**Supporting Information**

**New room temperature nematogens by cyano tail termination of alkoxy and alkylcyanobiphenyls and their anchoring behavior on metal salt-decorated surface**

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# SI.1 Synthesis of cyano tail-terminated cyanobiphenyl/terphenyl compounds



**n = 2, CN2OCB (using acrylonitrile)**

SI-14.tif

In a 200 ml recovery flask with stirbar was placed 4-hydroxycyanobiphenyl (1.95 gm, 10.0 mmol), acrylonitrile (20 ml), *t*-BuOH (30 mg, 0.04 mmol) and DMAP (50 mg, 0.04 mmol). The flask was fitted with a bump trap as condenser and the mixture was heated with stirring in a 90°C oil bath for 72 hours (after which time only a small amount of starting material remained). The mixture was stirred in an ice water bath and 2% aqueous HCl was added dropwise with stirring to fill the flask. A solid precipitate appeared and after stirring 15 min in the ice bath it was collected by suction filtration, washed well with water and air dried. This material was taken up in boiling methanol which was hot filtered. Upon cooling crystals appeared which were collected by suction filtration, washed with cold ethanol and air dried. The product was collected as white needle crystals in two crops totaling 2.17 gm (88%). MP: 186 °C. 1H NMR (400 MHz, CDCl3) δ (ppm): 7.71-7.61 (m, 4H), 7.52 (td, 1*J* = 8.4 Hz, 2*J* = 1.6 Hz, 2H), 6.98 (td, 1*J* = 8.8 Hz, 2*J* = 2.0 Hz, 2H), 4.26 (t, *J* = 6.4 Hz, 2H), 2.86 (t, *J* = 6.4 Hz, 2H); 13C NMR (100 MHz, CDCl3) δ (ppm): 158.6, 144.9, 132.9, 132.6, 128.6, 127.2, 118.8, 116.1, 115.4, 110.1, 62.9, 18.6; IR (cm-1): 2972, 2938, 2249, 2224, 1602, 1494, 1241, 1181, 813.

**General Procedure A for the synthesis of cyano tail-terminated alkoxy cyanobiphenyl compounds (n = 3-6)**

SI-13.tif

In a 200 ml round bottom flask was placed 4-cyano-4'-hydroxybiphenyl (1.0 equiv.), ,-bromoalkylnitrile (1.0 equiv.), dry DMF (1.0 ml per 1.0 mmol substrate), potassium carbonate (2.0 equiv.) and potassium iodide (0.1 equiv.). The resulting suspension was stirred overnight at room temperature and the reaction was monitored by TLC analysis. Upon completion, water was added dropwise with stirring to fill the flask and then the precipitate was collected by vacuum filtration. In some cases when no precipitate was found, the mixture was extracted with dichloromethane. The crude product was recrystallized from methanol.

**n = 3, CN3OCB (by General Procedure A)**

**SI-12.tif**

2.11 g, 81% yield after recrystallization from methanol.

1H NMR (400 MHz, CDCl3) δ (ppm): 7.69 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.53 (td, 1*J* = 8.8 Hz, 2*J* = 3.2 Hz, 2H), 7.00 (td, 1*J* = 9.2 Hz, 2*J* = 2.8 Hz, 2H), 4.14 (t, *J* = 6.0 Hz, 2H), 2.63 (t, *J* = 7.2 Hz, 2H), 2.18 (m, 2H); 13C NMR (100 MHz, CDCl3) δ (ppm): 159.0, 145.1, 132.6, 132.1, 128.5, 127.2, 119.1, 115.1, 110.3, 65.4, 25.4, 14.2. IR (cm-1): 2937, 2876, 2246, 2225, 1602, 1494, 1244, 1183, 826. GC-MS: 262.25 found 262.31 calc.

POM: K 138 I 79 N 71 K

DSC: K 137.9 I 79.0 N 70.9 K

**n = 4, CN4OCB (by General Procedure A)**

**SI-11.tif**

870 mg, 63% yield after recrystallization from methanol.

1H NMR (400 MHz, CDCl3) δ (ppm): 7.70 (td, 1*J* = 8.0 Hz, 2*J* = 0.8 Hz, 2H), 7.64 (td, 1*J* = 8.0 Hz, 2*J* = 0.8 Hz, 2H), 7.53 (td, 1*J* = 8.8 Hz, 2*J* = 2.8 Hz, 2H), 6.99 (td, 1*J* = 8.8 Hz, 2*J* = 2.8 Hz, 2H), 4.07 (t, *J* = 6.0 Hz, 2H), 2.47 (t, *J* = 6.8 Hz, 2H), 2.01-1.90 (m, 4H); 13C NMR (100 MHz, CDCl3) δ (ppm): 159.3, 145.1, 132.6, 131.8, 128.4, 127.1, 119.5, 119.1, 115.0, 110.2, 66.8, 28.2, 22.4, 17.1. IR (cm-1): 2937, 2876, 2243, 2221, 1601, 1493, 1249, 1179, 827. GC-MS: 276.24 found 276.33 calc.

DSC: K 93.1 I 61.2 N 37.8 K

POM: K 93 I 62 N 28 K

**n = 5, CN5OCB (by General Procedure A)**

**SI-10.tif**

1.0 g, 69% yield after recrystallization from methanol.

1H NMR (400 MHz, CDCl3) δ (ppm): 7.69 (td, 1*J* = 8.4 Hz, 2*J* = 1.6 Hz, 2H), 7.64 (dd, 1*J* = 8.0 Hz, 2*J* = 1.2 Hz, 2H), 7.53 (td, 1*J* = 8.8 Hz, 2*J* = 3.2 Hz, 2H), 6.99 (td, 1*J* = 8.8 Hz, 2*J* = 2.0 Hz, 2H), 4.03 (t, *J* = 6.0 Hz, 2H), 2.40 (t, *J* = 6.8 Hz, 2H), 1.85 (m, 2H), 1.79-1.65 (m, 4H); 13C NMR (100 MHz, CDCl3) δ (ppm): 159.5, 145.2, 132.6, 131.5, 128.4, 127.1, 119.6, 119.1, 115.1, 110.1, 67.5, 28.5, 25.4, 25.2, 17.2. IR (cm-1): 2950, 2909, 2872, 2244, 2223, 1600, 1494, 1246, 1180, 811. GC-MS: 290.23 found 290.36 calc.

DSC: K 65.8 N 76.7 I 75.6 N 4.9 K

POM: K 67.8 N 77.3 I 76.8 N

**n = 6, CN6OCB (by General Procedure A)**

**SI-9.tif**

1.2 g, 79% yield after recrystallization from methanol.

1H NMR (400 MHz, CDCl3) δ (ppm): 7.69 (td, 1*J* = 7.6 Hz, 2*J* = 1.2 Hz, 2H), 7.63 (dd, 1*J* = 6.8 Hz, 2*J* = 2.0 Hz, 2H), 7.53 (td, 1*J* = 6.4 Hz, 2*J* = 5.2 Hz, 2H), 6.99 (td, 1*J* = 8.8 Hz, 2*J* = 2.8 Hz, 2H), 4.02 (t, *J* = 6.0 Hz, 2H), 2.37 (t, *J* = 7.2 Hz, 2H), 1.83 (m, 2H), 1.73 (m, 2H), 1.57-1.53 (m, 4H); 13C NMR (100 MHz, CDCl3) δ (ppm): 159.6, 145.2, 132.6, 131.4, 128.4, 127.1, 119.7, 119.1, 115.1, 110.1, 67.8, 28.9, 28.4, 25.4, 25.3, 17.1. IR (cm-1): 2935, 2856, 2247, 2224, 1600, 1493, 1181, 818. GC-MS: 304.32 found 304.39 calc.

DSC: K 97.1 I 68.3 K

POM: K 97 I

**n = 5, Cl5OCB (by General Procedure A)**

1-Bromo-5-chloropentane (5.0 mmol, 927 mg) was used. White crystals recrystallized from methanol. (890 mg, yield: 60%)

1H NMR (400 MHz, CDCl3) δ (ppm): 7.70 (m, 2H), 7.64 (m, 2H), 7.53 (td, 1*J* = 8.8 Hz, 2*J* = 2.8 Hz, 2H), 6.99 (td, 1*J* = 8.8 Hz, 2*J* = 2.8 Hz, 2H), 4.03 (t, *J* = 5.6 Hz, 2H), 3.58 (t, *J* = 6.8 Hz, 2H), 1.91-1.82 (m, 4H), 1.65 (m, 2H); 13C NMR (100 MHz, CDCl3) δ (ppm): 159.3, 145.2, 132.6, 131.4, 128.4, 127.1, 119.1, 115.1, 110.1, 67.8, 44.9, 32.3, 28.5, 23.5. GC-MS:299.18 found 299.79 calc.

Synthesis of the cyano tail terminated compounds CN7OCB, CN5CB, CB6CB and CN7CB was accomplished by substitution of the relevant hydroxy tail terminated intermediates. (General Procedure B)

4'-[(7-Hydroxyheptyl)oxy]-4-cyanobiphenyl

SI-2.tif

In a 100 ml round bottom flask with stirbar was placed 4’-hydroxy-4-cyanobiphenyl (2.7 g, 13.8 mmol), triphenylphosphine (4.5 g, 16.5 mmol), 1,7-heptanediol (2.2 g, 16.5 mmol) and dry THF (25 ml). The resulting solution was chilled in an ice bath and diethylazodicarboxylate (94%, 3.5 g, 16.5 mmol) was added in portions over ten minutes. The mixture was allowed to warm to room temperature and monitored by TLC until completion. The mixture was allowed to stir overnight, and the reaction was terminated by addition of silica gel and the mixture was concentrated to dryness. The adsorbed material was placed at the top of a column made up with 20% ethyl acetate / 80% hexanes and eluted with a gradient up to ethyl acetate and hexanes (1:4). Fractions containing only the desired product were combined and concentrated to give the desired product as a white solid (2.4 g, 56%).

1H NMR (400 MHz, CDCl3) δ (ppm): 7.68 (dd, 1*J* = 6.4 Hz, 2*J* = 1.6 Hz, 2H), 7.63 (dt, 1*J* = 8.0 Hz, 2*J* = 1.6 Hz, 2H), 7.51 (dd, 1*J* = 7.2 Hz, 2*J* = 2.4 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.99 (t, *J* = 6.8 Hz, 2H), 3.65 (t, *J* = 6.4 Hz, 2H), 1.81 (m, 2H), 1.58 (q, *J* = 2.4 Hz, 2H), 1.51-1.40 (m, 6H); 13C NMR (100 MHz, CDCl3) δ (ppm): 159.8, 145.3, 132.6, 131.3, 128.3, 127.1, 119.2, 115.1, 110.0, 68.1, 62.9, 32.7, 29.2, 26.0, 25.7.

4’-[[7-[[(4-methylphenyl)sulfonyl]heptyl]oxyl]-4-cyanobiphenyl

SI-1.tif

A 100 mL flask was charged with 4'-[(7-hydroxyheptyl)oxy]-4-cyanobiphenyl (2.0 g, 6.7 mmol), triethylamine (0.89 g, 8.7 mmol) and DCM (6.0 mL). The mixture was cooled to a temperature of about 5°C to 15°C and cautiously charged with a solution of *p*-toluenesulfonyl chloride (1.28 g, 6.7 mmol) in DCM (5.0 mL) over 30 minutes via additional funnel. Once the addition was complete, the reaction mixture was warmed to 18 °C to 22 °C and stirred for 12 hours. To this solution was added 6N hydrochloric acid (0.55 mL) cautiously while maintaining temperature below 25 °C. The aqueous phase was removed, and the organic phase was washed with water and dried over magnesium sulfate. The product was purified by column chromatography to afford a low melting white solid (Yield: 2.1 g, 68%)

1H NMR (CDCl3, 400 MHz) δ (ppm): 7.78 (dt, 1*J* = 6.4 Hz, 2*J* = 2.0 Hz, 2H), 7.69-7.63 (m, 4H), 7.51 (m, 2H), 7.34 (m, 2H), 6.98 (m, 2H), 4.02 (m, 4H), 2.44 (s, 3H), 1.73 (m, 2H), 1.41 (m, 2H), 1.34-1.26 (m, 6H); 13C NMR (CDCl3, 100 MHz) δ (ppm): 159.7, 145.3, 144.7, 133.2, 132.6, 131.3, 129.8, 128.4, 127.9, 127.1, 119.2, 115.1, 110.2, 70.6, 68.0, 29.1, 28.8, 28.7, 25.8, 25.3, 21.7.

**n = 7, CN7OCB**

SI-8.tif

To a solution of 4’-[[7-[[(4-methylphenyl)sulfonyl]heptyl]oxyl]-4-cyanobiphenyl (1.1 g, 3.0 mmol) in DMSO (15 mL) was added NaCN (186 mg, 3.8 mmol). The mixture was stirred for 8 hours at 60 °C then at room temperature overnight. The residue was diluted with water (30 mL) and extracted with diethyl ether (15 mL). The organic phase was dried over magnesium sulfate and evaporated under reduced pressure. The desired product was separated by column chromatography eluted by ethyl acetate:hexane (1:4) as white crystals, which was then recrystallized from methanol as a white solid. (Yield: 440 mg, 46%)

1H NMR (CDCl3, 400 MHz) δ (ppm): 7.69 (td, 1*J* = 8.0 Hz, 2*J* = 0.8 Hz, 2H), 7.64 (td, 1*J* = 8.0 Hz, 2*J* = 1.2 Hz, 2H), 7.53 (td, 1*J* = 8.8 Hz, 2*J* = 2.4 Hz, 2H), 6.99 (dd, 1*J* = 6.4 Hz, 2*J* = 2.0 Hz, 2H), 4.01 (t, *J* = 6.4 Hz, 2H), 2.36 (t, *J* = 7.2 Hz, 2H), 1.82 (m, 2H), 1.69 (m, 2H), 1.52 (m, 4H), 1.43 (m, 2H); 13C NMR (CDCl3, 100 MHz) δ (ppm): 160.1, 145.7, 133.0, 132.9, 131.8, 128.7, 128.5, 119.5, 115.5, 110.5, 68.3, 29.5, 29.0, 28.9, 28.8, 26.2, 25.7, 17.5; IR (cm-1): 2933, 2866, 2246, 2219, 1600, 1494, 1248, 1179, 817; GC/MS: 318.25 found 318.41 calc.

POM: K 60.8 N 70.8 I 70.7 N 27 I

**The cyanoalkyl cyanobiphenyl compounds (n = 5-7) were synthesized by General Procedure B.**

**n = 5, CN5CB (by General Procedure B)**



800 mg, 80% yield. A white solid.

1H NMR (CDCl3, 400 MHz) δ (ppm): 7.72 (td, 1*J* = 8.0 Hz, 2*J* = 0.8 Hz, 2H), 7.66 (td, 1*J* = 8.0 Hz, 2*J* = 1.2 Hz, 2H), 7.52 (td, 1*J* = 8.8 Hz, 2*J* = 2.4 Hz, 2H), 7.28 (dd, 1*J* = 6.4 Hz, 2*J* = 2.0 Hz, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 2.35 (t, *J* = 7.2 Hz, 2H), 1.69 (m, 4H), 1.54 (m, 2H); 13C NMR (CDCl3, 100 MHz) δ (ppm): 145.5, 142.8, 136.8, 132.6, 129.2, 127.5, 127.2, 119.7, 119.0, 110.6, 35.3, 30.5, 28.3, 25.3, 17.1;

POM: K 65.8 I 25 K

**n = 6, CN6CB (by General Procedure B)**



32 mg, recrystallized from methanol, 40% yield.

1H NMR (CDCl3, 400 MHz) δ (ppm): 7.71 (td, 1*J* = 8.0 Hz, 2*J* = 0.8 Hz, 2H), 7.67 (td, 1*J* = 8.0 Hz, 2*J* = 1.2 Hz, 2H), 7.51 (td, 1*J* = 8.8 Hz, 2*J* = 2.4 Hz, 2H), 7.28 (dd, 1*J* = 6.4 Hz, 2*J* = 2.0 Hz, 2H), 2.68 (t, *J* = 7.6 Hz, 2H), 2.34 (t, *J* = 6.8 Hz, 2H), 1.66 (m, 4H), 1.50 (m, 2H), 1.42 (m, 2H); 13C NMR (CDCl3, 100 MHz) δ (ppm): 145.5, 143.2, 136.7, 132.6, 129.2, 127.5, 127.2, 119.7, 119.0, 110.6, 35.4, 31.0, 28.5, 28.4, 25.3, 17.1; IR (cm-1): 2935, 2857, 2247, 2226, 1605, 1494, 812; GC/MS: 288.26 found 288.39 calc.

DSC; K 61 I 35 N -7 K

POM: K 60 I 34 N

**n = 7, CN7CB (by General Procedure B)**

**07033KW**



29 mg,recrystallized from methanol, 24% yield.

1H NMR (CDCl3, 400 MHz) δ (ppm): 7.71 (td, 1*J* = 8.0 Hz, 2*J* = 0.8 Hz, 2H), 7.67 (td, 1*J* = 8.0 Hz, 2*J* = 1.2 Hz, 2H), 7.50 (td, 1*J* = 8.8 Hz, 2*J* = 2.4 Hz, 2H), 7.28 (dd, 1*J* = 6.4 Hz, 2*J* = 2.0 Hz, 2H), 2.67 (t, *J* = 7.2 Hz, 2H), 2.34 (t, *J* = 7.2 Hz, 2H), 1.66 (m, 4H), 1.46 (m, 2H), 1.39 (m, 4H); 13C NMR (CDCl3, 100 MHz) δ (ppm): 145.6, 143.4, 136.6, 132.6, 129.2, 127.5, 127.1, 119.8, 119.0, 110.6, 35.5, 31.2, 28.9, 28.6, 28.5, 25.3, 17.1; IR (cm-1): 2920, 2854, 2246, 2224, 1604, 1495, 820;GC/MS: 302.29.26 found 302..41 calc.

POM: K 66 I 36 K

**Synthesis of Cyano-terminated alkoxy cyanoterphenyl compounds CNnOCT**

**SI-3.tif**

Procedure for the synthesis of 1-bromo-4-hydroxybiphenyl

***4-acetoxybiphenyl.*** A 500 mL round bottom flask was charged with 4-phenylphenol (125 g, 0.7 mol), acetic anhydride (112.5 g, 1.1 mol), and concentrated sulfuric acid (cat.). The flask was fitted with a reflux condenser and was heated under nitrogen in an oil bath for 3 hours. Reaction progress was monitored by TLC, noting the disappearance of the spot for 4-phenylphenol and the appearance of a single spot for the product. The flask was removed from the oil bath, and water (~400 mL) was added to precipitate the product, and the product was dried by vacuum filtration. The product was purified by recrystallization from ethanol, giving the product as a white powder (152.8 g, 98%); mp 87 °C. 1H-NMR (400 MHz, CDCl3): 7.62 (d, J= 8.76 Hz, 2H); 7.59 (d, J= 7.04 Hz, 2H); 7.46 (dd, J= 7.52 Hz, 7.52 Hz, 2H); 7.38 (t, J= 7.34 Hz, 1H); 7.19 (d, J= 8.68 Hz, 2H); 2.36 (s, 3H).IR (Neat): 1748, 1598, 1515, 1484, 1428, 1372, 1217, 1193, 1165, 1106, 1052, 1017, 1008, 942, 906, 850, 832, 765, 735, 967, 650 cm-1.

***4-bromo-4’-acetoxybiphenyl.*** A 500 mL round bottom flask was charged with 4-acetoxybiphenyl (100.0 g, 471.0 mmol), sodium carbonate (149.8 g, 1.4 mol), and 1,1,2,2-tetrachloroethane (100 mL). A reflux condenser was attached, and the contents of the flask were heated under nitrogen to 50 °C in an oil bath. To this solution, a solution of bromine (113.0 g, 707.0 mmol) in 1,1,2,2-tetrachloroethane (100 mL) was added dropwise and the mixture was stirred overnight. Reaction completion was observed by TLC, noting the disappearance of the spot for 4-acetoxybiphenyl and the appearance of a new spot for the product. The solvent was removed under vacuum, and the product was washed with a 10% solution of sodium thiosulfate. The product was dried by vacuum filtration, giving the crude product. The crude product was purified by recrystallization from toluene, giving the product as white crystals (118.2 g, 86%); mp 132 °C. 1H-NMR (400 MHz, CDCl3): 7.59 (d, 2H); 7.57 (d, 2H); 7.44 (d, 2H); 7.19 (d, 2H); 2.35 (s, 3H). IR (Neat): 1747, 1479, 1194, 1071, 1001, 908, 822, 802, 746 cm-1.

***4-bromo-4’-hydroxybiphenyl.*** A 2 L round bottom flask was charged with 4-bromo-4’-acetoxybiphenyl (38.9 g, 133.0 mmol), and sodium hydroxide (38.9 g, 972.0 mmol, in 780 mL 80% aqueous ethanol). A reflux condenser was attached, and the solution was refluxed with stirring overnight. The contents of the flask were cooled to room temperature, and the ethanol was removed by rotary evaporation. Water (~700 mL) was added to the flask to redissolve the solid products, and the solution was neutralized with hydrochloric acid. The precipitate was collected and dried by vacuum filtration. The crude product was purified by recrystallization from a 1/4 solution of ethanol/water, giving the product as white crystals (31.1 g, 94%), mp 159 °C. NMR (400 MHz, CDCl3): 1H-NMR (400 MHz, CDCl3): 9.63 (s, 1H); 7.57 (d, J= 8.64 Hz, 2H); 7.53 (d, J= 8.68 Hz, 2H); 7.51 (d, J= 8.64 Hz, 2H); 6.85 (d, J= 8.64 Hz, 2H). IR (Neat): 3395, 1592, 1522, 1474, 1439, 1371, 1222, 1079, 998, 810, 727 cm-1.

The 4''-hydroxy-4-cyanoterphenyl was prepared by a Suzuki coupling of 1-bromo-4-hydroxybiphenyl with 4-cyanophenylboronic acid[[1]](#endnote-1).

**n = 3, CN3OCT (General Procedure A)**

SI-4.tif

110 mg, 57% yield after recrystallization from acetonitrile.

7.72 (m, 4H), 7.66 (m, 4H), 7.58 (td, 1*J* = 8.8 Hz, 2*J* = 3.2 Hz, 2H), 7.00 (td, 1*J* = 8.8 Hz, 2*J* = 2.8 Hz, 2H), 4.15 (t, *J* = 5.6 Hz, 2H), 2.63 (t, *J* = 6.8 Hz, 2H), 2.18 (m, 2H); 13C NMR (100 MHz, CDCl3) δ (ppm): 158.3, 145.2, 141.0, 137.4, 133.3, 132.7, 128.2, 127.6, 127.5, 127.4, 119.0, 114.9, 110.8, 65.4, 25.5, 14.2. IR (cm-1): 2949, 2927, 2877, 2251, 2225, 1597, 1487, 1254, 1045, 810. GC-MS: No peak

DSC: K 172 N 286 I 286 N 162 K

POM: K 173 N 284I 284 N 165 K

**n = 4, CN4OCT (General Procedure A)**

SI-5.tif

140 mg, 70% yield after recrystallization from acetonitrile.

1H NMR (400 MHz, CDCl3) δ (ppm): 7.73 (dt, 1*J* = 8.8 Hz, 2*J* = 1.2 Hz, 4H), 7.65 (m, 4H), 7.58 (td, 1*J* = 8.8 Hz, 2*J* = 2.8 Hz, 2H), 6.99 (td, 1*J* = 8.8 Hz, 2*J* = 3.2 Hz, 2H), 4.07 (t, *J* = 5.6 Hz, 2H), 2.48 (t, *J* = 6.8 Hz, 2H), 2.02-1.90 (m, 4H); 13C NMR (100 MHz, CDCl3) δ (ppm): 158.6, 145.2, 141.1, 137.4, 132.9, 132.7, 128.2, 127.6, 127.5, 127.3, 119.5, 119.0, 115.0, 110.8, 66.8, 28.2, 22.5, 17.0. IR (cm-1): 2937, 2876, 2243, 2228, 1598, 1488, 1255, 1029, 809. GC-MS: No peak

DSC: K 141 N 269 I 269 N 134 K

POM: K 140 N 267.1 I 267.1 N 136 K

**n = 5, CN5OCT (General Procedure A)**

SI-6.tif

182 mg, 62% yield after recrystallization from acetonitrile.

1H NMR (400 MHz, CDCl3) δ (ppm): 7.72 (d, *J* = 9.2 Hz, 4H), 7.66 (m, 4H), 7.57 (td, 1*J* = 8.8 Hz, 2*J* = 3.2 Hz, 2H), 6.99 (td, 1*J* = 9.2 Hz, 2*J* = 3.2 Hz, 2H), 4.04 (t, *J* = 6.0 Hz, 2H), 2.41 (t, *J* = 6.8 Hz, 2H), 1.86 (m, 2H), 1.77 (m, 2H), 1.68 (m, 2H); 13C NMR (100 MHz, CDCl3) δ (ppm): 158.8, 145.2, 141.2, 137.3, 132.7, 132.6, 128.1, 127.6, 127.5, 127.3, 119.0, 114.9, 110.8, 67.5, 28.5, 25.4, 25.2, 17.2. IR (cm-1): 2944, 2910, 2870, 2246, 2226, 1598, 1488, 1251, 808. GC-MS: No peak.

DSC: K 154 Sm 177 N 264 I 263 N 172 Sm 145 K

POM: K 155 Sm 177 N 258 I 257 N 172 Sm 145 K1 100 K

**n = 6, CN6OCT (General Procedure A)**

SI-7.tif

125 mg, 58% yield after recrystallization from acetonitrile.

1H NMR (400 MHz, CDCl3) δ (ppm): 7.71 (m, 4H), 7.66 (m, 4H), 7.57 (td, 1*J* = 8.8 Hz, 2*J* = 2.8 Hz, 2H), 6.99 (td, 1*J* = 8.8 Hz, 2*J* = 2.8 Hz, 2H), 4.02 (t, *J* = 6.4 Hz, 2H), 2.38 (t, *J* = 7.2 Hz, 2H), 1.84 (m, 2H), 1.72 (m, 2H), 1.55 (m, 2H); 13C NMR (100 MHz, CDCl3) δ (ppm): 159.0, 145.2, 141.2, 137.3, 132.6, 132.5, 128.5, 128.1, 127.6, 127.5, 127.3, 119.7, 119.0, 114.9, 110.8, 67.7, 29.0, 28.4, 25.4, 25.4, 17.1. IR (cm-1): 2933, 2861, 2251, 2227, 1600, 1490, 1468, 1252, 811. GC-MS: No peak

DSC: K 133 Sm 160 N 248 I 247 N 154 Sm 105 K

POM: K 146 Sm 158 N 244.7 I 244.6 N 154 Sm 105 K

# SI.2 Synthesis of PF6OCB

*Scheme 5.tif*

***4'-[(6-hydroxyhexyl)oxy]-4-cyanobiphenyl***. To a stirred solution of 4’-hydroxy-4-cyanobiphenyl (0.8 g, 4.6 mmol) in acetonitrile (35 mL) was added potassium carbonate (1.3 g, 9.2 mmol) and the mixture was kept under reflux for half an hour. Then 6-bromohexanol (1.0 g, 5.52 mmol) was added and the reaction was stirred overnight under reflux. After cooling, the solvent was removed under reduced pressure and the product was extracted with dichloromethane (50 mL), washed with water (150 mL), dried over magnesium sulfate filtered and evaporated. The crude product was subjected to flash column chromatography on silica gel (ethyl acetate and hexane 15%: 85%) to afford the desired product; (1.02 g, 75%).

1H NMR (400 MHz, CDCl3) δ (ppm): 7.68 (d, *J* = 8.68 Hz, 2H), 7.63 (d, *J* = 8.68 Hz, 2H), 7.52 (d, *J* = 8.88 Hz, 2H), 6.98 (d, J = 8.78 Hz, 2H), 4.01 (t, *J* = 6.49 Hz, 2H), 3.69-3.65 (m, 2H), 1.85-1.81 (m, 2H), 1.64-1.60 (m, 2H), 1.52-1.45 (m, 4H); 13C NMR (100 MHz, CDCl3) δ (ppm): 159.75, 145.28, 132.58, 131.31, 128.32, 127.09, 119.15, 115.08, 110.03, 68.01, 62.89, 32.67, 29.20, 25.90, 25.56.

***PF6OCB***. In a 200 ml round bottom flask was placed 4'-[(6-hydroxyhexyl)oxy]-4-cyanobiphenyl (2.95 g, 10.0 mmol), hexafluorobenzene (3.72 g, 20.0 mmol. 2.0 equiv.), dry DMF (15.0 ml), potassium carbonate (1.38 g, 10.0 mmol, 1.0 equiv.) and potassium iodide (0.1 equiv.). The resulting suspension was stirred at 40-50 °C overnight and the reaction was monitored by TLC analysis. Upon completion, water was added dropwise with stirring to fill the flask and then the mixture was extracted with ethyl acetate. The organic layers were washed with water and dried over MgSO4. The product was purified by flash chromatography as a low melting white solid. (2.6 g, 57%)

1H NMR (400 MHz, CDCl3) δ (ppm): 7.70 (m, 2H), 7.64 (m, 2H), 7.53 (dd, 1*J* = 6.8 Hz, 2*J* = 2.8 Hz, 2H), 6.99 (td, 1*J* = 8.8 Hz, 2*J* = 3.2 Hz, 2H), 4.17 (t, *J* = 6.4 Hz, 2H), 4.03 (t, *J* = 6.4 Hz, 2H), 1.87-1.80 (m, 4H), 1.58-1.55 (m, 4H); 13C NMR (100 MHz, CDCl3) δ (ppm): 159.7, 145.3, 132.6, 131.4, 128.4, 127.1, 119.1, 115.1, 110.1, 75.6, 67.9, 29.8, 29.1, 25.7, 25.3; 19F NMR (376 MHz, CDCl3) δ (ppm): -156.93 (m, 2F), -163.43 (m, 2F), -163.67 (m, 1F).

**Cl5OCB (General Procedure A)**



White crystals recrystallized from methanol. (890 mg, yield: 60%)

1H NMR (400 MHz, CDCl3) δ (ppm): 7.70 (m, 2H), 7.64 (m, 2H), 7.53 (td, 1*J* = 8.8 Hz, 2*J* = 2.8 Hz, 2H), 6.99 (td, 1*J* = 8.8 Hz, 2*J* = 2.8 Hz, 2H), 4.03 (t, *J* = 5.6 Hz, 2H), 3.58 (t, *J* = 6.8 Hz, 2H), 1.91-1.82 (m, 4H), 1.65 (m, 2H); 13C NMR (100 MHz, CDCl3) δ (ppm): 159.3, 145.2, 132.6, 131.4, 128.4, 127.1, 119.1, 115.1, 110.1, 67.8, 44.9, 32.3, 28.5, 23.5. GC-MS:299.18 found 299.79 calc.

# SI. 3 The NMR spectra of representative compounds

**CN3OCB-H.tifCN3OCB-C.tifCN4OCB-H.tifCN4OCB-C.tifCN5OCB-H.tifCN5OCB-C.tif**

**CN6OCB-H.tifCN6OCB-C.tif**

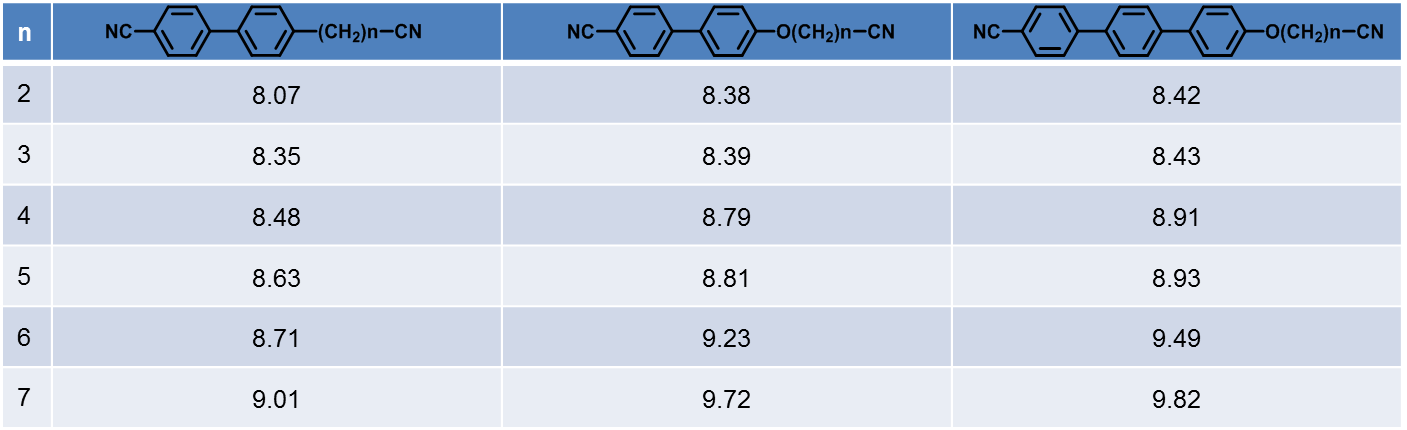
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# SI. 4 The DSC plots of the cyano tail terminated liquid crystals that are not shown in the main text. (The second heating cooling cycle is shown for all cases)

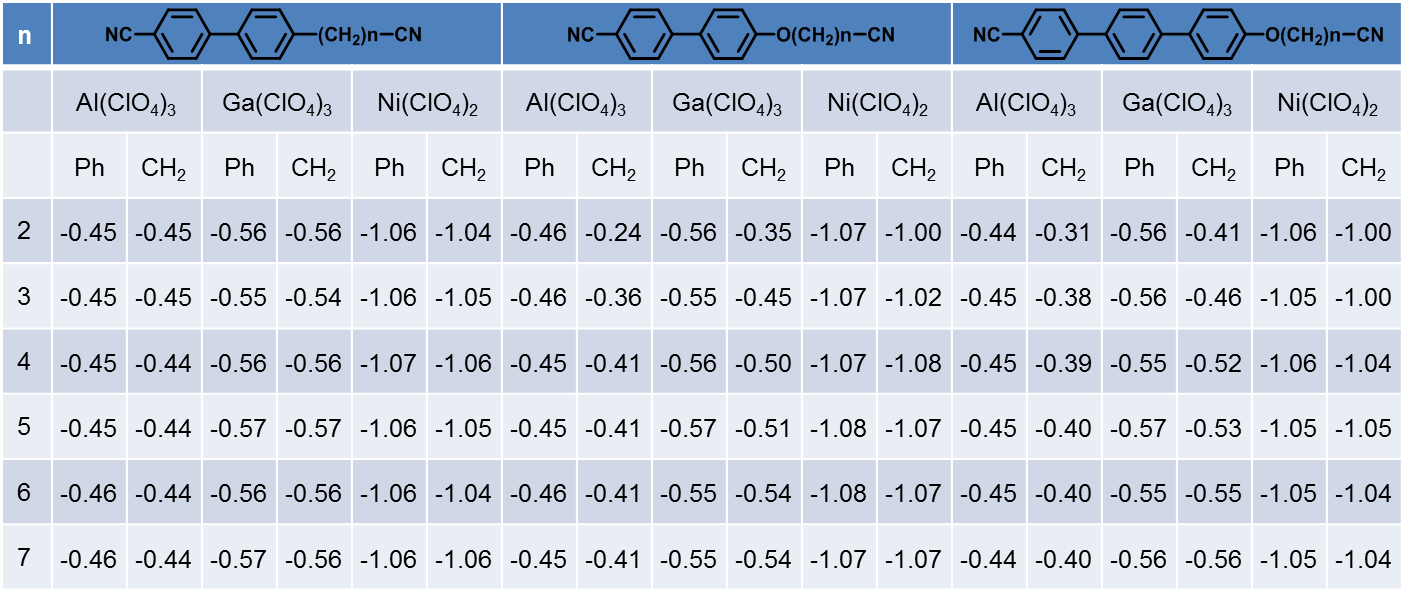
**CN3OCB.tifCN4OCB.tifCN7OCB.tifCN3OCT.tifCN5OCT.tifCN6OCT.tif**

# SI.5. Dipole moment and Gibbs Free Energy of adsorption for cyano-terminated compounds

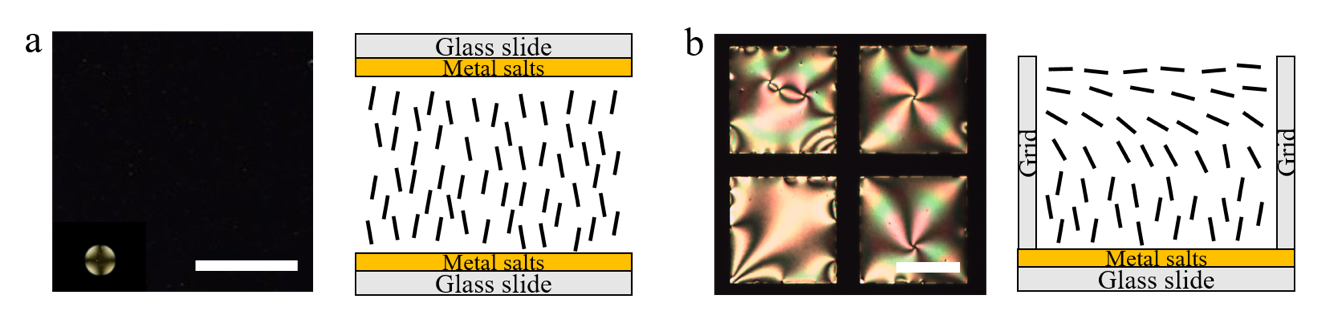
**Table SI.1.** Calculated dipole moment of the 4'-ω-cyanoalkyl-4-cyanobiphenyl, 4'-ω-cyanoalkoxy-4-cyanobiphenyl, and 4'-ω-cyanoalkoxy-4-cyanoterphenyl compounds. ‘n’ indicates the number of CH2 groups defined by the molecular formula in each column.



**Table SI.2.** Calculated Gibbs Free Energy of adsorption (GBE; in eV) for the 4'-ω-cyanoalkyl-4-cyanobiphenyl, 4'-ω-cyanoalkoxy-4-cyanobiphenyl, and 4'-ω-cyanoalkoxy-4-cyanoterphenyl compounds onto Al(ClO4)3, Ga(ClO4)3, and Ni(ClO4)2. Here ‘n’ indicates the number of CH2 groups defined by the molecular formula in each column. ‘Ph’ and ‘CH2’ refer to the neighboring group of the coordinating CN, thus identifying which CN end of the compound binds to the metal cation.



SI.6. Anchoring Study of the Binary Mixtures of PF6OCB and Cl5OCB in 50%:50% Molar Ratio on Ni(ClO4)2-Coated Surfaces and Air Free Interface

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1. Chen L, Chen Y, Zhou W, et al. Synthesis and properties of light-emitting polythiophene derivatives bearing terphenyl mesogenic pendant, Mol Cryst Liq Cryst*.* 2010; 518(1): 70–83. [↑](#endnote-ref-1)