Electronic Supporting Information

Frustrated phase driven by competition among layer structures

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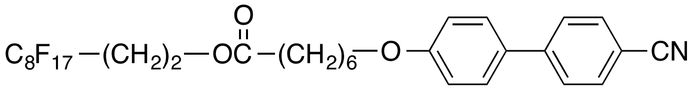
Materials

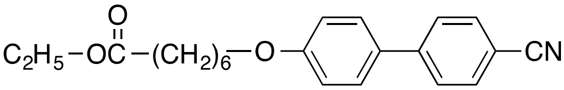
Spectroscopic analysis. Purity of the final compound was confirmed using elemental analysis (EA 1110; CE Instruments Ltd.). Infrared (IR) spectroscopy (FTS-30; Bio-Rad Laboratories Inc.) and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy (JNM-ECA500; JEOL) elucidated the structure of the final product.

Preparation of materials

1H, 1H, 2H, 2H-Heptadecafluorodecyl 7-{4-(4-cyanophenyl)phenyloxy}heptanoate (1).

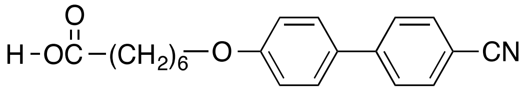


Potassium carbonate (0.90 g, 6.5 mmol) was added to a solution of 4-cyano-4'-hydroxybiphenyl (0.98 g, 5.0 mmol) and ethyl 7-bromoheptanoate (1.55 g, 6.5 mmol) in cyclohexanone (40 mL). The reaction mixture was stirred at 110 °C for 6.5 h. After filtration of the precipitate, the solvent was removed by evaporation. Then, using column chromatography, the residue was purified on silica gel with dichloromethane as the eluent. It was then recrystallized from ethanol to give ethyl 7-{4-(4-cyanophenyl)phenyloxy}heptanoate. Yield: 1.42 g (80.7%); mp 86.5–87.1 °C.



^{1}H-NMR (500 MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 7.68 (d, 2H, Ar-H, *J* = 8.6 Hz), 7.63 (d, 2H, Ar-H, *J* = 8.6 Hz), 7.52 (d, 2H, Ar-H, *J* = 9.1 Hz), 6.98 (d, 2H, Ar-H, *J* = 8.6 Hz), 4.12 (q, 2H, -C$\mathbf{H}_2$-O, *J* = 7.1 Hz), 4.00 (t, 2H, -C$\mathbf{H}_2$-O, *J* = 6.6 Hz), 2.31 (t, 2H, -OC-C$\mathbf{H}_2$-, *J* = 7.5 Hz), 1.82 (quint, 2H, -C$\mathbf{H}_2$-, *J* = 7.0 Hz), 1.67 (quint, 2H, -C$\mathbf{H}_2$-, *J* = 7.6 Hz), 1.50 (quint, 2H, -C$\mathbf{H}_2$-, *J* = 7.6 Hz), 1.41 (quint, 2H, -C$\mathbf{H}_2$-, *J* = 7.3 Hz), 1.25 (t, 3H, C$\mathbf{H}_3$-CH_2).

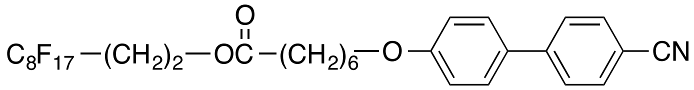
Ethyl 7-{4-(4-cyanophenyl)phenyloxy}heptanoate (1.52 g, 4.3 mmol) was added to a solution of NaOH (0.70 g, 12.8 mmol) in a THF (30 mL)/water (10 mL) mixture. The resulting solution was stirred at room temperature for 49 h. The solution was acidified using aq. HCl. The solution was extracted using dichloromethane (150 mL). The organic layers were combined, dried over magnesium sulphate, filtered, and evaporated. It was then recrystallized from ethanol, giving 7-{4-(4-cyanophenyl)phenyloxy}heptanoic acid. Yield: 1.15 g (82.0%); mp 118.9–120.0 °C.



^{1}H-NMR (500 MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 7.68 (d, 2H, Ar-H, *J* = 8.6 Hz), 7.63 (d, 2H, Ar-H, *J* = 8.6 Hz), 7.52 (d, 2H, Ar-H, *J* = 9.1 Hz), 6.98 (d, 2H, Ar-H, *J* = 9.1 Hz), 4.00 (t, 2H, -C$\mathbf{H}_2$-O, *J* = 6.3 Hz), 2.38 (t, 2H, -OC-C$\mathbf{H}_2$-, *J* = 7.4 Hz), 1.82 (quint, 2H, -C$\mathbf{H}_2$-, *J* = 7.0 Hz), 1.69 (quint, 2H, -C$\mathbf{H}_2$-, *J* = 7.6 Hz), 1.51 (quint, 2H, -C$\mathbf{H}_2$-, *J* = 7.6 Hz), 1.43 (quint, 2H, -C$\mathbf{H}_2$-, *J* = 7.0 Hz).

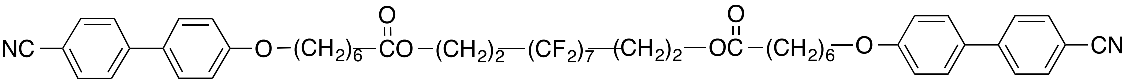
1H,1H,2H,2H-Heptadecafluoro-1-decanol (0.32 g, 0.7 mmol), *N,N'*-dicyclohexylcarbodiimide (0.15 g, 0.7 mmol) and 4-(*N,N*-dimethylamino)pyridine (0.01 g, 0.1 mmol) were added to a solution of 7-{4-(4-cyanophenyl)phenyloxy}heptanoic acid (0.17 g, 0.53 mmol) in dichloromethane (20 mL). The resulting solution was stirred at room temperature for 26 h. The precipitated materials were removed by filtration. After removal of the solvent by evaporation, the residue was purified using column chromatography on silica gel with a toluene : ethyl acetate (20:1) mixture as the eluent.

It was then recrystallized from ethanol, giving the desired compound. Yield: 258.5 mg (64.6%); mp 88.3–88.8 °C.



^{1}H-NMR (500 MHz, solvent CDCl$_3$, standard TMS) δ_{H}/ppm: 7.68 (d, 2H, Ar-H, J = 8.6 Hz), 7.63 (d, 2H, Ar-H, J = 8.6 Hz), 7.51 (d, 2H, Ar-H, J = 8.6 Hz), 6.97 (d, 2H, Ar-H, J = 8.6 Hz), 4.38 (t, 2H, -C**H**$_2$-O, J = 6.6 Hz), 4.00 (t, 2H, -C**H**$_2$-O, J = 6.3 Hz), 2.52–2.42 (m, 2H, -CF$_2$-C**H**$_2$-), 2.35 (t, 2H, -OC-C**H**$_2$-, J = 7.7 Hz), 1.81 (quint, 2H, -C**H**$_2$-, J = 7.0 Hz), 1.68 (quint, 2H, -C**H**$_2$-, J = 7.4 Hz), 1.51 (quint, 2H, -C**H**$_2$-, J = 7.6 Hz), 1.42 (quint, 2H, -C**H**$_2$-, J = 7.6 Hz). IR(KBr) $\nu_{\max}$cm^{-1} : 3462, 3071, 2940, 2869, 2232, 1737. Elemental Anal. Calcd. for $C_{30}H_{24}F_{17}NO_3$: C 46.83, H 3.14, N 1.82. Found: C 47.20, H 3.17, N 1.82.

1,9-Bis{7-[4-(4-cyanophenyl)phenyloxy]heptanoyloxy}-1H,1H,9H,9H-tetradecafluorononane (2)



1H,1H,9H,9H-Tetradecafluoro-1,9-nonandiol (0.16 g, 0.4 mmol), *N,N'*-dicyclohexylcarbodiimide (0.21 g, 1.0 mmol) and 4-(*N,N*-dimethylamino)pyridine (0.01 g, 0.1 mmol) were added to a solution of 7-{4-(4-cyanophenyl)phenyloxy}heptanoic acid (0.33 g, 1.0 mmol) in dichloromethane (10 mL). The resulting solution was stirred at room temperature for 24 h. The precipitated materials were removed by filtration. After removal of the solvent by evaporation, the residue was purified using column chromatography on silica gel with a toluene : ethyl acetate (20:1) mixture as the eluent. It was then recrystallized from toluene, giving the desired compound. Yield: 305.0 mg (75.8%); mp 107.5–108.3 °C.

^{1}H-NMR (500 MHz, solvent CDCl$_3$, standard TMS) δ_{H}/ppm: 7.68 (d, 4H, Ar-H, J = 8.6 Hz), 7.63 (d, 4H, Ar-H, J = 8.6 Hz), 7.51 (d, 4H, Ar-H, J = 8.6 Hz), 6.97 (d, 4H, Ar-H, J = 8.6 Hz), 4.58 (t, 4H, -CF$_2$-C**H**$_2$-O, J = 13.7 Hz), 4.00 (t, 4H, -C**H**$_2$-O, J = 6.6 Hz), 2.44 (t, 4H, -OCOC**H**$_2$-), 1.81 (quint, 4H, -C**H**$_2$-, J = 7.0 Hz), 1.70 (quint, 4H, -C**H**$_2$-, J = 7.6 Hz), 1.51 (quint, 4H, -C**H**$_2$-, J = 7.4 Hz), 1.42 (quint, 4H, -C**H**$_2$-, J = 7.6 Hz).

IR(KBr) ν_{max}cm^{-1}: 3459, 2942, 2867, 2232, 1747. Elemental Anal. Calcd. for $C_{33}H_{35}F_{17}N_2O_3$: C 57.54, H 4.34, N 2.74. Found: C 57.64, H 4.25, N 2.73.