

Chapter 8

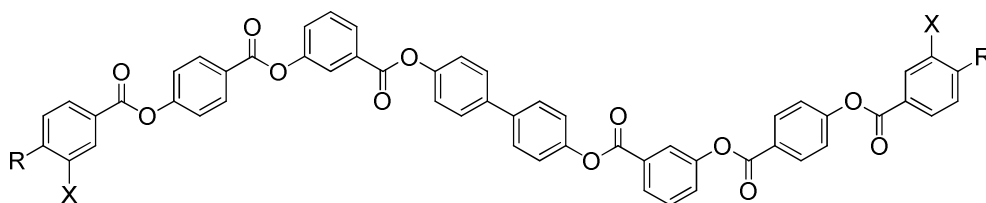
Synthesis and mesomorphic properties of

- (i) **Biphenyl-4-4'-dilyl bis(3-(4-(4-*n*-alkoxy)benzoyloxy)benzoyloxy)-benzoates, (compounds 8.A.1 to 8.A.11)**
- (ii) **Biphenyl-4-4'-dilyl bis(3-(4-(4-*n*-octadecyloxy)-3-fluorobenzoyloxy)benzoyloxy)benzoate, (compound 8.A.12)**
- (ii) **Biphenyl-4-4'-dilyl bis(3-(4-(4-*n*-hexadecyl)benzoyloxy)benzoyloxy)benzoate, (compound 8.A.13)**
- (iv) **Biphenyl-4-4'-dilyl bis(3-(4-(4-*n*-alkylbiphenyl)carbonyloxy)benzoates, (compounds 8.B.1 to 8.B.4)**
- (v) **4-(4-(3-(4-(4-*n*-Alkoxy)benzoyloxy)benzoyloxy)benzoyloxy)benzoyloxy)phenyl 3-(4-(4-*n*-alkoxy)benzoyloxy)benzoyloxy)benzoates, (compounds 8.C.1 to 8.C.9)**
- (vi) **4-((3-((4-(4-(3-(4-(3-Fluoro(4-*n*-hexadecyloxy)benzoyloxy)benzoyloxy)benzoyloxy)benzoyloxy)phenoxy)carbonyl)phenoxy)carbonyl)phenyl 3-fluoro(4-*n*-hexadecyloxy)benzoate, (compound 8.C.10)**
- (vii) **4-(4-(3-(4-(4-*n*-Hexadecylbenzoyloxy)benzoyloxy)benzoyloxy)benzoyloxy)phenyl 3-(4-(4-*n*-hexadecylbenzoyloxy)benzoyloxy)benzoate, (compound 8.C.11)**
- (viii) **3-((4-((4-(3-(-4'-*n*-Alkylbiphenylcarbonyloxy)benzoyloxy)phenoxy)carbonyl)phenoxy)carbonyl)phenyl 4'-*n*-alkylbiphenyl-4-carboxylates, (compounds 8.D.1 to 8.D.2)**

8.1: Introduction

The shape anisotropy of molecules in different organic compounds has yielded a variety of liquid crystalline phases. Compounds composed of banana-shaped or bent-core molecules have been extensively investigated due to the fact that many of them exhibit chiral phases even though the constituent molecules are achiral [1-4]. We have already seen in previous chapters results obtained on investigating a variety of bent-core compounds including those on dimeric systems. Many of the results obtained are really fascinating and exciting. In this chapter, we describe the design, synthesis and mesomorphic properties of compounds which are composed of Z or zigzag-shaped molecules. The idea to design such molecules occurred while investigating the structure of mesophases exhibited by hockey stick-shaped compounds [5-7]. The symmetric zigzag-shaped compounds may be viewed as bent-core dimers [8-11] without any spacers and as a result the polar directions get annuled and hence these do not have a net polarization.

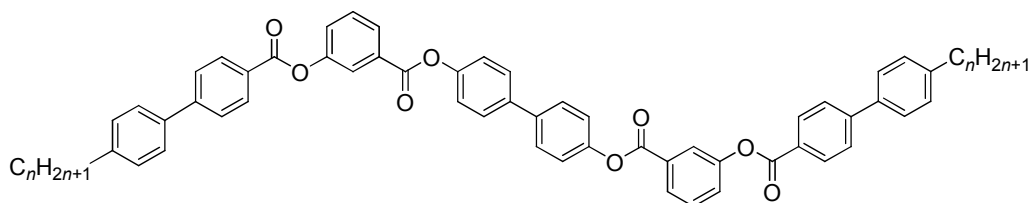
A total of eight different series/part of series of compounds have been synthesized. The influence of a lateral fluoro substituent, replacing a biphenyl moiety with a phenyl benzoate unit in the central position of the molecule and replacing the terminal *n*-alkoxy chain by a *n*-alkyl chain, on the mesomorphic properties have all been examined. Thus, the general structures of the zigzag-shaped compounds synthesized and investigated in this chapter are shown in general structure **8**. Interestingly, these compounds exhibit a columnar phase with either a rectangular lattice or an oblique lattice.



$R = OC_nH_{2n+1}$ $X = H$ $n = 7, 9, 10, 11, 12, 13, 14, 15, 16, 18, 20$ Series **8.A**

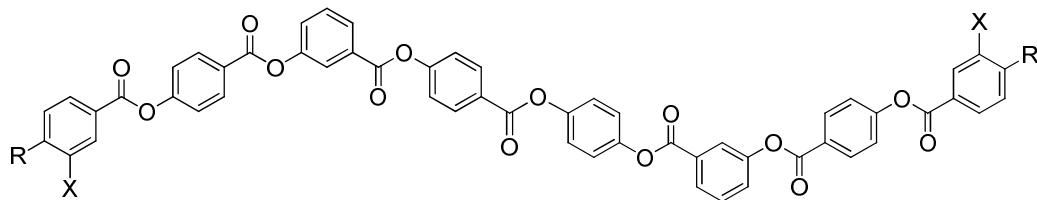
$R = OC_nH_{2n+1}$ $X = F$ $n = 18$ Series **8.A**

$R = C_nH_{2n+1}$ $X = H$ $n = 16$ Series **8.A**



$n = 12, 14, 16, 18$

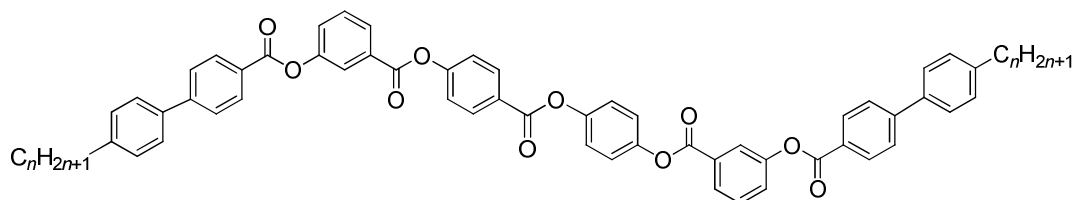
Series **8.B**



$R = OC_nH_{2n+1}$ $X = H$ $n = 7, 10, 11, 12, 13, 14, 16, 18, 20$ Series **8.C**

$R = OC_nH_{2n+1}$ $X = F$ $n = 16$ Series **8.C**

$R = C_nH_{2n+1}$ $X = H$ $n = 16$ Series **8.C**



$n = 12, 16$

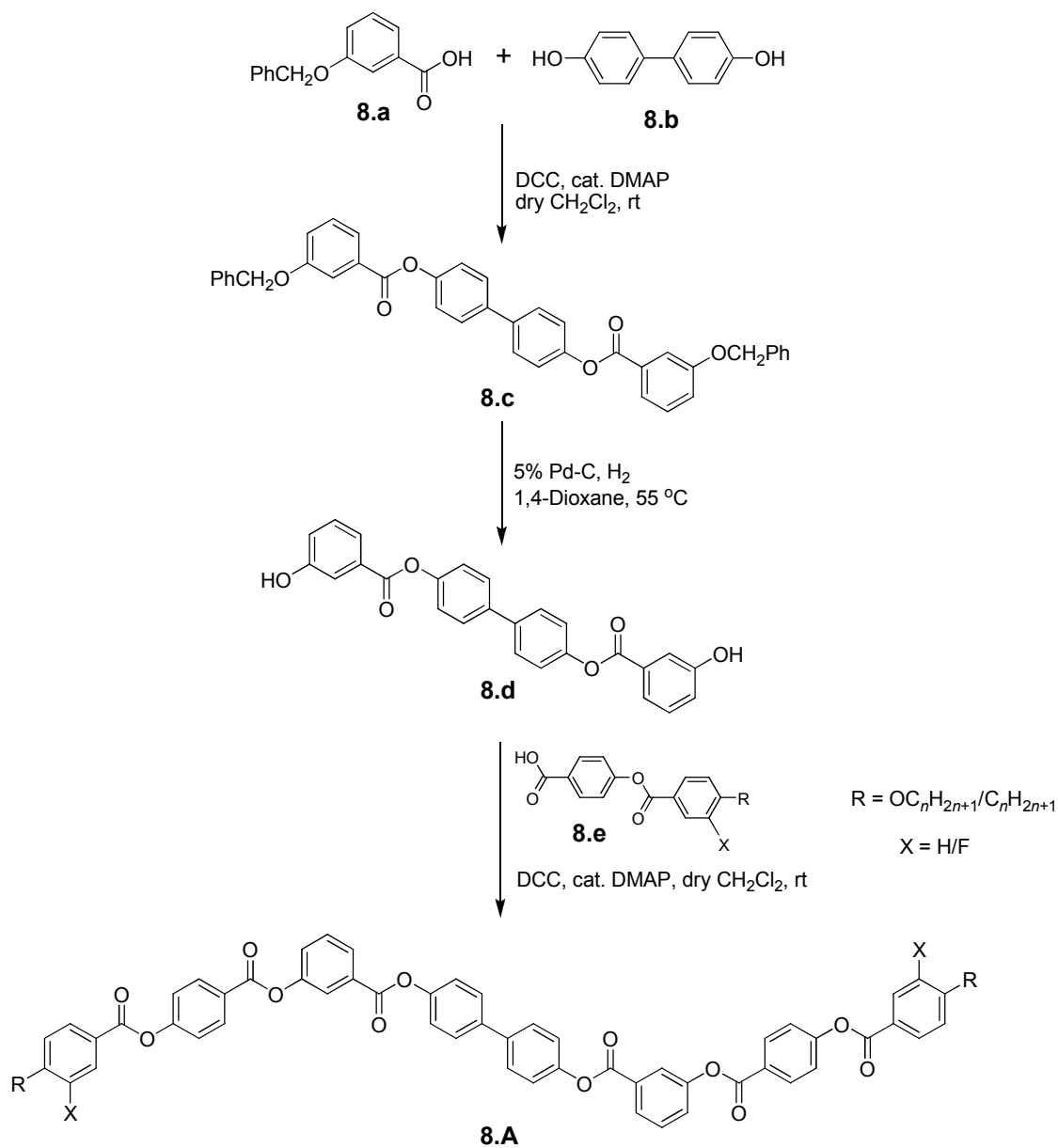
Series **8.D**

General structure 8

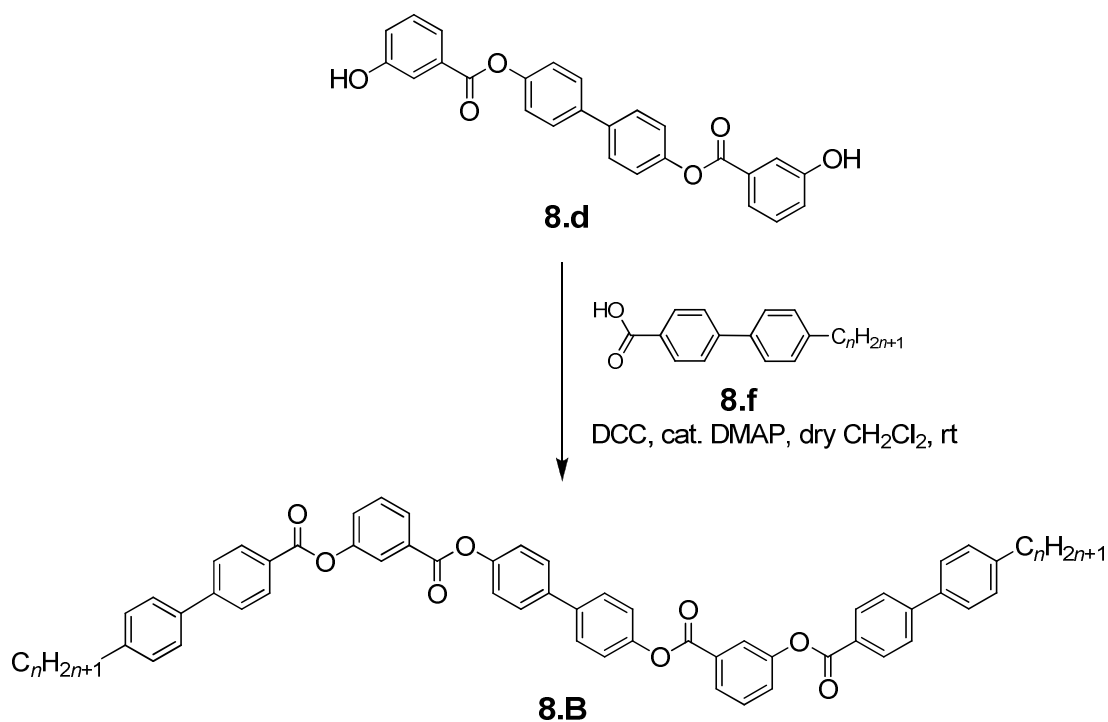
8.2: Synthesis

The symmetrical and unsymmetrical eight-ring zigzag-shaped compounds of series **8.A**, **8.B**, **8.C** and **8.D** were synthesized following the synthetic pathway shown in schemes **8.1**, **8.2**, **8.4** and **8.5** respectively. Biphenyl-4,4'-diol, 4-benzyloxyphenol and 3-hydroxybenzoic acids were obtained commercially from Merck/Aldrich and used without further purification. 3-Benzyloxybenzoic acid, **8.a** and 4-benzyloxybenzoic acid, **8.g** were synthesized according to a procedure described previously [12]. The synthesis of 4-*n*-alkoxybenzoyloxy-4-benzoic acids, **8.e** were described in chapter 2. Similarly, 4-*n*-alkylbenzoyloxy-4-benzoic acid and 4-*n*-alkoxy-3-fluorobenzoyloxy-4-benzoic acid, **8.e** were prepared. 4-*n*-Alkylbiphenyl-4-carboxylic acids, **8.f** were prepared following a procedure described in the literature [13]. 4-*n*-Alkoxybenzoic acids, 4-*n*-alkoxy-3-fluorobenzoic acid and 4-*n*-alkylbenzoic acid were prepared according to the procedure described in the literature [14-16]. 3-Benzyloxybenzoic acid, **8.a** was condensed with biphenyl-4,4'-diol, **8.b** in the presence of *N,N'*-dicyclohexylcarbodiimide (DCC) and a catalytic amount of 4-(*N,N*-dimethylamino)pyridine (DMAP). The dibenzyloxy ester **8.c**, thus obtained was subjected to hydrogenolysis in the presence of 5% Pd-C in 1,4-dioxane which yielded bisphenol **8.d**. Thus, the symmetrical zigzag-shaped compounds of series **8.A** and **8.B** were obtained by reacting one equivalent of bisphenol, **8.d** with two equivalents of corresponding two-ring acid, **8.e** and biphenyl acid, **8.f** respectively in presence of DCC and DMAP in dry dichloromethane at room temperature.

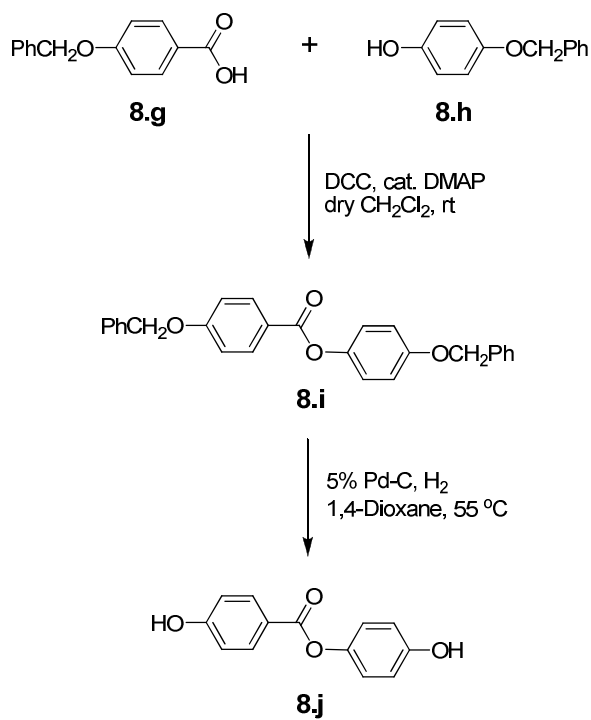
The ester linked unsymmetrical zigzag-shaped compounds of series **8.C** and **8.D** were synthesized as outlined in schemes **8.4** and **8.5** employing a series of esterification and hydrogenolysis reactions. The two-ring bisphenol **8.j** was prepared by condensing 4-benzyloxybenzoic acid, **8.g** with 4-benzyloxyphenol, **8.h** in presence of DCC and DMAP in dry DCM followed by hydrogenolysis using 5% Pd-C in 1,4-dioxane and the synthetic pathway followed is shown in scheme **8.3**. This bisphenol **8.j** was esterified with 3-benzyloxybenzoic acid, **8.a** and removal of benzyl group in the product obtained by hydrogenolysis provided four-ring bisphenol **8.i**. The target compounds of series **8.C** were synthesized by reacting one equivalent of four-ring bisphenol **8.i** with two equivalents of appropriate two-ring acid, **8.e**. Similarly, compounds of series **8.D** were prepared by reacting bisphenol **8.j** and a biphenyl acid, **8.f**. All compounds were



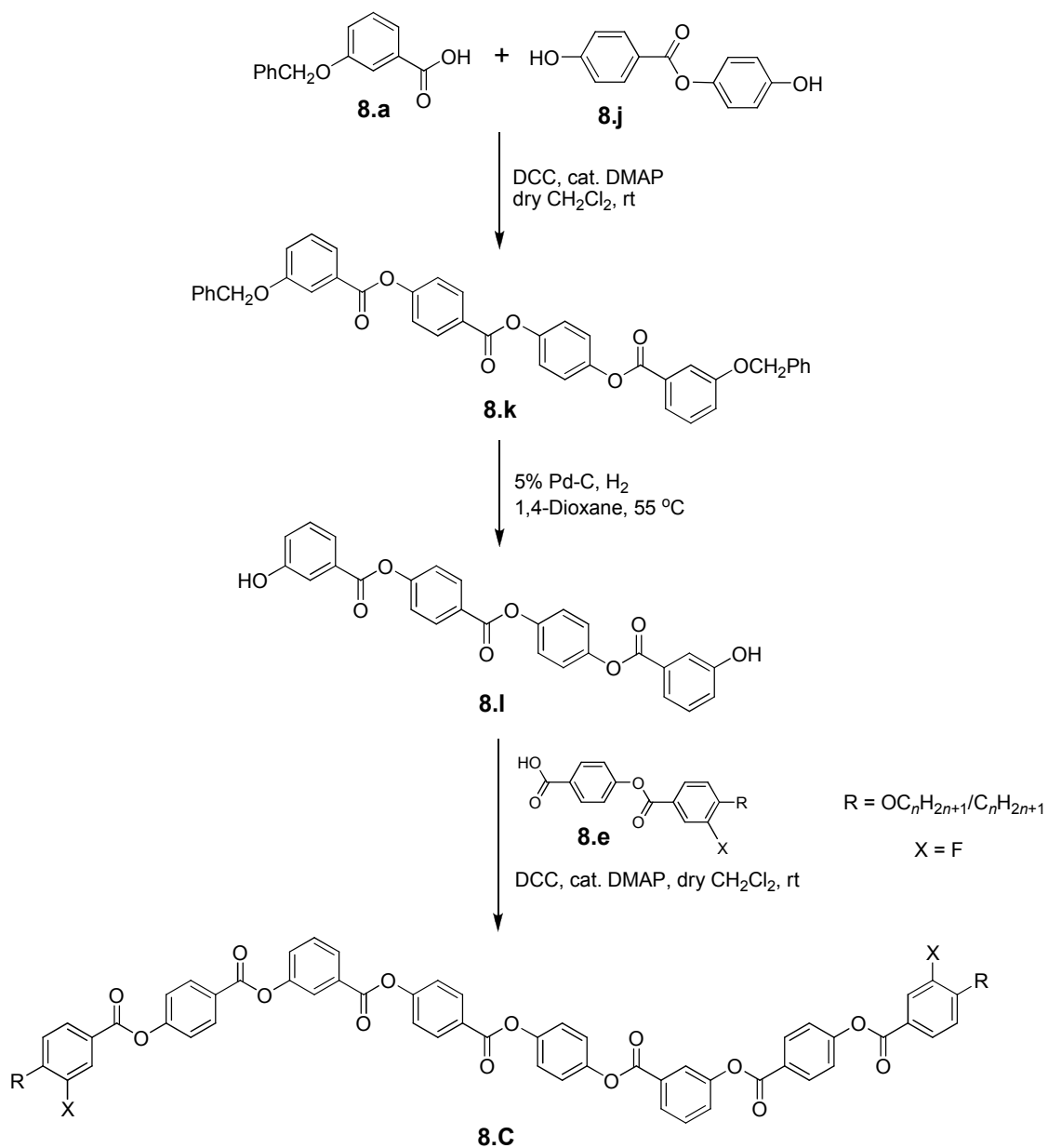
Scheme 8.1: Synthetic pathway followed for preparation of novel zigzag-shaped compounds of series 8.A.



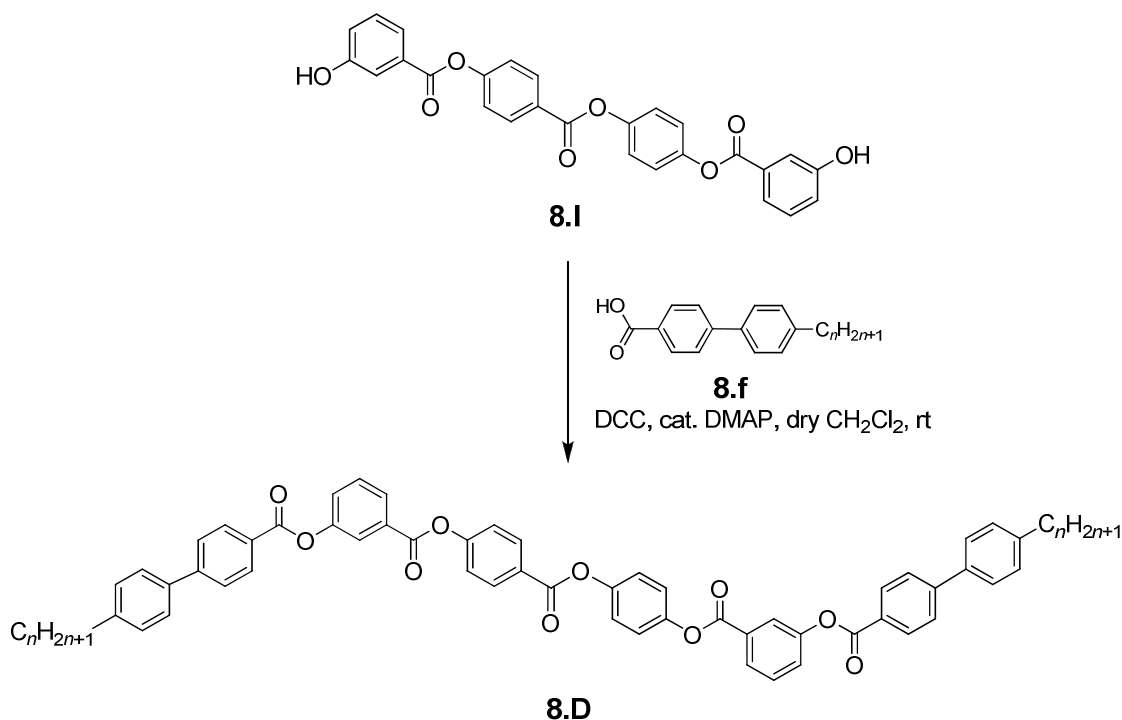
Scheme 8.2: Synthetic route followed to prepare compounds of series 8.B.



Scheme 8.3: Synthetic route used to prepare intermediate compound 8.j.



Scheme 8.4: Synthetic pathway employed to prepare compounds of series 8.C.



Scheme 8.5: Synthetic pathway followed to prepare compounds of series **8.D**.

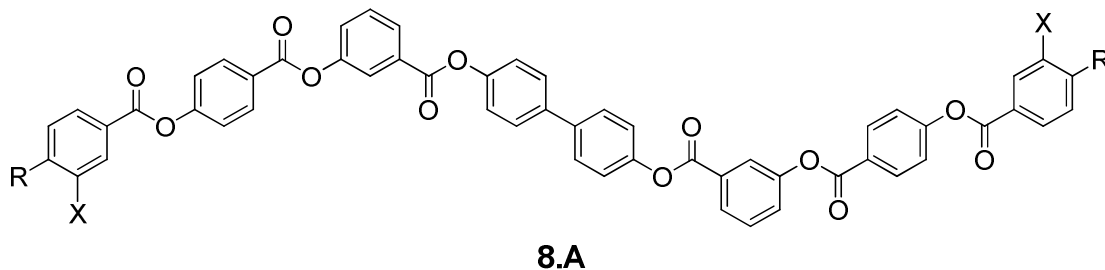
purified by column chromatography on silica gel (60-120 mesh) followed by repeated crystallization using suitable analytical grade solvents.

8.3: Results and discussion

8.3.1: Mesomorphic properties

The transition temperatures and the associated enthalpy values obtained for zigzag-shaped compounds of series **8.A**, **8.B**, **8.C** and **8.D** are summarized in tables **8.1**, **8.2**, **8.3** and **8.4** respectively. Interestingly, all these synthesized compounds are mesomorphic. In series **8.A**, as can be seen in table **8.1** compounds **8.A.1** to **8.A.5** are monotropic and exhibit only one mesophase. When a sample of compound **8.A.2** sandwiched between a glass plate and a coverslip was slowly cooled from the isotropic liquid and observed under a optical polarizing microscope, highly birefringent circular domains and banana leaf-like textures could be seen and

Table 8.1: Transition temperatures ($^{\circ}\text{C}$) and the associated enthalpy values (kJ mol^{-1}) (in italics) for compounds of series 8.A^a



Compound	n	X	R	Cr	T_{Cr}	ΔH_{Cr}	T_{Col_r}	ΔH_{Col_r}	$T_{\text{Col}_{\text{ob}}}$	$\Delta H_{\text{Col}_{\text{ob}}}$	I
8.A.1	7	H	$\text{OC}_n\text{H}_{2n+1}$	•	190.0*	(• 82.8)	183.5	-	-	-	•
8.A.2	9	H	$\text{OC}_n\text{H}_{2n+1}$	•	192.5*	(• 94.2)	184.5	-	-	-	•
8.A.3	10	H	$\text{OC}_n\text{H}_{2n+1}$	•	188.0*	(• 64.7)	184.5	-	-	-	•
8.A.4	11	H	$\text{OC}_n\text{H}_{2n+1}$	•	187.5*	(• 81.0)	183.5	-	-	-	•
8.A.5	12	H	$\text{OC}_n\text{H}_{2n+1}$	•	187.5*	(• 35.2)	180.5	-	-	-	•
8.A.6	13	H	$\text{OC}_n\text{H}_{2n+1}$	•	186.5*	(• 86.0)	-	(• 180.5)	-	(• 21.2)	•
8.A.7	14	H	$\text{OC}_n\text{H}_{2n+1}$	•	185.0*	(• 74.0)	-	(• 184.0)	-	(• 20.9)	•
8.A.8	15	H	$\text{OC}_n\text{H}_{2n+1}$	•	184.5*	(• 54.8)	-	• 187.0	-	• 20.4	•
8.A.9	16	H	$\text{OC}_n\text{H}_{2n+1}$	•	182.5*	(• 42.4)	-	• 188.5	-	• 19.6	•
8.A.10	18	H	$\text{OC}_n\text{H}_{2n+1}$	•	180.0*	(• 43.6)	-	• 190.0	-	• 18.6	•
8.A.11	20	H	$\text{OC}_n\text{H}_{2n+1}$	•	178.5*	(• 45.2)	-	• 191.5	-	• 17.2	•
8.A.12	18	F	$\text{OC}_n\text{H}_{2n+1}$	•	194.0*	(• 41.9)	-	• 199.0	-	• 18.4	•
8.A.13	16	H	$\text{C}_n\text{H}_{2n+1}$	•	176.5*	(• 31.1)	-	• 185.0	-	• 20.1	•

^aAbbreviations: Cr: crystalline phase; *has crystal-crystal transition and enthalpy denoted is the sum of all such transitions; Col_r : columnar phase with a rectangular lattice; Col_{ob} : columnar phase with an oblique lattice; I: isotropic phase; (•): phase is monotropic; •: phase exists; -: phase does not exist.

typical textures obtained for this compound are shown in figure **8.1.a** and **8.1.b**. These textures are very similar to those obtained for a rectangular columnar mesophase. On the basis of textural observations, X-ray diffraction and electro-optical studies (described later), the mesophase exhibited by these compounds have been characterized as columnar phase with a rectangular lattice (Col_r). Similar textural behaviour was observed for compounds **8.A.1**, **8.A.3**, **8.A.4** and **8.A.5** and the optical texture obtained for compound **8.A.3** is shown in figure **8.1.c**.

Interestingly, the higher homologues **8.A.6** to **8.A.11** show completely different optical textures which are again similar to those obtained for a two-dimensional columnar mesophase. Compounds **8.A.6** and **8.A.7** are monotropic and compounds **8.A.8** to **8.A.11** are enantiotropic. When a thin film of a sample of compound **8.A.9** was viewed under a polarizing microscope, on slow cooling from the isotropic liquid flower-like texture developed indicating a two-dimensional columnar structure which further grew and covered the entire field of view as shown in figures **8.2.a** and **8.2.b** respectively. The optical textures obtained for the same compound in different regions are also shown in figures **8.2.c** and **8.2.d**. Similar optical textures were observed in a cell treated for planar alignment. A DSC thermogram obtained for compound **8.A.11** is shown in figure **8.3**. All these compounds have crystal to crystal transition which can be seen in DSC thermograms. The accompanying enthalpy values of melting temperatures are in the range of 40-80 kJ mol^{-1} and clearing temperature enthalpy value decreases on ascending the series. Compound **8.A.11** shows a thermal range of 13 $^{\circ}\text{C}$ for Col_{ob} phase. X-Ray diffraction measurements of powder sample were carried out on the mesophase for the same sample. The X-ray intensity profile obtained for this compound is different from those obtained for lower homologues of the same series. On the basis of XRD measurements and optical textures, this mesophase has been identified as a columnar phase with an oblique lattice (Col_{ob}). The other homologues **8.A.6** to **8.A.8**, **8.A.10** and **8.A.11** exhibit optical textures and XRD data similar to that of compound **8.A.9**. Hence, the mesophase exhibited by all these compounds are the same viz. Col_{ob} phase.

A plot of transition temperature vs number of carbon atoms in the terminal chain obtained for this homologous series is shown in figure **8.4**. As can be seen, the Col_r phase to clearing transition temperature curve rises sharply and then falls as the series is ascended. However, a smooth rising curve is obtained for Col_{ob} phase on ascending the series. In order to examine the

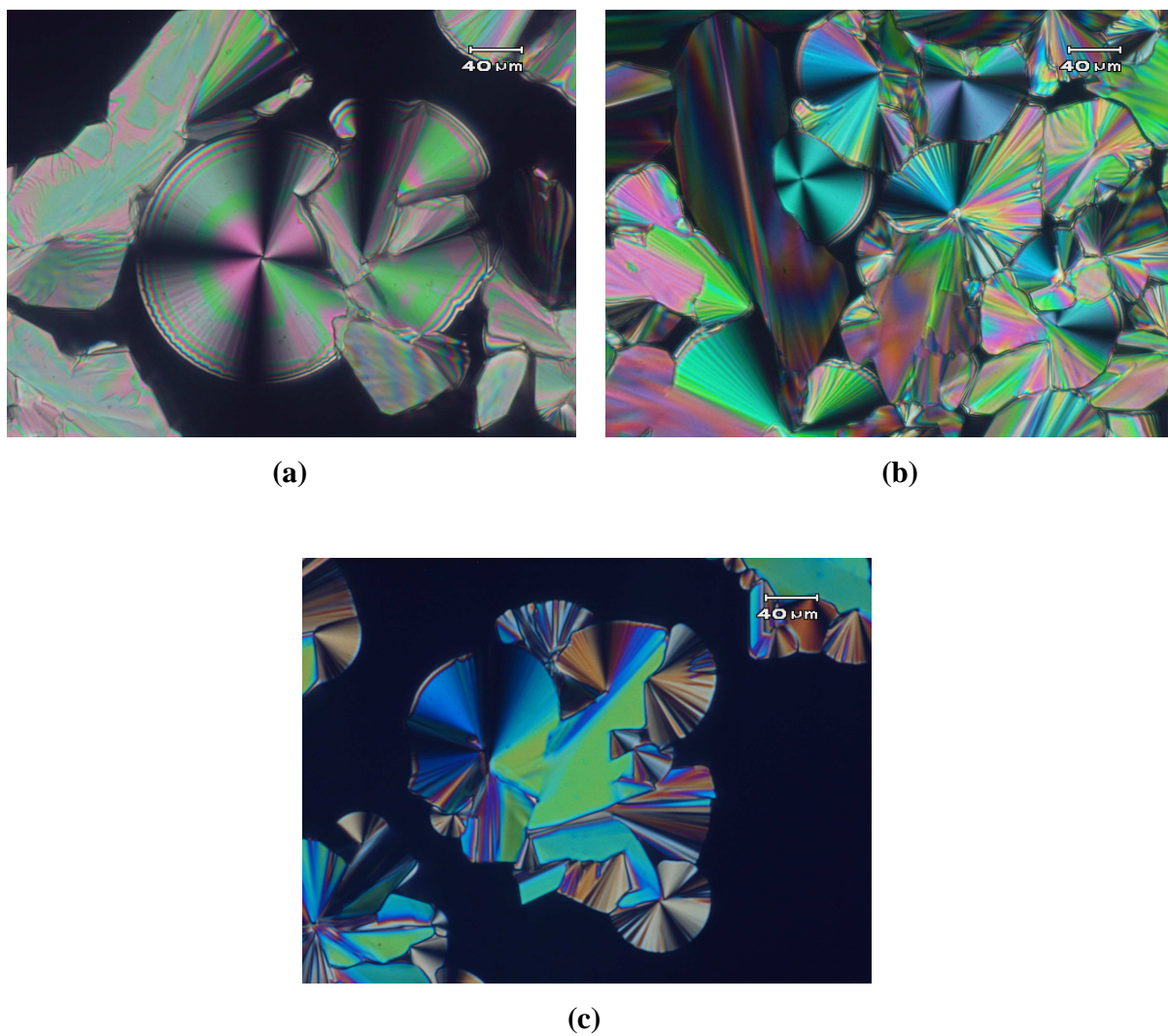


Figure 8.1: Photomicrographs of the textures obtained for Col_r mesophase of compounds 8.A.2 and 8.A.3 between glass plates without any treatment. (a) Circular domains at T = 182 °C, (b) T = 175 °C and (c) T = 184.6 °C.

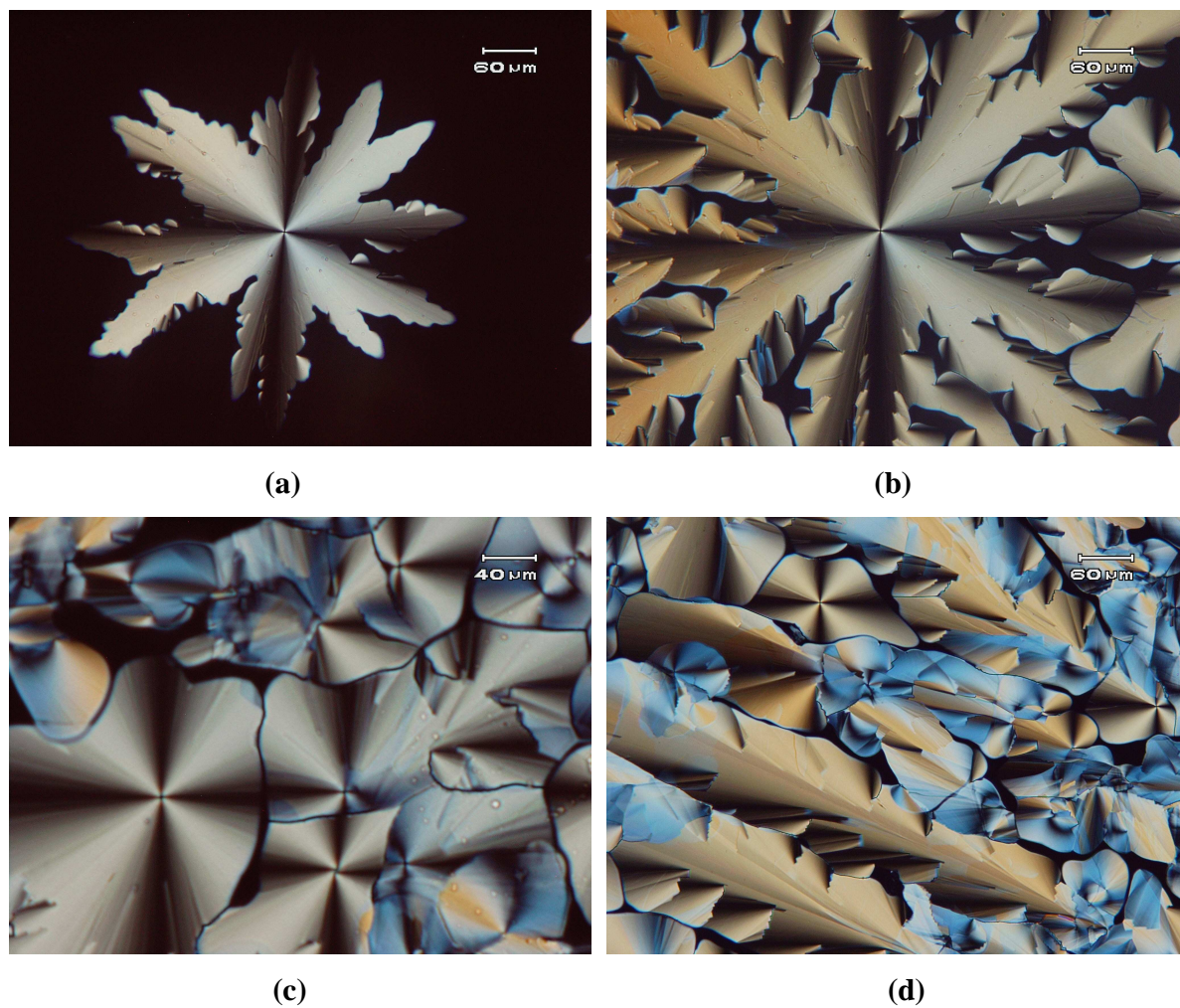


Figure 8.2: Textures obtained in Col_{ob} phase for compound 8.A.9 in a cell treated for homogeneous alignment. (a) Developing from isotropic liquid at $T = 187.5^{\circ}C$ and (b) $T = 187.3^{\circ}C$. Different regions of the same sample obtained on slow cooling, (c) $T = 186.5^{\circ}C$, (d) $T = 186.5^{\circ}C$.

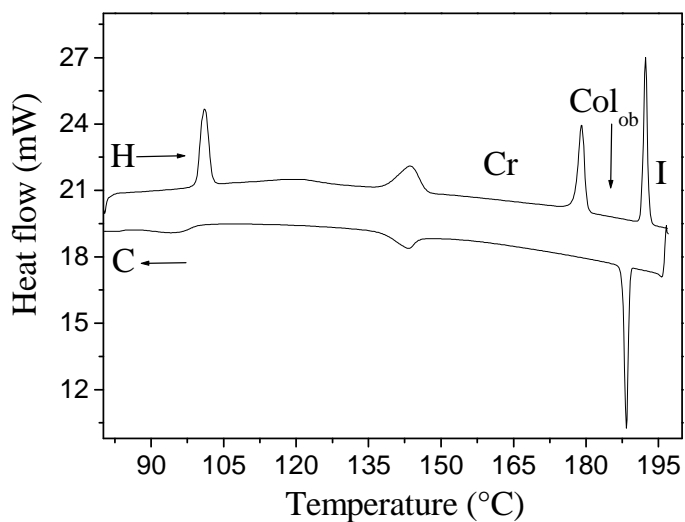


Figure 8.3: DSC thermogram of a sample of compound 8.A.11. (H) Heating cycle; (C) cooling cycle; rate $5^{\circ}\text{C min}^{-1}$.

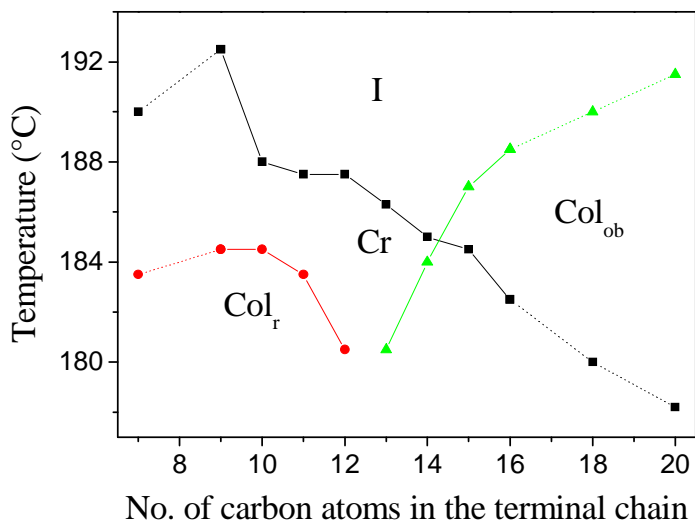
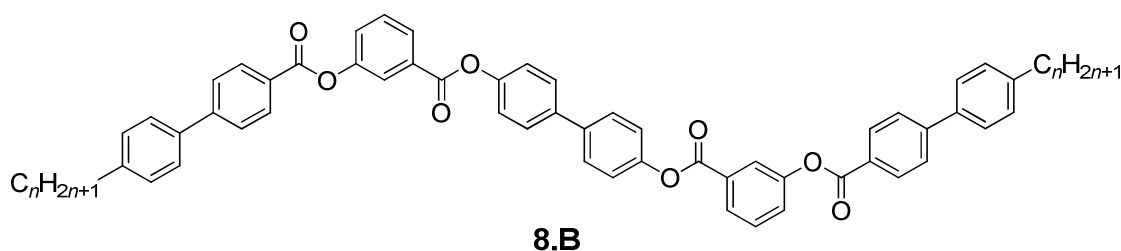


Figure 8.4: A plot of transition temperature as a function of the number of carbon atoms in the terminal chain for compounds of series 8.A.

influence of a fluoro substituent *ortho* to the terminal *n*-alkoxy chain, compound **8.A.12** was prepared. In addition, another compound **8.A.13** was prepared where the alkoxy chain was replaced by an alkyl chain. These compounds also showed textures similar to that of a two-dimensional Col_{ob} phase which was further confirmed by XRD measurements. It was observed that both the melting and clearing temperatures increased for fluoro substituted compound **8.A.12** as a result while the thermal mesophase range decreased. Interestingly, the thermal range increased with reduction of melting and clearing temperatures for compound **8.A.13** when compared to its alkoxy analogue.

Table 8.2: Transition temperatures (°C) and the associated enthalpy values (kJ mol⁻¹) (in italics) for compounds of series 8.B^a



Compound	<i>n</i>	Cr	Col _r	Col _{ob}	I
8.B.1	10	• 191.5 <i>60.4</i>	(• 187.5) <i>28.2</i>	-	•
8.B.2	12	• 190.5* <i>56.3</i>	-	(• 188.5) <i>24.8</i>	•
8.B.3	14	• 187.5* <i>47.7</i>	-	• 192.5 <i>25.0</i>	•
8.B.4	16	• 183.5* <i>36.4</i>	-	• 193.5 <i>23.4</i>	•

^aSee **Table 8.1**.

In order to understand the influence of variation in the structure, three other series of compounds **8.B**, **8.C** and **8.D** were synthesized and investigated, in addition to series **8.A**. Series **8.B** was synthesized using 4-*n*-alkylbiphenyl-4-carboxylic acids. The transition temperatures and enthalpy values obtained are summarized in table **8.2**. Compound **8.B.1** exhibits a monotropic columnar mesophase with a rectangular lattice (Col_r) whereas compound **8.B.2** to **8.B.4** show a Col_{ob} phase. The textural observations and X-ray diffraction patterns are similar to those obtained for compounds of series **8.A**. The thermal range of mesophase for compounds of this series increases with increase in melting and clearing temperatures when compared to the corresponding parent compound. In series **8.B**, compound **8.B.2** containing *n*-dodecyl chain shows Col_{ob} phase whereas the corresponding parent compound showed Col_r phase. A plot of transition temperature against the number of carbon atoms in the terminal chain for compounds of series **8.B** is shown in figure **8.5**. The slope of the curve obtained for clearing temperatures is similar to that obtained for series **8.A**.

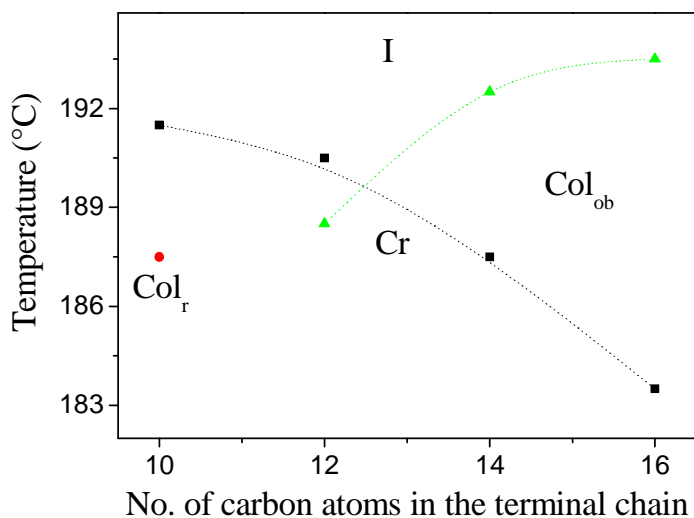
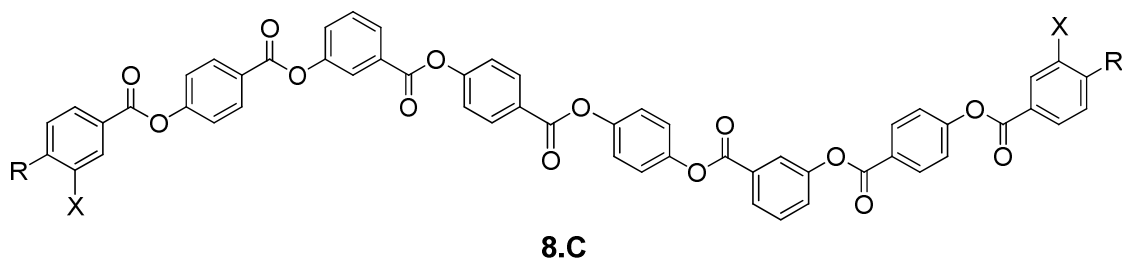


Figure 8.5: A plot of transition temperature against the number of carbon atoms in the terminal chain for compounds of series **8.B**.

The chemical nature of the parent compound (**8.A**) was further modified by introducing an ester group between the two phenyl groups of the biphenyl moiety and as a result series **8.C** was obtained. The transition temperatures and the associated enthalpy values obtained for this series is summarized in table **8.3**. Interestingly, this modification in the central part of the compound depressed the melting point considerably and it is remarkable that the thermal range increased on ascending the series whereas the clearing temperatures were lowered by about 10 °C only. Thus, the mesophases are well stabilized in this series and the mesomorphic behaviour of the compounds of this series is comparable to those of series **8.A**. As can be seen in table **8.3**, compounds **8.C.1** to **8.C.5** show columnar rectangular phase in which compounds **8.C.1** to **8.C.3** are monotropic whereas compounds **8.C.4** and **8.C.5** are enantiotropic. When a sample of compound **8.C.2** was filled in a cell treated for planar alignment in the isotropic state and cooled slowly under a polarizing microscope, optical textures similar to that obtained for columnar rectangular phase of compounds of series **8.A** were obtained. Hence the mesophase of compounds **8.C.1** to **8.C.5** was characterized as Col_r phase on the basis of textural observations and XRD measurements. A DSC thermogram recorded for compound **8.C.2** showing Col_r phase is depicted in figure **8.7.a**.

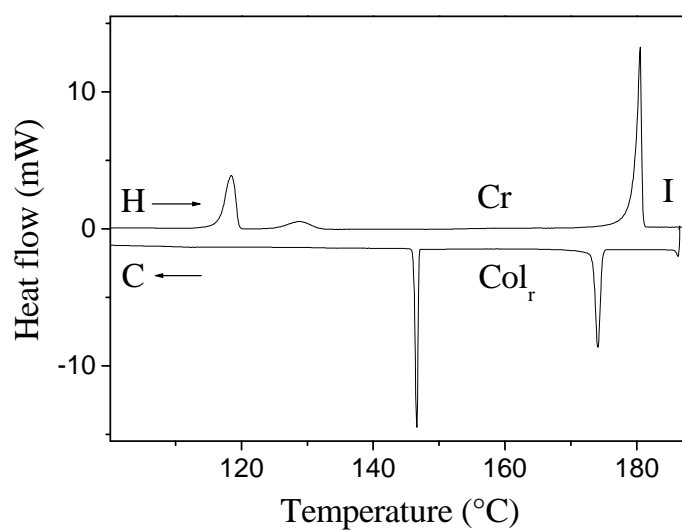
Compounds **8.C.6** to **8.C.9** are enantiotropic and the mesophase was characterized as Col_{ob} phase. A DSC thermogram obtained for compound **8.C.9** showing Col_{ob} phase is shown in figure **8.7.b**. Among all compounds in the four series, compound **8.C.9** shows the widest thermal range of 47.5 °C for Col_{ob} mesophase. The microscopic textures are very similar to those of higher homologues of series **8.A**. Further, the mesophase structure was confirmed by XRD measurements. A plot of transition temperature vs the number of carbon atoms in the terminal chain for this series is shown in figure **8.8**. It was found that the shape of clearing temperature curve for Col_r phase is different from that obtained for series **8.A** but similar to Col_{ob} phase. Compounds **8.C.10** and **8.C.11** also exhibited a two-dimensional columnar phase with an oblique lattice. It was found that melting as well as clearing temperatures increased for compound **8.C.10** and this behaviour is similar to that seen for compound **8.A.12** of series **A**. The thermal range of the mesophase decreased by about 10 °C for compound **8.C.11** with a slight increase in melting point and this is in contrast to compound **8.A.13**.

Table 8.3: Transition temperatures ($^{\circ}\text{C}$) and the associated enthalpy values (kJ mol^{-1}) (in italics) for compounds of series 8.C^a

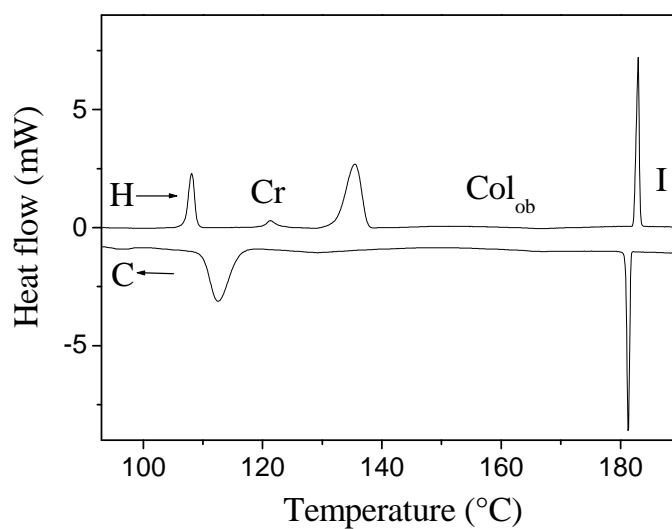


Compound	<i>n</i>	X	R	Cr	Col _r	Col _{ob}	I
8.C.1	7	H	OC _{<i>n</i>} H _{2<i>n</i>+1}	• 186.0* <i>50.9</i>	(• 175.5) <i>22.2</i>	-	•
8.C.2	10	H	OC _{<i>n</i>} H _{2<i>n</i>+1}	• 180.5* <i>75.8</i>	(• 174.0) <i>20.2</i>	-	•
8.C.3	11	H	OC _{<i>n</i>} H _{2<i>n</i>+1}	• 177.5* <i>80.1</i>	(• 174.0) <i>19.7</i>	-	•
8.C.4	12	H	OC _{<i>n</i>} H _{2<i>n</i>+1}	• 164.0* <i>59.4</i>	• 174.0 <i>20.5</i>	-	•
8.C.5	13	H	OC _{<i>n</i>} H _{2<i>n</i>+1}	• 164.5* <i>54.5</i>	• 173.0 <i>18.8</i>	-	•
8.C.6	14	H	OC _{<i>n</i>} H _{2<i>n</i>+1}	• 161.5* <i>49.4</i>	-	• 174.5 <i>18.3</i>	•
8.C.7	16	H	OC _{<i>n</i>} H _{2<i>n</i>+1}	• 140.5* <i>46.5</i>	-	• 178.5 <i>17.8</i>	•
8.C.8	18	H	OC _{<i>n</i>} H _{2<i>n</i>+1}	• 135.5* <i>44.0</i>	-	• 181.5 <i>16.8</i>	•
8.C.9	20	H	OC _{<i>n</i>} H _{2<i>n</i>+1}	• 135.5* <i>43.7</i>	-	• 183.0 <i>16.5</i>	•
8.C.10	16	F	OC _{<i>n</i>} H _{2<i>n</i>+1}	• 172.0* <i>62.1</i>	-	• 190.5 <i>18.8</i>	•
8.C.11	16	H	C _{<i>n</i>} H _{2<i>n</i>+1}	• 146.5* <i>40.7</i>	-	• 175.0 <i>17.7</i>	•

^aSee Table 8.1.



(a)



(b)

Figure 8.7: (a) DSC thermogram of a sample of compound 8.C.2 and (b) compound 8.C.9. (H) Heating cycle; (C) cooling cycle; rate 5 °C min⁻¹.

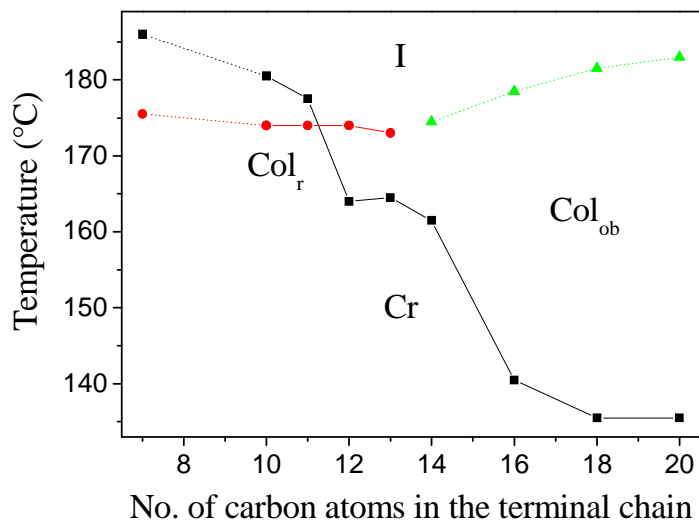
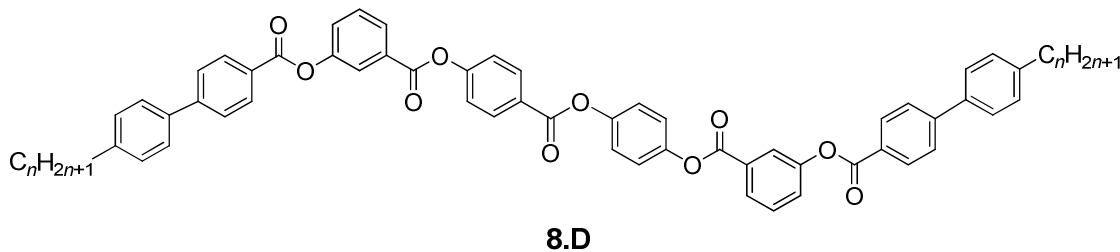


Figure 8.8: A plot of transition temperature *vs* the number of carbon atoms in the terminal chain for compounds of series 8.C.

Table 8.4: Transition temperatures (°C) and the associated enthalpy values (kJ mol⁻¹) (in italics) for compounds of series 8.D^a



Compound	<i>n</i>	Cr	Col _{ob}	I
8.D.1	12	• 184.5 <i>59.3</i>	(• 175.5) <i>22.0</i>	•
8.D.2	16	• 172.5 <i>39.1</i>	• 182.0 <i>19.7</i>	•

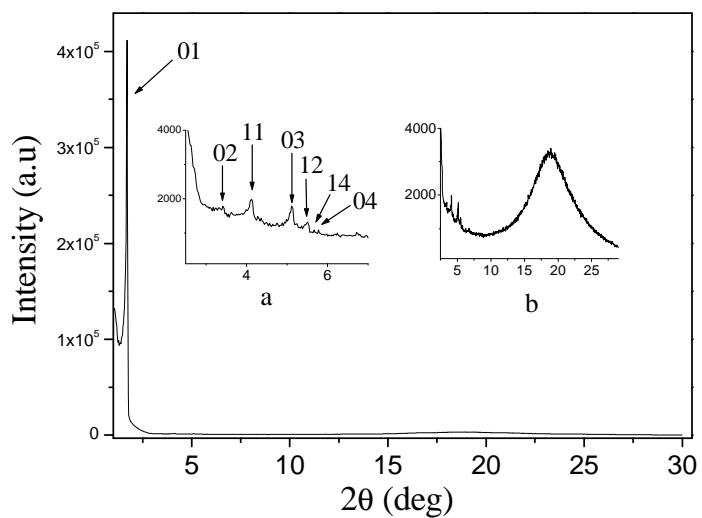
^aSee Table 8.1.

Only two compounds were synthesized in series **8.D**, which contain terminal *n*-alkyl chains and the transition temperature and the enthalpy values obtained for those are shown in table **8.4**. Both compounds show Col_{ob} mesophase in which it is metastable for compound **8.D.1** and compound **8.D.2** is enantiotropic. The mesophase was characterized by X-ray diffraction measurements. The mesomorphic behaviour of these two compounds are comparable to those of series **B**.

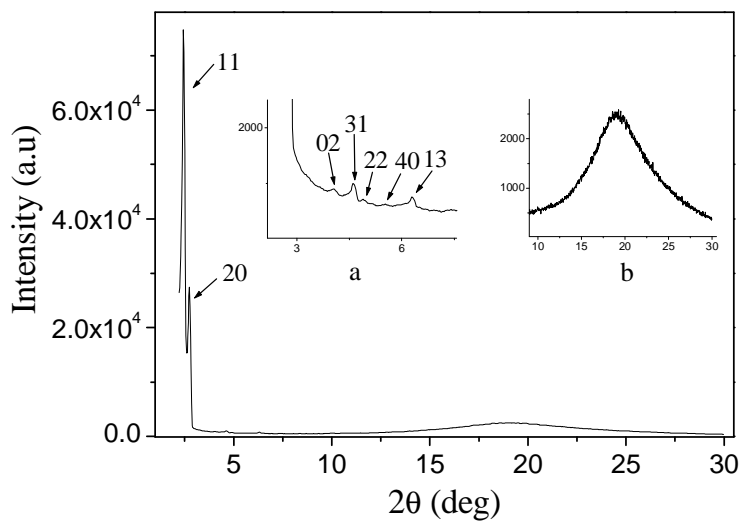
8.3.2: X-Ray diffraction measurements

The X-ray diffraction measurements were carried out on the mesophases of compounds of all the four series. The powder samples were filled in the isotropic state in Lindemann capillaries having a diameter of 1 mm and ends were sealed carefully. For example, compound **8.A.11** was cooled to mesophase and a typical intensity profile obtained is shown in figure **8.9.a**. It can be seen that there are many reflections in the small angle region indicating a two-dimensional structure with d-spacings of $d_1 = 51.78 \text{ \AA}$, $d_2 = 25.88 \text{ \AA}$, $d_3 = 21.43 \text{ \AA}$, $d_4 = 17.26 \text{ \AA}$, $d_5 = 16.03 \text{ \AA}$, $d_6 = 14.15 \text{ \AA}$, $d_7 = 13.06 \text{ \AA}$. The diffused peak in the wide angle region at 4.7 \AA indicates a liquid like in-plane order. The small angle reflections can be indexed to 01, 02, 11, 03, 12, 14 and 04 planes of an oblique lattice with lattice parameters $a = 32.07 \text{ \AA}$, $b = 57.76 \text{ \AA}$ and $\beta = 116.3^\circ$. The total number of molecules estimated is about 3 per unit cell.

Similar XRD measurements were carried out in the Col_r phase of compound **8.C.2** and the intensity profile obtained for this compound is shown in figure **8.9.b**. Four reflections can be seen in the small angle region and d-spacings correspond to $d_1 = 35.46 \text{ \AA}$, $d_2 = 30.62 \text{ \AA}$, $d_3 = 18.71 \text{ \AA}$, $d_4 = 14.27 \text{ \AA}$. These can be indexed to the 11, 20, 31 and 13 reflections of a columnar structure with a rectangular lattice. The calculated lattice parameters are $a = 61.24 \text{ \AA}$ and $b = 43.49 \text{ \AA}$. The broad peak at 4.7 \AA was also observed. These are typical values obtained for Col_{ob} and Col_r mesophases of compounds **8.A.11** and **8.C.2**. Similar experiments were carried out for other compounds as well. The d-spacings and the calculated lattice parameters obtained for compounds of series **8.A**, **8.B** and **8.C**, **8.D** are summarized in tables **8.5** and **8.6** respectively.



(a)



(b)

Figure 8.9: The XRD intensity profiles obtained for (a) Col_{ob} phase of compound 8.A.11 and (b) Col_r phase of compound 8.C.2.

Table 8.5: d-spacings obtained by XRD measurements and calculated lattice parameters for the mesophases of zigzag-shaped compounds of series 8.A and 8.B

Compound	d-spacings and Lattice parameters/(Å, °)	Phase type	T/(°C)
8.A.3	35.46(11), 30.62(20), 18.71(31), 14.27(13) a = 61.24; b = 43.49	Col _r	170
8.A.8	46.74(01), 23.53(02), 21.72(11), 16.66(1 $\bar{3}$), 15.73(03) a = 32.35; b = 50.54; β = 112.38	Col _{ob}	175
8.A.9	48.07(01), 24.03(02), 21.43(11), 17.0(1 $\bar{3}$), 16.10(03), 11.08(22); a = 31.18; b = 51.92; β = 112.21	Col _{ob}	170
8.A.10	50.17(01), 25.0(02), 21.15(11), 17.53(1 $\bar{3}$), 16.65(12), 11.9(21); a = 29.94; b = 54.14; β = 112.08	Col _{ob}	175
8.A.11	51.78(01), 25.88(02), 21.43(11), 17.26(03), 16.03(12), 14.15(20/14), 13.06(04); a = 32.07; b = 57.76; β = 116.3	Col _{ob}	175
8.A.12	56.1(01), 27.8(02), 24.74(11), 19.91(1 $\bar{3}$), 18.69(03), 11.44(14); a = 36.07; b = 60.80; β = 112.69	Col _{ob}	190
8.A.13	48.77(01), 24.38(02), 21.99(11), 16.34(12); a = 29.76; b = 50.94; β = 106.8	Col _{ob}	175
8.B.3	48.77(01), 36.5(1 $\bar{1}$), 24.56(02), 21.99(11), 19.03(1 $\bar{3}$); a = 37.32; b = 57.03; β = 121.2	Col _{ob}	185
8.B.4	50.99(01), 25.49(02), 21.43(11), 19.56(1 $\bar{3}$), 16.91(03), 13.19(04), 10.92(22); a = 34.31; b = 58.88; β = 120	Col _{ob}	185

Table 8.6: d-spacings obtained by XRD measurements and calculated lattice parameters for the mesophases of zigzag-shaped compounds of series 8.C and 8.D

Compound	d-spacings and Lattice parameters/(Å, °)	Phase type	T/(°C)
8.C.2	36.30(11), 32.14(20), 21.75(02), 19.16(31), 18.03(22), 15.98(40), 14.05(13); a = 64.28; b = 43.98	Col _r	160
8.C.3	37.8(11), 32.35(20), 23.21(02), 19.45(31), 16.03(40), 14.96(13), 10.7(24), 9.03(35), 8(06); a = 64.7; b = 46.57	Col _r	165
8.C.5	41.19(11), 33.08(20), 26.14(02), 20.43(31), 16.61(13 or 40); a = 66.16; b = 52.63	Col _r	160
8.C.6	47.61(01), 23.74(02), 16.84(1 $\bar{3}$), 15.94(03), 10.65(22); a = 31.05; b = 51.43; β = 112.23	Col _{ob}	160
8.C.7	50.47(01), 25.16(02), 22.48(11), 18.32(1 $\bar{3}$), 16.69(03/12); 11.7 (22); a = 33.92; b = 55.5; β = 114.6	Col _{ob}	165
8.C.8	52.90(01), 26.44(02), 22.29(11), 17.36(03), 16.58(12), 12.94(13); a = 33.4; b = 58.74; β = 115.86	Col _{ob}	168
8.C.9	53.43(01), 26.46(02), 22.42(11), 17.56(03), 16.5(12); a = 37.25; b = 63.14; β = 122.2	Col _{ob}	170
8.C.10	55.47(01), 27.65(02), 25.94(1 $\bar{1}$), 17.29(12); a = 26.83; b = 56.78; β = 102.36	Col _{ob}	175
8.C.11	49.49(01), 24.74(02), 17.09(1 $\bar{3}$), 16.92(12) 16.8(03); a = 33.21; b = 52.38; β = 109.13	Col _{ob}	160
8.D.2	51.78(01), 24.74(11), 14.83(1 $\bar{4}$); a = 43.36; b = 60.44; β = 121	Col _{ob}	165

8.3.3: Electro-optical studies

Electro-optical measurements were carried out on the mesophases of zigzag-shaped compounds using the standard triangular wave field method. As an example, a sample of compound **8.A.9** was filled in a commercial cell (EHC, Japan) having a thickness 6 μm , treated for homogeneous alignment. Then, the sample was cooled to mesophase and a triangular-wave field was applied. The mesophase did not show any polarization current peak to the applied electric field upto 360 V_{pp} and also there was no noticeable textural change seen indicating the apolar nature of the mesophase. It is expected that this type of compound would not respond to an applied electric field as all the dipolar components cancel with each other. Based on optical textures, XRD and electro-optical studies, possible models have been proposed for the molecular organization in the Col_{ob} and Col_r phases of these zigzag-shaped compounds and the same are shown in figures **8.10.a** and **8.10.b** respectively.

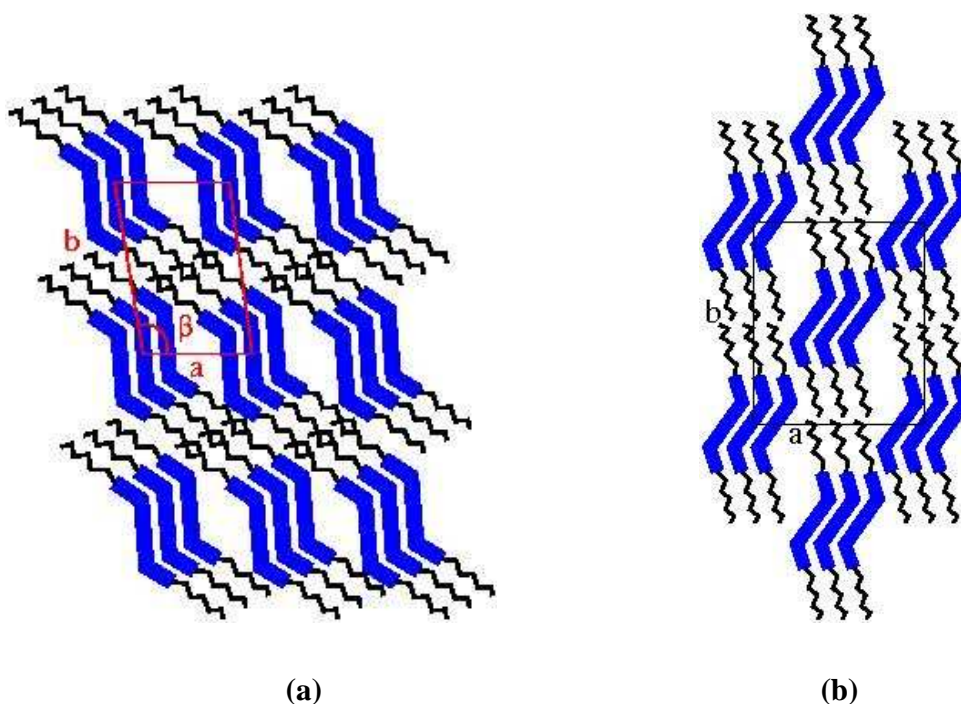


Figure 8.10: A proposed model structure for (a) Col_{ob} phase and (b) Col_r phase exhibited by the zigzag-shaped compounds.

Comparison of transition temperatures and thermal range of Col_{ob} phase in compounds of series 8.A, 8.B, 8.C and 8.D

The four series of compounds differ from one another in terms of terminal *n*-alkyl chain (compound 8.A.13 and 8.C.11), *n*-alkoxy chain (series 8.A and 8.C), 3-fluoro-*n*-alkoxy chain (compound 8.A.12 and 8.C.10) and 4-*n*-alkylbiphenyl groups (series 8.B and 8.D). For comparison the transition temperatures are shown as a bar diagram in figure 8.11. As can be seen in the diagram, the transition temperatures and the thermal range for the Col_{ob} phase of the *n*-alkyl- and *n*-alkoxy chain containing compounds are comparable. It is clear from this diagram, the melting points are low for series 8.C and the thermal range of the mesophase is quite large. Hence, more homologues of this series have been synthesized and investigated.

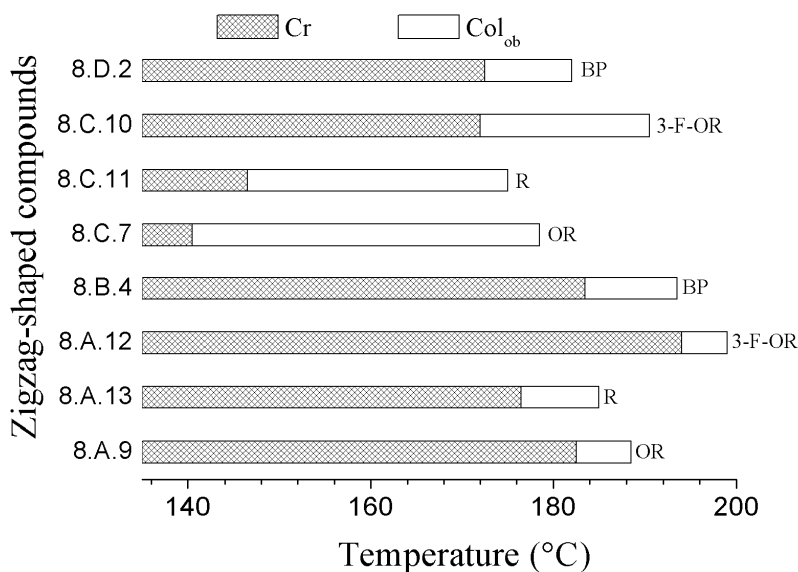


Figure 8.11: A bar diagram showing the transition temperatures and the thermal range of the mesophases for the four different series of compounds containing, *n*-alkyl, *n*-alkoxy, 3-fluoro-*n*-alkoxy and *n*-alkylbiphenyl units.

8.4: Summary

Several new series of symmetrical and unsymmetrical eight-ring zigzag-shaped compounds were designed and synthesized. All these compounds are derived from 3-hydroxybenzoic acid. In order to study the structure-property relationships, four series of compounds viz. **8.A**, **8.B**, **8.C** and **8.D** were synthesized and their mesomorphic properties investigated. The occurrence of the mesophase appears to depend mainly on the terminal chain length, and two different mesophases have been observed. The lower homologues exhibit a columnar phase with a rectangular lattice while the higher homologues exhibit a columnar phase with an oblique lattice and on the basis of experimental studies, these mesophases have been designated as Col_r and Col_{ob} phases respectively. These studies reveal that the mesophase gets stabilized in compounds of series **C** and interestingly the introduction of a fluoro substituent *ortho* to the terminal chain destabilizes the mesophase in contrast to that observed in polar BC compounds. To the best of our knowledge, these represent the first examples of zigzag-shaped compounds exhibiting a mesophase.

Experimental

3-(Benzyloxy)benzoic acid, **8.a**

This was prepared following a procedure described in the literature [12].

Biphenyl-4-4'-diyl bis(3-benzyloxybenzoate), **8.c**

A mixture of 3-benzyloxybenzoic acid, **8.c** (2.69 g, 11.82 mmol) and biphenyl-4,4'-diol, **8.b** (1.1 g, 5.91 mmol) was stirred in anhydrous dichloromethane in the presence of a catalytic amount of 4-(*N,N*-dimethylamino)pyridine (DMAP). To this reaction mixture was added *N,N'*-dicyclohexylcarbodiimide (DCC, 2.68 g, 13.01 mmol) and stirred overnight at room temperature. Thus, the dicyclohexylurea formed was filtered off and washed with chloroform several times. Removal of solvent from the filtrate gave a white material. This material was purified by column chromatography on silica gel using a mixture of 1% ethylacetate in chloroform as an eluent. Evaporation of the solvent from the eluate gave compound **8.c** which was further crystallized from a mixture of chloroform and acetonitrile. Yield: 3.2 g (89%); mp 214-215 °C; IR (nujol) ν_{\max} : 2953, 2924, 2854, 1735, 1728, 1599, 1591, 1492, 1440, 1377, 1321 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.85 (d, $J = 8$ Hz, 4H, Ar-H), 7.65 (d, $J = 8.4$ Hz, 4H, Ar-H), 7.49 (t, $J = 1.6$ Hz, 2H, Ar-H), 7.47-7.4 (m, 6H, Ar-H), 7.36 (d, $J = 7.2$ Hz, 2H, Ar-H), 7.3 (d, $J = 8.8$ Hz, 6H, Ar-H), 7.28 (dd, $J_1 = 1.1$ Hz, $J_2 = 4.4$ Hz, 2H, Ar-H), 5.16 (s, 4H, Ar-O-CH₂); Elemental analysis: $\text{C}_{40}\text{H}_{30}\text{O}_6$ requires C 79.19, H 4.97; found C 79.24, H 4.75%.

Biphenyl-4-4'-diyl bis(3-hydroxybenzoate), **8.d**

Compound **8.c** (3 g, 4.95 mmol) was dissolved in 1,4-dioxane and 5% Pd-C catalyst (0.6 g) was added to it. The reaction mixture was stirred at 55 °C in an atmosphere of hydrogen until the required quantity of hydrogen was absorbed. The reaction mixture was filtered hot and removal of the solvent under reduced pressure gave a white material which was crystallized from a mixture of 1,4-dioxane and hexane to give pure compound **8.d**. Yield: 1.68 g (80%); mp 296.5-298 °C; IR (nujol) ν_{\max} : 3427, 2925, 2926, 2854, 2794, 2652, 1716, 1685, 1602, 1491, 1456, 1375, 1363 cm^{-1} ; ^1H NMR (400 MHz, DMSO-d_6) δ : 9.95 (s, 2H, 2 × Ar-OH, exchangeable with D_2O), 7.77 (d, $J = 8.8$ Hz, 4H, Ar-H), 7.58 (d, $J = 8$ Hz, 2H, Ar-H), 7.52 (t, $J = 1.6$ Hz, 2H,

Ar-H), 7.42 (d, $J = 7.6$ Hz, 2H, Ar-H), 7.37 (d, $J = 8.4$ Hz, 4H, Ar-H), 7.12 (dd, $J_1 = 1.6$, $J_2 = 4.8$ Hz, 2H, Ar-H), Elemental analysis: $C_{26}H_{18}O_6$ requires C 73.23, H 4.25; found C 72.96, H 4%.

4-*n*-Alkoxybenzoyloxy-4-benzoic acids, 8.e

The synthesis of 4-*n*-alkoxybenzoyloxy-4-benzoic acids were described in chapter 2.

4-*n*-Alkylbiphenyl-4-carboxylic acids, 8.f

These alkylbiphenyl acids were synthesized following a procedure described in the literature [13].

Biphenyl-4-4'-dilyl bis(3-(4-(4-*n*-heptyloxy)benzoyloxy)benzoyloxy)benzoate, 8.A.1

This was synthesized following a procedure described for the preparation of compound 8.c using biphenyl-4-4'-dilyl bis(3-hydroxybenzoate), 8.d and compound 8.e. Yield: (75%); mp 190 °C; IR (KBr) ν_{\max} : 3072, 2953, 2922, 2854, 1747, 1737, 1608, 1514, 1496, 1377, 1311 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.3 (d, $J = 9.2$ Hz, 4H, Ar-H), 8.16 (d, $J = 7.2$ Hz, 6H, Ar-H), 8.09 (t, $J = 2$ Hz, 2H, Ar-H), 7.65 (d, $J = 8.8$ Hz, 4H, Ar-H), 7.6 (d, $J = 8$ Hz, 2H, Ar-H), 7.53 (dd, $J_1 = 1.2$ Hz, $J_2 = 4.8$ Hz, 2H, Ar-H), 7.39 (d, $J = 9.2$ Hz, 4H, Ar-H), 7.31 (d, $J = 8.8$ Hz, 4H, Ar-H), 6.99 (d, $J = 8.8$ Hz, 4H, Ar-H), 4.05 (t, $J = 6.4$ Hz, 4H, $2 \times \text{Ar-O-CH}_2$ -), 1.84-1.79 (quin, $J = 7.2$ Hz, 4H, $2 \times \text{Ar-O-CH}_2\text{-CH}_2$ -), 1.55-1.26 (m, 16H, $2 \times \text{-(CH}_2\text{)}_4$ -), 0.88 (t, $J = 6.8$ Hz, 6H, $2 \times \text{-CH}_3$); Elemental analysis: $C_{68}H_{62}O_{14}$ requires C 74.03, H 5.66; found C 73.84, H 5.32%.

Biphenyl-4-4'-dilyl bis(3-(4-(4-*n*-nonyloxy)benzoyloxy)benzoyloxy)benzoate, 8.A.2

Yield: (78%); mp 192.5 °C; IR (KBr) ν_{\max} : 3074, 2954, 2922, 2852, 2729, 2667, 1732, 1728, 1608, 1591, 1508, 1456, 1375 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.31 (d, $J = 8.5$ Hz, 4H, Ar-H), 8.16 (d, $J = 8$ Hz, 6H, Ar-H), 8.09 (t, $J = 2$ Hz, 2H, Ar-H), 7.65 (d, $J = 8.8$ Hz, 4H, Ar-H), 7.6 (d, $J = 8$ Hz, 2H, Ar-H), 7.53 (dd, $J_1 = 1.2$ Hz, $J_2 = 4.4$ Hz, 2H, Ar-H), 7.39 (d, $J = 8.8$ Hz, 4H, Ar-H), 7.31 (d, $J = 8.8$ Hz, 4H, Ar-H), 6.99 (d, $J = 8.8$ Hz, 4H, Ar-H), 4.05 (t, $J = 6.5$ Hz, 4H, $2 \times \text{Ar-O-CH}_2$ -), 1.85-1.8 (quin, $J = 7$ Hz, 4H, $2 \times \text{Ar-O-CH}_2\text{-CH}_2$ -), 1.37-1.28 (m, 24H, $2 \times \text{-(CH}_2\text{)}_6$ -), 0.89 (t, $J = 6.5$ Hz, 6H, $2 \times \text{-CH}_3$); Elemental analysis: $C_{72}H_{70}O_{14}$ requires C 74.59, H 6.08; found C 74.47, H 6.47%.

Biphenyl-4-4'-dilyl bis(3-(4-(4-*n*-decyloxy)benzoyloxy)benzoyloxy)benzoate, 8.A.3

Yield: (76%); mp 188 °C; IR (KBr) ν_{\max} : 3074, 2956, 2916, 2948, 2850, 1737, 1730, 1604, 1589, 1510, 1473, 1311 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.31 (d, $J = 8.8$ Hz, 4H, Ar-H), 8.16 (d, $J = 7.2$ Hz, 6H, Ar-H), 8.09 (t, $J = 2$ Hz, 2H, Ar-H), 7.65 (d, $J = 8.8$ Hz, 4H, Ar-H), 7.62 (d, $J = 8$ Hz, 2H, Ar-H), 7.53 (dd, $J_1 = 1.2$ Hz, $J_2 = 4.8$ Hz, 2H, Ar-H), 7.39 (d, $J = 9.2$ Hz, 4H, Ar-H), 7.31 (d, $J = 8.8$ Hz, 4H, Ar-H), 6.99 (d, $J = 8.8$ Hz, 4H, Ar-H), 4.05 (t, $J = 6.4$ Hz, 4H, $2 \times \text{Ar-O-CH}_2-$), 1.85-1.79 (quin, $J = 7.2$ Hz, 4H, $2 \times \text{Ar-O-CH}_2-\text{CH}_2-$), 1.55-1.25 (m, 28H, $2 \times -(\text{CH}_2)_{7-}$), 0.88 (t, $J = 6.8$ Hz, 6H, $2 \times -\text{CH}_3$); Elemental analysis: $\text{C}_{74}\text{H}_{74}\text{O}_{14}$ requires C 74.85, H 6.27; found C 74.75, H 6.25%.

Biphenyl-4-4'-dilyl bis(3-(4-(4-*n*-undecyloxy)benzoyloxy)benzoyloxy)benzoate, 8.A.4

Yield: (76%); mp 187.5 °C; IR (KBr) ν_{\max} : 3061, 2955, 2918, 2854, 2725, 1737, 1730, 1714, 1606, 1591, 1510, 1469, 1313 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.31 (d, $J = 8.5$ Hz, 4H, Ar-H), 8.16 (d, $J = 7.2$ Hz, 6H, Ar-H), 8.09 (t, $J = 2$ Hz, 2H, Ar-H), 7.65 (d, $J = 8.8$ Hz, 4H, Ar-H), 7.55 (d, $J = 8.1$ Hz, 2H, Ar-H), 7.53 (dd, $J_1 = 1.2$ Hz, $J_2 = 4.8$ Hz, 2H, Ar-H), 7.39 (d, $J = 9.2$ Hz, 4H, Ar-H), 7.31 (d, $J = 8.8$ Hz, 4H, Ar-H), 6.99 (d, $J = 8.68$ Hz, 4H, Ar-H), 4.05 (t, $J = 6.42$ Hz, 4H, $2 \times \text{Ar-O-CH}_2-$), 1.85-1.8 (quin, $J = 7.2$ Hz, 4H, $2 \times \text{Ar-O-CH}_2-\text{CH}_2-$), 1.5-1.26 (m, 32H, $2 \times -(\text{CH}_2)_{8-}$), 0.88 (t, $J = 6.6$ Hz, 6H, $2 \times -\text{CH}_3$); Elemental analysis: $\text{C}_{76}\text{H}_{78}\text{O}_{14}$ requires C 75.10, H 6.46; found C 74.75, H 6.70%.

Biphenyl-4-4'-dilyl bis(3-(4-(4-*n*-dodecyloxy)benzoyloxy)benzoyloxy)benzoate, 8.A.5

Yield: (78%); mp 187.5 °C; IR (KBr) ν_{\max} : 3072, 2951, 2920, 2850, 1732, 1728, 1608, 1556, 1510, 1456, 1375 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.31 (d, $J = 8.5$ Hz, 4H, Ar-H), 8.16 (d, $J = 7.2$ Hz, 6H, Ar-H), 8.09 (t, $J = 2$ Hz, 2H, Ar-H), 7.65 (d, $J = 8.8$ Hz, 4H, Ar-H), 7.6 (d, $J = 8$ Hz, 2H, Ar-H), 7.53 (dd, $J_1 = 1.2$ Hz, $J_2 = 4.8$ Hz, 2H, Ar-H), 7.39 (d, $J = 9.2$ Hz, 4H, Ar-H), 7.31 (d, $J = 8.8$ Hz, 4H, Ar-H), 6.99 (d, $J = 8.8$ Hz, 4H, Ar-H), 4.05 (t, $J = 6.5$ Hz, 4H, $2 \times \text{Ar-O-CH}_2-$), 1.85-1.79 (quin, $J = 7.2$ Hz, 4H, $2 \times \text{Ar-O-CH}_2-\text{CH}_2-$), 1.55-1.26 (m, 36H, $2 \times -(\text{CH}_2)_{9-}$), 0.88 (t, $J = 6.4$ Hz, 6H, $2 \times -\text{CH}_3$); Elemental analysis: $\text{C}_{78}\text{H}_{82}\text{O}_{14}$ requires C 75.34, H 6.64; found C 75.46, H 6.62%.

Biphenyl-4-4'-dilyl bis(3-(4-(4-*n*-tridecyloxy)benzoyloxy)benzoyloxy)benzoate, 8.A.6

Yield: (79%); mp 186.5 °C; IR (KBr) ν_{max} : 3063, 2955, 2922, 2850, 1737, 1714, 1608, 1589, 1506, 1469, 1454, 1313 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.3 (d, $J = 9.2$ Hz, 4H, Ar-H), 8.16 (d, $J = 7.2$ Hz, 6H, Ar-H), 8.09 (t, $J = 2$ Hz, 2H, Ar-H), 7.65 (d, $J = 8.5$ Hz, 4H, Ar-H), 7.6 (d, $J = 8$ Hz, 2H, Ar-H), 7.53 (dd, $J_1 = 1.2$ Hz, $J_2 = 4.8$ Hz, 2H, Ar-H), 7.39 (d, $J = 9.2$ Hz, 4H, Ar-H), 7.31 (d, $J = 8.8$ Hz, 4H, Ar-H), 6.99 (d, $J = 8.88$ Hz, 4H, Ar-H), 4.05 (t, $J = 6.4$ Hz, 4H, $2 \times \text{Ar-O-CH}_2$ -), 1.84-1.79 (quin, $J = 7$ Hz, 4H, $2 \times \text{Ar-O-CH}_2\text{-CH}_2$ -), 1.55-1.26 (m, 40H, $2 \times \text{-(CH}_2\text{)}_{10}$ -), 0.88 (t, $J = 6.8$ Hz, 6H, $2 \times \text{-CH}_3$); Elemental analysis: $\text{C}_{80}\text{H}_{86}\text{O}_{14}$ requires C 75.57, H 6.81; found C 75.17, H 6.85%.

Biphenyl-4-4'-dilyl bis(3-(4-(4-*n*-tetradecyloxy)benzoyloxy)benzoyloxy)benzoate, 8.A.7

Yield: (76%); mp 185 °C; IR (KBr) ν_{max} : 3045, 2956, 2916, 2850, 1735, 1730, 1604, 1591, 1512, 1471, 1440, 1311 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.3 (d, $J = 9.2$ Hz, 4H, Ar-H), 8.16 (d, $J = 7.2$ Hz, 6H, Ar-H), 8.09 (t, $J = 2$ Hz, 2H, Ar-H), 7.65 (d, $J = 8.8$ Hz, 4H, Ar-H), 7.6 (d, $J = 8$ Hz, 2H, Ar-H), 7.53 (dd, $J_1 = 1.2$ Hz, $J_2 = 4.8$ Hz, 2H, Ar-H), 7.39 (d, $J = 9.2$ Hz, 4H, Ar-H), 7.31 (d, $J = 8.8$ Hz, 4H, Ar-H), 6.99 (d, $J = 8.8$ Hz, 4H, Ar-H), 4.05 (t, $J = 6.4$ Hz, 4H, $2 \times \text{Ar-O-CH}_2$ -), 1.84-1.79 (quin, $J = 7.2$ Hz, 4H, $2 \times \text{Ar-O-CH}_2\text{-CH}_2$ -), 1.55-1.26 (m, 44H, $2 \times \text{-(CH}_2\text{)}_{11}$ -), 0.88 (t, $J = 6.8$ Hz, 6H, $2 \times \text{-CH}_3$); Elemental analysis: $\text{C}_{82}\text{H}_{90}\text{O}_{14}$ requires C 75.78, H 6.97; found C 76.11, H 7.29%.

Biphenyl-4-4'-dilyl bis(3-(4-(4-*n*-pentadecyloxy)benzoyloxy)benzoyloxy)benzoate, 8.A.8

Yield: (78%); mp 184.5 °C; IR (KBr) ν_{max} : 3063, 2953, 2916, 2848, 1737, 1730, 1695, 1606, 1591, 1494, 1469, 1440, 1396, 1311 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.31 (d, $J = 8.8$ Hz, 4H, Ar-H), 8.16 (d, $J = 8.8$ Hz, 6H, Ar-H), 8.1 (t, $J = 2$ Hz, 2H, Ar-H), 7.65 (d, $J = 8.4$ Hz, 4H, Ar-H), 7.61 (d, $J = 7.6$ Hz, 2H, Ar-H), 7.54 (dd, $J_1 = 1.2$ Hz, $J_2 = 4.8$ Hz, 2H, Ar-H), 7.4 (d, $J = 9.2$ Hz, 4H, Ar-H), 7.32 (d, $J = 6.8$ Hz, 4H, Ar-H), 6.99 (d, $J = 9.2$ Hz, 4H, Ar-H), 4.06 (t, $J = 8$ Hz, 4H, $2 \times \text{Ar-O-CH}_2$ -), 1.85-1.8 (quin, $J = 7.2$ Hz, 4H, $2 \times \text{Ar-O-CH}_2\text{-CH}_2$ -), 1.5-1.27 (m, 48H, $2 \times \text{-(CH}_2\text{)}_{12}$ -), 0.89 (t, $J = 6.4$ Hz, 6H, $2 \times \text{-CH}_3$); Elemental analysis: $\text{C}_{84}\text{H}_{94}\text{O}_{14}$ requires C 75.99, H 7.13; found C 76.19, H 7.35%.

Biphenyl-4-4'-dilyl bis(3-(4-(4-*n*-hexadecyloxy)benzoyloxy)benzoyloxy)benzoate, 8.A.9

Yield: (77%); mp 182.5 °C; IR (KBr) ν_{\max} : 3074, 2955, 2916, 2848, 1735, 1732, 1606, 1510, 1500, 1471, 1440, 1311 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.31 (d, $J = 8.8$ Hz, 4H, Ar-H), 8.16 (d, $J = 8$ Hz, 6H, Ar-H), 8.09 (t, $J = 2$ Hz, 2H, Ar-H), 7.65 (d, $J = 8.8$ Hz, 4H, Ar-H), 7.6 (d, $J = 8$ Hz, 2H, Ar-H), 7.53 (dd, $J_1 = 1.2$ Hz, $J_2 = 4.4$ Hz, 2H, Ar-H), 7.39 (d, $J = 8.8$ Hz, 4H, Ar-H), 7.31 (d, $J = 8.8$ Hz, 4H, Ar-H), 6.99 (d, $J = 8.8$ Hz, 4H, Ar-H), 4.05 (t, $J = 6.8$ Hz, 4H, 2 \times Ar-O-CH₂-), 1.86-1.79 (quin, $J = 6.8$ Hz, 4H, 2 \times Ar-O-CH₂-CH₂-), 1.5-1.26 (m, 52H, 2 \times -(CH₂)₁₃-), 0.88 (t, $J = 6.8$ Hz, 6H, 2 \times -CH₃); Elemental analysis: C₈₆H₉₈O₁₄ requires C 76.26, H 7.25; found C 76.14, H 7.1%.

Biphenyl-4-4'-dilyl bis(3-(4-(4-*n*-octadecyloxy)benzoyloxy)benzoyloxy)benzoate, 8.A.10

Yield: (76%); mp 180 °C; IR (KBr) ν_{\max} : 3074, 2955, 2914, 2848, 2756, 1735, 1730, 1695, 1604, 1589, 1471, 1440, 1311 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.31 (d, $J = 8.8$ Hz, 4H, Ar-H), 8.16 (d, $J = 8$ Hz, 6H, Ar-H), 8.1 (t, $J = 3.6$ Hz, 2H, Ar-H), 7.66 (d, $J = 8.8$ Hz, 4H, Ar-H), 7.61 (d, $J = 8$ Hz, 2H, Ar-H), 7.54 (dd, $J_1 = 1.2$ Hz, $J_2 = 4.8$ Hz, 2H, Ar-H), 7.4 (d, $J = 8.8$ Hz, 4H, Ar-H), 7.32 (d, $J = 8.8$ Hz, 4H, Ar-H), 7 (d, $J = 8.8$ Hz, 4H, Ar-H), 4.06 (t, $J = 6.4$ Hz, 4H, 2 \times Ar-O-CH₂-), 1.85-1.79 (quin, $J = 8$ Hz, 4H, 2 \times Ar-O-CH₂-CH₂-), 1.5-1.26 (m, 60H, 2 \times -(CH₂)₁₅-), 0.88 (t, $J = 8$ Hz, 6H, 2 \times -CH₃); Elemental analysis: C₉₀H₁₀₆O₁₄ requires C 76.57, H 7.56; found C 76.67, H 7.89%.

Biphenyl-4-4'-dilyl bis(3-(4-(4-*n*-icosodecyloxy)benzoyloxy)benzoyloxy)benzoate, 8.A.11

Yield: (75%); mp 178.5 °C; IR (KBr) ν_{\max} : 3074, 3063, 2955, 2916, 2848, 2771, 1737, 1730, 1695, 1604, 1589, 1471, 1440, 1311 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.31 (d, $J = 9.2$ Hz, 4H, Ar-H), 8.16 (d, $J = 7.2$ Hz, 6H, Ar-H), 8.1 (t, $J = 2$ Hz, 2H, Ar-H), 7.65 (d, $J = 8.8$ Hz, 4H, Ar-H), 7.61 (d, $J = 8$ Hz, 2H, Ar-H), 7.54 (dd, $J_1 = 1.2$ Hz, $J_2 = 4.8$ Hz, 2H, Ar-H), 7.39 (d, $J = 9.2$ Hz, 4H, Ar-H), 7.31 (d, $J = 8.8$ Hz, 4H, Ar-H), 6.99 (d, $J = 8.8$ Hz, 4H, Ar-H), 4.05 (t, $J = 6.4$ Hz, 4H, 2 \times Ar-O-CH₂-), 1.84-1.79 (quin, $J = 7.2$ Hz, 4H, 2 \times Ar-O-CH₂-CH₂-), 1.55-1.26 (m, 68H, 2 \times -(CH₂)₁₇-), 0.88 (t, $J = 8$ Hz, 6H, 2 \times -CH₃); Elemental analysis: C₉₄H₁₁₄O₁₄ requires C 76.93, H 7.82; found C 76.50, H 8.21%.

Biphenyl-4-4'-dilyl bis(3-(4-(4-*n*-octadecyloxy)-3-fluorobenzoyloxy)benzoyloxy)benzoate, 8.A.12

Yield: (70%); mp 194 °C; IR (KBr) ν_{\max} : 3063, 2922, 2952, 2725, 1737, 1732, 1695, 1604, 1589, 1471, 1454, 1377, 1311 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 8.31 (d, $J = 8.8$ Hz, 4H, Ar-H), 8.16 (d, $J = 8$ Hz, 2H, Ar-H), 8.09 (t, $J = 2$ Hz, 2H, Ar-H), 7.97 (d, $J = 9.2$ Hz, 2H, Ar-H), 7.91 (d, $J = 9.6$ Hz, 2H, Ar-H), 7.66-7.59 (m, 6H, Ar-H) 7.54 (dd, $J_1 = 1.2$ Hz, $J_2 = 6$ Hz, 2H, Ar-H), 7.39 (d, $J = 8.8$ Hz, 4H, Ar-H), 7.31 (d, $J = 8.8$ Hz, 4H, Ar-H), 7.05 (t, $J = 8$ Hz, 2H, Ar-H), 4.13 (t, $J = 6.8$ Hz, 4H, $2 \times \text{Ar-O-CH}_2^-$), 1.87-1.83 (quin, $J = 7.2$ Hz, 4H, $2 \times \text{Ar-O-CH}_2-\underline{\text{CH}}_2^-$), 1.51-1.26 (m, 60H, $2 \times -(\text{CH}_2)_{15}-$), 0.87 (t, $J = 6.8$ Hz, 6H, $2 \times -\text{CH}_3$); Elemental analysis: $\text{C}_{90}\text{H}_{104}\text{F}_2\text{O}_{14}$ requires C 74.66, H 7.24; found C 74.27, H 7.12%.

Biphenyl-4-4'-dilyl bis(3-(4-(4-*n*-hexadecyl)benzoyloxy)benzoyloxy)benzoate, 8.A.13

Yield: (68%); mp 176.5 °C; IR (KBr) ν_{\max} : 3074, 2953, 2920, 2850, 2725, 1735, 1730, 1602, 1591, 1471, 1444, 1377 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 8.31 (d, $J = 6.8$ Hz, 4H, Ar-H), 8.16 (d, $J = 7.6$ Hz, 2H, Ar-H), 8.14 (d, $J = 8.4$ Hz, 2H, Ar-H), 8.09 (t, $J = 2$ Hz, 2H, Ar-H), 7.64 (d, $J = 6.8$ Hz, 4H, Ar-H), 7.6 (d, $J = 8$ Hz, 2H, Ar-H), 7.54 (dd, $J_1 = 1.2$ Hz, $J_2 = 4.4$ Hz, 2H, Ar-H), 7.39 (d, $J = 8.8$ Hz, 4H, Ar-H), 7.32 (t, $J = 8.32$ Hz, 8H, Ar-H), 2.71 (t, $J = 7.6$ Hz, 4H, $2 \times \text{Ar-CH}_2^-$), 1.71-1.63 (quin, $J = 7.6$ Hz, 4H, $2 \times \text{Ar-CH}_2-\underline{\text{CH}}_2^-$), 1.37-1.29 (m, 52H, $2 \times -(\text{CH}_2)_{13}-$), 0.88 (t, $J = 6.4$ Hz, 6H, $2 \times -\text{CH}_3$); Elemental analysis: $\text{C}_{86}\text{H}_{98}\text{O}_{12}$ requires C 78.04, H 7.45; found C 77.88, H 7.49%.

Biphenyl-4-4'-dilyl bis(3-(4-(4-*n*-decylbiphenyl)carbonyloxy)benzoate, 8.B.1

Yield: (65%); mp 191.5 °C; IR (KBr) ν_{\max} : 3074, 2955, 2922, 2852, 2721, 1745, 1728, 1604, 1593, 1471, 1460, 1377, 1311 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 8.28 (d, $J = 8.4$ Hz, 4H, Ar-H), 8.16 (d, $J = 8$ Hz, 2H, Ar-H), 8.1 (t, $J = 2$ Hz, 2H, Ar-H), 7.75 (d, $J = 8.8$ Hz, 4H, Ar-H), 7.65 (d, $J = 8.5$ Hz, 4H, Ar-H), 7.62 (t, 2H, Ar-H), 7.59 (d, $J = 8.2$ Hz, 4H, Ar-H), 7.53 (dd, $J_1 = 1.4$ Hz, $J_2 = 6.5$ Hz, 2H, Ar-H), 7.31 (dd, $J_1 = 2$ Hz, $J_2 = 6$ Hz, 8H, Ar-H), 2.67 (t, $J = 7.5$ Hz, 4H, $2 \times \text{Ar-CH}_2^-$), 1.69-1.61 (quin, $J = 7.5$ Hz, 4H, $2 \times \text{Ar-CH}_2-\underline{\text{CH}}_2^-$), 1.38-1.27 (m, 28H, $2 \times -(\text{CH}_2)_{7}-$), 0.88 (t, $J = 6.5$ Hz, 6H, $2 \times -\text{CH}_3$); Elemental analysis: $\text{C}_{72}\text{H}_{74}\text{O}_8$ requires C 81.03, H 6.98; found C 81.23, H 7.03%.

Biphenyl-4-4'-dilyl bis(3-(4-(4-*n*-dodecylbiphenyl)carbonyloxy)benzoate, 8.B.2

Yield: (63%); mp 190.5 °C; IR (KBr) ν_{\max} : 3072, 2953, 2920, 2752, 2727, 1735, 1728, 1618, 1593, 1471, 1462, 1454, 1377 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.27 (d, $J = 8.4$ Hz, 4H, Ar-H), 8.16 (d, $J = 8$ Hz, 2H, Ar-H), 8.1 (t, $J = 2$ Hz, 2H, Ar-H), 7.75 (d, $J = 8.2$ Hz, 4H, Ar-H), 7.64 (d, $J = 8.8$ Hz, 4H, Ar-H), 7.61 (t, 2H, Ar-H), 7.59 (d, $J = 8$ Hz, 4H, Ar-H), 7.53 (dd, $J_1 = 1.5$ Hz, $J_2 = 6.5$ Hz, 2H, Ar-H), 7.31 (dd, $J_1 = 2$ Hz, $J_2 = 6$ Hz, 8H, Ar-H), 2.67 (t, $J = 7.4$ Hz, 4H, $2 \times \text{Ar-CH}_2$ -), 1.69-1.62 (quin, $J = 7.2$ Hz, 4H, $2 \times \text{Ar-CH}_2\text{-CH}_2$ -), 1.39-1.27 (m, 36H, $2 \times \text{-(CH}_2\text{)}_9$ -), 0.88 (t, $J = 6.8$ Hz, 6H, $2 \times \text{-CH}_3$); Elemental analysis: $\text{C}_{76}\text{H}_{82}\text{O}_8$ requires C 81.25, H 7.35; found C 81.65, H 7.79%.

Biphenyl-4-4'-dilyl bis(3-(4-(4-*n*-tetradecylbiphenyl)carbonyloxy)benzoate, 8.B.3

Yield: (68%); mp 187.5 °C; IR (KBr) ν_{\max} : 3074, 2955, 2918, 2850, 2756, 1743, 1735, 1732, 1695, 1604, 1591, 1471, 1456, 1375, 1311 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.27 (d, $J = 8.4$ Hz, 4H, Ar-H), 8.16 (d, $J = 8$ Hz, 2H, Ar-H), 8.1 (t, $J = 2$ Hz, 2H, Ar-H), 7.74 (d, $J = 8.8$ Hz, 4H, Ar-H), 7.64 (d, $J = 8.8$ Hz, 4H, Ar-H), 7.61 (t, 2H, Ar-H), 7.59 (d, $J = 8$ Hz, 4H, Ar-H), 7.53 (dd, $J_1 = 1.5$ Hz, $J_2 = 6.5$ Hz, 2H, Ar-H), 7.31 (dd, $J_1 = 2$ Hz, $J_2 = 6$ Hz, 8H, Ar-H), 2.67 (t, $J = 7.6$ Hz, 4H, $2 \times \text{Ar-CH}_2$ -), 1.69-1.62 (quin, $J = 7.2$ Hz, 4H, $2 \times \text{Ar-CH}_2\text{-CH}_2$ -), 1.39-1.27 (m, 44H, $2 \times \text{-(CH}_2\text{)}_{11}$ -), 0.88 (t, $J = 6.8$ Hz, 6H, $2 \times \text{-CH}_3$); Elemental analysis: $\text{C}_{80}\text{H}_{90}\text{O}_8$ requires C 81.46, H 7.68; found C 81.01, H 7.39%.

Biphenyl-4-4'-dilyl bis(3-(4-(4-*n*-hexadecylbiphenyl)carbonyloxy)benzoate, 8.B.4

Yield: (65%); mp 183.5 °C; IR (KBr) ν_{\max} : 3062, 2953, 2922, 2852, 2725, 1745, 1730, 1606, 1593, 1491, 1467, 1454, 1377, 1313 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.27 (d, $J = 8.4$ Hz, 4H, Ar-H), 8.16 (d, $J = 7.6$ Hz, 2H, Ar-H), 8.1 (t, $J = 1.6$ Hz, 2H, Ar-H), 7.74 (d, $J = 8.8$ Hz, 4H, Ar-H), 7.64 (d, $J = 8.8$ Hz, 4H, Ar-H), 7.61 (t, 2H, Ar-H), 7.59 (d, $J = 8.4$ Hz, 4H, Ar-H), 7.54 (dd, $J_1 = 1.2$ Hz, $J_2 = 7.2$ Hz, 2H, Ar-H), 7.31 (dd, $J_1 = 2.4$ Hz, $J_2 = 6$ Hz, 8H, Ar-H), 2.67 (t, $J = 7.6$ Hz, 4H, $2 \times \text{Ar-CH}_2$ -), 1.69-1.61 (quin, $J = 7.2$ Hz, 4H, $2 \times \text{Ar-CH}_2\text{-CH}_2$ -), 1.39-1.27 (m, 52H, $2 \times \text{-(CH}_2\text{)}_{13}$ -), 0.87 (t, $J = 6.4$ Hz, 6H, $2 \times \text{-CH}_3$); Elemental analysis: $\text{C}_{84}\text{H}_{98}\text{O}_8$ requires C 81.65, H 7.98; found C 81.29, H 7.90%.

4-Benzyloxyphenyl-4-benzyloxybenzoate, 8.i

This was synthesized following a procedure described for the preparation of compound **8.c** using 4-benzyloxybenzoic acid, **8.g** (4 g, 17.54 mmol), 4-benzyloxyphenol, **8.h** (3.85 g, 19.29 mmol) and DCC (3.98 g, 19.29 mmol) in the presence of a catalytic amount of DMAP in dichloromethane. This material was purified by column chromatography on silica gel using chloroform as an eluent. Evaporation of the solvent from the eluate gave compound **8.i** which was further crystallized from a mixture of chloroform and petroleum ether. Yield: 5.17 g (72%); mp 172.5-174 °C; IR (nujol) ν_{\max} : 3044, 2953, 2924, 2852, 2723, 1726, 1697, 1602, 1583, 1508, 1454, 1377 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.14 (d, $J = 8$ Hz, 2H, Ar-H), 7.46-7.33 (m, 10H, Ar-H), 7.11 (d, $J = 8.8$ Hz, 2H, Ar-H), 7.05 (d, $J = 8.8$ Hz, 2H, Ar-H), 7 (d, $J = 9.2$ Hz, 2H, Ar-H), 5.16 (s, 2H, Ar-O-CH₂-); 5.07 (s, 2H, Ar-O-CH₂-); Elemental analysis: C₂₇H₂₂O₄ requires C 79.01, H 5.39; found C 78.76, H 5.04%.

4-Hydroxyphenyl-4-hydroxybenzoate, 8.j

This was synthesized following a procedure described for the preparation of compound **8.d** using compound **8.i**. Yield: 2.46 g (88%); mp 248-249.5 °C; IR (nujol) ν_{\max} : 3319, 3248, 3064, 3010, 2955, 2924, 2854, 1693, 1681, 1612, 1591, 1508, 1446, 1377, cm^{-1} ; ^1H NMR (400 MHz, CD_3COCD_3) δ : 9.22 (s, 1H, Ar-OH, exchangeable with D₂O), 8.34 (s, 1H, Ar-OH, exchangeable with D₂O), 8 (d, $J = 8.8$ Hz, 2H, Ar-H), 7.02 (d, $J = 9.2$ Hz, 2H, Ar-H), 6.96 (d, $J = 8.8$ Hz, 2H, Ar-H), 6.86 (d, $J = 8.8$ Hz, 2H, Ar-H); Elemental analysis: C₁₃H₁₀O₄ requires C 67.82, H 4.37; found C 67.42, H 4.03%.

4-(4-(3-(Benzloxy)benzoyloxy)benzoyloxy)phenyl 3-benzyloxybenzoate, 8.k

This was synthesized following a procedure described for the preparation of compound **8.c** using 3-benzyloxybenzoic acid, **8.a** (4.16 g, 18.24 mmol), 4-benzyloxyphenol, **8.j** (2 g, 8.69 mmol) and DCC (3.94 g, 19.13 mmol) in the presence of a catalytic amount of DMAP in dichloromethane. Yield: 3.72 g (66%); mp 130-131.5 °C; IR (nujol) ν_{\max} : 3066, 2954, 2922, 2852, 2721, 2671, 1735, 1732, 1599, 1506, 1458, 1440, 1377, 1363 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.3 (d, $J = 8.8$ Hz, 2H, Ar-H), 7.81 (t, $J = 1.6$ Hz, 4H, Ar-H), 7.48-7.34 (m, 15H, Ar-H), 7.27 (d, $J = 9.2$ Hz, 5H, Ar-H), 5.15 (s, 2H, Ar-O-CH₂-); Elemental analysis: C₄₁H₃₀O₈ requires C 75.68, H 4.64; found C 75.48, H 4.70%.

4-(4-(3-(3-Hydroxybenzoyloxy)benzoyloxy)phenyl 3-hydroxybenzoate, 8.l

This was synthesized following a procedure described for the preparation of compound **8.d** using compound **8.k**. Yield: 2.3 g (90%); mp 251-252.5 °C; IR (nujol) ν_{\max} : 3462, 3066, 2955, 2922, 2854, 2723, 1732, 1712, 1602, 1504, 1491, 1454, 1377 cm^{-1} ; ^1H NMR (400 MHz, CD_3COCD_3) δ : 8.79 (s, 2H, 2 \times Ar-OH, exchangeable with D_2O), 8.3 (d, $J = 8.8$ Hz, 2H, Ar-H), 7.68-7.63 (m, 4H, Ar-H), 7.53 (d, $J = 8.8$ Hz, 2H, Ar-H), 7.45 (m, 6H, Ar-H), 7.19 (t, $J = 8.8$ Hz, 2H, Ar-H); Elemental analysis: $\text{C}_{27}\text{H}_{18}\text{O}_6$ requires C 68.93, H 3.85; found C 68.59, H 3.4%.

4-(4-(3-(4-(4-*n*-Heptyloxybenzoyloxy)benzoyloxy)benzoyloxy)benzoyloxy)phenyl 3-(4-(4-*n*-heptyloxybenzoyloxy)benzoyloxy)benzoate, 8.C.1

Yield: (72%); mp 186 °C; IR (KBr) ν_{\max} : 3074, 2955, 2848, 2721, 1735, 1730, 1604, 1589, 1506, 1471, 1377, 1311 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.31 (d, $J = 8.6$ Hz, 6H, Ar-H), 8.16 (d, $J = 8.6$ Hz, 6H, Ar-H), 8.09 (d, $J = 8$ Hz, 2H, Ar-H), 7.62 (d, $J = 8$ Hz, 2H, Ar-H), 7.54 (t, $J = 8.4$ Hz, 2H, Ar-H), 7.4 (dd, $J_1 = 4.4$ Hz, $J_2 = 8$ Hz, 6H, Ar-H), 7.3 (t, 4H, Ar-H), 6.99 (d, $J = 8.6$ Hz, 4H, Ar-H), 4.06 (t, $J = 6.8$ Hz, 4H, 2 \times Ar-O-CH₂-), 1.86-1.8 (quin, $J = 7.8$ Hz, 4H, 2 \times Ar-O-CH₂-CH₂-), 1.51-1.31 (m, 16H, 2 \times -(CH₂)₄-), 0.9 (t, $J = 8$ Hz, 6H, 2 \times -CH₃); Elemental analysis: $\text{C}_{69}\text{H}_{62}\text{O}_{16}$ requires C 72.24, H 5.44; found C 71.83, H 5.23%.

4-(4-(3-(4-(4-*n*-Decyloxybenzoyloxy)benzoyloxy)benzoyloxy)benzoyloxy)phenyl 3-(4-(4-*n*-decyloxybenzoyloxy)benzoyloxy)benzoate, 8.C.2

Yield: (74%); mp 180.5 °C; IR (KBr) ν_{\max} : 3063, 2953, 2922, 2852, 2725, 1735, 1730, 1604, 1589, 1508, 1460, 1377, 1340 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.31 (d, $J = 8.2$ Hz, 6H, Ar-H), 8.16 (d, $J = 8.2$ Hz, 6H, Ar-H), 8.09 (d, $J = 8.6$ Hz, 2H, Ar-H), 7.62 (d, $J = 8$ Hz, 2H, Ar-H), 7.54 (t, $J = 8.4$ Hz, 2H, Ar-H), 7.4 (dd, $J_1 = 4.2$ Hz, $J_2 = 8$ Hz, 6H, Ar-H), 7.3 (t, 4H, Ar-H), 6.99 (d, $J = 8.6$ Hz, 4H, Ar-H), 4.05 (t, $J = 6.8$ Hz, 4H, 2 \times Ar-O-CH₂-), 1.86-1.79 (quin, $J = 7.8$ Hz, 4H, 2 \times Ar-O-CH₂-CH₂-), 1.51-1.26 (m, 28H, 2 \times -(CH₂)₇-), 0.88 (t, $J = 8$ Hz, 6H, 2 \times -CH₃); Elemental analysis: $\text{C}_{75}\text{H}_{74}\text{O}_{16}$ requires C 73.15, H 6.05; found C 73.55, H 6.27%.

4-(4-(3-(4-(4-*n*-Undecyloxybenzoyloxy)benzoyloxy)benzoyloxy)benzoyloxy)phenyl 3-(4-(4-*n*-undecyloxybenzoyloxy)benzoyloxy)benzoate, 8.C.3

Yield: (74%); mp 177.5 °C; IR (KBr) ν_{\max} : 3074, 2955, 2922, 2852, 1737, 1732, 1604, 1591, 1508, 1462, 1454, 1377, 1311 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.30 (d, $J = 8.8$ Hz, 6H, Ar-H), 8.15 (d, $J = 8.4$ Hz, 6H, Ar-H), 8.09 (d, $J = 8$ Hz, 2H, Ar-H), 7.62 (d, $J = 8$ Hz, 2H, Ar-H), 7.54 (t, $J = 8.4$ Hz, 2H, Ar-H), 7.4 (dd, $J_1 = 3.8$ Hz, $J_2 = 8$ Hz, 6H, Ar-H), 7.3 (t, 4H, Ar-H), 6.99 (d, $J = 8.8$ Hz, 4H, Ar-H), 4.05 (t, $J = 6.8$ Hz, 4H, $2 \times \text{Ar-O-CH}_2$ -), 1.86-1.79 (quin, $J = 7.4$ Hz, 4H, $2 \times \text{Ar-O-CH}_2\text{-CH}_2$ -), 1.50-1.26 (m, 32H, $2 \times \text{-(CH}_2\text{)}_8$ -), 0.88 (t, $J = 8.2$ Hz, 6H, $2 \times \text{-CH}_3$); Elemental analysis: $\text{C}_{77}\text{H}_{78}\text{O}_{16}$ requires C 73.43, H 6.24; found C 73.21, H 6.52%.

4-(4-(3-(4-(4-*n*-Dodecyloxybenzoyloxy)benzoyloxy)benzoyloxy)benzoyloxy)phenyl 3-(4-(4-*n*-dodecyloxybenzoyloxy)benzoyloxy)benzoate, 8.C.4

Yield: (71%); mp 164 °C; IR (KBr) ν_{\max} : 3074, 2953, 2920, 2850, 2726, 1737, 1732, 1606, 1591, 1471, 1454, 1377, 1311 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.3 (d, $J = 8.2$ Hz, 6H, Ar-H), 8.15 (d, $J = 8.88$ Hz, 6H, Ar-H), 8.09 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.61 (d, $J = 8.2$ Hz, 2H, Ar-H), 7.55 (t, $J = 8$ Hz, 2H, Ar-H), 7.4 (dd, $J_1 = 4$ Hz, $J_2 = 7.8$ Hz, 6H, Ar-H), 7.3 (t, 4H, Ar-H), 6.99 (d, $J = 8.8$ Hz, 4H, Ar-H), 4.05 (t, $J = 6.4$ Hz, 4H, $2 \times \text{Ar-O-CH}_2$ -), 1.86-1.79 (quin, $J = 8$ Hz, 4H, $2 \times \text{Ar-O-CH}_2\text{-CH}_2$ -), 1.51-1.26 (m, 36H, $2 \times \text{-(CH}_2\text{)}_9$ -), 0.88 (t, $J = 8$ Hz, 6H, $2 \times \text{-CH}_3$); Elemental analysis: $\text{C}_{79}\text{H}_{82}\text{O}_{16}$ requires C 73.70, H 6.41; found C 73.49, H 6.34%.

4-(4-(3-(4-(4-*n*-Tridecyloxybenzoyloxy)benzoyloxy)benzoyloxy)benzoyloxy)phenyl 3-(4-(4-*n*-tridecyloxybenzoyloxy)benzoyloxy)benzoate, 8.C.5

Yield: (73%); mp 164.5 °C; IR (KBr) ν_{\max} : 3063, 2953, 2922, 2854, 2727, 1735, 1730, 1604, 1591, 1508, 1454, 1377, 1311 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.31 (d, $J = 8.4$ Hz, 6H, Ar-H), 8.16 (d, $J = 8.6$ Hz, 6H, Ar-H), 8.09 (d, $J = 8$ Hz, 2H, Ar-H), 7.62 (d, $J = 8$ Hz, 2H, Ar-H), 7.54 (t, $J = 8.4$ Hz, 2H, Ar-H), 7.4 (dd, $J_1 = 4.2$ Hz, $J_2 = 8$ Hz, 6H, Ar-H), 7.3 (t, 4H, Ar-H), 6.99 (d, $J = 8.6$ Hz, 4H, Ar-H), 4.05 (t, $J = 6.8$ Hz, 4H, $2 \times \text{Ar-O-CH}_2$ -), 1.86-1.79 (quin, $J = 7.8$ Hz, 4H, $2 \times \text{Ar-O-CH}_2\text{-CH}_2$ -), 1.51-1.26 (m, 40H, $2 \times \text{-(CH}_2\text{)}_{10}$ -), 0.88 (t, $J = 8$ Hz, 6H, $2 \times \text{-CH}_3$); Elemental analysis: $\text{C}_{81}\text{H}_{86}\text{O}_{16}$ requires C 73.95, H 6.59; found C 74.18, H 6.83%.

4-(4-(3-(4-(4-*n*-Tetradecyloxybenzoyloxy)benzoyloxy)benzoyloxy)benzoyloxy)phenyl 3-(4-(4-*n*-tetradecyloxybenzoyloxy)benzoyloxy)benzoate, 8.C.6

Yield: (72%); mp 161.5 °C; IR (KBr) ν_{\max} : 3074, 2955, 2922, 2852, 2721, 1735, 1732, 1604, 1591, 1456, 1377 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.31 (d, $J = 8.6$ Hz, 6H, Ar-H), 8.16 (d, $J = 8.6$ Hz, 6H, Ar-H), 8.09 (d, $J = 8$ Hz, 2H, Ar-H), 7.62 (d, $J = 8$ Hz, 2H, Ar-H), 7.54 (t, $J = 8.4$ Hz, 2H, Ar-H), 7.4 (dd, $J_1 = 4.5$ Hz, $J_2 = 8$ Hz, 6H, Ar-H), 7.3 (t, 4H, Ar-H), 6.99 (d, $J = 8.4$ Hz, 4H, Ar-H), 4.05 (t, $J = 6.6$ Hz, 4H, $2 \times \text{Ar-O-CH}_2$ -), 1.85-1.8 (quin, $J = 7.8$ Hz, 4H, $2 \times \text{Ar-O-CH}_2\text{-CH}_2$ -), 1.51-1.26 (m, 44H, $2 \times \text{-(CH}_2\text{)}_{11}$ -), 0.88 (t, $J = 8$ Hz, 6H, $2 \times \text{-CH}_3$); Elemental analysis: $\text{C}_{83}\text{H}_{90}\text{O}_{16}$ requires C 74.2, H 6.74; found C 74.43, H 6.42%.

4-(4-(3-(4-(4-*n*-Hexadecyloxybenzoyloxy)benzoyloxy)benzoyloxy)benzoyloxy)phenyl 3-(4-(4-*n*-hexadecyloxybenzoyloxy)benzoyloxy)benzoate, 8.C.7

Yield: (76%); mp 140.5 °C; IR (KBr) ν_{\max} : 3066, 2953, 2916, 2850, 2719, 1735, 1732, 1604, 1589, 1471, 1454, 1377 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.31 (d, $J = 8.8$ Hz, 6H, Ar-H), 8.15 (d, $J = 8.8$ Hz, 6H, Ar-H), 8.09 (d, $J = 8$ Hz, 2H, Ar-H), 7.61 (d, $J = 8$ Hz, 2H, Ar-H), 7.54 (t, $J = 8.4$ Hz, 2H, Ar-H), 7.4 (dd, $J_1 = 4.5$ Hz, $J_2 = 8$ Hz, 6H, Ar-H), 7.3 (t, 4H, Ar-H), 6.99 (d, $J = 8.8$ Hz, 4H, Ar-H), 4.06 (t, $J = 6.8$ Hz, 4H, $2 \times \text{Ar-O-CH}_2$ -), 1.86-1.8 (quin, $J = 7.8$ Hz, 4H, $2 \times \text{Ar-O-CH}_2\text{-CH}_2$ -), 1.5-1.26 (m, 52H, $2 \times \text{-(CH}_2\text{)}_{13}$ -), 0.88 (t, $J = 8$ Hz, 6H, $2 \times \text{-CH}_3$); Elemental analysis: $\text{C}_{87}\text{H}_{98}\text{O}_{16}$ requires C 74.66, H 7.05; found C 74.32, H 7.42%.

4-(4-(3-(4-(4-*n*-Octadecyloxybenzoyloxy)benzoyloxy)benzoyloxy)benzoyloxy)phenyl 3-(4-(4-*n*-octadecyloxybenzoyloxy)benzoyloxy)benzoate, 8.C.8

Yield: (79%); mp 135.5 °C; IR (KBr) ν_{\max} : 3074, 2954, 2922, 2850, 2721, 1737, 1732, 1604, 1591, 1471, 1440, 1377, 1311 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.3 (d, $J = 8.8$ Hz, 6H, Ar-H), 8.15 (d, $J = 8.8$ Hz, 6H, Ar-H), 8.09 (d, $J = 8$ Hz, 2H, Ar-H), 7.62 (d, $J = 8$ Hz, 2H, Ar-H), 7.54 (t, $J = 8.8$ Hz, 2H, Ar-H), 7.4 (dd, $J_1 = 3.6$ Hz, $J_2 = 7.8$ Hz, 6H, Ar-H), 7.3 (t, 4H, Ar-H), 6.99 (d, $J = 8.8$ Hz, 4H, Ar-H), 4.05 (t, $J = 6.8$ Hz, 4H, $2 \times \text{Ar-O-CH}_2$ -), 1.86-1.79 (quin, $J = 7.4$ Hz, 4H, $2 \times \text{Ar-O-CH}_2\text{-CH}_2$ -), 1.51-1.26 (m, 60H, $2 \times \text{-(CH}_2\text{)}_{15}$ -), 0.88 (t, $J = 8$ Hz, 6H, $2 \times \text{-CH}_3$); Elemental analysis: $\text{C}_{91}\text{H}_{106}\text{O}_{16}$ requires C 75.08, H 7.33; found C 74.70, H 7.03%.

4-(4-(3-(4-(4-*n*-Icosyloxybenzoyloxy)benzoyloxy)benzoyloxy)benzoyloxy)phenyl 3-(4-(4-*n*-icosyloxybenzoyloxy)benzoyloxy)benzoate, 8.C.9

Yield: (75%); mp 135.5 °C; IR (KBr) ν_{\max} : 3074, 3063, 2955, 2914, 2848, 2627, 1737, 1730, 1604, 1591, 1508, 1471, 1440, 1311 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.31 (d, $J = 8.4$ Hz, 6H, Ar-H), 8.16 (d, $J = 8.6$ Hz, 6H, Ar-H), 8.09 (d, $J = 8$ Hz, 2H, Ar-H), 7.61 (d, $J = 8$ Hz, 2H, Ar-H), 7.54 (t, $J = 8.8$ Hz, 2H, Ar-H), 7.4 (dd, $J_1 = 4$ Hz, $J_2 = 8$ Hz, 6H, Ar-H), 7.3 (t, 4H, Ar-H), 6.99 (d, $J = 8.8$ Hz, 4H, Ar-H), 4.05 (t, $J = 6.6$ Hz, 4H, $2 \times \text{Ar-O-CH}_2-$), 1.85-1.80 (quin, $J = 7.2$ Hz, 4H, $2 \times \text{Ar-O-CH}_2-\text{CH}_2-$), 1.51-1.29 (m, 68H, $2 \times -(\text{CH}_2)_{17}-$), 0.87 (t, $J = 7.8$ Hz, 6H, $2 \times -\text{CH}_3$); Elemental analysis: $\text{C}_{95}\text{H}_{114}\text{O}_{16}$ requires C 75.47, H 7.60; found C 75.83, H 7.39%.

4-((3-((4-(4-(3-(4-(3-Fluoro-4-*n*-hexadecyloxybenzoyloxy)benzoyloxy)benzoyloxy)benzoyloxy)phenoxy)carbonyl)phenoxy)carbonyl)phenyl 3-fluoro-4-*n*-hexadecyloxy benzoate, 8.C.10

Yield: (70%); mp 171.5 °C; IR (KBr) ν_{\max} : 3064, 2955, 2916, 2852, 2729, 1735, 1732, 1618, 1589, 1508, 1456, 1440, 1375 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.31 (d, $J = 8.8$ Hz, 6H, Ar-H), 8.15 (d, $J = 8.82$ Hz, 2H, Ar-H), 8.08 (d, $J = 6.8$ Hz, 2H, Ar-H), 7.62 (d, $J = 7.68$ Hz, 3H, Ar-H), 7.54 (t, $J = 6.8$ Hz, 3H, Ar-H), 7.4 (dd, $J_1 = 3.6$ Hz, $J_2 = 8$ Hz, 6H, Ar-H), 7.30 (t, 2H, Ar-H), 7.05 (t, $J = 8.4$ Hz, 2H, Ar-H), 4.13 (t, $J = 6.4$ Hz, 4H, $2 \times \text{Ar-O-CH}_2-$), 1.89-1.83 (quin, $J = 6.8$ Hz, 4H, $2 \times \text{Ar-O-CH}_2-\text{CH}_2-$), 1.53-1.25 (m, 52H, $2 \times -(\text{CH}_2)_{13}-$), 0.88 (t, $J = 6.8$ Hz, 6H, $2 \times -\text{CH}_3$); Elemental analysis: $\text{C}_{87}\text{H}_{96}\text{F}_2\text{O}_{16}$ requires C 72.78, H 6.73; found C 72.86, H 6.98%.

4-(4-(3-(4-(4-*n*-Hexadecylbenzoyloxy)benzoyloxy)benzoyloxy)benzoyloxy)phenyl 3-(4-(4-*n*-hexadecylbenzoyloxy)benzoyloxy)benzoate, 8.C.11

Yield: (65%); mp 146.5 °C; IR (KBr) ν_{\max} : 3066, 2953, 2922, 2852, 2719, 1735, 1732, 1602, 1502, 1460, 1454, 1377, 1311 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.31 (d, $J = 7.2$ Hz, 6H, Ar-H), 8.16 (d, $J = 7.6$ Hz, 6H, Ar-H), 8.09 (d, $J = 6.4$ Hz, 2H, Ar-H), 7.62 (d, $J = 6.8$ Hz, 2H, Ar-H), 7.55 (t, $J = 6$ Hz, 2H, Ar-H), 7.41 (d, $J = 6.8$ Hz, 6H, Ar-H), 7.33 (d, $J = 8.4$ Hz, 6H, Ar-H), 7.31 (t, 2H, Ar-H), 2.71 (t, $J = 7.6$ Hz, 4H, $2 \times \text{Ar-CH}_2-$), 1.71-1.63 (quin, $J = 7.2$ Hz, 4H, $2 \times \text{Ar-CH}_2-\text{CH}_2-$), 1.37-1.29 (m, 52H, $2 \times -(\text{CH}_2)_{13}-$), 0.88 (t, $J = 7.2$ Hz, 6H, $2 \times -\text{CH}_3$); Elemental analysis: $\text{C}_{87}\text{H}_{98}\text{O}_{14}$ requires C 76.40, H 7.22; found C 76.76, H 7.08%.

3-((4-((4-(3-(-4'-*n*-Dodecylbiphenylcarbonyloxy)benzoyloxy)phenoxy)carbonyl)phenoxy)carbonyl)phenyl 4'-*n*-dodecylbiphenyl-4-carboxylate, 8.D.1

Yield: (70%); mp 184.5 °C; IR (KBr) ν_{\max} : 3064, 2953, 2922, 2852, 2726, 1735, 1730, 1604, 1593, 1508, 1454, 1377, 1311 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.31 (d, $J = 6.8$ Hz, 2H, Ar-H), 8.27 (d, $J = 8.8$ Hz, 4H, Ar-H), 8.15 (d, $J = 7.4$ Hz, 2H, Ar-H), 8.09 (d, $J = 6.8$ Hz, 2H, Ar-H), 7.75 (d, $J = 7.6$ Hz, 4H, Ar-H), 7.64-7.54 (m, 8H, Ar-H), 7.41 (d, $J = 8.8$ Hz, 2H, Ar-H), 7.3 (t, $J = 4.8$ Hz, 8H, Ar-H), 2.67 (t, $J = 7.6$ Hz, 4H, $2 \times \text{Ar-CH}_2-$), 1.69-1.63 (quin, $J = 6.8$ Hz, 4H, $2 \times \text{Ar-CH}_2-\text{CH}_2-$), 1.37-1.26 (m, 36H, $2 \times -(\text{CH}_2)_9-$), 0.88 (t, $J = 8$ Hz, 6H, $2 \times -\text{CH}_3$); Elemental analysis: $\text{C}_{77}\text{H}_{82}\text{O}_{10}$ requires C 79.22, H 7.07; found C 79.01, H 6.71%.

3-((4-((4-(3-(-4'-*n*-Hexadecylbiphenylcarbonyloxy)benzoyloxy)phenoxy)carbonyl)phenoxy)carbonyl)phenyl 4'-*n*-hexadecylbiphenyl-4-carboxylate, 8.D.2

Yield: (68%); mp 172.5 °C; IR (KBr) ν_{\max} : 3074, 2952, 2922, 2854, 2725, 1735, 1730, 1604, 1593, 1508, 1454, 1377, 1311 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.31 (d, $J = 6.8$ Hz, 2H, Ar-H), 8.27 (d, $J = 8.4$ Hz, 4H, Ar-H), 8.15 (d, $J = 8$ Hz, 2H, Ar-H), 8.09 (d, $J = 6.8$ Hz, 2H, Ar-H), 7.74 (d, $J = 8$ Hz, 4H, Ar-H), 7.64-7.53 (m, 8H, Ar-H), 7.41 (d, $J = 8.8$ Hz, 2H, Ar-H), 7.30 (t, $J = 4.6$ Hz, 8H, Ar-H), 2.67 (t, $J = 7.8$ Hz, 4H, $2 \times \text{Ar-CH}_2-$), 1.69-1.62 (quin, $J = 6.8$ Hz, 4H, $2 \times \text{Ar-CH}_2-\text{CH}_2-$), 1.37-1.26 (m, 52H, $2 \times -(\text{CH}_2)_{13}-$), 0.87 (t, $J = 8$ Hz, 6H, $2 \times -\text{CH}_3$); Elemental analysis: $\text{C}_{85}\text{H}_{98}\text{O}_{10}$ requires C 79.78, H 7.72; found C 80.17, H 8.16%.

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