

Electronic Supporting Information

Polar order of an achiral taper-shaped liquid crystal in the uniaxial smectic A phase

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Experimental

Materials

For use in this study, 4-hydroxyphenyl-1-[4-(2-tetrahydropyranyloxy)phenyl]-2,3-difluorobenzene and 5-octyl-2-(4-hydroxyphenyl)pyrimidine were purchased from Midori Kagaku Co. Ltd. The purity of the final compound was confirmed using elemental analysis (EA 1110; CE Instruments Ltd.). Infrared (IR) spectroscopy (FTS-30; Bio-Rad Laboratories Inc.) and proton nuclear magnetic resonance (^1H NMR) spectroscopy (JNM-ECA500; JEOL) elucidated the structure of the final product.

6-[4-(4-Cyanophenyl)phenoxy]hexyl 2-{7-{4-[4-(4-hexylphenyl)-2,3-difluorophenyl]phenoxy}heptanoyloxy}-4-{6-[4-(5-octylpyrimidin-2-yl)phenoxy]hexyloxy}benzoate (**1**)

Potassium carbonate (0.42 g, 3.0 mmol) was added to a solution of 5-octyl-2-(4-hydroxyphenyl)pyrimidine (0.86 g, 3.0 mmol) and 1,6-dibromohexane (1.10 g, 4.5 mmol) in cyclohexanone (15 ml). The reaction mixture was stirred at 70 °C for 6 h, then stirred at 80 °C for 3 h. After filtration of the precipitate, the solvent was removed by evaporation. Then the residue was purified using column chromatography on silica gel with a toluene : ethyl acetate (20:1) mixture as the eluent. The obtained white solid was washed with hexane to give 5-octyl-2-{4-(6-bromohexyl)phenyl}pyrimidine. Yield: 0.58 g (43%).

Potassium carbonate (0.17 g, 1.2 mmol) was added to a solution of 5-octyl-2-{4-(6-bromohexyloxy)phenyl}pyrimidine (0.54 g, 1.2 mmol) and methyl 2,4-dihydroxybenzoate (0.24 g, 1.4 mmol) in cyclohexanone (20 ml). The reaction mixture was stirred at 70 °C for 5 h, then stirred at 80 °C for 5 h. After filtration of the precipitate, the solvent was removed by evaporation. Then the residue was purified using column chromatography on silica gel with a toluene : ethyl acetate (5:1) mixture as the eluent. Methyl 4-{6-[4-(5-octylpyrimidin-2-yl)phenoxy]hexyloxy}-2-hydroxybenzoate was obtained. Yield: 0.19 g (30%).

Methyl 4-{6-[4-(5-octylpyrimidin-2-yl)phenoxy]hexyloxy}-2-hydroxybenzoate (0.23 g, 0.4 mmol) was added to a solution of NaOH (0.15 g, 3.8 mmol) in an ethanol (30 ml) / water (10 ml) mixture. The resulting solution was stirred under reflux for 4 h. The solution was acidified using aq. HCl. The solution was extracted using dichloromethane (60 ml), and then using chloroform (120 ml). The organic layers were combined, dried over magnesium sulphate, filtered, and evaporated. 4-{6-[4-(5-Octylpyrimidin-2-yl)phenoxy]hexyloxy}-2-hydroxybenzoic acid was obtained. Yield: 0.12 g (54%).

Potassium carbonate (681 mg, 4.9 mmol) was added to a solution of 1-cyano-4-(4-hydroxyphenyl)benzene (812 mg, 4.0 mmol) and 6-bromohexanol (730 mg, 4.0 mmol) in cyclohexanone (20 ml). The reaction mixture was stirred at 120 °C for 6 h. After filtration of the precipitate, the solvent was removed by evaporation. Then the residue was purified using column chromatography on silica gel with a toluene : ethyl acetate (3:1) mixture as the eluent. It was then washed from hexane to give 1-cyano-4-(4-[6-hydroxyhexyloxy]phenyl)benzene. Yield: 915 mg (77%).

Potassium carbonate (268 mg, 2.1 mmol) was added to a solution of 4-(4-hexylphenyl)-1-(4-hydroxyphenyl)-2,3-difluorobenzene (722 mg, 2.0 mmol) and ethyl 7-bromoheptanoate (480 mg, 2.0 mmol) in cyclohexanone (20 ml). The reaction mixture was stirred at 120 °C for 10 h. After filtration of the precipitate, the solvent was removed by evaporation. Then the residue was purified using column chromatography on silica gel with dichloromethane as the eluent. It was then washed from hexane to give ethyl 7-{4-[2,3-difluoro-4-(4-hexylphenyl)phenyl]phenyloxy}heptanoate. Yield: 802 mg (79%).

Ethyl 7-{4-[2,3-difluoro-4-(4-hexylphenyl)phenyl]phenyloxy}heptanoate (810 mg, 1.6 mmol) was added to a solution of NaOH (476 mg, 11.9 mmol) in an ethanol (30 ml) / water (10 ml) mixture. The resulting solution was stirred at 100 °C for 3 h. The solution was acidified using aq. HCl. The solution was extracted using dichloromethane (60 ml). The organic layers were combined, dried over magnesium sulphate, filtered, and evaporated. 7-{4-[2,3-Difluoro-4-(4-hexylphenyl)phenyl]phenyloxy}heptanoic acid was obtained. Yield: 704 mg (89%).

1-Cyano-4-(4-[6-hydroxyhexyloxy]phenyl)benzene (402 mg, 1.4 mmol), *N, N'*-dicyclohexylcarbodiimide (167 mg, 0.8 mmol), and 4-(*N, N*-dimethylamino)pyridine (25 mg, 0.2 mmol) were added to a solution of 4-{6-[4-(5-Octylpyrimidin-2-yl)phenyloxy]hexyloxy}-2-hydroxybenzoic acid (377 mg, 0.8 mmol) in dichloromethane (30 mL). The resulting solution was stirred at room temperature for 19 h. The precipitated materials were removed by filtration. After removal of the solvent by evaporation, the residue was washed from ethanol. The obtained solid was purified using HPLC with chloroform as the eluent to give 6-[4-(4-Cyanophenyl)phenyloxy] hexyl4-{6-[4-(5-octylpyrimidin-2-yl)phenyloxy] hexyloxy}-2-hydroxybenzoate. Yield: 132 mg (22%).

6-[4-(4-Cyanophenyl)phenyloxy] hexyl4-{6-[4-(5-octylpyrimidin-2-yl)phenyloxy]hexyloxy}-2-hydroxybenzoate (120 mg, 0.2 mmol), *N, N'*-dicyclohexylcarbodiimide (50 mg, 0.2 mmol), and 4-(*N, N*-dimethylamino)pyridine (9 mg, 0.07 mmol) were added to a solution of 7-{4-[2,3-Difluoro-4-(4-hexylphenyl)phenyl]phenyloxy}heptanoic acid (105 mg, 0.2 mmol) in dichloromethane

(30 mL), The resulting solution was stirred at room temperature for 30 h. The precipitated materials were removed by filtration. After removal of the solvent by evaporation, the residue was washed from hot ethanol (70 °C). The obtained solid was purified using HPLC with chloroform as the eluent to give the desired compound. Yield: 105 mg (55%). ¹H-NMR(500 MHz, solvent CDCl₃, standard TMS) TM_H /ppm : 8.56(s, 2H, **H9**), 8.33(d, 2H, **H10** *J* = 8.5 Hz), 7.95(d, 1H, **H19**, *J* = 9.2 Hz), 7.66(d, 2H, **H29**, *J* = 8.0 Hz), 7.61(d, 2H, **H30**, *J* = 8.6 Hz), 7.51-7.48(m, 6H, **H28**, **H38**, **H41**), 7.27(d, 2H, **H42**, *J* = 8.6 Hz), 7.23-7.18(m, 2H, **H39**, **H40**), 6.98-6.96(m, 6H, **H11**, **H27**, **H37**), 6.77(dd, 1H, **H18**, *J* = 8.2 Hz, *J* = 2.3 Hz), 6.58(d, 1H, **H20**, *J* = 2.3 Hz), 4.24(t, 2H, **H21**, *J* = 6.6 Hz), 4.05-3.98(m, 8H, **H12**, **H17**, **H26**, **H36**), 2.66(t, 4H, **H8**, **H43**, *J* = 7.4 Hz), 2.59(t, 2H, **H31**, *J* = 7.7 Hz), 1.84-1.75(m, 12H, **H13**, **H16**, **H22**, **H25**, **H32**, **H35**), 1.68-1.48(m, 16H, **H7**, **H14**, **H15**, **H23**, **H24**, **H33**, **H34**, **H44**), 1.40-1.21(m, 16H, **H2**, **H3**, **H4**, **H5**, **H6**, **H45**, **H46**, **H47**), 0.91-0.86(m, 6H, **H1**, **H48**). IR(KBr)_{v_{max}}cm⁻¹ : 2933, 2857, 2226, 1756, 1697, 1609, 1253. Elemental anal. Calcd. for C₈₁H₉₃F₂N₃O₈ : C 76.33 , H 7.35 , N 3.30 . Found : C 76.61 , H 7.21 , N 3.43.

