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Photonic Bandgap in Achiral Liquid Crystals—A Twist on a Twist

Damian Pociecha,* Nataša Vaupotič, Magdalena Majewska, Ewan Cruickshank, Rebecca Walker, John M. D. Storey, Corrie T. Imrie, Cheng Wang, and Ewa Gorecka

Achiral mesogenic molecules are shown to be able to spontaneously assemble into liquid crystalline smectic phases having either simple or double-helical structures. At the transition between these phases, the doublehelical structure unwinds. As a consequence, in some temperature range, the pitch of the helix becomes comparable to the wavelength of visible light and the selective reflection of light in the visible range is observed. The photonic bandgap phenomenon is reported for achiral liquid crystals.

1. Introduction

A photonic bandgap crystal is a periodic structure through which light may either propagate or not, depending on the energy of the photons. For photonic crystals that operate in the visible part of the spectrum, the wavelengths of interest are from around 350 to 750 nm. The disallowed wavelengths of light are referred to as a photonic bandgap, and the periodicity of the photonic crystal structure must be close to a half

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of the wavelength of light to be diffracted. The fabrication of a periodic structure on this length scale is highly challenging but offset by a huge application potential, ranging from color changing inks to components for optical computers. In nature, photonic crystals are widespread and responsible for structural colors, such as the iridescent color of opals,^[1] animal reflectors found in butterfly wings^[2] or a metallic luster in some beetle shells.^[3] In

the latter case, it is a liquid crystalline microstructure of the shells that accounts for the photonic band structure. Indeed, the simplest 1D examples of a photonic crystal in soft matter are helical structures of a chiral nematic (cholesteric) and chiral smectic C phase; in both phases, the helical organization is a consequence of the molecular chirality. The chiral intermolecular interactions impose a small twist between the neighboring molecules, leading to a helically modulated structure. If the wavelength of light fits the periodicity of the helix, then the circularly polarized incident light with the same handedness as the helix is reflected while that of the opposite handedness propagates through the structure.^[4] Through molecular design, one may vary both the period of the helix, as well as the width of the stopband, which is determined by the ordinary (n_0) and extraordinary (n_e) refractive indices of the liquid crystal material. Furthermore, the susceptibility of liquid crystalline phases to external fields allows the bandgap to be tuned by electric or magnetic fields, or by temperature, giving the possibility to fabricate devices with readily reconfigurable optical properties.^[5] For many decades it was generally believed that intrinsic molecular chirality was a prerequisite to drive the helical structure of a liquid crystalline phase. More recently, however, it was shown that achiral mesogenic molecules may also form helical phases, and this raises an intriguing possibility of fabricating photonic bandgap structures using achiral materials. In this communication, we demonstrate for the first time that this can indeed be achieved. The twist-bend nematic phase, N_{TB}, was the first example of a liquid crystalline phase with helices assembled from achiral molecules.^[6–9] The N_{TB} phase has a heliconical structure, in which the molecules are tilted at an oblique angle with respect to the helix axis. As the mirror symmetry is spontaneously broken at the transition to the N_{TB} phase, there is an equal probability of the formation of the right- and left-handed helices, and chiral domains are observed in the N_{TB} phase. Electro-optical studies of chiral domains suggested that the director rotates on the cone,^[10,11] and the structural characterization of the N_{TB} phase showed that the helical pitch length is

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approximately 8–10 nm.^[8–9,12] Upon its discovery, the N_{TB} phase immediately became the hottest topic in the field, and the phase was found in numerous odd-membered liquid crystal dimers (see, for example refs. [13-17]). Unfortunately, in the present context of the photonic bandgap structures, the helical pitch of the N_{TB} phase is very short, and far from the optical range. As also found for solid crystals having a helical structure composed of achiral objects, for example, sodium chlorate, cesium copper chloride, quartz or oligobipyridine complexes (helicates),^[18,19] the pitch of the helix in the N_{TB} phase is just a few molecular lengths because it is determined mainly by steric interactions. Recent studies have shown that the lamellar (smectic) analogue of the N_{TB} phase also exists,^[20,21] and we termed this the SmC_{TB} phase. For some systems, the SmC_{TB} phase has a simple heliconical arrangement with the molecules changing azimuthal direction of tilt by a constant angle when going from layer to layer, i.e., forming a clock-like structure,^[21,22] and the helical pitch being as short as that found for the N_{TB} phase, about 3–4 smectic layers. For other systems, however, the SmC_{TR} structure is more complex, with an additional longer helix with the pitch of the order of tens of smectic layers superimposed on a short helix.^[23] Here we present systems, in which the transition between a phase with a single short helix and phase with a double helix takes place. We report on a fascinating observation that upon approaching this transition, the longer helix unwinds, and thus, in a given temperature range, the system exhibits a photonic bandgap for visible light, a phenomenon that has to date been observed exclusively for chiral liquid crystals having helical structures.

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Figure 1. A) Molecular structure of the compounds studied and B) phase diagram for the homologous CB6O.m series.

2. Results

The materials studied here are dimers, in which two semi-rigid mesogenic units are linked by a flexible chain containing an odd number of atoms. An odd-membered spacer constrains the mesogenic units to be inclined with respect to each other, thus the molecule is bent. This molecular curvature is widely believed to be a prerequisite for the formation of the N_{TB} phase.^[24] The focus of this study is the CB6O.*m* homologues,^[25] in which the molecules contain cyanobiphenyl and benzylideneaniline mesogenic units linked by a hexyloxy chain and the length (*m*) of the terminal alkyl chain is varied (Figure 1A). We will also describe the behavior of CB6O-9 in which the Schiff's base link has been reversed with respect to that in CB6O.9 (Figure 1A).

The shorter homologues of the CB6O.*m* series with m < 10show exclusively nematic (N) and N_{TB} phases, whereas the decyl homologue, CB6O.10, shows an N--NTB-SmCTB phase sequence, and was described in detail previously.^[23] For the longer homologues reported here, in the temperature range below the N phase, a sequence of smectic phases was observed (Figure 1, Table S1, Supporting Information). The highest temperature smectic phase observed for the homologues with $m \ge 12$, is an optically uniaxial SmA phase which is a nontilted smectic phase, and the layer spacing (d) corresponds to two molecular lengths. This bilayer structure is due to the broken up-down symmetry of the molecules in consecutive layers giving a higher concentration of polar cyano groups in every second layer interface. The layer thickness increases strongly with decreasing temperature in the SmA phase (Figure 2). This is a typical behavior for nonlinear molecules that gradually stop rotating around their long molecular axes on decreasing temperature, and thus the extent of interdigitation of their terminal chains between the layers also decreases.^[26]

In homeotropic cells (or surface-free films), the SmA phase appears uniformly black between crossed polarizers, and on cooling to the lower temperature SmX phase, a schlieren texture is observed (Figure 3A, for planar textures, see Figure S1 in the Supporting Information) indicating optical biaxiality.



Figure 2. Temperature (T) dependence of the layer spacing (d) for homologues of the CB6O.m series.







Figure 3. A) Optical textures of the CB6O.14 homologue observed between crossed polarizers in a 3 μ m thick cell with a homeotropic anchoring. B) Temperature dependence of the optical birefringence for green light ($\lambda = 532$ nm) for CB6O.14, measured in a planar cell (3 μ m thick). The green line is a fit to the critical dependence in the N and SmA phases, with the critical exponents β equal to 0.17 and 0.27, respectively. The inset: the in-plane birefringence of the SmX phase, determined in a cell with homeotropic anchoring.

The difference in the in-plane refractive indices for the light propagating along the layer normal grows continuously from zero at the SmA–SmX phase transition (inset in Figure 3B).

Reducing the temperature further leads to the transition to the SmY phase, at which the homeotropic texture is restored, suggesting that the SmY phase is uniaxial (as will be explained later, the SmY phase is, in fact, a double helix SmC_{TB} phase). For the homologues with m = 14, 16, and 18, at temperatures below the SmY phase, another lamellar phase (SmZ) is observed, and this exhibits a noncharacteristic, weakly birefringent texture in homeotropic cells. While for the SmA, SmX, and SmY phases only short-range correlations of molecular positions are evidenced by a broad X-ray diffraction signal at high diffraction angles, the SmZ phase exhibits an increased in-plane correlation length typical for hexatic-type smectic phases (Figure S2, Supporting Information). In the SmX and SmY phases, the layer spacing grows monotonically on cooling with nearly the same expansion coefficients, and these are considerably smaller than those in the SmA phase (Figure 2). To check if the biaxiality of the SmX phase is due to the tilting of molecules (a SmC-type phase) or is it a consequence of a hindered molecular rotation in an orthogonal phase (SmA_b phase), an experiment with chiral doping was performed. In a tilted phase, the chirality of the mixture should induce a helix (i.e., the SmC*







Figure 4. A,B) Temperature evolution of the resonant X-ray scattering signals for the CB6O.12 homologue observed on heating (A) and cooling (B). C) Scattered intensity versus wavevector (q) measured in a heating run across the SmX–SmC_{TB} phase transition.

phase), and therefore, the phase would become optically uniaxial, whereas the structure of the SmA_b phase should be insensitive to the chirality.^[27] For the SmX phase, it was observed that it became optically uniaxial upon chiral doping, and therefore we conclude it is a tilted smectic phase. For the chirally doped material filled in a cell with a homeotropic alignment, all three phases, SmA, SmX* and SmY* are optically uniaxial and practically indistinguishable in the polarized-light optical microscopy observations. Very small changes in birefringence were observed only in cells with planar anchoring for an oblique light transmission. These changes correspond to changes in birefringence observed in the pure compound (Figure 3B). The optical birefringence, Δn , measured in the planar cell increases quickly in the nematic phase following a critical behavior $(T - T_c)\beta$, where T_c is a clearing temperature and β , the critical exponent for the Iso-N phase transition (Figure 3 and Figure S3, Supporting Information). At the N-SmA phase transition, the birefringence grows as the orientational order of the long axes increases due to its coupling to the positional order.^[28,29] In the SmX phase, Δn is smaller than expected from the extrapolation of the critical behavior in the SmA phase. At the SmX-SmY transition, the birefringence increases slightly, indicating a weakly first-order transition, but still remains below the value expected from the critical dependence found in the SmA phase (Figure 3 and Figure S3, Supporting Information). By analyzing the departure of the measured birefringence from the extrapolated critical behavior,^[30] the tilt of the long molecular axis from the helix axis may be estimated to be not larger than 20°.

Based on the texture changes and the birefringence and calorimetric measurements, the phase diagram for the series was constructed (Figure 1B). From the resonant soft X-ray scattering measurements (RSoXS, an X-ray scattering method sensitive to the spatial variation of the orientation of molecules)^[31] performed previously for CB6O.10^[23] the phase formed below the N_{TB} phase in this homologue was assigned as a SmC_{TB} phase with a helical four-layer basic crystallographic unit and a longer helix superimposed on it. It is reasonable to expect a similar structure for the SmY phase exhibited by the longer homologues studied here.

The resonant X-ray scattering studies performed for the CB6O.12 homologue, in the temperature range of the SmX phase, revealed only a signal corresponding to the periodicity of four molecular layers (**Figure 4**), indicating that this phase also has a four-layer repeating unit.

In the nonresonant X-ray diffraction experiments, an electron density modulation with a periodicity of twice the molecular length (a bilayer structure) was detected (Figure 2 and Figure S2, Supporting Information). Thus the four-layer structure observed by RSoXS must be related solely to the modulation of molecular orientation. Upon entering the SmC_{TB}

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a structure analogous to that of the SmC_{Fi2} phase.^[32] In the optically uniaxial SmC_{TB} phase, averaging of the azimuthal tilt directions takes place, which occurs by superimposing an additional azimuthal angle shift, ε , between the consecutive layers, so that the sequence of azimuthal positions of molecules becomes 0, $\delta+\varepsilon$, $\pi+2\varepsilon$, $\pi+\delta+3\varepsilon$ (Figure 5 and Figure S4, Supporting Information).

A non-zero value of ε is responsible for the rotation of the four-layer unit cell and the formation of a secondary helix. The pitch of the secondary helix can be calculated from the splitting of the RSoXS signals.^[23,33] Far from the phase transition, the pitch of the helix is only about 16 molecular layers. As the temperature increases, the helix elongates to about 23 layers and close to the transition to the SmX phase, it jumps to 46 layers (160 nm). It appears that the helical pitch unwinds upon approaching the transition to the SmX phase, and as we determined previously for the CB6O.10 homologue, such a change of the helical pitch reflects the evolution of the system from a bilayer structure towards four layer with interchanging synclinic and anticlinic interfaces. The discontinuous nature of this process for CB6O.12 might result from surface interactions. The equal intensities of the RSoXS satellite signals observed in the SmC_{TB} phase show that the value of the angle δ is small^[23] (a strongly distorted-clock basic four-layer unit, with the consecutive layer interfaces being nearly synclinic and anticlinic). It should be noted that for CB6O.10, in which the SmC_{TB} phase is formed from the N_{TB} phase, a much larger value of $\delta \approx 70^\circ$ was determined (a weakly distorted-clock basic four-layer unit) from the strong asymmetry of the satellite signal intensities.^[23] Careful optical observation of the SmC_{TB} phase of CB6O.12 (and also of the longer homologues) reveals that very close to the transition to the SmX phase there is a narrow temperature range in which the secondary helix is much longer than the one determined from the RSoXS studies, and comparable to optical wavelengths. In homeotropic cells, in a range smaller than 0.1 K, selective reflection colors appear covering the whole optical spectrum (Figure 6A).

As this temperature range is very narrow, it was not possible to follow the helix unwinding using a spectroscopic method. Therefore, we decided to make several small modifications to the molecular structure, searching for materials that would have a similar phase sequence but a broader range of temperature over which the optical bandgap may be observed. One of these structural changes was to reverse the direction of the imine link in the mesogenic unit (compound CB6O-9, Figure 1). The phase sequence found for CB6O-9 was N-N_{TB}-SmX-SmC_{TB} (Table S1 and Figures S5-S7, Supporting Information), and at the SmC_{TB}-SmX phase transition the selective reflection of visible light was observed over an increased temperature range of 0.5 K. Spectroscopic measurements performed as a function of temperature clearly show the critical unwinding of the helix on approaching the SmX phase (Figure 6B,C). To ensure that the effect is not related to surface-induced structure or defects, the observations were also performed for freely suspended films, and similar results were found. In order to eliminate the possibility that the selective light reflection is due to the rotation of layers (i.e., that the SmC_{TB} phase is a type of TGB phase^[34]), atomic force microscopy (AFM) studies were performed as a function of temperature, which showed that the orientation of



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Figure 5. A–D) Models of the double-helical structures formed by changes in the azimuthal direction of molecular tilt in the consecutive layers, with the periodicity of the longer helix being 15 layers (A), 23 layers (B), 46 layers (C), and 100 layers (D). For clarity of the picture, only director projections onto the smectic layers are drawn. In the lower part of the figures the top views of the first four layers of the helix are shown; as the temperature decreases, the system gradually evolves from four layer structure with synclinic and anticlinic interfaces towards a bilayer structure by increasing the ε angle.

(SmY) phase, the symmetric satellites of the resonant signal start to develop and have almost equal intensities (Figure 4). The appearance of these satellites is accompanied by a significant decrease in the intensity of the main signal related to the four-layer periodicity. The satellites are a sign of an additional modulation superimposed on the four-layer structure. Interestingly, the satellites change their position discontinuously with temperature, whereas for the previously studied CB6O.10 homologue, the splitting of the main signal developed continuously with temperature when cooled across the N_{TB} -SmC_{TB} phase transition. For CB6O.12, far from the $SmX-SmC_{TB}$ phase transition, the splitting is $2q_m = 0.0232$ Å⁻¹, and on heating it decreases discontinuously to $2q_m = 0.0155$ Å⁻¹ and finally, near the SmC_{TB} -SmX phase transition, the splitting jumps to $2q_{\rm m}=0.0079$ Å^-1. In cooling scans, the temperature range with the splitting $2q_{\rm m} = 0.0079$ Å⁻¹ can be either narrow, or absent, due to the overcooling of the SmX phase. What are the possible structures that may account for the observed resonant X-ray scattering patterns? Both the SmX and SmC_{TB} phases have a periodic structure related to molecular orientation with the same basic periodicity of four layers. There are no changes in the layer thickness at the SmX-SmC_{TB} phase transition implying the same magnitude of tilt in both phases. The SmX phase is optically biaxial whereas the SmC_{TB} phase is optically uniaxial, and so a model of the SmC_{TB} phase has to include an averaging of molecular orientations along the layer normal. The biaxial optical properties of the SmX phase suggest a distorted-clock structure of the four-layer helix with the azimuthal direction of the molecules in the consecutive layers being in the sequence 0, δ , π , π + δ (Figure S4, Supporting Information),



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Figure 6. A) Optical texture of CB6O.12 taken in a 3 µm thick cell with a homeotropic anchoring at the transition from the SmC_{TB} to the SmX phase. The rainbow colors due to a selective reflection appear simultaneously because of a small temperature gradient in the sample. B) A sequence of optical textures taken as a function of temperature at the SmC_{TB}-SmX phase transition for CB6O-9. C) Transmission spectra taken from a 20 µm size spot in the SmC_{TB} phase of CB6O-9 as a function of temperature. The inset: position of the selective reflection band (λ_{SR}) versus temperature (*T*).

the smectic layers is only weakly affected by the SmX–SmC_{TB} phase transition (Figure S8, Supporting Information). This confirms that the helix must be formed by a change in the azimuthal orientation of the molecules within the layers. The chiral nature of the phase is reflected also by the presence of the strong circular dichroism signal recorded in the temperature range of the SmC_{TB} phase, the signal sign is positive or negative depending on predominance of the right- or left-handed helix in the tested area (Figure S9, Supporting Information).

3. Conclusion

Although helical structures formed by achiral materials are not particularly unusual among solid crystals, in soft matter they are observed much less frequently. Recently, such structures were reported for liquid crystalline phases without or with a limited positional order, composed of bent mesogens. However, in crystals as well as in the twist–bend nematic phase, the pitch of the helix is in the range of a few to several nanometers, and far from the optical range. In the analogous twist–bend smectic phase, the molecular organization can be more complex, and our results show that the helix locks to four molecular lengths but is distorted from the ideal clock structure due to the interlayer interactions that force molecules in the neighboring layers to tilt but stay in the same plane ("all-in-one-plane", synclinic, or anticlinic structures). For the materials studied here, the transition between the distorted-clock four-layer structure (SmX) and a phase with a more complex molecular arrangement, in which a longer helix is superimposed on the four-layer repeating unit (SmC_{TB}) was found. Such a structure can be viewed as an intermediate stage between a four layer and bilayer structure. The pitch of the longer helix is temperature dependent, because the four-layer clock-like structure (favored at higher temperature) evolves gradually towards a bilayer, nearly anticlinic arrangement of molecules in the neighboring layers favored at lower temperature. In the temperature range close to the transition to the SmX phase, the secondary helix unwinds and its pitch becomes comparable to the optical wavelength. This leads to the well-known phenomenon of the selective reflection of light with an energy bandgap in the visible range. This effect, although common for chiral liquid crystal phases, is reported here for the first time for achiral mesogens. It should be noted, however, that whereas in the case of helical LC structures made from chiral molecules the handedness of the helix is unique, defined by the configuration of chiral center in molecules, the helical structures in the here reported compounds are formed spontaneously and thus their twisting sense is degenerated. The photonic bandgap for chiral compounds thus appears for one type of circular polarization of light, while for the SmC_{TR} phase a selective reflection is expected for both types of circular polarization of light. In the case of a statistical distribution of right- and left-handed domains each circular polarization is extinguished only partially.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Keywords

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Supporting Information

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Photonic Bandgap in Achiral Liquid Crystals—A Twist on a Twist

Damian Pociecha,* Nataša Vaupotič, Magdalena Majewska, Ewan Cruickshank, Rebecca Walker, John M. D. Storey, Corrie T. Imrie, Cheng Wang, and Ewa Gorecka

ADVANCED MATERIALS

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Materials and Methods

<u>Calorimetric studies</u> were performed by using either a Mettler Toledo DSC1 or DSC3 differential scanning calorimeter equipped with TSO 801RO sample robots and calibrated using indium and zinc standards. Heating and cooling rates were 10 K/min, with a 3-minute isotherm between either heating or cooling and all samples were measured under a nitrogen atmosphere. Transition temperatures and associated enthalpy changes were extracted from the second heating trace unless otherwise noted. For each sample, two aliquots were measured, and the data listed are the average of the duplicate measurements.

<u>Optical observations</u> were performed by using the Zeiss Imager A2m polarizing microscope equipped with Linkam heating stage. Samples were observed in glass cells with various thickness: from 1.8 to 10 μ m, having either planar or homeotropic anchoring polymer layers, the cells were provided by MUT.

<u>The broad angle X-ray diffraction</u> was obtained with the Bruker D8 GADDS system (CuK α line, Goebel mirror, point beam collimator, Vantec2000 area detector). Samples were prepared as droplets on a heated surface. The temperature dependence of the layer thickness was determined from the small-angle X-ray diffraction experiments performed with the Bruker D8 Discover system (CuK α line, Goebel mirror, Anton Paar DCS350 heating stage, scintillation counter) working in the reflection mode. Homeotropically aligned samples were used, prepared as a thin film on a silicon reflectionless wafer.

<u>The resonant x-ray experiments</u> were performed on the soft x-ray scattering beam line (11.0.1.2) at the Advanced Light Source of Lawrence Berkeley National Laboratory. The energy of the incident beam was tuned to the K-edge of the carbon absorption (~280 eV). Samples with thickness lower than 1 μ m were placed between two 100-nm-thick Si3N4 slides (Norcada). The scattering intensity was recorded using the Princeton PI-MTE CCD detector, cooled to -45°C, having a pixel size of 27 μ m, with an adjustable distance from the sample. The adjustable position of the detector allowed to cover a broad range of *q* vectors, corresponding to periodicities from approximately 5.0 – 500 nm.

<u>The birefringence</u> was calculated from the optical retardation measured with a setup based on a photoelastic modulator (PEM-90, Hinds) working at a modulation frequency f = 50 kHz; as a light source a halogen lamp (Hamamatsu LC8) was used equipped with a narrow band pass filter (532 nm). The signal from a photodiode (FLC Electronics PIN-20) was deconvoluted by a lock-in amplifier (EG&G 7265) into 1f and 2f components to yield the retardation induced by the sample. Knowing the sample thickness, the retardation was recalculated into optical birefringence. For measurements $3 \mu m$ – thick cells were used with a planar alignment layer.

<u>Selective reflection</u> was measured by using Craic micro-spectrophotometric system working in UV-visible-NIR range, equipped with Linkam heating stage. The measurements were performed with \sim 20 micron thick cells with homeotropic anchoring. The tested sample area was confined to 50 microns.

<u>The AFM images</u> were taken with the Bruker Dimension Icon microscope, equipped with heating stage, working in the tapping mode at the liquid crystalline-air surface. Cantilevers with a low spring constant of 0.4 N/m were used, the resonant frequency was in the range of 70 - 80 kHz, a typical scan frequency was 1 Hz. Samples for the AFM imaging were prepared on a microscopy cover glass.

<u>All reagents and solvents</u> that were available commercially were purchased from Sigma Aldrich, Fisher Scientific, TCI Chemicals or Fluorochem and were used without further purification unless otherwise stated.

<u>Thin layer chromatography</u> was performed to monitor the reaction progress using the appropriate solvent system and aluminium-backed plates with a coating of Merck Kieselgel 60 F254 silica which were purchased from Merck KGaA. The spots on the plate were visualised by UV light (254 nm) or by oxidation using either a potassium permanganate stain or iodine dip.

<u>Column chromatography</u> was carried out using silica gel grade 60 Å, 40-63 μ m particle size, purchased from Fluorochem and using an appropriate solvent system. In addition, some normal phase separations were carried out using a Biotage Selekt system with Biotage Sfar Silica High Capacity Duo Columns of 50 g or 100 g load capacity. The desired spots were identified using a UV detector which was set to 254 nm and the instrument collected the spots when a threshold of 250 mAU was surpassed.

Structure characterization of all final products and intermediates that were synthesised was performed by using ¹H NMR, ¹³C NMR and infrared spectroscopies. The ¹H and ¹³C NMR spectra were recorded on either a 400 MHz Bruker Avance III HD NMR spectrometer, or a 300 MHz Bruker Ultrashield NMR spectrometer. The infrared spectra were recorded on a Thermal Scientific Nicolet IR100 FTIR spectrometer with an ATR diamond cell.

<u>Purity analysis</u> of the final products was completed by elemental analysis and/or highresolution mass spectrometry. C, H, N, S microanalysis were carried out by the Sheffield Analytical and Scientific Services Elemental Microanalysis Service at the University of Sheffield using an Elementar Vario MICRO Cube or by the Elemental Analysis Service at OEA Laboratories Limited using a CE Instruments EA1110 CHNS-O Elemental Analyser. The instruments were calibrated using series of different masses of sulphanilamide and acetanilide.

Synthesis of CB6O.m





The synthesis of the CB6O.*m* series follows the steps outlined in **Scheme S1**. In the synthesis of the CB6O.*m* series, 6-bromohexanoyl chloride underwent a Friedel-Crafts acylation, hydrosilane reduction, Williamson's ether reaction and a Rosenmund-von Braun cyanation reaction in a method described by Abberley *et al.*^[1] to form 4'-[6-(4-formylphenoxy)hexyl]-[1,1'-biphenyl]-4-carbonitrile (**1.4**). A Friedel-Crafts acylation reaction was followed by a Schmidt

reaction and subsequently an amide hydrolysis reaction to form 4-alkylanilines (1.7) using a method described by Henderson *et al.*^[2] Compounds 1.4 and 1.7 were combined in a Schiff's base reaction^[3] to form the desired product.

6-Bromo-1-(4'-bromo[1,1'-biphenyl]-4-yl)hexan-1-one (1.1)

To pre-dried flask flushed with argon, aluminium chloride (7.25 g, 0.0564 mol) was added along with dry dichloromethane (60 mL) while being stirred. The outside of the flask was wrapped in aluminium foil to prevent light from interfering with the reaction and was placed into an ice bath in order to keep the reaction mixture at 0 °C. 4-Bromobiphenyl (12.1 g, 0.0517 mol) and 6-bromohexanoyl chloride (7.19 mL, 10.0 g, 0.0470 mol) were mixed along with dry dichloromethane (60 mL) before being added dropwise into the flask. The ice bath was removed, and the reaction proceeded at room temperature overnight. The extent of the reaction was monitored by TLC using dichloromethane as the solvent system (RF values quoted in the product data). The mixture was added to a slurry of ice (50 g) with 6 M hydrochloric acid (12 mL) and extracted with dichloromethane (200 mL). The extracted organic layer was washed with water (3 × 50 mL) and dried over anhydrous magnesium sulfate. The magnesium sulfate was removed using vacuum filtration and the solvent evaporated under vacuum to leave an off-white solid which was recrystallised using hot ethanol (250 mL).

Yield: 10.15 g, 53.2 %. RF: 0.53. MP: 81 °C

v_{max}/cm⁻¹: 2938, 1678, 1604, 1477, 1389, 1365, 1262, 1208, 1189, 1070, 1000, 969, 822, 794, 723, 664, 574

 δ_{H} /ppm (400 MHz, CDCl₃): 8.02 (2 H, d, J 8.3 Hz, Ar-H), 7.65 (2 H, d, J 8.3 Hz, Ar-H), 7.59 (2 H, d, J 8.4 Hz, Ar-H), 7.49 (2 H, d, J 8.4 Hz, Ar-H), 3.44 (2 H, t, J 7.1 Hz, Br-<u>CH₂</u>-CH₂-), 3.03 (2 H, t, J 7.1 Hz, C(=O)-<u>CH₂</u>-CH₂-), 1.93 (2 H, quin, J 7.1 Hz, Br-CH₂-<u>CH₂</u>-CH₂-), 1.79 (2 H, quin, J 7.1 Hz, C(=O)-CH₂-<u>CH₂</u>-CH₂-), 1.56 (2 H, quin, J 7.1 Hz, Br-CH₂-CH₂-CH₂-)

δ_C/ppm (100 MHz, CDCl₃): 199.45, 144.40, 138.78, 135.94, 132.11, 128.82, 128.73, 127.07, 122.66, 38.37, 33.65, 32.64, 27.90, 23.37

Data consistent with reported values.^[1]

4-Bromo-4'-(6-bromohexyl)-1,1'-biphenyl (1.2)

To a pre-dried flask flushed with argon, compound **1.1** (10.0 g, 0.0244 mol) was added. The flask was then placed into an ice bath in order to maintain the temperature at 0 °C. The solid was solubilised using trifluoroacetic acid (100 mL, 149 g, 1.31 mol) and dry dichloromethane (40 mL) along with stirring. Finally, triethylsilane (20.0 mL, 14.6 g, 0.125 mol) was added to the flask and the ice bath was removed. The reaction was left for 24 h and the extent of the reaction was monitored by TLC using dichloromethane as the solvent system (RF values quoted in the product data). Once complete, the mixture was added to a beaker with dichloromethane (100 mL) and water (300 mL). The organic layer was separated and washed with water (3×50 mL). This was dried using anhydrous magnesium sulfate, which was removed by vacuum filtration, and the solvent evaporated under vacuum to leave a white solid which was recrystallised using hot ethanol (150 mL).

Yield: 6.77 g, 70.8 %. RF: 0.67. MP: 76 °C

v_{max} /cm⁻¹: 2931, 2856, 1479, 1454, 1390, 1235, 1189, 1077, 1000, 804, 726, 646, 503 δ_H/ppm (400 MHz, CDCl₃): 7.55 (2 H, d, J 8.2 Hz, Ar-H), 7.46 (4 H, m, Ar-H), 7.24 (2 H, d, J 8.2 Hz, Ar-H), 3.41 (2 H, t, J 6.8 Hz, Br-CH₂-CH₂-), 2.66 (2 H, t, J 7.3 Hz, Ar-CH₂-CH₂-), 1.87

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(2 H, tt, J 7.3 Hz, 6.8 Hz, Br-CH₂-CH₂-CH₂-CH₂-), 1.67 (2 H, quin, J 7.3 Hz, Ar-CH₂-CH₂-CH₂-), 1.48
(2 H, quin, J 7.3 Hz, Br-CH₂-CH₂-CH₂-CH₂-), 1.40 (2 H, quin, J 7.3 Hz, Ar-CH₂-CH₂-CH₂-CH₂-), δ_C/ppm (100 MHz, CDCl₃) 142.18, 140.03, 137.42, 131.81, 128.96, 128.57, 126.82, 121.21, 35.44, 33.95, 32.73, 31.21, 28.40, 28.03

Data consistent with reported values.^[1]

4-{[6-(4'-Bromo[1,1'-biphenyl]-4-yl)hexyl]oxy}benzaldehyde (1.3)

To a pre-dried flask flushed with argon and fitted with a condenser, 4-hydroxybenzaldehyde (1.87 g, 0.0153 mol) and potassium carbonate (3.84 g, 0.0278 mol) were added. Dimethylformamide (30 mL) was added with compound **1.2** (5.51 g, 0.0139 mol) and stirred. The reaction was heated to 90 °C, left overnight and the extent of the reaction monitored by TLC using dichloromethane as the solvent system (RF value quoted in the product data). The reaction mixture was cooled to room temperature, and poured into water (150 mL). The resulting white precipitate was vacuum filtered and recrystallised from hot ethanol (100 mL).

Yield: 3.64 g, 60.0 %. RF: 0.33. MP: 92 °C

v_{max}/cm⁻¹: 2930, 2857, 1691, 1600, 1577, 1507, 1481, 1431, 1392, 1300, 1243, 1216, 1166, 1106, 1078, 1012, 1001, 837, 805, 767, 752, 732, 652, 619, 517, 505, 481

 δ_{H} /ppm (400 MHz, CDCl₃): 9.88 (1 H, s, (C=O)-H), 7.82 (2 H, d, J 8.3 Hz, Ar-H), 7.55 (2 H, d, J 8.0 Hz, Ar-H), 7.46 (4 H, m, Ar-H), 7.25 (2 H, d, J 7.7 Hz, Ar-H), 6.98 (2 H, d, J 8.3 Hz, Ar-H), 4.04 (2 H, t, J 6.5 Hz, O-<u>CH₂</u>-CH₂-), 2.67 (2 H, t, J 7.6 Hz, Ar-<u>CH₂</u>-CH₂-), 1.83 (2 H, tt, J 6.9 Hz, 6.5 Hz, O-CH₂-<u>CH₂</u>-CH₂-), 1.71 (2 H, quin, J 7.6 Hz, Ar-CH₂-<u>CH₂</u>-CH₂-), 1.45 (4 H, m, Ar-CH₂-CH₂-CH₂-CH₂-))

δ_C/ppm (100 MHz, CDCl₃): 190.80, 164.21, 142.22, 140.00, 137.41, 132.00, 131.82, 129.79, 128.97, 128.55, 126.81, 121.22, 114.75, 68.32, 35.47, 31.30, 28.99, 28.94, 25.87

Data consistent with reported values.^[1]

4'-[6-(4-Formylphenoxy)hexyl][1,1'-biphenyl]-4-carbonitrile (1.4)

To a pre-dried flask flushed with argon and fitted with a condenser, compound 1.3 (5.25 g, 0.0120 mol) was added along with N-methyl-2-pyrrolidone (50 mL) and stirred. In addition, the flask was connected to a Drechsel bottle filled with sodium hypochlorite. Using respiration protection, copper (I) cyanide (2.15 g, 0.0240 mol) was added to the flask. After use, all equipment was placed into a sodium hypochlorite bath for 24 h. The mixture was heated to 200 °C for 4 h and subsequently cooled to 60 °C. In a separate flask, iron (III) chloride (19.5 g, 0.120 mol), 32 % hydrochloric acid (18.8 mL, 21.9 g, 0.600 mol) and water (45 mL) were added, mixed at 60 °C and added to the reaction flask all at one. The resultant mixture was kept at 60 °C for 30 min and afterwards cooled to room temperature. The mixture was stirred at room temperature for 1 h. The mixture was added to a beaker containing water (200 mL) and dichloromethane (200 mL). The organic layer was separated and washed with water (3×100 mL). The organic layer was dried using anhydrous magnesium sulfate. The magnesium sulfate was removed using vacuum filtration and the solvent evaporated under vacuum to leave a brown liquid. This liquid was added to water (200 mL) which generated a brown precipitate which was collected by vacuum filtration. The crude product was purified using a silica gel column with 10 % 40:60 petroleum ether and 90 % dichloromethane as eluent (RF value quoted in product data). The eluent fractions of interest were evaporated under vacuum to leave an off-white/pale vellow solid which was recrystallised from hot ethanol (40 mL).

Yield: 2.82 g, 61.3 %. RF: 0.16

T_{Cr}-: 84 °C T_{NI} (46 °C)

v_{max}/cm⁻¹: 2943, 2852, 2221, 1689, 1598, 1574, 1508, 1492, 1472, 1422, 1396, 1313, 1302, 1249, 1211, 1160, 1111, 1031, 1005, 846, 834, 813, 781, 647, 620, 546, 516

 $δ_{\rm H}$ /ppm (400 MHz, CDCl₃): 9.88 (1 H, s, (C=O)-H), 7.82 (2 H, d, J 8.3 Hz, Ar-H), 7.71 (2 H, d, J 8.0 Hz, Ar-H), 7.66 (2 H, d, J 8.0 Hz, Ar-H), 7.51 (2 H, d, J 7.8 Hz, Ar-H), 7.28 (2 H, d, J 7.8 Hz, Ar-H), 6.98 (2 H, d, J 8.3 Hz, Ar-H), 4.04 (2 H, t, J 6.5 Hz, O-<u>CH₂-CH₂-), 2.69 (2 H, t, J 7.7 Hz</u>, Ar-<u>CH₂-CH₂-), 1.83 (2 H, tt, J 7.1 Hz</u>, 6.5 Hz, O-CH₂-<u>CH₂-CH₂-), 1.70 (2 H, quin, J 7.7 Hz</u>, Ar-CH₂-<u>CH₂-CH₂-), 1.48 (4 H, m, Ar-CH₂-CH₂-CH₂-)</u>

δ_C/ppm (100 MHz, CDCl₃): 190.78, 164.18, 145.54, 143.44, 136.58, 132.58, 131.99, 129.81, 129.18, 127.48, 127.12, 119.02, 114.74, 110.60, 68.29, 35.51, 31.25, 28.99, 28.94, 25.86

Data consistent with reported values.^[1]

1-(4-Undecylphenyl)ethan-1-one (1.5)

To a pre-dried flask flushed with argon, aluminium chloride (3.84 g, 0.0288 mol) and acetyl chloride (1.92 mL, 2.12 g, 0.0270 mol) were added along with dry dichloromethane (70 mL) while being stirred. The outside of the flask was wrapped in aluminium foil to prevent light from interfering with the reaction and placed into an ice bath in order to keep the reaction mixture at 0 °C. Undecylbenzene (6.52 g, 5.58 g, 0.0240 mol) was added slowly dropwise to the stirred mixture and once completed the ice bath was removed. The reaction was left to stir at room temperature overnight. The extent of the reaction was monitored by TLC using dichloromethane as the solvent system (RF value quoted in the product data). The mixture was added to a slurry of ice (70 g) with 6 M hydrochloric acid (20 mL) and extracted with dichloromethane (150 mL). The extracted organic layer was washed with water (3×50 mL) and dried over anhydrous magnesium sulfate. The magnesium sulfate was removed using vacuum filtration and the solvent evaporated under vacuum to leave a colourless oil which was used without purification.

Yield: 5.46 g, 82.9 %. RF: 0.43

v_{max}/cm⁻¹: 2923, 2853, 1683, 1606, 1466, 1412, 1356, 1266, 1181, 1017, 955, 843, 817, 737, 722, 690

 δ_{H} /ppm (400 MHz, CDCl₃): 7.88 (2 H, d, J 8.1 Hz, Ar-H), 7.26 (2 H, d, J 8.1 Hz, Ar-H), 2.66 (2 H, t, J 7.4 Hz, Ar-<u>CH₂</u>-CH₂-), 2.58 (3 H, s, (C=O)-<u>CH₃</u>), 1.61 (2 H, quin, J 7.4 Hz, Ar-CH₂-<u>CH₂-CH_{2</u>}

 δ_C/ppm (100 MHz, CDCl_3): 197.72, 148.78, 134.89, 128.57, 128.45, 36.00, 31.93, 31.14, 29.67, 29.64, 29.58, 29.48, 29.36, 29.28, 26.49, 22.71, 14.13

N-(4-Undecylphenyl)acetamide (1.6)

To a pre-dried flask flushed with argon, compound **1.5** (2.40 g, 8.74×10^{-3} mol), 70 % sulfuric acid (20 mL) and dry dichloromethane (6 mL) were added with stirring. The flask was placed into a water/ice bath in order to maintain the temperature under 20 °C. Sodium azide (0.683 g, 0.0105 mol), was added very slowly portion wise to the flask, allowing for the evolution of nitrogen to stop before the next portion was added. The extent of the reaction was monitored by TLC using dichloromethane as the solvent system (RF value quoted in the product data). The reaction was left overnight and after completion was added to a mixture of dichloromethane (150 mL) and water (200 mL). The organic layer was washed with water (3 × 50 mL) and dried over anhydrous magnesium sulfate. The magnesium sulfate was removed by vacuum filtration and the solvent

evaporated under vacuum to leave a yellow oil which was added to 40:60 petroleum ether (150 mL). The resulting white precipitate was collected and recrystallised from hot ethanol (100 mL).

Yield: 2.19 g, 86.6 %. RF: 0.59. MP: 97 °C

v_{max}/cm⁻¹: 3296, 2955, 2917, 2849, 1661, 1605, 1548, 1514, 1466, 1410, 1369, 1321, 1269, 1012, 829, 806, 743, 721, 605, 551, 515

δ_H/ppm (400 MHz, CDCl₃): 7.38 (2 H, d, J 8.3 Hz, Ar-H), 7.17 (1 H, br, NH), 7.12 (2 H, d, J 8.3 Hz, Ar-H), 2.58 (2 H, t, J 7.6 Hz, Ar-<u>CH₂</u>-CH₂-), 2.58 (3 H, s, (C=O)-<u>CH₃</u>), 1.58 (2 H, quin, J 7.6 Hz, Ar-CH₂-<u>CH₂</u>-CH₂-) 1.27 (16 H, m, Ar-CH₂-CH₂-<u>CH₂-C</u>

 δ_C /ppm (100 MHz, CDCl₃): 168.16, 139.14, 135.40, 128.86, 119.98, 35.37, 31.93, 31.52, 29.68, 29.64, 29.61, 29.52, 29.35, 29.26, 24.55, 22.70, 14.13

4-Undecylaniline (1.7, *m*=11)

To a pre-dried flask flushed with argon and fitted with a condenser, compound **1.6** (2.00 g, $6.91 \times 10-3$ mol) was added. Ethanol (70 mL) was added along with 32 % hydrochloric acid (16 mL) and stirred. The reaction was heated at reflux overnight and the extent of the reaction monitored by TLC using 80 % dichloromethane and 20 % ethyl acetate as the solvent system (RF value quoted in the product data). The reaction mixture was cooled to room temperature, poured into ice (100 g), and made alkaline using 15 M sodium hydroxide solution. The resulting brown solid was vacuum filtered and was recrystallised from hot ethanol (100 mL).

Yield: 1.65 g, 96.5 %. RF: 0.28. MP: 33 °C

v_{max} /cm⁻¹: 3395, 3316, 3219, 2956, 2917, 2849, 1619, 1517, 1469, 1270, 1178, 1125, 826, 746, 717, 563, 809, 477

 δ_{H} /ppm (400 MHz, CDCl₃): 6.97 (2 H, d, J 8.3 Hz, Ar-H), 6.62 (2 H, d, J 8.3 Hz, Ar-H), 3.53 (2H, br, NH₂), 2.49 (2 H, t, J 7.4 Hz, Ar-CH₂-CH₂-CH₂-), 1.56 (2 H, quin, J 7.4 Hz, Ar-CH₂-CH₂-CH₂-), 1.27 (16 H, m, Ar-CH₂-

 δ_C/ppm (100 MHz, CDCl_3): 143.95, 133.19, 129.13, 115.23, 35.10, 31.94, 31.84, 29.70, 29.66, 29.64, 29.57, 29.36, 29.31, 22.71, 14.14

4-Dodecylaniline, **4-tetradecylaniline**, **4-hexadecylaniline**, and **4-octadecylaniline** were available commercially from Sigma Aldrich and used without further purification.

4'-[6-(4-{(E)-[(4-Alkylphenyl)imino]methyl}phenoxy)hexyl][1,1'-biphenyl]-4carbonitriles, CB6O.*m* series (1.8)

To a pre-dried flask flushed with argon and fitted with a condenser, compound **1.4** (1 eq, 0.200 g, $5.22 \times 10^{-4} \text{ mol}$) and compound **1.7** (2 eq, $1.04 \times 10^{-4} \text{ mol}$) of the appropriate chain length were added along with ethanol (20 mL) and the mixture was then stirred. The reaction was heated to reflux and *p*-toluenesulfonic acid (catalytic amount) was added before being left overnight. The reaction mixture was then cooled to room temperature and a white precipitate formed which was collected by vacuum filtration. The solid was recrystallized from hot ethanol (15 mL).

CB60.11 Yield: 0.162 g, 50.6 % T_{Cr}- 65 °C T_{SmCTBSmX} 71 °C T_{SmXN} 82 °C T_{NI} 106 °C *v_{max}* /cm⁻¹: 2920, 2850, 2228, 1625, 1606, 1572, 1510, 1495, 1467, 1422, 1394, 1304, 1247, 1193, 1166, 1106, 1039, 1021, 1005, 974, 885, 838, 810, 723, 635, 625, 560, 542

 $δ_{\rm H}$ /ppm (400 MHz, CDCl₃): 8.39 (1 H, s, (C=N)-H), 7.82 (2 H, d, J 8.6 Hz, Ar-H), 7.71 (2 H, d, J 8.5 Hz, Ar-H), 7.67 (2 H, d, J 8.5 Hz, Ar-H), 7.51 (2 H, d, J 8.1 Hz, Ar-H), 7.29 (2 H, d, J 8.1 Hz, Ar-H), 7.19 (2 H, d, J 8.3 Hz, Ar-H), 7.13 (2 H, d, 8.3 Hz, Ar-H), 6.95 (2 H, d, J 8.6 Hz, Ar-H), 4.02 (2 H, t, 6.4, O-<u>CH₂-CH₂-), 2.69 (2 H, t, J 7.5 Hz</u>, Ar-<u>CH₂-CH₂-), 2.61 (2 H, t, 7.7 Hz, Ar-CH₂-CH₂-), 1.82 (2 H, tt, 7.1 Hz, 6.4 Hz, O-CH₂-<u>CH₂-CH₂-), 1.68 (4 H, m, Ar-CH₂-CH₂-CH₂-, Ar-CH₂-CH₂-), 1.48 (4 H, m, Ar-CH₂-CH₂-CH₂-CH₂-), 1.29 (16 H, m, Ar-CH₂-C</u></u>

δ_C/ppm (100 MHz, CDCl₃): 161.64, 158.91, 149.90, 145.57, 143.50, 140.51, 136.55, 132.57, 130.37, 129.29, 129.20, 129.07, 127.48, 127.12, 120.75, 119.04, 114.65, 110.57, 68.03, 35.51, 35.50, 31.94, 31.59, 31.26, 29.69, 29.66, 29.63, 29.55, 29.37, 29.34, 29.10, 28.94, 25.88, 22.71, 14.15

Elemental Analysis: Calculated for $C_{43}H_{52}N_2O$: C = 84.27 %, H = 8.55 %, N = 4.57 %; Found: C = 84.35 %, H = 8.54 %, N = 4.28 %

CB60.12

Yield: 0.241 g, 73.6 %

T_{Cr-} 73 °C T_{SmCTBSmX} (73 °C) T_{SmXSmA} 87 °C T_{SmAN} 87 °C T_{NI} 103 °C

v_{max}/cm⁻¹: 2919, 2849, 2228, 1624, 1606, 1572, 1510, 1495, 1466, 1422, 1394, 1305, 1247, 1194, 1166, 1106, 1040, 1005, 974, 885, 839, 819, 809, 723, 626, 542

 $δ_{\rm H}$ /ppm (400 MHz, CDCl₃): 8.39 (1 H, s, (C=N)-H), 7.82 (2 H, d, J 7.9 Hz, Ar-H), 7.70 (2 H, d, J 7.9 Hz, Ar-H), 7.67 (2 H, d, J 7.9 Hz, Ar-H), 7.50 (2 H, d, J 7.7 Hz, Ar-H), 7.29 (2 H, d, J 7.7 Hz, Ar-H), 7.19 (2 H, d, J 7.9 Hz, Ar-H), 7.13 (2 H, d, 7.9 Hz, Ar-H), 6.95 (2 H, d, J 7.9 Hz, Ar-H), 4.02 (2 H, t, 6.5, O-<u>CH₂</u>-CH₂-), 2.69 (2 H, t, J 7.5 Hz, Ar-<u>CH₂</u>-CH₂-), 2.61 (2 H, t, 7.6 Hz, Ar-<u>CH₂</u>-CH₂-) 1.82 (2 H, tt, 7.2 Hz, 6.5 Hz, O-CH₂-<u>CH₂</u>-CH₂-), 1.67 (4 H, m, Ar-CH₂-<u>CH₂</u>-CH₂-, Ar-CH₂-<u>CH₂-CH₂-), 1.49 (4 H, m, Ar-CH₂-CH₂-CH₂-CH₂-), 1.26 (18 H, m, Ar-CH₂-CH₂-<u>CH₂-</u></u>

 δ_{C} /ppm (100 MHz, CDCl₃): 161.64, 158.91, 149.90, 145.57, 143.50, 140.51, 136.55, 132.57, 130.37, 129.29, 129.20, 129.07, 127.49, 127.12, 120.75, 119.04, 114.65, 110.57, 68.03, 35.51, 35.50, 31.94, 31.59, 31.26, 29.70, 29.69, 29.66, 29.63, 29.55, 29.38, 29.34, 29.10, 28.94, 25.88, 22.71, 14.15

Elemental Analysis: Calculated for $C_{44}H_{54}N_2O$: C = 84.30 %, H = 8.68 %, N = 4.47 %; Found: C = 84.66 %, H = 8.68 %, N = 4.40 %

CB60.14

Yield: 0.284 g, 83.1 %

T_{Cr-} 76 °C T_{SmZSmCTB} (60 °C) T_{SmCTBSmX} 77 °C T_{SmXSmA} 94 °C T_{SmAN} 99 °C T_{NI} 103 °C

v_{max}/cm⁻¹: 2918, 2849, 2231, 1623, 1606, 1571, 1509, 1495, 1469, 1422, 1393, 1305, 1247, 1167, 1106, 1025, 1005, 973, 886, 838, 817, 721, 625, 636, 563, 539, 520

 δ_{H} /ppm (400 MHz, CDCl₃): 8.39 (1 H, s, (C=N)-H), 7.82 (2 H, d, J 8.0 Hz, Ar-H), 7.70 (2 H, d, J 8.0 Hz, Ar-H), 7.67 (2 H, d, J 8.0 Hz, Ar-H), 7.51 (2 H, d, J 7.7 Hz, Ar-H), 7.29 (2 H, d, J 7.7 Hz, Ar-H), 7.19 (2 H, d, J 8.0 Hz, Ar-H), 7.13 (2 H, d, 8.0 Hz, Ar-H), 6.96 (2 H, d, J 8.0 Hz, Ar-H), 4.02 (2 H, t, 6.5, O-<u>CH₂-CH₂-), 2.69 (2 H, t, J 7.6 Hz, Ar-<u>CH₂-CH₂-), 2.61 (2 H, t, 7.5 Hz, Ar-H)</u></u>

<u>CH</u>₂-CH₂-) 1.82 (2 H, tt, 7.0 Hz, 6.5 Hz, O-CH₂-<u>CH</u>₂-CH₂-), 1.66 (4 H, m, Ar-CH₂-<u>CH</u>₂-CH₂-, Ar-CH₂-<u>CH</u>₂-CH₂-), 1.48 (4 H, m, Ar-CH₂-CH₂-<u>CH</u>₂-CH₂-), 1.26 (22 H, m, Ar-CH₂-CH₂-<u>CH₂-CH</u>

 δ_C/ppm (100 MHz, CDCl₃): 161.64, 158.91, 149.90, 145.58, 143.50, 140.51, 136.55, 132.57, 130.36, 129.29, 129.20, 129.07, 127.49, 127.11, 120.75, 119.04, 114.65, 110.57, 68.03, 35.51, 35.50, 31.95, 31.59, 31.26, 29.70 (4 x C), 29.67, 29.63, 29.54, 29.38, 29.34, 29.10, 28.94, 25.88, 22.71, 14.15

Elemental Analysis: Calculated for $C_{46}H_{58}N_2O$: C = 84.35 %, H = 8.93 %, N = 4.28 %; Found: C = 84.56 %, H = 8.91 %, N = 4.20 %

CB60.16

Yield: 0.187 g, 52.4 %

T_{Cr}- 76 °C T_{SmZSmCTB} (67 °C) T_{SmCTBSmX} 80 °C T_{SmXSmA} 98 °C T_{SmAN} 103 °C T_{NI} 103 °C

v_{max} /cm⁻¹: 2918, 2848, 2233, 1606, 1571, 1509, 1495, 1470, 1421, 1393, 1306, 1248, 1168, 1106, 1056, 1025, 1005, 886, 837, 819, 754, 720, 637, 625, 564, 540, 520

 $δ_{H}$ /ppm (400 MHz, CDCl₃): 8.39 (1 H, s, (C=N)-H), 7.82 (2 H, d, J 8.0 Hz, Ar-H), 7.71 (2 H, d, J 7.9 Hz, Ar-H), 7.67 (2 H, d, J 7.9 Hz, Ar-H), 7.51 (2 H, d, J 7.7 Hz, Ar-H), 7.30 (2 H, d, J 7.7 Hz, Ar-H), 7.18 (2 H, d, J 7.9 Hz, Ar-H), 7.13 (2 H, d, 7.9 Hz, Ar-H), 6.96 (2 H, d, J 8.0 Hz, Ar-H), 4.02 (2 H, t, 6.4, O-<u>CH₂-CH₂-), 2.69 (2 H, t, J 7.6 Hz</u>, Ar-<u>CH₂-CH₂-), 2.61 (2 H, t, 7.4 Hz</u>, Ar-<u>CH₂-CH₂-) 1.82 (2 H, tt, 7.0 Hz, 6.4 Hz, O-CH₂-<u>CH₂-CH₂-), 1.66 (4 H, m, Ar-CH₂-CH₂-CH₂-, Ar-CH₂-<u>CH₂-CH₂-), 1.49 (4 H, m, Ar-CH₂-CH₂-CH₂-CH₂-CH₂-), 1.26 (26 H, m, Ar-CH₂-<u>CH₂-</u></u></u></u>

 δ_{C} /ppm (100 MHz, CDCl₃): 161.64, 158.91, 149.90, 145.57, 143.50, 140.51, 136.55, 132.57, 130.37, 129.29, 129.20, 129.07, 127.49, 127.12, 120.75, 119.04, 114.65, 110.57, 68.03, 35.51, 35.50, 31.95, 31.59, 31.26, 29.72 (4 x C), 29.69 (2 x C), 29.68, 29.63, 29.55, 29.38, 29.34, 29.10, 28.94, 25.88, 22.71, 14.15

Elemental Analysis: Calculated for $C_{48}H_{62}N_2O$: C = 84.41 %, H = 9.15 %, N = 4.10 %; Found: C = 84.73 %, H = 9.16 %, N = 4.02 %

CB60.18

Yield: 0.351 g, 94.6 %

T_{Cr-} 73 °C Т_{SmZSmCTB} 78 °C Т_{SmCTBSmX} 85 °C Т_{SmXSmA} 101 °C Т_{SmAI} 106 °C

v_{max}/cm⁻¹: 2916, 2849, 2232, 1607, 1573, 1511, 1495, 1470, 1421, 1394, 1305, 1249, 1167, 1106, 1020, 1005, 972, 889, 829, 814, 720, 627, 624, 540

 $δ_{\rm H}$ /ppm (400 MHz, CDCl₃): 8.39 (1 H, s, (C=N)-H), 7.82 (2 H, d, J 8.0 Hz, Ar-H), 7.71 (2 H, d, J 7.9 Hz, Ar-H), 7.67 (2 H, d, J 7.9 Hz, Ar-H), 7.51 (2 H, d, J 7.7 Hz, Ar-H), 7.29 (2 H, d, J 7.7 Hz, Ar-H), 7.19 (2 H, d, J 8.0 Hz, Ar-H), 7.13 (2 H, d, 8.0 Hz, Ar-H), 6.95 (2 H, d, J 8.0 Hz, Ar-H), 4.02 (2 H, t, 6.6, O-<u>CH₂-CH₂-), 2.69 (2 H, t, J 7.7 Hz, Ar-CH₂-CH₂-), 2.61 (2 H, t, 7.5 Hz, Ar-H), 4.02 (2 H, tt, 7.1 Hz, 6.6 Hz, O-CH₂-<u>CH₂-CH₂-), 1.66 (4 H, m, Ar-CH₂-<u>CH₂-CH₂-</u>, Ar-CH₂-<u>CH₂-CH₂-), 1.48 (4 H, m, Ar-CH₂-CH₂-CH₂-CH₂-CH₂-), 1.26 (30 H, m, Ar-CH₂-<u>CH₂-CH_{2</u></u></u></u>}

 δ_C/ppm (100 MHz, CDCl₃): 161.64, 158.92, 149.90, 145.58, 143.50, 140.52, 136.55, 132.57, 130.37, 129.28, 129.19, 129.07, 127.48, 127.11, 120.75, 119.04, 114.65, 110.57, 68.03, 35.51, 35.50, 31.95, 31.59, 31.26, 29.72 (6 x C), 29.69 (2 x C), 29.68, 29.63, 29.55, 29.38, 29.34, 29.10, 28.94, 25.88, 22.71, 14.14

Elemental Analysis: Calculated for $C_{50}H_{66}N_2O$: C = 84.45 %, H = 9.36 %, N = 3.94 %; Found: C = 84.28 %, H = 9.38 %, N = 3.84 %

Synthesis of CB6O-9

The synthesis of the CB6O-*m* series follows the steps outlined in **Scheme S2**. CB6O-9 (**1.13**) was synthesised by using 4-bromo-4'-(6-bromohexyl)-1,1'-biphenyl (**1.2**), described in **Scheme S1**, in a Williamson's ether reaction^[4] followed by a modified Rosenmund-von Braun cyanation reaction^[5] and subsequently an amide hydrolysis reaction^[2] to form 4'-[6-(4-Aminophenoxy)hexyl]-[1,1'-biphenyl]-4-carbonitrile (**1.11**). A Duff reaction^[6] was used to generate 4-nonylbenzaldehyde (**1.12**). Compounds **1.11** and **1.12** were subsequently combined in a Schiff's base reaction^[3] to form the desired product.



Scheme S2. Synthesis of CB6O-9.

N-(4-{[6-(4'-Bromo[1,1'-biphenyl]-4-yl)hexyl]oxy}phenyl)acetamide (1.9)

To a pre-dried flask flushed with argon and fitted with a condenser, 4-acetamidophenol (4.62 g, 0.0305 mol) and potassium carbonate (8.43 g, 0.0610 mol) were added.

Dimethylformamide (150 mL) was added with compound **1.2** (12.1 g, 0.0305 mol) and then stirred. The reaction was heated to 90 °C, left overnight and monitored by TLC using dichloromethane as the solvent system (RF value quoted in the product data). The reaction mixture was then cooled to room temperature and poured into water (250 mL). The resulting white precipitate was vacuum filtered, and recrystallized from hot ethanol (250 mL).

Yield: 10.1 g, 71.0 %. RF: 0.31. MP: 151 °C

v_{max}/cm⁻¹: 3276, 2922, 2821, 1658, 1606, 1547, 1509, 1480, 1408, 1393, 1371, 1324, 1243, 1230, 1172, 1108, 1000, 920, 820, 804, 774, 733, 639, 587, 556, 526, 494, 472

 δ_{H} /ppm (400 MHz, CDCl₃): 7.54 (2 H, d, J 8.6 Hz, Ar-H), 7.45 (4 H, m, Ar-H), 7.38 (2 H, d, J 8.8 Hz, Ar-H), 7.25 (2 H, d, J 8.2 Hz, Ar-H), 7.15 (1 H, br, NH), 6.84 (2 H, d, J 8.8 Hz, Ar-H), 3.92 (2 H, t, J 6.5 Hz, O-<u>CH₂</u>-CH₂-), 2.66 (2 H, t, J 7.7 Hz, Ar-<u>CH₂</u>-CH₂-), 2.15 (3 H, s, (C=O)-<u>CH₃</u>) 1.72 (4 H, m, Ar-CH₂-<u>CH₂-CH₂-</u>CH₂-, O-CH₂-<u>CH₂-CH₂-), 1.47 (4 H, m, Ar-CH₂-CH₂-<u>CH₂-CH₂-CH₂-), CH₂-CH₂-)</u></u>

δ_C/ppm (100 MHz, CDCl₃): 168.14, 155.99, 142.33, 140.05, 137.35, 131.79, 130.79, 128.97, 128.56, 126.80, 121.89, 121.17, 114.78, 68.16, 35.48, 31.33, 29.19, 28.98, 25.91, 24.39

N-(4-{[6-(4'-Cyano[1,1'-biphenyl]-4-yl)hexyl]oxy}phenyl)acetamide (1.10)

To a pre-dried flask flushed with argon and fitted with a condenser, compound 1.9 (9.33 g, 0.0200 mol) was added along with N-methyl-2-pyrrolidone (40 mL) and stirred. The flask was connected to a Drechsel bottle filled with sodium hypochlorite. Using respiration protection, copper (I) cyanide (3.58 g, 0.0400 mol) was added to the flask. After use, all equipment was placed into a sodium hypochlorite bath for 24 h. The mixture was heated to 200 °C for 4 h and subsequently cooled to 60 °C. In a separate flask, iron (III) chloride (32.4 g, 0.200 mol), 32 % hydrochloric acid (31.5 mL, 36.5 g, 1.00 mol) and water (65 mL) were added, mixed at 60 °C and added to the reaction flask all at once. The resultant mixture was kept at 60 °C for 30 min and afterwards cooled to room temperature. The mixture was stirred at room temperature for 1 h. The mixture was added to a beaker containing water (200 mL) and dichloromethane (200 mL). The organic layer was separated and washed with water (3×100 mL). The organic layer was dried using anhydrous magnesium sulfate. The magnesium sulfate was removed using vacuum filtration and the solvent evaporated under vacuum to leave a brown liquid. This liquid was added to water (200 mL) giving a brown precipitate which was collected by vacuum filtration. The crude product was purified using a silica gel column with 30 % 40:60 petroleum ether and 70 % ethyl acetate as eluent (RF value quoted in product data). The eluent fractions of interest were evaporated under vacuum to leave an off-white solid which was recrystallised from hot ethanol (60 mL).

Yield: 3.27 g, 39.6 %. RF: 0.34. MP: 136 °C

v_{max} /cm⁻¹: 3287, 2933, 2854, 2225, 1656, 1604, 1595, 1511, 1491, 1477, 1412, 1395, 1373, 1297, 1236, 1110, 1053, 1027, 1007, 856, 828, 814, 793, 732, 606, 570, 556, 540, 522

 δ_{H} /ppm (400 MHz, CDCl₃): 7.71 (2 H, d, J 8.4 Hz, Ar-H), 7.67 (2 H, d, J 8.4 Hz, Ar-H), 7.51 (2 H, d, J 8.2 Hz, Ar-H), 7.37 (2 H, d, J 8.9 Hz, Ar-H), 7.29 (2 H, d, J 8.2 Hz, Ar-H), 7.05 (1 H, br, NH), 6.84 (2 H, d, J 8.9 Hz, Ar-H), 3.93 (2 H, t, J 6.5 Hz, O-<u>CH₂-CH₂-)</u>, 2.68 (2 H, t, J 7.7 Hz, Ar-<u>CH₂-CH₂-)</u>, 2.15 (3 H, s, (C=O)-<u>CH₃</u>) 1.77 (2 H, tt, J 7.4 Hz, 6.5 Hz, O-CH₂-<u>CH₂-CH₂-), 1.70 (2 H, tt, J 7.7 Hz, 7.4 Hz, Ar-CH₂-CH₂-CH₂-), 1.46 (4 H, m, Ar-CH₂-CH₂-CH₂-CH₂-)</u>

δ_C/ppm (100 MHz, CDCl₃): 168.07, 167.70, 155.99, 145.60, 143.54, 136.52, 132.57, 129.19, 127.49, 127.10, 121.87, 119.06, 114.78, 110.04, 68.13, 35.51, 31.27, 29.18, 28.95, 25.89, 24.41

4'-[6-(4-Aminophenoxy)hexyl][1,1'-biphenyl]-4-carbonitrile (1.11)

To a pre-dried flask flushed with argon and fitted with a condenser, compound **1.10** (2.50 g, 6.06×10^{-3} mol) was added. Ethanol (70 mL) was added along with 32 % hydrochloric acid (20.0 mL, 23.2 g, 0.636 mol) and then stirred. The reaction was heated at reflux overnight and monitored by TLC using dichloromethane as the solvent system (RF value quoted in the product data). The reaction mixture was then cooled to room temperature, poured into ice (100 g) and made alkaline using 15 M sodium hydroxide solution. The resulting brown solid was vacuum filtered and was recrystallised from ethanol (50 mL).

Yield: 2.23 g, 98.4 %. RF: 0.63. MP: 116 °C

v_{max} /cm⁻¹: 3453, 3367, 2932, 2854, 2229, 1603, 1604, 1510, 1493, 1476, 1468, 1391, 1278, 1228, 1125, 1028, 859, 818, 771, 728, 570, 556, 540, 517

 δ_{H} /ppm (400 MHz, CDCl₃): 7.71 (2 H, d, J 8.5 Hz, Ar-H), 7.67 (2 H, d, J 8.5 Hz, Ar-H), 7.51 (2 H, d, J 8.2 Hz, Ar-H), 7.29 (2 H, d, J 8.2 Hz, Ar-H), 6.73 (2 H, d, J 8.8 Hz, Ar-H), 6.63 (2 H, d, J 8.8 Hz, Ar-H), 3.88 (2 H, t, J 6.5 Hz, O-<u>CH₂</u>-CH₂-), 3.40 (2 H, br, NH₂), 2.67 (2 H, t, J 7.6 Hz, Ar-<u>CH₂</u>-CH₂-), 1.72 (4 H, m, Ar-CH₂-<u>CH₂</u>-CH₂-), 0-CH₂-<u>CH₂</u>-CH₂-), 1.45 (4 H, m, Ar-CH₂-CH₂-CH₂-), CH₂-CH₂-CH₂-)

δ_C/ppm (100 MHz, CDCl₃): 152.27, 145.62, 143.59, 139.87, 136.50, 132.56, 129.19, 127.49, 127.10, 119.06, 116.39, 115.65, 110.54, 68.55, 35.52, 31.28, 29.35, 29.00, 25.93

4-Nonylbenzaldehyde (1.12)

To a pre-dried flask flushed with argon and fitted with a condenser, hexamethylenetetramine (2.24 g, 0.0160 mol) and trifluoroacetic acid (20.0 mL 29.8 g, 0.261 mol) were added. Nonylbenzene (3.45 mL, 2.96 g, 0.0145 mol) was added and the reaction mixture was then stirred. The reaction mixture was heated at reflux overnight. The reaction was cooled to room temperature and the solvent removed under vacuum. The oil remaining was then made alkaline by the addition of 6 M sodium hydroxide before being extracted by diethyl ether (3×50 mL). The diethyl ether was removed under vacuum to leave an orange/brown oil. The crude product was purified using a silica gel column with 90 % 40:60 petroleum ether and 10 % ethyl acetate as eluent (RF value quoted in product data). The eluent fractions of interest were evaporated under vacuum to leave a pale-yellow oil.

Yield: 2.61 g, 77.4 %. RF: 0.51

v_{max} /cm⁻¹: 2924, 2853, 1702, 1606, 1576, 1466, 1305, 1212, 1167, 824, 779, 747, 722, 698, 622, 533

 δ_{H} /ppm (400 MHz, CDCl₃): 9.95 (1 H, s, (C=O)-H), 7.78 (2 H, d, J 8.2 Hz, Ar-H), 7.33 (2 H, d, J 8.2 Hz, Ar-H), 2.68 (2 H, t, J 7.8 Hz, Ar-<u>CH₂-CH₂-), 1.62</u> (2 H, m, Ar-CH₂-<u>CH₂-CH₂-), 1.29</u> (12 H, m, Ar-CH₂-CH₂-<u>CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂), 0.88 (3 H, t, J 7.0 Hz, Ar-CH₂-C</u>

δ_C/ppm (100 MHz, CDCl₃): 191.90, 150.45, 134.40, 129.90, 129.08, 36.21, 31.92, 31.09, 29.58, 29.45, 29.38, 29.23, 22.68, 14.12

Data consistent with reported values.^[7]

4'-[6-(4-{(E)-[(4-Nonylphenyl)methylidene]amino}phenoxy)hexyl][1,1'-biphenyl]-4carbonitrile, CB6O-9 (1.13)

To a pre-dried flask flushed with argon and fitted with a condenser, compound **1.11** (1 eq, 0.100 g, 2.70×10^{-4} mol) and compound **1.12** (0.094 g, 4.05×10^{-4} mol) were added along with ethanol (15 mL) and the mixture was then stirred. The reaction was heated to reflux and *p*-

toluenesulfonic acid (catalytic amount) was then added before being left overnight. The reaction mixture was then cooled to room temperature and a purple precipitate formed which was collected by vacuum filtration. The purple solid was recrystallised from hot ethanol (10 mL).

Yield: 0.055 g, 42.7 %

T_{Cr-} 75 °C T_{SmCTBSmX} (66 °C) T_{SmXNTB} (76 °C) T_{NTBN} 80 °C T_{NI} 108 °C

v_{max} /cm⁻¹: 2921, 2851, 2232, 1622, 1607, 1577, 1498, 1475, 1392, 1285, 1243, 1173, 1160, 1110, 1030, 1006, 966, 886, 830, 816, 783, 731, 638, 563, 539, 520, 417

 $δ_{\rm H}$ /ppm (400 MHz, CDCl₃): 8.44 (1 H, s, (C=N)-H), 7.79 (2 H, d, J 8.0 Hz, Ar-H), 7.71 (2 H, d, J 8.5 Hz, Ar-H), 7.67 (2 H, d, J 8.5 Hz, Ar-H), 7.50 (2 H, d, J 8.1 Hz, Ar-H), 7.29 (4 H, m, Ar-H), 7.20 (2 H, d, J 8.8 Hz, Ar-H), 6.91 (2 H, d, J 8.8 Hz, Ar-H), 3.97 (2 H, t, J 6.4 Hz, O-CH₂-CH₂-CH₂-), 2.67 (4 H, m, Ar-CH₂-CH₂-, Ar-CH₂-CH₂-), 1.80 (2 H, tt, J 7.0 Hz, 6.4 Hz, O-CH₂-CH₂-CH₂-), 1.67 (4 H, m, Ar-CH₂-CH₂-CH₂-, Ar-CH₂-CH₂-CH₂-), 1.49 (4 H, m, Ar-CH₂-C

 δ_C /ppm (100 MHz, CDCl₃): 158.46, 157.63, 146.57, 145.60, 145.03, 143.55, 136.52, 134.06, 132.57, 129.20, 128.86, 128.58, 127.49, 127.11, 122.12, 119.05, 114.96, 110.54, 68.13, 36.02, 35.51, 31.90, 31.30, 31.27, 29.56, 29.51, 29.33, 29.29, 29.22, 28.96, 25.91, 22.69, 14.14

Elemental Analysis: Calculated for $C_{41}H_{48}N_2O$: C = 84.20 %, H = 8.27 %, N = 4.79 %; Found: C = 83.70 %, H = 8.18 %, N = 4.80 %

Supplementary results



Figure S1. Optical textures of smectic phases formed by the CB6O.14 homologue observed between crossed polarizers (oriented along image edges) in a $3-\mu$ m-thick cell with planar anchoring. Arrow indicates the rubbing direction.



Figure S2. Broad-angle XRD patterns recorded in the smectic phases of the CB6O.18 homologue. Narrowing of the high-angle signal in the SmZ phase indicates an increased correlation length of the positional order within the smectic layers.



Figure S3. Temperature (T) dependence of the optical birefringence (Δn) for the CB6O.m homologues, measured with a green light (λ =532 nm) in a 3-µm-thick planar cell.



Figure S4. Models of the four layer repeating units in the (A) SmX and (B) SmC_{TB} phases. Elipsoids represent a top view of tilted molecules in layers 1-4 (projections onto the smectic plane). The sequence of azimuthal positions of molecules on the tilt cone in the consecutive layers is: 0, δ , π , π + δ for smectic X, and 0, δ + ε , π +2 ε , π + δ +3 ε for the SmC_{TB} phase.



Figure S5. (A) Temperature (*T*) dependence of the layer spacing (*d*) for compound CB6O-9. (B) Broad-angle XRD patterns recorded in the consecutive LC phases of the CB6O-9 compound.



Figure S6. Optical textures of liquid crystal phases formed by the CB6O-9 compound observed between crossed polarizers (oriented along image edges) in a cell with homeotropic anchoring.



Figure S7. Temperature dependence of the optical birefringence for CB6O-9 compound, measured with a green light (λ =532 nm) in a 1.6-µm-thick planar cell. The green line is a fit to the critical dependence in the N phase, with the critical exponents β equal 0.20.



Figure S8. AFM images recorded in the SmC_{TB} and SmX phases in the vicinity of the phase transition for compound CB6O-9. The smectic layers are only weakly affected by the phase transition. In the inset: an optical image of the tested area, the rainbow colors visible are due to the selective reflection observed in the SmC_{TB} on approaching the SmX phase. Scale bars correspond to 10 μ m.



Figure S9. Circular dichroism (CD) measured for the CB6O-9 compound aligned on a surface with homeotropic anchoring. The clear CD signal is recorded near the absorption band of the material at 280 and 340 nm, showing that molecules are in a chiral environment. The sign of the recorded signal in the SmC_{TB} is negative or positive depending on the handedness of the helix in the tested area.

Table S1.

	m.p.	SmZ	:	SmC _{тв}		SmX		SmA	Ντι	3	Ν	Iso
CB60.11	64.9			٠	71.0	٠	81.8				٠	105.7 •
	(28.7)				(0.053)		(0.42)					(0.75)
CB6O.12	73.3			•	72.7	•	86.5	٠	86.7		•	103.3 •
	(38.3)				(0.050)		*(1.12)		*(1.12)			(0.88)
CB6O.14	75.9	•	60.0	٠	76.7	٠	94.4	٠	99.0		•	102.7 •
	(30.7)		(4.36)		(0.044)		(0.42)		(0.38)			(0.72)
CB6O.16	76.0	•	67.2	•	79.6	٠	97.5	•	102.6		•	102.8 •
	(28.4)		(7.08)		(0.035)		(0.32)		*(3.25)			*(3.25)
CB6O.18	73.0	•	77.6	•	85.3	٠	100.6	•	106.2			•
	(35.6)		(9.67)		(0.024)		(0.28)		(4.95)			
CB6O-9	75.1			•	65.6	•	76.2			• 79.9	•	107.9 •
	(58.2)				(≈ 0)		(0.01)			(0.001)		(1.0)

Phase transition temperatures (°C) and (in brackets) the associated enthalpy changes (kJ mol⁻¹) for the studied compounds.

* Overlap between the exotherms associated with both transitions

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