Synthesis and Properties of Fluorine tail-terminated Cyanobiphenyls and Terphenyls for Chemoresponsive Liquid Crystals

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Abstract

A series of fluorine tail-terminated alkoxy and alkyl cyanobiphenyl compounds and some cyano-p-terphenyl derivatives were synthesized and mesogenic properties described. Comparison with the non-fluorinated K series and M series indicates that the terminal fluorine atom generally decreases the transition temperatures and, more interestingly, depresses the formation of a smectic phase. Several binary LC mixtures formed by the fluorine tail-terminated compounds were found exhibiting promising room temperature nematic phases with wide ranges. The mixture F7OCB and F8OCB shows homeotropic ordering at the metal salts-decorated surfaces and planar ordering at the free surface, which may have potential application in designing a more sensitive and faster LC system to targeted analytes.

1. Introduction

Amongst the many thousands of liquid crystal (LC) molecules, the K series 4-alkyl-4'-cyanobiphenyls (CB) and the M series 4-alkoxy-4'-cyanobiphenyls (OCB) originally

synthesized by G. Gray et al. have found wide applications in the field of liquid crystal displays (LCD) [1]. The best-known compound in this series is probably 4-pentyl-4'-cyanobiphenyl (5CB) due to its convenient room temperature nematic phase. The strong electron withdrawing effect of the cyano group contributes to the high polarizability of these molecules and thus stable nematic liquid crystal phases and opto-electronic properties including the optical and electronic anisotropies [2,3]. Later, larger conjugated systems, 4-alkyl-4"-cyano-*p*-terphenyls (CT) [4] and 4-alkoxy-4"-cyano-*p*-terphenyls (OCT) [5], were also examined. Since their discovery a considerable effort has been made on structural modifications of these cyanobiphenyl/terphenyl mesogens. For example, fluorination or chlorination on the aromatic rings of cyanooligophenyl derivatives have been examined [6-10]. Furthermore, the fluorination has been also installed in various ways in the aliphatic tails [11,12]. In contrast to the numerous modifications that have been accomplished in the core regions of these molecules relatively less attention has been paid to study of the tail sections of the cyanobiphenyls/terphenyls. Studies have shown that the insertion of a halogen atom (chlorine or bromine) to the tails strongly promotes the formation of a smectic A phase in difluoroterphenyl system [13] and this is also the case in phenylpyrimidine derivatives [14]. Recently a systematic study of chlorine- and bromine-terminated alkoxy cyanobiphenyls demonstrated the influence of terminal halogenation on the mesogenic properties [15]. An and coworkers investigated some tolane mesogens terminated by 2,2-difluorovinyloxyl group [16]. Some other termini such as siloxanes [13] or the hydroxy group [17] have also been investigated (some of the hydroxy-terminated compounds have been previously reported as synthetic intermediates for LC dimers/trimers [18,19]). Most of these compounds were found to be nematic mesogens as well as important precursors for the target molecules described here.

In this work, a series of monofluorine tail-terminated alkoxycyanobiphenyl and alkylcyanobiphenyl have been prepared and their mesogenic properties examined in order to search for novel nematic mesogens that are suitable for chemoresponsive sensors [20,21]. Some analogous cyano-*p*-terphenyl derivatives were also synthesized and similarly examined. The fluorine atom is more electronegative than chlorine and bromine yet much smaller. As such, how will terminal fluorination impact the liquid crystal properties? Previous work on fluorination of the aliphatic tails has been focused on the study of

multifluorination or even perfluorination [11,12]. This might due to the relative synthetic difficulty of monofluorination. Here an efficient approach was utilized to prepare these monofluorine-terminated cyanobiphenyls by substitution of the hydroxy tail-terminated cyanobiphenyl precursors [17]. The mesogenic behavior of these fluorinated derivatives was compared with their non-fluorinated parent compounds and two main influences were identified. First, the terminal fluorine atom generally decreases the transition temperatures. Second, and more interesting, the formation of a smectic phase is depressed. Calculations indicate that these fluorine tail terminated molecules are able to bind with different metal salt surfaces and homeotropic alignment at the mesogen-metal salt interface, which is confirmed by optical study of LC cells made of LC mixture and metal salt. Several binary mixtures were examined and exhibited nematic phases that were close to ambient temperature, which may find further LC sensor applications with faster rates of responses and greater sensitivity to targeted analytes due to the none homeotropic ordering at the free interface.

2. Experimental Section

Commercial-grade solvents were used without further purification. $PdCl_2$ was obtained 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 [22]. Triphenylphosphine and ethylenediamine were purchased from Sigma-Aldrich. The terminal hydroxyacetylenes were purchased from GFS Organic Chemicals (Columbus, OH). The methanol was purchased from VMR (West Chester, PA). The compressed hydrogen was purchased 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).

Construction of LC Optical Cells from Glass Substrates with two symmetric metal salt surface: Metal salts were deposited onto glass substrates by spin-coating ethanolic solutions (100 μL) of metal perchlorates. Two metal salt-coated substrates were aligned facing each other, spaced apart using a glass spacer of 20 μm. Next, 2 μL of LC was drawn by capillarity into the cavity between the two surfaces of the optical cell.

Formation of Micrometer-thick films of LC with one metal salt surface and one air surface: After coating the surface with metal salts, as described above, a 18 μm-thick copper-coated was deposited to the salt-coated surface. The grid defined square pores with lateral dimensions of 285 μm. The grids were filled with LC using a microcapillary tube at room temperature.

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

The catalyst was prepared using a literature method [23]. 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'-ω-hydroxyalkoxy-4-cyanobiphenyl compounds

In a 100 ml round bottom flask with stirbar was placed 4'-hydroxy-4-cyanobiphenyl (10.0-15.0 mmol, 1.0 equiv.), triphenylphosphine (1.2 equiv.), commercial alkanediols (1.2 equiv.) and dry THF (25 ml). The resulting solution was chilled in an ice bath and diisopropylazodicarboxylate (1.2 equiv.) was added in portions over ten minutes. The mixture was allowed to warm to room temperature and monitored by TLC until completion. 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 (1:2). Fractions containing only the monoadduct were combined and concentrated to give the desired product.

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

A 100 ml flask was charged with the 4'-ω-hydroxyalkoxy-4-cyanobiphenyls (2.0-5.0 mmol), triethylamine (1.3 equiv.) and DCM (5.0-10.0 mL). The mixture was cooled to a temperature between 5°C-15°C and a solution of *p*-toluenesulfonyl chloride (1.0 equiv.) in DCM (5.0-10.0 mL) was added slowly via a additional funnel. Once the addition was complete, the reaction mixture was warmed to ambient and stirred for 12 hours. The reaction was monitored by TLC until completion and was terminated by addition of silica gel and the mixture was concentrated to dryness. The desired product was obtained after column chromatography with eluent of hexanes and ethyl acetate (4:1).

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

These reactions were carried out according to a literature method [24]. To a solution of 4'-[ω-[(4-methylphenyl)sulfonyl]alkoxy]-4-cyanobiphenyls (1.0-5.0 mmol) in *t*-amyl alcohol (15.0-25.0 mL) was added CsF (2.0 equiv.). The resulting mixture was stirred for 12 hours at reflux. The reaction was monitored by TLC until completion. The mixture was cooled to room temperature, water (15 mL) was added 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 (1:5). The solid products were recrystallized from appropriate solvents while the liquid products were kept under vacuum to remove volatile impurities.

The synthesis of 4'-ω-fluoroalkyl-4-cyanobiphenyl compounds was similar to the procedure used for the alkoxy derivatives. For complete experimental procedures, see supplemental information.

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

These reactions were carried out according to a literature method [25]. 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 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

The alkyne reduction was perfurmed by a literature method [14,15]. In a 100 ml round bottom flask was placed 4'-(ω-hydroxyalkynyl)-4-cyanobiphenyls (1.0 g-2.0 g), Pd/C(en) (10%-30% weight of the substrate), and ethyl acetate (20.0-25.0 mL). The air inside the reaction flask was replaced with hydrogen via three vacuum/hydrogen cycles. The homogenous 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 mixture was filtered through a Celite pad and the filtrate was concentrated to afford the product.

Formation of LC films confined by two metal salt-decorated surfaces

Metal salts were deposited onto glass substrates by spin-coating ethanolic solutions (100 μL) of metal perchlorates. The density of metal salts is controlled to be 94.2 ± 2.5 pmol mm^{-2}. Two metal salt-coated substrates were aligned facing each other, spaced apart using a glass spacer of 20 μm. Next, 2 μL of LC was drawn by capillarity into the cavity between the two surfaces of the optical cell.

Formation of thin films of LC supported on metal salt-decorated surfaces

Metal salts were deposited onto the glass surfaces by spin-coating ethanolic solutions of metal salts. The density of metal salts is controlled to be 94.2 ± 2.5 pmol mm^{-2}. After coating the surface with metal salt, an 18 mm-thick copper TEM grid (Electron Microscopy Sciences, Hatfield, PA) was put on the surface. The TEM grid was composed of squares with lateral dimensions of 285 mm and an overall diameter of 3 mm. The grids were filled with LC using a microcapillary.

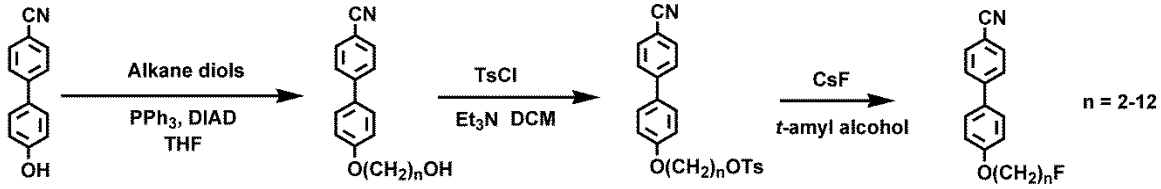
Computational methods

All calculations were carried out using Gaussian 09 version D.01 [26]. Geometry optimizations were performed using density functional theory (DFT) at the PBE-D3(SMD=benzonitrile)/def2-SVP level of theory [27-30]. Subsequently, dipole moments were calculated for each optimized structure at the M06-2X-D3(SMD=benzonitrile)/def2-TZVP level of theory [31]. The described method has been successfully utilized previously

to model mesogen properties including dipole moments [17,21]. To obtain appropriate statistical sampling of the conformational modes of the aliphatic chains, the complete conformational space was generated 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 were maximized to 2000 conformers 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.

Binding free energy (G_{BE}) calculations were executed at the M06-2X-D3/def2-TZVP//PBE-D3/def2-SVP level of theory using the Neutral Anion Model (NAM) which has been shown to provide good agreement with experiments as described in detail previously [32-34]. G_{BE} of mesogens are calculated as $G_{BE} = G_{Model+LC} - G_{Model} - G_{LC}$, where $G_{Model+LC}$ is the total free energy of the metal salt cluster with the bound mesogen, G_{Model} is the free energy of the naked metal salt cluster and G_{LC} is the free energy of the mesogen molecule in the gas phase. Negative values of G_{BE} (i.e., binding) were found to correlate with homeotropic ordering of 5CB whereas positive G_{BE} indicated planar ordering. For the sake of simplicity and consistency, we investigated only the energetically most stable anti conformation of the aliphatic chain of the mesogens to calculate G_{BE}.

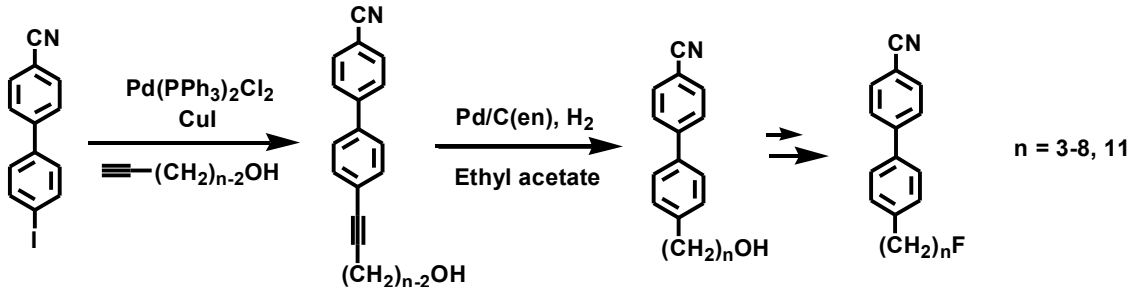
3. Synthesis



Scheme 1. Synthesis of 4'-ω-fluoroalkoxy-4-cyanobiphenyl compounds FnOCB.

Our main strategy to introduce the terminal fluorine was the substitution of the relevant terminal alcohols. Thus, the terminal hydroxyalkoxy cyanobiphenyl compounds were first prepared by a standard Mitsunobu reaction between commercial precursors—4'-hydroxy-4-cyanobiphenyl and α,ω-alkane diols (Scheme 1) or simple alkylation using

α,ω-bromoalcohols. The desired mono adducts were obtained in modest to good yields by use of excess diols. The exceptions are for the target molecules that bear propyloxy, butyloxy and pentyloxy side chains. We found commercial bromofluoroalkanes (n = 3–5) and so the desired fluorine-terminated alkoxy CBs were obtained directly by a standard alkylation [35]. Next, the terminal alcohols were tosylated by *p*-TsCl in the presence of triethylamine in good to excellent yields. The fluorination was then accomplished smoothly using CsF in *t*-amyl alcohol and the desired 4'-ω-fluoroalkoxy-4-cyanobiphenyl compounds were obtained quantitatively [24]. No major byproducts were found and the desired products were obtained by flash chromatography. The solid products which are crystalline at room temperature were recrystallized from *iso*-octane or hexanes while the non-crystalline products were dried by Kugelrohr prior to thermal analysis.



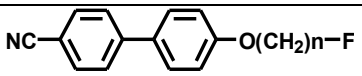
Scheme 2. Synthesis of 4'-ω-fluoroalkyl-4-cyanobiphenyl compounds FnCB.

As far as synthesis of the alkyl analogues, the challenge involves how to install the terminal hydroxyalkyl group into the cyanobiphenyl structure. Our approach started from the preparation of an important precursor 4'-cyano-4-iodobiphenyl according to a literature method [22] (Scheme 2). This iodide was treated with freshly generated $Pd(PPh_3)_2Cl_2$ /$Cu(PPh_3)_3I$ in diisopropylamine and reacted with commercial terminal hydroxy alkynes under the standard Sonogashira coupling condition and the desired alkynyl products were obtained in modest to good yields. Next, a poisoned palladium/carbon reagent—Pd/C (en) was utilized for the hydrogenation reaction to ensure that the cyano group will not be reduced [23]. With the 4'-hydroxy-terminated alkyl-4-cyanobiphenyl compounds in hand, the relevant fluorine-terminated derivatives were synthesized via the previous approach used for the alkoxy compounds.

In order to compare the influence of a terminal fluorine to a larger system as well, we also synthesized a few cyano-*p*-terphenyl analogues. The key intermediate—4'''-hydroxy-4-cyano-*p*-terphenyl was prepared according to the literature method [36]. However, the subsequent Mitsunobu reaction did not work as efficiently as with the biphenyl compounds. As a result, we utilized some commercial bromofluoro alkanes and reacted them with the terphenyl alcohol to afford the desired products in modest yields.

4. Mesogenicity study and discussions

The thermal behavior of the fluorine-terminated cyanobiphenyl/terphenyl compounds was analyzed using differential scanning calorimetry (DSC) and polarized optical microscopy (POM). The data is compiled in Table 1 through Table 4. The thermal behavior of the corresponding non-fluorinated cyanobiphenyls is also provided for comparison.

Compound #	n	 F-terminated M series Thermal behavior (°C)	 M series Thermal behavior (°C)
F2OCB	2	K 97 I 70 N 52 K	K 102 (N 91) I
F3OCB	3	K 78 I 53 N 25 K	K 72 (N 64) I
F4OCB	4	K 88 I 70 N 58 K	K 78 (N 76) I
F5OCB	5	K 47 N 61 I	K 50 N 68 I
F6OCB	6	K_1 47 K_2 55 K_3 61 N 67 I	K 57 N 76 I
F7OCB	7	K 51 N 67 I	K 54 N 74 I
F8OCB	8	K_1 32 K_2 37 K_3 53 N 70 I	K 55 SmA 67 N 80 I
F9OCB	9	K_1 47 K_2 55 N 67 I	K 64 SmA 78 N 80 I
F10OCB	10	K 52 N 67 I	K 59.5 SmA 89 I
F11OCB	11	K 63.5 N 68.7 I	K 71.5 SmA 87.5 I

F12OCB	12	K 68.6 N 69 I 68.2 N 46.6 K	K 70 SmA 90 I

Table 1. The thermal behavior of 4'-ω-fluoroalkoxy-4-cyanobiphenyl compounds FnOCB. (K = Crystal, N = Nematic, SmA = Smectic A, I = Isotropic) Data available for the analogous parent nonsubsitituted alkoxy series is provided for comparison [37].

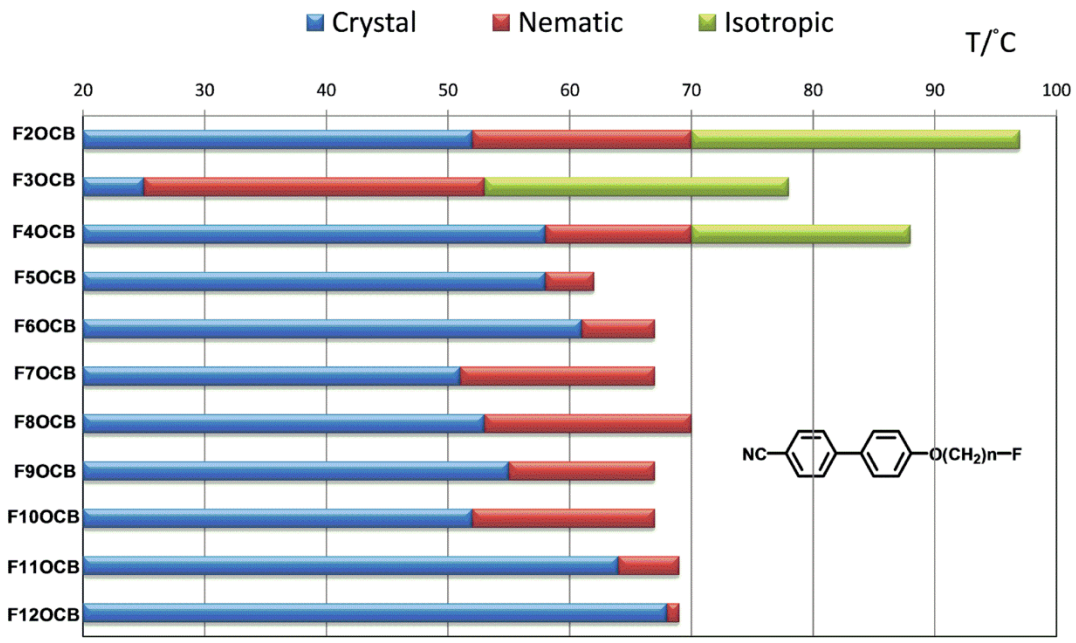


Chart 1. The thermal behavior of 4'-ω-fluoroalkoxy-4-cyanobiphenyl compounds FnOCB. (F2OCB, F3OCB and F4OCB are monotropic and therefore only cooling cycles are shown; for F5OCB through F12OCB heating cycles are shown).

As seen from Table 1, the 4'-ω-fluoroalkoxy-4-cyanobiphenyl compounds generally exhibit nematic mesogenic properties (Figure 1 for nematic phase texture of F8OCB), besides some crystal-crystal transitions found for a few cases (n = 6, 8, 9) by DSC. The clearing points of this series show a similar trend compared to the non-fluorinated analogues and compound F5OCB has the lowest clearing point. The K-N transition temperatures range from 50 to 60 °C. An interesting phenomenon is that some these compounds show super-cooling property—during the cooling cycle, the nematic phase persists for a quite wide temperature range, sometimes below ambient temperature as shown in Figure 1A, the DSC plot of F8OCB. By comparing the data with that of the

non-fluorinated versions, we found that the terminal fluorination decreases the clearing points (5-20 °C lower). As far as the K-N transition temperatures, compounds F7OCB, F8OCB, F9OCB, F10OCB and F11OCB show 5-20 °C lower temperature than the relevant non-fluorinated compounds. In addition, compounds F2OCB, F3OCB and F4OCB all display monotropic behavior with a nematic phase during cooling, which is consistent with the non-fluorinated analogues. Furthermore, the phase behavior of compounds F8OCB, F9OCB, F10OCB and F11OCB indicated that the terminal fluorination suppresses the formation of smectic phase, which has been observed in analogues bearing longer length tails. This phenomenon was also observed for chlorine and bromine terminated CBs [15]. F12OCB displays a very narrow range (within 0.5 °C) of nematic phase during heating, which was only observed by POM at a very slow heating rate. Even so, there is no evidence for the existence of a smectic phase for F12OCB. It is of interest that this influence from the fluorine atom remains in such long tails.

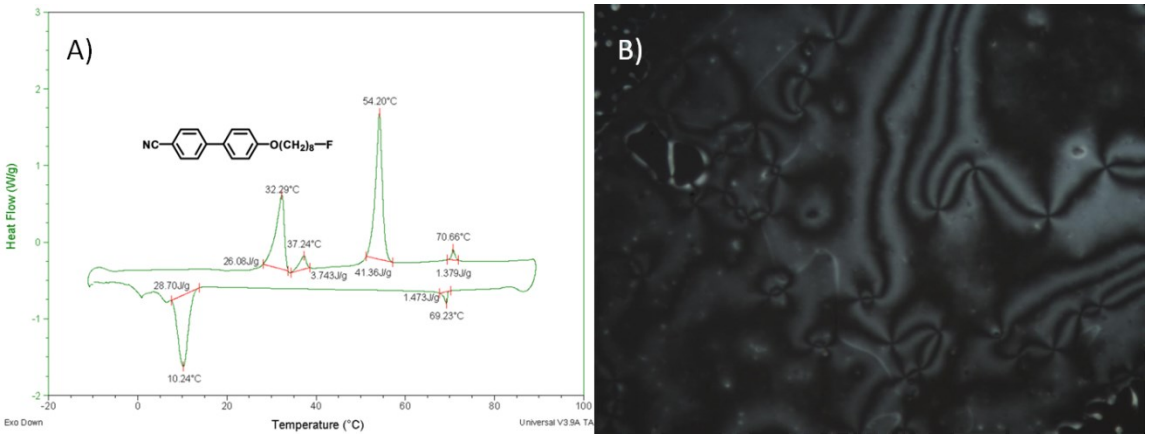


Figure 1. A) The DSC of F8OCB. The nematic phase remained until 10.2 °C during cooling. B) Optical microscopy image (crossed-polars) of F8OCB at 60 °C.

Next, two enantiotropic nematics, compounds F7OCB and F8OCB, were selected to investigate the mesogenic property of their mixtures in different ratios (Table 2). All the mixtures show lower phase clearing points than the individual components as we expected. When these two compounds are in equal amount (50%:50%), the mixture transform to the nematic phase below ambient temperature and the clearing point is 67 °C according to POM.

Composition	F7OCB	F8OCB
100%: 0%	DSC: K 51.84 N 67.29 I POM: K 50.8 N 66.8 I	
5%: 95%	DSC: K 35.14 N 64.87 I POM: K 50 (broad) N 64.9 (broad) I	
25%: 75%	DSC: K 27.89 N 69.65 (broad) I POM: K 47.6 (broad) N 70.3 I	
50%: 50%	DSC: K 47.66 (broad) N 68.97 I POM: N 66.6 I	
75%: 25%	DSC: K 44.43 (broad) N 68.91 (broad) I POM: K 43 (broad) N 67 (broad) I	
95%: 5%	DSC: K 49.28 N 68.95 (broad) I POM: K 47 (broad) N 67 (broad) I	
0%: 100%		DSC: K_1 32.29 K_2 37.24 K_3 54.20 N 70.66 I POM: K 53.0 N 70.2 I

Table 2. The thermal behavior of the binary mixture of F7OCB and F8OCB by DSC and POM.

The story of the 4'-ω-fluoroalkyl-4-cyanobiphenyl compounds is more complicated than the alkoxy versions as shown in Table 3. Depending on the commercial availability of the relevant hydroxy-terminated alkyne precursors, only the listed targets were synthesized. Only a nematic phase was found for all the alkyl derivatives. Compounds F3CB, F4CB, F5CB and F11CB all exhibit monotropic nematic behavior. Specifically, F3CB and F4CB display 10-20 $^{\circ}$C higher clearing points than their non-fluorinated versions 3CB and 4CB and such monotropic behavior is consistent. The phase behavior of the two enantiotopic nematics, F6CB and F7CB, were confirmed by DSC and POM but they have narrow nematic ranges compared to the non-fluorinated version (Figure 2A–B for F7CB). We were surprised to find that F5CB shows a 11 $^{\circ}$C higher clearing point than that of the well-known room temperature LC 5CB (Figure 2C). Due to the temperature limitations of the microscope hot-stage on our microscope, we were unable to observe the phase transitions that appear by POM below ambient temperature evident in DSC. As a result,

the phase appears at 15 °C during cooling for 3CB was assigned as a nematic phase considering the enthalpy change. F8CB is an isotropic liquid at ambient temperature and there is only one phase transition found on DSC at 19 °C upon cooling down to -40 °C. This transition turned out to be a N-I transition after we observed it by cooling the sample slide in a freezer and rapidly placing it in the microscope stage (Figure 2D). Just as in the case of the alkoxy derivatives, terminal fluorination of the alkane tails suppresses the formation of a smectic phase as well, as seen for the comparison between F8CB, F11CB and 8CB, 11CB. Additionally, according to the DSCs, most of these compounds show supercooling properties, too, as shown in Figure 2A for F7CB.

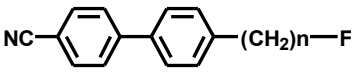
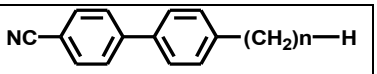
Compound #	n	 F-terminated K series Thermal behavior (°C)	 K series Thermal behavior (°C)
F3CB	3	K 84 I 16 N 10 K	K 66 I 26 N
F4CB	4	K 57 I 36 N 29 K	K 46 I 16 N
F5CB	5	K 46 I 28 N -15 K	K 22.5 N 35 I
F6CB	6	K 28 N 32 I	K 15 N 30 I
F7CB	7	K 31 N 35 I	K 31 N 44 I
F8CB	8	K [a] N 19 I	K 20 Sm 34 N 41 I
F11CB	11	K 54 I 44 N 19 K	K 53 Sm 57 N 58 I

Table 3. The thermal behavior of 4'-ω-fluoroalkyl-4-cyanobiphenyl compounds FnCB. a: the crystal-nematic transition was not found on DSC as low as -40 °C. (K = Crystal, N = Nematic, Sm = Smectic, I = Isotropic) Data available for the analogous parent nonsubsitituted alkyl series is provided for comparison [38].

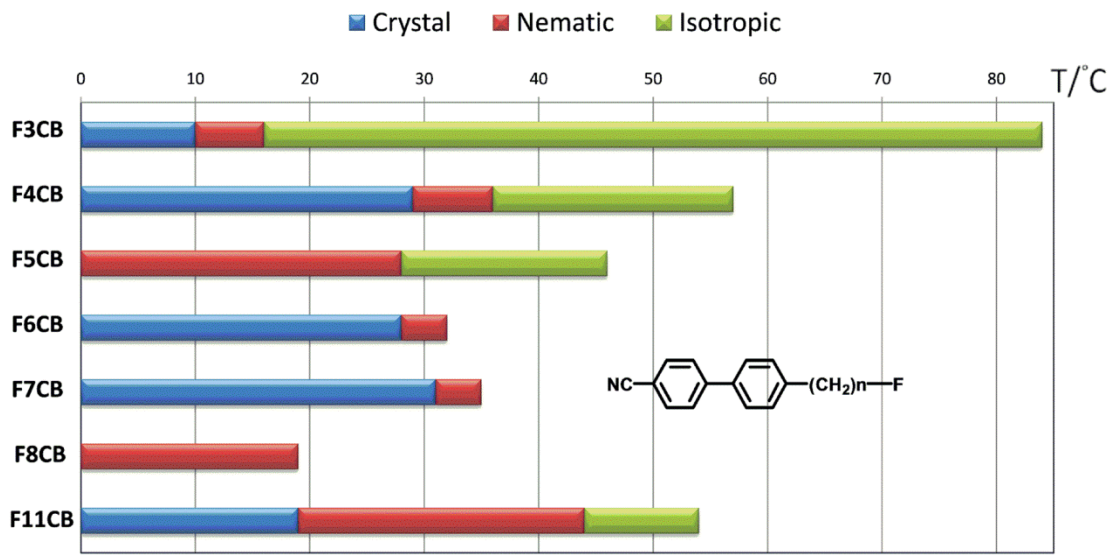


Chart 2. The thermal behavior of 4'-ω-fluoroalkyl-4-cyanobiphenyl compounds FnCB. (Compound F3CB, F4CB, F5CB and F11CB are monotropic therefore only cooling cycle shown)

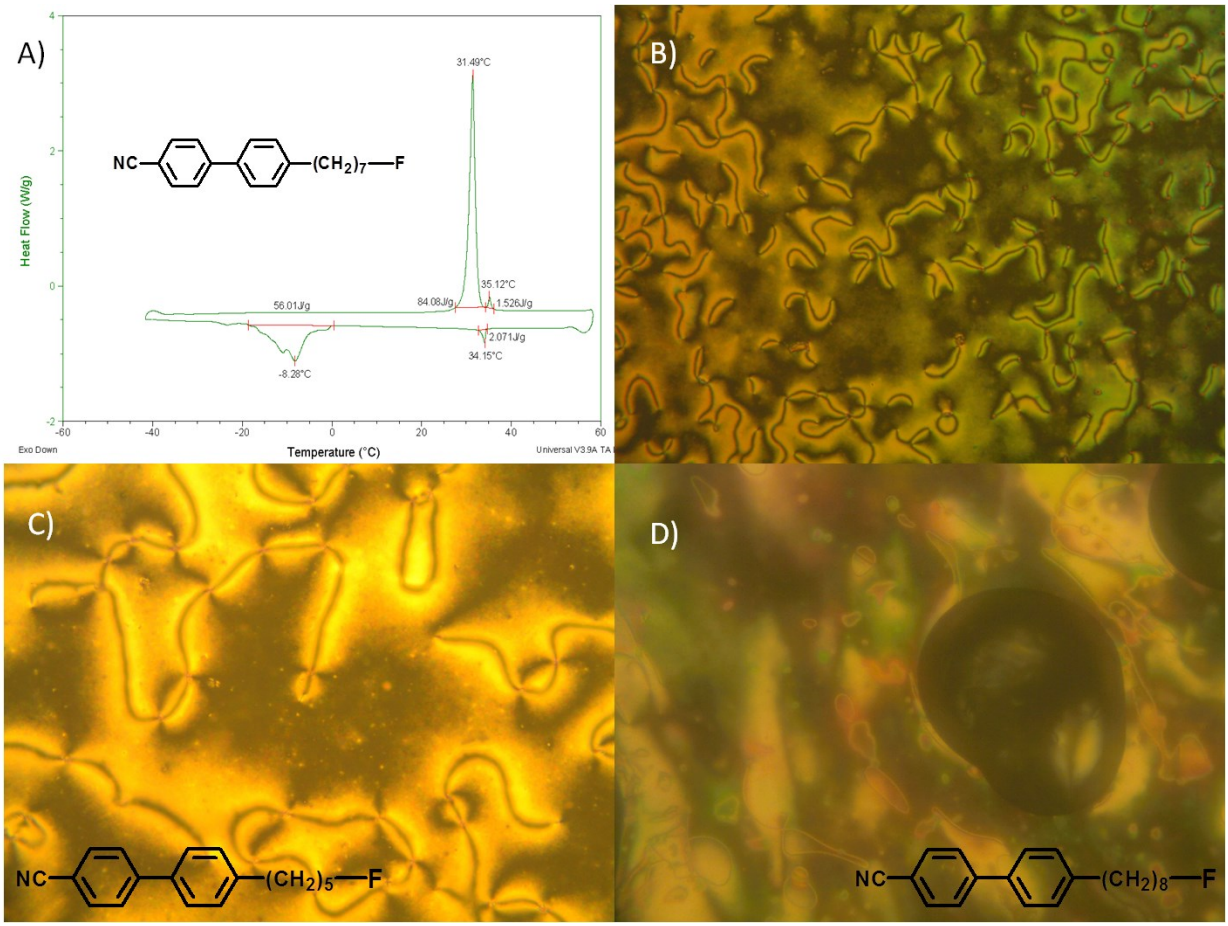


Figure 2. A) The DSC of F7CB (K 31.5 N 35.1 I 34.2 N -8.3 K). B) Optical microscopy image (crossed-polars) of F7CB at 25 °C during. C) Optical microscopy image (crossed-polars) of F5CB at 29 °C during. D) Optical microscopy image (crossed-polars) of F8CB at ~15 °C (image is foggy due to the absorbed moisture when the glass slide moved from freezer).

Next, two enantiotropic candidates F6CB and F7CB were selected to investigate the thermal behavior of their mixtures. The ratio of 50%:50% (Figure 3) and 75%: 25% both gave room temperature nematic mixtures. Similar to the individual component, these mixtures show supercooling properties. This 12 °C nematic phase found for the 50%:50% mixture is a good start but we are not satisfactory because of the relatively low clearing point (29.3 °C), which might hinder further applications.

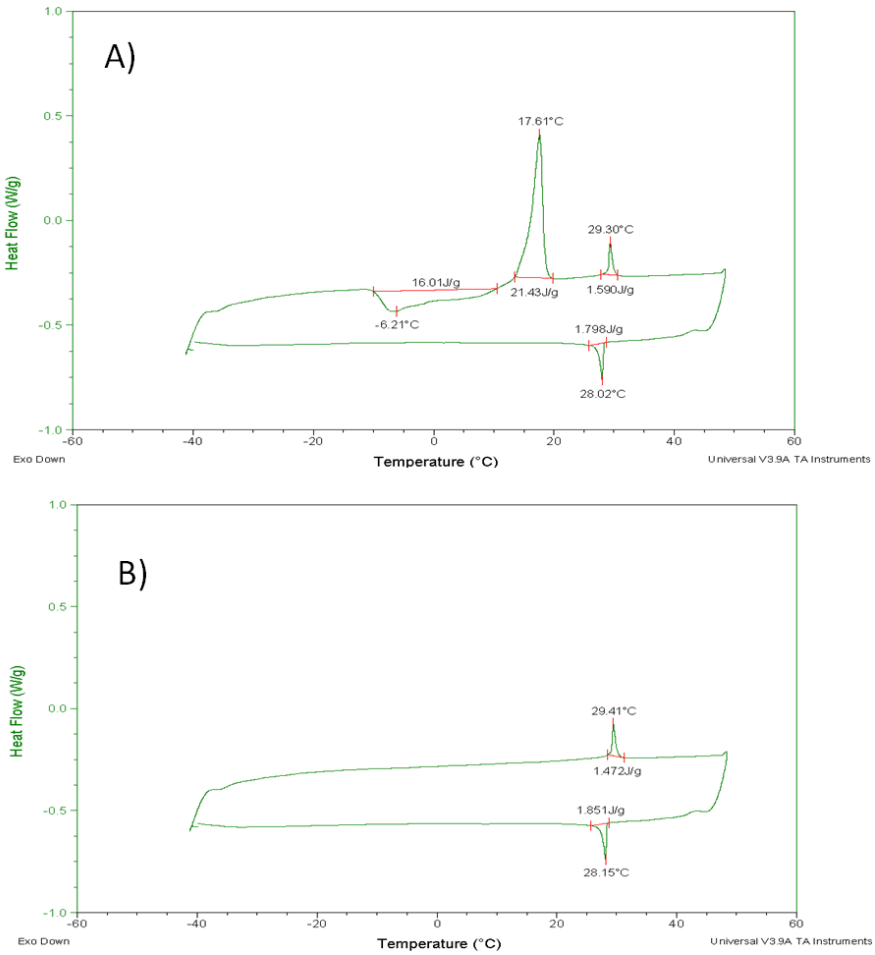


Figure 3. The DSC of the 50%:50% mixture of F6CB and F7CB. A) the second cycle. B) the third cycle. The sample didn't crystallize as low as -40 °C.

The behavior of a binary mixture made from one fluoroalkoxy cyanobiphenyl compound F6OCB and one fluoroalkyl cyanobiphenyl compound F6CB was then examined. We are delighted to see that when the molar percentage of F6CB ranges from 25% to 85% the resulting mixtures possesses a remarkably broad nematic phase down to -40 °C (the low temperature limitation of the DSC) (Figure 4). For example, the 50%:50% mixture exhibits a nematic phase from -40 to 46.6 °C (Figure 5). This may derive from the higher clearing point of F6OCB as well as the supercooling properties of both components. The mixture of F6CB (15%) and F6OCB (85%) also shows this supercooling property during the cooling cycle but then converts to crystal phase at about -40 °C. This sample also crystallized after one day storage whereas the other samples did not crystallize over a number of weeks.

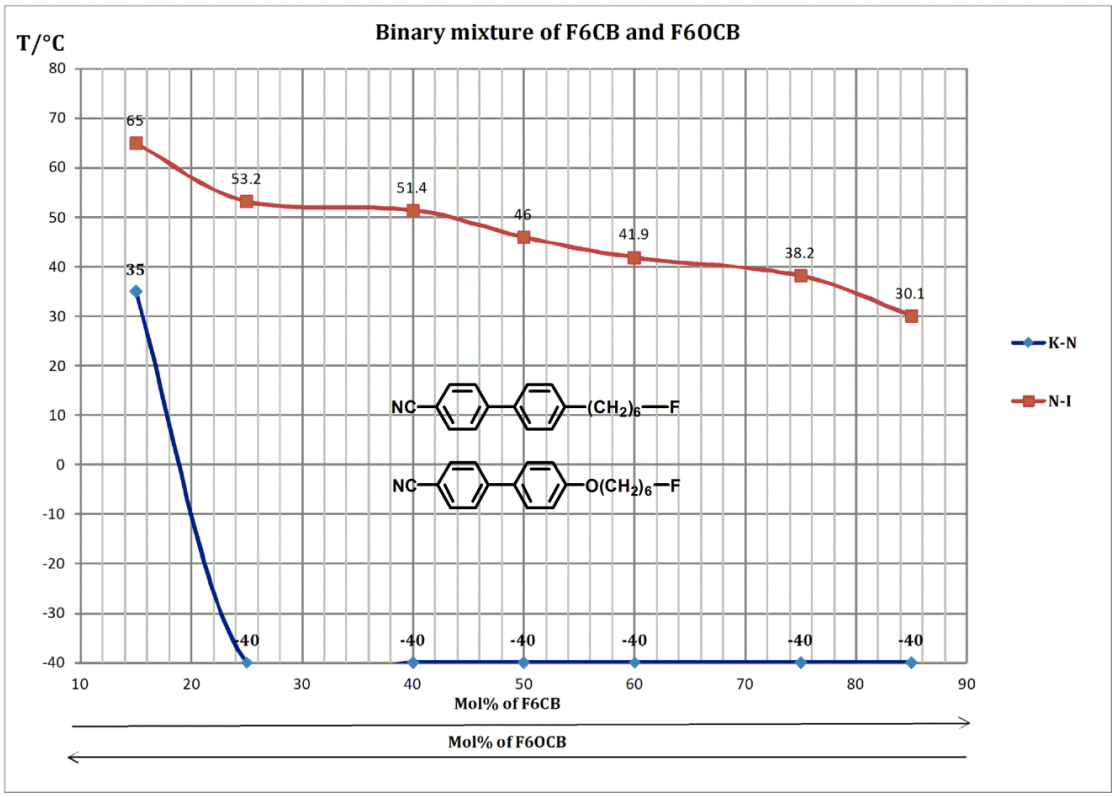


Figure 4. The phase behavior data of the binary mixtures of F6CB and F6OCB. (The lowest cooling temperature was down to -40 ˚C due to the limitations of the DSC).

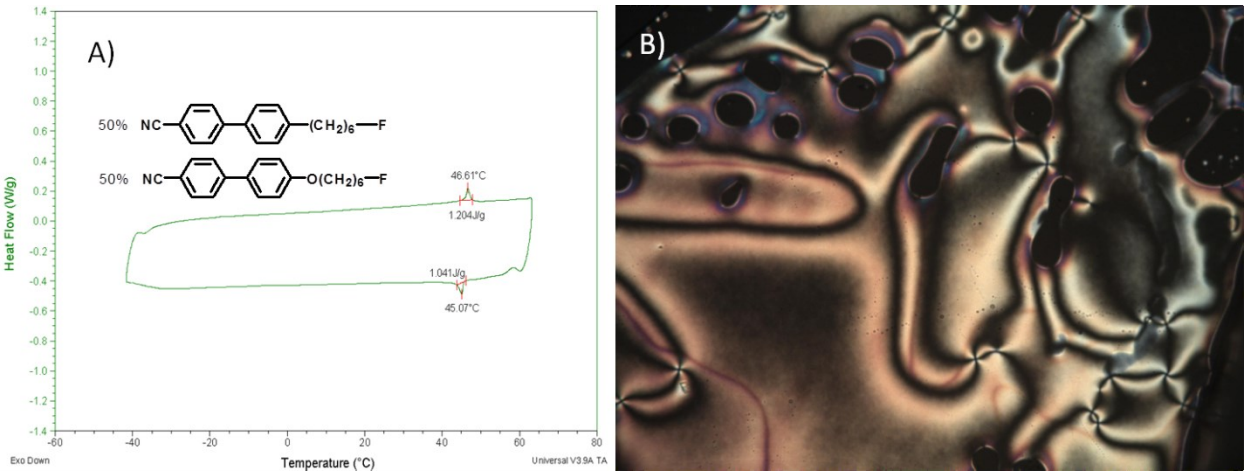


Figure 5. A) The DSC plot of the 50%:50% mixture of F6CB and F6OCB (the behavior repeats for three cycles). B) Optical microscopy image (crossed-polars) of the 50%:50% mixture of F6CB and F6OCB at 45 ˚C.

Another fluorinated K series compound F8CB, which exhibits a nematic phase below 19 °C, might not be a very useful mesogen by itself but a promising component to make liquid crystal mixtures with near ambient nematic phase. The idea is mixing it with other mesogens with higher nematic range. The first trial was a 50%:50% mixture of F8CB and F3OCB and the clearing point (T_{NI}) turned out to be 29 °C and not a significant improvement (Figure 6A). Next, F6OCB, which shows several K-K transitions during heating according to DSC (SI Figure 5), was mixed with F8CB in equal amount and the resulting mixture has a T_{NI} of 43 °C (Figure 6B). In addition, a 50%:50% mixture of F8CB and F8OCB was examined and the T_{NI} was increased to 40 °C (Figure 6C–D). These three mixtures all display supercooling properties according to DSC plots (no crystallization found). It seems that mesogens with an even higher nematic range are required to increase the T_{NI} of the mixtures for wider nematic range.

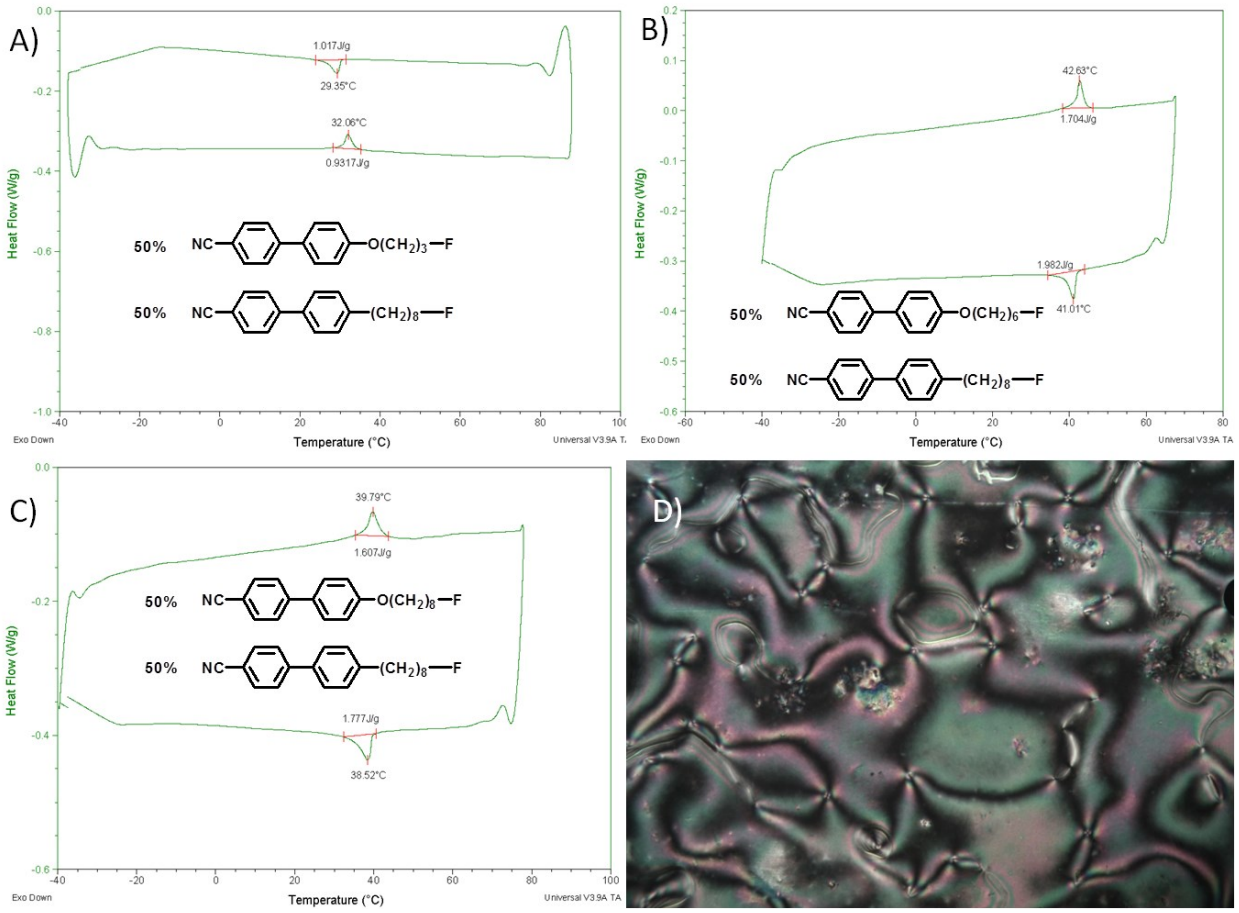


Figure 6. A) The DSC plot of the 50%:50% mixture of F3OCB and F8CB. B) The DSC plot of the 50%:50% mixture of F6OCB and F8CB. C) The DSC plot of the 50%:50% mixture of F8OCB and F8CB. D) Optical microscopy image (crossed-polars) of the 50%:50% mixture of F8OCB and F8CB at 38 °C.

In order to examine the influence of the terminal fluorination on a larger system, several alkoxycyano-*p*-terphenyl derivatives were prepared (Table 4, DSC plot of F5OCT is shown in Figure 7A). As expected, the K-N transition temperatures of these compounds are lower than the non-fluorinated versions while the clearing points slightly higher, resulting in a wider nematic range. Again, the formation of the smectic phase was suppressed by terminal fluorination. The thermal stability is consistent with the non-fluorinated analogues as DSC showed decompositions above ~280 °C (a trend of decreasing enthalpy changes in sequential cycles).

Furthermore, a 50%:50% mixture of F8CB and F5OCT was examined. Only one transition appears in DSC below 200 °C during heating (Figure 7B). However, POM observation shows that the clearing point is 168 °C. The mixture turns out to be a "soft" crystal at 25 °C, which may be explained that F8CB is in nematic state while F5OCT still in crystal phase. Upon heating, the whole mixture transfers to nematic phase at 115 °C. This binary mixture failed to form a uniform liquid crystal mixture in 50%:50% ratio.

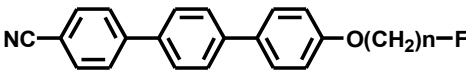
Compound #	n		
		F-terminated Thermal behavior (°C)	Non-F-version Thermal behavior (°C)
F3OCT	3	K 186 N 286 I Decomposed by DSC	K 190 SmB 207 N 282 I Decomposed by DSC
F4OCT	4	K 162 N 276 I Decomposed by DSC	K 121 Sm 185 N 272 I Decomposed by DSC
F5OCT	5	K 155 N 265 I Decomposed by DSC	K 104 SmF 130 SmB 172 N 253 I

Table 4. The thermal behavior of 4"-ω-fluoroalkoxy-4-cyano-*p*-terphenyl compounds FnOCT. (K = Crystal, N = Nematic, Sm = Smectic, SmA = Smectic A, SmB = Smectic B, SmF = Smectic F, I = Isotropic) Data available for the analogous parent nonsubsitituted alkoxy series is provided for comparison [4].

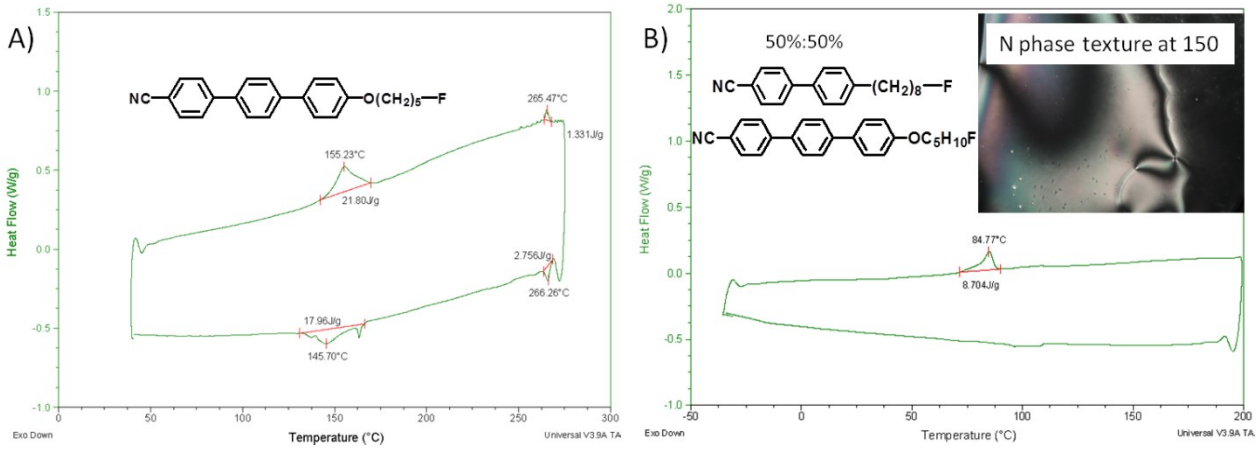


Figure 7. A) The DSC plot of F5OCT (K 155 N 265 I). B) The DSC plot and optical microscopy image (crossed-polars) of the 50%:50% mixture of F8CB and F5OCT.

5. Calculations of dipole moment and binding free energy (G_{BE})

To gain more insight into the effect of the fluorine-termination on the molecular properties, we calculated the dipole moment of the newly synthesized 4'-ω-fluoroalkoxy-4-cyanobiphenyl and 4'-ω-fluoroalkyl-4-cyanobiphenyl compounds. Figure 8 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 the dipole moments of 4'-ω-fluoroalkoxy-4-cyanobiphenyl and 4'-ω-fluoroalkyl-4-cyanobiphenyl compounds follow the same qualitative trend. 4'-ω-fluoroalkoxy-4-cyanobiphenyl compounds however have higher dipole moment than that of the corresponding 4'-ω-fluoroalkyl-4-cyanobiphenyl compound with the same alkyl chain length by ~0.8 D which reflects the effect of the electronegative O atom in the alkoxy tail. Both fluorine terminated alkoxy and alkyl series show a maximum in dipole moment at n=10 that is similar to hydroxyl-terminated mesogens which we investigated previously [17]. The gradually increasing dipole moment with increasing alkyl chain length up to n=10 is the consequence of the increasing distance between the polar CN and F ends in the molecules. However for longer alkyl

chain lengths, the aliphatic tail 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 mesogens. We note that our observations are similar to what have been found for surfactants; after a critical alkyl chain length the effective size of the surfactant molecules decreases due to conformational entropy effects [39-41].

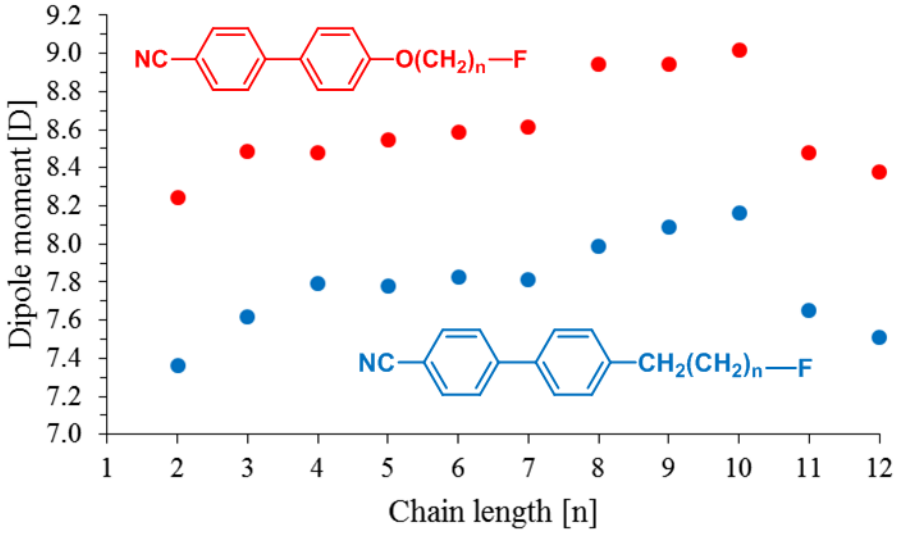


Figure 8. Calculated dipole moment (in Debye) as a function of chain length (n) , shown in the molecular formula of each mesogen class, for 4'-ω-fluoroalkoxy-4-cyanobiphenyl (red) and 4'-ω-fluoroalkyl-4-cyanobiphenyl compounds (blue).

To understand more about the interfacial ordering of the fluorine-terminated mesogens, we calculated the G_{BE} of the 4'-ω-fluoroalkoxy-4-cyanobiphenyl and 4'-ω-fluoroalkyl-4-cyanobiphenyl compounds together with the G_{BE} of the parent 4'-alkyl-4-cyanobiphenyl series using $Al(ClO_4)_3$, $Ga(ClO_4)_3$, and $Ni(ClO_4)_2$ metal salts (see details in the computational methods section). All calculated results can be found in Table.SI.2. We find that in all cases the calculated G_{BE} do not show any change as a function of the alkyl chain length within rounding error (0.01 eV). Additionally, different mesogen series, having different aliphatic tails, possess the same G_{BE} for the respective metal salts. Therefore, we conclude that the distant fluorine termination has no effect on the binding properties of the mesogen. This result is consistent with our previous findings that even PhCN can be a rational surrogate of 4'-pentyl-4-cyanobiphenyl (5CB) in G_{BE} calculations

[21,32-34]. We do see, however, difference between the G_{BE} of mesogens related to different metal salts. G_{BE} of each CN terminated mesogens are -0.46, -0.57, and -1.08 eV for $Al(ClO_4)_3$, $Ga(ClO_4)_3$, and $Ni(ClO_4)_2$ metal salts, respectively. Based on previous results [21,32-34], negative G_{BE} predicts homeotropic alignment at the mesogen-metal salt interface.

6. Optical study of the mixture of F7OCB and F8OCB on metal salt surfaces

Guided by the computational prediction that 4'-ω-fluoroalkoxy-4-cyanobiphenyl and 4'-ω-fluoroalkyl-4-cyanobiphenyl compounds should adopt homeotropic ordering, we performed the experiments using LC cells composed of two identically prepared metal salts-decorated surfaces to eliminate the confounding influence of LC-air interface on the orientation of LC. Consistent with the negative G_{BE} values, F7OCB and F8OCB mixtures (50 mol%:50 mol%) adopted homeotropic ordering on surfaces supported with $Al(ClO_4)_3$, $Ga(ClO_4)_3$, and $Ni(ClO_4)_2$ metal salts individually (Figure 9). Moreover, we hypothesize that a fluorine substituted chain may frustrate the smetic layer which would result in homeotropic orientation of LC at the free surface [21]. To study the anchoring at LC-air interface, we deposited LC mixtures in TEM grids with bottom surfaces coated with $Al(ClO_4)_3$, $Ga(ClO_4)_3$, and $Ni(ClO_4)_2$ metal salts individually, leaving the top surface exposed to air. We observed planar ordering of LC confined in TEM grids (Figure 9). The observation shows that the anchoring of LC mixtures at LC-air interface is not homeotropic, because the anchoring of LC at LC-metal salts surface is controlled to be homeotropic. This planar anchoring at the free surfaces has the potential application in designing a more sensitive and faster LC system to targeted analytes, because the elastic energy stored in the initial state of the LC can be released during the response.

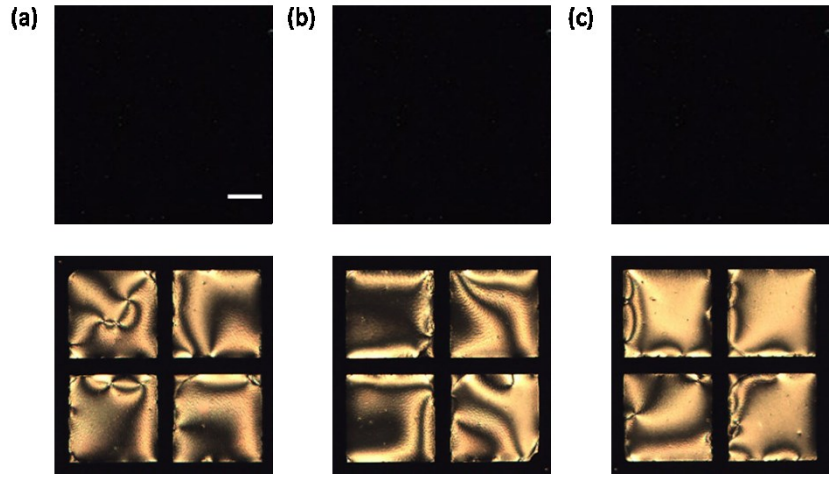


Figure 9. Optical micrographs (crossed polars) of LCs comprised of F7OCB and F8OCB (C_{F7OCB} = 50 mol%) mixtures supported on surfaces decorated with (a) $Al(ClO_4)_3$ (b) $Ga(ClO_4)_3$ (c) $Ni(ClO_4)_2$ (upper picture: sandwich cell, lower picture: TEM grid). Scale bar: 100 μm.

7. Conclusions

In this work the synthesis a series of fluorine tail-terminated alkoxy and alkyl cyanobiphenyl compounds and some cyano-*p*-terphenyl derivatives were presented and thermal behavior investigated. Comparison with the non-fluorinated K series and M series indicates that terminal fluorination generally decreases the K-N transition temperatures and the clearing points. Furthermore, the fluorination suppresses the formation of the smectic phase typically seen in M- and K- series compounds with longer length tails. In addition, several binary LC mixtures formed by the fluorine-terminated compounds were investigated and found exhibiting promising room temperature nematic phases with wide ranges. Optical study of a binary mixture F7OCB and F8OCB shows homeotropic ordering at the metal salts-decorated surfaces and planar ordering at the free surface. Further chemoresponsive analysis of these fluorinated materials is underway.

Acknowledgements

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external computational resource facilities at: the DoD High Performance Computing Modernization Program (US Air Force Research Laboratory DoD Supercomputing Resource Center (AFRL DSRC), the US Army Engineer Research and Development Center (ERDC), and the Navy DoD Supercomputing Resource Center (Navy DSRC), ARONC43623362), supported by the Department of Defense; the National Energy Research Scientific Computing Center (NERSC) through the U.S. DOE, Office of Science under Contract No. DE-AC02-05CH11231; and the Center for Nanoscale Materials (CNM) at Argonne National Laboratory (ANL) through the U.S. DOE, Office of Science under Con-tract No. DE-AC02-06CH11357.

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Synthesis and Properties of Fluorine tail-terminated Cyanobiphenyls and Terphenyls for Chemoresponsive Liquid Crystals

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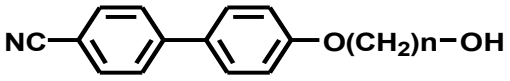
SI.1. Materials

Commercial-grade solvents were used without further purification. $PdCl_2$ was purchased 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 [1]. The 4-hydroxy-4'-bromobiphenyl was prepared according to literature method[2]. Triphenylphosphine and ethylenediamine were bought from Sigma-Aldrich. The terminal hydroxyacetylenes were purchased from GFS Organic Chemicals (Columbus, OH). 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.

SI.2. Synthesis of fluorine tail terminated alkoxy cyanobiphenyl/terphenyl compounds

SI.2.1 Synthesis of hydroxyalkoxy cyanobiphenyl compounds



n = 2

In a 250 ml round bottom flask with stir bar and bubbler was placed 4-cyano-4-hydroxydiphenyl (3.9 g 0.02 mmol, ethylene carbonate (3.6 g, 0.04 mmol), and dry DMF (30ml). Next, potassium carbonate (5.6 g, 0.04 mmol) was added and the mixture was stirred overnight at room temperature. There were some starting materials in TLC plate (25% EtOAC) and then it was heated up to 120°C. Then ethylene carbonate (1.8 g, 0.02 mmol) and potassium carbonate (3.6 g, 0.025 mmol). After 30 hours heating was removed. Bright yellow color solid was there with two by products. Mixture of water and 10% HCL (150 ml) was added drop wise to the mixture and product was filtered by suction filtration.

Yield- 4.69g (90.1%)

^{1}H NMR (400MHz, $CDCl_3$) δ (ppm): 2.08 (1H, t, *J* = 4.8 Hz), 4.02 (1H, q, *J* = 5.4 Hz), 4.17 (2H, m), 7.05 (2H, m), 7.55 (2H, m), 7.66 (2H, m),7.72 (2H, m); ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm): 61.4, 69.3, 110.2, 115.1, 119.0, 127.1, 128.4, 132.0, 132.5, 145.1, 159.2.

n = 6

To a stirred solution of 4'-hydroxy-4-cyanobipheyl (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. Next, 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 in 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%).

^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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

The data is consistent with the reference[3].

n = 7

In a 100 ml round bottom flask with stirbar was placed 4'-hydroxy-4-cyanobipheyl (2.7 g, 13.8 mmol), triphenylphosphine (4.5 g, 16.5 mmol), 1,8-heptanediol (2.2 g, 16.5 mmol) and dry THF (25 ml). The resulting solution was chilled in an ice bath and diisopropylazodicarboxylate (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%).

^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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.

n = 8

In a 100 ml round bottom flask with stirbar was placed 4'-hydroxy-4-cyanobipheyl (1.6 g, 9.6 mmol), triphenylphosphine (3.0 g, 11.5 mmol), 1,8-octanediol (1.7 g, 11.5 mmol) and dry THF (20 ml). The resulting solution was chilled in an ice bath and diisopropylazodicarboxylate (94%, 2.3 g, 11.5 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 2% ethyl acetate / 98% 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 white crystals (1.9 g, 64%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.69 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.8 Hz, 2H), 6.98 (d, J = 8.4 Hz, 2H), 3.99 (t, J = 6.4 Hz, 2H), 3.64 (q, J = 6.4 Hz, 2H), 1.85-1.81 (m, 2H), 1.64-1.60 (m, 2H), 1.52-1.45 (m, 2H), 1.43-1.36 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 159.8, 145.3, 132.6, 131.3, 128.3, 127.1, 119.1, 115.1, 110.0, 68.1, 63.0, 32.7, 29.3, 29.2, 26.0, 25.7, 22.0; GC/MS: only fragment found 243.18; 323.43 calc.

The data is consistent with the reference[4].

n = 9

To a stirred solution of 4'-hydroxy-4-cyanobipheyl (3.0 g, 15.0 mmol) in acetonitrile (50 mL) was added potassium carbonate (4.2 g, 30.0 mmol) and the mixture was kept under reflux for half an hour. Next, 9-bromononanol (3.4 g, 15.0 mmol) was added and the reaction was stirred overnight under reflux. The reaction was monitored by TLC until completion. The solvent was removed under reduced pressure and the product was extracted in 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 1: 4) to afford the desired product as white crystals (3.5 g, 69%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.69 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 4.00 (t, *J* = 6.8 Hz, 2H), 3.64 (t, *J* = 6.4 Hz, 2H), 1.84-1.77 (m, 2H), 1.61-1.54 (m, 2H), 1.49-1.44 (m, 2H), 1.38-1.30 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 159.8, 145.3, 132.6, 131.3, 128.3, 127.1, 119.1, 115.1, 110.0, 70.1, 68.1, 63.1, 32.8, 29.5, 29.4, 29.3, 29.2, 26.0, 25.7.

n = 10

In a 100 ml round bottom flask with stirbar was placed 4'-hydroxy-4-cyanobipheyl (1.6 g, 9.6 mmol), triphenylphosphine (3.0 g, 11.5 mmol), 1,10-decanediol (2.0 g, 11.5 mmol) and dry THF (20 ml). The resulting solution was chilled in an ice bath and diisopropylazodicarboxylate (94%, 2.3 g, 11.5 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 2% ethyl acetate / 98% 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 white crystals (1.9 g, 64%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.66 (dd, ^{1}J = 6.4 Hz, ^{2}J = 1.2 Hz, 2H), 7.63 (dd, ^{1}J = 6.4 Hz, ^{2}J = 1.6 Hz, 2H), 7.52 (dd, ^{1}J = 6.8 Hz, ^{2}J = 2.4 Hz, 2H), 6.99 (dd, ^{1}J = 6.8 Hz, ^{2}J = 2.0 Hz, 2H), 4.00 (t, J = 6.4 Hz, 2H), 3.64 (t, J = 6.8 Hz, 2H), 1.81 (m, 2H), 1.77 (m, 2H), 1.56 (m, 2H), 1.43 (m, 2H), 1.36-1.32 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 159.8, 145.3, 132.6, 131.2, 128.3, 127.1, 119.1, 115.1, 110.0, 70.0, 68.2, 29.6, 29.5, 29.4, 29.3, 29.2, 26.0, 25.8, 22.0.
The data is consistent with the reference[5].

n = 11

In a 100 ml round bottom flask with stirbar was placed 4'-hydroxy-4-cyanobipheyl (1.6 g, 9.6 mmol), triphenylphosphine (3.0 g, 11.5 mmol), 1,11-undecanediol (2.2 g, 11.5 mmol) and dry THF (20 ml). The resulting solution was chilled in an ice bath and diisopropylazodicarboxylate (94%, 2.3 g, 11.5 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 2% ethyl acetate / 98% 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 white crystals (1.9 g, 64%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.69 (dd, ^{1}J = 6.4 Hz, ^{2}J = 1.6 Hz, 2H), 7.63 (dd, ^{1}J = 6.4 Hz, ^{2}J = 3.2 Hz, 2H), 7.52 (dt, ^{1}J = 8.8 Hz, ^{2}J = 2.0 Hz, 2H), 6.98 (dt, ^{1}J = 8.8 Hz, ^{2}J = 3.2 Hz, 2H), 4.00 (t, J = 6.8 Hz, 2H), 3.64 (t, J = 6.8 Hz, 2H), 1.81 (m, 2H), 1.55 (m, 2H), 1.47 (m, 2H), 1.36-1.31 (m, 12H).
The data is consistent with the reference[3].

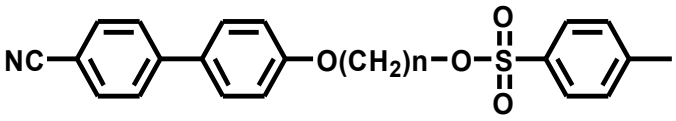
n = 12

In a 100 ml round bottom flask with stirbar was placed 4'-hydroxy-4-cyanobipheyl (1.6 g, 9.6 mmol), triphenylphosphine (3.0 g, 11.5 mmol), 1,12-dodecanediol (2.2 g, 11.5 mmol) and dry THF (20 ml). The resulting solution was chilled in an ice bath and

diisopropylazodicarboxylate (94%, 2.3 g, 11.5 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 2% ethyl acetate / 98% 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 white crystals (1.9 g, 64%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.66 (dd, ^1J = 6.4 Hz, ^2J = 1.6 Hz, 2H), 7.62 (dd, ^1J = 6.4 Hz, ^2J = 3.2 Hz, 2H), 7.51 (dt, ^1J = 8.8 Hz, ^2J = 2.0 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 3.98 (t, J = 6.4 Hz, 2H), 3.61 (q, J = 6.0 Hz, 2H), 1.82 (m, 2H), 1.62 (m, 2H), 1.50 (m, 2H), 1.33-1.26 (m, 14H).
The data is consistent with the reference[5].

SI.2.2 Synthesis of 4'-[[ω-[[(4-methylphenyl)sulfonyl]alkyl]oxyl]-4-cyanobiphenyls



n = 2

4'-[[2-[[(4-Methylphenyl)sulfonyl]ethyl]oxyl]-4-cyanobiphenyl

In a 100ml flask 4-(2-hydroxyalkyloxy)-4-cyanobiphenyl, (1.2 g, 5.0 mmol), triethylamine (0.67 g, 6.57 mmol) and 10 ml of DCM was added. The mixture was cooled to a temperature about 0-5°C and cautiously charged with a solution of p-toluenesulfonyl chloride (0.87 g, 4.5 mmol) in DCM (2.5 ml) over 30 minutes via additional funnel. Once the addition was complete, the reaction mixture was warmed to 18°C- 22°C and stirred overnight. To this solution was added 6N hydrochloric acid (0.55ml) cautiously while maintaining temperature below 25°C. Then 25 ml of DCM and

25 ml of water were added. The aqueous phase was removed, and the organic phase was washed with water, dried over magnesium sulfate, filtered over Celite. The filtrate was concentrated and the residue was purified by a silica gel column eluted by (90% of Hexane and 10% of Ethylacetate, polarity was increased gradually up to 40%), affording a white crystallized solid as final product. NMR was carried out for the main product (Yield: 1.78gm, 91.7%).

^{1}H NMR (400MHz, $CDCl_3$) δ (ppm): 7.6 (2H, d), 7.5 (2H, q), 7.5 (2H, q), 7.3(2H, quin), 7.2 (2H, d), 6.9 (2H, d), 4.4 (2H, d), 4.2 (2H, d), 1.5 (4H,q); ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm): 158.6, 145.04, 144.99, 132.83, 132.62, 132.27, 129.90, 128.41, 128.04, 127.18, 115.16, 67.95, 65.58, 21.3.

n = 6

4'-[[6-[[(4-Methylphenyl)sulfonyl]hexyl]oxyl]-4-cyanobiphenyl

A 100 mL flask was charged with 4'-[(6-hydroxyhexyl)oxy] -4-cyanobiphenyl (2.0 g, 6.8 mmol), triethylamine (1.2 mL, 0.89 g, 8.8 mmol) and DCM (5 mL). The mixture was cooled to a temperature of about 0-5°C and cautiously charged with a solution of *p*-toluenesulfonyl chloride (1.2 g, 6.1 mmol) in DCM (2.5 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, dried over magnesium sulfate, filtered over Celite. The filtrate was concentrated and the residue was dissolved in heptane and concentrated again to afford a final product (Yield: 2.2 g, 72.3%)
mp 120°C; FTIR 3515.66, 3037.61, 2941.39, 2867.82, 2218.74, 1336.05, 1523.55, 1178.28 $cm^{-1;}$ ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.69 (d, *J* = 9.0 Hz, 2H), 7.63 (d, *J* = 8.64 Hz, 2H), 7.57 (d, *J* = 8.84 Hz, 2H), 6.99 (d, *J* = 8.84 Hz, 2H), 4.46 (dt, *J* = 47.37 Hz, 6.08 Hz, 2H), 4.01 (t, *J* = 6.42 Hz, 2H), 1.83 (quint, J = 6.86 Hz, 2H), 1.81-1.68 (m, 2H), 1.56-1.51 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 159.72, 145.28, 132.59,

131.35, 128.36, 127.10, 119.14, 115.07, 110.06, 84.88, 83.25, 67.93, 30.45, 30.26, 29.13, 25.75, 25.07, 25.02

n = 7

4'-[[7-[[(4-Methylphenyl)sulfonyl]heptyl]oxyl]-4-cyanobiphenyl

A 100 mL flask was charged with 4'-[(7-hydroxyheptyl)oxy]-4-cyanobiphenyl (2.2 g, 7.2 mmol), triethylamine (0.89 g, 8.7 mmol) and DCM (6.0 mL). The mixture was cooled to a temperature of about 0-5°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%)
^{1}H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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 = 8

4'-[[8-[[(4-Methylphenyl)sulfonyl]octyl]oxyl]-4-cyanobiphenyl

A 100 mL flask was charged with 4'-[(8-hydroxyoctyl)oxy]-4-cyanobiphenyl (2.4 g, 7.4 mmol), triethylamine (1.34 mL, 0.98 g, 9.6 mmol) and DCM (6.0 mL). The mixture was cooled to a temperature of about 0-5°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: 2.5 g, 71%)

mp 72.6-73.5°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.79 (d, *J* = 8.8 Hz, 2H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 4.01 (m, 4H), 2.44 (s, 3H), 1.77 (m, 2H), 1.64 (m, 2H), 1.43 (m, 2H), 1.34-1.26 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 159.8, 145.3, 144.7, 133.2, 132.6, 131.3, 129.8, 128.3, 127.9, 127.1, 119.2, 115.1, 110.0, 70.6, 68.1, 29.2, 29.1, 28.9, 28.8, 25.9, 25.3, 21.3.

n = 9

4’-[[9-[[(4-Methylphenyl)sulfonyl]nonyl]oxyl]-4-cyanobiphenyl

A 100 mL flask was charged with 4'-[(9-hydroxynonanyl)oxy]-4-cyanobiphenyl (2.5 g, 7.4 mmol), trimethylamine (1.34 mL, 0.98 g, 9.6 mmol) and DCM (6.0 mL). The mixture was cooled to a temperature of about 0-5 °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: 2.3 g, 63%)

mp 73.3-74.5°C;^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.79 (d, *J* = 8.8 Hz, 2H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 4.01 (m, 4H), 2.45 (s, 3H), 1.77 (m, 2H), 1.68 (m, 2H), 1.47 (m, 2H), 1.38-1.28 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 159.8, 145.3, 144.6, 133.3, 132.6, 129.8, 128.3, 127.9, 127.1, 119.1, 115.1, 110.1, 70.7, 68.2, 29.4, 29.3, 29.2, 28.9, 26.0, 25.3, 21.6.

n = 10

4’-[[10-[[(4-Methylphenyl)sulfonyl]decyl]oxyl]-4-cyanobiphenyls

A 100 mL flask was charged with 4'-[(10-hydroxydecanyl)oxy]-4-cyanobiphenyl (3.5 g, 10.0 mmol), triethylamine (1.8 g, 17.8 mmol) and DCM (20.0 mL). The mixture was cooled to a temperature of about 0-5 °C and cautiously charged with a solution of *p*-toluenesulfonyl chloride (2.6 g, 13.7 mmol) in DCM (10.0 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 (0.7 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: 4.0 g, 80%)
^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.79 (dd, ^{1}J = 6.4 Hz, ^{2}J = 1.6 Hz, 2H), 7.69 (dd, ^{1}J = 6.8 Hz, ^{2}J = 2.0 Hz, 2H), 7.64 (dd, ^{1}J = 8.0 Hz, ^{2}J = 1.6 Hz, 2H), 7.53 (dd, ^{1}J = 6.4 Hz, ^{2}J = 2.0 Hz, 2H), 7.35 (dd, ^{1}J = 8.4 Hz, ^{2}J = 2.0 Hz, 2H), 6.99 (dd, ^{1}J = 6.8 Hz, ^{2}J = 2.0 Hz, 2H), 4.02 (m, 4H), 2.44 (s, 3H), 1.79 (m, 2H), 1.62 (m, 2H), 1.45 (m, 2H), 1.32-1.25 (m, 14H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 159.8, 145.3, 144.6, 133.3, 132.6, 129.8, 128.3, 127.9, 127.1, 119.2, 115.1, 110.1, 70.7, 68.1, 29.4, 29.3, 29.2, 28.9, 28.8, 26.0, 25.3, 21.7.

n = 11

4’-[[11-[[(4-Methylphenyl)sulfonyl]undecyl]oxyl]-4-cyanobiphenyl

A 100 mL flask was charged with 4'-[(11-hydroxyundecanyl)oxy]biphenyl-4-cyanobiphenyl (2.6 g, 7.0 mmol), triethylamine (1.3 g, 12.5 mmol) and DCM (20.0 mL). The mixture was cooled to a temperature of about 0-5 °C and cautiously charged with a solution of *p*-toluenesulfonyl chloride (1.83 g, 9.6 mmol) in DCM (10.0 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: 1.8 g, 50%)

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.79 (d, J = 8.8 Hz, 2H), 7.69-7.62 (m, 4H), 7.52 (dd, ^{1}J = 6.4 Hz, ^{2}J = 2.0 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 6.98 (dd, ^{1}J = 6.4 Hz, ^{2}J = 1.6 Hz, 2H), 4.01 (m, 4H), 2.44 (s, 3H), 1.79 (m, 2H), 1.63 (m, 2H), 1.46 (m, 2H), 1.33-1.24 (m, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 159.8, 145.3, 144.6, 133.3, 132.6, 129.8, 128.3, 127.9, 127.1, 119.1, 115.1, 110.1, 70.7, 68.2, 29.5, 29.4, 29.3, 29.2, 28.9, 28.8, 26.0, 25.3, 21.6.

n = 12

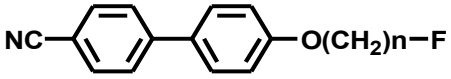
4'-[[12-[[(4-Methylphenyl)sulfonyl]dodecyl]oxyl]-4-cyanobiphenyl

A 100 mL flask was charged with 4'-[(12-hydroxydodecanyl)oxy]-4-cyanobiphenyl (2.7 g, 7.0 mmol), triethylamine (1.3 g, 12.5 mmol) and DCM (20.0 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 (1.83 g, 9.6 mmol) in DCM (10.0 mL) over 30 minutes via additional funnel. Once the addition was complete, the reaction mixture was warm 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: 1.6 g, 44%)

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.79 (dd, ^{1}J = 8.4 Hz, ^{2}J = 1.6 Hz, 2H), 7.69 (dd, ^{1}J = 8.0 Hz, ^{2}J = 1.6 Hz, 2H), 7.64 (dd, ^{1}J = 8.0 Hz, ^{2}J = 2.0 Hz, 2H), 7.52 (d, ^{1}J = 7.6 Hz, ^{2}J = 2.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 6.99 (dd, ^{1}J = 8.8 Hz, ^{2}J = 2.4 Hz, 2H), 4.01 (m, 4H), 2.45 (s, 3H), 1.80 (m, 2H), 1.63 (m, 2H), 1.46 (m, 2H), 1.30-1.24 (m, 14H); ^{13}C

NMR ($CDCl_3$, 100 MHz) δ (ppm): 159.8, 145.3, 144.6, 133.3, 132.6, 141.2, 129.8, 129.6, 128.3, 127.9, 127.1, 119.1, 115.1, 110.0, 70.7, 68.2, 29.6, 29.5, 29.4, 29.3, 29.2, 28.9, 28.8, 26.0, 25.3, 21.6.

SI.2.3 Synthesis of 4'-(ω-fluoroalkoxy)-4-cyanobiphenyls



n = 2

4'-(2-Fluoroethoxy)-4-cyanobiphenyl

To a solution of 4'-[[2-[[(4-methylphenyl)sulfonyl]diyl]oxyl][1,1'-biphenyl]-4-carbonitrile (0.762 g, 2.0 mmol) in *t*-amylalcohol (20 mL) was added CsF (0.607g, 4.0mmol). The mixture was heated up to 70℃ and stirred for12 hours at reflux. When checked by TLC starting material remained, and so an additional 20% of CsF(0.176g) was added. Reaction was heated for another 4 hours in same temperature. Water (30 mL) and diethyl ether (30 mL) were added and the phases were separated. The organic phase was dried over magnesium sulfate and evaporated under reduced pressure. The desired product was purified by column chromatography using ethyl acetate:hexane (1:4) as eluent (Yield: 0.35 g, 72.6%)

^{1}H NMR (400MHz, $CDCl_3$) δ (ppm): 4.30 (2H, m), 4.83 (2H, m), 7.06 (2H, dt, ^1J = 6.8 Hz, ^2J = 2.8 Hz), 7.57 (2H, dt, ^1J = 8.4 Hz, ^2J = 1.2 Hz), 7.66 (2H, dt, ^1J = 8.0 Hz, ^2J = 0.8 Hz), 7.73 (2H, dt, ^1J = 8.0 Hz, ^2J = 0.8 Hz); ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm): 67.2 (d, J = 20.5 Hz, 1C), 81.8 (d, J = 230.1 Hz, 1C), 110.2, 115.2, 119.0, 127.1, 128.4, 132.1, 132.6, 145.0, 159.0; ^{19}FNMR (376 MHz, $CDCl_3$) δ -223.83 (m, 1F); IR (cm^{-1}): 3040, 2967, 2888, 2223, 1600, 1491, 1242, 1047, 813; GC/MS: 241.12 found 241.26 calc.

DSC phase transition: K 97 I N 70 K

POM phase transition: K 95.6 N 69.4.

n = 3

4'-(3-Fluoropropoxy)-4-cyanobiphenyl (F3OCB)

To a clean dry Schlenk flask 4-hydroxy-4'-cyanobiphenyl (2.0 g, 10.24 mmol) was added to a suspension of DMF (35 mL) and potassium carbonate (1.7 g. 12.3 mmol) and stirred for 1 hour. To this solution was added 1-bromo-3-fluoropentane (1.73 g, 12.3 mmol) and the reaction mixture was heated at 102°C for 12 hours. The reaction mixture was monitored by TLC which indicated the absence of reactants. The reaction was cooled to room temperature and poured into the ice water. The precipitate was filtered and dried under vacuum. The mixture was separated by column chromatography using hexane:ethyl acetate (17:3); (Yield: 1.98 g, 68.2%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.72 (dt, ^{1}J = 8.0 Hz, ^{2}J = 0.8 Hz, 2H), 7.68 (dt, ^{1}J = 8.0 Hz, ^{2}J = 0.8 Hz, 2H), 7.56 (m, 2H), 7.03 (dt, ^{1}J = 6.8 Hz, ^{2}J = 2.0 Hz, 2H), 4.71 (dt, ^{1}J = 47.2. Hz, ^{2}J = 6.4 Hz, 2H), 4.19 (t, J = 6.0 Hz, 2H), 2.27 (m, 2H); ^{13}CNMR (100 MHz, $CDCl_3$) δ (ppm): 159.4, 145.2, 132.6, 131.7, 128.4, 127.1, 119.1, 115.1, 110.2, 80.6 (d, J = 163.6 Hz), 63.7 (d, J = 4.9 Hz), 30.4 (d, J = 19.9 Hz); ^{19}FNMR (376 MHz, $CDCl_3$) δ -222.40 (m, 1F); IR (cm^{-1}): 2973, 2908, 2880, 2230, 1604, 1494, 1178, 818; GC/MS: 255.10 found 255.29 calc.

DSC phase transition: K 78.2 N 53.1 I

POM phase transition: K 78.0 N 60 I

n = 4

4'-(4-Fluorobutoxy)-4-cyanobiphenyl (F4OCB)

To a clean dry Schlenk flask was added 4-hydroxy-4'-cyanobiphenyl (2.0 g, 10.24 mmol) in a suspension of DMF (35 mL) and potassium carbonate (1.7 g. 12.3 mmol) and stirred for 1 hour. To this solution was added 1-bromo-4-fluorobutane (1.91 g. 12.3 mmol) and the reaction mixture was heated at 120°C for 12 hours. The reaction mixture was monitored by TLC which indicated the absence of reactants. The reaction was stopped and cooled to room temperature and poured into the ice water. The precipitate was filtered and dried under vacuum. The mixture was separated by column chromatography using hexane:ethyl acetate (17:3); (Yield: 1.98 g, 68.2%); ^{1}H NMR (400 MHz, $CDCl_3$) δ

(ppm): 7.72-7.62 (m, 4H), 7.54 (d, J = 8.8 Hz, 2H), 7.01 (d, J = 8.8 Hz, 2H), 4.57 (dt, ^{1}J = 52.3. Hz, ^{2}J = 6.0 Hz, 2H), 4.08 (t, J = 6.0 Hz, 2H), 1.95 (m, 4H); ^{13}CNMR (100 MHz, $CDCl_3$) δ (ppm): 159.6, 145.2, 132.6, 131.4, 128.4, 127.1, 119.1, 115.1, 110.1, 83.8 (d, J = 163.8 Hz), 67.5, 27.2 (d, J = 19.9 Hz), 25.4 (d, J = 4.9 Hz); ^{19}FNMR (376 MHz, $CDCl_3$) δ (ppm): -218.34 (m, 1F); IR (cm^{-1}): 3076, 2947, 2928, 2225, 1600, 1493, 1251, 1053, 812; GC/MS: 269.09 found 269.31 calc.

DSC Phase Transition: K 69.6 N 65 I

POM Phase Transition: K 67.5 N 65 I

n = 5

4'-(5-Fluoropentyloxy)-4-cyanobiphenyl (F5OCB)

To a clean dry Schlenk flask was added 4-hydroxy-4'-cyanobiphenyl (2.0 g, 10.24 mmol) in a suspension of DMF (35 mL) and potassium carbonate (1.7 g. 12.3 mmol) and stirred for 1 hour. To this solution was added 1-bromo-5-fluoropentane (2.08 g, 12.3 mmol) and the reaction mixture was heated at 120°C for 12 hours. The reaction mixture was monitored by TLC which indicated the absence of reactants. The reaction was stopped and cooled to room temperature and poured into the ice water. The precipitate was filtered and dried under vacuum. The mixture was separated by column chromatography using hexane:ethyl acetate (17:3); (Yield: 1.98, 68.2%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.72 (dt, ^{1}J = 8.0 Hz, ^{2}J = 0.8 Hz, 2H), 7.67 (dt, ^{1}J = 8.0 Hz, ^{2}J = 0.8 Hz, 2H), 7.55 (d, ^{1}J = 8.0 Hz, ^{2}J = 0.8 Hz, 2H), 7.01 (dd, ^{1}J = 6.8 Hz, ^{2}J = 2.0 Hz, 2H), 4.52 (dt, ^{1}J = 47.2 Hz, ^{2}J = 6.0 Hz, 2H), 4.06 (t, J = 6.4 Hz, 2H), 1.92-1.77 (m, 4H), 1.65 (m, 2H); ^{13}CNMR (100 MHz, $CDCl_3$) δ (ppm): 159.7, 145.3, 132.6, 131.4, 128.4, 127.1, 119.1, 115.1, 110.1, 84.0 (d, J = 163.6 Hz), 67.8, 30.2 (d, J = 19.5 Hz), 28.9, 22.0 (d, J = 9.2 Hz); ^{19}FNMR (376 MHz, $CDCl_3$) δ (ppm): -218.47 (m, 1F). IR (cm^{-1}): 3044, 2742, 2865, 2223, 1600, 1494, 1178, 1051, 810; GC/MS: 283.08 found 283.34 calc.

DSC Phase Transition: K 46.5 N 61.2 I

POM Phase Transition: K 46.6 N 60.8 I

n = 6

4'-(6-Fluorohexyloxy)-4-cyanobiphenyl (F6OCB)

To a solution of 4'-[[6-[[(4-methylphenyl)sulfonyl]hexyl]oxyl][1,1'-biphenyl]-4-carbonitrile (2.2 g, 4.89 mmol) in t-amylalcohol (25 mL) was added CsF (1.48g, 9.78 mmol). The mixture was stirred over 12 hours at reflux. The residue was dissolved in water (15 mL) and extracted from the aqueous phase 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 using ethyl acetate:hexane (1:4) as eluent (Yield: 0.8 g, 55%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.71 (dt, ^{1}J = 8.0 Hz, ^{2}J = 0.8 Hz, 2H), 7.66 (dt, ^{1}J = 8.4 Hz, ^{2}J = 0.8 Hz, 2H), 7.55 (d, ^{1}J = 8.0 Hz, ^{2}J = 1.2 Hz, 2H), 7.01 (dd, ^{1}J = 6.8 Hz, ^{2}J = 2.0 Hz, 2H), 4.52 (dt, ^{1}J = 47.2 Hz, ^{2}J = 6.0 Hz, 2H), 4.05 (t, J = 6.4 Hz, 2H), 1.86 (m, 2H), 1.83-1.72 (m, 2H), 1.58-1.52 (m, 4H); ^{13}CNMR (100 MHz, $CDCl_3$) δ (ppm): 159.7, 145.3, 132.6, 131.4, 128.3, 127.1, 119.1, 115.1, 110.1, 84.0 (d, J = 163.4 Hz), 67.9, 30.3 (d, J = 19.4 Hz), 29.1, 25.7, 25.0 (d, J = 5.2 Hz); ^{19}FNMR (376 MHz, $CDCl_3$) δ (ppm): -218.34 (m, 1F); IR (cm^{-1}): 2944, 2872, 2223, 1601, 1116, 1053, 812; GC/MS: 297.15 found 297.37 calc.

DSC phase transition: K1 46.5 K2 55.25 K3 61.19 N 66.99 I

POM phase transition: K1 48.5 K2 57.5 N 66.57 I

n = 7

4'-(7-Fluoroheptyloxy)-4-cyanobiphenyl (F7OCB)

To a solution of 4'-[[7-[[(4-methylphenyl)sulfonyl]heptyl]oxyl]-4-cyanobiphenyl (1.84 g, 4.0 mmol) in *t*-amyl alcohol (25 mL) was added CsF (1.21g, 8.0 mmol). The mixture was stirred over 12 hours at reflux. The residue was dissolved in water (15 mL) and extracted from the aqueous phase 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 (1:20) as white

crystals, which was then recrystallized from *iso*-octane as white crystals. (Yield: 708 mg, 59%)

^{1}H NMR ($CDCl_3$, 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), 4.45 (td, ^{1}J = 47.2 Hz, ^{2}J = 6.4 Hz, 2H), 4.01 (t, J = 6.0 Hz, 2H), 1.80 (m, 2H), 1.69 (m, 2H), 1.51-1.42 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 159.8, 145.3, 132.6, 131.3, 128.3, 127.1, 119.1, 115.1, 110.0, 84.6 (d, J = 163.0 Hz), 68.0, 30.3 (d, J = 19.4 Hz), 29.1, 29.0, 26.0, 25.1 (d, J = 5.3 Hz); ^{19}FNMR ($CDCl_3$, 376 MHz) δ (ppm): -218.14 (m, 1F); IR (cm^{-1}): 3043, 2938, 2860, 2226, 1601, 1494, 1248, 1177, 822; GC/MS: 311.25 found 311.39 calc.

DSC phase transition: K 51.84 N 67.29 I

POM Phase transition: K 50.8 N 66.8 I

n = 8

4'-(8-Fluorooctyloxy)-4-cyanobiphenyl (F8OCB)

To a solution of 4'-[[8-[[(4-methylphenyl)sulfonyl]octyl]oxyl]-4-cyanobiphenyl (1.9 g, 4.0 mmol) in *t*-amylalcohol (25 mL) was added CsF (1.21g, 8.0 mmol). The mixture was stirred over 12 hours at reflux. The residue was dissolved in water (15 mL) and extracted from the aqueous phase with diethyl ether (15 mL). The organic phase was dried over magnesium sulfate and evaporated under reduced pressure. The desired product was purified by column chromatography eluted by ethyl acetate:hexane (1:20) as a oil, which was then crystallized as white crystals. (Yield: 1.2 g, 92%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.69 (td, ^{1}J = 8.4 Hz, ^{2}J = 1.6 Hz, 2H), 7.63 (td, ^{1}J = 8.0 Hz, ^{2}J = 1.2 Hz, 2H), 7.53 (td, ^{1}J = 8.8 Hz, ^{2}J = 2.0 Hz, 2H), 6.99 (td, ^{1}J = 8.8 Hz, ^{2}J = 2.0 Hz, 2H), 4.44 (td, ^{1}J = 47.2 Hz, ^{2}J = 6.4 Hz, 2H), 4.00 (t, J = 6.8 Hz, 2H), 1.81 (m, 2H), 1.77-1.65 (m, 2H), 1.51-1.39 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 159.8, 145.3, 132.6, 131.3, 128.3, 127.1, 119.2, 115.1, 110.0, 84.07 (d, J = 163.0 Hz), 68.1, 30.4 (d, J = 19.2 Hz), 29.4, 29.3, 29.2, 26.0, 25.1 (d, J = 5.3 Hz); ^{19}FNMR ($CDCl_3$,

376 MHz) δ (ppm): -218.09 (m, 1F); IR (cm^{-1}): 3043, 2938, 2860, 2226, 1601, 1494, 1248, 1177, 822; GC/MS: 325.26 found 325.42 calc.

DSC phase transition: K1 32.29 K2 37.24 K3 54.20 N 70.66 I

POM phase transition: K 53.0 N 70.2 I

n = 9

4'-(9-Fluorononyloxy)-4-cyanobiphenyl (F9OCB)

To a solution of 4'-[[9-[[(4-methylphenyl)sulfonyl]nonanyl]oxyl]-4-cyanobiphenyl (2.0 g, 4.0 mmol) in *t*-amylalcohol (25 mL) was added CsF (1.21g, 8.0 mmol). The mixture was stirred over 12 hours at reflux. The residue was dissolved in water (15 mL) and extracted from the aqueous phase 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 (1:20) as a white solid (Yield: 0.98 g, 72%), which was then recrystallized from hexanes as a white powder. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.68 (d, J = 7.6 Hz, 2H), 7.64 (dt, ^{1}J = 7.6 Hz, ^{2}J = 1.6 Hz, 2H), 7.53 (dd, ^{1}J = 6.8 Hz, ^{2}J = 2.0 Hz, 2H), 6.99 (dd, ^{1}J = 6.8 Hz, ^{2}J = 2.0 Hz, 2H), 4.49 (td, ^{1}J = 47.2 Hz, ^{2}J = 6.4 Hz, 2H), 4.00 (t, J = 6.8 Hz, 2H), 1.82-1.79 (m, 2H), 1.77-1.65 (m, 2H), 1.49-1.35 (m, 10H); ^{12}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 159.8, 145.3, 132.6, 131.3, 128.3, 127.1, 119.2, 115.1, 110.0, 84.1 (d, J = 162.9 Hz), 68.1, 30.4 (d, J = 19.2 Hz), 29.4, 29.3, 29.2, 29.1, 26.0, 25.1 (d, J = 5.3 Hz); ^{19}FNMR ($CDCl_3$, 376 MHz) δ (ppm): -218.02 (m, 1F). GC/MS: 339.26 found 339.45 calc.

DSC phase transition: K1 47.90 K2 54.05 N 67.75 I

POM phase transition: K1 47.4 K2 52.5 N 67.4 I

n = 10

4'-(10-Fluorodecyloxy)-4-cyanobiphenyl (F10OCB)

To a solution of 4'-[[10-[[(4-methylphenyl)sulfonyl]decanyl]oxyl]-4-cyanobiphenyl (2.0 g, 4.0 mmol) in *t*-amylalcohol (25 mL) was added CsF (1.21g, 8.0 mmol). The mixture

was stirred over 12 hours at reflux. The residue was dissolved in water (15 mL) and extracted from the aqueous phase 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 (1:20) as a white solid (Yield: 0.85 g, 60%), which was then recrystallized from *iso*-octane as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.72 (dt, ^{1}J = 8.0 Hz, ^{2}J = 0.8 Hz, 2H), 7.66 (dt, ^{1}J = 8.4 Hz, ^{2}J = 1.2 Hz, 2H), 7.55 (dd, ^{1}J = 6.8 Hz, ^{2}J = 2.0 Hz, 2H), 7.01 (dd, ^{1}J = 6.4 Hz, ^{2}J = 2.0 Hz, 2H), 4.47 (td, ^{1}J = 47.2 Hz, ^{2}J = 6.4 Hz, 2H), 4.03 (t, J = 6.4 Hz, 2H), 1.83 (m, 2H), 1.72 (m, 2H), 1.52-1.35 (m, 12H); ^{12}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 159.8, 145.3, 132.6, 131.3, 128.3, 127.1, 119.2, 115.1, 110.0, 84.3 (d, J = 162.9 Hz), 68.2, 30.4 (d, J = 19.3 Hz), 29.5, 29.4, 29.2, 26.0, 25.1 (d, J = 5.4 Hz); ^{19}FNMR ($CDCl_3$, 376 MHz) δ (ppm): -217.87 (m, 1F). IR (cm^{-1}): 2922, 2853, 2224, 1604, 1496, 1248, 823; GC/MS: 353.23 found 353.47 calc.

DSC phase transition: K 51.91 N 67.49 I 66.40 N 18.11 K

POM Phase transition: K 50.5 N 68.0 I 67.6 N until 25

n = 11

4'-(11-Fluoroundecyloxy)-4-cyanobiphenyl (F11OCB)

To a solution of 4'-[[11-[[(4-methylphenyl)sulfonyl]undecanyl]oxyl]-4-cyanobiphenyl (1.0 g, 2.0 mmol) in *t*-amylalcohol (15 mL) was added CsF (0.6 g, 4.0 mmol). The mixture was stirred over 12 hours at reflux. The residue was dissolved in water (15 mL) and extracted from the aqueous phase 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 (1:20) as a white solid (510 mg, 72%), which was then recrystallized from heptane as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.70 (dt, ^{1}J = 8.0 Hz, ^{2}J = 0.8 Hz, 2H), 7.66 (dt, ^{1}J = 8.4 Hz, ^{2}J = 1.6 Hz, 2H), 7.53 (dd, ^{1}J = 6.8 Hz, ^{2}J = 2.4 Hz, 2H), 7.00 (dd, ^{1}J = 6.4 Hz, ^{2}J = 2.0 Hz, 2H), 4.44 (td, ^{1}J = 47.2 Hz, ^{2}J = 6.4 Hz, 2H), 4.01 (t, J = 6.8 Hz, 2H), 1.81

(m, 2H), 1.72 (m, 2H), 1.66 (m, 2H), 1.49-1.31 (m, 12H); ^{12}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 159.8, 145.3, 132.6, 131.3, 128.3, 127.1, 119.2, 115.1, 110.0, 84.3 (d, J = 162.9 Hz), 68.2, 30.4 (d, J = 19.3 Hz), 29.6, 29.5, 29.4, 29.3, 29.2, 26.0, 25.1 (d, J = 5.4 Hz); ^{19}FNMR ($CDCl_3$, 376 MHz) δ (ppm): -218.00 (m, 1F). IR (cm^{-1}): 2935, 2920, 2851, 2235, 1605, 1495, 1463, 1251, 824; GC/MS: 367.23 found 367.50 calc.

DSC phase transition: K 63.46 N 68.67 I 67.84 N 50.36 K

POM Phase transition: K 61.0 N 68.4 I 68.3 N 48 K

n = 12

4'-(12-fluorododecyloxy)-4-cyanobiphenyl (F12OCB)

To a solution of 4'-[[12-[[(4-methylphenyl)sulfonyl]dodecanyl]oxyl]-4-cyanobiphenyl (1.0 g, 4.0 mmol) in *t*-amylalcohol (15 mL) was added CsF (0.6 g, 4.0 mmol). The mixture was stirred over 12 hours at reflux. The residue was dissolved in water (15 mL) and extracted from the aqueous phase 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 (1:20) as a white solid (Yield: 490 mg, 65%), which was then recrystallized from heptane as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.70 (dt, ^1J = 8.0 Hz, ^2J = 0.8 Hz, 2H), 7.64 (dt, ^1J = 8.0 Hz, ^2J = 1.6 Hz, 2H), 7.52 (dd, ^1J = 6.8 Hz, ^2J = 2.4 Hz, 2H), 6.99 (dd, ^1J = 6.8 Hz, ^2J = 2.4 Hz, 2H), 4.43 (td, ^1J = 47.2 Hz, ^2J = 6.4 Hz, 2H), 4.01 (t, J = 6.8 Hz, 2H), 1.81 (m, 2H), 1.69 (m, 2H), 1.49-1.30 (m, 16H); ^{12}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 159.8, 145.3, 132.6, 131.3, 128.3, 127.1, 127.0, 119.1, 115.1, 110.0, 84.2 (d, J = 163.0 Hz), 68.2, 30.4 (d, J = 19.2 Hz), 29.6, 29.5, 29.4, 29.3, 29.2, 26.0, 25.1 (d, J = 5.4 Hz); ^{19}FNMR ($CDCl_3$, 376 MHz) δ (ppm): -217.80 (m, 1F). IR (cm^{-1}): 2962, 2925, 2851, 2222, 1603, 1495, 1251, 827; GC/MS: 339.26 found 381.53 calc.

DSC phase transition: K 68.62 N 70.02 I 68.29 N 47.15 K

POM Phase transition: K 67.8 N 70.5 I 70.3 N 54 K

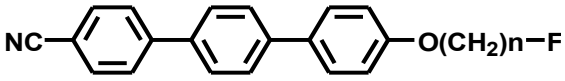
SI.2.4 Synthesis of fluorine tail terminated alkoxy cyanoterphenyl compounds

4-Bromo-4''-hydroxy[1,1';4',1'']terphenyl

In a 200 ml round bottom flask fitted with a magnetic stirbar was dissolved 4-hydroxy-4'-bromobiphenyl (5.0 g, 20.0 mmol) in a mixture of H_2O (12 ml) and 1,4-dioxane (30 ml) to give a light yellow solution. $Pd(PPh_3)_4$ (230 mg, 1 mol%) and 4-cyanophenylboronic acid (3.4 g, 1.5 equiv., 30.0 mmol) were added to the solution and the mixture was stirred at room temperature for 5 minutes. Next, potassium carbonate (5.5 g, 2.0 equiv.) was added and the mixture was stirred and refluxed for 48 hours until TLC analysis indicated the completion of the reaction. The mixture was cooled and 100 ml water was added. The precipitate was filtered by vacuum. The crude product was recrystallized from methanol as a green powder, 2.8 g, 52 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.73 (s, 4H), 7.65 (s, 4H), 7.53 (d, J = 8.4 Hz, 2H 2H), 6.92 (d, J = 8.4 Hz, 2H); GC/MS: 271.33 found 271.31 calc.

The data is consistent with the literature [6].



n = 5 (F5OCT)

In a 50 ml round bottom flask was placed 4-bromo-4''-hydroxy[1,1';4',1'']terphenyl (0.57 mmol, 155 mg), 5-bromofluoropentane (0.57 mmol, 96 mg, 1.0 equiv.), dry DMF (5.0 ml), potassium carbonate (157 mg, 2.0 equiv.) and potassium iodide (9.5 mg, 0.1 equiv.). The resulting suspension was stirred overnight at room temperature and the reaction was monitored by TLC analysis. Once completion, water was added dropwise with stirring to fill the flask and then the precipitate was collected by vacuum filtration. The crude product was recrystallized from acetonitrile as white crystals (133 mg, 65% yield).

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.74 (m, 4H), 7.67 (m, 4H), 7.57 (dt, ^1J = 8.8 Hz, ^2J = 2.8 Hz, 2H), 7.00 (m, dt, ^1J = 8.8 Hz, ^2J = 2.8 Hz, 2H), 4.55 (t, J = 6.4 Hz, 1H), 4.44 (t, J = 6.0 Hz, 1H), 4.04 (t, J = 6.0 Hz, 2H), 1.90-1.75 (m, 4H), 1.64 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 159.0, 145.2, 141.2, 137.3, 132.7, 132.5, 128.1, 127.6, 127.5,

127.3, 119.0, 115.0, 110.8, 84.0 (d, J = 163.6 Hz), 67.8, 30.1 (d, J = 19.4 Hz), 28.9, 22.0 (d, J = 5.3 Hz); ^{19}FNMR ($CDCl_3$, 376 MHz) δ (ppm): -218.43 (m, 1F). IR (cm^{-1}): 2928, 2868, 2231, 1580, 1488, 1254, 1051, 810.

POM phase transition: K 165 N 259.3 I 259.2 N 160 K

DSC phase transition: decomposition/sublimation

n = 4 (F4OCT)

In a 50 ml round bottom flask was placed 4-bromo-4"-hydroxy[1,1';4',1"]terphenyl (1.0 mmol, 271 mg), 4-bromofluorobutane (1.2 mmol, 180 mg, 1.2 equiv.), dry DMF (5.0 ml), potassium carbonate (276 mg, 2.0 equiv.) and potassium iodide (18 mg, 0.1 equiv.). The resulting suspension was stirred overnight at room temperature and the reaction was monitored by TLC analysis. Once completion, water was added dropwise with stirring to fill the flask and then the precipitate was collected by vacuum filtration. The crude product was recrystallized from acetonitrile as a light yellow solid (205 mg, 60% yield).

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.73 (m, 4H), 7.65 (m, 4H), 7.57 (dt, ^1J = 8.8 Hz, ^2J = 3.2 Hz, 2H), 7.00 (dt, ^1J = 8.8 Hz, ^2J = 3.2 Hz, 2H), 4.62 (t, J = 6.0 Hz, 1H), 4.49 (t, J = 6.0 Hz, 1H), 4.07 (t, J = 6.0 Hz, 2H), 1.98-1.88 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 158.9, 145.2, 141.2, 137.3, 132.6, 128.1, 127.6, 127.5, 127.3, 119.0, 114.9, 110.8, 83.79 (d, J = 163.7 Hz), 67.4, 27.2 (d, J = 19.8 Hz), 25.3 (d, J = 5.1 Hz); ^{19}FNMR ($CDCl_3$, 376 MHz) δ (ppm): -218.55 (m, 1F). IR (cm^{-1}): 2968, 2912, 2230, 1599, 1488, 1252, 1039, 810.

POM phase transition: K 165 N 273.1 I 273.1 N 150 K

DSC phase transition: decomposition/sublimation

n = 3 (F3OCT)

In a 100 ml round bottom flask with stirbar was placed 4-bromo-4"-hydroxy[1,1';4',1"]terphenyl (271 mg, 1.0 mmol), triphenylphosphine (314 mg, 1.15

mmol), 3-fluoropropanol (95 mg, 1.2 mmol) and dry THF (5.0 ml). The resulting solution was chilled in an ice bath and diethylazodicarboxylate (94%, 254 mg, 1.15 mmol) was added in portions over two 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 ethyl acetate / hexanes (1:5) 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 grey solid after recrystallization from hexanes/dichloromethane (80 mg, 25% yield).

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.74 (m, 4H), 7.66 (m, 4H), 7.57 (dt, ^{1}J = 8.8 Hz, ^{2}J = 3.2 Hz, 2H), 7.01 (dt, ^{1}J = 9.2 Hz, ^{2}J = 2.8 Hz, 2H), 4.74 (t, J = 5.6 Hz, 1H), 4.62 (t, J = 5.6 Hz, 1H), 4.16 (t, J = 6.0 Hz, 2H), 2.27-2.15 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 158.9, 145.2, 141.1, 137.3, 132.8, 132.6, 128.2, 127.6, 127.5, 127.3, 119.0, 114.9, 110.8, 80.7 (d, J = 163.7 Hz), 63.6 (d, J = 5.0 Hz), 30.4 (d, J = 20.0 Hz); ^{19}FNMR ($CDCl_3$, 376 MHz) δ (ppm): -222.32 (m, 1F). IR (cm^{-1}): 2968, 2912, 2230, 1599, 1488, 1252, 1039, 810.

POM phase transition: K 165 N 273.1 I 273.1 N 150 K

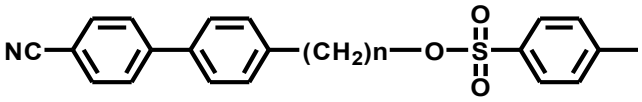
DSC phase transition: decomposition/sublimation

SI.3. Synthesis of fluorine tail terminated alkylcyanobiphenyl compounds

SI.3.1 Synthesis of hydroxy tail terminated alkylcyanobiphenyl compounds

The procedures follow those described in this paper[7].

SI.3.2 Synthesis of 4'-[[ω-[[(4-methylphenyl)sulfonyl]undecyl]yl]-4-cyanobiphenyls



n = 3

4'-[[3-[[(4-Methylphenyl)sulfonyl]propyl]yl]-4-cyanobiphenyl

A 100 mL flask was charged with 4'-(3-hydroxypropyl)-4-cyanobiphenyl (475 mg, 2.0 mmol), triethylamine (0.27 g, 2.6 mmol) and DCM (5.0 mL). The mixture was cooled to a temperature of about 0-5 °C to 15 °C and cautiously charged with a solution of *p*-toluenesulfonyl chloride (0.38 g, 2.0 mmol) in DCM (5.0 mL) over 20 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 (0.4 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 colorless oil (Yield: 780 mg, 93%)

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.72 (dd, ^1J = 8.8 Hz, ^2J = 2.0 Hz, 2H), 7.72-7.66 (m, 4H), 7.47 (dd, ^1J = 6.4 Hz, ^2J = 2.0 Hz, 2H), 7.34 (dd, ^1J = 8.0 Hz, ^2J = 1.6 Hz, 2H), 7.21 (dd, ^1J = 8.4 Hz, ^2J = 2.0 Hz, 2H), 4.06 (t, J = 6.0 Hz, 2H), 2.72 (t, J = 7.6 Hz, 2H), 2.45 (s, 3H), 2.01 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 145.3, 144.8, 141.2, 137.1, 133.1, 132.6, 129.9, 129.2, 127.9, 127.5, 127.3, 119.0, 110.7, 69.4, 31.2, 30.4, 21.7; IR (cm^{-1}): 2957, 2942, 2926, 2221, 1604, 1494, 1356, 1173, 913, 809.

n = 4

4'-[[4-[[(4-Methylphenyl)sulfonyl]butyl]yl]-4-cyanobiphenyl

The procedure is similar to (n = 3) described above. Here 2.0 mmol of the hydroxy compound was used. 530 mg, a light yellow solid, 65% yield

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.79 (dd, ^1J = 6.4 Hz, ^2J = 1.6 Hz, 2H), 7.72 (dt, ^1J = 8.8 Hz, ^2J = 2.0 Hz, 2H), 7.66 (dd, ^1J = 6.8 Hz, ^2J = 2.0 Hz,, 2H), 7.49 (dd, ^1J = 8.4 Hz, ^2J = 2.0 Hz, 2H), 7.33 (dd, ^1J = 8.0 Hz, ^2J = 1.6 Hz, 2H), 7.21 (dd, ^1J = 8.0 Hz, ^2J = 2.0

Hz, 2H), 4.05 (t, *J* = 6.0 Hz, 2H), 2.63 (t, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 1.70 (t, *J* = 2.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 145.5, 144.8, 142.4, 136.8, 133.1, 132.6, 129.9, 129.2, 127.9, 127.5, 127.2, 119.0, 110.6, 70.3, 34.8, 28.4, 27.0, 21.7; IR (cm^{-1}): 2943, 2919, 2859, 2221, 1604, 1492, 1353, 1170, 931, 809.

n = 5

4'-[[5-[[(4-Methylphenyl)sulfonyl]pentyl]yl]-4-cyanobiphenyl

The procedure is similar to (n = 3) described above. Here 2.0 mmol of the hydroxy compound was used. 560 mg, white crystals, 67%

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.79 (dt, ^{1}J = 8.4 Hz, ^{2}J = 2.0 Hz, 2H), 7.72 (dt, ^{1}J = 8.4 Hz, ^{2}J = 2.0 Hz, 2H), 7.67 (dd, ^{1}J = 6.8 Hz, ^{2}J = 2.4 Hz,, 2H), 7.50 (dt, ^{1}J = 8.4 Hz, ^{2}J = 2.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 9.2 Hz, 2H), 4.03 (t, *J* = 6.4 Hz, 2H), 2.63 (t, *J* = 7.6 Hz, 2H), 2.44 (s, 3H), 1.73-1.57 (m, 4H), 1.40 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 145.5, 144.7, 143.0, 136.7, 133.2, 132.6, 129.8, 129.2, 127.9, 127.5, 127.2, 119.0, 110.6, 70.4, 35.3, 30.6, 28.7, 25.0, 21.7; IR (cm^{-1}): 2928, 2863, 2225, 1605, 1495, 1351, 1187, 951, 810.

n = 6

4'-[[6-[[(4-Methylphenyl)sulfonyl]hexyl]yl]-4-cyanobiphenyl

A 100 mL flask was charged with 4'-(6-hydroxyhexyl)-4-cyanobiphenyl (560 mg, 2.0 mmol), triethylamine (0.27 g, 2.6 mmol) and DCM (5.0 mL). The mixture was cooled to a temperature of about 0-5 °C and cautiously charged with a solution of *p*-toluenesulfonyl chloride (0.38 g, 2.0 mmol) in DCM (5.0 mL) over 20 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 (0.4 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: 580 mg, 68%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.77 (dd, ^{1}J = 6.8 Hz, ^{2}J = 0.8 Hz, 2H), 7.72-7.66 (m, 4H), 7.51 (dd, ^{1}J = 6.8 Hz, ^{2}J = 1.2 Hz, 2H), 7.34 (dd, ^{1}J = 8.8 Hz, ^{2}J = 0.8 Hz, 2H), 7.26 (dd, ^{1}J = 6.4 Hz, ^{2}J = 1.6 Hz, 2H), 4.02 (t, J = 6.4 Hz, 2H), 2.62 (t, J = 7.8 Hz, 3H), 2.44 (s, 3H), 1.68-1.57 (m, 4H), 1.38-1.29 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 145.6, 144.7, 143.3, 136.6, 133.2, 132.6, 129.8, 129.1, 128.3, 127.9, 127.1, 119.1, 110.6, 70.6, 35.4, 31.1, 28.8, 28.6, 25.3, 21.7. IR (cm^{-1}): 2929, 2854, 2222, 1602, 1495, 1354, 1174, 919, 814.

n = 7

4’-[[7-[[(4-Methylphenyl)sulfonyl]heptyl]yl]-4-cyanobiphenyl

A 100 mL flask was charged with 4'-(7-hydroxyheptyl)-4-cyanobiphenyl (586 mg, 2.0 mmol), triethylamine (0.27 g, 2.6 mmol) and DCM (5.0 mL). The mixture was cooled to a temperature of about 0-5 °C and cautiously charged with a solution of *p*-toluenesulfonyl chloride (0.38 g, 2.0 mmol) in DCM (5.0 mL) over 20 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 (0.4 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 colorless oil (Yield: 680 mg, 76%).
^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.71 (dd, ^{1}J = 6.4 Hz, ^{2}J = 1.2 Hz, 2H), 7.68-7.65 (m, 4H), 7.51 (dt, ^{1}J = 8.4 Hz, ^{2}J = 2.0 Hz, 2H), 7.34 (dd, ^{1}J = 8.8 Hz, ^{2}J = 0.8 Hz, 2H), 7.27 (dd, ^{1}J = 8.4 Hz, ^{2}J = 1.6 Hz, 2H), 4.01 (t, J = 6.4 Hz, 2H), 2.63 (t, J = 7.6 Hz, 3H), 2.44 (s, 3H), 1.65 (m, 4H), 1.38-1.29 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 145.6, 144.7, 143.5, 136.5, 133.2, 132.6, 129.8, 129.2, 127.9, 127.5, 127.1, 119.1, 110.5, 70.6, 35.5, 31.2, 29.0, 28.8, 28.6, 25.3, 21.7; IR (cm^{-1}): 2928, 2855, 2225, 1605, 1493, 1355, 1174, 924, 812.

n = 8

4’-[[8-[[(4-methylphenyl)sulfonyl]octyl]yl]-4-cyanobiphenyl

A 100 mL flask was charged with 4'-(8-hydroxyoctyl)-4-cyanobiphenyl (614 mg, 2.0 mmol), triethylamine (0.27 g, 2.6 mmol) and DCM (5.0 mL). The mixture was cooled to a temperature of about 0-5 °C and cautiously charged with a solution of *p*-toluenesulfonyl chloride (0.38 g, 2.0 mmol) in DCM (5.0 mL) over 20 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 (0.4 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 colorless oil (Yield: 750 mg, 81%). Melting point: 65-66 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.78 (dd, ^{1}J = 6.4 Hz, ^{2}J = 2.0 Hz, 2H), 7.72-7.66 (m, 4H), 7.51 (dd, ^{1}J = 6.4 Hz, ^{2}J = 2.0 Hz, 2H), 7.34 (dt, ^{1}J = 7.6 Hz, ^{2}J = 0.8 Hz, 2H), 7.28 (dd, ^{1}J = 6.4 Hz, ^{2}J = 1.6 Hz, 2H), 4.01 (t, J = 6.4 Hz, 2H), 2.64 (t, J = 7.6 Hz, 2H), 2.44 (s, 3H), 1.62 (m, 4H), 1.38-1.29 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 145.6, 144.7, 143.6, 136.5, 133.2, 132.6, 129.8, 129.2, 127.9, 127.5, 127.1, 119.1, 110.5, 70.6, 35.6, 31.3, 29.2, 29.1, 28.9, 28.8, 25.3, 21.7; IR (cm^{-1}): 2976, 2935, 2921, 2851, 2223, 1605, 1494, 1346, 1169, 954, 812.

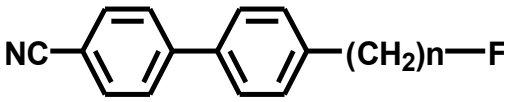
n = 11

4'-[[11-[[(4-methylphenyl)sulfonyl]undecyl]yl]-4-cyanobiphenyl

The procedure is similar to (n = 3) described above. Here 2.0 mmol of the hydroxy compound was used. 670 mg, a white solid, 86% yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.78 (dt, ^{1}J = 8.4 Hz, ^{2}J = 2.0 Hz, 2H), 7.72-7.66 (m, 4H), 7.51 (dt, ^{1}J = 8.4 Hz, ^{2}J = 2.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 7.6 Hz, 2H), 4.01 (t, J = 6.4 Hz, 2H), 2.66 (t, J = 7.6 Hz, 2H), 2.45 (s, 3H), 1.63 (m, 4H), 1.32-1.22 (m, 14H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 145.6, 144.6, 143.8, 136.5, 132.6, 129.8, 129.2, 127.9, 127.5, 127.1, 119.1, 110.5, 70.7, 35.6, 31.4, 29.5, 29.4, 29.3, 29.2, 28.9, 28.8, 25.3, 21.7; IR (cm^{-1}): 2928, 2863, 2225, 1605, 1495, 1351, 1187, 951, 810.

SI.3.3 Synthesis of 4'-(ω-fluoroalkyl)-4-cyanobiphenyls



n = 3

4'-(3-Fluoropropyl)-4-cyanobiphenyl (F3CB)

To a solution of 4'-[3-[[(4-methylphenyl)sulfonyl]propyl]-4-cyanobiphenyl (586 mg, 1.5 mmol) in *t*-amylalcohol (15 mL) was added CsF (0.45 g, 3.0 mmol). The mixture was stirred over 12 hours at reflux. The residue was dissolved in water (15 mL) and extracted from the aqueous phase with diethyl ether (15 mL). The organic phase was dried over magnesium sulfate and evaporated under reduced pressure. The desired product was purified by column chromatography eluted by ethyl acetate:hexane (1:10) as a light yellow solid (316 mg, 88%), which was then recrystallized from heptane as a white solid (30 mg, 10% recovery for crop 1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.74-7.66 (m, 4H), 7.67 (dt, ^{1}J = 8.0 Hz, ^{2}J = 1.2 Hz, 2H), 7.53 (dt, ^{1}J = 6.4 Hz, ^{2}J = 2.0 Hz, 2H), 7.32 (dt, ^{1}J = 6.4 Hz, ^{2}J = 2.0 Hz, 2H), 4.56 (t, J = 5.6 Hz, 1H), 4.43 (t, J = 6.0 Hz, 1H), 2.82 (t, J = 7.6 Hz, 2H), 2.03 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 145.4, 141.9, 137.0, 132.6, 129.3, 127.5, 127.3, 119.0, 110.7, 83.3 (d, J = 164.0 Hz), 31.9 (d, J = 19.7 Hz), 31.0 (d, J = 5.2 Hz); ^{19}FNMR ($CDCl_3$, 376 MHz) δ (ppm): -220.12 (m, 1F); IR (cm^{-1}): 2961, 2929, 2899, 2863, 2223, 1604, 1492, 1186, 1025, 809; GC/MS: 309.32 found 309.42 calc.

DSC phase transition: K 84 I 16 N 10 K

n = 4

4'-(4-Fluorobutyl)-4-cyanobiphenyl (F4CB)

The procedure is similar to (n = 3) described above. Here 1.5 mmol of the relevant tosylate was used. 133 mg of a colorless liquid, 44% yield

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.73-7.66 (m, 4H), 7.51 (dt, ^{1}J = 8.4 Hz, ^{2}J = 2.0 Hz, 2H), 7.30 (dt, ^{1}J = 8.8 Hz, ^{2}J = 2.0 Hz, 2H), 4.54 (m, 1H), 4.42 (t, J = 6.0 Hz, 1H),

2.73 (t, J = 7.2 Hz, 2H), 1.82-1.71 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 145.5, 142.8, 136.8, 132.6, 129.2, 127.5, 127.2, 119.0, 110.6, 83.9 (d, J = 163.5 Hz), 35.1, 29.9 (d, J = 19.7 Hz), 26.9 (d, J = 4.9 Hz); ^{19}FNMR ($CDCl_3$, 376 MHz) δ (ppm): -218.43 (m, 1F); IR (cm^{-1}): 2963, 2898, 2225, 1605, 1494, 822; GC/MS: 253.23 found 253.31 calc.

DSC phase transition: K 57 I 36 N 29 K

POM phase transition: unable to confirm the phase.

n = 5

4'-(5-Fluoropentyl)-4-cyanobiphenyl (F5CB)

The procedure is similar to (n = 3) described above. Here 1.5 mmol of the relevant tosylate was used. 112 mg of white crystals, 35% yield after recrystallization from hexanes.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.72-7.66 (m, 4H), 7.51 (dt, ^1J = 8.4 Hz, ^2J = 2.0 Hz, 2H), 7.30 (dt, ^1J = 8.0 Hz, ^2J = 2.0 Hz, 2H), 4.52 (t, J = 6.4 Hz, 1H), 4.40 (t, J = 6.0 Hz, 1H), 2.69 (t, J = 7.6 Hz, 2H), 1.81-1.67 (m, 4H), 1.48 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 145.6, 143.2, 136.6, 132.6, 129.2, 127.5, 127.2, 119.0, 110.6, 84.0 (d, J = 163.4 Hz), 35.5, 31.0, 30.3 (d, J = 19.4 Hz), 24.9 (d, J = 5.3 Hz); ^{19}FNMR ($CDCl_3$, 376 MHz) δ (ppm): -218.20 (m, 1F); IR (cm^{-1}): 2934, 2856, 2226, 1604, 1493, 975, 812; GC/MS: 267.24 found 267.34 calc.

DSC phase transition: K 46 I 28 N

POM phase transition: K 45.5 I 29 N

n = 6

4'-(6-Fluorohexyl)-4-cyanobiphenyl (F6CB)

To a solution of 4'-[6-[[(4-methylphenyl)sulfonyl]octyl]-4-cyanobiphenyl (455 mg, 1.0 mmol) in *t*-amylalcohol (15 mL) was added CsF (0.3 g, 2.0 mmol). The mixture was stirred over 12 hours at reflux. The residue was dissolved in water (15 mL) and extracted from the aqueous phase with diethyl ether (15 mL). The organic phase was dried over magnesium sulfate and evaporated under reduced pressure. The desired product was purified by column chromatography eluted by ethyl acetate:hexane (1:20) as a yellow oil (200 mg, 71%), which was then recrystallized from heptane as a white solid.

^{1}H NMR ($CDCl_3$, 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 = 8.4 Hz, ^{2}J = 2.0 Hz, 2H), 7.29 (td, ^{1}J = 8.4 Hz, ^{2}J = 1.6 Hz, 2H), 4.50 (t, J = 6.0 Hz, 1H), 4.38 (t, J = 6.0 Hz, 1H), 2.67 (t, J = 7.6 Hz, 2H), 1.75-1.64 (m, 4H), 1.48-1.40 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 145.6, 143.5, 136.6, 132.6, 129.2, 127.5, 127.1, 119.0, 110.6, 84.07 (d, J = 163.1 Hz), 35.5, 31.2, 30.3 (d, J = 19.2 Hz), 28.9, 25.1 (d, J = 5.3 Hz); ^{19}FNMR ($CDCl_3$, 376 MHz) δ (ppm): -218.40 (m, 1F). IR (cm^{-1}): 2959, 2936, 2923, 2850, 2223, 1605, 1494, 975, 825. GC/MS: 281.28 found 281.37 calc.

DSC phase transition: K 28.32 N 32.08 I

POM phase transition: N 33 I

n = 7

4'-(7-Fluoroheptyl)-4-cyanobiphenyl (F7CB)

To a solution of 4'-[7-[[(4-methylphenyl)sulfonyl]heptyl]-4-cyanobiphenyl (560 mg, 1.2 mmol) in *t*-amylalcohol (15 mL) was added CsF (0.36 g, 2.4 mmol). The mixture was stirred over 12 hours at reflux. The residue was dissolved in water (15 mL) and extracted from the aqueous phase with diethyl ether (15 mL). The organic phase was dried over magnesium sulfate and evaporated under reduced pressure. The desired product was purified by column chromatography eluted by ethyl acetate:hexane (1:10) as a colorless oil (334 mg, 94%), which was then recrystallized from heptane as a white solid (67 mg, 20% recovery for crop 1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.72-7.66 (m, 4H), 7.67 (dt, ^{1}J = 8.0 Hz, ^{2}J = 1.2 Hz, 2H), 7.51 (m, 2H), 7.28 (dd, ^{1}J = 6.4 Hz, ^{2}J = 2.0 Hz, 2H), 4.50 (t, J = 6.4 Hz, 1H), 4.38 (t, J = 6.0 Hz, 1H), 2.66 (t, J = 7.6 Hz, 2H), 1.74-1.63 (m, 4H), 1.43-1.36 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 145.6, 143.6, 136.5, 132.6, 129.2, 127.5, 127.1, 119.1, 110.5, 84.2 (d, J = 162.9 Hz), 35.6, 31.3, 30.4 (d, J = 19.1), 29.2, 29.1, 25.1 (d, J = 5.2 Hz); ^{19}FNMR ($CDCl_3$, 376 MHz) δ (ppm): -218.01 (m, 1F). IR (cm^{-1}): 2967, 2926, 2856, 2226, 1606, 1496, 969, 801. GC/MS: 295.27 found 295.39 calc.

DSC phase transition: K 31.49 N 35.12 I

POM phase transition: K 31.4 N 35.9 I

n = 8

4'-(8-Fluorooctyl)-4-cyanobiphenyl (F8CB)

To a solution of 4'-[8-[[(4-methylphenyl)sulfonyl]octyl]-4-cyanobiphenyl (650 mg, 1.4 mmol) in *t*-amylalcohol (15 mL) was added CsF (0.42 g, 2.8 mmol). The mixture was stirred over 12 hours at reflux. The residue was dissolved in water (15 mL) and extracted from the aqueous phase with diethyl ether (15 mL). The organic phase was dried over magnesium sulfate and evaporated under reduced pressure. The desired product was purified by column chromatography eluted by ethyl acetate:hexane (1:10) as a colorless oil (340 mg, 78%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.72-7.66 (m, 4H), 7.51 (dd, ^{1}J = 6.4 Hz, ^{2}J = 1.6 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 4.49 (t, J = 6.4 Hz, 1H), 4.38 (t, J = 6.0 Hz, 1H), 2.66 (t, J = 7.6 Hz, 2H), 1.73-1.61 (m, 4H), 1.48-1.35 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 145.6,143.7, 136.5, 132.6, 129.2, 127.5, 127.1, 119.1, 110.5, 84.2 (d, J = 162.9 Hz), 35.6, 31.4, 30.4 (d, J = 19.3 Hz), 29.4, 29.2, 29.1, 28.7, 25.1 (d, J = 5.2 Hz); ^{19}FNMR ($CDCl_3$, 376 MHz) δ (ppm): -218.02 (m, 1F); IR (cm^{-1}): 2927, 2854, 2225, 1606, 1494, 1006, 815; GC/MS: 309.32 found 309.42 calc.

DSC phase transition: K ? N 19.3 I

POM phase transition: N 19 I (approximately)

n = 11

4'-(11-Fluoroundecyl)-4-cyanobiphenyl (F11CB)

The procedure is similar to (n = 3) described above. Here 1.5 mmol of the relevant tosylate was used. 305 mg, white crystals, 72% yield after recrystallization from methanol.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.73-7.66 (m, 4H), 7.51 (td, ^{1}J = 8.4 Hz, ^{2}J = 2.0 Hz, 2H), 7.29 (td, ^{1}J = 8.4 Hz, ^{2}J = 2.0 Hz, 2H), 4.49 (t, J = 6.4 Hz, 1H), 4.38 (t, J = 6.0 Hz, 1H), 2.66 (t, J = 7.6 Hz, 2H), 1.73-1.61 (m, 4H), 1.39-1.29 (m, 14H); ^{13}C NMR

($CDCl_3$, 100 MHz) δ (ppm): 145.6,143.8, 136.5, 132.6, 129.2, 127.5, 127.1, 119.1, 110.7, 84.3 (d, J = 163.0 Hz), 35.6, 31.4, 30.4 (d, J = 19.3 Hz), 29.5, 29.4, 29.3, 29.2, 25.1 (d, J = 5.4 Hz); ^{19}FNMR ($CDCl_3$, 376 MHz) δ (ppm): -218.00 (m, 1F); IR (cm^{-1}): 2918, 2849, 2222, 1605, 823, 810; GC/MS: 351.35 found 351.50 calc.

POM phase transition: K 54 I 44 N 26 K

DSC phase transition: K 53 I 43 N 19 K

SI.4. The DSC of fluorine terminated compounds in this work.

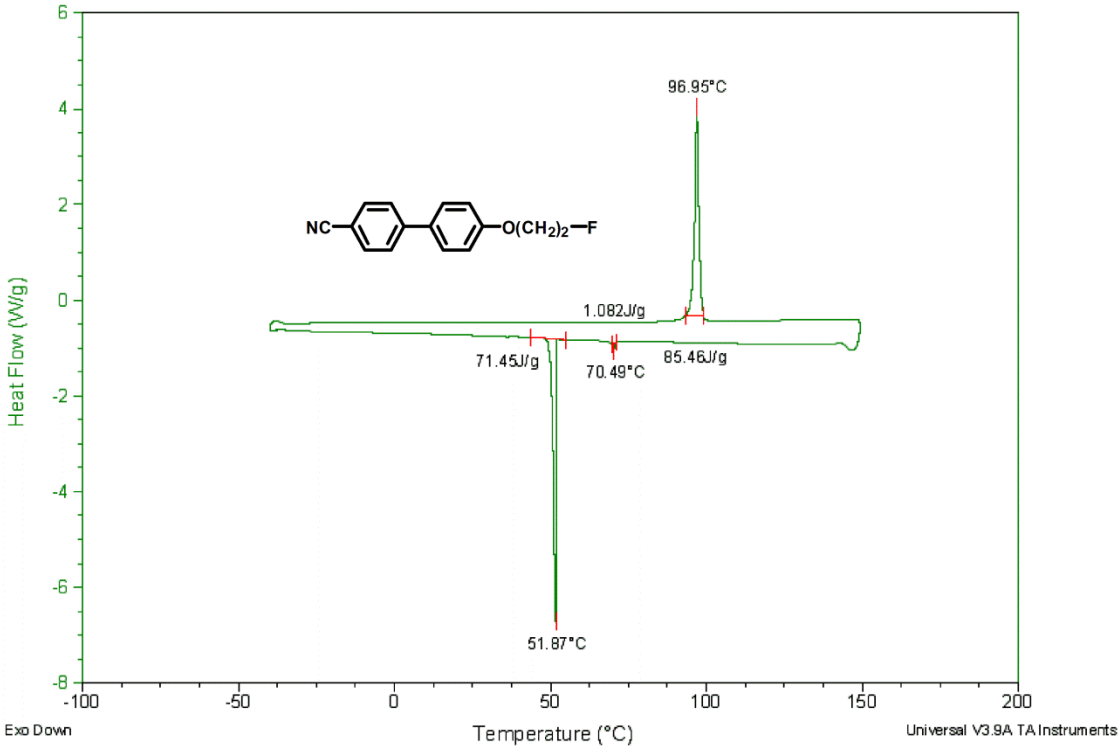


Figure SI.1 DSC of F2OCB. (K 97.0 I 70.5 N 51.9 K)

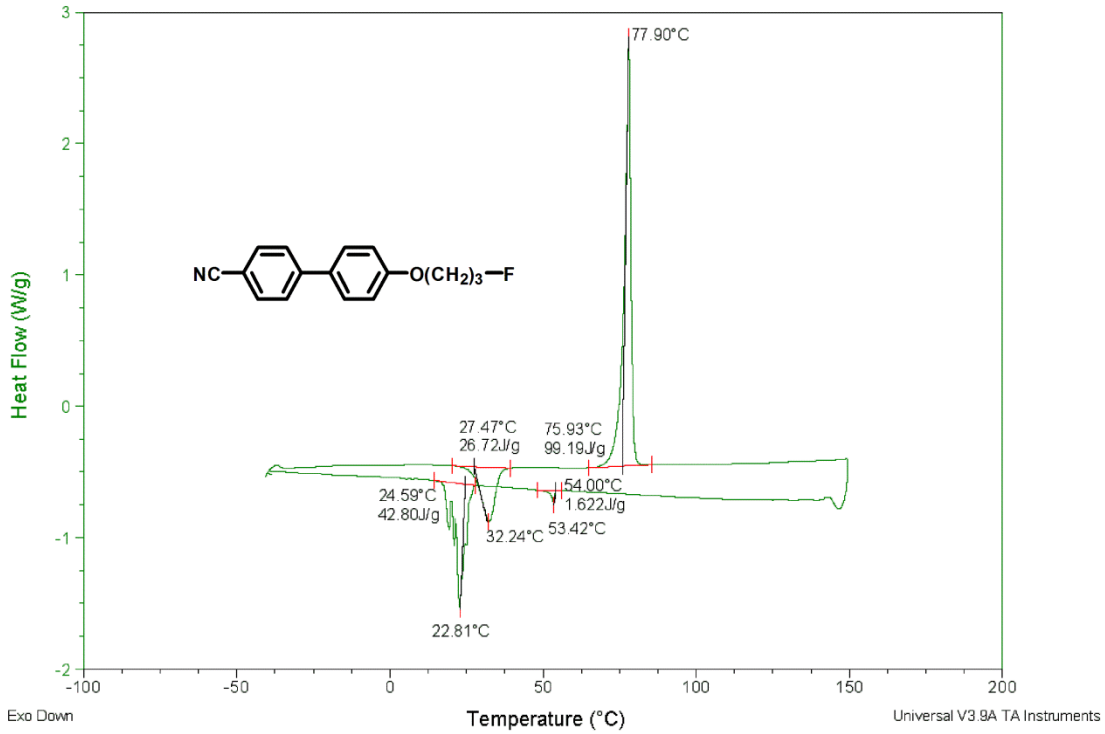


Figure SI.2 DSC of F3OCB. (K 77.9 I 53.4 N 22.8 K)

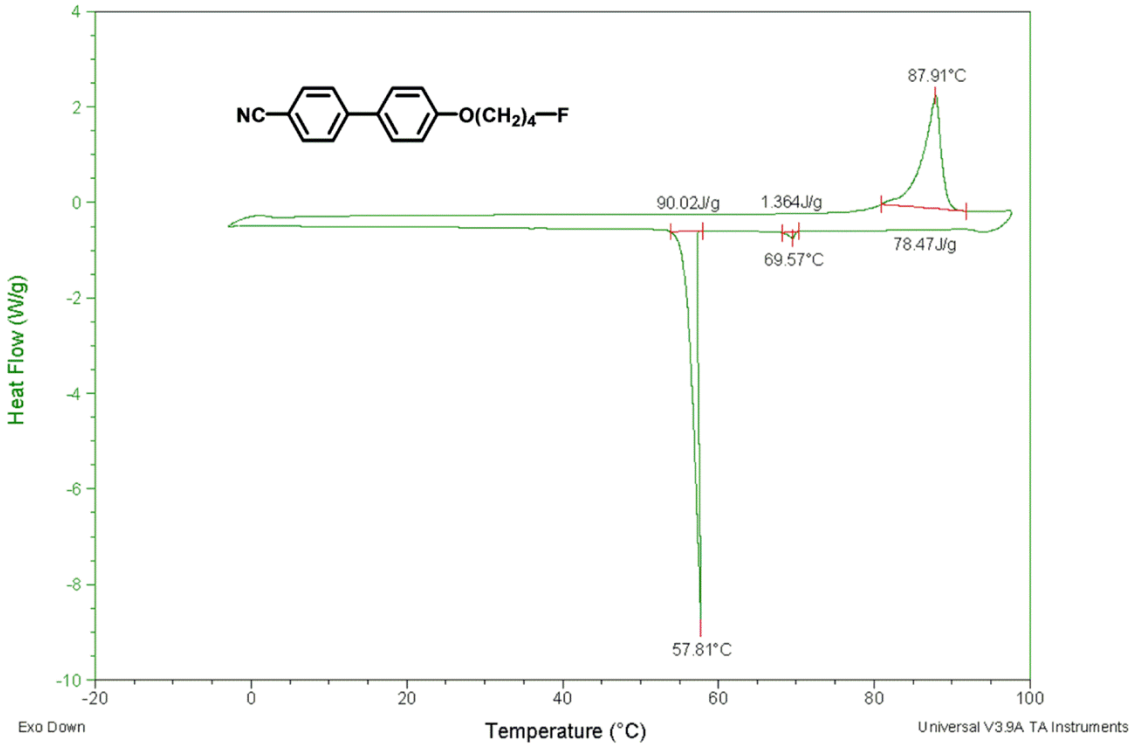


Figure SI.3 DSC of F4OCB. (K 87.9 I 69.6 N 57.8 K)

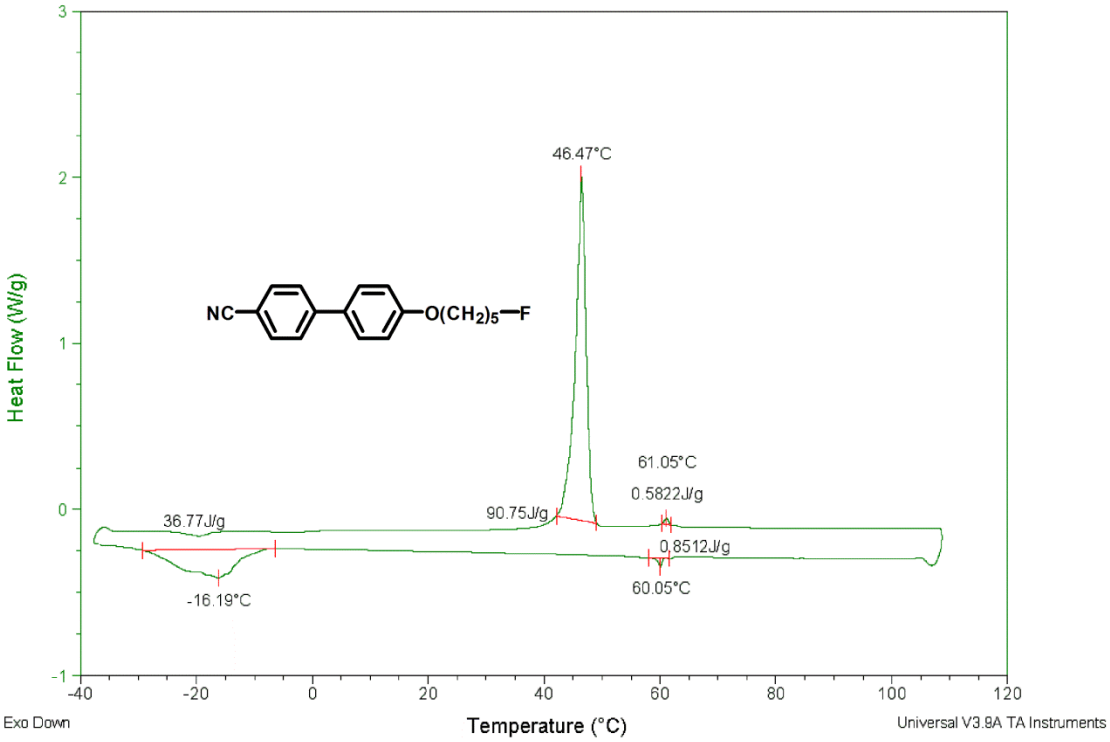


Figure SI.4 DSC of F5OCB. (K 46.5 N 61.1 I 60.1 N -16.2 K)

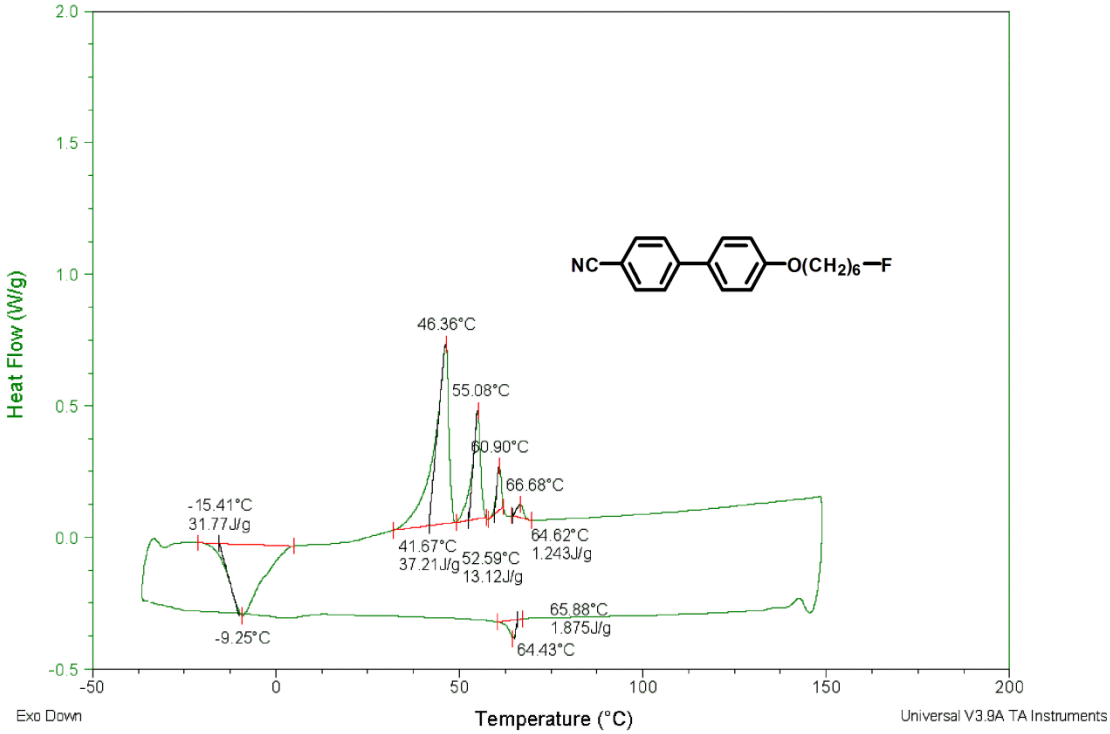


Figure SI.5 DSC of F6OCB. (K1 45.4 K2 55.1 K3 60.9 N 66.7 I 64.4 N -9.3 K)

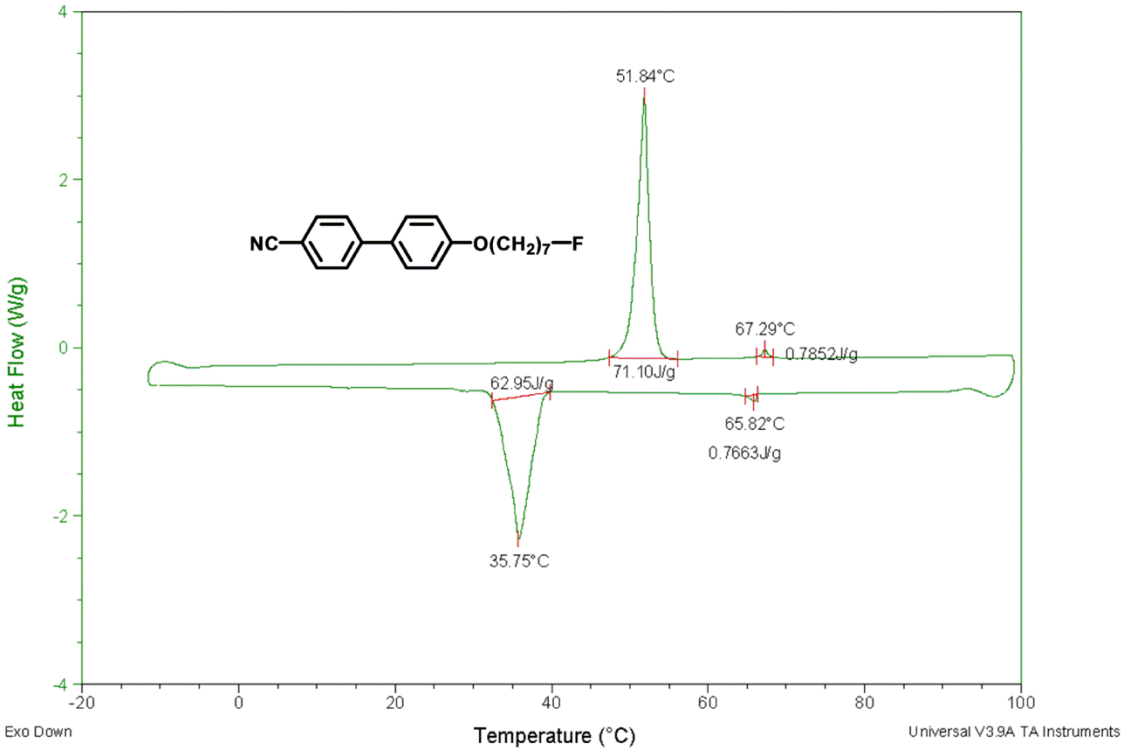


Figure SI.6 DSC of F7OCB. (K 51.8 N 67.3 I 65.8 N 35.8 K)

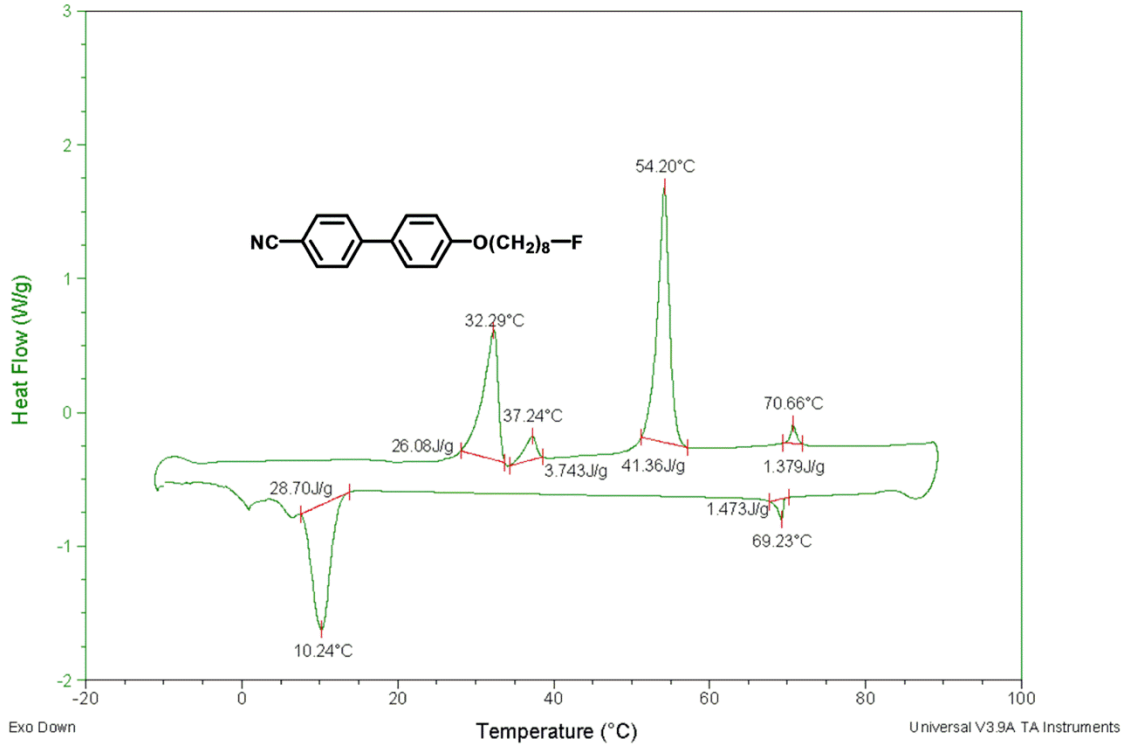


Figure SI.7 DSC of F8OCB. (K_1 32.3 K_2 37.2 K_3 54.2 N 70.7 I 69.2 N 10.4 K)

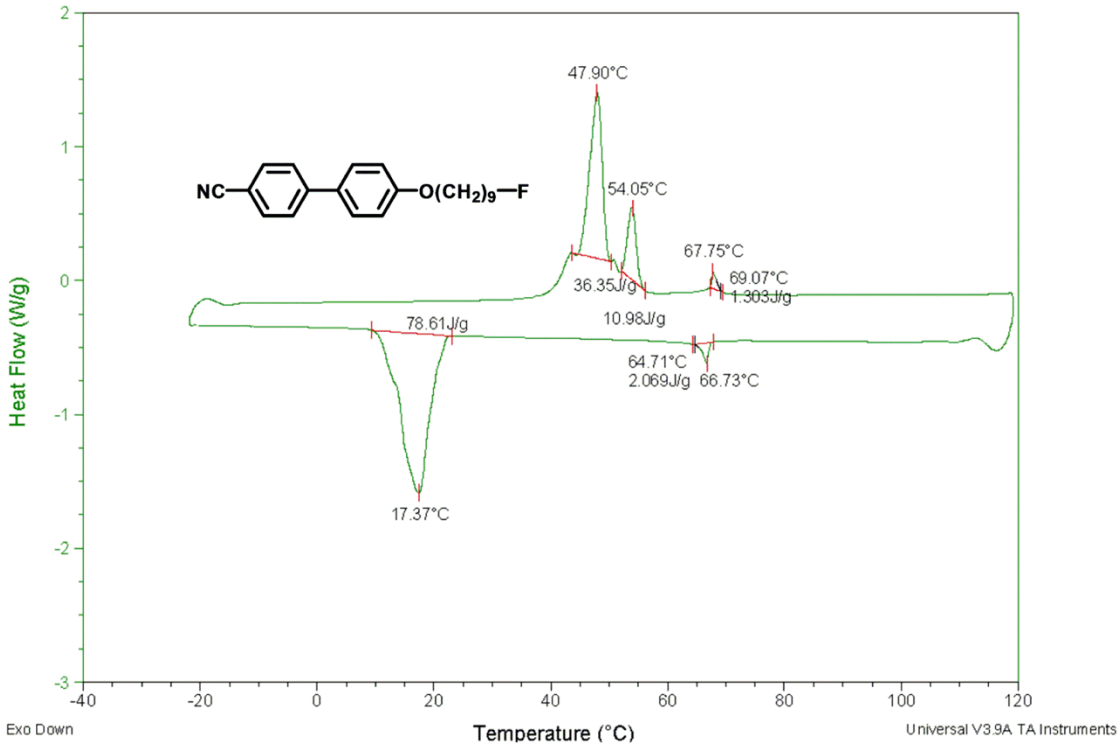


Figure SI.8 DSC of F9OCB. (K_1 47.9 K_2 54.1 N 67.8 I 64.7 N 17.4 K)

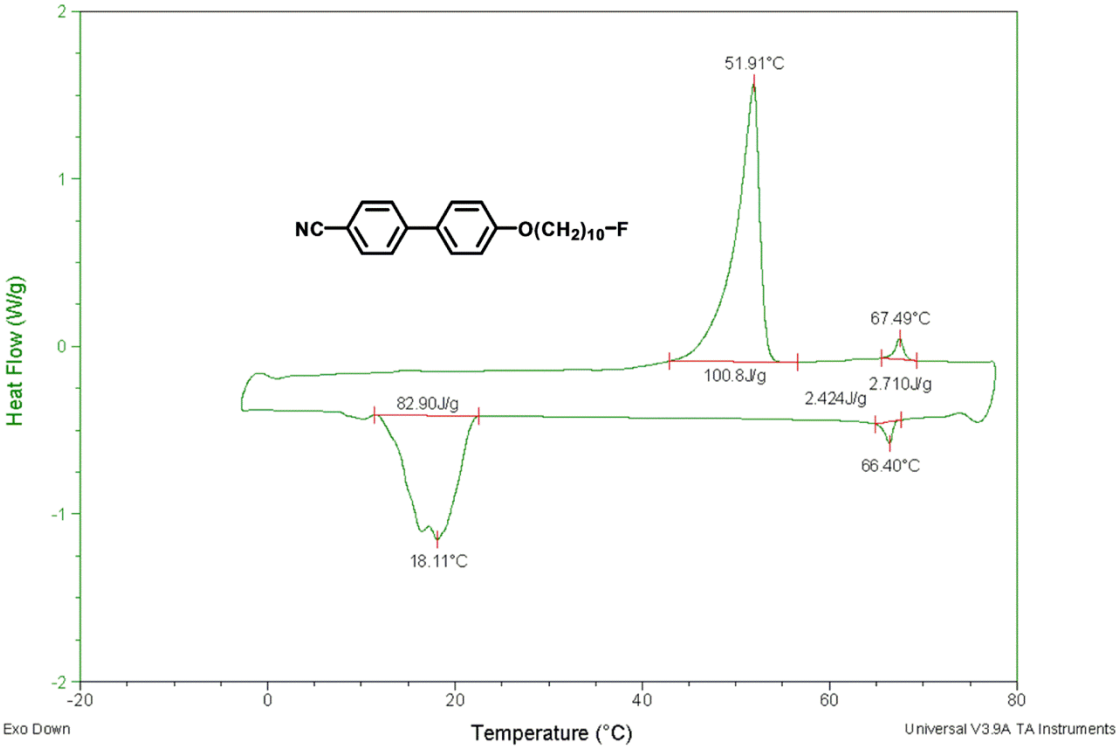


Figure SI.9 DSC of F10OCB. (K 51.9 N 67.5 I 66.4 N 18.1 K)

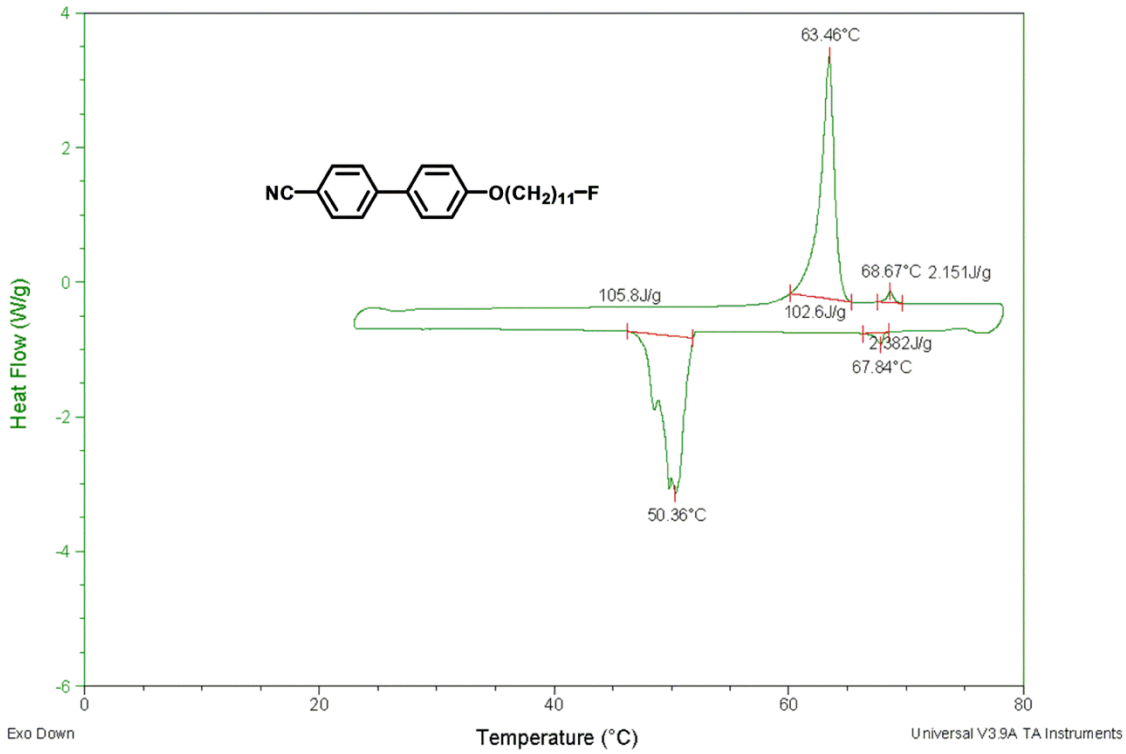


Figure SI.10 DSC of F11OCB. (K 63.5 N 68.7 I 67.8 N 50.4 K)

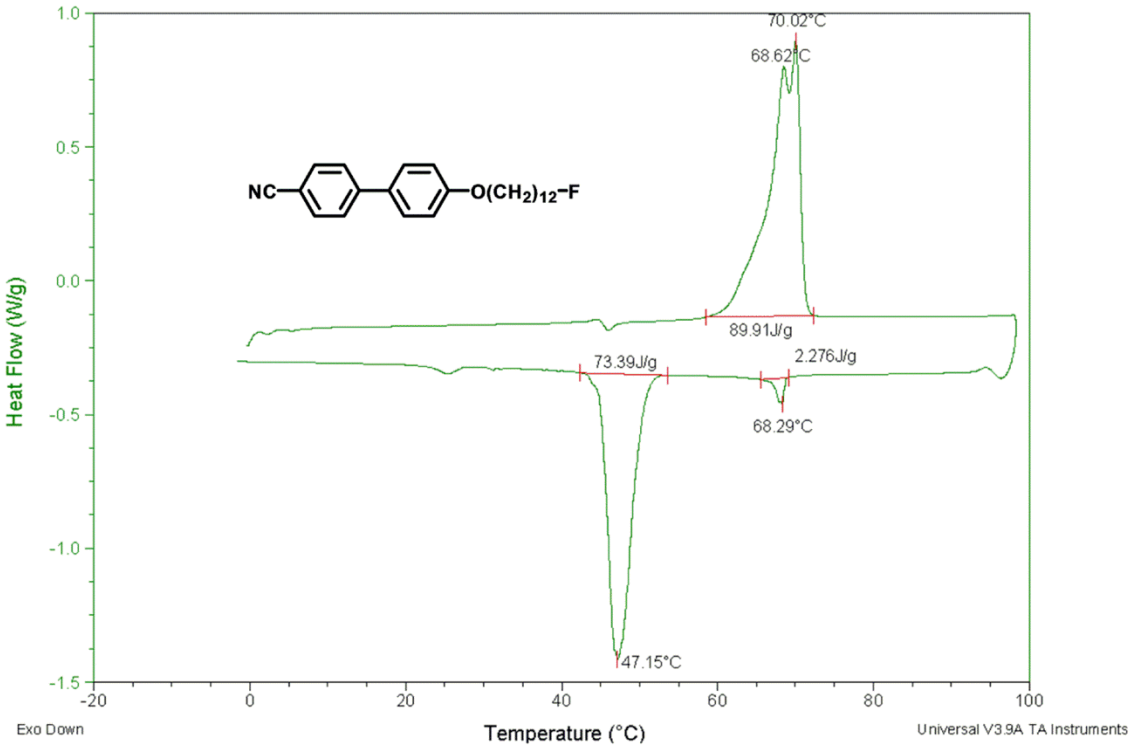


Figure SI.11 DSC of F12OCB. (K 68.6 N 70.0 I 68.3 N 47.2 K)

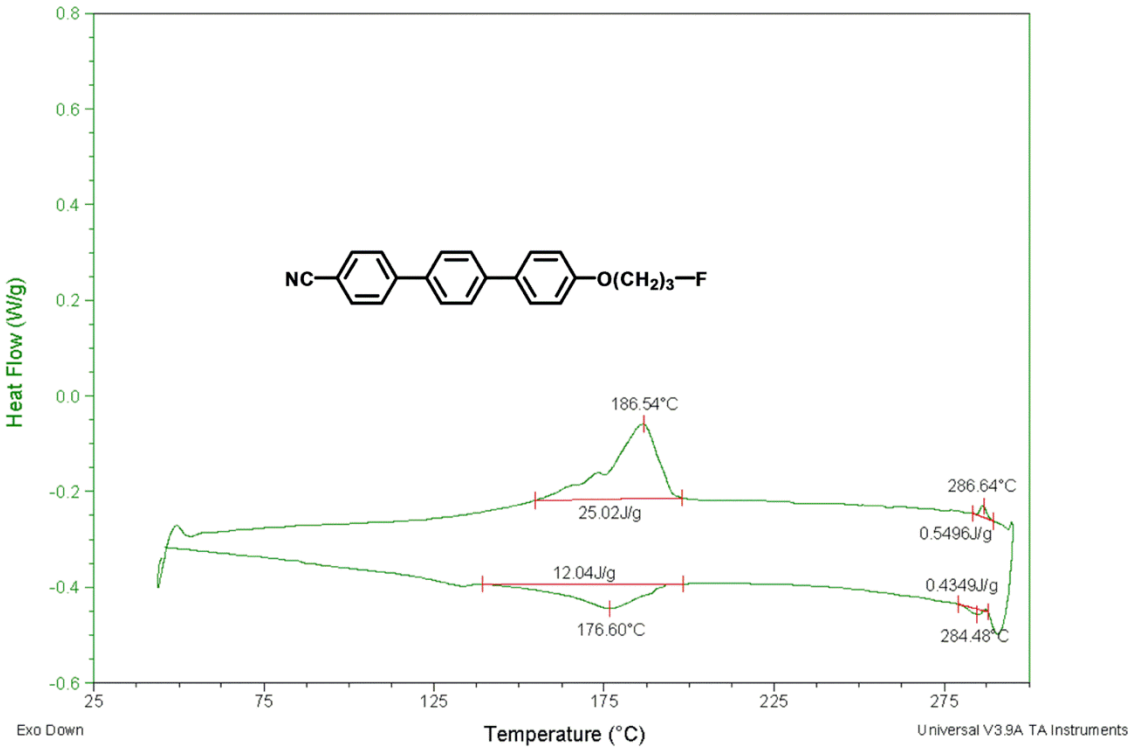


Figure SI.12 DSC of F3OCT. (K 186.5 N 286.6 I 284.5 N 176.6 K)

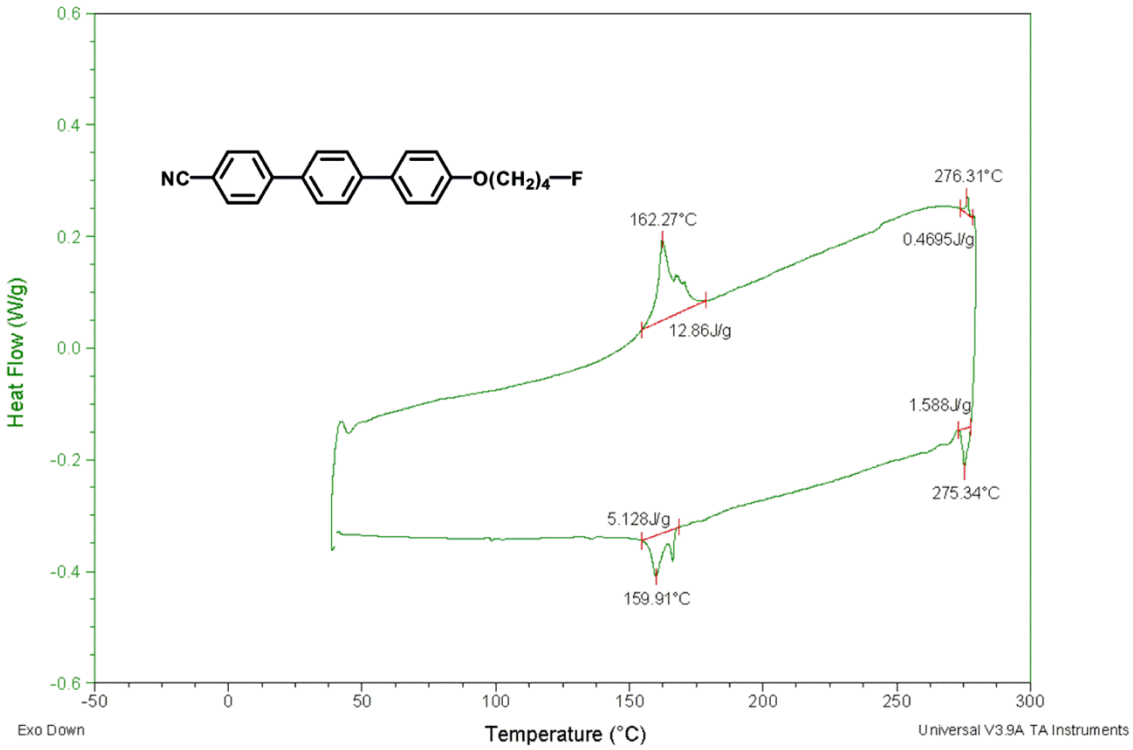


Figure SI.13 DSC of F4OCT. (K 162.3 N 276.3 I 275.3 N 160.0 K)

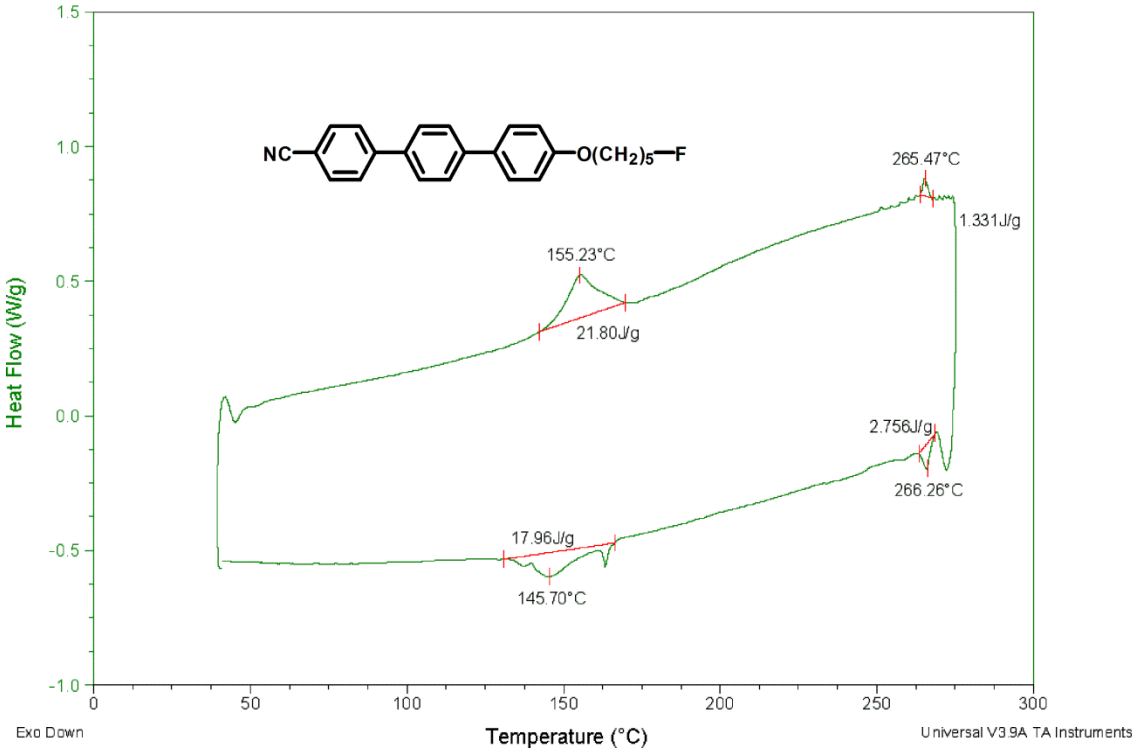


Figure SI.14 The DSC plot of F5OCT. (K 155 N 265 I)

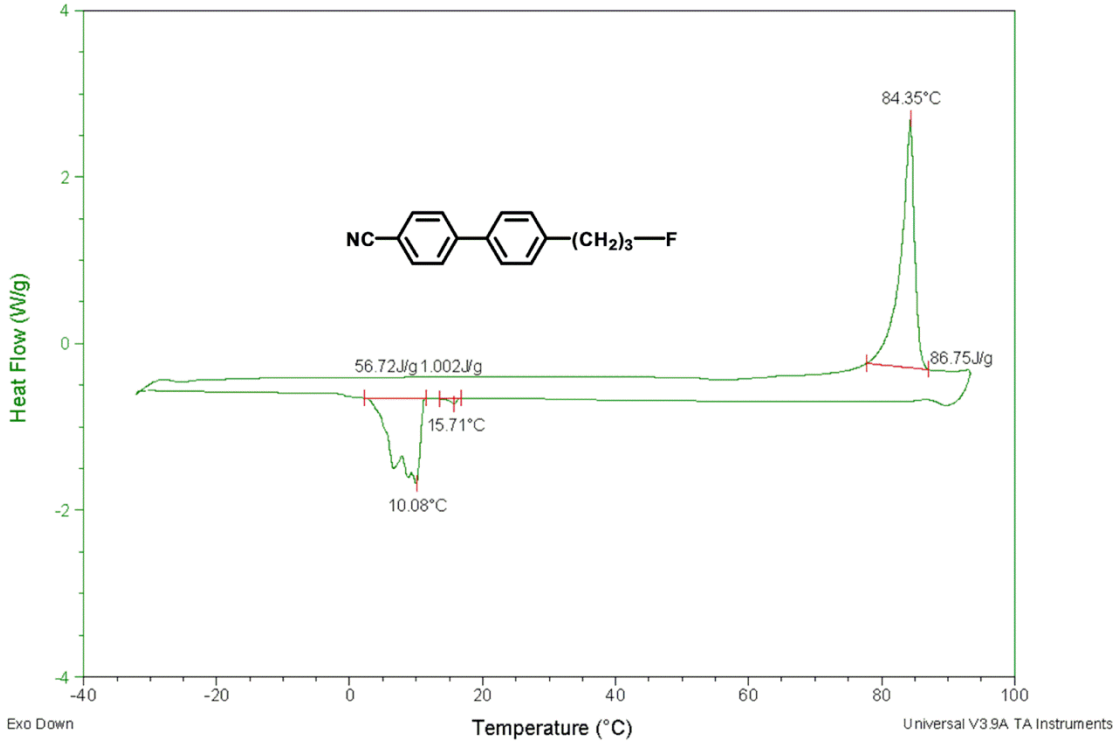


Figure SI.15 DSC of F3CB. (K 84.4 I 15.7 N 10.1 K)

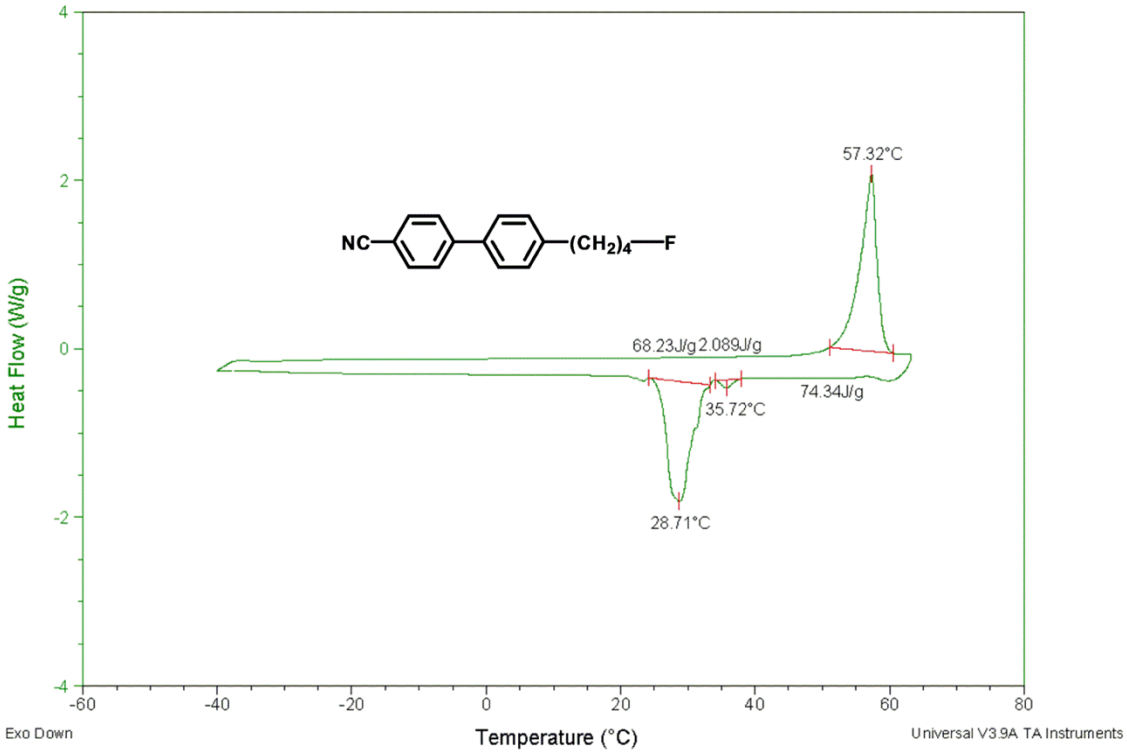


Figure SI.16 DSC of F4CB. (K 57.3 I 35.7 N 28.7 K)

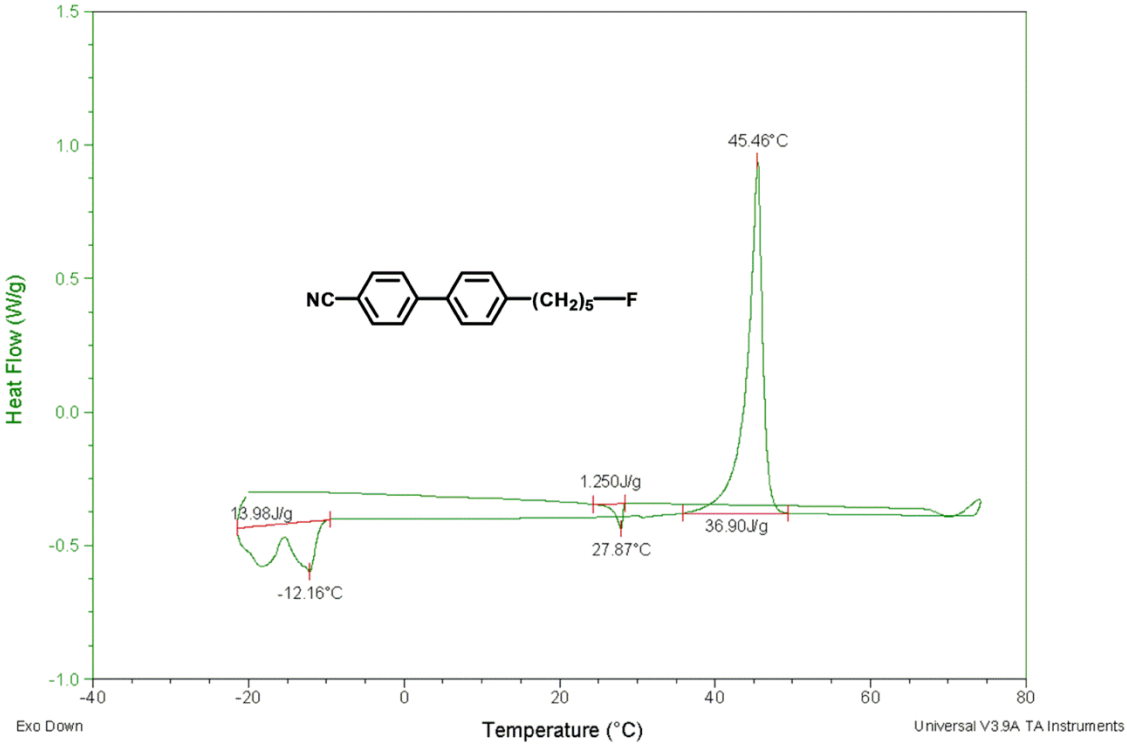


Figure SI.17 DSC of F5CB. (K 45.5 I 27.9 N -12.2 K)

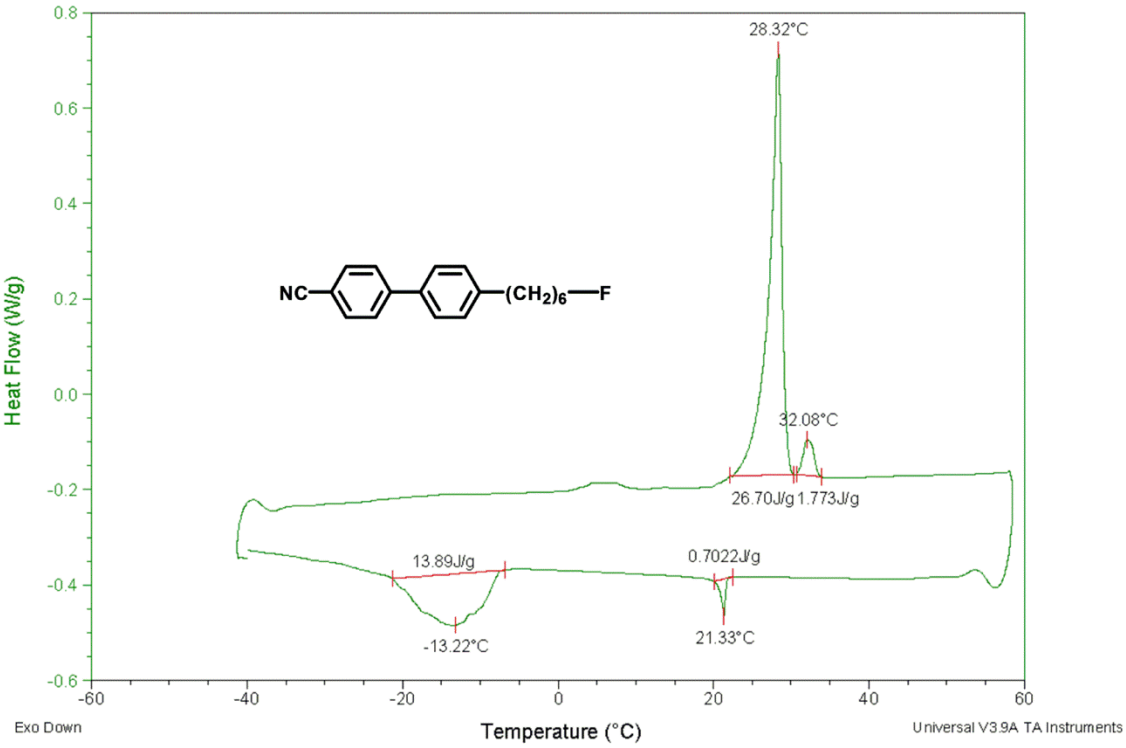


Figure SI.18 DSC of F6CB. (K 28.3 N 32.1 I 21.3 N -13.2 K)

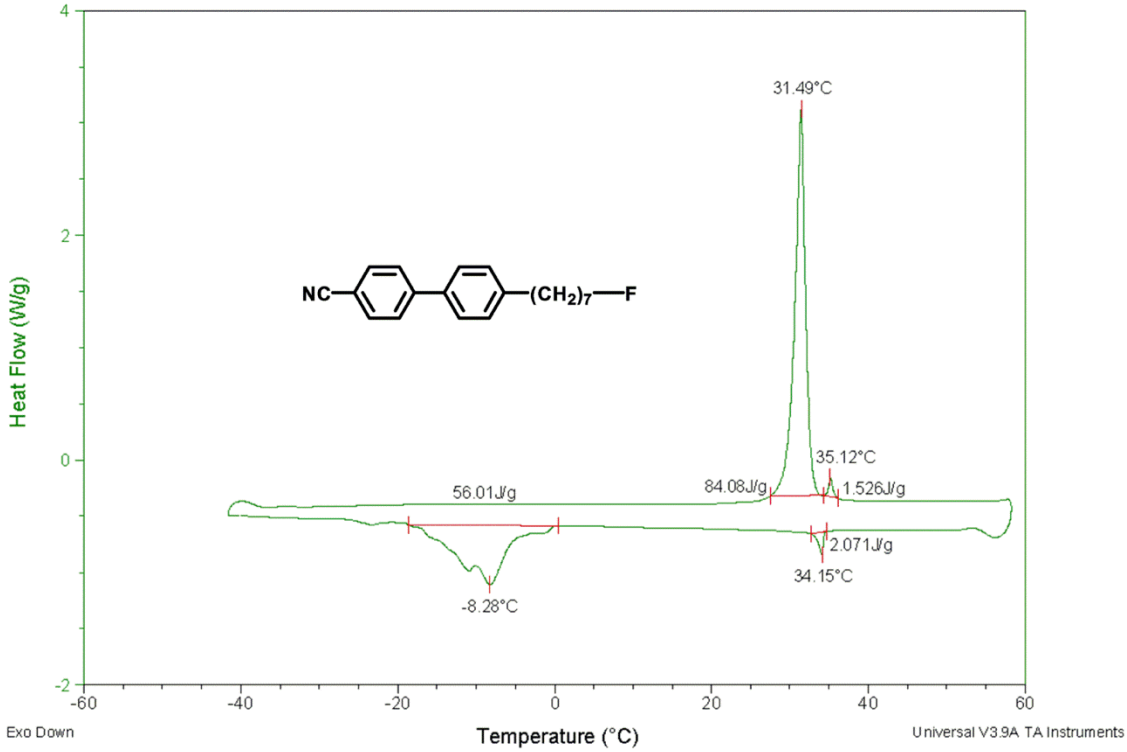


Figure SI.19 DSC of F7CB. (K 31.5 N 35.1 I 34.2 N -8.28 K)

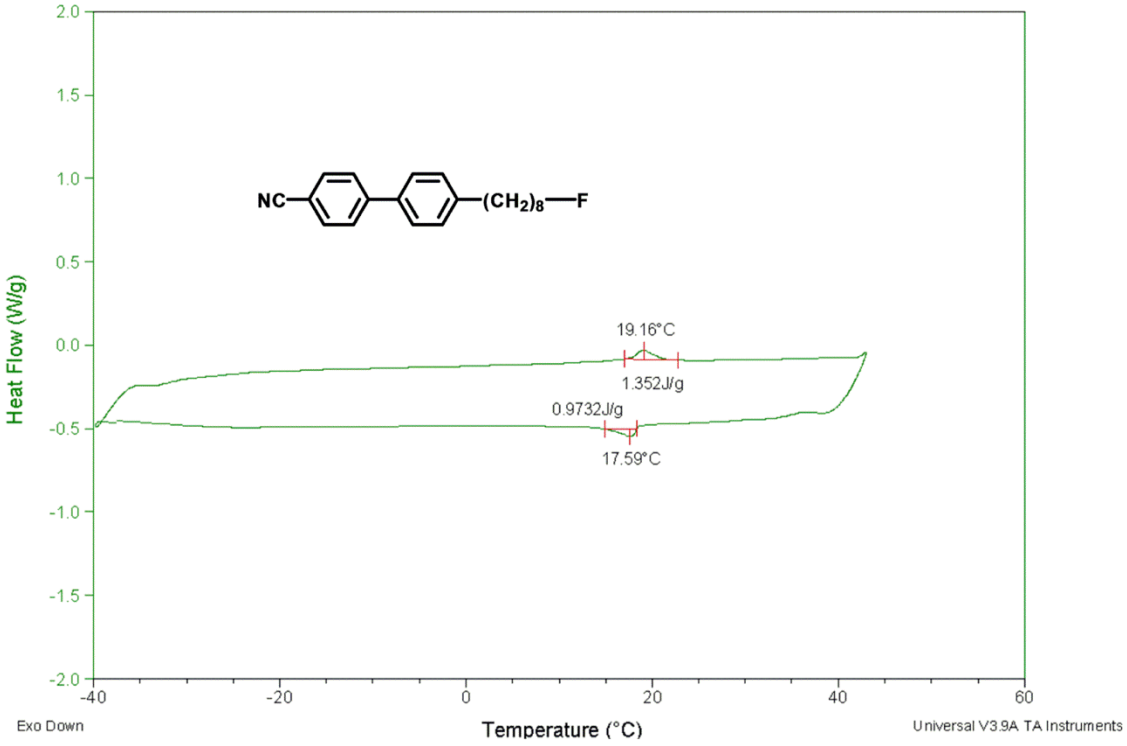


Figure SI.20 DSC of F8CB. (K ? N 19.2 I 17.6 N ? K)

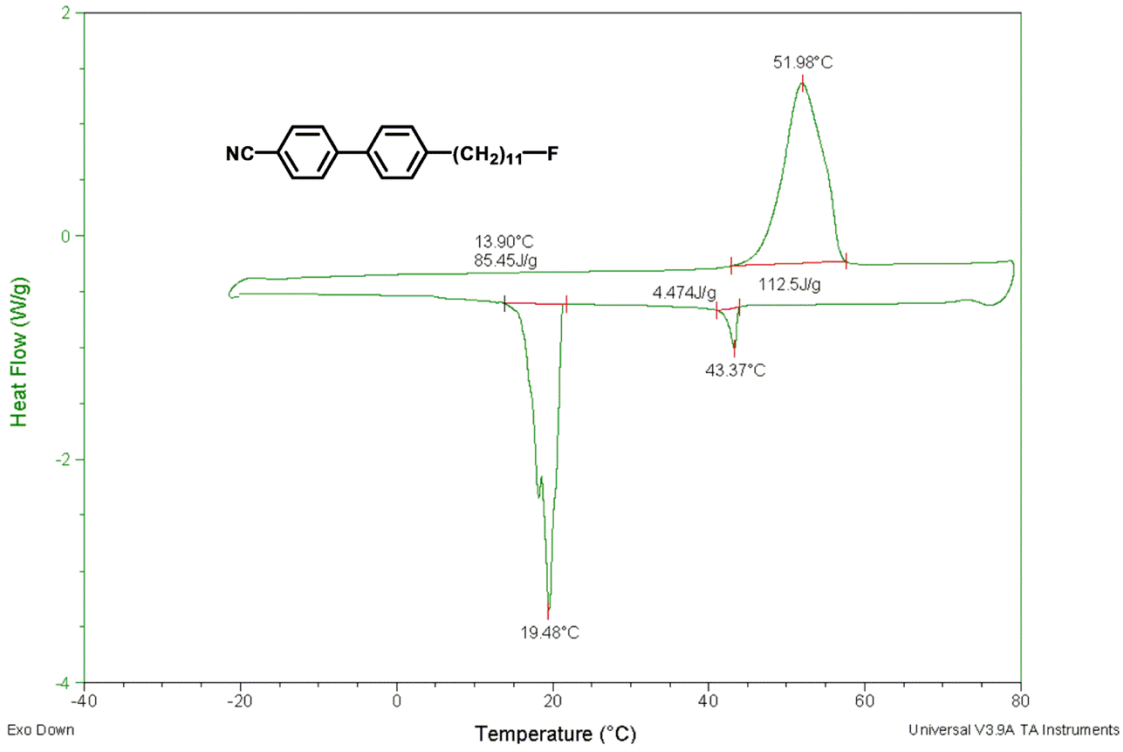


Figure SI.21 DSC of F11CB. (K 52.0 I 43.4 N 19.5 K)

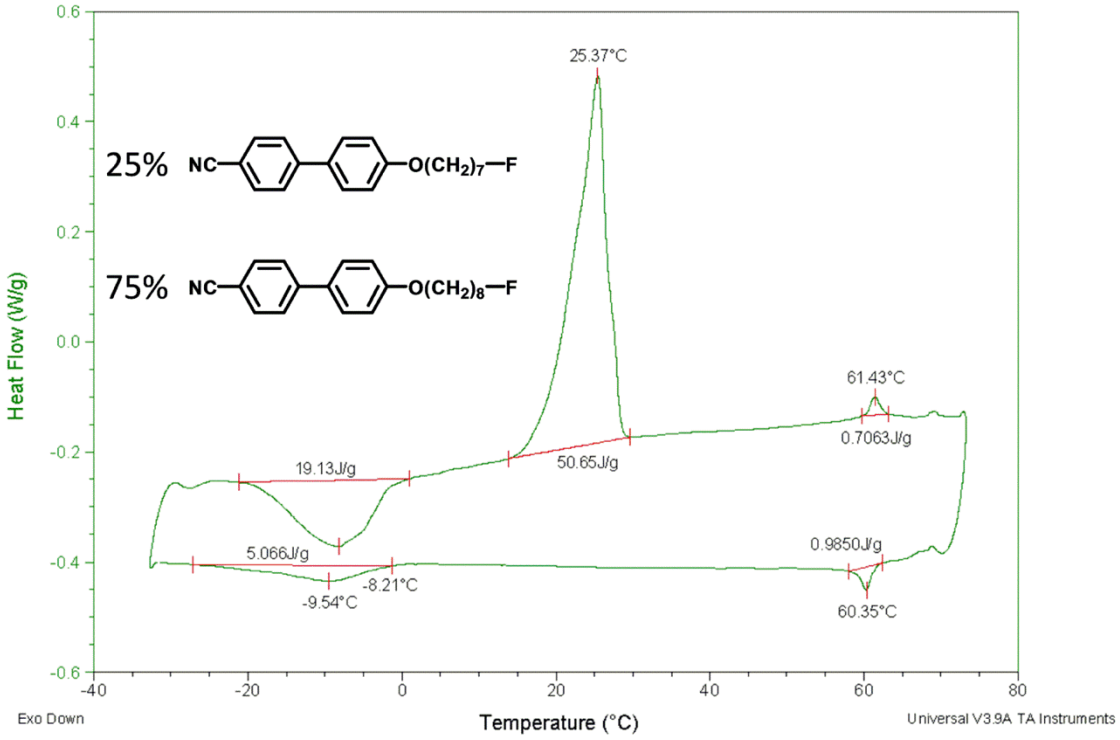


Figure SI.22 DSC of a 25%:75% mol mixture of F7OCB and F8OCB. [K 25.4 N 61.4 I 60.4 N -9.54 K (crystallization found in next heating cycle)]

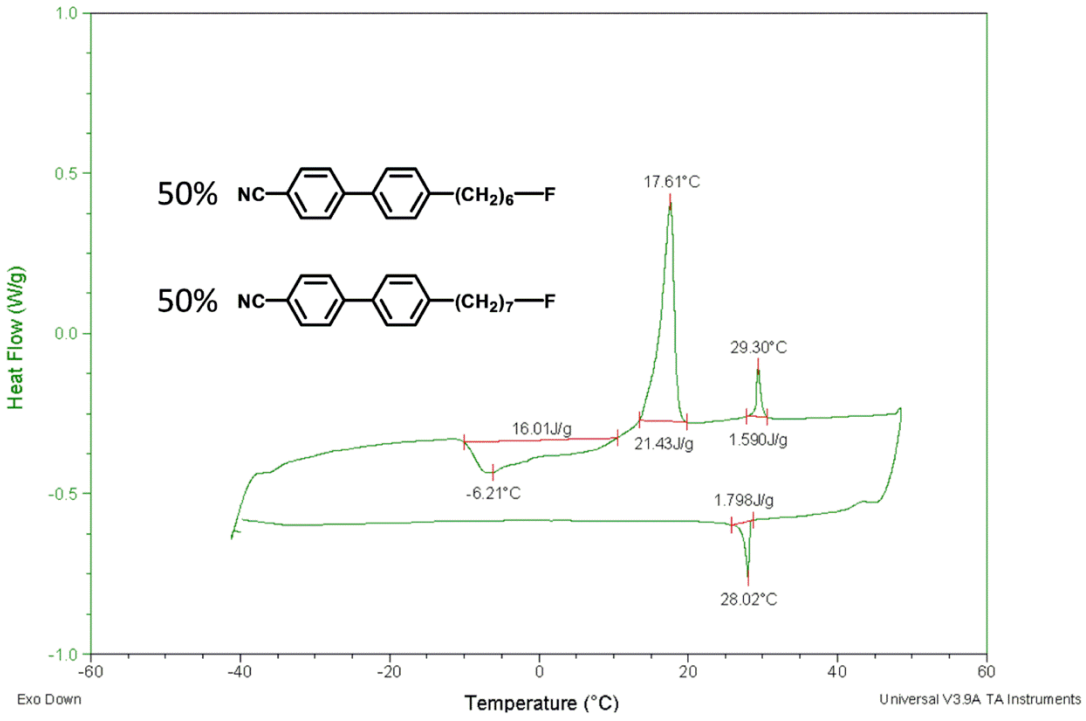
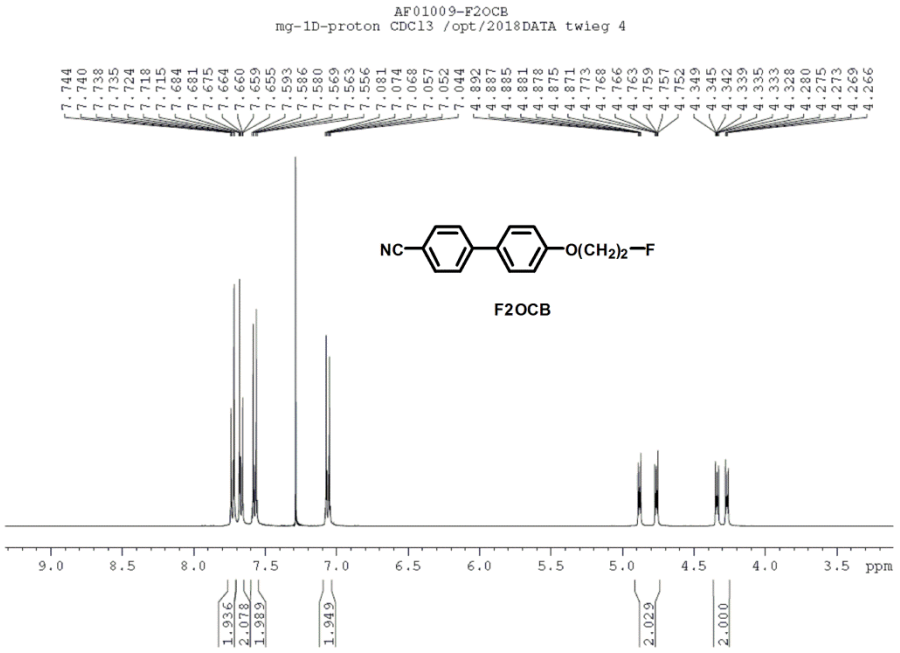
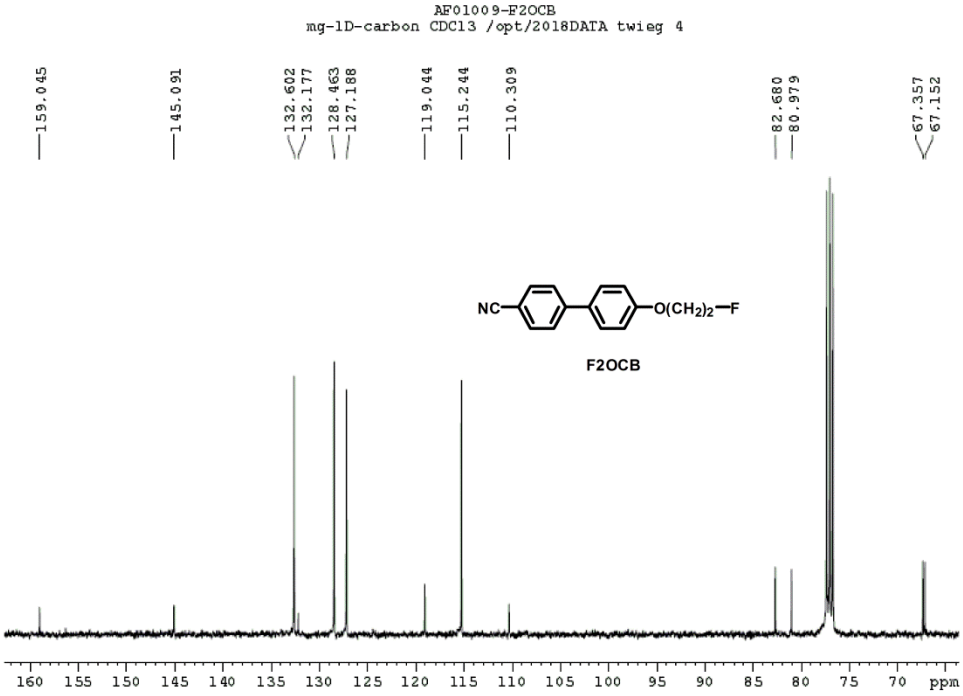


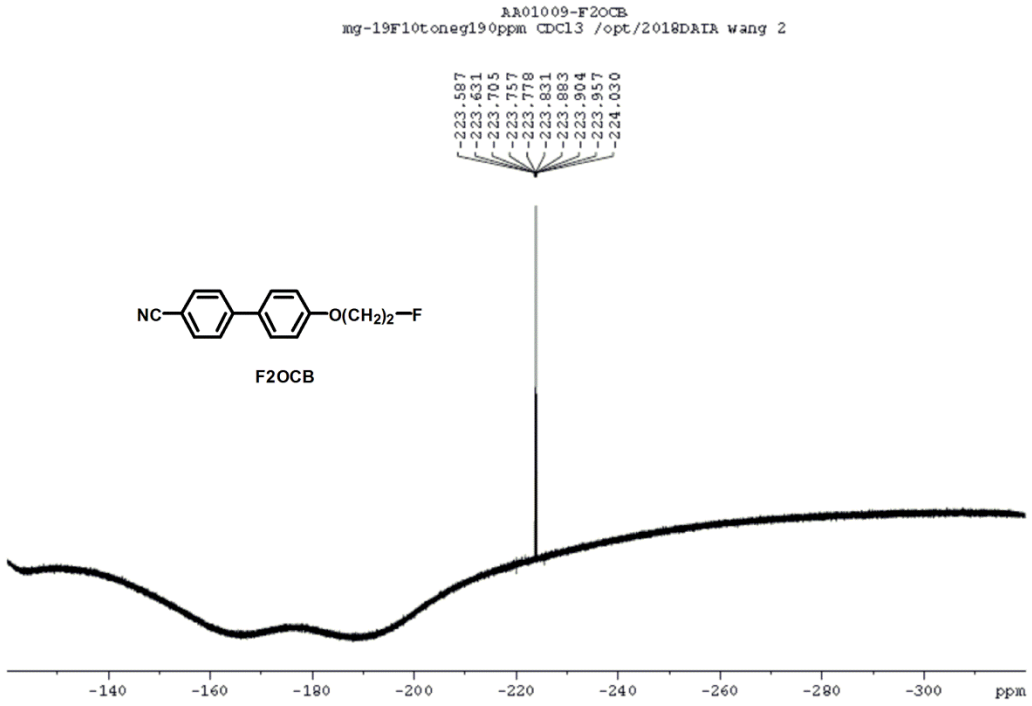
Figure SI.23 DSC of a 50%:50% mol mixture of F6CB and F7CB. [K 17.6 N 29.3 I 28.0 N -6.21 K (crystallization found in next heating cycle)]

SI.5. The NMR spectra of fluorine-terminated liquid crystals

FnOCB series



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-223.831
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-223.904
-223.957
-224.030
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F2OCB
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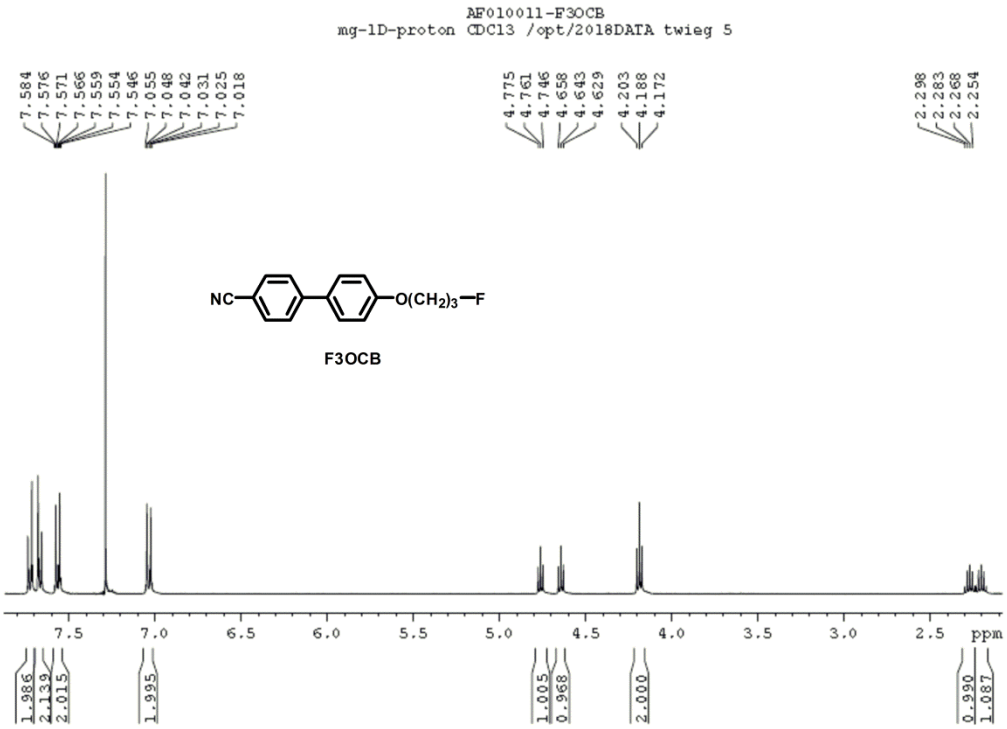
-180
-200
-220
-240
-260
-280
-300
ppm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7.571
7.566
7.559
7.554
7.546
7.055
7.048
7.042
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4.761
4.746
4.658
4.643
4.629
4.203
4.188
4.172
2.298
2.283
2.268
2.254
NC
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F3OCB
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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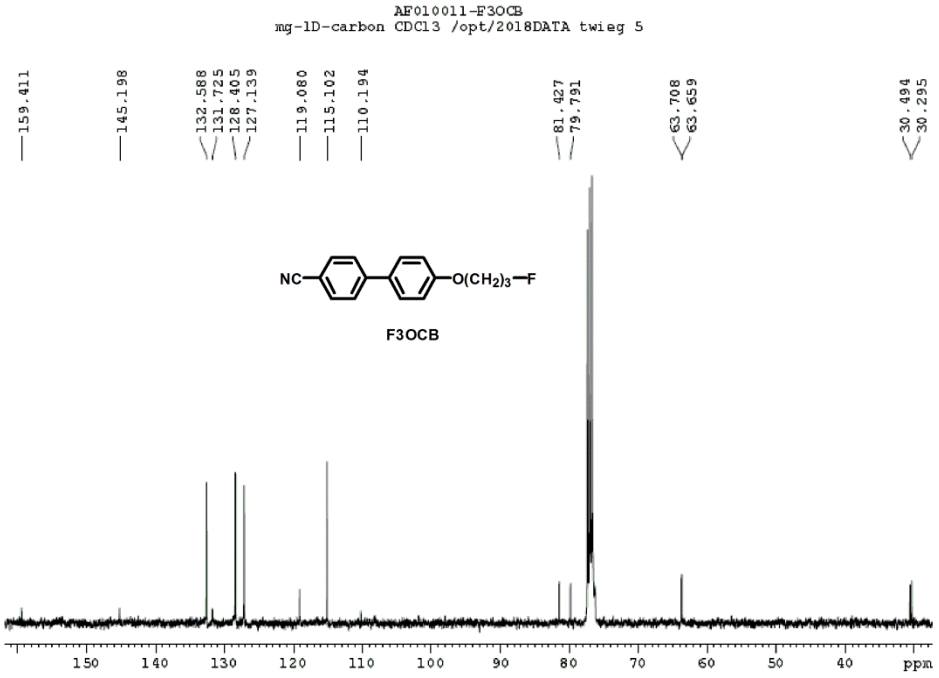
1.087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119.080
115.102
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81.427
79.791
63.708
63.659
30.494
30.295
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F3OCB
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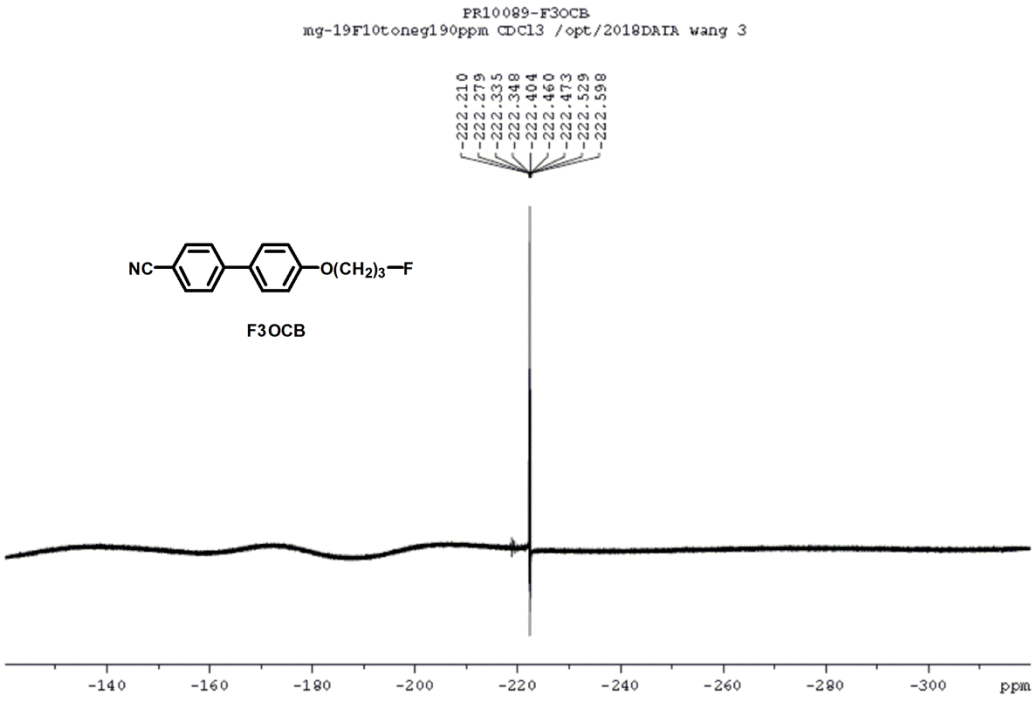
120
110
100
90
80
70
60
50
40
ppm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-222.335
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NC
O(CH2)3F
F3OCB
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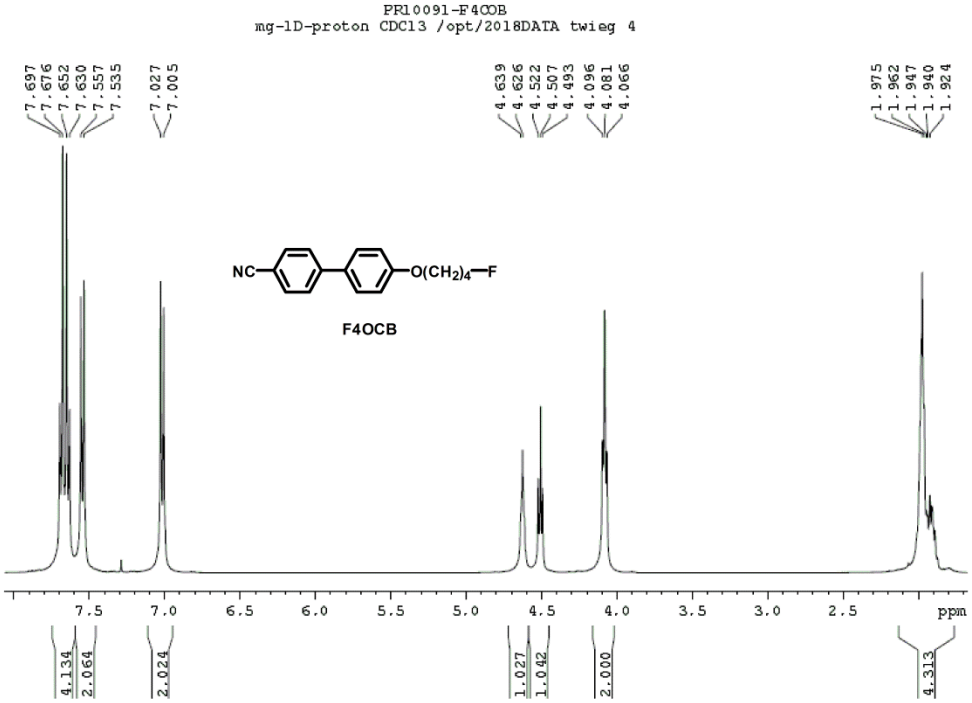
-180
-200
-220
-240
-260
-280
-300
ppm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7.652
7.630
7.557
7.535
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1.947
1.940
1.924
NC
O(CH2)4F
F4OCB
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
2.5
ppm
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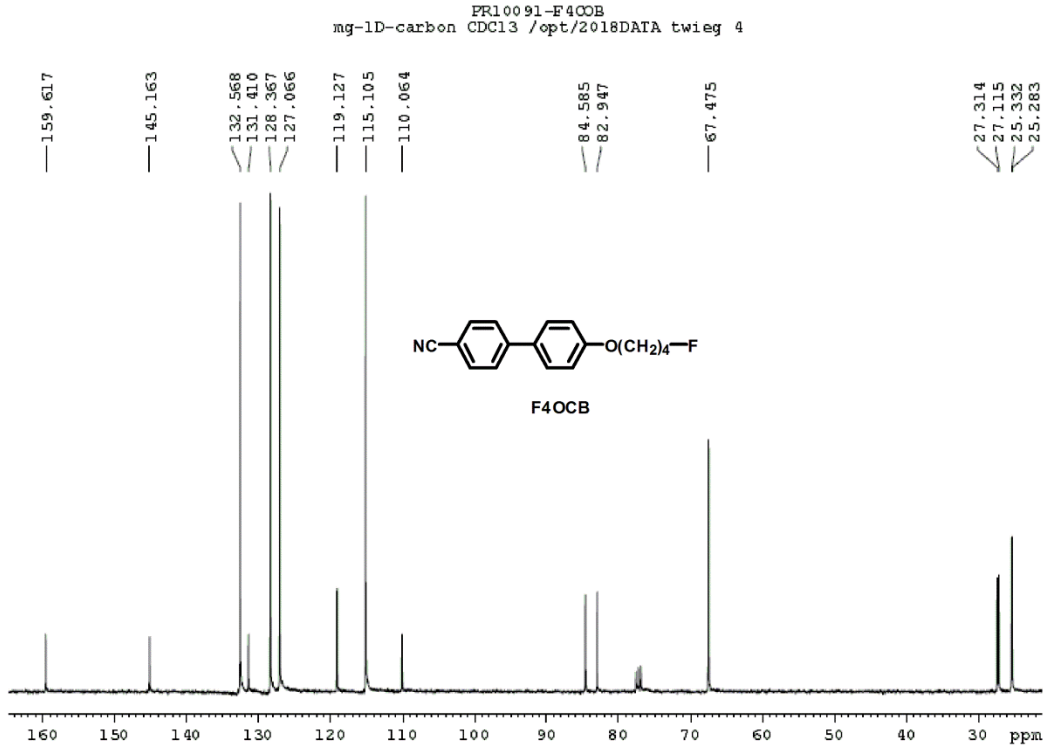
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119.127
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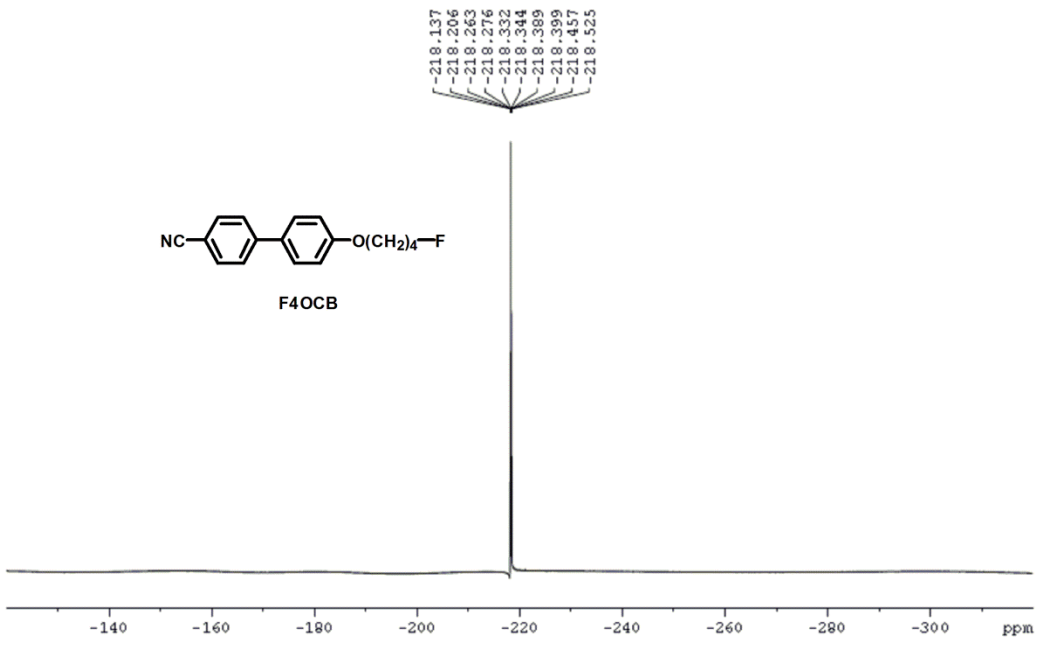
110.064
84.585
82.947
67.475
27.314
27.115
25.332
25.283
NC
O(CH2)4F
F4OCB
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

PR10091-4FOCB
mg-19F1Otoneg190ppm CDCl3 /opt/2018DATA twieg 4



PR1004-5FOCB
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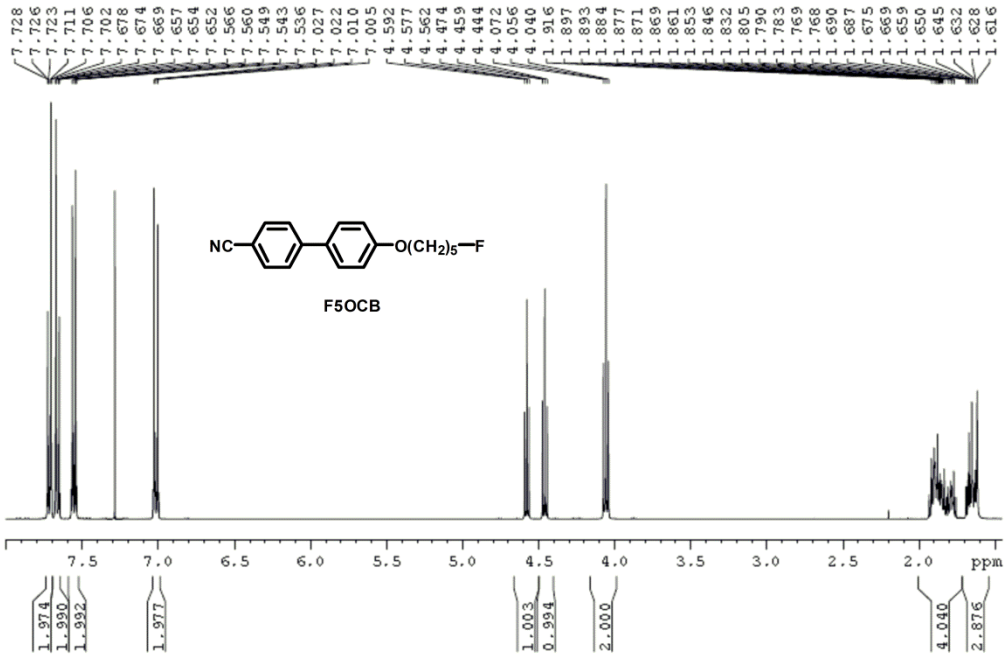

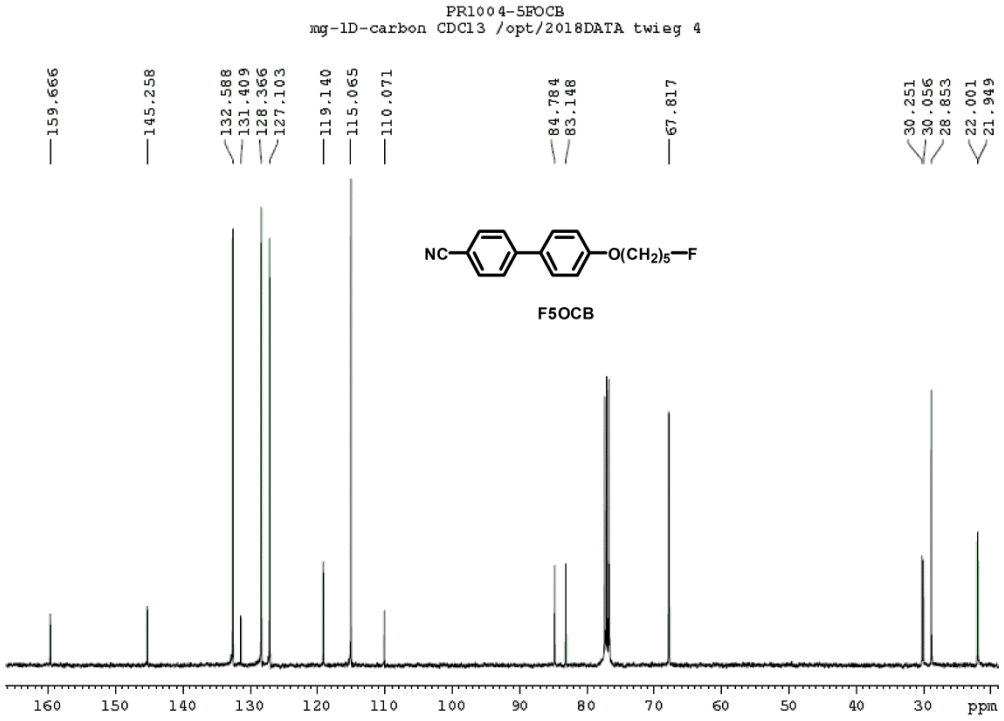
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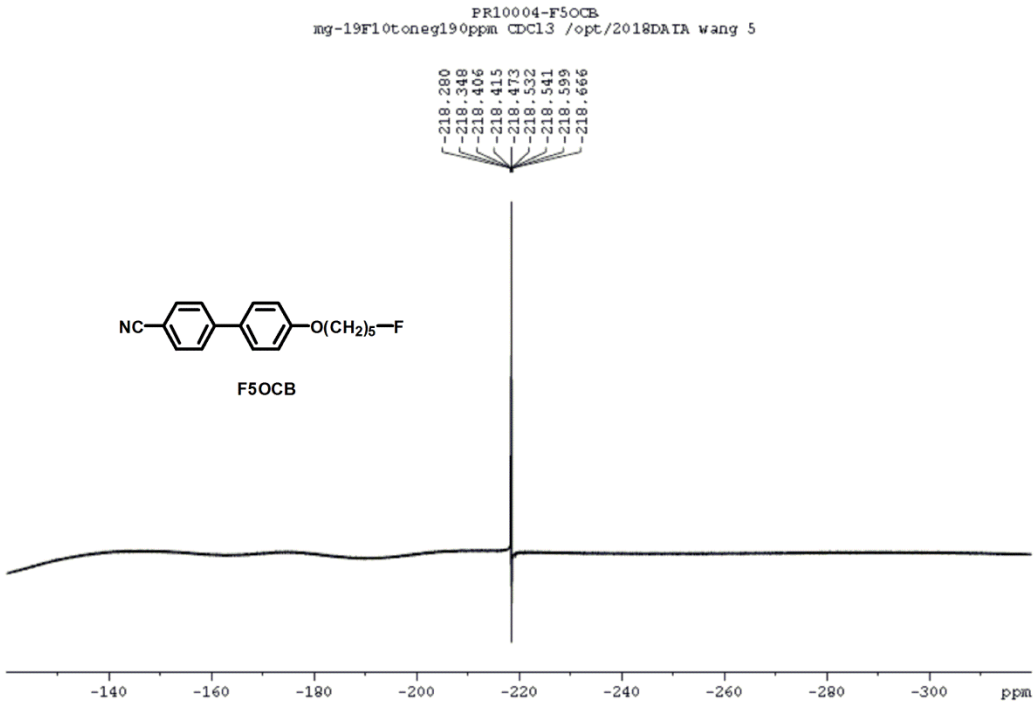
127.103
119.140
115.065
110.071
84.784
83.148
67.817
30.251
30.056
28.853
22.001
21.949
NC
O(CH2)5F
F5OCB
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


PR10004-F5OCB
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-218.406
-218.415
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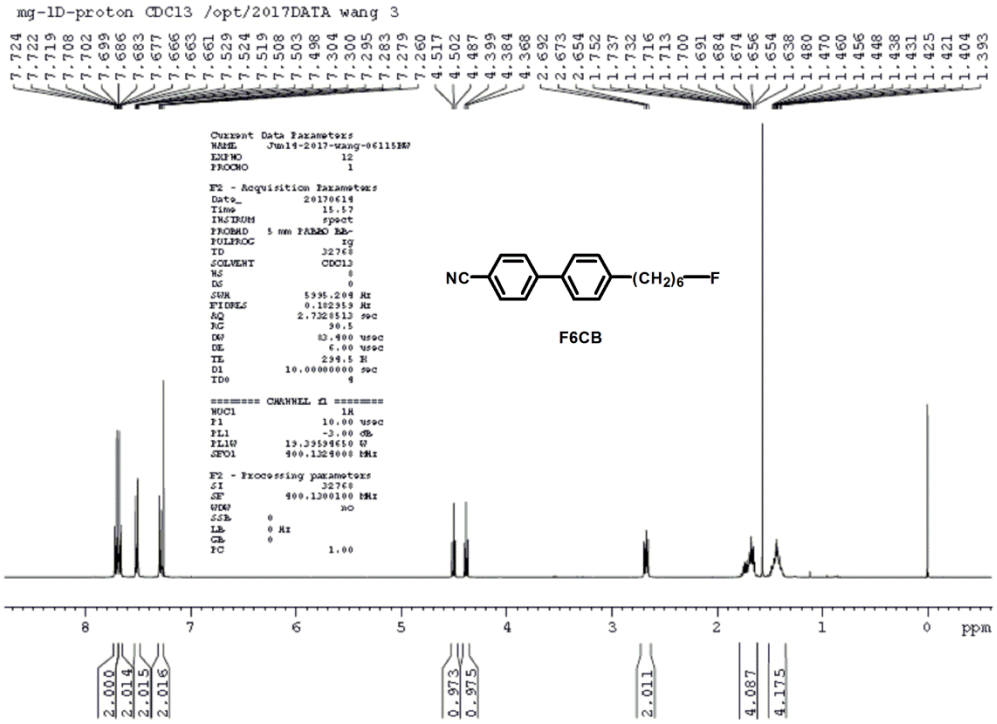
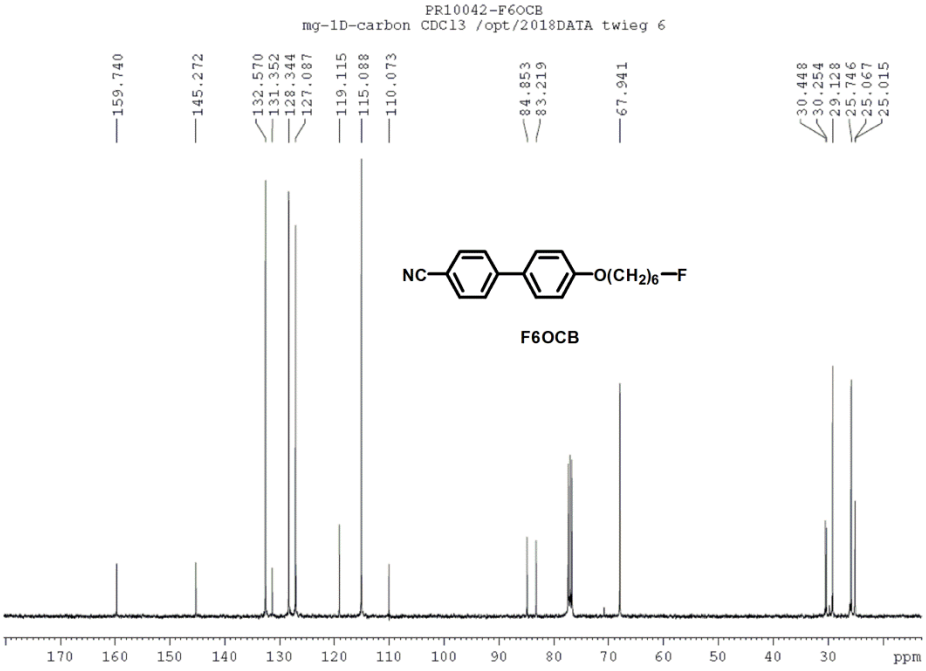
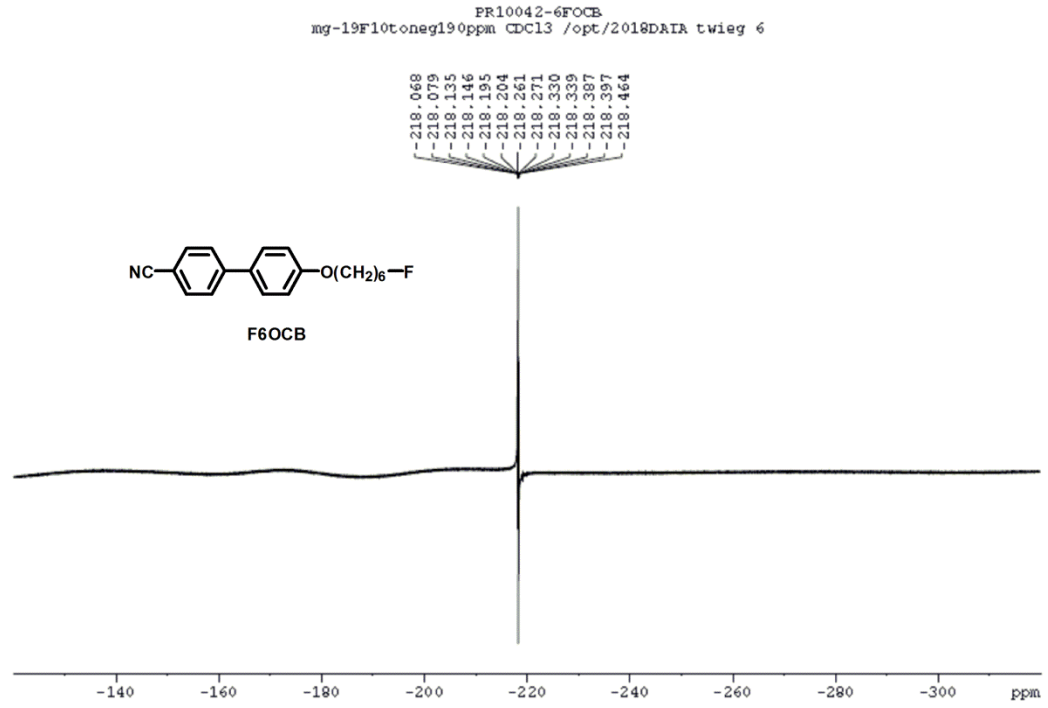
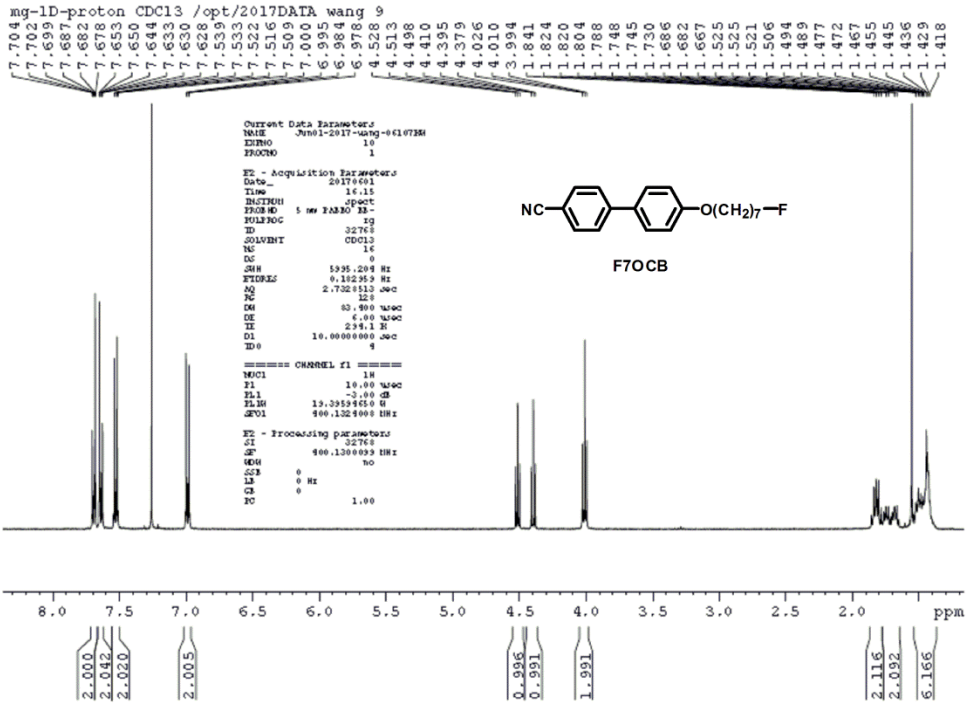
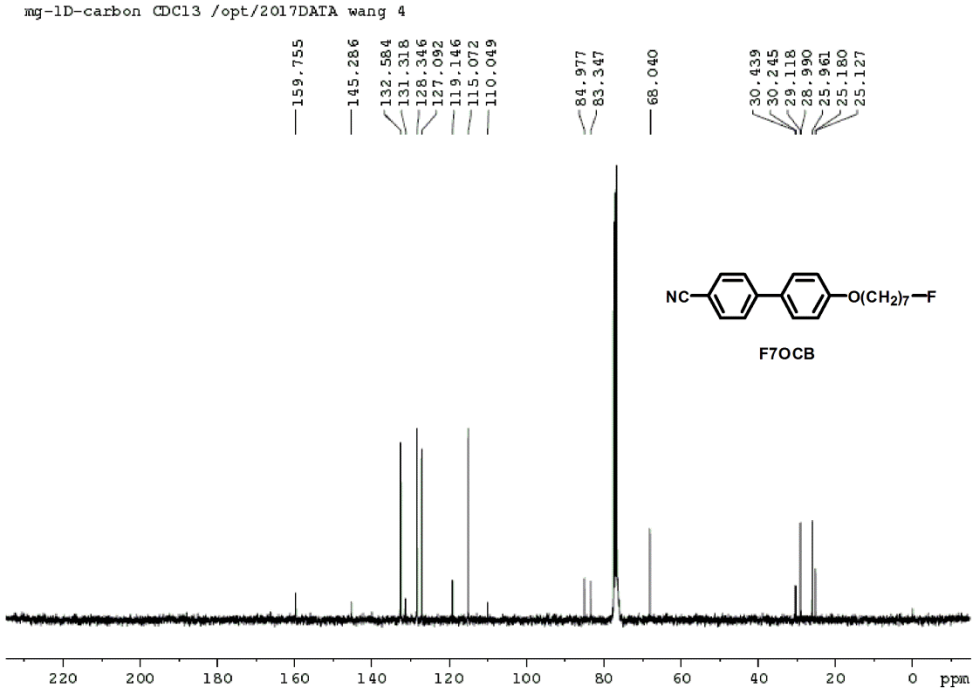
-180
-200
-220
-240
-260
-280
-300
ppm

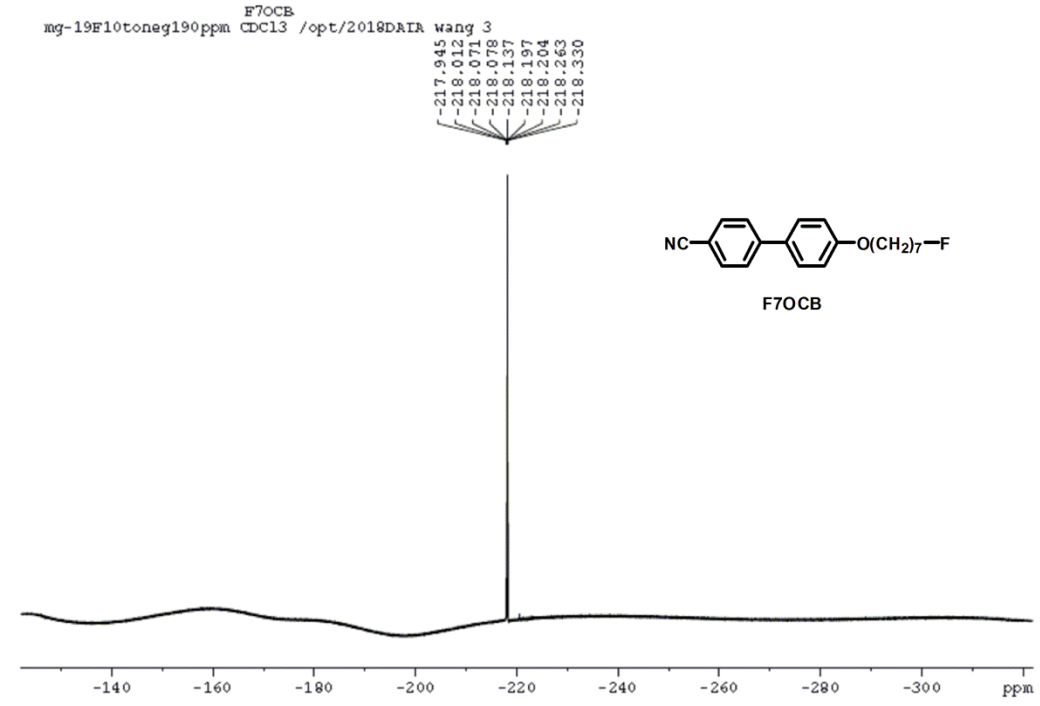

mg-1D-proton CDCl3 /opt/2017DATA wang 3
7.724 7.722 7.719 7.708 7.702 7.699 7.686 7.683 7.677 7.666 7.663 7.661 7.529 7.524 7.519 7.508 7.503 7.498 7.304 7.300 7.295 7.283 7.279 7.260 4.517 4.502 4.487 4.399 4.384 4.368 2.692 2.673 2.654 1.752 1.737 1.732 1.716 1.713 1.700 1.691 1.684 1.674 1.656 1.654 1.638 1.480 1.470 1.460 1.456 1.448 1.438 1.431 1.425 1.421 1.404 1.393
Current Data Parameters
NAME Jun19-2017-wang-06115367
EXPNO 12
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170619
Time 15.57
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7321512 sec
RG 30.5
DW 83.400 usec
DE 6.00 usec
TE 298.5 K
D1 10.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 -3.00 dB
PL10 13.39594650 W
SFO1 400.1324000 MHz
F2 - Processing parameters
SI 32768
SF 400.1300100 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.00
NC
(CH2)6—F
F6CB
8 7 6 5 4 3 2 1 0 ppm
2.000 2.014 2.015 2.016 0.973 0.975 2.011 4.087 4.175

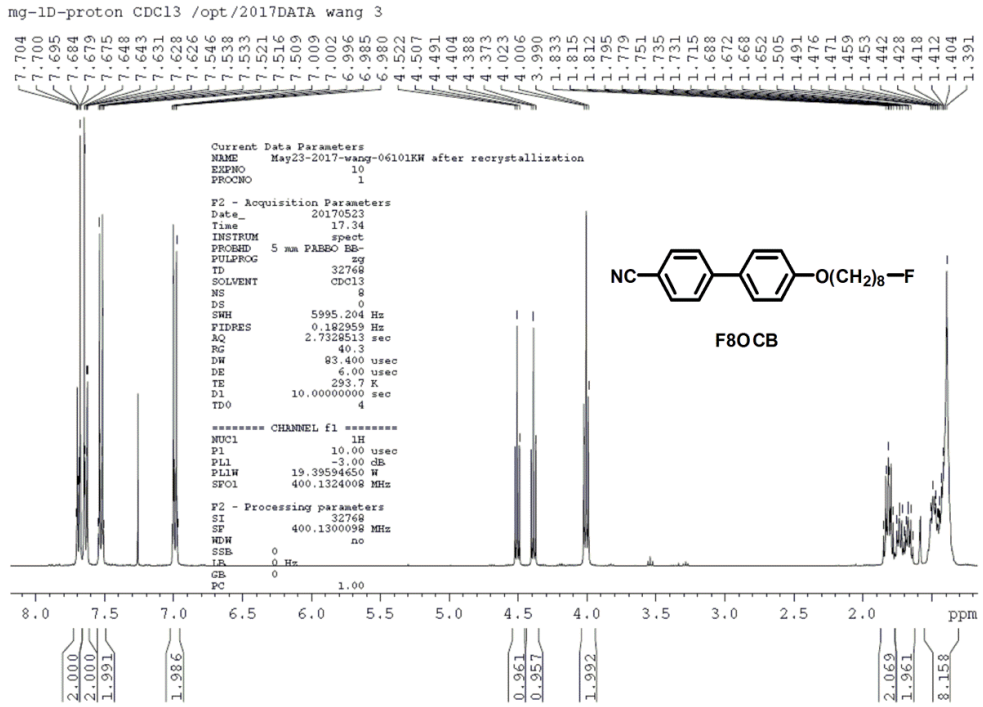

PR10042-F6OCB
mg-1D-carbon CDCl3 /opt/2018DATA twieg 6
159.740 145.272 132.570 131.352 128.344 127.087 119.115 115.088 110.073 84.853 83.219 67.941 30.448 30.254 29.128 25.746 25.067 25.015
NC
O(CH2)6—F
F6OCB
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm

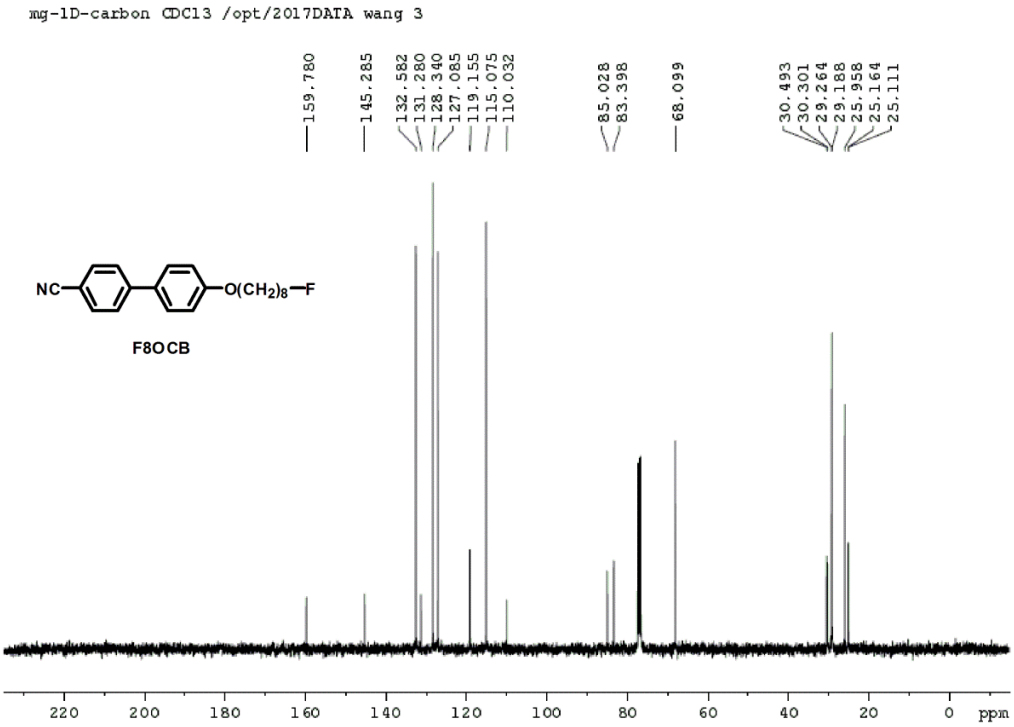

PR10042-6FOCB
mg-19F10toneg190ppm CDCl3 /opt/2018DATA twieg 6
-218.068
-218.079
-218.135
-218.146
-218.195
-218.204
-218.261
-218.271
-218.330
-218.339
-218.387
-218.397
-218.464
NC
O(CH2)6—F
F6OCB
-140
-160
-180
-200
-220
-240
-260
-280
-300
ppm

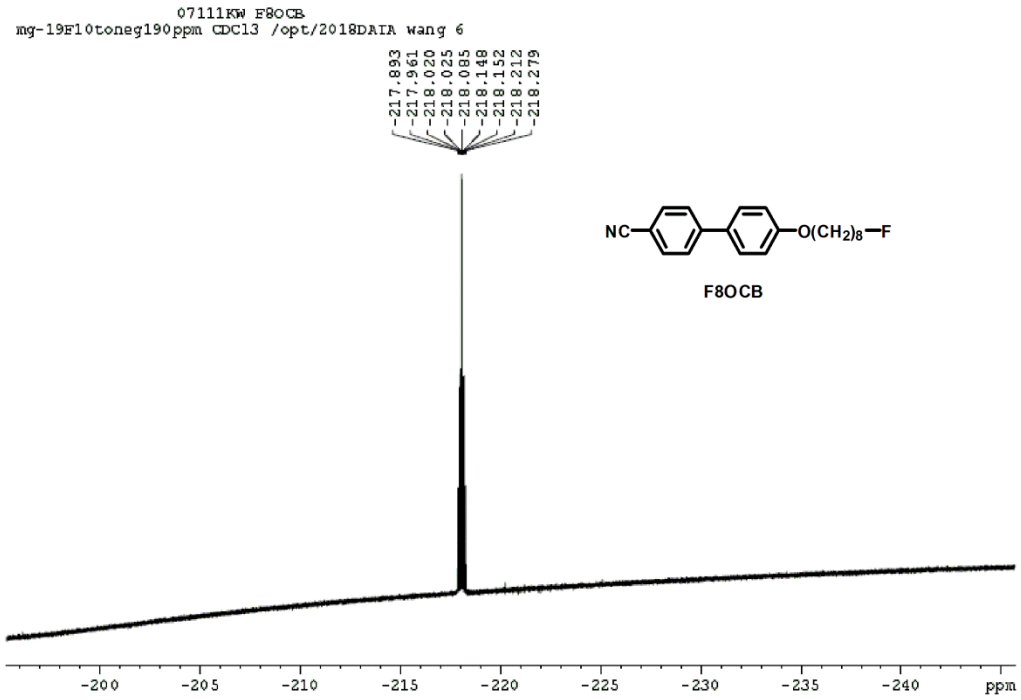

mg-1D-proton CDCl3 /opt/2017DATA wang 9
7.704
7.702
7.699
7.687
7.682
7.678
7.653
7.650
7.644
7.633
7.630
7.628
7.539
7.533
7.522
7.516
7.509
7.000
6.995
6.984
6.978
4.528
4.513
4.498
4.410
4.395
4.379
4.026
4.010
3.994
1.841
1.824
1.820
1.804
1.788
1.748
1.745
1.730
1.686
1.682
1.667
1.525
1.525
1.521
1.506
1.494
1.489
1.477
1.472
1.467
1.455
1.445
1.436
1.429
1.418
Current Data Parameters
NAME Jun01-2017-wang-0617HH
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170601
Time 16.15
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7328113 sec
RG 128
DW 83.900 usec
DE 6.00 usec
TE 294.1 K
D1 10.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 -3.00 dB
PL1H 19.3959450 W
SFO1 400.1324000 MHz
F2 - Processing parameters
SI 32768
SF 400.1300093 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.00
NC
O(CH2)7—F
F7OCB
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
2.000
2.042
2.020
2.005
0.996
0.991
1.991
2.116
2.092
6.166

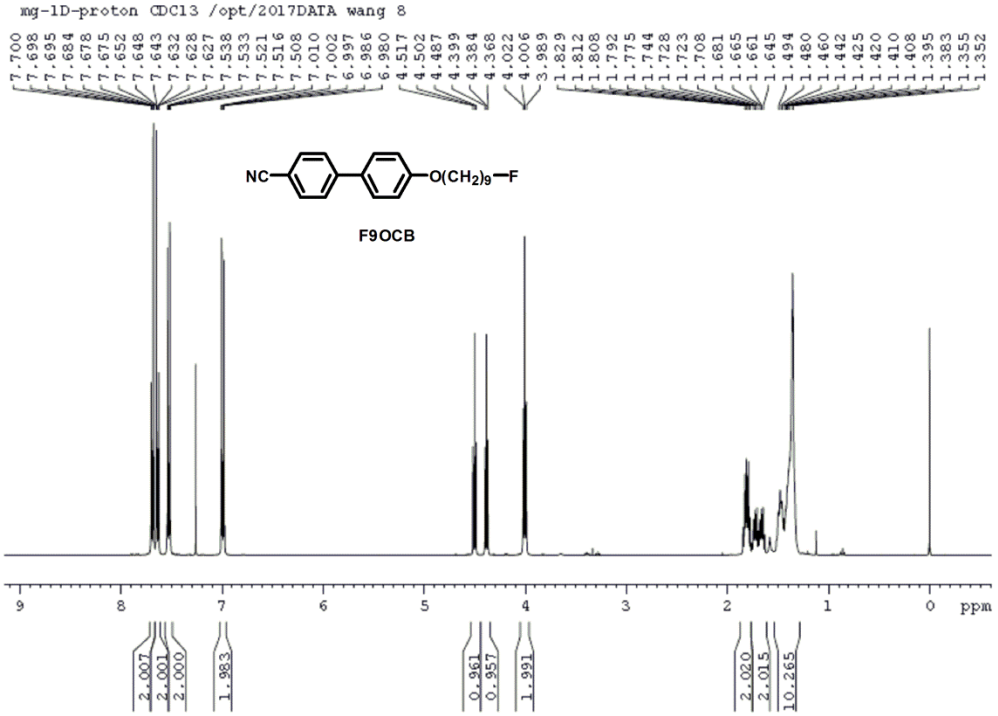

mg-1D-carbon CDCl3 /opt/2017DATA wang 4
159.755
145.286
132.584
131.318
128.346
127.092
119.146
115.072
110.049
84.977
83.347
68.040
30.439
30.245
29.118
28.990
25.961
25.180
25.127
NC
O(CH2)7F
F7OCB
220
200
180
160
140
120
100
80
60
40
20
0
ppm

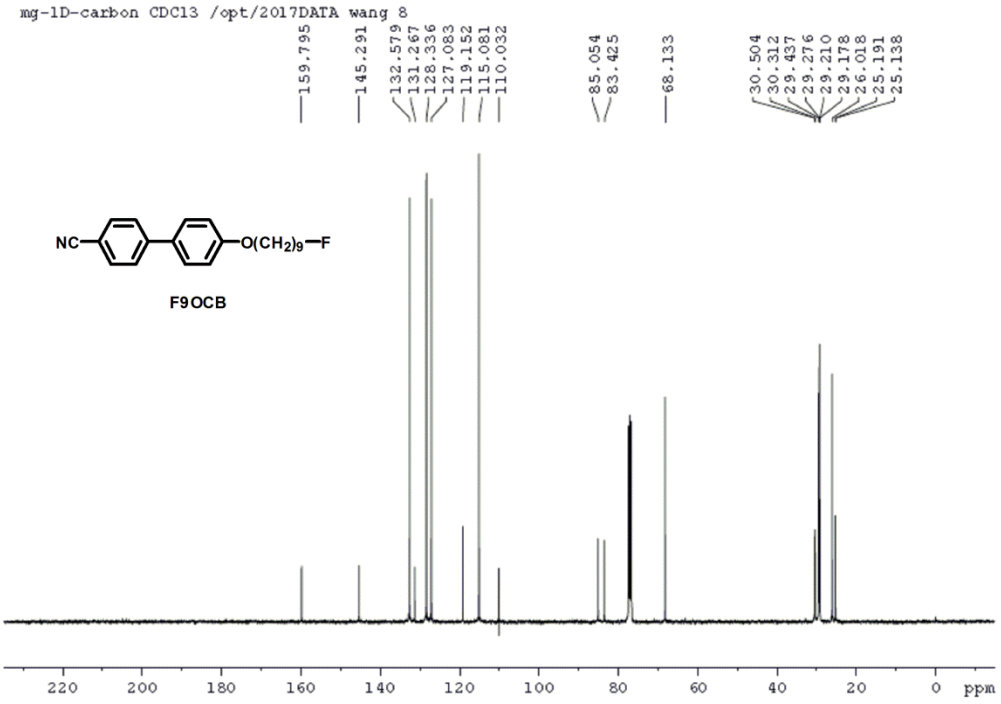

F7OCB
mg-19F10toneg190ppm CDCl3 /opt/2018DATA wang 3
-217.945
-218.012
-218.071
-218.078
-218.137
-218.197
-218.204
-218.263
-218.330
NC
O(CH2)7F
F7OCB
-140
-160
-180
-200
-220
-240
-260
-280
-300
ppm

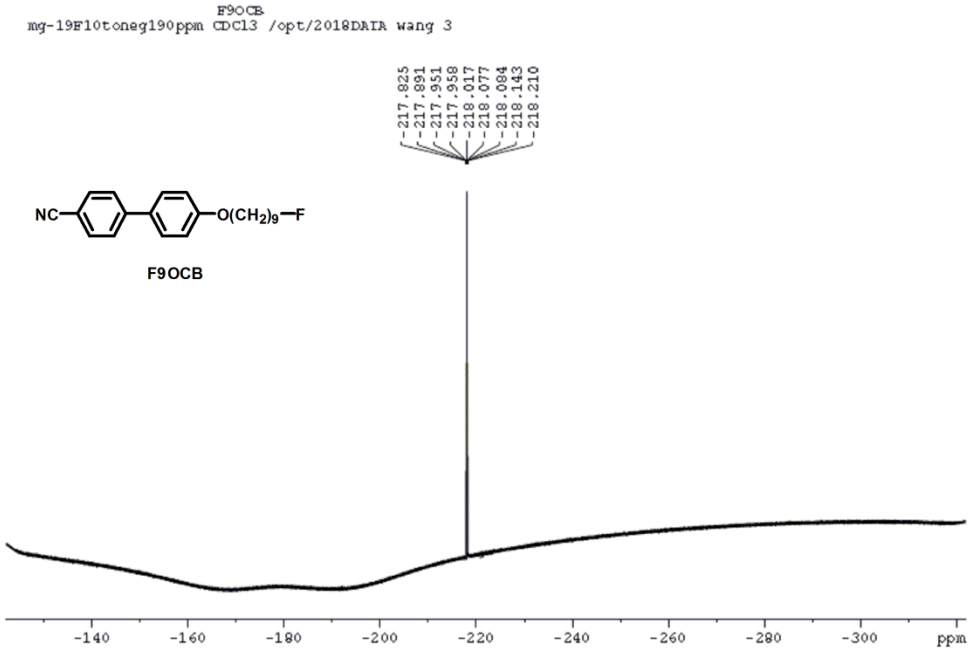

mg-1D-proton CDCl3 /opt/2017DATA wang 3
Current Data Parameters
NAME May23-2017-wang-06101KW after recrystallization
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170523
Time 17.34
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7328513 sec
RG 40.3
DW 83.400 usec
DE 6.00 usec
TE 293.7 K
D1 10.00000000 sec
TD0 4
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 -3.00 dB
PL1W 19.39594650 W
SFO1 400.1324008 MHz
F2 - Processing parameters
SI 32768
SF 400.1300098 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.00
NC
O(CH2)8F
F8OCB
ppm

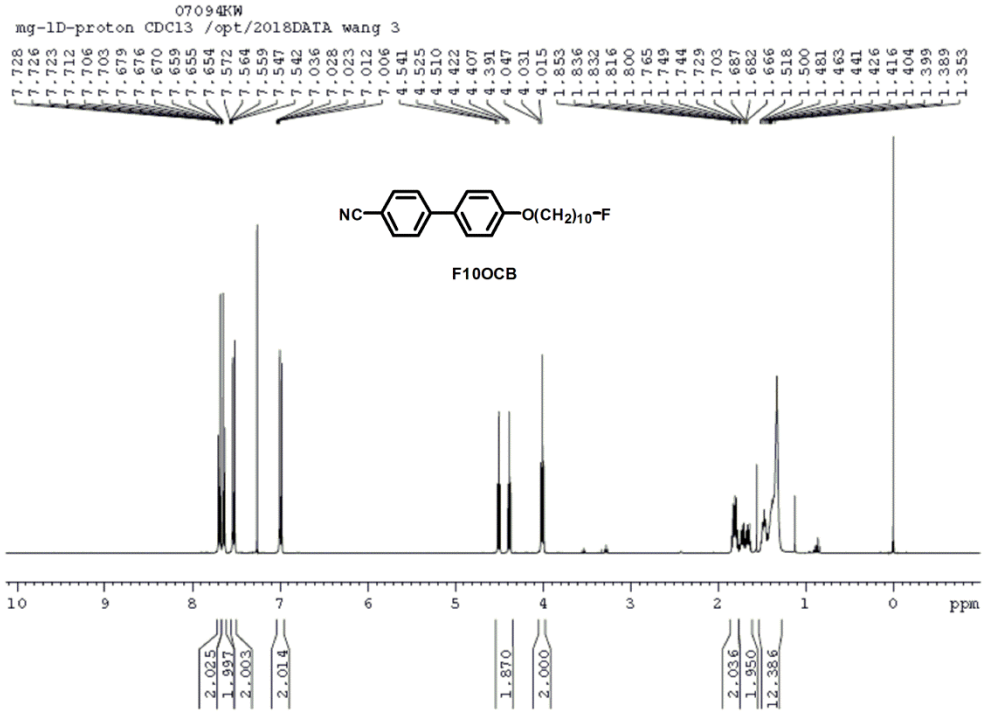

mg-1D-carbon CDCl3 /opt/2017DATA wang 3
159.780
145.285
132.582
131.280
128.340
127.085
119.155
115.075
110.032
85.028
83.398
68.099
30.493
30.301
29.264
29.188
25.958
25.164
25.111
NC
O(CH2)8F
F8OCB
ppm

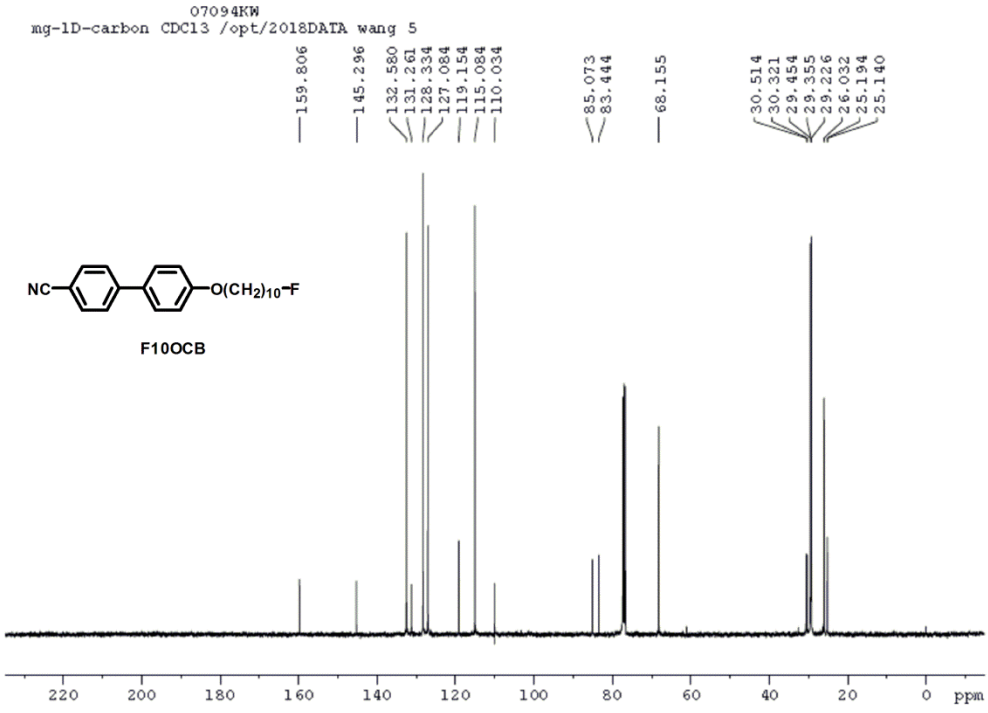

07111KW F8OCB
mg-19F10toneg190ppm CDCl3 /opt/2018DATA wang 6
-217.893
-217.961
-218.020
-218.025
-218.085
-218.148
-218.152
-218.212
-218.279
NC
O(CH2)8F
F8OCB
-200
-205
-210
-215
-220
-225
-230
-235
-240
ppm

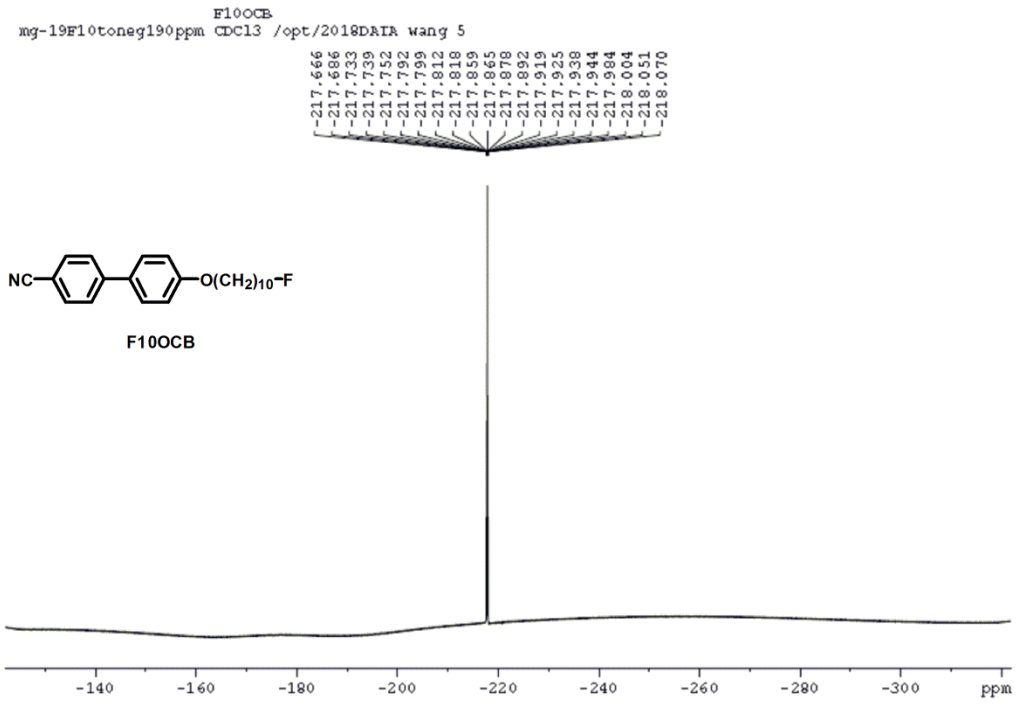

mg-1D-proton CDCl3 /opt/2017DATA wang 8
7.700
7.698
7.695
7.684
7.678
7.675
7.652
7.648
7.643
7.632
7.628
7.627
7.538
7.533
7.521
7.516
7.508
7.010
7.002
6.997
6.986
6.980
4.517
4.502
4.487
4.399
4.384
4.368
4.022
4.006
3.989
1.829
1.812
1.808
1.792
1.775
1.744
1.728
1.723
1.708
1.681
1.665
1.661
1.645
1.494
1.480
1.460
1.442
1.425
1.420
1.410
1.408
1.395
1.383
1.355
1.352
NC
O(CH2)9F
F9OCB
9
8
7
6
5
4
3
2
1
0
ppm
2.007
2.001
2.000
1.983
0.961
0.957
1.991
2.020
2.015
10.265

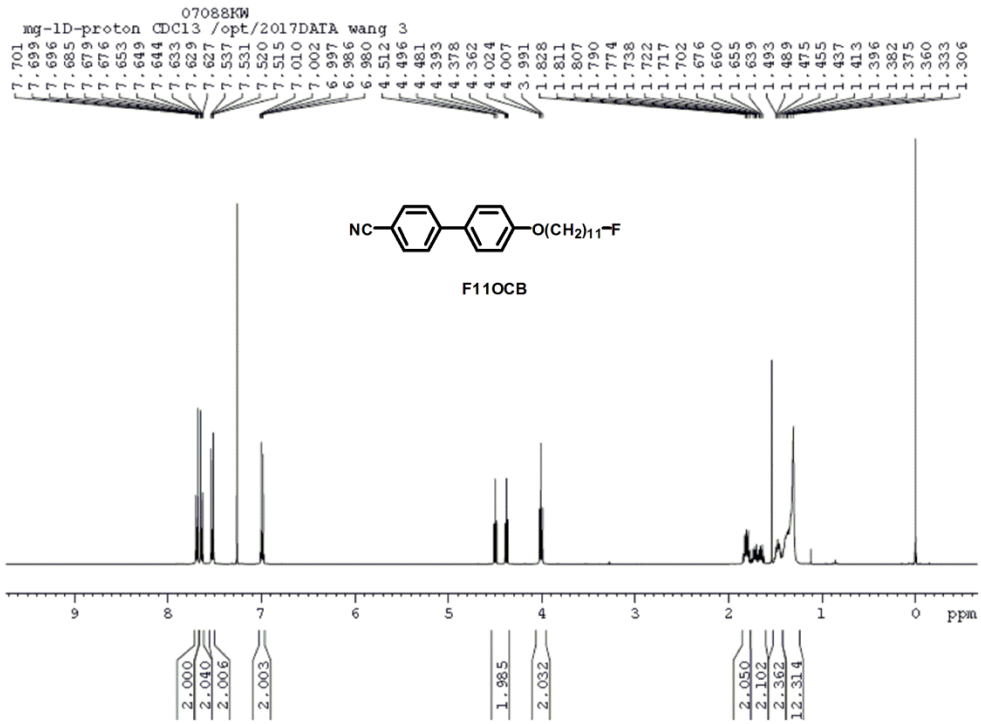

mg-1D-carbon CDCl3 /opt/2017DATA wang 8
159.795
145.291
132.579
131.267
128.336
127.083
119.152
115.081
110.032
85.054
83.425
68.133
30.504
30.312
29.437
29.276
29.210
29.178
26.018
25.191
25.138
NC
O(CH2)9F
F9OCB
220
200
180
160
140
120
100
80
60
40
20
0
ppm

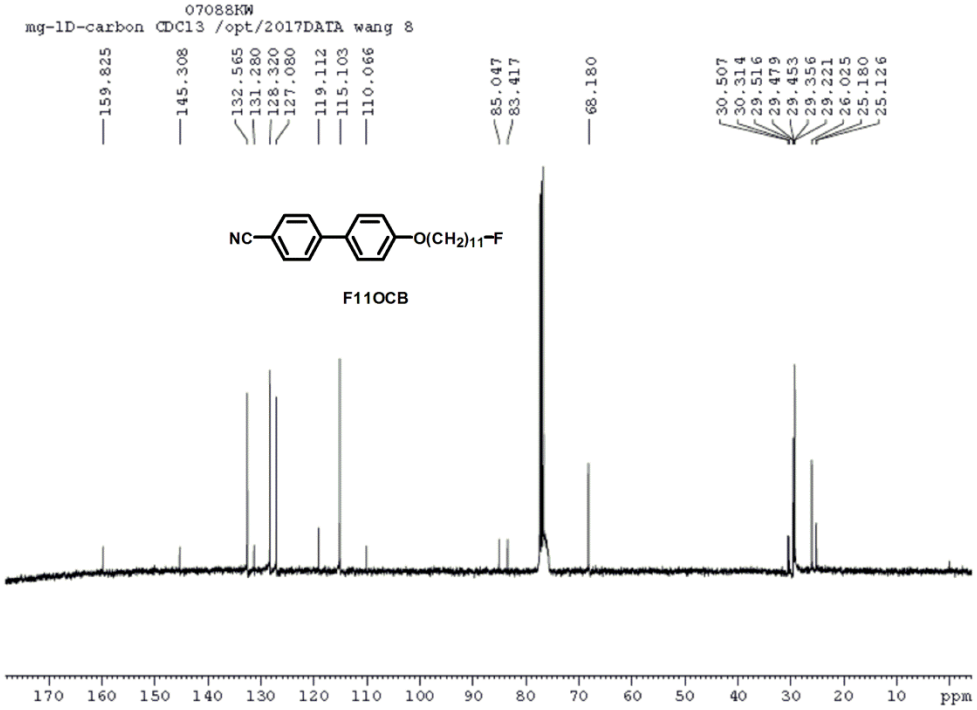

F9OCB
mg-19F10toneg190ppm CDCl3 /opt/2018DATA wang 3
-217.825
-217.891
-217.951
-217.958
-218.017
-218.077
-218.084
-218.143
-218.210
NC
O(CH2)9F
F9OCB
-140
-160
-180
-200
-220
-240
-260
-280
-300
ppm

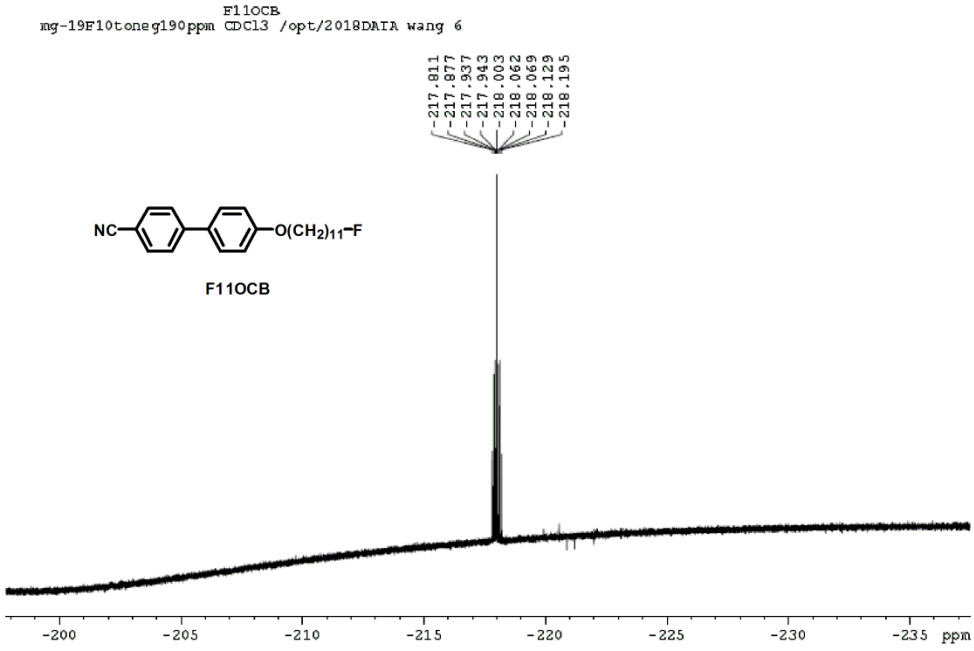

07094KW
mg-1D-proton CDCl3 /opt/2018DATA wang 3
7.728
7.726
7.723
7.712
7.706
7.703
7.679
7.676
7.670
7.659
7.655
7.654
7.572
7.564
7.559
7.547
7.542
7.036
7.028
7.023
7.012
7.006
4.541
4.525
4.510
4.422
4.407
4.391
4.047
4.031
4.015
1.853
1.836
1.832
1.816
1.800
1.765
1.749
1.744
1.729
1.703
1.687
1.682
1.666
1.518
1.500
1.481
1.463
1.441
1.426
1.416
1.404
1.399
1.389
1.353
NC
O(CH2)10F
F10OCB
10
9
8
7
6
5
4
3
2
1
0
ppm
2.025
1.997
2.003
2.014
1.870
2.000
2.036
1.950
12.386

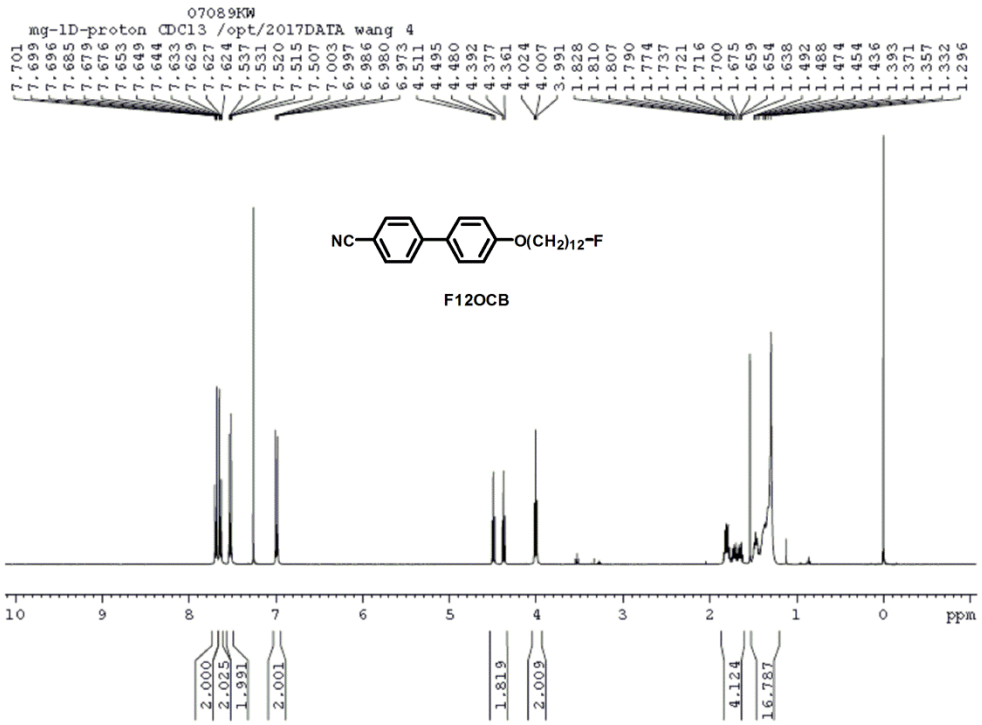

07094KW
mg-1D-carbon CDCl3 /opt/2018DATA wang 5
159.806
145.296
132.580
131.261
128.334
127.084
119.154
115.084
110.034
85.073
83.444
68.155
30.514
30.321
29.454
29.355
29.226
26.032
25.194
25.140
NC
O(CH2)10F
F10OCB
220
200
180
160
140
120
100
80
60
40
20
0
ppm

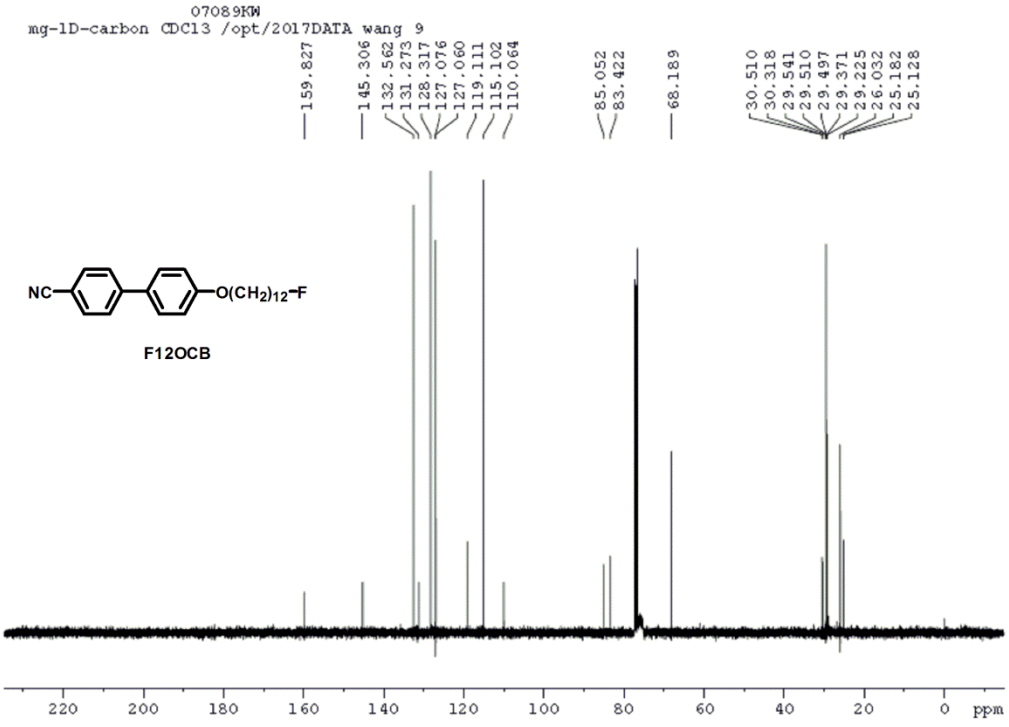

F10OCB
mg-19F10toneg190ppm CDCl3 /opt/2018DATA wang 5
-217.666
-217.686
-217.733
-217.739
-217.752
-217.792
-217.799
-217.812
-217.818
-217.859
-217.865
-217.878
-217.892
-217.919
-217.925
-217.938
-217.944
-217.984
-218.004
-218.051
-218.070
NC
O(CH2)10F
F10OCB
-140
-160
-180
-200
-220
-240
-260
-280
-300
ppm

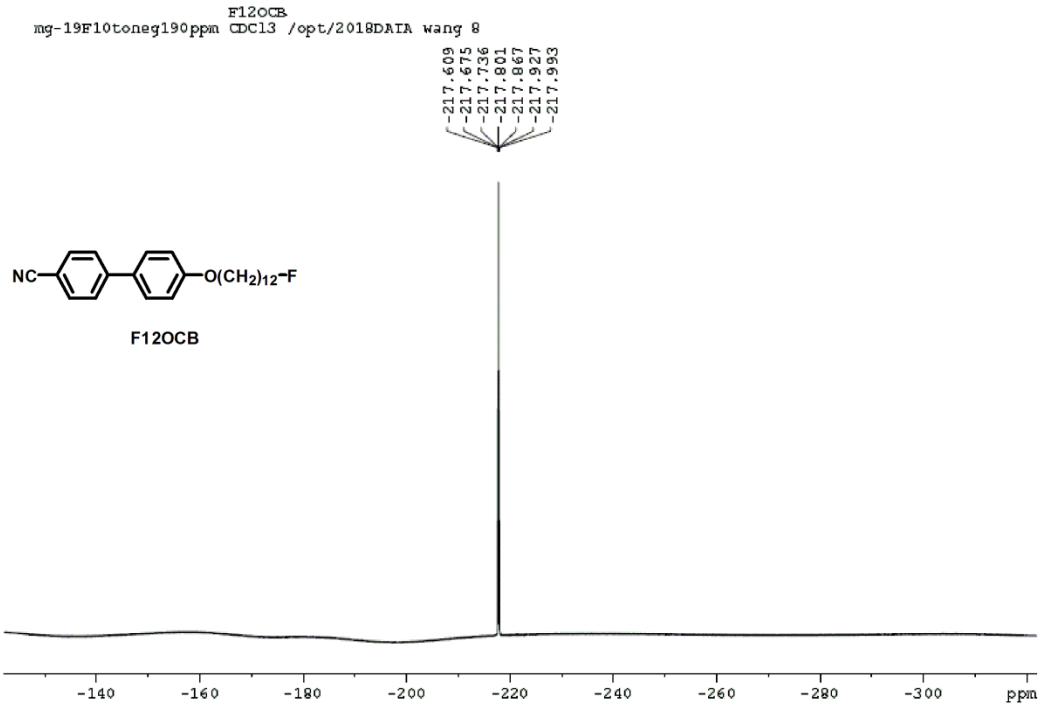

07088KW
mg-1D-proton CDCl3 /opt/2017DATA wang 3
7.701
7.699
7.696
7.685
7.679
7.676
7.653
7.649
7.644
7.633
7.629
7.627
7.537
7.531
7.520
7.515
7.010
7.002
6.997
6.986
6.980
4.512
4.496
4.481
4.393
4.378
4.362
4.024
4.007
3.991
1.828
1.811
1.807
1.790
1.774
1.738
1.722
1.717
1.702
1.676
1.660
1.655
1.639
1.493
1.489
1.475
1.455
1.437
1.413
1.396
1.382
1.375
1.360
1.333
1.306
NC
O(CH2)11F
F11OCB
9
8
7
6
5
4
3
2
1
0
ppm
2.000
2.040
2.006
2.003
1.985
2.032
2.050
2.102
2.362
12.314


07088KW
mg-1D-carbon CDCl3 /opt/2017DATA wang 8
159.825
145.308
132.565
131.280
128.320
127.080
119.112
115.103
110.066
85.047
83.417
68.180
30.507
30.314
29.516
29.479
29.453
29.356
29.221
26.025
25.180
25.126
NC
O(CH2)11F
F11OCB
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

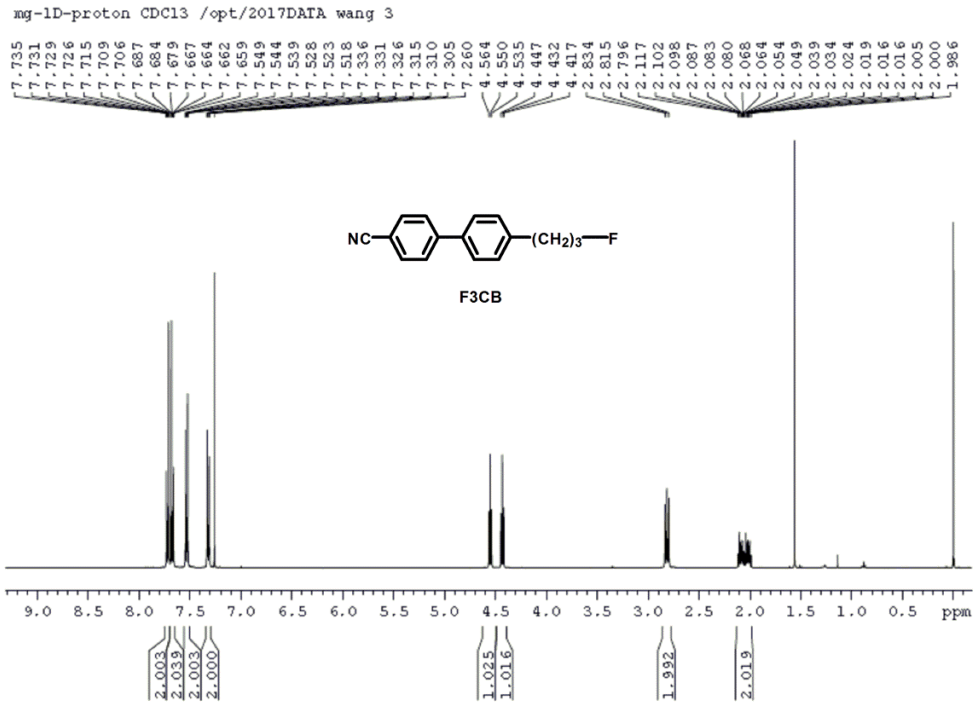

F11OCB
mg-19F10toneg190ppm CDCl3 /opt/2018DATA wang 6
-217.811
-217.877
-217.937
-217.943
-218.003
-218.062
-218.069
-218.129
-218.195
NC
O(CH2)11F
F11OCB
-200 -205 -210 -215 -220 -225 -230 -235 ppm

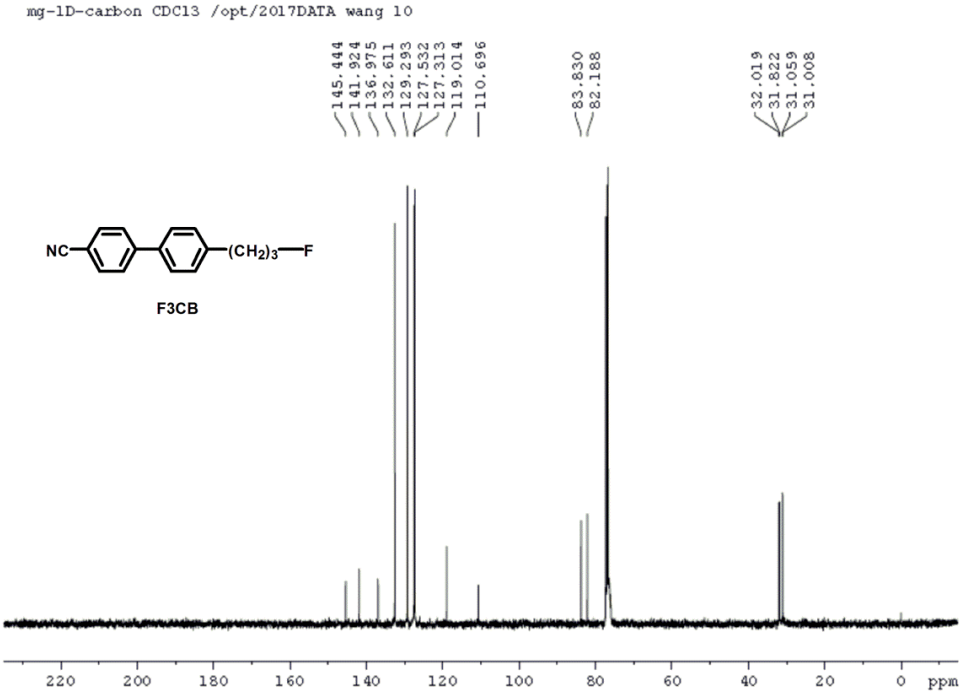

07089KW
mg-1D-proton CDCl3 /opt/2017DATA wang 4
7.701
7.699
7.696
7.685
7.679
7.676
7.653
7.649
7.644
7.633
7.629
7.627
7.624
7.537
7.531
7.520
7.515
7.507
7.003
6.997
6.986
6.980
6.973
4.511
4.495
4.480
4.392
4.377
4.361
4.024
4.007
3.991
1.828
1.810
1.807
1.790
1.774
1.737
1.721
1.716
1.700
1.675
1.659
1.654
1.638
1.492
1.488
1.474
1.454
1.436
1.393
1.371
1.357
1.332
1.296
NC
O(CH2)12F
F12OCB
10
9
8
7
6
5
4
3
2
1
0
ppm
2.000
2.025
1.991
2.001
1.819
2.009
4.124
16.787

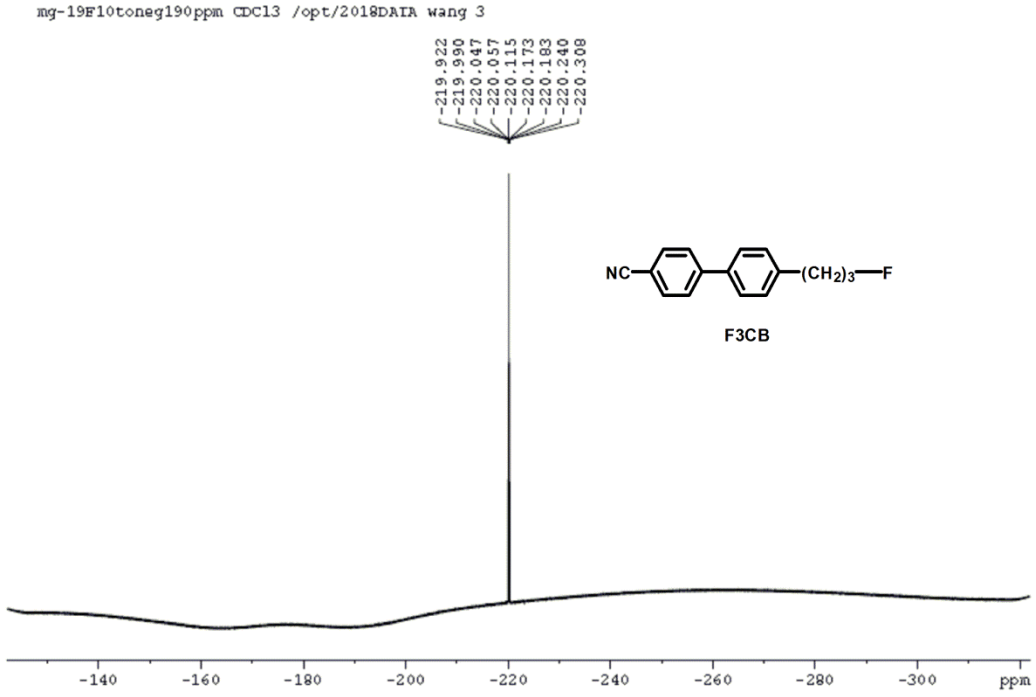

07089KW
mg-1D-carbon CDCl3 /opt/2017DATA wang 9
159.827
145.306
132.562
131.273
128.317
127.076
127.060
119.111
115.102
110.064
85.052
83.422
68.189
30.510
30.318
29.541
29.510
29.497
29.371
29.225
26.032
25.182
25.128
NC
O(CH2)12F
F12OCB
220
200
180
160
140
120
100
80
60
40
20
0
ppm

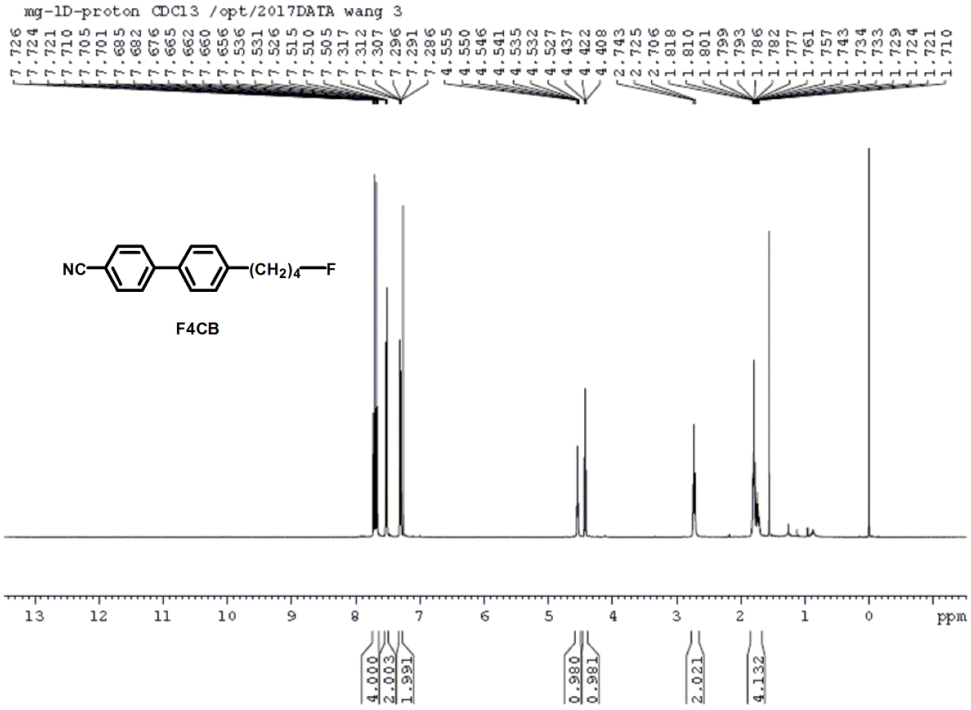

F12OCB
mg-19F10toneg190ppm CDCl3 /opt/2018DATA wang 8
-217.609
-217.675
-217.736
-217.801
-217.867
-217.927
-217.993
NC
O(CH2)12F
F12OCB
-140
-160
-180
-200
-220
-240
-260
-280
-300
ppm

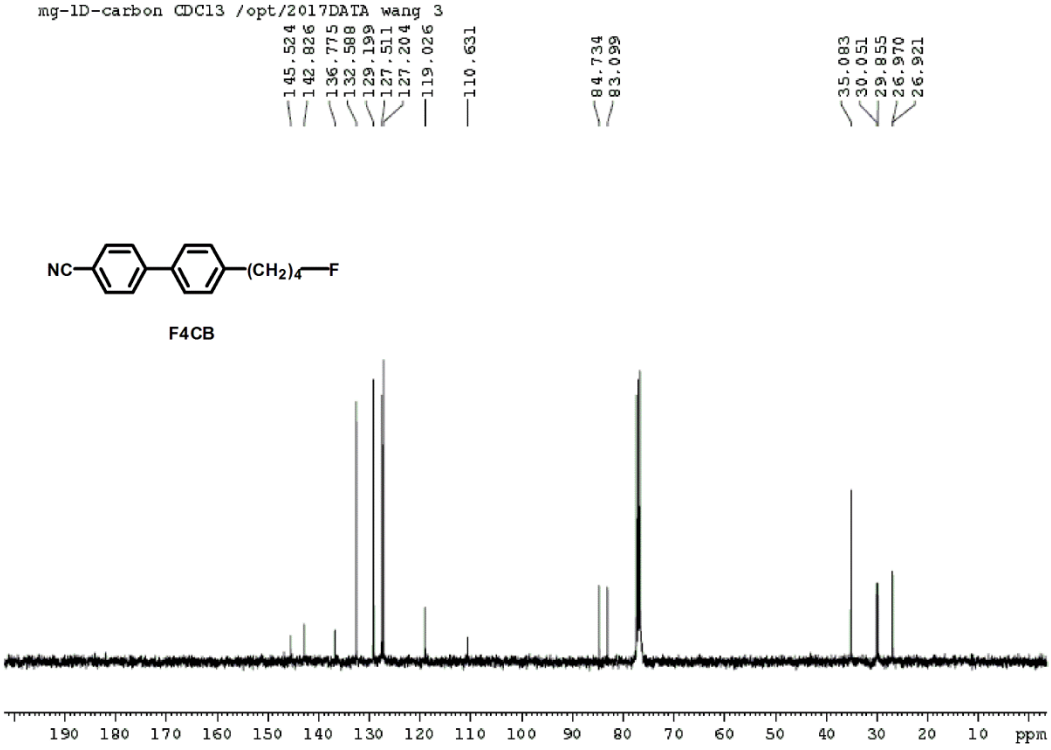
FnCB series

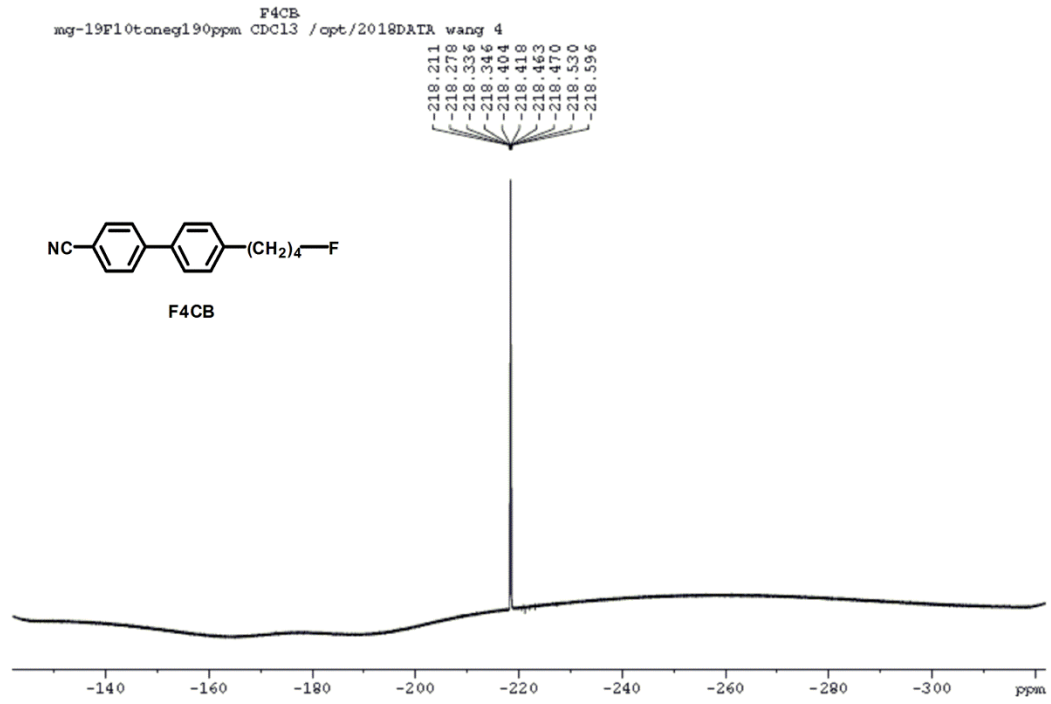

mg-1D-proton CDCl3 /opt/2017DATA wang 3
NC
(CH2)3
F
F3CB
ppm
2.003
2.039
2.003
2.000
1.025
1.016
1.992
2.019

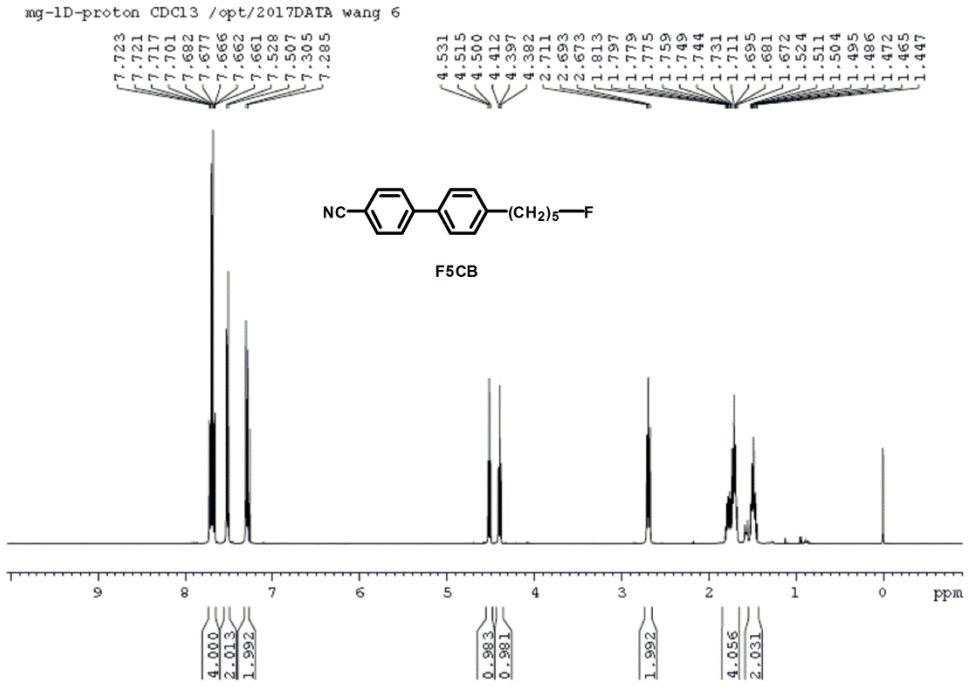

mg-1D-carbon CDCl3 /opt/2017DATA wang 10
145.444
141.924
136.975
132.611
129.293
127.532
127.313
119.014
110.696
83.830
82.188
32.019
31.822
31.059
31.008
NC
(CH2)3
F
F3CB
ppm

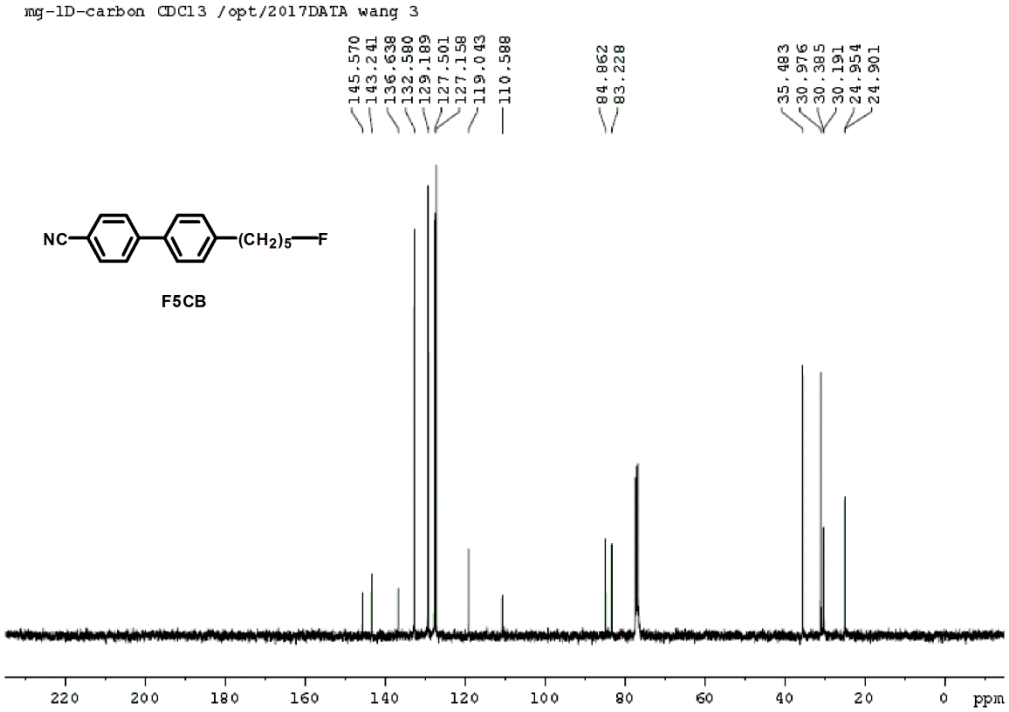

mg-19F10toneg190ppm CDCl3 /opt/2018DATA wang 3
-219.922
-219.990
-220.047
-220.057
-220.115
-220.173
-220.183
-220.240
-220.308
NC
(CH2)3
F
F3CB
-140
-160
-180
-200
-220
-240
-260
-280
-300
ppm

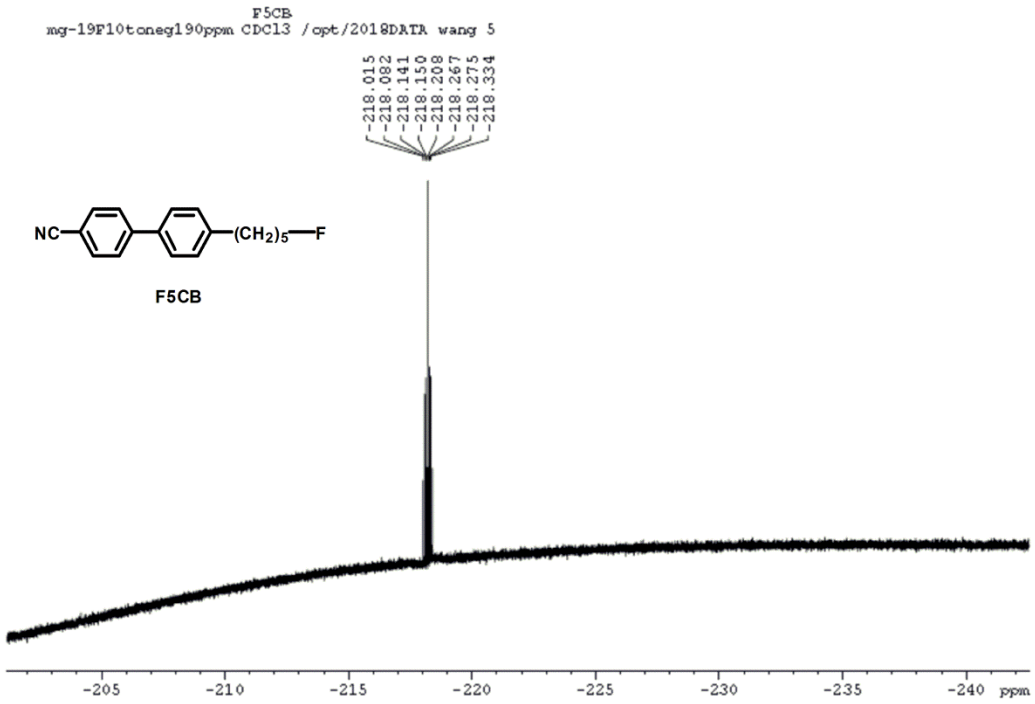

mg-1D-proton CDCl3 /opt/2017DATA wang 3
7.726
7.724
7.721
7.710
7.705
7.701
7.685
7.682
7.676
7.665
7.662
7.660
7.656
7.536
7.531
7.526
7.515
7.510
7.505
7.317
7.312
7.307
7.296
7.291
7.286
4.555
4.550
4.546
4.541
4.535
4.532
4.527
4.437
4.422
4.408
2.743
2.725
2.706
1.818
1.810
1.801
1.799
1.793
1.786
1.782
1.777
1.761
1.757
1.743
1.734
1.733
1.729
1.724
1.721
1.710
NC
(CH2)4
F
F4CB
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
4.000
2.003
1.991
0.980
0.981
2.021
4.132

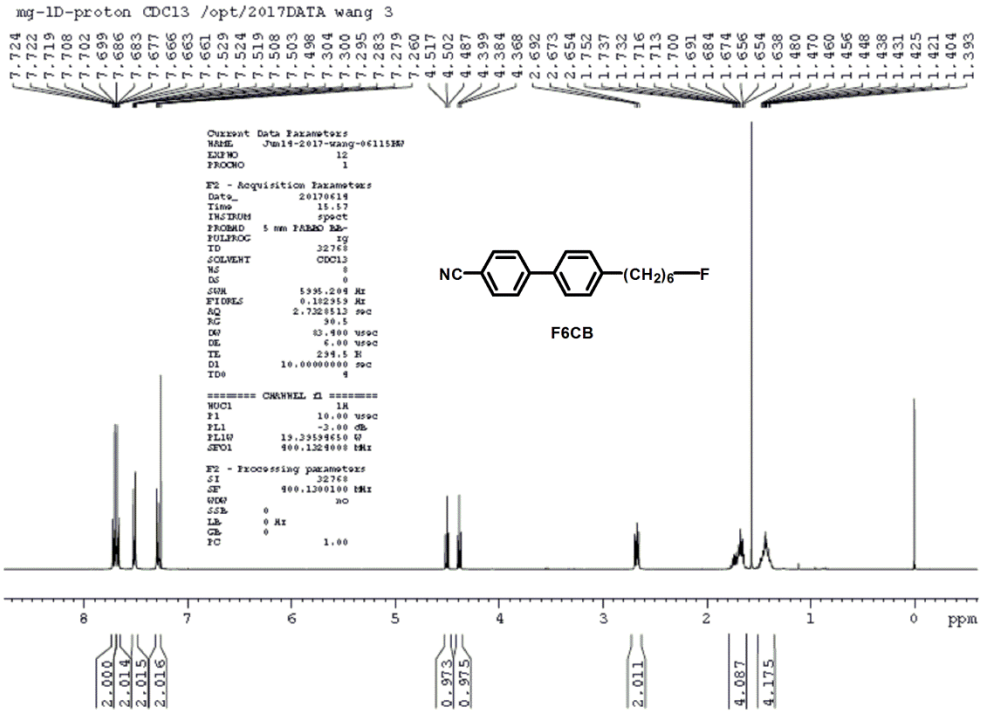

mg-1D-carbon CDCl3 /opt/2017DATA wang 3
145.524
142.826
136.775
132.588
129.199
127.511
127.204
119.026
110.631
84.734
83.099
35.083
30.051
29.855
26.970
26.921
NC
(CH2)4
F
F4CB
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

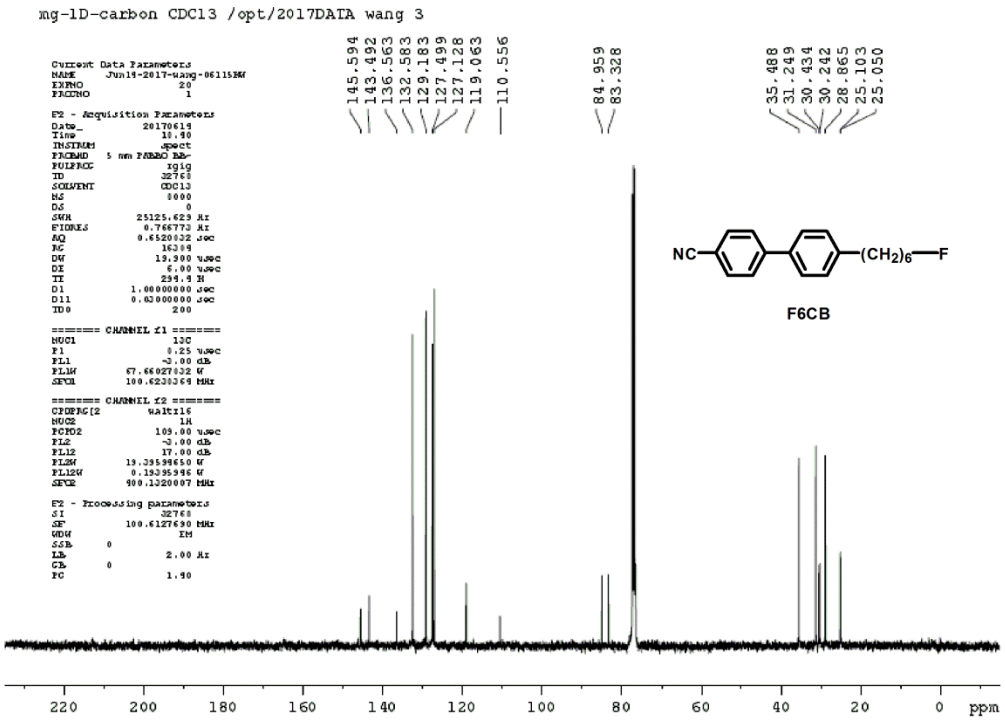

F4CB
mg-19F10toneg190ppm CDCl3 /opt/2018DATA wang 4
-218.211
-218.278
-218.336
-218.346
-218.404
-218.418
-218.463
-218.470
-218.530
-218.596
NC
(CH2)4
F
F4CB
-140 -160 -180 -200 -220 -240 -260 -280 -300 ppm

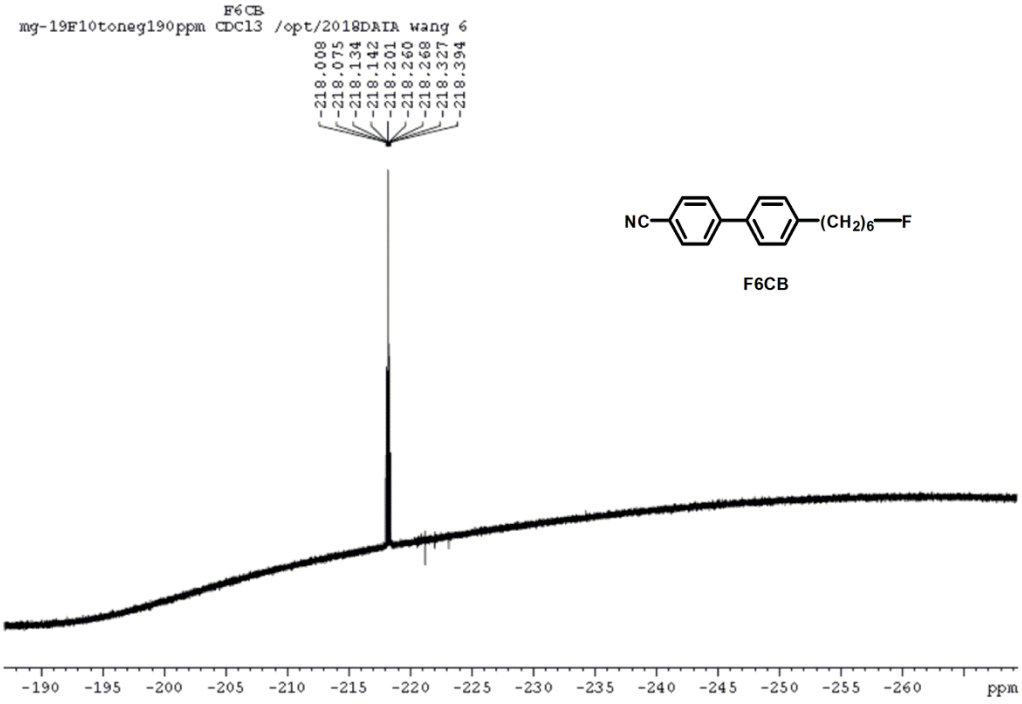

mg-1D-proton CDCl3 /opt/2017DATA wang 6
7.723
7.721
7.717
7.701
7.682
7.677
7.666
7.662
7.661
7.528
7.507
7.305
7.285
4.531
4.515
4.500
4.412
4.397
4.382
2.711
2.693
2.673
1.813
1.797
1.779
1.775
1.759
1.749
1.744
1.731
1.711
1.695
1.681
1.672
1.524
1.511
1.504
1.495
1.486
1.472
1.465
1.447
NC
(CH2)5
F
F5CB
9
8
7
6
5
4
3
2
1
0
ppm
4.000
2.013
1.992
0.983
0.981
1.992
4.056
2.031

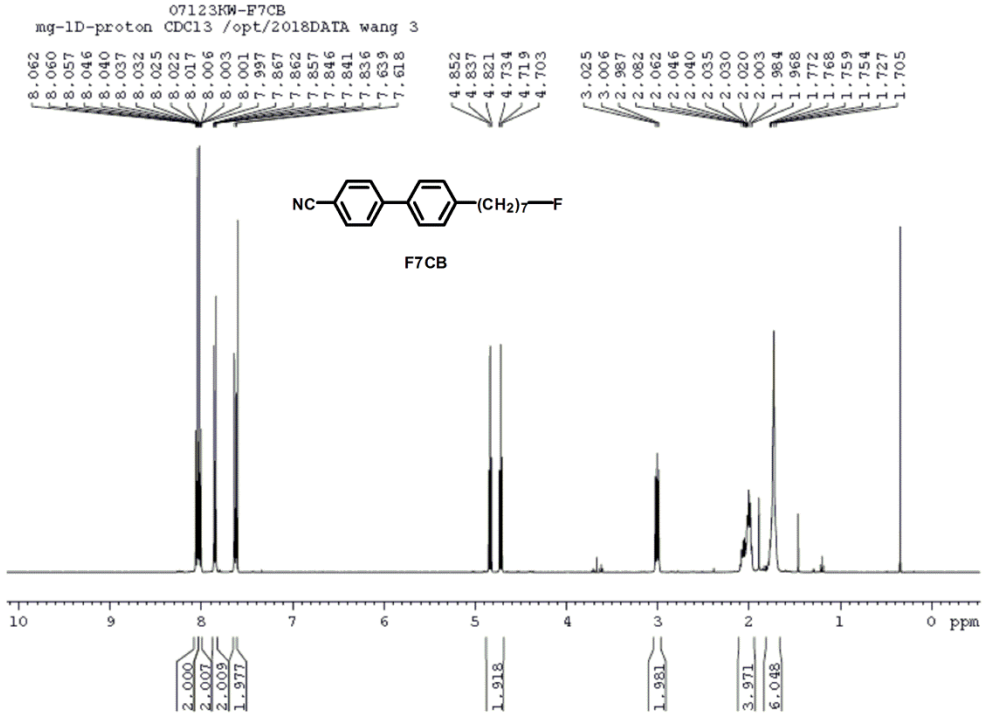

mg-1D-carbon CDCl3 /opt/2017DATA wang 3
145.570
143.241
136.638
132.580
129.189
127.501
127.158
119.043
110.588
84.862
83.228
35.483
30.976
30.385
30.191
24.954
24.901
NC
(CH2)5
F
F5CB
220
200
180
160
140
120
100
80
60
40
20
0
ppm

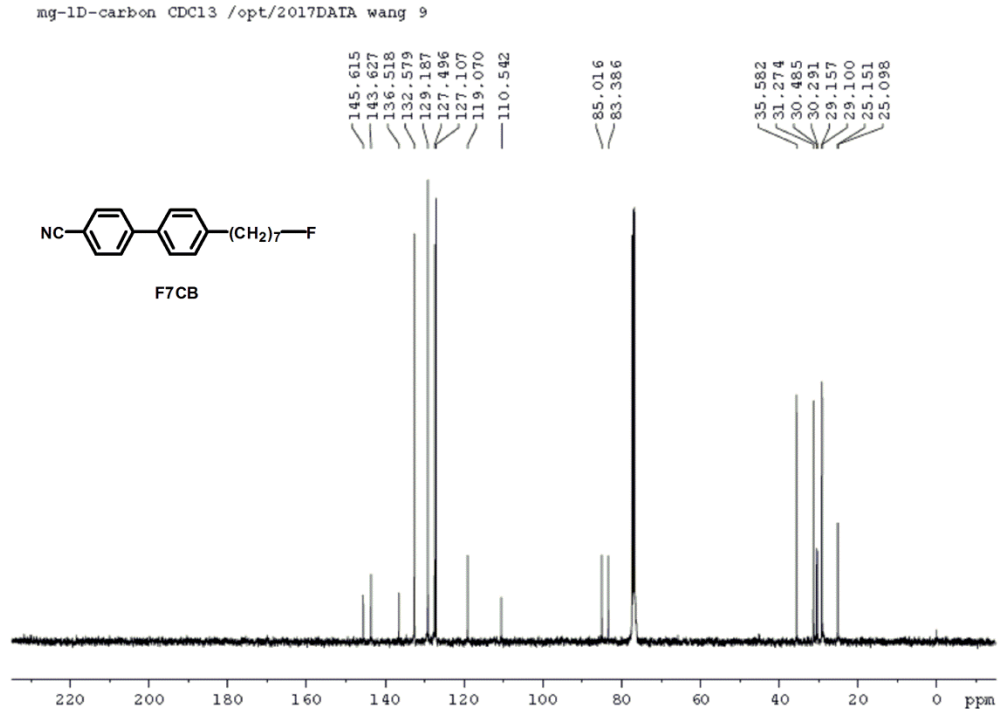

F5CB
mg-19F10tonegl90ppm CDCl3 /opt/2018DATA wang 5
-218.015
-218.082
-218.141
-218.150
-218.208
-218.267
-218.275
-218.334
NC
(CH2)5
F
F5CB
-205
-210
-215
-220
-225
-230
-235
-240
ppm

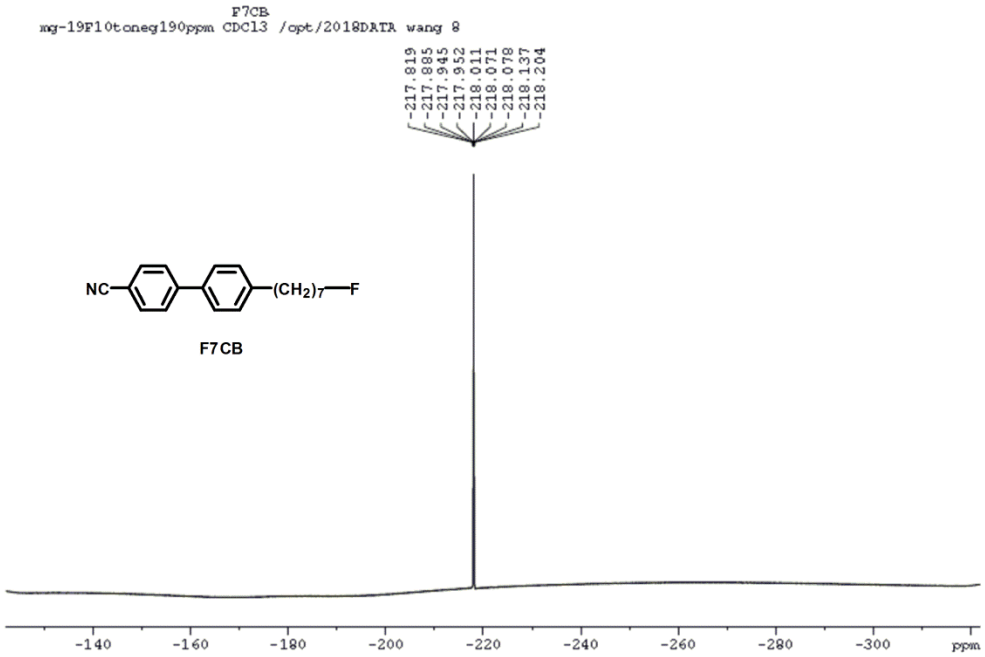

mg-1D-proton CDCl3 /opt/2017DATA wang 3
7.724
7.722
7.719
7.708
7.702
7.699
7.686
7.683
7.677
7.666
7.663
7.661
7.529
7.524
7.519
7.508
7.503
7.498
7.304
7.300
7.295
7.283
7.279
7.260
4.517
4.502
4.487
4.399
4.384
4.368
2.692
2.673
2.654
1.752
1.737
1.732
1.716
1.713
1.700
1.691
1.684
1.674
1.656
1.654
1.638
1.480
1.470
1.460
1.456
1.448
1.438
1.431
1.425
1.421
1.404
1.393
Current Data Parameters
NAME Jun14-2017-wang-06115BR7
EXPNO 12
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170614
Time 15.57
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 5995.208 Hz
FIDRES 0.182959 Hz
AQ 2.7328512 sec
RG 30.5
DW 83.400 usec
DE 6.00 usec
TE 294.5 K
D1 10.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 -3.00 dB
PL1W 19.39594650 W
SFO1 400.1324000 MHz
F2 - Processing parameters
SI 32768
SF 400.1300100 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.00
NC
(CH2)6
F
F6CB
8
7
6
5
4
3
2
1
0
ppm
2.000
2.014
2.015
2.016
0.973
0.975
2.011
4.087
4.175

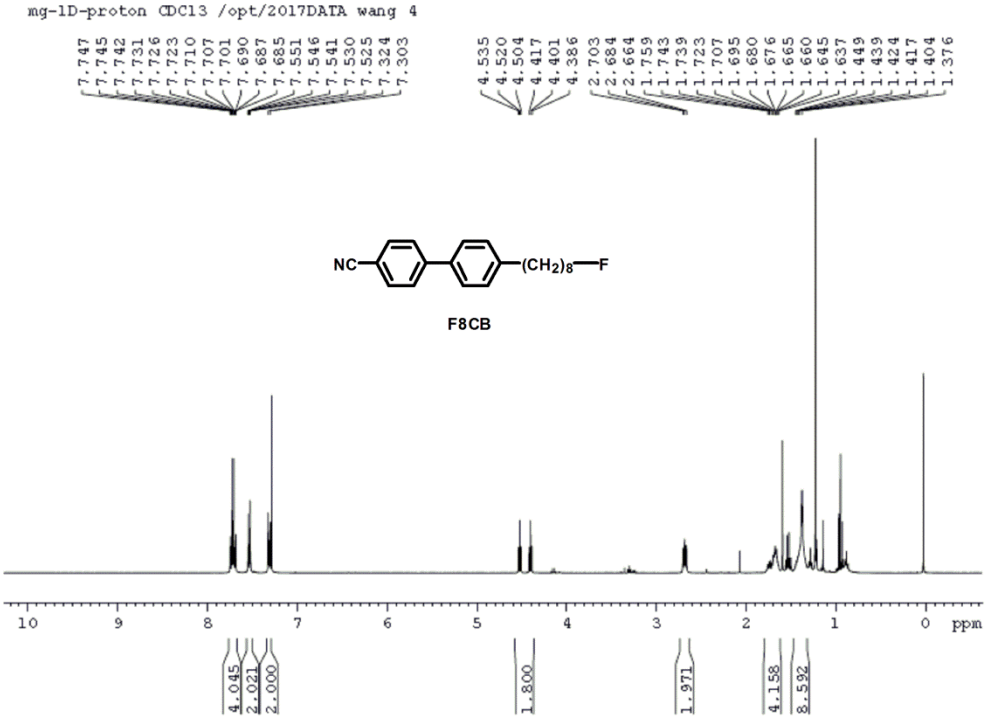

mg-1D-carbon CDCl3 /opt/2017DATA wang 3
145.594
143.492
136.563
132.583
129.183
127.499
127.128
119.063
110.556
84.959
83.328
35.488
31.249
30.434
30.242
28.865
25.103
25.050
NC
(CH2)6
F
F6CB
220
200
180
160
140
120
100
80
60
40
20
0
ppm

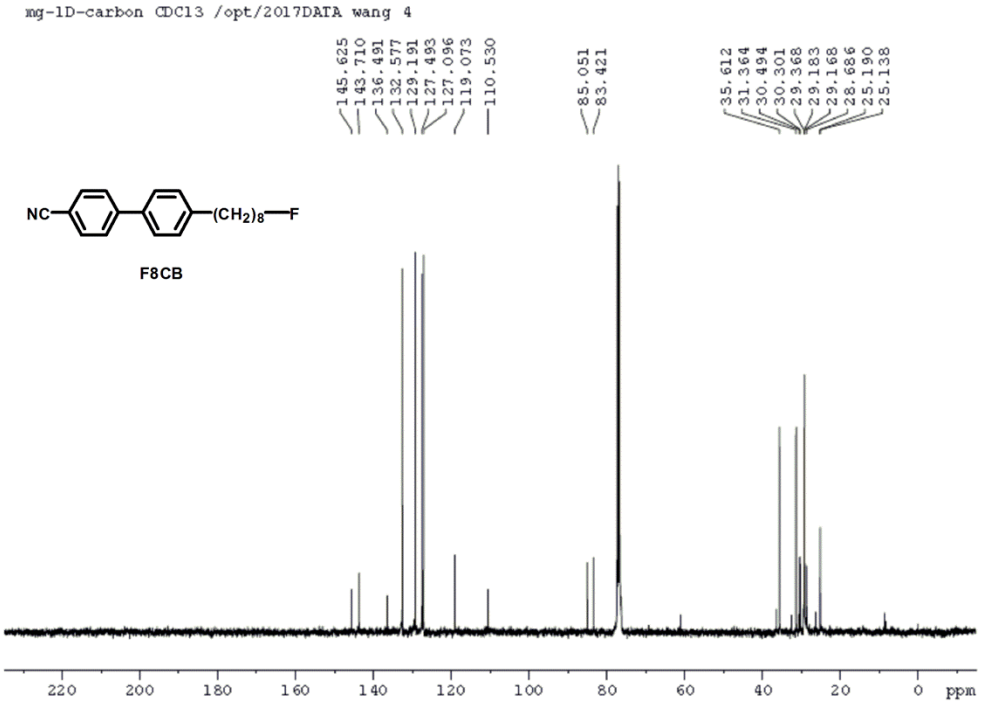

F6CB
mg-19F10toneg190ppm CDCl3 /opt/2018DATA wang 6
-218.008
-218.075
-218.134
-218.142
-218.201
-218.260
-218.268
-218.327
-218.394
NC
(CH2)6
F
F6CB
-190
-195
-200
-205
-210
-215
-220
-225
-230
-235
-240
-245
-250
-255
-260
ppm

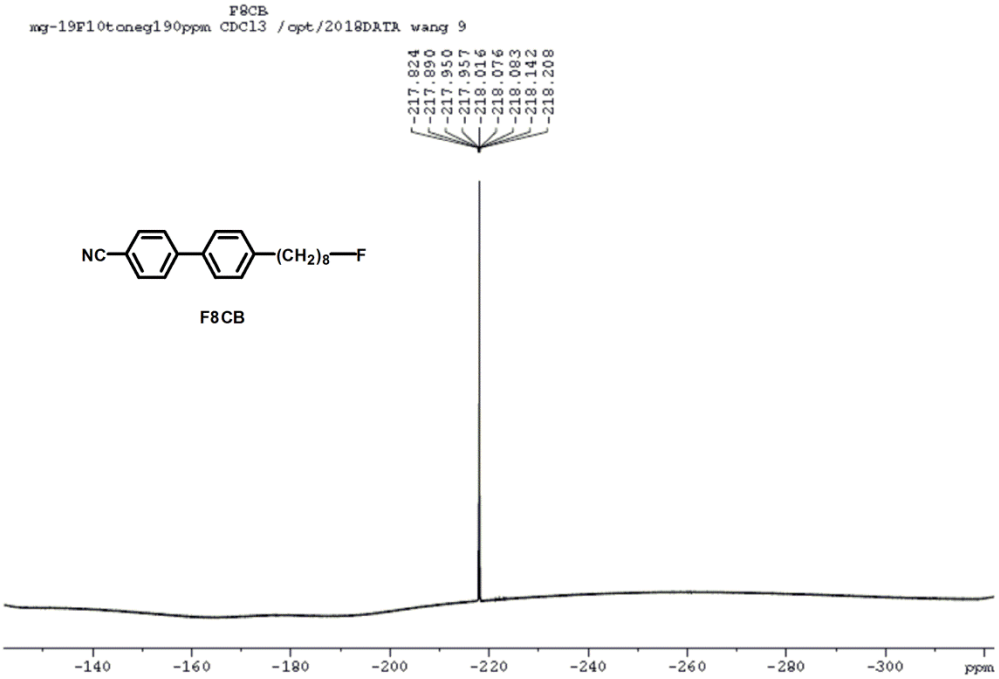

07123KW-F7CB
mg-1D-proton CDCl3 /opt/2018DATA wang 3
8.062
8.060
8.057
8.046
8.040
8.037
8.032
8.025
8.022
8.017
8.006
8.003
8.001
7.997
7.867
7.862
7.857
7.846
7.841
7.836
7.639
7.618
4.852
4.837
4.821
4.734
4.719
4.703
3.025
3.006
2.987
2.082
2.062
2.046
2.040
2.035
2.030
2.020
2.003
1.984
1.968
1.772
1.768
1.759
1.754
1.727
1.705
NC
(CH2)7
F
F7CB
10
9
8
7
6
5
4
3
2
1
0 ppm
2.000
2.007
2.009
1.977
1.918
1.981
3.971
6.048

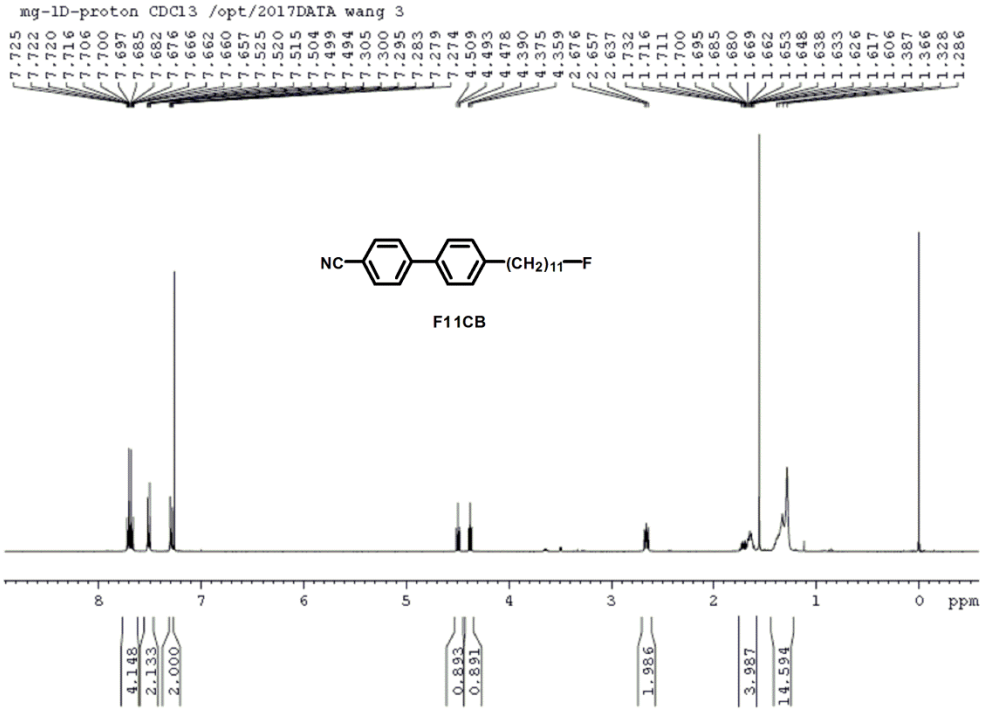

mg-1D-carbon CDCl3 /opt/2017DATA wang 9
145.615
143.627
136.518
132.579
129.187
127.496
127.107
119.070
110.542
85.016
83.386
35.582
31.274
30.485
30.291
29.157
29.100
25.151
25.098
NC
(CH2)7
F
F7CB
220
200
180
160
140
120
100
80
60
40
20
0 ppm

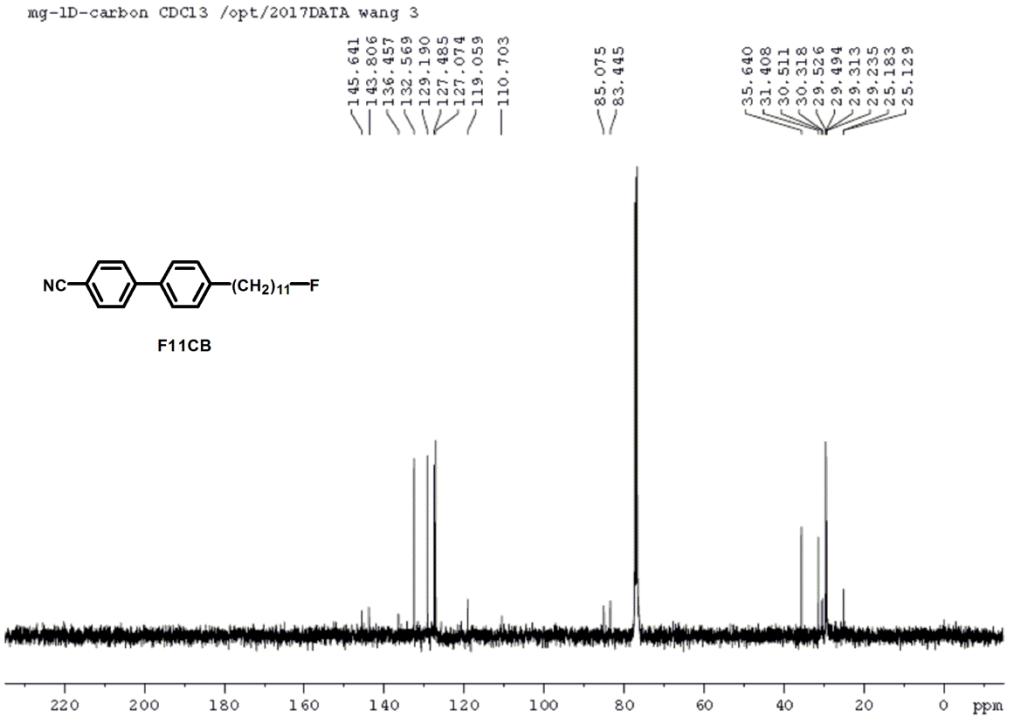

F7CB
mg-19F10toneg190ppm CDCl3 /opt/2018DATA wang 8
-217.819
-217.885
-217.945
-217.952
-218.011
-218.071
-218.078
-218.137
-218.204
NC
(CH2)7
F
F7CB
-140
-160
-180
-200
-220
-240
-260
-280
-300
ppm

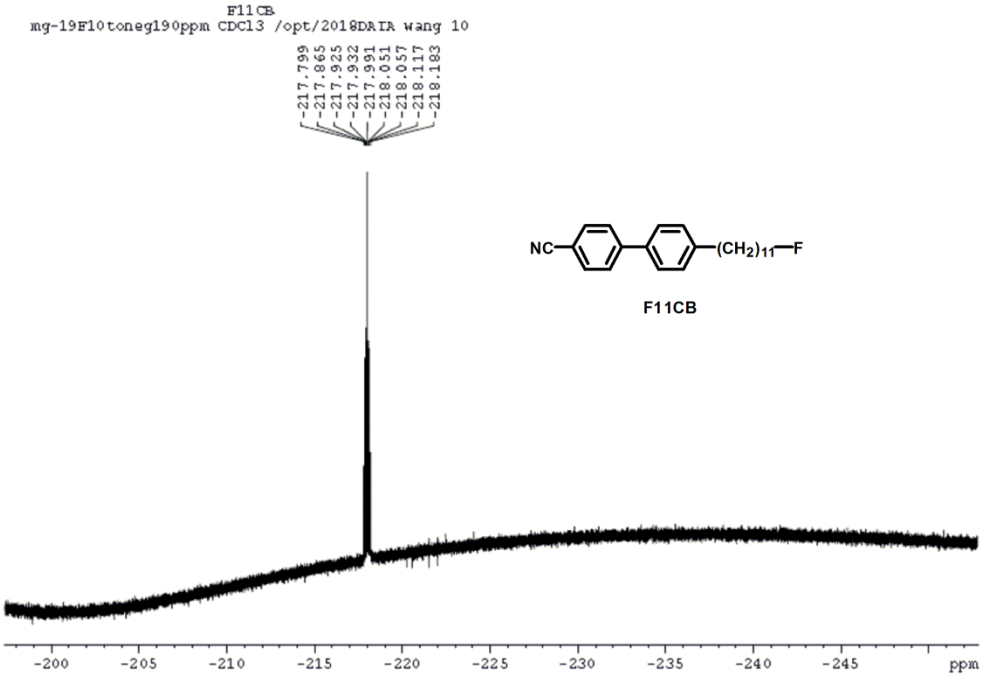

mg-1D-proton CDCl3 /opt/2017DATA wang 4
7.747
7.745
7.742
7.731
7.726
7.723
7.710
7.707
7.701
7.690
7.687
7.685
7.551
7.546
7.541
7.530
7.525
7.324
7.303
4.535
4.520
4.504
4.417
4.401
4.386
2.703
2.684
2.664
1.759
1.743
1.739
1.723
1.707
1.695
1.680
1.676
1.665
1.660
1.645
1.637
1.449
1.439
1.424
1.417
1.404
1.376
NC
(CH2)8
F
F8CB
10
9
8
7
6
5
4
3
2
1
0
ppm
4.045
2.021
2.000
1.800
1.971
4.158
8.592


mg-1D-carbon CDCl3 /opt/2017DATA wang 4
145.625
143.710
136.491
132.577
129.191
127.493
127.096
119.073
110.530
85.051
83.421
35.612
31.364
30.494
30.301
29.368
29.183
29.168
28.686
25.190
25.138
NC
(CH2)8
F
F8CB
220
200
180
160
140
120
100
80
60
40
20
0
ppm

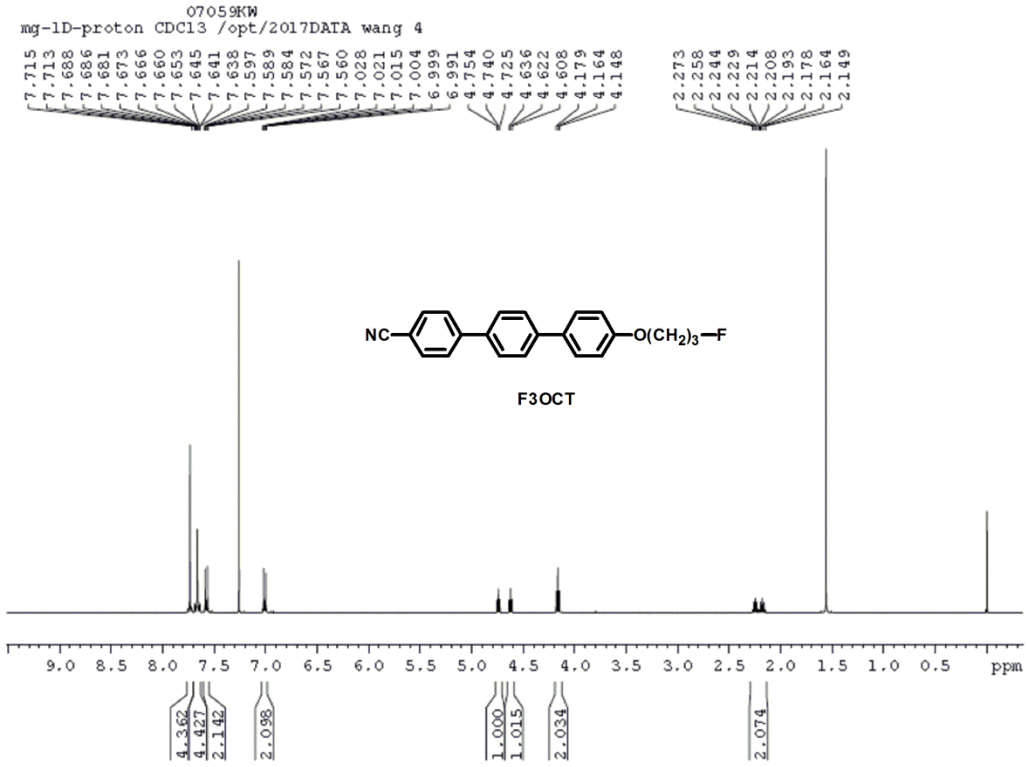

F8CB
mg-19F10toneg190ppm CDCl3 /opt/2018DATA wang 9
-217.824
-217.890
-217.950
-217.957
-218.016
-218.076
-218.083
-218.142
-218.208
NC
(CH2)8
F
F8CB
-140
-160
-180
-200
-220
-240
-260
-280
-300
ppm

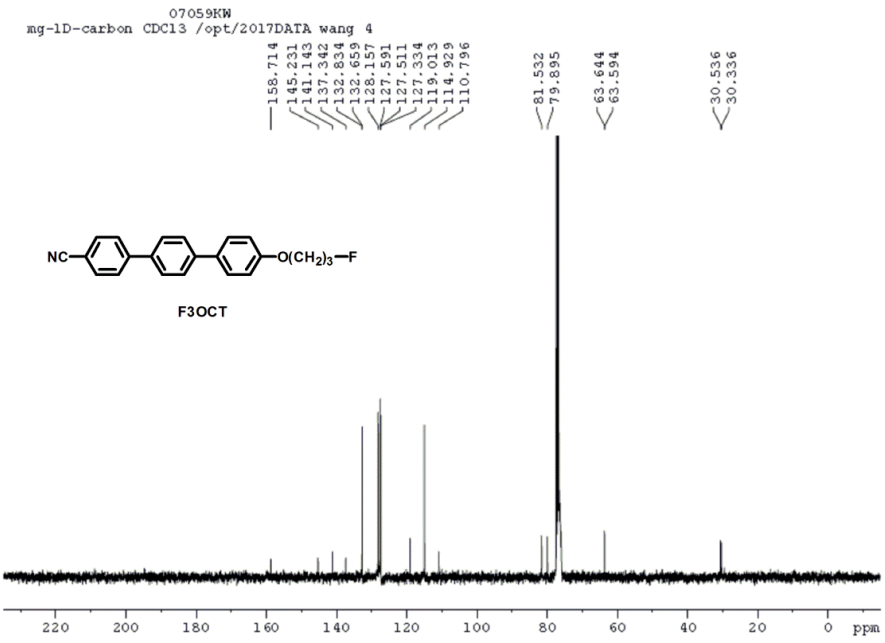

mg-1D-proton CDCl3 /opt/2017DATA wang 3
7.725
7.722
7.720
7.716
7.706
7.700
7.697
7.685
7.682
7.676
7.666
7.662
7.660
7.657
7.525
7.520
7.515
7.504
7.499
7.494
7.305
7.300
7.295
7.283
7.279
7.274
4.509
4.493
4.478
4.390
4.375
4.359
2.676
2.657
2.637
1.732
1.716
1.711
1.700
1.695
1.685
1.680
1.669
1.662
1.653
1.648
1.638
1.633
1.626
1.617
1.606
1.387
1.366
1.328
1.286
NC
(CH2)11
F
F11CB
8
7
6
5
4
3
2
1
0
ppm
4.148
2.133
2.000
0.893
0.891
1.986
3.987
14.594

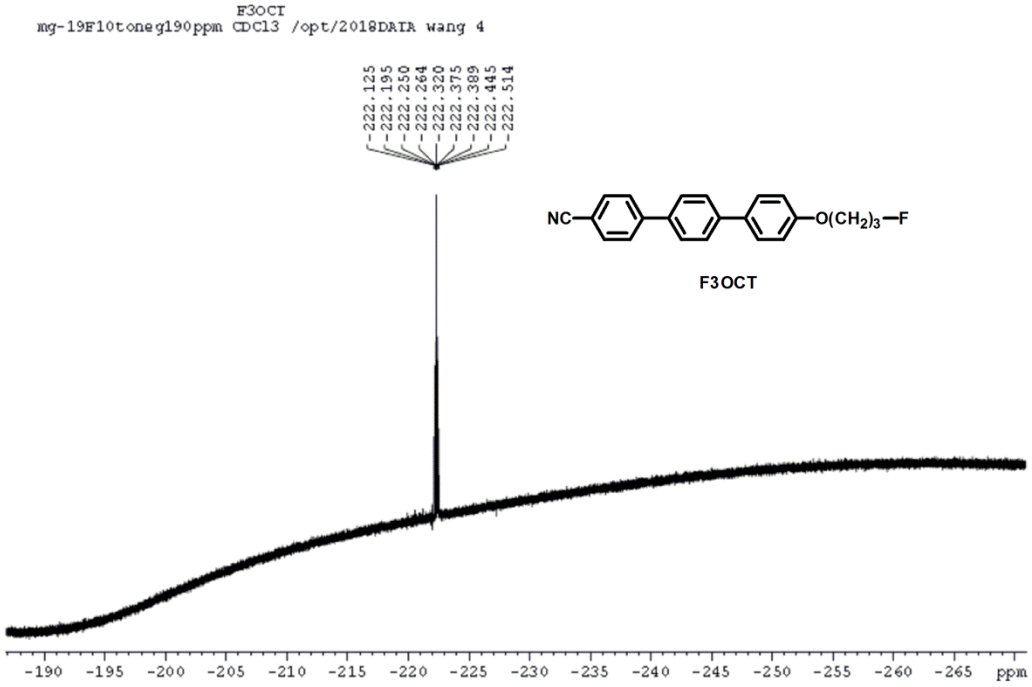

mg-1D-carbon CDCl3 /opt/2017DATA wang 3
145.641
143.806
136.457
132.569
129.190
127.485
127.074
119.059
110.703
85.075
83.445
35.640
31.408
30.511
30.318
29.526
29.494
29.313
29.235
25.183
25.129
NC
(CH2)11
F
F11CB
220
200
180
160
140
120
100
80
60
40
20
0
ppm

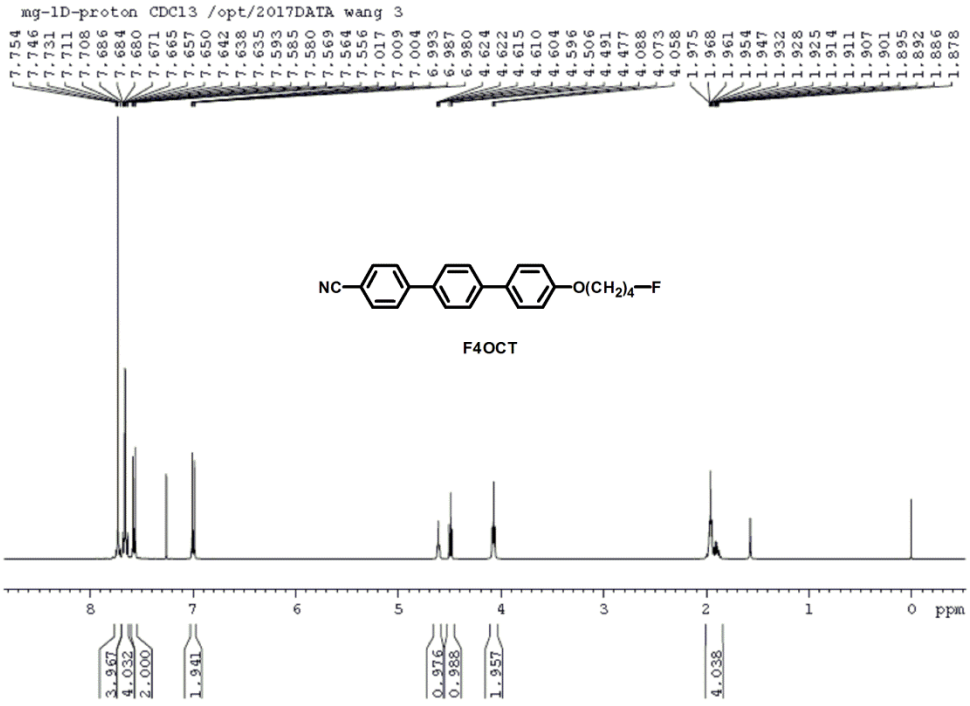

F11CB
mg-19F10toneg190ppm CDCl3 /opt/2018DATA wang 10
-217.799
-217.865
-217.925
-217.932
-217.991
-218.051
-218.057
-218.117
-218.183
NC
(CH2)11
F
F11CB
-200
-205
-210
-215
-220
-225
-230
-235
-240
-245
ppm

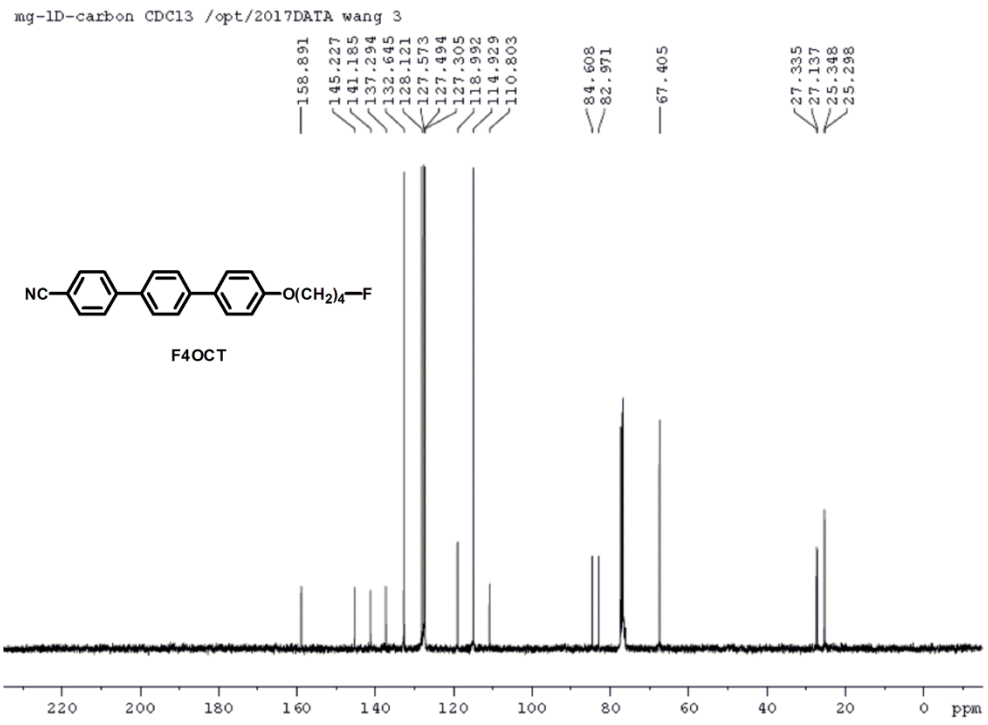
FnOCT series

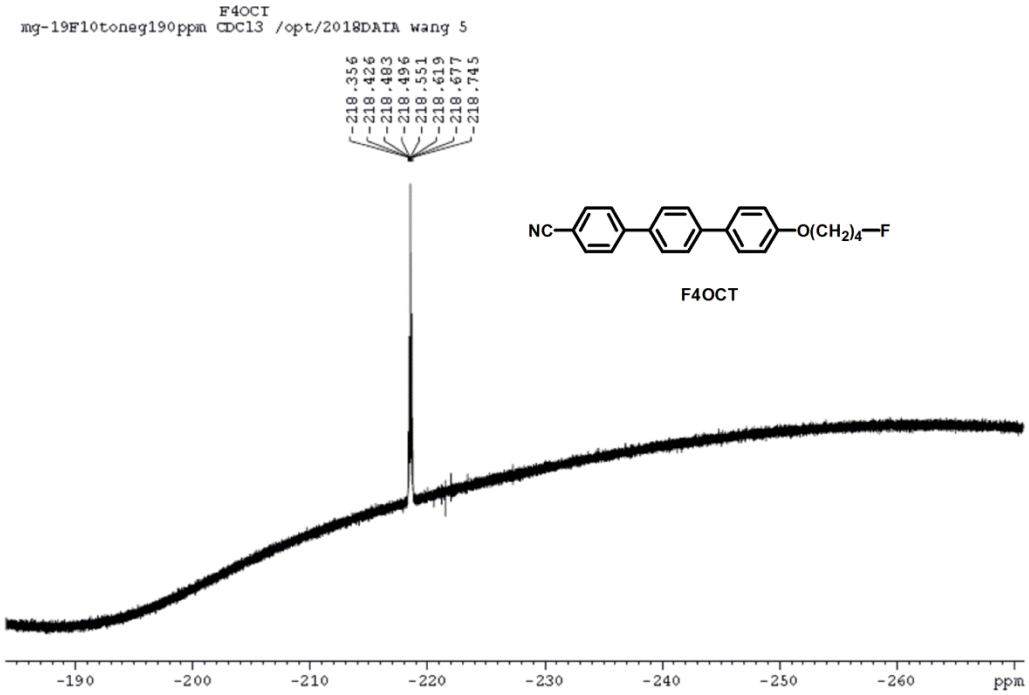


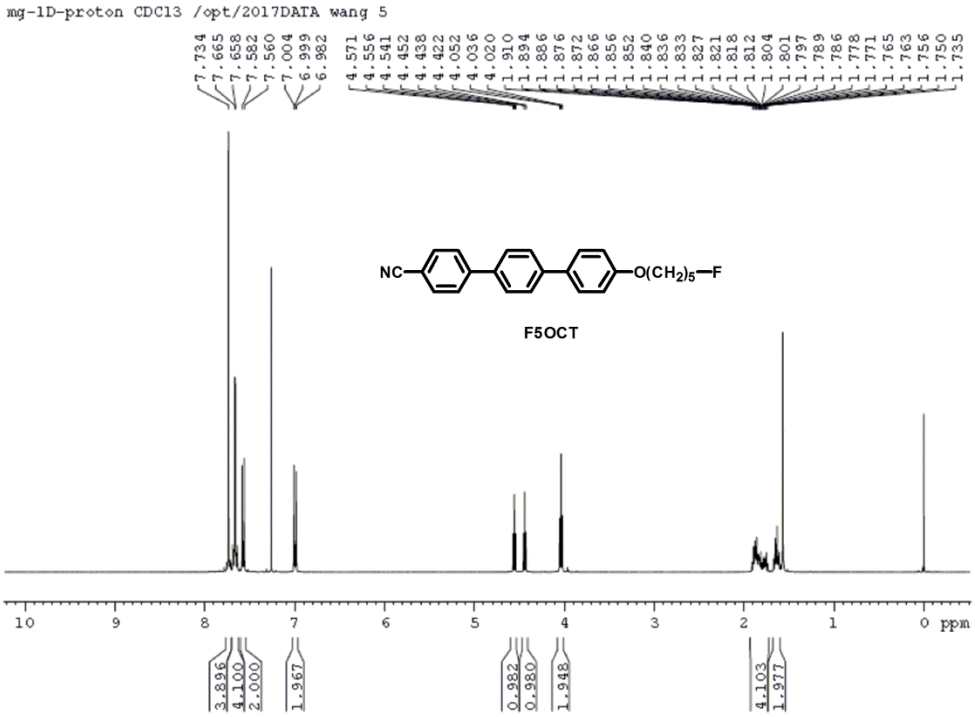


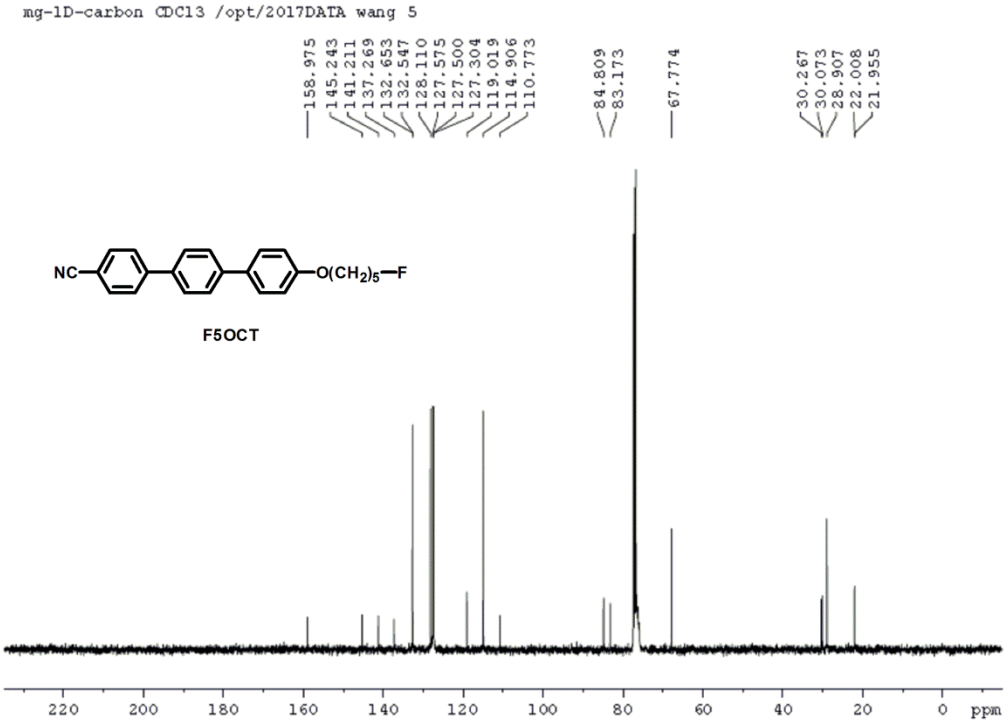

F3OCT
mg-19F10toneg190ppm CDCl3 /opt/2018DATA wang 4
222.125
222.195
222.250
222.264
222.320
222.375
222.389
222.445
222.514
NC
O(CH2)3—F
F3OCT
-190 -195 -200 -205 -210 -215 -220 -225 -230 -235 -240 -245 -250 -255 -260 -265 ppm

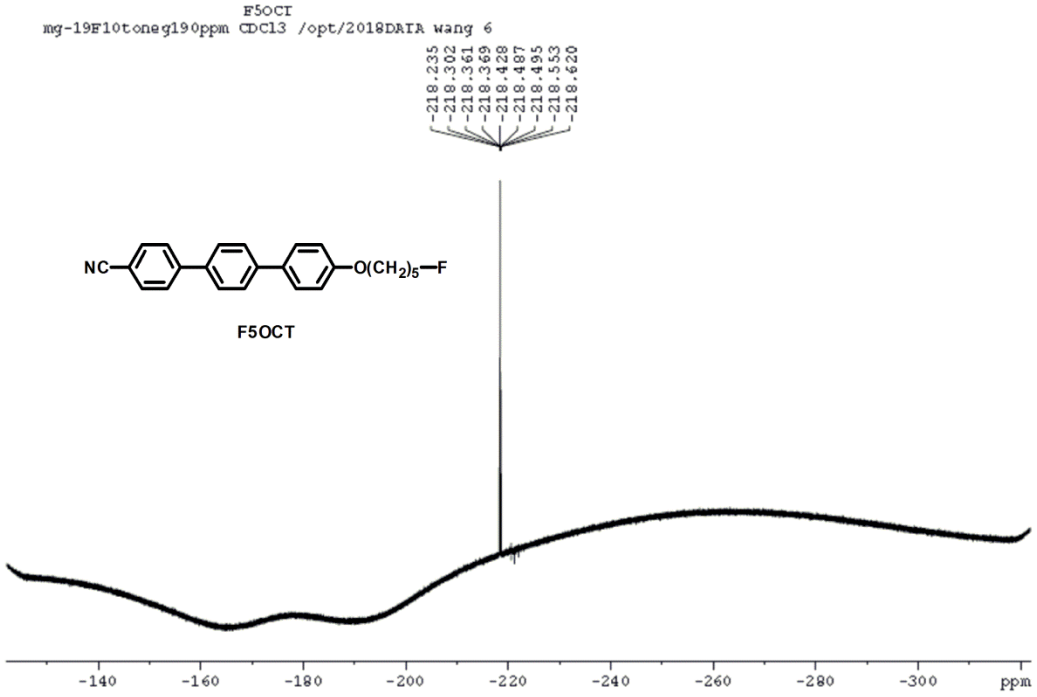

mg-1D-proton CDCl3 /opt/2017DATA wang 3
7.754
7.746
7.731
7.711
7.708
7.686
7.684
7.680
7.671
7.665
7.657
7.650
7.642
7.638
7.635
7.593
7.585
7.580
7.569
7.564
7.556
7.017
7.009
7.004
6.993
6.987
6.980
4.624
4.622
4.615
4.610
4.604
4.596
4.506
4.491
4.477
4.088
4.073
4.058
1.975
1.968
1.961
1.954
1.947
1.932
1.928
1.925
1.914
1.911
1.907
1.901
1.895
1.892
1.886
1.878
NC
O(CH2)4—F
F4OCT
8 7 6 5 4 3 2 1 0 ppm
3.967
4.032
2.000
1.941
0.976
0.988
1.957
4.038


mg-1D-carbon CDCl3 /opt/2017DATA wang 3
158.891
145.227
141.185
137.294
132.645
128.121
127.573
127.494
127.305
118.992
114.929
110.803
84.608
82.971
67.405
27.335
27.137
25.348
25.298
NC
O(CH2)4F
F4OCT
220
200
180
160
140
120
100
80
60
40
20
0
ppm


F4OCT
mg-19F10toneg190ppm CDCl3 /opt/2018DATA wang 5
-218.356
-218.426
-218.483
-218.496
-218.551
-218.619
-218.677
-218.745
NC
O(CH2)4F
F4OCT
-190
-200
-210
-220
-230
-240
-250
-260
ppm


mg-1D-proton CDCl3 /opt/2017DATA wang 5
7.734
7.665
7.658
7.582
7.560
7.004
6.999
6.982
4.571
4.556
4.541
4.452
4.438
4.422
4.052
4.036
4.020
1.910
1.894
1.886
1.876
1.872
1.866
1.856
1.852
1.840
1.836
1.833
1.827
1.821
1.818
1.812
1.804
1.801
1.797
1.789
1.786
1.778
1.771
1.765
1.763
1.756
1.750
1.735
NC
O(CH2)5—F
F5OCT
10
9
8
7
6
5
4
3
2
1
0 ppm
3.896
4.100
2.000
1.967
0.982
0.980
1.948
4.103
1.977


mg-1D-carbon CDCl3 /opt/2017DATA wang 5
158.975
145.243
141.211
137.269
132.653
132.547
128.110
127.575
127.500
127.304
119.019
114.906
110.773
84.809
83.173
67.774
30.267
30.073
28.907
22.008
21.955
NC
O(CH2)5—F
F5OCT
220
200
180
160
140
120
100
80
60
40
20
0 ppm



SI.6. The calculation of dipole moment of the fluorine-terminated compounds

Table SI.1. Calculated dipole moment of the 4'-ω-fluoroalkyl-4-cyanobiphenyl and 4'-ω-fluoroalkoxy-4-cyanobiphenyl compounds. Here 'n' refers to the number of CH_2 groups as defined in the molecular formula in each column.

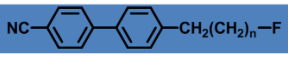
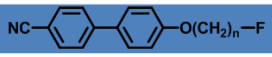
n		
2	7.36	8.24
3	7.62	8.49
4	7.80	8.48
5	7.78	8.55
6	7.83	8.58
7	7.81	8.61
8	7.99	8.94
9	8.09	8.94
10	8.16	9.02
11	7.65	8.48
12	7.51	8.38

Table SI.2. Calculated binding free energies (G_{BE}; in eV) of the 4'-alkyl-4-cyanobiphenyl, 4'-ω-fluoroalkyl-4-cyanobiphenyl, and 4'-ω-fluoroalkoxy-4-cyanobiphenyl compounds to $Al(ClO_4)_3$, $Ga(ClO_4)_3$, and $Ni(ClO_4)_2$. Here 'n' refers to the number of CH_2 groups as defined in the molecular formula in each column.

n	NC—⟨⟩—⟨⟩—$CH_2(CH_2)_n$—H			NC—⟨⟩—⟨⟩—$CH_2(CH_2)_n$—F			NC—⟨⟩—⟨⟩—$O(CH_2)_n$—F		
	$Al(ClO_4)_3$	$Ga(ClO_4)_3$	$Ni(ClO_4)_2$	$Al(ClO_4)_3$	$Ga(ClO_4)_3$	$Ni(ClO_4)_2$	$Al(ClO_4)_3$	$Ga(ClO_4)_3$	$Ni(ClO_4)_2$
2	-0.46	-0.57	-1.08	-0.47	-0.58	-1.09	-0.47	-0.57	-1.08
3	-0.47	-0.57	-1.08	-0.46	-0.57	-1.08	-0.46	-0.58	-1.08
4	-0.46	-0.57	-1.09	-0.46	-0.57	-1.09	-0.46	-0.57	-1.08
5	-0.46	-0.57	-1.08	-0.46	-0.57	-1.08	-0.46	-0.58	-1.08
6	-0.46	-0.57	-1.09	-0.47	-0.57	-1.08	-0.46	-0.57	-1.08
7	-0.47	-0.57	-1.08	-0.46	-0.57	-1.08	-0.47	-0.57	-1.08
8	-0.47	-0.58	-1.08	-0.46	-0.57	-1.09	-0.46	-0.57	-1.09
9	-0.46	-0.57	-1.09	-0.46	-0.57	-1.08	-0.46	-0.57	-1.08
10	-0.46	-0.57	-1.08	-0.46	-0.57	-1.08	-0.46	-0.57	-1.09
11	-0.46	-0.57	-1.09	-0.46	-0.57	-1.08	-0.47	-0.58	-1.08
12	-0.46	-0.57	-1.08	-0.47	-0.57	-1.08	-0.46	-0.58	-1.08

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