Synthesis and properties of hydroxy tail terminated cyanobiphenyl liquid crystals

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Abstract

Two series of new hydroxy tail terminated cyanobiphenyl compounds are described. The 4'-ω-hydroxyalkynyl-4-cyanobiphenyl compounds (**1a-1g**) were synthesized as the key intermediates to the 4'-ω-hydroxyalkyl-4-cyanobiphenyl compounds (**2a-2g**) obtained upon reduction of the acetylenes. Many of these ω-hydroxyalkynyl and ω-hydroxyalkyl cyanobiphenyl compounds exhibit nematic mesophases and they also serve as precursors for the synthesis of other interesting materials. Using density functional theory, we calculate the dipole moment of all relevant ω-hydroxyalkynyl and ω-hydroxyalkyl cyanobiphenyl compounds and find a correlation between the calculated dipole moments and measured crystalline to nematic or isotropic liquid transition temperatures.

Key words: hydroxy terminated, cyanobiphenyl, nematic phases.

1. Introduction

The molecule 4-pentyl-4'-cyanobiphenyl (5CB) is probably the best-known single

compound amongst the many thousands of liquid crystalline (LC) molecules. In part this importance is due to its room temperature nematic phase that makes it so convenient to study in a wide range of applications. The entire family of 4-alkyl-4'-cyanobiphenyls (CB, K-series) and 4-alkoxy-4'-cyanobiphenyls (OCB, M-series) were originally synthesized by Gray et al. and have found broad applications in liquid crystal science [1]. The strong electron withdrawing effect of the cyano group contributes to the high polarizability of these molecules and thus to their stable nematic liquid crystal phases and opto-electronic properties including the optical and electronic anisotropies [2,3].

Since their discovery a considerable effort has been made on structural modifications of these cyanobiphenyls [4-7]. For instance, substitution of the core hydrogen atoms by other atoms (F, Cl, etc.) or other functional groups has a dramatic influence on the mesogenic properties [8-10]. Previously, Gray et al. [11] investigated some 2-fluoro and 2'-fluoro-4-alkyl CB/OCBs and the FCB derivatives show higher clearing points compared to the parent CBs while the clearing points of FOCB derivatives are lower. Most of these fluorinated cyanobiphenyls are nematic mesogens with some being monotropic. Our group synthesized 3-fluoro-4-pentyl-4'-cyanobiphenyl and in this case the insertion of fluorine atom eliminated the mesophases [12]. In addition to the modifications that have been examined in the core regions of these molecules attention has also been paid to study of the tail sections of the cyanobiphenyls (these tail modifications include branching, inclusion of unsaturation and the like). The tail terminus is a functionalization site of particular interest and, for example, a number of hydroxy-terminated alkoxycyanobiphenyls have already been synthesized. In many cases these hydroxy-terminated alkoxycyanobiphenyls were prepared as synthetic intermediates with the terminal hydroxyl group available as a site of further derivatization [13-15]. However, there is also reported a more systematic study of hydroxy-terminated

alkoxycyanobiphenyls and most of these compounds exhibit nematic phases. A related derivative from the literature is the cyclohexylcyanobenzene bearing a hydroxy terminus [16,17] and it is also a nematic mesogen.

In contrast to the hydroxy tail terminated alkyloxycyanobiphenyls the hydroxy tail terminated alkylcyanobiphenyls have received very little attention. In part this is due to the relative synthetic inaccessibility of the hydroxy terminated alkyl materials compared to the hydroxy terminated alkoxy materials. For another study underway we required the hydroxy tail terminated alkylcyanobiphenyls as intermediates and here a method for their synthesis is described as well as their phase behavior compared to the related alkoxycyanobiphenyls. Since it is evident from previous examples that alkylcyanobiphenyl compounds generally display nematic phases at lower temperature ranges than their alkoxycyanobiphenyl counterparts, we believe the hydroxy tail terminated alkylcyanobiphenyls analogues are also of interest and suitable for further applications and may also themselves serve as valuable intermediates. Therefore, in this work the synthesis and mesogenic properties of a series of these 4'-ω-hydroxyalkyl-4-cyanobiphenyl compounds is presented.

The synthesis devised involves the preparation of hydroxy-terminated alkynyl cyanobiphenyl compounds as key intermediates and they are also new structures. Many of these ω-hydroxyalkynyl cyanobiphenyl compounds were also found to have nematic phases, which will be discussed in detail. The hydroxy-terminated alkynyl materials provide the hydroxy-terminated alkyl materials upon reduction of the acetylene. The thermal behavior of these compounds is compared with the previous analogous examples. In order to elucidate the influence of the terminal hydroxy group, the dipole moments of these compounds were calculated and the results are discussed in comparison to the K series counterparts.

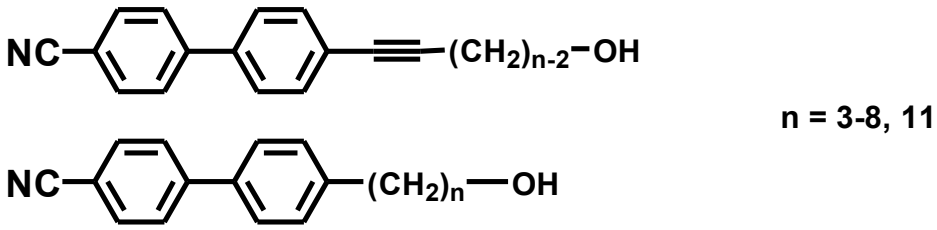


Figure 1. Two series of new hydroxy tail terminated cyanobiphenyl compounds obtained in this work. Top: the 4'-ω-hydroxyalkynyl-4-cyanobiphenyl compounds. Bottom: 4'-ω-hydroxyalkyl-4-cyanobiphenyl compounds.

2. Experimental Section

Commercial-grade solvents were used without further purification. $PdCl_2$ was bought from Pressure Chemical (Pittsburgh, PA). Palladium on carbon (5%), diisopropylamine, ether and copper iodide were purchased from Acros. The precursor 4'-cyano-4-iodobiphenyl was prepared using a literature method [19]. Triphenylphosphine and ethylenediamine were bought from Sigma-Aldrich. The terminal α,ω-hydroxyalkylacetylenes were purchased from GFS Organic Chemicals (Columbus, OH). The methanol was purchased from VMR (West Chester, PA). The compressed hydrogen was bought from Linde Gas. The products were purified by column chromatography using silica gel (60–120 mesh) and/or by recrystallization from analytical grade solvents.

Polarized optical microscopy (POM): Nikon ECLIPSE E600 Microscope & SPOT^{TM} idea COMS and Mettler Toledo FP90 central processor with FP82HT hot stage.

IR analysis was accomplished by using a Bruker Vector 33 FTIR spectrometer (Bruker Optics Inc, Billerica, MA, USA). The data obtained was processed and plotted using OPUS software.

A Bruker 400 NMR was used for NMR data acquisition (Frequency: 400 MHz for 1H-NMR; 100 MHz for ^{13}C-NMR and 376 MHz for ^{19}F-NMR) and the plots were generated by TOPSPIN 2 software.

A Thermo Finnigan Trace - GC 2000 (Thermo Scientific, Austin, TX, USA) and Polaris Q Mass Spectrometer (Thermo Scientific, Austin, TX, USA) were used to follow the reactions and assay product purity. The GC-MS data was collected and processed via Xcalibur software (Ver. 1.4, Thermo Scientific, San Jose, CA, USA).

Differential scanning calorimetry (DSC) analysis was run on a 2920 Modulated DSC from TA instruments (TA Instruments Inc., New Castle, DE, USA). Experimental data was analyzed and exported by using the Thermal Advantage software (Version 1.1A, TA Instruments Inc., New Castle, DE, USA).

Palladium Ethylenediamine on Activated Carbon [Pd/C (en)][20]

Into a 100-mL round bottom flask was placed 5% palladium on carbon (3.00 g, 0.15 g Pd, 1.41 mmol Pd), and the flask was degassed with nitrogen for 30 minutes. Ethylenediamine (5.93 g, 98.67 mmol) dissolved in methanol (50 mL) was then added. The resulting suspension was stirred under nitrogen for 48 hours. At this point, the suspension was filtered under vacuum on a filter paper, and the black solid remaining was washed with methanol (100 mL) and then with diethyl ether (100 mL). The solid was then dried for 48 hours under vacuum. (2.88 g, 93 % yield).

General Procedure for the synthesis of 4'-(hydroxyalkynyl)-4-cyanobiphenyl compounds

These reactions were carried out using a literature method [21]. A 100 ml round bottom flask fitted with a condenser and a stirbar was charged with degassed diisopropylamine (3.0 equiv.), triphenylphosphine (6.0 mol%), $PdCl_2$ (2.0 mol%), CuI (1.0 mol%),

anhydrous dimethylformamide (20 ml for 10 mmol iodide) and the resulting mixture was stirred at 60 °C for one and a half hours under a nitrogen atmosphere until the triphenylphosphine complexes of the metal salts were completely formed. After cooling to room temperature, 4'-cyano-4-iodobiphenyl (5.0-10.0 mmol) and the relevant commercially available hydroxy-terminated alkyne (1.0-1.5 equiv.) was added. This mixture was then stirred at 85 °C for 6-12 hours with the formation of a white precipitate. The reaction was monitored by TLC until completion. The resulting mixture was then carefully transferred to a 250 ml round bottom flask and the solvent was removed by rotary evaporation. The residue was absorbed on silica gel and subjected to chromatography on a short silica gel column eluted with a mixture of hexanes and ethyl acetate to give the desired products.

General Procedure for the synthesis of 4'-ω-hydroxyalkyl-4-cyanobiphenyl compounds

In a 100 ml round bottom flask was placed the 4'-(hydroxyalkynyl)-4-cyanobiphenyl (1.0 g-2.0 g), Pd/C(en) (10%-30% weight of the substrate, ref. 10% used), and ethyl acetate (20-25 mL). The air inside the reaction flask was replaced with hydrogen via three vacuum/hydrogen cycles. The black suspension was then stirred at room temperature for 12-72 hours under hydrogen until GC-MS indicated that the reaction went to completion. The resulting mixture was filtered through a Celite pad and the filtrate was concentrated to afford the product. The products were purified by column chromatography using silica gel and/or by recrystallization from analytical grade solvents.

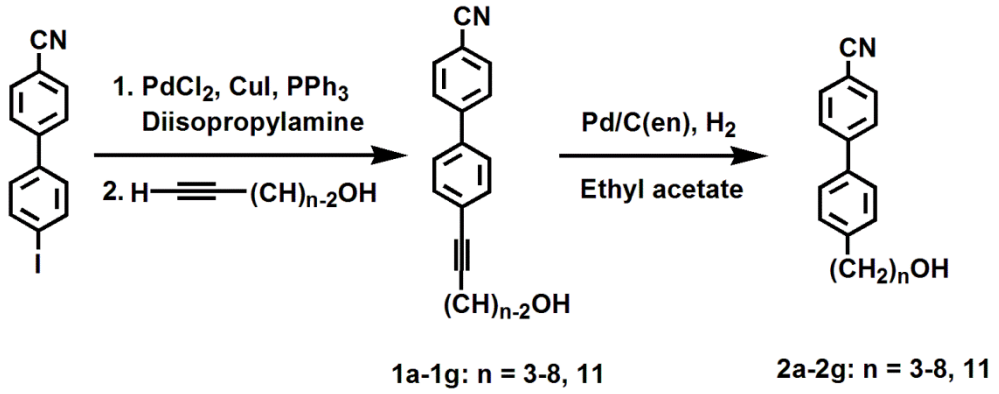
For detailed experimental procedures, see the supplemental information.

Computational methods

All calculations were performed using Gaussian 09 [22]. Geometry optimizations were

carried out using density functional theory (DFT) at the PBE-D3(SMD=benzonitrile)/def2-SVP level of theory [23-26]. Subsequently dipole moments were calculated for each obtained structure at the M06-2X-D3(SMD=benzonitrile)/def2-TZVP level of theory [27], as that method has been successfully implemented previously to model mesogen properties [28-30]. To obtain appropriate statistical sampling of the conformational modes of the aliphatic chains, the complete conformational was generated space by assuming three stable conformations (one anti and two gauches) for each C-C and C-O single bonds. To limit computational cost, the number of randomly chosen conformers we maximized at 2000 for each compound. These conformers were then employed in the dipole moment calculations. To obtain the average dipole moment for each compound, the Boltzmann weighted sum of the dipole moment was calculated for each relevant conformer.

3. Synthesis



Scheme 1. Synthesis of the 4'-(hydroxyalkynyl)-4-cyanobiphenyl compounds (**1a**-**1g**) and their reduction to the respective 4'-ω-hydroxyalkyl-4-cyanobiphenyl compounds (**2a**-**2g**).

As noted, the 4'-ω-hydroxyalkyl-4-cyanobiphenyl compounds are more challenging to

prepare than the 4'-ω-hydroxyalkyloxy-4-cyanobiphenyl compounds. Our approach adopted a Sonagashira coupling route that started with the important precursor 4'-cyano-4-iodobiphenyl, itself prepared using a literature method involving iodination of 4-cyanobiphenyl. Next, this aryliodide was reacted with a commercial terminal α,ω-hydroxyalkylacetylene in the presence of a catalyst system prepared from $PdCl_2$ and CuI with excess triphenylphosphine in diisopropylamine. The desired 4-(hydroxyalkynyl)cyanobiphenyl products (**1a-1g**) were obtained in modest to good yields (Scheme 1). This set of acetylene containing intermediates were examined for their intrinsic mesogenic properties and they also serve as precursors for the ω-hydroxyalkylcyanobiphenyls.

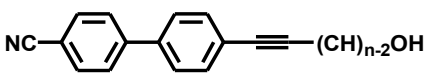
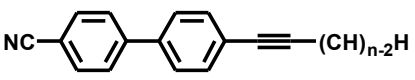
Our attempts to reduce the alkyne in the presence of the cyano group with a standard palladium on carbon catalyst proved problematic. It is known that the cyano group can be reduced using palladium on carbon under such conditions to the imine, then to the amine and even, finally, hydrogenolysis to the methyl group [31]. As a consequence, an alternative poisoned palladium/carbon reagent— Pd/C (en) was prepared according to a literature method [20]. This catalyst was originally designed for a mild reduction of olefins without the deprotection of the *O*-benzyl or *O*-Cbz groups and in this work the Pd/C (en) was utilized and reduction of the alkyne was accomplished without affecting the cyano group. Interestingly, the reduction seems to proceed faster for shorter tail alkynes ($n < 6$). They were reduced within 24 hours in the presence of 10% weight percent of catalyst while the reaction time was as long as 3 days for longer tail alkynes and required as much as 20%-30% by weight of the catalyst. The products obtained from the reduction were purified by column chromatography on silica gel and/or recrystallized from appropriate solvents prior to the phase behavior analysis by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). While

less than ideal this overall reaction scheme produced sufficient quantities of the required materials in good purity.

4. Results and Discussions

The phase behavior of the series of 4'-(hydroxyalkynyl)-4-cyanobiphenyl compounds **1a-1g** is found in Table 1. Compounds **1a**, **1b** and **1g** show only crystal to isotropic transitions. Compounds **1c**, **1e** and **1f** show monotropic nematic phases during cooling and these phases generally persist for 10 °C or less (compound **1f**). Compound **1d** exhibits an enantiotropic nematic phase from 69 °C to 94 °C during heating and an additional smectic A phase was observed during cooling. The clearing points in this series tend to decrease as the number of carbons increases but in an "odd/even" pattern. The even-numbered compounds have lower clearing points than the neighboring ones, which might be some even/odd effect. Compared to the few reported alkynyl CB compounds with no terminal functionality with the same number of carbons in the tail, the hydroxy tail-terminated derivatives show clearing point temperatures on the order of 30-50 °C higher (Table 1).

Table 1. The phase behavior of 4'-(hydroxyalkynyl)-4-cyanobiphenyl compounds **1a-1g**. Literature data available for the analogous parent unsubstituted alkynyl series is provided for comparison (K = Crystal, N = Nematic, I = Isotropic). Compound numbers (#) apply to the 4'-ω-hydroxyalkynyl-4-cyanobiphenyl compounds.

n	Compound #	Phase behavior (°C)	
			
3	**1a**	K 199.9 I 191.5 K	N/A
4	**1b**	K 128.3 I 115.6 K	N/A

5	**1c**	K 138.1 I 132.8 N 121.3 K	N/A
6	**1d**	K 69.5 N 93.4 I 92.2 N 47.7 SmX 25.8 K	K 63.4 (N 39.6) I [32]
7	**1e**	K 104.5 I 89.6 N 70.0 K	K 51.6 (N 49.1) I [32]
8	**1f**	K 81.4 I 73.1 N 63.7 K	K 32.7 N 42.1 I [32]
11	**1g**	K 92.8 I 81.1 K	N/A

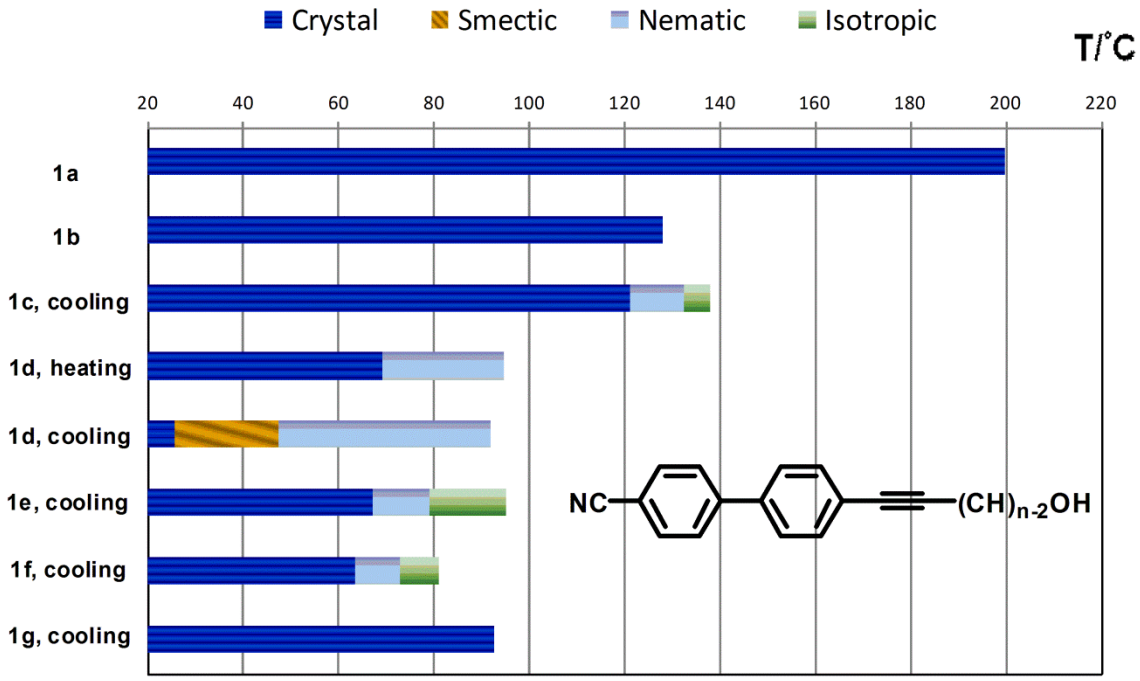
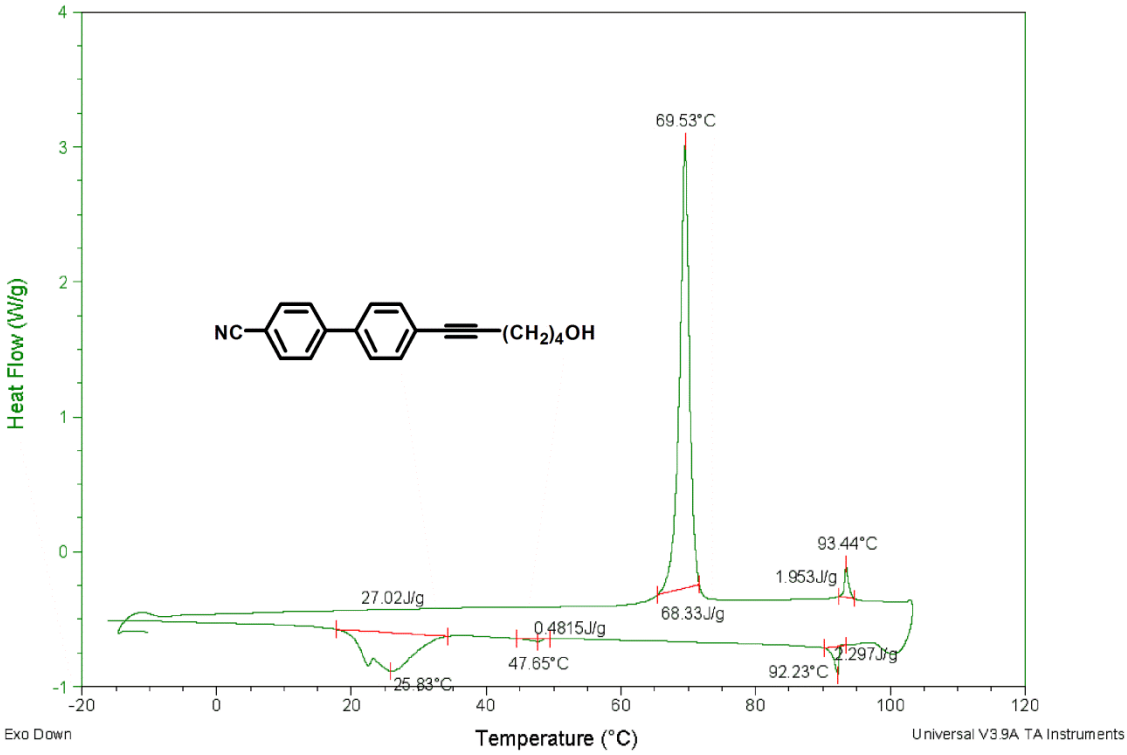
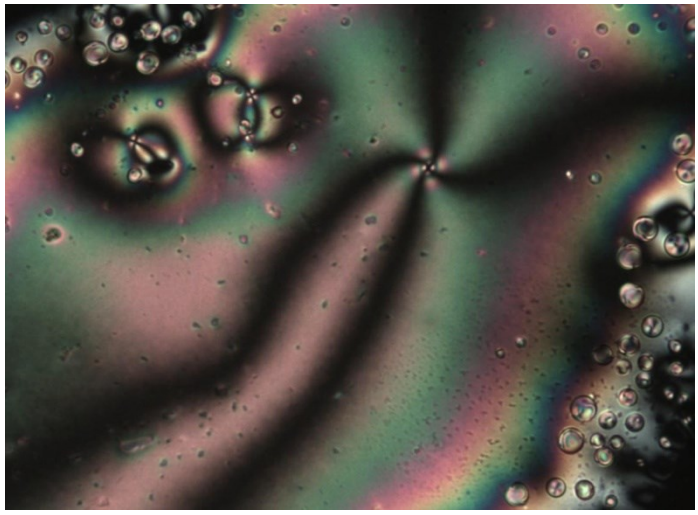


Chart 1. Thermal data of hydroxy-terminated alkynyl CB compounds **1a** to **1g**. Compounds **1c** (n = 5), **1e** (n = 7) and **1f** (n = 8) exhibit a monotropic nematic phase and only cooling cycles are shown; the cooling cycle for **1d** is shown for the smectic phase.


Heat Flow (W/g)
Temperature (°C)
Exo Down
Universal V3.9A TA Instruments
NC
(CH2)4OH
69.53°C
93.44°C
1.953J/g
27.02J/g
68.33J/g
0.4815J/g
47.65°C
2.297J/g
92.23°C
25.83°C



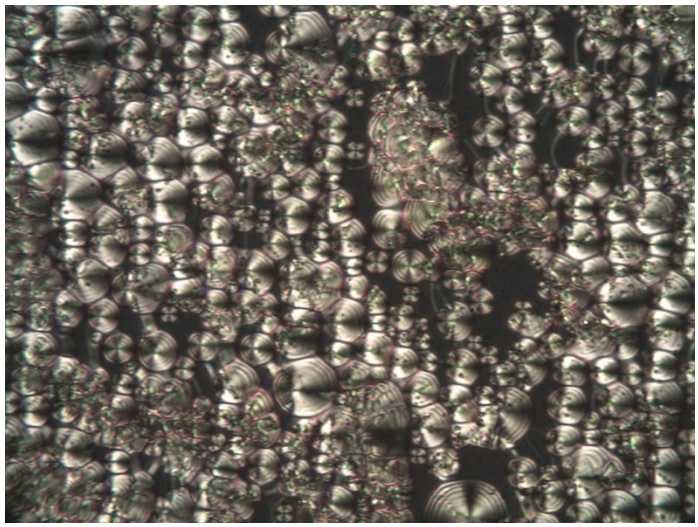


Figure 2. Top: The DSC plot of compound **1d** (K 69.5 N 93.4 I 92.2 N 47.7 SmX 25.8 K); Center: the texture of the nematic phase during cooling; Bottom: the unassigned smectic phase that appears at 48.0 °C during cooling.

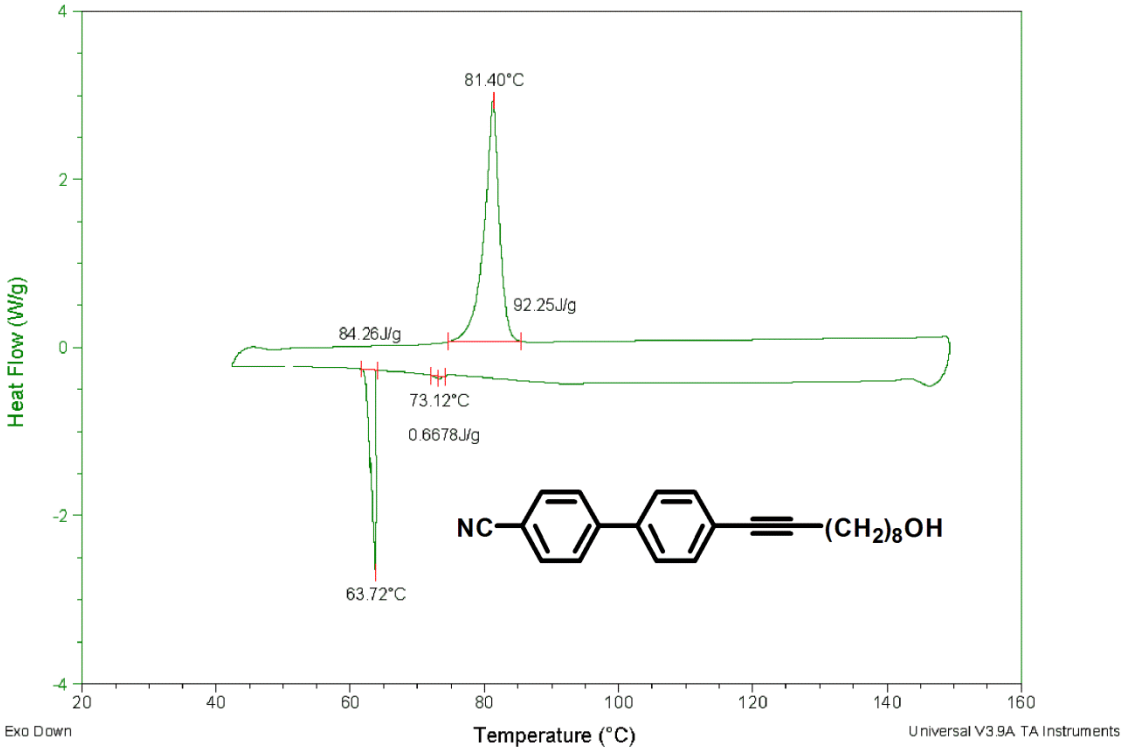
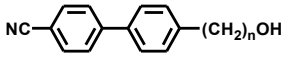
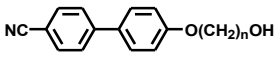
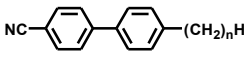


Figure 3. The DSC plot of compound **1f** (K 81.4 I 73.1 N 63.7 K).

The thermal phase data for the 4'-ω-hydroxyalkyl-4-cyanobiphenyl compounds **2a**-**2g** are shown in Table 2. As expected, the clearing points of these compounds appear 10-30 °C lower than the corresponding 4'-ω-hydroxyalkoxy-4-cyanobiphenyl analogues. Also, as expected in the series of 4'-ω-hydroxyalkoxy-4-cyanobiphenyl compounds the clearing point temperatures decrease as the number of carbons increases and compound **2f** possesses the lowest clearing point temperature of all (Figure 4 and 5). Compounds **2c**, **2e** and **2f** are enantiotropic nematic mesogens with narrow temperature ranges (3-4 °C). The alkoxy counterparts show broader mesomorphic ranges (13-22 °C). The remaining compounds **2a**, **2b**, **2d** and **2g** in this family all exhibit monotropic nematic properties. For compounds **2b** and **2g**, the monotropic behavior is consistent with the relevant alkoxy versions. As far as the comparison with the non-substituted alkyl CBs, it is not surprising to find the hydroxy tail-terminated compounds show higher mesogenic temperature

ranges. It is also of interest that the introduction of the hydroxyl terminus suppresses the formation of a smectic phase as seen in two compounds **2f** and **2g** with the longest tails.

Table 2. The phase behavior of 4'-ω-hydroxyalkyl-4-cyanobiphenyl compounds **2a** to **2g**. Data available for the analogous hydroxy terminated alkoxy CB series [16,17] and the parent unsubsitituted alkyl CB series is provided for comparison (K = Crystal, N = Nematic, Sm = Smectic, I = Isotropic). Compound numbers (#) apply to the 4'-ω-hydroxyalkyl-4-cyanobiphenyl compounds.

n	#	Phase behavior (°C)		
				
3	**2a**	K_1 52.5 K_2 107.6 I 105.6 N 101.1 K_1 47.1 K_2	K 76 N 116 I	K 66 I 26 N [33]
4	**2b**	K 94.2 I 72.3 N 49.8 K	K 132 (N 120) I	K 46 I 16 N [33]
5	**2c**	K 85.7 N 88.2 I 86.5 N 64.0 K	K 90 N 104 I	K 22.5 N 35 I [33]
6	**2d**	K 78.9 I 69.9 N 53.3 K	K 97 N 109 I	K 15 N 30 I [33]
7	**2e**	K 74.0 N 79.4 I 78.3 N 52.4 K	K 78 N 100 I	K 31 N 44 I [33]
8	**2f**	K 65.9 N 69.5 I 67.7 N 46.2 K	K 89 N 102 I	K 20 Sm 34 N 41 I [33]
11	**2g**	K 84.5 I 73.6 N 69.2 K	K 91.6 N 96.4 I	K 53 Sm 57 N 58 I [33]

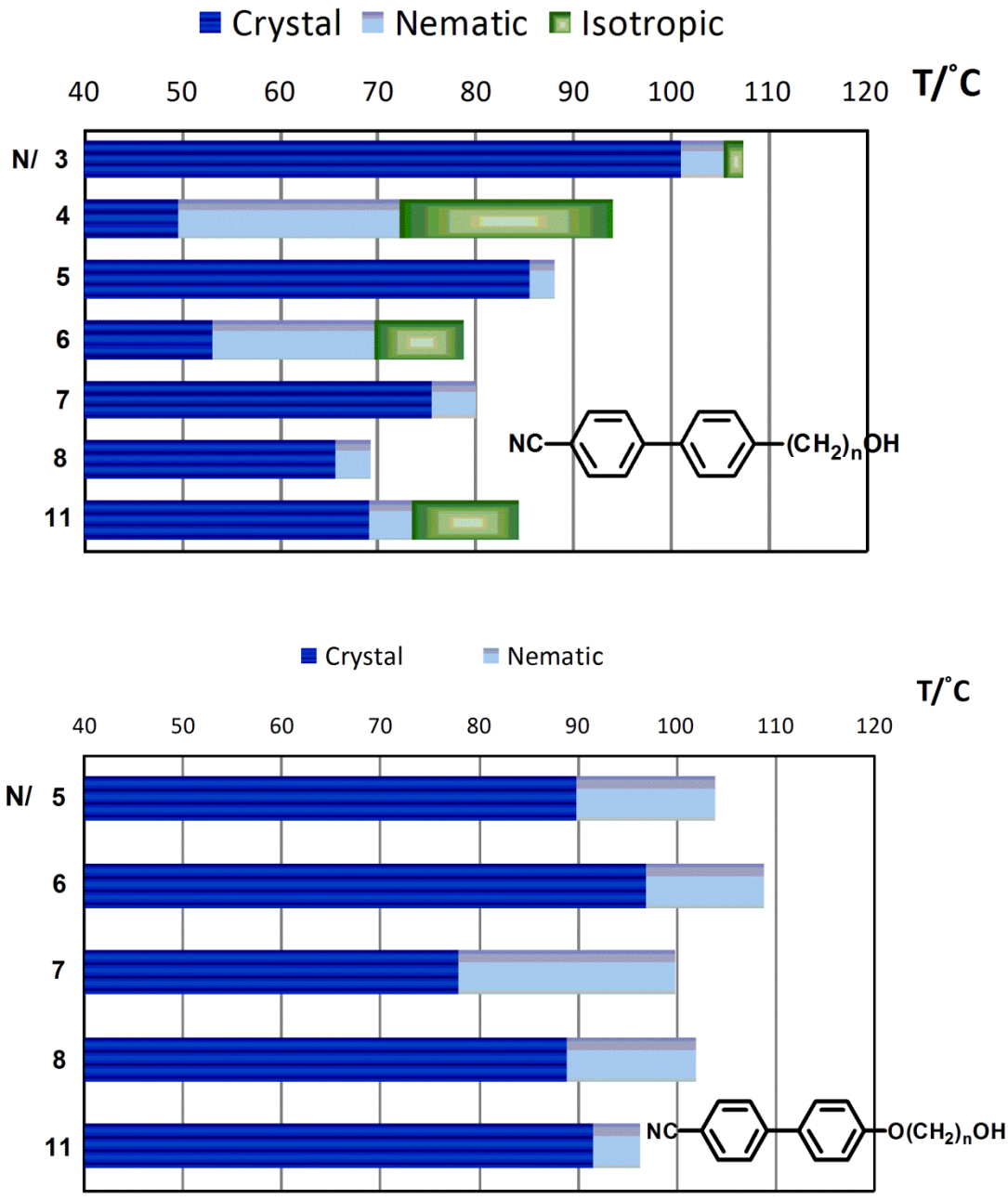


Chart 2. Top: the thermal data of 4'-ω-hydroxyalkyl-4-cyanobiphenyl compounds **2a** to **2g** (top). (Compounds **2a** (n = 3), **2b** (n = 4), **2d** (n = 6) and **2g** (n = 11) exhibit a monotropic nematic phase and only cooling cycles were shown; otherwise heating cycles shown) Bottom: the thermal data of relevant 4'-ω-hydroxyalkyloxy-4-cyanobiphenyl analogues [16,17] (n = 5-8, 11; all these nematic phases are enantiotropic).

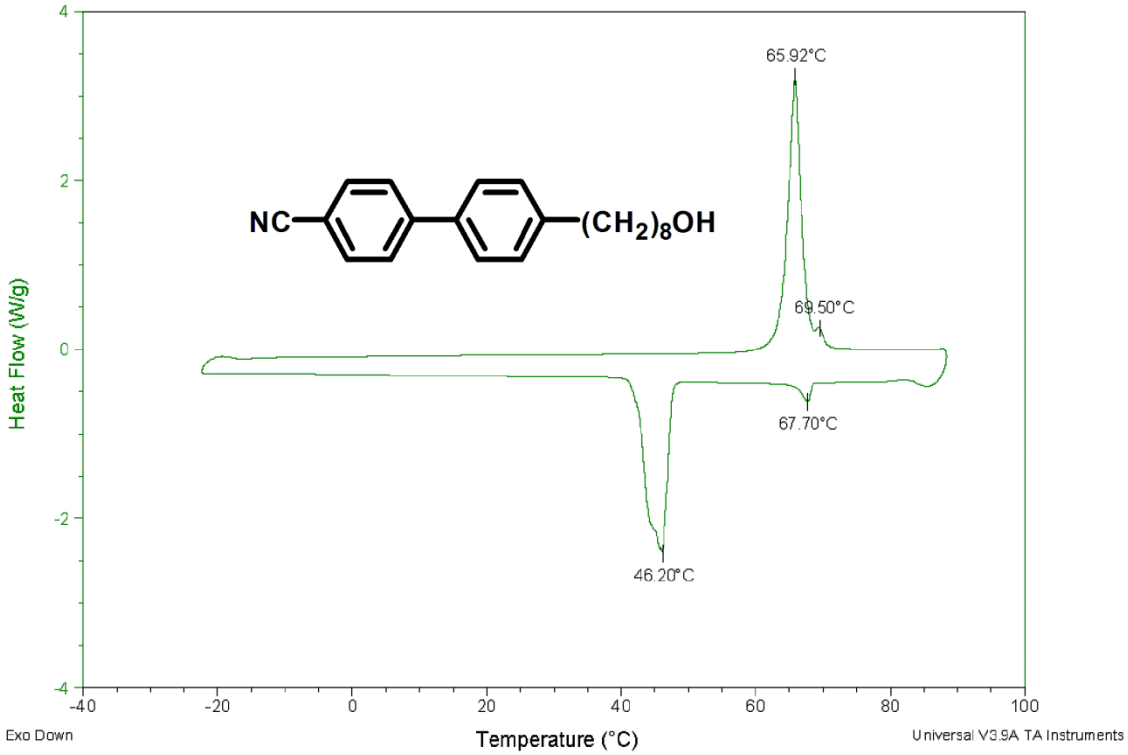


Figure 4. The DSC plot of compound **2f** (K 65.9 N 69.5 I 67.7 N 46.2 K). (The phase behavior is repeatable for three cycles)

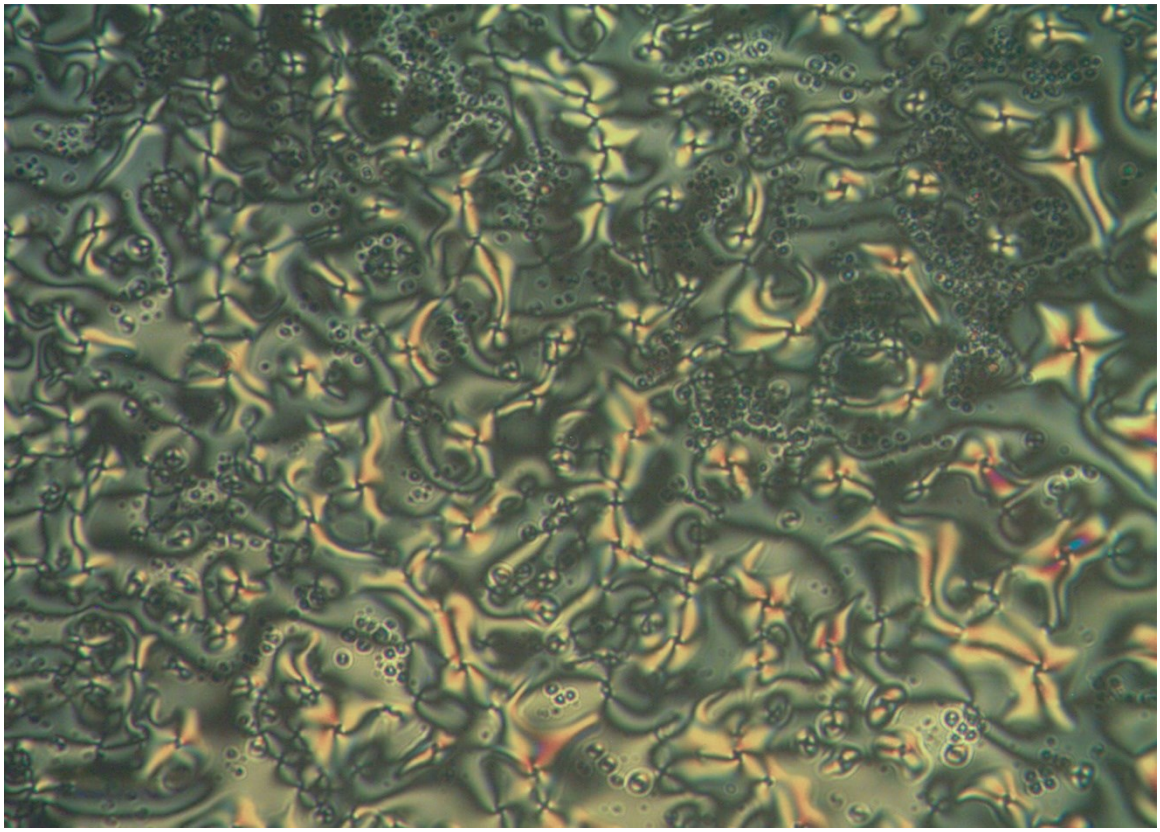


Figure 5. The Schlieren phase texture observed by POM for compound **2f** captured at 69 °C during cooling indicates the formation of a nematic phase.

Overall, most of the members of the two new series of hydroxy-terminated alkynyl and hydroxy-terminated alkyl CB derivatives obtained in this work exhibit nematic properties. Clearly the attachment of the hydroxyl group at the terminal position of the side chain does not eliminate the mesomorphic properties that are well-known in the series with no functional termination. Introduction of the terminal hydroxyl group on to the alkyl and alkoxycyanobiphenyls influences their mesomorphic properties by a variety of interactions that are not available in the systems containing just a simple aliphatic tail.

To gain more insight into the effect of the hydroxyl-termination on the molecular properties, the dipole moment of the hydroxy-terminated alkynyl CB derivatives, the hydroxy-terminated alkyl CB derivatives, and the parent CB compounds with alkyl chain (K series) were calculated. Figure 6 shows the calculated dipole moment as a function of the alkyl chain length (n) (detailed results are also provided in Table SI.1). We find that for the parent alkyl terminated CB compounds, the dipole moment does not change as a function of the alkyl chain length (n). This behavior is expected because of the lack of a polar end group. We note that the ~0.01 D fluctuation in the numbers (Table SI.1) is within the error bar of the statistical sampling. The introduction of OH termination results in an increasing dipole moment (Figure 6) from n=3 (7.40 D) up to n=9 (7.98 D), but then the dipole moment quickly decreases till n=11 (7.52 D). The gradually increasing dipole moment from n=3 to n=9 is the consequence of the increasing distance between the polar CN and OH ends in the molecules. For n>9, the long alkyl chain can curve itself backwards in considerable number of conformations thereby decreasing the distance between the end tail groups in the molecules, leading to a decrease in the overall dipole moment of the molecules. Similar phenomena have been found for surfactants; after a

critical alkyl chain length the effective size of the surfactant molecules decreases because the alkyl chain curves backwards due to conformational entropy effects [34-36].

Further modification of the molecular structure introduced by the addition of an alkynyl tail, again leads to a dipole moment increase from n=3 up to n=11 (Figure 6) but the effect is larger (from 5.81 D (n=3) to 7.74 D (n=11)) than that found for hydroxy-terminated alkyl CB derivatives. The key to understand the differences in dipole moment between the hydroxy-terminated alkynyl and alkyl CB derivatives is to consider the acetylene moiety of the alkynyl derivatives as part of the core instead of the tail of the molecules. The *sp* hybridized carbon atoms directly interact with the biphenyl π-system and they lack the conformational mobility of the sp^3 hybridized tail carbons. Therefore, we ought to compare alkynyl and alkyl CB derivatives with the same number of sp^3 hybridized tail carbons ($n_{alkynyl}=n_{alkyl}-2$) and recognize that the calculated dipole moment of alkynyl and alkyl CB derivatives shows very similar dipole moments; for example, for $n_{alkyl}=3$, D=7.40 while for $n_{alkynyl}=5$, D=7.38. We can also rationalize the relatively smaller dipole moment for $n_{alkynyl}=3$ and 4 (D=5.81 and 6.81, respectively). Because of its close proximity of the acetylene moiety, there is strong interaction between the OH group and the biphenyl-acetylene π-system that lowers the extreme electron density distribution in the molecules and thus their dipole moment. Similarly, because of the acetylene moiety, we cannot observe the decrease of dipole moment for alkynyl CB derivatives for alkyl chains as long as with $n_{alkynyl}=11$, as that would correspond to $n_{alkyl}=9$ which is the maximum in dipole moment for alkyl CB derivatives.

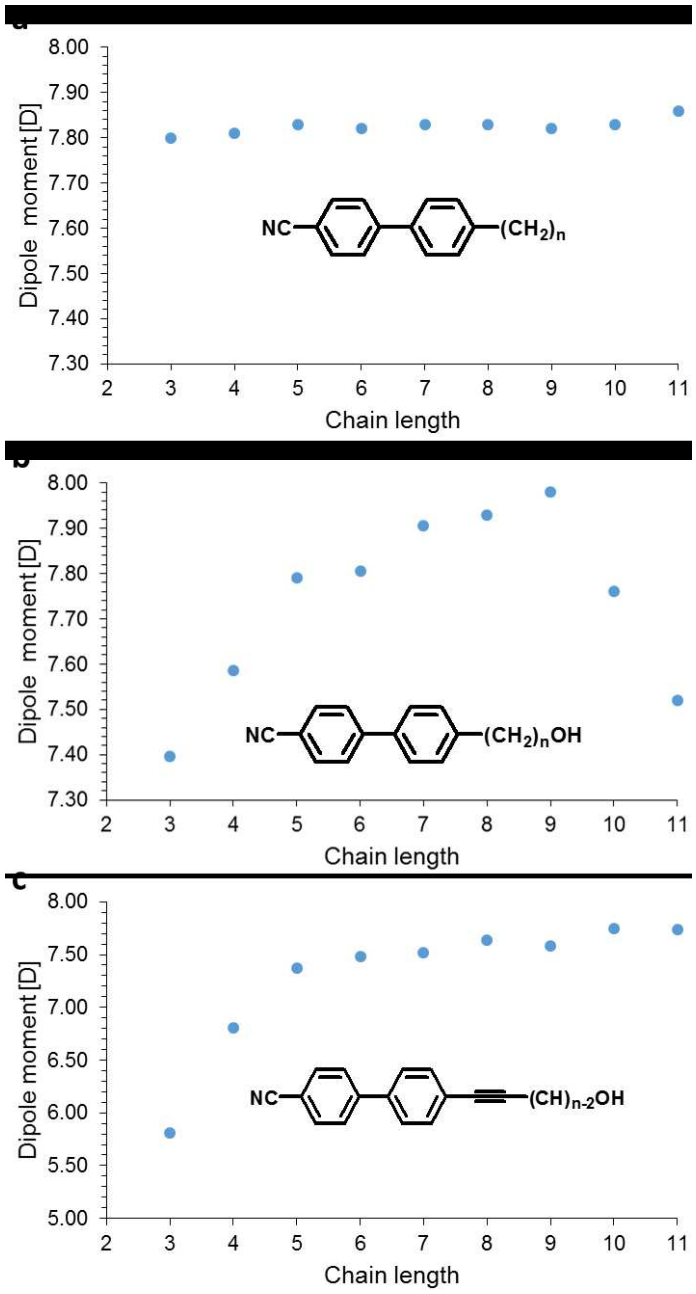


Figure 6. Calculated dipole moment (in Debye) as a function of chain length (n) for: (a) parent CB compounds with alkyl chain, (b) hydroxy-terminated alkyl CB derivatives, and (c) hydroxy-terminated alkynyl CB derivatives (note different dipole moment axis).

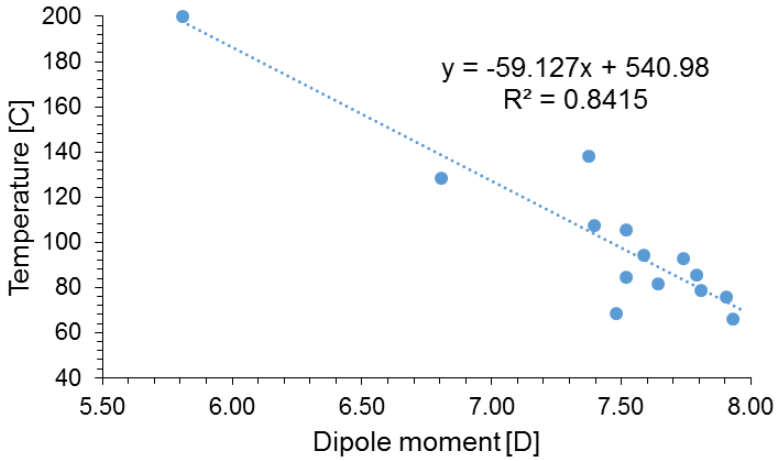


Figure 7. Correlation between calculated dipole moment (in Debye) and measured crystalline to nematic or isotropic transition temperature (in °C) for hydroxy-terminated alkyl and alkynyl CB derivatives.

Because we find similar trends between the dipole moment of hydroxy-terminated alkyl and hydroxy-terminated alkynyl CB derivatives and also between the measured crystalline to nematic or isotropic liquid transition temperatures of hydroxy-terminated alkyl and hydroxy-terminated alkynyl CB derivatives we are interested in whether there is correlation between calculated dipole moment and measured crystalline to nematic or isotropic liquid transition temperature (Figure 7). Interestingly, we find a very good correlation ($R^2 = 0.84$) including all hydroxy-terminated alkyl and alkynyl CB derivatives (Figure 7). In fact, we find a similar quality correlation and essentially the same fitted trend line when we plot the results separately for hydroxy-terminated alkyl and alkynyl CB derivatives (Figure SI.9). Based on this very good universal correlation, we conclude that the dipole moment of the hydroxyl terminated compounds has significant influence on the crystalline to liquid transition temperature. This finding can help in the future to design new compounds having crystalline to nematic transition temperature below room temperature. Of course, other interactions including hydrogen bonding will contribute to the net bulk structure and properties of these alcohol functionalized systems.

Finally, we note that the successful preparation of these hydroxy-terminated alkyl cyanobiphenyl compounds provides us with precursors for the synthesis of a variety of other interesting materials. For instance, the hydroxyl group can be efficiently converted into other common functional groups [37]. In addition, by application of the Mitsunobu reaction, numerous asymmetric dimeric LCs (with one alkynyl or alkyl connection and one ether connection) become feasible [38]. The use of the Sonagashira chemistry here sometimes provides only moderate yields and some improvements in this synthesis or alternative approaches will ultimately be useful.

5. Conclusion

A series of hydroxy tail terminated cyanobiphenyl compounds were synthesized in two steps from 4'-cyano-4-iodobiphenyl. Most of these hydroxy tail terminated cyanobiphenyl compounds, including the alkynyl intermediates, were found to be nematic mesogens. The alkyl compounds obtained generally show lower mesomorphic temperature ranges compared to the analogous alkoxy analogues. Using density functional theory, we calculate the dipole moment of all relevant ω-hydroxyalkynyl and ω-hydroxyalkyl cyanobiphenyl compounds and find a correlation between the calculated dipole moments and measured crystalline to nematic or isotropic liquid transition temperatures. Furthermore, these new hydroxy tail terminated mesogens can also act as interesting precursors for the synthesis of other terminal-functionalized cyanobiphenyl derivatives and this work is underway.

Acknowledgements

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Synthesis and properties of hydroxy tail terminated cyanobiphenyl liquid crystals

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Materials. Commercial-grade solventswere used without further purification.$PdCl_2$ was bought from Pressure Chemical (Pittsburgh, PA). Palladium on carbon, diisopropylamine, ether and copper iodide were purchased from Acros. Triphenylphosphine and ethylenediamine were bought from Sigma-Aldrich. The hydroxyacetylenes were purchased from GFS Organic Chemicals (Columbus, OH). The methanol was purchased from VMR (West Chester, PA). The compressed hydrogen was bought from Linde Gas. The products were purified by column chromatography using silica gel (60–120 mesh) and/or by recrystallization from analytical grade solvents. The purity of products were demonstrated by combination of TLC, NMR and DSC.

SI.1. Synthesis of 4'-cyano-4-iodobiphenyl

4-Phenylbenzonitrile

To a 200-mL round bottom flask containing dimethyl sulfoxide (55 mL) was added hydroxylamine hydrochloride (3.53 g, 50.8 mmol) and 4-phenylbenzaldehyde (5.0 g, 27.4 mmol). The mixture was stirred overnight at 100 °C and at this point, a clear, light yellow solution was present and ^{1}HNMR indicated that the reaction had proceeded to completion. The solution was subsequently allowed to cool to room temperature. Water (150 mL) was added, and the resulting mixture was extracted with ethyl acetate (3 x 200 mL). The combined organic layers were washed with water (200 mL), brine (200 mL) and finally they were then dried over magnesium sulfate, and the solvent was removed under reduced pressure. The crude solid remaining was triturated with hexane (25 mL), yielding 3.102 g (63.2% yield) of a light yellow solid.

^{1}HNMR (400 MHz, $CDCl_3$) δ: 7.71 (d, 2H, J = 8.68 Hz), 7.67 (d, 2H, J = 8.60 Hz), 7.59-7.56 (m, 2H), 7.49-7.45 (m, 2H), 7.43-7.41(m, 1H)

The data is consistent with the reference [1].

4'-Cyano-4-iodobiphenyl

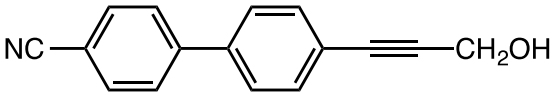
The 4-phenylbenzonitrile (2.0 g, 11.2 mmol) was suspended in a mixture of glacial acetic acid (5.5 mL), 95-98% sulfuric acid (0.17 mL) and water (1.12 mL) in a 50-mL round bottom flask. Iodine (1.46 g, 5.7 mmol) and periodic acid (0.56 g, 2.4 mmol)

were added, and the suspension was heated to 70 °C with stirring. The resulting dark purple solution was stirred overnight at 70 °C. At this point, a light yellow precipitate had formed, and ^{1}HNMR indicated that all of the 4-phenylbenzonitrile had been consumed. The suspension was allowed to cool to room temperature, and the solvents were removed by vacuum filtration. The remaining crude solid was washed with hexane (25 mL), leaving 1.963 g (57.4% yield) of a tan solid.

^{1}HNMR (400 MHz, DMSO) δ: 7.94 (d, 2H, *J* = 8.8 Hz), 7.88 (d, 2H, *J* = 8.4 Hz), 7.88 (d, 2H, *J* = 8.4 Hz), 7.56 (d, 2H, *J* = 8.8 Hz)
The data is consistent with the reference [2]

SI.2. Synthesis of 4'-hydroxy-terminated alkynyl-4-cyanobiphenyl compounds 1a-1g.

4-[4-(3-hydroxyprop-1-yn-1-yl)phenyl]benzonitrile (1a)



In a 250-mL round bottom flask fitted with a stir bar, reflux condenser, and nitrogen inlet was placed PPh_3 (130 mg, 0.50 mmol), anhydrous dimethylformamide (25 mL), and diethylamine (10 mL). The system was purged with nitrogen, and $PdCl_2$ (12 mg, 0.10 mmol) and copper(I) iodide (10 mg, 0.050 mmol) were added. The mixture was subsequently warmed to 65° in an oil bath. After stirring for a few minutes, the mixture became homogeneous, and 4-cyano-4'-iodobiphenyl (3.05 g, 10.0 mmol) and propargyl alcohol (0.84 g, 15.0 mmol) were added. After six hours, TLC indicated that all of the iodobiphenyl was consumed. The mixture was cooled to room temperature, and the volatile solvents were removed under vacuum. Next, THF (25 mL), methanol (25 mL), and silica gel (15 cc) were added. The solvents were stripped off by rotary evaporation, leaving the crude product mixture absorbed on silica gel. This mixture was then subjected to column chromatography, and the fractions containing the product were combined (eluent: hexane/ethyl acetate = 4: 1). The solvent was removed from these fractions under vacuum, leaving a light brown solid. Because TLC revealed that

residual impurities were present, the product was recrystallized from 1-propanol, yielding 1.559 g (66.9% yield) of a light brown solid.

^{1}HNMR (400 MHz, DMSO) δ: 7.93 (d, 2H, *J* = 8.8 Hz), 7.89 (d, 2H, *J* = 8.8 Hz), 7.76 (d, 2H, *J* = 8.4 Hz), 7.54 (d, 2H, *J* = 8.4 Hz), 5.40 (t, 1H, *J* = 6.0 Hz), 4.33 (d, 2H, *J* = 5.6 Hz)

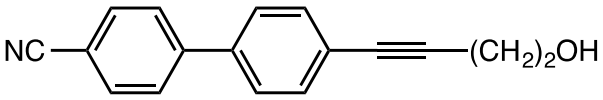
^{13}CNMR (100 MHz, DMSO) δ: 143.6, 138.0, 132.9, 132.0, 127.5, 127.3, 122.8, 118.8, 110.4, 91.4, 83.2, 49.5

FTIR: 3451.81, 2874.89, 2229.69, 1602.74, 1491.58, 1428.80, 1395.78, 1284.17, 1258.21, 1186.64, 1038.78, 1005.52, 860.39, 815.22, 738.31, 711.41, 651.71, 581.08, 567.03, 555.36 cm^{-1}

DSC: K 199.9 I 191.5 K

POM: K 199 I 184 K

4-[4-(4-Hydroxybut-1-yn-1-yl)phenyl]benzonitrile (1b)



A 100-mL round bottom flask was degassed with nitrogen for 30 minutes, and triphenylphosphine (0.30 g, 1.15 mmol), anhydrous dimethylformamide (16.4 mL), and diisopropylamine (2.48 g, 24.6 mmol) were added. The resulting solution was heated to 60 °C with stirring and palladium(II) chloride (0.028 g, 0.16 mmol) was added, and the reaction mixture was stirred for 15 minutes. Copper(I) iodide (0.016 g, 0.082 mmol) was then added, and the reaction mixture was stirred for another 15 minutes. Subsequently, 4-cyano-4'-iodobiphenyl (2.50 g, 8.19 mmol) was added, and the resulting suspension was stirred for 90 minutes. At this point, some solid 4-cyano-4'-iodobiphenyl remained undissolved, so anhydrous dimethylformamide and diisopropylamine were added until most of it dissolved. Next 1-butyn-4-ol (1.03 g, 12.3 mmol) was added, and the temperature was gradually raised from 60 °C to 85 °C over two hours with stirring. The reaction mixture was then stirred overnight at 85 °C under nitrogen. At this point, the reaction mixture was dark brown and TLC indicated that the reaction had gone to completion. The mixture was cooled and THF (25 mL) and silica gel (25 cc) were added, and the volatile solvents were removed under vacuum overnight. The adsorbed material was placed at the top of a silica gel column, and it was

eluted with a gradient of ethyl acetate/hexane from 5% / 95% to 30% / 70%. The fractions containing only the product were combined, and concentrated under reduced pressure. The residue remaining was recrystallized from a mixture of 1-propanol and water, and a light yellow crystalline solid was collected in two crops (0.969 g, 47.8% yield).

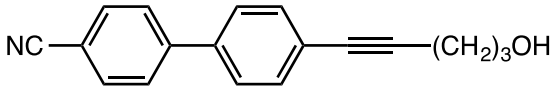
^{1}HNMR (400 MHz, DMSO) δ: 7.93 (d, 2H, *J* = 8.8 Hz), 7.90 (d, 2H, *J* = 8.8 Hz), 7.75 (d, 2H, *J* = 8.8 Hz), 7.52 (d, 2H, *J* = 8.4 Hz), 4.94 (t, 1H, *J* = 5.6 Hz), 3.61 (q, 2H, *J* = 6.8 Hz), 2.60 (t, 2H, *J* = 6.8 Hz)

^{13}CNMR (100 MHz, DMSO) δ: 143.6, 137.4, 132.9, 132.0, 127.4, 127.2, 123.6, 118.8, 110.2, 90.3, 80.6, 59.7, 23.4

FTIR: 3260.51, 2928.58, 2226.72, 1724.50, 1601.54, 1489.15, 1398.69, 1277.04, 1181.67, 1128.21, 1042.64, 1004.07, 820.00, 714.77, 618.65, 600.91, 562.78 cm^{-1}

DSC: K 128.3 I 115.6 K

4-[4-(5-Hydroxypent-1-yn-1-yl)phenyl]benzonitrile (1c)



A 200-mL round bottom flask was purged with nitrogen gas for 20 minutes and triphenylphosphine (0.367 g, 1.4 mmol), diisopropylamine (3.03 g, 30.0 mmol), and anhydrous dimethylformamide (20 mL) were then added. The resulting mixture was heated with stirring to 60 °C and palladium(II) chloride (0.023 g, 0.2 mmol) was added, and the mixture was stirred for 20 minutes. Copper (I) iodide (0.018 g, 0.1 mmol) was then added, and the mixture was stirred for an additional 20 minutes. Next, 4-cyano-4'-iodobiphenyl (3.05 g, 10.0 mmol) was added, and the mixture was stirred for one hour and 30 minutes, at which point some 4-cyano-4'-iodobiphenyl remained undissolved. Next, pent-4-yn-1-ol (1.26 g, 15.0 mmol) was added, and the resulting suspension was stirred for two hours under nitrogen while it was gradually heated from 60 °C to 85 °C. At this point, TLC indicated that 4-cyano-4'-iodobiphenyl was still present, so the reaction mixture was stirred overnight at 85 °C under nitrogen. After this time, TLC showed that some 4-cyano-4'-iodobiphenyl still remained, so bis(triphenylphosphine)palladium(II) dichloride (0.035 g, 0.05 mmol) and pent-4-yn-1-ol (0.17 g, 2.0 mmol) were added, and the reaction mixture was stirred for an additional seven hours at 85 °C. At this point, TLC indicated that all the 4-cyano-4'-iodobiphenyl

had been consumed, so the reaction mixture was allowed to cool to room temperature. The volatile solvents were removed under vacuum, and ethyl acetate (25 mL), THF (25 mL), and silica gel (40 cc) were added. These solvents were then removed under reduced pressure. The adsorbed material was placed at the top of a silica gel 5 x 22 cm silica gel column, and it was eluted with a gradient of ethyl acetate/hexane from 10% / 90% to 35% / 65%. The fractions containing only the product were combined and concentrated under reduced pressure. The crude solid was recrystallized from a mixture of acetonitrile and water, and a light yellow solid was collected in two crops (0.709 g, 27.1% yield).

^{1}HNMR (400 MHz, DMSO) δ: 7.93 (d, 2H, *J* = 8.8 Hz), 7.89 (d, 2H, *J* = 8.8 Hz), 7.74 (d, 2H, *J* = 8.4 Hz), 7.51 (d, 2H, *J* = 8.4 Hz), 4.55 (t, 1H, *J* = 5.2 Hz), 3.53 (m, 2H), 2.50 (t, 2H, *J* = 7.2 Hz), 1.71 (m, 2H)

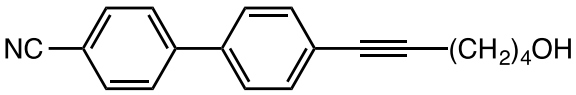
^{13}CNMR (100 MHz, DMSO) δ: 143.4, 137.2, 132.6, 131.7, 127.2, 127.0, 123.5, 118.6, 110.0, 92.0, 79.8, 59.2, 31.3, 15.2

FTIR: 3499.87, 2926.14, 2231.64, 1602.34, 1489.81, 1394.94, 1309.75, 1066.15, 1004.31, 908.72, 821.35, 716.28, 569.43, 541.79, 521.54, 512.12, 507.84, 503.75, 497.95, 493.93, 487.98, 482.52, 474.93, 470.64, 457.73, 453.22, 447.42, 441.62, 434.74, 424.07, 418.13, 411.95, 406.08 cm^{-1}

DSC: K 138.1 I 132.8 N 121.3 K

POM: K 137 I 132 N 120 K

4-[4-(6-Hydroxyhex-1-yn-1-yl)phenyl]benzonitrile (1d)



In a 200-mL recovery flask with a stir bar, condenser, and nitrogen inlet was placed triphenylphosphine (0.734 g, 2.8 mmol), anhydrous dimethylformamide (40 mL), and diisopropylamine (6.06 g, 60.0 mmol). This mixture was heated in an oil bath to 60 °C with a nitrogen purge and palladium (II) chloride (46 mg, 0.4 mmol) was added. The resulting mixture was stirred at 60 °C for 20 minutes and copper (I) iodide (36 mg, 0.2 mmol) was added. The mixture was stirred at 60 °C for an additional 20 minutes. Next, 4-cyano-4'-iodobiphenyl (6.10 g, 20.0 mmol) was added, and after it all dissolved, 5-hexyn-1-ol (2.94 g, 30.0 mmol) was added. The mixture was stirred under nitrogen, and the temperature was gradually raised to 85 °C over the next four hours. After this time,

the reaction was complete by TLC and the mixture was cooled to room temperature and the volatile components were removed under vacuum. The residue was stirred with ethyl acetate (50 mL) and THF (50 mL) and transferred to a one-liter flask with the aid of some ethyl acetate. Silica gel (60 cc) was added and then the solvent was removed by rotary evaporation. The adsorbed material was placed at the top of a column of silica gel (6 cm by 20 cm) and eluted with a gradient (10-40%) of ethyl acetate in hexane. Fractions containing the product were combined and concentrated, and the crude solid was recrystallized from a mixture of acetonitrile/H_2O. The product was obtained in two crops totalling 3.66 g (66%).

^{1}HNMR (400 MHz, DMSO) δ: 7.91 (d, 2H, *J* = 8.8 Hz), 7.87 (d, 2H, *J* = 8.8 Hz), 7.72 (d, 2H, *J* = 8.4 Hz), 7.49 (d, 2H, *J* = 8.4 Hz), 4.47 (t, 1H, *J* = 5.2 Hz), 3.45 (m, 2H, *J* = 5.2 Hz), 2.45 (t, 2H, *J* = 6.8 Hz), 1.57 (m, 4H)

^{13}CNMR (100 MHz, DMSO) δ: 143.7, 137.4, 132.9, 132.0, 127.5, 127.2, 123.8, 118.8, 110.2, 92.5, 80.2, 60.2, 31.7, 24.9, 18.6

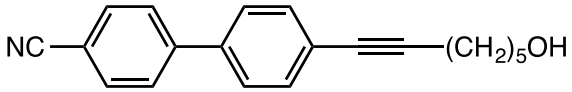
FTIR: 3353.58, 2940.94, 2229.61, 1605.06, 1491.06, 1397.45, 1181.96, 1057.72, 994.68, 859.93, 820.49, 716.51, 564.98 cm^{-1}

DSC: K 68.3 N 93.7 I 91.9 N 47.0 SmA 21.6 K

POM: K 80 N 94 I 88 N 36 K

The data is consistent with the reference [3].

4-[4-(7-Hydroxyhept-1-yn-1-yl)phenyl]benzonitrile (1e)



In a 200 ml recovery flask with stirbar, condenser and nitrogen inlet was placed triphenylphosphine (0.367 g, 1.4 mmol), anhydrous dimethylformamide (20ml) and diisopropylamine (3.03 gm, 30.0 mmol). This mixture was heated in an oil bath to 60 °C with a nitrogen purge and palladium (II) chloride (23 mg, 0.2 mmol) was added. The resulting mixture was stirred at 60°C for 20 minutes and then copper (I) iodide (18 mg, 0.1 mmol) was added and the mixture was stirred at 60 °C for 20 min more. Next, the 4-cyano-4'-iodobiphenyl (3.05 gm, 10.0 mmol) was added and after it all dissolved 6-heptyn-1-ol (1.68 gm, 15.0 mmol) was added. The mixture was stirred under nitrogen and the temperature was gradually raised to 85 °C over the next two hours and maintained at this temperature for two additional hours. After this time the reaction was

complete by TLC and the mixture was cooled to room temperature and the volatile components were removed under vacuum. The residue was stirred with ethyl acetate (25 ml) and THF (25 ml) and transferred to a one liter flask with the aid of some ethyl acetate. Silica gel (40 cc) was added and then the solvent was removed by rotary evaporation. The adsorbed material was placed at the top of a column of silica gel (6 cm by 15 cm) and eluted with a gradient (10-50%) of ethyl acetate in hexane. Fractions containing the product were combined and concentrated and the crude solid was crystallized from a mixture of acetonitrile/H_2O. Three crops of crystals were obtained pure (total, 1.73 gm, 60%).

^{1}HNMR (400 MHz, DMSO) δ: 7.92 (d, 2H, *J* = 8.8 Hz), 7.88 (d, 2H, *J* = 8.4 Hz), 7.73 (d, 2H, *J* = 8.8 Hz), 7.49 (d, 2H, *J* = 8.8 Hz), 3.41 (t, 2H, *J* = 5.6 Hz), 2.44 (t, 2H, *J* = 6.8 Hz), 1.56 (m, 2H, *J* = 6.8 Hz), 1.45 (m, 4H)

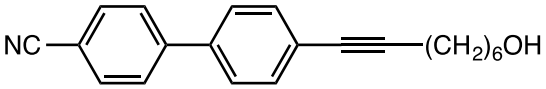
^{13}CNMR (100 MHz, DMSO) δ: 143.7, 137.4, 132.9, 131.9, 127.4, 127.2, 123.8, 118.8, 110.2, 92.4, 80.2, 60.6, 32.0, 28.1, 24.9, 18.8

FTIR: 3244.66, 2942.37, 2863.48, 2232.93, 1601.20, 1490.70, 1459.87, 1388.41, 1312.23, 1286.69, 1181.42, 1146.67, 1073.80, 1045.95, 1014.84, 1003.68, 985.23, 958.31, 880.39, 863.17, 844.29, 822.16, 718.47, 638.93, 567.80 cm^{-1}

DSC: K_1 73.3 K_2 105.4 I 89.2 N 67.5 K

POM: K 106 I 91 N 67 K

4-[4-(8-Hydroxyoct-1-yn-1-yl)phenyl]benzonitrile (1f)



In a 200 ml recovery flask with stirbar, condenser and nitrogen inlet was placed triphenylphosphine (0.367 g, 1.4 mmol), anhydrous dimethylformamide (20ml) and diisopropylamine (3.03 gm, 30.0 mmol). This mixture was heated in an oil bath to 60 °C with a nitrogen purge and palladium (II) chloride (23 mg, 0.2 mmol) was added. The resulting mixture was stirred at 60°C for 20 min and then copper (I) iodide (18 mg, 0.1 mmol) was added and the mixture was stirred at 60 °C for 20 min more. Next, the 4-cyano-4'-iodobiphenyl (3.05 gm, 10.0 mmol) was added and after it all dissolved 7-octyn-1-ol (1.89 gm, 15.0 mmol) was added. The mixture was stirred under nitrogen and the temperature was gradually raised to 85 °C over the next two hours. After this time the reaction was complete by TLC and the mixture was cooled to room temperature and the volatile components were removed under vacuum. The residue was

stirred with ethyl acetate (25 ml) and THF (25) and transferred to a one liter flask with the aid of some ethyl acetate. Silica gel (40 cc) was added and then the solvent was removed by rotary evaporation. The adsorbed material was placed at the top of a column of silica gel (6 cm by 15 cm) and eluted with a gradient (10-40%) of ethyl acetate in hexane. Fractions containing the product were combined and concentrated and the crude solid was crystallized from a mixture of acetonitrile/H_2O. Two crops were obtained pure (1.90 gm, 62%) and (0.28 gm, 7%). Total yield 69%.

^{1}HNMR (400 MHz, DMSO) δ: 7.91 (d, 2H, *J* = 8.4 Hz), 7.87 (d, 2H, *J* = 8.8 Hz), 7.72 (d, 2H, *J* = 8.4 Hz), 7.49 (d, 2H, *J* = 8.4 Hz), 3.40 (t, 2H, *J* = 6.4 Hz), 2.44 (t, 2H, *J* = 6.8 Hz), 1.55 (m, 2H, *J* = 7.2 Hz), 1.42 (m, 4H), 1.32 (m, 2H)

^{13}CNMR (100 MHz, DMSO) δ: 143.7, 137.3, 132.9, 131.9, 127.4, 127.2, 123.7, 118.8, 110.2, 92.4, 80.2, 60.6, 32.4, 28.23, 28.17, 25.0, 18.7

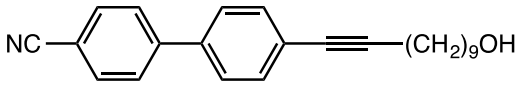
FTIR: 3359.66, 2936.51, 2860.92, 2229.74, 1603.80, 1492.08, 1463.93, 1394.94, 1353.77, 1312.27, 1179.77, 1106.19, 1054.58, 1038.33, 1023.93, 1004.48, 859.94, 821.28, 717.41, 566.43 cm^{-1}

DSC: K 81.4 I 73.1 N 63.7 K

POM: K 82 I 77 N 60 K

The data is consistent with the reference [4].

4-[4-(11-Hydroxyundec-1-yn-1-yl)phenyl]benzonitrile (1g)



In a 200 ml recovery flask with stirbar, condenser and nitrogen inlet was placed triphenylphosphine (0.367 g, 1.4 mmol), anhydrous dimethylformamide (20ml) and diisopropylamine (3.03 gm, 30.0 mmol). This mixture was heated in an oil bath to 60 °C with a nitrogen purge and palladium (II) chloride (23 mg, 0.2 mmol) was added. The resulting mixture was stirred at 60 °C for 20 min and then copper (I) iodide (18 mg, 0.1 mmol) was added and the mixture was stirred at 60 °C for 20 min more. Next, the 4-cyano-4'-iodobiphenyl (3.05 gm, 10.0 mmol) was added and after it all dissolved 10-undecyn-1-ol (2.52 gm, 15.0 mmol) was added. The mixture was stirred under nitrogen and the temperature was gradually raised to 85 °C over the next two hours. After this time the reaction was complete by TLC and the mixture was cooled to room temperature and the volatile components were removed under vacuum. The residue was stirred with ethyl acetate (25 ml) and THF (25) and transferred to a one liter flask with

the aid of some ethyl acetate. Silica gel (40 cc) was added and then the solvent was removed by rotary evaporation. The adsorbed material was placed at the top of a column of silica gel (6 cm by 15 cm) and eluted with a gradient (10-20%) of ethyl acetate in hexane. Fractions containing the product were combined and concentrated and the crude solid was crystallized from acetonitrile. Two crops were obtained pure (2.45 gm, 71%) and the remaining material (0.14 gm, 4%) was contaminated with palladium and used for reduction. Total yield 75%.

^{1}HNMR (400 MHz, DMSO) δ: 7.93 (d, 2H, *J* = 8.4 Hz), 7.89 (d, 2H, *J* = 8.8 Hz), 7.74 (d, 2H, *J* = 8.8 Hz), 7.50 (d, 2H, *J* = 8.8 Hz), 4.32 (t, 1H, *J* = 5.2 Hz), 3.37 (m, 2H, J_1 = 6.4 Hz, J_2 = 5.2 Hz), 2.45 (t, 2H, *J* = 6.8 Hz), 1.56 (m, 2H, *J* = 7.6 Hz), 1.41 (m, 4H), 1.28 (m, 8H)

^{13}CNMR (100 MHz, DMSO) δ: 143.7, 137.4, 132.9, 131.9, 127.4, 127.2, 123.7, 118.8, 110.2, 92.4, 80.2, 60.7, 32.5, 29.0, 28.9, 28.5, 28.3, 28.1, 25.5, 18.7

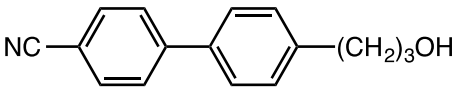
FTIR: 3244.04, 2916.97, 2852.59, 2228.67, 1604.41, 1490.02, 1468.81, 1335.66, 1181.12, 1147.66, 1110.75, 1073.17, 1056.96, 1038.36, 1004.88, 983.28, 952.54, 844.93, 820.75, 730.93, 716.79, 565.92, 552.63 cm^{-1}

DSC: K 92.8 I 81.1 K

POM: K 83 I 72 K

SI.3. Synthesis of 4'-ω-hydroxyalkyl-4-cyanobiphenyl compounds 2a-2g.

4-[4-(3-Hydroxypropyl)phenyl]benzonitrile (2a)



These reduction reactions were carried out using a literature method [5]. Compound **1a** (0.233 g, 1.00 mmol), Pd/C(en) (0.023 g, 10% weight of the substrate), and THF (5 mL) were combined in a 50-mL round bottom flask. Three evacuation/hydrogen addition cycles were performed, and the homogenous black suspension was stirred overnight under hydrogen at room temperature. At this point, ^{1}HNMR indicated that the reaction went to completion, so the catalyst was removed via suction filtration through a celite pad. The filtrate was combined with silica gel (15 cc) and ethyl acetate, the solvent was removed under reduced pressure, the adsorbed material was placed at the top of a silica

gel column, and it was eluted with ethyl acetate. The solvent was removed from the solution collected under reduced pressure. The solid remaining was recrystallized from cyclohexane/toluene (75% / 25%), yielding 0.052 g (21.7% yield) of a white crystalline solid.

^{1}HNMR (400 MHz, $CDCl_3$) δ: 7.72 (d, 2H, *J* = 8.8 Hz), 7.67 (d, 2H, *J* = 8.8 Hz), 7.52 (d, 2H, *J* = 8.4 Hz), 7.32 (d, 2H, *J* = 8.4 Hz), 3.71 (m, 2H), 2.78 (t, 2H, *J* = 7.6 Hz), 1.93 (m, 2H), 1.35 (s, 1H)

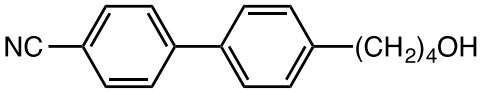
^{13}CNMR (100 MHz, $CDCl_3$) δ: 145.5, 142.7, 136.8, 132.6, 129.2, 127.5, 127.2, 119.0, 110.6, 62.2, 34.1, 31.7

FTIR: 3280.59, 2938.85, 2226.63, 1604.46, 1494.09, 1401.10, 1180.93, 1063.57, 1041.58, 1003.73, 906.94, 827.44, 808.27, 723.65, 543.79, 524.10, 505.76, 479.63, 468.32, 456.58, 446.59, 434.86, 406.18 cm^{-1}

DSC: K_1 52.5 K_2 107.6 I 105.6 N 101.1 K_1 47.1 K_2

POM: K 107 I 105 N 100 K

4-[4-(4-Hydroxybutyl)phenyl]benzonitrile (2b)



Compound **1b** (0.30 g, 1.21 mmol), Pd/C(en) (0.030 g, 10% weight of substrate), and THF (5 mL) were combined in a 50-mL round bottom flask. Three evacuation/hydrogen addition cycles were performed, and the reaction mixture was stirred overnight under hydrogen at room temperature. At this point, ^{1}HNMR indicated that the reaction went to completion. The catalyst was removed via suction filtration through a Celite pad. The filtrate was combined with silica gel (15 cc) and ethyl acetate, the solvent was removed under reduced pressure, the adsorbed material was placed at the top of a silica gel column, and it was eluted with ethyl acetate. The solvent was removed from the solution collected under reduced pressure. The solid remaining was recrystallized from a mixture of cyclohexane/toluene (75% / 25%), yielding 0.076 g (25.3% yield) of a light tan crystalline solid.

^{1}HNMR (400 MHz, $CDCl_3$) δ: 7.71 (d, 2H, *J* = 8.8 Hz), 7.67 (d, 2H, *J* = 8.4 Hz), 7.52 (d, 2H, *J* = 8.4 Hz), 7.30 (d, 2H, *J* = 8.4 Hz), 3.68 (m, 2H), 2.71 (t, 2H, *J* = 7.2 Hz), 1.73 (m, 2H), 1.63 (m, 2H), 1.27 (t, 1H, *J* = 4.8 Hz)

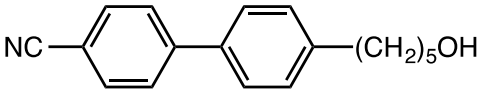
^{13}CNMR (100 MHz, $CDCl_3$) δ: 145.7, 143.3, 136.8, 132.7, 129.3, 127.6, 127.3, 119.2, 110.7, 62.9, 35.4, 32.4, 27.6

FTIR: 3451.75, 2938.79, 2224.16, 1603.56, 1493.38, 1395.98, 1178.89, 1067.41, 1030.84, 988.11, 861.17, 823.55, 568.22, 554.41, 536.20, 521.32, 509.69, 499.83, 476.85, 467.56, 458.05, 440.54, 424.37, 417.18 cm^{-1}

DSC: K 94.2 I 72.3 N 49.8 K

POM: K 93 I 72 N 49 K

4-[4-(5-Hydroxypentyl)phenyl]benzonitrile (2c)



Compound **1c** (0.576 g, 2.20 mmol) dissolved in tetrahydrofuran (15 mL) was combined with Pd/C(en) (0.058 g, 10% weight of substrate) in a 50-mL round bottom flask. Three cycles of evacuation/hydrogen addition were performed, and the black homogenous suspension was stirred for 72 hours under hydrogen at room temperature. At this point, ^{1}HNMR indicated that the reaction went to completion, so the catalyst was removed via suction filtration through a celite pad, and the solvent was removed under vacuum. The crude product was dissolved in hot acetonitrile, clay was added, and the resulting mixture was stirred for 10 minutes. The clay was removed via gravity filtration, and the product was recrystallized from acetonitrile/water, yielding 0.137 g (23.6% yield) of a tan crystalline solid.

^{1}HNMR (400 MHz, $CDCl_3$) δ: 7.71 (d, 2H, J = 8.4 Hz), 7.67 (d, 2H, J = 8.8 Hz), 7.51 (d, 2H, J = 8.4 Hz), 7.29 (d, 2H, J = 8.4 Hz), 3.66 (t, 2H, J = 6.4 Hz), 2.68 (t, 2H, J = 7.6 Hz), 1.67 (m, 4H), 1.43 (m, 2H), 1.37 (s, 1H)

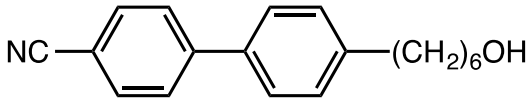
^{13}CNMR (100 MHz, $CDCl_3$) δ: 145.6, 143.4, 136.6, 132.6, 129.2, 127.5, 127.1, 119.1, 110.6, 62.9, 35.6, 32.6, 31.2, 25.4

FTIR: 3512.75, 2929.07, 2857.93, 2228.30, 1603.64, 1493.32, 1394.78, 1313.48, 1177.67, 1079.98, 1049.81, 963.42, 810.00, 737.72, 543.24, 517.22, 504.42, 494.80, 472.55, 456.44, 448.57, 429.16, 415.69, 405.88 cm^{-1}

DSC: K85.7 N 88.2 I 86.5 N 64.0 K

POM: K 86 N 88 I 87 N 67 K

4-[4-(6-Hydroxyhexyl)phenyl]benzonitrile (2d)



Compound **1d** (0.55 g, 2.00 mmol), Pd/C(en) (0.083 g, 15% weight of substrate), and ethyl acetate (30 mL) were combined in a 100-mL round bottom flask. Three cycles of evacuation/hydrogen addition were performed, and the reaction mixture was stirred overnight at room temperature under hydrogen. At this point, ^{1}HNMR indicated that the reaction went to completion, so the catalyst was removed via suction filtration through a celite pad. The filtrate was combined with silica gel (20 cc) and ethyl acetate, the solvent was removed under reduced pressure, the adsorbed material was placed at the top of a silica gel column, and it was eluted with ethyl acetate. The solvent was removed from the solution collected under reduced pressure. The solid remaining was recrystallized from a mixture of cyclohexane/toluene (75% / 25%), yielding 0.378 g (67.5% yield) of a white crystalline solid.

^{1}HNMR (400 MHz, $CDCl_3$) δ: 7.71 (d, 2H, *J* = 8.8 Hz), 7.67 (d, 2H, *J* = 8.8 Hz), 7.51 (d, 2H, *J* = 8.4 Hz), 7.29 (d, 2H, *J* = 8.4 Hz), 3.64 (m, 2H), 2.67 (t, 2H, *J* = 7.6 Hz), 1.65 (m, 2H), 1.57 (m, 2H), 1.39 (m, 4H), 1.23 (s, 1H)

^{13}CNMR (100 MHz, $CDCl_3$) δ: 145.7, 143.7, 136.7, 132.7, 129.3, 127.6, 127.2, 119.2, 110.7, 63.1, 35.7, 32.8, 31.5, 29.2, 25.7

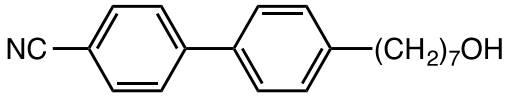
FTIR: 3226.26, 2919.71, 2851.32, 2227.49, 1606.06, 1493.47, 1395.10, 1180.85, 1118.92, 1052.98, 1025.72, 1005.84, 986.50, 812.45, 723.55, 540.12, 513.09, 497.52, 482.09, 475.05, 461.53, 438.90, 430.89, 411.53 cm^{-1}

DSC: K 78.9 I 69.9 N 53.3 K

POM: K 79 I 68 N 60 K

The data is consistent with the reference [3].

4-[4-(7-Hydroxyheptyl)phenyl]benzonitrile (2e)



Compound **1e** (0.90 g, 3.11 mmol) dissolved in ethyl acetate (40 mL) was combined with Pd/C(en) (0.27 g, 30% weight of substrate) in a 100-mL round bottom flask. Three cycles of evacuation/hydrogen addition were performed, and the black homogenous suspension was stirred for 72 hours under hydrogen at room temperature. At this point,

^{1}HNMR indicated that the reaction went to completion, so the catalyst was removed via suction filtration through a Celite pad. The filtrate was combined with silica gel (20 cc) and ethyl acetate, the solvent was removed under reduced pressure, the adsorbed material was placed at the top of a silica gel column, and it was eluted with ethyl acetate. The solvent was removed from the solution collected under reduced pressure. The crude solid remaining was recrystallized from a mixture of cyclohexane/toluene (75% / 25%), yielding 0.743 g (81.6% yield) of a white crystalline solid.

^{1}HNMR (400 MHz, $CDCl_3$) δ: 7.71 (d, 2H, *J* = 8.8 Hz), 7.67 (d, 2H, *J* = 8.8 Hz), 7.51 (d, 2H, *J* = 8.0 Hz), 7.29 (d, 2H, *J* = 8.4 Hz), 3.63 (m, 2H), 2.66 (t, 2H, *J* = 7.6 Hz), 1.59 (m, 4H), 1.38 (m, 6H), 1.28 (s, 1H)

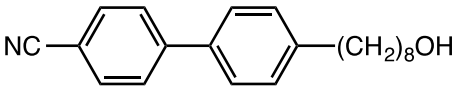
^{13}CNMR (100 MHz, $CDCl_3$) δ: 145.8, 143.8, 136.6, 132.7, 129.3, 127.6, 127.2, 119.2, 110.7, 63.1, 35.7, 32.9, 31.4, 29.4 (29.40), 29.4 (29.37), 25.8

FTIR: 3241.14, 2921.50, 2853.77, 2227.52, 1604.26, 1493.48, 1467.04, 1180.99, 1139.36, 1073.36, 1050.86, 1002.09, 981.10, 923.81, 801.32, 723.02, 557.96, 536.51, 516.08, 499.54, 486.72, 469.77, 447.49, 440.20, 421.12, 408.68 cm^{-1}

DSC: K 75.6 N 80.2 I 78.3 N 57.0 K_1 51.7 K_2

POM: K 75 N 81 I 78 N 51 K

4-[4-(8-Hydroxyoctyl)phenyl]benzonitrile (2f)



Compound **1f** (0.624 g, 2.06 mmol) dissolved in ethyl acetate (30 mL) was combined with Pd/C(en) (0.19 g, 30% weight of substrate) in a 100-mL round bottom flask. Three cycles of evacuation/hydrogen addition were performed, and the black homogenous suspension was stirred overnight under hydrogen at room temperature. At this point, ^{1}HNMR indicated that the reaction went to completion, so the catalyst was removed via suction filtration. To remove any remaining catalyst, the filtrate was combined with silica gel (20 cc) and ethyl acetate, the solvent was removed under reduced pressure, the adsorbed material was placed at the top of a silica gel column, and it was eluted with ethyl acetate. The solvent was removed from the solution collected under reduced pressure. The crude solid remaining was recrystallized from cyclohexane/toluene (75% / 25%), yielding 0.357 g (56.7% yield) of a cream colored crystalline.

^{1}HNMR (400 MHz, $CDCl_3$) δ: 7.73 (d, 2H, *J* = 8.8 Hz), 7.69 (d, 2H, *J* = 8.4 Hz), 7.53 (d, 2H, *J* = 8.4 Hz), 7.31 (d, 2H, *J* = 8.4 Hz), 3.66 (t, 2H, *J* = 6.8 Hz), 2.68 (t, 2H, *J* = 7.6 Hz), 1.62 (m, 4H), 1.39 (m, 8H), 1.29 (s, 1H)

^{13}CNMR (100 MHz, $CDCl_3$) δ: 145.8, 143.9, 136.6, 132.7, 129.3, 127.6, 127.2, 119.2, 110.6, 63.2, 35.7, 32.9, 31.5, 29.6, 29.5, 29.4, 25.9

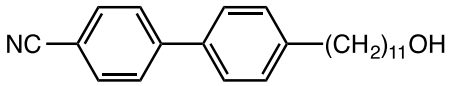
FTIR: 3333.40, 2923.52, 2848.82, 2227.39, 1604.68, 1493.88, 1465.93, 1398.82, 1353.84, 1181.91, 1053.48, 1024.26, 848.60, 813.28, 784.07, 724.88, 605.55, 563.49, 544.37, 525.37, 513.56, 472.98, 464.10, 457.44, 436.81, 420.23, 411.20 cm^{-1}

DSC: K 65.9 N 69.5 I 67.7 N 46.2 K

POM: K 65 N 70 I 69 N 47 K

The data is consistent with the reference [4].

4-[4-(11-Hydroxyundecyl)phenyl]benzonitrile (2g)



Compound **1g** (0.35 g, 1.00 mmol) dissolved in tetrahydrofuran (5 mL) was combined with Pd/C(en) (0.035 g, 10% weight of substrate) in a 50-mL round bottom flask. Three cycles of evacuation/hydrogen addition were performed, and the black homogenous suspension was stirred overnight under hydrogen at room temperature. At this point, ^{1}HNMR indicated that the reaction went to completion, so the catalyst was removed via suction filtration. To remove any remaining catalyst, the filtrate was combined with silica gel (20 cc) and ethyl acetate, the solvent was removed under reduced pressure, the adsorbed material was placed at the top of a silica gel column, and it was eluted with ethyl acetate. The solvent was removed from the solution collected under reduced pressure. The crude solid remaining was recrystallized from cyclohexane/toluene (75% / 25%), yielding 0.122 g (34.9% yield) of a white solid. ^{1}HNMR (400 MHz, $CDCl_3$) δ: 7.71 (d, 2H, *J* = 8.8 Hz), 7.67 (d, 2H, *J* = 8.4 Hz), 7.51 (d, 2H, *J* = 8.4 Hz), 7.29 (d, 2H, *J* = 8.4 Hz), 3.63 (m, 2H), 2.66 (t, 2H, *J* = 7.6 Hz), 1.64 (m, 2H), 1.55 (m, 2H), 1.32 (m, 14H), 1.21 (s, 1H)

^{13}CNMR (100 MHz, $CDCl_3$) δ: 145.8, 144.0, 136.6, 132.7, 129.3, 127.6, 127.2, 119.2, 110.7, 63.2, 35.8, 32.9, 31.5, 29.7 (29.72), 29.7 (29.70), 29.6 (29.63), 29.6 (29.56), 29.5, 25.9

FTIR: 3509.90, 2916.92, 2880.28, 2848.19, 2230.21, 1604.16, 1494.66, 1466.48, 1400.26, 1325.36, 1301.52, 1178.29, 1125.26, 1051.63, 1040.19, 1005.70, 983.17,

869.11, 851.16, 834.57, 817.60, 798.31, 772.19, 720.67, 563.29, 536.51, 521.60, 508.28, 495.23, 488.96, 477.95, 462.50, 454.31, 441.82, 433.46, 410.15 cm^{-1}

DSC: K 84.5 I 73.6 N 69.2 K

POM: K 82 I 73 N 70 K

SI.4. DSC of Representative Liquid Crystals

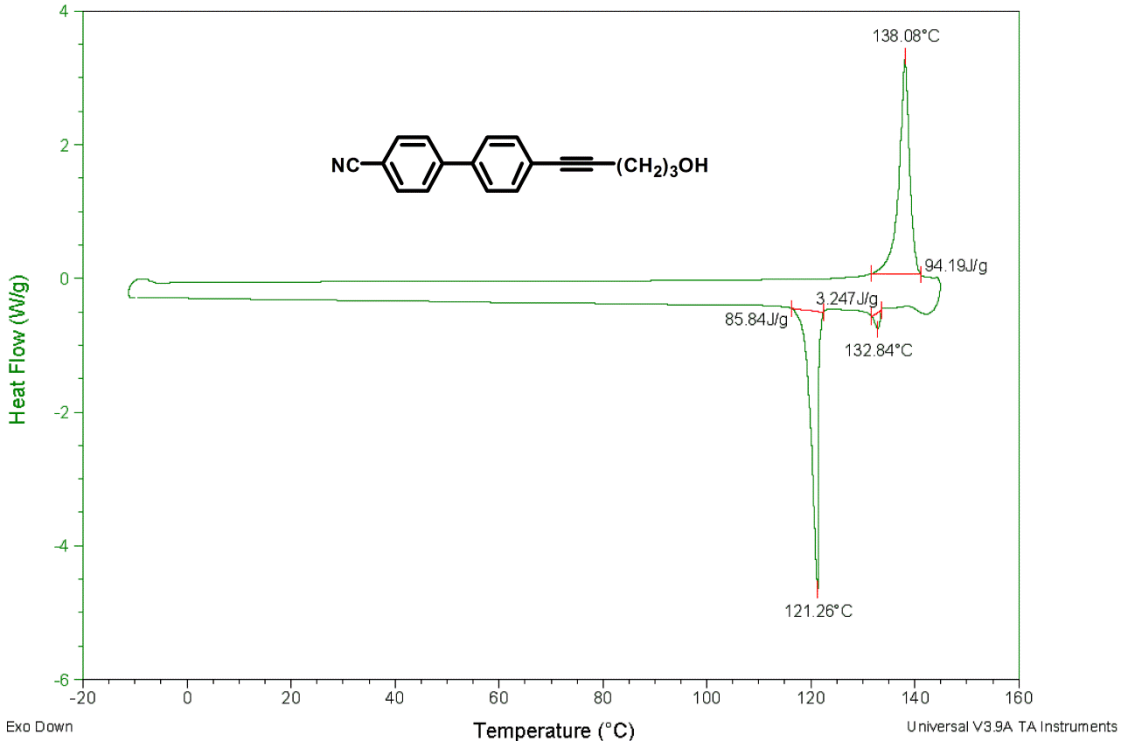


Figure SI.1. The DSC plot of compound **1c** (K 138.1 I 132.8 N 121.3 K).

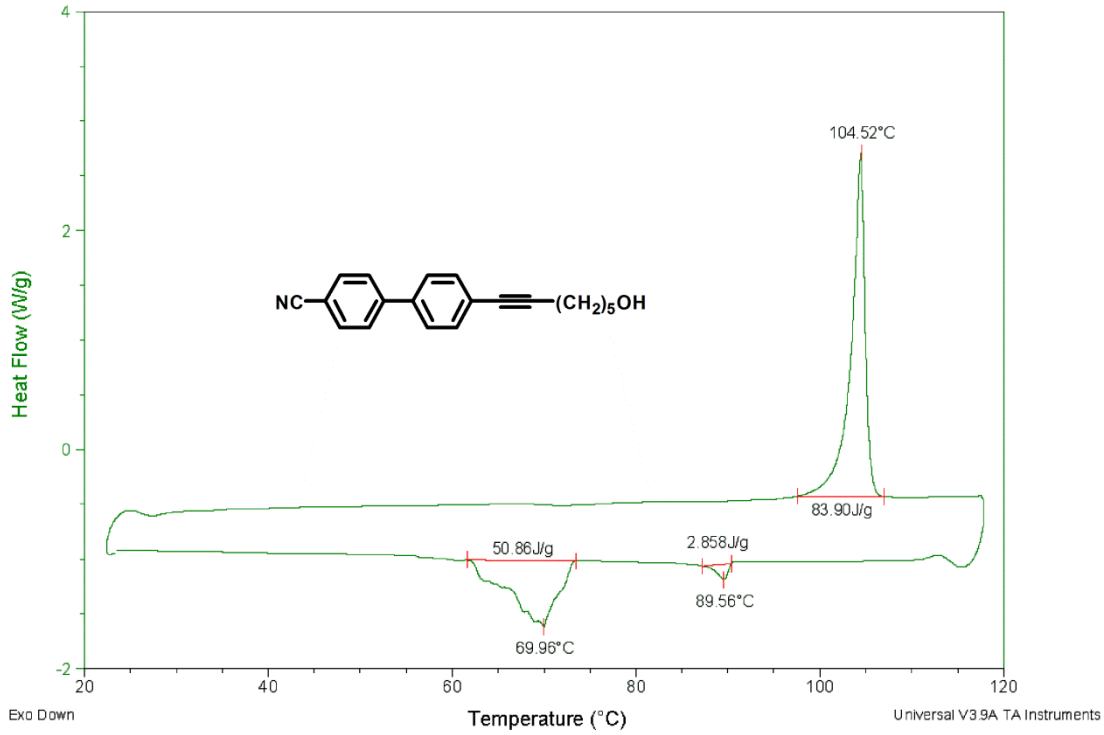


Figure SI.2. The DSC plot of compound **1e** (K 104.5 I 89.6 N 70.0 K).

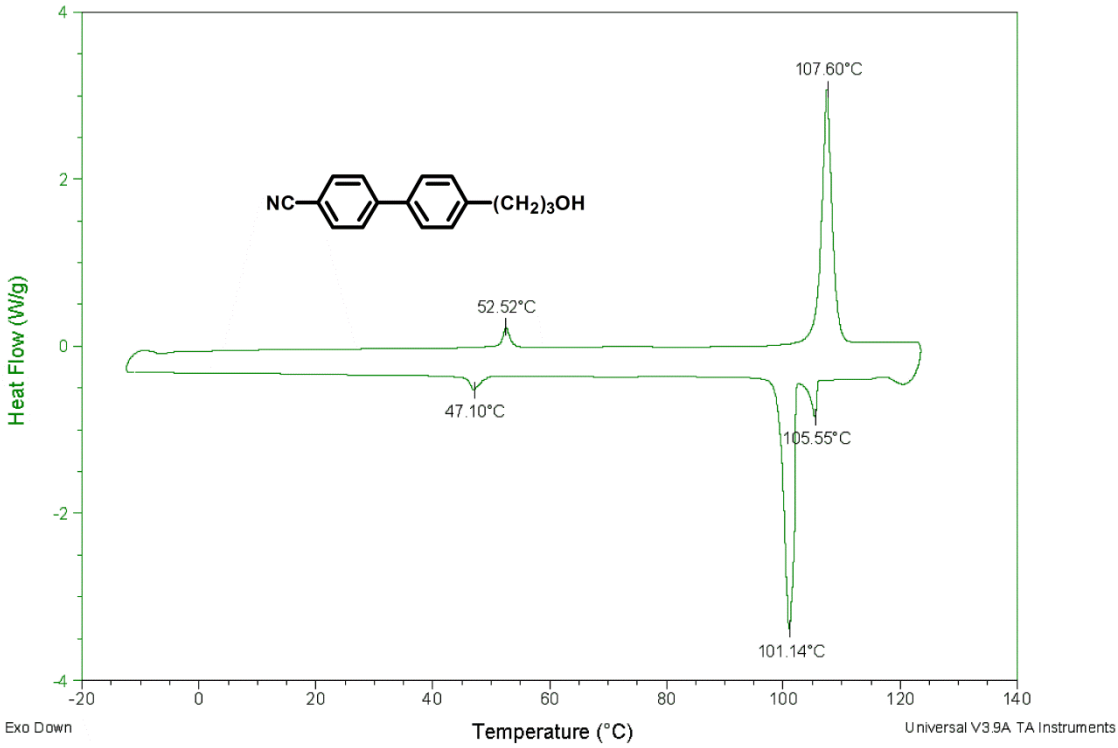


Figure SI.3. The DSC plot of compound **2a** (K_1 52.5 K_2 107.6 I 105.6 N 101.1 K_1 47.1 K_2).

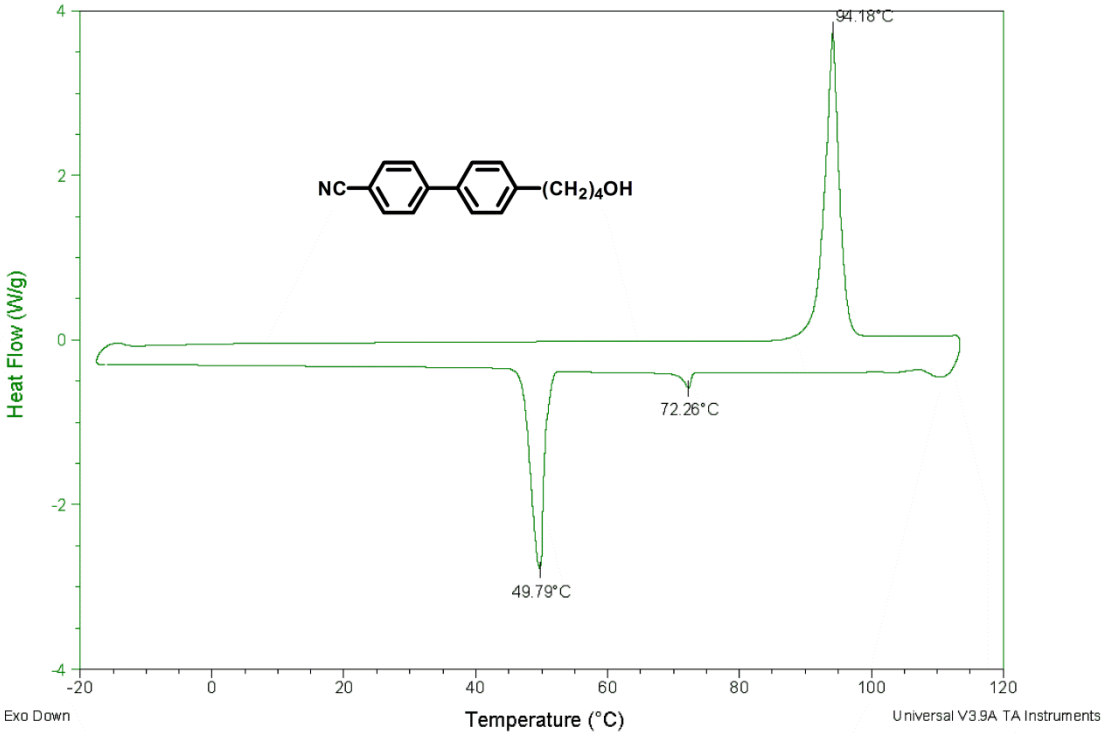


Figure SI.4. The DSC plot of compound **2b** (K 94.2 I 72.3 N 49.8 K).

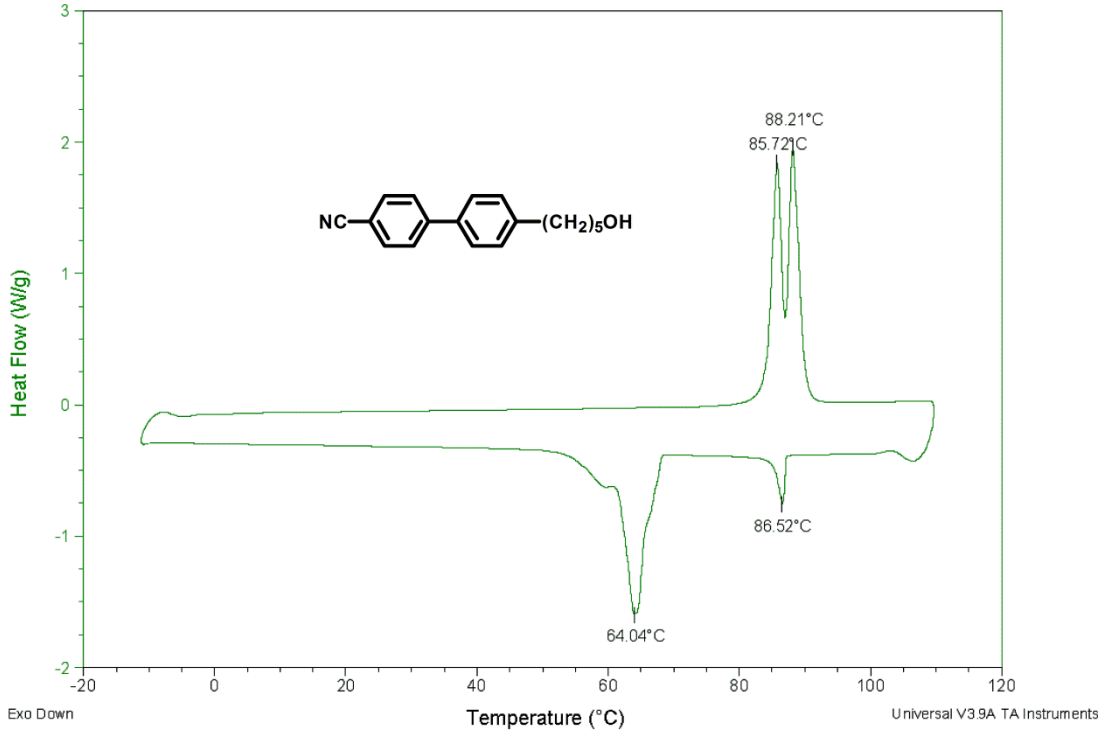


Figure SI.5. The DSC plot of compound **2c** (K 85.7 N 88.2 I 86.5 N 64.0 K).

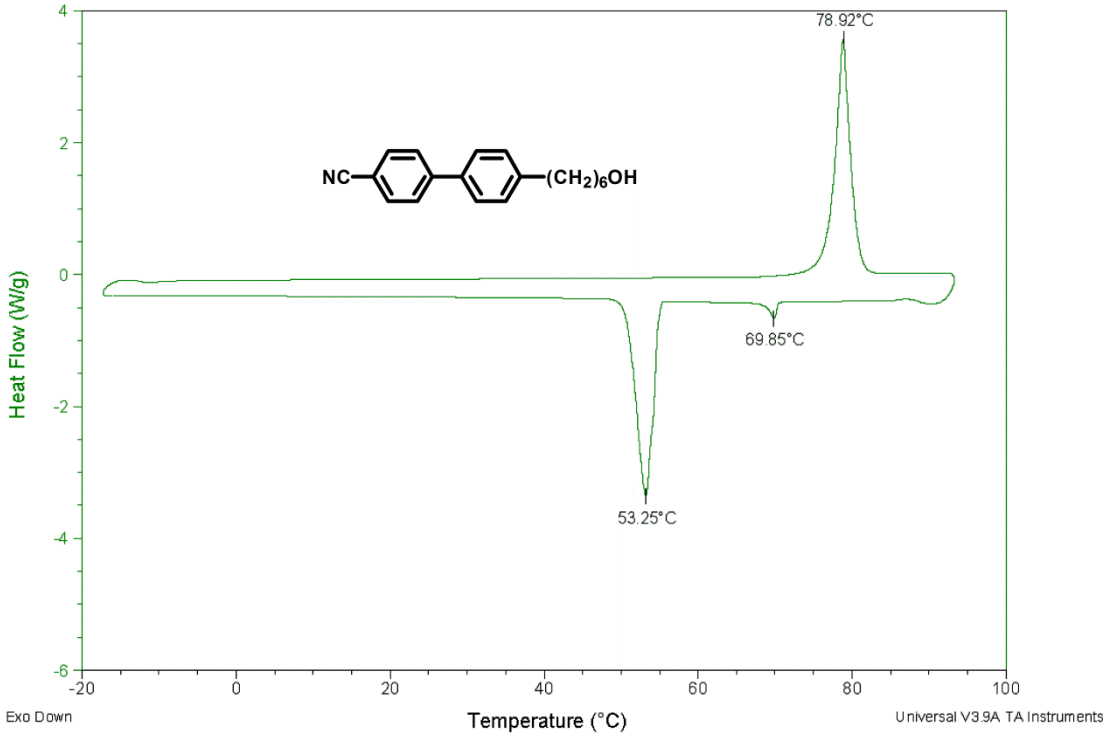


Figure SI.6. The DSC plot of compound **2d** (K 78.9 I 69.9 N 53.3 K).

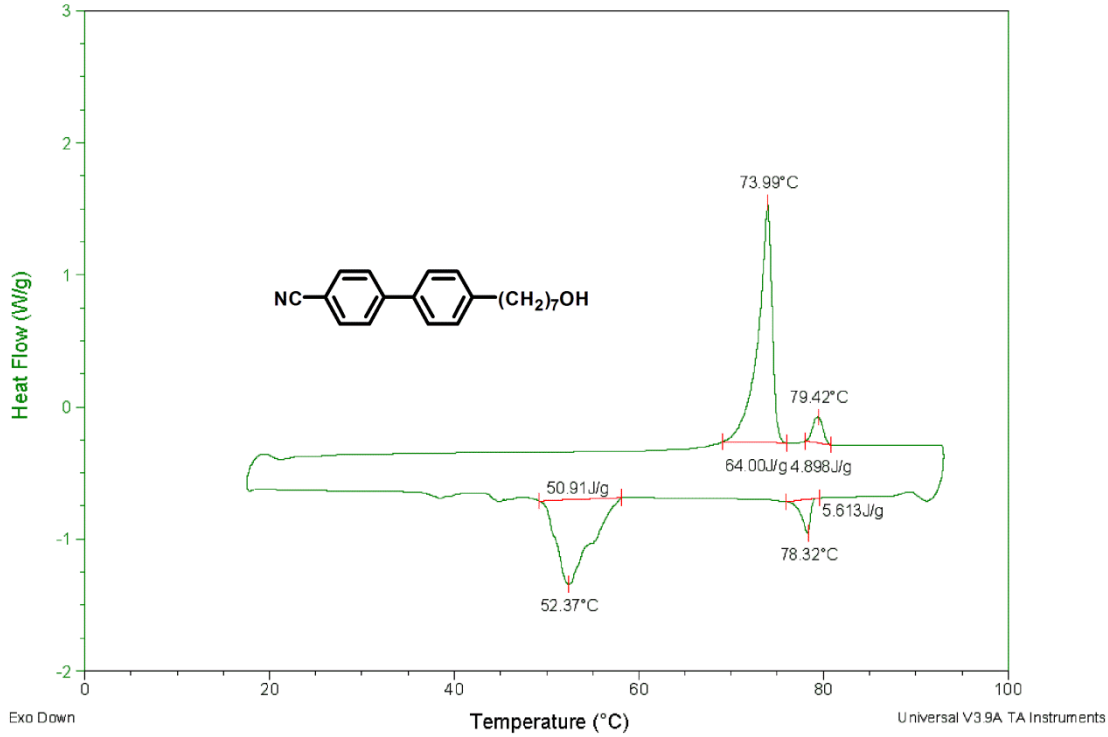


Figure SI.7. The DSC plot of compound **2e** (K 74.0 N 79.4 I 78.3 N 52.4 K).

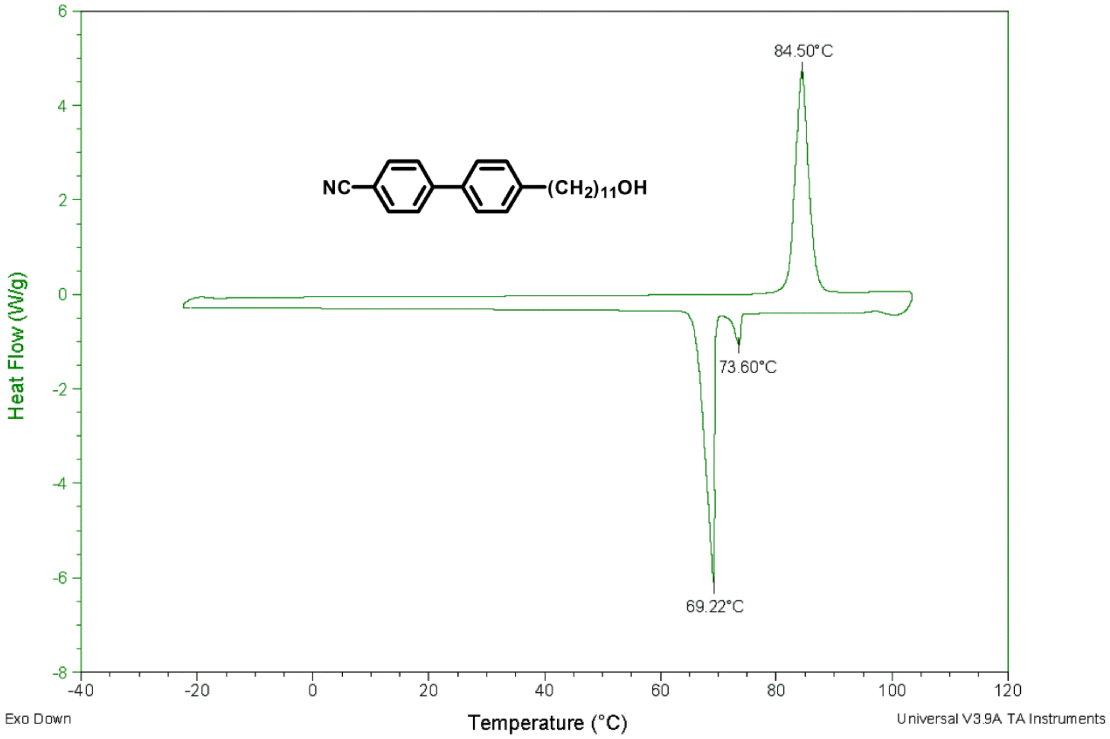


Figure SI.8. The DSC plot of compound **2g** (K 84.5 I 73.6 N 69.2 K).

Table SI.1. Calculated dipole moment of hydroxy-terminated alkynyl and hydroxy-terminated alkyl CB derivatives and parent CB compounds with alkyl chain. Here 'n' refers to the number of CH_2 groups in the molecule.

n	NC–(CH$_2$)$_n$H	NC–(CH$_2$)$_n$OH	NC–(CH)$_{n-2}$OH
3	7.80	7.40	5.81
4	7.81	7.59	6.81
5	7.83	7.79	7.38
6	7.82	7.81	7.48
7	7.83	7.91	7.52
8	7.83	7.93	7.64
9	7.82	7.98	7.58
10	7.83	7.76	7.75
11	7.86	7.52	7.74

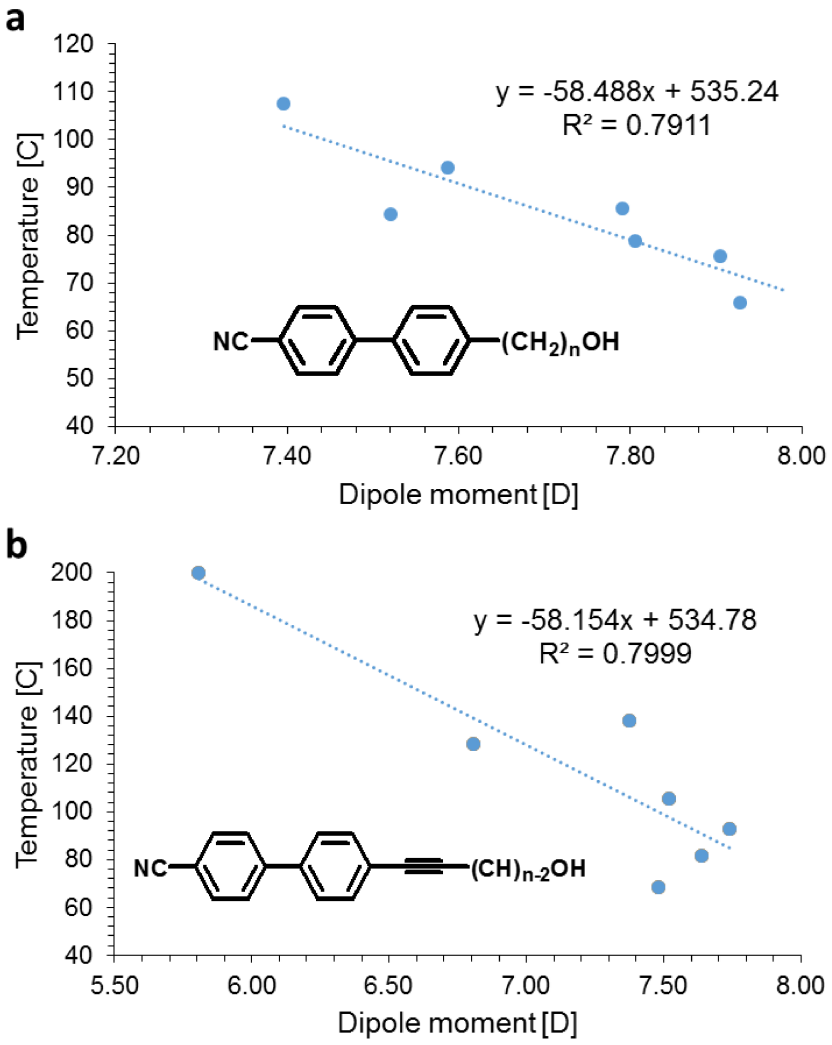


Figure SI.9. Correlation between calculated dipole moment (in Debye) and measured crystalline to nematic or isotropic transition temperature (in ºC) for (a) hydroxy-terminated alkyl CB derivatives and (b) hydroxy-terminated alkynyl CB derivatives.

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