## **Chapter 5**

## Synthesis and mesomorphic properties of

 (i) Apolar symmetric dimers composed of five-ring bent-core monomeric units separated by an alkylene spacer (compounds 5.D.1 to 5.D.42)

#### 5.1: Introduction

Liquid crystalline dimers are composed of molecules containing two mesogenic units connected by a flexible spacer, most commonly an alkyl chain. The interesting aspect of liquid crystalline dimers is that their mesomorphic behaviour is different from that of monomers.



#### Structure 5.1

The liquid crystalline dimers were discovered by Vorlander [1] in 1927. The first series of dimers were composed of rod-like molecules containing alkoxy azobenzenes and linked by ester groups which is shown in structure **5.1**. The liquid crystalline dimers re-emerged when Rault *et al.* reported [2] such materials in 1975. However, the significance of liquid crystalline dimers were realized when the transitional properties of a series of diesters were described by Griffin and Britt [3] in 1981. They proposed that these dimers could serve as model compounds for main-chain liquid crystal polymers due to their similarity in the mesophase behaviour. Since then, this subject has become an area of research interest.

In general, the dimers can be broadly classified into two types based on their chemical structure.

- 1. Symmetric dimers, in which the mesogenic units are identical.
- 2. Non-symmetric dimers, which contain two different mesogenic units.

A number of calamitic as well as discotic liquid crystalline dimers have been synthesized and investigated for their mesomorphic behaviour in detail, especially the former.

#### Structure-property relationships of liquid crystalline dimers

In 1992, eleven homologous series of symmetric rod-like dimers were synthesized by Date *et al.* [4] and a systematic study was made on the mesomorphic behaviour as a function of length of the spacer unit and the terminal chain. The investigated dimers are connected in terminal positions and belong to a series of bis[4-(4-*n*-alkylphenyliminomethyl)phenoxy] alkanes. It was found that a pronounced odd-even effect in the clearing temperatures as a function of the spacer length was observed. In addition, the length of the spacer containing an even number of methylene units has higher clearing temperatures than those containing an odd number. On the basis of this review and other studies [5], it has been found that the transition temperatures and mesomorphic properties of liquid crystalline dimers often strongly depend on the following factors:

- 1. the length and parity of the flexible spacer
- 2. the chemical nature of the spacer
- 3. the molecular structure of the mesogenic unit and
- 4. the nature of the terminal groups.

#### Laterally connected calamitic liquid crystalline dimers

The majority of calamitic liquid crystalline dimers reported in the literature are mostly connected in terminal positions although a very few number of laterally linked dimers are also known.

The first laterally connected rod-like dimers containing longer flexible spacer were reported by Weissflog *et al.* [6] in 1989. The general structure of this dimer is shown below in structure **5.2.** In this series, all the homologues exhibited a nematic mesophase and the lower homologues containing *n*-propyl, *n*-butyl- and *n*-pentyloxy- chain exhibited a smectic C phase in addition to the nematic phase. A pronounced odd-even effect was observed in the clearing temperatures for shorter spacer unit which became weaker as the spacer unit was lengthened. This behaviour is similar to that observed for terminally connected dimers. They also investigated the effect of incorporation of an aromatic ring in the spacer unit and also the

influence of lateral substituents such as -Cl,  $-CH_3$ ,  $-C_2H_5$  and  $-OCH_3$  on aromatic ring in the spacer unit for this type of dimer. It was found that all these dimers are liquid crystalline and exhibit nematic phase.



Structure 5.2

In 1996, Andersch *et al.* [7] reported the laterally connected dimers containing p-terphenyl units. It was found that the mesophase behaviour depended strongly on the length and structure of the spacer. It was shown that short as well as highly polar and rigid spacer units stabilize smectic phases with high transition temperature. They also investigated the effect of the position of a linking group on the mesomorphic properties of dimers [8]. These dimers are composed of p-terphenyl and rigid aromatic units connected by 2-oxapropylene spacer unit. It was observed that dimers connected by spacer at periphery stabilized the mesophase whereas in case of dimers connected at central position destabilized the phase compared to the monomer.

#### **Bent-core liquid crystalline dimers**

The bent-core liquid crystalline dimers are relatively new. The possibility of obtaining different types of such dimers have been pictorially shown in figure **5.1**. The first bent-core liquid crystalline dimers were reported by Dantlgraber *et al.* [9] in 2002 using dimethylsiloxane

spacer. It was also shown that a dimer containing a dimethyltrisiloxane spacer showed ferroelectric switching while that with dimethyltetrasiloxane spacer exhibited antiferroelectric characteristics. Thus, the parity of the flexible spacer has a strong influence on the mesomorphic properties. Later, Keith *et al.* [10] investigated the mesomorphic properties of dimers containing carbosilane spacer unit in place of oligosiloxane. In this dimer, the antiferroelectric to ferroelectric switching behaviour of the mesophase can be controlled by varying the spacer. It was found that on increasing the length of carbosilane unit in the spacer, ferroelectric phase at low temperature with broad mesophase range and high polarization value could be obtained.



Figure 5.1: Pictorial representation of the possibility of different types of bent-core dimers.

In 2006, Kosata *et al.* [11] reported systematic studies on symmetric twin molecules of two bent-core mesogenic units for the first time. It was shown that the formation of mesophases mainly depends on the chemical structure of the spacer. Symmetric dimers containing flexible alkylene spacer exhibited columnar mesophase.

Subsequently, Umadevi *et al.* [12, 13] reported symmetric bent-core dimers, in which the monomeric units are connected by flexible alkylene spacer unit. They studied the influence of

fluorine as a lateral substituent on aromatic rings and the effect on the mesomorphic behaviour of dimers. They also examined systematically the effect of varying the length of the terminal chain for fixed odd and even spacers, as well as varying the spacer length for a fixed terminal chain length on the mesomorphic properties of these symmetric dimers. On the basis of XRD and electro-optical studies, they proposed a structural model for the polar columnar mesophase. Very interestingly, all these dimers show the same type of polar columnar mesophase which has been characterized as a  $Col_{ob}P_{FE}$  phase.

In 2007, Achten *et al.* [14] reported the effect on the mesomorphic behaviour of bent-core dimers by varying the length of the spacer unit as well as length of the terminal chain. Most of these dimers are derived from resorcinol central unit and connected via trisiloxane spacer unit and alkylene spacer unit respectively for two different series. Dimers containing a trisiloxane spacer unit show a polar smectic C phase with ferroelectric properties irrespective of the spacer length and terminal chain. This supports that the decoupling of the layers by the siloxane units suppresses the antiferroelectric ground state of the monomeric precursors. In dimers containing an alkylene spacer, a mesophase is obtained only if the terminal chains are relatively long and these dimers show a strong tilted monolayer smectic phase. In all these cases, the bent-core units are connected in the terminal positions such that a polar order could still be retained.

Very recently, side-by-side as well as side-to-end connected bent-core dimers have been synthesized and investigated by Shankar *et al.* [15]. In side-by-side dimers, monomers are connected at *ortho* to the terminal ring using flexible alkylene spacer containing bis(dimethylsilane) unit in the middle. Whereas in case of side-to-end dimer, monomers are connected using the same spacer. However, 4-cyanoresorcinol which is well known to form nematic phase was used as a central unit, thus both the dimers exhibited nematic phase in addition to SmC phase.

We designed a new type of dimer in which the individual monomers are connected at the apex positions via flexible alkylene spacers. We also assumed that a dimer of this type would be apolar as all the dipolar components of the individual monomeric units cancel with each other. With this in view, a new kind of symmetric five-ring BC dimers were designed and synthesized using 5-hydroxyisophthalic acid as central unit. In this chapter, the synthesis and the

mesomorphic properties of these new dimers in which the monomeric bent-core units are linked via an ether or an ester linkage are described. The general structure of this new type of bent-core dimers is shown in structure **5.3**.



#### Structure 5.3

#### 5.2: Synthesis

The symmetrical five-ring bent-core dimers in which monomers are connected at apex positions to alkylene spacer via a ether or ester linkage were synthesized as shown in schemes **5.3** and **5.4** respectively. We chose 5-hydroxyisophthalic acid as a central unit for making this type of dimers since we had already obtained interesting results by converting the 5-hydroxy group to 5-methoxyisophthalic acid for making both five-ring and seven-ring bent-core systems [16, 17]. 5-Hydroxyisophthalic acid, dibromoalkanes and alkanedioic acids were obtained commercially and used without further purification. The central unit of ether linkage dimers were synthesized as shown in scheme **5.1**. 5-Hydroxyisophthalic acid, **5.a** was refluxed in



Scheme 5.1: Synthetic route followed to prepare the intermediate compounds.



Scheme 5.2: Synthetic path used for preparation of two-ring phenol 5.j.



Series 5.D.I, II and III

# Scheme 5.3: The final step used for preparing dimers containing alkylene spacer belonging to series 5.D.I, 5.D.II and 5.D.III.

methanol with a catalytic amount of sulphuric acid to obtain dimethyl 5-hydroxyisophthalate, **5.b**. Williamson ether synthesis using a dibromoalkane with dimethyl 5-hydroxyisophthalate, **5.b** led to the formation of compound **5.c**. This was saponified and after acidification provided the tetra carboxylic acid, **5.d**. The wings of the dimers were synthesized as shown in scheme **5.2**. 4-Benzyloxybenzoic acid, **5.h** was esterified with an appropriate 4-*n*-alkoxyphenol, **5.g** using



Scheme 5.4: Synthetic route followed for preparation of monomer 5.1 and dimers of series 5.D.IV, 5.D.V and 5.D.VI containing ester moiety in the spacer.

*N*,*N*'-dicyclohexylcarbodiimide (DCC) and a catalytic amount of 4-(*N*,*N*-dimethyamino)pyridine (DMAP) to provide compound **5.i**. The benzyl group in compound **5.i** was cleaved using H<sub>2</sub> and 5% Pd-C catalyst to obtain the two-ring phenol **5.j**. The dimers obtained via a ether linkage and belonging to series **5.D.I**, **5.D.II** and **5.D.III** were synthesized by condensing an appropriate tetra carboxylic acid **5.d** with four equivalents of two-ring phenol **5.j**.

Benzylation of dimethyl 5-hydroxyisophthalate, **5.b** with benzyl chloride provided dimethyl 5-benzyloxyisophthalate, **5.e** which on hydrolysis yielded 5-benzyloxyisophthalic acid, **5.f**. The five-ring bent-core compound **5.k** was synthesized by condensing 5-benzyloxyiso -phthalic acid, **5.f** with the two-ring phenol **5.j**. Removal of the benzyl group by hydrogenolysis gave monomer **5.l**. The dimers belonging to series **5.D.IV**, **5.D.V** and **5.D.VI** were synthesized by condensing commercially available and appropriate alkanedioic acid and two equivalents of monomer **5.l**.

#### 5.3: Results and discussion

#### **5.3.1: Mesomorphic properties**

A total of six different series of symmetric dimers composed of bent-core monomeric units were synthesized. In series **5.D.I**, **5.D.II** and **5.D.III** the monomeric units are connected by a flexible alkylene spacer via ether linkages whereas in series **5.D.IV**, **5.D.V** and **5.D.VI** the monomeric units are connected by a flexible alkylene spacer via ester linkages. The transition temperatures and the associated enthalpy values of dimers, **5.D** belonging to ether and ester linkage series are summarized in tables **5.1** to **5.3** and **5.4** to **5.6** respectively. All the dimers show mesophases except two of them.

In series **5.D.I**, the terminal chain length is fixed  $(n = C_{18}H_{37})$  while the linking methylene units (m) are varied. The transition temperatures and associated enthalpy values obtained for dimers of series **5.D.I** are summarized in table **5.1**. As can be seen all the eight compounds are dimesomorphic in nature and show the same type of mesophases.

The characterization of the mesophases was carried out as follows. When a sample of compound **5.D.8** was filled in a cell treated for planar alignment in the isotropic phase and cooled slowly, batonnets appeared which coalesced to form a fan-shaped texture as shown in figures **5.2.a** and **5.2.b** respectively and this texture is typical for SmA phase. On cooling further another phase transition takes place, which can be clearly seen under a polarizing microscope and the optical texture obtained is shown in figure **5.2.c.** When the same compound was filled in a cell treated for homeotropic alignment and cooled slowly, dark regions with some defects were observed in the higher temperature phase which indicated that the phase is a SmA phase and absence of schlieren texture ruled out a smectic C phase. However, noticeable change was not observed on further cooling into the lower temperature phase. The optical textures obtained at various temperatures are shown in figures **5.2.d** to **5.2.f.** 

Compound	<i>n/m</i> (Et)	Cr		SmA'		SmA		Ι
5.D.1	18/5Et	•	67.5	(•	59.0)	•	122.0	•
			27.5		6.4		1.5	
5.D.2	18/6Et	•	66.5	(•	55.5)	•	119.0	•
			29.5		6.0		2.0	
5.D.3	18/7Et	•	65.5	(•	57.5)	•	115.0	•
			30.0		7.4		2.0	
<b>5.D.4</b>	18/8Et	•	64.5	(•	54.0)	•	110.0	•
			31.0		2.5		2.5	
5.D.5	18/9Et	•	64.0	(•	55.5)	•	104.0	•
			32.5		11.6		2.7	
<b>5.D.6</b>	18/10Et	•	64.0	(•	53.5)	•	98.0	•
			31.0		10.3		2.8	
5.D.7	18/11Et	•	63.0	(•	53.5)	•	91.5	•
			35.0		11.2		2.7	
5.D.8	18/12Et	•	63.5	(•	51.5)	•	84.5	•
			36.0		9.1		2.7	

Table 5.1: Transition temperatures (°C) and the associated enthalpy values (kJ mol<sup>-1</sup>)(in italics) for compounds of series 5.D.I<sup>a</sup>

<sup>a</sup>Abbreviations: Cr: crystalline phase; SmA': variant of smectic A phase; SmA: smectic A phase; I: isotropic phase; ( ): phase is monotropic; •: phase exists.



(c)

(**f**)

Figure 5.2: Photomicrographs of the textures obtained for SmA phase of dimer 5.D.8 in a cell treated for planar alignment. (a)  $T = 82.6 \degree C$ ; (b)  $T = 80 \degree C$  and (c) SmA' phase at  $T = 30 \degree C$ . Dark texture exhibited for dimer 5.D.8 in the SmA phase in a cell treated for homeotropic alignment (d)  $T = 80 \degree C$ ; (e)  $T = 70 \degree C$  and (f) SmA' phase at  $T = 30 \degree C$ .



Figure 5.3: A DSC thermogram obtained for dimer 5.D.7; (a) showing two phase transitions; inset shows SmA-SmA' transition; (b) showing phase transitions at same temperatures after 1 h and 30 min; (H) heating cycle; (C) cooling cycle; rate 5 °C min<sup>-1</sup>.

A DSC thermogram obtained for compound **5.D.7** is depicted in figure **5.3**. It can be clearly seen from the thermogram that the higher temperature phase is enantiotropic whereas lower temperature phase is monotropic. Interestingly, the same phase transiton temperatures were obtained without showing a peak corresponding to melting when repeating DSC scan even after 1 h and 30 min. This clearly indicates that crystallization of this type of dimers is very slow. The enthalpy value for the clearing temperature for the series **5.D.I** varies from about 1.5 to 3 kJmol<sup>-1</sup> which is far less than what is generally obtained for a banana (B) phase. The textures and the enthalpy values obtained suggest that higher temperature mesophase could be SmA and the lower temperature phase is a variant of SmA phase which has been designated as SmA' phase. In addition, on the basis of XRD measurements and electro-optical studies which are described later, the higher temperature phase is characterized as SmA phase and lower temperature phase.



Figure 5.4: Plot of transition temperature as a function of number of methylene units in the spacer for series 5.D.I.

A plot of the transition temperature as a function of spacer length for series **5.D.I** is shown in figure **5.4**. A wide thermal range of about 54 °C for SmA phase was observed for dimer **5.D.1** containing a shorter spacer (m = 5) which decreased to 21 °C for dimer **5.D.8** having a longer spacer (m = 12). It can be clearly seen from figure **5.4** that a smooth falling curve is obtained for the clearing temperatures of SmA phase whereas odd-even effect is observed for SmA-SmA' phase transition as the series is ascended and the melting points are almost the same for all dimers.

In order to study the structure-property relationships, the terminal chain length was varied for fixed odd and even spacers, and thus series **5.D.II** and **5.D.III** were synthesized. The mesomorphic properties of dimers of series **5.D.II** containing an odd spacer (m = 9) and series **5.D.III** containing an even spacer (m = 12) were investigated. The transition temperatures and associated enthalpy values obtained for these two series are summarized in tables **5.2** and **5.3** respectively. As can be seen in tables **5.2** and **5.3** all the dimers are mesomorphic except dimer **5.D.15**. When a sample of dimer **5.D.17** filled in the isotropic phase in a cell treated for planar

Compound	<i>n/m</i> (Et)	Cr		SmA'		SmA	A	Ι
5.D.9	11/9Et	٠	124.5	-		(•	66.5)	٠
			57.5				2.2	
5.D.10	12/9Et	•	112.0	-		(•	77.0)	•
			45.5				2.7	
5.D.11	13/9Et	•	108.0	-		(•	84.5)	•
			39.5				2.8	
5.D.12	14/9Et	•	105.5	-		(•	91.5)	•
			15.5				3.0	
5.D.13	15/9Et	•	50.5	-		•	96.5	•
			18.5				3.0	
5.D.14	16/9Et	•	56.5	-		•	99.5	•
			26.5				2.7	
5.D.5	18/9Et	•	64.0	(•	55.5)	•	104.0	•
			32.5		11.6		2.7	

Table 5.2:	Transition temperatures (°C) and the associated enthalpy values (kJ $mol^{-1}$ )
	(in italics) for compounds of series 5.D.II <sup>a</sup>

<sup>a</sup>See table **5.1**.

 Table 5.3: Transition temperatures (°C) and the associated enthalpy values (kJ mol<sup>-1</sup>)

 (in italics) for compounds of series 5.D.III<sup>a</sup>

Compound	<i>n/m</i> (Et)	Cr		SmA'		SmA		Ι
5.D.15	11/12Et	•	75.3	-		-		-
			15.5					
5.D.16	12/12Et	•	65.3	-		(•	45.0)	•
			43.0				0.6	
5.D.17	13/12Et	•	45.5	-		•	59.0	٠
			3.0				1.7	
5.D.18	14/12Et	•	44.5	-		•	67.0	•
			9.4				2.5	
5.D.19	15/12Et	•	52.5	-		•	73.5	•
			27.0				2.7	
5.D.20	16/12Et	•	54.5	-		•	78.0	•
			29.5				2.9	
5.D.8	18/12Et	•	63.5	(•	51.5)	•	84.5	٠
			36.0		9.1		2.7	



(a)



**(b)** 



(c)

Figure 5.5: Optical photomicrographs of textures obtained for SmA phase of dimer 5.D.17 in a cell treated for planar alignment. (a)  $T = 51 \degree C$ ; (b)  $T = 44.5 \degree C$  and (c)  $T = 30 \degree C$ .



Figure 5.6: A DSC thermogram obtained for compound 5.D.17 showing phase transitions; (H) heating cycle; (C) cooling cycle; rate 5 °C min<sup>-1</sup>.

alignment and cooled slowly, optical textures were obtained at various temperatures and the same are shown in figures **5.5.a** to **5.5.c.** These two series of dimers show a SmA phase. Remarkably, in all cases the mesophase is stable upto room temperature and we did not see any transition on cooling in DSC even after 1 h. However, over a period of time, it is possible that this may go to a glassy state. A DSC thermogram obtained for dimer **5.D.17** showing only one mesophase is depicted in figure **5.6**.

A plot of transition temperatures *vs* number of carbon atoms in the terminal chain is shown in figures **5.7.a** and **5.7.b** for series **5.D.II** and **5.D.III** respectively. It can be seen from figures **5.7.a** and **5.7.b** that the clearing points decrease as a function of decreasing number of carbon atoms in the terminal chain length. In other words, the mesophase is destabilized and it becomes monotropic for the lower homologues **5.D.9** to **5.D.12** of series **5.D.II** and **5.D.16** of series **5.D.III**. As a result, the thermal range increases and smooth curves are observed on ascending the series in both cases. However, there is a variation of the slope in the two series of dimers. Interestingly, all the dimers exhibit the same type of mesophase and there is no change



Figure 5.7: Plot of transition temperature as a function of number of carbon atoms in the terminal chain for fixed methylene units in the spacer (a) m = 9; (b) m = 12 for series 5.D.II and 5.D.III respectively.

in the mesophase on variation of the terminal chain except  $n = C_{18}$  chain (series **5.D.I** which is dimesomorphic in nature).

In order to study the influence of a linkage group, additionally three different series of dimers were synthesized and investigated. The dimers containing an ester linkage were synthesized following the pathway which is different for those used for ether linkage dimers. First, phenolic five-ring bent-core compounds, which are intermediates for ester linkage dimers were synthesized. These monomeric five-ring BC compounds are also mesomorphic in nature. The higher homologues such as compounds 5.1-18 to 5.1-13 exhibit polymesomorphism. When a thin film of sample 5.1-18 was cooled slowly from the isotropic phase to mesophase, batonnets appeared which became dark and on cooling further filament-like textures were obtained in the lower temperature phase and these are shown in figures 5.8.a and 5.8.b. A different texture obtained on further cooling is also shown in figure 5.8.c. When the same sample was filled in the isotropic phase in a cell treated for planar alignment and cooled slowly, smooth fan-shaped texture was obtained and on further cooling to lower temperature phase, lines developing across the fans could be seen. On cooling even further, arcs across the fans along with lines were seen and the optical textures obtained are shown in figures 5.8.d to 5.8.f. The lower homologues 5.1-12 to 5.1-10 are dimesomorphic in nature. The photomicrographs of the textures obtained for BC compound 5.I-11 are depicted in figures 5.9.a and 5.9.b. Detailed studies of X-ray diffraction measurements and electro-optics were not possible due to thermal instability of these phenolic monomeric five-ring BC compounds and hence the mesophases could not be characterized.

In series 5.D.IV, 5.D.V and 5.D.VI, the monomeric units are connected by a flexible alkylene spacer via ester groups. The transition temperatures and the associated enthalpy values of the dimers of series 5.D.IV are summarized in table 5.4. In this series, the terminal chain (n = 18) is fixed while flexible methylene spacer is varied (m = 6-14). It can be seen from table 5.4 that the dimers are dimesomorphic in nature and the behaviour is very similar to ether series 5.D.I.

When dimer **5.D.24** was filled in a cell treated for homogeneous alignment and cooled slowly and viewed under a polarizing microscope, a fan-shaped texture was obtained on cooling and the textures at various temperatures are shown in figures **5.10.a** to **5.10.c**. Photomicrographs



Figure 5.8: Optical textures obtained for the mesophases of monomer 5.1-18 in a cell treated for homeotropic alignment at various temperatures (a-c). (a) T = 185 °C;
(a) T = 172 °C and (c) T = 168 °C. Textures of the same mesophases in a cell treated for homogeneous alignment (d-f). (d) T = 185 °C; (e) T = 173 °C and (f) T = 169.5 °C.



Figure 5.9: Photomicrographs of the optical textures shown by monomer 5.1-11 in a cell treated for homeotropic alignment for the two mesophases (a and b).
(a) T = 176 °C and (b) T = 156 °C.

Table 5.4:	Transition temperatures (°C) and the associated enthalpy values (kJ mol	-1)
	(in italics) for compounds of series 5.D.IV <sup>a</sup>	

Compound	<i>n/m</i> (Es)	Cr		SmA'		SmA		Ι
5.D.21	18/6Es	•	65.5	(•	56.0)	•	127.0	•
			21.0		7.2		1.6	
5.D.22	18/7Es	•	65.5	(•	56.5)	•	119.5	٠
			29.5		8.2		1.5	
5.D.23	18/8Es	•	65.5	(•	54.0)	•	112.5	•
			32.0		5.7		1.9	
5.D.24	18/9Es	•	65.5	(•	54.5)	•	106.0	•
			32.0		9.3		2.0	
5.D.25	18/10Es	•	63.0	(•	51.5)	•	101.0	•
			36.5		5.2		2.4	
5.D.26	18/11Es	•	63.0	(•	52.5)	•	94.0	•
			30.5		9.1		2.0	
5.D.27	18/12Es	•	108.5	(•	51.5)	(•	87.5)	•
			54.5		7.6		2.3	
5.D.28	18/14Es	•	101.0	(•	50.5)	(•	71.0)	•
			70.5		5.8		1.5	







(c)

(**d**)



**(e)** 

Figure 5.10: Optical textures exhibited by dimer 5.D.24 in a cell treated for planar alignment at various temperatures. SmA phase at (a) T = 101 °C;
(b) T = 80 °C and (c) T = 65 °C. SmA' phase at (d) T = 51 °C and (e) T = 30 °C.

obtained for SmA' phase are also shown in figures **5.10.d** to **5.10.e**. The dimer **5.D.21** (m = 6) exhibits the widest thermal range of 65 °C for SmA phase and on increasing the methylene spacer length this range decreased to 30 °C for the dimer **5.D.26** (m = 11). It becomes metastable for longer spacer length such as m = 12 and 14 for dimers **5.D.27** and **5.D.28** respectively.

A plot of transition temperature *vs* number of methylene units in the spacer is depicted in figure **5.11.** As expected, a smooth falling curve is observed for the clearing points on increasing the spacer length whereas odd-even effect is observed for SmA-SmA' phase transition. Noticeably, the melting points are almost the same for dimers showing enantiotropic SmA phase.

Not only for comparison with ether dimers (series **5.D.II** and **5.D.II**) but also to study the mesomorphic behaviour as a function of terminal chain length for fixed odd and even spacer, two series **5.D.V** (m = 7) and **5.D.VI** (m = 10) of dimers have been synthesized and examined. The transition temperatures and the associated enthalpy values obtained for these two series of dimers are presented in tables **5.5** and **5.6** respectively. As can be seen in these tables, all the dimers are mesomorphic in nature and show only one mesophase except for dimer **5.D.36**.



Figure 5.11: Plot of transition temperature as a function of number of methylene units in the spacer for ester series 5.D.IV.

Compound	<i>n/m</i> (Es)	Cr		SmA'		SmA		Ι
5.D.29	10/7Es	•	141.5	_		(•	77.0)	•
			54.5				1.9	
5.D.30	11/7Es	•	121.5	-		(•	97.5)	•
			33.0				2.8	
5.D.31	12/7Es	•	120.5	-		(•	97.0)	٠
			39.0				2.5	
5.D.32	13/7Es	•	111.0	-		(•	108.5)	٠
			3.0				2.8	
5.D.33	14/7Es	•	112.0	-		(•	107.0)	٠
			43.0				2.5	
5.D.34	15/7Es	•	55.0	-		•	119.5	٠
			10.2				2.6	
5.D.35	16/7Es	•	59.0	-		•	114.5	٠
			22.5				2.1	
5.D.22	18/7Es	•	66.0	(•	56.5)	•	118.5	•
			29.5		8.2		1.5	

Table 5.5:	Transition temperatures (°C) and the associated enthalpy values (kJ mol $^{-1}$ )
	(in italics) for compounds of series 5.D.V <sup>a</sup>

Table 5.6: Transition temperatures (°C) and the associated enthalpy values (kJ mol<sup>-1</sup>) (in italics) for compounds of series 5.D.VI<sup>a</sup>

Compound	<i>n/m</i> (Es)	Cr		SmA'		SmA		Ι
5.D.36	10/10Es	•	86.0	-		-		٠
			41.0					
5.D.37	11/10Es	•	84.0	-		(•	54.5)	•
			42.0				1.0	
5.D.38	12/10Es	•	86.0	-		(•	69.0)	•
			41.0				1.7	
5.D.39	13/10Es	•	78.5	-		(•	79.0)	•
			37.0				2.2	
<b>5.D.40</b>	14/10Es	•	82.5	-		•	86.0	•
			39.5				2.3	
<b>5.D.41</b>	15/10Es	•	53.0	-		•	92.0	•
			23.0				2.2	
5.D.42	16/10Es	•	58.0	-		•	95.5	•
			28.0				2.5	
5.D.25	18/10Es	•	63.0	(•	51.5)	•	101.0	•
			36.5		5.2		2.5	



Figure 5.12: Plot of transition temperature as a function of number of carbon atoms in the terminal chain for ester linkage dimers of series (a) 5.D.V and (b) series 5.D.VI.



Figure 5.13: The dependence of clearing temperature on the length of terminal chains.
(a) series 5.D.II (m = 9) and 5.D.III (m = 12) of ether series; (b) 5.D.V (m = 7) and 5.D.VI (m = 10) of ester series.

In series 5.D.V, the spacer length is fixed as m = 7 and the terminal chain length is varied from n = 10-18. It can be seen from table 5.5 that the dimers 5.D.29 to 5.D.33 exhibit monotropic SmA phase while dimers 5.D.34, 5.D.35 and 5.D.22 show a wide thermal range of enantiotropic phase. A plot of transition temperature as a function of terminal chain length for this series is shown in figure 5.12.a. Interestingly, an odd even effect is observed in the clearing temperatures on variation of the terminal chain for fixed odd spacer (m = 7). It is also observed that clearing temperatures of homologues containing odd number of methylene units are higher than those containing even number of methylene units.

In series **5.D.VI**, the terminal chain length is varied for a fixed even spacer (m = 10) and their mesomorphic behaviour is investigated. The textures obtained for compounds of both series **5.D.V** and **5.D.VI** are similar to those seen for series **5.D.II** and **5.D.III** and all these four series of dimers exhibit only one mesophase which has been characterized as SmA. A plot of the dependence of transition temperature on the length of the terminal chain length is shown in figure **5.12.b.** There is no odd-even effect observed in the clearing points as seen in series **5.D.V**.

It is interesting to point out here that the clearing temperatures of dimers containing odd number of spacer units (series **5.D.II** and series **5.D.IV**) are higher than those of dimers containing an even number of spacer units (series **5.D.V** and series **5.D.VI**) and plots are given in figures **5.13.a** and **5.13.b** respectively. These results are in contrast to the symmetrical calamitic dimers [4, 6] but similar to the terminally connected bent-core dimers [10, 11].

#### **5.3.2: X-Ray diffraction measurements**

In order to confirm the structure of the mesophases exhibited by this new type of dimers, X-ray diffraction measurements were carried out on the mesophase for some representative dimers. Powder samples were examined in Lindemann capillaries (0.7 mm diameter) and the samples were filled in isotropic state and the ends were sealed. For example, a sample of dimer **5.D.7** was cooled slowly from isotropic state to mesophase and on irradiation at T = 80 °C, showed two reflections in the small angle with d-spacing of  $d_1 = 54.83$  Å (01),  $d_2 = 27.41$  Å (02).

The diffuse chain scattering in the wide angle region at about 4.5 Å, indicating a liquid-like ordering of the molecules, was also seen. The d-spacings in the small angle are in the ratio of 1 : 1/2 and this suggests a layer structure of the molecules in the mesophase. The layer spacing determined from X-ray measurements is lower than the calculated molecular length (L = 77 Å, assuming that all the methylene units in the alkoxy chain are in the fully extended all *trans* conformation). This can be accounted as follows:

1. Packing of aromatic part can be disturbed by lateral linking group of alkylene spacer.

2. Thus, free volume developed by distortion can be filled by alkoxy terminal chains by adopting mostly the *gauche* conformation which will lead to smaller d-spacing.

When the same sample was cooled to the lower temperature phase at T = 40 °C, the following reflections were obtained. The d-spacing of  $d_1 = 63.07$  Å (01),  $d_2 = 31.56$  Å (02) were observed in the small angle region, along with a wide angle reflection at about 4.4 Å. Interestingly, these d-spacings correspond to a layer structure. However, increase in d-spacing of about 8 Å was observed in the lower temperature mesophase and this could happen only when a few methylene units are coming out from the above packing and going to higher order *trans* conformation. The wide angle reflection obtained in this mesophase is slightly sharper than the higher temperature mesophase and this observation strongly suggests the methylene units in the lower temperature mesophase is having more *trans* conformation than the higher temperature mesophase. Whereas in the higher temperature mesophase, the methylene units are mostly in gauche conformation. The intensity profile obtained for both the mesophases is given in figure 5.14. For comparison, a powder sample of dimer 5.D.7 which is in crystalline form was filled in a capillary without going to isotropic phase and X-ray measurement was carried out at room temperature. The reflections obtained in the small angle region correspond to d-spacing of  $d_1 = 47.46$  Å,  $d_2 = 23.73$  Å and a sharp reflection in the wide angle region at about 4.13 Å were The intensity profile obtained for crystal is given in figure 5.14 along with the seen. mesophases. The wide angle reflection of the lower temperature phase is slightly shifted and is sharper than higher temperature phase indicating an ordered conformation of methylene units. It is clearly noticeable that it is not as sharp as crystal. These experimental results strongly suggest that the structures of higher and lower temperature mesophases are different from crystal.



Figure 5.14: XRD intensity profile of powder sample of dimer 5.D.7 in the higher and lower temperature mesophases along with that obtained for crystal. Inset shows(a) expanded region of second order reflection; and (b) wide angle region respectively.

Similar experiments were carried out for some of the other samples of series **5.D.II** and **5.D.III**. The d-values obtained for ether series are summarized in table **5.7**.

For a better understanding of the molecular order, XRD measurements of a monodomain sample were carried out on a glass plate for a few samples. A partially aligned pattern was obtained in the higher temperature phase. On cooling down to the lower temperature phase, the same pattern was obtained with increase in d-spacing as seen in powder pattern. However, the wide angle region did not align in both the mesophases which may be due to disordering of the alkoxy chains.

To investigate further, temperature dependent layer spacing measurements were carried out for a few samples. For example, samples of dimer **5.D.3**, **5.D.7** and **5.D.17** were taken for investigations. The d-spacings obtained by this study for these three different dimers are plotted



Figure 5.15: Plot of d-spacings as a function of temperature for dimers 5.D.3, 5.D.7 and 5.D.17.

and shown in figure **5.15.** It can be seen from this figure **5.15** that d-spacing increases as a function of decreasing temperature for samples of **5.D.3** and **5.D.7**, and thus the d-values are highly temperature dependent in the higher temperature phase. On the other hand d-spacings of lower temperature phase is temperature independent as can be seen. The sample of dimer **5.D.17** containing only one mesophase was also examined. It was found that no significant variation in the d-spacing as a function of temperature was seen as shown in figure **5.15**.

Similar measurements were carried out for some of the samples of ester dimers belonging to series **5.D.IV**, **5.D.V** and **5.D.VI**. The d-spacings obtained are collected in table **5.8**. It was observed that the d-spacing obtained for the fixed terminal chain length on variation of spacer is almost the same whereas d-spacings increased on ascending the series for a fixed spacer.

Compound	d-spacing (Å)	Phase type	T (°C)
5.D.3	55.66 (01), 27.83 (02) 63.07 (01), 31.56 (02)	SmA SmA'	99 40
5.D.7	54.83 (01), 27.45 (02) 63.07 (01), 31.56 (02)	SmA SmA'	80 40
5.D.8	54.25 (01), 27.12 (02) 62.62 (01), 31.31 (02)	SmA SmA'	75 40
5.D.9	46.64 (01), 23.32 (02)	SmA	30
5.D.10	48.58 (01), 24.29 (02)	SmA	30
5.D.11	51.13 (01), 25.56 (02)	SmA	30
5.D.12	51.10 (01), 25.55 (02)	SmA	75
5.D.13	50.24 (01), 25.12 (02)	SmA	85
5.D.14	52.20 (01), 26.10 (02)	SmA	85
5.D.16	46.78 (01)	SmA	30
5.D.17	48.98 (01), 24.49 (02)	SmA	50
5.D.18	49.85 (01), 24.92 (02)	SmA	58
5.D.19	50.68 (01), 25.34 (02)	SmA	65
5.D.20	52.50 (01), 26.25 (02)	SmA	68

### Table 5.7: The d-spacings obtained from XRD measurements for dimers of ether series

Compound	d-spacing (Å)	Phase type	T (°C)
5.D.23	56.37 (01) 65.01 (01)	SmA SmA'	95 35
5.D.24	54.56 (01) 62.61(01)	SmA SmA'	100 40
5.D.27	56.19 (01) 63.79 (01)	SmA SmA'	80 30
5.D.28	57.15 (01) 62.61 (01)	SmA SmA'	65 30
5.D.29	44.44 (01), 22.22 (02)	SmA	50
5.D.30	47.86 (01), 23.93 (02)	SmA	30
5.D.31	46.63 (01)	SmA	80
5.D.32	51.8 (01), 25.9 (02)	SmA	30
5.D.33	51.1 (01), 25.55 (02)	SmA	95
5.D.34	52.46 (01), 26.23 (02)	SmA	100
5.D.35	50.92 (01), 25.46 (02)	SmA	105
5.D.37	45.89 (01)	SmA	30
5.D.38	46.07 (01), 23.78 (02)	SmA	50
5.D.39	48.70 (01), 24.35 (02)	SmA	68
5.D.40	49.19 (01), 24.59 (02)	SmA	78
5.D.41	50.31 (01), 25.15 (02)	SmA	80
5.D.42	52.04 (01), 26.02 (02)	SmA	85

## Table 5.8: Layer spacings obtained from XRD measurements for ester linkage dimers

#### 5.3.3: Electro-optical measurements

Inorder to examine the effect of electric-field on the mesophases, electro-optical studies were carried using the standard triangular-wave method. As an example, a sample of dimer **5.D.7** was filled in a commercial cell (EHC, Japan) having a thickness 8  $\mu$ m, treated for homogeneous alignment. Then, the sample was cooled to mesophase and a triangular-wave field was applied. As expected, the mesophase did not respond to the applied electric field upto 350  $V_{pp}$  and also there was no noticeable textural change seen indicating the apolar nature of the mesophase. It is reasonable to assume that a dimer of this type would not respond to an applied electric field as all the dipolar components of the individual monomeric units cancel with each other. Based on optical textures, XRD and electro-optical studies, possible models have been proposed for the molecular organization in the SmA and SmA' phases of dimers connected at apex positions and the same are shown in figure **5.16**.



Figure 5.16: Schematic representation of apolar bent-core dimers. (a) SmA phase; (b) SmA' phase.

#### **5.4: Conclusions**

A new type of symmetrical dimers composed of five-ring BC monomeric units, which are connected at the apex positions via flexible alkylene spacers have been designed. In order to understand the structure-property relationships, a total of six different series of dimers using 5-hydroxyisophthalic acid central unit connected by two different linkages have been synthesized and investigated. In series, 5.D.I to 5.D.III and 5.D.IV to 5.D.VI the monomeric units are connected by flexible alkylene spacers via ether and ester linkages respectively. The chemical structure has been characterized by a combination of spectroscopic techniques. The mesophases have been studied using polarizing optical microscopy, differential scanning calorimetry and X-ray diffraction measurements. The occurrence of the mesophase depends mainly on the terminal chain length and as a result series **5.D.I** and **5.D.IV** are dimesomorphic in nature and exhibit SmA and SmA' phases. The remaining series of dimers exhibit only SmA phase irrespective of the spacer and the terminal chain lengths. Interestingly, an odd-even effect is observed in the clearing temperatures as a function of terminal chain length for the ester linkage dimers containg a fixed odd spacer (m = 7). Very surprisingly, a phase transition between two orthogonal mesophases which are different only in their layer spacings has been observed. This has been attributed to conformational changes in the chains. Remarkably, the mesophases of all these dimers are stable upto room temperature. On the basis of our experiments, a model has been proposed for the packing of the dimeric molecules in the two orthogonal mesophases.

#### **Experimental**

#### **Dimethyl 5-hydroxyisophthalate, 5.b**

To a solution of 5-hydroxyisophthalic acid, **5.a** (25 g) in methanol (300 mL), a catalytic amount of conc. sulphuric acid was added and the resulting mixture was refluxed for about 24 h. Excess of methanol was distilled off, the reaction mixture was cooled and poured into ice-cold water. This mixture was extracted using ether (4 × 150 mL) and the combined ethereal solution was washed with 5% NaHCO<sub>3</sub> solution (2 × 150 mL) and then with brine solution several times and dried over anhydrous sodium sulphate. The solvent was evaporated and the residue obtained was passed through a column of silica gel and eluted using a mixture of 5% methanol in chloroform. The product **5.b** obtained after removal of the solvent was crystallized using chloroform. Yield: 25 g (86%); mp 161-163 °C; IR (nujol)  $\nu_{max}$ : 3357, 2923, 2852, 1726, 1703, 1654, 1618, 1598, 1463, 1431 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 8.25 (t, *J* = 1.08 Hz, 1H, Ar-H), 7.76 (d, *J* = 1.08 Hz, 2H, Ar-H), 3.94 (s, 6H, 2 × Ar-COO-CH<sub>3</sub>); Elemental analysis: C<sub>10</sub>H<sub>10</sub>O<sub>5</sub> requires C 57.14, H 4.78; found C 56.79, H 4.37%.

#### Tetramethyl-5,5'-(pentane-1,5-diylbis(oxy))diisophthalate, 5.c (n = 5)

A mixture of dimethyl 5-hydroxyisophthalate, **5.b** (1.91 g, 9.13 mmol), 1,5-dibromopentane (1 g, 4.3 mmol) and anhydrous potassium carbonate (3.6 g, 26.08 mmol) in anhydrous butan-2-one (150 mL) was refluxed for 24 h. Excess solvent was distilled off, the reaction mixture was cooled and poured into ice-cold water. This mixture was extracted using chloroform ( $3 \times 100$  mL). The organic solution was washed with aqueous 5% NaOH solution ( $2 \times 100$  mL) followed by water ( $3 \times 100$  mL) and dried over anhydrous sodium sulphate. The solvent was removed and the residue obtained was passed through a column of silica gel and eluted using chloroform. The product thus obtained on removal of the solvent was crystallized using chloroform and hexane. Yield: 1.95 g (92%); mp 111-113 °C; IR (nujol) v<sub>max</sub>: 3072, 2923, 2854, 1732, 1724, 1618, 1595, 1456, 1434, 1342 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.26 (t, 2H, Ar-H), 7.74 (d, J = 1.34 Hz, 4H, Ar-H), 4.08 (t, J = 6.19 Hz, 4H,  $2 \times$  Ar-O-CH<sub>2</sub>-), 1.71-1.67 (m, 2H, -(CH<sub>2</sub>)-); Elemental analysis: C<sub>25</sub>H<sub>28</sub>O<sub>10</sub> requires C 61.47, H 5.77; found C 61.3, H 5.92%.

#### 5,5'-(Pentane-1,5-diylbis(oxy))diisophthalic acid, 5.d (n = 5)

To a solution of tetramethyl-5,5'(pentane-1,5-bis(oxy))diisophthalate, **5.c** (1.8 g, 3.68 mmol) in ethanol (50 mL), potassium hydroxide (1.65 g, 29.5 mmol) and water (10 mL) were added and refluxed overnight. The excess of ethanol was distilled off, reaction mixture cooled and poured into ice-cold water. The resulting solution was acidified with conc. HCl and heated on a water-bath for an hour and cooled. The white precipitate thus obtained was filtered off, washed several times with ice-cold water until the washings were neutral to litmus and dried. The material **5.d** so obtained was crystallized using hexamethyl phosphoric acid triamide (HMPA) and water. Yield: 1.43 g (90%); mp > 250 °C; IR (nujol)  $v_{max}$ : 3352, 3089, 2922, 2852, 2671, 1735, 1732, 1681, 1606, 1542, 1456, 1406, 1377 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 13.28 (s, 4H, 4 × Ar-COOH, exchangeable with D<sub>2</sub>O), 8.07 (t, 2H, Ar-H), 7.64 (d, *J* = 1.25 Hz, 4H, Ar-H), 4.01 (t, *J* = 6.25 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 1.96-1.83 (quin, *J* = 6.74 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-C<u>H</u><sub>2</sub>-), 1.63-1.61 (m, 2H, -(CH<sub>2</sub>)-); Elemental analysis: C<sub>21</sub>H<sub>20</sub>O<sub>10</sub> requires C 58.33, H 4.65; found C 58.68, H 5.04%.

#### Tetramethyl-5,5'-(Hexane-1,6-diylbis(oxy))diisophthalate, 5.c (n = 6)

Yield: (92%); mp 137-138.5 °C; IR (nujol)  $\nu_{max}$ : 2922, 2852, 1737, 1722, 1618, 1595, 1460, 1436, 1348 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.26 (t, 2H, Ar-H), 7.73 (d, J = 1.32 Hz, 4H, Ar-H), 4.06 (t, J = 6.34 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 3.93 (s, 12H, 4 × Ar-COO-CH<sub>3</sub>), 1.88-1.83 (quin, J = 6.19 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.59-1.55 (m, 4H, -(CH<sub>2</sub>)<sub>2</sub>-); Elemental analysis: C<sub>26</sub>H<sub>30</sub>O<sub>10</sub> requires C 62.14, H 6.01; found C 61.81, H 6.26%.

#### 5,5'-(Hexane-1,6-diylbis(oxy))diisophthalic acid, 5.d (n = 6)

Yield: (95%); mp > 250 °C; IR (nujol)  $v_{max}$ : 3352, 3090, 2923, 2852, 2671, 1735, 1732, 1681, 1606, 1542, 1454, 1407, 1377 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 13.25 (s, 4H, Ar-COOH, exchangeable with D<sub>2</sub>O), 8.04 (t, 2H, Ar-H), 7.62 (d, *J* = 1.1 Hz, 4H, Ar-H), 4.08 (t, *J* = 6.2 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 1.8-1.74 (quin, *J* = 6.4 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-C<u>H</u><sub>2</sub>-), 1.59-1.49 (m, 4H, -(CH<sub>2</sub>)<sub>2</sub>-); Elemental analysis: C<sub>22</sub>H<sub>22</sub>O<sub>10</sub> requires C 59.17, H 4.97; found C 58.78, H 5.38%.

#### Tetramethyl-5,5'-(heptane-1,7-diylbis(oxy))diisophthalate, 5.c (n = 7)

Yield: (94%); mp 77-78.5 °C; IR (nujol)  $v_{max}$ : 2923, 2852, 1730, 1718, 1618, 1595, 1456, 1436, 1340 cm<sup>-1</sup>; H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.25 (t, 2H, Ar-H), 7.74 (d, J = 1.12 Hz, 4H, Ar-H), 4.04 (t, J = 6.3 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 3.93 (s, 12H, 4 × Ar-COO-CH<sub>3</sub>), 1.87-1.79 (quin, J = 6.4 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.52-1.45 (m, 6H, 2 × -(CH<sub>2</sub>)<sub>3</sub>-); Elemental analysis: C<sub>27</sub>H<sub>32</sub>O<sub>10</sub> requires C 62.78, H 6.24; found C 62.55, H 6.46%.

#### 5,5'-(Heptane-1,7-diylbis(oxy))diisophthalic acid, 5.d (n = 7)

Yield: (91%); mp > 250 °C; IR (nujol)  $v_{max}$ : 3352, 3087, 2923, 2852, 2673, 1732, 1727, 1681, 1603, 1542, 1456, 1406, 1377 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 13.25 (s, 4H, 4 × Ar-COOH, exchangeable with D<sub>2</sub>O), 8.04 (t, 2H, 2 × Ar-H), 7.61 (d, *J* = 1.32 Hz, 4H, Ar-H), 4.06 (t, *J* = 6.3 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 1.74-1.67 (quin, *J* = 6.74 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-C<u>H</u><sub>2</sub>-), 1.42-1.32 (m, 6H, -(CH<sub>2</sub>)<sub>3</sub>-); Elemental analysis: C<sub>23</sub>H<sub>24</sub>O<sub>10</sub> requires C 60 H 5.24; found C 59.8, H 5.39%.

#### Tetramethyl-5,5'-(octane-1,8-diylbis(oxy))diisophthalate, 5.c (n = 8)

Yield: (92%); mp 104-105 °C; IR (nujol)  $v_{max}$ : 2923, 2852, 1737, 1722, 1618, 1595, 1456, 1427, 1350 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.26 (t, 2H, Ar-H), 7.74 (d, J = 1.31 Hz, 4H, Ar-H), 4.04 (t, J = 6.39 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 3.93 (s, 12H, 4 × Ar-COO-CH<sub>3</sub>), 1.85-1.78 (quin, J = 6.88 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.49-1.4 (m, 8H, -(CH<sub>2</sub>)<sub>4</sub>-); Elemental analysis: C<sub>28</sub>H<sub>34</sub>O<sub>10</sub> requires 63.38, H 6.45; found C 62.99, H 6.55%.

#### 5,5'-(Octane-1,8-diylbis(oxy))diisophthalic acid, 5.d (n = 8)

Yield: (93%); mp > 250 °C; IR (nujol)  $v_{max}$ : 3354, 3089, 2923, 2852, 2669, 1737, 1732, 1681, 1606, 1542, 1454, 1406, 1377 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 13.25 (s, 4H, 4 × Ar-COOH, exchangeable with D<sub>2</sub>O), 8.04 (t, 2H, Ar-H), 7.61 (d, *J* = 1.1 Hz, 4H, Ar-H), 4.05 (t, *J* = 6.3 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 1.74-1.69 (quin, *J* = 6.7 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-C<u>H<sub>2</sub>-), 1.42-1.35 (m, 8H, -(CH<sub>2</sub>)<sub>4</sub>-); Elemental analysis: C<sub>24</sub>H<sub>26</sub>O<sub>10</sub> requires C 60.75, H 5.52; found C 60.78, H 5.8%.</u>

#### Tetramethyl-5,5'-(nonane-1,9-diylbis(oxy))diisophthalate, 5.c (n = 9)

Yield: (92%); mp 80-81 °C; IR (nujol)  $v_{max}$ : 2923, 2852, 1735, 1728, 1618, 1595, 1461, 1434, 1344 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.24 (t, 2H, Ar-H), 7.74 (d, J = 1.24 Hz, 4H, Ar-H), 4.04 (t, J = 6.6 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 3.93 (s, 12H, 4 × Ar-COO-CH<sub>3</sub>), 1.84-1.78 (quin, J = 6.88 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-C<u>H<sub>2</sub>-</u>), 1.42-1.35 (m, 10H, -(CH<sub>2</sub>)<sub>5</sub>-); Elemental analysis: C<sub>29</sub>H<sub>36</sub>O<sub>10</sub> requires 63.96, H 6.65; found C 63.66, H 6.3%.

#### 5,5'-(Nonane-1,9-diylbis(oxy))diisophthalic acid, 5.d (n = 9)

Yield: (94%); mp > 250 °C; IR (nujol)  $v_{max}$ : 3346, 3089, 2922, 2852, 2667, 1735, 1732, 1681, 1606, 1542, 1456, 1406, 1377 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 13.26 (s, 4H, 4 × Ar-COOH, exchangeable with D<sub>2</sub>O), 8.04 (t, 2H, Ar-H), 7.61 (d, *J* = 1.3 Hz, 4H, Ar-H), 4.05 (t, *J* = 6.2 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 1.73-1.70 (quin, *J* = 6.9 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-C<u>H<sub>2</sub>-), 1.47-1.24 (m, 10H, -(CH<sub>2</sub>)<sub>5</sub>-); Elemental analysis: C<sub>25</sub>H<sub>28</sub>O<sub>10</sub> requires C 61.47, H 5.78; found C 61.21, H 5.46%.</u>

#### Tetramethyl-5,5'-(decane-1,10-diylbis(oxy))diisophthalate, 5.c (n = 10)

Yield: (95%); mp 101.5-103 °C; IR (nujol)  $v_{max}$ : 2922, 2852, 1737, 1722, 1618, 1595, 1458, 1377, 1348 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.25 (t, 2H, Ar-H), 7.73 (d, J = 1.2 Hz, 4H, Ar-H), 4.04 (t, J = 6.45 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 3.93 (s, 12H, 4 × Ar-COO-CH<sub>3</sub>), 1.82-1.78 (quin, J = 6.62 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.47-1.34 (m, 12H, -(CH<sub>2</sub>)<sub>6</sub>-); Elemental analysis: C<sub>30</sub>H<sub>38</sub>O<sub>10</sub> requires C 64.5, H 6.85; found C 64.11, H 7.15%.

#### 5,5'-(Decane-1,10-diylbis(oxy))diisophthalic acid, 5.d (n = 10)

Yield: (93%); mp > 250 °C; IR (nujol)  $v_{max}$ : 3352, 3089, 2923, 2852, 2671, 1735, 1732, 1681, 1606, 1542, 1456, 1406, 1377 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 13.24 (s, 4H, 4 × Ar-COOH, exchangeable with D<sub>2</sub>O), 8.04 (t, 2H, Ar-H), 7.61 (d, *J* = 1.1 Hz, 4H, Ar-H), 4.04 (t, *J* = 6.3 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 1.72-1.67 (quin, *J* = 6.7 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-C<u>H<sub>2</sub>-), 1.4-1.28</u> (m, 12H, -(CH<sub>2</sub>)<sub>6</sub>-); Elemental analysis: C<sub>26</sub>H<sub>30</sub>O<sub>10</sub> requires C 62.14, H 6.01; found C 61.72, H 6.06%.

#### Tetramethyl-5,5'-(undecane-1,11-diylbis(oxy))diisophthalate, 5.c (n = 11)

Yield: (92%); mp 83-84.5 °C; IR (nujol)  $v_{max}$ : 2922, 2852, 1735, 1728, 1618, 1595, 1456, 1377, 1344 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.25 (t, 2H, Ar-H), 7.74 (d, J = 1.3 Hz, 4H, Ar-H), 4.03 (t, J = 6.45 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 3.93 (s, 12H, 4 × Ar-COO-CH<sub>3</sub>), 1.82-1.77 (quin, J = 7 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.48-1.32 (m, 14H, -(CH<sub>2</sub>)<sub>7</sub>-); Elemental analysis: C<sub>31</sub>H<sub>40</sub>O<sub>10</sub> requires C 65.02, H 7.03; found C 64.91, H 6.8%.

#### 5,5'-(Undecane-1,11-diylbis(oxy))diisophthalic acid, 5.d (n = 11)

Yield: (94%); mp > 250 °C; IR (nujol)  $v_{max}$ : 3354, 3089, 2923, 2852, 2669, 1732, 1728, 1681, 1606, 1542, 1456, 1406, 1377 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 13.25 (s, 4H, 4 × Ar-COOH, exchangeable with D<sub>2</sub>O), 8.04 (t, 2H, Ar-H), 7.6 (d, *J* = 1.1 Hz, 4H, Ar-H), 4.04 (t, *J* = 6.2 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 1.72-1.63 (quin, *J* = 6.7 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-C<u>H</u><sub>2</sub>-), 1.4-1.27 (m, 14H, -(CH<sub>2</sub>)<sub>7</sub>-); Elemental analysis: C<sub>27</sub>H<sub>32</sub>O<sub>10</sub> requires C 62.78, H 6.23; found C 62.35, H 6.19%.

#### Tetramethyl-5,5'-(dodecane-1,12-diylbis(oxy))diisophthalate, 5.c (n = 12)

Yield: (92%); mp 104-105.5 °C; IR (nujol)  $v_{max}$ : 2923, 2852, 1737, 1722, 1618, 1595, 1460, 1377, 1348 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.25 (t, 2H, Ar-H), 7.73 (d, J = 1.24 Hz, 4H, Ar-H), 4.03 (t, J = 6.45 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 3.93 (s, 12H, 4 × Ar-COO-CH<sub>3</sub>), 1.82-1.76 (quin, J = 6.88 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.47-1.3 (m, 16H, -(CH<sub>2</sub>)<sub>8</sub>-); Elemental analysis: C<sub>32</sub>H<sub>42</sub>O<sub>10</sub> requires C 65.51, H 7.21; found C 65.4, H 7.07%.

#### 5,5'-(dodecane-1,12-diylbis(oxy))diisophthalic acid, 5.d (n = 12)

Yield: (91%); mp > 250 °C; IR (nujol)  $v_{max}$ : 3342, 2922, 2825, 2671, 1735, 1681, 1606, 1541, 1456, 1377 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 13.26 (s, 4H, 4 × Ar-COOH, exchangeable with D<sub>2</sub>O), 8.04 (t, 2H, Ar-H), 7.61 (d, J = 1.25 Hz, 4H, Ar-H), 4.04 (t, J = 6.25 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 1.75-1.65 (quin, J = 6.74 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-C<u>H<sub>2</sub>-</u>), 1.4-1.25 (m, 16H, -(CH<sub>2</sub>)<sub>8</sub>-); Elemental analysis: C<sub>28</sub>H<sub>34</sub>O<sub>10</sub> requires C 63.38, H 6.45; found C 62.99, H 6.24%.

#### 4-*n*-Decyloxyphenyl-4-benzyloxybenzoate, 5.i (n = 10)

4-*n*-Decyloxyphenol, **5.g** (5 g, 20 mmol) was mixed with 4-benzyloxybenzoic acid, **5.h** (4.56 g, 20 mmol) in dry dichloromethane (50 mL) in the presence of a catalytic amount of DMAP and stirred for 10 min. To this mixture, DCC (4.53 g, 22 mmol) was added and stirring continued for 24 h at room temperature. The precipitated dicyclohexylurea was filtered off and washed with chloroform several times. Evaporation of the solvent from the filtrate gave a white material. This material was purified by column chromatography on silica gel using chloroform as an eluent. Removal of the solvent from the eluate gave compound **5.i** which was crystallized from ethanol. Yield: 8.74 g (95%); mp 121.5-122 °C; IR (nujol) v<sub>max</sub>: 2922, 2852, 1724, 1739, 1606, 1510, 1454, 1377, 1280 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.14 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.48-7.33 (m, 5H, Ar-H), 7.09 (d, *J* = 8.96 Hz, 2H, Ar-H), 7.05 (d, *J* = 8.92 Hz, 2H, Ar-H), 6.91 (d, *J* = 9 Hz, 2H, Ar-H), 5.15 (s, 2H, -O-CH<sub>2</sub>-Ar), 3.95 (t, *J* = 6.54 Hz, 2H, Ar-O-CH<sub>2</sub>-), 1.81-1.74 (quin, *J* = 6.64 Hz, 2H, Ar-O-CH<sub>2</sub>-C<u>H</u><sub>2</sub>-), 1.45-1.29 (m, 14H, -(CH<sub>2</sub>)<sub>7</sub>-), 0.89 (t, *J* = 6.52 Hz, 3H, -CH<sub>3</sub>); Elemental analysis: C<sub>30</sub>H<sub>36</sub>O<sub>4</sub> requires C 78.23, H 7.87; found C 78.42, H 8.01%.

#### 4-*n*-Decyloxyphenyl-4-hydroxybenzoate, 5.j (n = 10)

Compound **5.i** (8 g, 17.39 mmol) was dissolved in 1,4-dioxane (50 mL) and 5% Pd-C catalyst (1.6 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 mixture was filtered, the solvent removed under reduced pressure and the residue was crystallized from a mixture of 1,4-dioxane and hexane. Thus, pure compound **5.j** was obtained. Yield: 5.66 g (88%); mp 145-146 °C; IR (nujol)  $v_{max}$ : 3377, 2922, 2852, 1730, 1705, 1608, 1514, 1458 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.09 (d, *J* = 8.68 Hz, 2H, Ar-H), 7.09 (d, *J* = 8.92 Hz, 2H, Ar-H), 6.92-6.89 (m, 4H, Ar-H), 3.94 (t, *J* = 6.52 Hz, 2H, Ar-O-CH<sub>2</sub>-), 1.81-1.74 (quin, *J* = 6.72 Hz, 2H, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.46-1.28 (m, 14H, -(CH<sub>2</sub>)<sub>7</sub>-), 0.88 (t, *J* = 6.88 Hz, 3H, -CH<sub>3</sub>); Elemental analysis: C<sub>23</sub>H<sub>30</sub>O<sub>4</sub> requires C 74.57, H 8.15; found C 74.28, H 8.41%.

#### 4-*n*-Undecyloxyphenyl-4-benzyloxybenzoate, 5.i (n = 11)

Yield: (87%); mp 121-122 °C; IR (nujol)  $v_{max}$ : 2922, 2852, 1724, 1606, 1510, 1463, 1377, 1282, 1253 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.14 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.48-7.33

(m, 5H, Ar-H), 7.09 (d, J = 8.96 Hz, 2H, Ar-H), 7.05 (d, J = 8.92 Hz, 2H, Ar-H), 6.91 (d, J = 9 Hz, 2H, Ar-H), 5.15 (s, 2H, -O-CH<sub>2</sub>-Ar), 3.95 (t, J = 6.54 Hz, 2H, Ar-O-CH<sub>2</sub>-), 1.81-1.74 (quin, J = 6.64 Hz, 2H, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.45-1.29 (m, 16H, -(CH<sub>2</sub>)<sub>8</sub>-), 0.89 (t, J = 6.52 Hz, 3H, -CH<sub>3</sub>); Elemental analysis: C<sub>31</sub>H<sub>38</sub>O<sub>4</sub> requires C 78.45, H 8.06; found C 78.01, H 8.3%.

#### 4-*n*-Undecyloxyphenyl-4-hydroxybenzoate, 5.j (*n* = 11)

Yield: (89%); mp 140.5-141.5 °C; IR (nujol)  $v_{max}$ : 3375, 2922, 2852, 1728, 1708, 1610, 1596, 1514, 1463 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.09 (d, *J* = 8.68 Hz, 2H, Ar-H), 7.09 (d, *J* = 8.92 Hz, 2H, Ar-H), 6.92-6.89 (m, 4H, Ar-H), 3.94 (t, *J* = 6.52 Hz, 2H, Ar-O-CH<sub>2</sub>-), 1.81-1.74 (quin, *J* = 6.72 Hz, 2H, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.46-1.28 (m, 16H, -(CH<sub>2</sub>)<sub>8</sub>-), 0.88 (t, *J* = 6.88 Hz, 3H, -CH<sub>3</sub>); Elemental analysis: C<sub>24</sub>H<sub>32</sub>O<sub>4</sub> requires C 74.97, H 8.38; found C 74.59, H 8.1%.

#### 4-*n*-Dodecyloxyphenyl-4-benzyloxybenzoate, 5.i (*n* = 12)

Yield: (88%); mp 119-120 °C; IR (nujol)  $v_{max}$ : 2920, 2852, 1724, 1606, 1510, 1463, 1456, 1377, 1280, 1255 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.14 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.48-7.33 (m, 5H, Ar-H), 7.09 (d, *J* = 8.96 Hz, 2H, Ar-H), 7.05 (d, *J* = 8.92 Hz, 2H, Ar-H), 6.91 (d, *J* = 9 Hz, 2H, Ar-H), 5.15 (s, 2H, -O-CH<sub>2</sub>-Ar), 3.95 (t, *J* = 6.54 Hz, 2H, Ar-O-CH<sub>2</sub>-), 1.81-1.74 (quin, *J* = 6.64 Hz, 2H, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.45-1.29 (m, 18H, -(CH<sub>2</sub>)<sub>9</sub>-), 0.89 (t, *J* = 6.52 Hz, 3H, -CH<sub>3</sub>); Elemental analysis: C<sub>32</sub>H<sub>40</sub>O<sub>4</sub> requires C 78.66, H 8.24; found C 78.23, H 8.59%.

#### 4-*n*-Dodecyloxyphenyl-4-hydroxybenzoate, 5.j (*n* = 12)

Yield: (90%); mp 137-138.5 °C; IR (nujol)  $v_{max}$ : 3375, 2922, 2852, 1728, 1706, 1610, 1596, 1514, 1463 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.09 (d, *J* = 8.68 Hz, 2H, Ar-H), 7.09 (d, *J* = 8.92 Hz, 2H, Ar-H), 6.92-6.89 (m, 4H, Ar-H), 3.94 (t, *J* = 6.52 Hz, 2H, Ar-O-CH<sub>2</sub>-), 1.81-1.74 (quin, *J* = 6.72 Hz, 2H, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.46-1.28 (m, 18H, -(CH<sub>2</sub>)<sub>9</sub>-), 0.88 (t, *J* = 6.88 Hz, 3H, -CH<sub>3</sub>); Elemental analysis: C<sub>25</sub>H<sub>34</sub>O<sub>4</sub> requires C 75.34, H 8.59; found C 75.12, H 8.62%.

#### 4-*n*-Tridecyloxyphenyl-4-benzyloxybenzoate, 5.i (n = 13)

Yield: (92%); mp 119.5-121 °C; IR (nujol) v<sub>max</sub>: 2922, 2852, 1727, 1606, 1510, 1463,

1456, 1377, 1282, 1255 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.14 (d, *J* = 8.5 Hz, 2H, Ar-H), 7.48-7.33 (m, 5H, Ar-H), 7.09 (d, *J* = 8.94 Hz, 2H, Ar-H), 7.05 (d, *J* = 8.88 Hz, 2H, Ar-H), 6.91 (d, *J* = 8.9 Hz, 2H, Ar-H), 5.15 (s, 2H, -O-CH<sub>2</sub>-Ar), 3.95 (t, *J* = 6.4 Hz, 2H, Ar-O-CH<sub>2</sub>-), 1.81-1.74 (quin, *J* = 6.68 Hz, 2H, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.47-1.3 (m, 20H, -(CH<sub>2</sub>)<sub>10</sub>-), 0.88 (t, *J* = 6.44 Hz, 3H, -CH<sub>3</sub>); Elemental analysis: C<sub>33</sub>H<sub>42</sub>O<sub>4</sub> requires C 78.86, H 8.47; found C 78.9, H 8.88%.

#### 4-*n*-Tridecyloxyphenyl-4-hydroxybenzoate, 5.j (n = 13)

Yield: (90%); mp 136.5-138 °C; IR (nujol)  $v_{max}$ : 3375, 2922, 2852, 1728, 1708, 1608, 1596, 1514, 1463 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.09 (d, *J* = 8.68 Hz, 2H, Ar-H), 7.09 (d, *J* = 8.92 Hz, 2H, Ar-H), 6.92-6.89 (m, 4H, Ar-H), 3.94 (t, *J* = 6.52 Hz, 2H, Ar-O-CH<sub>2</sub>-), 1.81-1.74 (quin, *J* = 6.72 Hz, 2H, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.46-1.28 (m, 20H, -(CH<sub>2</sub>)<sub>10</sub>-), 0.88 (t, *J* = 6.88 Hz, 3H, -CH<sub>3</sub>); Elemental analysis: C<sub>26</sub>H<sub>36</sub>O<sub>4</sub> requires C 75.69, H 8.78; found C 75.96, H 8.69%.

#### 4-*n*-Tetradecyloxyphenyl-4-benzyloxybenzoate, 5.i (*n* = 14)

Yield: (89%); mp 117-118 °C; IR (nujol)  $v_{max}$ : 2922, 2850, 1724, 1606, 1512, 1463, 1377, 1282, 1255 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.14 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.48-7.33 (m, 5H, Ar-H), 7.09 (d, *J* = 8.96 Hz, 2H, Ar-H), 7.05 (d, *J* = 8.92 Hz, 2H, Ar-H), 6.91 (d, *J* = 9 Hz, 2H, Ar-H), 5.15 (s, 2H, -O-CH<sub>2</sub>-Ar), 3.95 (t, *J* = 6.54 Hz, 2H, Ar-O-CH<sub>2</sub>-), 1.81-1.74 (quin, *J* = 6.64 Hz, 2H, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.45-1.29 (m, 22H, -(CH<sub>2</sub>)<sub>11</sub>-), 0.89 (t, *J* = 6.52 Hz, 3H, -CH<sub>3</sub>); Elemental analysis: C<sub>34</sub>H<sub>44</sub>O<sub>4</sub> requires C 79.03, H 8.57; found C 78.62, H 8.93%.

#### 4-*n*-Tetradecyloxyphenyl-4-hydroxybenzoate, 5.j (*n* = 14)

Yield: (92%); mp 138-139 °C; IR (nujol)  $v_{max}$ : 3377, 2920, 2852, 1728, 1708, 1606, 1596, 1514, 1461 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.09 (d, *J* = 8.68 Hz, 2H, Ar-H), 7.09 (d, *J* = 8.92 Hz, 2H, Ar-H), 6.92-6.89 (m, 4H, Ar-H), 3.94 (t, *J* = 6.52 Hz, 2H, Ar-O-CH<sub>2</sub>-), 1.81-1.74 (quin, *J* = 6.72 Hz, 2H, Ar-O-CH<sub>2</sub>-C<u>H</u><sub>2</sub>-), 1.46-1.28 (m, 22H, -(CH<sub>2</sub>)<sub>11</sub>-), 0.88 (t, *J* = 6.88 Hz, 3H, -CH<sub>3</sub>); Elemental analysis: C<sub>27</sub>H<sub>38</sub>O<sub>4</sub> requires C 76.03, H 8.97; found C 75.6, H 9.07%.

#### 4-*n*-Pentadecyloxyphenyl-4-benzyloxybenzoate, 5.i (n = 15)

Yield: (88%); mp 119-121 °C; IR (nujol)  $v_{max}$ : 2922, 2852, 1724, 1681, 1606, 1510, 1463, 1454, 1377, 1280, 1253 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.14 (d, J = 8.2 Hz, 2H, Ar-H), 7.48-7.33 (m, 5H, Ar-H), 7.09 (d, J = 8.7 Hz, 2H, Ar-H), 7.05 (d, J = 8.9 Hz, 2H, Ar-H), 6.91 (d, J = 8.8 Hz, 2H, Ar-H), 5.15 (s, 2H, -O-CH<sub>2</sub>-Ar), 3.95 (t, J = 6.4 Hz, 2H, Ar-O-CH<sub>2</sub>-), 1.81-1.74 (quin, J = 6.42 Hz, 2H, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.45-1.29 (m, 24H, -(CH<sub>2</sub>)<sub>12</sub>-), 0.89 (t, J = 6.54 Hz, 3H, -CH<sub>3</sub>); Elemental analysis: C<sub>35</sub>H<sub>46</sub>O<sub>4</sub> requires C 79.21, H 8.72; found C 79.21, H 9.1%.

#### 4-*n*-Pentadecyloxyphenyl-4-hydroxybenzoate, 5.j (*n* = 15)

Yield: (90%); mp 135-136.5 °C; IR (nujol)  $v_{max}$ : 3379, 2920, 2852, 1728, 1706, 1610, 1596, 1514, 1463, 1377 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.09 (d, *J* = 8.68 Hz, 2H, Ar-H), 7.09 (d, *J* = 8.94 Hz, 2H, Ar-H), 6.92-6.89 (m, 4H, Ar-H), 3.94 (t, *J* = 6.54 Hz, 2H, Ar-O-CH<sub>2</sub>-), 1.81-1.74 (quin, *J* = 6.76 Hz, 2H, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.46-1.28 (m, 24H, -(CH<sub>2</sub>)<sub>12</sub>-), 0.88 (t, *J* = 6.82 Hz, 2H, -CH<sub>3</sub>); Elemental analysis: C<sub>28</sub>H<sub>40</sub>O<sub>4</sub> requires C 76.33, H 9.14; found C 76.63, H 9.52%.

#### 4-*n*-Hexadecyloxyphenyl-4-benzyloxybenzoate, 5.i (*n* = 16)

Yield: (90%); mp 119-119.5 °C; IR (nujol)  $v_{max}$ : 2954, 2920, 2850, 1739, 1610, 1514, 1463, 1377, 1286, 1251 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.14 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.48-7.33 (m, 5H, Ar-H), 7.09 (d, *J* = 8.96 Hz, 2H, Ar-H), 7.05 (d, *J* = 8.92 Hz, 2H, Ar-H), 6.91 (d, *J* = 9 Hz, 2H, Ar-H), 5.15 (s, 2H, -O-CH<sub>2</sub>-Ar), 3.95 (t, *J* = 6.54 Hz, 2H, Ar-O-CH<sub>2</sub>-), 1.81-1.74 (quin, *J* = 6.64 Hz, 2H, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.45-1.29 (m, 26H, -(CH<sub>2</sub>)<sub>13</sub>-), 0.89 (t, *J* = 6.52 Hz, 3H, -CH<sub>3</sub>); Elemental analysis: C<sub>36</sub>H<sub>48</sub>O<sub>4</sub> requires C 79.37, H 8.87; found C 79.45, H 9.24%.

#### 4-*n*-Hexadecyloxyphenyl-4-hydroxybenzoate, 5.j (*n* = 16)

Yield: (90%); mp 135.6-136.5 °C; IR (nujol)  $v_{max}$ : 3379, 2920, 2850, 1728, 1708, 1705, 1610, 1596, 1514, 1465 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.09 (d, J = 8.68 Hz, 2H, Ar-H), 7.09 (d, J = 8.92 Hz, 2H, Ar-H), 6.92-6.89 (m, 4H, Ar-H), 3.94 (t, J = 6.52 Hz, 2H, Ar-O-CH<sub>2</sub>-), 1.81-1.74 (quin, J = 6.72 Hz, 2H, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.46-1.28 (m, 26H, -(CH<sub>2</sub>)<sub>13</sub>-), 0.88 (t,

J = 6.88 Hz, 3H, -CH<sub>3</sub>); Elemental analysis: C<sub>29</sub>H<sub>42</sub>O<sub>4</sub> requires C 76.61, H 9.3; found C 76.25, H 9.62%.

#### 4-*n*-Octadecyloxyphenyl-4-benzyloxybenzoate, 5.i (*n* = 18)

Yield: (89%); mp 118-118.5 °C; IR (nujol)  $v_{max}$ : 2954, 2920, 2850, 1741, 1739, 1610, 1514, 1463, 1377, 1251 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.14 (d, J = 8.8 Hz, 2H, Ar-H), 7.48-7.33 (m, 5H, Ar-H), 7.09 (d, J = 8.96 Hz, 2H, Ar-H), 7.05 (d, J = 8.92 Hz, 2H, Ar-H), 6.91 (d, J = 9 Hz, 2H, Ar-H), 5.15 (s, 2H, -O-CH<sub>2</sub>-Ar), 3.95 (t, J = 6.54 Hz, 2H, Ar-O-CH<sub>2</sub>-), 1.81-1.74 (quin, J = 6.64 Hz, 2H, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.45-1.29 (m, 30H, -(CH<sub>2</sub>)<sub>15</sub>-), 0.89 (t, J = 6.52 Hz, 3H, -CH<sub>3</sub>); Elemental analysis: C<sub>38</sub>H<sub>52</sub>O<sub>4</sub> requires C 79.68, H 9.14; found C 79.4, H 8.81%.

#### 4-*n*-Octadecyloxyphenyl-4-hydroxybenzoate, 5.j (*n* = 18)

Yield: (93%); mp 132-133 °C; °C IR (nujol)  $v_{max}$ : 3386, 2922, 2850, 1728, 1610, 1598, 1514, 1454 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.09 (d, J = 8.68 Hz, 2H, Ar-H), 7.09 (d, J = 8.92 Hz, 2H, Ar-H), 6.92-6.89 (m, 4H, Ar-H), 3.94 (t, J = 6.52 Hz, 2H, Ar-O-CH<sub>2</sub>-), 1.81-1.74 (quin, J = 6.72 Hz, 2H, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.46-1.28 (m, 30H, -(CH<sub>2</sub>)<sub>15</sub>-), 0.88 (t, J = 6.88 Hz, 3H, -CH<sub>3</sub>); Elemental analysis: C<sub>31</sub>H<sub>46</sub>O<sub>4</sub> requires C 77.14, H 9.59; found C 76.72, H 9.97%.

#### Dimethyl 5-benzyloxyisophthalate, 5.e

This was prepared following a procedure described for the synthesis of compound **5.c**, by using compound **5.b**, benzyl chloride and anhydrous potassium carbonate in butan-2-one. Yield: 26 g (91%); mp 92-93 °C; IR (nujol)  $v_{max}$ : 2923, 2825, 1720, 1595, 1460, 1433, 1346, 1249 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.28 (t, *J* = 1.48 Hz, 1H, Ar-H), 7.83 (d, *J* = 1.44 Hz, 2H, Ar-H), 7.45-7.33 (m, 5H, Ar-H), 5.14 (s, 2H, -O-CH<sub>2</sub>-Ar), 3.93 (s, 6H, 2 × Ar-COO-CH<sub>3</sub>); Elemental analysis: C<sub>17</sub>H<sub>16</sub>O<sub>5</sub> requires C 67.99, H 5.37; found C 67.59, H 5.56%.

#### 5-Benzyloxyisophthalic acid, 5.f

This was synthesized following a procedure described for the synthesis of compound **5.d**, by using dimethyl 5-benzyloxyisophthalate, **5.e**, 10% ethanolic potassium hydroxide and water. Yield: 16.3 g (90%); mp >250 °C; IR (nujol)  $v_{max}$ : 2923, 2854, 2644, 2557, 2503, 1697, 1693, 1981, 1593, 1454 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>COCD<sub>3</sub>)  $\delta$ : 8.29 (t, *J* = 1.4 Hz, 1H, Ar-H), 7.85

(d, J = 1.44 Hz, 2H, Ar-H), 7.53 (d, J = 7.36 Hz, 2H, Ar-H), 7.4 (t, J = 8.4 Hz, 2H, Ar-H), 7.33 (t, J = 7.2 Hz, 1H, Ar-H), 5.28 (s, 2H, Ar-O-CH<sub>2</sub>-); Elemental analysis: C<sub>15</sub>H<sub>12</sub>O<sub>5</sub> requires C 66.18, H 4.43; found C 66.54, H 4.06%.

#### **5-Benzyloxy bis**[4-(*n*-decyloxyphenyloxycarbonyl)phenylisophthalate], **5.**k (*n* = 10)

This was prepared following the procedure described for the synthesis of compound **5.i**, by using compound **5.f** and compound **5.j** in dry dichloromethane. Yield: (85%); mp 111-112.5 °C; IR (nujol)  $v_{max}$ : 2923, 2852, 1747, 1732, 1730, 1604, 1596, 1512, 1465, 1377, 1344, 1271, 1255 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.64 (t, 1H, Ar-H), 8.3 (d, J = 8.72 Hz, 4H, Ar-H), 8.08 (d, J = 1.4 Hz, 2H, Ar-H), 7.49-7.43 (m, 5H, Ar-H), 7.39 (d, J = 8.76 Hz, 4H, Ar-H), 7.12 (d, J = 9 Hz, 4H, Ar-H), 6.93 (d, J = 9 Hz, 4H, Ar-H), 5.24 (s, 2H, -O-CH<sub>2</sub>-Ar), 3.96 (t, J = 6.52 Hz, 4H,  $2 \times \text{Ar-O-CH}_2$ -), 1.82-1.75 (quin, J = 6.76 Hz, 4H,  $2 \times \text{Ar-O-CH}_2$ -CH<sub>2</sub>-), 1.49-1.25 (m, 28H,  $2 \times -(\text{CH}_2)_7$ -), 0.87 (t, J = 6.52 Hz, 6H,  $2 \times -\text{CH}_3$ ); Elemental analysis: C<sub>61</sub>H<sub>68</sub>O<sub>11</sub> requires C 74.98, H 7.01; found C 74.56, H 6.75%.

#### 5-Hydroxy bis[4-(n-decyloxyphenyloxycarbonyl)phenylisophthalate], 5.1 (n = 10)

This was synthesized following a procedure described for the synthesis of compound **5.j**, by using compound **5.k** as starting material. Yield: (85%); mp 185 °C; IR (nujol)  $v_{max}$ : 3562, 3070, 2920, 2852, 1737, 1732, 1602, 1512, 1454, 1377, 1344, 1290, 1253 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.62 (t, 1H, Ar-H), 8.28 (d, J = 8.72 Hz, 4H, Ar-H), 7.94 (d, J = 1.4 Hz, 2H, Ar-H), 7.39 (d, J = 8.72 Hz, 4H, Ar-H), 7.12 (d, J = 9 Hz, 4H, Ar-H), 6.92 (d, J = 9 Hz, 4H, Ar-H), 3.96 (t, J = 6.52 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 1.80-1.76 (quin, J = 6.4 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.39-1.26 (m, 28H, 2 × -(CH<sub>2</sub>)<sub>7</sub>-), 0.87 (t, J = 6.56 Hz, 6H, 2 × -CH<sub>3</sub>); Elemental analysis: C<sub>54</sub>H<sub>62</sub>O<sub>11</sub> requires C 73.12, H 7.04; found C 72.85, H 7.22%.

#### 5-Benzyloxy bis[4-(*n*-undecyloxyphenyloxycarbonyl)phenylisophthalate], 5.k (*n* = 11)

Yield: (90%); mp 121-122 °C; IR (nujol)  $v_{max}$ : 2923, 2852, 1747,1745, 1732, 1730, 1652, 1595, 1510, 1465, 1377, 1271, 1255 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.64 (t, 1H, Ar-H), 8.30 (d, J = 8.72 Hz, 4H, Ar-H), 8.08 (d, J = 1.4 Hz, 2H, Ar-H), 7.49-7.43 (m, 5H, Ar-H), 7.39 (d, J = 8.76 Hz, 4H, Ar-H), 7.12 (d, J = 9 Hz, 4H, Ar-H), 6.93 (d, J = 9 Hz, 4H, Ar-H), 5.24 (s, 2H, -O-CH<sub>2</sub>-Ar), 3.96 (t, J = 6.52 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 1.82-1.75 (quin, J = 6.76 Hz, 4H,

2 × Ar-O-CH<sub>2</sub>-C<u>H</u><sub>2</sub>-), 1.49-1.25 (m, 32H, 2 × -(CH<sub>2</sub>)<sub>8</sub>-), 0.87 (t, J = 6.52 Hz, 6H, 2 × -CH<sub>3</sub>); Elemental analysis: C<sub>63</sub>H<sub>72</sub>O<sub>11</sub> requires C 75.22, H 7.21; found C 74.73, H 7.35%.

#### **5-Hydroxy bis**[4-(*n*-undecyloxyphenyloxycarbonyl)phenylisophthalate], **5.** (*n* = 11)

Yield: (88%); mp 181.5 °C; IR (nujol)  $v_{max}$ : 3560, 2918, 2850, 1737, 1732, 1602, 1510, 1463, 1377, 1288, 1253 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.62 (t, 1H, Ar-H), 8.28 (d, J = 8.72 Hz, 4H, Ar-H), 7.94 (d, J = 1.4 Hz, 2H, Ar-H), 7.39 (d, J = 8.72 Hz, 4H, Ar-H), 7.12 (d, J = 9 Hz, 4H, Ar-H), 6.92 (d, J = 9 Hz, 4H, Ar-H), 3.96 (t, J=6.52 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 1.80-1.76 (quin, J = 6.4 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.39-1.26 (m, 32H, 2 × -(CH<sub>2</sub>)<sub>8</sub>-), 0.87 (t, J = 6.56 Hz, 6H, 2 × -CH<sub>3</sub>); Elemental analysis: C<sub>56</sub>H<sub>66</sub>O<sub>11</sub> requires C 73.4, H 7.27; found C 73.62, H 7.41%.

#### **5-Benzyloxy bis**[4-(*n*-dodecyloxyphenyloxycarbonyl)phenylisophthalate], **5.**k (*n* = 12)

Yield: (92%); mp 110.5-111.5 °C; IR (nujol)  $v_{max}$ : 2922, 2852, 1747, 1745, 1732, 1730, 1595, 1463, 1377, 1269, 1253 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.64 (t, 1H, Ar-H), 8.3 (d, J = 8.72 Hz, 4H, Ar-H), 8.08 (d, J = 1.4 Hz, 2H, Ar-H), 7.49-7.43 (m, 5H, Ar-H), 7.39 (d, J = 8.76 Hz, 4H, Ar-H), 7.12 (d, J = 9 Hz, 4H, Ar-H), 6.93 (d, J = 9 Hz, 4H, Ar-H), 5.24 (s, 2H, -O-CH<sub>2</sub>-Ar), 3.96 (t, J = 6.52 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 1.82-1.75 (quin, J = 6.76 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.49-1.25 (m, 36H, 2 × -(CH<sub>2</sub>)<sub>9</sub>-), 0.87 (t, J = 6.52 Hz, 6H, 2 × -CH<sub>3</sub>); Elemental analysis: C<sub>65</sub>H<sub>76</sub>O<sub>11</sub> requires C 75.55, H 7.41; found C 75.15, H 7.5%.

#### **5-Hydroxy bis**[4-(*n*-dodecyloxyphenyloxycarbonyl)phenylisophthalate], **5.** (*n* = 12)

Yield: (85%); mp 179.5 °C; IR (nujol)  $v_{max}$ : 3560, 2918, 2850, 1739, 1733, 1602, 1512, 1463, 1377, 1276, 1253 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.62 (t, 1H, Ar-H), 8.28 (d, J = 8.72 Hz, 4H, Ar-H), 7.94 (d, J = 1.4 Hz, 2H, Ar-H), 7.39 (d, J = 8.72 Hz, 4H, Ar-H), 7.12 (d, J = 9 Hz, 4H, Ar-H), 6.92 (d, J = 9 Hz, 4H, Ar-H), 3.96 (t, J = 6.52 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 1.80-1.76 (quin, J = 6.4 Hz, 4H, 2×Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.39-1.26 (m, 36H, 2 × -(CH<sub>2</sub>)<sub>9</sub>-), 0.87 (t, J = 6.56 Hz, 6H, 2 × -CH<sub>3</sub>); C<sub>58</sub>H<sub>70</sub>O<sub>11</sub> requires C 73.87, H 7.47; found C 73.49, H 7.57%.

#### **5-Benzyloxy bis**[4-(*n*-tridecyloxyphenyloxycarbonyl)phenylisophthalate], **5.**k (*n* = 13)

Yield: (88%); mp 101.5-103 °C; IR (nujol) v<sub>max</sub>: 2922, 2852, 1749, 1737, 1604, 1596,

1465, 1377, 1344, 1271, 1255 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.64 (t, 1H, Ar-H), 8.30 (d, J = 8.72 Hz, 4H, Ar-H), 8.08 (d, J = 1.2 Hz, 2H, Ar-H), 7.50-7.42 (m, 5H, Ar-H), 7.39 (d, J = 8.4 Hz, 4H, Ar-H), 7.12 (d, J = 8.9 Hz, 4H, Ar-H), 6.94 (d, J = 8.8 Hz, 4H, Ar-H), 5.24 (s, 2H, -O-CH<sub>2</sub>-Ar), 3.96 (t, J = 7.4 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 1.82-1.75 (quin, J = 6.6 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.46-1.27 (m, 40H, 2 × -(CH<sub>2</sub>)<sub>10</sub>-), 0.88 (t, J = 6.56 Hz, 6H, 2 × -CH<sub>3</sub>); Elemental analysis: C<sub>67</sub>H<sub>80</sub>O<sub>11</sub> requires C 75.82, H 7.59; found C 75.43, H 7.74%.

#### 5-Hydroxy bis[4-(*n*-tridecyloxyphenyloxycarbonyl)phenylisophthalate], 5.l (*n* = 13)

Yield: (85%); mp 174.5 °C; IR (nujol)  $v_{max}$ : 3560, 2954, 2918, 2850, 1739, 1733, 1602, 1512, 1463, 1377, 1276, 1253 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.62 (t, 1H, Ar-H), 8.28 (d, J = 8.73 Hz, 4H, Ar-H), 7.95 (d, J = 1.3 Hz, 2H, Ar-H), 7.40 (d, J = 8.72 Hz, 4H, Ar-H), 7.12 (d, J = 8.8 Hz, 4H, Ar-H), 6.93 (d, J = 8.92 Hz, 4H, Ar-H), 3.96 (t, J = 6.9 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 1.82-1.76 (quin, J = 6.54 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.38-1.26 (m, 40H, 2 × -(CH<sub>2</sub>)<sub>10</sub>-), 0.87 (t, J = 6.52 Hz, 6H, 2 × -CH<sub>3</sub>); Elemental analysis: C<sub>60</sub>H<sub>74</sub>O<sub>11</sub> requires C 74.21, H 7.67; found C 74.56, H 7.95%.

#### **5-Benzyloxy bis**[4-(*n*-tetradecyloxyphenyloxycarbonyl)phenylisophthalate], **5.**k (*n* = 14)

Yield: (88%); mp 98-99 °C; IR (nujol)  $v_{max}$ : 2922, 2852, 1755, 1732, 1598, 1508, 1456, 1377, 1338, 1271, 1251 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.64 (t, 1H, Ar-H), 8.3 (d, J = 8.72 Hz, 4H, Ar-H), 8.08 (d, J = 1.4 Hz, 2H, Ar-H), 7.49-7.43 (m, 5H, Ar-H), 7.39 (d, J = 8.76 Hz, 4H, Ar-H), 7.12 (d, J = 9 Hz, 4H, Ar-H), 6.93 (d, J = 9 Hz, 4H, Ar-H), 5.24 (s, 2H, -O-CH<sub>2</sub>-Ar), 3.96 (t, J = 6.52 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 1.82-1.75 (quin, J=6.76 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.49-1.25 (m, 44H, 2 × -(CH<sub>2</sub>)<sub>11</sub>-), 0.87 (t, J = 6.52 Hz, 6H, 2 × -CH<sub>3</sub>); Elemental analysis: C<sub>69</sub>H<sub>84</sub>O<sub>11</sub> requires C 76.08, H 7.77; found C 75.8, H 7.61%.

#### 5-Hydroxy bis[4-(*n*-tetradecyloxyphenyloxycarbonyl)phenylisophthalate], 5.I (*n* = 14)

Yield: (83%); mp 171.5 °C; IR (nujol)  $v_{max}$ : 3560, 2918, 2850, 1739, 1732, 1600, 1514, 1454, 1377, 1276, 1253 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.62 (t, 1H, Ar-H), 8.28 (d, J = 8.72 Hz, 4H, Ar-H), 7.94 (d, J = 1.4 Hz, 2H, Ar-H), 7.39 (d, J = 8.72 Hz, 4H, Ar-H), 7.12 (d, J = 9 Hz, 4H, Ar-H), 6.92 (d, J=9 Hz, 4H, Ar-H), 3.96 (t, J = 6.52 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 1.8-1.76 (quin, J = 6.4 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.39-1.26 (m, 44H, 2 × -(CH<sub>2</sub>)<sub>11</sub>-), 0.87 (t,

J = 6.56 Hz, 6H, 2 × -CH<sub>3</sub>); Elemental analysis: C<sub>62</sub>H<sub>78</sub>O<sub>11</sub> requires C 74.52, H 7.87; found C 74.16, H 8.14%.

#### **5-Benzyloxy bis**[4-(*n*-pentadecyloxyphenyloxycarbonyl)phenylisophthalate], **5.**k (*n* = 15)

Yield: (86%); mp 102-103.5 °C; IR (nujol)  $v_{max}$ : 2923, 2852, 1747, 1735, 1732, 1604, 1595, 1465, 1377, 1344, 1271, 1255 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.64 (t, 1H, Ar-H), 8.29 (d, *J* = 8.7 Hz, 4H, Ar-H), 8.08 (d, *J* = 1.4 Hz, 2H, Ar-H), 7.49-7.42 (m, 5H, Ar-H), 7.39 (d, *J* = 8.76 Hz, 4H, Ar-H), 7.12 (d, *J* = 8.8 Hz, 4H, Ar-H), 6.94 (d, *J* = 6.9 Hz, 4H, Ar-H), 5.24 (s, 2H, -O-CH<sub>2</sub>-Ar-), 3.96 (t, *J* = 6.2 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 1.82-1.75 (quin, *J* = 6.76 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.48-1.25 (m, 48H, 2 × -(CH<sub>2</sub>)<sub>12</sub>-), 0.88 (t, *J* = 6.2 Hz, 6H, 2 × -CH<sub>3</sub>); Elemental analysis: C<sub>71</sub>H<sub>88</sub>O<sub>11</sub> requires C 76.31, H 7.93; found C 76.62, H 7.99%.

#### 5-Hydroxy bis[4-(*n*-pentadecyloxyphenyloxycarbonyl)phenylisophthalate], 5.l (*n* = 15)

Yield: (85%); mp 170.5 °C; IR (nujol)  $v_{max}$ : 3560, 2918, 2850, 1739, 1733, 1602, 1512, 1463, 1377, 1309, 1290, 1276 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.62 (t, 1H, Ar-H), 8.28 (d, J = 8.72 Hz, 4H, Ar-H), 7.94 (d, J = 1.4 Hz, 2H, Ar-H), 7.39 (d, J = 8.7 Hz, 4H, Ar-H), 7.12 (d, J = 9 Hz, 4H, Ar-H), 6.92 (d, J = 8.9 Hz, 4H, Ar-H), 3.96 (t, J = 6.5 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 1.80-1.76 (quin, J = 6.36 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.39-1.26 (m, 48H, 2 × -(CH<sub>2</sub>)<sub>12</sub>-), 0.87 (t, J = 6.56 Hz, 6H, 2 × -CH<sub>3</sub>); Elemental analysis: C<sub>64</sub>H<sub>82</sub>O<sub>11</sub> requires C 74.82, H 8.04; found C 75.13, H 7.87%.

#### **5-Benzyloxy bis**[4-(*n*-hexadecyloxyphenyloxycarbonyl)phenylisophthalate], **5.**k (*n* = 16)

Yield: (88%); mp 100-101.5 °C; IR (nujol)  $v_{max}$ : 2922, 2852, 1737, 1749, 1595, 1510, 1461, 1377, 1276, 1247 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.64 (t, 1H, Ar-H), 8.3 (d, J = 8.72 Hz, 4H, Ar-H), 8.08 (d, J = 1.4 Hz, 2H, Ar-H), 7.49-7.43 (m, 5H, Ar-H), 7.39 (d, J = 8.76 Hz, 4H, Ar-H), 7.12 (d, J = 9 Hz, 4H, Ar-H), 6.93 (d, J = 9 Hz, 4H, Ar-H), 5.24 (s, 2H, -O-CH<sub>2</sub>-Ar), 3.96 (t, J = 6.52 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 1.82-1.75 (quin, J = 6.76 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.49-1.25 (m, 52H, 2 × -(CH<sub>2</sub>)<sub>13</sub>-), 0.87 (t, J = 6.52 Hz, 6H, 2 × -CH<sub>3</sub>); Elemental analysis: C<sub>73</sub>H<sub>92</sub>O<sub>11</sub> requires C 76.54, H 8.08; found C 76.17, H 8.33%.

#### **5-Hydroxy bis**[4-(*n*-hexadecyloxyphenyloxycarbonyl)phenylisophthalate], **5.** (*n* = 16)

Yield: (82%); mp 167.5 °C; IR (nujol)  $v_{max}$ : 3558, 2918, 2850, 1739, 1728, 1602, 1512, 1463, 1377, 1276, 1253 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.62 (t, 1H, Ar-H), 8.28 (d, J = 8.72 Hz, 4H, Ar-H), 7.94 (d, J = 1.4 Hz, 2H, Ar-H), 7.39 (d, J = 8.72 Hz, 4H, Ar-H), 7.12 (d, J = 9 Hz, 4H, Ar-H), 6.92 (d, J = 9 Hz, 4H, Ar-H), 3.96 (t, J = 6.52 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 1.80-1.76 (quin, J = 6.4 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-C<u>H<sub>2</sub></u>-), 1.39-1.26 (m, 52H, 2 × -(CH<sub>2</sub>)<sub>13</sub>-), 0.87 (t, J = 6.56 Hz, 6H, 2 × -CH<sub>3</sub>); Elemental analysis: C<sub>66</sub>H<sub>86</sub>O<sub>11</sub> requires C 75.11, H 8.2; found C 74.67, H 8.38%.

#### **5-Benzyloxy bis**[4-(*n*-octadecyloxyphenyloxycarbonyl)phenylisophthalate], **5.**k (*n* = 18)

Yield: 3.8 g (86%); mp 102-103 °C; IR (nujol)  $v_{max}$ : 2920, 2850, 1755, 1739, 1732, 1596, 1508, 1456, 1377, 1272, 1249 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.64 (t, 1H, Ar-H), 8.3 (d, J = 8.72 Hz, 4H, Ar-H), 8.08 (d, J = 1.4 Hz, 2H, Ar-H), 7.49-7.43 (m, 5H, Ar-H), 7.39 (d, J = 8.76 Hz, 4H, Ar-H), 7.12 (d, J = 9 Hz, 4H, Ar-H), 6.93 (d, J = 9 Hz, 4H, Ar-H), 5.24 (s, 2H, -O-CH<sub>2</sub>-Ar), 3.96 (t, J = 6.52 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 1.82-1.75 (quin, J = 6.76 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.49-1.25 (m, 60H, 2 × -(CH<sub>2</sub>)<sub>15</sub>-), 0.87 (t, J = 6.52 Hz, 6H, 2 × -CH<sub>3</sub>); C<sub>77</sub>H<sub>100</sub>O<sub>11</sub> requires C 76.97, H 8.38; found C 76.58, H 8.33%.

#### 5-Hydroxy bis[4-(n-octadecyloxyphenyloxycarbonyl)phenylisophthalate], 5.l (n = 18)

Yield: (90%); mp 160.5 °C; IR (nujol)  $v_{max}$ : 3558, 2918, 2848, 2673, 1739, 1602, 1512, 1463, 1377, 1290, 1247 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.62 (t, 1H, Ar-H), 8.28 (d, J = 8.72 Hz, 4H, Ar-H), 7.94 (d, J = 1.4 Hz, 2H, Ar-H), 7.39 (d, J = 8.72 Hz, 4H, Ar-H), 7.12 (d, J = 9 Hz, 4H, Ar-H), 6.92 (d, J = 9 Hz, 4H, Ar-H), 3.96 (t, J = 6.52 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 1.80-1.76 (quin, J = 6.4 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.39-1.26 (m, 60H, 2 × -(CH<sub>2</sub>)<sub>15</sub>-), 0.87 (t, J = 6.56 Hz, 6H, 2 × -CH<sub>3</sub>); Elemental analysis: C<sub>70</sub>H<sub>94</sub>O<sub>11</sub> requires C 75.65, H 8.52; found C 75.8, H 8.55%.

#### Dimer 5.D.1 (m = 5, n = 18)

This was synthesized following a procedure described for the synthesis of compound **5.i**, by using compounds **5.d** and **5.j**. Quantities: compound **5.d** (0.050 g, 0.115 mmol), compound **5.j** (0.223 g, 0.462 mmol), DCC (0.114 g, 0.555 mmol), DMAP (catalytic amount) and dry

dichloromethane (15 mL). The product was crystallized from a mixture of chloroform and acetonitrile. Yield: 0.105 g (40%); mp 67.5 °C; IR (KBr)  $v_{max}$ : 3072, 3051, 2918, 2904, 2848, 2769, 2636, 1753, 1745, 1737, 1730, 1604, 1504, 1469, 1454, 1413, 1394 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.62 (t, 2H, Ar-H), 8.29 (d, J = 8.3 Hz, 8H, Ar-H), 7.99 (d, J = 1.2 Hz, 4H, Ar-H), 7.39 (d, J = 8.2 Hz, 8H, Ar-H), 7.11 (d, J = 8.1 Hz, 8H, Ar-H), 6.93 (d, J = 8.7 Hz, 8H, Ar-H), 4.19 (t, J = 6.5 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 3.96 (t, J = 6.2 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 2.4-1.98 (quin, J = 6.1 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.82-1.76 (quin, J = 6.8 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.49-1.25 (m, 122H, 4 × -(CH<sub>2</sub>)<sub>15</sub>- + -(CH<sub>2</sub>)-), 0.87 (t, J = 6.5 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>145</sub>H<sub>196</sub>O<sub>22</sub> requires C 76.02, H 8.63; found C 75.74, H 8.62%.

#### Dimer 5.D.2 (m = 6, n = 18)

This compound and other homologues of this series were prepared following the procedure described for the preparation of compound **5.D.1**.

Yield: (45%); mp 66.5 °C; IR (KBr)  $v_{max}$ : 3072, 3052, 2918, 2902, 2846, 2767, 2636, 1745, 1732, 1730, 1604, 1506, 1469, 1454, 1413, 1394 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.62 (t, 2H, Ar-H), 8.28 (d, J = 8.1 Hz, 8H, Ar-H), 7.97 (d, J = 1.16 Hz, 4H, Ar-H), 7.38 (d, J = 8.8 Hz, 8H, Ar-H), 7.11 (d, J = 8.4 Hz, 8H, Ar-H), 6.92 (d, J = 9 Hz, 8H, Ar-H), 4.16 (t, J = 6.3 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 3.96 (t, J = 6.1 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 1.97-1.92 (quin, J = 6.2 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.82-1.76 (quin, J = 6.6 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.49-1.25 (m, 124H, 4 × -(CH<sub>2</sub>)<sub>15</sub>- + -(CH<sub>2</sub>)<sub>2</sub>-), 0.87 (t, J = 6.2 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>146</sub>H<sub>198</sub>O<sub>22</sub> requires C 76.07, H 8.65; found C 76.39, H 8.90%.

#### Dimer 5.D.3 (m = 7, n = 18)

Yield: (42%); mp 65.5 °C; IR (KBr)  $v_{max}$ : 3072, 3053, 2918, 2904, 2848, 2769, 2636, 1747, 1732, 1728, 1604, 1504, 1469, 1454, 1413, 1394 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.62 (t, 2H, Ar-H), 8.29 (d, J = 8.4 Hz, 8H, Ar-H), 7.98 (d, J = 1.24 Hz, 4H, Ar-H), 7.39 (d, J = 8.5 Hz, 8H, Ar-H), 7.12 (d, J = 8.4 Hz, 8H, Ar-H), 6.93 (d, J = 9 Hz, 8H, Ar-H), 4.15 (t, J = 6.3 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 3.96 (t, J = 6.1 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 1.92-1.85 (quin, J = 6.4 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-C<u>H<sub>2</sub>-), 1.83-1.75 (quin, J = 6.1 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.49-1.25 (m, 126H, 4 × -(CH<sub>2</sub>)<sub>15</sub>- + -(CH<sub>2</sub>)<sub>3</sub>-), 0.87 (t, J = 6.5 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>147</sub>H<sub>200</sub>O<sub>22</sub> requires C 76.14, H 8.68; found C 76.09, H 8.75%.</u>

#### Dimer 5.D.4 (*m* = 8, *n* = 18)

Yield: (43%); mp 64.5 °C; IR (KBr)  $v_{max}$ : 3071, 3052, 2920, 2904, 2850, 2769, 2636, 1745, 1737, 1730, 1604, 1504, 1469, 1454, 1413, 1394 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.62 (t, 2H, Ar-H), 8.29 (d, J = 8 Hz, 8H, Ar-H), 7.98 (d, J = 1.22 Hz, 4H, Ar-H), 7.39 (d, J = 8.3 Hz, 8H, Ar-H), 7.12 (d, J = 8.5 Hz, 8H, Ar-H), 6.93 (d, J = 8.9 Hz, 8H, Ar-H), 4.15 (t, J = 6.1 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 3.96 (t, J = 6.3 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 1.92-1.87 (quin, J = 6.8 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-C<u>H<sub>2</sub>-), 1.82-1.76 (quin, J = 6.6 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-C<u>H<sub>2</sub>-), 1.49-1.26 (m, 128H, 4 × -(CH<sub>2</sub>)<sub>15</sub>- + -(CH<sub>2</sub>)<sub>4</sub>-), 0.87 (t, J = 6.1 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>148</sub>H<sub>202</sub>O<sub>22</sub> requires C 76.19, H 8.71; found C 76.93, H 8.75%.</u></u>

#### Dimer 5.D.5 (m = 9, n = 18)

Yield: (40%); mp 64 °C; IR (KBr)  $v_{max}$ : 3072, 3051, 2918, 2850, 2769, 2636, 1745, 1730, 1604, 1504, 1467, 1456, 1413, 1396 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.62 (t, 2H, Ar-H), 8.29 (d, J = 8.5 Hz, 8H, Ar-H), 7.98 (d, J = 1.3 Hz, 4H, Ar-H), 7.39 (d, J = 8.6 Hz, 8H, Ar-H), 7.11 (d, J = 8.9 Hz, 8H, Ar-H), 6.93 (d, J = 9 Hz, 8H, Ar-H), 4.13 (t, J = 6.1 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 3.96 (t, J = 6.5 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 1.91-1.86 (quin, J = 6.4 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.82-1.75 (quin, J = 6.1 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.48-1.26 (m, 130H, 4 × -(CH<sub>2</sub>)<sub>15</sub>- + -(CH<sub>2</sub>)<sub>5</sub>-), 0.87 (t, J = 7 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>149</sub>H<sub>204</sub>O<sub>22</sub> requires C 76.25, H 8.75; found C 76.65, H 8.7%.

#### Dimer 5.D.6 (*m* = 10, *n* = 18)

Yield: (44%); mp 64 °C; IR (KBr)  $v_{max}$ : 3072, 3051, 2918, 2848, 2769, 2632, 1747, 1735, 1606, 1504, 1469, 1454, 1415, 1394 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.62 (t, 2H, Ar-H), 8.29 (d, J = 8.2 Hz, 8H, Ar-H), 7.98 (d, J = 1.1 Hz, 4H, Ar-H), 7.39 (d, J = 8.5 Hz, 8H, Ar-H), 7.12 (d, J = 8.6 Hz, 8H, Ar-H), 6.93 (d, J = 8.4 Hz, 8H, Ar-H), 4.12 (t, J = 8 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 3.96 (t, J = 6.8 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 1.9-1.82 (quin, J = 6.9 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.87-1.77 (quin, J = 6.5 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.49-1.26 (m, 132H, 4 × -(CH<sub>2</sub>)<sub>15</sub>- + -(CH<sub>2</sub>)<sub>6</sub>-), 0.88 (t, J = 6.2 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>150</sub>H<sub>206</sub>O<sub>22</sub> requires C 76.31, H 8.78; found C 76.06, H 8.81%.

#### Dimer 5.D.7 (*m* = 11, *n* = 18)

Yield: (43%); mp 63 °C; IR (KBr)  $v_{max}$ : 3072, 3051, 2904, 2852, 2771, 2636, 1745, 1730, 1604, 1506, 1471, 1456, 1413, 1394 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.62 (t, 2H, Ar-H), 8.29 (d, J = 8.7 Hz, 8H, Ar-H), 7.98 (d, J = 1.3 Hz, 4H, Ar-H), 7.39 (d, J = 8.7 Hz, 8H, Ar-H), 7.11 (d, J = 9 Hz, 8H, Ar-H), 6.93 (d, J = 9 Hz, 8H, Ar-H), 4.12 (t, J = 8 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 3.95 (t, J = 6.53 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 1.9-1.82 (quin, J = 7.7 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.8-1.77 (quin, J = 6 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.49-1.26 (m, 134H, 4 × -(CH<sub>2</sub>)<sub>15</sub>- + -(CH<sub>2</sub>)<sub>7</sub>-), 0.87 (t, J = 6.49 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>151</sub>H<sub>208</sub>O<sub>22</sub> requires C 76.36, H 8.81; found C 76.23, H 8.92%.

#### Dimer 5.D.8 (m = 12, n = 18)

Yield: (40%); mp 63.5 °C; IR (KBr)  $v_{max}$ : 3072, 3051, 2921, 2850, 2769, 2636, 1747, 1737, 1730, 1604, 1506, 1469, 1456, 1413, 1396 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.62 (t, 2H, Ar-H), 8.29 (d, J = 8.65 Hz, 8H, Ar-H), 7.98 (d, J = 1.03 Hz, 4H, Ar-H), 7.39 (d, J = 8.67 Hz, 8H, Ar-H), 7.11 (d, J = 8.93 Hz, 8H, Ar-H), 6.93 (d, J = 8.99 Hz, 8H, Ar-H), 4.12 (t, J = 8 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 3.95 (t, J = 6.46 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 1.9-1.88 (quin, J = 8 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.82-1.75 (quin, J = 6.84 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.42-1.26 (m, 136H, 4 × -(CH<sub>2</sub>)<sub>15</sub>- + -(CH<sub>2</sub>)<sub>8</sub>-), 0.89 (t, J = 6.42 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>152</sub>H<sub>210</sub>O<sub>22</sub> requires C 76.41, H 8.85; found C 76, H 8.45%.

#### Dimer 5.D.9 (m = 9, n = 11)

Yield: (45%); mp 124.5 °C; IR (KBr)  $v_{max}$ : 3072, 3051, 2922, 2850, 2769, 2636, 1745, 1735, 1730, 1604, 1506, 1469, 1456, 1413, 1396 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.61 (t, 2H, Ar-H), 8.29 (d, J = 8.7 Hz, 8H, Ar-H), 7.98 (d, J = 1.2 Hz, 4H, Ar-H), 7.39 (d, J = 8.58 Hz, 8H, Ar-H), 7.12 (d, J = 8.99 Hz, 8H, Ar-H), 6.93 (d, J = 9 Hz, 8H, Ar-H), 4.13 (t, J = 6.2 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 3.96 (t, J = 6.5 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 1.91-1.86 (quin, J = 7.05 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.83-1.76 (quin, J = 6.5 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.48-1.27 (m, 74H, 4 × -(CH<sub>2</sub>)<sub>8</sub>- + -(CH<sub>2</sub>)<sub>5</sub>-), 0.88 (t, J = 6.5 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>121</sub>H<sub>148</sub>O<sub>22</sub> requires C 74.36, H 7.62; found C 74.15, H 7.72%.

#### Dimer 5.D.10 (m = 9, n = 12)

Yield: (40%); mp 112 °C; IR (KBr)  $v_{max}$ : 3072, 3051, 2918, 2848, 2772, 2636, 1745, 1737, 1728, 1606, 1504, 1469, 1456, 1413, 1396 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.61 (t, 2H, Ar-H), 8.29 (d, J = 8.6 Hz, 8H, Ar-H), 7.98 (d, J=1.4 Hz, 4H, Ar-H), 7.39 (d, J = 8.6 Hz, 8H, Ar-H), 7.12 (d, J = 9 Hz, 8H, Ar-H), 6.93 (d, J = 9.03 Hz, 8H, Ar-H), 4.13 (t, J = 6 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 3.96 (t, J = 6.5 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 1.91-1.86 (quin, J = 7.3 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.82-1.75 (quin, J = 7.1 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.48-1.26 (m, 82H, 4 × -(CH<sub>2</sub>)<sub>9</sub>- + -(CH<sub>2</sub>)<sub>5</sub>-), 0.88 (t, J = 6.36 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>125</sub>H<sub>156</sub>O<sub>22</sub> requires C 74.67, H 7.81; found C 74.36, H 7.81%.

#### Dimer 5.D.11 (*m* = 9, *n* = 13)

Yield: (43%); mp 108 °C; IR (KBr)  $v_{max}$ : 3072, 3051, 2920, 2906, 2848, 2769, 2636, 1747, 1735, 1730, 1604, 1506, 1469, 1456, 1413, 1394 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.62 (t, 2H, Ar-H), 8.29 (d, J = 8.68 Hz, 8H, Ar-H), 7.98 (d, J = 1.3 Hz, 4H, Ar-H), 7.39 (d, J = 8.7 Hz, 8H, Ar-H), 7.11 (d, J = 6.9 Hz, 8H, Ar-H), 6.93 (d, J = 9 Hz, 8H, Ar-H), 4.13 (t, J = 6.1 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 3.96 (t, J = 6.5 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 1.91-1.85 (quin, J = 6.2 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-C<u>H</u><sub>2</sub>-), 1.83-1.75 (quin, J = 6.2 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-C<u>H</u><sub>2</sub>-), 1.48-1.26 (m, 90H, 4 × -(CH<sub>2</sub>)<sub>10</sub>- + -(CH<sub>2</sub>)<sub>5</sub>-), 0.88 (t, J = 6.7 Hz, 12H, 4×-CH<sub>3</sub>); Elemental analysis: C<sub>129</sub>H<sub>164</sub>O<sub>22</sub> requires C 74.97, H 7.99; found C 74.78, H 8.33%.

#### Dimer 5.D.12 (m = 9, n = 14)

Yield: (41%); mp 105.5 °C; IR (KBr)  $v_{max}$ : 3072, 3052, 2918, 2904, 2852, 2769, 2636, 1745, 1737, 1730, 1604, 1504, 1467, 1454, 1413, 1394 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.61 (t, 2H, Ar-H), 8.29 (d, J = 8.65 Hz, 8H, Ar-H), 7.98 (d, J = 1.24 Hz, 4H, Ar-H), 7.39 (d, J = 8.6 Hz, 8H, Ar-H), 7.11 (d, J = 8.99 Hz, 8H, Ar-H), 6.93 (d, J = 9 Hz, 8H, Ar-H), 4.13 (t, J = 6.6 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 3.96 (t, J = 6.52 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 1.91-1.86 (quin, J = 6.82 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.82-1.75 (quin, J = 6.56 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.48-1.26 (m, 98H, 4 × -(CH<sub>2</sub>)<sub>11</sub>- + -(CH<sub>2</sub>)<sub>5</sub>-), 0.88 (t, J = 7.12 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>133</sub>H<sub>172</sub>O<sub>22</sub> requires C 75.25, H 8.16; found C 74.88, H 8.17%.

#### Dimer 5.D.13 (m = 9, n = 15)

Yield: (44%); mp 50.5 °C; IR (KBr)  $v_{max}$ : 3072, 3051, 2918, 2848, 2771, 2637, 1747, 1737, 1730, 1606, 1504, 1469, 1454, 1396 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.61 (t, 2H, Ar-H), 8.29 (d, J = 8.8 Hz, 8H, Ar-H), 7.98 (d, J = 1.2 Hz, 4H, Ar-H), 7.39 (d, J = 8.5 Hz, 8H, Ar-H), 7.12 (d, J = 8.78 Hz, 8H, Ar-H), 6.93 (d, J = 8.9 Hz, 8H, Ar-H), 4.13 (t, J = 6.4 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 3.96 (t, J = 6.42 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 1.91-1.85 (quin, J = 6.78 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.83-1.76 (quin, J = 6.6 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.49-1.26 (m, 106H, 4 × -(CH<sub>2</sub>)<sub>12</sub>- + -(CH<sub>2</sub>)<sub>5</sub>-), 0.86 (t, J = 7.05 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>137</sub>H<sub>180</sub>O<sub>22</sub> requires C 75.53, H 8.32; found C 75.8, H 8.72%.

#### Dimer 5.D.14 (m = 9, n = 16)

Yield: (42%); mp 56.5 °C; IR (KBr)  $v_{max}$ : 3072, 3051, 2918, 2904, 2852, 2769, 2638, 1745, 1735, 1730, 1606, 1506, 1469, 1454, 1413, 1396 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.61 (t, 2H, Ar-H), 8.29 (d, J = 8.7 Hz, 8H, Ar-H), 7.98 (d, J = 1.12 Hz, 4H, Ar-H), 7.39 (d, J = 8.3 Hz, 8H, Ar-H), 7.12 (d, J = 8.7 Hz, 8H, Ar-H), 6.93 (d, J = 9 Hz, 8H, Ar-H), 4.13 (t, J = 6.1 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 3.96 (t, J = 6.2 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 1.91-1.86 (quin, J = 6.9 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-C<u>H</u><sub>2</sub>-), 1.84-1.76 (quin, J = 6.4 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-C<u>H</u><sub>2</sub>-), 1.47-1.26 (m, 114H, 4 × (CH<sub>2</sub>)<sub>13</sub>- + -(CH<sub>2</sub>)<sub>5</sub>-), 0.88 (t, J = 7 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>141</sub>H<sub>188</sub>O<sub>22</sub> requires C 75.77, H 8.47; found C 75.62, H 8.59%.

#### Dimer 5.D.15 (*m* = 12, *n* = 11)

Yield: (43%); mp 75.3 °C; IR (KBr)  $v_{max}$ : 3072, 3053, 2922, 2904, 2852, 2769, 2636, 1743, 1735, 1730, 1604, 1506, 1469, 1456, 1413, 1394 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.61 (t, 2H, Ar-H), 8.29 (d, J = 8.56 Hz, 8H, Ar-H), 7.98 (d, J = 1.3 Hz, 4H, Ar-H), 7.39 (d, J = 8.7 Hz, 8H, Ar-H), 7.11 (d, J = 8.97 Hz, 8H, Ar-H), 6.93 (d, J = 8.95 Hz, 8H, Ar-H), 4.12 (t, J = 6.8 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 3.95 (t, J = 6.6 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 1.9-1.83 (quin, J = 8.4 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-C<u>H</u><sub>2</sub>-), 1.82-1.75 (quin, J = 6.54 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-C<u>H</u><sub>2</sub>-), 1.42-1.26 (m, 80H, 4 × -(CH<sub>2</sub>)<sub>8</sub>- + -(CH<sub>2</sub>)<sub>8</sub>-), 0.89 (t, J = 6.96 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>124</sub>H<sub>154</sub>O<sub>22</sub> requires C 74.58, H 7.76; found C 74.53, H 8.09%.

#### Dimer 5.D.16 (*m* = 12, *n* = 12)

Yield: (40%); mp 65.3 °C; IR (KBr)  $v_{max}$ : 3072, 3051, 2918, 2904, 2848, 2769, 2636, 1747, 1737, 1730, 1606, 1504, 1469, 1456, 1413, 1396 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.61 (t, 2H, Ar-H), 8.29 (d, J = 8.65 Hz, 8H, Ar-H), 7.98 (d, J = 1.2 Hz, 4H, Ar-H), 7.39 (d, J = 8.67 Hz, 8H, Ar-H), 7.12 (d, J = 8.93 Hz, 8H, Ar-H), 6.93 (d, J = 9 Hz, 8H, Ar-H), 4.12 (t, J = 6.2 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 3.96 (t, J = 6.5 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 1.9-1.83 (quin, J = 8.2 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.82-1.75 (quin, J = 6.84 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.42-1.26 (m, 88H, 4 × -(CH<sub>2</sub>)<sub>9</sub>- + -(CH<sub>2</sub>)<sub>8</sub>-), 0.88 (t, J = 7.06 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>128</sub>H<sub>162</sub>O<sub>22</sub> requires C 74.90, H 7.94; found C 74.87, H 8.11%.

#### Dimer 5.D.17 (m = 12, n = 13)

Yield: (40%); mp 45.5 °C; IR (KBr)  $v_{max}$ : 3072, 3053, 2918, 2906, 2848, 2769, 2636, 1745, 1732, 1730, 1606, 1504, 1469, 1456, 1413, 1394 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.61 (t, 2H, Ar-H), 8.29 (d, J = 8.5 Hz, 8H, Ar-H), 7.98 (d, J = 1.2 Hz, 4H, Ar-H), 7.39 (d, J = 8.3 Hz, 8H, Ar-H), 7.12 (d, J = 9 Hz, 8H, Ar-H), 6.93 (d, J = 8.9 Hz, 8H, Ar-H), 4.12 (t, J = 6.3 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 3.96 (t, J = 6.9 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 1.9-1.83 (quin, J = 7.1 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-C<u>H</u><sub>2</sub>-), 1.82-1.75 (quin, J = 6.8 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-C<u>H</u><sub>2</sub>-), 1.42-1.26 (m, 96H, 4 × -(CH<sub>2</sub>)<sub>10</sub>- + -(CH<sub>2</sub>)<sub>8</sub>-), 0.88 (t, J = 7 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>132</sub>H<sub>170</sub>O<sub>22</sub> requires C 75.19, H 8.11; found C 75.49, H 8.41%.

#### Dimer 5.D.18 (*m* = 12, *n* = 14)

Yield: (42%); mp 44.5 °C; IR (KBr)  $v_{max}$ : 3071, 3053, 2918, 2906, 2848, 2769, 2636, 1745, 1732, 1730, 1604, 1506, 1469, 1454, 1413, 1394 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.61 (t, 2H, Ar-H), 8.29 (d, J = 8.52 Hz, 8H, Ar-H), 7.98 (d, J = 1.2 Hz, 4H, Ar-H), 7.39 (d, J = 8.56 Hz, 8H, Ar-H), 7.11 (d, J = 8.88 Hz, 8H, Ar-H), 6.93 (d, J = 8.75 Hz, 8H, Ar-H), 4.12 (t, J = 8.1 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 3.96 (t, J = 6.6 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 1.9-1.83 (quin, J = 8.3 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.82-1.75 (quin, J = 6.84 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.41-1.27 (m, 104H, 4 × -(CH<sub>2</sub>)<sub>11</sub>- + -(CH<sub>2</sub>)<sub>8</sub>-), 0.88 (t, J = 6.12 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>136</sub>H<sub>178</sub>O<sub>22</sub> requires C 75.45, H 8.28; found C 75.07, H 8.11%.

#### Dimer 5.D.19 (*m* = 12, *n* = 15)

Yield: (44%); mp 52.5 °C; IR (KBr)  $v_{max}$ : 3072, 3053, 2918, 2850, 2769, 2637, 1742, 1737, 1732, 1604, 1506, 1469, 1456, 1413, 1394 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.61 (t, 2H, Ar-H), 8.29 (d, J = 8.4 Hz, 8H, Ar-H), 7.98 (d, J = 1.2 Hz, 4H, Ar-H), 7.38 (d, J = 8.7 Hz, 8H, Ar-H), 7.12 (d, J = 8.98 Hz, 8H, Ar-H), 6.93 (d, J = 9.1 Hz, 8H, Ar-H), 4.12 (t, J = 6.1 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 3.96 (t, J = 6.45 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 1.9-1.83 (quin, J = 8.2 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.82-1.76 (quin, J = 6.86 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.4-1.26 (m, 112H, 4 × -(CH<sub>2</sub>)<sub>12</sub>- + -(CH<sub>2</sub>)<sub>8</sub>-), 0.88 (t, J = 6.2 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>140</sub>H<sub>186</sub>O<sub>22</sub> requires C 75.71, H 8.43; found C 75.37, H 8.43%.

#### Dimer 5.D.20 (m = 12, n = 16)

Yield: (45%); mp 54.5 °C; IR (KBr)  $v_{max}$ : 3072, 3051, 2918, 2906, 2848, 2771, 2636, 1747, 1737, 1732, 1604, 1506, 1469, 1456, 1413, 1394 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.62 (t, 2H, Ar-H), 8.29 (d, J = 8.7 Hz, 8H, Ar-H), 7.98 (d, J = 1.2 Hz, 4H, Ar-H), 7.39 (d, J = 8.7 Hz, 8H, Ar-H), 7.12 (d, J = 8.96 Hz, 8H, Ar-H), 6.93 (d, J = 9 Hz, 8H, Ar-H), 4.12 (t, J = 6.4 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-), 3.95 (t, J = 6.48 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 1.89-1.83 (quin, J = 8.4 Hz, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.82-1.76 (quin, J = 8.1 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.42-1.26 (m, 120H, 4 × -(CH<sub>2</sub>)<sub>13</sub>- + -(CH<sub>2</sub>)<sub>8</sub>-), 0.88 (t, J = 6.4 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>144</sub>H<sub>194</sub>O<sub>22</sub> requires C 75.96, H 8.57; found C 75.6, H 8.54%.

#### Dimer 5.D.21 (m = 6, n = 18)

Yield: (50%); mp 65.5 °C; IR (KBr)  $v_{max}$ : 2922, 2850, 1753, 1745, 1735, 1604, 1504, 1467, 1394 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.9 (t, 2H, Ar-H), 8.30 (d, J = 8.6 Hz, 8H, Ar-H), 8.21 (d, J = 1.4 Hz, 4H, Ar-H), 7.39 (d, J = 8.64 Hz, 8H, Ar-H), 7.12 (d, J = 8.96 Hz, 8H, Ar-H), 6.93 (d, J = 9 Hz, 8H, Ar-H), 3.96 (t, J = 6.52 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 2.65 (t, J = 6.52 Hz, 4H, 2 × Ar-OCO-CH<sub>2</sub>-), 1.8-1.77 (quin, J = 6.64 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.45-1.26 (m, 128H, 4 × -(CH<sub>2</sub>)<sub>15</sub>- + -(CH<sub>2</sub>)<sub>4</sub>-), 0.87 (t, J = 6.4 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>148</sub>H<sub>198</sub>O<sub>24</sub> requires C 75.29, H 8.44; found C 74.9, H 8.79%.

#### Dimer 5.D.22 (*m* = 7, *n* = 18)

Yield: (55%); mp 65.5 °C; IR (KBr) v<sub>max</sub>: 2922, 2850, 1739, 1735, 1602, 1508, 1465,

1377, 1271 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.9 (t, 2H, Ar-H), 8.30 (d, J = 8.6 Hz, 8H, Ar-H), 8.21 (d, J = 1.4 Hz, 4H, Ar-H), 7.39 (d, J = 8.64 Hz, 8H, Ar-H), 7.12 (d, J = 8.96 Hz, 8H, Ar-H), 6.93 (d, J = 9 Hz, 8H, Ar-H), 3.96 (t, J = 6.52 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 2.65 (t, J = 6.52 Hz, 4H, 2 × Ar-OCO-CH<sub>2</sub>-), 1.8-1.77 (quin, J = 6.64 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.45-1.26 (m, 130H, 4 × -(CH<sub>2</sub>)<sub>15</sub>- + -(CH<sub>2</sub>)<sub>5</sub>-), 0.87 (t, J = 6.4 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>149</sub>H<sub>200</sub>O<sub>24</sub> requires C 75.35, H 8.47; found C 75.02, H 8.7%.

#### Dimer 5.D.23 (m = 8, n = 18)

Yield: (52%); mp 65.5 °C; IR (KBr)  $v_{max}$ : 2922, 2852, 1753, 1739, 1602, 1508, 1456, 1377, 1271 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.9 (t, 2H, Ar-H), 8.30 (d, J = 8.6 Hz, 8H, Ar-H), 8.21 (d, J = 1.4 Hz, 4H, Ar-H), 7.39 (d, J = 8.64 Hz, 8H, Ar-H), 7.12 (d, J = 8.96 Hz, 8H, Ar-H), 6.93 (d, J = 9 Hz, 8H, Ar-H), 3.96 (t, J = 6.52 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 2.65 (t, J = 6.52 Hz, 4H, 2 × Ar-OCO-CH<sub>2</sub>-), 1.80-1.77 (quin, J = 6.64 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.45-1.26 (m, 132H, 4 × -(CH<sub>2</sub>)<sub>15</sub>- + -(CH<sub>2</sub>)<sub>6</sub>-), 0.87 (t, J = 6.4 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>150</sub>H<sub>202</sub>O<sub>24</sub> requires C 75.41, H 8.51; found C 75.58, H 8.76%.

#### Dimer 5.D.24 (*m* = 9, *n* = 18)

Yield: (53%); mp 65.5 °C; IR (KBr)  $v_{max}$ : 3072, 2922, 2852, 1755, 1739, 1602, 1508, 1463, 1377, 1271 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.9 (t, 2H, Ar-H), 8.30 (d, J = 8.6 Hz, 8H, Ar-H), 8.21 (d, J = 1.4 Hz, 4H, Ar-H), 7.39 (d, J = 8.64 Hz, 8H, Ar-H), 7.12 (d, J = 8.96 Hz, 8H, Ar-H), 6.93 (d, J = 9 Hz, 8H, Ar-H), 3.96 (t, J = 6.52 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 2.65 (t, J = 6.52 Hz, 4H, 2 × Ar-OCO-CH<sub>2</sub>-), 1.80-1.77 (quin, J = 6.64 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.45-1.26 (m, 126H, 4 × -(CH<sub>2</sub>)<sub>14</sub>- + -(CH<sub>2</sub>)<sub>7</sub>-), 0.87 (t, J = 6.4 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>151</sub>H<sub>204</sub>O<sub>24</sub> requires C 75.47, H 8.54; found C 75.66, H 8.81%.

#### Dimer 5.D.25 (m = 10, n = 18)

Yield: (51%); mp 63 °C; IR (KBr)  $v_{max}$ : 2920, 2850, 1739, 1735, 1604, 1508, 1467, 1394, 1271 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.9 (t, 2H, Ar-H), 8.30 (d, *J* = 8.6 Hz, 8H, Ar-H), 8.21 (d, *J* = 1.4 Hz, 4H, Ar-H), 7.39 (d, *J* = 8.64 Hz, 8H, Ar-H), 7.12 (d, *J* = 8.96 Hz, 8H, Ar-H), 6.93 (d, *J* = 9 Hz, 8H, Ar-H), 3.96 (t, *J* = 6.52 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 2.65 (t, *J* = 6.52 Hz, 4H, 2 × Ar-OCO-CH<sub>2</sub>-), 1.80-1.77 (quin, *J* = 6.64 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-C<u>H<sub>2</sub>-</u>), 1.45-1.26 (m, 136H,

 $4 \times -(CH_2)_{15^-} + -(CH_2)_{8^-}$ , 0.87 (t, J = 6.4 Hz, 12H,  $4 \times -CH_3$ ); Elemental analysis:  $C_{152}H_{206}O_{24}$  requires C 75.53, H 8.58; found C 75.17, H 9.02%.

#### Dimer 5.D.26 (*m* = 11, *n* = 18)

Yield: (53%); mp 63 °C; IR (KBr)  $v_{max}$ : 2922, 2852, 1753, 1741, 1602, 1508, 1461, 1377, 1271 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.9 (t, 2H, Ar-H), 8.3 (d, J = 8.6 Hz, 8H, Ar-H), 8.21 (d, J = 1.4 Hz, 4H, Ar-H), 7.39 (d, J = 8.64 Hz, 8H, Ar-H), 7.12 (d, J = 8.96 Hz, 8H, Ar-H), 6.93 (d, J = 9 Hz, 8H, Ar-H), 3.96 (t, J = 6.52 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 2.65 (t, J = 6.52 Hz, 4H, 2 × Ar-OCO-CH<sub>2</sub>-), 1.8-1.77 (quin, J = 6.64 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-C<u>H<sub>2</sub>-), 1.45-1.26 (m, 138H, 4 × -(CH<sub>2</sub>)<sub>15</sub>- + -(CH<sub>2</sub>)<sub>9</sub>-), 0.87 (t, J = 6.4 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>153</sub>H<sub>208</sub>O<sub>24</sub> requires C 75.58, H 8.61; found C 75.93, H 8.86%.</u>

#### Dimer 5.D.27 (m = 12, n = 18)

Yield: (52%); mp 108.5 °C; IR (KBr)  $v_{max}$ : 2922, 2850, 1753, 1739, 1604, 1508, 1465, 1377, 1271 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.9 (t, 2H, Ar-H), 8.3 (d, J = 8.6 Hz, 8H, Ar-H), 8.21 (d, J = 1.4 Hz, 4H, Ar-H), 7.39 (d, J = 8.64 Hz, 8H, Ar-H), 7.12 (d, J = 8.96 Hz, 8H, Ar-H), 6.93 (d, J = 9 Hz, 8H, Ar-H), 3.96 (t, J = 6.52 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 2.65 (t, J = 6.52 Hz, 4H, 2 × Ar-OCO-CH<sub>2</sub>-), 1.8-1.77 (quin, J = 6.64 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.45-1.26 (m, 140H, 4 × -(CH<sub>2</sub>)<sub>15</sub>- + -(CH<sub>2</sub>)<sub>10</sub>-), 0.87 (t, J = 6.4 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>154</sub>H<sub>210</sub>O<sub>24</sub> requires C 75.64, H 8.64; found C 75.25, H 8.9%.

#### Dimer 5.D.28 (*m* = 14, *n* = 18)

Yield: (45%); mp 101.5 °C; IR (KBr)  $v_{max}$ : 2922, 2850, 1753, 1739, 1604, 1508, 1465, 1377, 1271 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.9 (t, 2H, Ar-H), 8.3 (d, J = 8.6 Hz, 8H, Ar-H), 8.21 (d, J = 1.4 Hz, 4H, Ar-H), 7.39 (d, J = 8.64 Hz, 8H, Ar-H), 7.12 (d, J = 8.96 Hz, 8H, Ar-H), 6.93 (d, J = 9 Hz, 8H, Ar-H), 3.96 (t, J = 6.52 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 2.65 (t, J = 6.52 Hz, 4H, 2 × Ar-OCO-CH<sub>2</sub>-), 1.8-1.77 (quin, J = 6.64 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.45-1.26 (m, 144H, 4 × -(CH<sub>2</sub>)<sub>15</sub>- + -(CH<sub>2</sub>)<sub>12</sub>-), 0.87 (t, J = 6.4 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>156</sub>H<sub>214</sub>O<sub>24</sub> requires C 75.76, H 8.71; found C 75.65, H 8.68%.

#### Dimer 5.D.29 (m = 7, n = 10)

Yield: (50%); mp 141.5 °C; IR (KBr)  $v_{max}$ : 2923, 2852, 1755, 1753, 1732, 1604, 1510, 1461, 1377, 1271cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.9 (t, 2H, Ar-H), 8.3 (d, J = 8.6 Hz, 8H, Ar-H), 8.21 (d, J = 1.4 Hz, 4H, Ar-H), 7.39 (d, J = 8.64 Hz, 8H, Ar-H), 7.12 (d, J = 8.96 Hz, 8H, Ar-H), 6.93 (d, J = 9 Hz, 8H, Ar-H), 3.96 (t, J = 6.52 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 2.65 (t, J = 6.52 Hz, 4H, 2 × Ar-OCO-CH<sub>2</sub>-), 1.8-1.77 (quin, J = 6.64 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.45-1.26 (m, 66H, 4 × -(CH<sub>2</sub>)<sub>7</sub>- + -(CH<sub>2</sub>)<sub>5</sub>-), 0.87 (t, J = 6.4 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>117</sub>H<sub>136</sub>O<sub>24</sub> requires C 72.95, H 7.1; found C 72.56, H 6.99%.

#### Dimer 5.D.30 (m = 7, n = 11)

Yield: (48%); mp 121.5 °C; IR (KBr)  $v_{max}$ : 2923, 2852, 1755, 1753, 1735, 1733, 1604, 1508, 1463, 1377, 1271 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.9 (t, 2H, Ar-H), 8.3 (d, J = 8.6 Hz, 8H, Ar-H), 8.21 (d, J = 1.4 Hz, 4H, Ar-H), 7.39 (d, J = 8.64 Hz, 8H, Ar-H), 7.12 (d, J = 8.96 Hz, 8H, Ar-H), 6.93 (d, J = 9 Hz, 8H, Ar-H), 3.96 (t, J = 6.52 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 2.65 (t, J = 6.52 Hz, 4H, 2 × Ar-OCO-CH<sub>2</sub>-), 1.8-1.77 (quin, J = 6.64 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 2.65 (t, J = 6.52 Hz, 4H, 2 × Ar-OCO-CH<sub>2</sub>-), 1.8-1.77 (quin, J = 6.64 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.45-1.26 (m, 74H, 4 × -(CH<sub>2</sub>)<sub>8</sub>- + -(CH<sub>2</sub>)<sub>5</sub>-), 0.87 (t, J = 6.4 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>121</sub>H<sub>144</sub>O<sub>24</sub> requires C 73.31, H 7.31; found C 73.12, H 7.5%.

#### Dimer 5.D.31 (m = 7, n = 12)

Yield: (52%); mp 120.5 °C; IR (KBr)  $v_{max}$ : 2922, 2852, 1755, 1732, 1604, 1508, 1456, 1377, 1271 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.9 (t, 2H, Ar-H), 8.3 (d, J = 8.6 Hz, 8H, Ar-H), 8.21 (d, J = 1.4 Hz, 4H, Ar-H), 7.39 (d, J = 8.64 Hz, 8H, Ar-H), 7.12 (d, J = 8.96 Hz, 8H, Ar-H), 6.93 (d, J = 9 Hz, 8H, Ar-H), 3.96 (t, J = 6.52 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 2.65 (t, J = 6.52 Hz, 4H, 2 × Ar-OCO-CH<sub>2</sub>-), 1.80-1.77 (quin, J = 6.64 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.45-1.26 (m, 82H, 4 × -(CH<sub>2</sub>)<sub>9</sub>- + -(CH<sub>2</sub>)<sub>5</sub>-), 0.87 (t, J = 6.4 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>125</sub>H<sub>152</sub>O<sub>24</sub> requires C 73.65, H 7.51; found C 73.58, H 7.74%.

#### Dimer 5.D.32 (m = 7, n = 13)

Yield: (48%); mp 111 °C; IR (KBr)  $\nu_{max}$ : 2922, 2852, 1753, 1737, 1606, 1508, 1456, 1377, 1271 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.9 (t, 2H, Ar-H), 8.3 (d, J = 8.6 Hz, 8H, Ar-H), 8.21 (d, J = 1.4 Hz, 4H, Ar-H), 7.39 (d, J = 8.64 Hz, 8H, Ar-H), 7.12 (d, J = 8.96 Hz,

8H, Ar-H), 6.93 (d, J = 9 Hz, 8H, Ar-H), 3.96 (t, J = 6.52 Hz, 8H,  $4 \times \text{Ar-O-CH}_2$ -), 2.65 (t, J = 6.52 Hz, 4H,  $2 \times \text{Ar-O-CH}_2$ -), 1.8-1.77 (quin, J = 6.64 Hz, 8H,  $4 \times \text{Ar-O-CH}_2$ -CH<sub>2</sub>-), 1.45-1.26 (m, 90H,  $4 \times -(\text{CH}_2)_{10}$ - + -(CH<sub>2</sub>)<sub>5</sub>-), 0.87 (t, J = 6.4 Hz, 12H,  $4 \times -\text{CH}_3$ ); Elemental analysis: C<sub>129</sub>H<sub>160</sub>O<sub>24</sub> requires C 73.97, H 7.69; found C 74.03, H 7.96%.

#### Dimer 5.D.33 (m = 7, n = 14)

Yield: (65%); mp 112 °C; IR (KBr)  $v_{max}$ : 2922, 2852, 1755, 1735, 1604, 1508, 1456, 1377, 1271 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.9 (t, 2H, Ar-H), 8.3 (d, J = 8.6 Hz, 8H, Ar-H), 8.21 (d, J = 1.4 Hz, 4H, Ar-H), 7.39 (d, J = 8.64 Hz, 8H, Ar-H), 7.12 (d, J = 8.96 Hz, 8H, Ar-H), 6.93 (d, J = 9 Hz, 8H, Ar-H), 3.96 (t, J = 6.52 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 2.65 (t, J = 6.52 Hz, 4H, 2 × Ar-OCO-CH<sub>2</sub>-), 1.8-1.77 (quin, J = 6.64 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.45-1.26 (m, 98H, 4 × -(CH<sub>2</sub>)<sub>11</sub>- + -(CH<sub>2</sub>)<sub>5</sub>-), 0.87 (t, J = 6.4 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>133</sub>H<sub>168</sub>O<sub>24</sub> requires C 74.27, H 7.87; found C 74.14, H 8.07%.

#### Dimer 5.D.34 (m = 7, n = 15)

Yield: (50%); mp 55 °C; IR (KBr)  $v_{max}$ : 2922, 2852, 1747, 1735, 1604, 1508, 1456, 1377, 1271 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.9 (t, 2H, Ar-H), 8.3 (d, J = 8.6 Hz, 8H, Ar-H), 8.21 (d, J = 1.4 Hz, 4H, Ar-H), 7.39 (d, J = 8.66 Hz, 8H, Ar-H), 7.12 (d, J = 8.96 Hz, 8H, Ar-H), 6.93 (d, J = 9 Hz, 8H, Ar-H), 3.96 (t, J = 6.52 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 2.65 (t, J = 6.52 Hz, 4H, 2 × Ar-OCO-CH<sub>2</sub>-), 1.8-1.77 (quin, J = 6.64 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.45-1.26 (m, 106H, 4 × -(CH<sub>2</sub>)<sub>12</sub>- + -(CH<sub>2</sub>)<sub>5</sub>-), 0.87 (t, J = 6.24 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>137</sub>H<sub>176</sub>O<sub>24</sub> requires C 74.56, H 8.03; found C 75, H 8.37%.

#### Dimer 5.D.35 (m = 7, n = 16)

Yield: (51%); mp 59 °C; IR (KBr)  $v_{max}$ : 2922, 2852, 1753, 1741, 1604, 1508, 1456, 1377, 1271 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.9 (t, 2H, Ar-H), 8.3 (d, J = 8.6 Hz, 8H, Ar-H), 8.21 (d, J = 1.4 Hz, 4H, Ar-H), 7.39 (d, J = 8.64 Hz, 8H, Ar-H), 7.12 (d, J = 8.96 Hz, 8H, Ar-H), 6.93 (d, J = 9 Hz, 8H, Ar-H), 3.96 (t, J = 6.52 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 2.65 (t, J = 6.52 Hz, 4H, 2 × Ar-OCO-CH<sub>2</sub>-), 1.8-1.77 (quin, J = 6.64 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.45-1.26 (m, 114H, 4 × -(CH<sub>2</sub>)<sub>13</sub>- + -(CH<sub>2</sub>)<sub>5</sub>-), 0.87 (t, J = 6.4 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>141</sub>H<sub>184</sub>O<sub>24</sub> requires C 74.84, H 8.19; found C 74.71, H 8.31%.

#### Dimer 5.D.36 (m = 10, n = 10)

Yield: (50%); mp 86 °C; IR (KBr)  $v_{max}$ : 2923, 2852, 1749, 1755, 1732, 604, 1510, 1461, 1377, 1271 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.9 (t, 2H, Ar-H), 8.3 (d, J = 8.6 Hz, 8H, Ar-H), 8.21 (d, J = 1.4 Hz, 4H, Ar-H), 7.39 (d, J = 8.64 Hz, 8H, Ar-H), 7.12 (d, J = 8.96 Hz, 8H, Ar-H), 6.93 (d, J = 9 Hz, 8H, Ar-H), 3.96 (t, J = 6.52 Hz, 8H,  $4 \times \text{Ar-O-CH}_2$ -), 2.65 (t, J = 6.52 Hz, 4H, 2 × Ar-OCO-CH<sub>2</sub>-), 1.8-1.77 (quin, J = 6.64 Hz, 8H,  $4 \times \text{Ar-O-CH}_2$ -CH<sub>2</sub>-), 1.45-1.26 (m, 72H,  $4 \times -(\text{CH}_2)_7$ - + -(CH<sub>2</sub>)<sub>8</sub>-), 0.87 (t, J = 6.4 Hz, 12H,  $4 \times -\text{CH}_3$ ); Elemental analysis: C<sub>120</sub>H<sub>142</sub>O<sub>24</sub> requires C 73.22, H 7.26; found C 72.93, H 7.52%.

#### Dimer 5.D.37 (m = 10, n = 11)

Yield: (52%); mp 84 °C; IR (KBr)  $v_{max}$ : 2922, 2852, 1753, 1739, 1604, 1508, 1456, 1377, 1272 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.9 (t, 2H, Ar-H), 8.3 (d, J = 8.6 Hz, 8H, Ar-H), 8.21 (d, J = 1.4 Hz, 4H, Ar-H), 7.39 (d, J = 8.64 Hz, 8H, Ar-H), 7.12 (d, J = 8.96 Hz, 8H, Ar-H), 6.93 (d, J = 9 Hz, 8H, Ar-H), 3.96 (t, J = 6.52 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 2.65 (t, J = 6.52 Hz, 4H, 2 × Ar-OCO-CH<sub>2</sub>-), 1.8-1.77 (quin, J = 6.64 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.45-1.26 (m, 80H, 4 × -(CH<sub>2</sub>)<sub>8</sub>- + -(CH<sub>2</sub>)<sub>8</sub>-), 0.87 (t, J = 6.4 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>124</sub>H<sub>150</sub>O<sub>24</sub> requires C 73.57, H 7.46; found C 73.18, H 7.55%.

#### Dimer 5.D.38 (*m* = 10, *n* = 12)

Yield: (48%); mp 86 °C; IR (KBr)  $v_{max}$ : 2922, 2852, 1755, 1739, 1737, 1604, 1508, 1456, 1377, 1271 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.9 (t, 2H, Ar-H), 8.3 (d, J = 8.6 Hz, 8H, Ar-H), 8.21 (d, J = 1.4 Hz, 4H, Ar-H), 7.39 (d, J = 8.64 Hz, 8H, Ar-H), 7.12 (d, J = 8.96 Hz, 8H, Ar-H), 6.93 (d, J = 9 Hz, 8H, Ar-H), 3.96 (t, J = 6.52 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 2.65 (t, J = 6.52 Hz, 4H, 2 × Ar-OCO-CH<sub>2</sub>-), 1.8-1.77 (quin, J = 6.64 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.45-1.26 (m, 88H, 4 × -(CH<sub>2</sub>)<sub>9</sub>- + -(CH<sub>2</sub>)<sub>8</sub>-), 0.87 (t, J = 6.4 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>128</sub>H<sub>158</sub>O<sub>24</sub> requires C 73.88, H 7.65; found C 73.51, H 7.70%.

#### Dimer 5.D.39 (*m* = 10, *n* = 13)

Yield: (46%); mp 84.5 °C; IR (KBr)  $v_{max}$ : 2922, 2852, 1755, 1732, 1604, 1508, 1456, 1377, 1271 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.9 (t, 2H, Ar-H), 8.3 (d, J = 8.62 Hz, 8H, Ar-H), 8.21 (d, J = 1.4 Hz, 4H, Ar-H), 7.39 (d, J = 8.64 Hz, 8H, Ar-H), 7.12 (d, J = 8.96 Hz,

8H, Ar-H), 6.93 (d, J = 9 Hz, 8H, Ar-H), 3.96 (t, J = 6.56 Hz, 8H,  $4 \times \text{Ar-O-CH}_2$ -), 2.65 (t, J = 6.54 Hz, 4H,  $2 \times \text{Ar-O-CH}_2$ -), 1.8-1.77 (quin, J = 6.66 Hz, 8H,  $4 \times \text{Ar-O-CH}_2$ -CH<sub>2</sub>-), 1.45-1.26 (m, 96H,  $4 \times -(\text{CH}_2)_{10}$ - + -(CH<sub>2</sub>)<sub>8</sub>-), 0.87 (t, J = 6.4 Hz, 12H,  $4 \times -\text{CH}_3$ ); Elemental analysis: C<sub>132</sub>H<sub>166</sub>O<sub>24</sub> requires C 74.2, H 7.82; found C 74.26, H 8.04%.

#### Dimer 5.D.40 (*m* = 10, *n* = 14)

Yield: (52%); mp 82.5 °C; IR (KBr)  $v_{max}$ : 2922, 2852, 1755, 1739, 1604, 1508, 1463, 1377, 1271 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.9 (t, 2H, Ar-H), 8.3 (d, J = 8.6 Hz, 8H, Ar-H), 8.21 (d, J = 1.4 Hz, 4H, Ar-H), 7.39 (d, J = 8.6 Hz, 8H, Ar-H), 7.12 (d, J = 8.96 Hz, 8H, Ar-H), 6.93 (d, J = 9 Hz, 8H, Ar-H), 3.96 (t, J = 6.52 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 2.65 (t, J = 6.52 Hz, 4H, 2 × Ar-OCO-CH<sub>2</sub>-), 1.8-1.77 (quin, J = 6.64 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.45-1.26 (m, 104H, 4 × -(CH<sub>2</sub>)<sub>11</sub>- + -(CH<sub>2</sub>)<sub>8</sub>-), 0.87 (t, J = 6.4 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>136</sub>H<sub>174</sub>O<sub>24</sub> requires C 74.49, H 7.99; found C 74.4, H 8.28%.

#### Dimer 5.D.41 (m = 10, n = 15)

Yield: (48%); mp 53 °C; IR (KBr)  $v_{max}$ : 2922, 2852, 1747, 1735, 1602, 1508, 1460, 1377, 1271 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.9 (t, 2H, Ar-H), 8.3 (d, J = 8.62 Hz, 8H, Ar-H), 8.21 (d, J = 1.4 Hz, 4H, Ar-H), 7.39 (d, J = 8.62 Hz, 8H, Ar-H), 7.12 (d, J = 8.88 Hz, 8H, Ar-H), 6.93 (d, J = 9 Hz, 8H, Ar-H), 3.96 (t, J = 6.56 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 2.65 (t, J = 6.52 Hz, 4H, 2 × Ar-OCO-CH<sub>2</sub>-), 1.8-1.77 (quin, J = 6.66 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.45-1.26 (m, 112H, 4 × -(CH<sub>2</sub>)<sub>12</sub>- + -(CH<sub>2</sub>)<sub>8</sub>-), 0.87 (t, J = 6.4 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>140</sub>H<sub>182</sub>O<sub>24</sub> requires C 74.77, H 8.14; found C 75.02, H 8.21%.

#### Dimer 5.D.42 (m = 10, n = 16)

Yield: (50%); mp 58 °C; IR (KBr)  $v_{max}$ : 2922, 2852, 1751, 1735, 1602, 1508, 1460, 1377, 1271 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.9 (t, 2H, Ar-H), 8.3 (d, *J* = 8.6 Hz, 8H, Ar-H), 8.21 (d, *J* = 1.4 Hz, 4H, Ar-H), 7.39 (d, *J* = 8.64 Hz, 8H, Ar-H), 7.12 (d, *J* = 8.96 Hz, 8H, Ar-H), 6.93 (d, *J* = 9 Hz, 8H, Ar-H), 3.96 (t, *J* = 6.52 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-), 2.65 (t, *J* = 6.52 Hz, 4H, 2 × Ar-OCO-CH<sub>2</sub>-), 1.8-1.77 (quin, *J* = 6.62 Hz, 8H, 4 × Ar-O-CH<sub>2</sub>-C<u>H</u><sub>2</sub>-), 1.45-1.26 (m, 120H, 4 × -(CH<sub>2</sub>)<sub>13</sub>- + -(CH<sub>2</sub>)<sub>8</sub>-), 0.87 (t, *J* = 6.4 Hz, 12H, 4 × -CH<sub>3</sub>); Elemental analysis: C<sub>144</sub>H<sub>190</sub>O<sub>24</sub> requires C 75.04, H 8.30; found C 75.24, H 8.51%.

#### Chapter 5

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