_1$ (300 MHz; CDCl$_3$) 0.89 (3 H, t, $J$ = 6.87, CH$_3$CH$_2$), 1.29–1.43 (14 H, m, CH$_2$CH$_2$CH$_2$), 1.76–1.85 (2 H, m, CH$_2$CH$_2$O), 3.99 (2 H, t, $J$ = 6.60, CH$_2$CH$_2$O), 6.83 (1 H, t, $J$ = 8.67, Ar-H), 7.15–7.26 (2 H, m, Ar-H). Elemental analysis: [found: C, 55.42; H 6.68%; C$_{14}$H$_{28}$BrFO requires C, 55.46; H 6.65%; M, 303.01].

4-bromo-1-decyloxy-2-fluorobenzene (3b): Yield is about 85.0%. $^1$H NMR: $\delta_1$ (300 MHz; CDCl$_3$) 0.89 (3 H, t, $J$ = 6.86, CH$_3$CH$_2$), 1.29–1.43 (14 H, m, CH$_2$CH$_2$CH$_2$), 1.76–1.87 (2 H, m, CH$_2$CH$_2$O), 3.99 (2 H, t, $J$ = 6.62 Hz, CH$_2$CH$_2$O), 6.83 (1 H, t, $J$ = 8.67, Ar-H), 7.15–7.26 (2 H, m, Ar-H). Elemental analysis: [found: C, 57.94; H 7.21%; C$_{16}$H$_{32}$BrFO requires C, 58.01; H 7.30%; M, 331.26].

4-bromo-1-dodecyloxy-2-fluorobenzene (3c): Yield is about 88.4%. $^1$H NMR: $\delta_1$ (300 MHz; CDCl$_3$) 0.88 (3 H, t, $J$ = 6.86, CH$_3$CH$_2$), 1.29–1.43 (14 H, m, CH$_2$CH$_2$CH$_2$), 1.76–1.87 (2 H, m, CH$_2$CH$_2$O), 3.98 (2 H, t, $J$ = 6.64, CH$_2$CH$_2$O), 6.83 (1 H, t, $J$ = 8.66, Ar-H), 7.14–7.26 (2 H, m, Ar-H). Elemental analysis: [found: C, 60.09; H 7.70%; C$_{18}$H$_{36}$BrFO requires C, 61.17; H, 7.85%; M, 359.31].

4-bromo-1-pentadecyloxy-2-fluorobenzene (3d): Yield is about 86.3%. $^1$H NMR: $\delta_1$ (300 MHz; CDCl$_3$) 0.89 (3 H, t, $J$ = 6.84, CH$_3$CH$_2$), 1.29–1.43 (24 H, m, CH$_2$CH$_2$CH$_2$), 1.75–1.88 (2 H, m, CH$_2$CH$_2$O), 3.99 (2 H, t, $J$ = 6.60, CH$_2$CH$_2$O), 6.83 (1 H, t, $J$ = 8.60, Ar-H), 7.15–7.26 (2 H, m, Ar-H). Elemental analysis: [found: C, 62.78; H 8.60%; C$_{21}$H$_{44}$BrFO requires C, 62.84; H 8.54%; M, 401.39].

4-bromo-1-hexadecyloxy-2-fluorobenzene (3e): Yield is about 88.0%. $^1$H NMR: $\delta_1$ (300 MHz; CDCl$_3$) 0.88 (3 H, t, $J$ = 6.86, CH$_3$CH$_2$), 1.28–1.43 (26 H, m, CH$_2$CH$_2$CH$_2$), 1.74–1.87 (2 H, m, CH$_2$CH$_2$O), 3.98 (2 H, t, $J$ = 6.64, CH$_2$CH$_2$O), 6.82 (1 H, t, $J$ = 8.64, Ar-H), 7.13–7.24 (2 H, m, Ar-H). Elemental analysis: [found: C, 63.60; H, 8.76%; C$_{22}$H$_{46}$BrFO requires C, 63.61; H, 8.73%; M, 415.42].
Synthesis of boronate esters (4a–4e):
The compounds obtained in the previous step, 4-bromo-1-alkyloxy-2-fluorobenzenes (3a–3e) are converted into the corresponding boronate esters by following the reported [37] procedure. The products are purified by column chromatography using silica gel as the stationary phase and the ethylacetate:hexane (2:98) mixture as the solvent system.

2-(4-octyloxy-3-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4a): Yield is about 74.9%. H NMR: δ 8.28 (1 H, d, J = 8.0 Hz, Ar-H), 7.46–7.50 (2 H, m, Ar-H). Elemental analysis: [found: C, 68.61; H, 9.12%, C20H13BFO requires C, 68.58; H, 9.21%; M, 350.27].

2-(4-decyloxy-3-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4b): Yield is about 76.3%. H NMR: δ 8.28 (1 H, d, J = 8.0 Hz, Ar-H), 7.46–7.50 (2 H, m, Ar-H). Elemental analysis: [found: C, 68.62; H, 9.63%, C22H15BFO requires C, 69.84; H, 9.59%; M, 378.32].

2-(4-dodecyloxy-3-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4c): Yield is about 75.0%. H NMR: δ 8.28 (1 H, d, J = 8.0 Hz, Ar-H), 7.44–7.47 (2 H, m, Ar-H). Elemental analysis: [found: C, 70.86; H, 9.81%, C24H16BFO requires C, 70.93; H, 9.92%; M, 406.38].

2-(4-pentadecyloxy-3-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4d): Yield is about 71.1%. H NMR: δ 8.28 (1 H, d, J = 8.0 Hz, Ar-H), 7.46–7.50 (2 H, m, Ar-H). Elemental analysis: [found: C, 72.26; H, 10.40% C27H18BFO requires C, 72.31; H, 10.34%; M 488.46].

2-(4-hexadecyloxy-3-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4e): Yield is about 72.3%. H NMR: δ 8.28 (1 H, d, J = 8.0 Hz, Ar-H), 7.46–7.50 (2 H, m, Ar-H). Elemental analysis: [found: C, 72.68; H, 10.36% C28H18BFO requires C, 72.72; H, 10.46%; M 462.48].

Synthesis of octyl 4-(5-((3’-fluoro-4’-alkoxy-biphenyl-4-yl)-1,2,4-oxadiazol-3-yl)benzoates (5a–5e):
The final products of the present study, 5a–5e (C4–Ox.FBP.Cn) are prepared by treating the bromo substituted 1,2,4-oxadiazole (I) with the boronate esters, 4a–4e under Suzuki conditions by following the reported [37] procedure. A detailed synthetic procedure for the preparation of bromo substituted 1,2,4-oxadiazole (I) starting from 4-cyanobenzoic acid is described [37] in our previous report. The 1H NMR and 13C NMR spectra of 5c (C4.Ox.FBP.C13) is given in supplementary information file as representatives of the series.

Octyl 4-(5-(3’-fluoro-4’-octyloxy-biphenyl-4-yl)-1,2,4-oxadiazol-3-yl)benzoate (5a): Yield is about 32.3%. H NMR: δ 8.28 (1 H, d, J = 8.0 Hz, Ar-H), 7.46–7.50 (2 H, m, Ar-H). Elemental analysis: [found: C, 72.89; H, 7.60; N, 4.62%; C25H14FNO4 requires C, 73.97; H, 7.55; N, 4.66%; M 600.76].

Octyl 4-(5-((3’-fluoro-4’-decyloxy-biphenyl-4-yl)-1,2,4-oxadiazol-3-yl)benzoate (5b): Yield is about 40.8%. H NMR: δ 8.28 (1 H, d, J = 8.0 Hz, Ar-H), 7.44–7.50 (2 H, m, Ar-H). Elemental analysis: [found: C, 72.26; H, 10.40% C27H18BFO requires C, 72.31; H, 10.34%; M 488.46].
Elemental analysis: [found: C, 74.44; H, 7.79; N, 4.49%; C_{39}H_{50}F_{2}N_{2}O_{4} requires C, 74.49; H, 7.85; N, 4.45%; M 628.81].

**Octyl 4-(5-(3′-fluoro-4′-dodecyloxy-biphenyl-4-yl)-1,2,4-oxadiazol-3-yl)benzoate (5c):** Yield is about 35.0%. ¹H NMR: δ_H (400 MHz; CDCl₃) 0.90 (6 H, t, J = 6.66, CH₃CH₂), 1.28–1.39 (24 H, m, CH₂CH₂CH₂), 1.44–1.52 (4 H, m, CH₂CH₂CH₂CH₂O), 1.77–1.90 (4 H, m, CH₂CH₂O), 4.10 (2 H, t, J = 6.64, CH₂CH₂O), 4.37 (2 H, t, J = 6.72, COOC₂H₅), 7.07 (1 H, t, J = 8.36, Ar-H), 7.40 (2 H, t, J = 10.01, Ar-H), 7.73 (2 H, d, J = 8.52, Ar-H), 8.19 (2 H, d, J = 7.67, Ar-H), 8.28 (4 H, d, J = 8.4, Ar-H).

¹³C NMR: δ_C (100 MHz; CDCl₃) 14.01, 22.57, 22.61, 25.84, 25.96, 28.63, 29.11, 29.18, 29.28, 29.48, 29.51, 29.56, 29.58, 31.72, 31.84, 65.45, 69.48, 114.69, 114.94, 122.53, 122.79, 122.83, 123.11, 127.40, 128.68, 129.95, 130.86, 132.37, 132.77, 144.10, 147.42, 165.96, 168.28, 175.76.

IR (cm⁻¹): 3076 (Ar-C-H), 2917, 2850 (C-H), 1716 (C=O), 1604, 1469 (C-C in ring), 1409 (C-H bend), 1287 (C-O-C), 1133 (C-C) 1102 (C-N).

Elemental analysis: [found: C, 74.97; H, 8.13; N, 4.52%; M 656.86].

**Octyl 4-(5-(3′-fluoro-4′-pentadecyloxy-biphenyl-4-yl)-1,2,4-oxadiazol-3-yl)benzoate (5d):** Yield is about 34.1%. ¹H NMR: δ_H (400 MHz; CDCl₃) 0.90 (6 H, t, J = 6.68, CH₃CH₂), 1.27–1.35 (30 H, m, CH₂CH₂CH₂), 1.45–1.58 (4 H, m, CH₂CH₂CH₂O), 1.79–1.88 (4 H, m, CH₂CH₂O), 4.10 (2 H, t, J = 6.64, CH₂CH₂O), 4.37 (t, J = 6.72, COOC₂H₅), 7.07 (1 H, t, J = 8.60 Hz, Ar-H), 7.40 (2 H, t, J = 12.12 Hz, Ar-H), 7.73 (2 H, d, J = 6.76 Hz, Ar-H), 8.19 (2 H, d, J = 6.80, Ar-H), 8.28 (4 H, d, J = 6.72, Ar-H).

¹³C NMR: δ_C (100 MHz; CDCl₃) 14.01, 22.57, 22.61, 25.84, 25.97, 28.63, 29.12, 29.18, 29.28, 29.48, 29.52, 29.58, 29.61, 31.72, 31.85, 65.45, 69.48, 114.69, 114.94, 122.53, 122.78, 122.83, 127.40, 128.68, 129.95, 130.86, 132.37, 132.77, 144.08, 147.57, 151.64, 165.96, 168.28, 175.76.

IR (cm⁻¹): 3061 (Ar-C-H), 2915, 2848 (C-H), 1707 (C=O), 1609, 1499 (C-C in ring), 1413(C-H bend), 1275 (C-O-C), 1137 (C-F) 1107 (C-N).

Elemental analysis: [found: C, 75.76; H, 8.68; N, 3.99%; C_{45}H_{53}F_{2}N_{2}O_{4} requires C, 75.81; H, 8.62; N, 3.93%; 712.97].

### 3.2. Phase characterisation by POM, DSC and electro-optical studies

The mesophases exhibited by this series, C₈Ox.FBP.Cₙ (n = 8, 10, 12, 15 and 16) of compounds are characterised using a POM attached with a hot stage. On cooling the sample, batonnets are formed and they coalesce to form a focal conic fan texture. Simultaneously, pseudo isotropic texture is noticed in homeotropic regions. These textural changes are similar to the textural changes reported [49] for smectic-A (SmA) of a calamitic LC viz., N-(tridecyloxybenzylidene)-4-methylaniline. These observations confirm [50] that the phase is an orthogonal smectic-A (SmA) mesophase. Similar observations are noticed in all other compounds of this series. The characteristic texture of SmA exhibited by 5a is given in *Figure 1* as a representative of the series. On further cooling, the focal conic fan texture is changed into a paramorphotic broken focal conic fan texture. A schlieren texture is noticed in the homeotropic regions simultaneously on shearing. This infers [50] that the phase is a tilted phase. This texture is similar to the...
texture reported [37] for B\textsubscript{2} phase of octyl-4-(5-(4'-(decyloxy)-biphenyl-4-yl)-1,2,4-oxadiazol-3-yl) benzoate (C\textsubscript{6}C\textsubscript{10}) compound of achiral FE compounds. All the compounds of this series are found to exhibit bistable switching by application of an electric field, which is observed clearly in the polarising microscope. The switching is observed both in heating and cooling cycles in applied electric fields. A single polarisation current peak per half period of triangular wave voltage is found in this phase. Since there is no chiral centre in the molecule and showing a bistable switching, the phase is confirmed as a ferroelectric smectic i.e., B\textsubscript{2} phase. All the compounds in the series are found to exhibit similar textural changes. A characteristic texture of B\textsubscript{2} phase exhibited by 9\textsubscript{a} is given in Figure 2 as a representative of the series. The phase transition temperatures observed in the cooling cycle of POM studies are tabulated in Table 1 along with the DSC data.

Figure 2. (colour online) B\textsubscript{2} phase exhibited by 5\textsubscript{a} (C\textsubscript{6}OxFBP.C\textsubscript{6}) at 55.4°C (10x).

The heating or cooling rate applied for studies are 10°C/min. It is noticed that the 1-D orthogonal SmA mesophase is an enantiotropic in all the compounds of the present series, whereas the polar smectic B\textsubscript{2} phase is a monotropic in 5\textsubscript{a} and 5\textsubscript{b} compounds and is an enantiotropic in higher homologues of the series viz., 5\textsubscript{c}, 5\textsubscript{d} and 5\textsubscript{e}. The DSC thermograms of the compounds 5\textsubscript{b} and 5\textsubscript{d} are given in Figure 3 as representatives of the series. The phase transition viz., Iso.–SmA, is obtained as a prominent peak for all the compounds in both heating and cooling cycles. But the SmA–B\textsubscript{2} phase transition is not well resolved in 5\textsubscript{a} and 5\textsubscript{b} compounds but the same phase transition is well resolved for other compounds (5\textsubscript{c}, 5\textsubscript{d} and 5\textsubscript{e}) of the series. This may be due to the weakly first order or second order nature of the orthogonal SmA to tilted B\textsubscript{2} phase transition, which are also reflected in their enthalpy change values. An attempt is made to resolve these phase transitions by recording the thermograms at slow scan rate, 5°C/min. Even at slow scan rate, the SmA–B\textsubscript{2} phase transition is not well resolved in 5\textsubscript{a} and 5\textsubscript{b} compounds but is resolved in the other compounds of the series. The DSC thermograms of 5\textsubscript{c} recorded at 5°C/min. is given in supplementary information file as a representative case along with the enlarged graph in the region of SmA–B\textsubscript{2} phase transition. The enthalpy changes (\(\Delta H\) in kJ/mol) across the phase transitions are computed and are given in parenthesis in Table 1 along with the transition temperatures obtained from DSC studies. The \(\Delta H\) values for Iso.–SmA transitions are found to be 10 ± 2 kJ/mol whereas for SmA–B\textsubscript{2} phase transitions, it is 0.4 ± 0.1 kJ/mol i.e., the enthalpy change across the SmA–B\textsubscript{2} transitions are one order less than that of the Iso.–SmA transitions. This shows that the structural changes at SmA–B\textsubscript{2} are not substantial as in the case of Iso.–SmA transitions. A phase

| Compound | Method | Cryst. | B\textsubscript{2} | SmA | Iso. |
|----------|--------|--------|-------------------|------|------|
| 5\textsubscript{a} | POM (c) | ● | 52.0 | 133.0 | 183.0 |
| DSC (h) | ● | 74.9 (42.5) | – | 180.0 (12.73) |
| DSC (c) | ● | 50.2 (20.18) | 130.0\textsuperscript{5} | 178.1 (10.17) |
| 5\textsubscript{b} | POM (c) | ● | 54.8 | 172.8 | 183.1 |
| DSC (h) | ● | 77.8 (98.65) | – | 182.7 (8.58) |
| DSC (c) | ● | 52.9 (33.23) | 173.1\textsuperscript{5} | 181.2 (10.19) |
| 5\textsubscript{c} | POM (c) | ● | 55.0 | 169.0 | 184.1 |
| DSC (h) | ● | 80.0 (81.91) | 173.1 (0.52) | 183.9 (10.10) |
| DSC (c) | ● | 51.5 (32.15) | 169.3 (0.49) | 180.1 (10.24) |
| 5\textsubscript{d} | POM (c) | ● | 68.2 | 157.0 | 170.9 |
| DSC (h) | ● | 93.9 (116.84) | 157.5 (0.44) | 170.4 (8.72) |
| DSC (c) | ● | 65.2 (122.42) | 154.6 (0.34) | 167.0 (8.71) |
| 5\textsubscript{e} | POM (c) | ● | 64.1 | 156.0 | 170.7 |
| DSC (h) | ● | 86.0 (148.15) | 157.0 (0.50) | 170.3 (11.59) |
| DSC (c) | ● | 60.7 (134.50) | 154.7 (0.29) | 166.0 (10.78) |

Note: \(^{5}\)not well resolved; c: cooling; h: heating.
The ferroelectric switching behaviour of these compounds is studied by using a modified Sawyer-Tower bridge and a 10 Vpp of 100 Hz triangular wave is applied. An ITO coated buffed cells (Instec. Inc., USA) of 5.5 μm thickness are used for studies. The bridge was calibrated with a standard ferroelectric material (DOBAMBC) of known $P_s$ and the $P_s$ of the materials of the present study is computed by comparing the areas under the peaks obtained for each sample and at each temp. The $P_s$ profile of 5b at 72.0°C is given in Figure 5 as a representative of the series. In achiral systems, the supramolecular macroscopic chiral domains are forming which orient in the direction of external stimuli and results the $P_s$. The temp. variable $P_s$ is studied in all the compounds. The $P_s$ is found to increase with decreasing the temp. and attained a max. (saturated) value. The temp. dependent $P_s$ for 5a compound of the series is given in Figure 6 as a
representative of the series. The same trend of temp.
variable \( P_s \) is noticed in all other compounds of the
series. The observed maximum values of \( P_s \) for 5a–5e
compounds are about 100, 85, 72, 68 and 65 nC/cm²
respectively.

Recently, we have reported [37,46] the synthesis and
caracterisation of 3,5-disubstituted 1,2,4-oxadiazoles
with and without chiral centre, exhibiting the conven-
tional and FE smectic phases. The general molecular
structures of the different series of compounds are
given below for convenient comparative studies.

\[
\text{Series – I (C}_8\text{C}_n \text{series) [37]}
\]

\[
\text{Series – II (C}_8\text{Ox}_n\text{FBP}_n\text{C}_n \text{) (Phase variant: SmA and B}_2 \text{) [Present investigations]}
\]

\[
\text{Series – III (SmA) [46]}
\]

\[
\text{Series – IV (SmA and SmC*) [46]}
\]

All these series (I–IV) contain the same 1,2,4-oxa-
diazole central core with different substitutions at
C-3 and C-5 positions. It is observed that the end
moieties on either sides influence the phase variant,
mesomorphic thermal ranges and the phase transi-
tion temperatures. One common feature of all the
series is the exhibition of SmA phase. In series-I
viz., octyl-4-(5′-(alkoxy)-biphenyl-4-yl)-1,2,4-
oxadiazol-3-yl)benzoate (C\( _8\text{C}_n\), \( n = 8, 9, 10, 12, 15 \)
and 16), the end moieties are flexible chains without a
lateral substitution on the biphenyl moiety. It is
found that the compounds of this series are exhibiting
orthogonal smectic phases along with the polar
smectic phases. In series-II, the molecular frame
and the end groups are similar to that of the ser-
ies-I, except a lateral ‘F’ substituent on the biphenyl
moiety (at C-5 of the oxadiazole core), which are
found to exhibit SmA and B₂ mesophases. The
compounds of series-III and series-IV possess the
same central core, but the end groups are different.
The series-III compounds are found [46] to exhibit
SmA mesophase whereas the series-IV compounds
are found to exhibit both SmA and SmC* (FE)
mesophases. Series-I and series-II compounds con-
tain an ester and an ether linkage whereas the
series-III and series-IV contain three ester groups.
Except the series-III compounds, the remaining
three series of compounds are exhibiting the ferro-
electric mesophases. It infers that the molecular
structure including the substituents and the linking
(functional) groups influence the stability of the
mesophase structures.

The mesomorphic thermal ranges of various phases
exhibited by series-II compounds are computed from
their DSC heating cycle data and are given in Table 2.
It is noticed that the thermal range of SmA mesophase
of 5c–5e compounds are almost the same in both
heating and cooling cycles. But in case of 5a and 5b,
the B₂–SmA transition is not obtained in the heating
cycle while it is noticed as an unresolved peak in the
cooling cycle. It is observed that the thermal range of
SmA phase in 5a and 5b compounds in POM studies
during heating are in concurrence with their DSC cool-
ing cycle data (given in Table 2). The thermal range of
B₂ mesophase is more in cooling cycle due to super-
cooling of about 20–25°C below to their respective
melting temperatures (Cryst.–B₂/SmA).

The lower members of the series (5a, 5b and 5c)
are found to possess almost the same mesomorphic
thermal range (104.5 ± 0.6°C) and may be attributed
to the high dipolar interactions between the molecules
with an optimum rigidity and flexibility. The other
two higher members of the series (5d and 5e) are
found to possess low \( \Delta T_{LC} \) values and may be attributed
to the dilution [51] of the core in comparison
with the other members of the series. \( \Delta T_{SmA} \) of
the compounds (except 5a) in the series (5b–5e) increases
upon increasing the alkyl chain length. The FE B₂

| Compound | \( \Delta T_{SmA} \) | \( \Delta T_{FE} \) | \( \Delta T_{LC} \) |
|----------|----------------|----------------|----------------|
| 5a       | 48.0*          | 57.1           | 105.1          |
| 5b       | 8.0*           | 96.9           | 104.9          |
| 5c       | 10.8           | 93.1           | 103.9          |
| 5d       | 12.9           | 63.6           | 76.5           |
| 5e       | 13.3           | 71.0           | 84.3           |

Note: *POM data.
phase abundance (ranging from 57–97°C) changed appreciably in this series of compounds. The compound 5b contains ten carbons in the alkyl chain possessing the highest $\Delta T_{FE}$ value in the series. This chain length (C10) may be the optimum for stabilising the polar smectic mesophase in this series. It is well established that the mesomorphic thermal ranges are influenced [42,43] by the polarity, polarisability and intermolecular interactions of the molecules. The fluorine atom is more electronegative and the C–F bond length (135 pm) is more than the C–H bond length (109 pm). The electronegative fluorine atom influence [52] the delocalised $\pi$-electron density of aromatic rings which further influence the $\pi-\pi$ stacking and $\pi\cdots C$–H electrostatic interactions between the aromatic rings and the overall polarisability of the conjugated system. The fluorine atom also influences [53] the conformation of the groups/substituents present in its vicinity (i.e., neighbouring molecules) and consequently the net intermolecular interactions. As a result of the net interactions, the mesophase thermal range may be stabilised (induced) or destabilised or eliminated completely.

Torgova et. al., have studied the mesomorphism [24,54,55] in various compounds of the 1,2,4-oxadiazole core with unsymmetrical substitutions at C-3 and C-5 positions. It was reported that the compounds with five aromatic rings were exhibiting nematic and smectic phases with switching in both the phases due to the longitudinal molecular dipole moment. However, the derivatives of 1,2,4-oxadiazoles with four aromatic rings are reported [24] to exhibit the conventional smectic phases. It is believed that if the exocyclic bond angle between the rod-like moieties at the central core is greater than 140°, the molecules may prefer to exhibit conventional calamitic smectic phases and if it is close to 120° as in the case of 1,3-substituted phenylene systems may exhibit the polar smectic phases. The compounds of 2,5-disubstituted 1,3,4-oxadiazoles with an exocyclic bond angle of about 134° were reported [24] with conventional smectic mesophases (even though the exocyclic bond angle is 134° i.e., <140°), but are not exhibiting the polar smectic phases. But in the present series of 1,2,4-oxadiazole compounds consisting four aromatic rings i.e., a benzoate moiety at C-3 and a fluoro substituted biphenyl moiety at C-5 (exocyclic bond angle [41] is 140°) are found to exhibit an orthogonal SmA and polar smectic (B2) phase with FE switching. It infers that the substituents at C-3 as well as at C-5 are crucial to realise the supramolecular FE phase structures in oxadiazole systems. The wide range polar smectic phase in the present series of compounds may be due to the presence of a fluoro substituted non-coplanar biphenyl moiety at the C-5 position of the oxadiazole core, in which long range intermolecular interactions due to the conformation of molecules in adjacent layers are expected.

The lower homologues of the series-II (5a, 5b and 5c) are found to have the isotropic temperatures of about 180 ± 2°C, whereas the higher members of the series-II (5d and 5e) are found to have the isotropic temperatures of about 168 ± 2°C. The isotropic temperatures of the structurally similar compounds of series-I are about 20°C higher than the corresponding fluoro substituted compounds of series-II. The lowering of the isotropic temperatures in the present investigations of series-II can be argued due to the presence of ‘F’ substitution at the ortho position to the alkoxy chain. The crystallisation temperatures (cooling cycle) of the compounds 5a, 5b, 5c, 5d and 5e are 50.2, 52.9, 51.5, 65.2 and 60.7°C, respectively. Interestingly, the clearing temperatures of series-III are still lower than series-II. In series-III, the end moiety at C-3 of oxadiazole is a bulky phenyl and is a flexible long alkyl chain in the other three series (I, II and IV) of compounds. It may be argued due to the bulky phenyl moiety, which increase the interlayer distances and may possess lower London dispersions in comparison with the other series of compounds. The crystallisation temperatures (cooling cycle) of series-II are found to be lesser than that of the series-III and series-IV due to supercooling.

4. Summary

A new series of achiral FE LC materials of four aromatic rings with 1,2,4-oxadiazole as a central core are synthesised and characterised. A lateral fluoro substituent is introduced in the molecular structure and the mesomorphism is studied by POM, DSC and electro-optical studies. The low clearing and crystallisation temperatures are achieved with the fluorine substitution in the present series of compounds. The FE phase stability is found to vary with the flexible alkoxy end chain length of the compounds in this series. The polar smectic (FE) mesomorphism is observed over a wide range of temperatures (about 57–97°C) in the present series of compounds containing four aromatic rings with fluorine substitution in comparison with a similar central core with five or more aromatic rings. The fluoro substituted non-coplanar biphenyl moiety at C-5 of the oxadiazole core is found to play a crucial role in stabilising the FE mesomorphism in 1,2,4-oxadiazole achiral systems.

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**References**

[1] Lagerwall Jan PF, Schütz C, Salajkova M, et al. Cellulose nanocrystal-based materials: from liquid crystal self-assembly and glass formation to multifunctional thin films. NPG Asia Mater. 2014;6:e80. DOI: 10.1038/am.2013.69.

[2] Tiwari A, Uzun L, editors. Advanced functional materials. New Jersey: John Wiley & Sons and Massachusetts: Scrivener Publishing LLC; 2015.

[3] Kato T, Mizoshita N, Kishimoto K. Functional liquid-crystalline assemblies: self-organized soft materials. Angew Chem Int Ed. 2006;45:38–68. DOI: 10.1002/anie.200501384.

[4] Miller DS, Wang X, Abbott NL. Design of functional materials based on liquid crystalline droplets. Chem Mater. 2014;26:496–506. DOI: 10.1021/cm4025028.

[5] Goodby JW. The nanoscale engineering of nematic liquid crystals for displays. Liq Cryst. 2011;38(11–12):1363–1387. DOI: 10.1080/02678292.2011.614700.

[6] Yang D, Wu S. Fundamentals of liquid crystal devices. 1st ed. Chichester: Wiley; 2006.

[7] Carlton RJ, Hunter JT, Miller DS, et al. Chemical and biological sensing using liquid crystals. Liq Cryst Rev. 2013;1(1):29–51. DOI: 10.1016/B978-0-08-093963-6.00031-0.

[8] Guo C, Wang J, Cao F, et al. Lyotropic liquid crystal systems in drug delivery. Drug Discov Today. 2010;15(23–24):1032–1040. DOI: 10.1016/j.drudis.2010.09.006.

[9] Chandrashekar S, editor. Liquid crystals. 2nd ed. Cambridge: Cambridge University Press; 1992.

[10] Kumar S. Functional discotic liquid crystals. Isr J Chem. 2012;52:820–829. DOI: 10.1002/ijch.201200035.

[11] Malthête J, Nguyen HT, Delaude C. Phasms and polycatenar mesogens. Liq Cryst. 1993;13:171–187. DOI: 10.1080/02678299308026292.

[12] Niori T, Sekine T, Watanabe J, et al. Distinct ferroelectric smectic liquid crystals consisting of banana shaped achiral molecules. J Mater Chem. 1996;6:1231–1233. DOI: 10.1039/JM9960601231.

[13] Kihara H, Kato T, Uryu T, et al. Supramolecular liquid-crystalline networks built by self-assembly of multifunctional hydrogen-bonding molecules. Chem Mater. 1996;8:961–968. DOI: 10.1021/cm9505456.

[14] Muniprasad M, Srinivasulu M, Chalapathi PV, et al. Influence of chemical moieties and the flexible chain for the tilted smectic phases in linear hydrogen bonded liquid crystals with Schiff based pyridine derivatives. J Mol Struct. 2012;1015:181–191. DOI: 10.1016/j.molstruc.2011.10.007.

[15] Bruce D, Dunmur DA, Maitlis PM, et al. High-birefringence materials using metal-containing liquid crystals. J Mater Chem. 1991;1:255–258. DOI: 10.1039/JM9910100255.

[16] Meyer RB, Liebert L, Strzelecki L, et al. Ferroelectric liquid crystals. J Phys Lett (Paris). 1975;36:69–71. DOI: 10.1051/jphyslet:0197500360306900.

[17] Reddy RA, Tschierske C. Bent-core liquid crystals: polar order, superstructural chirality and spontaneous desymmetrisation in soft matter systems. J Mater Chem. 2006;16:907–961. DOI: 10.1039/B504400F.

[18] Takezoe H, Takanishi Y. Bent-core liquid crystals: their mysterious and attractive world. Jpn J Appl Phys. 2006;45:597–625. DOI: 10.1143/JJAP.45.597.

[19] Kovalenko L, Schröder MW, Reddy RA, et al. Unusual mesomorphic behaviour of new bent-core mesogens derived from 4-cyanoresorcinol. Liq Cryst. 2005;32:857–865. DOI: 10.1080/02678290500231687.

[20] Reddy RA, Sadashiva BK. Synthesis and mesomorphic properties of banana-shaped compounds derived from 2,7-dihydroxynaphthalene. Liq Cryst. 2000;27:1613–1623. DOI: 10.1080/026782900750037176.

[21] Walba DM, Korbilova E, Shao R, et al. A ferroelectric liquid crystal conglomerate composed of racemic molecules. Science. 2000;288:2181–2184. DOI: 10.1126/science.288.5474.2181.

[22] Mohiuddin G, Punjani V, Pal SK. Three ring based room temperature bent core nematic compounds: synthesis and characterization. ChemPhysChem. 2013;16:2739–2744. DOI: 10.1002/cphc.201300435.

[23] Bedel JP, Rouillon JC, Marcero JP, et al. New switchable smectic phases in banana-shaped compounds. Liq Cryst. 2001;28:1285–1292. DOI: 10.1080/026782900750039949.

[24] Torgovska SI, Geivandova TA, Francescangeli O, et al. Banana-shaped 1,2,4-oxadiazoles. Pramana – J Phys. 2003;61:239–248. DOI: 10.1007/BF02708306.

[25] Keith C, Lehmann A, Baumeister U, et al. Nematic phases of bent-core mesogens. Soft Matter. 2010;6:1704–1721. DOI: 10.1039/B923262A.

[26] Dingemans TJ, Madsen LA, Francescangeli O, et al. The biaxial nematic phase of oxadiazole biphenol mesogens. Liq Cryst. 2013;40(12):1655–1677. DOI: 10.1080/02678292.2013.824119.

[27] Nagaraj M, Usami K, Zhang Z, et al. Unusual electric-field-induced transformations in the dark conglomerate phase of a bent-core liquid crystal. Liq Cryst. 2014;41(6):800–811. DOI: 10.1080/02678292.2014.885602.

[28] Glebowski A, Vita F, Francescangeli O, et al. Molecular engineering room-temperature bent-core nematics. Liq Cryst. 2015;42(5–6):829–839. DOI: 10.1080/02678292.2014.987709.

[29] Weissflog W, Baumeister U, Tamba M-G, et al. Unexpected liquid crystalline behaviour of three-ring bent-core mesogens: bis(4-subst.-phenyl)2-methyl-isob
liquid crystals: influence of the size and position of a substituent. J Mol Liq. 2013;186:56–62. DOI:10.1016/j.molliq.2013.05.013.

[43] Bhagavath P, Bhat SG, Mahabaleshwara S, et al. Induced smectic-A phase at low temperatures through self-assembly. J Mol Struct. 2013;1039:94–100. DOI:10.1016/j.molstruc.2013.01.053.

[44] Spruce G, Pringle RD. Measurement of spontaneous polarisation by field reversal. J Phys E:Sci Instrum. 1988;21:268–271. DOI:10.1088/0022-3735/21/3/006.

[45] Madhu Mohan MLN, Goud BVS, Kumar PA, et al. Design and fabrication of an automated technique: measurement of spontaneous polarization in two new Schiff base ferroelectric liquid crystals. Mater Res Bull. 1999;34:2167–2175. DOI:10.1016/S0025-5408(00)00173-2.

[46] Subrao M, Potukuchi DM, Sharada Ramachandra G, et al. Novel biphenyl-substituted 1,2,4-oxadiazole ferroelectric liquid crystals: synthesis and characterization. Beilstein J Org Chem. 2015;11:233–241. DOI:10.3762/bjoc.11.26.

[47] Ishiyama T, Murata M, Miyaura N, Palladium(0)-catalyzed cross-coupling reaction of alkoxydiboron with halogenated arylboronic esters. J Org Chem. 1995;60:7508–7510. DOI:10.1021/jo00128a024.

[48] Miyaura N, Suzuki A. Palladium catalysed cross coupling reactions of organoboron compounds. Chem Rev. 1995;95:2457–2483. DOI:10.1021/cr00039a007.

[49] Padmaja S, Srinivasulu M, Pisipati VGKM. Higher homologues of mesomorphic benzylidene anilines: manifestation of smectic polymorphism. Z Naturforsch. 2003;58a:573–580.

[50] Dierking I. Textures of liquid crystals. Weinheim: Wiley-VCH Verlag GmbH KGaA; 2003.

[51] Berdagué P, Bayle JP, Ho M-S, et al. New laterally aromatic branched liquid crystal materials with large nematic ranges. Liq Cryst. 1993;14(3):667–674. DOI:10.1080/02678299308027746.

[52] Banks RE, Smart BE, Tatlow JC, editors. Organofluorine chemistry principles and commercial applications. New York (NY): Plenum Press; 1994.

[53] Reddy RA, Sadashiva BK. Ferroelectric properties exhibited by mesophases of compounds composed of achiral banana-shaped molecules. J Mater Chem. 2002;12:2627–2632. DOI:10.1039/B204474A.

[54] Karamysheva LA, Torgova SI, Agaforonova IF, et al. Dependence of mesomorphic properties of 3,5-disubstituted 1,2,4-oxadiazoles on geometric and electronic factors. Mol Cryst Liq Cryst. 1995;260:217–225. DOI:10.1080/10587259508038693.

[55] Karamysheva LA, Agaforonova IF, Torgova SI, et al. Liquid crystalline pyridine containing 1,2,4-oxadiazoles. Mol Cryst Liq Cryst. 2001;364:547–556. DOI:10.1080/10587250108025024.