Electronic Supplementary Information

Novel achiral four-ring bent-shaped nematic liquid crystals with trifluoromethyl and methyl substituents in central molecular core: Unusual large Kerr constant in blue phase III of nematic-chiral dopant mixture.

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Procedure for the Synthesis of the compounds:

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DMAP, DCC and DCM

H_{2n+1}C_mO
\[\text{1} \quad \text{2}\]

\text{stir 48 hrs}

\text{m-3CF}_3\text{-2Me-n}
\text{m = n = 5; m = 5, n = 12; m = 12, n = 5; m = n = 12}

\text{Scheme 1: Synthesis of m-3CF}_3\text{-2Me-n series}
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4-[N-(4ʹ-(n-pentyloxy-2-hydroxybenzylidene)amino]-3-trifluoromethylphenyl-4yl 3-[N-(4ʹ-n-pentyloxy-2-hydroxybenzylidene)amino]-2-methylbenzoate, 5-3CF₃-2M-5:

3-[N-(4ʹ-n-pentyloxy-2-hydroxybenzylidene)amino]-2-methylbenzoic acid (0.68g; 2 mmol) was dissolved in dichloromethane, stirred on a magnetic stirrer and a catalytic amount of N,N’-dimethylaminopyridine (DMAP) was added to the solution. To the stirred reaction mixture a solution 4-[N-(4ʹ-n-pentyloxy-2-hydroxybenzylidene)amino]-3-trifluoromethyl phenol (0.73g, 2 mmol) was slowly added. To the resulting solution an equimolar quantity of dicyclohexylcarbodiimide (DCC) (0.412g, 2 mmol) was added and stirred for 48 hours. After the completion of stirring, the dicyclohexylurea thus formed in the reaction mixture was
filtered off. Evaporation of the solvent gave the crude product which was then recrystallized several times from ethanol to obtain the pure product 4-[N-(4ʹ-(n-pentyloxy-2-hydroxybenzylidene)amino] 3-trifluoromethylphenyl-4yl 3-[N-(4ʹ-n-pentyloxy-2-hydroxybenzylidene)amino]-2-methylbenzoate, 5-3CF3-2M-5, as yellow solid. Yield: 0.96g, (70%); IR $\nu_{\text{max}}$ in cm$^{-1}$: 1619 ($\nu_{\text{CH=O}, \text{imine}}$); 1759 ($\nu_{\text{C=O}, \text{ester}}$), 3070 ($\nu_{\text{O-H}, \text{H-bonded}}$), 1H NMR (CDCl$_3$, 400 MHz): 13.46 (s, 1H, -OH), 12.94 (s, 1H, -OH), 8.52 (s, 1H, -CH=N-), 8.45 (s, 1H, -CH=N-), 8.00 (dd, 1H, J = 1.2 Hz, J = 7.6 Hz, ArH), 7.58 (d, 1H, J = 2.4 Hz, ArH), 7.49 (dd, 1H, J = 2.4 Hz, J = 8.4 Hz, ArH), 7.39 (t, 1H, J = 8.0 Hz, ArH), 7.31-7.27 (4H, ArH), 6.52-6.50 (4H, ArH), 4.01 (t, 4H, J = 6.8 Hz, -OCH$_2$-), 2.67 (s, 3H, Ar-CH$_3$), 1.83-1.36 (m, 12H, -(CH$_2$)$_6$-), 0.94 (t, 6H, J = 7.6 Hz, 2x -CH$_3$), 19F NMR 60.93. Elemental Analysis calculated for C$_{39}$H$_{41}$F$_3$N$_2$O$_6$: C, 67.81; H, 5.98 %, N = 4.06%; Found: C, 67.18; H, 5.89%, N = 4.00%.

Using the same procedure as described above, the other compounds of n-3CF$_3$-2Me-m series (n = 5, m =12), (n = 12, m = 5) and (n = m =12), with varying the number of carbon atoms (n) and (m) in the terminal alkyloxy chains using starting compounds in appropriate molar ratios were synthesized.

4-[N-(4ʹ-(n-pentyloxy-2-hydroxybenzylidene)amino] 3-trifluoromethylphenyl-4yl 3-[N-(4ʹ-n-dodecyloxy-2-hydroxybenzylidene)amino]-2-methylbenzoate, 5-3CF$_3$-2M-12: Yield: 1.19g, (76%); IR $\nu_{\text{max}}$ in cm$^{-1}$: 1622 ($\nu_{\text{CH=O}, \text{imine}}$); 1762 ($\nu_{\text{C=O}, \text{ester}}$), 3105 ($\nu_{\text{O-H}, \text{H-bonded}}$), 1H NMR (CDCl$_3$, 400 MHz): 13.48 (s, 1H, -OH), 12.96 (s, 1H, -OH), 8.54 (s, 1H, -CH=N-), 8.47 (s, 1H, -CH=N-), 8.00 (dd, 1H, J = 1.2 Hz, J = 7.6 Hz, ArH), 7.58 (d, 1H, J = 2.4 Hz, ArH), 7.49 (dd, 1H, J = 2.4 Hz, J = 8.4 Hz, ArH), 7.39 (t, 1H, J = 8.0 Hz, ArH), 7.31-7.27 (4H, ArH), 6.52-6.50 (4H, ArH), 4.03 (t, 4H, J = 6.8 Hz, -OCH$_2$-), 2.69 (s, 3H, Ar-CH$_3$), 1.84-1.29 (m, 26H, -(CH$_2$)$_{13}$-), 0.94 (t, 6H, J = 7.6 Hz, 2x -CH$_3$), 19F NMR 60.93. Elemental Analysis calculated for C$_{46}$H$_{55}$F$_3$N$_2$O$_6$: C, 70.03; H, 7.03 %, N = 3.55%; Found: C, 69.37; H, 6.99 %, N = 3.55%.

4-[N-(4ʹ-(n-dodecyloxy-2-hydroxybenzylidene)amino] 3-trifluoromethylphenyl-4yl 3-[N-(4ʹ-n-pentyloxy-2-hydroxybenzylidene)amino]-2-methylbenzoate, 12-3CF$_3$-2M-5: Yield: 1.22g, (78%); IR $\nu_{\text{max}}$ in cm$^{-1}$: 1628 ($\nu_{\text{CH=O}, \text{imine}}$); 1749 ($\nu_{\text{C=O}, \text{ester}}$), 3103 ($\nu_{\text{O-H}, \text{H-bonded}}$), 1H NMR (CDCl$_3$, 400 MHz): 13.46 (s, 1H, -OH), 12.94 (s, 1H, -OH), 8.52 (s, 1H, -CH=N-), 8.45 (s, 1H, -CH=N-), 8.00 (dd, 1H, J = 1.2 Hz, J = 7.6 Hz, ArH), 7.58 (d, 1H, J = 2.4 Hz, ArH), 7.49 (dd, 1H, J = 2.4 Hz, J = 8.4 Hz, ArH), 7.39 (t, 1H, J = 8.0 Hz, ArH), 7.31-7.27 (4H, ArH), 6.52-6.50 (4H, ArH), 4.03 (t, 4H, J = 6.8 Hz, -OCH$_2$-), 2.69 (s, 3H, Ar-CH$_3$), 1.84-1.29 (m, 26H, -(CH$_2$)$_{13}$-), 0.94 (t, 3H, J = 7.6 Hz, -CH$_3$), 0.90 (t, 3H, J = 7.6 Hz, -CH$_3$). Elemental Analysis calculated for C$_{46}$H$_{55}$F$_3$N$_2$O$_6$: C, 70.03; H, 7.03 %, N = 3.55%; Found: C, 69.37; H, 6.99 %, N = 3.55%.
Hz, -CH₃). Elemental Analysis calculated for C₄₆H₅₅F₃N₂O₆: C, 70.03%; H, 7.03 %, N = 3.55%; Found: C, 69.44; H, 6.88; N = 3.55%.

4-[N-(4’-(n-dodecyloxy-2-hydroxybenzylidene)amino] 3-trifluoromethylphenyl-4yl 3-[N-(4’-n-dodecyloxy-2-hydroxybenzylidene)amino]-2-methylbenzoate, 12-3CF₃-2M-12:

Yield: 1.31g, (74%); IR νₓ max in cm⁻¹: 1622 (νCH=N, imine); 1761 (νC=O, ester), 3114νO-H, H-bonded; ¹H NMR (CDCl₃, 400 MHz): 13.46 (s, 1H, -OH), 12.94 (s, 1H, -OH), 8.52 (s, 1H, -CH=N-), 8.45 (s, 1H, -CH=N-), 8.00 (dd, 1H, J = 1.2 Hz, J = 7.6 Hz, ArH), 7.58 (d, 1H, J = 2.4 Hz, ArH), 7.49 (dd, 1H, J = 2.4 Hz, J = 8.4 Hz, ArH), 7.39 (t, 1H, J = 8.0 Hz, ArH), 7.31-7.27 (4H, ArH), 6.52-6.50 (4H, ArH), 4.01 (t, 4H, J = 6.8 Hz, -OCH₂-), 2.67 (s, 3H, Ar-CH₃), 1.83-1.27 (m, 40H, -(CH₂)₂-), 0.88 (t, 6H, J = 6.8 Hz, 2 x -CH₃). Elemental Analysis calculated for C₅₃H₆₉F₃N₂O₆: C, 71.76; H, 7.84 %, N = 3.16; Found: C, 71.01; H, 7.45 %, N = 3.15%.

Figure 1a: ¹H-NMR and ¹⁹F-NMR spectra of representative compound 5-3CF₃-2M-5
Figure 1b: FT-IR spectra of 5-3CF3-2M-5

Figure 1c: $^1$H-NMR and $^{19}$F-NMR spectra of representative compound 5-3CF3-2M-12
Figure 1d: $^1$H-NMR spectra of representative compound 12-3CF$_3$-2M-5

Figure 1e: $^1$H-NMR spectra of representative compound 12-3CF$_3$-2M-12
Figure 1a: Differential scanning calorimetry thermogram of compound 5-3CF_3-2M-5 in the second heating and cooling at 5°C/min.

Figure 1b: Differential scanning calorimetry thermogram of compound 5-3CF_3-2M-12 in the second heating and cooling at 5°C/min.
Figure 1c: Differential scanning calorimetry thermogram of compound 12-3CF₃-2M-5 in the second heating and cooling at 5°C/min.

Figure 1d: Differential scanning calorimetry thermogram of compound 12-3CF₃-2M-12 in the second heating and cooling at 5°C/min.
2. Polarizing Optical micrographs of BPIII:

Figure 2a: POM images exhibiting Iso-BPIII-N* transition in a planar cell of thickness 4µm for the mixture 5-3CF3-2M-5 + 30% S811
Figure 2b: POM images exhibiting Iso-BPIII-N* transition in a planar cell of thickness 4µm for the mixture 5-3CF3-2M-12 + 30% S811.