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Synthesis and characterization of novel chiral dimers exhibiting highly frustrated liquid crystal phases

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ABSTRACT

Two novel series of optically active dimers comprising cholesterol and biphenyl-4-yl 4-(*n*-alkoxy)benzoate cores interlinked though either an odd-parity/even-parity spacer have been prepared and characterized. They stabilize an extremely complex, frustrated liquid crystalline state viz., the twist grain boundary (TGB) phase with chiral smectic C structure, denoted as TGBC* phase, over a wide (50–110 °C) temperature range. Notably, the dimers with an odd-parity spacer show an additional frustrated liquid crystal phase namely, the blue phase (BP). The presence of such frustrated phases suggests that the synthesized dimers are characterized by high enantiomeric excess and strong molecular chirality. Thus, 12 new optically active, nonsymmetric dimers reported herein constitute new examples of rarely found strongly chiral, optically pure dimers showing frustrated liquid crystal phase over an adequately wide thermal range.

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1. Introduction

Since the discovery of chiral liquid crystalline state by Reinitzer in 1888,^{1,2} mesogens possessing molecular chirality have been intensively investigated.^{3–9} In particular, a variety of new chiral mesogenic materials have been realized based on the rational molecular engineering.⁴ This has, in fact, resulted in the invention of a great variety of novel LC superstructures¹⁰⁻²⁰ that are enormously significant in the context of both basic research and various emerging technologies^{21,22} as well as bioscience.²³ In general, molecular chirality favours a twist in the orientation of LC molecules. However, interestingly, the invention of new phases appears to be associated with an increase of complexity of their structures. Their self-organization into an asymmetric chiral LC structure with a superimposed macroscopic twist of the constituent mesogens yields states such as N* and chiral smectic C (SmC*) phases, which are characterized by a helicoidal macroscopic structure; in these structures the helical arrangement is achieved without any defects. In chiral mesogens with high enantiomeric excess and strong molecular chirality⁵ (intrinsic high twisting power), the twisting structure accompanies defects that adds complexity in the structure. Frustrated LC phases namely BPs,^{6,16,22-26} and twist grain boundary (TGB) phases^{6,18–20,27,28} are well-known examples where the defects are not only present but are imperative in the formation and stabilization of these complex, superstructures.

Blue phases usually exist over a narrow thermal range $(\sim 0.5-2 \circ C)$ between the N*/smectic (Sm) phase and the isotropic liquid (I) phase. However, in recent times there have been efforts to improve vastly the thermal stabilities of these phases^{24,25} owing to their potential for photonic application.^{22,26} Three types of blue phase viz., BPI, BPII and BPIII are known to exist as a consequence of the competition among the chiral twisting force and the inclination of mesogens to pack so as to fill space uniformly. Their structure comprises double twist cylinders.^{6,16} In BPI and BPII, the packing of double twist cylinders give rise to body-centred cubic and simple cubic structures, respectively. Whereas in the BPIII phase, the orientational order of molecules is not periodic and the symmetry is the same as that of the isotropic phase. Thus, BPIII consists of double twist cylinders with arbitrary orientation. Analogous to BPs, TGB phases occur over a short temperature range at the phase transition from the isotropic (I) or chiral nematic (N*) to smectic A (SmA) or SmC* phases.^{6,17–20} Although their significance in applied science is vet to be figured out, they have attracted a considerable amount of attention in view of the fact that in 1988 Renn and Lubensky invented them as LC analogues of the Abrikosov phases exhibited by type-II superconductors in an external magnetic field.²⁷ They get stabilized when the constituent chiral mesogens endeavour to form helical (with the N* helix axis perpendicular to their long molecular axes) and lamellar (smectic) structures concurrently. These two structures, being opposite to or in conflict with each other, cannot coexist. However, the coexistence of layering and twist is attained by an array of screw dislocation wall twist grain boundaries in the layering, which basically segregate the





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structure into smectic slabs. Thus, different types of TGB phases varying in the local structure of smectic slabs have been theoretically predicted and discovered. However, three main types of TGB phases are the TGBA, TGBC and TGBC* where the slabs have orthogonal smectic A (SmA), tilted smectic C (SmC) and helical SmC* characters, respectively. Among these, the TGBC* phase is of outstanding interest as it is highly complex structure where a helix along the smectic layer normal direction exists (due to bulk SmC* phase), besides the TGB helix. Here, the helical axis of the smectic structure remains perpendicular to that of the TGB helix. Owing to its complex nature, the search for mesogens capable of exhibiting the TGBC* phase over wide thermal range has been a challenging venture for liquid crystal chemists where the generation of general strategy in the form of molecular engineering and synthesis of novel chiral LC materials is crucial.

In this paper, we report 12 novel LC dimers, belonging to two series, exhibiting the TGBC* phase over an exceptionally wide thermal (50–110 °C) range; notably, one of the series of dimers show BP additionally, albeit over only a short thermal width. The molecular design incorporates natural cholesterol covalently joining to a long, calamitic (three-ring ester) moiety though a flexible spacer. This particular design was conceived based on the literature reports that nonsymmetric dimers consisting of cholesterol as the chiral entity joined to different aromatic mesogens through a spacer show frustrated phases and unusual LC phase sequences.²⁸ In particular, in the context of present study, it must be mentioned here that dimers derived from cholesterol stabilize TGBC* phase (including other TGB phase/s) over a moderate 2^{28-33} to wide thermal range.^{34,35} For example, we have recently reported the existence of the TGBC* phase over an unprecedented thermal range in chiral dimers where a three-ring salicylaldimine core with an *n*alkoxy tail is covalently tethered to cholesterol through an evenparity (ω -oxyalkanoyloxy) spacer.³⁵ This remarkable behaviour is considered to be originating from the extended molecular length and thus, rigid rod-like geometry of the dimers. This observation motivated us to design similar lengthy, cholesterol-based dimers. Thus, in order to realize such dimers, we intended to interlink a three-ring anisometric moiety with cholesterol through an ω oxyalkanoyloxy spacer. To understand the structure-property correlations, we proposed to vary the lengths of the alkylene spacers as well as those of the terminal alkoxy chains attached to three-ring core. Specifically, both odd-parity (5-oxypentanoyloxy) and even-parity (6-oxyhexanoyloxy) spacers were chosen to link cholesterol and three-ring entities; *n*-alkoxy chains such as n-octyloxy, n-nonyloxy, n-decyloxy, n-undecyloxy, n-dodecyloxy and *n*-hexadecyloxy chains were selected as terminal substituents. Accordingly, two series of compounds namely 4'-((5cholesteryloxy-5-oxopentyl)oxy)biphenyl-4-yl 4-(n-alkoxy)-benzoates and 4'-((6-cholesteryloxy-6-oxohexyl)oxy)-biphenyl-4-yl 4-(*n*-alkoxy)benzoates (see Scheme 1) have been synthesized: for the sake of convenience they are hereafter referred to as **BD-4**,*m* and **BD-5**,*m* series where **B** denotes the presence of biphenyl moiety, **D** refers to dimer, 4 and 5 indicate the number of methylene units present in the spacers and *m* represents the length of the terminal tail.

2. Results and discussion

2.1. Synthesis and characterization

All the target compounds were prepared by the synthetic route depicted in Scheme 1. Mono O-alkylation of 4,4-dihydroxybiphenyl with cholesteryl 5-bromopentanoate (**1-4**) and cholesteryl 6-bromohexanoate (**1-5**)³⁶ under Williamson ether synthesis protocol respectively yielded cholesteryl 5-(4'-hydroxybiphenyl-4-oxy)pentanoate (**2-4**) and cholesteryl 6-(4'-hydroxybiphenyl-4-



Scheme 1.

oxy)hexaneate (**2-5**).³⁶ In the final step the phenols **2-4** and **2-5** were reacted with 4-(*n*-alkoxy)benzoic acids (**3-8**, **3-9**, **3-10**, **3-11**, **3-12** and **3-16**) in the presence of dicyclohexylcarbodiimide (DCC) and a catalytic amount of 4-dimethylaminopyridine (DMAP) in dichloromethane (DCM) for 24 h at refluxing temperature to obtain the final compounds in good yield. These acids were prepared starting from of ethyl 4-hydroxybenzoate; it was *O*-alkylated with 1-bromoalkanes in presence of a mild base to obtain ethyl 4-(*n*-alkoxy)benzoates, which upon subjecting to alkaline hydrolysis furnished 4-*n*-alkoxybenzoic acids in almost quantitative yields. The molecular structures of all the dimers and their intermediates were confirmed by standard spectroscopic methods of analyses and microanalytical data (see Experimental part for the details).

2.2. Mesomorphic behaviour

2.2.1. Optical and calorimetric studies. Having synthesized the dimeric molecules and confirmed their molecular structures, we examined these compounds for their thermal behaviour. It was accomplished with the help of polarizing optical microscope (POM) and differential scanning calorimeter (DSC). However, X-ray diffraction (XRD) measurement was also carried out for the essential LC phase of some selected samples of both the series. For preliminary POM observation, especially to verify the liquid crystal property (fluidity and birefringence) of the dimers, the sample placed between a clean untreated glass slide and a cover slip was used. For unequivocal mesophase assignment, two different surface coated slides, one treated for homogeneous (planar) alignment and another with homeotropic alignment, were employed. The phase transition temperatures noted during the POM study were found to be in good agreement with those of the calorimetric experiments. The phase sequences, transition temperatures and enthalpies of the phase transitions of both series of dimers are listed in Table 1.

It is apparent from the results accumulated in Table 1 that all the compounds exhibit enantiotropic LC behaviour. As can be seen, the two series of dimers synthesized primarily differ in the parity of central flexible (ω -oxyalkanoyloxy) spacer and thus, vary notably in their thermal behaviour. That is, the dimers of **BD-4**,*m* series are

Table 1 Phase transition temperatures $(^{\circ}C)^{a}$ and enthalpies $[J g^{-1}]^{b}$ of chiral dimers of **BD-4**.*m* and **BD-5**.*m* series

Dimers	Heating	Cooling		
BD-4,8	Cr 136.9 [25] ^c TGBC* 159.1 [0.6]	I 223.3 [1.4] ^d BP-N* 157.9		
	N* 224.3 [1.4] I	[0.4] TGBC* 95.8 [13.4] Cr		
BD-4,9	Cr 130.6 [5.6] ^c TGBC* 172.1 [0.6]	I 222.6 [1.5] ^d BP-N* 170.7		
	N* 223.9 [1.5] I	[0.5] TGBC* 97.1 [11.8] Cr		
BD-4,10	Cr 122.7 [50.9] TGBC* 176.8 [0.7]	I 212.5 [1.4] ^d BP-N* 169.8		
	N* 216.1 [1.7] I	[0.6] TGBC* 83.5 [12.4] Cr		
BD-4,11	Cr 106.6 [15.5] TGBC* 170.3 [0.5]	I 204 [1.5] ^d BP-N* 168.8		
	N* 204.4 [1.6] I	[0.5] TGBC* 68.1 [8.7] Cr		
BD-4,12	Cr 119.2 [39.9] TGBC* 188.2 [0.7]	I 209 [1.8] ^d BP-N* 183.1		
	N* 211.5 [1.9] I	[0.5] TGBC* 71.5 [11.1] Cr		
BD-4,16	Cr 120.9 [27.5] TGBC* 190 [0.6]	I 196.2 [1.8] ^d BP-N* 185.9		
	N* 201.9 [2] I	[0.6] TGBC* 97.8 [13.6] Cr		
BD-5,8	Cr 142.4 [42.3] TGBC* 174.1 ^e	I 243.3 [3.7] N* 172.8 ^e TGBC*		
	N* 245.2 [3.9] I	116.6 [12.3] Cr		
BD-5,9	Cr 141.2 [48.2] TGBC* 186.6 ^e	I 232.5 [4.8] N* 185 ^e TGBC*		
	N* 235.3 [4.7] I	109.3 [50.4] Cr		
BD-5,10	Cr 146.1 [38.2] TGBC* 198.3 ^e	I 230.1 [4.7] N* 192.4 ^e TGBC*		
	N* 233.7 [4.7] I	88 [19.6] Cr		
BD-5,11	Cr 133.4 [41.4] TGBC* 204.9 [0.2]	I 240.8 [4.5] N* 203.8 [0.2]		
	N* 242 [4.2] I	TGBC* 93.3 [26.6] Cr		
BD-5,12	Cr 119 [34.1] TGBC* 200.6 ^e	I 235.1 [4.2] N* 199 ^e TGBC*		
	N* 235.3 [4.5] I	86.6 [26.6] Cr		
BD-5,16	Cr 132.7 [38.3] ^a TGBC* 214.7 ^e	I 227.2 [5.7] N* 211.7 ^e TGBC*		
	N* 227.9 [5.6] I	117.7 [29.9] Cr		

Cr: crystal; TGBC*: twist grain boundary phase having SmC* blocks; SmC*: chiral smectic C phase; N*: chiral nematic phase; BP: blue phase; I: isotropic phase.

^a Phase transition temperatures were determined by both POM ($5 \circ C \min^{-1}$) and DSC studies: peak temperatures in the DSC traces obtained during the first heating and cooling cycles (at $5 \circ C \min^{-1}$) coupled with optically measured temperatures are given.

^b Transition enthalpies were obtained from the DSC thermograms.

^c Additional crystal to crystal transitions have been observed for the compounds **BD-4,8** (129.3 [64.2]), **BD-4,9** (126.2 [38.9]) and **BD-5,16** (97.5 [11.8]).

 d BP is a transient phase and thus the ΔH represents the combined enthalpy for I–BP–N* transitions.

^e The phase transition was observed under POM; too weak to be recognized in DSC.

odd-members as they possess5-oxypentanoyloxy spacer where five carbon atoms separate the two segments while **BD-5**,*m* series of materials are even-homologues as they contain 6oxyhexanoyloxy spacer. As is well-known, the phase transitional properties including clearing transition temperature of dimers critically depend on the parity of the spacer. This behaviour is generally attributed to molecular shape of dimers in their all-trans conformation imposed by the number of atoms (generally carbons) present in the spacer. In dimers with an even-numbered spacer, the mesogenic units are anti-parallel to give an overall rod-like (calamitic) shape, while the odd-membered dimers attain bentshape as the mesogenic entities are inclined to each other. Fig. 1a



Fig. 1. Space-filling, energy-minimized molecular structures of dimers **BD-4**,**9** (odd-member) (a) and **BD-5**,**11** (even-member) (b); notice that dimer **BD-4**,**9** attains a bent-shape while compound **BD-5**,**11** has rod-like conformation.

and b, respectively, shows the space-filled, energy-minimized molecular structures of an odd-member (**BD-4,9**) and evenmember (**BD-5,11**) of the present series where the respective bent-structure and rod-like shape can be visualized. In essence, the effective change in molecular shape (geometry) evolving from the spacer parity affects the liquid crystalline behaviour of the present dimers. For instance, the dimers with even-parity spacers, regardless of variation in their terminal chain lengths, exhibit two enantiotropic mesophases such as N* and TGBC* phases whereas those with odd-numbered spacers additionally exhibit BP phase. The occurrence of these mesophases was established clearly with the help several complementary studies, which we describe as follows.

Firstly, we discuss about our studies concerning BD-5,m series of dimeric molecules where the two mesogenic segments are separated by an even-parity spacer. As mentioned earlier, all the members of this series show N* and TGBC* phases. These crystalline samples, held between a cover slip and untreated glass slide, upon heating, melt into the TGBC* phase exhibiting a hazy texture consisting of square grid pattern as well as undulated filaments, which arise due to planar and homeotropic orientations of mesogens, respectively. On heating the samples further, the TGBC* phase transforms into the N* phase exhibiting a planar texture having oily streaks that remains unaltered till isotropic liquid state. Upon cooling these samples gradually from the liquid state, the N* phase appears at a well defined temperature manifesting optically in the form of fan-like focal-conic domains. As a representative case, the microphotographs of such a textural pattern observed for dimer **BD-5.10** are shown in Fig. 2a.

It may be mentioned here that for the sake of completeness, we show other textural patterns observed on different occasions for this dimer only. On further cooling, the TGBC* phase comes into view with textural pattern shown in Fig. 2b where thick lines appearing like filaments are seen. However, when the N* phase with focal-conic texture was subjected to the gentle mechanical shearing, the pattern transformed sharply in to a planar texture where the director (*n*) remains parallel to the plane of the glass plates. This confirms that the helical axis is normal to the substrates, i.e., along the viewing direction. Further lowering of the sample temperature, the planar texture of the N* phase changes sharply to a square grid pattern. Fig. 2c shows a transition from the planar texture of the TGB phase to the square grid pattern of the TGBC* phase while Fig. 2d shows the texture for the completely formed TGBC* phase. When glass plates coated with a polyimide solution and unidirectionally rubbed (to account for planar anchoring) were used, the aforesaid characteristic textural patterns were observed for these two mesophases. In order to rule out the possibility that the presence of the square grid is due to some instability in the helical structure such as SmC* phase, the TGBC* phase of the samples was examined in slides treated for homeotropic anchoring where a filament texture was observed with an undulatory structure as shown in Fig. 2e.

Further, when the samples were examined in a wedge-type cell (where the thickness varies from one end to other end of the cell) with similar surface treatment to the parallel cell, an array of Grandjean Cano dislocation lines were observed for the N* phase; whereas, the TGBC* phase appeared with a striking square grid pattern forming over the dislocation lines (Fig. 2f). As mentioned earlier, in the TGBC* structure, besides a helical superstructure due to the TGB helix, there exists another helical structure due to bulk SmC* phase; the helical axis of the latter is perpendicular to that of the TGB helix. Such a complex organization of mesogens produces square grids over planar texture/Grandjean Cano dislocation lines.

In general, the DSC thermograms of these dimers exhibited two endothermic peaks in the heating cycle due to $Cr-N^*$ and N^*-I transitions; as expected, during cooling scan, the samples showed two exothermic peaks due to $I-N^*$ and N^*-Cr phase sequences.



Fig. 2. Polarized light micrographs of the textures of the N⁺ and TGBC⁺ phases observed for dimer **BD-5,10**: (a) the focal-conic texture of the N⁺ phase occurring just below the isotropic melt (229 °C); (b) texture of the TGBC⁺ phase grown on top of focal-conic pattern of the N⁺ phase (190 °C); (c) the square grid pattern of the TGBC⁺ phase (LHS) growing (243.6 °C) on top of the Granjean-planar texture of the N⁺ phase (RHS) (192.2 °C); (d) the square grid pattern of the completely formed TGBC⁺ phase (189 °C); (e) the undulated filamentary pattern of the TGBC⁺ phase seen when slides treated for homeotropic alignment were used (103 °C); (e) the texture showing Grandjean Cano dislocation lines superposed on the square grid pattern when the TGBC⁺ phase (186 °C) was viewed in a wedge-type cell with the glass plates treated for planar anchoring.

However, as shown in Fig. 3a, the DSC traces of both heating and cooling cycles of dimer **BD-5,11** displayed the peaks due to TGBC* $-N^*$ and N*-TGBC* transitions with the enthalpy value 0.2 J/g suggesting the phase transition being first order. Most importantly,

it is evident from Table 1 that these mesogens, the **BD-5**,*m* series of dimeric molecules, stabilize TGBC* phase in the thermal range of 55–110 °C, which is noteworthy given the highly complex and frustrated nature of the phase.



Fig. 3. DSC traces of the first heating (black-curve)-cooling (red-curve) cycles obtained for the dimers **BD-5,11** (a) and **BD-4,9** (b). Notice that in these traces the signatures due to TGBC*-N* phase transition can be distinctly seen (see insets).

We now discuss the thermal behaviour of **BD-4**,*m* series of dimers possessing an odd-membered (5-oxypentanoyloxy) spacer. It is apparent from the results summarized in Table 1 that all the members of the series behave analogously. They stabilize additionally, unlike their counterparts with even-parity spacer, the BP phase. That is, these dimers show BP. N* and TGBC* phases that were established, as before, with the help of calorimetric and POM studies. Clear signatures were seen in the DSC trances of the transitions between these phases. As an example, the DSC thermograms obtained during the first heating-cooling cycles for the dimer **BD-4,9** are shown in Fig. 3b. The heating curve (black-trace) shows, besides transformation between crystalline forms, shows three reversible transitions at 130.6 °C ($\Delta H=25 \text{ J/g}$), 172.1 °C (0.6 J/ g) and 224.3 °C (1.4 J/g) associated with the Cr–TGBC*, TGBC*–N* and N*–I phase transitions. The corresponding transitions of the cooling cycle were observed at 222.6 °C (1.5 J/g), 170.7 °C (0.5 J/g) and 97.1 °C (11.8 J/g); however, the enthalpy of the first transition (1.5 J/g) represents the combined value for N*-BP transition as the BP was clearly observed during the cooling cycle only. Again, unlike in the case of the dimers with even-parity spacer (except BD-5,11), the peak observed due to N*-TGBC* transition for all these oddmembers can be ascribed to the lower order parameter of the N* phase. Further, the N*–I transition enthalpy values, ranging from 1.4 to 1.8 J/g, found for these odd-members are lower than that obtained for dimers with even-parity spacers for which the values lie between 3.9 and 5.6 J/g. Such results certainly originate from the order parameter of the N* phase of a given dimer. Needless to say, molecular geometries of the dimers namely the bent-conformation and rod-like shape of the odd- and even-members, respectively, are responsible for such differences in order parameters of the N* phase.

As mentioned earlier, POM studies carried out for all the samples evidenced the presence of BP, N* and TGBC* phases. For example, on slow cooling (2 °C/min) the isotropic liquid of dimer **BD-4,9** placed between a clean glass slide and a cover slip, a textural pattern emanating from the black background was observed at 222.6 °C (Fig. 4a). This texture existing for a very short thermal range (0.3 °C) is typical of the BPI/BPII phase. On further cooling, a focal-conic texture (Fig. 4b) appeared, which upon shearing transformed into oily streak pattern occurring over a planar texture (Fig. 4c) signifying the presence of the N* phase. On cooling the planar texture of the N* phase, the TGBC* phase with characteristic square grid pattern appears at 170.7 °C that persists till the sample crystallizes out at 97 °C; thus, the TGBC* phase exists for about 73 °C. Likewise, other members of the series stabilize the TGBC* phase over wide thermal range (60–110 °C). The occurrence of the other frustrated mesophase viz., BP phase in these dimers is also noteworthy.

2.2.2. X-ray diffraction measurements. From the analysis of the foregoing experimental results it is clear that the chiral dimers realized in the present study display TGBC* phase over an exceptionally wide thermal range. The occurrence of such a frustrated phase was further substantiated by XRD measurements on unaligned (powder) samples with Cu K α (λ =0.15418 nm) radiation. Specifically, the lamellar ordering of the TGBC* phase was ascertained using dimers BD-4,9 and BD-5,11 as representative cases. The chosen samples were inserted into a Lindemann capillary (1 mm diameter) tube in the isotropic phase and both the ends of tube were flame sealed carefully. The samples, placed in a temperature-controlled device, were slowly cooled from the isotropic phase and the diffraction patterns were collected at different temperatures while cooling the TGBC* phase. Identical diffractograms were obtained for both the dimers and established the lavered structure of the mesophase. Fig. 5 illustrates the resemblance among one-dimensional intensity versus 2θ profiles obtained for BD-4,9 and BD-5,11 at 130 °C and 170 °C, respectively. As can be seen, each diffractogram shows two low-angle reflections, the first one very intense (d_1) and the other very weak (d_2) , and a diffuse reflection (d_3) at wide angles (see insets of Fig. 5).

Fig. 6 illustrates the layer spacings (d_1) of the low-angle Bragg reflections as a function of temperature. Needless to say, the spacing of the lowest angle intense peak corresponds to the smectic layer thickness in the TGBC* phase. The second peak seen is



Fig. 4. Microphotograph of the textures observed for the LC phases of dimer **BD-4,9**: (a) the platelet texture of the BPI/BPII (at 222.6 °C); (b) the focal-conic texture of the N* phase (at 220 °C); (c) the characteristic oily streak texture of the N* seen at 210 °C when the focal-conic pattern of the same phase was sheared gently; (d) the square grid pattern of the TGBC* phase (170.7 °C).



Fig. 5. The low-angle and wide-angle (inset) regions of the XRD patterns obtained for the TGBC- phase of dimer **BD-4,9** (blue traces) and **BD-5,11** (red-traces) at 130 °C and 170 °C, respectively.



Fig. 6. The layer spacing (d_1) as a function of temperature obtained in the TGBC⁺ phase for the nonsymmetric dimers **BD-4.9** (blue-trace) and **BD-5,11** (red-trace).

a characteristic feature of dimeric molecules and is known to stemm from the two individual mesogenic entities²⁸ interlinked via a flexible spacer to form the dimer. The diffuse reflection at wide angles spacing (d_3) corresponds to the inter-molecular separation within the smectic layer arising due to the liquid-like positional correlation within the smectic layer.

Table 2 gives the spacings corresponding to the low-angle and wide-angle reflections as well as the ratio d_1/l , where *l* signifies the estimated molecular length (in all-trans from) derived from

Table 2 The all-trans molecular length (l/Å) of dimers, the measured spacings of the lowangle and wide-angle reflections of TGBC* phase of **BD-4,9** and **BD-5,11** and d_1/l ratio

Dimer (<i>l</i> /Å)	Temperature/°C	$d_1/\text{\AA}$	$d_2/\text{\AA}$	<i>d</i> ₃ /Å	d_1/l
BD-4,9 (42)	150	39.66	19.88	5.31	0.94
	130	39.21	19.49	5.31	0.93
	120	38.72	19.41	5.31	0.92
BD-5,11 (55.4)	180	42.72	21.43	4.97	0.77
	170	41.67	20.93	4.97	0.75
	160	40.96	20.51	4.97	0.74
	140	39.95	20.05	4.97	0.72
	120	39.35	19.83	4.97	0.71

a Chem3D molecular model. It is perceptible from the results (Table 2) that the layer spacing d_1 is less than the molecular length (l) (also see Fig. 1) and thus, the d_1/l ratio falls below 1. This is predictable given the situation that in the SmC* layers of the TGBC* phase, the constituent mesogens tilt with respect to the layer normal direction. It can also be seen that the d_1 -value decreases progressively when the TGBC* phase is cooled. This means that the tilt angle of the dimers within the SmCtic blocks increases on decreasing the temperature. Thus, the XRD study clearly supports the tilted orientation of dimers within the smectic blocks and thus validates the presence of TGBC* phase unequivocally.

2.3. Analysis of the results

In essence, it is thus evident from the collected experimental results that the thermal behaviour of the present dimers shows critical dependence on the parity of the spacer as well as on the structure of three-ring calamitic unit namely, biphenyl-4-yl 4-(nalkoxy)benzoate attached to cholesterol. In particular, the effect of the parity of the central spacer on the clearing temperature is notable. That is, the dimers of **BD-4**,*m* series with a 5oxypentanoyloxy (odd-parity; C₅) spacer show lower clearing temperatures when compared to that of even-members (BD-5,m series of dimers). As discussed earlier, such a behaviour can be interpreted in terms of the overall molecular shape of the dimer imposed by the geometry and flexibility of the spacer. The enthalpy values associated with N*-I phase transitions also exhibit odd-even effect. The reduction in the shape anisotropy, due to bent-conformation, lowers the clearing temperatures and their enthalpy values effectively. From the results it can also be seen that on increasing the length of the terminal tails within the series the clearing temperature generally shows a decreasing trend that can be ascribed to the progressive softening of the mesogens. Most importantly, the thermal range of the TGBC* appears to widen with the increase in the length of terminal tail attached to biphenyl-4-yl 4-(*n*-alkoxy)benzoate core supporting our earlier observation that moderately lengthy, three-ring dimers derived from cholesterol stabilize TGBC* phase over a wide thermal range.³⁵ Needless to say, the three-ring biphenyl-4-yl 4-(*n*-alkoxy)benzoate core present in the molecular design also favours the stabilization of frustrated phase; this observation is in agreement with the earlier observations that cholesterol-based dimers having 4,4'-disubstituted phenylbenzoate core stabilize frustrated phases.^{28,37}

3. Summary

Twelve new lengthy dimers belonging to two different series have been synthesized and their phase transitional behaviour has been evaluated by several complementary studies. They are made by covalently joining cholesterol and three-ring mesogenic entities through an ω -oxyalkanoyloxy spacer. They have been especially designed and realized to explore the possibility of stabilizing frustrated phase(s). The lengths of the central flexible spacers as well as those of the *n*-alkoxy chains attached to terminus of three-ring core have been varied to understand how chemical structure influences the occurrence of frustrated phase(s). In particular, both odd-parity (5-oxypentanoyloxy) and even-parity (6oxyhexanoyloxy) spacers have been employed to covalently join cholesterol and three-ring entities; n-alkoxy tails such as n-octyloxy to *n*-dodecyloxy and *n*-hexadecyloxy chains were used as terminal substituents. The dimeric molecules with even-parity spacer show enantiotropic N* and TGBC* phases whereas their counterparts comprising odd-parity spacer display BP additionally. As expected, both the series of dimers show thermodynamically stable TGBC* phase over an exceedingly wide thermal range. This is profoundly interesting and noteworthy given the complex and highly frustrated nature of the TGBC* phase. We attribute this behaviour to the combined effect of extended geometry (conformation), strong chirality and the enantiomeric excess of the molecules. Although there is a striking similarity between the two series of compounds in the context of stabilizing TGBC* phase, several significant differences in their transitional behaviour were also observed. For example, the dimers with odd-parity spacer, unlike even-members, show another frustrated phase namely, the BP phase. The clearing transition temperatures and the associated enthalpies alternate where the odd-members exhibit lower values when compared to those of even-members. These results clearly demonstrate that the geometry (rod-like and bent-conformation) and the thermal behaviour of dimers are greatly influenced by the spacer parity.

Thus, the dimers reported in this work constitute new examples of rarely encountered strongly chiral, optically pure dimers showing the TGBC* phase over a notable thermal width. We believe that the molecular design approach adopted in this work facilitates the efforts of realizing chiral mesogens capable of stabilizing frustrated phase(s) with sufficiently wide thermal range.

4. Experimental

4.1. Materials

The essential starting chemicals such as cholesterol, 6bromohexanioc acid, 5-bromovaleric acid, 4,4-dihydroxybiphenyl and 1-bromoalkanes procured from Aldrich were used as received. Deuterated chloroform (CDCl₃) obtained from same company was used to record NMR of the samples. The reagent grade solvents (DMF and dichloromethane) purchased were distilled over appropriate drying agents. Thin layer chromatography (TLC) was performed on aluminium sheets pre-coated with silica gel (Merck, Kieselge 60, F_{254}). The target compounds and some of the intermediates were purified by column chromatographic technique using either silica gel (100–200 mesh) as stationary phase. The target dimeric molecules were further purified by repeated recrystallizations from a mixture of two solvents until the constant clearing temperatures were obtained.

4.2. Instrumentation

The ^1H and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker AMX-400 (400 MHz) using CDCl₃. Chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS; SiMe₄) as an internal standard. IR spectra were recorded using Perkin Elmer Spectrum 1000 FT-IR spectrometer. Elemental analyses were carried out by Eurovector model EA 3000 elemental analyzer. Phase transition temperatures and textures of the mesophases were determined using an Olympus BX50 microscope equipped with a digital camera and a programmable hot stage (Mettler FP90). The melting transitions of non-mesogenic compounds were recorded using the same setup. The enthalpies of the transitions were determined from the thermograms recorded on a differential scanning calorimeter (Perkin Elmer DSC7) at the operating rate of 5 °C/min. Powder XRD data were collected using the PANalytical X'Pert PRO MP X-ray diffractometer consisting of a focussing elliptical mirror and a fast resolution detector (PIXCEL). The energy-minimized space-filling molecular structures of dimers were obtained using MM2 computations of the CS ChemDraw3D (version 5) program.

4.3. Synthesis and characterization data

4.3.1. General procedure for the preparation of **BD-4**,**m** and **BD-5**,**m** series of dimers. An oven-dried, 100-mL, round-bottomed flask

equipped with a magnetic stirring bar, reflux condenser and argon inlet was charged with cholesteryl ω -(4'-hydroxybiphenyl-4-oxy) alkanoate (2-4/2-5) (0.3 mmol, 1 equiv), 4-(n-alkoxy)benzoic acid (3-8/3-9/3-10/3-11/3-12/3-16) (0.33 mmol, 1.1 equiv), dichloromethane (25 ml), DCC (0.74 g, 0.36 mmol, 1.2 equiv) and DMAP (catalytic amount). The flask was flushed with argon and the reaction mixture was stirred at 40 °C for 24 h. The resulting reaction mixture was cooled, diluted with 10 ml of chloroform and stirred at room temperature for 2 h. The urea separated from the reaction was removed by filtration through Celite bed and the filtrate was evaporated to dryness in vacuo. The off-white residue obtained was purified by column chromatography on silica gel (100-200 mesh). Elution with a mixture of dichloromethane/hexanes (1:3) afforded the product. It was further purified by repeated recrystallizations from a mixture of dichloromethane/hexanes (1:2) to obtain pure compound in 67–82% yield.

4.3.1.1. **BD-4,8**: 4'-((5-cholesteryloxy-5-oxopentyl)oxy)biphenyl-4-yl 4-(octyloxy)benzoate. Yield: 81%; a bright yellow solid. Found: C, 79.5; H, 9.0; C₅₉H₈₂O₆ requires C, 79.87; H, 9.32; IR (KBr Pellet): $\nu_{\rm max}$ in cm⁻¹ 2933, 2868, 1730, 1605, 1469 and 1379; ¹H NMR (400 MHz, CDCl₃): 8.16 (d, J=8.8 Hz, 2H, Ar), 7.58 (d, J=8.4 Hz, 2H, Ar), 7.51 (d, *I*=8.8 Hz, 2H, Ar), 7.25 (d, *I*=8.4 Hz, 2H, Ar), 6.98 (d, J=6 Hz, 2H, Ar), 6.96 (d, J=6 Hz, 2H, Ar), 5.38 (br d, J=4 Hz, 1H, 1×olefinic), 4.67 (m, 1H, 1×CHOCO), 4.06 (t, *J*=6.6 Hz, 2H, 1×OCH₂), 4.03 (t, *J*=4.4 Hz, 2H, 1×OCH₂), 2.40–1.08 (m, 49H, 6×CH, 20×CH₂, 1×CH₃), 1.02 (s, 3H, 1×CH₃), 0.92 (d, *J*=6.8 Hz, 3H, 1×CH₃), 0.88 (d, *J*=1.6 Hz, 3H, 1×CH₃), 0.86 (d, *J*=1.6 Hz, 3H, 1×CH₃) and 0.68 (s, 3H, $1 \times CH_3$): ¹³C NMR (100 MHz, CDCl₃): δ 172.84, 165.03, 163.55, 158.55, 150.04, 139.66, 138.49, 132.98, 132.28, 128.11, 127.67, 122.64, 121.98, 121.58, 114.81, 114.30, 73.91, 68.34, 67.49, 56.69, 56.15, 50.03, 42.32, 39.74, 39.52, 38.16, 37.00, 36.60, 36.19, 35.79, 34.30, 29.32, 29.21, 29.10, 28.68, 28.22, 28.01, 27.82, 25.98, 24.28, 23.83, 22.80, 22.64, 22.55, 21.74, 21.03, 19.31, 18.71, 14.08 and 11.85.

4.3.1.2. **BD-4,9**: 4'-((5-cholesteryloxy-5-oxopentyl)oxy)biphenyl-4-yl 4-(nonyloxy)benzoate. Yield: 80%; a bright yellow solid. Found: C, 80.0; H, 9.2; C₆₀H₈₄O₆ requires C, 79.96; H, 9.39; IR (KBr Pellet): $\nu_{\rm max}$ in cm⁻¹ 2942, 2868, 1730, 1604, 1501, 1469 and 1380; ¹H NMR (400 MHz, CDCl₃): 8.16 (d, *J*=8.4 Hz, 2H, Ar), 7.58 (d, *J*=8 Hz, 2H, Ar), 7.51 (d, J=8.4 Hz, 2H, Ar), 7.25 (d, J=8.4 Hz, 2H, Ar), 6.98 (d, J=6.8 Hz, 2H, Ar), 6.96 (d, J=6.8 Hz, 2H, Ar), 5.37 (br d, J=4.4 Hz, 1H, 1×olefinic), 4.64 (m, 1H, 1×CHOCO), 4.06 (t, *J*=6.4 Hz, 2H, 1×OCH₂), 4.04 (t, *J*=6.8 Hz, 2H, 1×OCH₂), 2.38–1.08 (m, 51H, 6×CH, 21×CH₂, 1×CH₃), 1.02 (s, 3H, 1×CH₃), 0.92 (d, J=6 Hz, 3H, 1×CH₃), 0.87 (d, *J*=1.6 Hz, 3H, 1×CH₃), 0.86 (d, *J*=1.6 Hz, 3H, 1×CH₃) and 0.68 (s, 3H, $1 \times CH_3$); ¹³C NMR (100 MHz, CDCl₃): δ 172.87, 165.06, 163.59, 158.59, 150.08, 139.70, 138.52, 133.02, 132.32, 128.15, 127.71, 122.67, 122.01, 121.62, 114.85, 114.34, 73.95, 68.38, 67.53, 56.73, 56.19, 50.07, 42.36, 39.78, 39.56, 38.20, 37.04, 36.64, 36.23, 35.83, 34.34, 31.94, 31.90, 29.54, 29.44, 29.40, 29.28, 29.14, 28.72, 28.26, 28.04, 27.86, 26.02, 24.32, 23.87, 22.84, 22.70, 22.65, 22.59, 21.78, 21.07, 19.35, 18.75, 14.13 and 11.89.

4.3.1.3. **BD-4,10**: 4'-((5-cholesteryloxy-5-oxopentyl)oxy)biphenyl-4-yl 4-(decyloxy)benzoate. Yield: 82%; a bright yellow solid. Found: C, 79.9; H, 9.5; C₆₁H₈₆O₆ requires C, 80.04; H, 9.47; IR (KBr Pellet): ν_{max} in cm⁻¹ 2951, 2857, 1728, 1605, 1496, 1468 and 1381; ¹H NMR (400 MHz, CDCl₃): 8.16 (d, J=8.8 Hz, 2H, Ar), 7.58 (d, J=8.8 Hz, 2H, Ar), 7.51 (d, J=8.8 Hz, 2H, Ar), 7.25 (d, J=8.8 Hz, 2H, Ar), 6.98 (d, J=6 Hz, 2H, Ar), 6.96 (d, J=5.6 Hz, 2H, Ar), 5.37 (br d, J=4 Hz, 1H, 1×olefinic), 4.67 (m, 1H, 1×CHOCO), 4.06 (t, J=6.6 Hz, 2H, 1×OCH₂), 4.03 (t, J=4.4 Hz, 2H, 1×OCH₂), 2.40–1.04 (m, 53H, 6×CH, 22×CH₂, 1×CH₃), 1.02 (s, 3H, 1×CH₃), 0.92 (d, J=6.8 Hz, 3H, 1×CH₃), 0.88 (d, J=1.6 Hz, 3H, 1×CH₃), 0.86 (d, J=1.6 Hz, 3H, 1×CH₃) and 0.68 (s, 3H, 1×CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 172.82, 165.02, 163.55, 158.55, 150.04, 139.70, 138.48, 132.98, 132.28, 128.11, 127.67, 122.63, 121.97, 121.58, 114.81, 114.30, 73.90, 68.34, 67.49, 56.69, 56.15, 50.04, 42.32, 39.74, 39.52, 38.16, 37.00, 36.60, 36.19, 35.79, 34.30, 31.88, 29.54, 29.35, 29.30, 29.10, 28.68, 28.22, 28.00, 27.82, 25.98, 24.28, 23.83, 22.80, 22.67, 22.55, 21.74, 21.03, 19.31, 18.71, 14.09 and 11.85.

4.3.1.4. **BD-4,11**: 4'-((5-cholesteryloxy-5-oxopentyl)oxy)biphenyl-4-vl 4-(undecvloxy)benzoate. Yield: 78%: a bright vellow solid. Found: C, 79.8; H, 9.4; C₆₂H₈₈O₆ requires C, 80.13; H, 9.54; IR (KBr Pellet): v_{max} in cm⁻¹ 2961, 2851, 1729, 1605, 1496 and 1467; ¹H NMR (400 MHz, CDCl₃): 8.16 (d, *J*=8.8 Hz, 2H, Ar), 7.58 (d, *J*=8.8 Hz, 2H, Ar), 7.51 (d, *J*=8.8 Hz, 2H, Ar), 7.25 (d, *J*=8.8 Hz, 2H, Ar), 6.98 (d, J=5.6 Hz, 2H, Ar), 6.96 (d, J=5.6 Hz, 2H, Ar), 5.38 (br d, J=4.4 Hz, 1H, 1×olefinic), 4.67 (m, 1H, 1×CHOCO), 4.06 (t, *J*=6.6 Hz, 2H, 1×OCH₂), 4.03 (t, *J*=4.4 Hz, 2H, 1×OCH₂), 2.38–1.08 (m, 55H, 6×CH, 23×CH₂, 1×CH₃), 1.02 (s, 3H, 1×CH₃), 0.92 (d, *J*=6.8 Hz, 3H, 1×CH₃), 0.88 (d, *J*=1.6 Hz, 3H, 1×CH₃), 0.86 (d, *J*=1.6 Hz, 3H, 1×CH₃) and 0.68 (s, 3H, 1×CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 172.84, 165.02, 163.55, 158.55, 150.04, 139.66, 138.48, 132.98, 132.28, 128.11, 127.67, 122.64, 121.97, 121.58, 114.81, 114.30, 73.91, 68.34, 67.49, 56.69, 56.15, 50.03, 42.32, 39.74, 39.52, 38.16, 37.00, 36.60, 36.19, 35.79, 34.30, 31.90, 29.58, 29.55, 29.35, 29.10, 28.68, 28.22, 28.00, 27.82, 25.98, 24.28, 23.83, 22.80, 22.67, 22.55, 21.74, 21.03, 19.31, 18.71, 14.10 and 11.85.

4.3.1.5. BD-4,12: 4'-((5-cholesteryloxy-5-oxopentyl)oxy)biphenyl-4-yl 4-(dodecyloxy)benzoate. Yield: 80%; a bright yellow solid. Found: C, 80.1; H, 9.6; C₆₃H₉₀O₆ requires C, 80.21; H, 9.62; IR (KBr Pellet): *v*_{max} in cm⁻¹ 2926, 2851, 1728, 1605, 1495 and 1380; ¹H NMR (400 MHz, CDCl₃): 8.16 (d, J=8.8 Hz, 2H, Ar), 7.58 (d, J=8.8 Hz, 2H, Ar), 7.51 (d, J=8.8 Hz, 2H, Ar), 7.25 (d, J=8.8 Hz, 2H, Ar), 6.98 (d, *J*=5.6 Hz, 2H, Ar), 6.96 (d, *J*=5.6 Hz, 2H, Ar), 5.38 (br d, *J*=3.6 Hz, 1H, 1×olefinic), 4.67 (m, 1H, 1×CHOCO), 4.06 (t, *J*=5.6 Hz, 2H, 1×OCH₂), 4.02 (t, J=4.4 Hz, 2H, 1×OCH₂), 2.38–1.06 (m, 57H, 6×CH, 24×CH₂, 1×CH₃), 1.02 (s, 3H, 1×CH₃), 0.92 (d, *J*=6.8 Hz, 3H, 1×CH₃), 0.87 (d, J=1.6 Hz, 3H, 1×CH₃), 0.86 (d, J=1.6 Hz, 3H, 1×CH₃) and 0.68 (s, 3H, $1 \times CH_3$); ¹³C NMR (100 MHz, CDCl₃): δ 172.82, 165.02, 163.55, 158.55, 150.04, 139.66, 138.48, 132.98, 132.28, 128.11, 127.67, 122.64, 121.98, 121.58, 114.81, 114.30, 73.90, 68.34, 67.49, 56.70, 56.15, 50.04, 42.32, 39.74, 39.52, 38.17, 37.00, 36.60, 36.19, 35.79, 34.30, 31.91, 29.63, 29.58, 29.55, 29.35, 29.10, 28.68, 28.22, 28.01, 27.83, 25.98, 24.28, 23.83, 22.80, 22.68, 22.55, 21.75, 21.03, 19.31, 18.72, 14.10 and 11.85.

4.3.1.6. BD-4,16: 4'-((5-cholesteryloxy-5-oxopentyl)oxy)biphenyl-4-yl 4-(hexadecyloxy)benzoate. Yield: 71%; a bright yellow solid. Found: C, 80.6; H, 9.9; C₆₇H₉₈O₆ requires C, 80.51; H, 9.88; IR (KBr Pellet): v_{max} in cm⁻¹ 2924, 2850, 1730, 1604, 1468 and 1379; ¹H NMR (400 MHz, CDCl₃): 8.16 (d, J=9.2 Hz, 2H, Ar), 7.58 (d, J=8.4 Hz, 2H, Ar), 7.51 (d, J=8.8 Hz, 2H, Ar), 7.25 (d, J=8.8 Hz, 2H, Ar), 6.99 (d, *I*=5.6 Hz, 2H, Ar), 6.96 (d, *I*=5.6 Hz, 2H, Ar), 5.37 (br d, *I*=4 Hz, 1H, 1×olefinic), 4.67 (m, 1H, 1×CHOCO), 4.06 (t, *J*=6.6 Hz, 2H, 1×OCH₂), 4.03 (t, *J*=4.4 Hz, 2H, 1×OCH₂), 2.40–1.08 (m, 65H, 6×CH, 28×CH₂, 1×CH₃), 1.02 (s, 3H, 1×CH₃), 0.92 (d, *J*=6.8 Hz, 3H, 1×CH₃), 0.87 (d, J=1.6 Hz, 3H, 1×CH₃), 0.86 (d, J=2 Hz, 3H, 1×CH₃) and 0.68 (s, 3H, $1 \times CH_3$); ¹³C NMR (100 MHz, CDCl₃): δ 172.83, 165.02, 163.55, 158.55, 150.04, 139.66, 138.48, 132.98, 132.27, 128.11, 127.67, 122.64, 121.97, 121.59, 114.81, 114.30, 73.90, 68.34, 67.48, 56.69, 56.15, 50.03, 39.74, 39.52, 38.17, 37.00, 36.19, 35.79, 34.30, 31.92, 31.87, 29.69, 29.65, 29.58, 29.55, 29.36, 29.10, 28.68, 28.22, 28.00, 27.82, 25.98, 24.28, 23.83, 22.80, 22.55, 21.74, 19.31, 18.71, 14.13 and 11.85.

4.3.1.7. **BD-5,8**: 4'-((6-cholesteryloxy-6-oxohexyl)oxy)biphenyl-4-yl 4-(octyloxy)benzoate. Yield: 80%; a bright yellow solid. Found: C, 80.2; H, 9.2; C_{60} H₈₄O₆ requires C, 79.96; H, 9.39; IR (KBr Pellet): ν_{max} in cm⁻¹ 2937, 2857, 1729, 1604, 1497 and 1376; ¹H NMR (400 MHz, CDCl₃): 8.15 (d, *J*=8.8 Hz, 2H, Ar), 7.57 (d, *J*=8.8 Hz, 2H, Ar), 7.50 (d, *J*=8.8 Hz, 2H, Ar), 7.24 (d, *J*=8.8 Hz, 2H, Ar), 6.98 (d, *J*=7.6 Hz, 2H, Ar), 6.95 (d, *J*=7.6 Hz, 2H, Ar), 5.37 (br d, *J*=4 Hz, 1H, 1×olefinic), 4.62 (m, 1H, 1×CHOCO), 4.05 (t, *J*=6.4 Hz, 2H, 1×OCH₂), 4.0 (t, *J*=6.4 Hz, 2H, 1×OCH₂), 2.34–1.04 (m, 51H, 6×CH, 21×CH₂, 1×CH₃), 1.02 (s, 3H, 1×CH₃), 0.91 (d, *J*=6.4 Hz, 3H, 1×CH₃), 0.87 (d, *J*=1.6 Hz, 3H, 1×CH₃), 0.86 (d, *J*=2 Hz, 3H, 1×CH₃) and 0.68 (s, 3H, 1×CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 173.03, 165.03, 163.55, 158.64, 150.02, 139.68, 138.5, 132.91, 132.27, 128.10, 127.66, 122.61, 121.97, 121.58, 114.8, 114.3, 73.82, 68.34, 67.74, 56.69, 56.15, 50.04, 42.32, 39.74, 39.51, 38.16, 37.0, 36.60, 36.18, 35.78, 34.59, 31.90, 31.87, 31.79, 29.31, 29.20, 29.10, 28.96, 28.22, 28.0, 27.82, 25.98, 25.63, 24.80, 24.28, 23.83, 22.80, 22.64, 22.55, 21.03, 19.31, 18.71, 14.08 and 11.85.

4.3.1.8. **BD-5,9**: 4'-((6-cholesteryloxy-6-oxohexyl)oxy)biphenyl-4-yl 4-(nonyloxy)benzoate. Yield: 79%; a bright yellow solid. Found: C, 80.3; H, 9.3; C₆₁H₈₆O₆ requires C, 80.04; H, 9.47; IR (KBr Pellet): $\nu_{\rm max}$ in cm⁻¹ 2929, 2852, 1728, 1601, 1499 and 1376; ¹H NMR (400 MHz, CDCl₃): 8.16 (d, J=8.8 Hz, 2H, Ar), 7.58 (d, J=8.4 Hz, 2H, Ar), 7.51 (d, J=8.8 Hz, 2H, Ar), 7.25 (d, J=8.8 Hz, 2H, Ar), 6.98 (d, J=7.2 Hz, 2H, Ar), 6.96 (d, J=7.2 Hz, 2H, Ar), 5.37 (br d, J=4.8 Hz, 1H, 1×olefinic), 4.66 (m, 1H, 1×CHOCO), 4.06 (t, *J*=6.6 Hz, 2H, 1×OCH₂), 4.01 (t, *J*=6.4 Hz, 2H, 1×OCH₂), 2.34–1.08 (m, 53H, 6×CH, 22×CH₂, 1×CH₃), 1.01 (s, 3H, 1×CH₃), 0.90 (d, J=6 Hz, 3H, 1×CH₃), 0.87 (d, *J*=1.6 Hz, 3H, 1×CH₃), 0.85 (d, *J*=1.6 Hz, 3H, 1×CH₃) and 0.67 (s, 3H, $1 \times CH_3$); ¹³C NMR (100 MHz, CDCl₃): δ 173.02, 165.03, 163.55, 158.64, 150.03, 139.69, 138.50, 132.91, 132.28, 128.10, 127.67, 122.61, 121.97, 121.59, 114.80, 114.30, 73.81, 68.34, 67.74, 56.70, 56.15, 50.04, 42.32, 39.74, 39.52, 38.17, 37.00, 36.60, 36.19, 35.79, 34.59, 31.91, 31.86, 29.50, 29.36, 29.24, 29.10, 28.97, 28.22, 28.00, 27.82, 25.98, 25.63, 24.80, 24.28, 23.83, 22.80, 22.66, 22.55, 21.03, 19.31, 18.71, 14.09 and 11.85.

4.3.1.9. **BD-5,10**: 4'-((6-cholesteryloxy-6-oxohexyl)oxy)biphenyl-4-*vl* 4-(*decyloxy*)*benzoate*. Yield: 80%; a bright yellow solid. Found: C, 80.0; H, 9.1; C₆₂H₈₈O₆ requires C, 80.13; H, 9.54; IR (KBr Pellet): $v_{\rm max}$ in cm⁻¹ 2936, 2860, 1730, 1605, 1499 and 1378; ¹H NMR (400 MHz, CDCl₃): 8.16 (d, J=8.8 Hz, 2H, Ar), 7.58 (d, J=8.8 Hz, 2H, Ar), 7.51 (d, J=8.8 Hz, 2H, Ar), 7.25 (d, J=8.4 Hz, 2H, Ar), 6.98 (d, *J*=7.6 Hz, 2H, Ar), 6.96 (d, *J*=7.2 Hz, 2H, Ar), 5.37 (br d, *J*=5.2 Hz, 1H, 1×olefinic), 4.66 (m, 1H, 1×CHOCO), 4.06 (t, *J*=6.6 Hz, 2H, 1×OCH₂), 4.02 (t, *J*=6.4 Hz, 2H, 1×OCH₂), 2.34–1.04 (m, 55H, 6×CH, 23×CH₂, 1×CH₃), 1.01 (s, 3H, 1×CH₃), 0.90 (d, *J*=6.8 Hz, 3H, 1×CH₃), 0.87 (d, *I*=1.6 Hz, 3H, 1×CH₃), 0.85 (d, *I*=2 Hz, 3H, 1×CH₃) and 0.67 (s, 3H, $1 \times CH_3$); ¹³C NMR (100 MHz, CDCl₃): δ 173.04, 165.04, 163.55, 158.65, 150.03, 139.69, 138.51, 132.92, 132.28, 128.11, 127.67, 122.62, 121.97, 121.59, 114.81, 114.31, 73.82, 68.34, 67.74, 56.70, 56.15, 50.04, 42.32, 39.74, 39.52, 38.17, 37.00, 36.60, 36.19, 35.79, 34.60, 33.96, 31.91, 31.88, 29.54, 29.35, 29.30, 29.10, 28.97, 28.22, 28.01, 27.83, 25.98, 25.64, 24.93, 24.80, 24.28, 23.83, 22.80, 22.67, 22.55, 21.03, 19.31, 18.71, 14.09 and 11.85.

4.3.1.10. **BD-5,11**: 4'-((6-cholesteryloxy-6-oxohexyl)oxy)biphenyl-4-yl 4-(undecyloxy)benzoate. Yield: 82%; a bright yellow solid. Found: C, 80.4; H, 9.4; $C_{63}H_{90}O_6$ requires C, 80.21; H, 9.62; IR (KBr Pellet): ν_{max} in cm⁻¹ 2937, 2856, 1731, 1623, 1498 and 1377; ¹H NMR (400 MHz, CDCl₃): 8.17 (d, *J*=8.8 Hz, 2H, Ar), 7.58 (d, *J*=8.8 Hz, 2H, Ar), 7.51 (d, *J*=8.8 Hz, 2H, Ar), 7.25 (d, *J*=8.4 Hz, 2H, Ar), 6.99 (d, *J*=7.6 Hz, 2H, Ar), 6.96 (d, *J*=7.6 Hz, 2H, Ar), 5.38 (br d, *J*=4 Hz, 1H, 1×olefinic), 4.64 (m, 1H, 1×CHOCO), 4.06 (t, *J*=6.6 Hz, 2H, 1×OCH₂), 4.02 (t, *J*=6.4 Hz, 2H, 1×OCH₂), 2.35–1.04 (m, 57H, 6×CH, 24×CH₂, 1×CH₃), 1.02 (s, 3H, 1×CH₃), 0.92 (d, *J*=6.8 Hz, 3H, 1×CH₃), 0.89 (d, *J*=1.6 Hz, 3H, 1×CH₃), 0.87 (d, *J*=2 Hz, 3H, 1×CH₃) and 0.67 (s, 3H, 1×CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 173.01, 165.01, 163.54, 158.64, 150.02, 139.68, 138.49, 132.90, 132.27, 128.09, 127.66, 122.61, 121.96, 121.58, 114.80, 114.29, 73.80, 68.33, 67.73, 56.69, 56.14, 50.03, 42.31, 39.73, 39.51, 38.16, 36.99, 36.59, 36.18, 35.78, 34.58, 31.89, 29.58, 29.54, 29.35, 29.09, 28.96, 28.21, 28.00, 27.82, 25.97, 25.63, 24.79, 24.27, 23.83, 22.80, 22.67, 22.55, 21.03, 19.30, 18.71, 14.09 and 11.85.

4.3.1.11. **BD-5,12**: 4'-((6-cholesteryloxy-6-oxohexyl)oxy)biphenyl-4-yl 4-(dodecyloxy)benzoate. Yield: 75%; a bright yellow solid. Found: C, 79.9; H, 9.8; C₆₄H₉₂O₆ requires C, 80.29; H, 9.69; IR (KBr Pellet): v_{max} in cm⁻¹ 2931, 2863, 1730, 1604, 1495 and 1378; ¹H NMR (400 MHz, CDCl₃): 8.16 (d, J=9.2 Hz, 2H, Ar), 7.58 (d, J=8.8 Hz, 2H, Ar), 7.51 (d, J=8.4 Hz, 2H, Ar), 7.25 (d, J=8.8 Hz, 2H, Ar), 6.98 (d, *I*=7.2 Hz, 2H, Ar), 6.96 (d, *I*=7.2 Hz, 2H, Ar), 5.37 (br d, *I*=4 Hz, 1H, 1×olefinic), 4.66 (m, 1H, 1×CHOCO), 4.06 (t, *J*=6.6 Hz, 2H, 1×OCH₂), 4.02 (t, J=6.4 Hz, 2H, 1×OCH₂), 2.34–1.08 (m, 59H, 6×CH, 25×CH₂, 1×CH₃), 1.01 (s, 3H, 1×CH₃), 0.92 (d, *J*=6.8 Hz, 3H, 1×CH₃), 0.87 (d, J=1.6 Hz, 3H, 1×CH₃), 0.85 (d, J=2 Hz, 3H, 1×CH₃) and 0.67 (s, 3H, 1×CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 173.02, 165.02, 163.54, 158.63, 150.02, 139.67, 138.49, 132.90, 132.27, 128.09, 127.65, 122.60, 121.96, 121.57, 114.79, 114.29, 73.81, 68.33, 67.73, 56.68, 56.14, 50.03, 42.31, 39.73, 39.51, 38.15, 36.99, 36.59, 36.18, 35.78, 34.58, 31.89, 31.86, 29.57, 29.54, 29.48, 29.33, 29.09, 28.95, 28.21, 27.99, 27.81, 25.97, 25.62, 24.79, 24.27, 23.82, 22.79, 22.67, 22.54, 21.02, 19.30, 18.70, 14.09 and 11.84.

4.3.1.12. **BD-5.16** : 4'-((6-cholesteryloxy-6-oxohexyl)oxy)biphenyl-4-yl 4-(hexadecyloxy)benzoate. Yield: 67%; a bright yellow solid. Found: C, 81.0; H, 9.6; C₆₈H₁₀₀O₆ requires C, 80.58; H, 9.94; IR (KBr Pellet): *v*_{max} in cm⁻¹ 2928, 2858, 1731, 1603, 1497 and 1379; ¹H NMR (400 MHz, CDCl₃): 8.16 (d, *J*=8.8 Hz, 2H, Ar), 7.58 (d, *J*=8.4 Hz, 2H, Ar), 7.51 (d, J=8.8 Hz, 2H, Ar), 7.25 (d, J=8.8 Hz, 2H, Ar), 6.98 (d, *I*=7.2 Hz, 2H, Ar), 6.96 (d, *I*=7.2 Hz, 2H, Ar), 5.37 (br d, *I*=4 Hz, 1H, 1×olefinic), 4.66 (m, 1H, 1×CHOCO), 4.05 (t, *J*=6.6 Hz, 2H, 1×OCH₂), 4.01 (t, *J*=6.4 Hz, 2H, 1×OCH₂), 2.34–1.04 (m, 67H, 6×CH, 29×CH₂, 1×CH₃), 1.01 (s, 3H, 1×CH₃), 0.92 (d, *J*=6.8 Hz, 3H, 1×CH₃), 0.87 (d, J=1.6 Hz, 3H, 1×CH₃), 0.85 (d, J=1.2 Hz, 3H, 1×CH₃) and 0.67 (s, 3H, 1×CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 173.02, 165.02, 163.55, 158.64, 150.02, 139.68, 138.50, 132.91, 132.27, 128.09, 127.66, 122.61, 121.97, 121.58, 114.80, 114.30, 73.81, 68.33, 67.73, 56.69, 56.15, 50.04, 42.31, 39.74, 39.52, 38.16, 37.00, 36.60, 36.19, 35.79, 34.59, 31.91, 31.87, 29.69, 29.65, 29.58, 29.55, 29.35, 29.10, 28.96, 28.22, 28.00, 27.82, 25.98, 25.63, 24.80, 24.28, 23.83, 22.80, 22.68, 22.55, 21.03, 19.31, 18.71, 14.10 and 11.85.

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